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Metallurgical Project
A. H. Compton, Project Director

* * * *

Clinton Laboratories

M. D. Whitaker, Director

S. W. Pratt, Plant Manager

* * * *

Production Division

J. P. Sinclair, Production Superintendent

* * * *

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Progress Report

First Nine Months Operation of

Separations Plant

This document has been approved for release to the public by:

David R Hamrin 9/20/95
Technical Information Officer Date
ORNL Site

December, 1943 to September, 1944

Submitted by: A. C. Cox

Approved by: W. Q. Smith

Received Clinton: 10/9/44 Series A Issued: 10/9/44
Received Chicago: Series B Issued:

[redacted]

[redacted]

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INTRODUCTION

There have been two objectives in the operation of the Separations Plant at Clinton. The first has been to recover the maximum quantity of product from the uranium reacted in the pile in order to make it available to the various groups within the project. The second objective has been to demonstrate the separations process for the Hanford plant as defined by the research and process development groups. Because of the large number of groups concerned all process modifications were cleared through the Process Steering Committee. The plant strictly observed this procedure and did not make process modifications unless they had been cleared, with the exception of isolated inadvertant deviations.

The purpose of this report is to present all pertinent information on the operation of the Separations Plant. A large part of this information has already been presented in other reports but will be included here to gather all of this information in one report.

Process problems encountered in the Clinton Separations Plant have been given almost complete coverage in two reports (CN 1446 and CN 1894) issued by the Plant Assistance Group and, therefore, Section II (Process) of this report, except for a few changes and additions, was prepared by joining together sections of these two reports.

Information for Section I, Materials of Construction and Maintenance of Equipment, was obtained from the following reports:

200 Area Operating Reports.
200 Area Individual Run Summary Reports.
Start-Up History on Bldg. 205 - by R. S. Wangelin.
Corrosion Studies - CN 1628 - by M. D. Peterson
200 Area Operating Logs.

Reports of Assistance in Assembly of Section III, Radiation and Chemical Hazards and Disposal of Radioactive Wastes, were:

Monthly Reports - issued by the Health Physics Section.
Data and Reports from the files of the Health Physics Section.
200 Area Operating Reports.
Handling of Wastes from 200 Area - by W. Q. Smith.
Equipment Decontamination - CN 1617 - by M. D. Peterson
Report on Iodine and Xenon in the Stack Gases - by G. M. Branch, Jr.

SUMMARY

MATERIALS OF CONSTRUCTION AND MAINTENANCE OF EQUIPMENT

The equipment as initially designed for the separations plant has proven well suited to the operation of the bismuth phosphate process with only minor exceptions. The amount of maintenance required in the plant has been relatively small, but when necessary it has been possible to decontaminate the equipment so that no excess exposure to radiation has occurred while making repairs. Process investigations have been responsible for the major part of the modifications made in the equipment.

Stainless steel, 25-12 S Cb, has proven to be very satisfactory as the material of construction for most of the equipment exposed to process solutions. Failures have occurred in equipment handling fluoride solutions, but evidence seems to indicate that these were due to localized overheating or to faulty welding. Saran piping and tubing has proven to be quite unsatisfactory and in most cases it has been replaced. The gasketing as now used has given little trouble where properly installed and packing materials with the exception G-X, have given satisfactory service. It seems probable that good results would be obtained with G-X packing also, if it could be obtained in properly braided form.

On the whole, the centrifuges have given excellent service. All of the troubles encountered have been readily corrected with no major modifications being required. The original agitators installed in the solution tanks and the Room D precipitator failed shortly after start-up because of faulty design, and were replaced with lower speed units which have given good service. The agitators in the precipitators generally have given good service, the principle difficulty encountered being motor lubrication. Jets have performed satisfactorily, except in Cell 4. Difficulties here have been due to plugging by bits of the Saran HF dip pipe which decomposed. This caused localized overheating, thus accelerating corrosion. Pulsafeeder pumps used in Room D were replaced soon after start-up with air-actuated jets because their operation was unsatisfactory. Pumps handling process chemicals have been satisfactory, except that the Viking pump handling anhydrous HF required a great deal of care. Tanks in the separations area have given satisfactory service with the exception of the steel ferrous ammonium sulfate storage tank which developed leaks after eight months of service. This has been repaired with a lead liner. The stack equipment and metal conveyor have given good service. The Ring Balance liquid level and specific gravity recorders have required frequent checking to maintain calibration.

PROCESS

The bismuth phosphate process for the separation of product from uranium and uranium fission products has given high recovery of product, adequate decontamination and satisfactory production rates. Eighty-five percent of the product received from the 100 Area was recovered and transferred for isolation, with 97.7% of it being accounted for. In the operation of the process it has never been necessary to exceed the tolerance dosage for radiation for any of the personnel involved and in general the exposure to radiation has been well under tolerance. The schedule for processing of uranium has been met in all cases, and so the product production has been determined by the operation of the pile.

A number of process and equipment modifications have been made which have improved yield and decontamination but there have been no basic changes in the process. The modifications in the separation process which will be desirable for its operation at Hanford and which have primarily been defined by laboratory studies, have been demonstrated in the plant with satisfactory results. It is concluded from these runs that the Hanford process as now proposed will give adequate decontamination and high recovery of product, but that even higher yields can be obtained by some simplification of the scavenger treatment and still obtain adequate decontamination.

Two procedures for the removal of the aluminum jackets from the metal slugs have been used. The first is to dissolve the aluminum in 10% nitric acid, the reaction being catalysed by a small quantity of mercuric nitrate. The other procedure is to dissolve the aluminum in a 10% sodium hydroxide, 20% sodium nitrate mixture. The principal advantage of the alkaline mixture is that it is more effective than the acid in removing the aluminum silicon bonding alloy which will be used at Hanford. Product losses in the coating waste are slightly lower with this procedure.

The uranium metal after removal of the coating is dissolved in 60% nitric acid. The only significant change which was made in the operating procedure was to charge 3 batches (1 ton) of metal and dissolve it in thirds. The advantage of this procedure is that the number of charging and coating removal operations are decreased and the dissolving time for the first two batches is shortened because of the increased metal surface exposed.

The pre-extraction treatment of the 40% UNH solution in the dissolver with formic acid was originally designed to decompose excess nitric acid in the solution and to reduce any product which may have been oxidized to the plus 6 state. It developed that the dissolver operation could be controlled so that the residual nitric acid was not excessive and it was shown that there was only a small amount of oxidized product in the UNH. However, when the formic acid pre-treatment was discontinued waste losses in the extraction step increased from the normal 1 - 2% to 10 to 20%. The plant Assistance Group found that the UNH solution contains hydrazine, that this interferes with carrying of product and that nitrite formed by the decomposition of formic acid in the UNH or added as sodium nitrite will react with the hydrazine and prevent its interference with carrying. Sodium nitrite (0.1M) pre-treatment was substituted for the formic acid principally on the basis that it presents less of a problem in handling.

In the extraction step the effects of strike and digestion temperature, rate of striking, phosphoric acid concentration and concentration of inactive fission products have been investigated. Lowering the strike and digestion temperature to 55° does not noticeably affect the waste losses in the extraction step. In a 30 minute strike bismuth precipitates more rapidly than the product while in a 2 hour strike they precipitate at about the same rate. Lowering the phosphoric acid does not exercise a marked effect on extraction yield unless it is decreased to .3M or less. The effect of increased concentration of inactive fission products (to W level) has been small if any on yield.

In operations without added fission products (Clinton process) the only two factors which have affected decontamination appreciably, and both of these increased it, were the change from the hot reverse to the hot direct strike in the extraction step, and the inclusion of a lanthanum fluoride by-product precipitation in the cross-over. Decontamination (through the cross-over step) was not significantly affected by the cooling time of the metal (20 to 60 days) by changes in the coating removal procedure or pre-extraction treatment, the reduction of H_3PO_4 concentration from .1M to .02M in the by-product precipitation of the decontamination cycle, or the change from a product followed by a by-product precipitation in the same vessel, to these operations carried out in separate vessels.

Losses with the Clinton process (no scavengers) in the bismuth phosphate by-product precipitate of the decontamination cycle were decreased from 12% to .7% by making equipment and process modifications to eliminate pick-up, by the by-product solutions, of product which was precipitated in the product precipitation step. These were: change from hot reverse to hot direct strike to obtain a more readily soluble precipitate, installation of an acid distributor in the precipitator to remove product adhering to the surface before the by-product precipitation and replacement of the failed agitators in the product solution tanks.

The evaluation of the Hanford process was made with UNH fortified with inactive fission products. Three combinations of scavengers were tested for their effect on decontamination and waste losses. The use of a double cerium-zirconium precipitation in each of two cycles gave the best decontamination at the end of the decontamination cycles but the other combinations, Ce-Zr; Ce in both cycles and Ce-Zr; Ce in first cycle with $(NH_4)_2SiF_6$ in the second, also met the goal factor of 10^5. The waste losses were lowest with the Ce-Zr; Ce - $(NH_4)_2SiF_6$ combination (5%) and highest with the Ce-Zr; Ce-Zr in both cycles (12%). The Ce-Zr; Ce $(NH_4)_2SiF_6$ combination seemed to have a slight edge at the end of the cross-over on decontamination. Runs were also made with inactive solutions to find the optimum operating procedure for handling scavenger precipitates.

Product losses in the bismuth phosphate by-product precipitation step of the cross-over cycle were high (3.6%) in the early runs due principally to a reducing agent in the phosphoric acid. With this correction and with the installation of an acid distributor in the precipitator and replacement of the mechanical agitator in the oxidation tank, the losses fell to .4%.

The cross-over cycle did not include a lanthanum fluoride by-product precipitation on most of the Clinton runs because the additional decontamination was not needed and because high losses were obtained in the early runs made with the procedure then being used. An improved procedure was used on the Hanford demonstration runs which gave consistantly low losses (1.3%).

Oxalic acid was substituted for hydrogen peroxide reduction in the cross-over with the result that waste losses decreased from 3.8% to .9%. The oxalic acid reduction temperature was subsequently lowered from 75° C and manganous nitrate added as a catalyst with no significant change in results.

A number of modifications in the lanthanum fluoride product precipitation step of the cross-over were studied. It was concluded that a preformed product precipitate is preferable to a coformed one, that aresklene is not satisfactory as a flocculating agent (under the conditions tested), that washing of the lanthanum fluoride product precipitate will decrease the phosphoric acid going into Room D, and that the concentration of HF can be reduced from 1N to .5N and the lanthanum used for carrying reduced from 225 to 125 mg/liter without increasing waste losses.

The principal process changes in Room D were from metathesis of the lanthanum fluoride in the centrifuge bowl to metathesis in the precipitator and from H_2O_2 reduction to oxalic acid reduction. The metathesis change resulted in a better operational procedure but did not appreciably increase yields. The change in reduction procedure decreased waste losses about 2%. A decrease in product loss in the by-product lanthanum fluoride precipitates resulted from more complete washing of these precipitates (from about 3 to 1%). Metathesis of the lanthanum fluoride with a mixture of potassium carbonate and potassium hydroxide was used on a few runs. The resulting lanthanum hydroxide dissolved readily in nitric acid but it was not possible to omit zirconium from the oxidation and by-product precipitation steps without increasing the LaF_3 by-product waste losses.

Material balances over individual steps of the process were not satisfactory during the early periods of operations. Overall material balances, however, were reasonably good, indicating that the individual inaccuracies were not accumulative. These difficulties have been largely overcome by modifications in the equipment to eliminate hold-up of product, modifications in the sampling devices and improvement in the analytical procedures. The largest factor appears to have been the sampler modifications.

RADIATION AND CHEMICAL HAZARD AND DISPOSAL OF RADIOACTIVE WASTES

The original design bases for the separations plant, both as far as the chemical process and amount of radioactive materials to be handled are concerned, were changed after the plant construction was started. However, it has been possible to operate the plant without excessive radiation in the operating areas or excessive exposure of the operating personnel at any point. The radioactive wastes have been stored or disposed of safely, although modification of the disposal system for chemical wastes were made to increase the safety factor on the material being discharged to the creek.

Excessive exposure to operating personnel has not been encountered in the operating areas. Room C, the control room from which cell equipment is operated, is protected by 5 feet of concrete shielding, which has proven to be adequate. Room D was originally designed without shielding, but during early runs, protection was found desirable and a 12 inch concrete block wall was erected around the area occupied by the process equipment. The remaining hazard of contamination of the operating areas and personnel with product has been largely eliminated by modifying Room D to remote control operation. Some exposure to radiation is involved in the operation of the samplers for cell process vessels, but the amount of sample is small and handling time short and tolerance dosage is not approached.

It has been necessary during the first 9 months of operation to enter all cells except Cell 1 for maintenance or inspections. Due to high radiation, these cells are entered only when an emergency warrants the effort of cleaning them to allow entrance for the time required.

Storage or disposal of radioactive wastes has been accomplished safely. Volatile wastes that are liberated during metal dissolving are disposed of through the stack with large dilution by air, metal waste is stored separately in the underground tanks and all others go first to underground tanks where some settling and decay of active materials occurs. The supernatant is jetted at a rate to maintain a constant level in the tanks, to the settling basin where it is diluted with cooling water from the operating areas. A considerable amount of the activity precipitates and remains in the basin while a solution well below tolerance is discharged to the creek. This was not the original procedure for these wastes. After about three months accumulation was in the tanks, the supernatant was jetted to the ponds and went out to the creek with the cooling water. It was found that on dilution a precipitate was formed that, if retained, would considerably lower the activity entering the creek. Therefore, the present settling basin was constructed and placed in service.

The principal chemical hazard encountered has been in the handling of anhydrous HF and of formic acid. Improvement in equipment and operating procedure have considerably reduced the danger from HF, and process changes have eliminated the use of formic acid.

APPENDIX

In the appendix, there are given flowsheets of the process at Clinton at start-up, after about four months of operation and after about nine months of operation. Yield and material balance averages at the various sample points for groups of eight runs are presented, and waste losses and decontamination results for individual runs are graphed. The letters covering process modifications that were made in the separations process are listed with page numbers referring to the discussion of the changes.

MATERIALS OF CONSTRUCTION

AND

MAINTENANCE OF EQUIPMENT

MATERIALS OF CONSTRUCTION

Stainless Steel, 25-12 S Cb

The standard material of construction for handling process solutions in the Separations Plant is 25-12 S Cb stainless steel. This has proven eminently satisfactory except for a few special cases when handling fluoride solutions.

The most frequently occurring corrosion difficulty has been with the spray nozzles in the centrifuges handling fluoride solutions; that is, in Cell 4 centrifuge and in the 26" Room D centrifuge. The spray nozzles have been completely changed twice in Room D and three times in Cell 4. In every instance, corrosion was most severe on the top spray which is never immersed in the process solutions and was least on the bottom spray which is at times immersed and during centrifuging is sprayed with the process solutions. Inspection of the centrifuge bowl at the time of each failure showed no evidence of corrosion. Analysis of one of the spray nozzles from the first failure in Cell 4 showed the content of nickel and chromium to be within the specifications for 25-12 S Cb. Corrosion studies also indicated the nozzle to be heat-treated 25-12 S Cb but somewhat less corrosion resistant than a standard 25-12 test sample. See Table I. This evidence, however, in no way accounts for the rapid failure of such equipment by normal contact with the fluoride solutions at process temperatures. It appears that spray nozzle corrosion has been aggravated by partial plugging of the steam jets feeding the centrifuges which resulted in steam being blown into the centrifuge intermittently. This caused over-heating and consequently rapid corrosion of the parts not cooled by the liquid. Since eliminating the source* of the material plugging the transfer jets, the sprays have not been replaced, but there has not been sufficient operating time since to demonstrate that corrosion is no longer a problem at this point.

TABLE I

RELATIVE CORROSION OF PLANT CENTRIFUGE SPRAY NOZZLE

Solution: 6.2% HNO_3 (1 M), 2.0% HF (1 N), 0.98% H_3PO_4 (0.1 M) Room Temp.

Penetration Rate (inches/month)				
Spray Nozzle		25-12 Test Sample		18-8
As heceived	Heat-Treated	Un-Heat-Treated	Heat-Treated	Heat-Treated
.0015	.00028		.00004	.0052
.00014	.00020	.00092, .00090	.00003	.0019
.0005	.00018		.00005	.0062

Three failures of Thermohm wells have occurred in Cell 4 where fluoride solutions are handled. One leak occurred at a weld, apparently due to removal of flux from an occlusion rather than from corrosion of the metal. The other two

*Saran particles from HF dip pipe which failed.

were due to corrosion of the weld closing the end of the tubes. The closures were made by welding over the opening (1/8") between a cylindrical insert and the tube wall. Clearance between the insert and tube wall had evidently been large which resulted in a heavy weld. The parent metal did not show any appreciable attack. The wells were repaired by driving a tight-fitting plug into the end of the tube and running a small bead around it. No failures have occurred with this type of closure.

Two samplers in Cell 4 have failed due to corrosion in the vicinity of the steam jet. Over-heating from the steam was certainly a contributing factor. Air is now being used on all of the sampler jets and will be used on the Hanford samplers. The sampler on the metal dissolver and the sampler on the Cell 5 by-product holding tank both failed near the steam jets. The former was definitely the result of faulty construction. These are the only corrosion difficulties encountered with 25-12 S Co other than when handling fluoride solutions. One sampler handling fluoride solutions (43 H) failed due to corrosion of the suction line at a butt weld where two lengths of tubing were joined. The sampler lines were not heat-treated before installation because of difficulties in handling the long pieces and this is believed to be the reason for the rapid corrosion.

One steam transfer jet failed in service in Cell 4 where fluoride solutions are handled. This jet had been examined a month before the failure after four months' service and it appeared that it would last at least another four months. At this time there were no signs of corrosions on the steam nozzle or throat although considerable pitting had occurred on the surface of and adjacent to the steam nozzle. The failure occurred at the junction between the steam nozzle and the jet body and was caused by plugging of the throat by pieces of foreign material (Saran) which resulted in over-heating of the solutions.

The corrosion samples placed in Cell 4 precipitator before operations were started were checked after two months' elapsed time in the plant. These samples were heat-treated 25-12 stainless, but did not contain any welds. Corrosion rates were 0.00012 and 0.00013 inches/month total elapsed time. No pitting had occurred. During a second exposure of three additional months, corrosion rates were 0.00054 to 0.00078 inches/month elapsed time, five or six times as great as during the first exposure, yet still not high. The samples then showed shallow trenches in the surfaces outlining the "GX" gaskets used to separate them, and the surfaces of the samples appeared to be roughened from slight pitting.

Laboratory tests were also made with plant solution and with solutions of the same composition made in the laboratory. Similar penetration rates were obtained, (0.00013-0.0004 inches/month). The substitution of 1% H_2O_2 for the 0.05M oxalic acid reducing agent made no significant change in corrosion rate (0.0002-0.0009 inches/month), but reduction in the concentration of HF from 1N to 0.5N reduced the corrosion to 0.0005-0.0001 inches/month (laboratory tests). Corrosion samples from the first catch tank in Room D showed only very slight corrosion (0.00004 inches/month total elapsed time).

The failures which have occurred in the Separations Plant cannot be satisfactorily explained on the basis of data obtained from corrosion test but must be due to localized over-heating of fluoride process solutions or to faulty welding.

Saran Equipment

In a number of places throughout the Separations Plant saran piping and tubing was used and in practically every service it has proven unsatisfactory.

Anhydrous HF is introduced into the precipitator tanks in both Cell 4 and Room D through a 25-12 S Cb stainless steel dip pipe through which was inserted a saran pipe as a liner. Inspection of the liner in Cell 4 after seven months' service showed it to be the source of large black particles which had been causing plugs in the transfer jet on this and other vessels. The saran had hardened and cracked and only six inches of the original seven feet remained in the 25-12 supporting tube. This stainless tube was corroded thin at the end but was still effective as an addition line. A similar inspection in Room D showed that saran liner to be in good condition. However, Cell 4 uses approximately 26 times as much anhydrous HF as does Room D and it can be safely stated that saran is undesirable for anhydrous HF service.

Saran tubing had been installed initially for process lines in Room D. Dummy process runs demonstrated this type of piping to be totally inadequate. Leaks were frequent and could only be stopped by installation of new saran piping, and the plastic would creep and sag at temperatures only slightly above normal. Before start-up, all saran tubing was replaced with 25-12 S Cb stainless steel lines.

Saran tubing was used initially on the liquid level and density instruments. Considerable leakage was also encountered here and much of the saran was soon replaced with copper tubing.

Gasketing

Cells - The standard gasket material in the vessels and lines used for handling process solution is G-9 a compressed, rubber-impregnated, blue African asbestos. This material was installed throughout Cells 1 through 3 and to a large extent throughout Cell 4 where fluoride containing solutions are encountered. Only in positions where fluoride solutions at elevated temperature are expected has "G-9" not been used. In such places in Cell 4 GX (PTFE) gasket material was installed and may be found in the line from the precipitator to the centrifuge, in the HF addition line, and in a few flanges on the discharge side of the transfer jets which move process solution from the catch tank to the precipitator and from the catch tank to waste. Both types of gaskets have given admirable service throughout eight months of operation.

Only a few gasket leaks have occurred during the operation of the plant. A G-9 gasket located between the flanges connecting the throat and nozzle of 2" steam jet from the catch tank to the precipitator in Cell 4, failed after about nine months' service. An improved design might have averted the failure since the holding ledge between the flanges at this spot in the jet is quite narrow. However, the gasket had become quite hard which could only result from over-heating or chemical attack. The GX gaskets in the remaining flanges of this jet were examined also, and were found to be in good condition. In hydrogen peroxide service there are indications that G-9 is not satisfactory; a gasket in a dismantled line which had been in this service showed definite signs of chemical attack.

It was initially planned to use Koroseal gaskets in all cell equipment and this material had been installed throughout by construction. During equipment testing, it was soon discovered that slightly elevated temperatures softened the Koroseal sufficiently to cause considerable creeping which opened up the flanges. In addition, that portion of the gasket which worked its way into the process line became hard and brittle and constituted a potential jet plugging hazard. Before operations commenced, therefore, all Koroseal gasketing was removed except from the centrifuge casing where very little temperature variation was expected.

Room D - GX gasketing material is used universally throughout the process lines and vessels in Room D. Here all the equipment is in contact with fluoride containing solution and most of it is subjected to strong (15%) caustic solutions at one time or another in the processing of each charge. The GX gasket material has withstood these conditions without a single failure and inspection of gaskets which have been in service for eight months show no signs of chemical attack.

Room A - The following gaskets have been used for handling chemicals outside the cells: GX for the most severe service (HF systems), G-9 for all other acid equipment, G-1 (white asbestos, rubber impregnated) for caustic and steam, and G-5 (red rubber) for water service. Long life has been obtained from each type when used according to the above code. Failures have been few where the gaskets were properly installed and service in general has been satisfactory.

Packing

Three types of packing material are used in the Separations Plant which correspond in service and composition to the three types of gasketing material. GX packing is used in the most severe service (HF systems), R-4-X (blue African asbestos) in all acid equipment, and R-1 (white asbestos) in caustic, steam and water service. It is of course evident that no packing normally is subjected to contact with active process solutions since valves and pumps are not a part of process equipment. On the whole, the various types of packing have given good service except for GX. This material is excellent from the standpoint of resistance to chemical attack, but mechanically it has caused difficulty. Extreme care must be exercised in packing HF valves with GX or a tight fit around the valve stem will not result. For a considerable period numerous designs and methods for packing pumps with "GX" were tried without success and it was finally necessary to return to packing all but the HF pump with R-4-X packing. The difficulty appeared to be in winding the "GX" shavings into a suitable rope before inserting it into the packing gland. The feeling is that could it be obtained in a properly braided form "GX" could be used satisfactorily for packing pumps.

MAINTENANCE

Centrifuges

Three types of centrifuges essentially different only in their size are used for solids separation in the Clinton Separations Plant (205 Bldg.). All machines are Bird solid bowl centrifuges, the wetted parts of which are 25-12 S Cb. A 40 inch diameter bowl machine is used in each of the cells where the large volume slurries of the extraction, decontamination and cross-over cycles are processed. A 26 inch diameter bowl machine is used for the first concentration cycle and a 12 inch machine for the final concentration cycle. The two larger type centrifuges are similar and operate at bowl speeds of 870 or 1740 RPM (430 or 1730 G for the 40" machines and 280 or 1120 G for the 26" machines). The higher speed is not necessary for bismuth phosphate, but must be used for lanthanum fluoride. The 12 inch centrifuge differs from the other in that it is equipped with a variable speed drive and can be set to operate at any speed between 1400 and 3200 RPM (340 to 1770 G). The operating speed used at Clinton is 3000 RPM (1550 G).

The 40 inch and 26 inch machines are essentially the same as those which will be used at Hanford except that at Hanford, those in the cells will be equipped for remote control maintenance. Only the Cell 3 centrifuge at Clinton is equipped with a hydraulically operated skimmer, while all such skimming mechanisms at Hanford are hydraulically actuated. Before operations commenced, mechanical wooble indicators were installed on the 40 inch centrifuge drive heads which have proven valuable in the operation of the machines.

The centrifuges in the Separations Plant at Clinton have given excellent service. Many of the troubles encountered might well have been corrected before the machine left the vendor. In the following paragraphs are discussed the centrifuge difficulties for the first nine months of operation grouped according to type or size of machine.

40" Centrifuge - The Cell #5 centrifuge upon arrival was found to contain several small cracks in the weld attaching the 8 inch discharge nozzle to the centrifuge shell. The cracks leaked on hydrostatic testing and it was decided to return the defective centrifuge to the vendor for repairs.

While moving a centrifuge plow into position to start adjustment of the clearance stops, the bushing in the bracket supporting the shaft galled and stuck on the shaft. The bushing of Carpenter 7 MO apparently did not have the correct properties to operate on a 25-12 shaft. All similar bushings in plow and skimmer shaft brackets were changed to bronze. After seven months' operation, the skimmers and plows have worked satisfactorily. Some green discoloration or scale has appeared around the bearings, but there has not been sufficient corrosion to adversely affect operation.

Inspection of the centrifuge motor bearings disclosed that they had been lubricated improperly by the motor manufacturer. It was necessary, therefore, to dismantle each motor, clean the bearing of the excess seal grease, repack and reassemble. The Cell 2 motor and drive head on which the bearings had overheated during centrifuge testing were replaced by a spare.

In order to repack the centrifuge motor bearing it was necessary to remove the tachometer. After a short period of operation, a tachometer shaft on one of the reassembled motors was cut in two as a result of contact with the motor housing. The top motor housing was found to require extremely close setting with reference to the 1 inch tachometer shaft, and it was necessary to increase clearances by 0.015 inches.

The make up oil collector rings, held to the suspension head housings by three set screws, were originally positioned too high with the result that centrifuge wobble forced the collector rings down and bent the 1/8 inch pipe connection. The ring was set down 1/4 inch and the strain in the 1/8 inch tube removed.

Shortly after the Separations Plant start-up, the plows in both the Cell 2 and 3 centrifuges began striking the baffles in the bowl. Subsequent inspection revealed that the plows were striking the top of the baffles in one machine and the bottom of the baffles in the other. Information from the manufacturer indicated that some vertical movement of the bowl might be expected due to changes with use of the neoprene ring in the drive head. Correction of the plow setting would, therefore, appear to give only temporary relief. Had the setting been adjusted from time to time as the machines became run in, possibly a satisfactory adjustment might have finally been reached. It is evident, however, that 1/4 inch clearance between plow and baffles was not adequate, at least for these machines. Efforts to work out a procedure which would not necessitate the use of plows were successful and their use was discontinued after the first month of operation.

The hydraulic mechanism for the Cell 3 centrifuge skimmer had been in service 8 months, when failure of the mechanism to function revealed that solid material (dirt, scale) had lodged under a rubber piston cup. This unit, as first installed, was in extremely dirty condition but presumably was carefully cleaned before start of operations. There were, however, no scars or obvious signs of wear to indicate any cause other than foreign material for the failure. Trouble was again experienced several weeks later when loss of compression allowed the skimmer to "float" into the torus of the bowl during the centrifuge operation. Investigation in the cell revealed a faulty union on the line to the "out" side of the hydraulic piston chamber which allowed oil leakage. At this same time new cups were installed in the compression chamber, but later inspection revealed the old ones to be in perfect condition.

It was necessary during the first nine months of operation to replace the Cell 4 centrifuge skimmer pipe twice. The first failure occurred after the original pipe had been in service seven months and the replacement failed approximately six weeks after being installed. Examination of both pipes showed only minor corrosion and subsequent corrosion studies confirmed that both were of properly heat-treated 25-12 S Co stainless steel. Both pipes broke off at the point of greatest physical stress close to the weld on the bottom of the hollow shaft and photo micrographic studies indicated that the pipes broke as a result of stress failure rather than fatigue.

The Cell 4 centrifuge, the only 40" machine in which failure of the skimmer pipe has occurred, is subject to contact with fluoride solutions and is operated normally at 1740 RPM, although skimming is carried out at 870 RPM. The skimmer unit consists of a curved 1/2" pipe with the liquid pick up about 9" from the

vertical axis of rotation and 3" below the plane of the weld, so that the metal near the weld (the point of failure) is subject to combined shear and bending stress. Stresses were estimated by the plant assistance group at the 2 speeds (1740 and 870 RPM) assuming the force at the skimmer tip to be equal to the velocity head of the liquid acting on the cross-sectional area of the 1/2" pipe. These estimates are about 78,000 PSI and 19,000 PSI respectively, and are large enough to cause failure if applied suddenly. These stresses correspond to forces of 670 lbs. and 155 lbs. on the skimming lever at the operating board. Forces of this magnitude have not been observed by the operator. Since it is probable that the Cell 4 failure resulted from stress, the forces must momentarily occur at times and are damped out in the heavy linkage between the centrifuge and the operator. Investigation of the Cell 4 skimmer linkage following the second failure gave no evidence of mechanical trouble. It has also been noted that forces are far more pronounced through the hydraulic skimmer on Cell 3 where inertia is much less important than through the mechanically linked skimmers in the other cells.

The skimmer pipe failures indicate that design is inadequate at this point. The plant assistance group suggests the use of a heavy (Schedule 160) 1" pipe reduced to a pick up tip of the present size. They calculate this would reduce the stress at the weld to about 17,000 PSI and 4,000 PSI for the two speeds and would thus allow an adequate safety factor at the low speed.

After about nine months of operation, the Cell 3 centrifuge motor was replaced to permit closer examination of the shaft, bearings, winding and the housing of the original motor. The condition of all parts within the total enclosure was extremely good. No grease had been added since installation and the original quantity of Starfax No. 2 was found intact. The grease was darkened somewhat, however no evidence of grease disintergration was observed. The seal grease was found to be in excellent condition. On the basis of this inspection, one ounce of Starfax No. 2 was added to each centrifuge and no further addition is planned for the next six months. The inspection also revealed that considerable rusting of the inner surfaces of the top of bell had occurred, with the screen being particularly corroded. It is planned to paint these surfaces with a bakelite resin coating before reusing.

<u>26" Centrifuge</u> - Only minor corrections were necessary on the 26 inch centrifuge before its acceptance from Construction. While skimming the machine, the shaft tended to bind and liquor would also leak up around this shaft on to the cover plate. The Koroseal gasket below the casing collar was replaced and a new Koroseal gasket was installed around the skimmer rod above the casing collar. This gasket was held in place with a 25-12 wearing washer plate. Satisfactory operation resulted.

Just after start-up the plows on the 26" centrifuge were cut down and equipped with GX gasket wipers. These together with high pressure water (80 - 90 lbs.) introduced through the centrifuge sprays have proven satisfactory for removing fluoride precipitates from the centrifuge bowl.

The original 26" centrifuge after about two months' service developed a serious vibration at high speed and the complete assembly was replaced with the spare. The replacement had been in operation only a month when it too began to vibrate under the same conditions as the original machine. The manufacturer suggested that the neoprene buffer rings supporting the drive head may have shrunk causing the peculiar behavior. Inspection of the buffer rings showed that they had shrunk and did not properly support the drive head. Also, it was found that the rings were neither neoprene nor rubber. New tight fitting rubber rings were installed in the two machines and both have given excellent performance since. Similar difficulty had been experienced in the 12" Semi-Works machines where the rubber rings got oil on them (both Chicago and Clinton).

12" Centrifuge - Seven months after start-up, the per cent of product in the waste effluents from the 12 inch centrifuge became abnormally high and it seemed probable that leaks had developed in the bowl. Inspection of the bowl disclosed a number of cracks. Those which leaked upon addition of water to the bowl were around the top of the weld joining the top plate to the side wall and on the side of the bowl extending up from the bottom butt weld. Other cracks which were evidently only surface deep were in the area where the balance pads had been welded on and their appearance indicated that they probably resulted from faulty welding. The over-all appearance of the bowl was good in that it did not show noticeable signs of corrosion. The liquids handled, however, do contain HF which tests have shown to be a corrosive agent characterized by selective intergranular attacks on welds which have not been properly heat-treated. All visible cracks were peened closed and the bowl was returned to service following a water test. The peened bowl remained in service for six weeks before being replaced. Waste losses during this period were only slightly above normal.

Agitators

All precipitator and solution tanks at Clinton are equipped with agitators. The cell precipitator tanks are agitated by a centrally located vertical 25-12 S Cb shaft fitted with two sets of paddles and driven at 150 RPM by a 5 HP motor. The corresponding agitators at Hanford are fitted with two sets of paddles and are driven by a 15 HP motor at 68 RPM. The calculated agitation obtained in the Clinton precipitator tanks is 1.1 HP/1,000 gallons, and the measured agitation as obtained from the difference in motor load while an extraction precipitation was in progress and when the tank was empty is 0.9 HP/1,000 gallons.

The solution tanks and the Room D precipitator tank were equipped initially with 1/2 HP, 400 RPM agitators which were found before start-up to run at a critical speed for their length of shaft and provisions were made then for their replacement as soon as practicable. The plant started up, however, without replacements and the original agitators failed early (Cell 4 - Run 17, Cell 2 - Run 22, Cell 3 - Run 34). For a considerable period, agitation was provided in these tanks by air spargers. New mechanical agitators were installed in the precipitator in Room D prior to Runs 30 and 31 and in Cells 2, 3, and 4 solution tanks prior to Run 84. The agitators have centrally located vertical 25-12 S Cb shafts fitted with one set of paddles and are driven by a 2 HP motor at 150 RPM. The corresponding agitators at Hanford are fitted with one set of paddles and are driven by a 5 HP motor at 100 RPM. The calculated power obtained in the Clinton

solution tanks assuming no baffles is .197 HP/1,000 gallons, while assuming the dip pipes are equivalent to 1 baffle it is .90 HP/1,000 gallons. The measured agitation obtained from the motor loads with the tank empty and with 90 gallons of 10N HNO_3 in the tank is .90 HP/1,000 gallons.

Following installation of the new agitator in Room D, the assembly gave some difficulty with oil leakage due to positioning the oil outlet line from the gear reducer too high. This was corrected on the cell solution tank units before they were installed.

During the test runs before start-up, the agitator motor on the Cell 5 solution tank over-heated and kicked out. Investigation disclosed that the motor fan had not been pinned to the shaft and had worked loose. Examination of other motors revealed that they had not been pinned either and this was corrected.

The overflow of oil from the gear reducer on the Cell 2 precipitator initiated an investigation which revealed that water had been building up in the waste oil receiver. The water resulted from the condensation of steam which had followed up the oil overflow line from the sewer funnel. To prevent a recurrence, the top half of a horizontal section of all cell oil overflow lines were cut out and the lines were pitched to give good drainage, thus allowing wet vapors to escape.

It was intended originally that the top bearings on all cell agitator motors would be lubricated at regular intervals. Grease lines had been installed for this purpose, but the limited clearance allowed by the motor fan restricted the size of the outlet grease lines to 1/8 inch. This design appeared undesirable in that during lubrication the bearing housing might fill up with grease and develop pressure. On the manufacturers' recommendation, therefore, the grease lines were removed and the bearings were sealed. The motors were then run for a number of hours with thermocouples installed to check for over-heating. After six months' operation, the agitator on the Cell 2 precipitator failed during Run 123. Throughout the previous ten runs, its operation had become increasingly noisy accompanied by a gradual build-up in the electrical load. The damaged motor reducer unit was removed and replaced. Inspection of the unit revealed that the top motor bearing had failed completely apparently due to lack of lubrication. The residual lubricant was carbonized. The gear reducer, however, was in good condition. Failure of the top motor bearing resulted in excessive shaft whippage which cut and grounded the motor windings to the extent that off-the-plant repairs would have been required. The motor, however, was found by the Health Group to be contaminated in spite of the intensive external washings; hence, no effort was made to repair it. As a result of this failure, the 5 HP precipitator motors in the other cells were inspected and grease was added. The bearings were found to be in good condition, but the Lubrico 00 grease generally was frothy and was considerably less than had been present initially. An average of 4 oz. of Lubrico 00 grease was necessary to refill the bearings. The grease addition lines were reconnected and the practice of adding 1 oz. of Lubrico 00 grease per month was established.

Grease lines were also provided for the 2 HP agitator motors on the solution tanks, although inspection of the Cell 4 unit after 4 months' operation showed the bearings to be in excellent condition. These motors are receiving 3/4 oz. of Lubrico 00 grease every two months.

In conjunction with the inspection of motor bearings, the Cell 3 precipitator motor housing was found to be badly rusted and as a precaution, was exchanged with the corresponding Cell 5 unit. Both motor housings were internally cleaned and coated with a thin layer of Parmo grease. Future protection will, however, follow Design Division's recommendations that a bakelite resin paint such as Glyptal be tried.

Jets

All process solutions are moved between vessels and to waste by means of steam syphons of 25-12 S Cb construction. There are two sizes of jets used in the cells: nominal one and nominal two inch, the smaller size always being used for transfer to the centrifuges. The syphons in the cells at Clinton are similar to those which will be used at Hanford except that for a corresponding size, the jets at Hanford will have a slightly higher rate. The one inch and two inch jets at Clinton have a rate of 14 to 75 GPM respectively, but jetting rates can be and are varied appreciably by varying the steam pressure to the jets with steam control valves. The steam control valves are located on the proper panel boards, together with air valves which serve after completion of a transfer to blow out the steam which might otherwise condense in the lines to the jet, produce a vacuum, and draw radioactive solution into the operating room.

The original installation for control of the steam to each syphon comprised three-way air and steam plug cock valves designed such that in order to shut off the steam after transfer, air must be introduced through the lines as the valves were closed. During the testing period before start-up a number of steam jets became plugged with a hard material about the size of a pea which was subsequently identified as plug cock lubricant. Some attempts were made to find a suitable solvent to remove the obstruction without entering the cells. Sulfuric acid was the only inorganic acid which attacked the material. Solvents such as pyridene dissolved the grease, but organic acids and alcohols did not. The plug cock valves prior to start-up were removed and they were replaced with an assembly of standard valves; globe valves on the steam and air lines and gate valves on the bleed and cell lines. In addition, strainers were placed in each cell line just before it passed through the concrete wall to the jet. Since removal of the plug cocks and installation of the strainers, there have been no plug ups or stoppage due to material accumulating in the jets, except in Cell 4. Stoppages have occurred, however, as a result of pipe scale accumulating in the strainers, which are easily cleaned out. Also, after about nine months' operation, the 1" jet feeding 22 centrifuge from 21 precipitator was partially stopped by failure of the G-9 asbestos gasket between the throat and the body of the jet. A similar condition was found to exist in the same location in Cell 3. In Cell 4, both the jet from the precipitator to the centrifuge and from the solution tank to Room D have plugged as a result of Saran accumulation in the suction side. The Saran liner in the dip pipe used for addition of HF to the Cell 4 precipitator tank failed and pieces of the Saran carried through plugging these jets from time to time as well as the 1/2" jet in Room D.

The Room D jets are of 1/2 inch size and are steam operated throughout the first concentration cycle, giving a rate of approximately 4 GPM. This rate is considerably too high for final concentration cycle work where the rate of feed to the 12" centrifuge must not exceed 1/4 GPM. Here 1/2 inch size jets are also

used, but they are placed at the bottom of the tank from which they transfer and are fed with air, incorporating both a jetting and air lift principle. The method allows considerable leeway in transfer rate within the range desired. Pulsafeeder pumps were used to feed the 12" centrifuge throughout the first month of operation. These, however, proved unsatisfactory and the air lift jet system for feeding was installed.

Operation of the jets in Room D on the whole has been satisfactory. Some difficulty was encountered with air leaks in the line on the suction side of the jet from the precipitator tank to the 26" centrifuge. Plugs were caused by the inadvertent addition of foreign material (wood from caustic containers, etc.) into the process tanks.

Pumps

In the Clinton Separations Plant, pumps are used for the movement of process chemicals to and from storage and for high pressure (70-80#/in.^{2}) addition of water to the centrifuges through the sprays. In no case are pumps involved in the movement of active process solutions. When the plant started up, however, Pulsafeeder pumps were used for transferring process solution to the 12" centrifuge. Losses and delays due to stoppages in the pumps necessitated their replacement after one month's service and an air lift jet system was installed to feed the small centrifuge.

Durco centrifugal pumps which have given good service are used for movement of all process chemicals except anhydrous HF and sodium carbonate solution. A Durco pump was initially installed in the carbonate system, but was replaced by a steam jet which has proven a better method of handling 30% Na_2CO_3 solutions since such solutions freeze at slightly below room temperature.

A Viking positive displacement gear pump is used in the anhydrous HF system and has given some difficulty. After the pump has been in contact with HF it tends to lock or freeze in the packing gland. This would occur even if the pump were operated for a few minutes each shift. The present practice is to remove the pump after use, flush with water, and fill it with oil so that it will be ready when again needed.

Goulds centrifugal pumps are successfully used for supplying water to the centrifuges through the sprays. To obtain the desired pressure, however, it was necessary to install two of these pumps in series.

Process Chemicals Equipment

The various process chemicals are stored in Room A of the Separations Building. All acid containing solutions are kept in 18-8 or 25-12 S Co stainless steel tanks, while anhydrous HF, sodium carbonate solutions and ferrous ammonium sulfate solutions are held in steel. The process chemical storage equipment has given no difficulties throughout eight months' service, except for the steel tank used for storage of ferrous ammonium sulfate solutions. This tank became pitted and developed leaks after eight months' use. Following failure a lead liner was installed and several strips of steel have been placed in the tank to maintain the ferrous solution in the reduced state.

Process Tanks

All process tanks at Clinton and Hanford can be grouped into three classifications according to their use in the separations process. They are precipitator tanks, catch tanks, and solution tanks. All are constructed of 25-12 S Cb stainless steel and two at Clinton, the precipitator and solution tanks, have cooling and heating jackets of 18-8 S Cb stainless steel. At Hanford, however, all three types have the 18-8 S Cb cooling and heating jackets. The precipitator tanks, catch tanks, and solution tanks at Clinton are 7' x 7', 8' x 6' and 3' x 5' respectively; the corresponding tanks at Hanford are 9' x 9', 9' x 9', and 6' 10½" x 4' 5¼" respectively. Baffles are installed in all process tanks at Hanford, while only the precipitators at Clinton contain such equipment. All flat-bottomed tanks at both sites are pitched to insure adequate drainage. The differences in tanks between Clinton and Hanford from a process viewpoint are insignificant and vary only to the extent that the latter have been designed to handle larger volumes and to give better agitation.

The vessels at Clinton have given satisfactory service during eight months of operation and only minor changes were required before start-up. The bottoms of several of the tanks were bowed upon arrival and required straightening to obtain proper drainage. The lifting ears on the precipitators were filled with asphalt to eliminate a pocket which might collect process solutions from any subsequent spillage.

During the test runs considerable water hammer was encountered when heating the jackets of the large precipitator tanks. This was corrected by changing to top inlet and bottom outlet connections. The bottom discharge was connected to a standpipe which overflowed above the top level of the jacket thus maintaining a positive pressure within the jackets at all times. Small by-pass lines were also installed between the top of the jackets and the discharge risers to prevent air locking. One-inch orifice plates were installed in the inlet pipes to prevent excessive flow of steam or cooling water through the jackets which would in turn overflow the sewer funnels. These revisions have been incorporated in Hanford design.

Waste Tanks

The waste storage tanks at Clinton are 25' and 50' Gunite tanks painted internally with bitumastic paint on top of which has been added an inner-liner consisting of two layers of bitumen coated fabric covered with 1½" of Gunite. At Hanford these tanks are 75' concrete vessel with a steel inner-liner. The inner-liners were installed at Clinton before start-up, but not until after one of the tanks was found to leak on testing with water. After eight months of service there has been no leakage of process solutions as indicated by analysis of the drainage water from around the base of the tanks.

Auxiliary Equipment

Stack - The stack equipment has operated without incident for eight months except for a failure before start-up of the belts to the steam-driven fan. The belts were found to be too light and were replaced with the proper size.

Metal Conveyor - Following minor adjustment immediately after its installation the long arm metal conveyor has given satisfactory and uninterrupted service.

Liquid Level and Specific Gravity Recorders - Frequent checking of the Ring Balance liquid level and specific gravity recorders has been required in order to keep them properly calibrated. An early source of difficulty was due to leaks in the saran connecting lines and iron valves, but this was largely eliminated by the installation of copper tubing and brass valves. Corrosion of the rings by the sealing liquid, acetylene tetrabromide, has also been a problem, although no instruments have failed completely because of this.

PROCESS

ALUMINUM JACKET REMOVAL

Removal with 10% Nitric Acid and Mercury Catalyst

The coating removal method used at Clinton during the initial 7 months of operation (Runs 1 - 181) consisted of dissolving the aluminum jackets with 10% nitric acid, the reaction being catalyzed by Hg^{+2} (0.06% as $Hg(NO_3)_2 \cdot 1\frac{1}{2} H_2O$).* This method proved satisfactory for removal of the aluminum jackets but has the disadvantage of developing a vigorous reaction. A few instances have occurred when the rate of reaction has been sufficiently rapid to foam out of the dissolver.

The 10% HNO_3 coating removal procedure consisted of adding 2684 lbs. of a 10% HNO_3 solution and $1\frac{1}{2}$ lbs. of ($Hg(NO_3)_2 \cdot 1\frac{1}{2} H_2O$) to a 3 batch charge of Clinton slugs in the dissolver. This corresponds to a HNO_3 aluminum ratio of 11 to 1 and a $Hg(NO_3)_2 \cdot 1\frac{1}{2} H_2O$ - aluminum ratio of 1 to 16. The reaction was started by raising the temperature to 50° C whereupon the heat of reaction raised the temperature to the boiling point. After digesting for an hour at 95° - 100° the solution was cooled and jetted to waste.

The residual 10% acid was then washed from the decoated slugs and the dissolver with a 400 lbs. water rinse. The start-up flowsheet called for a rinse of 400 lbs. of a 2% HNO_3 on the basis that alumina might precipitate when the residual aluminum solution was diluted with water. The use of acid in the rinse was discontinued following Run 26 without adverse affect.**

It is not contemplated that the 10% HNO_3 method for coating removal will be used at Hanford, since the jackets there are bonded to the slugs by a silicon alloy which is not dissolved by nitric acid.

Aluminum Jacket Removal with $NaOH$-$NaNO_3$ Solution

A satisfactory coating removal procedure using 10% NaOH-20% $NaNO_3$*** has been demonstrated on the Clinton plant scale (Runs 182 - 201). About 900 lbs. of 10% NaOH-20% $NaNO_3$ solution were used to remove the 20-mil Al jackets from each one ton batch of X slugs. This represents a 300% excess above stoichiometric requirements and gives an eight inch liquid depth in the dissolver. The NaOH-$NaNO_3$ solution was prepared by adding 60% HNO_3 to 50% NaOH in the dissolver before charging the metal. In normal operation the temperature is adjusted to 40° C and three buckets of metal are charged over a half-hour period.

Shortly after charging the third bucket of metal the temperature rises to about 100° C for 5 - 10 minutes. After the reaction subsides the temperature is maintained at 100° C for one hour with steam. The coating removal is followed by a 400 lbs. water wash and a 440 lbs. 5% HNO_3 wash.

*See Section A of Appendix for details of operating procedure.
**Recommended in a letter from M. F. Acken to W. C. Kay (1-25-44).
***Conditions given in letter R. S. Apple to W. C. Kay (7-12-44). Details of the operating procedure given in Section A of the Appendix.

Two runs (charges 202 - 207) have been made using slugs with 35- instead of 20-mil aluminum jackets*, with no other change in the procedure. (This condition more closely approximates the Hanford ratio of Al to NaOH.) The column back-pressure increased somewhat, but remained below the usual level observed with three-batch charges of 20-mil slugs dissolved in the HNO_3-Hg mixture.

The time cycle for this operation has averaged about six hours as compared to about five hours for the previous HNO_3-Hg catalyzed procedure. Maximum column pressure drop observed on the runs using 20-mil jackets was two to three inches water. Product losses in these runs have been reported less than 0.1%, while plant data indicate that in cases where the sampler was well flushed out the loss in the HNO_3-Hg runs was 0.5% to 0.8%. These figures are open to some question, however, since (1) the same sampler is used for sampling the coating removal waste and the metal solution and, therefore, some cross-contamination is possible, and (2) quantitative separation of a small amount of product from a large amount of aluminum is difficult.

*Conditions for removal of 35 mil jackets given in letter from R. S. Apple to W. C. Kay (8-4-44).

METAL DISSOLVING

No difficulty has been experienced at Clinton with metal dissolving with either single or triple batches charged to the dissolver.* Runs 1 through 27 were dissolved as single batches. After Runs 28 and 29 (double batch), all batches have been dissolved, with a few exceptions, on the triple batch basis.** Advantage to be gained by multiple charge dissolving is mainly that of saving in time. The time required for dissolving a single batch under the original operating procedure ran, on the average, 18 hours. With multiple charging (three batches to the dissolver at a time) the time requirement runs, on average, as follows:

1st batch - 5 hours
2nd batch - 9 hours
3rd batch - 15 hours

The saving in time is due to the fact that a greater surface area is presented for attack by the dissolving acid on each batch of a multiple charge, than for one batch charged and dissolved singly. Also the aluminum jackets can be removed from three batches at once in about the same time as required for one batch.

It has been found that the product content of the metal solution changes from batch to batch on a triple charge due to the varying product content within the slugs. The percentage of the total product which is dissolved in each batch varies somewhat but averages about as follows:

1st batch - 39%
2nd batch - 33%
3rd batch - 28%

There is little difference, from the operating standpoint, between the two methods of dissolving. However, the reaction starts much more readily with the multiple charge and requires closer operational control at the beginning than does the single charge. During this period it is often necessary to shut off the steam to the dissolver coils to maintain the column pressure drop within limits experience has shown most desirable.

*For details of the operating procedure see Section A of the Appendix.
**Requested by TNX Technical Division. See memo F. B. Vaughan to W. C. Kay (2-8-44).

PRE-EXTRACTION TREATMENT OF METAL SOLUTION

The pre-extraction treatment of the uranyl nitrate solution with formic acid was originally introduced in the process to reduce oxidized product to the plus four state, and to decompose the excess nitric acid. It developed that there was very little oxidized product in the metal solution and that the dissolver operation could be controlled to hold the free nitric acid to a satisfactorily low value. The pre-extraction treatment was therefore discontinued; however, the waste losses in the extraction step increased to 10 - 20%. A study made by the Plant Assistance Group showed that the cause of the high waste losses is hydrazine and that it is destroyed by the nitrite formed in the decomposition of nitric acid with formic acid. The nitrite can also be obtained from sodium nitrite and so this was substituted for formic acid with satisfactory results. A discussion of the work on this problem with the supporting evidence on the conclusions is presented below.

The Role of Formic Acid and Nitrites

Summary

a. Analyses indicate that the high metal waste losses occurring in the absence of pre-extraction treatment cannot be explained on the basis of Pu VI being present.

b. A series of laboratory experiments have shown that of the possible side reaction products (hydroxylamine, hydrazine and hydrazoic acid) present in the metal solution, only hydrazine seriously interferes with $BiPO_4$ carrying of product.

c. Hydrazine in concentrations of 0.0002M to 0.0008M has been found in plant metal solution. This concentration of material does not interfere with laboratory extractions unless conditions are made critical by using a rapid (two minute) strike.

d. Using the rapid strike, easy differentiation between the rate of $BiPO_4$ carrying from untreated and formic treated plant metal solution is possible.

e. Nitrite is a specific reactant for hydrazine and may be obtained by the $HCOOH-HNO_3$ reaction or may be added as the Na or K salt.

f. The mechanism of hydrazine interference is probably that of reduction of the product to the plus three state where it is not satisfactorily carried on $BiPO_4$. Further work on this problem is being carried out by the chemistry sections.

g. Based on plant experience at Clinton Product level, either formic acid or sodium nitrite will be satisfactory for the Hanford plant metal solution pre-extraction treatment.

Effect of HCOOH Neutralization upon the Extraction Step

Early experiments with metal of very low product concentration indicated the possibility of oxidizing large fractions (up to 50%) of product during the metal dissolving step. Likewise, initial laboratory and semi-works results suggested that high HNO_3 concentrations in the UNH solution might be deleterious to extraction yield. Therefore, formic acid reduction at the end of the solution step was added to the process to (1) insure reduction of product, and (2) destroy the excess HNO_3 remaining after metal solution.

Experience obtained in operating the plant dissolver established a procedure which left the HNO_3 in the UNH solution at the end of the dissolving step very low. A comparison of metal waste losses with HNO_3 concentration formic acid neutralization failed to establish any correlation. (See Table I.)

TABLE I

Run Number	HNO_3 Concentration	Waste Loss	Run Number	HNO_3 Concentration	Waste Loss
65	0.0%	1.2%	78	0.0%	0.8%
66	0.0	0.6	79	0.0	4.3
67	0.0	0.6	80	0.7	0.7
68	0.0	0.9	81	0.45	1.5
76	0.0	1.7	82	0.0	2.0
77	0.0	1.3	83	0.33	4.4

Control analyses made on the dissolver solutions indicated varying, but usually very small, amounts of product in the oxidized state. The results of a number of such analyses are given in Table II.

TABLE II

Analysis of Unreduced Metal Solution for Oxidized Product

Plant Run Nos.	30	37	39	40	41	42	43	44	45	46	47	Ave.
% Pu Oxidized	0.6	0.6	1.0	0.9	1.1	1.2	0.8	1.2	0.4	1.7	0.6	0.9

The method used (fluoride precipitation, H_2O_2 reduction of the supernatant, fluoride precipitation) was checked against phosphate precipitation for reduced Pu with a $Bi(OH)_3$ precipitation for the oxidized fraction and also against phosphate precipitation, H_2O_2 reduction, fluoride precipitation, with excellent results. Product precipitates were taken through an oxidation-reduction cycle to eliminate background uranium counts and fission activity. More recent data obtained with the Berkley Method (Run 92) are in agreement with the results shown in this table.

On the basis of these data, formic acid was omitted from Run 61* (made at 55° C strike and digestion temperature) with the following results:

Extraction waste loss = 15.8%
Oxidized product in waste = 1.1% (by LaF_3 method)

Additional runs were made later (at 75° strike and digestion temperature) without formic acid neutralization with the following results:

TABLE III

Total and Oxidized Product in Metal Waste

Run Number	%HNO_3 in 40% UNH	Product in Metal Waste	
		Oxidized	Total
85	8.5	3.3%	14.5%
86	2.4	1.4%	14.6%
87	1.9	----	12.8%

These results indicate that the high waste losses associated with the omission of HCOOH result from incomplete product carrying rather than from oxidized product. The following results support this view:

TABLE IV

Extraction Conditions Compared with Oxidized Product and Total Product in Metal Waste

Run Numbers	Conditions of Extraction	Product in Metal Waste (Control Laboratory)	
		Oxidized	Total
**88	0.01M U^{+4} added to precipitator, 30 minute strike	1.9	12.1
**89	ditto	1.9	20.8
***91	0.05M HCOOH added to precipitator, 30 minute strike	0.8	3.8
***92	ditto	0.3	1.9
96-107	0.05M HCOOH added to dilution H_2O	2.3 (av.)	1.2 (av.)
****108	No HCOOH added to dilution H_2O	3.2	21.2
108 Waste	30 minute strike, 1/2 Bi^{+3}	---	17.9
108A Waste	0.05M HCOOH added, 30 minute strike	---	2.5
****109	No HCOOH added, 120 minute strike	1.4	20.9
109 Waste	0.05M HCOOH added, 30 minute strike, 1/2 Bi^{+3}	---	8.5

*Conditions for run outlined in letter from R. S. Apple to W. C. Kay (3-11-44).
**Conditions for runs outlined in letter from R. S. Apple to W. C. Kay (4-12-44).
***Conditions for runs outlined in letter from F. B. Vaughan to W. C. Kay (4-15-44).
****Conditions for runs outlined in letter from R. S. Apple to W. C. Kay (4-24-44).

The rates of carrier and product precipitation in Runs 107, 108 and 109 are shown in Figures 1, 2, and 3.

The high waste losses (10 - 20%) encountered in these trial runs (61, 85, 86, 87, 108, 109) focussed interest on the mechanism of the formic acid reaction. Further confirmation that these losses were not the result of oxidation was given by the failure of a U^{+4} pre-treatment (Runs 88 - 89) to produce results comparable to the formic treatment. Several hypotheses as to the mechanism whereby HCOOH pre-treatment exercises an effect on the rate of carrying have been proposed. Information obtained during a study of the formic reaction pointed to the existance of some "compound X" formed by a side reaction during metal solution which interfered with the carrying of product on $BiPO_4$ and which was removed during the HCOOH-HNO_3 reaction.

Rate of HCOOH Decomposition in Metal Solution and the Formation of Nitrite by HCOOH-HNO_3 Reaction

The initial indication of some "compound X" was noted in an investigation of the rate of decomposition of HCOOH during the pre-treatment period by a series of alkaline $KMnO_4$ and Ce^{+4} titrations to determine free HCOOH concentration; the presence of some reducing material other than HCOOH was indicated and its existance in the metal solution before pre-treatment was confirmed by Ce^{+4} titration in the absence of NO (qualitative test). NO was found in diluted metal solution (21 MR) during the HCOOH pre-treatment period (α-naphtaylamine test); its effect on $BiPO_4$ carrying was checked in the laboratory and found to be negligible. Data on the rate of formic decomposition are shown in Tables V and VI. The results of this study indicate:

(1) Most of the formic acid decomposes immediately after it is added to the metal solution with the dilution water.

(2) Decomposition of the formic acid does not produce an appreciable quantity of stable nitrite until H_2SO_4 is added. For a period after addition of H_2SO_4 the nitrite concentration increases as the HCOOH decreases.

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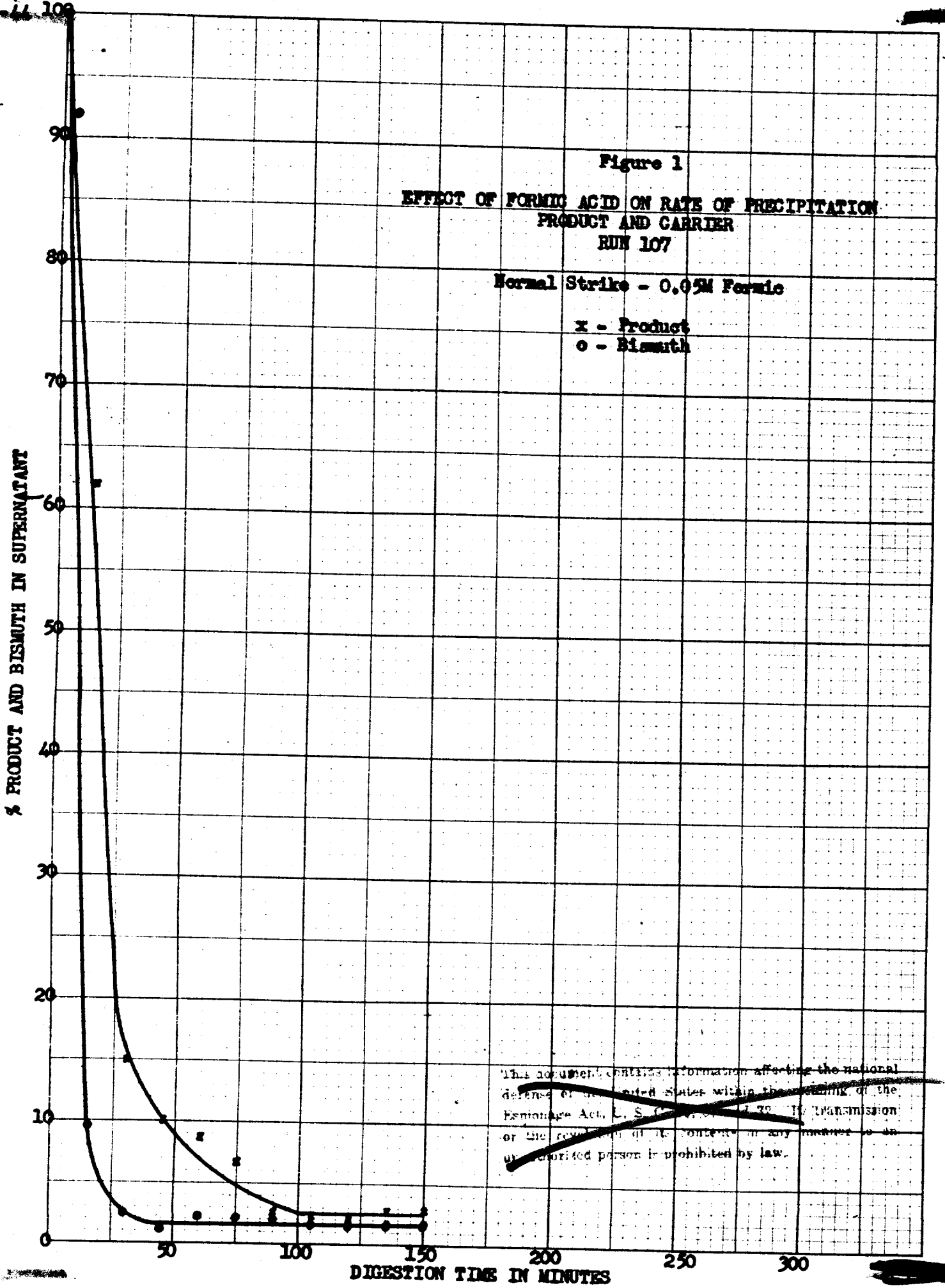

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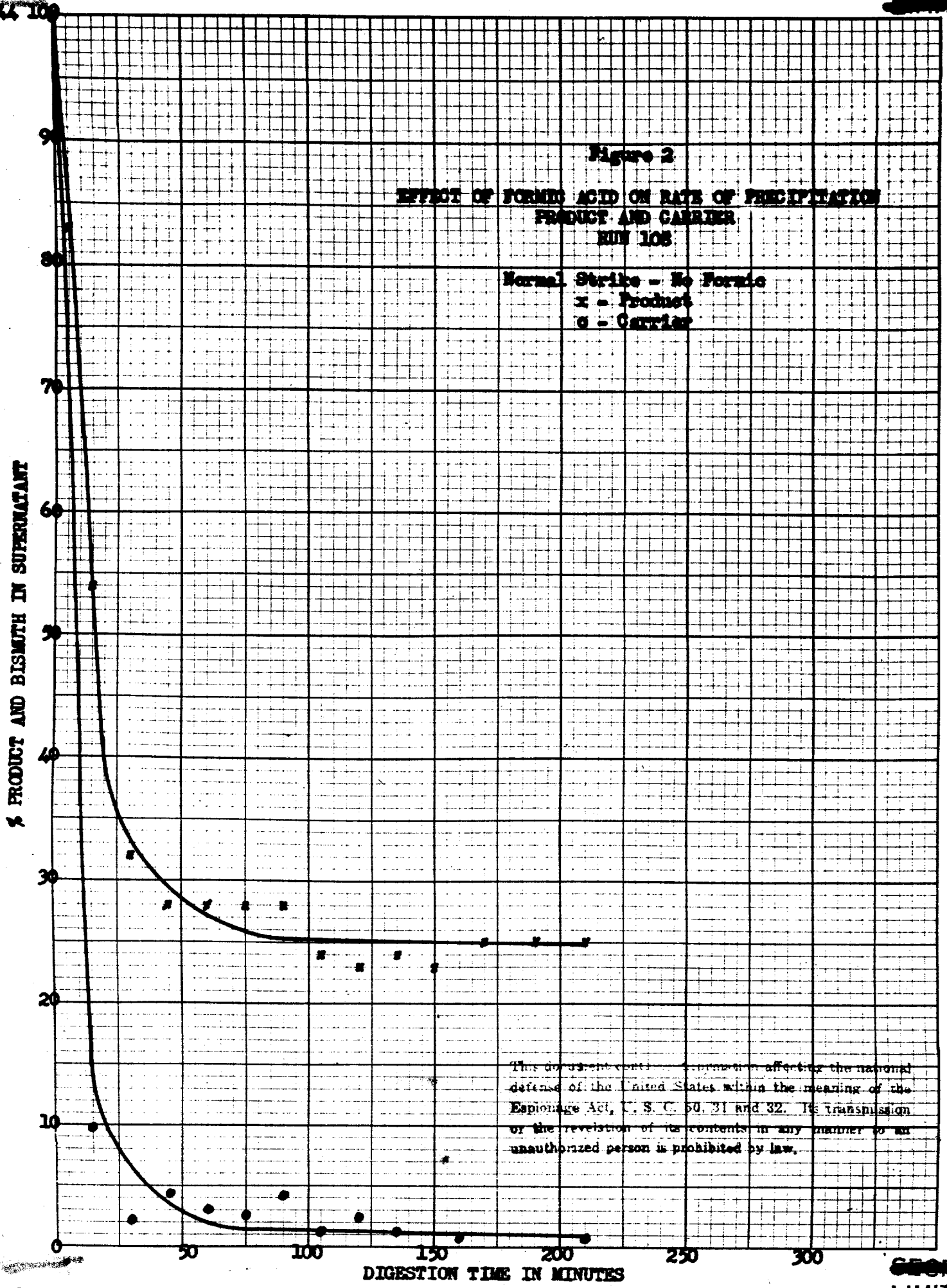

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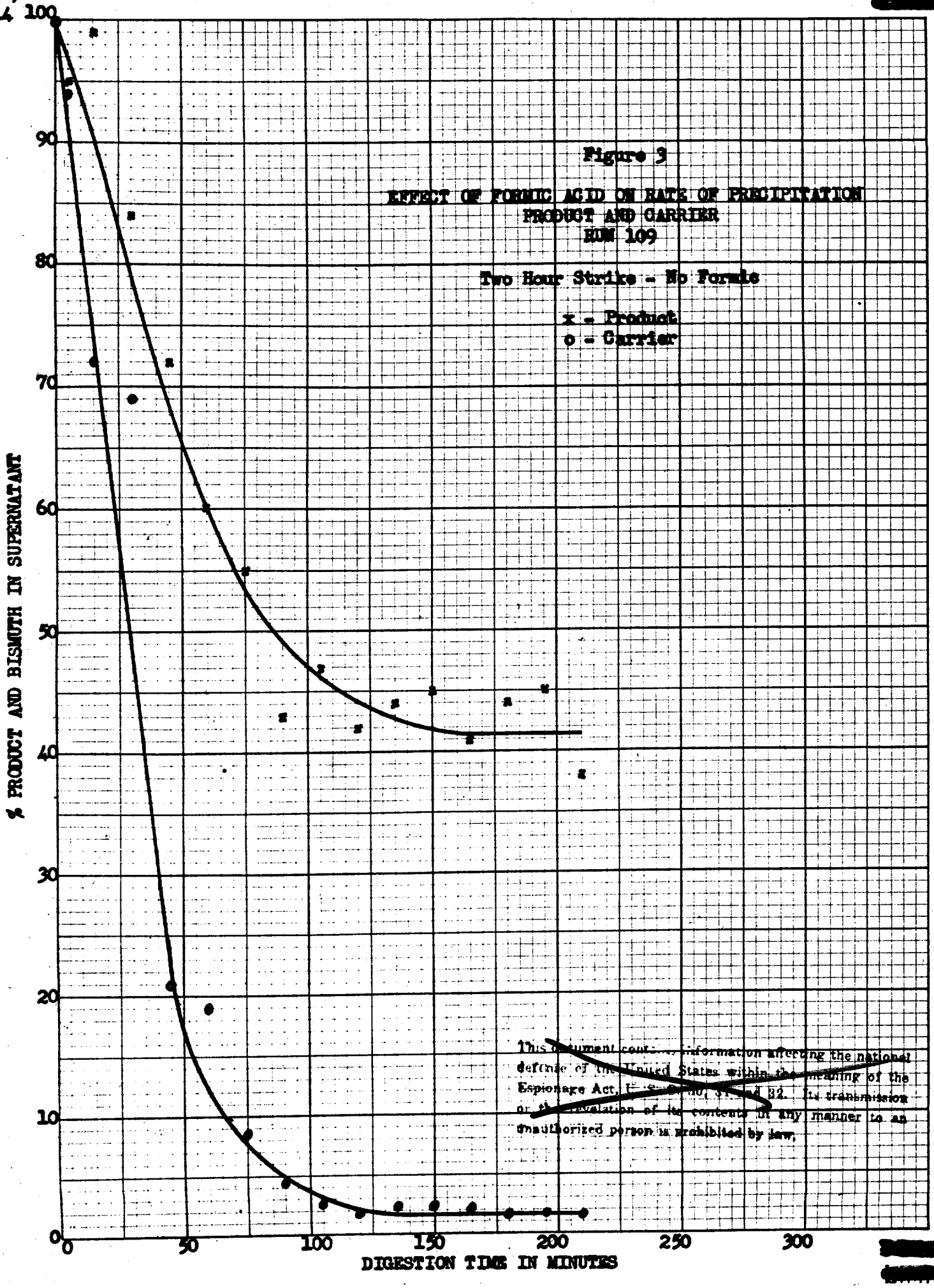

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TABLE V

FORMIC CONCENTRATION IN ZIRR SOLUTION

(Determined by difference between alkaline $KMnO_4$ and acid Ce^{+4} titrations)

Run Number	Formic Acid Added in Dilution Water	Formic Acid Found 30 Minutes After Dilution
90	7 lbs. (0.02M in 20% UNH)	1.68 lbs.
91	17 lbs. (0.05M in 20% UNH)	3.03 lbs.

TABLE VI

CONCENTRATION OF REDUCING MATERIALS IN METAL SOLUTION DURING EXTRACTION PRECIPITATION

(Reported as grams per liter HCOOH, 0.05M HCOOH - 20% UNH - pre-treatment)

Sample Time	Run 97			Run 98			Run 99		
	Alkaline $KMnO_4$	Ce^{+4}	Nitrite Test*	Alkaline $KMnO_4$	Ce^{+4}	Nitrite Test*	Alkaline $KMnO_4$	Ce^{+4}	Nitrite Test*
Dilution H_2O and HCOOH mixed with metal solution at 25° C.	0.592	0.069	Neg.	0.722	0.115	Trace	0.428	0.106	Tra
After H_2SO_4 addition agitated at 75° C.	0.418	0.147	Red.	0.358	0.161	Red.	0.358	0.179	Red
One hour after H_3PO_4 addition	0.364	0.308	Dark	0.262	0.161	Red.	0.346	0.290	Dar
Two hours after H_3PO_4 addition	0.161	?	Neg.	0.161	0.156	Trace	?	0.198	Ne

*Test not very sensitive in these solutions.

Laboratory Extraction Conditions Which Differentiate Between Plant Treated And Untreated Metal Solution

The scale of laboratory experiments with plant 21BR solution is limited by the radiation hazard and shielding requirements. However, the Plant Assistance Group operated at full Clinton plant level on the 100 cc. scale, and Chemistry Section I performed numerous extractions on the 1000 cc. scale. All laboratory extractions on either scale using plant procedure (either 30 minute or two hour direct strike) with untreated 11B solution diluted to 20% UNH, gave waste losses of less than 4.0% after two hours' digestion.

The Plant Assistance Group found that on the 100 cc. scale, conditions are made critical by using a short (2 minute) direct strike in 20% UNH followed by the usual two hour digestion. Varying waste losses were obtained from different batches of plant metal solution. A marked difference between rates of $BiPO_4$ carrying was found in plant treated and untreated metal solution. Rate of precipitation curves were obtained using semi-micro scale sampling (See Figure 4).

Correlation of Potentiometric Ce^{+4} Titrations of 11 B with Rate of Carrying by $BiPO_4$

The data on Runs 85, 87, 89, 90 and 91 as reported above indicated that a small amount of reducing material is in the metal solution before any pretreatment agent is added. Investigation in several later runs showed that the titratable reducing material in the 40% UNH is of two forms: one is removed by aeration of the solution or aging for a period of days (probably dissolved gases), while the other is quite stable. Good correlation has been obtained between the concentration of the stable material (aerated samples) and the corresponding rate of carrying on $BiPO_4$ from the untreated metal solution from Runs 158, 159, 160 (one dissolver charge), and 185, 186, 187. See Table VII and Figures 5 and 6. No correlation has been obtained between the concentration of stable reducing agent and dissolving time, temperature, residual HNO_3, or number of the batch (three batches are charged at once).

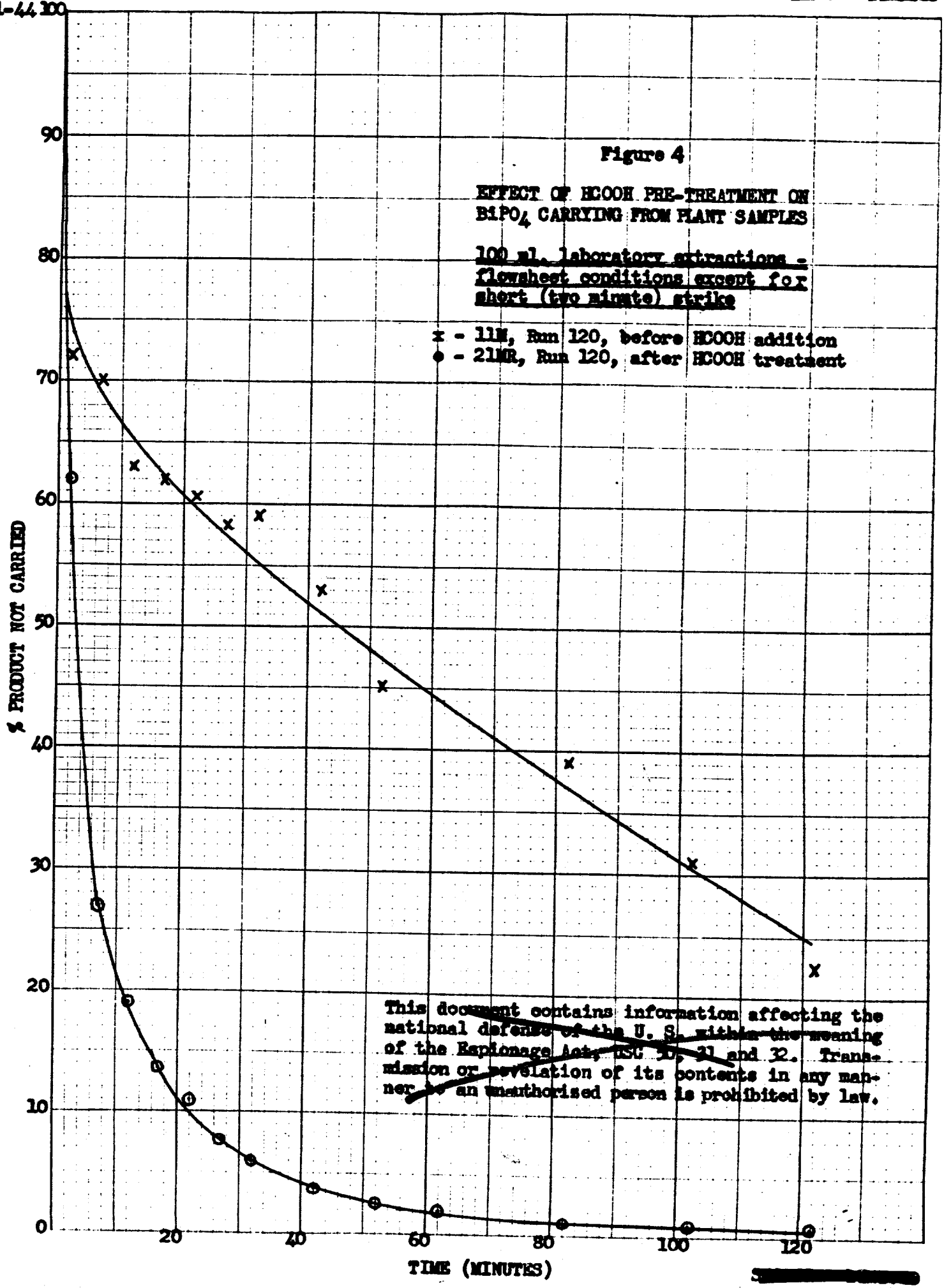

Figure 4

EFFECT OF HCOOH PRE-TREATMENT ON $BiPO_4$ CARRYING FROM PLANT SAMPLES

100 ml. laboratory extractions - flowsheet conditions except for short (two minute) strike

x - 11M, Run 120, before HCOOH addition
● - 21MR, Run 120, after HCOOH treatment

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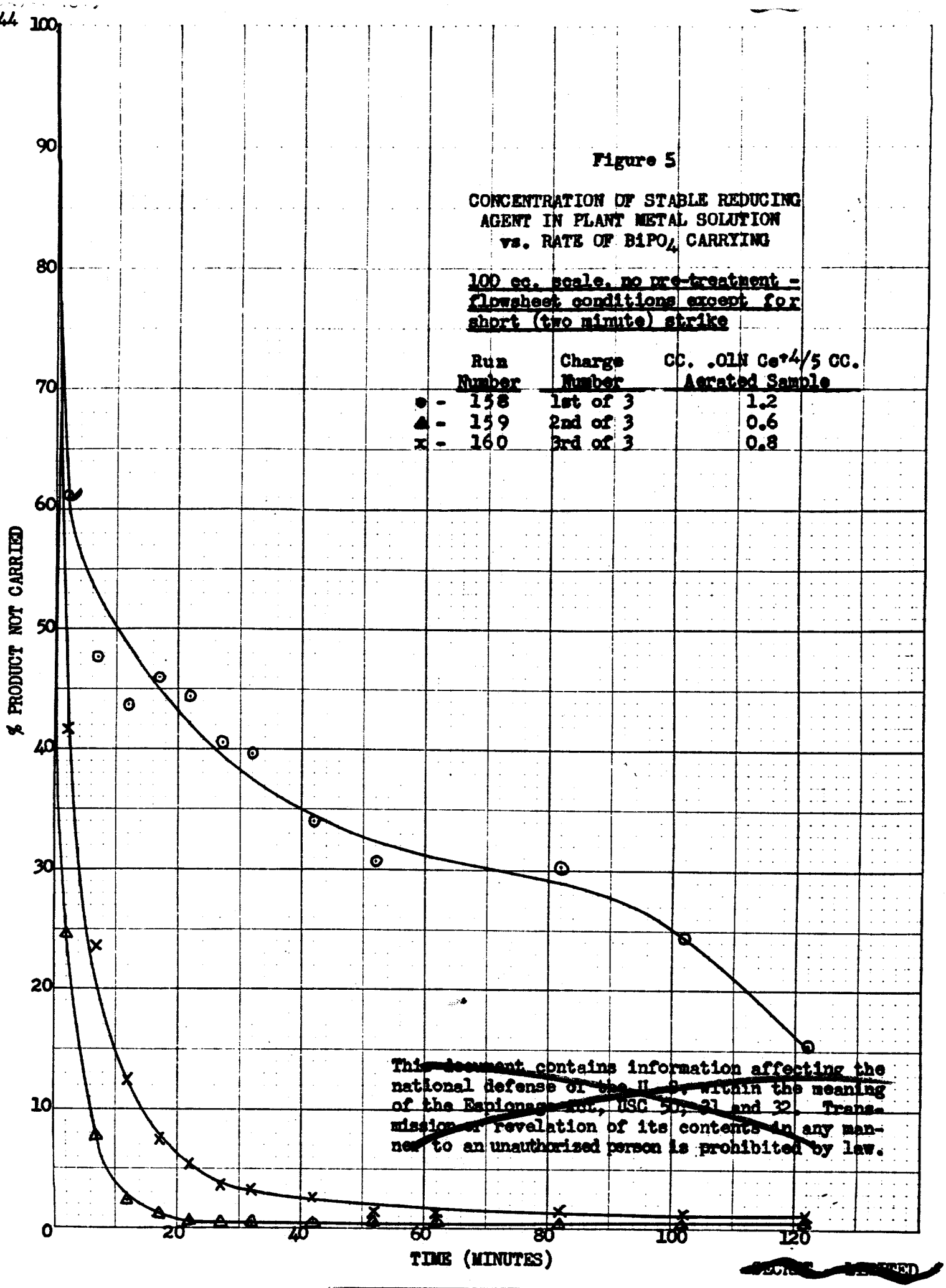

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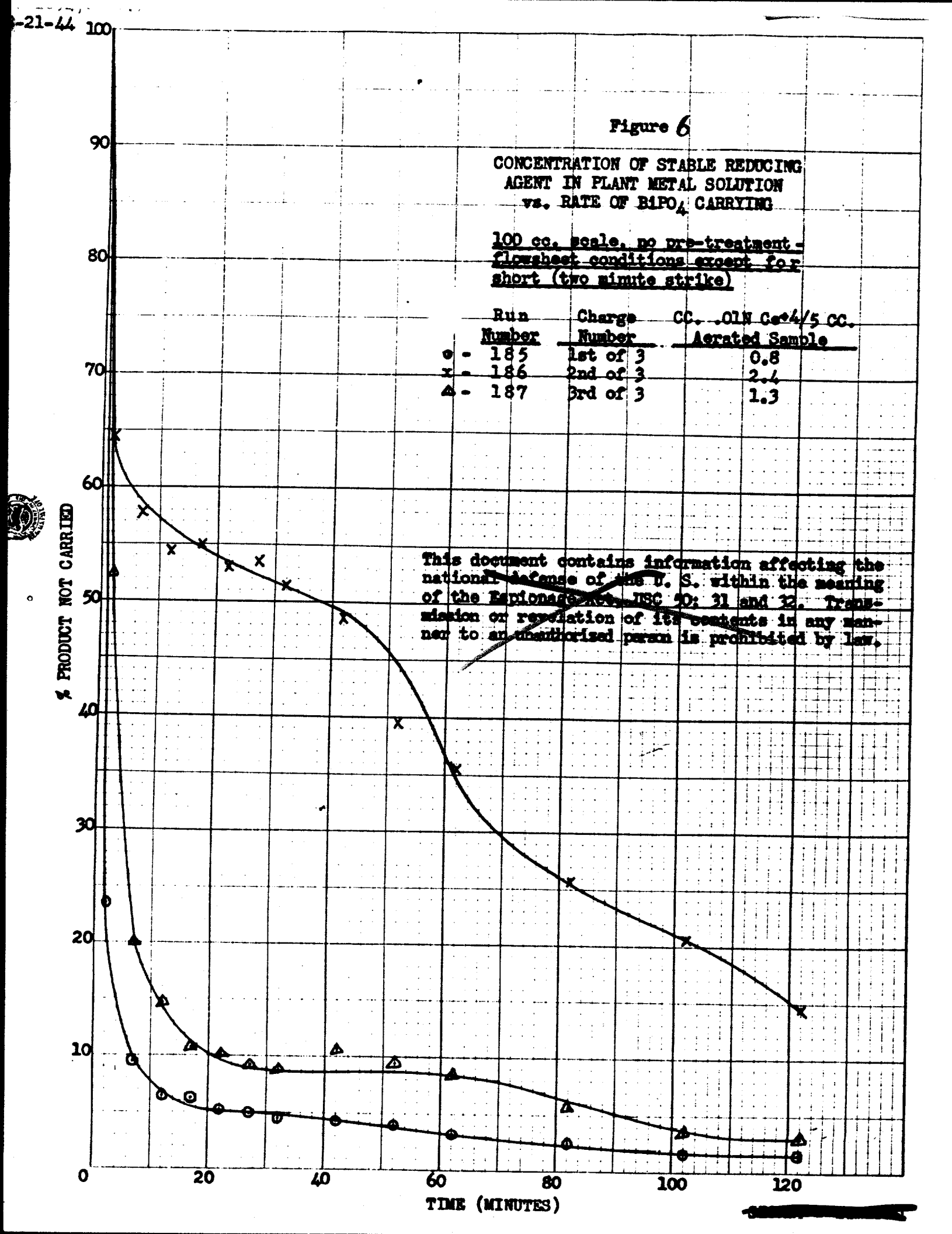

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TABLE VII

Concentration of Compound X in 11M vs. Metal Waste Losses
(100 cc. scale extraction, 2 minute strike, otherwise flowsheet conditions)

Run Nos.	Charge Nos.	0.01N Ce+4 Potentiometric Titration (Aerated Samples)	Concentration as N_2H_4	% Waste Loss
158	1st of 3	1.2 cc/9 cc. sample	0.00038M	15.3
159	2nd of 3	0.6	0.00019	0.5
160	3rd of 3	0.8	0.00026	1.1
185	1st of 3	0.8	0.00024	1.6
186	2nd of 3	2.7	0.00077	14.5
187	3rd of 3	1.3	0.00042	3.0

Effect of Possible Side Reaction Products from Metal Solution on $BiPO_4$ Carrying

A survey of possible reducing materials other than nitrogen oxides which might be produced in the metal solution step was made by the Plant Assistance Group. The three most logical possibilities were hydroxylamine, hydrazine and hydrazoic acid. Laboratory extraction studies were made to check the effect of small concentrations of these materials on $BiPO_4$ carrying. Hydroxylamine and hydrazine were added as the sulfates; hydrazoic acid was produced by addition of sodium azide. Hydroxylamine produced no carrying difficulties; hydrazoic acid produced a slight effect on rate of carrying, but hydrazoic acid is so volatile that at the end of a two-hour digestion, waste losses were normal. Only hydrazine produced a marked effect on carrying efficiency.

TABLE VIII

Effect of Possible Side Reaction Products
of Metal Solution on $BiPO_4$ Carrying

(Laboratory extractions 100 cc. scale; product added to inactive UNH plus tracer, 2 minute strike, 2 hour digestion; otherwise flowsheet conditions)

Date	Material Added	Concentration	Metal Waste Loss
4-26-44	None	Control	1.0%
	NH_2OH	0.05M	0.5
	HN_3	0.01M initially plus periodic addition to give total concentration of 0.07M	2.6
	N_2H_4	0.05M initially plus periodic addition to give total concentration of 0.1M	94.0
	N_2H_4	0.01M	64.0
	N_2H_4	0.004M	23.0
	N_2H_4	0.001M	5.0

Some investigation of the mechanism whereby hydrazine inhibits the carrying of product on $BiPO_4$ has been made, and at present it is being studied by the Chemistry Sections. Using the spectro-photometer, Chemistry Group I found that 0.1 hydrazine would maintain product 100% in the plus 3 state for three hours at 75° C. The carrying of product in the plus 3 state by $BiPO_4$ is poor and there is some question as to whether it is carried at all unless it undergoes oxidation to the plus 4 state. The presence of product in the plus 3 state might explain the high extraction waste losses which occur when pre-extraction treatment is omitted.

Identification of N_2H_4 in Metal Solution

Initial analytical efforts to identify N_2H_4 in plant metal solution were not successful (ferric chloride drop test). The Analytical Division obtained a more sensitive reagent (o-hydroxybenzaldehyde) which will detect hydrazine in the concentrations indicated by Ce^{+4} titrations. Addition of this reagent to plant 11M (diluted to 10% UNH) produced a cloudiness, which could be centrifuged out. A sufficient quantity of precipitate was obtained from 400 cc. of 11M (Runs 202 - 205) to allow centrifugation, drying, recrystallization from alcohol and a melting point determination to be made. The melting point was 211.5° C, compared to 212.5° C for a similar precipitate thrown down in inactive UNH solution to which hydrazine sulfate had been added. A precipitate obtained from a distilled water solution of C.P. hydrazine sulfate with o-hydroxybenzaldehyde recrystallized from alcohol melted at 212.5° C. The melting point given in the literature is 213° C.* A mixed melting point of material obtained from 11M and from C.P. materials melted at 211.5° C.

Mechanism of Formic Acid and Nitrite Treatments

It has been found in the plant that nitrite is a product of the formic-nitric reaction and laboratory experiments have shown that the formic treatment is of no value unless this reaction occurs. The presence of an appreciable quantity of hydrazine (0.01M) inhibits the formic-nitric reaction, but it can be made to go at 95° C. after an induction period if the nitric concentration is high (10%). Addition of the extraction concentration of H_2SO_4 to the solution decreases the induction time. With laboratory procedure using 0.01M N_2H_4 and 5% free HNO_3 plus the H_2SO_4, reaction of 1.5 mols HCOOH per mol HNO_3 resulted in a metal waste loss of 0.6% while the control run with no formic gave a 75% loss. A similar effect is obtained with nitrite pre-treatment of a solution (inactive UNH, no free HNO_3) containing hydrazine as shown in Table IX below.

*Meiffer and Fitzner, J. Pract. Chem., 145, 243-256 (1936), C.A., 30, 5197.

TABLE IX

Effect of KNO_2 Pre-Treatment of Metal Solution Containing N_2H_4 on $BiPO_4$ Carrying

(50 cc. scale, glass apparatus, 2 minute strike)

Sample	Product Not Carried	
	0.01M N_2H_4	0.01M N_2H_4 + 0.025M KNO_2
Starting solution	100.0%	100.0%
15 minute digestion	61.0	----
30 " "	58.0	1.7
45 " "	60.0	1.8
60 " "	60.0	2.1
90 " "	59.0	1.4
120 " "	62.0	0.9

The KNO_2 was added to the cold 20% UNH containing N_2H_4, the solution heated to 75° C, and the precipitation carried out.

The reaction between N_2H_4 and HNO_2 can be written as follows:

$$N_2H_4 + HNO_2 \longrightarrow HN_3\uparrow + 2H_2O$$

Substitution of $NaNO_2$ for HCOOH in the Plant

Laboratory tests were made to compare the efficiency of the formic pre-treatment with nitrite pre-treatment on the 100 cc. scale. Low waste losses were obtained with only 0.026M KNO_2. (See Figure 7). A study of the effect of KNO_2 concentration indicated that 0.05M was more satisfactory (See Figure 8) and 0.1M was recommended for plant use.* Formic acid was replaced by 0.1M $NaNO_2$ added with the dilution water to the metal solution in Cell 2. The 20% UNH solution was agitated for thirty minutes at 40° C, and heated to 75° C before addition of the H_2SO_4, Bi^{+3}, etc. The average metal waste loss for the first ten plant runs using $NaNO_2$ (166 - 175) was 1.6%, and the average waste loss for the preceding ten runs using HCOOH (156 - 165) was 1.6%. Other factors affecting metal waste losses (W fission products, addition to H_2SO_4 to the dissolver) will be discussed later. The rate of precipitation of product in plant Run 168 ($NaNO_2$ treated) as compared to Run 134 (HCOOH treatment) is shown in Figure 9.

Some recent fluctuations in waste losses (1-4%) indicate that experiments should be carried out in the plant to determine optimum nitrite concentration and treatment temperature. The rate of $NaNO_2$ decomposition in Run 192 is shown in Table X.

*Addition methods for substitution of $NaNO_2$ for HCOOH given in letter from R. S. Apple to L. C. Kay (6-22-44).

CN-1894, CN-1879
8-22-44

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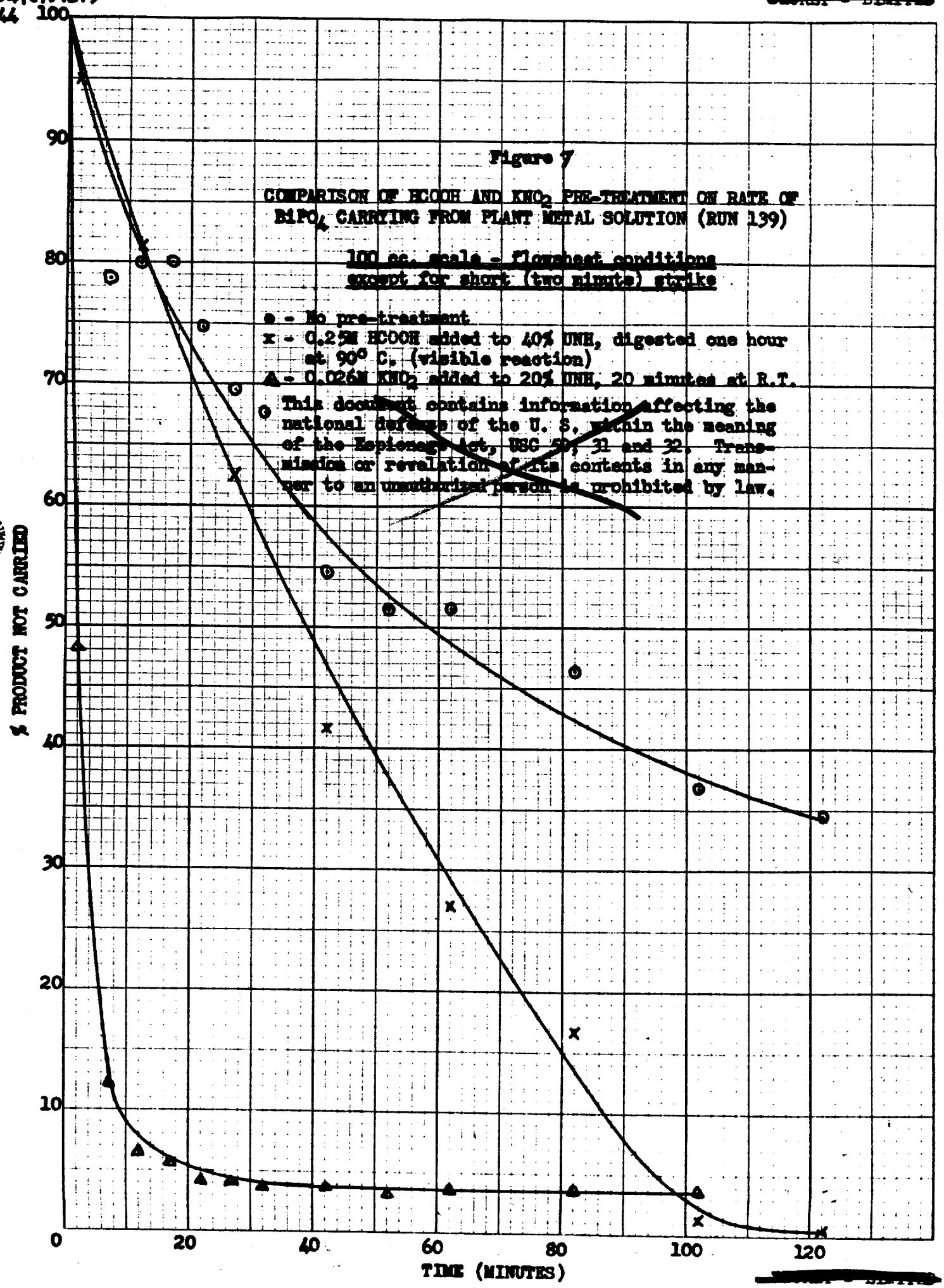

Figure 7

COMPARISON OF HCOOH AND KNO_2 PRE-TREATMENT ON RATE OF $BiPO_4$ CARRYING FROM PLANT METAL SOLUTION (RUN 139)

100 cc. scale - flowsheet conditions except for short (two minute) strike

● - No pre-treatment
x - 0.25M HCOOH added to 40% UNH, digested one hour at 90° C. (visible reaction)
▲ - 0.026M KNO_2 added to 20% UNH, 20 minutes at R.T.

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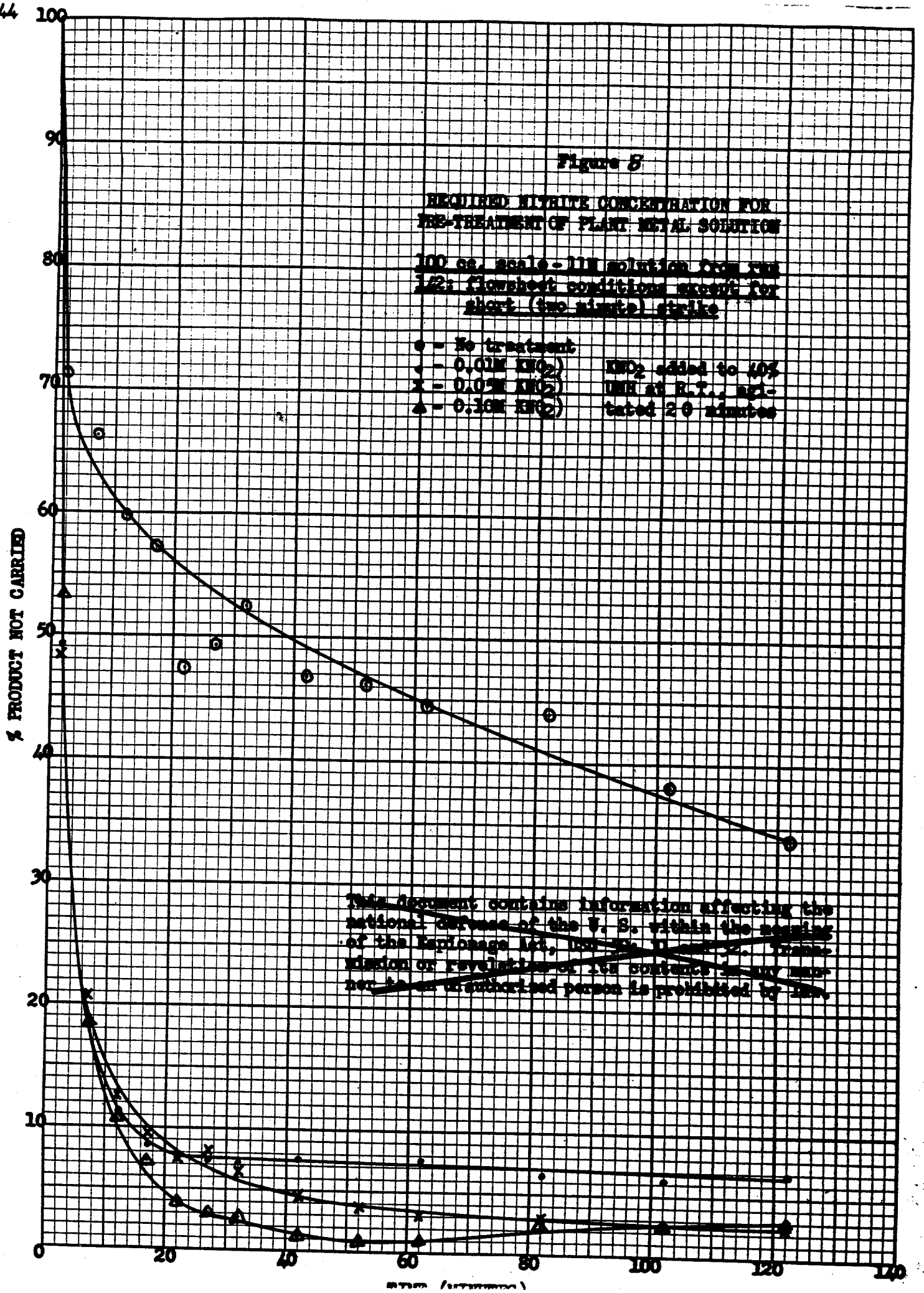

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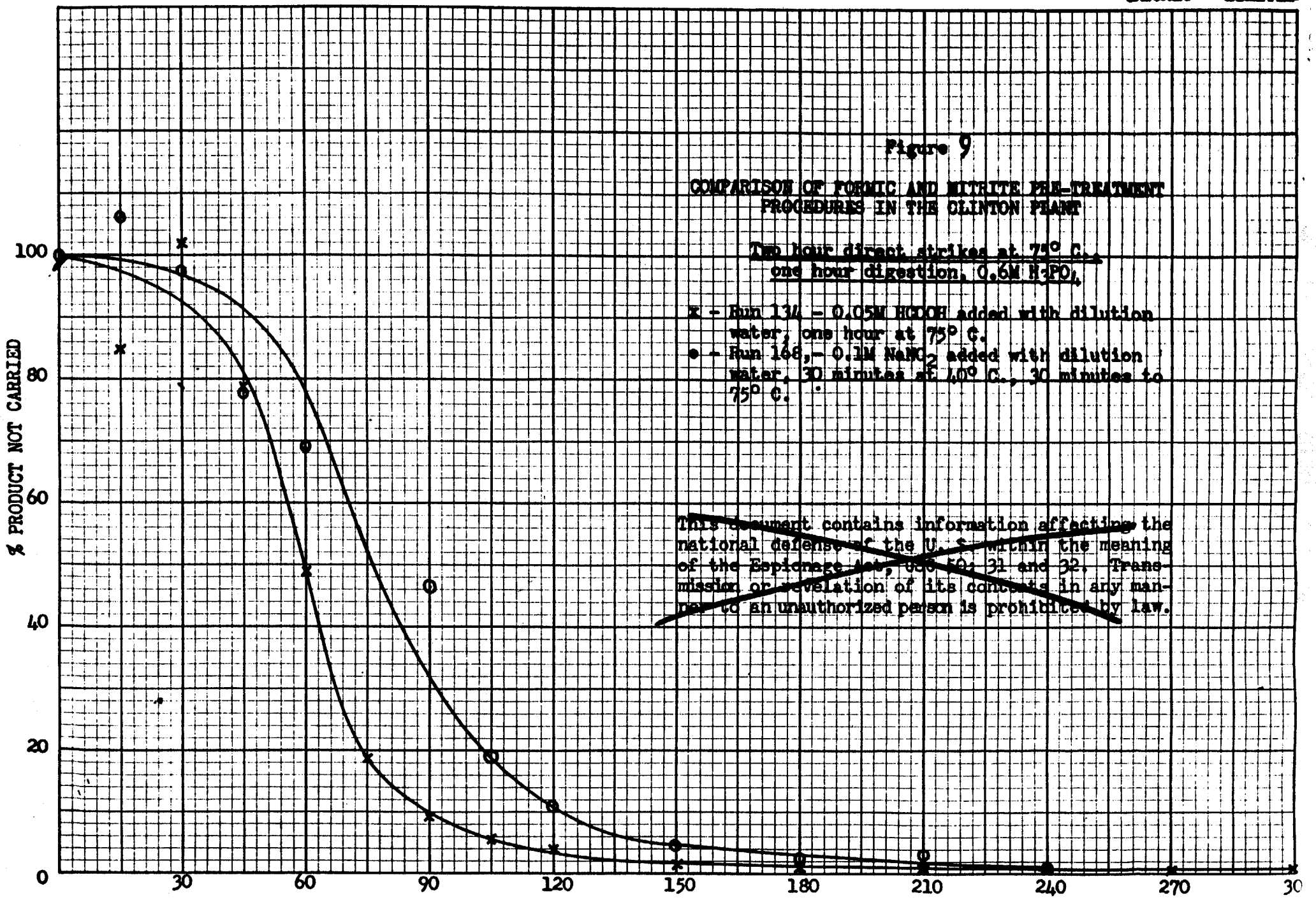

Figure 9

COMPARISON OF FORMIC AND NITRITE PRE-TREATMENT PROCEDURES IN THE CLINTON PLANT

Two hour direct strikes at 75° C., one hour digestion, 0.6M H_3PO_4

x - Run 134 - 0.05M HCOOH added with dilution water, one hour at 75° C.

● - Run 168,- 0.1M $NaNO_2$ added with dilution water, 30 minutes at 40° C., 30 minutes to 75° C.

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TABLE X

RATE OF DECOMPOSITION OF $NaNO_2$ IN 20% UNH - RUN 192

Sample	Conditions	Temperature	% Total Product Oxidized	% Product Not Carried	Molarity $NaNO_2$	% $NaNO_2$ Remaining
11M	Before jetting to 21	42° C.	0.7	------	------	------
21MR	Diluted in H_2O $NaNO_2$ added to UNH in 21	40	---	------	0.079	64
21MR	After 30 minutes	40	2.1	------	0.062	51.
21MR	Heated to 75° C.	75	?	------	0.027	22.
21MR	H_2SO_4 added	75	2.3	100.	0.018	15.
23MW	Middle of strike	75	---	------	0.010	9.3
23MW	End of strike	75	0.23	21.	0.005	4.6
23MW	End digestion	75	0.18	6.0	0.0032	2.9
23MW	End cooling	45	0.63	4.4	0.0026	2.5
23MS	Plant waste	--	---	2.3	------	------

EXTRACTION STEP

The initial separation between the product and uranium is made in the extraction step. This step has given satisfactory recovery of product during all of the operation of the Clinton plant except for losses caused by omitting the pre-extraction treatment as discussed in the preceding section. A number of process variables have been studied in order to obtain information on the process conditions proposed for Hanford. The result of these studies are presented in the following pages.*

Effect of Variation of Temperature During Strike and Digestion Period

In order to determine the effect of digestion temperature on yield losses in the extraction step, special runs were made in the plant in which the temperature of digestion was decreased from 75° C to 55° C in 10° increments.** Samples were taken at frequent intervals from Cell 2 precipitator tank, centrifuged in the laboratory to remove the solids and the supernatants analyzed for product and bismuth. The results of these tests are shown in Table XI and Figures 10, 11 and 12.

TABLE XI

Sample Time	Run 79 (75° C)		Run 54 (65° C)		Run 58 (55° C)	
	Product	Bismuth	Product	Bismuth	Product	Bismuth
0 min.	100. %	100. %	100. %	100. %	100. %	100. %
5 min. (1/6 H_3PO_4 in)	92. %	100. %	117. %	81. %	91. %	80. %
15 min. (1/2 H_3PO_4 in)	45. %	22. %	46. %	50. %	23. %	12. %
30 min. (all H_3PO_4 in)	12.%	1.5%	15. %	2.1%	20. %	5.0%
15 min. digestion	11. %	1.4%	9.9%	1.9%	8.6%	2.0%
30 min. digestion	5.4%	0.6%	7.9%	2.4%	6.9%	4.9%
45 " "	1.8%	0.7%	3.9%	1.1%	13.3%***	9.3%
60 " "	1.7%	0.8%	3.5%	1.2%	8.3%***	5.5%
75 " "	1.6%	0.8%	2.8%	1.1%	6.5%***	5.3%
90 " "	1.4%	0.8%	2.5%	1.1%	4.5%	7.7%
120 min. digestion	0.7%	0.7%	1.9%	1.1%	3.2%	4.8%
150 " "	0.6%	0.6%	1.3%	1.0%	2.2%	1.2%
180 " "	1.2%	0.6%	1.2%	1.1%	1.6%	3.6%
After two-hour cooling	1.1%	0.6%	----	----	----	----
23MS	0.75****	---	0.8%	----	1.1%	----

*The operating details for the extraction step are given in Section A of the Appendix. A graph of the extraction waste losses with notes on the process changes is given in Section C of the Appendix.

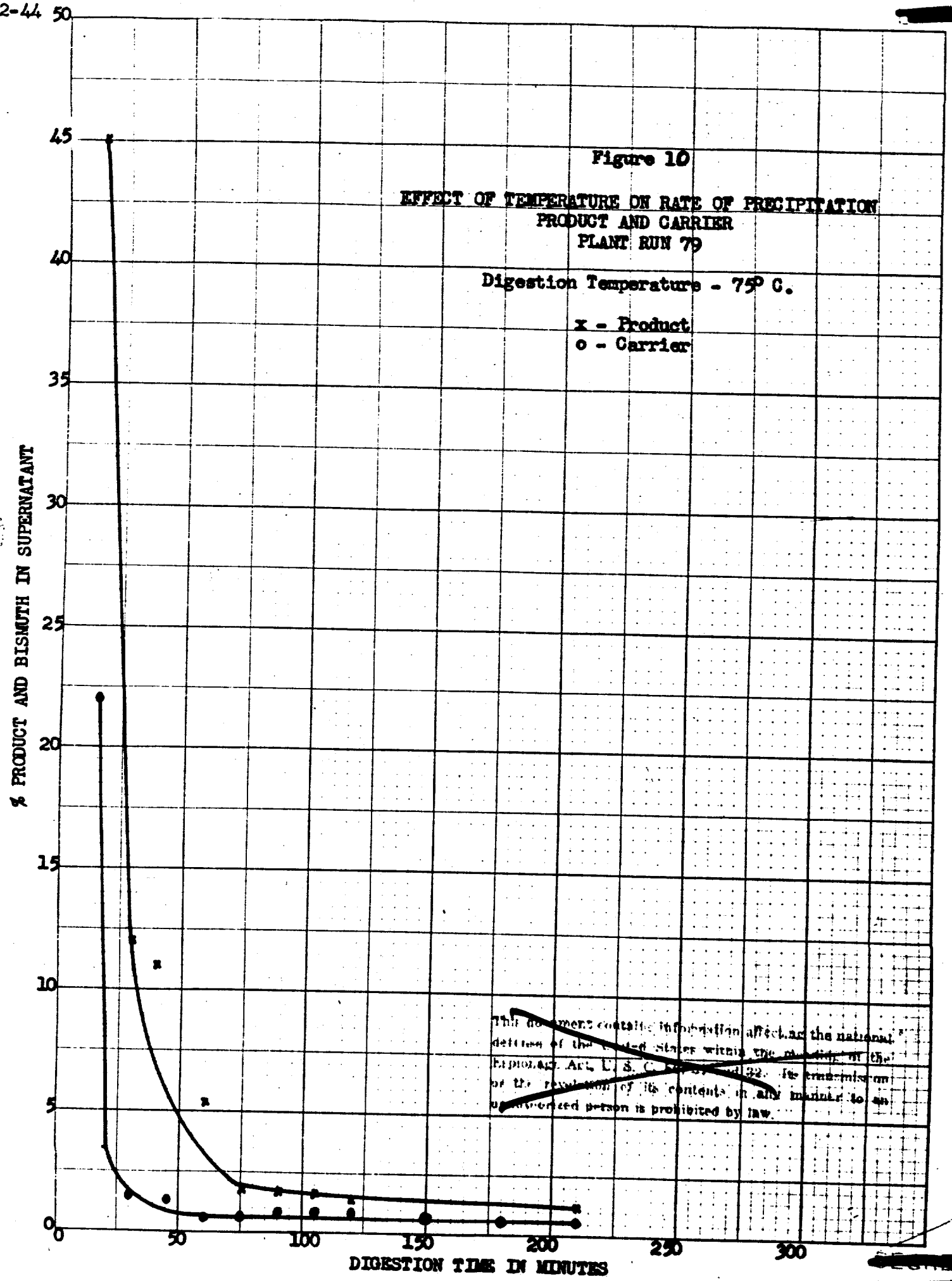
**Procedure recommended by R. S. Apple in letter to W. C. Kay (3-2-44).

***Power failure - no agitation on tank.

****23MS.

6-2-44

[redacted]



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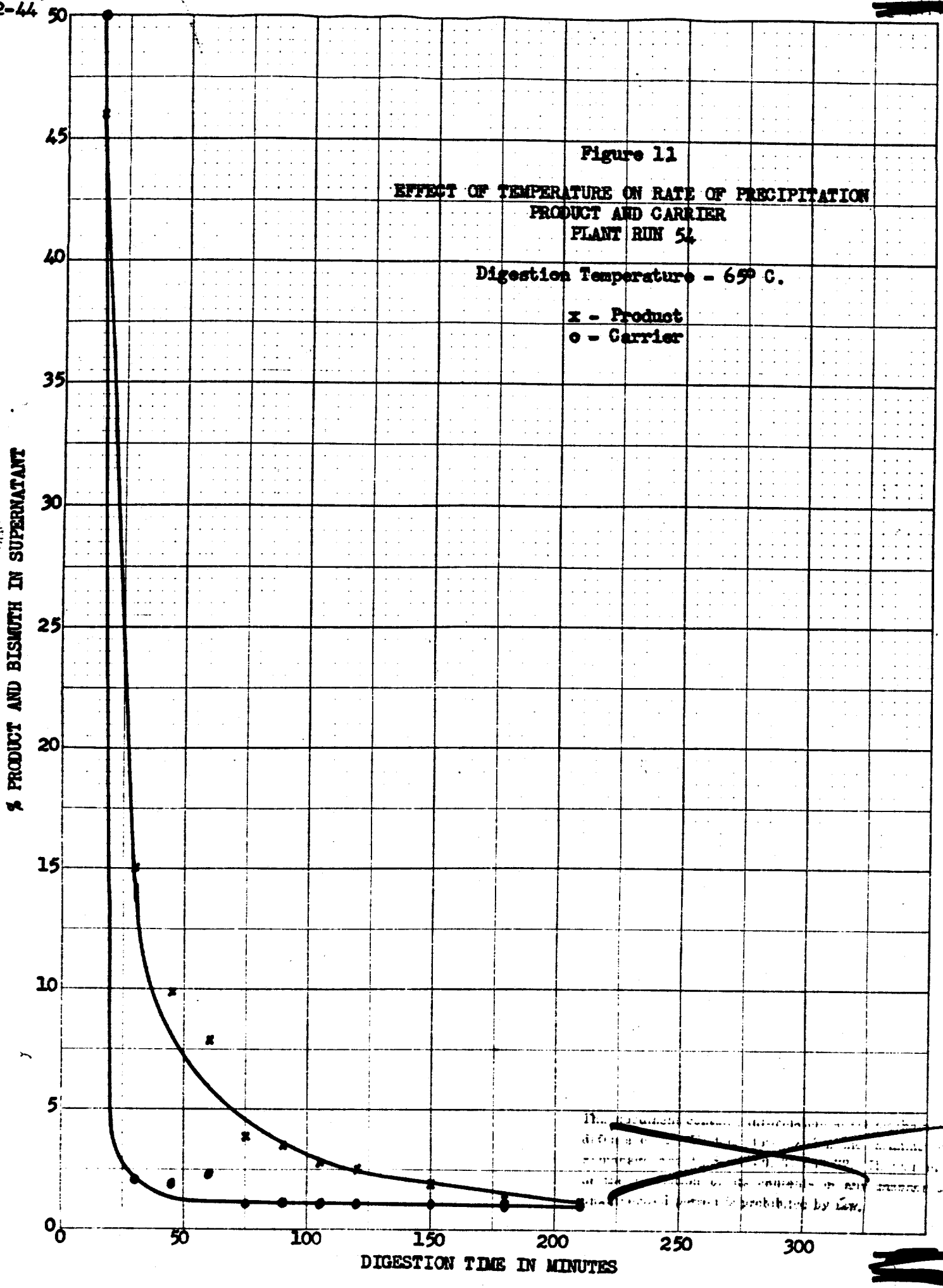

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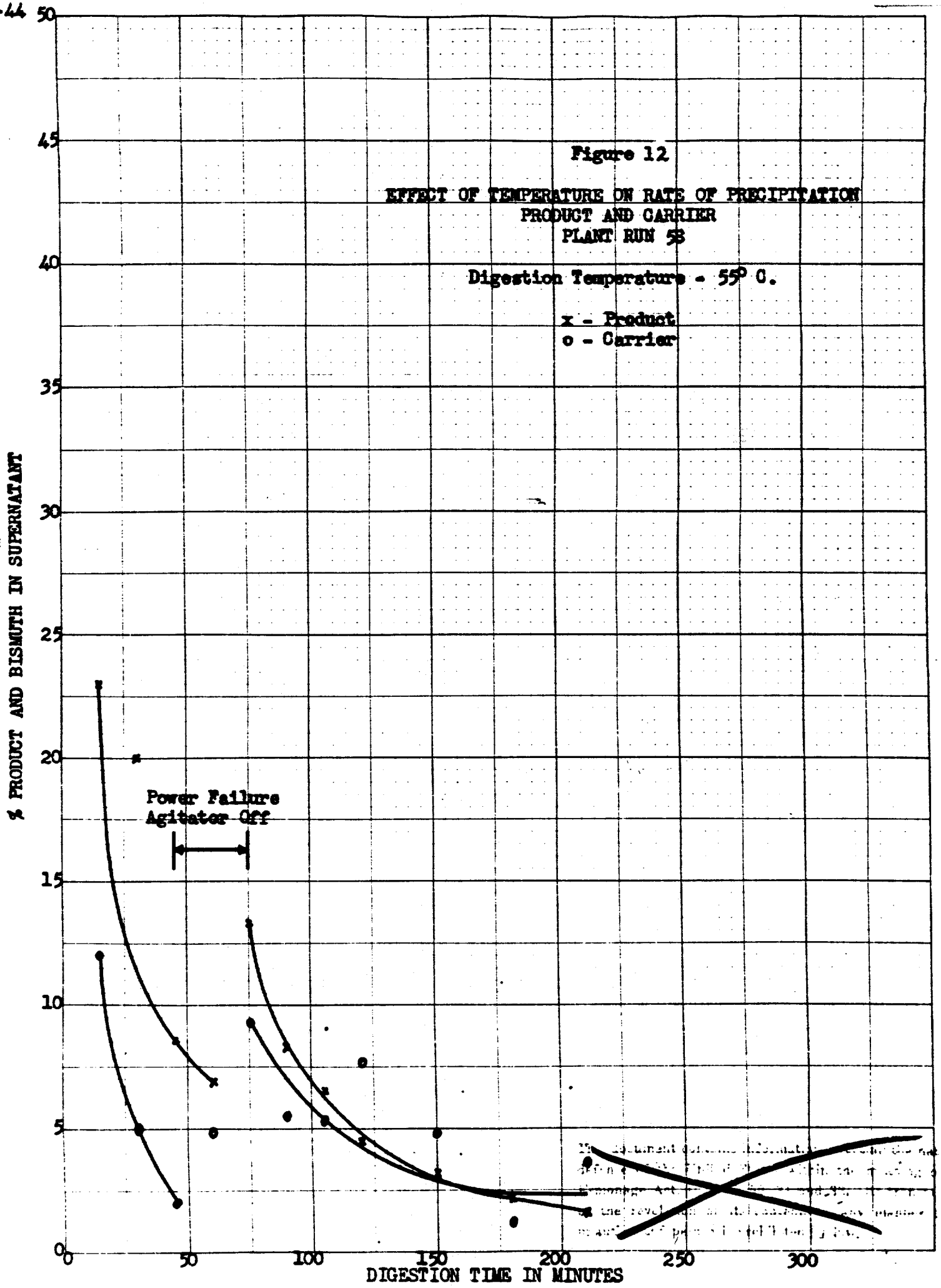
Figure 12
EFFECT OF TEMPERATURE ON RATE OF PRECIPITATION
PRODUCT AND CARRIER
PLANT RUN 58
Digestion Temperature - 55° C.
x - Product
o - Carrier
Power Failure
Agitator Off
% PRODUCT AND BISMUTH IN SUPERNATANT
DIGESTION TIME IN MINUTES
0
5
10
15
20
25
30
35
40
45
50
0
50
100
150
200
250
300

Four normal runs were made at the 65° strike and digestion temperature and three at the 55° temperature. Average waste losses and decontamination factors are given in Table XII. On the basis of the average waste losses and decontamination factors, decreasing the strike and digestion temperature to 55° had little effect on the efficiency of the extraction step.

TABLE XII

Run Numbers	Strike and Digestion Temperature	Average Waste Loss	Decontamination Factors*
50-53	75° C	1.3%	13.6, 5.9, 6.4, 10.9
54-57	65° C	1.0%	16.7, 24.**, 36., 13.3
58-60	55° C	1.7%	13.7, 24., 17.6
62-65	75° C	1.1%	14., 9.3, 15.3, 12.3

Comparison of Thirty Minute and Two Hour Direct Strikes

The precipitation time on the extraction step was extended from thirty minutes to two hours and the digestion time was reduced from two hours to one hour starting with Run 130.*** Laboratory work at Clinton product concentration had indicated that extraction waste losses decreased as the striking time increased, although the effect of variation in the striking time was not great. Similar runs at [illegible] product concentration greatly magnified the effect of strike time giving a reduction in waste loss from 10 - 20% for thirty minute striking time to 1 - 2% for two hour striking time (CN-1870). Data from a study of product and carrier behaviour during the strike show:

a. In the short thirty minute strike the rate of carrier precipitation is very rapid and a large portion of the product is carried on a preformed $BiPO_4$ precipitate.

b. In the long two hour strike the rate of carrier and product precipitation are approximately equal and the major portion of the product is carried by a coformed $BiPO_4$ precipitate.

No marked change was noted in plant extraction waste losses as a result of change to a two hour strike. Improved overall decontamination resulted from the change. Comparative data are given in Table XIII. Figure 13 shows the relative rate of product precipitation in plant Run 107 (thirty minute strike) and Run 130 (two hour strike).

*These changes in decontamination factors were not reflected in material entering Room D.
**First run after equipment clean-out.
***Conditions for runs given in letter from E. S. Apple to E. C. Kay (5-26-44).

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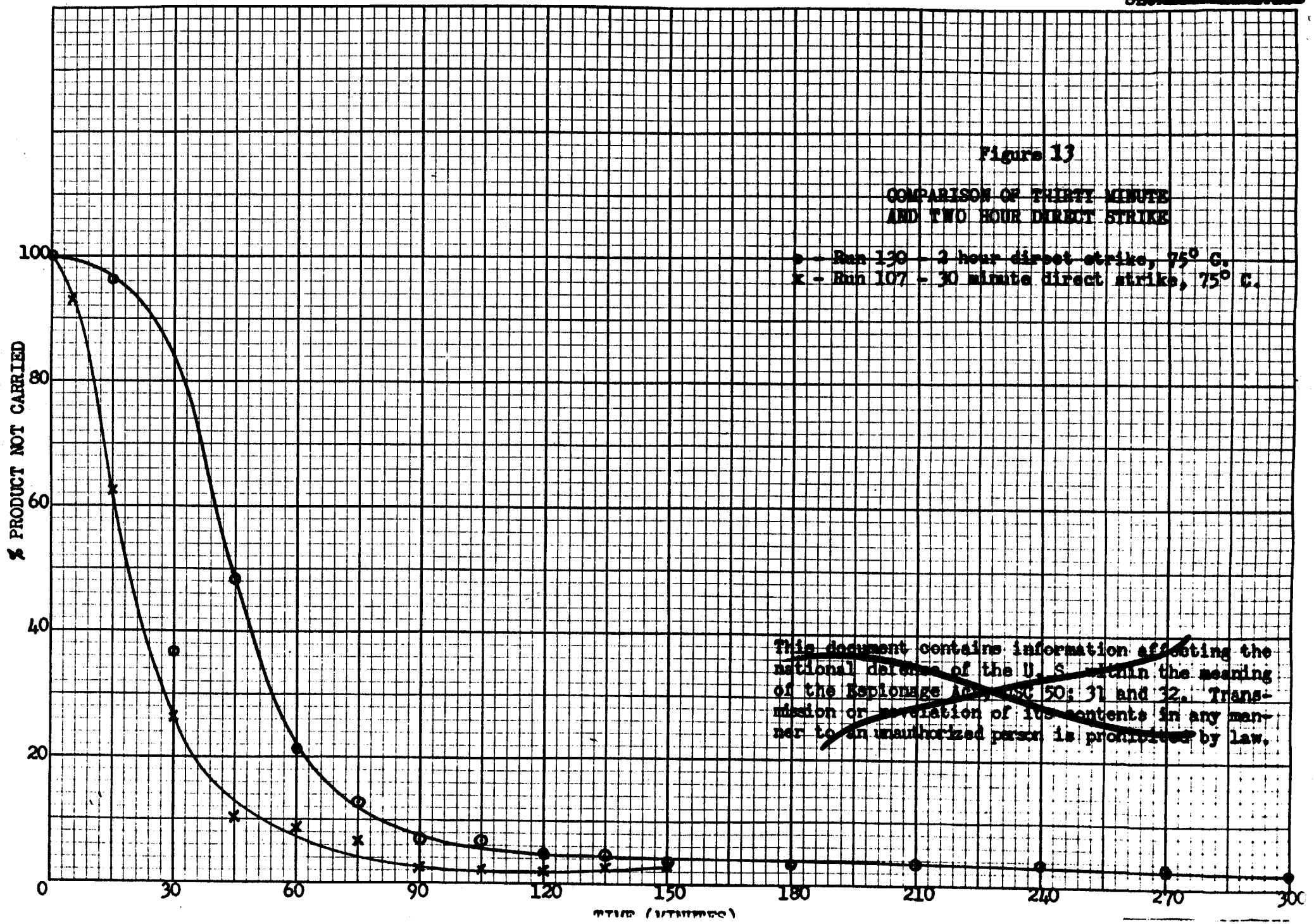

Figure 13

COMPARISON OF THIRTY MINUTE AND TWO HOUR DIRECT STRIKE

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TABLE XIII

Comparison of Thirty Minute and Two Hour Direct Strikes

Run Numbers	Number Runs	Molarity H_3PO_4	Time		% Waste Loss		Decontamination	
			Strike	Digestion	Range	Average	Extraction	Crossover
115-125*	10	0.8	30 min.	2 hrs.	0.5-1.8	0.8	11.7	16,000
130-133	4	0.8	2 hrs.	1 hr.	0.4-1.9	1.0	10.2	48,000

Effect of H_3PO_4 Concentration (0.3M to 0.8M) on Extraction Yield

In order to determine the effect of H_3PO_4 concentration on yield losses in the extraction step, sixteen special runs (130 - 146) were made in the plant in which the H_3PO_4 concentration was decreased from 0.8M to 0.6M, 0.4M and 0.3M, four runs being made at each concentration.**

On the first run of each set samples were taken at frequent intervals from Tank 21, centrifuged immediately to remove the solids and the supernatants analyzed for product and bismuth. The results of these rate of precipitation tests are shown in Tables XIV and XV, and Figures 14 to 17. The H_3PO_4 concentration does not exercise a marked effect on extraction yield unless it is decreased to the point where a large fraction of the bismuth is not precipitated. The hot direct two hour strike which was initiated at the start of this series of runs, and 0.6M H_3PO_4, were made standard plant practice for subsequent operation. The H_3PO_4 concentration appears to have little effect on decontamination. The factor in the extraction step decreased with decreased H_3PO_4 concentration and the over-all factor through the crossover remained approximately constant.

*Except 123.
**Letters R. S. Apple to R. C. Kay (5-26-44 and 6-9-44).

[redacted]

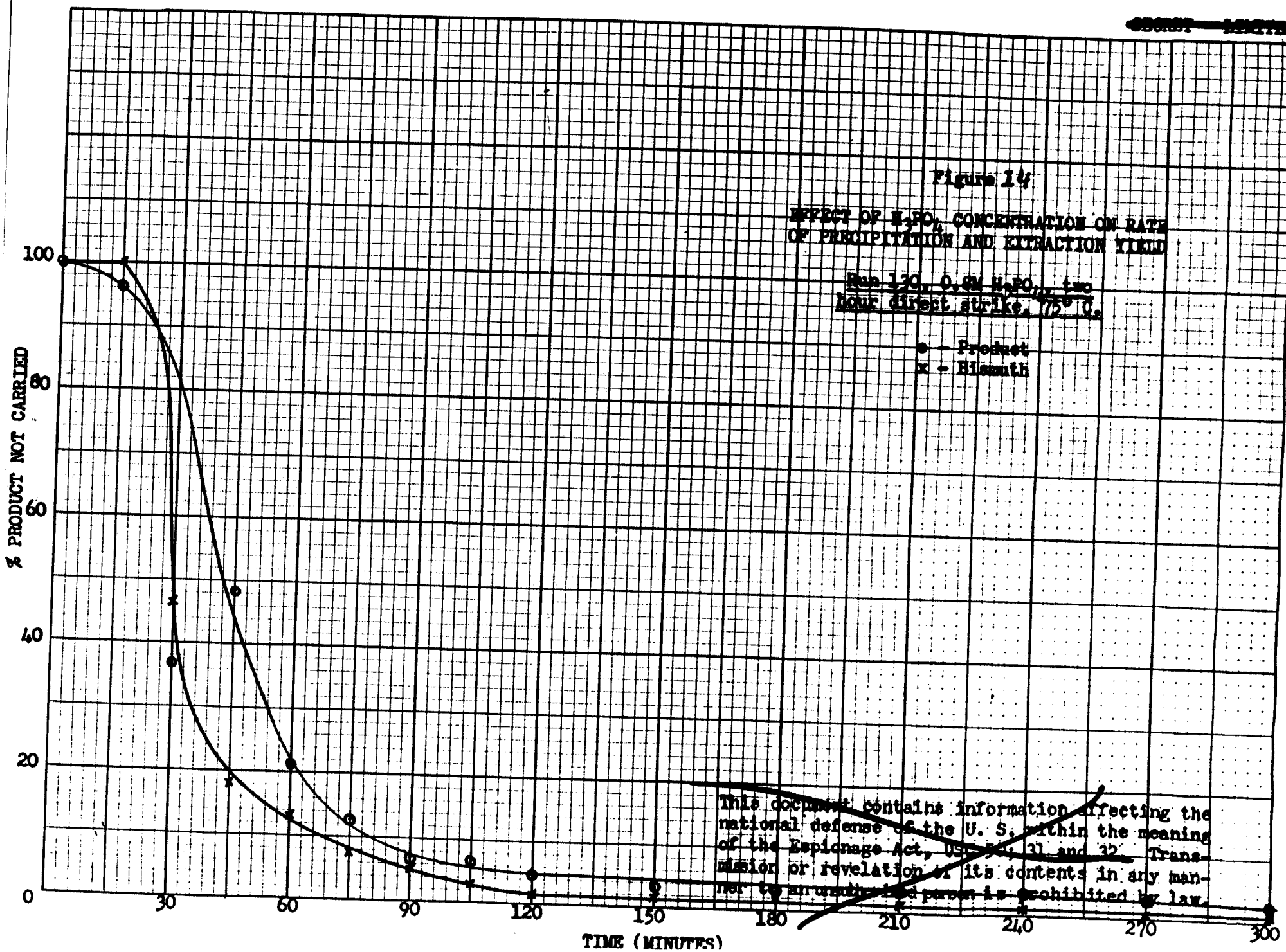

Figure 14

EFFECT OF H_3PO_4 CONCENTRATION ON RATE OF PRECIPITATION AND EXTRACTION YIELD

Run 120, 0.84 H_3PO_4, two hour direct strike, 75° C.

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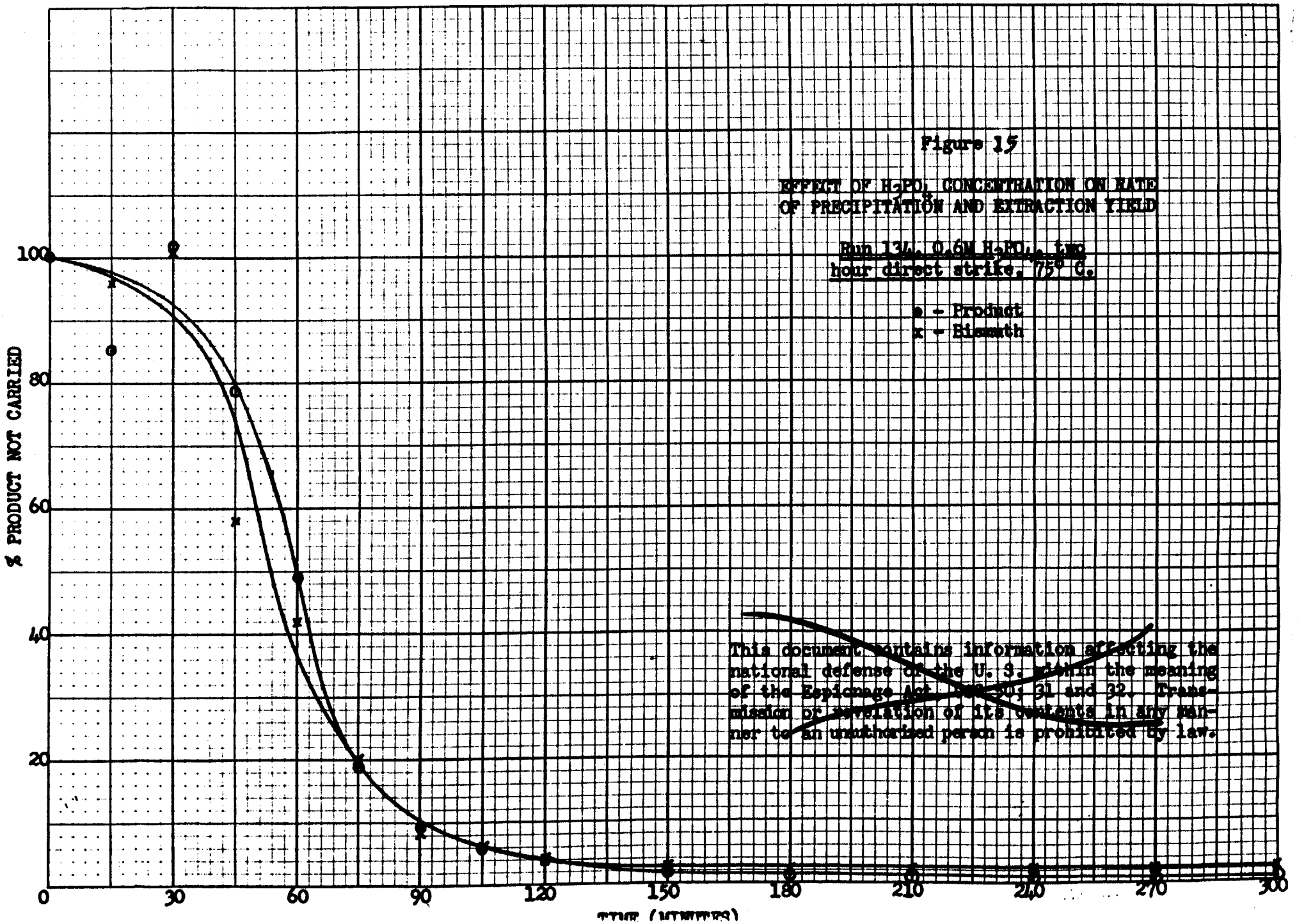

Figure 15

EFFECT OF H_3PO_4 CONCENTRATION ON RATE OF PRECIPITATION AND EXTRACTION YIELD

Run 134, 0.6M H_3PO_4, two hour direct strike, 75° C.

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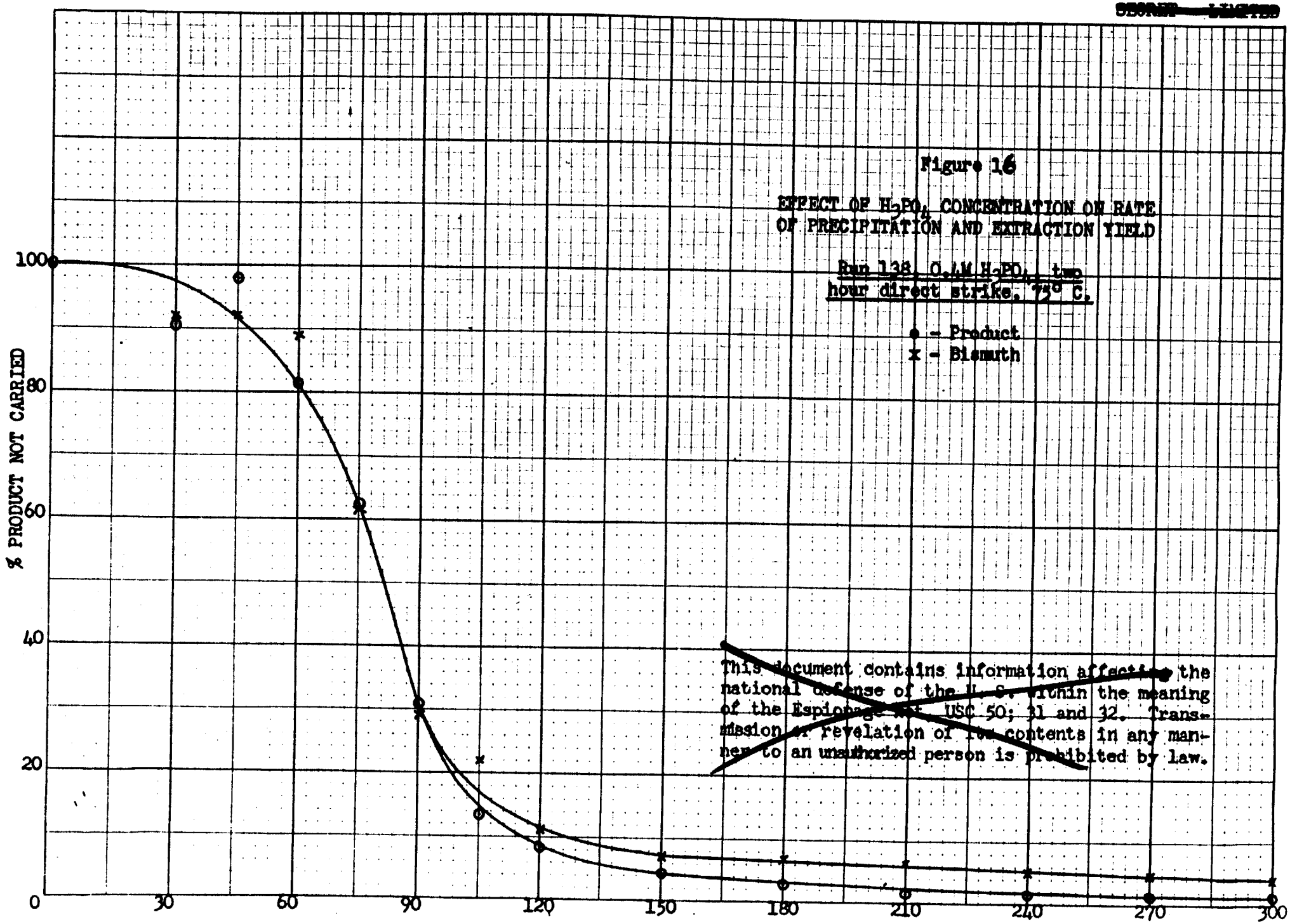

Figure 16

EFFECT OF H_3PO_4 CONCENTRATION ON RATE OF PRECIPITATION AND EXTRACTION YIELD

Run 138, 0.4M H_3PO_4, two hour direct strike, 75° C.

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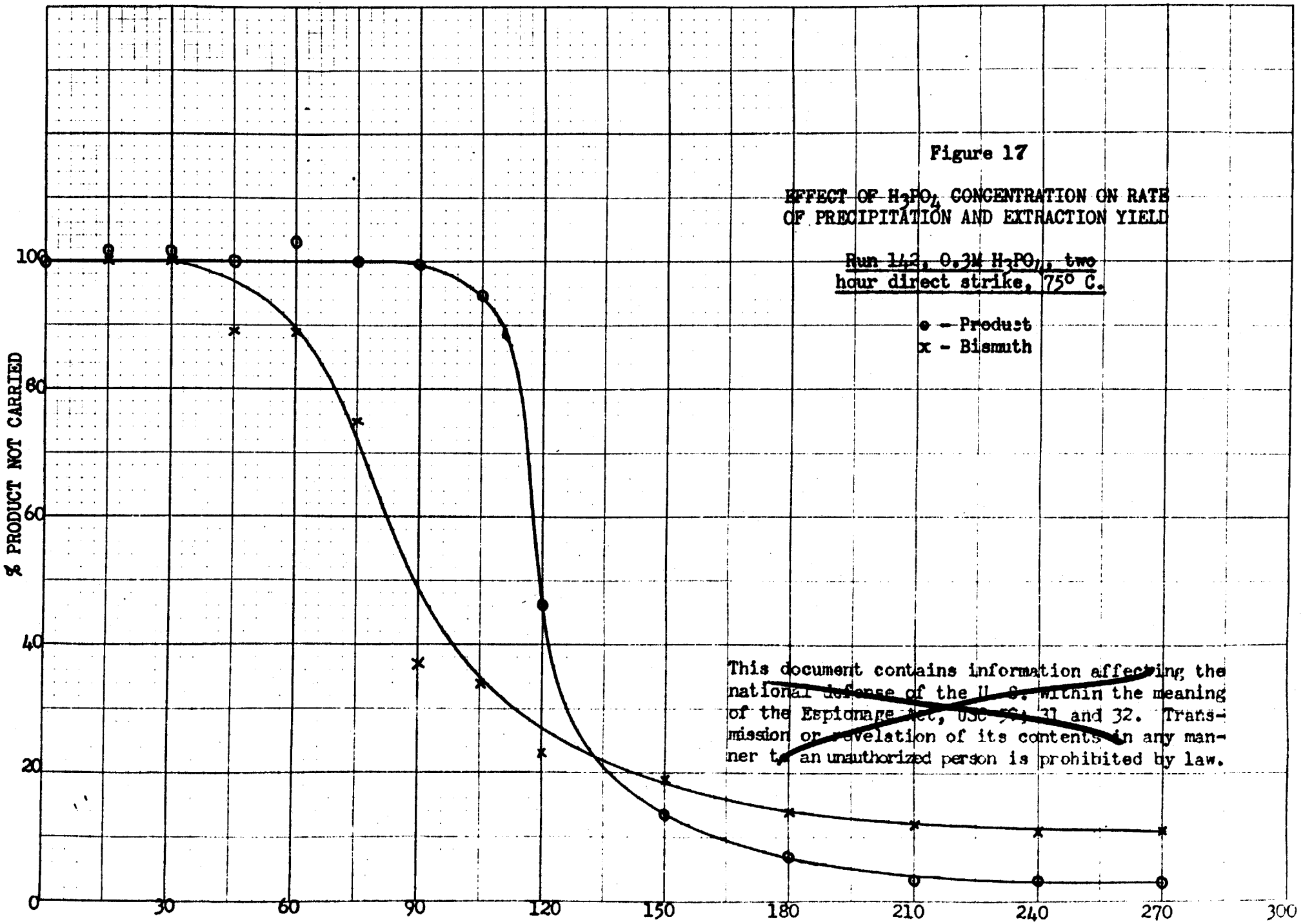

Figure 17

EFFECT OF H_3PO_4 CONCENTRATION ON RATE OF PRECIPITATION AND EXTRACTION YIELD

Run 1/2, 0.3M H_3PO_4, two hour direct strike, 75° C.

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TABLE XIV

EFFECT OF H_3PO_4 CONCENTRATION ON EXTRACTION YIELD - DIRECT STRIKE, 75° C.

Run Numbers	Number Runs	Molarity H_3PO_4	Time		Yield Loss		Decontamination Through		% Bismuth in Metal Waste
			Strike	Digestion	Range	Average	Extraction	Cross-Over	
115-125*	10	0.8	30 min.	2 hrs.	0.5-1.8	0.8	11.7	16,000	0.6 (Run 79) 1.7 (Run 107)
130-133	4	0.8	2 hrs.	1 hr.	0.4-1.9	1.0	10.2	46,000	1.0 (Run 130)
134-137	4	0.6	2 hrs.	1 hr.	0.6-1.4	1.0	8.3	39,000	2.3 (Run 134)
138-141	4	0.4	2 hrs.	1 hr.	1.2-1.9	1.5	8.0	41,000	4.0 (Run 138)
142-145	4	0.3	2 hrs.	1 hr.	2.0-2.5	2.4	6.9	54,000	11.0 (Run 142)

*Excepting run 123-123A

TABLE XVI

EFFECT OF W FISSION PRODUCTS AND POINT OF H_2SO_4 ADDITION ON EXTRACTION

Run Numbers	% Loss in Metal Waste		Decontamination Factors		Remarks
	Range	Average	Range	Average	
154-161	0.6-2.2	1.4	2.0-9.3	6.0	Prior to fission product addition
162-169	0.8-3.1	1.7	4.3-9.5	6.8	Prior to fission product addition
170-177	1.1-2.2	1.7	4.6-7.7	5.5	Fission product addition started run 170 - no Ru, Pr, Sm, La
178-185	2.7-9.7	4.1	4.1-10.0	[illegible]	H_2SO_4 addition to 40% UNi in tank 11 runs 178-185 only
186-193	1.9-4.8	3.1	4.1-9.8	6.7	New solution five times too much Ru, no Pr, Sm, Eu
194-201	1.1-4.1	2.4	3.4-16.0	7.6	All fission product elements except Ru
170-201	1.1-9.7	2.8	3.4-16.0	6.3	Average

TABLE XV

EFFECT OF H_3PO_4 CONCENTRATION ON RATE OF PRODUCT AND CARRIER PRECIPITATION

Time	Conditions	Run 130 0.8M H_3PO_4		Run 134 0.6M H_3PO_4		Run 138 0.4M H_3PO_4		Run 142 0.2M H_3PO_4	
		Product	Bismuth	Product	Bismuth	Product	Bismuth	Product	Bismuth
0 minutes	no H_3PO_4 in	100. %	100. %	100. %	100. %	100. %	100. %	100. %	100 %
15 "	1/8 " "	96.2	100.	85.2	96.	------	------	101.5	100.
30 "	1/4 " "	36.7	56.4	102.	101.	90.5	92.	101.6	100.
45 "	3/8 " "	48.3	18.0	78.8	58.	98.	92.	1.0.	89.
60 "	1/2 " "	21.4	13.4	49.2	42.	81.3	89.	102.9	89.
75 "	5/8 " "	12.8	7.8	19.1	20.	62.4	62.	100.	75.
90 "	3/4 " "	6.8	5.3	9.6	8.9	30.9	29.	99.6	37.
105 "	7/8 " "	6.8	2.9	5.9	5.9	13.6	22.	94.6	34.
120 "	all " "	4.6	1.7	4.0	4.0	8.3	11.	46.1	23.
150 "		3.3	1.8	1.7	2.8	4.4	7.2	13.4	19.
180 "	end digestion	3.1	2.0	1.0	2.3	2.7	6.9	6.8	14.
210 "		3.4	1.6	0.8	2.2	1.7	6.3	3.3	12.
240 "		3.6	1.0	0.6	2.3	1.6	5.1	3.4	11.
270 "		2.9	0.8	0.5	2.4	1.4	4.7	2.8	11.
300 "	end cooling	2.2	1.0	0.7	2.3	1.0	4.0	------	------

Effect of Fission Product Addition and Point of H_2SO_4 Addition on the Extraction Step

Inactive fission elements were added to the dissolver in concentrations prior to the metal solution step for a series of Hanford runs with scavengers starting with Run 170.* While product losses have increased generally since the addition of fission products, the effect on extraction has been small and somewhat inconsistent as shown by a summary of the runs in Table XVI.

Beginning with Run 178 the H_2SO_4 to be used in the extraction step was added to the 40% UNH solution in the dissolver in an attempt to obtain more representative sampling.** The average extraction waste loss for the eight Runs 178 - 185 was 4.1%, compared with an average of 1.6% for the twenty-four preceding runs. On Run 186 the H_2SO_4 was added to the 20% UNH according to previous practice, but the waste losses remained high. (See Table XVI.) Laboratory extractions duplicating the H_2SO_4 addition of the 40% UNH gave no indication of any adverse effect. (See Figure 18.) The sharp rise in waste losses coincident with the change in the point of H_2SO_4 addition is apparently due to some combination of factors other than this single variable.

Comparison of Extraction Losses with Time of Storage of Metal Solution

Averages of a large number of runs in the plant showed a trend toward increased waste losses with increasing holding time of the UNH before extraction. Individual runs both in the plant and in the semi-works, however, do not follow this pattern. To check this aging effect, further laboratory $BiPO_4$ extractions were made on UNH solution from Run 60 aged in stainless steel, both in the presence and absence of uranium metal. No effect was observed.

TABLE XIX

Aging Time (hours)	Loss in Metal Waste: No Metal Present	Loss in Metal Waste: Metal Present	Aging Time (hours)	Loss in Metal Waste: No Metal Present	Loss in Metal Waste: Metal Present
0	1.2%	1.2%	46	1.2%	2.4%
6	0.8%	1.9%	92	1.0%	1.9%
19	0.8%	0.8%	239	2.0%	1.1%

Subsequent laboratory and semi-works results indicate that storage of metal solutions for periods as long as a month has no adverse effect on extraction yields.

*Letter J. B. Sutton to H. C. Kay (6-5-44).
**See letter H. S. Apple to H. C. Kay (3-21-44).

[redacted]

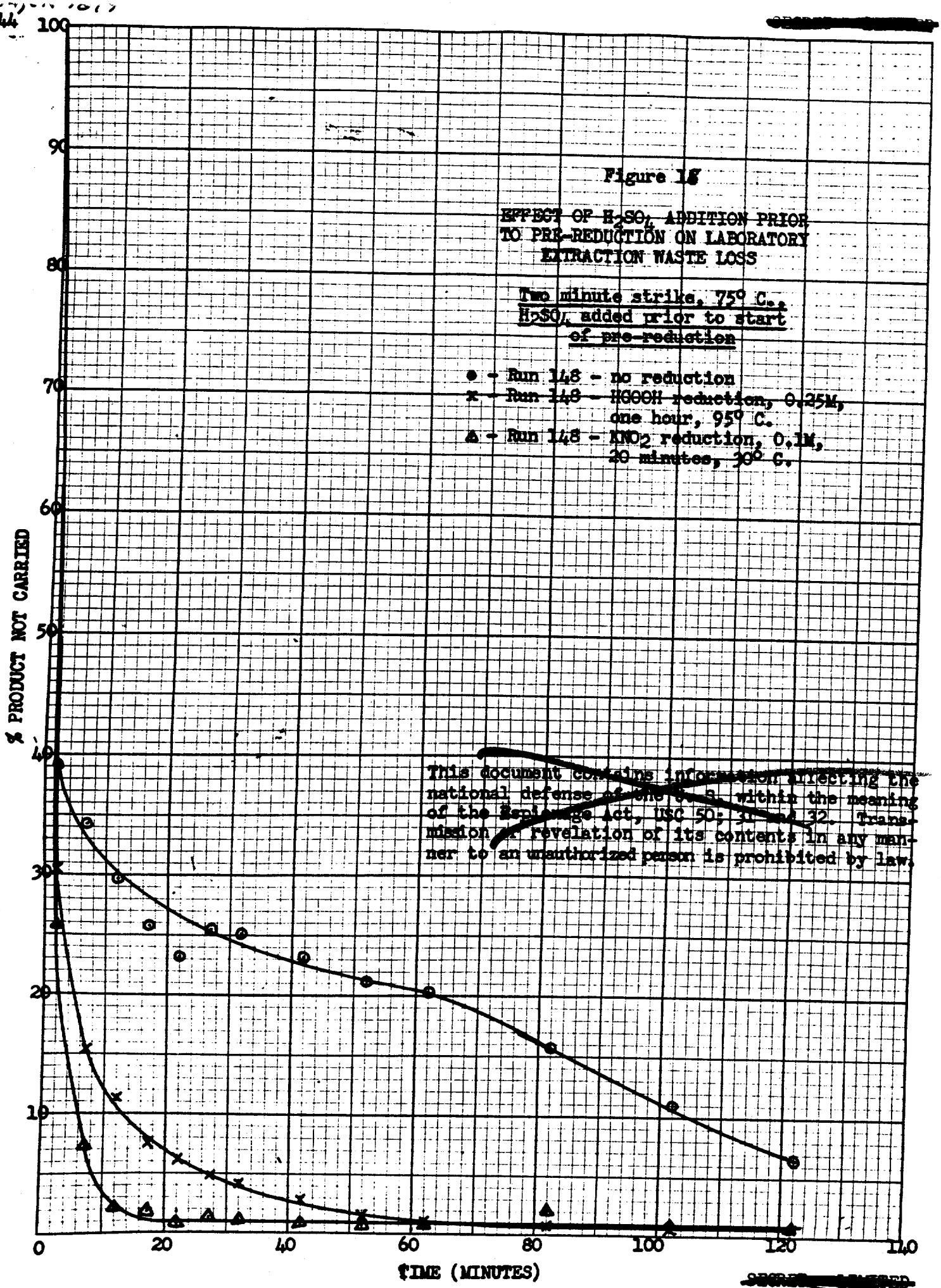

Figure 18

EFFECT OF H_2SO_4 ADDITION PRIOR TO PRE-REDUCTION ON LABORATORY EXTRACTION WASTE LOSS

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DECONTAMINATION CYCLE

The purpose of the decontamination cycle is to remove the radioactive fission products which are separated with the product from the uranium. The product must be sufficiently purified of these materials so that it can be handled during the concentration and isolation steps with very little or no shielding. One bismuth phosphate oxidation reduction cycle has satisfactorily accomplished this for the Clinton plant except for a few instances during the early operation. Equipment and minor process modifications were responsible for eliminating the early difficulties.*

The waste losses in the by-product precipitate with the Clinton process (no scavengers) have been consistantly low since making modifications in the equipment and process to eliminate pick up of product precipitated in the product precipitation steps.

At Hanford the decontamination factor which will be required will be greater than at Clinton by a factor of 10 to 100. A large number of runs have been made with metal solution to which was added inactive fission products in order to simulate Hanford metal. Most of the runs were made with two decontamination cycles and all with scavenger precipitations. All of the procedures surpassed the goal decontamination factor of 10^5 through two cycles. The goal of 10^7 at the end of the crossover was essentially obtained in all cases with some of the factors being slightly higher than this and some a little lower.

The use of scavengers resulted in a relatively large increase in waste losses. The losses varied with the particular type of scavenger used, being highest with the double Ce-Zr precipitations in each cycle. The use of ammonium fluosilicate decreases the waste losses from the product precipitation steps which otherwise are increased somewhat by the use of scavengers.

The choice of the scavenger combination for Hanford must be made by balancing the waste losses against the factor of safety in obtaining the required decontamination. The double cerium-zirconium precipitations in each cycle was recommended as the preferred process primarily on the basis that it offered the greatest factor of safety in obtaining the required decontamination at the end of two cycles. However, should more decontamination be obtained than is needed a definite improvement in yield would result from omitting the zirconium from the second shot in each cycle, or from omitting scavengers altogether in the second cycle and using ammonium fluosilicate.

Clinton Process

Factors Affecting Gamma Decontamination - In a pair of early runs (4 - 5) in the Clinton plant, sufficient by-product gamma activity came into Room D with the LaF_3 slurry to necessitate the use of concrete blocks and lead shielding around the equipment pieces. Since it was planned to handle more active starting material (by factors of 10 - 50) in the plant, the problem of improving the decontamination in the canyon was considered urgent.

*The operating details for the decontamination cycle are given in Section A of the Appendix. Graphs of the waste losses are given in Section C and of the decontamination in Section D with notes on each as to process or equipment changes which are likely to affect them.

First attempts to improve the situation were through the use of a LaF_3 by-product precipitate in the cross-over cycle (Run 13).* Subsequent use of the "hot direct" extraction precipitation procedure** (for the primary purpose of decreasing yield losses) resulted in improved decontamination. (Run 16.) The LaF_3 by-product precipitation was eliminated because of high product losses in the cross-over cycle. The improvement in decontamination from this procedure was only about three fold due primarily, it is believed, to incomplete separation of the lanthanum fluoride by-product precipitate. On Runs 126 and 127 a by-product lanthanum fluoride precipitation was again made,*** but on these runs the lanthanum was added in two shots with centrifuging after each. The improvement in the decontamination factor on these runs was about 10 fold.

Results obtained on a three-liter laboratory scale showed that approximately ten-fold improved gamma decontamination was obtained by precipitating the by-product $BiPO_4$ in 0.02M instead of 0.1M H_3PO_4 (CN 1655). This procedure was written into the plant flowsheet on Run 112 and was continued until the scavenger procedure tests were started on Run 170.**** Results on plant Runs 112 - 120 (exceptin, 115 made with 0.1M H_3PO_4) show decontamination factors at the end of the first decontamination cycle about twice those obtained on the ten normal preceding runs. This cycle improvement did not show up at the end of the crossover, where the principal activities are rare earth rather than phosphate insoluble species. The possible advantage resulting from this procedure is a more rapid decontamination with respect to phosphate insolubles, resulting in a lower activity level in subsequent cells. The rates of by-product and Bi^{+3} precipitation in plant Run 112 are shown in Table XX. Based on this study and a large amount of supporting laboratory evidence, the digestion time for this precipitate was reduced from one hour to thirty minutes on Run 130; the additional digestion time is of no value.*****

*Conditions outlined in letter from J. B. Sutton to L. C. Kay (1-11-44).
**Conditions outlined in letter from E. F. Acken to L. C. Kay (1-14-44).
***See letter from R. W. Smith to L. C. Kay (5-20-44) concerning request of J. H. Peterson for these runs.
****Modification recommended in letter from R. S. Apple to L. C. Kay (4-25-44).
*****Recommended in letter from R. S. Apple to L. C. Kay (4-26-44).

TABLE XX

RATE OF BY-PRODUCT PRECIPITATION
WITH 0.02M H_3PO_4 - RUN 112

Sample	Origin	Gamma Activity cpm/gm UNH	% 11 L Gamma Activity	Bi^{+3} Concentration grams/liter	% Bi^{+3}
11 L		1.68×10^6	100. %		
24 P		1.33×10^5	7.9		100
A	Solution after dilution before H_3PO_4	2.42×10^4	1.4	1.776	43
B	5 minutes after H_3PO_4	2.32×10^4	1.4	0.226	15.
C	20 " " "	2.12×10^4	1.3	0.067	[illegible]
D	40 " " "	2.10×10^4	1.3	0.059	[illegible]
E	60 " " "	2.12×10^4	1.3	0.079	4.4

The logarithm of the decontamination factors (dF's) obtained at each step in the process are shown graphically in Figures A 13 and A 14, Section D of the Appendix. Also noted on the graphs are the various process and equipment modifications which are likely to affect decontamination. The conclusions are summarized below:

1. Neither reaction time in the pile nor cooling time appeared to have a marked effect on decontamination factors obtained. Reaction times have varied from approximately 20 days to approximately 100 days, and cooling times have varied from approximately 20 days to approximately 50 days.

2. A change in the extraction striking procedure from "hot reverse" to "hot direct" starting on Run 16 resulted in an increase in "canyon" decontamination of at least three-fold.

3. The inclusion of a single LaF_3 by-product precipitate in the crossover cycle on Runs 13 - 17, 19 - 23, 25 and 27 improved the "canyon" decontamination about three-fold. It is probable that poor centrifuging efficiency of the by-product precipitate limited the decontamination obtained in this step. A double LaF_3 by-product precipitate (Runs 126 - 127) improved decontamination by a factor of 10.

4. The change in coating removal procedure from nitric acid plus mercury catalyst solution to caustic-sodium nitrate solution had no marked effect on decontamination (Runs 184 - 185 vs. 170 - 177).

5. The effect on decontamination of changing the pre-extraction treatment from formic acid to sodium nitrite requires further confirmation. On the basis of the first four runs, $NaNO_2$ reduced overall decontamination, but further conclusions cannot be drawn because of additional variables in succeeding runs (Runs 166 - 169 vs. 162 - 165).

6. The reduction in H_3PO_4 concentration from 0.1M to 0.02M in the first by-product precipitation (decontamination cycle) starting with Run 112 increased about two-fold the decontamination factors through the decontamination cycle. This improvement did not carry through to DIP (Room D).

7. The adoption of a equipment arrangement (one operation per cell) had no significant effect on decontamination after the first two-timer (Runs 159, 160) had been processed.

Product Losses in Decontamination Cycle - Shortly after the start-up of the plant the by-product losses in the decontamination cycle increased until they averaged 12% for Runs 11, 12, 13 and 14. Analyses of the oxidized solution immediately prior to making the by-product precipitation failed to show incomplete oxidation. Analyses of the by-product slurries (analyses of slurry samples are always subject to uncertainties) failed to indicate the same order of magnitude of product in the precipitate as was later found in the solution of the by-product precipitate. Investigation of the extraction precipitate

dissolving procedure (three one-hour treatments) revealed that it failed to completely dissolve the cake. In Run 10 the centrifuge bowl was washed clean before centrifuging the extraction precipitate, the centrifuged cake then dissolved in the usual manner, and the centrifuge bowl washed again:

1st wash	contained	9.7%	product
2nd "	"	1.7%	"
3rd "	"	0.4%	"

Laboratory data showed that $BiPO_4$ made by the hot reverse strike (start-up procedure) was more sticky and more difficult to dissolve than that made by the hot direct strike. (See Table XXI.) Following successful semi-works trials, the plant striking procedure was changed on Run 16 to the hot direct precipitation.* The by-product precipitate losses decreased to an average of 4.7% (range 2.6 - 7.2%) on the 11 runs from 16 to 26.

TABLE XXI

Acid Concentration (%)	Time for Apparent Solution (in minutes) at 25° C					
	27	36	44	53	60	67
Hot reverse precipitate	22.	11.	9.	17.	18.	22.
Hot direct precipitate	5.	3.	1.5	1.5	1.5	1.5

Weight HNO_3/ weight $BiPO_4$ = 23.6

During Run 26 it was found that sufficient corrosion was occurring in the stainless steel phosphoric acid storage tank and lines to build up a concentration of reducing material and corrosion products in the acid. Since some H_3PO_4 is used for by-product precipitation, this situation was corrected by adding H_3PO_4 directly from carboys, and later by storing the H_3PO_4 with HNO_3 inhibitor. The 53BF1 loss decreased to an average of 4.0% for the eighteen runs 27 - 45 (range 1.9% - 7.7%).

Following Run 45 an acid distributor was installed in the precipitator used for both the extraction and the by-product precipitation of the decontamination cycle. This allowed the precipitator to be washed before the by-product precipitation thus removing the reduced product which is left on the tank walls after the product precipitation and preventing it from being picked by the by-product precipitate. The product cake solution acid is used for this wash. The by-product cake losses decreased to an average of 1.4% on Runs 46 - 83.

After Run 84 a mechanical agitator was installed in the oxidation tank (24) which resulted in a further decrease in the by-product loss because it insured complete solution of the product cake before oxidation. After this change the losses averaged .7% (Runs 85 - 169).

The product losses in the waste solution on the product precipitation step averaged 1.3% on Runs 1 - 169. There have been no process changes which have affected these waste losses appreciably.

*Conditions outlined in letter H. F. Acken to H. C. May (1-14-44).

Hanford Process with Similated Hanford Metal

The problem of decontamination at Hanford is more difficult than at Clinton both because the starting metal will be more active, thus requiring a greater decontamination factor, and because it contains a higher concentration of the elements formed by the fission of uranium which interfere with decontamination. In order to study the Hanford decontamination process at Clinton inactive fission elements are added to the dissolver before the metal solution begins, thus simulating as nearly as possible the Hanford metal.* The required decontamination factors for the Hanford Plant have been calculated to be 10^5 at the end of the decontamination cycles and 10^7 at the end of the crossover.

Laboratory studies indicated that two decontamination cycles are not adequate for obtaining the factor of 10^5 unless scavengers are used and therefore scavengers have been used on all plant runs when inactive fission products have been added to the metal dissolver. A number of combinations of scavengers gave the required decontamination in the laboratory and so the more promising of these were studied in the plant. These investigations included a study of the behavior of the precipitates in the centrifuge operation, their effectiveness as scavengers and their effect on waste losses.

Handling Characteristics of Scavenger Precipitates - Before starting regular runs in the plant with scavengers three scavenger combinations were investigated to determine their centrifuging characteristics, the best cake washing procedure, and a satisfactory procedure for removal of the cakes from the centrifuge bowl. The scavengers tested were:

Ce-Zr; Ce-Zr	50 mg/l. each element each pptn.
Ce-Zr; Ce	50 mg/l. each element each pptn.
Ce-Zr-Ba; Ce	50 mg/l. Ce and Zr and 1 g/l. Ba

The detailed procedure for the Ce-Zr; Ce-Zr scavenger precipitation is given in Section A (run 193) of the Appendix.* Briefly the procedure is to dilute the oxidized 5N nitric acid solution to 1.25N to precipitate the $BiPO_4$. Additional bismuth is then added to decrease the phosphoric acid remaining in solution, and this is followed by the first scavenger solution (Ce-Zr). Phosphoric acid is then added to precipitate these scavengers. This precipitate consisting of bismuth, cerium and zirconium phosphates is separated by centrifugation. A second precipitate is made by adding additional cerium-zirconium solution which is removed by a second centrifugation. All precipitates are removed from the centrifuge bowl at once. The Ce-Zr; Ce procedure is the same as the above except that no zirconium is added for the last precipitation.** The Ce-Zr-Ba; Ce procedure is the same as the Ce-Zr; Ce procedure except that sulfuric acid and then barium nitrate are added to give a barium sulfate precipitate before the cerium and zirconium precipitates are formed.***

The conclusions which were reached on the scavenger runs without activity were as follows:

*Outlined in letters from J. B. Sutton to W. C. Kay (6-5-44 and 6-8-44).
**Outlined in letters from J. B. Sutton to W. C. Kay (6-5-44 and 6-8-44).
***Outlined in letters from J. B. Sutton to W. C. Kay (6-22-44).

1. The centrifuge efficiency with all of the precipitates is roughly 95% determined by measuring the volume of solids which can be batch centrifuged out of the plant centrifugate in the laboratory. This checked roughly the efficiency of the semi-works separations.

2. The cake volumes for Clinton size (1/3 ton) batches were approximately 10 gallons for the Ce-Zr; Ce-Zr and Ce-Zr; Ce scavengers and 6 gallons for the Ce-Zr-Ba; Ce scavenger. For the Hanford size (1 ton) batches the volumes were 28 gallons for the Ce-Zr; Ce-Zr scavenger and 14 gallons for the Ce-Zr-Ba; Ce scavenger. See Figure 19 for the distribution of these precipitates in the centrifuge bowl.

3. The preferred washing procedure for the Ce-Zr; Ce-Zr and Ce-Zr; Ce scavengers was to skim 40 gallons of the liquid from the bowl (30 gals. for Hanford size cakes), wash once with water and skim again. The Ce-Zr-Ba; Ce cake can be skimmed more closely since this precipitate is more dense.

4. Any of the by-product precipitates may be removed from the centrifuge bowl by a multi-batch nitric acid - hydrogen peroxide treatment. Because of rapid decomposition of the peroxide it must be added directly to the bowl and cannot be recirculated through the precipitator. The Hanford size cakes can be removed with the same amount of HNO_3-H_2O_2 as the Clinton size cakes.* See Section A, Run 193 of Appendix for details of the preferred procedure.

5. Bismuth and ceric phosphates are dissolved by the HNO_3-H_2O_2 treatment. Zirconium phosphate remains as a light, gelatinous precipitate which suspends readily and may be transferred without difficulty. Barium sulfate likewise must be handled as a suspension and while no trouble was experienced with it in these tests, there is some question as to whether this scavenger will be practical for use in the canyon, the principal concern being the possibility of depositing an insoluble precipitate in which the hard gamma emitter lanthanum would grow.

Decontamination and Waste Losses with Scavengers - Three combinations of scavenger precipitations have been studied in the plant. These are Ce-Zr; Ce-Zr in each of two cycles,** Ce-Zr; Ce in each of two cycles*** and Ce-Zr; Ce in the first cycle followed by one cycle with no scavengers but with ammonium fluosilicate added before the product precipitation.**** The procedure for the scavengers were the same as outlined for the inactive runs. The ammonium fluosilicate was added immediately before the ferrous reduction step to make the solution .05 M in this constituent. The role of the fluosilicate is to solubilize the colloidal materials such as zirconium phosphate so that they remain in solution during the product precipitation. The results of these runs are summarized in Table XXII. A more condensed summary is given below (Table XXIII), and is useful for comparing the relative merits of the three scavenger combinations.

*Procedure for dummy runs with Hanford size cakes is outlined in letter from J. B. Sutton to W. C. Kay (6-16-44).

**Procedure recommended in letters from J. B. Sutton to W. C. Kay (7-17-44 and 7-18-44).

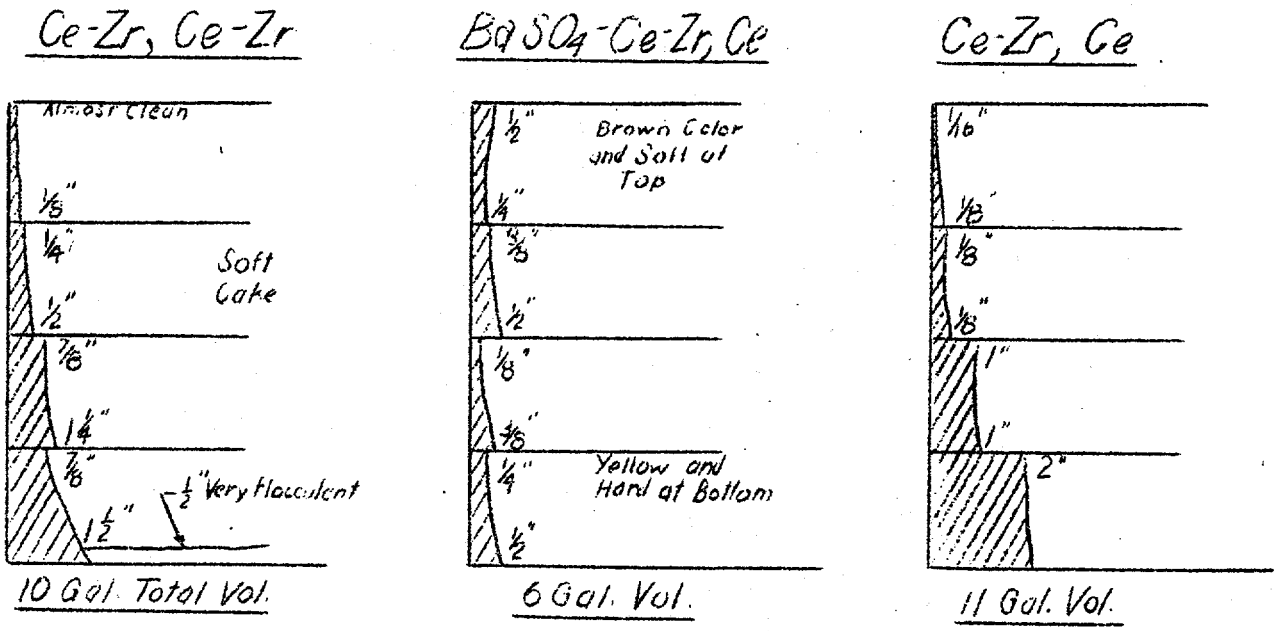
***Procedure recommended in letter from J. B. Sutton to W. C. Kay (7-28-44).

****Procedure recommended in letter from J. B. Sutton to W. C. Kay (8-10-44).

FIGURE 19

SCAVENGER CAKE DISTRIBUTION IN CENTRIFUGE

CLINTON CAKES



HANFORD CAKES

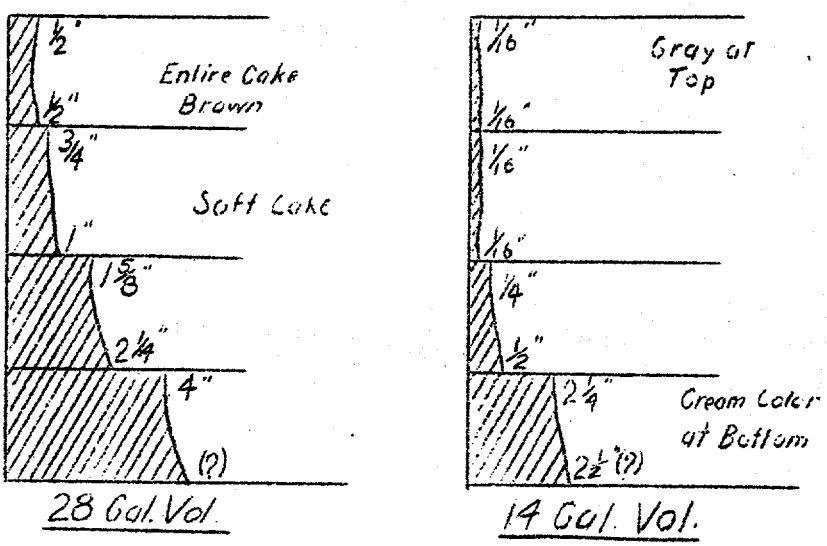


TABLE XXIII

Scavenger Combination	1st cycle 2nd cycle	Ce-Zr; Ce-Zr Ce-Zr; Ce-Zr	Ce-Zr; Ce Ce-Zr; Ce	Ce-Zr; Ce $(NH_4)_2 SiF_6$
Run Numbers		186-193; 210-217	194-201	202-209
Waste Losses % Orig. Prod:	1st cycle 2nd cycle Total	6.0; 6.9 6.5; 0.7 12.5; 11.6	3.9 3.8 7.7	4.0 .9 4.9
Decontamination dF thru:	2nd cycle Crossover	5.6; 5.8 6.3; 5.9*	5.3 6.7	5.3 7.1*

*Possibly low due to recycle of peroxide supernatant and precipitate.

TABLE XXII

SUMMARY OF CLINTON PLANT SCAVENGER TESTS - % EQUIPMENT ARRANGEMENT

Run Numbers	162-169	170-177	178-185	186-193	194-201	202-209	210-2
Conditions							
Number of decontamination cycles	1	1	1	2	2	2	2
% concentration of fission products	no	yes*	yes*	yes	yes	yes	yes
Average age of metal, days	59	55	55	52	62	37	43
Scavengers							
1st cycle							
1st shot		Ce-Zr	Ce-Zr	Ce-Zr	Ce-Zr	Ce-Zr	Ce-Z
2nd shot		Ce-Zr	Ce-Zr	Ce-Zr	Ce	Ce	Ce-Z
2nd cycle							
1st shot				Ce-Zr	Ce-Zr	none	Ce-Z
2nd shot				Ce-Zr	Ce		Ce-Z
Ammonium fluosilicate in second cycle	no	no	no	no	no	yes	no
Cross-over LaF_3 by-product	no	no	no	yes	yes	yes	yes
Product losses							
Extraction	1.8	1.7	4.0	2.9	2.4	2.0	1.9
1st cycle	2.0	5.7	6.6	6.0	3.9	4.0	6.9
2nd cycle	---	---	---	6.5	3.8	0.9	4.7
Cross-over (including metathesis)	2.9	5.3	5.5	6.4	5.1	f	f
Total	6.7	12.7	16.1	21.8	15.2		
Decontamination (dF)[a] thru							
Extraction	0.8	0.8	0.7	0.8	0.8	1.0	0.9
1st cycle	3.5	3.6	3.4[b]	3.7	3.5	3.7	3.7
2nd cycle	---	---	---	5.6	5.3	5.3	5.8
Cross-over	4.2	4.4	4.0	6.3[c]	6.7[c]	7.1[d,e]	6.9

[a]Averages of the individual dF values. (dF = log of the ratio of gamma counts of starting material to gamma counts at point sampled)
[b]Scavenger precipitate washed three times on five runs (178-182).
[c]Value on first two runs of series omitted since solution contained recycled by-product cake from previous final concentration cycle.
[d]Based on 150 cc. of DIS instead of 25 cc. of DIP, as in former runs.
[e]May be low due to recycle of peroxide precipitate and supernatant.
[f]Omitted since losses were affected by recycling of product.

*Conditions for these runs outlined in letter from J. B. Sutton to W. C. Kay (7-4-44).

From the above tables the following conclusions may be drawn:

a. The use of Ce-Zr; Ce-Zr scavenger result in a waste loss of 6% per cycle. This is the average of 48 results.

b. The use of Ce-Zr; Ce scavenger results in a waste loss of 3.7% per cycle. This is the average of 24 results.

c. Omitting all scavengers but using ammonium fluosilicate results in a waste loss of .9% per cycle. This is the average of 8 results. Apparently this complexing agent decreases the waste losses since the average for the decontamination cycle on Runs 85 to 169 was 2.0%. This improvement was predicted from laboratory results.

d. The best decontamination at the end of the second cycle was obtained with Ce-Zr; Ce-Zr in each cycle. However, this was not much better than the other two scavenger combinations in view of the normal fluctuations in results. All combinations gave decontamination factors of better than the goal factor of 10^5.

e. The best decontamination at the end of the crossover was obtained with the Ce-Zr; Ce scavenger in the first cycle and ammonium fluosilicate in the second cycle. Results at the end of the crossover may have reflected changes in the operating procedure for handling recycle materials. Thus in the series of runs 202 - 217 product was recycled from the isolation studies in order to build up its concentration and in the accounting the amount of gamma activity recycled was assumed to be negligible. The results, particularly the dF of 6.9 on the Ce-Zr; Ce-Zr in both cycles, may be low due to this recycle.

f. The Ce-Zr; Ce-Zr scavenger precipitate on Runs 178 - 182 was washed 3 times instead of once in an attempt to lower the waste losses.* The losses decreased about 25% but the decontamination appeared to be poorer by a factor of 2 and so this was discontinued.

*Recommended in letter from J. B. Sutton to W. C. Kay (7-12-44).

CROSSOVER CYCLE

The crossover cycle includes the operations incident to changing from bismuth phosphate as a carrier to lanthanum fluoride as a carrier by separation of the product from the bismuth by making a by-product bismuth phosphate precipitation and precipitation of the product with lanthanum fluoride. A lanthanum fluoride by-product precipitation is made if additional decontamination is desired in the process. Most of the Clinton runs have not included this operation since the decontamination was not required. However, sufficient runs have been made with this step to demonstrate the process for Hanford since it will be required there.

There have been only minor difficulties in these steps of the process with the exception of losses in the early runs with the by-product lanthanum fluoride. Following further laboratory investigations the operating procedure was changed and the product and by-product precipitations made in separate cells with the result that losses dropped to about 1% in the lanthanum fluoride by-product. The results of the investigations made in connection with the crossover cycle are presented below.*

Losses in the Bismuth Phosphate By-Product Precipitation of the Crossover Cycle

The product loss in the bismuth phosphate by-product precipitate of the crossover cycle has decreased during continued plant operation, although improvement has not been as large as was noted for the by-product precipitate of the decontamination cycle. A chronological summary of operational changes with their effect on losses follows:

TABLE XXIV

Run Numbers	Average Loss in 533P2	Remarks
8-26	3.6%	Mechanical agitation in Tank 34 No washing of Tank 31 H_3PO_4 found to contain reducing material - corrected on runs 27 et seq.
27-35	1.5%	Mechanical agitation in Tank 34 No washing of Tank 31
36-50	1.9%	No mechanical agitation in Tank 34 Tank 31 washed after product precipitation only
51-84	1.1%	No mechanical agitation in Tank 34 Tank 31 washed after both product and by-product precipitations
84-118	0.4%	Mechanical agitation in Tank 34 Tank 31 washed after both product and by-product precipitations

*Details of the operating procedure are given in Section A of the Appendix. Waste losses in the crossover are graphed in Section C, with notes on the curves to indicate significant process and equipment changes.

Use of 0.02M H_3PO_4 for $BiPO_4$ By-Product Precipitation in the Cross-Over Cycle

Some difficulty had been experienced in obtaining complete oxidation of the first metathesis solution in Room D prior to Run 159. If complete oxidation was not obtained in the normal time, the usual procedure followed was addition of more zirconium, more dichromate, and re-oxidation. On several occasions the addition of more zirconium increased the amount of precipitate (zirconium phosphate) in the slurry. In order to reduce carry-through of phosphate into Room D, the H_3PO_4 concentration used for the crossover phosphate by-product precipitation was reduced from 0.1M to 0.02M for Runs 159 to 162.* Oxidation difficulties were not experienced in Room D during this period, but bismuth remaining in solution after by-product removal caused precipitation of bismuth oxalate during reduction with subsequent non-representative sampling in Cell 4. The bismuth followed through the metathesis and again precipitated as the oxalate in the first concentration cycle. In view of these difficulties the H_3PO_4 concentration was returned to 0.1M.

LaF_3 By-Product Precipitation in the Crossover Cycle and Its Development for the Hanford Procedure

The LaF_3 by-product precipitation was introduced in the crossover cycle of Runs 13 - 23 for the purpose of reducing the radiation from material entering Room D.** During this period product losses in the cycle wastes averaged 12% - about 3% in the $BiPO_4$ by-product precipitate (not a result of the LaF_3 by-product), 5% in the LaF_3 by-product precipitate, and 4% in the product precipitate effluent. (Effluent losses in Runs 8 - 12 averaged 1.8%.) In Run 17 the $Na_2Cr_2O_7$ holding oxidant was increased from 0.002N to 0.01N** in an effort to prevent product reduction and subsequent loss in the fluoride by-product precipitate, but results were not encouraging; the losses in the by-product precipitate increased from an average of 4.5% to an average of 6.5%, and the waste effluent losses increased from an average of 3.1% to an average of 6.4%.

The decontamination factor was also not improved appreciably throughout these runs (a factor of about 3) and after changing the striking procedure in Cell 2 to a hot direct strike which was first made on Run 16, it became apparent that adequate decontamination could be obtained without the LaF_3 by-product precipitation and it was omitted to improve yields.

In an effort to develope a satisfactory crossover procedure for Hanford a two shot LaF_3 by-product precipitation with double centrifugation was tried on Runs 126 - 127.*** Decontamination factors for the cycle averaged 84; factors for this cycle of preceding runs averaged only 7.5 (111 - 125). This cycle decontamination improvement was much larger than the factor of about 3 shown in early runs (13 - 23) using the single precipitation. However, product loss with the double precipitation was again excessive (12% loss in the two precipitates of Run 127). This necessitated the development of a procedure which would prevent product reduction during the increased time (more than doubled) of exposure of the fluoride solution to the stainless steel surface.

*Recommended in letter from R. S. Apple to W. C. Kay (6-24-44).
**See letter J. B. Sutton to W. C. Kay (1-11-44).
***Requested by J. H. Peterson. See letter W. W. Smith to W. C. Kay (5-20-44).

Laboratory work by the Plant Assistance Group indicated that product reduction and subsequent product losses in the LaF_3 by-product precipitate would be decreased by:

a. Conditioning of the stainless steel by pre-treating with an oxidizing agent.

b. Reoxidation of the product solution after by-product $BiPO_4$ precipitation prior to the addition of HF.

c. Low HF concentrations.

d. Low temperature.

e. Change in the holding oxidant concentration.

On the basis of these data, LaF_3 by-product studies were made in the semi-works, the results of which indicated that all of the above changes were required to insure low product losses.

The following procedure was recommended to the plant for the LaF_3 by-product precipitation:*

Condition equipment prior to the first run by treating for one hour at 75° with 0.1N $KMnO_4$-1% HNO_3.

Reoxidize product-containing effluent from $BiPO_4$ by-product precipitation using 0.01M $KMnO_4$ at 75° C for one hour.

Precipitate by-product LaF_3 (preformed) at 35° C in 0.2N HF with 125 mg/liter La, centrifuge, reprecipitate (125 mg/liter La) and centrifuge.

The first eight runs made in the plant (186 - 193) under the above procedure resulted in an average product loss in the two precipitates of 1.2%, with extremes of 0.8% to 2.0%. In the second eight runs (194 - 201) the total product loss in the by-product LaF_3 varied between 0.7% and 2.1%, averaging 1.4%.

Decontamination factors for the crossover on these eight runs ranged from only 4.5 to 6.8. However, the crossover cycles were run following two scavenger decontamination cycles and the gamma activity level was too low for accurate measurement.

Substitution of Oxalic Acid for Hydrogen Peroxide Reduction

In an attempt to reduce the crossover cycle effluent waste loss and to reduce corrosion in the Cell 4 equipment, Separations Development Section S-11 recommended** that oxalic acid be substituted for hydrogen peroxide as a reducing agent and that 0.2N HF be used instead of 1N HF to precipitate a single co-formed LaF_3 product precipitate rather than the split pre-formed

*See letter R. S. Apple to W. C. Kay (7-22-44) and letter J. B. Sutton to W. C. Kay (7-25-44).
**Letters J. B. Sutton to W. C. Kay (2-9-44 and 2-12-44).

precipitation with double centrifuging. The average loss in the waste using this procedure (Runs 40 - 45) was 10.5%, including Run 45 with an HF concentration of 0.4N. The original procedure except for the peroxide reduction was resumed and waste losses dropped to 1.5% in Runs 46 - 48.

Comparing the effectiveness of oxalic acid and H_2O_2 as reducing agents, the average waste loss for 17 normal runs using oxalic acid (46 - 62) was 0.9% and the average of 12 normal runs using H_2O_2 was 3.8% (28 - 39).

Substitution of Mn^{+2}-Oxalic Reduction at Low Temperature for Oxalic Reduction at 75° C

A low temperature reduction procedure is a prerequisite for use of the LaF_3 by-product precipitation in the crossover cycle. The procedure for oxalic reduction at 75° was changed to Mn^{+2}-oxalic reduction at 35 - 50° C (0.003% Mn^{+2}, 0.05% $H_2C_2O_4$) starting with Run 146.* Results of subsequent runs are shown in Table XXV, with a comparison with the previous high temperature procedure. Slightly higher waste losses are indicated with the low temperature procedure.

TABLE XXV

Mn^{+2}-Oxalic Reduction at 30 - 50° C vs. Oxalic Reduction at 75° C

Run Nos.	Conditions Mn^{+2}-$H_2C_2O_4$	% Reduction	Waste Loss - Double Centrifugation, Two-Shot Precipitation - 1N HF
146	1 hour at 30° C	not checked	1.9%
147	ditto	99%	1.5
148	ditto	97	0.8
149	1 hour at 50° C	99	1.5
150	ditto	99	1.0
151	ditto	99	0.6
152	ditto	not checked	1.0
153	ditto	not checked	1.2
129-139	1 hour at 75° C**	not checked	0.4

*Letter T. A. Smith to T. C. Kay (5-30-44) and letter R. S. Apple to B. C. Nylen (6-20-44).
**No Mn^{+2}.

Flocculation Studies on the LaF_3 Product Precipitation in the Cross-Over

The effectiveness of Aresklene as a flocculating agent for lanthanum fluoride was studied in Runs 119 and 120, following the procedure recommended by the S-II Section of the Separations Development Division.* For these tests the following revisions to the standard operating procedure were recommended:

1. Make one full LaF_3 precipitation instead of two, one-half LaF_3 precipitations with centrifuging after each.

2. Make a coformed LaF_3 precipitate (La first) rather than a preformed precipitate.

3. Reduce the HF concentration from 1 to 0.2 normal.

Run 119 LaF_3 product precipitation was carried out according to the revisions listed above. Aresklene equal to 20% by weight of the La ion present was added after the product precipitation and the slurry was centrifuged at 1740 RPM. The effluent contained 14.1% of the original product. This waste was reworked by increasing the HF concentration of 0.4 normal and making a second precipitation using one half the normal amount of La. This decreased the loss of 1.3% of the original product.

The conditions for Run 120 were revised when the results from Run 119 were obtained. Two product precipitations and centrifugations were made instead of one, half the total Aresklene was added after each precipitation, and the HF concentration was raised to 0.4 N on the second precipitation. The effluent from the first precipitation contained 15.5% of the original product and the final waste 1.5%.

These tests did not indicate that Aresklene would not improve the centrifuging characteristics of LaF_3 since the other conditions varied at the same time tended to increase waste losses. However, it is clear that Aresklene will not overcome all of these disadvantages.

Effect of Washing LaF_3 Product Precipitates with 1N HNO_3

Clinton plant procedure up to Run 158 had not included washing of the product LaF_3 precipitate at the end of the cross-over cycle. In an effort to reduce the PO_4^{-3} carry-through into Room D, a single HNO_3 wash of the precipitate was made in Runs 168 - 169.** Fluoride waste losses on these runs averaged 1.7% (including the wash) compared to 1.4% for the ten preceding runs (158 - 167). The solids in the product solution after metathesis and zirconium addition were reduced to about one-third the normal amount. These solids contained the usual Zr and P with some Fe and Si. Further washing tests have not been made during the testing of the scavenger procedures.

*Letter J. H. Balthis to W. C. Kay (5-12-44).
**Recommended in letter from R. S. Apple to W. C. Kay (6-24-44).

Preformed vs. Coformed LaF_3 Product Precipitation

At the request of Section S-II of the Separations Development Section a series of eight runs was made in which preformed and coformed LaF_3 precipitates were compared for carrying efficiency and ease of centrifugation.* The results checked earlier findings in that the separation of the coformed precipitate in the large scale centrifuge is very difficult. Results are summarized in Table XVI.

TABLE XVI

Comparison of Preformed vs. Coformed LaF_3 Precipitates

Run	Conditions	Fluoride Waste Loss
138	1N HF, 2 shot, preformed	0.2%
139	(La^{+3} strike) precipitate	0.4
140	0.5N HF, 2 shot, preformed	0.8
141	(La^{+3} strike) precipitate	0.6
142	0.5N HF, 2 shot, 1st shot	2.4
143	coformed (HF strike)	2.2
144	1N HF, 2 shot, 1st shot	1.0
145	coformed (HF strike)	1.9

Substitution of 0.5N HF for 1N HF in the Cross-Over Product Precipitation

The HF concentration used in the precipitation of the two preformed LaF_3 carriers was decreased from 1N to 0.5N in the cross-over cycle beginning with Run 154.** Satisfactory results are obtained at this concentration; the fluoride waste losses for Runs 154 - 163 averaged 1.1%, while the losses on Runs 146 - 153 (1N HF) averaged 1.2%.

Use of Low La^{+3} Concentration (125 Mg/Liter Total) in the Two-Shot Product Precipitation

Clinton plant runs prior to 186 used 225 mg/liter of La^{+3} for the LaF_3 product precipitation in the cross-over cycle. In order to approximate the conditions set up for the Hanford flowsheet, the La^{+3} concentration was decreased to 125 mg/liter, or 60-65 mg/liter per shot.*** This quantity of LaF_3 carries efficiently. The fluoride waste losses on Runs 186 - 201 have averaged 1.9%.

A Summary of Results of Two-Shot Product Precipitations

Samples have been taken from several runs between the first and second LaF_3 product precipitations, which allows evaluation of the second precipitation and centrifugation. Some of the results (shown in Table XXVII) are summarized here for reference.

*Letter J. H. Balthis to W. C. Kay - W. Q. Smith (5-30-44).
**Letter R. S. Apple to W. C. Kay - B. C. Nylen (6-26-44).
***Letter R. S. Apple to W. C. Kay (7-22-44).

TABLE XXVII

CROSS-OVER CYCLE: LaF_3 PRECIPITATION AND CENTRIFUGATION DATA

(First shot - 125 mg/liter La^{+3}, second shot - 100 mg/liter La^{+3})

Run No.	Type of Precipitate	HF Concentration	Loss after First Precipitation	Loss after Rework (1N HF)	Remarks
42	single shot coformed	0.2 N	7.7%	1.9%	Solids not centrifuged - 5.8%
43	ditto	0.2	22.9	2.3	
44	ditto	0.43	6.9	2.3	
45	ditto	0.43	16.4	2.7	
			Loss after		
			First Precipitate	Second Precipitate	Third Centrifugation
48	preformed two shot	1. N	2.7%	1.8%	
49	ditto	1.	4.4	0.6	
50	ditto	1.	---	5.6[a]	1.0%[b]
51	ditto	1.	10.4[a]	2.8[a]	1.3 [b]
52	ditto	1.	3.6	1.0	
53	ditto	1.	4.2	0.8	
55	ditto	1.	13.4	0.6	
57	ditto	1.	6.5	0.2	
59	ditto	1.	4.4	0.8	
60	ditto	1.	6.4	1.4	
158	ditto	0.5	8.5	1.1	
159	ditto	0.5	3.8	1.5	
		(125 mg/liter La^{+3} total)			
194	ditto	0.5	7.2	1.4	
195	ditto	0.5	8.1	1.1	
196	ditto	0.5	6.6	1.1	
197	ditto	0.5	6.8	1.6	
198	ditto	0.5	11.7	1.0	
199	ditto	0.5	8.3	1.8	
200	ditto	0.5	5.2	1.2	
201	ditto	0.5	8.7	1.6	

[a] 870 r.p.m. [b] 1740 r.p.m.

ROOM D OPERATIONS

The purpose of the operations in Room D at Clinton is to concentrate the product in a small amount of lanthanum fluoride so that it can be isolated on a laboratory scale. These operations have no counter-part at Hanford since there will be sufficient product present for isolation of the product without the preliminary concentration.

A concentration factor of 400 is accomplished in Room D by going through two lanthanum fluoride oxidation reduction cycles, decreasing the volume and amount of lanthanum used on each by a factor of 20. These operations have been carried out with a minimum of difficulty process-wise and equipment-wise. The waste losses have been consistantly low and the recovery of product excellent. There follows a discussion of the process modifications and studies which have been made in the course of these operations.*

Oxalic Acid Reduction

Very shortly after the start of operations it was recommended by the Separations Development Section SII that oxalic acid reduction, catalysed by manganous nitrate, be substituted for hydrogen peroxide in the concentration cycles.** The waste losses in the product precipitation step averaged 1.6% on the four runs with hydrogen peroxide reduction, while with oxalic acid they were less than 1%. The reductions were made with .1 M oxalic acid and .005 M manganous nitrate, heated for 1 hour at 50° C.

Change in Oxidation Procedure

The original conditions for the oxidation step in the concentration cycles did not consistantly give satisfactory oxidation, and it was frequently necessary to reheat the solution in order to bring the oxidation up to 90%. In order to avoid this delay and the additional analyses, an oxidation temperature of 85° C held for 1½ hours was adopted as standard procedure. Zirconium (5 g/l) was added to complex the fluoride ion while the dichromate concentration was left unchanged (0.015 molal).***

Tank Metathesis

Following procedures recommended by the Separations Development Section S-II, tank metathesis of the crossover LaF_3 was substituted for bowl metathesis starting with Runs 36 - 36A.**** From the standpoint of losses in the metathesis wastes a review of a large number of runs indicated that neither procedure was superior to the other. Water wash and caustic wash wastes for Runs 10 - 36 average 0.9 and for Runs 36 - 60 average 1.0. However, the effect of increasing the caustic concentration in the water wash from ½% to 2% to prevent peptization of the LaF_3 or $La(OH)_3$ cakes influenced these averages to some extent. Advantages of tank metathesis are (a) less centrifuge operation, and (b) less exposure of the personnel to radiation due to increased ease of manipulation.

*Details of the operating procedure are given in Section A of the Appendix. The effects of process and equipment changes on waste losses are shown on graphs of the waste losses in Section C of the Appendix.

**See letter by J. B. Sutton (report) Jan. 5, 1944.

***See note from W. J. Smith to W. C. Kay (1-19-44)

****Letters (memo) J. B. Sutton 1-4-44 and 1-5-44.

Tank operation was used in the final metathesis step from start-up. The only change in this was the lowering of the KOH concentration from 30% to 10%* with no noticeable change in product losses.

Solubility Study of the First Metathesis $La(OH)_3$ Precipitate

In order to determine the minimum amount of nitric acid required to dissolve the first metathesis $La(OH)_3$ cake an experiment was carried out on a double charge (Run 48 - 49).** Successive amounts of 60% HNO_3 up to the Clinton flowsheet quantity was added to the $La(OH)_3$ cake in the centrifuge bowl. This was followed with the flowsheet quantity of Zr^{+4} and the solution was then transferred to the precipitator tanks and diluted to give a HNO_3 concentration of 1N. Samples were obtained at each step with the following results:

TABLE XXVIII

% of Total HNO_3 used	Conc. of HNO_3	Kg Product in Solution	% Product in Solution (based on total product in 1N HNO_3 Solution)
50	36	224	39.5
75	41.5	310	54.6
100	45.0	344	60.6
100-Zr^{+4}	39.0	384	67.5
100 diluted to 1N	6.0	568	100.0

Losses in LaF_3 By-Product Precipitation and Oxidation Difficulties

Prior to Run 68 the product losses in the LaF_3 by-product precipitates of the concentration cycles were usually 1 - 2% greater than the amount of unoxidized product remaining after the oxidation step. It was found that the anhydrous HF used for the LaF_3 precipitation contained ~0.1% reducing material (as SO_2) by weight. Since it was possible that this material caused product reduction and loss, the HF used in the final by-product precipitation of Runs 39 - 45A was pre-treated with $Na_2Cr_2O_7$ to oxidize the reducing material. No improvement was observed: the oxidation check indicated 1.1% in the reduced state and the by-product loss was 2.6%.

Further investigation showed that by-product losses could be reduced by more thorough washing of the by-product cake. In most runs since 68, by-product losses have been as low or lower than the indicated unoxidized product. An average of the oxidation checks (Run 68 - 91) showed 0.9% of the product unoxidized before centrifugation while the corresponding by-product waste losses averaged 0.8%. At the present time the by-product precipitate in the final concentration is not washed because of the health hazard. No net loss results since the precipitate is recycled.

*Recommended in memo from J. B. Sutton (1-5-44).
**Requested by the TNX Technical Division.

During June and July, starting with Run 123 - 123A, poor oxidation checks were frequently reported on the solution from the first metathesis. From one to three reoxidations with extra zirconium, dichromate or both were required before good oxidation checks (99% oxidized) could be obtained on these runs. A survey of plant results and process changes as far back as Run 77 is given in Table XXIX. These runs can be divided into five groups:

a. Runs 77 - 122, in which only one reoxidation was necessary and the checks, with one exception, were above 99% on the first try.

b. Runs 123 - 135, in which the use of carbonate-assisted metathesis without zirconium and a faulty temperature recorder on the metathesis tank caused numerous oxidation difficulties.

c. Runs 138 - 155, in which frequent reoxidations were necessary in spite of the fact that new and more vigorous metathesis conditions were adopted.

d. Runs 156 - 169, in which oxidation checks that would formerly have been considered unsatisfactory were accepted, with no increase in by-product losses.

e. Runs 170 - 185, containing [illegible] fission elements, in which occasional poor oxidation checks continued to occur, but by-product losses were normal.

TABLE XXIX

SUMMARY OF OXIDATION DIFFICULTIES AFTER FIRST ROOM D METATHESIS

Run No.	D4BF	D10
77-122	0.78 (avg.)	1 reoxidation, 2 others less than 99%, of 22 runs
123-131	1.3 (avg.)	3 reoxidations, KOH/K_2CO_3 metathesis
132-133	1.9	2 reoxidations
134-135	0.9	2 reoxidations, D-1 temperature corrected
136-137	0.7	98.7, extra Zr included
138-139	0.9	99.9, metathesis revised to 1½ hours at 80° C instead of 1 hour at 75° C
140-155	0.66 (avg.)	5 reoxidations in 8 runs
156-157	0.8	98.6
158-159	0.6	99.3
160-161	0.6	99.1 5 out of 7 runs less than 99% oxidized;
162-163	1.1	98.9
164-165	0.4	97.5 no reoxidations
166-167	0.4	96.0
168-169	0.4	96.7
156-169	0.61 (avg.)	
170-171	0.4	94.9
172-173	1.1	97.7 Runs with % fission elements;
174-175	0.5	98.0
176-177	0.2	99.5
178-179	0.9	99.3 no reoxidations;
180-181	0.8	96.0
182-183	0.7	99.6 5 out of 8 runs less than 99% oxidized
184-185	0.6	97.9
170-185	0.61 (avg.)	

Fifteen consecutive runs have been made without reoxidation or above-normal by-product losses, although no evidence is available as to why the oxidation checks are not as consistently high as formerly. At the time that poor oxidation checks appeared, definite amounts of precipitate were observed in D1P and D1O. (It is not certain whether the precipitate first appeared at this time or was present in earlier runs also.) Results of spectrographic and chemical analyses of these precipitates are given in Table XXX. The principal constituent appears to be zirconium phosphate.

When the precipitate was identified as zirconium phosphate it was considered probable that phosphate coming through with the Cell 4 precipitate was reacting with the zirconium used as an aid in dissolving D1P. Precipitation of the zirconium would make it ineffective in dissolving residual fluoride and hence might lead to poor oxidation. Accordingly, in Runs 158 - 161 inclusive, the second phosphate by-product precipitation was made from 0.02M H_3PO_4, instead of the usual 0.1M.* This reduced phosphate contamination of the fluoride product cake, and Runs 158 - 9 and 160 - 1 were oxidized above 99% without difficulty. The low phosphoric acid by-product precipitation was discontinued, however, when it was found to cause analytical difficulties with the reduced fluoride solution in the crossover. Washing of the LaF_3 product cake in Cell 4 (Runs 168 - 169) reduced the solids in the solution of the first metathesis cake to about one-third the normal amount.** The oxidation check showed 97% and the by-product loss was 0.4%.

TABLE XXX

ANALYSES OF SOLIDS IN SOLUTION OF FIRST METATHESIS CAKE (AFTER Zr ADDITION)

Run Number	Sample	Chemical Analysis	Spectrographic Analysis
148-149	D1O	Zr	Zr, P
150-151	D1P	Zr, PO_4^{-3}, Bi, Mn (trace), Fe (trace)	Zr, Bi, P, Mn, Fe
152-153	D1P	----------	Zr, La
168-169	D1P	----------	Cb, Fe, P, Si, Zr
170-171	D1P	----------	Bi, Fe, P, Zr
172-173	D1P	----------	Bi, P, Si, Zr

Carbonate Metathesis Tests

The first Room D metathesis of Runs 123 - 127 employed 10% K_2CO_3 in addition to the usual 15% KOH. No zirconium was used in Runs 123 - 125.*** The solution resulting from these metatheses contained a small amount of solid compared to the usual cloudy solutions (no zirconium phosphate precipitated) but difficulty was experienced with oxidation in the absence of zirconium.

*Conditions outlined in letter R. S. Apple to W. C. Ray (6-24-44).
**Conditions outlined in letter R. S. Apple to W. C. Ray (6-24-44).
***Requested in letter J. B. Sutton to W. C. Ray (5-10-44).

a. Runs 123 - 123A

Oxidized at end of normal period	78. %
Oxidized after additional 1½ hours	83.
Additional hour with 10% extra dichromate	97.
By-product loss (D4BP)	4.3

b. Run 124 - 125

Oxidized at end of normal period	88. %
Additional hour with 10% extra dichromate	99.
By-product loss (D4BP)	6.7

c. Runs 126 - 127 (LaF_3 by-product in crossover cycle)

Zirconium was added prior to oxidation and no difficulty was encountered.

Oxidized at end of normal period	99.6%
By-product loss (D4BP)	1.0

Normal (D4BP) by-product losses at this point average 0.8% (Runs 93 - 122).

Elimination of ZrO^{+2} in the Second Metathesis

Zirconium has been omitted from the second metathesis in Room D starting with Run 170.* This change was requested by the Isolation Group since it interferes with the precipitation of the product peroxide. Slightly higher concentrations of product (about 6%) appeared in the final by-product precipitates of Runs 170 - 177 and 178 - 185, compared to the previous Runs 154 - 161 and 162 - 169 (about 4%). This product is recovered by recycling the precipitate. A large part of the product can be removed by washing, but no washing is done because of the health hazard.

Oil Contamination in Room D

At various times oil has appeared in the final product slurry from Room D. During the isolation process additional operations are necessary to eliminate this oil, in order that a clean final product can be obtained.

In May, two equipment changes were made to eliminate suspected sources of oil contamination:

a. An oil guard was installed around the drip pan on D-2 centrifuge so that any splashed oil is drained away from the machine. Also, oil circulation was adjusted to minimize accumulation in the drip pan.

b. A glass wool filter was placed in the line supplying air to Room D spargers and to the air jets feeding D-5 centrifuge.

*See letter from I. Perlman to H. C. Johnson (6-28-44).

These changes were completed prior to Runs 130 - 137 and since that time only one case of oil contamination has been reported by the Isolation Group.

Samples were taken from Room D process solutions at various points by the Plant Assistance Group to determine the sources of oil contamination and the course followed by the oil through a series of operations. Small amounts of oil were rather consistently found in P-2 and the following oxidized solution (FO). As nearly as the analytical accuracy permits it may be concluded that this oil is carried down with the by-product precipitate and eliminated with the FBP. No significant amount of oil has been found in any final product slurry examined, and the Isolation Group has confirmed that these runs were satisfactorily free from oil. The source of the oil was not discovered.

MATERIAL BALANCES

Confidence in any chemical operation is considerably increased if it is possible to obtain a balance on the material involved in the operation. If this cannot be done then either the accounting on the material entering or leaving is in error, or there are unknown losses, or there is mixing of batches due to varying accumulations of the material in the process vessels. It was recognized early in the operation of the separations plant that material balances were poor over individual steps of the process, being sometimes over and sometimes under 100 percent. However, the overall material balances for the whole process have been reasonably satisfactory, in view of the large number of steps, and this indicates that there has not been any large amount of material being lost from the system or going to waste without being accounted for. For individual steps therefore the difficulty must lie either with variable hold-up in the equipment or improper accounting on the transfers. Checks on analytical procedures and tank calibrations indicated that these were unlikely sources of difficulty. Attention was first given to hold-up in plant equipment and certain equipment modifications were made to eliminate the questionable as well as known points of hold-up. These changes removed some of the sources of difficulty but the material balances were still far from satisfactory on individual steps. Attention was then focused on reproducibility of analytical results and on sampling. From this study it developed that the assay on the starting solution was often incorrect due to failure to obtain a sample representative of the contents of the dissolver. The samplers were modified and refinements were made in the analytical procedures with the result that the reproducibility of individual samples on the starting solution was quite good. The overall material balances on the process increased to somewhat over 100% after these changes but were more consistant and nearer 100% than before.

Material balances still are not as good as it is believed the analyses should give. However, in view of the extended study of this problem there does not appear to be any reason to believe that there are unaccounted for losses from the system or that conclusions as to the efficiency of the process can be appreciably affected by this obvious inconsistancy.

There follows a more detailed discussion of modifications made in the equipment in order to decrease hold-up of product and in the samplers in order to obtain more representative samples.

Equipment Modifications

Analysis of plant data on Runs 8 to 22 revealed an average unaccounted-for loss in both Cells 2 and 3 of approximately 17 mg. per run (21%). In order to obtain additional information on this, the extraction step of plant Run 25 was followed by an inactive chemical run which simulated and preceded the regular oxidation and by-product digestion. The results of this runs are shown below:

TABLE XXXI

Code	Sample	Total Product
24O	Synthetic Oxidized Product Solution	0.3 mg.
21	Special Dilution Water	0.3
21O	Synthetic By-Product Slurry Before Heating	17.6*
21S	Solution Separated from By-Product Slurry During Centrifuging	0.3
23OS	Effluent from By-Product Precipitate	0.3
53BP1	Solution of By-Product Precipitate	10.3
31OP	Oxidized Solution from 23 After Jetting to 31	9.7
31R	31OP Solution Reduced	1.6

These figures indicate that some of the unusual plant results were caused by hold-up in the precipitators, since the product found in the 21 slurry had to come into the inactive oxidized solution from the walls of the precipitator. A large fraction (approximately 4.5% of run 25) of this material went out in the synthetic by-product precipitate. This was significant in that normal losses in this precipitate at that time were 4 - 5%. Coupled with this information was the fact that previous semi-works investigations had shown that product hold-up on that scale of operation amounted to about 25% and that most of the material held on the side walls of the vessel could be removed by washing with 60% nitric acid introduced through a centrifugal distributor. After rinsing the precipitator walls, the wash acid was used for dissolving the bismuth phosphate cake in the normal manner.

On the strength of the foregoing evidence, a centrifugal acid distributor was installed on the agitator shaft of Tank 31. At the time of installation a heavy coating of $BiPO_4$ was found on the inside of the tank. Analysis of this solid indicated a product and by-product concentration about equivalent to that in the normal decontamination cycle product precipitate. The distributor was put into operation after the decontamination cycle product precipitation on Run 36, and used in a series of chemical runs (36A - 36D). A summary of the results including Run 36 (36B, C, D were HNO_3 washes of Tank 31) follows:

Estimated amount of $BiPO_4$ removed from Tank 31 walls - 56 lbs.
Estimated amount of product removed from Tank 31 walls - 315 mg.
Estimated amount of product recovered from Tank 31 walls - 260 mg.

(Some additional product - approximately 60 mg. - was removed by acid washes during Run 35.)

*Questionable value.

Shortly after installation of the centrifugal acid distributor in Tank 31, a single acid spray, similar in design to that proposed for Hanford precipitators, was placed in operation in Tank 21. The initial acid treatment with this spray removed 115 mg. of product and 23 pounds of $BiPO_4$.

On Runs 55 and 56 the performance of the spray and distributor were studied with the following results:

TABLE XXXII

Run 56: Tank 21 Wash (Acid Spray)
Charged 789 lbs. HNO_3 (60%) after centrifugation and washing of extraction precipitate

Sample Number	Washing Time	%HNO_3	$BiPO_4$	Product
1	0 min.	56.4	1.5 g./l.	4.7 mg.
2	5	53.2	1.7	9.0
3	10	52.5	1.9	10.1
4	15	51.7	1.6	10.5
5	20	50.7	---	11.5
6	25	50.0	1.6	12.8
7	30	49.5	1.9	13.2

TABLE XXXIII

Run 55: Tank 31 Wash (Centrifugal Distributor)
Charged 789 lbs. HNO_3 (60%) after centrifugation and washing of product precipitate

Sample Number	Washing Time	%HNO_3	$BiPO_4$	Product
1	0 min.	54.2	3.0 g./l.	8.3 mg.
2	5	54.2	2.7	10.5
3	10	53.5	2.6	11.1
4	15	53.5	---	11.4
5	20	52.2	2.7	11.5
6	25	51.1	2.4	12.0
7	30	50.8	2.8	11.9

The $BiPO_4$ precipitate dissolving tanks (24, 34, 44) were equipped initially with agitators which ran at a critical speed for their length of shaft. These failed early (Tk. 44 on Run 17, Tk. 24 on Run 22, and Tk. 34 on Run 44), and were replaced by air spargers. The average material balance into Room D before agitator failure was 85.1% (Runs 1 - 16). After their failure and after installation of the acid distributors in the precipitators the average material balance into Room D was 82.2% (Runs 45 - 79. No credit is given for "clean-out" runs.)

Starting with Run 53, unusually low extraction yields were obtained. Investigation showed the active material to be in Tank 24 although normal sampling of the 24 product solution did not show it. An acid wash of Tank 24 (Run 56A) picked up about 400 mg. of product and ten pounds of solids in about twenty-four hours. The material dissolved very slowly. The acid was not heated since an air sparger was used for agitating the tank. Small scale air agitation tests in the laboratory and semi-works indicated that the air agitation is ineffective in suspending $BiPO_4$ and because of this the rate of solution is very slow. Analyses of 24P solutions and testing for $BiPO_4$ saturation indicated that solids hold-up in 24 was not a result of precipitation, but rather incomplete solution of the extraction cake.

In order to prevent build-up of solids in Tanks 24 and 34, a procedure was adopted of adding the cake dissolving acid to Tanks 24 and 34, agitating with air for several hours, and then jetting to Tanks 21 or 31 for washing. Results are shown in Table XXXIV. These figures indicate that in general, solution of the decontamination cycle product is essentially complete at the end of the oxidation step, but the solution of the extraction cake is complete only in a few cases.

TABLE XXXIV

Run Number	Product in 60% HNO_3 Added to Run (Left from Previous Run)	
	24A (Extraction)	34A (Decontamination)
61	6.7%	0.8%
62	4.1%	0.5%
63	11.2%	0.4%
64	24.2%	0.9%
65	no sample	----
66	10.4%	0.9%
67	0.1%	0.6%
68	3.3%	0.1%
69	7.3%	0.1%
70	0.2%	0.1%
71	0.9%	0.6%
72	0.3%	----
73	10.5%	0.2%
74	1.7%	0.4%
75	8.0%	0.4%

As a result of this information, an extensive investigation was undertaken by the Plant Assistance Group to determine the solubility and rate of solution of $BiPO_4$, prepared under different conditions, in various strengths of nitric acid. These studies included an investigation of the beta or "insoluble" form of $BiPO_4$. The results of these studies are presented on pages 14 - 18 of CN 1894. The conclusion to be drawn from these experiments was that the beta

form of $BiPO_4$ is not formed under the conditions of the extraction precipitation, but that even if it were formed, the flowsheet quantity of nitric acid would dissolve the material if adequate agitation were supplied. In experiments performed with air agitation, similar to plant conditions, the solids were not suspended. The fine material apparently stirred and dissolved readily while the remainder of the solids settled to the bottom of the container and dissolved slowly from the outer surface.

In view of the inefficiency of air agitation, mechanical agitators were reinstalled in Tanks 24, 34, and 44, and material balances into Room D increased (Runs 84 - 118; precipitator cleaning plus mechanical agitators) to an average of 93.6%.

Other factors influencing material balances which have been investigated are tank calibrations and density corrections for temperature variations in process solutions. A survey by the Plant Assistance Group of process material transfers from scale tanks to cell vessels and from vessels in one cell to those in another cell in a large number of runs (65 - 82) revealed only minor discrepancies of a few percent.

Only little information was available to the operating group on the temperature-density relationships of the process solutions. The following correction factors were determined in the laboratory by the Plant Assistance Group:

TABLE XXXV

Solution	Factor to Correct to 25° C	Temperature Range
40% UNH	+0.00052/° C	25-75° C
20% UNH	+0.00040	25-75° C
20% UNH-1N H_2SO_4	+0.00056	25-85° C
6N HNO_3-17.3 g. $BiPO_4$/l.	+0.0008	25-60° C
5N HNO_3-14.4 g. $BiPO_4$/l.	+0.0006	25-60° C
4N HNO_3-11.5 g. $BiPO_4$/l.	+0.0007	25-60° C

Sampler Modifications

Starting with Run 130 four samples were taken of the 40% UNH solution in the dissolver and each was analysed by two different analysts. From the study of these results it became apparent that many of the samples are not representative of the contents of the dissolver because of evaporation of water from the sample. This was indicated by an increase in specific gravity of the samples over the gravity of the material in the dissolver. It was discovered that the orifice in the air line was plugged which prevented the operation of the sampler in the normal fashion as a combination vacuum plus air lift. The discharge of steam from the sampler jet heated the suction line causing the UNH solution to boil, creating a vapor lift, thus giving circulation through the sampler. The vaporization resulted in a concentration of product and UNH

in the sampler and an increase in gravity of the sample. As would be expected with such a mechanism the product content and the specific gravity of different samples varied considerably. However, when the assays were corrected for the increase in product on the basis of the increase in UNH excellent checks were obtained. The increase in UNH concentration was calculated from the increase in gravity of the sample over the gravity of the solution in the dissolver as indicated by the plant specific gravity instrument. Table XXXVI shows the assays on Run 134 on the starting UNH in the dissolver (11 M) and in the extraction precipitator (21 MR) and the corrected values of the dissolver samples. This particular run was the first on which the correction was made and it so happens that it is the most dramatic illustration of this point. However, it is true that on all samples studied in this fashion better agreement was obtained after making these corrections than before.

TABLE XXXVI

Starting Assay on Run 134
(First 11 M = 100%)

Sample No.	11 M	11 M Corrected	21 MR
1	100%	100%	95%
2	124%	100%	97%
3	125%	97.5%	95%
4	112.5%	98.%	94%
Max. Spread	24%	2.5%	3%

As a result of this study air was substituted for steam on the circulating jets on all the samplers and shields were placed over the air orifices to decrease the chance of their plugging. This eliminated the increase in concentration of product in the dissolver sampler, indicated by the fact that the gravity of all samples checked the plant gravity within experimental error. As anticipated this brought the maximum spread between these samples down to a much lower figure.

A modification was made in the samplers so that the samples are taken directly into a test tube which is carried to the laboratory and used for storage of the sample rather than into a permanent cup in the sampler from which it must be transferred via a pipette to the laboratory container. (See Figure 20.) This modification eliminated poor samples due to hold-up of liquid or solids in the sampler cup and contamination from the transfer pipette. A further improvement in analytical checks resulted.

Table XXXVII presents a summary of the analytical results obtained in these studies. Figure 21 gives a more detailed breakdown of these results of the 11 M and 21 MR analyses.

Revised Roof Sampler

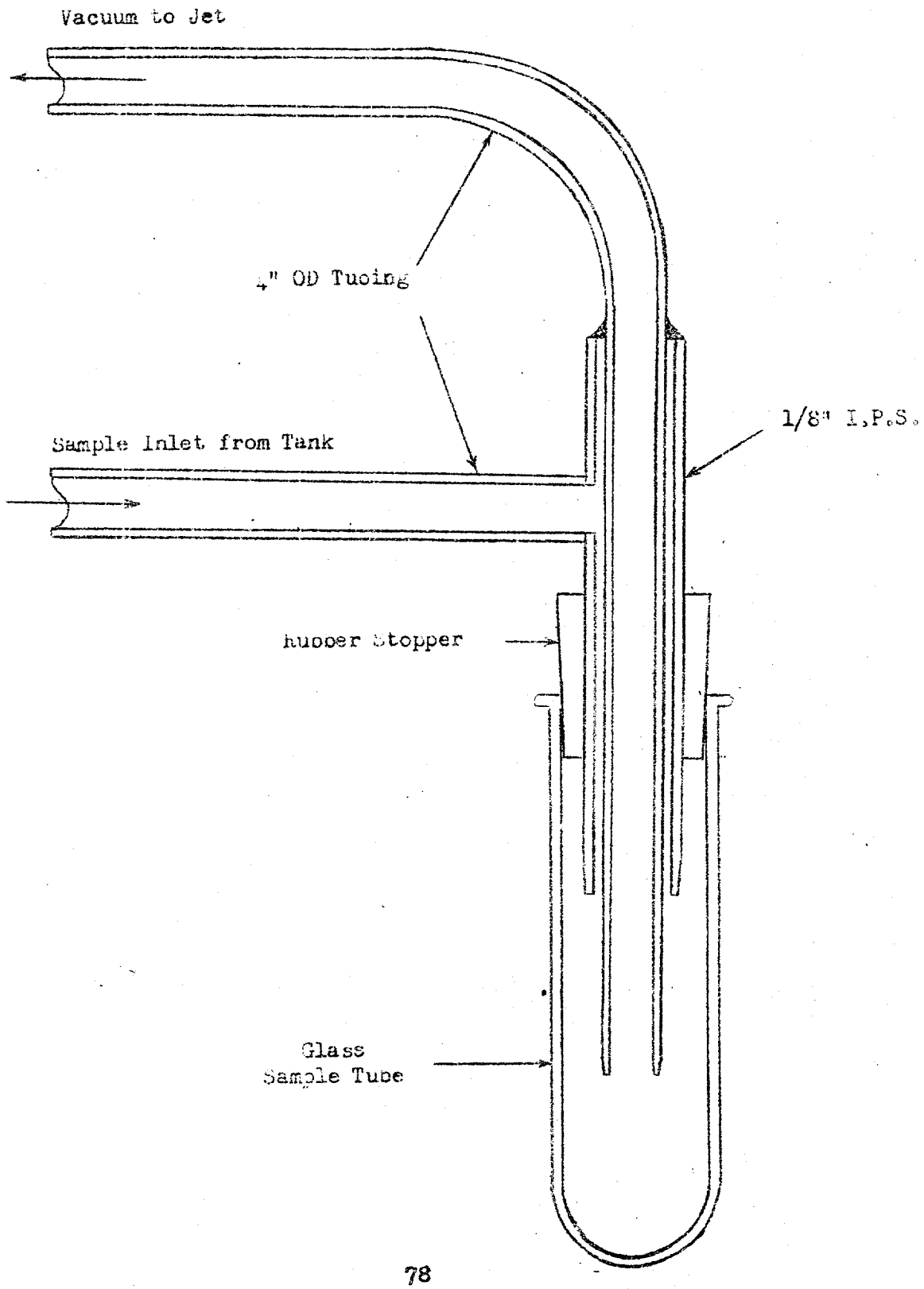


TABLE XXXVII

EFFECT OF CHANGES IN SAMPLER DESIGN AND OPERATION ON PLANT MATERIAL BALANCES

Runs	Average Through				Maximum Deviation Through				Average Deviation Through			
	21MR	24P	34P	D1P	21MR	24P	34P	D1P	21MR	24P	34P	D1P
111-139*	99%	89%	86%	89%	27%	18%	24%	28%	9%	7%	6%	12%
140-193**	102	96	98	101	22	16	19	30	4	6	6	11
194-217***	101	97	102	---	15	10	10	--	3	4	3	--

100% = 11M = 40% metal solution
21MR = 20% metal solution prior to extraction
24P = product solution at end of extraction
34P = product solution at end of first decontamination
D1P = product solution at end of crossover

*Runs 111 - 139 - Steam on samplers.
**Runs 140 - 193 - Air on samplers.
***Runs 194 - 217 - Air on samplers, improved analytical techniques and sample taken directly into test tube.

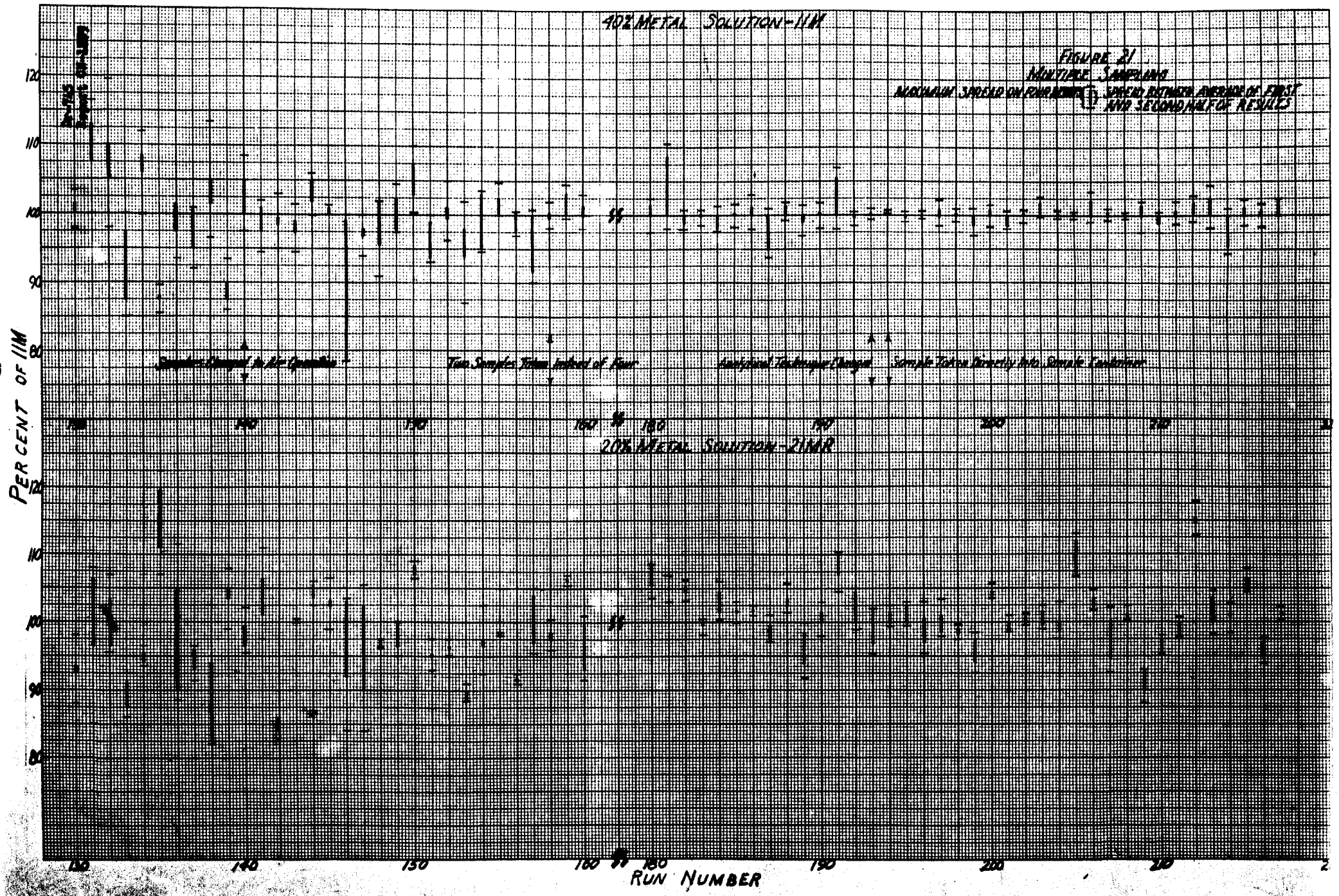


FIGURE 21
MULTIPLE SAMPLING
MAXIMUM SPREAD ON FOUR RUNS [illegible] SPREAD BETWEEN AVERAGE OF FIRST AND SECOND HALF OF RESULTS

RADIATION AND CHEMICAL HAZARDS

AND

DISPOSAL OF RADIOACTIVE WASTES

RADIATION IN OPERATING AREAS

The operating areas in the Clinton Separations Plant not including Room A (chemical preparation) are divided into three sections: Room C, the roof over the Cells and Room D. In and from these areas the various steps for the separation, decontamination and crude isolation of product are carried out. Each area is, therefore, involved to a greater or lesser degree in the handling of radioactive solution and is subject to the hazard involved.

Radiation Detection Meters

Protection of the operating personnel from dangerous amounts of radiation was of vital concern in the design of the plant and in instrumentation for the detection of radiation. There are four types of instruments used; three are sensitive to beta or gamma radiation; the fourth is sensitive to beta, gamma and alpha radiation but is used primarily for detection of the latter. A detection instrument for monitoring of fixed critical areas in Room C and Room D is the integrating radiation meter built by the Victoreen Company known as an Integron. These Integrons have been placed so as to record radiation behind each instrument panel in Room C and beside the 26" centrifuge in Room D. They give a permanent record of the total exposure, full scale on the instrument recording meter being a dosage of 100 milliroentgens. The meters automatically reset to zero every 8 hours at shift change. Very little maintenance has been required by these instruments with the exception that it has been difficult to keep the automatic reset mechanism in proper adjustment. Efforts are being made to improve this device and it is felt when proper adjustment is obtained, the Integron will give satisfactory and uninterrupted service.

In conjunction with the Integron meters, a G-E ionization chamber which is connected to a Beckman amplifier and in turn to a Leeds Northrup Micromax recorder was installed adjacent to the precipitator tank in Room D. Similar circuits were initially installed in Room C with the G-E chamber situated behind the instrument panel. These circuits differed from the one in Room D to the extent that the amplifier was made by the Harvey Company and the recorder was made by the Esterline Angus Company. Shortly after operations commenced, the G-E chambers in Room C were removed from behind the instrument panels and were placed in the cells. The chamber circuit in Room D has been in service for 8 months and has proven valuable as an immediate indication of the activity in charges received from the cells. Some early difficulty was encountered with the leads from the ionization chamber to the amplifier. Originally these were not enclosed in conduit and disturbance of the leads or particularly spillage of liquid on them would throw the circuit out of adjustment. This was also found to be the case with all similar circuits in the Separations Plant and all such leads are protected from external disturbance with suitable conduit.

A third type of radiation detection meter which has been used extensively is the Lauritsen Electroscope. It is made portable by mounting in a case containing batteries for charging and a flash light bulb for illumination. This survey

meter has proven very dependable and continues to function satisfactorily even when subjected to reasonably rough treatment. In Room D, it is used for making routine surveys of all tanks containing process solutions and serves to keep the operators continually aware of the activity in each vessel in use. Throughout the building the Lauritsen is used for monitoring areas suspected or known to contain radioactive material.

The fourth type of instrument is used exclusively in Room D for detection of alpha particles. It is a portable unit developed in the Metallurgical Laboratories at Chicago and was built by the Hallicrafters, Inc. The instrument is actually sensitive to all three types of radiation and, therefore, can be used as an alpha detector only where the beta and gamma backgrounds are slight. "Pluto" as it is called, has been useful for detecting product spillage on the equipment, shielding and floor in Room D. The instrument, however, requires considerable minor repairs.

Radiation in Room C

Room C is the gallery from which the cell equipment is operated by remote control. It is situated above and separated from the process vessels by 5' of concrete shielding; the other three sides and the floor of the cells are 4' thick. Shielding is necessary to protect the plant personnel from the intense radiation emitted by the radioactive fission products and is required through metal solution, extraction, decontamination and cross-over. The waste from the Separations Plant also contains radioactive fission products removed from the product-containing solution and must be neutralized behind shielding in Cell 5. The cell shielding has proven entirely adequate for the intensities of radiation encountered at Clinton and consequently during the initial 8 months of operation, the radiation hazard in Room C has been of little consequence. However, the possibility does exist of inadvertently drawing radioactive solution into the operating gallery by improper operation of the steam jets. The presence of a small amount of radioactive material on the strainer and in the steam line leading to the Cell 1 steam jet, indicates that a suck-back might have occurred. The activity might also have come from vapors being forced up this line from the dissolver.

Radiation on the Roof Above the Cells

Samples for control of the separation process through metal solution, extraction, decontamination and the cross-over are obtained from samplers located on the roof over the cells. Sampling of the intensely radioactive solutions in the cells, particularly the 40% UNH solution and the solution of the first product cake, involve to a limited extent exposure to radiation. The size of the normal control sample is, however, small and by keeping a reasonable distance from it, the tolerance rate for an 8-hr. exposure is not exceeded. At a distance of 1' from a 2 cc. sample of the most active solution (40% UNH) the radiation intensity is approximately 10 mr/hr. Control samples as large as 5 cc. are obtained from other cell process solutions, but here the hazard is less than when obtaining a 2 cc. sample of the 40% UNH solution. At Clinton a large number of special samples have been taken ranging as large as 2.3 liters of 40% UNH and 50 gallons of the solution of the second product cake. It is obvious that in such instances extra precaution and shielding are required.

The hazard involved in obtaining a sample depends to a large extent on the design of the sampling device. At Clinton each cell vessel is equipped with a sampling device which is situated on the cell roof and is connected to the vessel by two lines extending up through the roof. The solution is drawn to the sampler through one of these two lines with an air jet and is returned to the vessel through the other line in which the air jet is installed. The ends of these two lines are inserted through a small rubber stopper into a 15 cc. test tube. When a sample is desired, air is turned on the jet and liquid circulated through the permanent test tube for 10 min. This test tube is then removed and a clean tube put in place. After the solution has circulated sufficiently to insure a representative sample, the test tube is removed before the air jet is turned off and the permanent tube replaced. It is important to keep air on the jet while changing tubes because in this way drops of radioactive solution, which would other wise form, drop from the ends of the pipes and contaminate the area, are sucked by the vacuum into the lines and returned to the cell vessel. The assembly is shielded with lead for locations where the solutions are sufficiently radioactive to require it. Radiation measurements taken on the 40% UNH sampler while in operation gave readings of 11 mr/hr. against the shield (1/4" lead) and the same figure at one foot away with the lead shielding removed. To insure that the operator remains at a safe distance, the test tube in which the sample is obtained is handled with an 18" clamp. The sampling mechanism discussed above was installed for process reasons after the plant had been operating for 8 months and does not constitute a safety hazard at the radiation levels encountered at this site.

The sampler originally installed was similar to the one which will be used at Hanford and operates on the same principle as the one now in use at Clinton. It differs only to the extent that the solution in the cell vessel was drawn into a cup with an overflow positioned such that the cup could hold no more than 10 cc. To obtain a sample, a portion of the solution in the cup was drawn off with a pipette. This assembly was encased in a 2" lead shield. The lead thickness over the top was later reduced to 3/4" and this proved entirely adequate.

The sampling hazard is also increased if process solutions are spilled on the roof or around the sampler, and if leaks develop in the sampling assembly above the roof. Routine surveys give evidence of spillage around nearly all samplers and particularly around the one attached to the Cell 1 precipitator tank. The spills were probabl caused by faulty sampling technique and by pouring active samples no longer of value back down the sampler pipes. One leak has occurred in the assembly above the roof and developed on the Cell 1 sampler. The leak was detected during a routine survey and was the result of faulty construction. The concrete shielding and the adjoining roof had absorbed large quantities of active solution. The area was flushed with water numerous times and was even given a dilute nitric acid wash without appreciably decreasing the activity (200 mr/hr. at 1").

Radiation in Room D

The crude product after passing through the extraction, decontamination and cross-over is brought out from behind the cell shielding into Room D. Enough of the intensely radioactive fission products of the pile chain reaction have been removed so that remote control to the extent required in the cells is no longer

necessary. The operating gallery and process equipment for carrying out the first and final concentration cycles are both within Room D and the process vessels are placed along the inner wall. At present the room is equipped for remote control operation. Such an arrangement developed as a result of experience gained during the early months of running, since the radiation hazards in these operations were not clearly understood or anticipated before the plant started up. As the hazards were recognized and understood, methods of operation and equipment alterations were developed to reduce them to a safe level. In general, the hazards assume two forms: exposure to excessive amounts of radiation as a result of inadequate decontamination in the cell, and contamination of the operating area and the personnel with product containing material which might subsequently be ingested or inhaled by the operators. The latter form has been by far the greater problem and the majority of the alterations in Room D have been made to eliminate product contamination.

At the time Room D operation was started, the equipment was totally unshielded and its operation required that the personnel be on and around the process vessels. High pressure water sprays had not been tied into the 26" centrifuge sprays and to remove the lanthanum fluoride precipitates from the bowl, it was necessary for the operator to use a manual scraper inserted through the centrifuge sight glass window. A scraper was also used for the same purpose on the 12" centrifuge where the lanthanum fluoride cake contains considerably more product. The large process vessels were covered, but were vented into the room, while the small vessels used for the final concentration cycle were equipped with no covers whatsoever. The room was ventilated with two fans situated on the roof.

The first charge received (Run 1) was relatively low in activity giving a reading of 2 mr/hr. at the precipitator on the Lauritsen electroscope. The second charge (Runs 2 - 3), however, gave a radiation intensity of twice that figure and the third charge (Runs 4 - 5) gave an intensity of 11.5 mr/hr. or a tolerance dose for an 8-hr. period. Radiation intensities of twice the above figure were obtained at the centrifuge after the by-product centrifugation. The activity of the charges decreased to insignificance following removal of this by-product cake. On Runs 4 - 5, however, part of the by-product cake through an operating error was carried over into the following final concentration cycle by-product precipitation with the result that the radiation intensity at one foot from the 12" centrifuge was 26 mr/hr. or twice tolerance. At no time during these runs did any of the pocket radiation meters worn by the personnel indicate an over-exposure. However, shielding was installed around all process equipment. A 12" wall of concrete blocks was placed in front of the operating vessels and lead covers 1" thick were placed over the centrifuge casing and around the bowl. Also, the practice of making hourly surveys of tanks containing process solutions was initiated in order to keep the operators continually aware of the activity on each vessel. Since the installation of the shielding, the hazard of radiation from the process solutions in this area has been small, even though charges have been received having a higher activity than was encountered with the the first three. A completely satisfactory explanation for the high activity or poor decontamination is not known. Efforts to tie it in with the metal age have proven futile. The highest activity encountered in Ro m D was through Runs 45 to 53. These runs immediately followed the installation of the acid spray in the Cell 3 precipitator tank and might be explained on this basis.

Shortly after corrective measures were taken to reduce the hazard of radiation from the process solutions, investigations were begun on the possibility of contamination of the operating area with product. Upon the advice of the Medical Department, a preliminary set of tests were run in February 1944 which showed that there were alpha emitting substances in the air and on the surfaces of the operating area. This information indicated a very serious potential hazard might exist since if this were product, it was probably finding its way into the lungs of the operating personnel. This could occur in two ways; either by directly inhaling mists or vapors from the process solutions or by inhaling the product containing dust which must subsequently be formed wherever product is deposited. Spills, hot vapors from the tanks, windage from the centrifuges and thus entrainment, contamination of gloves and clothing, all could account for the presence of product in the room. In no case, was the alpha count, assuming it all came from product, above the tolerance established by the Medical Department except where known spillages had occurred. However, a series of revisions in operating technique and equipment were begun. Efforts were made to avoid handling of product containing solution and slurries. Changing from a bowl to a tank metathesis was a step in this direction as well as discontinuing the practice of washing the by-product cake in the small centrifuge. More extensive use of gloves was advised and all tanks and vessels were kept covered as much as possible. By April 1 a ventilation system was provided for exhausting fumes from all tanks. A program of washing down the room thoroughly every eight hours was adopted and on April 3 - 6 the room was painted in a concerted effort to keep the amount of product to as low a level as possible.

During this period, an extensive program of testing was initiated in an effort to obtain a quantitative understanding of the product hazard. Air contamination was investigated by having the Room D personnel wear respirators masks while they worked and by drawing air from various positions throughout the plant area through respirator pads. These pads as well as those from the respirators worn by the operators were subsequently ashed, dissolved in nitric acid and analyzed for product. Surface contamination was studied by using the so-called smear test whereby various locations about the room and throughout the plant were wiped with filter papers and the papers analyzed by the same procedure used for the respirator pads.

Results of these tests were difficult to interpret and in the light of more recent information, it is evident that the tests were quite inadequate. The technique was faulty in that it did not detect all of the product and further, the importance of naturally occurring alpha emitting substances was not appreciated. This substance (radium and thorium active deposits) has a short half-life and results would vary according to the lapse of time between sampling and analyzing. The tests, however, did give some indication that the average level of activity was reduced by installation of the tank ventilation system. On this basis and because at the time it was evident that a reasonably accurate evaluation of the product hazard had not been obtained, steps were taken for the early conversion of Room D over to remote control operation. This method of operation, it was felt, would give a large enough margin of safety for the worst condition expected. Remote control operation was installed for the large Room D equipment on July 23 - 29 and for the small on August 3 - 11 after the plant had been operating approximately 8 months.

Shortly after Room D had been equipped with a tank ventilation system and prior to the installation of remote control operation, two product detecting instruments, one for monitoring air and another for monitoring surfaces, became available and have proven of considerable aid in estimating the hazard. The air

monitoring instrument, called a "Precipitron", collects the solids from the air by precipitating them electrostatically on a paper which is then counted for alpha activity. Tests have shown the device recovers on an average 70% of the product in the air. Normally, the instrument draws $11\frac{1}{2}$ cfm and is operated for 30 min. for each sample. The natural alpha emitting materials normally present in the air are also precipitated, but by following the count of each sample for two days, a correction is obtained for the thorium active deposits, while the radium active deposits are eliminated.

Table I is a list of the amounts of product found in the air in Room D as obtained by the "Precipitron". The tolerance amount has been established by the Medical Department to be

$$5 \times 10^{-10} \text{ micrograms/cc.}$$

TABLE I

SURVEYS IN ROOM D
Measurement by D. J. Rendell and T. W. Bloss

Date	Location	μmg Prod./cc x 10^{-10}	Date	Location	μmg Prod./cc x 10^{-10}
6/15/44	D-1	0.16	6/9/44	D-5	0.51
6/20/44	"	0.32	6/21/44	"	0.16
6/21/44	"	0.02	7/10/44	"	0.63
7/ 3/44	"	0	7/12/44	"	0.16
7/ 8/44	"	21.80	7/17/44	"	0.28
7/10/44	"	0.02			
7/12/44	"	0.23	6/20/44	D-7	0.98
7/13/44	"	0.14	6/21/44	"	4.80
7/14/44	"	0.14			
7/15/44	"	0	7/10/44	West Wall	4.66
7/17/44	"	0.30	7/13/44	" "	0.44
7/20/44	"	0.25	7/14/44	" "	4.71
			7/15/44	" "	2.17
6/12/44	D-2	0.16	7/17/44	" "	0.33
6/21/44	"	0.45	7/22/44	" "	0.20
7/ 3/44	"	3.47			
7/12/44	"	0.23	6/15/44	East Wall	0.32
7/14/44	"	0.67	7/31/44	" "	0.14
7/15/44	"	0.12			
7/31/44	"	0.23	8/2/44	General Survey	0.49
			8/4/44	" "	0.47

It will be noted from Table I that in general all readings are well below the tolerance level. There is no explanation for the high reading obtained on 7/8/44 over Tank D-1. The sample was taken approximately 2' above a 3" outlet on the tank. The most consistently high readings were obtained along the west wall of the room for which there is also no reasonable explanation. There is no operating equipment near the west wall, only a wash basin and rack for storage of rubber gloves. Since conversion to remote control operation all "Precipitron" readings have fallen practically to zero.

The instrument for monitoring surfaces, called "Pluto", is essentially an ion collector and is used to give an approximate indication of the amount of product within the surface area covered by the instrument. The tolerance amount has been established by the Medical Department to be 0.05μ gm. The device has proven of considerable value in monitoring of equipment and operating area surfaces as well as determining if rubber gloves worn by the operators are fit for further use. In the latter service, a reading of 0.05μ gm is maximum. All gloves giving readings above this figure are scrubbed and rechecked. If the reading is still above 0.05μgm the gloves are discarded. Recent checks have shown that approximately 10% of the gloves are lost each week by using this procedure.

Immediately prior to the installation of remote control operation, it was necessary to thoroughly clean up all contaminated areas around the equipment before proceeding with the work. Work was started on the large equipment first and preliminary readings in excess of tolerance were obtained with "Pluto" on the floor around the process vessels, on the wooden covering over the concrete tank shielding, and around the sight glass windows of the large centrifuge. After scrubbing the floors well with soap and water, covering the woodwork with a film of Usilon paint, and cleaning all stainless steel surfaces with a nitric acid - zirconium nitrate solution the readings dropped well below tolerance. The Medical Department allowed the conversion to be made without requiring the mechanics to wear respirators.

Cleanup of the small equipment was found more difficult. There were places on the floor around the operating vessels where no amount of scrubbing with soap and water or washing with nitric - zirconium solution would remove the activity. The Medical Department, however, allowed the work to be done without requiring the mechanics to wear respirators on the basis that if the activity could not be removed by the methods tried it certainly could not be kicked into the air as a dust and thus create a hazard.

Results obtained with both the "Precipitron" and "Pluto" indicate that under the present conditions, the product hazard in Room D is slight. It seems probable that this would not be the case with increased product levels had conditions remained the same as when the plant started up in December.

RADIATION IN NON-OPERATING AREAS

The non-operating areas in the Clinton Separations Plant are the Cells in which are situated the vessels for handling the highly radioactive solution. The cell equipment is all located along the side of the chamber opposite the doorway through which the cell is entered and the closest piece is approximately 10' from the entrance. The equipment consists of a precipitator tank, centrifuge, catch tank, and solution tank. The latter two tanks are set on the floor of the chamber and the precipitator and centrifuge are supported above the floor on steel frames. Adjacent to each cell vessel is an ionization chamber, and although these chambers are used primarily for following the process, a discussion of their function is included in this section since they are radiation detection instruments.

Because of the high radiation in the cells, they are entered only on rare occasions, when the urgency is sufficient to warrant the time and effort required to clean up the equipment.

Cell Decontamination and Maintenance

During the first 9 months of operation, all the cells except Cell 1 were entered at one time or another for purposes of maintenance or inspection of equipment. Before work was done in any cell, a survey of the activity throughout was made by the Medical Department, and a maximum time that any one individual could remain in the working area was established. The time of exposure per man is established on the basis of less than 0.1 roentgens/8 hr. day. The cell activity varied from cell to cell according to the degree of decontamination of the process solutions handled and in those cells where the activity was high, it was necessary before entry to clean the equipment and in some instances the walls and floor of the cell. Activity builds up within the cell vessels either by accumulation of the process precipitates on the inside of the tank or by adsorption or plating out of specific fission elements on the metal surfaces. Active material gets outside of the vessels and onto the walls and floor of the cells either by deposition of volatile fission elements (I, Ru) evolved from the process solution or through entrainment of process solutions. In a few instances active solutions have leaked or been spilled from the equipment as a result of equipment failure or faulty operating technique. When this occurred, the cell intensity increased appreciably and subsequent cell decontamination was rendered more difficult. At the present product level a clean out before entry is always required for cells in which the process steps of extraction, decontamination, and waste neutralization (Cells 2, 3, and 5 before June 20 and Cells 2, 3, 5, 6 and 7 after) are carried out.

The general clean out procedure now used at Clinton is as follows:

1. The cell vessels are given a wash (4 to 10 hours) with successive amounts of 60% HNO_3 (usually two washes). The nitric acid washes have proven effective in removing active $BiPO_4$ residues which have accumulated on the inner surfaces of the tanks. Nitric acid does not appear to be too effective in removing the remaining activity deposited or absorbed directly on the metal equipment surfaces. Indications are that 1N HNO_3 - 1N HF wash solutions (fluoride wastes) are effective in removing such activity, but this wash must not be heated or it will become corrosive to 25 - 12 stainless steel. NaOH wash solutions also appear promising.

2. The cell cover on the roof is removed and the equipment, floor and walls of the cell are thoroughly washed down with a high pressure stream of water. This procedure has proven quite effective in removing some of the external contamination loosely attached to the cell surfaces. No effective method for complete decontamination of concrete is known.

3. The cell vessels are finally washed and filled with water. The extra shielding gained by the addition of water to the cell tanks has in some instances doubled the working time per man and has decreased the general activity to an extent equal to that of the two preceding steps of the clean out procedure.

A detailed discussion of cell decontamination follows.

Tank 31 Clean-Out for Installation of Centrifugal Acid Distributor

After Run 35, a centrifugal acid distributor was installed on the agitator shaft of the Cell 3 precipitator (Tank 31) to facilitate cleaning the interior surfaces of this vessel. In Run 35, the 10N HNO_3 used to dissolve the Cell 3 product precipitate was first added to the precipitator and agitated therein to dissolve active residue from the bottom of the tank. However, the activity near the bottom of the precipitator, below the jacket, was 180 mr./hr. both before and after this treatment. The acid distributor was then installed, and the vessel cleaned further with three separate washes of 10N HNO_3, each circulated through the distributor and through the vessel for one-half hour (solutions not heated except by the steam jet used for transfer; cooling water running through the precipitator jacket). After these three additional HNO_3 treatments, the activity near the bottom of the precipitator was reduced to 6 mr./hr.

Approximately 360 mg of product and 60 pounds of $BiPO_4$ were picked up from the Cell 3 precipitator in these four HNO_3 solutions. Clearly, therefore, this clean-out involved the solution of a thick layer of active $BiPO_4$ from the walls of the vessel, more than the deactivation of a contaminated, but otherwise relatively clean, metal surface.

Tank 21 Clean-Out for Installation of Acid Spray

A spray was installed in the Cell 2 precipitator (Tank 21) after Run 45 to allow recirculation of acid over the interior surfaces of the vessel for dissolving off the $BiPO_4$ residues.

A survey in Cell 2 after Run 45 showed too high an activity level for installation of the spray, so the level was reduced by washing the precipitator with the normal amount of 10N HNO_3, agitated therein for ten hours without heating, then processing this solution in the standard manner for a product precipitate solution in order to recover the product picked up. (See Table II) The spray was then installed, and three separate washes made with 10N HNO_3, each circulated through

the spray and precipitator one-half hour without heating (with jacket cooling water on), to remove product remaining in the vessel. (See Table III). Here, also, the large initial activity reduction is due to the removal of the active, product-containing $BiPO_4$ residue.

TABLE II

PRODUCT PICKED UP IN 10N HNO_3 WASHES OF CELL 2 PRECIPITATOR

1st wash (before spray installed)	88 mg
2nd wash	22
3rd wash	5
4th wash	1

TABLE III

ACTIVITY LEVEL NEAR CELL 2 PRECIPITATOR

Survey	Mr./Hr. Near Precipitator		Precipitator
	Bottom	Top	
After Run 45	6,000	67	Full of water
After first HNO_3 wash	450	55	Full of water
After final HNO_3 wash	220	100	Empty

Clinton Plant Cell 2 Wall Activity

During the installation of the spray in the Cell 2 precipitator, high hand counts were noted, which contamination was traced to the cell walls. Smears from thirty locations indicated that all surfaces in the cell were contaminated. Though readily detectable, the contamination was not sufficient to affect the general radiation level in the cell. Tests by L. C. Peery, G. M. Branch Jr., and G. R. Leader on samples from the Cell 2 exit air duct indicated that at least three-fourths of the activity was due to iodine and ruthenium, with roughly ten times as much iodine as ruthenium.

Two chips of the painted concrete from Cell 2 were tested - one from the floor near the precipitator and catch tank vents counted 3,500 beta counts per minute per square inch, and one from the east wall, 2,900. Neither chip was reduced in activity by as much as half by treatment with a hard direct spray of water for five minutes, followed by three hours in running water.

No such contamination was found in Cells 3 or 4, nor in any of the semi-works cells.

Plant Clean-Out Before Determination of Product in Metal of Known Power Level

Immediately before plant Runs 84 and 85 in which the amounts of product in special batches of metal were determined, the extraction plant equipment was cleaned out with HNO_3 washes, and mechanical agitators were installed in Tanks 24 and 34 (oxidizers in Cells 2 and 3).

Cell 1 Clean-Out

To clean out the metal heel and the product remaining in the dissolver, a normal charge (1675 pounds) of 60% HNO_3 was digested in the dissolver at 100°C for twenty-five hours. A heel of approximately half a normal batch of metal was dissolved, and the final solution contained 24% HNO_3 and 94.4 mg of product. This was diluted as usual in the dissolver, but was not neutralized with HCOOH, and was then processed as special batch 83-A.

One thousand pounds of 60% HNO_3 were then digested in the dissolver for fifteen hours at 100°C. This solution picked up only 1.2 mg of product and was discarded. The dissolver was then rinsed with 500 pounds of water.

While the pick-up of HNO_3-recoverable product was nearly complete in the first hot HNO_3 treatment, the removal of fission activity from the dissolver by both treatments was not sufficient to allow entrance into the cell - electroscope readings in the doorway after the clean-out showed 560 mr/hr., nearly fifty times tolerance. No comparable value before the clean-out is available.

Cell 2 Clean-Out

The special batch 83-A from Cell 1, which contained 17% HNO_3 after dilution in the dissolver, was transferred to Tank 21, the normal amount of H_2SO_4 was added, and this solution was then used to wash all four equipment pieces in Cell 2. The solution was not heated, except by the jetting (temperatures not recorded), and was circulated or agitated in each vessel one to two hours. This solution was then returned to Tank 21, analyzed for acid (9.8% HNO_3), diluted to about 6% HNO_3 and processed from there on in the standard manner.

A special acid wash of 1,000 pounds of 60% HNO_3 was then circulated through 21, 22 and 24 (Cell 2 precipitator, centrifuge and oxidizer), diluted to 28% HNO_3 and agitated in 23 (catch tank), and then transferred to Cell 5 and stored there until used for washing Cell 3 also. Analysis of this special wash showed 9.9 mg of product and 2.4 g/l solids picked up in Cell 2.

Activities in Cell 2 before and after the clean-out are recorded in Table IV. These results are not directly comparable, as the tanks were filled with water for the readings after the clean-out, but not before, and the positions of the electroscope for the two sets of measurements were not exactly the same. However, it is clear that the removal of by-product activity was far from complete. A temporary wall of concrete blocks six inches thick was built around the oxidizer to increase the time (40 minutes) allowable for men to work on the installation of the agitator.

Cell 3 Clean-Out

After processing special batch 83-A through Cell 3, the acid wash from Cell 2, containing 28% HNO_3, 9.9 mg product and 2.4 g/l. solids, was used to wash out all four equipment pieces in Cell 3. As in Cell 2, this wash was agitated in or circulated through each vessel for one to two hours, with no heating other than that from jetting (temperatures not recorded). Two water rinses of 100 pounds each were added to the wash; the solution was then analyzed and discarded. The analysis showed 20% HNO_3, 24.9 mg product (a pick-up of 15 mg in Cell 3), and 0.6 g/l. solids. This analysis for solid content cannot be reconciled with that of 2.4 g/l. for the wash solution before treatment of Cell 3.

Activities in Cell 3 after cleaning are also shown in Table IV. Corresponding values immediately before treatment are not known, but values from earlier surveys indicate activities within the cell before clean-out to be generally but a few-fold greater than tolerance, and not much greater than those after the clean-out. Three hours of exposure per man was permitted by the Medical Department. In both Cells 2 and 3, the catch tank appears to have been decontaminated to a significantly greater extent than the other tanks.

Cell 4 Clean-Out

Following Run 83-A, all four equipment pieces in Cell 4 were washed out with a solution of 60 pounds zirconium carbonate gel in 1700 pounds 60% HNO_3 (8.7 g Zr/l.), circulated or agitated in each vessel at 50°C for one to four hours. When returned to the precipitator, analysis showed 17 mg of product had been picked up. The solutionswas then diluted to 9,000 pounds (flowsheet volume, 1.3 g Zr/l.), transferred to and digested in the Cell 4 vessels again, then returned to the precipitator, where the product analyzed 28 mg. This solution was then processed through Cell 4 with oxalic reduction and one-shot LaF_3 precipitation.

The activity within Cell 4 has never been sufficient to require a cell clean-out prior to entry. The purpose of the wash was merely to recover and remove product from the vessels.

Room D Clean-Out

The small tank and centrifuge in Room D were also cleaned out with HNO_3-Zr solution, as was Cell 4, yielding 13 mg of product. However, radiation from the Room D equipment was too low to be measured both before and after cleaning.

TABLE IV

ACTIVITIES IN PLANT CELLS 2 AND 3 BEFORE AND AFTER THE CLEAN-OUT FOLLOWING RUN 83-A

	Activity (mr./hr.)			
	Cell 2		Cell 3	
Adjacent to	4/7/44 After Clean-Out. Tanks Filled with Water	4/4/44 Before Clean-Out. Tanks Empty	After Clean-Out. Tanks Filled with Water	Before Clean-Out. from Earlier Surveys
Precipitator.				
bottom	1000	350(?)	26	---
middle of jacket	150	---	62	---
top of jacket	165	200	27	60 (2/7/44)
Centrifuge				
center of bowl	180	---	24	---
Catch Tank				
top	38	350	13	---
bottom	44	530	14	140 (2/7/44) 4 (3/7/44)
Oxidizer				
top	120	350	8	9 (3/7/44)
bottom	680*	705	29	32 (2/17/44) 65 (3/7/44)

* 100 mr./hr. outside concrete block wall erected around oxidizer.

Cell 2 Precipitator Clean-Out for Replacement of Agitator Motor

The agitator motor on the Cell 2 precipitator tank failed during the digestion of the extraction precipitate on Run 123. The charge was centrifuged without mechanical agitation in the precipitator and it was expected since the precipitate was not suspended in the effluent, that part of the cake would settle out on the bottom of the tank. To recover this precipitate and to decrease the activity within the tanks in preparation for replacing the agitator motor, all vessels in Cell 2 were successively washed with 1,000 lbs. of 60% HNO_3 during a 10-hr. period, including a final wash after dilution with an equal part of water. This wash picked up 134 mg of product, the major part of which must be attributed to that part of the product cake which settled out on the bottom of the tank. Although the activity in the cell and around the working area (on top of and above the precipitator) was still high, it was decided to attempt to reduce the activity sufficiently by filling the vessels with water and, also, by applying a hard stream of water for one hour against the reducer motor, around the top of the precipitator, and the surrounding walls. These measures reduced the activity to 84 mr/hr. and a second nitric wash was not required. One-half hour working time per man was permitted by the Health Group. The activity reading taken after clean-up and at various times throughout the clean-up are given in Table V. Note that radiation above the precipitator was reduced from 270 mr/hr. to 120 mr/hr. as a result of the water hosing. This suggests the presence of I and Ru on the surfaces of the motor and around the top of the vessel. A previous clean-

out of Cell 2 revealed that all surfaces in this cell have been contaminated with these radioactive elements. The table also shows the marked effect filling the tanks with water has on reducing the level of activity.

TABLE V

ACTIVITY READING TAKEN DURING AND AFTER
CELL 2 CLEAN-OUT PRIOR TO REPLACEMENT OF AGITATOR MOTOR

Conditions	Inside Cell Door	Activity (mr/hr.) Precipitator Tank		Catch Tank	
		Below	Above	Below	Above
Following acid wash Vessels empty	100	2500	---	230	250
60" Water in Precipitator and 12" in Catch Tank	75	800	270	---	---
Following External Washing of Top of Precipitator for 1 hour	---	---	120	280	---
Precipitator and Catch Tank Full of Water	---	---	84	90	---

Cell 5 Clean-Out for Conversion to Normal Process Cell

During June work was done on Cells 5, 6 and 7 in preparation for using all 7 cells in duplication of Hanford flow sheet conditions. Cell 5 was converted from the waste neutralization cell to a standard process cell and is normally used for carrying out the first product precipitation. The conversion of Cell 5 to a standard process cell called for extensive piping changes and relocation of the vessels, and in order to perform this work, a thorough decontamination of the cell equipment was necessary. The general activity level within the cell was high because active material had gotten from within the confines of the cell vessels and on to the outsides of the equipment, floor and walls of the room. This was brought about primarily by inadvertently allowing a too rapid evolution of CO_2 during waste neutralization and thus entraining active material or even foaming over the tank. A further cause of Cell 5 contamination resulted from a failure in a sampler discharge pipe above the roof which allowed leakage to seep down outside of the sampler pipe before repairs were made. Table VI gives a list of the primary measures taken for clean-out of Cell 5 and also activity readings taken at various times throughout the decontamination procedure.

TABLE VI

ACTIVITY READINGS TAKEN DURING CELL 5 CLEAN-OUT
(Clean-Out Started around Middle of May)

Conditions	Activity (mr/hr.)					
	Cell Entrance		By-Product Holding Tank		Neutralizer Tank	
	2' from Cell	2' in Cell	6' Away	4' Away	6' Away	4' Away
1.	---	1500	---	---	---	---
2.	160	---	---	---	---	---
3.	280	---	---	---	---	---
4.	115	---	---	---	---	---
5.	145	410	610	---	180	---
6.	68	420	600	---	120	---
7.	---	85	85	---	63	---
8.	---	52	48	275	35	70
9.	---	46	45	215	---	26

1. Reading taken on April 29 approximately 2 weeks before clean-out. Cell vessels empty.

2. Tanks 51, 53 and 54 (Neutralizer, By-Product Holding Tanks) washed with a Cell 4 HNO_3 - HF waste for 17 hours.

3. Reading after first HNO_3 - HF wash. Cell vessels empty.

4. Tanks 53 and 54 (By-Product Holding Tanks) washed for 19 hours with second HNO_3 - HF waste.

5. After water wash vessels empty.

6. After 4-hr. wash of tanks 51, 53 and 54 with 24% HNO_3 at 50°C and use of Cell sprays for 8 hrs.

7. After 4 hrs. high pressure hosing from cell roof opening.

8. After 20 hrs. treatment of Tanks 51 and 53 with 25% NaOH at 50°C.

9. After 4 hrs. hosing from cell roof opening. 30% HNO_3 in Tanks 51 and 53.

Although no readings were taken immediately before the first chemical wash (HF-HNO_3), it appears from the reading taken on April 29, that this wash gave the most pronounced decontamination. The marked improvement in decontamination observed after the high pressure hosing is evidence that the greater portion of the radiation after the first wash was eminating from outside the process vessels. Observation of the cell sprays during the clean-out showed them to be quite ineffective in removing external contamination from cell equipment. Deposits of active precipitates on the cell vessels, walls and floor can only be removed by means of high pressure hosing.

Even after the cleaning measures outlined in Table VI, Cell 5 was not wholly tenable for eight hours of working time, and additional steps as follows were required:

1. The cell was entered and all equipment thoroughly hosed for 4 hrs.

2. Readings 4" away from the by-product holding tank sampler pipe were reduced from 4,000 to 50 mr/hr. after four 8-hr. treatments with 60% HNO_3. As a further precaution, the sampler mechanism was raised ten feet above the vessel.

3. Discharge lines leading from the neutraliser to the waste storage tanks were removed from the cells. The internal contamination in these lines was enough to give a reading of 600 mr/hr. against the pipe.

It is evident from the difficulty encountered in clean-out of Cell 5 that any leakage or spillage of process solution greatly increases the problem of decontamination.

Clean-Out of Cell 2 and 3 for Inspection of Equipment

Following Run 201, Cells 2 and 3 lay idle for a short period while operation for complete duplication of the Hanford Flow Sheet were carried out in Cells 4, 5 and 6. The idle time was used for making an inspection of the equipment in Cells 2 and 3 and it was necessary, therefore, to decontaminate these areas before entry. Two successive washes of 1000# of 60% HNO_3 were circulated through the tanks in both cells. The first wash picked up 31.2 mg of product and the second wash picked up 6 mg. Cell 2 was given a third wash which was transferred directly to waste and was not used for washing Cell 3 as were the others. This wash picked up 4 mg of product. Following the acid washes, the equipment, floor and walls in each cell were hosed down thoroughly with a stream of high pressure water. Before entry, the cell vessels were then washed and filled with water. Surveys made by the Health Group during the clean-out are given in Table 7. Upon entering the cells, the inside of the precipitator tanks were inspected and found to be free of adhering material, indicating that any $BiPO_4$ precipitate which might have been coated on the inside of the vessel prior to the clean-out was effectively removed by the nitric washes. It is doubtful, however, if any $BiPO_4$ cake accumulates on the walls of the vessels since installation of the sprays for recycling of acid over the interior surfaces. Electroscope readings of highest intensity were obtained at the bottom of the catch tanks in the two cells. The vent line from both the precipitator and the catch tanks discharge close to where the high readings were obtained. Hosing down the cell produced a marked decrease in external contamination. It seems probable that most of the external contamination arises from entrainment of process solution although deposition of volatile iodine may have been a contributing factor. This conclusion is drawn from the observation that there was a fair degree of activity on the surfaces in Cell 3 where the concentration of iodine in the process solution is known to be quite low, even at the present time when Cell 3 is used for making the first by-product precipitation. Surveys taken during clean-out again demonstrated the marked decrease in cell activity brought about by filling the vessels with water.

TABLE VII

ACTIVITY IN CELL 2 AND 3
AFTER CLEAN-OUT FOLLOWING RUN 201

Cell 2

Position	(1)	(2)	(3)	(4)	(5)
Doorway	700	430	120	92	235
Top of 21 Tank	-	-	400	150	340
Top of 22 Centrifuge	-	-	46	32	120
Bottom of 23 Tank	-	-	2000	300	2000
Bottom of 24 Tank	-	-	95	37	52
Top of 24 Tank	-	-	390	260	235

all readings in mr/hr.

(1) Before clean-up, cell equipment empty.
(2) After two nitric acid and one water wash.
(3) After one more nitric acid wash and hosing down equipment and walls with fire hose.
(4) After hosing once more and putting water into 21 and 23 Tanks.
(5) Cell equipment empty prior to resuming operations.

Cell 3

Position	(1)	(2)	(3)	(4)	(5)
Doorway	150	30	16	14	20
Top of 31 Tank	-	200	110	59	200
Bottom of 31 Tank	-	125	72	69	165
Top of 32 Centrifuge	-	150	44	62	120
Bottom of 33 Tank	-	230	170	74	125
Top of 33 Tank	-	94	56	54	-
Bottom of 34 Tank	-	-	-	21	27

all readings in mr/hr.

(1) Before clean-up cell equipment empty.
(2) After two acid washes and one water wash, equipment empty.
(3) After hosing down cell equipment and walls, tanks empty.
(4) After another hosing as above and adding water to 31 and 33 Tanks.
(5) Cell tanks empty prior to going back into use.

Ionization Chambers in the Cells

Single ionization chambers in the cells which were installed prior to start-up responded to movement of active solution in the cells. Additional chambers were subsequently installed in the cells in order to accumulate information relative to the possibilities of using ionization chambers to determine decontamination factors, hold-up of process solutions or precipitates in vessels, and as an aid in following cell transfers and other processing steps.

Cells 2, 3 and 4 were each equipped with 4 G-E 8" ionization chambers, one placed adjacent to each cell vessel. Amphenol-Copolene cables connect the chambers via a four point selector switch to a Harvey B4 amplifier and single point Esterline Angus recording milliameter. Cells 1 and 5 were provided before start with single Mack chambers positioned on a bracket shelf considerably above the cell vessels and serve primarily to record general activity level in these cells.

The G-E chambers are located several inches from the vessels in comparable positions with respect to vessels of the same type. The effect of activity emanating from other vessels is minimized by taking advantage of structural shielding. However, the installation is far from perfect from this standpoint. The chambers at the catch tanks in Cells 2 and 3 are shielded with 4" of lead bricks and the chamber serving the Cell 2 oxidizer is within a 6" concrete wall.

From a study of the data collected with this arrangement the following conclusions may be drawn:

1. Chambers located adjacent to cell vessels can be used to detect wide divergence of decontamination in runs when compared to normal results. They have also been valuable in detecting hold-up of process solutions and precipitates in the vessels due to mechanical failures.

2. Chambers serve as an additional guide in assisting the operators in following movement of active process solutions and slurries. Vessel rinsing and centrifuge operation are also aided by responses recorded on chamber instruments.

3. Gamma activity measurement made in Cell 4 following the LaF_3 cross-over cycle serve to forecast the level to be expected in Room D before the double charge is transferred out of the canyon.

4. Ionization chambers placed adjacent to cell vessels should not, however, be expected to replace laboratory analysis for fission products. Rather good correlation was obtained in a few instances on decontamination factors across Cells 2 and 3, however, the influence of variable background readings, self-adsorption within process solutions of different volumes as well as instrument drift and gradual changes in amplifier calibration all tend to affect ionization chamber readings. Furthermore, interpretation of the readings is time-consuming and involved, hence cannot be regarded as a

quick substitute for laboratory decontamination analyses. Many of the shortcomings of this type of installation might be overcome by locating the chambers adjacent to a sample container outside the cell. It would then be possible to calibrate the whole system frequently, to take background readings which would not be affecte by the movement of the solutions in the vessels, and to maintain geometry factors uniform for all locations in the process. The complexity of this system, however, probably makes it less attractive than the standard procedure.

An illustration of the method used for calculation of decontamination factors from data obtained with the cell chambers and also calculations for comparison with laboratory data are as follow:

Reading in mr/hr. - Run 80

Tank 22 (Cell 2 Centrifuge)			Tank 32 (Cell 3 Centrifuge)		
Background Bowl Empty	Extraction Cake in Bowl	Net (Background Subtracted)	Background Bowl Empty	1st Product Cake in Bowl	Net (Background Subtracted)
183	2684	2501	2	45	43

Decontamination Factor $\cong \frac{2501}{43} \cong 58$

GdF $\cong$ Log of Decontamination Factor $\cong$ 1.8

Laboratory Analysis

Cell 2 Product Cake dGF $\cong$ 2.9

Cell 3 Product Cake dGF $\cong$ 1.0

Comparable Laboratory dGF $\cong$ 1.9

Figure I shows graphically a comparison of dGF obtained from cell chamber reading and Laboratory Analyses.

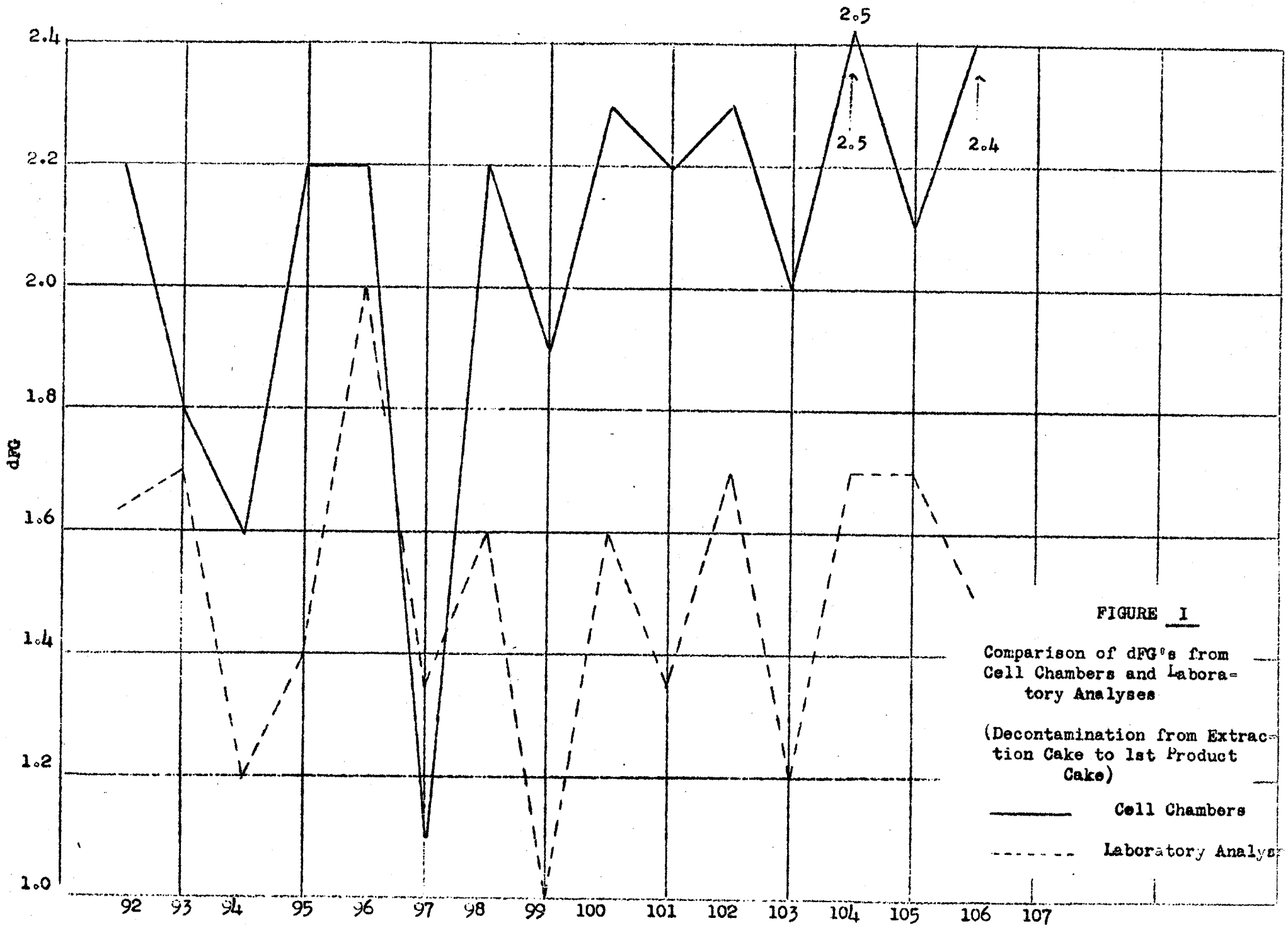


FIGURE I

Comparison of dFG's from Cell Chambers and Laboratory Analyses

(Decontamination from Extraction Cake to 1st Product Cake)

CHEMICAL HAZARDS

Since the hazards involved in handling chemicals have received much attention for many years and since the majority of the people concerned with this report are already familiar with the problems involved, no effort is made to discuss in detail the method and difficulties encountered in handling the numerous chemicals used at the Clinton Separations Plant. Only those reagents which have given abnormal difficulty (anhydrous hydrofluoric acid and formic acid) are herein discussed.

Handling of Anhydrous HF

Two completely separate systems for the addition of anhydrous HF to the process solutions have been set up at the Clinton Separations Plant. One is used for supplying the chemical in relatively large amounts (100 lbs./run) to the precipitator in Cell 4, the other is for adding a smaller amount (15 lbs./run) to the large precipitator tank in Room D. HF is added in the final concentration cycle from wax bottles containing a 48% solution.

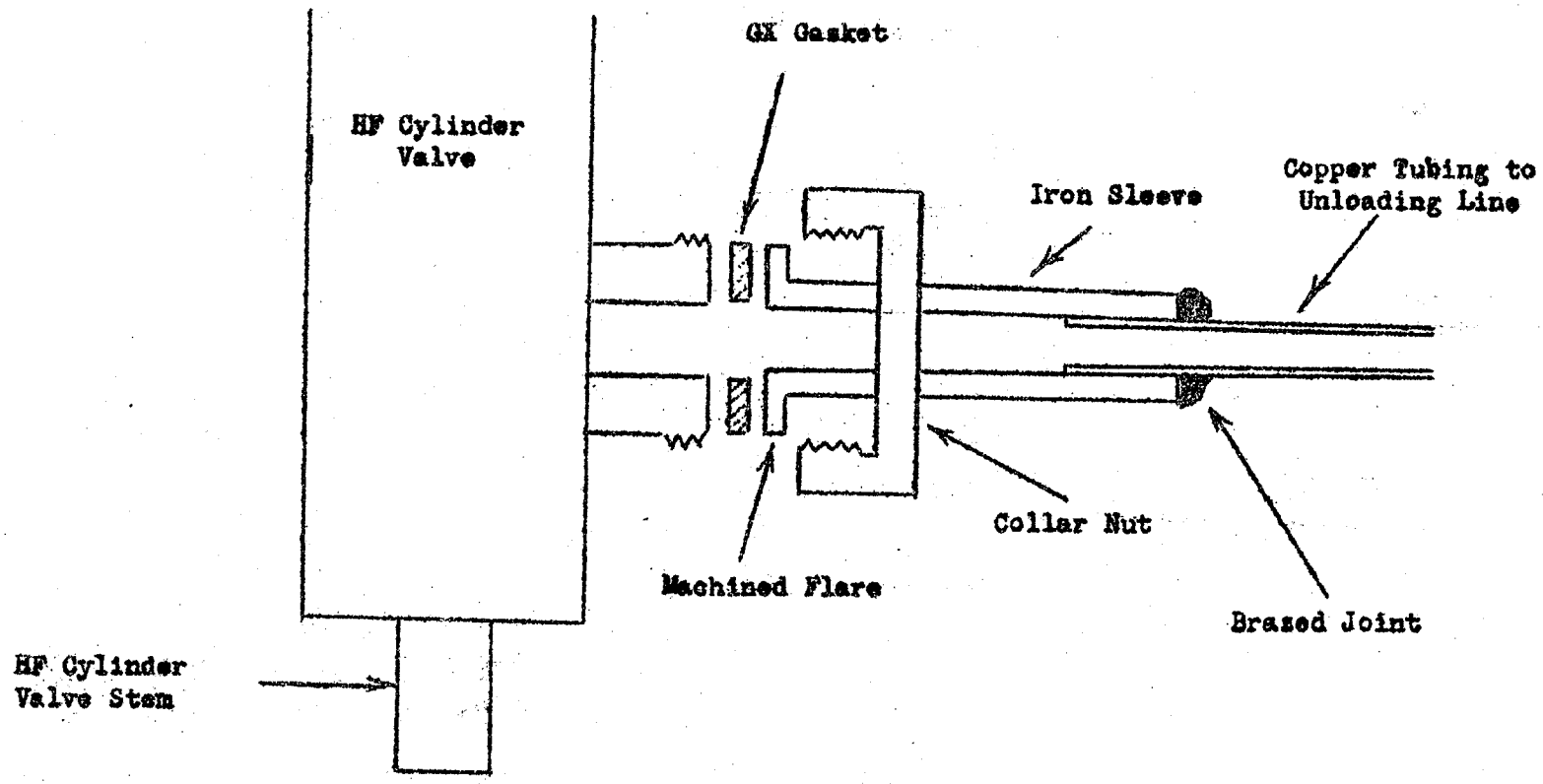
The standard HF cylinder is a clumsy device to handle. It weighs about 200 lbs. when full, contains about 100 lbs. of HF and must be inverted valve-end down, to unload the liquid. A rack must, therefore, be designed to decrease the handling problem and to hold the cylinders in the inverted position while they are unloaded.

One of the greatest difficulties with handling HF at Clinton has been in obtaining a satisfactory connection between the cylinder valve and the line through which the HF is unloaded. The HF cylinders are not uniform in dimensions and the position of the valve opening when placed in the HF rack varies as much as an inch from cylinder to cylinder. This difficulty is overcome by brazing a short section of copper tubing on the end of the HF line, to which in turn is brazed a short section of steel pipe with a machined flare. (See Figure 2) The copper tubing thus gives enough flexibility to the line to allow for variation in the position of the cylinder valve. The short end section of steel pipe with the flare is necessary instead of just flaring the end of the copper tube because threaded fittings after being in HF service become frozen and require considerable pressure to be broken loose and the copper tubing would become bent and torn while breaking the union.

Difficulty has, also, been encountered with the pump used for the movement of anhydrous HF. After the pump has been in contact with HF, it tends to lock or freeze in the packing gland. This would occur even if the pump were operated for a few minutes each shift. The present practice is to remove the pump to the shop after use, flush with water, and fill it with oil so it will be ready when again needed. It is also repacked in the shop with GX packing, since a better job can be done there. Difficulties have been experienced in packing all pumps with GX, in the Separations Plant. The feeling is, however, that could GX be obtained in a properly braided form, it could be used satisfactorily. When packing gland leaks develop on the HF pump, sometimes the addition of large quantities of parmo grease through the grease cap will help.

FIGURE II

Connector for HF Cylinder Valve and Unloading Line



At Clinton, the following precautions are required before doing any work whatsoever with or on the HF system:

A complete rubber suit, rubber gloves, and rubber hood or goggles must be worn.

Two men, one of whom is a supervisor, must be present.

A hose with running water and a gas mask are to be placed nearby.

The area around the pump and HF rack must be roped off and "Danger" sign placed before starting work.

Formic Acid Accident

Prior to Run 166, formic acid was used for the pre-treatment of metal solution before the extraction step. On one occasion (April 9, 1944), a sudden evolution of gas in the formic acid weigh tank (capacity 50 gal.) blew the cover from the tank and caused moderate damage to piping, to the east end of the Separations Building and to adjacent instruments. There were no serious or permanent injuries to personnel. On the previous shift, 100 lbs. of nitric acid had been transferred to the dissolver through this tank. This was not standard procedure and was occasioned by the need of small increments of acid to insure complete solution of a special metal charge. The formic acid weigh tank was washed twice with water before transfer of formic acid, but all evidence indicates that about 20 ft. of ½" transfer line from the carboy unloading station to the weigh tank was neither drained nor washed. A partially empty carboy containing 39 lbs. of formic acid had been transferred to C-12 and 22 lbs. of formic acid from a full carboy had been transferred when the accident occurred. Analyses of wash liquors remaining in used carboys indicate that they contained the proper materials. It is believed that products from the reaction of the small quantity of nitric acid in the transfer line with the formic acid being charged to the tank and the vapors from the heat liberated by this reaction could not be relieved rapidly enough by the 2" diam. vent line on the tank. This accident dramatically demonstrates that every precaution must be taken to prevent mixing of even small quantities of formic and nitric acids.

DISPOSAL OF RADIOACTIVE WASTES

The process wastes from the Separations Plant (205 Bldg.) contain the radioactive fission products of the pile chain reaction, the uranium metal salts and all of the process chemicals. A few of the fission products are completely or partially volatile and are evolved during metal solution and to a slight extent during extraction. These are dissipated to the atmosphere through the Separations Plant stack, the rest of the fission products remain in the waste solutions. All of the waste solutions are treated in Cell 7 with sodium carbonate to neutralize the acidity, raising the pH to about 8. Neutralization was originally carried out in Cell 5 until about June 1. Because of the possible value of the uranium containing waste for future recovery of the uranium, this is not combined with other materials, but is stored separately after neutralization. The other wastes--hereafter called chemical wastes--consist of the waste solution from the aluminum coating removal, the solution of the bismuth phosphate by-product precipitates, the waste supernatants from both the bismuth phosphate and the lanthanum fluoride product precipitates in the cells and the various wastes from the product concentration steps in Room D. These chemical wastes are discharged from the plant to underground tanks. From these tanks, the supernatant is jetted at a fixed rate into cooling water which in turn passes through a settling basin where part of the activity is removed by solids which precipitate on dilution.

Volatile Wastes

In the first steps of the separations process when the uranium is dissolved in Cell 1, there are released volatile fission products which constitute a source of radiation hazard. These products, together with the solution reaction off-gases and the purging air, are drawn through a 4" stainless steel line to the base of the 200 Area stack from whence they are discharged into the atmosphere.

Since there is a hold-up time of about 30 to 50 days between the time of the discharging of the metal from the pile and its dissolving in Cell 1, most of the short-lived activities have decayed to practically zero. At the time of the dissolving, only the relatively long-lived volatile fission products, 8.0-day iodine and 5.3-day xenon, are observed in the off-gases. Evidence of a volatile oxide of ruthenium has been found in Cell 2, but has not been detected in the stack. *

As reported in CP-1615, Kanne and Branch of the Physics Section computed the activities of iodine and xenon to be present in the metal at the time of discharge and at the time of the dissolving and set up apparatus in Bldg. 204, the Separations Area Stack building, to measure directly the activities in the off-gases. At a time when the pile was operating at 1000 KW they computed that a one-third-ton batch of metal (the amount of one run in the dissolver), discharged from a region of average neutron intensity contained 4.35×10^4 curies of 5.3 day xenon and 1.92×10^4 curies of 8.0 day iodine. After a hold-up time of about a month, this metal would contain about 7 curies of xenon and 12 curies of iodine.

Observations show that for a hold-up time of one month, 5 to 15 curies of xenon and 0.5 to 1.5 curies of iodine, depending upon the product concentration in the metal, are released into the atmosphere during each run. When the hold-up time is lengthened to about 50 days, the amount of xenon released ranges from 0.4 to 1.1 curies and the amount of iodine from 0.1 to 0.3 curies.

Two complete cycles of three dissolver runs each were monitored and material balances of these two fission products computed. In both cases, approximately 100% of the xenon and from 2 to 5% of the iodine were found to be discharged into the stack. Of the iodine in the off-gases about $2\frac{1}{2}$ to 5%, or less than $\frac{1}{4}$ of 1% of the total iodine in the metal before solution, is absorbed in the stack drainage.

During Runs 113, 114 and 115, not only were the off-gases monitored but also samples were taken at various stages of the solution and separation process and analyzed by Mr. Martens of the Analytical Division. The amount of xenon calculated to be in the metal at the time of these runs was 34 curies, of which 31.3 curies, or 100% within the experimental error, was observed to be discharged in the stack. Of the 64 curies of iodine calculated to be in the metal, 5.3 curies was observed to be discharged into the stack. The analyses showed that 38.4 curies of iodine remained in Cell 1 after the metal solution. Thus, probably because of the large experimental error, only about 65% of the iodine activity is accounted for. Of the 38.4 curies that remained in solution, 30.8 was retained in the waste and about 0.15 curies was carried down with the first precipitate. Some iodine contamination has been observed at the vent of Cell 2, but the exact amount, the accumulation of many runs, was not determined.

Figure III shows the distribution of iodine and xenon activities with time for Runs 113, 114 and 115. These curves are representative of all runs, although the peak and average intensities are a function of the hold-up time, pile intensity and flux factor of the region from whence the metal came, and the solution reaction rate. The smooth unbroken curve shows the relatively sharp peaks of xenon activity which coincide closely with the actual time the solution reaction is maintained, and the dotted line connects points that indicate the observed iodine intensities. The experimental procedure of obtaining this data and the calculations are discussed in GP-1615.

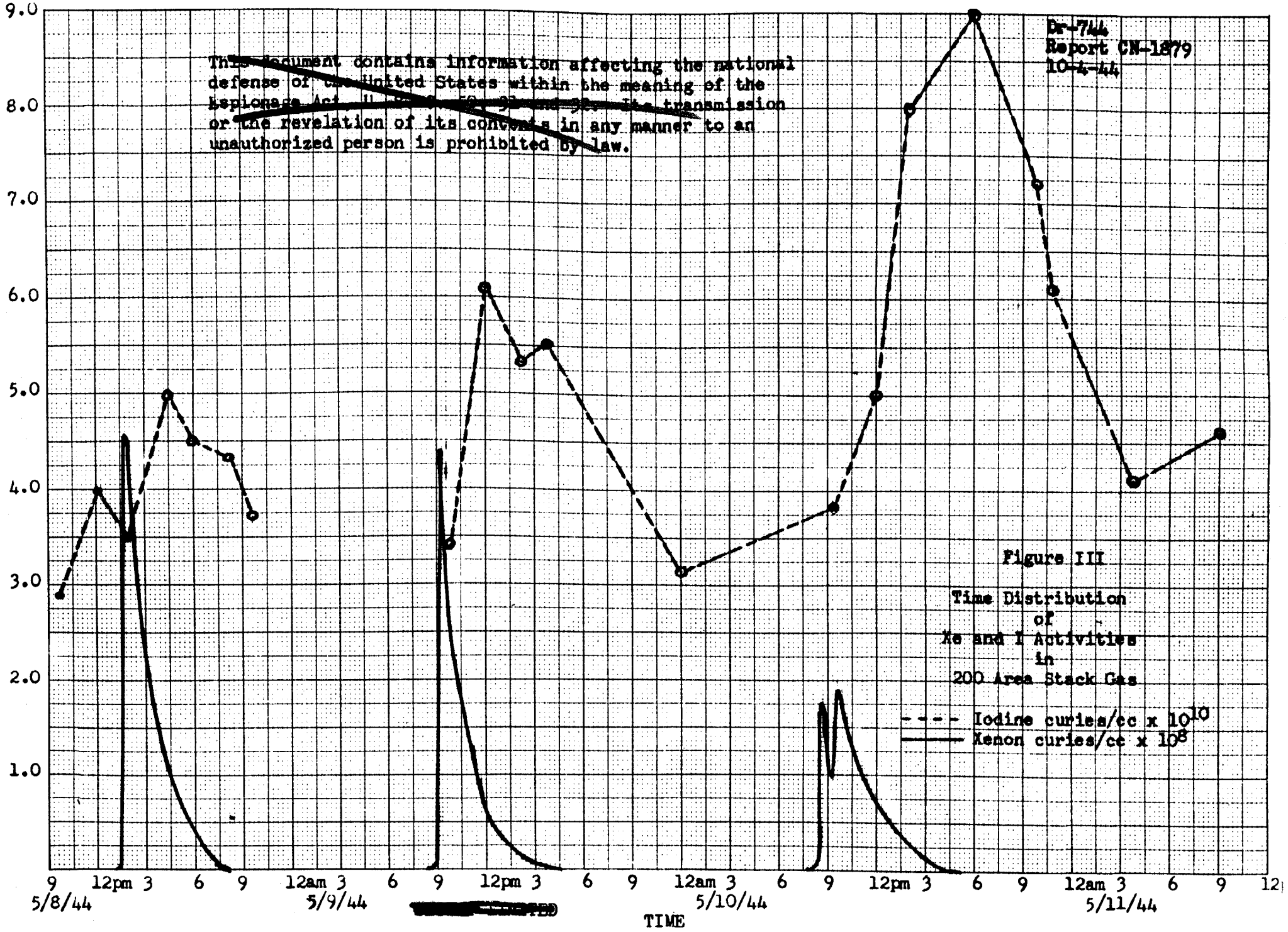
The average xenon intensity in the off-gases is about 10^{-8} curies/cc during the time of solution, with peaks for short periods as high as 5×10^{-8} curies/cc. The iodine intensity in the off-gases is about 2×10^{-10} curies/cc. At the base of the stack the off-gases are diluted by a factor of 400 to 500 by the Separation Plant ventilating air, consequently the activity concentrations of xenon discharged into the atmosphere is 2×10^{-11} curies/cc and of iodine is about 4×10^{-13} curies/cc.

For a person to obtain an 8-hr. dose of 100 mr, the concentrations of xenon and iodine as calculated by J. A. Lane would have to be 6.4×10^{-13} curies/cc and 2.0×10^{-13} curies/cc respectively. From these figures, it is evident that very little further dilution of the off-gas is required after leaving the stack. Frequent checks have been made in the vicinity of the plant on radiation from the stack gas. On occasion, readings above background have been obtained, but they have always been well below tolerance.

Metal Wastes

The uranium containing waste after neutralization has a volume of 1670 gallons for each 1/3 ton batch of metal processed. Its approximate composition is: H_2O - 71.3%; $UO_2(NO_3)_2 \cdot 6H_2O$ - 8.7%; Na_2CO_3 - 5.2%; $NaHCO_3$ - 5.5%; $NaNO_3$ - .5%; Na_3PO_4 - 4.9%; Na_2SO_4 - 2.5%. The approximate quantities of the various radioactive fission products are given in Table VIII. Sodium carbonate neutralization of the metal waste gives an essentially clear solution, since the uranyl nitrate forms a

[redacted]



[redacted]

soluble complex with the excess carbonate. Figure IV shows schematically the arrangement of the storage tanks for the metal wastes. The waste is discharged to W-3 or 4 and then jetted to W-9. When this was filled (about May 1), it began overflowing to W-10. W-7 and W-8 were made available for metal waste by removing the chemical wastes

Chemical Wastes

The approximate composition and volumes of the individual components which make up the chemical wastes are given in Table IX. The distribution of the radioactive fission products in each component is given in Table VIII. About 93% of the activity in these wastes is carried by the precipitate formed when the solution is neutralized with sodium carbonate. In the storage tank this precipitate settles out on standing, leaving a supernatant with about 7% of the original activity.

Figure V shows schematically the arrangement of the storage tanks and the two retention ponds. Also included in Figure V is a broken line sketch of the settling basin which was built during June and put into operation on July 1, 1944.

Briefly stated, the operation of the waste tanks, ponds, and settling basin were as follows: Beginning with the initial operation of the Separations Plant in December 1943, and up to April 27, 1944, the chemical wastes were run to storage tank W-5. This tank was filled and began overflow to W-6 about February 14. On March 6, discharge was started of the clear supernatant from W-6 to the plant cooling water going to the ponds. This was discontinued on April 27 and the chemical waste was run to W-7 until July 1, 1944. This tank was filled and began overflowing to W-8 about June 1. Prior to July 1, 1944, the waste cooling waters from the pile and Separations Plant flowed into the ponds and was monitored before being discharged to the White Oak Creek. On July 1, 1944, the plant cooling water was diverted from the retention ponds into the basin and discharge from W-6 into this water was recommenced on July 3. The wastes from the plant were started into W-5 again at the same time. The rate of discharge from W-6 exceeded considerably the rate wastes were entering the storage tanks, and the plant was able to empty W-7 and W-8 by jetting to W-5 during the period of July 15 to August 26 making these tanks available for storage of metal waste.

The Clinton Separations Plant was initially designed for the Lanthanum Fluoride Process and on this basis sufficient storage capacity was provided to store all wastes for a period of one year. In June 1943 it was decided that the Bismuth Phosphate Process was the one preferred for operation at Hanford, and consequently it was decided that this process would be the first piloted at Clinton. It was recognized that the neutralized waste volume from the bismuth phosphate process was almost double that for the fluoride process and that storage capacity corresponded to about six months of operation.

Following the decision to use the phosphate process, the only modifications made in the plant were those which were required and every effort was made to hold these changes to a minimum in order not to delay start-up of the plant. At this time the construction of the buried waste storage tanks was well under way and since they were one of the late items on the completion list, it was planned to start operations without further increase. It was realized that considerable decontamination of

FIGURE IV

METAL WASTE STORAGE TANKS

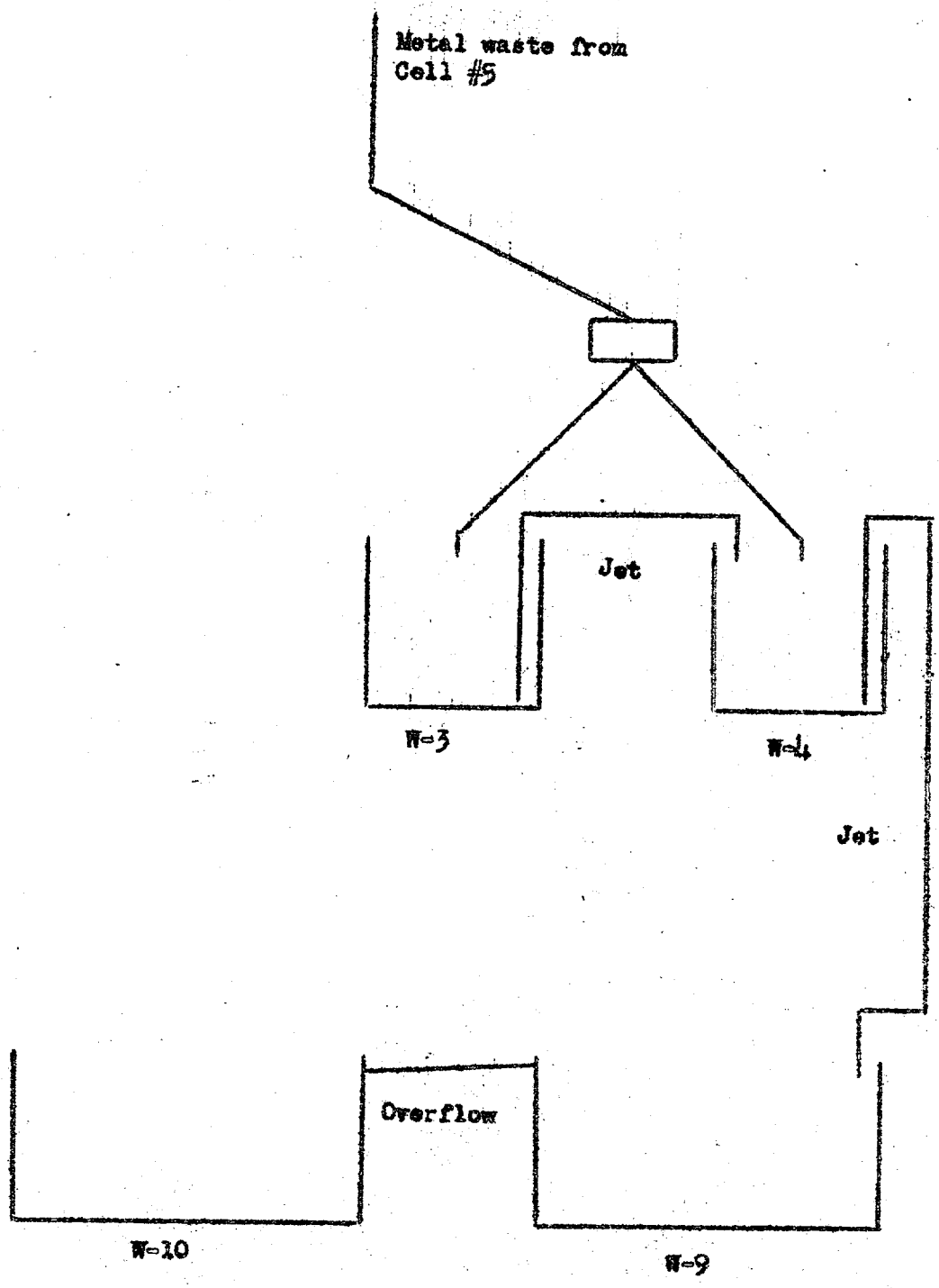


TABLE VIII

MILLICURIES OF FISSION PRODUCTS IN PLANT WASTES:*

Basis: One-third ton metal containing 1 gram product, made in 100 days and cooled 40 days.

ELEMENT	Zr	Cb	Ba	Sr	Pr	Y	La	Ce	I	Te	Cs	Totals
Total Millicuries	125,000	110,000	50,000	180,000	130,000	200,000	60,000	130,000	6,250	5,700	2,000	999,000
Millicuries in Metal Coating Waste	250	220	100	360	260	400	120	260	12	11	4	2,000
Millicuries in Extracted Metal Waste	89,000	98,000	49,000	178,000	95,000	196,000	58,500	114,000	6,250	5,400	1,980	891,000
Millicuries in First By-Product Bismuth Waste	35,000	11,000	270	2,050	13,000	600	1,500	15,000	0	0	---	75,000
Millicuries in Decontamination Waste Centrifugate	62	190	530	20	21,000	3,200	4,000	580	6.5	280	20	30,000
Millicuries in Second By-Product Bismuth Waste	44	480	.6	.02	270	6	6	42	.28	4.6	--	850
Millicuries in Fluoride Waste Centrifugate	.2	9	.3	.02	380	10	68	2	--	.5	.2	470
Millicuries in Room D Wastes	.8	.9	3	.08	310	24	10	.1	--	--	--	350
Total Millicuries to W-5 and 6	35,000	12,000	900	2,400	34,000	4,200	3,000	16,000	19	296	24	108,000

* Calculated from data in CN-1309, CC-829 and data from D. N. Hume.

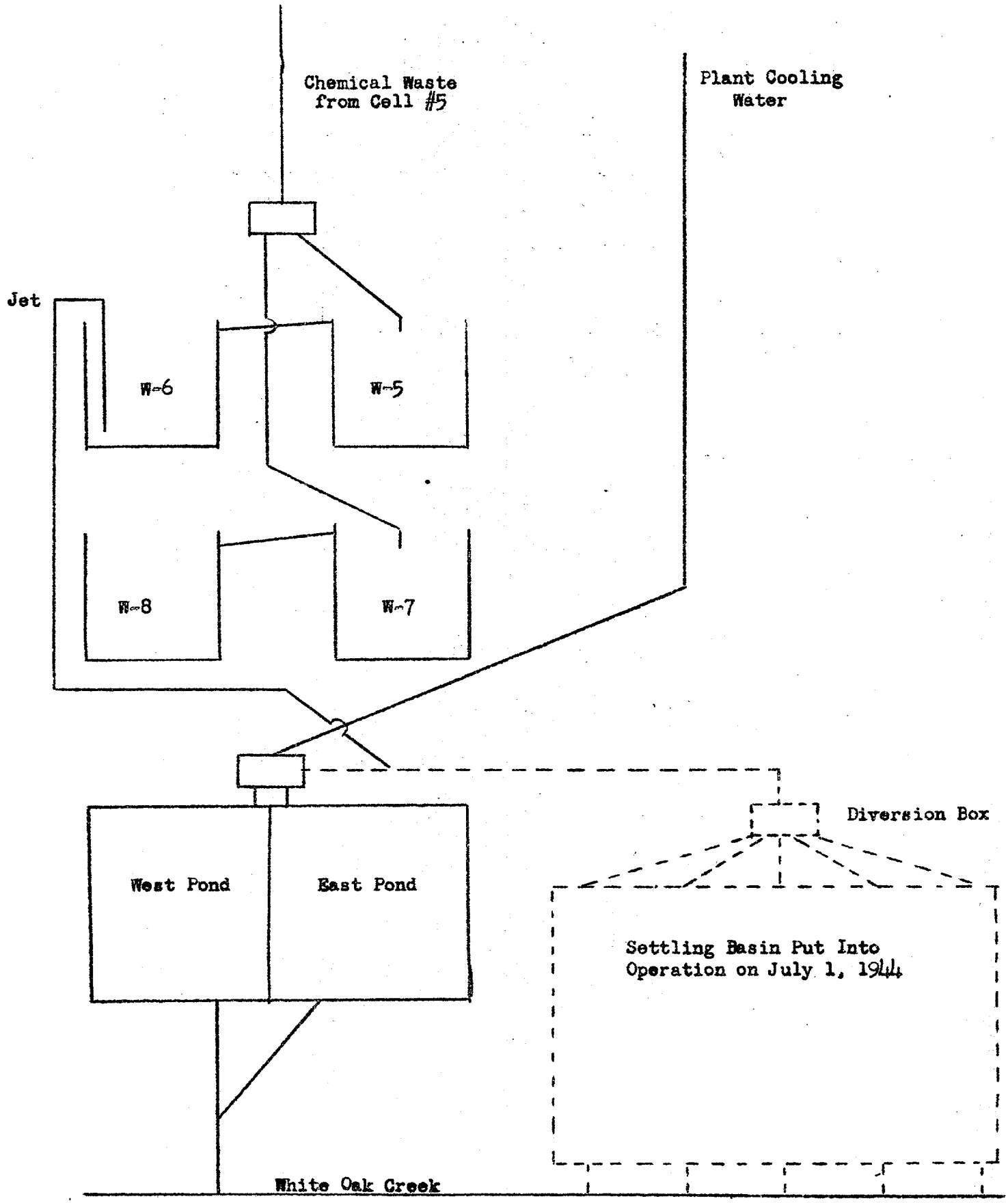
TABLE IX

CHEMICAL WASTES - COMPOSITIONS AND VOLUMES

	Gals	% H_2O	% $Al(NO_3)_3$	% $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$	% $BiPO_4$	% Na_2CO_3	% $NaHCO_3$	% $NaNO_3$	% Na_3PO_4	% NaF	% KOH	% KF	% KNO_3
Aluminum Coating Waste	203	86.6	3.4			6.6	1.1	1.7					
$BiPO_4$ By-Product Wastes	540	64.9			.7	1.9	5	22.8					
$BiPO_4$ Supernatant Wastes	1971	81.3		.5		2.3	5.7	3.9	4.8				
LaF_3 Supernatant Wastes	1802	85.3				.6	5.1	3.9	.8	2.5			
Composite Room D Wastes	508	94.3									1.2	.9	3.0
Total Chemical Wastes	5016	83.7	.13	.22	.09	1.61	4.77	5.80	2.27	.90	.11	.09	.28

FIGURE V

CHEMICAL WASTE STORAGE TANK AND SETTLING BASIN



the chemical wastes would result from the precipitation of solids formed on neutralization and that if this were sufficient, it might be possible to dispose of the supernatant from the chemical wastes thus increasing the life of the installed tanks to well over a year. If it developed that the supernatant could not be disposed of, then a number of months would be available for increasing the storage capacity or for installing equipment for further treatment of the supernatant.

In February 1944, approximately two months after beginning operation of the separations plant, analyses were run on the supernatant in the waste tanks which indicated that dilution with the available plant waste water to below tolerance levels would allow disposal of waste at the rate of input into the tanks.

Discharge of the supernatant from the waste tanks was started on March 6, 1944. Samples were taken of each pond before discharge to the creek in order to ensure that a body submersed in the water would not obtain more than .1 r in 24 hours. Also, the water in White Oak Creek was collected behind a dam near the discharge of the creek into the Clinch River and this water was monitored. The maximum reading obtained on this water at any time was less than 0.1 milliroentgen per hour. A few days after discharge of the waste started, it was observed that a precipitate was collecting in the ponds and that a large fraction of it washed into White Oak Creek when the pond valves were opened. On March 15 a sample of the slurry from the bottom of the ponds was found to contain 27,300 beta and 900 gamma counts per 5 cc, while the supernatant from the slurry contained 410 beta counts. The following day another sample of this precipitate taken from the exit ditch from the pond showed 32,500 beta counts/5 cc, while the supernatant from this sample gave only 75 beta counts. Thus the precipitate was carrying a large fraction of the activity from the waste. It was observed at this time that this precipitate was carrying into White Oak Creek and down the creek a ways. On the same day, samples of water dipped out of the creek gave the following counts per minute (5 cc): Before first gap: 8 betas; lagoon just beyond this gap: 7 betas; and exit of the dike below lagoon: 4 betas.

Recognizing that the precipitate formed was likely due to the calcium in the water, laboratory tests were carried out on March 18-26 which demonstrated that the addition of calcium chloride to the waste tanks would decontaminate the wastes by a factor of about 10. See Table X. The addition of calcium chloride was started on April 17 and continued until the discharge to the ponds was discontinued on April 27. This treatment decreased the activity in W-5 by a factor of about 2, and was just beginning to take effect on W-6 when the discharge was discontinued. See Table XI.

TABLE X

LABORATORY DECONTAMINATION OF PLANT CHEMICAL WASTES WITH $CaCO_3$

Days of Treatment	1	2	3	5	6	7	8	9
			Per Cent of Original Activity					
Sample A	43	44	39	40	39	40	40	40
Sample B	49	28	18	13	12	10	9	8

A: .04% $CaCl_2$ added once only (equivalent to 500 lbs. $CaCl_2$ in W-5).
B: .04% $CaCl_2$ added each day.
Continuous air agitation of liquid phase in both.

tab

TABLE XI

PLANT DECONTAMINATION OF CHEMICAL WASTES WITH $CaCl_2$

Date Sampled	Number of 500# Batches of $CaCl_2$ Previously Added to W-5	% of Original Activity in Supernatant W-5	W-6
4/17/44	0	100	100
4/18/44	1	72	99
4/19/44	2	68	98
4/20/44	3	58	93
4/21/44	4	45	91
4/22/44	5	38	82
4/23/44	6	--	--
4/24/44	7	46	82
4/25/44	8	45	73
4/26/44	9	54	74
4/27/44	9	54	78

On April 25, 1944, a more complete survey of White Oak Creek was made by Overstreet and Jacobson. On April 27, discharge of the waste was discontinued on the basis that if the activity found in the creek bed were of a species which was rapidly absorbed in the body or was one which had a long half-life, then continued discharge into the creek might create a hazard. The elements responsible for the activity in the mud was not known nor were tolerance limits for the possible elements available. Table XII shows the results of this survey and others taken at later dates in terms of microcuries per gram of mud. The first survey was taken after 52 days of discharging of waste to the retention pond. The second survey was taken over a period of 5 days and approximately 40 days after discharge to the ponds had been stopped. The activity in the clay appears to have decreased by a factor of 10 to 100 from the first survey. The third survey agrees in general with the second. It will be noted, however, that the results vary considerably. This may be due to the location of the samples, although numerous other factors are no doubt involved.

Analyses for specific fission products distribution of activity were also made on the mud at various places along the creek bed. Results are summarized in Table XIII.

TABLE XII

MUD ACTIVITY SURVEY ON WHITE OAK CREEK

Key to Sampling Spots on Figure VI	1st Survey Sampled 4/25/44 After 52 Days of Waste Discharge from W-6	2nd Survey Samples 6/9/44 to 6/19/44 After Approx. 40 Days of No Discharge	3rd Survey Sampled 7/4/44 Discharge to Settling Basin Started 7/3/44
Location	μ c/gm Dry Mud	μ c/gm Dry Mud	μ c/gm Dry Mud
1	2.0	0.0011	
2	4.3	0.0024	0.0042
3	1.5	0.0001	0.0001
4	0.037		0.0029
5	0.37		
6	0.29		
7	0.30		
8	1.4		
9	0.096		
10	0.038		0.0128
11	0.41	0.0031	0.0468
12	0.77	0.0004	0.0033
13	0.011	0.00007	0.00002
14	0.0093	0.00004	0
15	0.011	0.00004	0.00001
16	0.007		0.00002
17		0.00004	0
18	0.01	0.00007	0.000004
19	Background		
20			0.0027

TABLE XIII

PER CENT DISTRIBUTION OF ACTIVITY IN CLAY/GM DRY CLAY

Location	1	2	12	14
Ba + Sr	.96%	.70%	.98%	1.4%
Zr	50	55	47	41
Cb	37	28	32.5	38
Ce	8	12	14	13
Y + Pr	4	4	5.5	5.6
Total in μ c/gm	6.7	0.19	0.038	0.0069

FIGURE VI

Survey Points of White Oak Creek

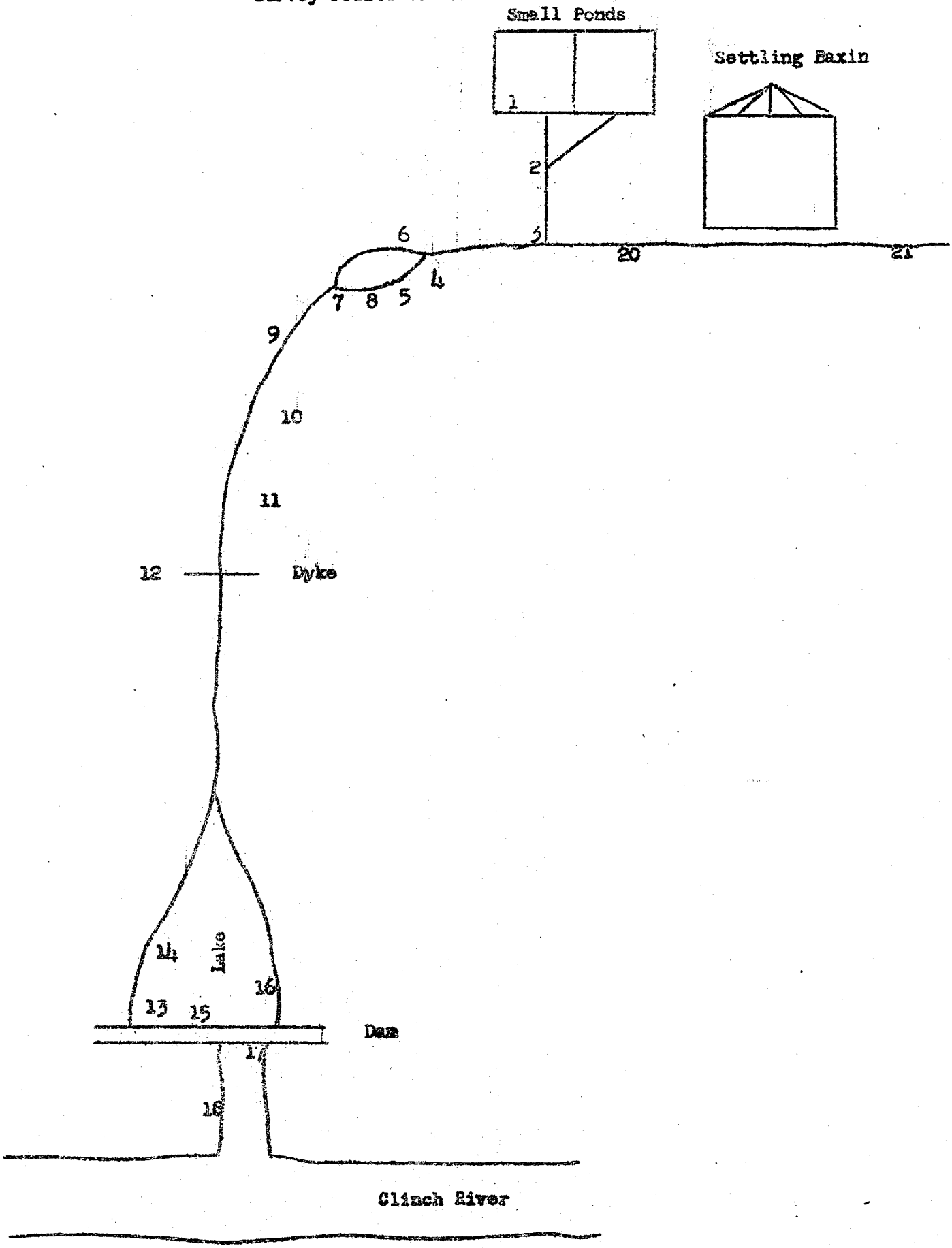


Table XIV shows the result of similar analyses on the supernatant from W-6 and the precipitate formed on dilution.

TABLE XIV

ANALYSES OF ACTIVITY IN W-6 SOLUTION AND PRECIPITATE FROM DILUTION OF W-6 WASTE WITH THIRTY-FIVE PARTS OF PLANT WATER

Element	Distribution of Activity in Precipitate		Distribution of Activity in Solution	
	Beta[3]	Gamma	Beta[3]	Gamma
Cb	7. %	48. %	12. %	88. %
Ce	46.	0.	7.	0.
Cs	0.3	0.	16.	0.
Ru	0.6	0.	58.	10.
Sr	2.3	---	0.9	0.
Te	3.2	1.1	2.	0.5
Zr	43.	51	0.8	2.
Total	102. %	100. %	97. %	101. %

Two samples of the precipitate formed in the ponds were analyzed chemically, the results of which are given in Table XV.

TABLE XV

Determination	Method	Analysis: Sample #1 (Close to Ponds)	Analysis: Sample #4 (Farther from Ponds)
Si as SiO_2	gravimetric	67.4 %	81.5 %
Fe as Fe_2O_3	"	2.0	1.6
Al as Al_2O_3	"	12.5	7.2
Mg as MgO	"	2.1	0.9
Ca as CaO	"	3.8	0.7
$PO_4^{=3}$	"	0.4	---
F^-	gravimetric & volumetric	26.0	11.5

Laboratory tests demonstrated that the wastes could be decontaminated by a factor of about 9 by a 70-fold dilution with waste water. One set of data on this is given in Table XVI.

TABLE XVI

DECONTAMINATION OF PLANT WASTE ON DILUTION WITH POND WATER

Dilution Ratio	70-1	35-1	14-1	7-1	2.8-1	1-1
% of Original Activity Left in Solution	11.8	12.4	15.9	29.2	76	87.8

The precipitate formed in these tests was proportional to the amount of dilution water used and a ten to twenty-fold decontamination was obtained with 70 parts water. The precipitate amounted to about 2 to 3% of the dilution water volume and settled to this volume in about an hour (in 1 ft. of liquid depth). Additional data on settling rates and decontamination factors are given in CH 1852.

Methods of decontaminating the supernatant from the waste tanks other than dilution were investigated in the laboratory, with the conclusion that the most effective procedure is to add calcium chloride to the waste tanks, then dilute the supernatant with waste water and settle out the precipitated solids.

During the period a large part of the experimental data reported in the preceding paragraphs was being obtained, a settling basin was constructed. Its purpose was to effectively remove all precipitated solids resultant from adding W-6 waste to plant cooling water and thus prevent accumulation of hazardous amounts of radioactive fission products in White Oak Creek. The basin hold-up time was designed to be about 30 hours at a flow of 900,000 gal./day of plant cooling water. Construction was started on the basin before completion of all the confirmatory experiments, since the time allowed by the available space in the storage tanks was limited. The settling basin was put into operation on July 3, 1944.

Throughout the months of July and August with the settling basin in operation, the plant was able to discharge from W-6 at about double the rate waste entered the storage tanks and both W-7 and W-8 were emptied and made available for metal waste storage. Decontamination of the supernatant in W-5 with $CaCl_2$ was started on July 10 and since that time, 500 lbs. of the material has been added daily. In spite of the fact that wastes of continually increasing activities were being added to W-5, the use of $CaCl_2$ reduced the beta counts/cc of supernatant about 10-fold (from 4.9×10^4 on July 10 to 5.9×10^3 on August 2). Beginning July 5, 500 lbs. of $CaCl_2$ were added daily directly to the settling basin in an effort to obtain further decontamination by increasing the hardness of the cooling water. This was discontinued on July 24 without any noticeable effect on the efficiency of the settling basin.

The analyses, discussed earlier, for the specific activities occurring in the pond precipitate indicated that the elements of most concern, barium, strontium, tellurium, and cesium represent only a very small fraction of the total activity. J. G. Hamilton (letter to S. T. Cantril, 6/20/44) estimates that on the basis of this composition a tolerance limit of 1 curie per day would probably be a safe rate of discharge to White Oak Creek. H. M. Parker (CH-1889) seems to think that this is conservative and that a tolerance limit of 5 curies might be permissible under certain

conditions. This is about the average rate of discharge during the period of March 6 - April 27 when the active wastes were being added to the ponds.

Table XVII gives data on the per cent solids retained, as well as the curies of activity entering and leaving the basin. The figures listed are typical for a rate of discharge from K-6 of 10,000 gal./day.

TABLE XVII

Date	Per Cent Solids Retained in Basin	Total Curies/Day Inlet	Total Curies/Day Outlet
7/12/44	87	3.5	0.7
7/14/44	85	3.7	0.7
7/17/44	84	2.6	0.6
7/19/44	93	4.8	0.6
7/21/44	95	3.0	0.6
7/24/44	92	6.4	0.7
7/26/44	96	10.6	1.4*
7/27/44	85	5.2	1.0*
7/29/44	85	3.8	0.8
7/31/44	93	5.3	0.5
8/ 2/44	88	4.4	0.7

*Very low flow of plant cooling water.

The operation of the settling basin has been satisfactory, except for flotation of some of the active precipitate from the bottom by CO_2 formation. The mechanism by which the CO_2 forms is not clearly understood, perhaps through contact of the alkaline waste with the slightly acid (6 pH) cooling water or from plant life (algae) in the water. The floating material accumulates in the corners of the basin, according to the wind direction, and surveys made at the water's edge near such accumulations have given readings of as high as 350 mr/hr. After heavy rains or after playing a fire hose over the pond, the floating material is temporarily removed from the surface. Steps have been taken to prevent these solids from floating into the overflow from the basin and thus getting into White Oak Creek.

APPENDIX

APPENDIX

A. FLOWSHEETS OF SEPARATIONS PROCESSES AT CLINTON

Three flowsheets are presented to show in detail the procedures followed at various points in the development of the separations process at Clinton. The first is that which was followed on Run 1 at start-up. The second for Run 90 giving the procedure after about four months of operation is in diagramatic form to show arrangement of equipment and flow of process solutions. The last is that which was used after about nine months for Run 193 and is essentially a duplication of the procedure for Hanford as outlined by J. B. Work of the TNX Technical Division August 26, 1944. On the graphs of waste and decontamination results for individual runs (Figures A-1 to A-14) notations have been made to show the runs at which the various process modifications were made.

Compositions given at various points on the flowsheets were calculated values rather than analytical results.

PREPARATION OF METAL SOLUTION

Cell #1

A. COATING REMOVAL (Basis - 1 charge of 678 lbs. Clinton slugs)

1. Add 908 lbs. of a 10% HNO_3 solution to the dissolver Tank 11.
2. Add 12½ lbs. of a solution that contains 10 lbs. of H_2O, 2 lbs. of 60% HNO_3 and ½ lb. $Hg(NO_3)_2$.
3. Heat to 40° C with 10 lbs. steam on the sparger. Cut off sparger at 40° C and allow temperature to rise to 98° C and hold at 98° C for 1 hour.
4. Cool to 50° C with coils.
5. Jet to waste receiver 54.
6. Add 400 lbs. of a 2% HNO_3 solution for rinse.
7. Jet to waste receiver 54.

Solution Composition (coating removal solution):

HNO_3	10.0%
$Hg(NO_3)_2$	0.06%

B. METAL SOLUTION

1. Add 2000 lbs. of a 60% HNO_3 solution to 11.
2. Add 1151 lbs. process water to dissolver scale tank to be used for drowning the charge if necessary.
3. Heat with 15 lbs. steam until column differential pressure exceeds -8 in water. Digest for 24 hours.
4. Add 1511 lbs. of water and cool to 80° C.

Solution Composition (in dissolver)

HNO_3	4.0% +
UNH	40%

C. METAL SOLUTION REDUCTION

1. Add enough 60% HNO_3 to obtain 4% free HNO_3 in 40% UNH solution, if necessary.
2. Add 2000 lbs. water to dissolver scale tank to be used for drowning charge, if necessary.
3. Heat to 100° C with 15 lbs. steam of coil and hold at 100° C throughout formic acid addition.
4. Add sufficient formic acid to destroy all the excess free HNO_3.
5. Digest for ½ hour at 100° C; then cool to 35° C using coils and jacket.
6. Transfer from dissolver to Cell 2 precipitator Tank 21.
7. Add 2000 lbs. of water to 11.
8. Jet from 11 to 21.

PRODUCT EXTRACTION

Cell #2

A. PRECIPITATION

1. Receive metal solution and dilution water from 11 into precipitator 21.
2. Add 304 lbs. of 93% H_2SO_4 to 21 through funnel. Flush funnel with 10 lbs. of water and 5 lbs. 60% HNO_3.
3. Add 613 lbs. of 75% H_3PO_4. Flush with 50 lbs. of water.
4. Heat to 75° C using jacket.
5. Add 83.3 lbs. of a 24% Bi solution uniformly over 30 minutes through funnel. Flush with 5 lbs. of 60% HNO_3.
6. Digest 2 hours at 75° C.
7. Cool to 35° C before jetting to centrifuge 22.

Slurry Composition (in 21)

UNH	20%	0.48 M
HNO_3	0.5%	0.12 N
H_2SO_4	4.0%	1.0 N
H_3PO_4	6.5%	0.8 M
Bi ion		250 g/l

B. CENTRIFUGATION AND WASHING

1. Centrifuge at 870 RPM, 110 lbs./min. using 45 to 55 lbs. steam on jet.
2. When jet 21 to 22 gases, jet four 20 second shots from catch tank 23 to 21, then recycle 1000 lbs. from 23 to 21 to 22.
3. Skim to 5 gal. heel.
4. Add 250 lbs. water to 21 and jet to 22 as it is added to 21.
5. Skim to 5 gal. heel.
6. Plug centrifuge to 30 RPM and plow 1 minute.
7. With centrifuge rotating at 10 RPM, add 250 lbs. of water through sprays at 70 lbs. or greater pressure.
8. Bring 22 to 110 RPM, hold 2 minutes and plug to stop. Repeat twice.
9. Bring 22 to 870 RPM, hold 5 minutes and skim to 5 gal. Plug to 30 RPM.
10. Plug centrifuge to 30 RPM and plow 1 minute.
11. With centrifuge rotating at 10 RPM, add 250 lbs. of water through sprays at 70 lbs. or greater pressure.
12. Bring 22 to 110 RPM, hold 2 minutes and plug to stop. Repeat twice.
13. Bring 22 to 870 RPM, hold 5 minutes and skim to 5 gal. Plug to 30 RPM.
14. Jet waste and washings from 23 to waste receiver 54. Follow with a 250 lbs. water rinse.

C. CAKE SOLUTION

1. Plow centrifuge bowl for 1 minute at 30 RPM.
2. Add 263 lbs. of 60% HNO_3 to 22. Flush 22 scale tank with 66 lbs. water.

3. Slurry cake twice by bringing 22 to 110 RPM and plugging to 0 RPM.
4. Jet slurry from 22 to solution tank 24.
5. Start agitator in 24.
6. Plow centrifuge bowl for 1 minute at 30 RPM.
7. Add 263 lbs. of 60% HNO_3 to 22. Flush 22 scale tank with 66 lbs. water.
8. Slurry cake twice by bringing 22 to 110 RPM and plugging to 0 RPM.
9. Jet slurry from 22 to solution tank 24.
10. Plow centrifuge bowl for 1 minute at 30 RPM.
11. Add 263 lbs. of 60% HNO_3 to 22. Flush 22 scale tank with 66 lbs. water.
12. Bring 22 to 100 RPM. Hold at 100 RPM two minutes and then allow to coast to 80 RPM. Run plow in and out rapidly two times.
13. Slurry cake twice by bringing 22 to 110 RPM and plugging to 0.
14. Jet slurry from 22 to 24.
15. Agitate 24 for 15 minutes after all HNO_3 has been added.

Cake Solution Composition

HNO_3	10 M	20%
$BiPO_4$	0.09 M	2%

DECONTAMINATION

First By-Product Precipitation

Cell #2

A. OXIDATION

1. Add 690 lbs. water to 24 via centrifuge 22.
2. Add 45 lbs. of 10% $NaBiO_3$ solution to 24 through funnel. Flush funnel with 80 lbs. of water.
3. Agitate for 1 hour at 50° C.
4. Add 8 lbs. of a 10% $Na_2Cr_2O_7$ solution.
5. Cool to 35° C.
6. Jet to precipitator 21.

Solution Composition (in 24)

HNO_3	5 N	26%
$NaBiO_3$	0.0106 M	1.1%
$Na_2Cr_2O_7$		

7. Add 375 lbs. rinse water to 24 and agitate 5 minutes with air sparger.
8. Jet rinse water from 24 to 21.

B. BY-PRODUCT PRECIPITATION

1. Add 5000 lbs. of water to 21.
2. Receive oxidized solution and washings from 24.
3. Heat to 75° C.
4. Add 105 lbs. of 75% H_3PO_4 solution. Flush scale tank with 585 lbs. water.
5. Digest one hour at 75° C.
6. Cool to 35° C.

Slurry Composition (in 21)

HNO_3	0.99 N	20%
$BiPO_4$	0.106 M	0.3%
H_3PO_4		1.0%

C. CENTRIFUGATION AND WASHING

1. Centrifuge at 870 RPM, 110 lbs./min. using 45 to 55 lbs. steam on jet.
2. When jet 21 to 22 gases, jet four 20 second shots from 23 to 21, then recycle 1000 lbs. from 23 to 21 to 22.
3. Skim to 5 gal. heel.
4. Jet 23 to Cell 3 precipitator tank 31.
5. Add 250 lbs. of water to 21 and jet to 22.
6. Skim to 5 gal. heel.
7. Jet washing from 23 to 31.
8. Plug centrifuge 22 to 30 RPM.
9. Flow 22 for 1 minute.

10. With centrifuge rotating at 10 RPM, add 250 lbs. water through sprays at 70 lbs. or greater pressure.
11. Slurry cake twice by bringing 22 to 110 RPM and plugging to 0 RPM.
12. Bring 22 to 870 RPM and skim to 5 gal. heel.
13. Jet cake wash from 23 to 31.

D. BY-PRODUCT CAKE REMOVAL

1. Plow 22 for 1 minute at 30 RPM.
2. Add 263 lbs. of 60% HNO_3 and 30 lbs. water to 22.
3. Slurry cake twice by bringing 22 to 110 RPM and plugging to 0 RPM.
4. Jet from 22 to waste receiver 53.
5. Plow 22 for 1 minute at 30 RPM.
6. Add 263 lbs. of 60% HNO_3 and 66 lbs. of water.
7. Slurry cake twice by bringing 22 to 110 RPM and plugging to 0 RPM.
8. Jet from 22 to waste receiver 53.
9. Plow 22 for 1 minute at 30 RPM.
10. Add 263 lbs. of 60% HNO_3 and 30 lbs. water to 22.
11. Slurry cake twice by bringing 22 to 110 RPM and plugging to 0 RPM.
12. Jet from 22 to waste receiver 53.
13. Plow 22 for 1 minute at 30 RPM.
14. Add 263 lbs. of 60% HNO_3 and 60 lbs. of water.
15. Bring 22 to 100 RPM, hold 2 minutes and allow to coast to 80 RPM. Run plow in and out rapidly 2 times.
16. Slurry cake twice by bringing 22 to 110 RPM and plugging to 0 RPM.
17. Jet from 22 to waste receiver 53.
18. Rinse 22 with 125 lbs. of water and jet to waste receiver 53.

DECONTAMINATION

First Product Precipitation

Cell #3

A. REDUCTION AND PRECIPITATION

1. Receive oxidized effluent and washings from 23.
2. Add 515 lbs. of 20% ferrous ammonium sulfate solution to 31.
3. Heat to 75° C.
4. Agitate for 1 hour at 75° C.
5. Add 143 lbs. of 14% bismuth solution over a period of 30 minutes.
6. Agitate for 30 minutes at 75° C.
7. Add 615 lbs. of 75% H_3PO_4.
8. Agitate for 1 hour at 75° C.
9. Cool to 35° C before jetting to centrifuge 32.

Slurry Composition (in 31)

HNO_3	1 N
H_3PO_4	0.6 M
Fe^{+2}	0.03 M
Bi^{+3}	150 mg/l

B. CENTRIFUGATION AND WASHING

1. Jet from 31 to 32 to 33.
2. Centrifuge at 870 RPM, 110 lbs./min. using 45 to 55 lbs. steam on jet.
3. When jet 31 to 32 gases, jet four 20 second shots from catch tank 33 to 31, then recycle 1000 lbs. from 33 to 31 to 32.
4. Skim to 5 gal. heel.
5. Add 250 lbs. of water to 31 and jet to 32 as it is added to 31.
6. Skim to 5 gal. heel.
7. Plug centrifuge to 30 RPM and plow 1 minute.
8. With centrifuge rotating at 10 RPM, add 250 lbs. of water through sprays at 70 lbs. or greater pressure.
9. Bring 32 to 110 RPM, hold 2 minutes and plug to stop. Repeat twice.
10. Bring 32 to 870 RPM, hold 5 minutes and skim to 5 gal. Plug to 30 RPM.
11. Plug centrifuge to 30 RPM and plow 1 minute.
12. With centrifuge rotating at 10 RPM, add 250 lbs. of water through sprays at 70 lbs. or greater pressure.
13. Bring 32 to 110 RPM, hold 2 minutes and plug to stop. Repeat twice.
14. Bring 32 to 870 RPM, hold 5 minutes and skim to 5 gal. Plug to 30 RPM.
15. Jet waste and washings from 33 to waste receiver 54. Follow with a 250 lbs. water rinse.

C. CAKE SOLUTION

1. Transfer cakes from 32 to 34.
2. Flow centrifuge bowl for 1 minute at 30 RPM.
3. Add 263 lbs. of 60% HNO_3 to 32. Flush 32 scale tank with 66 lbs. water.
4. Slurry cake twice by bringing 32 to 110 RPM and plugging to 0 RPM.
5. Jet slurry from 32 to solution tank 34.
6. Start agitator in 34.
7. Flow centrifuge bowl for 1 minute at 30 RPM.
8. Add 263 lbs. of 60% HNO_3 to 32, flush 32 scale tank with 66 lbs. of water.
9. Slurry cake twice by bringing 32 to 110 RPM and plugging to 0 RPM.
10. Jet slurry from 32 to solution tank 34.
11. Flow centrifuge bowl for 1 minute at 30 RPM.
12. Add 263 lbs. of 60% HNO_3 to 32. Flush 32 scale tank with 66 lbs. water.
13. Bring 32 to 100 RPM. Hold at 100 RPM two minutes and then allow to coast to 80 RPM. Run flow in and out rapidly twice.
14. Jet slurry from 32 to 34.
15. Agitate 34 for 15 minutes after all HNO_3 has been added.

Solution Composition (in 34)

$BiPO_4$	0.0917 M	2%
HNO_3	10 N	

DECONTAMINATION

Second By-Product Precipitation

Cell #3

A. OXIDATION

1. Add 690 lbs. water to 34 via centrifuge 32.
2. Add 45 lbs. of 10% $NaBiO_3$ solution to 34 through funnel. Flush funnel with 80 lbs. of water.
3. Agitate for 1 hour at 50° C.
4. Add 8 lbs. of a 10% $Na_2Cr_2O_7$ solution.
5. Cool to 35° C.
6. Jet to precipitator 31.

Solution Composition (in 34)

HNO_3	26%	5 N
$NaBiO_3$		0.0106 M
$Na_2Cr_2O_7$		0.002 M

7. Add 375 lbs. rinse water to 34 and agitate 5 minutes with air sparger.
8. Jet rinse water from 34 to 31.

B. BY-PRODUCT PRECIPITATION

1. Add 500 lbs. of water to 31.
2. Receive oxidized solution and washings from 34.
3. Heat to 75° C.
4. Add 105 lbs. of 75% H_3PO_4 solution. Flush scale tank with 585 lbs. water.
5. Digest one hour at 75° C.
6. Cool to 35° C.

Solution Composition

HNO_3	0.99 N	20%
H_3PO_4	0.106 M	

C. CENTRIFUGATION AND WASHING

1. Centrifuge at 870 RPM, 110 lbs./min. using 45 to 55 lbs. steam on jet.
2. When jet 31 to 32 gases, jet four 20 second shots from 33 to 31, then recycle 1000 lbs. from 33 to 31 to 32.
3. Skim to 5 gal. heel.
4. Jet 33 to Cell 4 precipitator tank 41.
5. Add 250 lbs. of water to 31 and jet to 32.
6. Skim to 5 gal. heel.
7. Jet washing from 33 to 41.

8. Plug centrifuge 32 to 30 RPM.
9. Plow 32 for 1 minute.
10. With centrifuge rotating at 10 RPM, add 250 lbs. water through sprays at 70 lbs. or greater pressure.
11. Slurry cake twice by bringing 32 to 110 RPM and plugging to 0 RPM.
12. Bring 32 to 870 RPM and skim to 5 gal. heel.
13. Jet cake wash from 33 to 41.

D. BY-PRODUCT CAKE REMOVAL

1. Plow 32 for 1 minute at 30 RPM.
2. Add 263 lbs. of 60% HNO_3 and 30 lbs. water to 32.
3. Slurry cake twice by bringing 32 to 110 RPM and plugging to 0 RPM.
4. Jet from 32 to waste receiver 53.
5. Plow 32 for 1 minute at 30 RPM.
6. Add 263 lbs. of 60% HNO_3 and 66 lbs. of water.
7. Slurry cake twice by bringing 32 to 110 RPM and plugging to 0 RPM.
8. Jet from 32 to waste receiver 53.
9. Plow 32 for 1 minute at 30 RPM.
10. Add 263 lbs. of 60% HNO_3 and 30 lbs. water to 32.
11. Slurry cake twice by bringing 32 to 110 RPM and plugging to 0 RPM.
12. Jet from 32 to waste receiver 53.
13. Plow 32 for 1 minute at 30 RPM.
14. Add 263 lbs. of 60% HNO_3 and 60 lbs. of water.
15. Bring 32 to 100 RPM, hold 2 minutes and allow to coast to 80 RPM. Run plow in and out rapidly 2 times.
16. Slurry cake twice by bringing 32 to 110 RPM and plugging to 0 RPM.
17. Jet from 32 to waste receiver 53.
18. Rinse 32 with 125 lbs. of water and jet to 53.

DECONTAMINATION

LaF_3 Product Precipitation

Cell #4

A. REDUCTION AND INITIAL PRECIPITATION

1. Receive oxidized effluent and washings from 33 into 41.
2. Add 325 lbs. of a 27.5% solution of hydrogen peroxide to 41 via sparger.
3. Agitate for 1 hour at 75° C.
4. Cool to 25° C.
5. Add 200 lbs. of anhydrous HF.
6. Add 500 lbs. of a 1% La salt solution at a rate not to exceed 25 lbs./min.
7. Agitate for 1 hour at 25° C.
8. Cool to 20° C or below before centrifuging.

Slurry Composition

H_2O_2		1%
HF	1.0 N	2.2%
La	125 mg/l	

B. FIRST CENTRIFUGATION AND FINAL PRECIPITATION

1. Centrifuge at 870 RPM, 110 lbs./min. using 45 to 55 lbs. on steam jet.
2. Skim to 5 gal. heel.
3. Jet effluent from 43 to 41.
4. Add 400 lbs. 1% La salt solution at a rate not to exceed 25 lbs./min.
5. Agitate for 1 hour at 25° C.
6. Cool to 20° C or below before centrifuging.

Slurry Composition

La	100 mg/l

C. FINAL CENTRIFUGATION AND CAKE REMOVAL

1. Centrifuge at 870 RPM, 110 lbs./min. using 45 to 55 lbs. on steam jet.
2. Skim to 5 gal. heel.
3. Plug centrifuge speed to 10 RPM.
4. Add water at 70 lbs. pressure into 42 through sprays.
5. Just after sprays start, begin jetting from 42 to 44 and keep bowl empty during entire water addition by intermittingly stopping water to the sprays.
6. Continue spraying until 795 lbs. of water are in 44.
7. Agitate slurry in 44 until transferred to Room D.
8. When two charges have accumulated in 44, transfer to Room D.
9. Jet effluent in 43 to waste receiver 54.

FIRST CONCENTRATION

First KOH Metathesis

Room D

A. LaF_3 PRODUCT SLURRY TREATMENT AND CENTRIFUGATION

1. Receive two charges of LaF_3 product slurry from 44 into Room D precipitator tank D-1.
2. Add a calculated amount of solid KOH to make LaF_3 slurry 0.5% in KOH. Amount varies with the acidity of the slurry.
3. Agitate and heat to 75° C.
4. Cool to 25° C before centrifuging.
5. Jet from D-1 to 26" centrifuge D-2.
6. Centrifuge at 1800 RPM, 3 gal./min.
7. Recycle 90 gal. of effluent in 3 portions from catch tank D-3 to D-1 to D-2.
8. Pump effluent from D-3 to Room D waste storage tank D-4.

B. KOH TREATMENT

1. Add 87 lbs. of 30% KOH solution through centrifuge sprays to D-2 at approximately 10 lbs. pressure.
2. Rotate centrifuge bowl slowly during KOH addition and cut LaF_3 cake from the centrifuge wall.
3. Slurry cake in D-2 for 30 minutes, by rotating bowl slowly with plows half in and by running the bowl speed up to 100 RPM and plugging to 0 RPM.
4. Centrifuge KOH - LaF_3 slurry for 15 minutes at 1800 RPM.
5. Skim at 1800 RPM to 3 gal. heel.
6. Add 87 lbs. of 30% KOH solution through centrifuge sprays to D-2 at approximately 10 lbs. pressure.
7. Rotate centrifuge bowl slowly during KOH addition and cut LaF_3 cake from the centrifuge wall.
8. Slurry cake in D-2 for 30 minutes, by rotating bowl slowly with plows half in and by running the bowl speed up to 100 RPM and plugging to 0 RPM.
9. Centrifuge KOH-LaF_3 slurry for 15 minutes at 1800 RPM.
10. Skim at 1800 RPM to 3 gal. heel.
11. Add 87 lbs. of 30% KOH solution through centrifuge sprays to D-2 at approximately 10 lbs. pressure.
12. Rotate centrifuge bowl slowly during KOH addition and cut LaF_3 cake from centrifuge wall.
13. Slurry cake in D-2 for 30 minutes, by rotating bowl slowly with plows half in and by running the bowl speed up to 100 RPM and plugging to 0 RPM.
14. Centrifuge KOH-LaF_3 slurry for 15 minutes at 1800 RPM.
15. Skim at 1800 RPM to 3 gal. heel.

C. $La(OH)_3$ WATER WASH

1. Add 66 lbs. of water through centrifuge sprays to D-2 at approximately 10 lbs. pressure.

2. Rotate centrifuge bowl slowly during water addition and cut $La(OH)_3$ from the centrifuge wall.
3. Slurry cake in D-2 by running the bowl speed up to 100 RPM and plugging to 0 RPM.
4. Centrifuge $La(OH)_3$ water slurry for 15 minutes and skim to 3 gal. heel.
5. Repeat step 1 through 4 until F^- ion in the water wash skimming is nil (normally requires 6 water washes).
6. Pump KOH skimmings and water wash skimming from D-3 to D-4.

FIRST CONCENTRATION

First LaF_3 By-Product Precipitation

Room D

A. $La(OH)_3$ CAKE SOLUTION

1. Add 100 lbs. of 60% HNO_3 solution to D-2 through sprays.
2. Slurry $La(OH)_3$ cake from bowl wall.
3. Agitate in D-2 for 10 minutes and jet to precipitator tank D-1.
4. Add 667 lbs. of water to D-2 through sprays at 80 lbs. pressure.
5. Jet water from D-2 to D-1. Keep the level in D-2 less than 1½ inches water by stopping water addition to D-2 as necessary.

B. OXIDATION AND PRECIPITATION

1. Add 37 lbs. of 10% $Na_2Cr_2O_7$ to D-1.
2. Agitate for one hour at 75° C.
3. Cool to 25° C before adding HF.
4. Add 5 lbs. of anhydrous HF slowly to D-1.
5. Agitate ½ hour at 25° C or lower before centrifuging.
6. Centrifuge at 1800 RPM, at a rate low enough to give clear effluent.
7. Recycle 90 gal. of effluent in 3 portions from catch tank D-3 to D-1 to D-2.
8. Pump effluent from D-3 to precipitator D-1.

Slurry Composition

$Na_2Cr_2O_7$		0.48%
HF	0.34 N	0.65%

C. CAKE REMOVAL

1. Add water under 80 lbs. pressure to D-2.
2. Jet from D-2 to waste receiver D-4. Keep the level in D-2 less than 1½ inches of water by stopping water addition to D-2 as necessary.
3. Continue steps 1 and 2 until by-product cake has been completely slurried from D-2 into D-4.

FIRST CONCENTRATION

First LaF_3 Product Precipitation

A. REDUCTION AND INITIAL PRECIPITATION

1. Add 37 lbs. of 27.5% hydrogen peroxide solution to D-1 through sparger.
2. Agitate for 1 hour at 50° C.
3. Cool to 25° C.
4. Add 8 lbs. of anhydrous HF slowly to D-1.
5. Add 50 lbs. of La salt solution at a rate not to exceed 2.5 lbs./min.
6. Agitate for 1 hour at 25° C or lower before centrifuging.

Slurry Composition

HF	0.7 M
La	0.62 g/l

B. FIRST CENTRIFUGATION AND FINAL PRECIPITATION

1. Centrifuge at 1800 RPM, rate slow enough to give clear effluent.
2. Skim to 3 gal. heel.
3. Pump effluent and skimmings from catch tank D-3 to D-1.
4. Add 50 lbs. of La salt solution at a rate not to exceed 2.5 lbs./min.
5. Agitate for 1 hour at 25° C before centrifuging.

Slurry Composition

La	0.6 g/l

C. FINAL CENTRIFUGATION AND CAKE REMOVAL

1. Centrifuge 1800 RPM, rate slow enough to give clear effluent.
2. Recycle 90 gals. of effluent in 3 portions from catch tank D-3 to D-1 to D-2.
3. Skim to 3 gal. heel.
4. Pump effluent and skimmings from D-3 to Room D waste receiver D-4.
5. Add 150 lbs. of water to D-2 at 80 lbs. pressure.
6. Jet from D-2 to 50 gal. Room D precipitator D-7. Keep the level in D-2 less than 1½ inches of water by stopping water addition to D-2 as necessary.

FIRST CONCENTRATION

Second KOH Metathesis

Room D

A. KOH TREATMENT AND CENTRIFUGATION

1. Add 3 lbs. of solid 85% KOH to D-7 to neutralize excess acidity in LaF_3 slurry.
2. Add 100 lbs. of solid 85% KOH to D-7.
3. Agitate for 1½ hours at 60° C.
4. Cool to 35° C or below before centrifuging.
5. Transfer KOH-LaF_3 slurry from D-7 to 12" centrifuge D-5 with pump P-7.
6. Centrifuge at 3000 RPM, rate ¼ gal./min.
7. Skim to ½ gal. heel.

Solution Composition

KOH 30%

B. $La(OH)_3$ WATER WASH

1. Add 4.1 lbs. water to D-5 by hand.
2. Cut $La(OH)_3$ cake from centrifuge wall by hand and slurry by bringing centrifuge to slow speed and break to 0 RPM.
3. Centrifuge slurry at 3000 RPM for 10 minutes and skim to ½ gal. heel.
4. Transfer skimmings to catch tank D-8.
5. Repeat steps 1 through 5 until F^- in the water wash skimmings are nil (normally requires 7 water washes).
6. Pump KOH effluent and water wash skimming from D-8 to D-4.

C. $La(OH)_3$ CAKE SOLUTION

1. Add 5 lbs. of 60% HNO_3 solution to D-5.
2. Slurry in bowl until cake dissolves.
3. Siphon product solution from D-5 and pour into spare tank D-9.
4. Rinse D-5 bowl with 48.3 lbs. water washes. Add washes to D-9.
5. Hold until three more charges have accumulated for final concentration cycle.

FINAL CONCENTRATION

Final LaF_3 By-Product Precipitation

Room D

A. OXIDATION AND PRECIPITATION

1. Transfer cake solutions of 2 charges to D-7 and add 7.5 lbs. 10% $Na_2Cr_2O_7$. D-7 should be 20 gal.
2. Digest at 75° for 1 hour and cool to 25°.
3. Add 2 lbs. 48% HF and agitate for 1 hour below 25°.

Slurry Composition

HNO_3	0.6 M	3.60%
$Na_2Cr_2O_7$	0.018 M	0.67%
HF	0.3 M	0.58%
La	3.3 g/l	

B. BY-PRODUCT SEPARATION

1. Centrifuge from D-7 through D-5 to D-8 at 1800 G and at the rate of 4 g.p.m. Recycle 3 gal.
2. Skim to 2 gal. and slurry down precipitate wash with four ½ gal. portions of 6% HNO_3 skimming each to 2 gal. in D-5. Skimming to D-8.

C. CAKE REMOVAL

1. Slurry down cake and wash with ½ gal. water. Syphon out to flask. Wash bowl with water until clean.
2. Sample and return to D-1 for recycling if necessary.

FINAL CONCENTRATION

Final Product Precipitation

Room D

A. REDUCTION AND INITIAL PRECIPITATION

1. Add 7.5 lbs. of 27.5% H_2O_2, adjusting D-8 volume to 22.5 gal., digest at 50° for 1 hour and cool to 25°.
2. Add 6 lbs. of 48% HF. Make D-8 volume 25 gals.
3. Add 10 lbs. of 1% La salt slowly (5% per min.) and agitate for 1 hour at 20° - 25° C.

Slurry Composition

HF	0.68 M	1.7%
La	125 mg/l	

B. INITIAL PRODUCT CENTRIFUGATION

1. Centrifuge at 1800 G and ½ g.p.m. in D-5, running effluent to D-7. Hold temperature at 25°.
2. Recycle 3 gal. and skim to 4 gal.

C. FINAL PRODUCT PRECIPITATION

1. Add 9 lbs. of 1% La salt at the rate of 5% per min.
2. Agitate for 1 hour at 25° C.

Slurry Composition

La	120 mg/l

D. FINAL PRODUCT CENTRIFUGATION

1. Centrifuge at 1800 G and 2 g.p.m. in D-5, running effluent to D-8
2. Recycle 3 gals.
3. Sample effluent and recycle to D-1 if necessary.
4. Skim to 4 gal. (no wash).

E. CAKE REMOVAL

1. Slurry solid out of bowl with successive 4 gal. portions of H_2O. Syphon to flask.

WASTE DISPOSAL

Metal Waste

Cell #5

1. Add 12,630 lbs. of 20% Na_2CO_3 solution to waste receiver 54.
2. Receive metal waste solution and washings from 23 in to 54 at maximum rate of jet 23 to 54.
3. Adjust temperature to 40° C.
4. Jet neutralized metal waste solution to metal waste storage tank M-3.

COATING SOLUTION AND DECONTAMINATION WASTES

A. COATING REMOVAL SOLUTIONS

1. Add 775 lbs. of 20% Na_2CO_3 solution to waste receiver 54.
2. Receive coating removal and rinse solution from dissolver to 54 at maximum rate of jet 11 to 54.
3. Adjust temperature to 40° C.
4. Jet neutralized waste solution to M-5.

B. OXIDIZED CAKE SOLUTIONS

1. Add 2700 lbs. of 20% Na_2CO_3 solution to waste receiver 54.
2. Agitate by-product slurry in 53 and sample.
3. Jet oxidized cake solution from 53 to 54 at maximum rate of jet 53 to 54.
4. Adjust temperature to 40° C.
5. Jet neutralized waste solution to M-5.

C. $BiPO_4$ REDUCED EFFLUENT

1. Add 12,435 lbs. of 20% Na_2CO_3 solution to waste receiver 54.
2. Receive first reduced effluent from 33 into 54 at maximum rate of jet 33 to 54.
3. Adjust temperature to 40° C.
4. Jet neutralized waste solution to M-5.

D. LaF_3 REDUCED EFFLUENT

1. Add 8500 lbs. of 20% Na_2CO_3 to waste receiver 54.
2. Receive LaF_3 reduced effluent from 43 to 54 at maximum rate of jet 43 to 54.
3. Adjust temperature to 40° C.
4. Jet neutralized waste solution to M-5.

ROOM D WASTES

A. LETATRESIS WASTES (ALKALINE)

1. Received wastes from D-4 to 54 and jet directly to waste storage tank W-5.

B. REDUCED EFFLUENT - 1ST CONCENTRATION CYCLE

1. Add 482 lbs. 20% Na_2CO_3 to 54.
2. Receive waste from D-4.
3. Cool to 40° C.
4. Jet neutralized waste solution to W-5.

C. BY-PRODUCT SLURRY - 1ST CONCENTRATION CYCLE

1. Add 23 lbs. 20% Na_2CO_3 to 54.
2. Receive waste from D-4.
3. Cool to 40° C.
4. Jet waste to W-5.

D. BY-PRODUCT SLURRY AND REDUCED EFFLUENT - 2ND CONCENTRATION CYCLE

1. Add 106 lbs. 30% Na_2CO_3 to 54.
2. Receive waste from D-4.
3. Cool to 40° C.
4. Jet waste to W-5.

NOTE: Na_2CO_3 used was actually 27% - 30%, consequently the amount actually added was adjusted proportionally in each case.

~~SECRET LIMITED~~

CELL #1 RUN 90

Drawing 592
Report CA-1879

(A) COATING REMOVAL

(1) 920 LBS./CHARGE 10% HNO_3 CONTAINING 0.5 LBS. $Hg(NO_3)_2$

(2) HEAT 98° C.

(3) DIGEST ONE HR., AT 98° C.

(4) COOL TO 60° C.

(5) AIR SPARGE 30 MIN. THEN SAMPLE 11C.

(6) JET COATING SOLUTION TO #54.

(7) 400 LBS. H_2O.

(8) JET RINSE WATER TO #54.

(B) METAL SOLUTION

(1) 1625 LBS. 60% HNO_3.

(2) HEAT TO 110°-115° C.

(3) DIGEST UNTIL SPEC. GRAVITY = 1.78

(4) 1511 LBS. H_2O.

(5) COOL TO 50° C.

(6) AIR SPARGE 1.5 HRS. THEN TAKE SAMPLE 11M.

(C) REDUCTION

(1) HEAT TO 100° C.

(2) ADD 60% HNO_3 TO OBTAIN 2% HNO_3 IN METAL SOLUT.

(3) ADD [illegible] LBS. 90% HCOOH

(4) DIGEST FOR 30 MIN. AFTER COMPLETING ADDITION OF FORMIC.

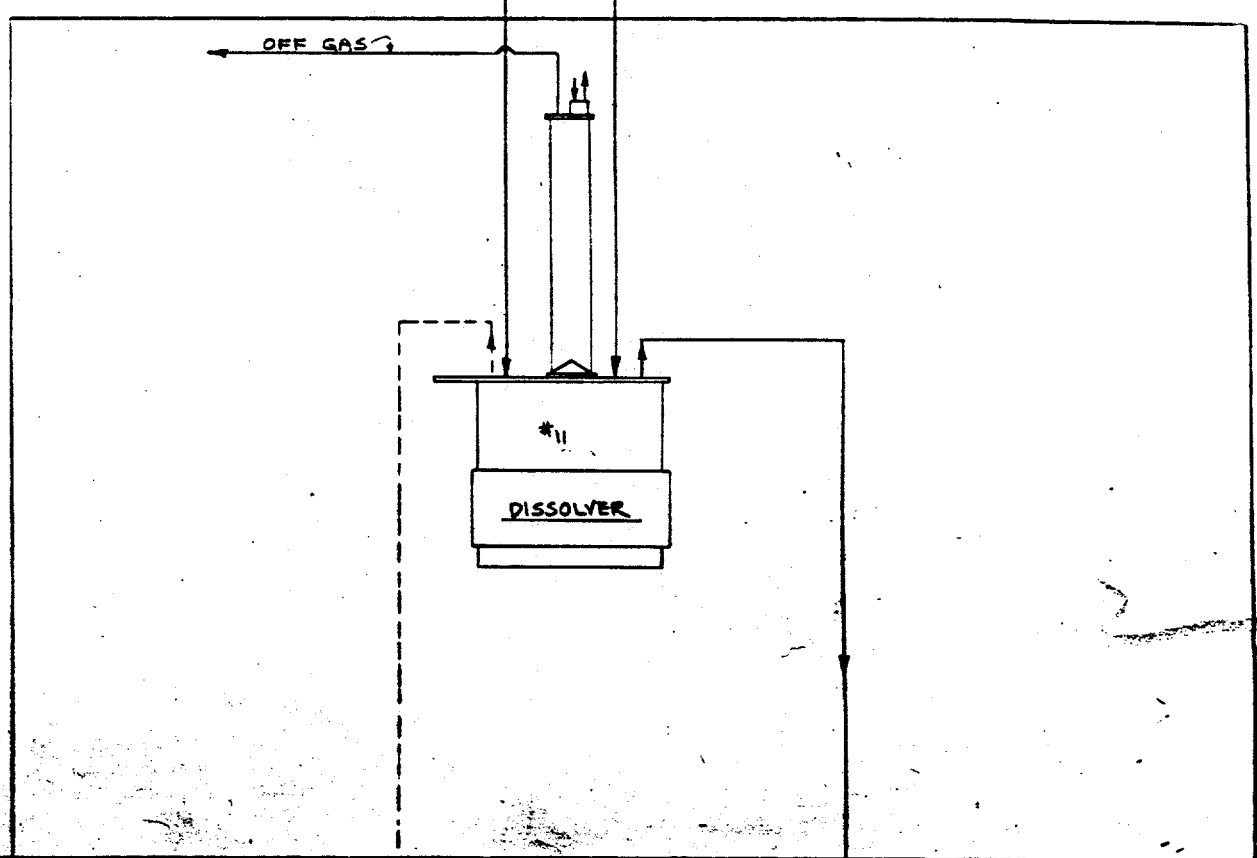
(5) COOL TO 60° C.

(6) AIR SPARGE 20 MIN. THEN TAKE SAMPLE 11MR

(7) JET METAL SOLUTION TO #2

(8) 2400 LBS. H_2O.

(9) JET DILUTION WATER TO #2



COATING SOLUTION TO #54

~~SECRET LIMITED~~

METAL SOLUTION TO #21

PIPE TUNNEL

(A) PRODUCT PRECIPITATION

(1) RECEIVE METAL SOLUTION & DILUTION WATER FROM #11.
(2) HEAT TO 55°C.
(3) 304 LBS. 93% H_2SO_4.
(4) 83.5 LBS. 24% Bi SALT SOLUTION
(5) 5 LBS. 60% HNO_3.
(6) DIGEST 15 MIN. AT 55°C.
(7) 613 LBS. 75% H_3PO_4.
(8) 100 LBS. H_2O.
(9) DIGEST 2 HRS. AT 55°C.
(10) COOL TO 35°C.

(B) PRODUCT SEPARATION & CAKE WASHING

(1) CENTRIFUGE 110 LBS./MIN. AT 870 R.P.M.
(2) JET 4 EFFLUENT WASHES FROM #33 TO #31.
(3) RECYCLE 1000 LBS. EFFLUENT FROM #23 TO #21 TO #22.
(4) AIR SPARGE #23 FOR 20 MIN. THEN TAKE SAMPLE 23 MW.
(5) SKIM TO #23.
(6) 250 LBS. H_2O VIA #21.
(7) SKIM TO #22.
(8) PLUG #22 TO 10 R.P.M.
(9) 250 LBS. H_2O VIA SPRAYS.
(10) BRING #22 TO 110 R.P.M., HOLD 2 MIN., PLUG TO STOP. REPEAT TWICE.
(11) BRING #22 TO 870 R.P.M., SKIM.
(12) REPEAT (8) (9) & (11).

(C) PRODUCT CAKE SOLUTION

(1) TAKE SAMPLE 24A.
(2) JET DISSOLVING ACID FROM #24 TO #21.
(3) CIRCULATE ACID 30 MIN. AT 35°C OR LOWER.
(4) JET 330 LBS. ACID FROM #21 TO #22.
(5) BRING #22 TO 110 R.P.M. HOLD 2 MIN. PLUG TO STOP. REPEAT TWICE.
(6) JET FROM #22 TO #24.
(7) REPEAT (4) (5) & (6) TWICE.
(8) AIR SPARGE #23 FOR 20 MIN. THEN TAKE SAMPLE 23 MS.
(9) JET FROM #23 TO #54.
(10) 250 LBS. H_2O VIA SPARGER.
(11) JET RINSE WATER TO #54.

(D) OXIDATION OF PRODUCT CAKE

(1) AIR SPARGE #24, 2 HRS. AT 50°C
(2) 500 LBS. H_2O TO #21. CIRCULATE 15 MIN. AT 35°C.
(3) JET H_2O FROM #21 TO #24 VIA #2
(4) HEAT #24 TO 50°C. WHILE SPARGING.
(5) TAKE SAMPLE 24P.
(6) 45 LBS. 10% $NaBiO_3$.
(7) 80 LBS. H_2O.
(8) DIGEST ONE HR. AT 50°C
(9) 16 LBS. 10% $Na_2Cr_2O_7$.
(10) COOL TO 35°C.
(11) JET TO #21.
(12) 375 LBS. H_2O.
(13) JET TO #21.
(14) 789 LBS. 60% HNO_3 VIA #2
(15) AIR SPARGE UNTIL ACID NEEDED FOR NEXT RUN.

(E) BY-PRODUCT PRECIPITATION

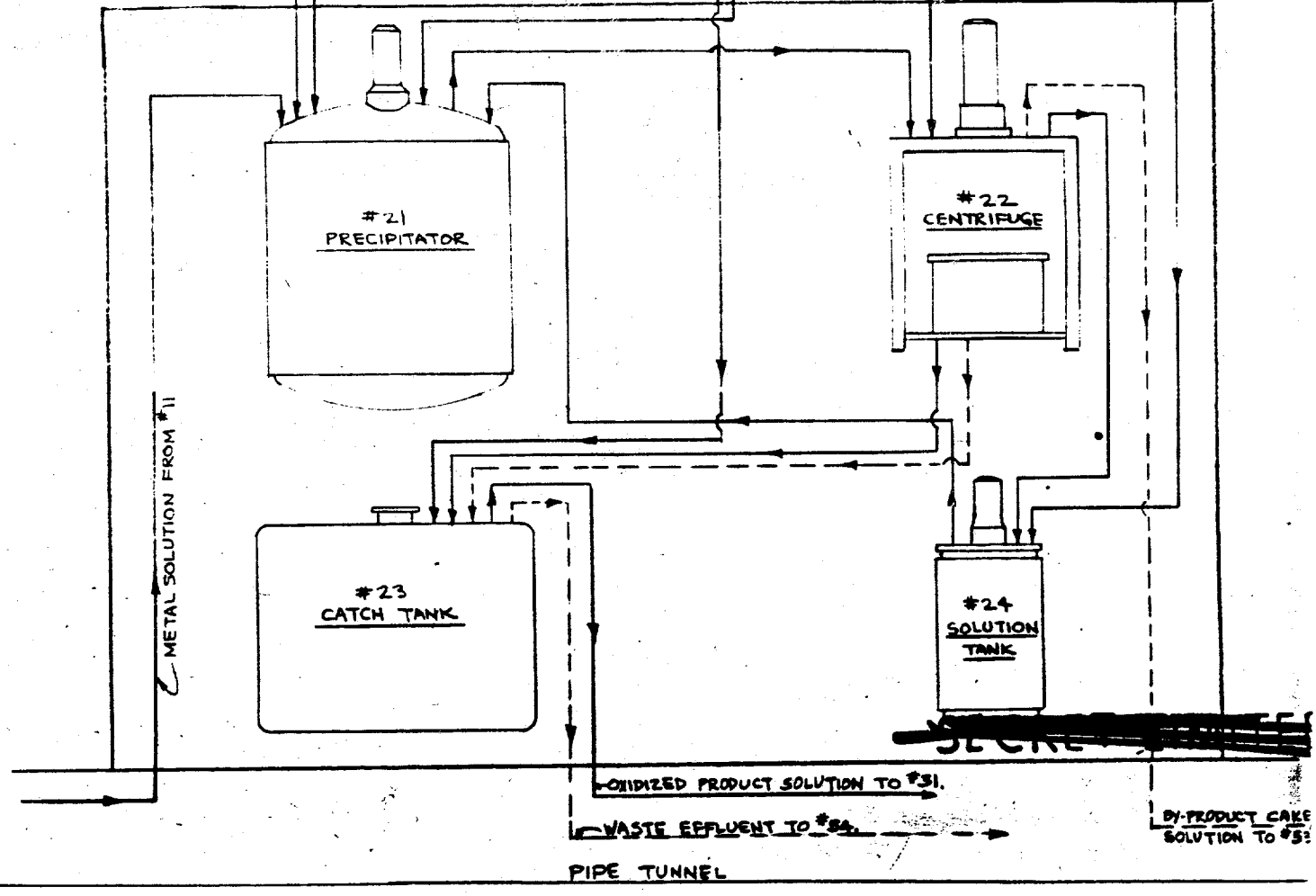
(1) 5000 LBS H_2O TO #21.
(2) HEAT TO 40°C
(3) RECEIVE OXIDIZED SOLUTION & RINSE FROM #24
(4) HEAT TO 75°C.
(5) 105 LBS. 75% H_3PO_4
(6) 585 LBS H_2O.
(7) DIGEST ONE HR. AT 75°C.
(8) COOL TO 50°C.

(F) BY-PRODUCT SEPARATION & CAKE WASHING

(1) CENTRIFUGE 110 LBS./MIN. AT 870 R.P.M.
(2) JET 4 EFFLUENT WASHES FROM #23 TO #21
(3) RECYCLE 1000 LBS. EFFLUENT FROM #23 TO #21 TO #22.
(4) SKIM TO #23.
(5) JET #23 TO #31.
(6) 250 LBS H_2O TO #22 VIA #31
(7) SKIM TO #23.
(8) JET #23 TO #31
(9) 250 LBS H_2O TO #22 AT 10 RPM VIA SPRAYS.
(10) BRING #22 TO 110 R.P.M. HOLD 2 MIN. PLUG TO STOP. REPEAT TWICE.
(11) BRING #22 TO 870 R.P.M. HOLD 5 MIN. SKIM TO #23
(12) JET #23 TO #31.

(G) BY-PRODUCT CAKE SOLUTION

(1) 789 LBS. 60% HNO_3 TO #21.
(2) CIRCULATE ACID IN #21 FOR 30 MIN AT 35°C. OR LOWER.
(3) WITH #22 AT 10 R.P.M., JET 330 LBS. OF ACID FROM #21.
(4) BRING #22 TO 110 R.P.M., HOLD 2 MIN., PLUG TO STOP. REPEAT TWICE.
(5) JET FROM #22 TO #53.
(6) REPEAT (3) (4) & (5) TWICE
(7) 125 LBS. H_2O TO #21
(8) CIRCULATE WATER IN #21 FOR 5 MIN.
(9) BRING #22 TO 10 RPM, JET WATER FROM #21 TO #22
(10) BRING #22 TO 110 RPM. PLUG TO STOP.
(11) JET FROM #22 TO #53



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CELL 3 RUN 70

Report CN-1899

(A) REDUCTION & PRODUCT PRECIPITATION

(1) RECEIVE PRODUCT SOLUTION & WASHES IN #31 FROM #23.
(2) 515 LBS. 20% Fe SALT SOLUTION.
(3) DIGEST ONE HR. AT 75°C.
(4) SAMPLE 31 R.
(5) HOLDING 75°C ADD 143 LBS. 14% Bi SOLUTION.
(6) 5 LBS. 60% HNO_3.
(7) DIGEST 30 MIN. AT 75°C.
(8) 615 LBS. 75% H_3PO_4.
(9) DIGEST 2 HRS. AT 75°C.
(10) COOL 50°C.

(B) PRODUCT SEPARATION & CAKE WASHING

(1) CENTRIFUGE 110 LBS./MIN. AT 870 RPM.
(2) JET 4 EFFLUENT WASHES FROM #33 TO #31.
(3) RECYCLE 1000 LBS. EFFLUENT FROM #33 TO #31 TO #32.
(4) SKIM TO #33.
(5) 250 LBS. H_2O TO #32 VIA #31.
(6) SKIM TO #33.
(7) PLUG #32 TO 10 RPM.
(8) 250 LBS. H_2O VIA SPRAYS.
(9) BRING #32 TO 110 RPM. HOLD 2 MIN. PLUG TO STOP. REPEAT TWICE.
(10) BRING #32 TO 870 RPM. HOLD 5 MIN. & SKIM.
(11) REPEAT (7)(8)(9) & (10).

(C) PRODUCT CAKE SOLUTION

(1) SAMPLE 34A.
(2) JET DISSOLVING ACID FROM #34 TO #31.
(3) CIRCULATE ACID IN #31 FOR 30 MIN. AT 35°C. OR LOWER.
(4) JET 330 LBS. ACID FROM #31 TO #32.
(5) BRING #32 TO 110 RPM. HOLD 2 MIN. PLUG TO STOP. REPEAT TWICE.
(6) JET FROM #32 TO #34.
(7) REPEAT (4)(5) & (6) TWICE.
(8) AIR SPARGE #33 FOR 20 MIN. SAMPLE 33 WS.
(9) JET FROM #33 TO #54.
(10) RINSE #33 WITH 250 LBS. H_2O.
(11) JET WASH TO #54.

(D) OXIDATION OF PRODUCT CAKE

(1) AIR SPARGE #34 FOR 2 HRS. AT 50°C.
(2) 500 LBS. H_2O TO #31. CIRCULATE 15 MIN. AT 5
(3) JET H_2O FROM #31 T #34 VIA #32.
(4) HEAT #34 TO 50°C WHILE SPARGING.
(5) TAKE SAMPLE 34P.
(6) 45 LBS. 10% $NaBiO_3$
(7) 80 LBS. H_2O.
(8) DIGEST 1 HR. AT 50°
(9) 8 LBS. 10% Na_2Cr_2O.
(10) COOL TO 35°C.
(11) JET TO #31.
(12) 375 LBS H_2O.
(13) JET TO #31.
(14) 789 LBS. 60% HNO_3 TO #34 VIA #32.
(15) AIR SPARGE #34 UNTIL ACID IS NEEDED FOR NEXT RUN.

(E) BY-PRODUCT PRECIPITATION

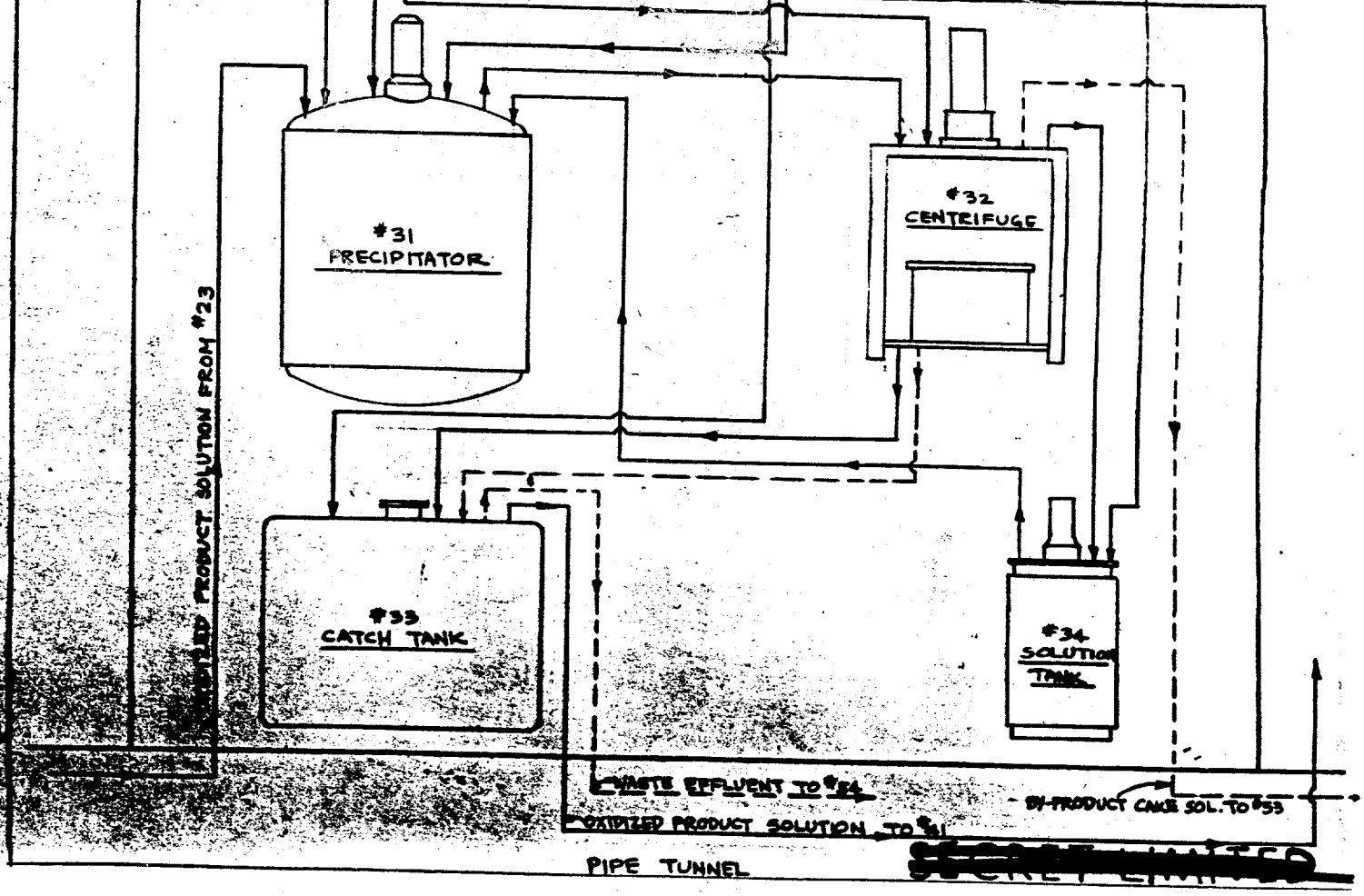
(1) 5400 LBS. H_2O TO #31.
(2) HEAT TO 40°C.
(3) RECEIVE OXIDIZED SOLUTION & RINSE FROM #34.
(4) HEAT TO 75°C.
(5) 105 LBS. 75% H_3PO_4.
(6) 185 LBS. H_2O.
(7) DIGEST ONE HR. AT 75°C.
(8) COOL TO 50°C.

(F) BY-PRODUCT SEPARATION & CAKE WASHING

(1) CENTRIFUGE 110 LBS./MIN. AT 870 RPM.
(2) JET 4 EFFLUENT WASHES FROM #33 TO #31.
(3) RECYCLE 1000 LBS. EFFLUENT FROM #33 TO #31 TO #32.
(4) SKIM TO #33.
(5) JET #33 TO #41.
(6) 250 LBS. H_2O TO #32 VIA #31.
(7) SKIM TO #33.
(8) JET #33 TO #41.
(9) 250 LBS. H_2O TO #22 AT 10 RPM VIA SPRAYS.
(10) BRING #32 TO 110 RPM, HOLD 2 MIN. PLUG TO STOP. REPEAT TWICE.
(11) BRING #32 TO 870 RPM, HOLD 5 MIN. SKIM TO #33.
(12) JET #33 TO #41

(G) BY-PRODUCT CAKE SOLUTION

(1) 789 LBS. 60% HNO_3 TO #31.
(2) CIRCULATE ACID IN #31 FOR 30 MIN. AT 35°C. OR LOWER.
(3) WITH #32 AT 10 RPM JET 330 LBS. ACID FROM #31 TO #32.
(4) BRING #32 TO 110 RPM, HOLD 2 MIN. PLUG TO STOP. REPEAT TWICE.
(5) JET FROM #32 TO #53.
(6) REPEAT (3)(4) & (5) TWICE
(7) 125 LBS. H_2O TO #31.
(8) CIRCULATE WATER IN #31 FOR 5 MIN.
(9) BRING #32 TO 10 RPM. JET WATER FROM #31 TO #32.
(10) BRING #32 TO 110 RPM. PLUG TO STOP.
(11) JET FROM #32 TO #53.



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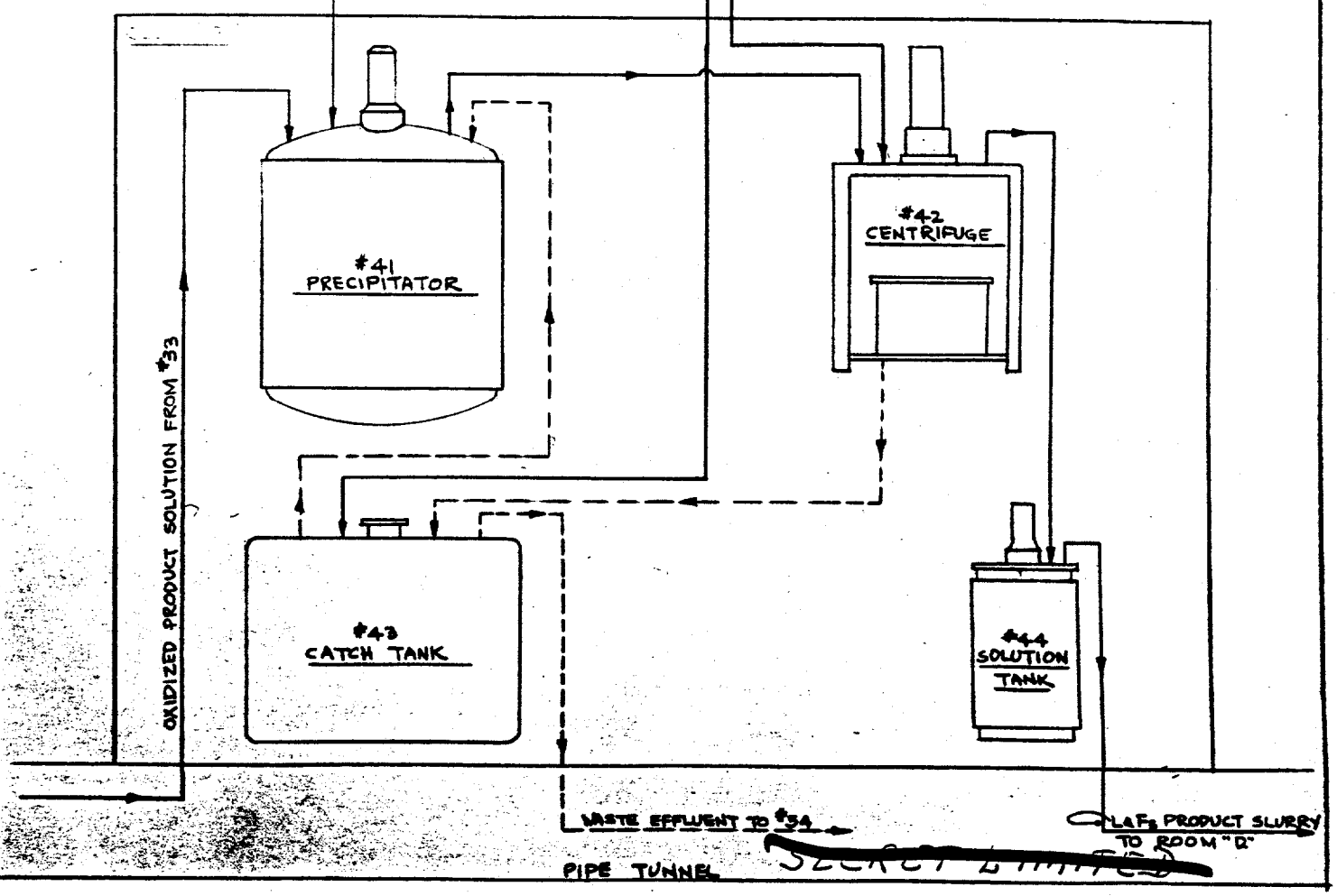
~~SECRET LIMITED~~ CELL #4 Run 90 Report CN-1879

(A) PRODUCT REDUCTION, FIRST PRECIPITATION AND SEPARATION

(1) RECEIVE PRODUCT SOLUTION FROM #33.
(2) 600 LBS. 9.2% $H_2C_2O_4$ SOLUTION.
(3) DIGEST ONE HR. AT 75°C.
(4) COOL TO 25°C.
(5) TAKE SAMPLE 41R.
(6) 200 LBS. HF.
(7) 500 LBS. 1% La SALT SOLUTION.
(8) DIGEST ONE HR. AT 25° C.
(9) CENTRIFUGE 90 LBS./MIN. AT 870 RPM.
(10) REDUCE #42 TO 870 RPM.
(11) AIR SPARGE #43 FOR 20 MIN. TAKE SAMPLE 43-W1

(B) SECOND PRODUCT PRECIPITATION AND SEPARATION

(1) JET SOLUTION FROM #43 TO #41
(2) COOL TO 25°C.
(3) 400 LBS. La SALT SOLUTION.
(4) DIGEST ONE HR. AT 25°C.
(5) CENTRIFUGE 90 LBS./MIN. AT 1870 RPM.
(6) REDUCE #42 TO 870 RPM & SKIM TO #43
(7) PLUG #42 TO 10 RPM.
(8) SLURRY CAKE FROM BOWL WITH WATER SPRAY JETTING TO #44 UNTIL 795 LBS. ARE IN #44.
(9) AIR SPARGE #UNTIL TWO CHARGES HAVE ACCUMULATED. TRANSFER TO ROOM "D."
(10) AIR SPARGE #43 FOR 20 MIN. TAKE SAMPLE 43 W.
(11) JET #43 TO #54.
(12) 250 LBS. H_2O.
(13) JET RINSE TO #54.



~~SECRET LIMITED~~

Agent 011-1577

[illegible] CONCENTRATION [illegible]

[illegible] SLURRY [illegible] FROM [illegible]
NEUTRALIZE WITH 85% KOH.
(2) 671 LBS. 85% KOH.
(3) BRING WEIGHT TO 2870 LBS. WITH H_2O.
(5) HEAT TO 75° C.
(6) DIGEST AT 75° C FOR ONE HOUR.
(7) COOL TO 25° C.

(B) $La(OH)_3$ SEPARATION
(1) CENTRIFUGE 20 LBS./MIN. @ 1800 R.P.M.
(2) SKIM TO D-3.
(3) TAKE SAMPLE D3-CW.
(4) JET D-3 TO D-4.
(5) JET D-4 TO 54.
(6) SCRAPE CAKE FROM D-2 BOWL WALL.
(7) WASH CAKE FROM BOWL JETTING SLURRY TO D-1.
(8) BRING D-1 WEIGHT TO 2081 LBS. WITH H_2O.
(9) 12 LBS. 85% KOH.
(10) AGITATE ONE HOUR AT 25° C.
(11) CENTRIFUGE 20 LBS./MIN. @ 1800 R.P.M.
(12) JET 3 EFFLUENT WASHES FROM D-3 TO D-1 TO D-2.
(13) SKIM D-2 TO D-3.
(14) AGITATE D-3 FOR 5 MIN. THEN TAKE SAMPLE DC-WW.
(15) JET D-3 TO D-4.
(16) JET D-4 TO 54.

(C) FIRST PRODUCT CAKE SOLUTION
(1) SCRAPE CAKE FROM D-2 BOWL WALL.
(2) 100 LBS. HNO_3 FROM D-6 TO D-2.
(3) ROTATE D-2 SLOWLY TO COMPLETE SOLUTION
(4) 25 LBS. 1.5% Zr SOLUTION FROM D-6 TO D-2
(5) ROTATE D-2 SLOWLY FOR 20 MIN.
(6) JET FROM D-2 TO D-1.

(D) FIRST OXIDATION OF PRODUCT CAKE
(1) 37 LBS. 10% $Na_2Cr_2O_7$ SOLUTION TO D-1.
(2) DIGEST 90 MIN. @ 85° C.
(3) TAKE SAMPLE D1-O.
(4) COOL TO 25° C.

(E) BY PRODUCT PRECIPITATION.
(1) 15 LBS. HF TO D-1.
(2) DIGEST 30 MIN. @ 25° C.

(F) BY-PRODUCT SEPARATION
(1) CENTRIFUGE 20 LBS./MIN. @ 1800 R.P.M.
(2) JET 3 EFFLUENT WASHES FROM D-3 TO D-1 TO D-2.
(3) SKIM TO D-3.
(4) PLUG D-2 TO STOP.
(5) 25.5 LBS. 6% HNO_3, 2% HF SOLUTION FROM D-6 TO D-2.
(6) CENTRIFUGE SLURRY 15 MIN @ 1800 R.P.M.
(7) SKIM TO D-3.
(8) REPEAT STEPS (4), (5), (6) & (7).
(9) AGITATE D-3 FOR 5 MIN. THEN TAKE SAMPLE D-3 OP.
(10) JET FROM D-3 TO D-1.
(11) 25 LBS. H_2O TO D-3.
(12) JET WASH TO D-1.

(G) BY-PRODUCT CAKE REMOVAL
(1) WASH CAKE FROM D-2 WITH H_2O JETTING TO D-4.
(2) AGITATE D-4 5 MIN. THEN TAKE SAMPLE D-4-BP.
(3) JET SLURRY FROM D-4 TO 54.

(H) REDUCTION & PRODUCT PRECIPITATION.
(1) 12.2 LBS. $H_2C_2O_4 \cdot 2H_2O$ TO D-1.
(2) 1.75 LBS. 50% $Mn(NO_3)_2$ SOL. TO D-1.
(3) DIGEST ONE HR. @ 35° C.
(4) TAKE SAMPLE D1-R.
(5) COOL TO 25° C.
(6) 50 LBS. 1% La SALT SOLUTION @ 2 LBS/MIN. TO D-1.
(7) AGITATE ONE HR. @ 25° C.

(I) PRODUCT SEPARATION
(1) CENTRIFUGE 20 LBS./MIN. @ 1800 R.P.M.
(2) SKIM D-2 TO D-3.
(3) JET D-3 TO D-1.
(4) 50 LBS. 1% La SALT SOLUTION @ 2 LBS./MIN. TO D-1.
(5) AGITATE ONE HR. @ 25° C.
(6) REPEAT STEP (1).
(7) JET 3 EFFLUENT WASHES FROM D-3 TO D-1 TO D-2.
(8) SKIM TO D-3.
(9) TAKE SAMPLE D3-W.
(10) JET D-3 TO D-4.
(11) JET D-4 TO 54.

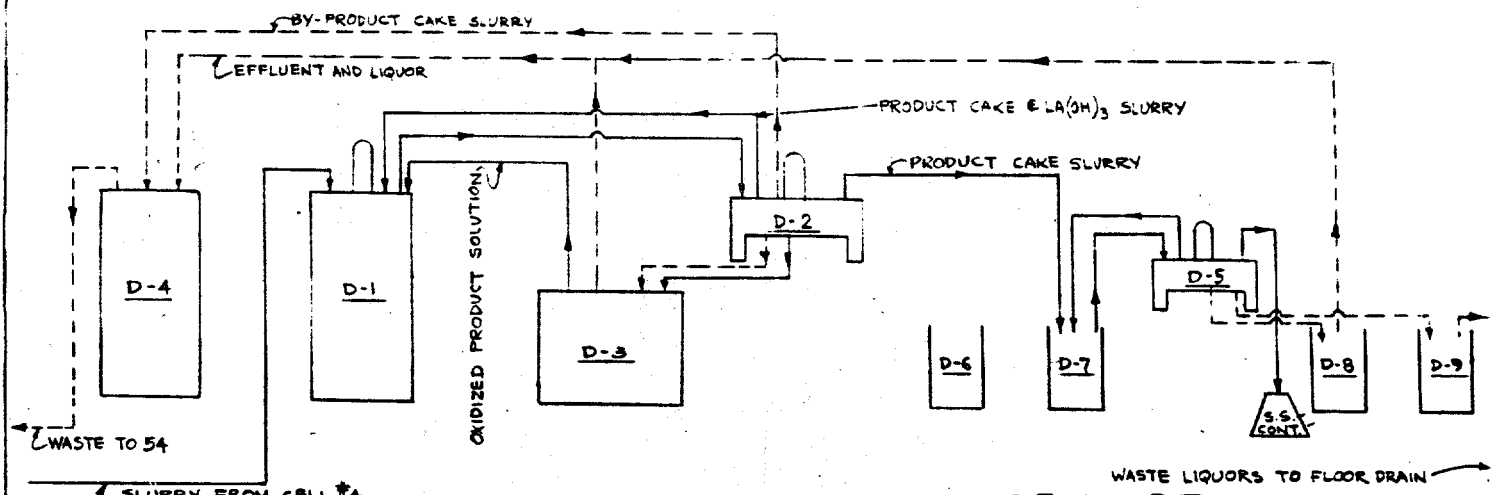
(J) PRODUCT CAKE REMOVAL
(1) WASH CAKE FROM BOWL WITH 300 LBS. H_2O JETTING SLURRY TO D-7.
(2) BRING WEIGHT TO 334 LBS. WITH H_2O.

(K) SECOND METATHESIS & CENTRIFUGATION
(1) NEUTRALIZE D-7 SLURRY WITH 85% KOH.
(2) 4.4 LBS. 85% KOH TO D-7.
(3) DIGEST ONE HR. @ 75° C.
(4) COOL TO 25° C.
(5) USING AIR JET, CENTRIFUGE 2 LBS./MIN. @ 3000 R.P.M.
(6) JET TWO EFFLUENT WASHES FROM D-8 TO D-7 TO D-5.
(7) SKIM D-5 TO D-8.
(8) AGITATE D-8 FOR 5 MIN., TAKE SAMPLE OW-2.
(9) JET D-8 TO D-4.
(10) 8 LBS. H_2O TO D-8.
(11) JET WASH TO D-4.
(12) JET D-4 TO 54.

(L) $La(OH)_3$ CAKE REMOVAL & WASH.
(1) SCRAPE CAKE FROM D-5 BOWL WALLS.
(2) 15 LBS. H_2O TO D-5.
(3) JET SLURRY TO D-7.
(4) WASH D-5 WITH SMALL PORTIONS H_2O JETTING EACH PORTION TO D-7.
(5) BRING WEIGHT OF D-7 TO 334 LBS. WITH H_2O.
(6) 2 LBS. 85% KOH TO D-7.
(7) AGITATE ONE HR. @ 25° C.

(M) FINAL $La(OH)_3$ CENTRIFUGATION
(1) USING AIR JET, CENTRIFUGE 3 LBS./MIN. @ 3000 R.P.M.
(2) JET TWO EFFLUENT WASHES FROM D-9 TO D-5.
(3) SKIM D-5 TO D-9.
(4) AGITATE D-9 FOR 5 MIN., TAKE SAMPLE WW2.
(5) DRAIN D-9 TO FLOOR DRAIN.

(N) FINAL SOLUTION OF $La(OH)_3$ CAKE
(1) 5 LBS. 60% HNO_3 TO D-5.
(2) SCRAPE CAKE FROM BOWL WALLS.
(3) AGITATE BOWL FOR 5 MIN.
(4) DIGEST IN D-5 FOR ONE HR.
(5) SYPHON FROM D-5 TO STAINLESS STEEL CONTAINER.
(6) 15 LBS H_2O IN 3 PORTIONS.
(7) SYPHON EACH PORTION TO S.S. CONTAINER.
(8) STIR SOLUTION IN S.S. CONTAINER WITH STAINLESS ROD.
(9) TAKE SAMPLE P-2.



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ROOM D RUN 50

Report GN-1879

FINAL CONCENTRATION

(A) FINAL OXIDATION
(1) PUT 4 DOUBLE CHARGES FROM G.S. CONTAINERS INTO D-7.
(2) BRING WEIGHT OF D-7 TO 180 LBS. WITH H_2O.
(3) AGITATE D-7 5 MIN., TAKE SAMPLE CP.
(4) 7.5 10% $Na_2Cr_2O_7$ SOLUTION TO D-7.
(5) 5.44 LBS. 1.5% Zr SOLUTION TO D-7.
(6) USING AIR JET CENTRIFUGE 2 LBS./MIN. @ 3000 R.P.M.
(7) 8 LBS. H_2O TO D-7 IN TWO PORTIONS.
(8) SKIM D-5 TO D-8.
(9) SLURRY SOLIDS FROM BOWL WALLS AND SYPHON TO S.S. CONTAINERS.
(10) WASH BOWL WITH SUCCESSIVE PORTIONS OF H_2O.
(11) SEPARATE SOLIDS FROM LIQUOR BY SWINGING @ 1500 R.P.M. FOR 15 MIN. IN INTERNATIONAL #2 CENTRIFUGE.
(12) POUR SUPERNATANT INTO D-8

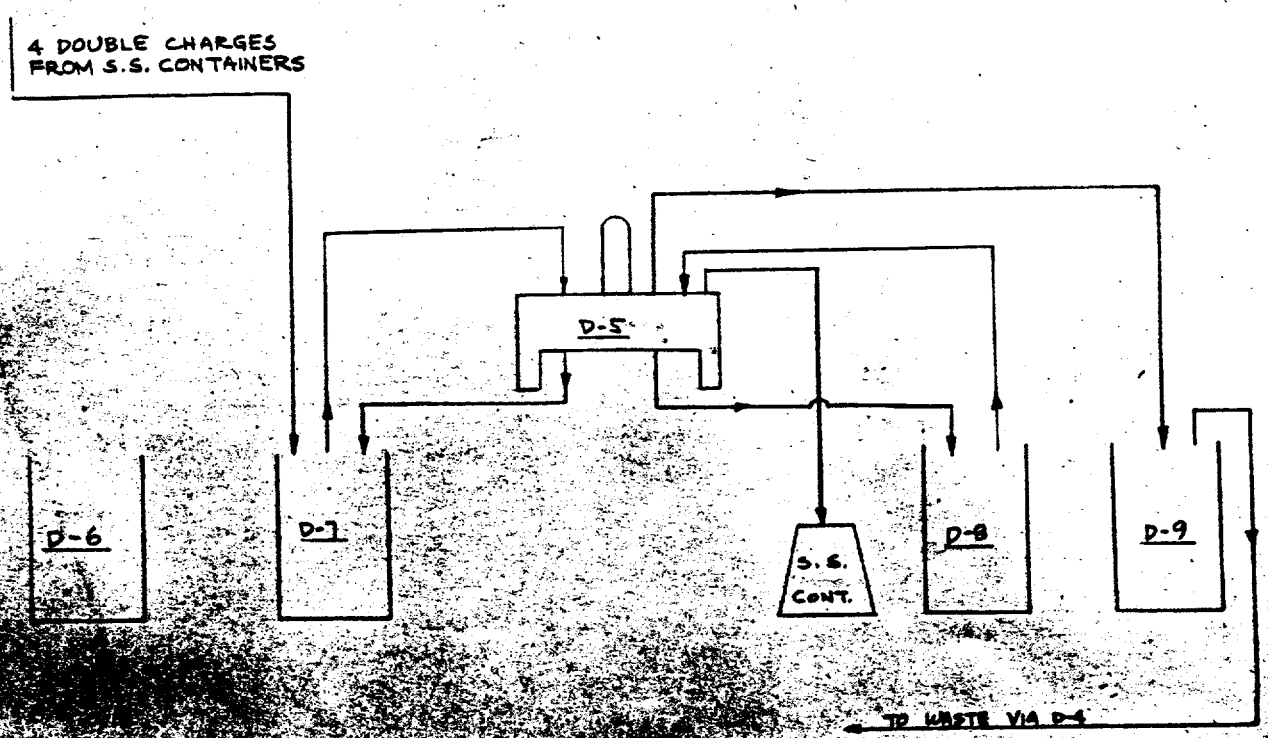
(B) FINAL BY-PRODUCT PRECIPITATION & CENTRIFUGATION
(1) 6 LBS. 48% HF TO D-8.
(2) AGITATE D-8 1 HR. @ 25°C.
(3) USING AIR JET CENTRIFUGE 2 LBS/MIN. @ 3000 R.P.M.
(4) SKIM D-5 TO D-7.
(5) 5 LBS. 6% HNO_3 - 5% HF SOLUTION TO D-5, MIX 3 MIN.
(6) BRING D-5 TO 3000 R.P.M. HOLD FOR 5 MIN.
(7) SKIM D-5 TO D-7
(8) REPEAT STEPS (5) (6) & (7).

(C) BY-PRODUCT CAKE REMOVAL
(1) 2 LBS. H_2O TO D-5.
(2) SLURRY CAKE IN BOWL FOR 5 MIN.
(3) JET SLURRY FROM D-5 TO D-9.
(4) REPEAT (1) (2) & (3) UNTIL BOWL IS CLEAN.
(5) AGITATE D-9. TAKE SAMPLE FBP.

(D) REDUCTION & PRODUCT PRECIPITATION
(1) 2.44 LBS. $H_2C_2O_4 \cdot 2H_2O$ TO D-7.
(2) 0.38 LBS. 50% $Mn(NO_3)_2$ SOLUTION TO D-7.
(3) AGITATE ONE HR. @ 35°C.
(4) TAKE SAMPLE FR.
(5) 10 LBS. 1% LA SALT SOLUTION TO D-7.
(6) AGITATE ONE HR. @ 25°C.

(E) PRODUCT SEPARATION
(1) USING AIR JET CENTRIFUGE 2 LBS./MIN. @ 3000 R.P.M.
(2) JET AN EFFLUENT WASH FROM D-8 TO D-5.
(3) SKIM D-5 TO D-8.
(4) 9 LBS. 1% LA SALT SOLUTION TO D-8.
(5) AGITATE ONE HR. @ 25°C.
(6) USING AIR JET CENTRIFUGE 2 LBS./MIN. @ 3000 R.P.M.
(7) JET AN EFFLUENT WASH FROM D-7 TO D-8 TO D-5.
(8) SKIM D-5 TO D-7
(9) AGITATE D-7 5 MIN. TAKE SAMPLE FW.
(10) JET D-7 TO WASTE. VIA D-4.

(F) FINAL PRODUCT CAKE REMOVAL
(1) SLURRY FROM BOWL WITH SMALL PORTIONS OF PROCESS WATER SIPHONING TO S.S. CONTAINER.
(2) WEIGH S.S. CONTAINER.
(3) AGITATE S.S. CONTAINER ONE HR. THEN TAKE SAMPLE FP.
(4) DELIVER TO 706 A BLDG.



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PREPARATION OF METAL SOLUTION

Cell #1

A. Coating Removal (Basis - 3 charges of 1/3 ton each).

		(Ave.)Ti in Mins
1.	Add 350 lbs. 50% NaOH and 330 lbs. water to dissolver tank 11.	
2.	Sparge with air and cool; add 224 lbs. 60% HNO_3 to dissolver tank at a controlled rate such that 11 temperature does not exceed 70° C.	36
3.	Cool to 40° C, and leave cooling water on; sparger off.	12
4.	Charge 3 buckets of metal to dissolver tank.	43
5.	Control reaction rate by use of coil cooling water. Maintain a column pressure drop of not more than 3" water until violent initial reaction subsides. Heat to 98° C with 20 lbs./sq. in. steam, maintaining column pressure drop of less than 3" of water. Digest 1 hour at 98° C.	53
6.	Cool to 35° C or below with water on coils and sparge with air while cooling.	44
7.	Jet coating removal solution to waste.	36
8.	Add 400 lbs. water to dissolver tank, air sparge for 10 min. and jet to waste.	24
9.	Add 400 lbs. water and 40 lbs. 60% HNO_3, air sparge for 10 min. and jet to waste.	26
		4 hrs. 34 min.

Solution Composition	
NaOH	10%
$NaNO_3$	20%

B. Metal Solution (Basis - 1/3 ton of metal).

1.	Drop 800 lbs. 60% HNO_3 to dissolver tank 11, followed by 1/2 gal. line flush of water.	16
2.	Add 267 cc F.P. stock solution #4 to dissolver, followed by 1/2 gal. water flush.*	3
3.	Drop 400 lbs. 60% HNO_3 to dissolver.	4
4.	Add F.P. stock solutions (267 cc each) to dissolver in order #1, 2, 3, 5, 6. Follow with 5 lbs. 60% HNO_3 flush.	12

*Time lapse from beginning of heating to reaction start.

FISSION ELEMENTS AND AMOUNTS IN 670 POUNDS OF METAL
Basis: 100 days @ 2500 KW/ton - 60 days cooling

SOLUTION NOS.	FISSION ELEMENT	GRAMS OF ELEMENT	PREFERRED SALT OR MOST READILY AVAILABLE SOURCE	GRAVIMETRIC FACTOR	GRAMS OF SALT
1	Y	2.5	$Y(NO_3)_3$ 6HOH	4.3	10.75
	Ce	9.67	$Ce(NO_3)_3$ 6HOH	3.09	29.9
	La	3.67	$La(NO_3)_3$ 6HOH (LL 23%)	4.35	15.95
	Ag	0.075	$Ag(NO_3)$	1.426	0.107
	Pr	4.33	$Pr(NO_3)_3$ 6HOH	3.08	13.35
	Nd	9.4	Neodymium ammon. nitrate	3.04(assay)	28.6
	Sm	2.75	$Sm(NO_3)_3$ 6HOH	2.95	8.1
	Eu	0.417	$Eu(NO_3)_3$ 6HOH	3.14	1.31
	Gd	0.0166	$Gd(BrO_3)_3$ 8HOH	4.3	0.0715
2	Ba	3.68	$Ba(NO_3)_2$	1.9	7.0
	Br	0.03	NaBr	1.29	0.0387
	Rb	1.5	$Rb(NO_3)$	1.73	2.59
	Cs	9.7	$Cs(NO_3)$	1.47	14.28
	Sr	3.57	$Sr(NO_3)_2$	2.41	8.6
3	Zr	8.85	Zirconium carbonate gel	by assay	
4	Cb	4.07	$KCoO_3$ 2HOH	2.6	10.6
	Mo	7.25	$(NH_4)_6Mo_7O_{24}$ 4HOH	1.85	13.4
	Sb	0.0166	$H_2K_2Sb_2O_7$ 4HOH	2.08	0.0345
5	I	0.585	HIO_3	1.39	0.814
	Se	0.0835	H_2SeO_4	1.0	0.156
	Te	1.08	Te metal	1.0	1.08
6	Ru	4.66	by assay		4.66
	Rh	0.833	" "		0.833
	Pd	0.5	" "		0.50

Run 193

		(Ave.)Ti in Mins
5.	Drop remaining 425 lbs. 60% HNO_3 to dissolver and air sparge for 15 minutes.	22
6.	Heat dissolver contents with 20 psi steam on coil and maintain steam unless column pressure drop exceeds 5" of water. Hold 5", if necessary, by water on coil.	35*
7.	Hold 1511 lbs. of water in C-11 for drowning charge in event of emergency.	
8.	Digest until Sp. Gr. of 1.79 is obtained, or for a total digestion time of 15 hours.	354
9.	At end of digestion period, drop 1511 lbs. water to dissolver and begin air sparging with 30 lbs. air. Cool while sparging (40° C).	27
10.	Jet 11 to 21.	41**
		8 hrs. 34 mi

Solution Composition

HNO_3	2%
UNH	40%

C. Dilution and Pre-Extraction Treatment.

1.	Add 1000 los. water to dissolver and sparge.	8
2.	Dissolve 42 lbs. $NaNO_2$ in 10 gal. water and add to dissolver.	13
3.	Drop 1250 los. water to dissolver and air sparge for 10 minutes.	17
4.	Jet 11 to 21.	8
		46 mins.

*Time lapse from beginning of heating to reaction start.
**Reflects 40 min. sparging, sampling of 11 M. Does not allow for hold up on Cell 2.

PRODUCT EXTRACTION

Cell #2

A. Product Precipitation.

		(Ave.)Ti in Mins.
1.	Receive metal solution and dilution water from 11 to precipitator 21.	50
2.	Adjust 21 temperature to 40° C, agitate 1/2 hour.	38
3.	Adjust 21 temperature to 75° C and add 304 lbs. 93% H_2SO_4, followed by 5 lbs. 60% HNO_3 flush.	63 46
4.	Add 83.5 lbs. 24% Bi solution A: 24% $BiONO_3$ 19% HNO_3 This solution is added rapidly and followed by 5 lbs. HNO_3 (60%) flush.	5
5.	Agitate 21 tank contents for 15 minutes and add 460 lbs. 73.5% H_3PO_4 uniformly over 2 hours. H_3PO_4 73.5% HNO_3 1.2%	141
6.	Add 100 lbs. water to 21 tank and digest 1 hour at 75° C after addition of all H_3PO_4	66
7.	Cool to 50° C and leave cooling water on during centrifugation.	70
		7 hrs. 58 min

Slurry Composition (in 21)

HNO_3	0.25 M	1.3%
UNH	0.48 M	20.0%
H_2SO_4	0.5 M	4.1%
H_3PO_4	0.6 M	4.9%
Bi	2.5 g/l	0.3%

B. Product Separation and Washing.

1.	Centrifuge at 870 RPM, rate 110 lbs./min. using 45 to 55 lbs. steam on jet.	64
2.	When jet gases, recycle from 23 to 21 for period of 10 to 30 seconds and repeat four times. Finally recycle 1000 lbs.	26
3.	After 5 min., skim 22.	10
4.	Add 250 lbs. water to 21, jetting to 22 as it is added to 21.	7
5.	Five minutes after completing (4), skim 22 and plug 22 to stop.	9
6.	With 22 turning at 10 RPM, add 250 lbs. water thru sprays at 70 lbs. pressure or higher. Bring 22 to 110 RPM, hold 2 min., plug to stop. The latter operation is repeated twice.	11
7.	Bring 22 to 870 RPM, hold 5 min. and skim. Plug to stop.	12
8.	With 22 turning at 10 RPM, add 250 lbs. water thru sprays at 70 lbs. pressure or higher. Bring 22 to 110 RPM, hold 2 min., plug to stop. The latter operation is repeated twice.	11
9.	Bring 22 to 870 RPM, hold 5 min. and skim. Plug to stop.	12
		2 hrs. 42 min

Run 193

D. Product Cake Solution.

		(Ave.)Ti in Mins
1.	Agitate 24 tank for 1 hour, transfer dissolving acid to 21. With 21 agitator running, jet thru 21 distributor for 30 min. with cooling water on jacket.	103*
2.	With 22 stopped, jet 330 lbs. acid from 21 to 22.	5
3.	Bring 22 to 110 RPM, hold 2 min., plug to stop. Repeat twice.	8
4.	With 22 stopped, jet 22 to 24 and start 24 agitator	5
5.	Jet 330 lbs. acid from 21 to 22.	3
6.	Bring 22 to 100 RPM, hold 2 min., plug to stop. Repeat twice.	8
7.	With 22 stopped, jet 22 to 24.	4
8.	Jet remaining acid to 22. (If 22 weight exceeds 400 lbs., immediately jet excess acid to 24.	3
9.	Bring 22 to 110 RPM, hold 2 min., plug to stop. Repeat twice.	8
10.	With 22 stopped, jet 22 to 24.	5
11.	Air sparge 22 for 40 min., sample, jet to waste - 475 min.**	
		2 hrs. 32 m

E. Oxidation of Product Cake.

1.	Agitate 24 for 2 hours at 50° C. (Do not exceed 50°)	120
2.	Start 21 agitator. Cooling water to jacket.	
3.	Add 500 lbs. water to 21 and distribute thru spray 4 for 15 min., holding 21 temperature below 35° C. (19)***	
4.	Upon completion of 2 hour agitation of 24, and with 22 stopped, jet 21 to 22 and 22 to 24 simultaneously.	5
5.	Adjust 24 temperature to 50° C and add 45 lbs. 10% $NaBiO_3$ followed by 80 lbs. process water.	26
6.	Agitate 24 at 50° C for 1 hour and add 16 lbs. 10% $Na_2Cr_2O_7$.	
7.	Cool 24 to 35° C.	75
		3 hrs. 46 mi

Solution Composition (in 24)

HNO_3	4.6 M	25%
$BiPO_4$		1.13%
$NaBiO_3$	0.009 M	0.22%
$Na_2Cr_2O_7$	.004 M	0.09%

*Step 1 is performed during preceding cake wash. Not to be included in overall cycle.

**This figure not included in overall time cycle.

***This time not included in overall time cycle. Operation performed simultaneously with Item 1.

DECONTAMINATION

First By-Product Precipitation - Cell #3

A. Initial By-Product Precipitation.

		(Ave.)Tim in Mins.
1.	Add 4000 lbs. water and heat to 40°. Receive oxidized solution from 24 and rinse 24 with 375 lbs. water. Jet rinse to 31 and agitate for 5 minutes.	14
2.	Add 42 lbs. of 24% Bi solution to 31 and follow with 5 lbs. 60% HNO_3 flush.	4
	24% $BiONO_3$ 19% HNO_3	
3.	Adjust temperature to 75° C and digest for 1 hour.	104
4.	Add 8 lbs. 10% $Na_2Cr_2O_7$ and cool 31 to 35° C, leaving cooling water on.	182
5.	Add 21 4/5 lbs. Ce-Zr solution to 31 and follow with 5 lbs. 60% HNO_3 flush.	3
6.	Digest for 10 min. after Ce-Zr addition.	10
7.	Add 82 lbs. 75% H_3PO_4 and 100 lbs. water flush.*	8
8.	Digest while cooling for 1 hour after H_3PO_4 additions.	60
		6 hrs. 25 m

9. Cool 31 to 30° C.

Slurry Composition (in 31)		
HNO_3	1.77 M	7.62%
H_3PO_4	0.095 M	0.89%
Bi	3.68 g/l	
Ce	50 mg/l	
Zr	50 mg/l	

Ce-Zr Solution Composition

Solution of Zr Carbonate Gel in HNO_3	20 3/5 lbs.	1.5%
Ceric Ammonium Nitrate (Salt)	1 1/5 lbs.	

B. Initial By-Product Separation.

1. With 32 at 870 RPM transfer slurry from 31 to 32 at 110 lbs./min. using 45 to 55 lbs. steam pressure.

2. When jet 31 to 32 gases, shut off jet, add 550 lbs. water to 31, distribute 5 min., and jet to 32. Leave 32 at 870 RPM. 86

1 hr. 26 mi

C. Final By-Product Precipitation.

1.	Transfer effluent from 1st by-product separation from 33 to 31 and cool to 35° C.	53
2.	Add 37 lbs. 10% $NaBiO_3$ (slurry).	2

*Flush addition time not included in cycle.

Run 193

	(Ave.)Ti in Mins.
3. Add 21 4/5 lbs. Ce-Zr solution made up as above.	2
Flush line with 5 lbs. 60% HNO_3	2
4. Digest 1 hour while cooling to 30° C.	60
	1 hr. 59

Slurry Composition (in 31)

HNO_3	1.18 M	7.15%
H_3PO_4	0.088 M	0.83%
Ce	50 mg/l	
Zr	50 mg/l	

D. Second By-Product Separation.

1. With 32 at 870 RPM, transfer 31 to 32 at 110 lbs./min.	64
2. When jet 31 to 32 gases, jet 33 to 31 for 10 to 30 seconds. Repeat four times, finally recycling 1000 lbs.	23
3. Add 550 lbs. process water to 31 and jet 31 - 31 distributor for 5 minutes with agitator running and cooling water on jacket.	13
4. Ten minutes after recycling 1000 lbs. above jet 31 to 32.	6
5. After 10 min., skim 32 and plug to 10 RPM.	17
6. Jet 33 to 51.	13
	2 hrs. 16 min

E. By-Product Cake Washing.

1. With 32 at 10 RPM, add 175 lbs. water thru spray.	2
2. Bring 32 to 140 RPM, hold 2 min., plug to stop. Repeat twice.	10
3. Bring 32 to 870 RPM, hold 10 min., skim, plug to stop.	19
4. Jet 33 to 51.	3
5. Jet 32 heel to waste. (4)*	
	34 min.

F. By-Product Cake Solution.

1. Add 1180 lbs. 60% HNO_3 to 31, turn cooling water on jacket and jet 31 - 31 distributor for 15 minutes.	15
2. Bring 32 to 10 RPM and jet 315 lbs. acid from 31 to 32	4
3. Add 20 lbs. 27 1/2% H_2O_2 to 32.	3
4. Bring 32 to 140 RPM, hold 2 min. Plug to stop. Repeat four times.	14
5. With 32 stopped, jet 32 to 71.	5
6. Bring 32 to 10 RPM and jet 315 lbs. acid from 31 to 32.	4
7. Add 20 lbs. 27 1/2% H_2O_2 to 32.	3
8. Bring 32 to 140 RPM, hold 2 min. Plug to stop. Repeat four times.	14.

*This figure not included in overall cycle.

		(Ave.)Tim in Mins.
9.	With 32 stopped, jet 32 to 71.	5
10.	Bring 32 to 10 RPM and jet 315 lbs. acid from 31 to 32.	4
11.	Add 20 lbs. 27 1/2% H_2O_2 to 32.	2
12.	Bring 32 to 140 RPM, hold 2 min. Plug to stop. Repeat four times.	15
13.	With 32 stopped jet 32 to 71.	5
14.	Jet remaining acid from 31 to 32.	3
15.	Add 20 lbs. 27 1/2% H_2O_2 to 32.	2
16.	Bring 32 to 140 RPM, hold 2 min. Plug to stop. Repeat four times.	16
17.	With 32 stopped jet 32 to waste.	5
18.	Add 252 lbs. water to 31 and jet to 32 with 32 at 10 RPM.	5
19.	Bring 32 to 140 RPM, hold 2 min. Plug to stop. Jet heel to waste.	5
20.	Add 28 lbs. 10% $Na_2Cr_2O_7$ to 31, 252 lbs. water, jet mixture to 32 (10 RPM). Bring 32 to 140 RPM, hold 2 min. Plug to stop.	10
21.	Jet 32 to waste.	3
		2 hrs. 22 mi

DECONTAMINATION

First Product Precipitation - Cell #5

A. Reduction in Precipitator.

	(Ave.)Time in Mins.
1. Receive product solution and washes from 33.	61
2. Add 500 lbs. 20% ferrous ammonium sulphate.	15
3. Heat to 75° C and digest for 1 hour.	118
	2 hrs. 14 min

B. Product Precipitation.

1. With temperature at 75° C add 143 lbs. 14% Bi solution, uniformly over 30 min. Flush with 5 lbs. 60% HNO_3. (14% $BiONO_2$, 52% HNO_3)	37
2. Digest 30 min. at 75° C.	30
3. Add 590 lbs. 75% H_3PO_4 to 51 and digest at 75° C for 2 hours.	131
4. Cool to 50° C; leave cooling water on.	64
	4 hrs. 22 min.

Slurry Composition (in 51)

HNO_3	1.09 M	6.36%
H_3PO_4	0.6 M	5.42%
Fe	0.03 M	
Bi	1.77 g/l	

C. Product Separation.

1. Bring 52 to 870 RPM and transfer slurry from 51 to 52 at 110 lbs./min. rate using 45 to 55 psi steam.	88
2. When jet 51 - 52 gases, recycle 53 to 51 for period of 10 to 30 seconds and repeat four times. Finally, recycle 1000 lbs.	24
3. Five minutes after completing (2) above, skim 52 and plug to stop.	11
	2 hrs. 3 min.

D. Product Cake Washing.

1. With 52 at 10 RPM add 250 lbs. water thru sprays at 70 lb. pressure or higher.	5
2. Bring 52 to 110 RPM, hold 2 min., plug to stop. Repeat twice.	10
3. Bring 52 to 870 RPM, hold 5 min., skim, plug to stop.	11
4. With 52 at 10 RPM, add 250 lbs. water thru sprays at 70 lb. pressure or higher.	3
5. Bring 52 to 110 RPM, hold 2 min., plug to stop. Repeat twice.	10
6. Bring 52 to 870 RPM, hold 5 min., skim, plug to stop.	13
	52 min.

E. Product Cake Solution.

		(Ave.)Tim in Mins
1.	Agitate 54 for 1 hour (contains acid for cake solution) and jet 58 to 51. With 91 agitator running, jet thru 51 distributor for 10 min, with cooling water on jacket. (98)*	
2.	Jet 330 lbs. acid from 51 to 52, bring 52 to 110 RPM, hold 2 min., plug to stop. Repeat twice.	14
3.	With 52 stopped, jet 52 to 54.	5
4.	Jet 330 lbs. acid from 51 to 52, bring 52 to 110 RPM, hold 2 min., plug to stop. Repeat twice.	14
5.	With 52 stopped, jet 52 to 54.	5
6.	Jet remaining acid to 52. (Jet excess above 400 lbs. directly to 54.)	5
7.	Bring 52 to 110 RPM, hold 2 min., plug to stop. Repeat twice.	9
8.	With 52 stopped jet 52 to 54.	5
9.	Jet waste effluent to waste disposal. (395)**	
		57 min.

F. Oxidation of product Cake.

1.	Agitate 54 for 2 hours at 50° C.	120
2.	Add 500 lbs. water to 51, agitate, distribute 5 min. (19)***	
3.	With 52 stopped, jet 51 to 52 and 52 - 54 simultaneously.	7
4.	With 54 at 50° C add 45 lbs. $NaBiO_3$ and add 80 lbs. water for flush.	16
5.	Agitate 54 at 50° C for 1 hour, then add 8 lbs. 10% $Na_2Cr_2O_7$.	61
6.	Cool 54 to 35° C.	22
		3 hrs. 46 min

Solution Composition (in 54)

HNO_3	4.6 M	25%
Na_2BiO_3	0.009 M	
$Na_2Cr_2O_7$	0.002 M	

*This item does not reflect time in overall cycle. Operation is performed during cake washing above.

**This item does not reflect time in overall cycle. Operation performed during product cake solution above.

***Not included in overall time cycle.

DECONTAMINATION

Second By-Product Precipitation - Cell #6

A. Initial By-Product Precipitation.

	(Ave.)Tim in Mins.
1. Add 4000 lbs. water to 61, heat to 40° C. Receive oxidized solution in 61 from 54. Rinse 54 with 375 lbs. water and after 5 min. agitation in 54, jet to 61. (14)*	
2. Add 42 lbs. 24% Bi solution to 61; rapidly, follow with 5 lbs. 60% HNO_3.	4
3. Adjust temperature to 75° C and digest for 1 hour.	104
4. Add 8 lbs. of 10% $Na_2Cr_2O_7$ to 61 and cool to 35° C.	182
5. Add 21 4/5 lbs. Ce-Zr solution to 61. Follow with 5 lbs. 60% HNO_3 flush. Digest 10 min.	13
6. Add 82 lbs. 75% H_3PO_4, followed by 100 lbs. water flush. (8)**	
7. Digest while cooling for 1 hour after H_3PO_4 addition.	60
8. Cool 61 to 30° C and leave cooling water on.	--
	6 hrs. 25 m

Slurry Composition (in 61)

HNO_3	1.27 M	7.62%
H_3PO_4	0.095 M	0.89%
Bi	3.68 g/l	
Ce	50 mg/l	
Zr	50 mg/l	

B. Initial By-Product Separation.

1. Bring 62 to 870 RPM and transfer slurry at rate of 110 lbs./min. using 45 to 55 lbs. in 2 steam.	
2. Just as jet 61 - 62 first gases, shut off jet.	
3. Add 550 lbs. water to 61, distribute 5 min., jet to 62 and leave 62 running at end (870 RPM).	86
	1 hr. 26 m

C. Final By-Product Precipitation.

1. With cooling water on 61, jet 63 to 61 and cool to 35° C.	53
2. Add 37 lbs. 10% $NaBiO_3$ to 61.	2
3. Add 21 4/5 lbs. Ce-Zr solution to 61, followed by 5 lbs. 60% HNO_3 flush.	3
4. Digest 1 hour while cooling to 30° C.	60
	1 hr. 58 m

Solution Composition

HNO_3	1.18 M	7.15%
H_3PO_4	0.088 M	0.83%
Ce	50 mg/l	
Zr	50 mg/l	

*This figure does not include time necessary to add water to 61 and heat to 40° C.

**Does not include flush addition time.

D. Final By-Product Separation.

		(Ave.)Time in Mins.
1.	With 62 at 870 RPM transfer slurry to 62 at 110 lbs./min. rate using 45 - 55 psi steam.	64
2.	As jet 61 - 62 gases jet from 73 to 61 for 10 to 30 seconds. Repeat this operation 5 times. At end, recycle 1000 lbs.	23
3.	Add 550 lbs. water to 61, distribute 5 min. and 10 min. after completion of 1000 lbs. recycle, jet to 62.	19
4.	After 10 min. skim 62 and plug 62 to 10 RPM.	17
5.	Jet 63 to 41.	13
		2 hrs. 16 min

E. By-Product Cake Washing.

1.	With 62 at 10 RPM add 175 lbs. water thru sprays at 70 lbs. or more pressure.	2
2.	Bring 62 to 140 RPM, hold 2 min., plug to stop. Repeat twice.	10
3.	Bring 62 to 870 RPM hold 10 min. and skim.	19
4.	Jet 63 to 41.	3
5.	Plug 62 to stop and jet 62 heel to waste. (4)	
		34 min.

F. By-Product Cake Solution.

1.	Add 1180 lbs. 60% HNO_3 to 61, agitate, cool and distribute for 5 min.	10
2.	Bring 62 to 10 RPM and jet 315 lbs. acid from 61 to 62.	4
3.	Add 20 lbs. 27 1/2% H_2O_2 to 62, bring 62 to 140 RPM, hold 2 min., plug to stop. Repeat four times.	17
4.	With 62 stopped, jet 62 to 71.	5
5.	Bring 62 to 10 RPM and jet 315 lbs. acid from 61 - 62.	4
6.	Add 20 lbs. 27 1/2% H_2O_2 to 62, bring 62 to 140 RPM, hold 2 min., plug to stop. Repeat four times.	17
7.	With 62 stopped jet 62 to 71.	5
8.	Bring 62 to 10 RPM and jet 315 lbs. acid from 61 - 62.	4
9.	Add 20 lbs. 27 1/2% H_2O_2 to 62, bring 62 to 140 RPM, hold 2 min., plug to stop. Repeat four more times.	17
10.	With 62 stopped jet 62 to 71.	5
11.	Jet remaining acid from 61 to 62. (Jet excess over 400 lbs. to 71.)	3
12.	Add 20 lbs. 27 1/2% H_2O_2 to 62, followed by 5 lbs. 60% HNO_3	3
13.	Bring 62 to 140 RPM, hold 2 min., plug to stop. Repeat four more times.	11
14.	With 62 stopped, jet 62 to 71.	5
15.	Add 252 lbs. water to 61. With 62 at 10 RPM jet to 62. Bring 62 to 140 RPM, hold 2 min., plug to stop.	9
16.	Jet 62 to 71.	5
17.	Add 28 lbs. 10% $Na_2Cr_2O_7$ to 61 and 252 lbs. water.	4
18.	With 62 at 10 RPM, jet the $Na_2Cr_2O_7$ solution from 61 to 62, bring 62 to 140 RPM, hold 2 min., plug to stop.	6
19.	Jet 62 to 71.	4
		2 hrs. 18 min.

DECONTAMINATION

Second Product Precipitation - Cell #4

A. Reduction in Precipitator.

	(Ave.)Ti in Mins
1. After product solution and cake washes are in 41, add 500 lbs. 20% ferrous ammonium sulphate, heat to 75° C and digest 1 hour.	194
	3 hrs. 14

Solution Composition (in 41)

HNO_3	1.00 M	5.83%
Fe	0.032 M	

B. Product Precipitation.

1. With temperature at 75° C, add 143 lbs. 14% Bismuth solution uniformly over 30 min., followed by 5 lbs. 60% HNO_3 flush.	37
2. Digest 30 min. at 75° C and add 590 lbs. 75% H_3PO_4	30
3. Digest at 75° C for 2 hours.	131
4. Cool to 50° C and leave cooling water on.	64
	4 hrs. 22

Slurry Composition (in 41)

HNO_3	1.09 M	6.36%
H_3PO_4	0.6 M	5.42%
Fe	0.03 M	
Bi	1.77 g/l	

C. Product Separation.

1. Bring 42 to 870 RPM and transfer slurry at rate of 110 lbs./min.	88
2. When jet gases, jet from 43 to 41 for 10 to 30 seconds. Repeat this operation four times. At end, recycle 1000 lbs.	24
3. Five minutes after 1000 lbs. recycle, skim 42.	11
4. Add 250 lbs. H_2O to 41, jet to 42 as it is added to 41.	5
5. Five minutes after above item, skim 42 and plug to stop.	15
	2 hrs. 23

D. Product Cake Washing.

1. With 42 at 10 RPM add 250 lbs. water thru sprays at 70 lb. pressure or higher, bring 42 to 110 RPM, hold 2 min, and plug to stop. Repeat twice.	15
2. Bring 42 to 870 RPM, hold 5 min. and skim. Plug to stop.	11
3. With 42 at 10 RPM add 250 lbs. water thru sprays at 70 lb. pressure or higher, bring 42 to 110 RPM, hold 2 min., and plug to stop. Repeat twice.	15
4. Bring 42 go 870 RPM, hold 5 min., skim. Plug to stop.	11
	52 min.

E. Product Cake Solution.

	(Ave.)Time in Mins.
1. After agitating 44 for 1 hour, transfer to 41 and distribute for 10 min., with 41 cooling water on. (78)*	
2. Stop 42 and jet 330 lbs. acid from 41 - 42. Bring 42 to 110 RPM, hold 2 min. and plug to stop. Repeat twice.	14
3. With 42 stopped, jet 42 to 44.	5
4. Jet 330 lbs. acid from 41 - 42. Bring 42 to 110 RPM, hold 2 min. and plug to stop. Repeat twice.	14
5. With 42 stopped jet 42 to 44.	5
6. Jet remaining acid from 41 to 42. Any excess over 400 lbs. to be jetted to 44. Bring 42 to 110 RPM, hold 2 min. and plug to stop. Repeat twice.	14
7. With 42 stopped, jet 42 to 44.	5
8. Jet waste in 43 to waste disposal. (395)*	
	57 min.

NOTE:

To simulate Hanford operating conditions thru two decontamination cycles plus extraction in the Clinton canyon, the following operating procedure was adopted:

Extraction

1. Cell 2 - Used only thru extraction.

Decontamination

1. Cell 3 - By-product $BiPO_4$.
2. Cell 5 - Product $BiPO_4$.
3. Cell 6 - By-product $BiPO_4$.
4. Cell 4 - Product $BiPO_4$

Crossover

1. Cell 6 - By-product $BiPO_4$.
2. Cell 4 - By-product double precipitation, double centrifugation LaF_3.
3. Cell 5 - Product double precipitation double centrifugation LaF_3.
4. Rood D.

*Not reflected in overall time cycle. Operation performed during centrifugation step.

CROSSOVER

Oxidation of Product Cake - Cell #5.

	(Ave.)Time in Mins.
1. Transfer product solution from 45 to 54 (1800 lbs.)	5
2. Add 53 lbs. 10% $NaBiO_3$ to 54, followed by 80 lb. water flush.	16
3. Agitate at 50° C for 1 hour, add 16 lbs. 10% $Na_2Cr_2O_7$ and cool to 35° C.	83
	1 hr. 44 min.

Solution Composition (in 54)

HNO_3	4.6 M	25%
$NaBiO_3$	0.009 M	
$Na_2Cr_2O_7$	0.004 M	

$BiPO_4$ By-Product Precipitation - Cell #6

A. By-Product Precipitation.

1. Add 4300 lbs. H_2O to 61 and heat to 40° C. Receive oxidized product from 54 and rinse 54 tank with 375 lbs. water.	23
2. Heat 61 to 75° C, add 90 lbs. 75% H_3PO_4 followed by 185 lbs. water.	50
3. Digest 61 at 75° C for 1 hour. Cool to 50° C and leave cooling water on.	120
	3 hrs. 13 min.

Slurry Composition (in 61)

HNO_3	1.39 M	8.38%
H_3PO_4	0.1 M	0.94%
Bi	2.7 g/l	

B. By-Product Separation.

1. With 62 at 870 RPM, transfer slurry from 61 to 62 at 110 lbs./min. rate using 45 - 55 lb. steam.	75
2. As jet 61 - 62 first gases, jet from 63 to 61 for 10 to 30 seconds. This is repeated four times. At end, recycle 1000 lbs.	29
3. Five minutes after recycling 1000 lbs., skim 62.	10
4. Jet 63 to 41.	16
5. Add 250 lbs. to 61, jet to 62 as it is added. Five minutes after water addition, skim 62 and plug to stop.	10
6. Jet 63 to 41.	2
	2 hrs. 22 min

C. By-Product Cake Washing.

1. With 62 at 10 RPM, add 250 lbs. water thru sprays at 70 lb. pressure or higher.	3
2. Bring 62 to 110 RPM, hold 2 min., plug to stop. Repeat twice.	9
3. Bring 62 to 870 RPM, hold 5 min., skim, plug to stop.	10
4. Jet 63 to 41.	3
	25 min.

D. By-Product Cake Solution.

		(Ave.)Ti in Mins
1.	Add 789 lbs. 60% HNO_3 to 61, agitate, distribute for 5 min. with cooling water on jacket. (15)*	
2.	Bring 62 to 10 RPM, jet 330 lbs. acid from 61 to 62.	5
3.	Bring 62 to 110 RPM, hold 2 min., plug to stop. Repeat twice.	10
4.	With 62 stopped, jet 62 to 71.	4
5.	Bring 62 to 10 RPM, jet 330 lbs. acid from 61 to 62.	5
6.	Bring 62 to 110 RPM, hold 2 min., plug to stop. Repeat twice.	10
7.	With 62 stopped, jet 62 to 71.	4
8.	Jet remaining acid from 61 - 62 (excess of 400 lbs. jet to 71 immediately.)	5
9.	Bring 62 to 110 RPM, hold two min., plug to stop. Repeat twice.	10
10.	With 62 stopped, jet 62 to 71.	4
11.	Add 125 lbs. water to 61, distribute 1 min., jet to 62 with 62 running at 10 RPM.	7
12.	Bring 62 to 110 RPM, plug to stop. Jet 62 to 71.	4
		58 min.

*This time not included in overall time cycle.

CROSSOVER

LaF_3 By-Product Precipitation - Cell #4

A. Initial By-Product Precipitation.

		(Ave.)Tim in Mins.
1.	Receive effluent and washes from Cell 6. Start heating 41 to 75° C. While heating, add 270 lbs. 5% $KMnO_4$ to 41, followed by 5 gal. water flush.*	
2.	Adjust temperature to 75° C and agitate 1/2 hour.	21
3.	Cool to 40° C and add 36 lbs. anhydrous HF to 41.	30
4.	Dissolve 4 1/2 lbs. La salt in 5 gal. water and add to 41 uniformly over 20 min.	70
5.	Digest 41 for 1 hour.	20
		60
		3 hrs. 21 m

Solution Composition		
HNO_3	1.26 M	7.63%
H_3PO_4	0.09 M	0.84%
HF	0.22 M	0.41%
La	0.131 g/l	

B. First By-Product Peparation.

1.	With 42 at 1740 RPM transfer slurry from 41 to 42 at rate of 70 lbs./min.	105
2.	When jet 41 - 42 gases shut off steam and reduce 42 speed to 870 RPM.	5
3.	Five minutes after reducing 42 speed to 870 RPM, skim.	4
		1 hr. 54 min

C. Final By-Product Precipitation.

1.	Jet from 43 to 41 using 60 lb. steam.	22
2.	Dissolve 4 1/2 lbs. La salt in 5 gal. water and add 41 uniformly over 20 min.	20
3.	Digest for 1 hour after addition of La salt, cool to 40° C or below.	60
		1 hr. 42 mi

Solution Composition		
HNO_3	1.20 M	7.14%
H_3PO_4	0.085 M	0.79%
HF	0.20 M	0.38%
La	0.137 g/l	

D. Second By-Product Separation.

1.	Bring 42 to 1740 RPM and transfer slurry from 41 to 42 at rate of 110 lbs./min.	118

*Heating time and $KMnO_4$ addition time combined.

	(Ave.)Ti in Mins
2. When 41 - 42 jet gases, cut off steam.	
3. Reduce 42 speed to 870 RPM, hold 5 min. and skim.	12
4. Plug 42 to 10 RPM.	2
5. Jet 43 to 51.	15
	2 hrs. 27

E. By-Product Cake Washing and Removal.

1. With 42 at 10 RPM add 225 lbs. water thru sprays at 70 lb. pressure or more, followed by 25 lbs. 60% HNO_3.	9
2. Bring 42 to 110 RPM, hold 2 min., plug to stop. Repeat twice.	7
3. Bring 42 to 1740 RPM, hold 10 min., reduce speed to 870 RPM, hold 5 min., and skim.	25
4. Jet 43 to 51.	4
5. With 42 at 10 RPM add 225 lbs. water thru sprays at 70 lb. pressure or more. (4)*	
6. Just after sprays start, begin jetting to 71. Continue spraying until 71 weight is 1500 lbs. (25)*	
	45 min.

NOTE:

Figures marked with asterisk are not included in overall time cycle. Operation proceeds normally from Step 4.

*This figure does not reflect time required for making up the reducing solution. This time is 30 minutes.

CROSSOVER

LaF_3 Product Precipitation - Cell 5

A. Product Reduction.

	(Ave.)Tim in Mins.
1. Receive effluent from 43 tank to 51 tank, add 850 lbs. 9.2% $H_2C_2O_4$ and digest 1 hour at 50° C. (84)*	84*
2. Cool 51 to 30° C.	115
	3 hrs. 19 m

Solution Composition (in 51)

HNO_3	0.95 M
HF	0.17 M
$H_2C_2O_4 \cdot 2H_2O$	0.048 M
$Mn(NO_3)_2$	0.008 M

B. Product Precipitation.

1. Add 75 lbs. anhydrous HF to 51. (Rm. D HF cylinder)	60
2. Add 230 lbs. 1% La salt solution uniformly over 20 min.	20
3. Digest 51 for 1 hour after La solution has been added at 40° C or below.	60
4. Cool to 30° or below.	--
	2 hrs. 20 mi

Slurry Composition

HNO_3	0.93 M	5.57%
H_3PO_4	0.070 M	0.65%
$H_2C_2O_4 \cdot 2H_2O$	0.047 M	
HF	0.57 M	
La	0.049 g/l	

C. First Product Separation.

1. Bring 52 to 1740 RPM and transfer slurry from 51 to 52 at rate of 70 lbs./min.	131
2. When jet from 51 to 52 gases, shut off steam.	1
3. Reduce 52 to 870 RPM and hold 5 min. Skim.	11
	2 hrs. 23 mi

D. Second Product Precipitation.

1. Jet from 53 to 51.	26
2. Add 230 lbs. 1% La solution to 51, uniformly over 20 min. and digest for 1 hour after the La salt is added.	80
3. Cool 51 to 30° C.	--
	1 hr. 46 min.

*This figure does not reflect time required for making up the reducing solution. This time is 30 min.

Slurry Composition			(Ave.)Time in Mins.
HNO_3	0.87 M	5.20%	
H_3PO_4	0.065 M	0.60%	
$H_2C_2O_4 \cdot 2H_2O$	0.044 M		
HF	0.53 M		
La	0.045 g/l		

B. Second Product Separation.

1.	Bring 52 to 1740 RPM and transfer slurry from 51 to 52 at 70 lbs./min. rate.	158
2.	When jet 51 to 52 gases, cut off steam.	1
3.	Add 500 lbs. water to 51, distribute 10 min., jet 51 to 52.	25
4.	Reduce 52 speed to 870 RPM, hold 5 min., skim.	12
5.	Plug 52 to stop.	3
		3 hrs. 19 min

NOTE:

The previous run, (192) through crossover, has been stored in 44 tank, waiting for completion of Run 193. Upon completion of Run 193, Run 192 is transferred to Room D before Run 193 is removed from the centrifuge bowl. The two runs combined are then processed in D-1.

Cake Removal

1.	Check Room D and transfer charge 192 from 44 to D-1.	13
2.	With 52 at 10 RPM, spray 250 lbs. water at 70 lb. pressure to 52; jet 52 to 44; keeping 52 empty.	14
3.	Agitate 44 and jet to D-1	13
4.	With 52 at 10 RPM, spray 250 lbs. water at 70 lb. pressure to 52; jet 52 to 44, keeping 44 empty.	6
5.	Agitate 44 and jet to D-1.	4
6.	With 52 at 10 RPM, spray 500 lbs. water at 70 lb. pressure to 52, jet 52 to 44, keeping 44 empty.	12
7.	Agitate 44 and jet to D-1	8
		1 hr. 10 min.

FIRST CONCENTRATION

Room D

	(Ave.)Tim in Mins.
A. First Metathesis.	
1. *Receive slurry of two runs from 44 into D-1. Start agitator.	
2. *Receive washes from Cell 4.	
3. Observe color of slurry.	30
4. Add 550 lbs. KOH to D-1	5
5. Heat to 80° C and hold at 80° C for 90 min.	117
6. Cool D-1 to 35° C.	42
KOH 15%	
	3 hrs. 14 m
B. $La(OH)_3$ Separation.	
1. Bring empty centrifuge to 1800 RPM.	
2. Transfer slurry from D-1 to D-2 using steam jet.	210
3. Start D-3 agitator.	
4. Skim D-2 to 3 - 5 gal. Stop D-2.	
5. Agitate 10 minutes and sample (18)**	
6. Jet from D-3 to D-4 (10)**	
7. Jet from D-4 to 72. (4)**	
	3 hrs. 30 m
C. $La(OH)_3$ Cake Removal.	
1. Scrape cake from D-2 bowl wall.	7
2. Wash cake from D-2 bowl with water at 80 lbs. pressure. Jetting slurry to D-1.	55
3. Make volume in D-1 up to 250 gal. with water.	10
	1 hr. 12 mi
D. Second $La(OH)_3$ wash.	
1. Add 49 lbs. 85% KOH to D-1	8
2. Agitate 1 hour at 35° C or lower.	60
KOH 2%	
	1 hr. 8 min
E. Second $La(OH)_3$ Centrifugation.	
1. Bring empty centrifuge to 1800 RPM.	
2. Transfer slurry from D-1 to D-2	217
3. Recycle 3 - 10 gal. washes from D-3 to D-1 and jet to D-2.	8

*Time involved in transfer of skimming and washes accounted for in cake removal.

**The times shown do not reflect time consumed in process, and are therefore not included in the overall time cycle.

		(Ave.)Tim in Mins.
4. Start D-3 agitator.		
5. Skim to 3 - 5 gal. in D-2 at 1800 RPM.		
6. Stop D-2.		13
7. Jet from D-3 to D-4.	(10)*	
8. Jet from D-4 to 72.	(4)*	
		3 hrs. 58 m

F. First Product Cake Solution.

1. Scrape cake from D-2 walls.	
2. Add 100 lbs. of 60% HNO_3 to D-6.	
3. While rotating D-2 slowly pump HNO_3 from D-6 into D-2 through sprays.	5
4. Rotate D-2 slowly for 10 min. to complete solution.	10
5. Jet solution from D-2 to D-1.	
6. Add 25 lbs. of 1.5% Zr^{+4} solution to D-6.	
7. While rotating D-2 slowly pump the Zr^{+4} solution from D-6 into D-2 through sprays.	
8. Rotate D-2 slowly for 20 minutes.	20
9. Jet solution from D-2 to D-1	
10. Rotate D-2 slowly and wash bowl with water and jet to D-1 until D-1 weight reaches 917 lbs.	
11. Agitate D-1 for 20 min. and sample.	20
	55 min.

G. First Oxidation of Product Cake.

1. Add 37 lbs. of 10% $Na_2Cr_2O_7$ to D-1.	56
2. Heat D-1 to 85° C. Hold 90 minutes.	90
3. Adjust volume in D-1 to 954 lbs.	
4. Cool to 35° C.	
	2 hrs. 26 m

Solution Composition

HNO_3	1.05 M	6.3%
$Na_2Cr_2O_7$	0.016 M	0.4%
Zr^{+4}	0.4 g/l	

H. By-Product Precipitation.

1. Add 17 lbs. anyhydrous HF.	
2. Digest 1/2 hour at 25° C or lower.	167
	2 hrs. 47 mi

Solution Composition

HNO_3	1.05M	6.2%
HF	0.92 M	1.8%
La	1.29 g/l	

*Not reflected in overall cycle.

I. By-Product Centrifugation and Washes.

		(Ave.) Time in Mins.
1.	Bring D-2 to 1800 RPM.	74
2.	Transfer slurry from D-1 to D-2.	
3.	Recycle 100 lbs. from D-3 to D-1 to D-2.	
4.	Repeat Item 3, two times.	
5.	Skim D-2 at 1800 RPM.	19
6.	Plug D-2 to stop.	
7.	Jet solution from D-3 to D-1 and cool.	
8.	Add 176 lbs. water and 20 lbs. 60% nitric to D-6.	
9.	Pump 1/4 of the above solution through D-2 sprays and slurry for five minutes.	
10.	Centrifuge at 1800 RPM for 15 minutes.	
11.	Skim at 1800 RPM.	
12.	Repeat steps 9, 10, 11 three times using balance of solution in D-6.	
13.	Jet washes from D-3 to D-1.	
14.	Wash out D-3 with 3 gal. of water and jet to D-1.	107
		3 hrs. 20 min.

J. By-Product Cake Removal.*

1. With 80 lb. pressure through sprays start jetting from D-2 to D-4 until bowl is clean.
2. Jet from D-4 to 72.

K. First Reduction of Product.

1.	Start D-1 agitator.	
2.	Add 12.2 lbs. of solid $H_2C_2O_4 \cdot 2H_2O$ to D-1.	
3.	Add 1.75 lbs. of 50% $Mn(NO_3)_2$ solution to D-1.	
4.	Adjust temperature to 35° C and digest 1 hour.	
5.	Cool to 25° C.	62
		1 hr. 2 min.

Solution Composition

HNO_3	0.69 M	4.58%
HF	0.62 M	1.30%
$H_2C_2O_4 \cdot 2H_2O$	0.07 M	0.93%
$Mn(NO_3)_2$	0.035 M	0.067%

L. First Product Precipitation.

1.	Add 50 lbs. of 1% La salt solution to D-1 at the rate of 7 lbs./min.	30
2.	Agitate 1 hour at 25° C.	60
		1 hr. 30 min.

Slurry Composition

HNO_3	0.66 M	4.4%
$H_2C_2O_4 \cdot 2H_2O$	0.067 M	0.90%
HF	0.60 M	1.25%
La	0.35 g/l	

*Time not recorded - does not add to time cycle.

M. First Product Centrifugation.

	(Ave.)Time in Mins.
1. Bring D-2 up to 1800 RPM.	
2. Transfer slurry from D-1 to D-2 at the rate of 2 gals./min.	137
3. Eight minutes after transfer is complete skim D-2.	
4. Plug D-2 to stop.	11
5. Jet effluent and skimming from D-3 back to D-1.	
	2 hrs. 28 min

N. Second Product Precipitation.

1. Start D-1 agitator.	
2. Add 50 lbs. 1% La salt solution to D-1 at the rate of 2 lbs./min.	34
3. Agitate for 1 hour at 25° C.	60
	1 hr. 34 min

Slurry Composition

HNO_3	0.61 M	4.27%
$H_2C_2O_4 \cdot 2H_2O$	0.062 M	0.82%
HF	0.55 M	1.15%
La	0.32 g/l	

O. Second Product Centrifugation.

1. Bring D-2 to 1800 RPM.	
2. Transfer slurry from D-1 to D-2 at the rate of 2 GPM.	147
3. Recycle 100 lbs. of effluent from D-3 to D-1 to D-2, 3 times.	
4. Start D-3 agitator.	
5. Eight minutes after completion of transfer skim D-2.	
6. Plug D-2 to stop.	
7. Jet effluent from D-3 to D-4.	24
8. Jet contents of D-4 to 72.	
	2 hrs. 51 min

P. Product Cake Removal.

1. Rotate D-2 bowl slowly and wash cake from the walls with 300 lbs. process water at 80 lbs. pressure. Jet washes to D-7.
2. Make up volume in D-7 to 334 lbs.

Q. Second Metathesis.

1. Start agitation in D-7.	
2. Add 70 lbs. solid KOH (85%)	
3. Heat D-7 to 80° C.	41
4. Hold D-7 at 80° C for 90 min.	90
5. Cool D-7 to 35° C.	18
	2 hrs. 29 min.

Solution Composition

KOH 15%

Run 193

R. Second Centrifugation of $La(OH)_3$.

	(Ave.)Tim in Mins.
1. Bring D-5 centrifuge to 3000 RPM.	
2. Jet slurry from D-7 to D-5 at the rate of 1/4 gal. per min.	298
3. Wash D-7 twice with 1/2 gal. of water.	
4. Skim D-5.	
5. Stop D-5.	
6. Jet effluent from D-8 to D-4.	21
7. Jet D-4 to 72.	
	5 hrs. 19 min.

S. $La(OH)_3$ Cake Removal.

1. Scrape cake from walls of D-5.
2. Wash D-5 bowl with successive portions of water and jetting to D-7 until D-5 is clean.
3. Make D-7 weight up to 334 lbs. with water.

T. Second $La(OH)_3$ Wash.

1. Start D-7 agitator.	
2. Add 8 lbs. solid 85% KOH to D-7	42
3. Agitate for 1 hour.	60
	1 hr. 42 min

Solution Composition
KOH 2%

U. Final $La(OH)_3$ Centrifugation.

1. Bring D-5 centrifuge to 3000 RPM.	
2. Jet slurry from D-7 to D-5 at the rate of 1/4 gal./min., effluent to D-8.	236
3. Wash D-7 twice with 1/2 gal. of water.	
4. Skim D-5.	
5. Stop D-5.	
6. Jet effluent from D-8 to D-4.	26
7. Jet from D-4 to 72.	
	4 hrs. 22 min

V. Final HNO_3 solution of $La(OH)_3$ Cake.

1. Add 5 lbs. of 60% HNO_3 to D-5.	
2. Scrape cake from sides of bowl.	
3. Agitate bowl slowly for 5 minutes to dissolve cake.	18
4. Let solution stand in D-5 bowl for 1 hour.	60
5. Jet cake from bowl into D-9.	
6. Wash bowl with 3 successive 5 lb. additions of process water. Jet to D-9 after each wash.	13
7. Agitate solution in D-9 for 1/2 hour.	30
8. Hold for 8 times.	
	2 hrs. 1 min.

FINAL CONCENTRATION

Room D

	(Ave.)Time in Mins.
A. Charge to make up from First Cycle Solution.	
1. Jet HNO_3 solutions from four double charges from D-9 into D-7.	
2. Make volume in D-7 up to 180 lbs.	40
3. Agitate D-7 30 minutes.	32
	1 hr. 12 min
B. Final Oxidation.	
1. Add 7 lbs. 8 oz. 10% $Na_2Cr_2O_7$ solution to D-7.	
2. Heat to 85° C for 90 min.	90
3. Cool to 25° C and adjust weight to 193 lbs. if necessary.	30
	2 hrs. 11min

Solution Composition

HNO_3	1.03 M	6.22%
$Na_2Cr_2O_7$	0.016 M	0.39%

C. Final By-Product Precipitation.	
1. Start D-7 agitator.	
2. Add 6 lbs. 58% HF, holding temperature at 25° C or below.	74
3. Agitate D-7 for 1 hour at 25° C or below.	60
	2 hrs. 14 min

Slurry Composition

HNO_3	1.00 M	5.92%
HF	0.75 M	1.45%
La	5.5 g/l	

D. Final By-Product Centrifugation and Washing.	
1. Bring D-5 bowl to 3000 RPM.	
2. Using air jet, feed slurry from D-7 into D-5 at a rate slow enough to give a clean effluent into D-8.	155
3. Flush D-7 with 3 gal. process water.	8
4. Skim D-5 at 3000 RPM. Skim as closely as possible without disturbing the cake. Stop D-5.	11
	2 hrs. 54 min

E. Final By-Product Cake Removal.

1. Clean D-5 bowl by scraping down the cake, adding process water and slurrying in bowl.
2. Jet slurry out of bowl into D-9 tank.

Run 193

(Ave.)Time in Mins.

3. Routine the above procedure in successive washes until bowl is clean.
4. Stir slurry in D-9 until well mixed.
5. Sample, lable FBP, Run No., Date, Time Weight, and Sp. Gr.
6. Jet slurry from D-9 to D-1.

F. Final Reduction of Product.

1. Start agitator in L-8.
2. Add 2 lbs. 7 oz. of solid $H_2C_2O_4 \cdot 2H_2O$.
3. Add 6 oz. of 50% $Mn(NO_3)_2$.
4. Adjust temperature to 35° C. 7
5. Agitate for 1 hour at 35° C. 60
6. Sample D-8 for reduction.
7. Cool to 25° C. 7

1 hr. 14 min.

Solution Composition

HNO_3	0.87 M	5.16%
$H_2C_2O_4 \cdot 2H_2O$	0.83 M	1.1%
$Mn(NO_3)_2$	0.043 M	0.082%

G. First Final Product Precipitation.

1. Add 10 lbs. 1% La salt solution at rate of 2%/min. 50
2. Agitate for 1 hour at 25° C. 60

1 hr. 50 min

Slurry Composition
La 0.12 g/l

H. Final Product Centrifugation (First half)

1. Bring D-5 up to 3000 RPM and transfer slurry from D-8 at a rate slow enough to give a clear effluent. Effluent to D-7. 177
2. Clean slurry from D-8 by recycling 3 gal. of effluent from D-7 6
3. Skim D-5 to within 1/4" of the cake. 7
4. Shut down D-5.

3 hrs. 10 min

I. Second Half Final Product Precipitation.

1. Start agitator in D-7 tank.
2. Add 9 lbs. 1% La salt solution at rate of 2%/min. 49
3. Agitate 1 hour at 25° C or lower. 60

1 hr. 49 min.

Slurry Composition
La 0.095 g/l

J. Final Product Centrifugation (Second half)

		(Ave.)Time in Mins.
1.	Bring D-5 up to 3000 RPM.	
2.	Transfer slurry from D-7 to D-5 at a rate slow enough to obtain a clear effluent. Effluent to D-8.	159
3.	Clean slurry from D-7 by recycling 3 gal. of effluent from D-8.	16
4.	Shut down D-5.	
5.	Agitate D-8 for 5 min., sample, label FW, Date, Time, Chg. Nos., Weight, Sp. Gr. Wait for results.	180
6.	Transfer solution from D-8 to D-4.	
7.	Jet solution from D-4 to 54.	
		5 hrs. 55 min

K. Removal of Final Product Cake from Centrifuge.

1.	Slurry solid from bowl with small portions of process water, siphoning out into s.s. flask after each slurry. Wash until absolutely clean. All washes are to be sent to the s.s. container.	62
2.	Bolt cover on s.s. container and weigh.	
3.	Monitor s.s. container 1" from container.	
4.	Set up container in pipe tunnel and agitate slurry for 1 hour.	
5.	Take 10 cc sample in pipe turned using special pipette. Bring sample to Control Laboratory. Label FF, Chg. No., Date, Time, Weight, and Sp. Gr.	
6.	Bolt cover on s.s. container.	
7.	Deliver to 706-A Building.	

WASTE DISPOSAL

Cell 7

A. Coating Removal Solution.

1. Receive coating removal solution and washes from 11 into 72 and jet directly to waste storage tank W-5.

B. Metal Waste.

1. Receive 1/2 of metal waste solution from 23 into 72.
2. Add 3000 lbs. 30% Na_2CO_3 to 72 maintaining temperature between 30 - 45° C.
3. Jet to metal waste storage tank W-3.
4. Receive remainder of metal waste solution and washes from 23 into 72.
5. Add 3000 lbs. 30% Na_2CO_3 to 72 maintaining temperature between 30 - 45° C.
6. Jet to metal waste storage tank W-3.

C. Oxidized $BiPO_4$ Cake Solution.

1. Agitate waste receiver (71 or 73) for 2 hours and sample.
2. Jet to 72.
3. Add 1435 lbs. 30% Na_2CO_3 to 72, maintaining temperature between 30 - 45° C.
4. Jet to waste storage tank W-5.

D. Oxidized LaF_3 slurry.

1. Agitate in waste receiver (71 or 73) for 2 hours and sample.
2. Jet to 72 and directly out to waste storage tank W-5.

E. $BiPO_4$ Reduced Effluents.

1. Receive 1/2 of waste solution into 72.
2. Add 2000 lbs. 30% Na_2CO_3, maintaining temperature between 30 - 45° C.
3. Jet to waste storage tank W-5.
4. Receive remainder of waste solution and washes into 72.
5. Add 2000 lbs. 30% Na_2CO_3, maintaining temperature between 30 - 45° C.
6. Jet to waste storage tank W-5.

F. LaF_3 Reduced Effluent.

1. Receive 1/2 of waste solution into 72.
2. Add 1665 lbs. 30% Na_2CO_3, maintaining temperature between 30 - 45° C.
3. Jet to waste storage tank W-5.
4. Receive remainder of waste solution and washes into 72.
5. Add 1665 lbs. 30% Na_2CO_3, maintaining temperature between 30 - 45° C.
6. Jet to waste storage tank W-5.

G. Metathesis Wastes.

1. Receive wastes in 72 from D-4 and jet directly to waste storage tank W-5.

H. Reduced Effluent - 1st Concentration Cycle.

1. Receive reduced effluent waste in 72 from D-4.
2. Add 320 lbs. 30% Na_2CO_3, maintaining temperature between 30 - 45° C.
3. Jet to waste storage tank W-5.

I. By-Product Slurry - 1st Concentration Cycle.

1. Receive slurry waste in 72 from D-4.
2. Add 15 lbs. of 30% Na_2CO_3, maintaining temperature between 30 - 45° C.
3. Jet to waste storage tank K-5.

J. Reduced effluent - Final Concentration Cycle.

1. Receive reduced effluent waste in 72 from D-4.
2. Add 10 lbs. of 30% Na_2CO_3, maintaining temperature between 30 - 45° C.
3. Jet to waste storage tank K-5.

B. YIELD AND MATERIAL BALANCES

Tables showing yields and material balances for "eight-timers" at various sample points are given. An "Eight-Timer" is taken to mean a series of runs, usually eight, that are combined to make a batch for final concentration and isolation. Values given have been adjusted for any appreciable amounts of product removed from the process in special samples.

TABLE

Percent Yield

Run Numbers		1-3	4-11	12-19	20-27	28-34	35-38	39-45	46-53	54-60	61-68	69-[illegible]
% Ori[illegible] prod. in extr. ppt.	24-P	70.4	62.2	79.5	86.2	83.9	92.0	86.0	85.0	99.0	81.0	77
% Ori[illegible] prod. after 1st by-prod. ppt.	31-R	85.8	76.3	93.3	93.9	93.0	105.0	98.0	89.0	108.0	92.0	92
% Ori[illegible] prod. in 1st prod. ppt.	34-P	71.8	57.8	71.4	74.1	76.0	120.0	85.0	88.0	92.0	79.0	78
% Ori[illegible] prod. after 2nd by-prod. ppt.	41-R	63.9	64.5	59.5	72.5	80.0	121.0	83.0	80.0	97.0	86.0	84
% Ori[illegible] prod. in LaF_3 pr. slurry	41R-43	58.8	62.4	54.3	69.7	78.0	117.0	78.0	79.0	96.0	85.0	83
% Ori[illegible] prod. in sol. of LaF_3 pr. slurry	D-I-P	44.8	63.7	68.3	61.7	64.0	115.4	73.0	66.0	82.0	64.0	85
% Ori[illegible] prod. in oxid. sol. 1st cycle	D-I-R	37.6	54.6	61.8	57.4	54.0	111.2	74.0	65.0	81.0	63.0	84
% Ori[illegible] prod. in prod. cake sol. 1st cycle	CP	43.4	50.4	57.1	56.8	49.0	85.1	72.0	67.0	76.0	66.0	78
% Ori[illegible] prod. in oxid. prod. sol. final cycle	FR	39.0	40.2	56.6	59.5	62.0	107.6	74.0	67.0	83.0	64.0	81
% Ori[illegible] prod. in final cake slurry	FP	40.5	46.0	59.7	59.7	72.0	107.2	81.5	72.0	85.0	60.0	75

Percent Yield (Contd.)

Run Numbers	77-83	84-91	92-99	100-107	108-114	115-122	123-129	130-137	138-145	146-153	154-161	162-169	170-177	178-185	186-193	194-201
24-P	82.4	75.0	80.8	88.6	86.5	85.2	84.0	86.1	91.8	93.1	92.6	93.6	93.1	97.2	93.9	92.8
31-R	101.0	92.5	94.3	95.2	103.0	93.5	95.5	90.4	102.2	103.9	96.2	100.5	99.9	98.2	97.8	102.8
34-P	84.0	73.6	84.0	88.5	86.6	84.3	86.0	85.7	89.5	91.5	88.2	94.2	88.7	94.9	89.5	96.1
41-R	90.0	85.3	92.5	95.5	95.5	95.5	120.2	90.5	97.6	99.0	72.8	87.5	72.2	93.4	101.3	92.4
41R-43	89.0	84.5	91.5	94.5	94.8	93.5	119.7	90.1	96.4	97.7	71.6	85.9	88.6	91.2	85.4*	93.3*
D-I-P	97.5	79.5	88.2	85.5	102.4	81.0	75.1	84.9	81.3	91.5	94.0	105.8	92.7	93.0	85.8	96.2
D-I-R	101.7	87.0	81.2	87.0	95.4	87.5	92.2	83.4	87.9	91.2	88.0	115.2	94.8	99.8	99.0	96.5
CP	89.6	85.3	86.5	96.7	97.6	104.6	91.9	103.5	98.4	86.0	85.4	106.6	94.0	97.9	90.4	94.7
FR	83.5	74.1	88.0	78.6	94.6	84.6	75.0	92.0	92.9	96.8	85.4	101.4	92.2	87.2	89.9	82.6
FP	82.3	85.0	86.6	82.5	91.7	69.5	84.4	89.5	94.5	93.8	88.2	103.5	93.7	89.0	81.9	87.0

*151-153

Percent Material Balance

Run Numbers		1-3	4-11	12-19	20-27	28-34	35-38	39-45	46-53	54-60	61-68	69-76	77-83	84-91	92-9
Through 1st by-pr. ppt.	31R	110.3	87.8	102.3	99.0	98	109	104	93	112	97	94	105.3	105.0	96
Through 2nd by-pr. ppt.	41R	79.3	81.2	77.6	89.3	68	137	92	85	103	93	87	93.4	99.5	96
Through sol. of LaF_3 pr. slurry	D-I-P	69.9	84.7	92.7	77.9	82	127	86	73	[illegible]	73	91	110.8	95.8	93
Through 1st conc. cycle	CP	71.4	74.6	86.5	77.6	83	118	90	80	[illegible]	77	87	95.5	103.2	93
Through final conc. cycle	FP	68.9	76.4	91.1	82.8	68	134	93	86	98	71	85	95.4	104.0	93

Percent Material Balance (Cont.)

Run Numbers		100-107	108-114	115-122	123-129	130-137	138-145	146-153	154-161	162-169	170-177	178-185	186-193	194-201
	31R	96.9	107.5	95.0	97.0	92.3	106.3	106.3	98.2	102.7	105.1	106.8	104.6	108.0
	41R	98.5	101.7	98.3	123.2	94.1	104.3	103.3	76.9	91.8	101.4	106.3	114.7	101.8
	D-I-P	90.5	110.8	86.5	80.5	89.9	90.5	79.9	99.9	112.4	104.4	109.2	107.3	111.4
	CP	103.2	109.0	113.0	101.3	111.1	110.1	89.3	91.4	109.7	97.5	116.7	114.6	112.3
	FP	90.0	103.2	78.3	94.4	97.1	106.0	102.7	96.3	112.6	108.7	107.7	105.9	104.7

Yields in Crossover
Using Hanford Procedure

Run Numbers		186-193	194-201
% Orig. prod. in 2nd prod. ppt.	44P	86.7	89.6
% Orig. in composite of 2nd prod. ppt.	45P	80.5	94.8
% Orig. *(Aver.) prod. in 2nd prod. ppt.	154P	90.5	95.8
% Orig. *(Aver.) prod. in oxidized 2nd prod. ppt.	154O	89.0	93.6
% Orig. *(Aver.) prod. after LaF_3 by-pr. ppt.	151R	91.7	94.6

*Basis here is 1/8th of total of orig. prod. for the 8 runs since all were collected in tank No. 45 and 1/8th removed for each run.

C. GRAPHS OF WASTE LOSSES FOR INDIVIDUAL RUNS

The following graphs show the waste results by individual runs with notations of the process modifications that were made throughout the development of the process. The effect of these changes, therefore, can be seen and waste results compared with other runs. In most cases where high values were obtained, the wastes were reworked to recover a large proportion of the product that otherwise would have been lost.

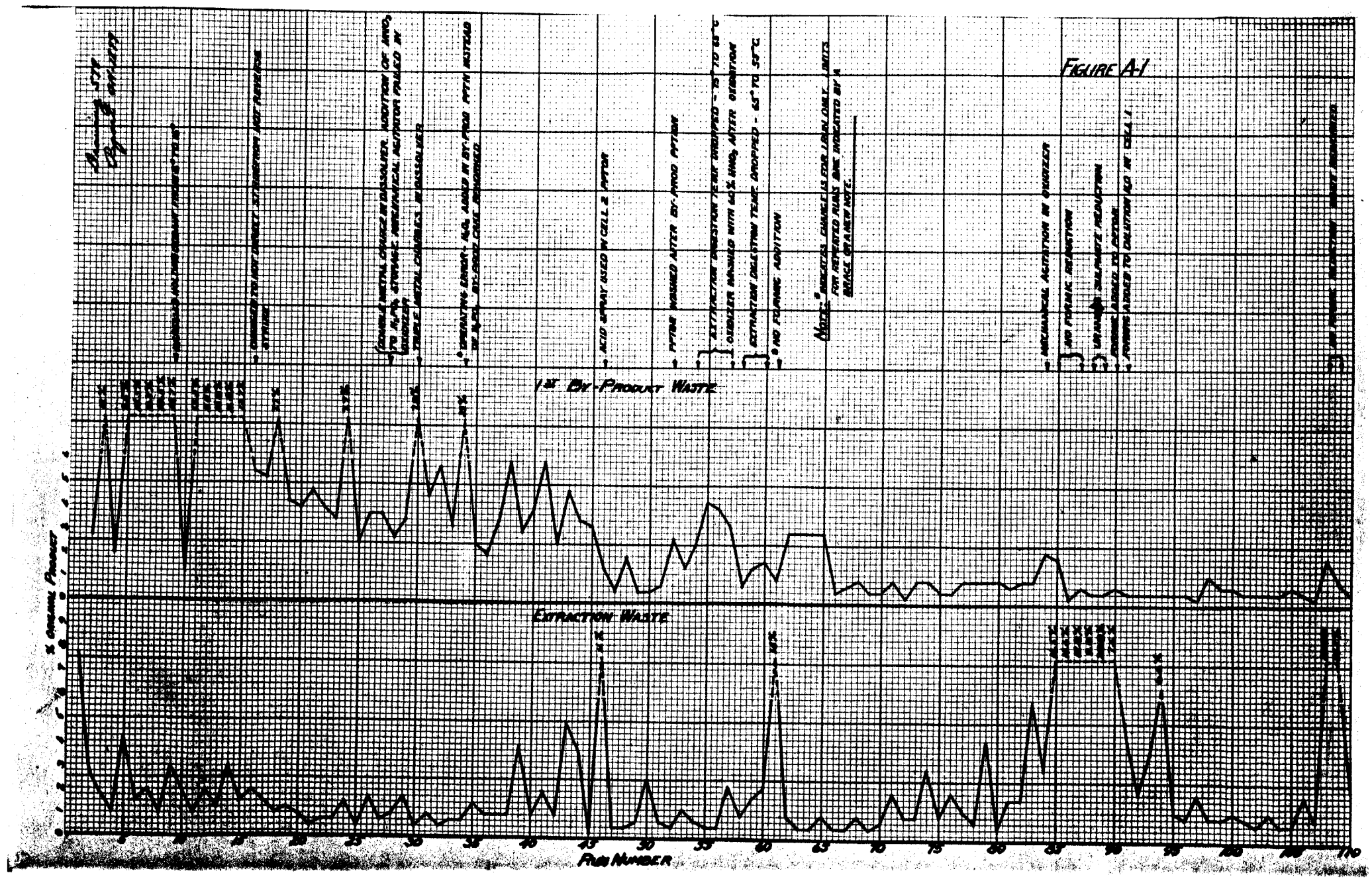

FIGURE A-1
1st By-Product Waste
Extraction Waste
% Original Product
Run Number
ACID SPRAY USED IN CELL 2 PPTOR
PPTOR WASHED AFTER BY-PROD PPTION
EXTRACTION DIGESTION TEMP. DROPPED - 75° TO 65°C
OXIDIZER WASHED WITH 60% HNO3 AFTER OXIDATION
EXTRACTION DIGESTION TEMP. DROPPED - 65° TO 55°C
NO FORMIC ADDITION
MECHANICAL AGITATION IN OXIDIZER
NO FORMIC REDUCTION

Decont.

Run 159 6 cells in operation

Run 170 W-F-P [illegible] Scav. on 1st BP [illegible]

Run 186 W procedure Scav in 2 dec. cycles

Run 193 [illegible] in decont cycles.

Runs 2[illegible]5-231 [illegible] dF [illegible]
W Runs

Runs 24[illegible]-2[illegible]7 Between FP [illegible]

Runs 202 - [illegible] runs
[illegible]
Runs 202-217

Single Cycle Runs 236-254, 264-299

Two Cycl Runs 202-235 & 255-263

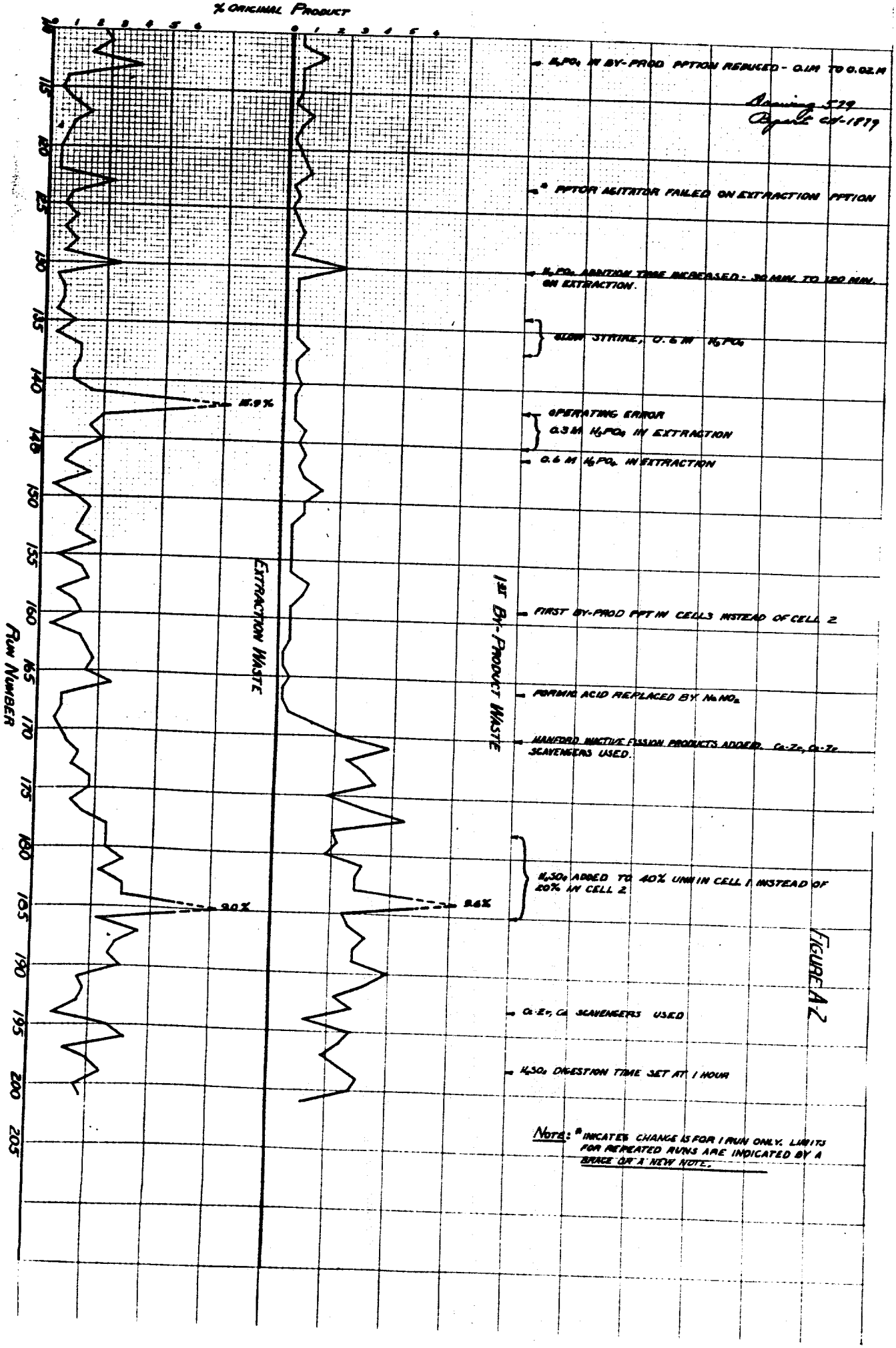
% ORIGINAL PRODUCT
0 1 2 3 4 5 6
0 1 2 3 4 5 6
RUN NUMBER
115
120
125
130
135
140
145
150
155
160
165
170
175
180
185
190
195
200
205
15.9%
9.0%
9.6%
EXTRACTION WASTE
1ST BY-PRODUCT WASTE
H3PO4 IN BY-PROD PPTION REDUCED - 0.1M TO 0.02M
Drawing 579
Report CH-1879
* PPTOR AGITATOR FAILED ON EXTRACTION PPTION
H3PO4 ADDITION TIME INCREASED - 30 MIN. TO 120 MIN. ON EXTRACTION.
GLOW STRIKE, 0.6 M H3PO4
OPERATING ERROR
0.3 M H3PO4 IN EXTRACTION
0.6 M H3PO4 IN EXTRACTION
FIRST BY-PROD PPT IN CELL 3 INSTEAD OF CELL 2
FORMIC ACID REPLACED BY NaNO2
HANFORD INACTIVE FISSION PRODUCTS ADDED. Ca-Zr, Ca-Zr SCAVENGERS USED.
H2SO4 ADDED TO 40% UNH IN CELL 1 INSTEAD OF 20% IN CELL 2
Ca-Zr, Ca SCAVENGERS USED
H2SO4 DIGESTION TIME SET AT 1 HOUR
NOTE: * INDICATES CHANGE IS FOR 1 RUN ONLY. LIMITS FOR REPEATED RUNS ARE INDICATED BY A BRACE OR A NEW NOTE.

FIGURE A-2

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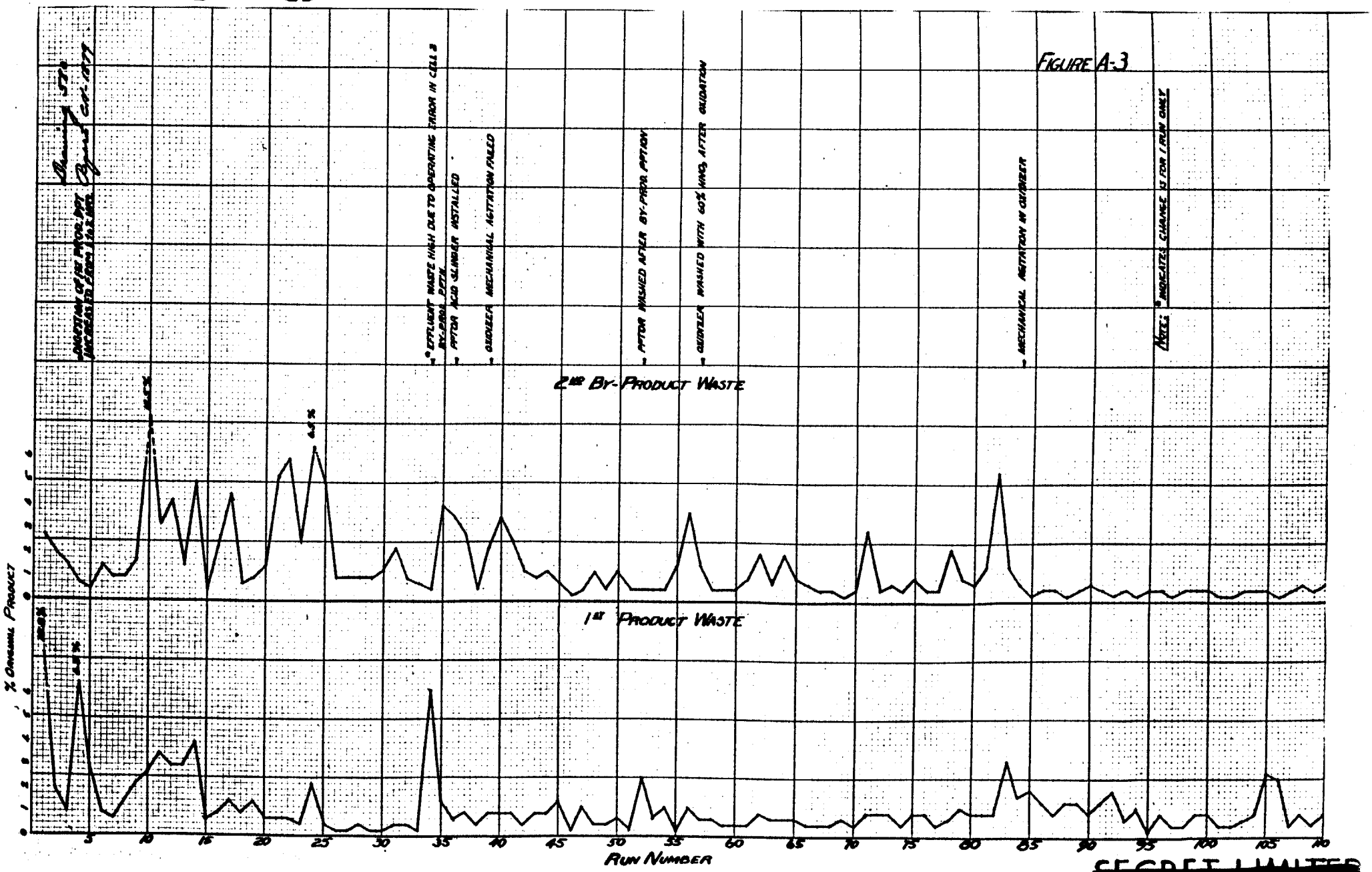

~~SECRET LIMITED~~

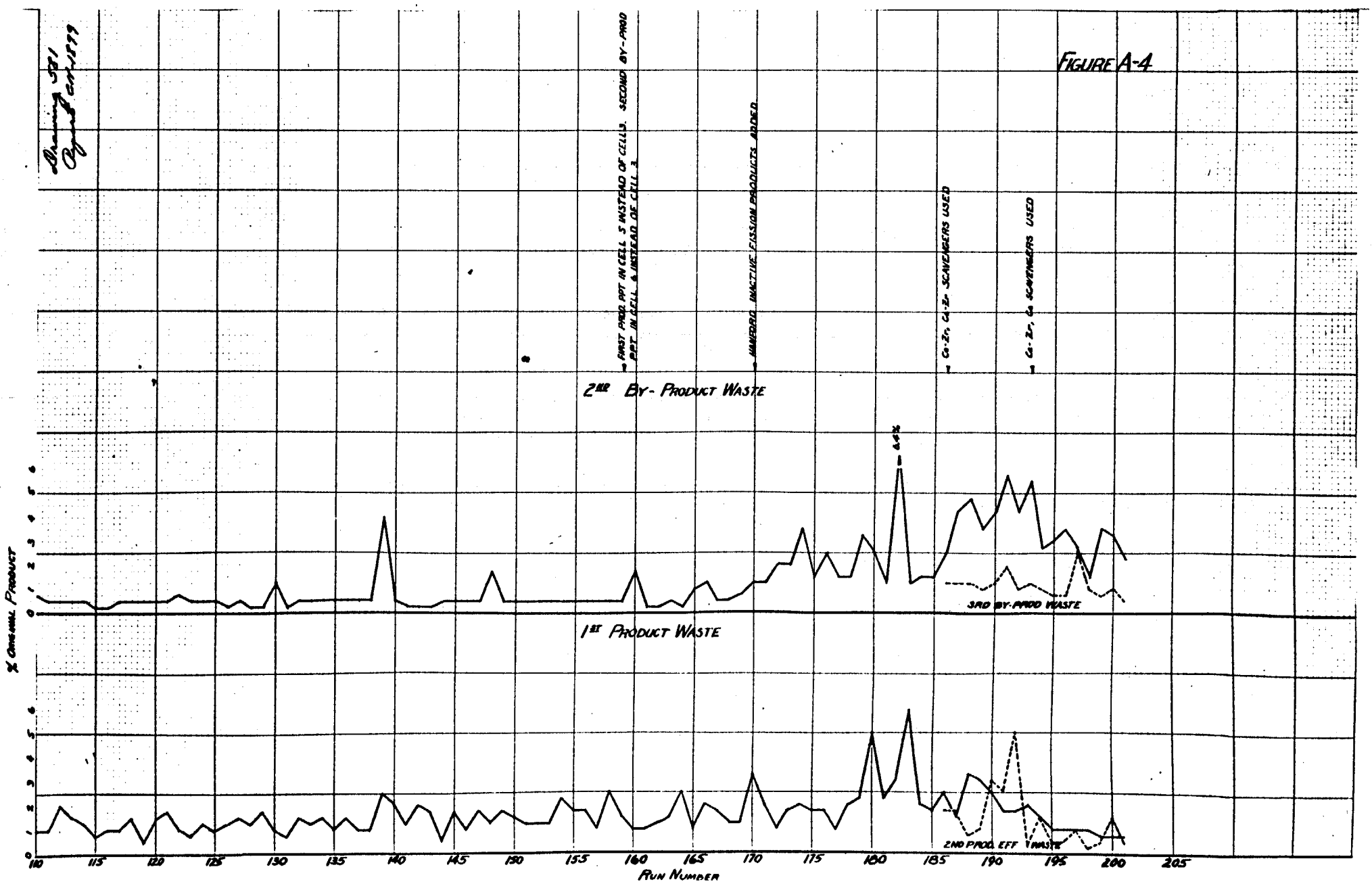
FIGURE A-4
FIRST PROD PPT IN CELL 5 INSTEAD OF CELL 3. SECOND BY-PROD PPT IN CELL 6 INSTEAD OF CELL 3
HANFORD INACTIVE FISSION PRODUCTS ADDED
Co-Zr, Cd-Zr SCAVENGERS USED
Co-Zr, Co SCAVENGERS USED
2ND BY-PRODUCT WASTE
3RD BY-PROD WASTE
1ST PRODUCT WASTE
2ND PROD. EFF WASTE
% ORIGINAL PRODUCT
RUN NUMBER
0
1
2
3
4
5
6
110
115
120
125
130
135
140
145
150
155
160
165
170
175
180
185
190
195
200
205

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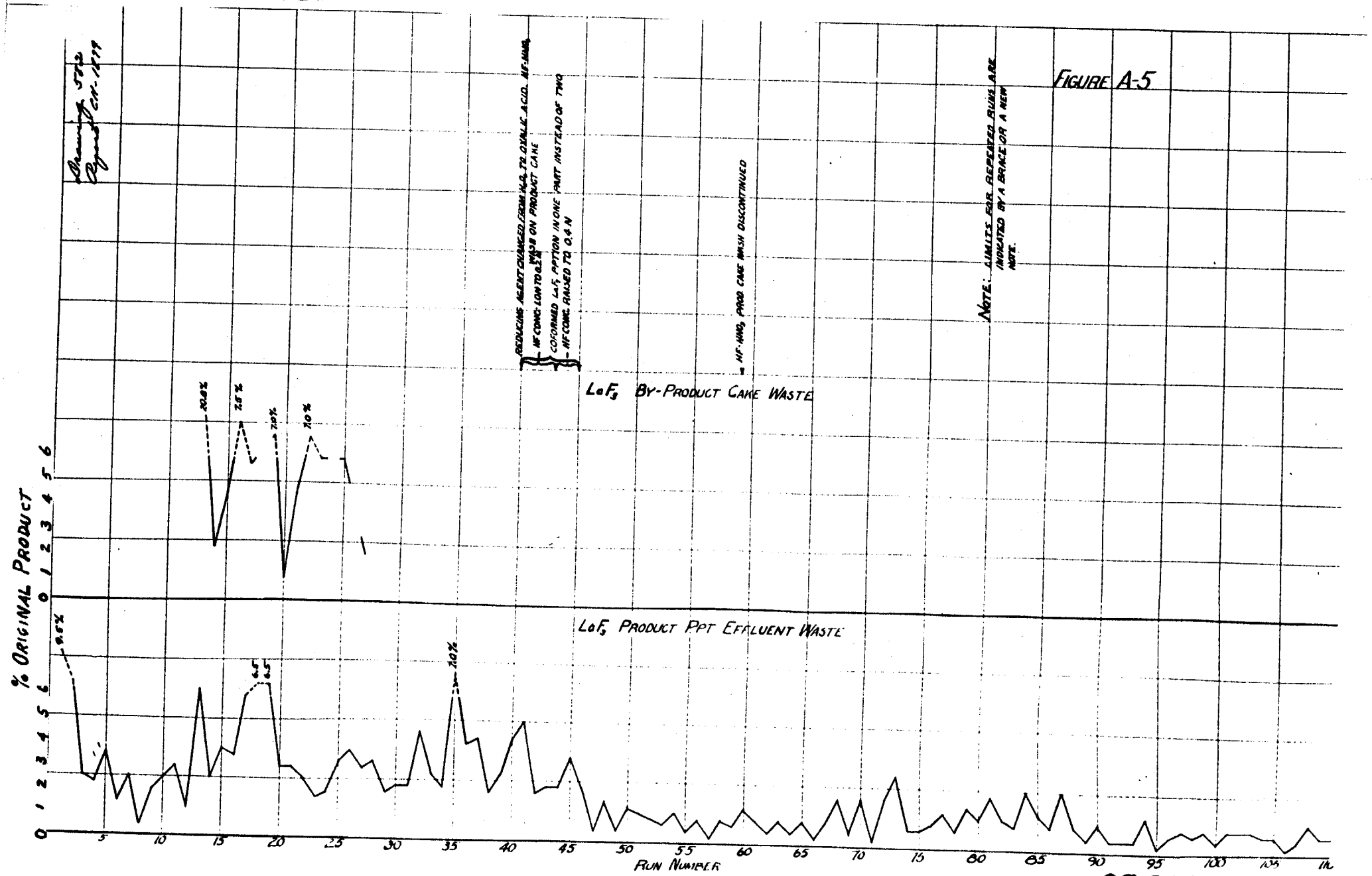

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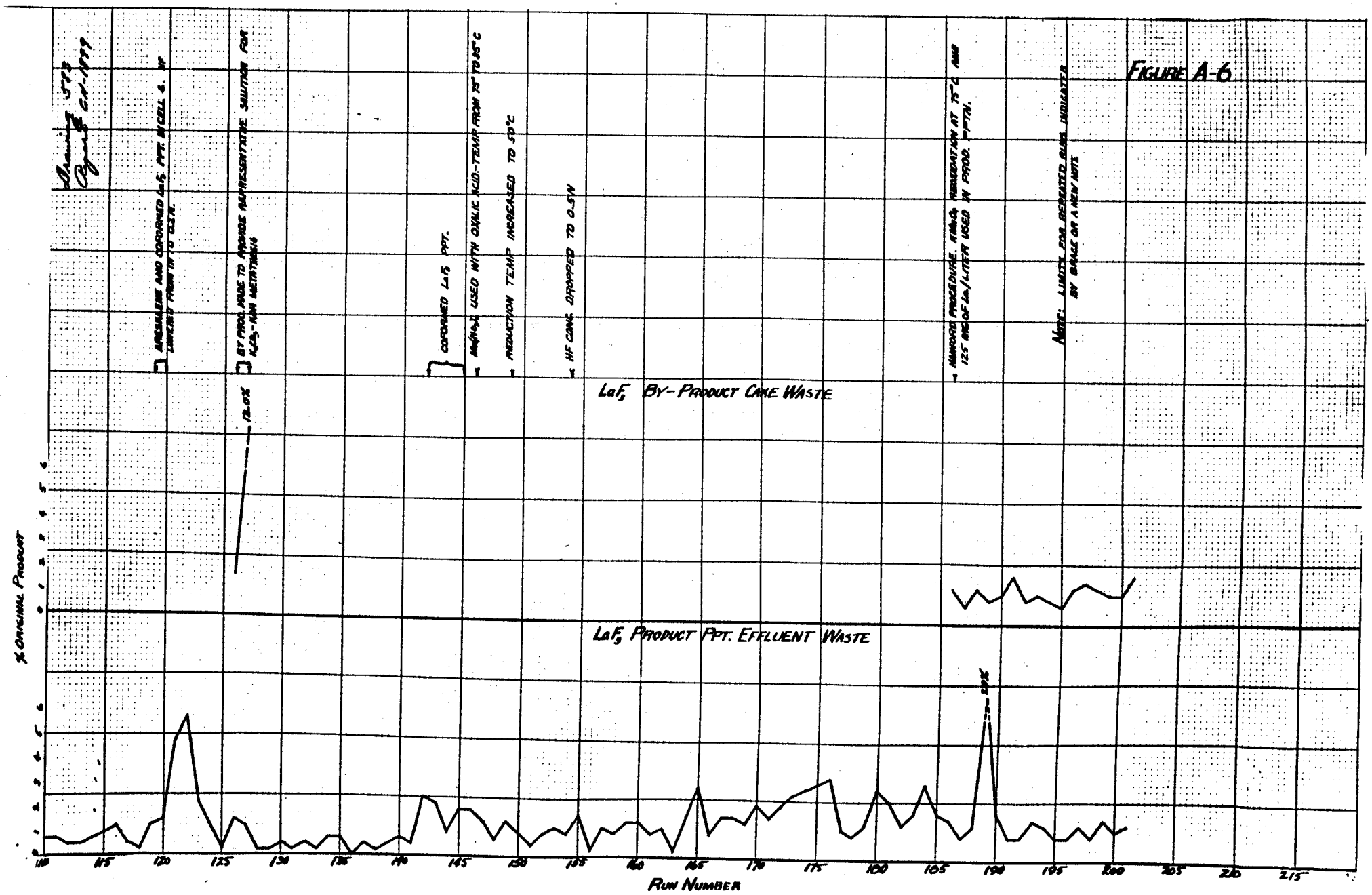
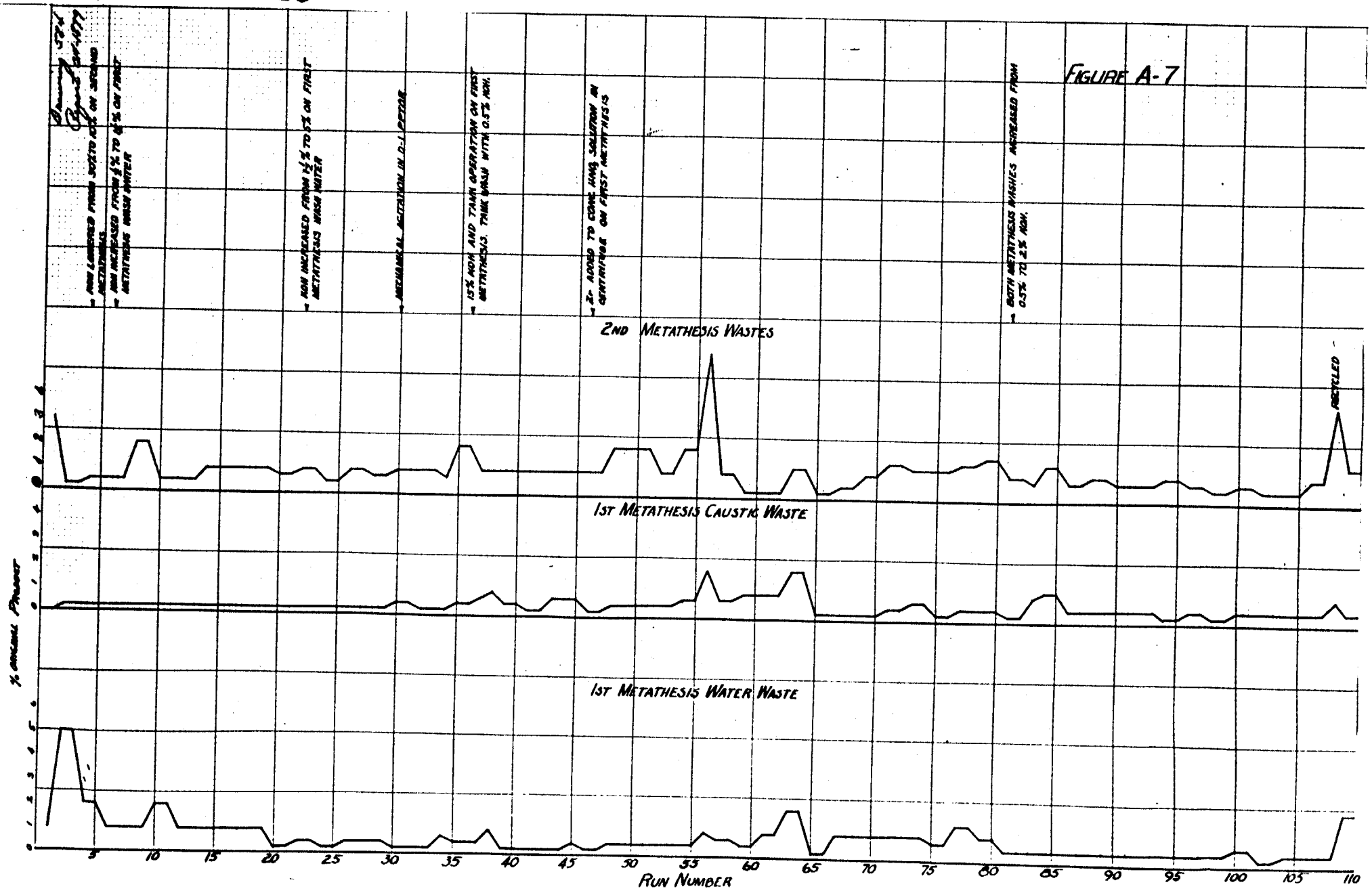


Drawing 583
Report CN-1799
ARESKLENE AND COFORMED LaF3 PPT. IN CELL 4. HF LOWERED FROM 1N TO 0.2N.
BY PROD. MADE TO PROVIDE REPRESENTATIVE SOLUTION FOR K2CO3-KOH METATHESIS
12.0%
COFORMED LaF3 PPT.
Mn(NO3)2 USED WITH OXALIC ACID-TEMP FROM 75° TO 35°C
REDUCTION TEMP INCREASED TO 50°C
HF CONC. DROPPED TO 0.5N
HANFORD PROCEDURE. KMnO4 REOXIDATION AT 75°C AND 125 MG OF La/LITER USED IN PROD. PPTN.
NOTE: LIMITS FOR REPEATED RUNS INDICATED BY BRACE OR A NEW NOTE
LaF3 BY-PRODUCT CAKE WASTE
LaF3 PRODUCT PPT. EFFLUENT WASTE
29%
% ORIGINAL PRODUCT
RUN NUMBER
110
115
120
125
130
135
140
145
150
155
160
165
170
175
180
185
190
195
200
205
210
215

FIGURE A-6

~~SECRET LIMITED~~



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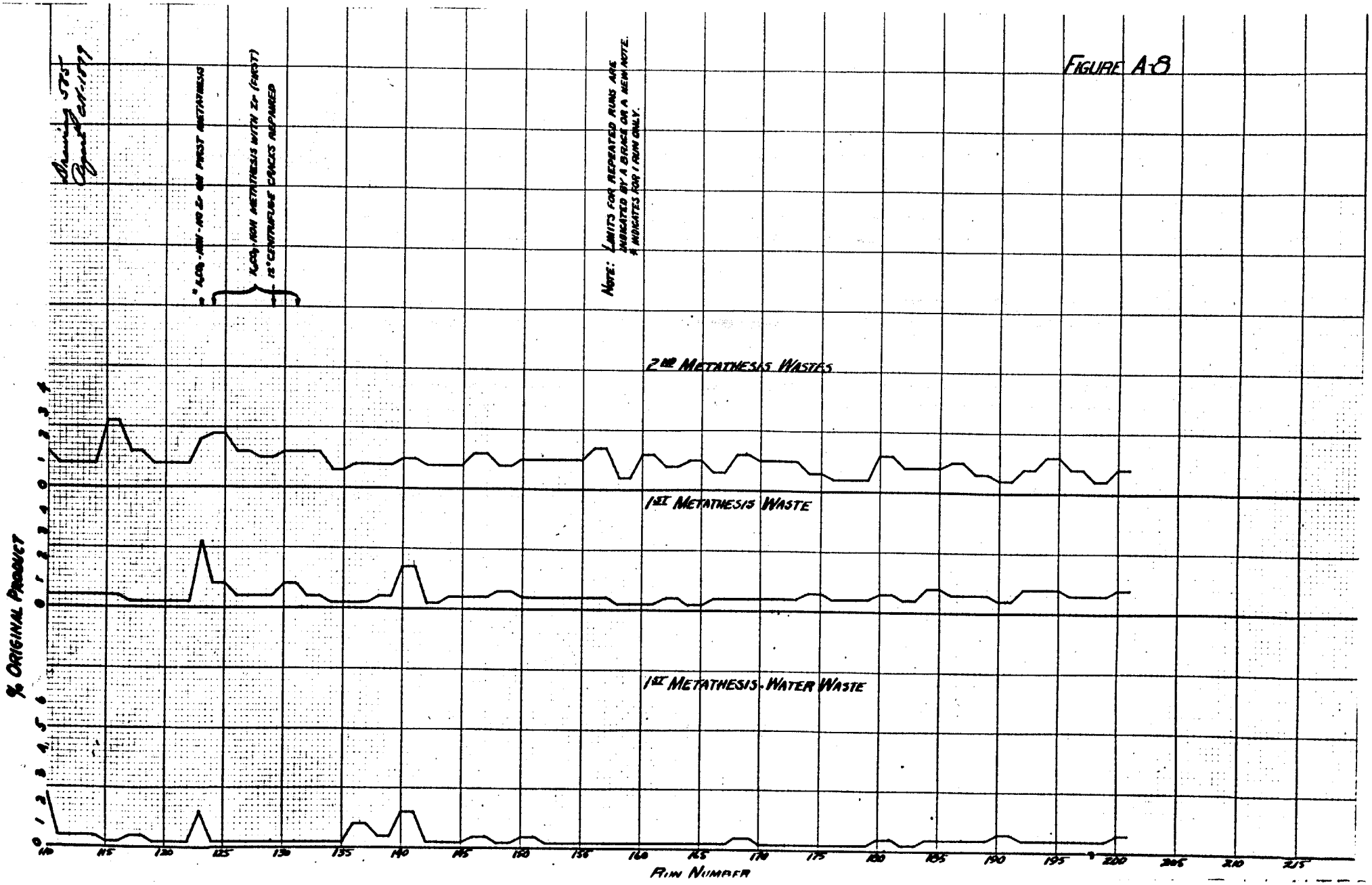
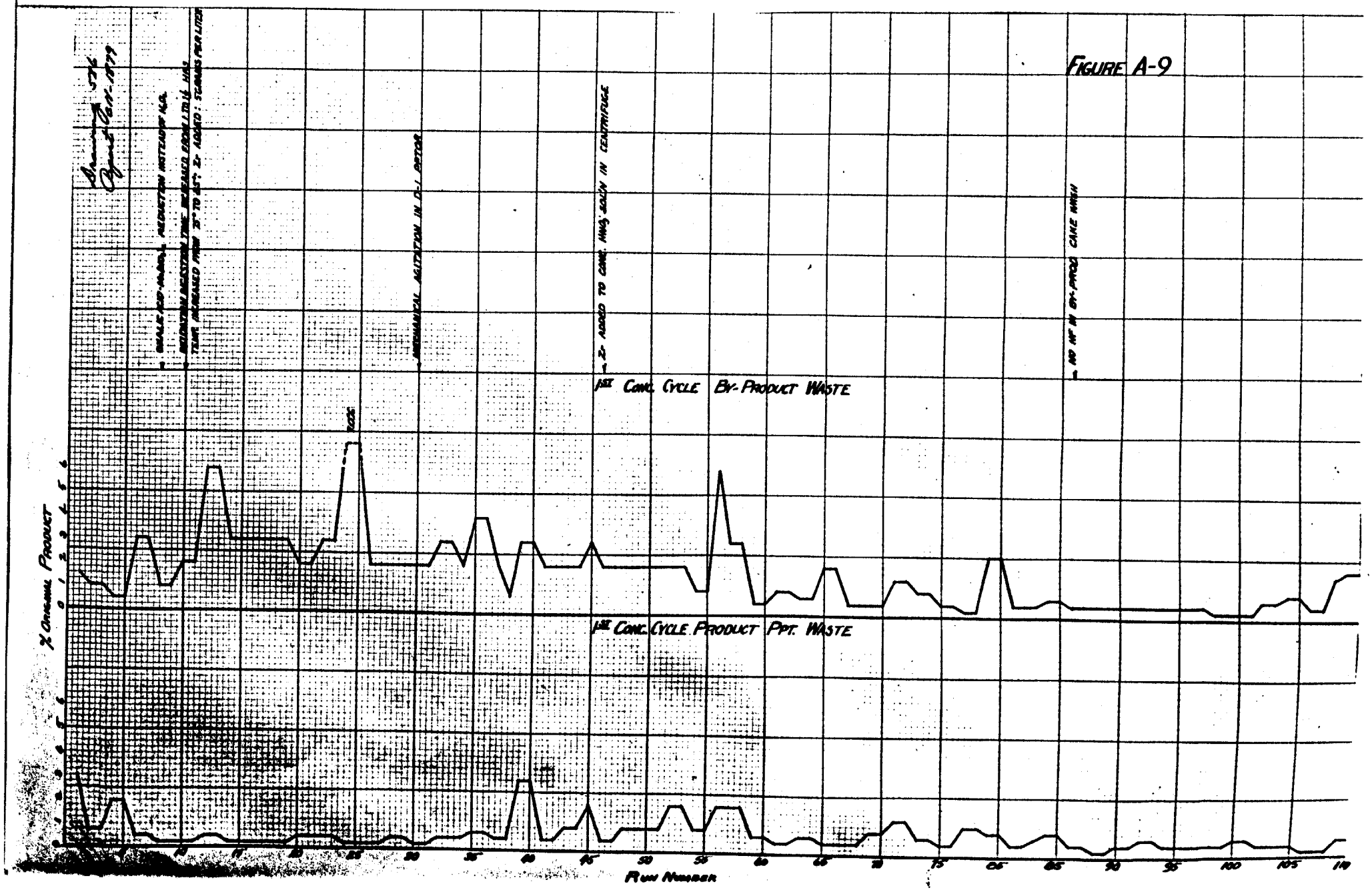
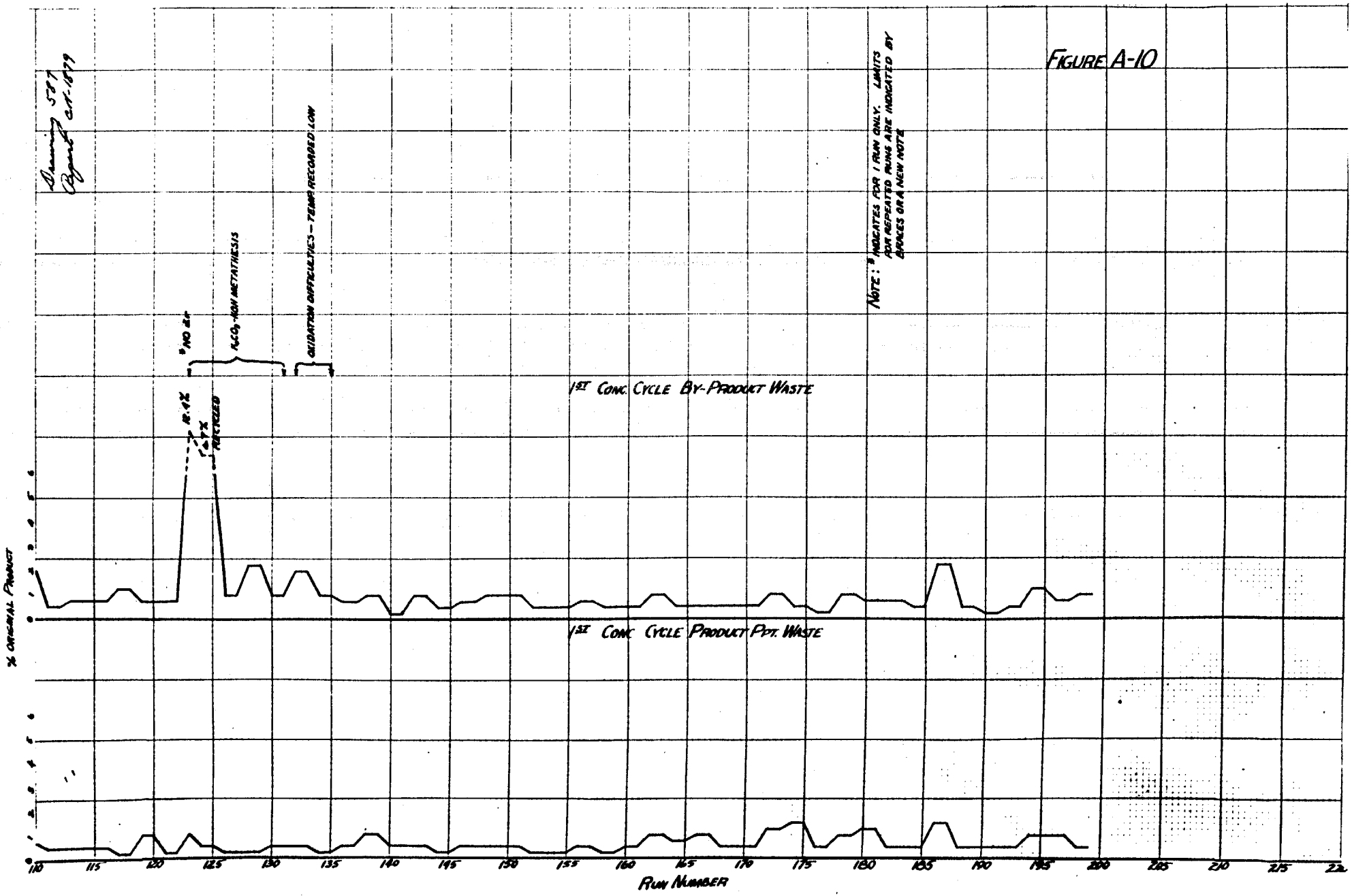




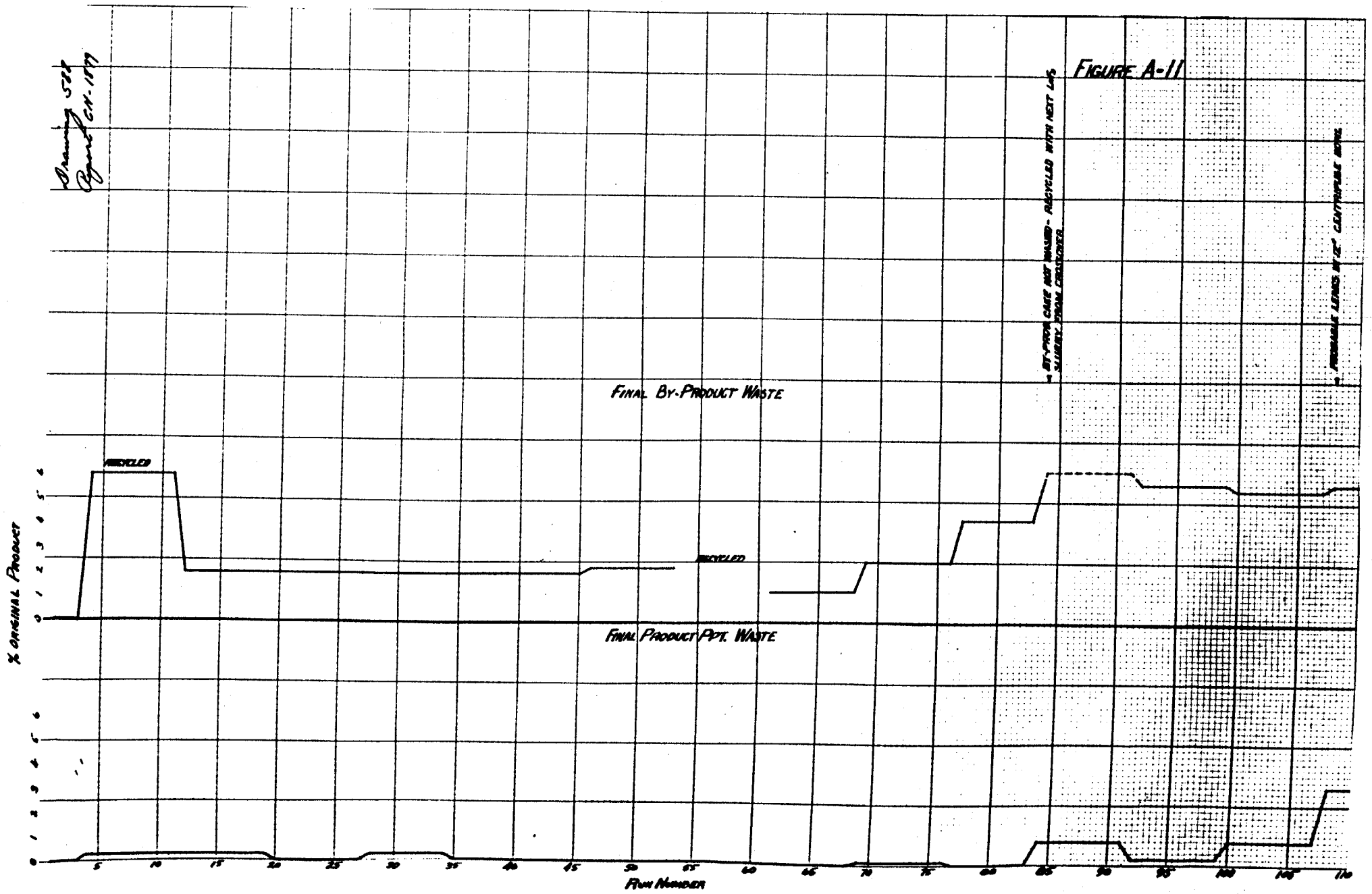
Drawing 576
Report Con-1879
REDUCTION INSTEAD OF H_2O_2
MECHANICAL AGITATION IN D-1 PRTOR
Zr ADDED TO CONC. HNO_3 SOL'N IN CENTRIFUGE
NO HF IN BY-PROD CAKE WASH
1st CONC. CYCLE BY-PRODUCT WASTE
1st CONC. CYCLE PRODUCT PPT. WASTE
% ORIGINAL PRODUCT
RUN NUMBER

FIGURE A-9

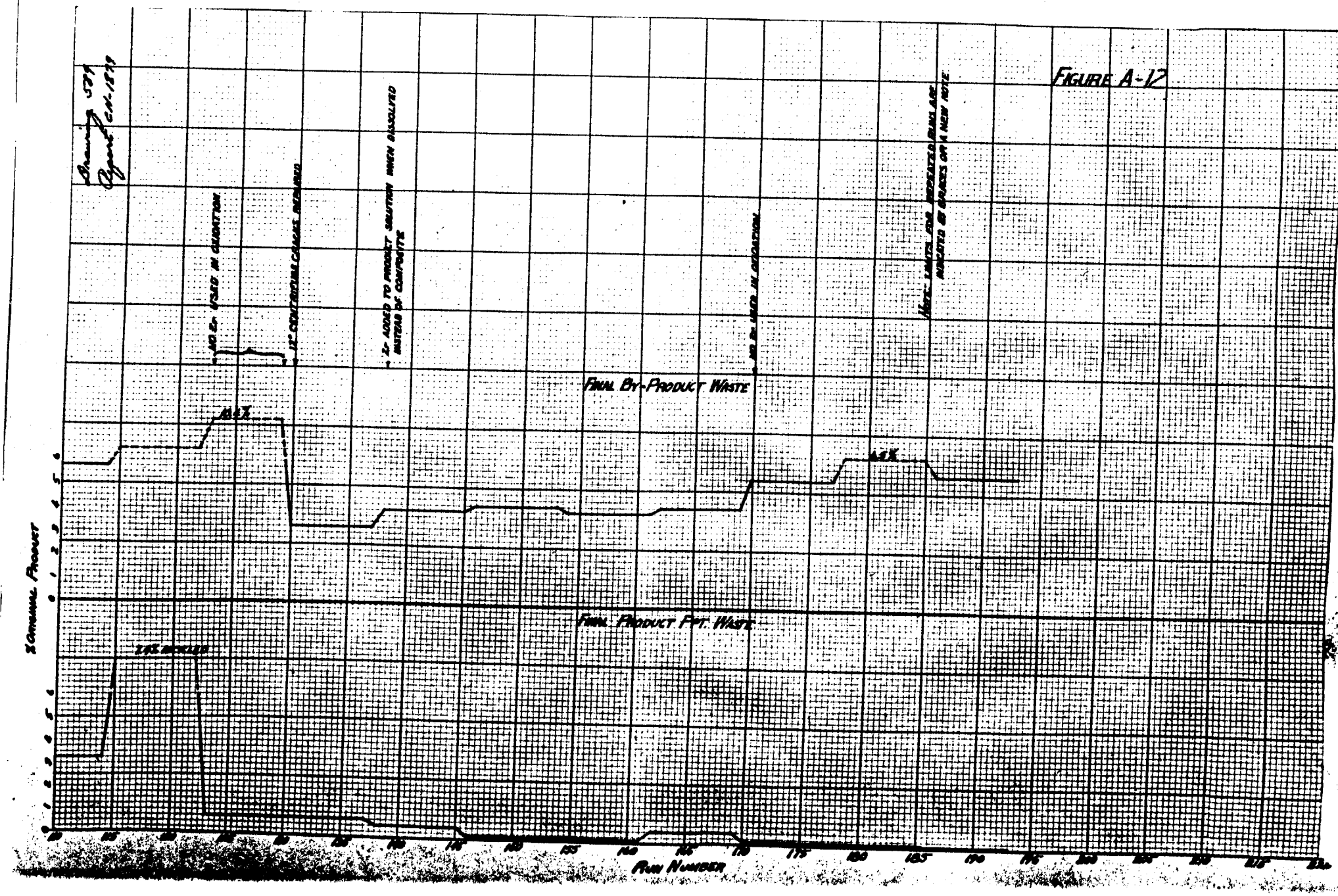


Drawing 587
Report CN-1879
NOTE: * INDICATES FOR 1 RUN ONLY. LIMITS FOR REPEATED RUNS ARE INDICATED BY BRACES OR A NEW NOTE
OXIDATION DIFFICULTIES — TEMP. RECORDED LOW
1ST CONC. CYCLE BY-PRODUCT WASTE
1ST CONC. CYCLE PRODUCT PPT. WASTE
% ORIGINAL PRODUCT
RUN NUMBER
110
115
120
125
130
135
140
145
150
155
160
165
170
175
180
185
190
195
200
205
210
215

FIGURE A-10



Drawing 588
Report CN-1879
FIGURE A-11
BY-PROD. CAKE NOT WASHED - RECYCLED WITH NEXT LOT
SLURRY FROM CROSSOVER
PROBABLE LEAKS IN 12" CENTRIFUGE BOWL
FINAL BY-PRODUCT WASTE
RECYCLED
RECYCLED
FINAL PRODUCT PPT. WASTE
% ORIGINAL PRODUCT
RUN NUMBER



Drawing 589
Report CN-1879
NO Zr USED IN OXIDATION
12" CENTRIFUGE CRACKS REPAIRED
Zr ADDED TO PRODUCT SOLUTION WHEN DISSOLVED INSTEAD OF COMPOSITE
NO Zr USED IN OXIDATION
NOTE: LIMITS FOR REPEATED RUNS ARE INDICATED BY BRACES OR A NEW NOTE
FINAL BY-PRODUCT WASTE
FINAL PRODUCT PPT. WASTE
% ORIGINAL PRODUCT
RUN NUMBER

FIGURE A-12

D. GRAPHS OF DECONTAMINATION FOR INDIVIDUAL RUNS

Gamma dF's for individual runs have been plotted with notations of process modifications included at the runs on which the changes were made. The unit used to express decontamination, Gamma dF, is the log of the ratio of the Gamma activity in the original solution to the Gamma activity in the solution at the sample point.

E. RECOMMENDATIONS AND APPROVALS FOR PROCESS MODIFICATIONS

All modifications of the process at Clinton were made upon the recommendation of the research and development groups after approval by the Process Steering Committee. The letters concerning these changes are listed here with page numbers referring to the discussion of them in this report.

Coating Removal

M. F. Acken to W. C. Kay (1-25-44) - Elimination of 2% HNO_3 Rinse in Dissolver — Page 28

R. S. Apple to W. C. Kay (7-12-44) - Change in Operating Procedure - 205 Building Removing Slug Jackets with $NaOH$-$NaNO_3$ Mixture — Page 28

R. S. Apple to W. C. Kay (8-4-44) - Coating Removal, Three-Batch Charges of 35-mil Jacketed Slugs — Page 29

Metal Dissolving

F. B. Vaughan to W. C. Kay, Memo, (2-8-44) - Multiple Charges to Dissolver - Building 205 — Page 30

Pre-Extraction Treatment of Metal Solution

R. S. Apple to W. C. Kay (3-11-44) - Change in Operating Procedure - 205 Building Elimination of HCOOH Neutralization — Page 33

R. S. Apple to W. C. Kay (4-12-44) - Use of $U(SO_4)_2 \cdot 4H_2O$ as Replacement for HCOOH — Page 33

F. B. Vaughan to W. C. Kay (4-15-44) - Pre-Reduction Step - Separations Process — Page 33

R. S. Apple to W. C. Kay (4-24-44) - Proposed Experimental Runs - 205 Building — Page 33

R. S. Apple to W. C. Kay (6-22-44) - Change in Operating Procedure - 205 Building Substitution of $NaNO_2$ for HCOOH — Page 39

Extraction Step

R. S. Apple to W. C. Kay (3-2-44) - Investigation of Extraction Temperature and Time of Digestion in 205 Building — Page 41

R. S. Apple to W. C. Kay (3-21-44) - Addition of H_2SO_4 to 11 MR Solution — Page 46

R. S. Apple to W. C. Kay (5-26-44) -
Proposed Change in Operating Procedure - 205 Building
Reduced H_3PO_4 Concentration in the Extraction Step — Pages 42 & 43

J. B. Sutton to W. C. Kay (6-5-44) -
Suggested Process Flowsheet Revision
for Separations Plant Hanford Runs with Scavengers — Page 46

R. S. Apple to W. C. Kay (6-9-44) -
Proposed Change in Operating Procedure - 205 Building
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Decontamination

J. B. Sutton to W. C. Kay (1-11-44) -
Proposed Flowsheet Changes - LaF_3
By-Product Precipitate in the Cross-Over Cycle — Page 48

M. F. Acken to W. C. Kay (1-14-44) -
Recommended Change in Extraction Strike Procedure — Pages 48 & 51

R. S. Apple to W. C. Kay (4-25-44) -
Change in Procedure in Cell 2 — Page 48

R. S. Apple to W. C. Kay (4-26-44) -
Proposed Change in Operating Procedure - 205 Building
Reduced H_3PO_4 Concentration in Extraction Step — Page 48

W. Q. Smith to W. C. Kay (5-20-44) -
Lanthanum Fluoride By-Product Precipitation
in Cell 4 — Page 48

J. B. Sutton to W. C. Kay (6-5-44) -
Suggested Process Flowsheet Revisions for
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J. B. Sutton to W. C. Kay (6-8-44) -
Supplementary Flowsheet Suggestions for Hanford
Scavenger Test Runs at Clinton — Page 52

J. B. Sutton to W. C. Kay (6-16-44)
Suggested Procedure for Dummy Scavenger Runs
in Cell 6 with Hanford By-Product Cake Volumes — Page 53

J. B. Sutton to W. C. Kay (6-22-44) -
Procedure for Hanford Scale Dummy Runs
in Cell 5 with Ce-Zr-Ba Scavenging — Page 52

J. B. Sutton to W. C. Kay (7-4-44) -
Process Flowsheet Revision for Separations
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J. B. Sutton to W. C. Kay (7-12-44) -
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J. B. Sutton to W. C. Kay (7-17-44) -
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J. B. Sutton to W. C. Kay (7-18-44) -
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J. B. Sutton to W. C. Kay (7-28-44) -
Separations Plant Runs with Two Cycle Decontamination — Page 53

J. B. Sutton to W. C. Kay (8-10-44) -
Procedure for Separations Plant Test Runs 202 to 209
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Cross-Over Step

J. B. Sutton to W. C. Kay (1-11-44) -
LaF_3 By-Product Precipitation in the Cross-Over Cycle — Page 59

J. B. Sutton to W. C. Kay (2-9-44) -
Proposed Flowsheet Change - Oxalic Acid
Reduction in the Cross-Over Cycle — Page 60

J. B. Sutton to W. C. Kay (2-12-44) -
Proposed Flowsheet Change - Oxalic Acid
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J. H. Balthis to W. C. Kay (5-12-44) -
Plant Test of Flocculation — Page 62

W. Q. Smith to W. C. Kay (5-20-44) -
Lanthanum Fluoride By-Product Precipitation
in Cell 4 — Page 59

W. Q. Smith to W. C. Kay (5-30-44) -
Modification of Reduction Procedure, Cell 4 — Page 61

J. H. Balthis to W. C. Kay (5-30-44) -
LaF_3 Precipitation in Cell 4 — Page 63

R. S. Apple to B. C. Nylen (6-20-44) -
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R. S. Apple to W. C. Kay (6-24-44) -
Oxidation Difficulties in Room D - Changes
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R. S. Apple to W. C. Kay (6-26-44) -
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R. S. Apple to W. C. Kay (7-22-44) -
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J. B. Sutton to W. C. Kay (7-25-44) -
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J. B. Sutton (Memo) (1-4-44) -
Proposed Flowsheet Change - Tank Metathesis in the Cross-Over Cycle — Page 65

J. B. Sutton (Memo) (1-5-44) -
Tank Metathesis and Washing in the Room D First Concentration Cycle — Pages 65 & 66

J. B. Sutton (to Report) (1-5-44) -
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W. Q. Smith to W. C. Kay (1-19-44) -
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R. S. Apple to W. C. Kay (6-24-44) -
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I. Perlman to W. C. Johnson (6-28-44) -
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SUPPLEMENT TO:

CN-1879

Progress Report

Last Five Months Operation of

Separations Plant

September, 1944 to February, 23, 1945

March 31, 1945

Submitted by: E. C. Stewart
D. F. Ryder
E. A. Pritchard

Approved by: B. C. Nylen

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I. INTRODUCTION

The final months of separations plant operation found increasing emphasis being placed on the improvement of an operating process rather than the demonstration of laboratory studies. Facilities for the isolation of product were completed and operating procedures developed for similar work to be carried on at the Hanford plant.

Additional information was gathered in the protection of personnel from exposure to radiation, particularly in the handling of product. Rigid safety procedures were adopted as operating levels increased, and instruments of higher sensitivity developed for detection of alpha activity were utilized for frequent monitoring throughout the area.

Following processing of the final run (no. 299) early in January, 1945, an extensive program was carried out to decontaminate all processing equipment and surrounding surfaces before placing the buildings in standby condition.

The following report, covering all phases of the work during this final period, has been prepared in the form of a supplement to the "Progress Report - First Nine Months of Operation of Separations Plant" (CN-1879).

II. SUMMARY

A. MATERIALS OF CONSTRUCTION AND MAINTENANCE OF EQUIPMENT.

The additional processing of chemicals under flowsheet conditions completed better than one year of operation in the separations plant using 25-12 S Cb equipment as the primary material of construction. In general, the performance of 25-12 S Cb has served to confirm its adequacy as a material resistant to the corrosive action of the process chemicals involved. Failures were largely confined to welds in new piping installed without the prescribed heat treatment or to machined centrifuge spray nozzles used in lanthanum fluoride service. The metal dissolver coils failed at three points at the end of final clean-up operations, and considerable corrosion of dip tube welds was found upon inspection. However, the severe penetration is attributed to the drastic flushing procedure required for decontamination rather than to normal operating conditions. Final internal inspection of representative cell equipment revealed only unusual corrosion of the Cell 4 centrifuge bowl used for lanthanum fluoride separation. The corrosion in this case was restricted to a partial surface of the outer vertical wall, indicating improper treatment of the original metal.

The adoption of a schedule for regular addition of lubricant resulted in trouble free performance of cell agitator motors, except in one instance when failure was caused by a defective field coil. Thermoguards on centrifuge motors failed to open and close properly in a few cases and precautionary replacements of the motors were made. Thermocouples were installed in the field windings of the re-installed motors as an added guide to observance of coil temperatures.

Instrumentation proved satisfactory for the remote control operation except that frequent maintenance of the Ring balance recorders was required due to corrosion of bearing surfaces by steam vapors. The loud speaker facilities installed in connection with Cells 6 and 7 process vessels proved more sensitive than instruments furnished for the original equipment and assisted materially in following the process.

Several types of equipment were used in the development of a product isolation process. The final assembly proved adequate from the standpoint of corrosion and layout. Several shortcomings were recognized, however, and suggested corrections have been incorporated into the Hanford design.

B. PROCESS.

The bismuth phosphate process for the separation of product continued to give high recovery, adequate decontamination and satisfactory production rates.

A review of product recovery realized from the entire period of 200 Area operations reveals that an overall yield of 94.6% was obtained. This figure is based on analyses made on dissolved metal prior to extraction and decontamination and should be weighed against a comparable overall material balance of 107.8%. The high material balance is not entirely explainable, however, it is recognized that the carrier precipitation procedure used for analyses of starting solution and wastes results in values ranging from 3% to 6% less than that obtained with the direct evaporation procedure used for final product analysis. If the direct evaporation method is assumed to be correct, and the starting analyses are raised by an average figure of 4½%, the overall yield becomes 90.5%.

It is interesting to note that the 100 Area estimate of total product content in metal delivered to the 200 Area is 8.6% above the actual starting analyses, and is in close agreement with the material balance of 107.8%. The overall yield was 87.2% based on 100 Area estimates.

There were no basic changes in the process, however, the 200 Area was expanded to include isolation of the product which operation was formerly done by a laboratory group.

The 10% NaOH - 20% $NaNO_3$ procedure for coating removal was used on all batches since its demonstration during the last period with no operational difficulties. One change in procedure was made to more closely duplicate the Hanford procedure, namely, the metal was charged into a neutral solution of $NaNO_3$ and the excess NaOH then added at a controlled rate instead of charging the metal into the complete solution. This procedure gave a more easily controlled reaction.

The metal dissolution step has also continued satisfactorily and with no operational difficulties even though the amount of metal per run was increased from 1/3 ton to 1/2 ton and later to 2/3 ton. Closer attention was required with the larger batches during the initial period of the reaction, but control was easily maintained by means of a small amount of water through the coil. Experience showed that in order to use the specific gravity as an indication of the free acid remaining it is necessary that the control be standardized.

While satisfactory results were usually obtained with the pre-extraction treatment of the metal solution, occasional high extraction losses indicate that there are factors involved that have not yet been recognized. From the study of variation of the sodium nitrite concentration, it was indicated that 0.025M will result in the best yield. The effect of storing metal solution was also studied, but the results obtained only serve to emphasize the fact that this step is not well understood. The potassium permanganate-oxalic acid pre-treatment procedure gave fairly good results, but only where the temperature of oxidation with permanganate was 75° C. Lower temperature gave high waste losses (12% - 21%). Sulfuric acid addition to the 70% UNH solution instead of to the 20% solution apparently had no adverse affect.

Very little was done during this latter period on the extraction step itself, most attention having been given to the pre-extraction treatment. A 90% direct - 10% reverse strike was demonstrated on four runs with no significant change in waste losses. 14% bismuth solution was substituted for 24% solution with no change in waste losses. Because of limited tank capacities, it was necessary when changing to 2/3 ton of metal per run to extract from a 22% UNH solution rather than 20%. This resulted in an increase of about 1% in waste losses.

Additional demonstration runs of the Hanford two cycle decontamination process were made with two new methods of using scavengers and ammonium fluosilicate. The first was the use of both Ce-Zr; Ce-Zr and ammonium fluosilicate in the first cycle and ammonium fluosilicate alone in the second cycle. Decontamination was equal to the best obtained with Ce-Zr; Ce-Zr, both cycles and waste losses were about 5% lower. This process has been recommended for use at Hanford. The other process was the use of ammonium fluosilicate alone in both cycles with no scavengers. An

additional improvement of more than 3% in waste losses was realized, however, decontamination with this process was not up to the goal factor of 7.0 (the average was 6.2). The lower decontamination resulted mostly from lower decontaminating efficiency in the crossover cycle. Studies of the behavior of individual fission product elements in the crossover step of these runs lead to the use of a barium sulfate scavenger precipitation along with the LaF_3 by-product precipitation step which improved decontamination especially in runs made from metal of relatively short cooling time where the amount of active barium would be high. Another process wherein two product reprecipitations were made in 0.5M ammonium fluosilicate in place of the second decontamination cycle was demonstrated. Waste losses were higher and decontamination lower than the regular ammonium fluosilicate process.

Operation of the crossover cycle continued satisfactorily and there were only a few modifications. Supernatants, washes and filter cake leachings were recycled into this step with no operational difficulties, a 1N HNO_3 wash was used on the LaF_3 product cake with no apparent increase in waste losses, and the concentration of La^{+3} in the product step was reduced to 90 mg per liter (Hanford concentration) which allowed the combination of 3 third ton (or 2 half ton) runs for metathesis in Room D again with no change in waste losses. A summary of the study of the behavior of fission product elements is given in this report.

Room D operations during this period consisted of running the metathesis step only, since with the start up of 204 Building, product was isolated directly from the solution of the LaF_3 cake from the crossover step. At first, a K_2CO_3 assisted KOH metathesis was used which resulted in rather high product content of the effluents necessitating their being reworked. Later, however, a straight KOH metathesis was used with no adverse effect in isolation and consequently with a decrease in waste losses from this step.

Since isolation wastes were recycled into the LaF_3 by-product step, it was necessary to decompose the H_2O_2 in the recycle solutions. This was done with $NaNO_2$ in Room D since facilities were available.

Isolation of product has been carried out in the 204 Building during the entire period following the recommended Hanford procedure wherein the product is precipitatedas a peroxide directly from a HNO_3 solution of the LaF_3 product cake from the crossover step. The process gave excellent results and there were no operational difficulties except on the first run where it was found that the H_2O_2 decomposed at the precipitation temperature of 60° C. Lowering this temperature to 20° C. eliminated this difficulty and still a precipitate formed that could easily be decanted. Considerable variation in the amount of product remaining in solution after precipitation was encountered and this was found to be due to some of the product being oxidized during the dissolving of the $La(OH)_3$ cake and not being reduced by the H_2O_2 at the low temperature of 20° C. It was found that this condition was improved by treating the solution with 1%

H_2O_2 at 50° C. for 1 hour. Laboratory studies have indicated that further improvement would result from the use of 0.1M hydroxylamine at 20° C. for 1 hour. This latter process would be better also from the standpoint of operability, since some gas evolution occurs with the 1% H_2O_2 treatment less time would be consumed in heating and cooling. Drying of the final isolated product was accomplished by evaporating the solution in the shipping tube by means of an electrically heated furnace and drawing pre-dried and pre-heated air through the vapor space of the tube. Time of drying has been 30 - 40 hours.

C. RADIATION HAZARD AND DISPOSAL OF RADIO-ACTIVE WASTES.

In spite of the higher operating levels attained during the final period of operation and the greater care required in sampling, overexposure of personnel was avoided. Increasing emphasis was placed upon protection of personnel from the dangers of product inhalation and ingestion, particularly in the isolation step where the product was handled in concentrated forms. Frequent surveys were made throughout the operating area for all types of radiation and increasingly sensitive instruments developed for the detection of alpha activity were placed in use. Notable among these was the portable alpha proportional counter.

The disposal of radio-active wastes followed the pattern established during previous operation and was essentially uneventful. Discharge of by-product chemical wastes into White Oak Creek was continued and held well within the tolerance limits established by the Health-Physics Section. A flash flood threatened to wash accumulated radio-active sediment from the settling basin, however, careful monitoring of the overflow water and subsequent surveys of the flooded area disclosed no significant contamination. Corrective measures were taken to prevent reoccurance.

D. FINAL DECONTAMINATION AND CLEAN-UP OF THE SEPARATIONS PLANT.

Following the final process run (299) and for several weeks thereafter an extended program was undertaken to remove radio-active substances from the equipment and surrounding surfaces in the cells, tunnel and processing rooms. The decontamination work consisted chiefly of a series of internal chemical flushes accompanied in the latter stages by intensive efforts to remove residual contamination from external surfaces, using a variety of chemicals as well as hard hose streams of water. Spindle oil and glycerin-liquid soap mixtures were employed in repeated applications for removal of product alpha activity in the isolation room.

The degree of success achieved in this work was such that beta and gamma radiations were brought within the tolerance range of 12.5 mr/hr in all but a few localized spots in the cells and tunnel. Final efforts were concentrated on the removal of alpha activity from all external surfaces and only a few readings as high as 50,000 disintegrations/minute were obtained in the cells, with most surfaces being reduced essentially to 0. An even greater degree of product decontamination was obtained in Room D and in the isolation room.

At the conclusion of the decontamination work, routine steps were taken to place the separations and isolation buildings in standby condition. Final survey data was posted within entrances leading to rooms in which radio-active work had been carried out. The facilities for storage and disposal of radio-active wastes continued to function for other departments with operational authority delegated to the Technical Division.

III. MATERIALS OF CONSTRUCTION AND MAINTENANCE OF EQUIPMENT

A. MATERIALS OF CONSTRUCTION.

Stainless Steel 25-12 S Cb - Additional processing in the 25-12 S Cb equipment has confirmed the overall adequacy of this material of construction for the flowsheet conditions involved. Several failures of 25-12 S Cb have occurred, but these have been largely confined to welds in equipment installed without heat treatment in Cells 5 and 6 or to corrosion encountered in Cell 4 where the LaF_3 process was used.

Corrosion difficulties that developed during the last five months of operation are discussed below along with the apparent causes. (Additional information pertaining to internal appearance of cell processing equipment will be found under the sub-heading "Final Inspection of Equipment" which is given later in this section of the report.)

1. Centrifuge Outer Spray Ring - two pin holes developed in the outer spray ring welds to the Cell 4 centrifuge (LaF_3 by-product). These lines were kept in almost constant contact with 0.2N to 0.5N HF solution which impinged upon the outer spray nozzles during centrifugation. Failure was attributed to the occlusion of flux at the welds.

2. Anhydrous HF Sparger - approximately 18 inches of the sparger, used to introduce anhydrous HF below the surface of the liquid in the LaF_3 by-product cell, corroded away after 11 months of service. Localized high concentrations of HF and excessive temperatures at the tip end of the sparger line are doubtless responsible for the failure.

3. Spool Piece in LaF_3 Waste Line - the HF solution attacked the line until the walls had become almost paper thin and failed completely at the flange welds. Analysis of the pipe revealed 15.25% Cr and less than 1% Ni, confirming the suspicion that 25-12 S Cb piping was not involved.

4. Scavenger Addition Line - considerable etching took place on the addition lines used to introduce Ce-Zr stock solutions to the precipitators. Laboratory data indicated that stock solutions, containing 15 g/l of each scavenger in 1N nitric, attacked 25-12 S Cb at a rate of 0.0024 in./mo. @ 25° C. Likewise solutions containing 50 mg/l of each element (comparable to process solutions) showed penetrating rates of 0.00013 in./mo. @ 75° C.

5. 3" 25-12 S Cb Centrifuge Line to Catch Tank - the welds of this installation in Cell 5 failed after only a few months service in the LaF_3 product cell. This installation was made without heat treatment to the line, in order to expedite the conversion for the two decontamination cycle runs. A 2" cold-bent 25-12 S Cb replacement showed no apparent corrosion for the remainder of operations, although its service was not sufficient for conclusive results.

Gasketing - Leaks and blown gaskets traced to chemical and thermal attack on G-9 gasketing material have been more evident during the last five months, and may be attributed to weakening caused by the hardening of the impregnating rubber or chemical solution of the rubber binder. The surface normally in contact with the solutions is relatively small; however, loosened nuts have been in evidence and have permitted the flanges to become separated so solution could pass onto the gasket, and permit excessive attack.

The blue asbestos (G-9) gaskets have been appreciably attacked in service lines carrying solutions of dilute HF, $NaNO_2$ and 30% hydrogen peroxide. For lines carrying these solutions care should be exercised in making up the flanges and using well cut gaskets which would have the inner periphery cut smooth.

Corrosion Samples - Upon completion of the runs and flushes the corrosion samples were removed from the LaF_3 by-product precipitator. These samples represent exposure in solutions of 0.2N HF for an operating period of five months. All samples were heat treated and the corrosion rates were 0.0005 inches per month and 0.0003 inches per month for welded and non-welded samples respectively. These rates are comparable or less to the rates found on the previous samples in this tank which, however, contained no welds but were subject to 1.0N HF solutions.

The corrosion samples that were placed in the dissolver before operations started were removed upon completion of the clean-up flush number twelve. These samples were heat treated 18-8 S Cb stainless and 25-12 S Cb stainless, but did not contain any welds. The corrosion rates were 0.0006 and 0.0030 inches/month for the total elapsed time of 13 months on the 25-12 S Cb and 18-8 S Cb respectively. This rate exceeds by a factor of 5 the rates found in the precipitator of Cell 4 in which fluoride solutions are handled.

Because of the necessity to decontaminate the dissolver before removing the corrosion samples the overall corrosion rates are not representative of normal dissolving alone, and must take into account the six flushes of nitric acid and ammonium fluosilicate solution having been boiled between the temperatures of 105 - 110° C., and also the effect of the inadvertent addition of H_2SO_4 to the boiling UNH solution of run 299.

There was no evidence of pitting of the 25-12 S Cb sample; however, the 18-8 S Cb showed definite trenching.

Final Inspection of Equipment - Upon sufficient completion of the final decontamination of the cells, at least one or more typical equipment pieces were inspected. A brief paragraph pertaining to each type of vessel for both the $BiPO_4$ and LaF_3 processes follows:

An overall inspection of the dissolver has revealed that there was strong etching of the inner surfaces and considerable corrosion of all welds inside of the dissolver. Particularly noticeable was the corrosion of the welds of the thermowell, sparger and instrument dip tubes where the welding material has been partially removed. The dissolver condenser coil was found

to be completely plugged with a white crystalline powder which undoubtedly was the cause of the very high column pressure drop during the flushes. The Raschig rings in the column were not similarly plugged though evidence of the solid powder was found on the upper few inches of rings, which may have dropped from the coils as they were removed. laboratory analysis indicated the solid material to be SiO_2 with evidence of a fair quantity of a fluoride being present. The source of this material was unquestionably from the $(NH_4)_2SiF_6$. During the digestion period of flush 12 the liquid level instrument of the dissolver showed an increase to a point beyond the capacity of the tank. An appreciable overflow was found to have accumulated in the diversion tanks connected to the floor drains, and this was found to be 5% HNO_3 which was promptly neutralized. The dissolver coils were found to be corroded through in three places. It was felt certain that most of the corrosion had occurred during the $(NH_4)_2SiF_6$ - H_2SO_4 clean-up treatment of run 299 and the HNO_3 - $(NH_4)_2SiF_6$ flushes, which were digested at high temperatures. No evidence of corrosion was detected on either the condenser column, the Raschig rings or the condenser coils.

Inspection of the Cell 3 precipitator and centrifuge, used in the $BiPO_4$ process and subjected to scavenger as well as $(NH_4)_2SiF_6$ process modifications, showed only slight signs of corrosion. Use of this equipment could have been indefinitely prolonged. The Cell 4 precipitator, used for both LaF_3 by-product and product precipitations, showed three distinct etched lines around the tank corresponding to the various solution levels used. Pitting was evident in a small section of the weld attaching a brace to one of the baffles in the upper part of the tank.

The Cell 4 centrifuge bowl inspection disclosed unusual corrosion of the outer wall starting at the vertical weld and extending about one-quarter of the distance around the circumference, gradually disappearing at this point. The wall was not attacked on the far side of the weld, and although the weld itself was darkened, no unusual corrosion had taken place. The affected surface of the bowl wall had an orange peel appearance varying in depth as great as one millimeter. It is felt that the corrosion resulted from imperfections in the original plate and could well have been responsible for unbalancing of the bowl as reflected by an excessive vibration of the "A" frame at the higher operating speed. Minor corrosion was evident in a comparable region of the inner bowl wall, but aside from this the bowl and casing showed only minor etching on exposed surfaces.

Several steam jets were inspected and in both $BiPO_4$ and LaF_3 service the machined surfaces of nozzles and throats were found to be free of corrosion. Some corrosion was found on line flange welds, the most pronounced being on flanges at the discharge side of steam jets. The corrosive action did not seem greater in welds used in LaF_3 service, and in no case was early failure indicated.

A few gaskets failed during flushing operations, however, these failures are attributed largely to the non-process solutions used. All of the gaskets were subsequently removed and in general found in good condition. The G-9 gaskets used throughout the process had become imbrittled around the inner periphery, however, when correctly installed, the remainder of the surface was found to remain effective. The G-X (P.T.F.E.) gaskets used in LaF_3 also

remained in good condition. Koroseal used around manhole covers and centrifuge casing covers were bleached and waved where exposed, but otherwise intact.

The equipment used in the concentration step in Room D was likewise inspected and no signs of excessive corrosion noted.

B. MAINTENANCE OF EQUIPMENT.

Centrifuges - The centrifuges have continued to give excellent service at Clinton. The primary trouble has been overheating the motors during cake washing and solution, resulting in their being kicked out by the thermoguards. One bearing failure has occurred on the 26" centrifuge, due to insufficient lubrication.

In the following paragraphs are discussed the centrifuge difficulties encountered during the last five months of operation.

1. 40" Centrifuge.

The thermoguard on Cell 3 centrifuge motor failed to close after cutting out the motor on run 223 after completing a cake solution and removal. Since investigation of the electrical circuits and the motor loads showed no apparent reason for failure, the motor was put back into operation by shunting out the thermoguard. After run 226 while the cell was idle, the motor was removed and replaced with a spare which had been equipped with a thermocouple in the motor windings. The thermocouple was installed for the purpose of indicating the motor temperature on a recording thermometer on the operating floor. The thermoguard had kicked out the motor during washing and dissolving of the product and by-product cakes and showed the motor temperature to be 97° C. A check on the amperage drawn by this motor was comparable to similar motors in Cells 5 and 6. Later on run 235 this replacement motor kicked out several times, presumably due to opening of the thermoguard since the internal thermocouple gave readings of 114°, 117° and 120° C. During a subsequent test operation on September 28, 1944, a short developed causing some damage to the wiring in the switch box and in the motor junction box. Later inspection revealed the coil windings of the motor to be sufficiently damaged to require replacement. The cause of the short was determined to be within the junction box at the motor where insufficient clearance and heavy cables prevented the use of varnished cambric and glyptal coating insulation at the lead junctures. A larger junction box was installed to avert recurrence.

Operation continued satisfactorily until the thermoguard kicked out the motor during run 290 when the thermocouple reading was 97° C. The motor was allowed to cool but the thermoguard failed to reset and was shunted across for the completion of the runs and flushes.

Intermittently, during runs 247 - 255 the Cell 5 centrifuge motor was kicked out by the thermoguard. This motor was replaced October 31, by a new motor in order to determine the possibility of a faulty thermoguard. It was noted in dismantling the removed motor that the drive arm, although keyed to the motor shaft, had sufficient play to allow it to drop down on the motor shaft.

It does not appear that this was responsible for thermoguard kicking out. Inspection of the motor revealed no shorting of the motor coils and the thermoguard was properly set at 108 - 112° C. The failure of the felt grease retainer ring in the lower bearing had permitted the grease to leak out, and it is possible that this was caused by insufficient clearance between the felt and the shaft since the felt had been torn by the shaft. The loss of grease resulted in the scoring of the balls and race. The top bearing had sufficient grease and was in good condition.

Installation of the thermocouples in the centrifuge motors of Cells 3, 4, 5, and 6 was completed November 1. A multi-point temperature recorder is used for the recording of these temperatures.

The high LaF_3 product waste losses occurring during runs 255 - 265, were not reduced appreciably by recentrifugation and making an additional La^{+3} strike. Examination of the centrifuge disclosed that the overshot nipple which throws the skimmings into the outer case had come off. This allowed a portion of the discharged skimmings to be thrown back into the upper compartment of the bowl thus dislodging some cake which was carried over the edge of the bowl in the effluent. The nipple was replaced and welding of this nipple to the skimmer assembly to prevent recurrence is recommended.

At the time of the Cell 3 clean-up following run 263, the hydraulic skimmer assembly was removed (from Cell 3) and replaced by the standard mechanical linkage design. The removal was prompted because of cumulative operating difficulties encountered.

2. 26" Centrifuge.

The top motor bearing on the 26" centrifuge in Room D, failed after twelve months of operation. Inspection of the bearing revealed the lack of sufficient lubrication. On the basis of this failure a new bearing was installed and a lubrication schedule established to provide the addition of one ounce of grease every six months.

Agitators - All agitator motors have continued to give excellent service; however, the agitator motor on 61 tank failed on 11-1-44 and was replaced. The failure was caused by the breaking of a defective wire in one of the field coils following 5 months of operation. The motor bearings had sufficient grease and the gear reducer was in good condition.

A study of the motor load on Cell 7 neutralizing tank was made during neutralization of metal wastes with Na_2CO_3 as compared with similar wastes neutralized with NaOH plus Na_2CO_3 as per Hanford procedure. No increase in the amperage drawn by the motor was shown during neutralization by either method. No indications of the formation of a heavy precipitate during the neutralization was shown by this test.

Jets - The jets have continued to operate satisfactorily for the remainder of the runs with only a small number becoming plugged. These stoppages have been predominant in the jet feeding the centrifuge in the extraction cycle and were freed by a water hammer effect by alternately filling the service line with water and adding 125 lbs. steam pressure momentarily to this line. The source of the material and its nature is not known, though possibly metal slivers from the dissolver may be the cause.

Installation of a Hanford jet in a process line in the LaF_3 by-product cell gave excessive jetting rates and the jet was removed. In the waste area, intra-tank transfer using Hanford jets has proven very satisfactory.

Hanford Gang Valve Operation - Operation of the Hanford gang valve was unsatisfactory upon installation due to the inability to control the jetting rate at low steam pressures. The plug of the steam valve was removed and a cylinder, slotted axially, was inserted in its place. This facilitated the adjustment of the steam feed by acting as an expanding orifice as the valve was opened; however, several minutes are required to attain a steady transfer rate while temperature expansion in the valve and steam reaches equilibrium. Good control has been obtained in subsequent trials.

Pumps, Stack Area, and Metal Conveyor - Service has been satisfactory throughout the completion of operations for this equipment in the separations plant.

Waste Area - Climatic conditions, maintenance difficulties and the nature of the solutions stored have necessitated that the manometer type liquid level indicators be replaced by bucket type float indicators which have proven more satisfactory.

Throughout the entire service of the gunite tanks in the waste area, there has been no leakage of process wastes as indicated by the analyses of the drainage water from the dry wells which collect any seepage from the tanks.

C. ISOLATION EQUIPMENT.

General - The choice of proper equipment for the isolation of product from slurries and later from solutions delivered from Room D required full recognition of the hazards involved in handling product in concentrated forms. Previous isolation work by the Research Group had demonstrated that extreme care was needed to prevent scattering of alpha activity into the room air and throughout the working area even when spills were avoided.

During the design and construction of the 204 Building isolation room, efforts were directly not only toward the procurement of suitable chemical processing equipment, but toward the installation of adequate room and hood ventilation with discharge of product laden air into the 200 Area stack duct. Several layers of Amercoat paint were applied to the room floor to achieve a smooth, acid resistant surface and particular care was taken to obtain smooth paint finishes within the hoods. Stainless steel pans were installed in all hoods to catch spillage and permit ease in cleaning.

The evolution of increasingly safer processing equipment based on experience and changes in process requirements followed three distinct steps.

1. The original equipment consisted of glass with polystryene covers in fixed positions, with the vessels placed on lifts to contact the covers during reactions. Hood contamination resulted when the vessels were lowered and mist or vapors dropped from the covers. Contamination also came from batch centrifugation of product precipitates and the transfer of liquids in uncovered containers. At elevated temperatures vapors escaped from the vessels resulting in product deposition generally throughout the hood.

2. A second set of equipment was installed to handle increased volumes involved in the ammonium sulfide process for iron removal. At this time glass was replaced entirely by stainless steel, with all transfers made using vacuum to draw solutions and slurries into head tanks followed by gravity flow into the proper vessels. Covers were placed on all tanks, however, the hoods again became contaminated and when a test showed heavy alpha activity in air drawn over the surface of an open reaction vessel, the need for independent equipment ventilation became apparent.

3. Based on the above experience equipment similar to that later installed at Hanford was designed and constructed. Stainless steel vessels, lines and valves (largely 18-8 S Cb) were used together with the vacuum head tank transfer and feed principle. Close fitting vessel covers were installed and in addition a separate ventilating system was employed to maintain all process vessels under greater negative pressure than the hoods. This improved equipment was used to process most of the product isolated in the 204 Building and proved to be fundamentally adequate and safe for production purposes. Some drawbacks remained from the standpoint of sampling devices together with the need for even more tightly sealed containers and further recommended improvements were incorporated into installations made at Hanford.

Details of Hanford Type Processing Equipment -

1. Filtration, decantation, and first peroxide precipitation.

The nitric solutions containing $La(NO_3)_2$ and product nitrate were removed by vacuum from the tightly closed 5 gallon stainless transfer containers and filtered through a neutsch equipped with an Aloxite filter plate. The solution was mixed with Hyflo-Supercel in the filter-aid tank and then gravitated through the neutsch. The filtrate was elevated to a head tank and then dropped into the precipitator for the first hydrogen peroxide precipitation. The filter was so constructed that the filter cake with the retained impurities could be washed and the leachings sent to the catch tank. The filter plate could also be backwashed to permit removal of the cake slurry and delivery to waste.

The precipitator and the catch tank for supernatant solution, as well as their auxiliary equipment, all closely approximated the design intended for use at Hanford. Due to the time element, however, no heat treatment followed fabrication, and 18-8 S Cb was successfully used in place of the preferred 25-12 S Cb metal. Both vessels were jacketed and brine cooling was provided in order to maintain temperatures at 20° C. during the peroxide precipitation, and at 0° - 5° C. during the several hour settling period which followed prior to decantation of the supernatant solution. The precipitator was provided with four stainless rods placed vertically around the edge of the tank to simulate the boron filled rods to be used at Hanford and in addition the original agitator consisted of a Hanford type disc superimposed upon the agitating blades. The disc, to be filled with boron at Hanford, was soon deleted from the Clinton precipitator due to heavy product deposition on the upper and lower surfaces. Agitation of the precipitator was furnished by a Chicago Pneumatic motor, while settling of post-precipitant was prevented in the catch tank by an electrically driven agitator similar in design to the original precipitator agitator.

The head, or vacuum transfer tanks, were cylindrical in shape with conical tops and bottoms. The vacuum lines entered the top cones, suction being provided by a jet and condensing system outside of the building exhausting into a sump tank. A second jet and condensing system exhausted into the same tank and served to maintain negative pressures on the process vessels used in the entire operation.

2. Second peroxide precipitation and drying.

The second peroxide precipitation was carried out in glass equipment utilizing a pair of four liter suction flasks as the precipitator and catch tank, two sintered glass filters for the necessary filtering and stainless steel head tanks for liquid transfer. Stainless steel lines were used throughout and agitation was provided by laboratory size electric stirrers. Temperature control for the precipitator and catch tank was maintained by a water jacket connected to a circulating tank where the water temperature was controlled by the use of ice or heater elements.

This final product solution was agitated thoroughly by passing into a 500 ml measuring graduate provided with an adjustable vernier for accurate reading. Transfer to the shipping tube which also served as a drying tube was also made by vacuum through an intermediate transfer vessel and sampler. The batches were evaporated to dryness for final shipment by heating the shipping tube in an electric furnace. The tube was placed in a stainless steel can inside an electric furnace and preheated air passed over the surface of the liquid. The rate and control of evaporation was increased by installing an infra-red heating lamp at the base of the drying unit. The maximum temperatures used in the drying were 140° C. in the inlet air, 110° C. at the bottom of the can and 125° C. at the top of the can.

3. Valves.

Three of the Hills-McCanna diaphragm valves used in controlling process solution movements failed in service after four weeks of operation. Investigation of these has shown that in two instances the tygon diaphragm had stiffened and the valve did not operate properly. In the other case the diaphragm was punctured, possibly by closing the valve too tightly or by not having the screw in the diaphragm screwed tightly into the stem, thus causing the diaphragm to be punctured by the protruding head of the bolt. Two more failures resulted during the remainder of the operating period due to similar causes. During the final clean-up operation inspection disclosed that all of the tygon diaphragms were in poor condition. These were all replaced with neophrene since several weeks operation with a neophrene disphragm gave excellent results.

4. Paint.

Difficulty was encountered in finding an acidproof paint which would anchor to the cement floor. Both "Ucilon" and "Amercoat" were tried and of the two the latter seemed somewhat the better. However, utmost care and strict adherence to the standard procedure defined by the manufacturer must be followed to get "Amercoat" to anchor satisfactorily. Once anchored it seemed to be quite acceptable in wearing and cleaning properties. A floor which has been etched with acid appears to present the best surface on which to apply the paint.

IV. PROCESS

A. ALUMINUM JACKET REMOVAL.

Aluminum Jacket Removal with $NaOH - NaNO_3$ Solution - The use of the $NaOH - NaNO_3$ coating removal procedure was continued on all charges since its demonstration on runs 182 - 183 - 184 with only one modification, instituted on charge 210 - 211 - 212, to duplicate more closely the Hanford procedure. Instead of charging the metal into the $NaNO_3$ solution already containing the excess NaOH, it was charged into the neutral $NaNO_3$ solution at 30° C. (made at Clinton by neutralizing 17% NaOH with 60% HNO_3 in the dissolver) and then the excess NaOH was added at such a rate that the column pressure drop did not exceed 5" H_2O. Cooling was maintained with both coil and jacket during the NaOH addition until the temperature reached a maximum and began to drop. The temperature was then allowed to reach 100° ± 5° C. and after the reaction subsided, the charge was digested for 1 hour at this temperature.

This procedure had the advantage over the standard Clinton procedure that the reaction rate could be controlled to some extent by the rate of addition of NaOH.

B. METAL DISSOLUTION.

The metal solution step continued satisfactorily and with no operational difficulty even though the batch size was increased. About 11 months after the start of operations, the process was changed to use 1/2 ton of metal per run instead of 1/3 ton and about 1 1/2 months later, changed again to 2/3 ton of metal per run. For the 1/2 ton runs, 1 ton of metal was charged as previously and for the 2/3 ton runs, 1 1/3 tons of metal was charged. The jackets were removed and the metal dissolved in two portions. No difficulty was experienced in controlling the reaction on either the coating removal or metal solution step, although with the increased quantities of metal and process chemicals, close attention was necessary during the first part of the reaction in order to prevent the column pressure drop from exceeding the desired point. Control of the metal solution reaction was easily affected by a small flow of water through the dissolver coil. The approximate dissolving time and distribution of product for each of the two runs dissolved from each batch charged for the 1/2 ton and 2/3 ton runs is shown below:

	Dissolving Time	Distribution of Product
1/2 ton - 1st	9	56%
- 2nd	13	44%
2/3 ton - 1st	10	56%
- 2nd	15	44%

Considerable variation from these average times was experienced possibly due to variations in the manner in which the reaction was controlled and, in the case of the last run dissolved from the double batches, variations in the amount of metal left as a heel.

On some of the charges (both first and last), the final specific gravity of 1.79 was not reached. Again this might have been due to the manner of control of the reaction. This serves to emphasize the point that in order to use the specific gravity as an indication of the free acid remaining it is necessary that the control be standardized.

C. PRE-EXTRACTION.

The cause of the variations in extraction waste losses is still not understood, except that the pre-extraction treatment appears to be the critical step. As discussed in the original part of this report (pp. 31 ff.), very little of the product after dissolution is in the + 6 state, while considerable proportions may be in the + 3 state, because of the formation of some strong reducing agents from side reactions during metal dissolution. Therefore, the aim of all procedures for pre-extraction treatment has been to raise the product from the + 3 to the + 4 valence by destroying these reducing materials. While satisfactory results have been obtained with most of the procedures tried, occasional high losses indicate that other factors not yet recognized are involved. The procedures that were studied and the results obtained are discussed in the following pages.

Variations in Sodium Nitrite Concentration - As pointed out in the discussion "Substitution of $NaNO_2$ for HCOOH in the Plant" on page 39 of the original section of this report, fluctuations in extraction waste losses while using 0.1M $NaNO_2$ indicated that experiments should be carried out in the plant to determine the optimum concentration and treatment temperature with $NaNO_2$. The table below shows the results obtained at the various concentrations studied. No change in the temperature conditions (40° C. for 1/2 hour and heating to 75° C. before adding H_2SO_4) was made other than to standardize at 1 hour the time the solution was held at 75° C., during which time the H_2SO_4 was added, before adding bismuth solution. The runs in which the UNH was 22% were runs processed with 2/3 ton of metal.

Table 38

Variations in $NaNO_2$ Concentration

Number of Runs	$NaNO_2$ (Molar.)	UNH Conc.	Losses	
			Avg.	Range
61	0.1	20%	2.4	0.8 - 9.0
5		22%	3.1	1.8 - 4.1
26	0.025	20%	1.9	0.5 - 5.6
7		22%	3.2	1.4 - 5.2
4	0.2	20%	2.2	1.3 - 3.8
3	0.1 + 0.1*	20%	2.0	1.3 - 2.6
3	0.4	20%	1.5	1.1 - 2.3
5	0.017	20%	2.2	1.0 - 3.2
2	0.012	20%	2.9	2.2 & 3.5

*100% excess $NaNO_2$ added to the precipitator just prior to the strike.

Accuracy Of Method For Analysis of Pu^{+3} - In the discussion that follows, figures are given for the Pu^{+3} content of metal solution of runs on which studies were being conducted in order to better understand the pre-extraction treatment step. The method for determining Pu^{+3} is not too accurate as shown by the fact that duplicate samples cannot be made to check better than 5% of each other (that is, one result may show 5% more or less + 3 than the other). Time necessary to improve the accuracy of the method has not been available. The results given, therefore, cannot be used as a definite indication of the condition of the metal solution.

A brief outline of the procedure is as follows:

From a hydrochloric acid solution of the sample, precipitate zirconium with phenylarsonic acid which precipitate carries the Pu^{+4}, and leaves a supernatant containing the Pu^{+3}, and Pu^{+6}. A LaF_3 precipitation removes the Pu^{+3} which may be counted. Counts are made on all solutions to check on material balance.

Effect of Holding Time of Metal Solution - Laboratory investigations indicated that the strong reducing agents (hydrazine and possibly others) present in the metal solution decompose on standing and that once they are decomposed, the natural oxidizing properties of the solution will oxidize the product to a higher valence. Also, if sulfuric acid is present the oxidation will proceed only from the plus 3 to the plus 4 state.

In order to demonstrate these findings in the plant, four runs were made. The conditions used and the results obtained are discussed below:

1. H_2SO_4 added to the 70% UNH solution, UNH diluted to 40% and stored about 4 days in Cell 2 (precipitator). No nitrite was added. Waste (23MS) - 0.7%.

Analytical Data

Days after Dissolution	1st	2nd	4th
Hydrazine (M)	$< 3 \times 10^{-5}$	$< 3 \times 10^{-5}$	-
Pu (6) (%)	<1	<1	<1
Pu (3) (%)	8	13	3

2. UNH diluted to 40% and stored 3 days in the dissolver in contact with metal heel. H_2SO_4 added to the 20% UNH as normal, but nitrite was omitted. Waste - 33.%. (This waste was reworked by treating with .07M $NaNO_2$ and 1/4 of the normal bismuth lowering the waste loss to 10%. This rework procedure was repeated using an additional .025M $NaNO_2$ resulting in a final waste of 9%.)

Analytical Data

Days after Dissolution	0	2nd	3rd	1st Waste	Final Waste
Hydrazine (M)	-	$< 3 \times 10^{-5}$	-		
Pu (6) (%)	-	1	1	1	1
Pu (3) (%)	12	-	2	-	-

3. H_2SO_4 added to 70% UNH_3 charge diluted to 50% and stored in Cell 2 2 1/2 days. Solution diluted to 22%, 0.1M $NaNO_2$ added and normal procedure followed. Waste - 4.3%.

Analytical Data

	After Dissolution	Before $NaNO_2$ Addition
Hydrazine (M)	$< 3 \times 10^{-5}$	nil
Pu (6) %	1.7	3
Pu (3) %	13	10

4. Charge diluted to 50% and held in the dissolver in contact with metal heel for 3 days. H_2SO_4 was then added in Cell 1 and normal procedure was followed, using 0.1M $NaNO_2$. Waste - 2.9%.

Analytical Data

	After Dissolution	Before $NaNO_2$ Addition
Hydrazine (M)	nil	-
Pu (6) (%)	2	2
Pu (3) (%)	19	2

From the results obtained on these runs, it is apparent that there are factors in this step that cannot be explained on the basis of present theories.

Potassium Permanganate - Oxalic Acid Pre-Treatment - In line with the theory that strong reducing materials hold some of the product in the + 3 state, a procedure was developed wherein the metal solution was oxidized with $KMnO_4$ and then reduced again with oxalic acid. With this method, it

was believed that all of reducing material would be destroyed during oxidation and that the reduction with oxalic acid would return the product to the + 4 state only. This procedure was used on the six runs processed for the recovery of 93 - 237 since $NaNO_2$ interferes with the yield of neptunium. The conditions for these runs are outlined below and the results obtained are shown in Table 39.

> Solution made 0.002M in $KMnO_4$ after addition of H_2SO_4 and heated 1 hour at 75° C. (on the first two runs 50° C. on one and 35° C. on three of the last four runs). Solution then made 0.035M in oxalic acid and after 15 minutes, 0.008M in manganous nitrate and digested at 75° C. 1 hour.

Table 39

Run Number	Oxid. Temp.	Pu (6)			Pu (3) after Reduct.	Loss (23MS)
		After Oxid.	After Reduct.	After Cent.		
266	75°	94	4	<1	8 - 23	2.4
267	75°	99	6 - 15	<1	8 - 23	4.4
294	35°	98	-	-	-	12.1
295	50°	98.7	1.7		8	15.5
296	35°	98.7	1.8		7.5	19.4
297	35°	99.2	2.5		8	21.0

It is indicated from the results of these runs that the reasoning behind the process is sound and that a temperature of 75° C. is necessary for oxidation. However, the results are not as good as with the normal procedure using $NaNO_2$ and the operation is more involved.

Sulfuric Acid Addition to 70% UNH - Sulfuric acid was added to the 70% UNH solution immediately after dissolution instead of to the solution prior to extraction on six runs, 0.025M $NaNO_2$ being used as the pre-treatment reagent. On the first two the UNH concentration at the time of precipitation was 20% UNH (1/2 ton of metal per charge) and the remaining four, 22% (2/3 ton of metal per charge). In the table below, the results obtained are compared with runs made under similar conditions except for this change. Because only a few runs can be compared, and also because of the variable results obtained during the runs of this period, no clearcut answer can be presented. However, it is indicated that no adverse effect results from this change.

Table 40

Number of Runs	% UNH at Extraction	Point of H_2SO_4 Addition	Extraction Waste Loss
4	20	20% UNH	2.4
2	20	70	2.1
3	22	22	3.7
4	22	70	3.0

D. EXTRACTION.

Attention for the past several months has been given mostly to the pre-extraction treatment step in an effort to improve losses in the extraction step. However, one different method of formation of the precipitate was studied, namely, a combination direct-reverse strike, demonstrated on four runs. Two modifications in the procedure were made also; (1) substitution of 14% bismuth solution for 24% and (2) increase of UNH concentration at the time of precipitation from 20% to 22% upon changing to runs using 2/3 ton of metal. These changes are discussed below.

Combination Direct-Reverse Strike - On runs 210 - 213 a two hour direct strike was made using 90% of the bismuth solution followed by a thirty minute reverse strike with the remaining bismuth solution. The waste losses did not show a significant change.

20% UNH vs. 22% UNH - In order to further study the two-cycle decontamination procedure using ammonium fluosilicate and no scavengers while at the same time not delay the processing of metal, 2/3 ton of metal was used for each run starting with run 280. The UNH solution from the dissolver was diluted only to 22% so that while still using the same bismuth concentration in grams per liter as before the amount of bismuth phosphate cake would be increased only 20%. This larger cake still could be dissolved in the same quantity of acid as used on the 1/2 ton runs so that, after extraction, solution volumes were the same as with 1/2 ton runs. From Table 40 above it can be seen that extraction waste losses ran about 1% higher with the higher UNH concentration.

14% Bi Solution in Place of 24% for Extraction - Starting with run 274, 14% Bi solution was substituted for 24% in the extraction precipitation step with no adverse effects. This was the same solution that was used for product precipitations in the decontamination cycles. The purpose of this change was to simplify solution make-up operations by using only one bismuth solution as well as the elimination of a solution in which the salt is more difficult to dissolve and to keep in solution.

E. DECONTAMINATION.

A great deal of attention was given during this period to the contaminating efficiency and the waste losses that result from various combinations of cerium and zirconium scavengers and the complexing agent ammonium fluosilicate used to gain the goal factor of 10^7 in decontamination established for Hanford operations.

Three of these processes are discussed in the original part of this report, namely, Ce-Zr; Ce-Zr in both cycles, Ce-Zr; Ce in both cycles, and Ce-Zr; Ce in the first cycle $(NH_4)_2SiF_6$ in the second cycle. Conclusions drawn from these demonstrations were that about equal decontamination was obtained with each, but that waste losses were highest with the first process, and lowest with the last process. Also, it was evident that $(NH_4)_2SiF_6$ in the product precipitation step actually lowered the loss from this step. Therefore, during this period, additional demonstrations were carried out to determine the way that $(NH_4)_2SiF_6$ could be employed to best advantage. Two methods were tried. The first was with both Ce-Zr; Ce-Zr and $(NH_4)_2SiF_6$ in the first cycle and $(NH_4)_2SiF_6$ alone in the second cycle. The second was the elimination of scavengers entirely and use of $(NH_4)_2SiF_6$ in both cycles. Since the Ce-Zr; Ce-Zr both cycles process was at first recommended for Hanford operations, this process was demonstrated on one more series of runs during this period.

Table 41 below shows the results obtained with these processes, with the data on the processes reported in the first section of this report repeated for easier comparison. On the second series of runs to demonstrate the processing with $(NH_4)_2SiF_6$ alone in both cycles, a barium sulfate scavenger precipitate was used in the LaF_3 crossover by-product step in an attempt to improve decontamination.

Another process was demonstrated on two runs wherein two product reprecipitations in 0.5M $(NH_4)_2SiF_6$ were made in place of the second decontamination cycle by-product and product steps. The result of this demonstration together with a description of the procedure is given in the discussion.

Table 41

Waste Losses and Decontamination

Process	Runs	Known Losses %		Gamma dF's	
		1st cycle	2nd cycle	Thru Decon. Cycles	Thru Cross-over Cycle
Ce-Zr; Ce - both cycles.	194-201	3.9	3.8	5.3	6.7
Ce-Zr; Ce - 1st cycle. $(NH_4)_2SiF_6$ - 2nd cycle.	202-209	4.0	0.9	5.3	7.1
Ce-Zr; Ce-Zr -both cycles.	186-193	6.0	6.5	5.6	6.3
Ce-Zr; Ce-Zr - both cycles.	210-217	6.9	4.7	5.8	6.9
Ce-Zr; Ce-Zr - both cycles.	227-235	5.7	5.0	5.8	7.4
Ce-Zr; Ce-Zr and $(NH_4)_2SiF_6$ - 1st cycle. $(NH_4)_2SiF_6$ alone - 2nd cycle.	218-226	4.5	1.5	5.6	7.4
$(NH_4)_2SiF_6$ alone - both cycles. (No $BaSO_4$ scavenger in crossover.)	255-263	2.2	0.5	5.2	6.1
$(NH_4)_2SiF_6$ alone - both cycles. ($BaSO_4$ scavenger in crossover.)	280-291	1.4	1.0	5.0	6.3

Ce-Zr; Ce-Zr Both Cycles - Nine additional runs (227 - 235) were processed using double cerium-zirconium scavengers in both cycles and the results confirmed that this process is adequate for obtaining the goal decontamination factors. The decontamination was even better than on the earlier runs. Waste losses, however, continued high when compared to runs without scavengers.

Ce-Zr; Ce-Zr and $(NH_4)_2SiF_6$, 1st cycle - $(NH_4)_2SiF_6$ alone, 2nd cycle - Nine runs were made to demonstrate this process. Waste losses for the first decontamination cycle were more than 1% lower than those obtained on runs where Ce-Zr; Ce-Zr scavengers alone were used in the first cycle (see Table 41 above), all of the improvement being realized in the product precipitation step as a result of using $(NH_4)_2SiF_6$. The waste losses in the second cycle were considerably lower, as expected. The decontamination for this series was as good as the best obtained on the runs demonstrating the Ce-Zr; Ce-Zr - both cycles process. Because of the equally good decontamination and an improvement of approximately 5% in yield was obtained, this process was later recommended for use at Hanford in place of the Ce-Zr; Ce-Zr - both cycles process that was first recommended.

Two Cycle Process with Ammonium Fluosilicate Only - In view of the improvement that resulted from the use of $(NH_4)_2SiF_6$ in the above studies, it was believed that scavengers might be eliminated entirely and use $(NH_4)_2SiF_6$ alone to obtain the goal factor of 10^7. Advantages of this, besides a lowering of waste losses, would be a decrease in the processing time in the by-product step (which is the limiting step in the scavenger process), a decrease in wear and consequently maintenance on the centrifuge by the elimination of the dual precipitation necessary with scavengers and elimination of an insoluble component (Zr) in the by-product precipitate which is difficult to rework if through some unforeseen contingency, it contains appreciable quantities of product. Further indication that this method would give the desired decontamination was given by the results of several one cycle runs in which some were run with $(NH_4)_2SiF_6$ and others with Ce-Zr; Ce-Zr. The results, tabulated below, show that while a lower factor was obtained with $(NH_4)_2SiF_6$ through the one decontamination cycle, the decontamination in the crossover was considerably better, resulting in better decontamination for the $(NH_4)_2SiF_6$ process.

Table 42

Decontamination

Run No.	Treatment	Gamma dF					
		64-P		41-OS		D1-S	
241	$(NH_4)_2SiF_6$	2.1		4.6		6.1	
242	"	2.6	2.8	4.2	4.2		5.8
243	"	3.1		3.9		5.6	
244	"	2.4		-			
245	Ce-Zr; Ce-Zr	3.6		3.6		5.2	
246	"	3.6	3.7	3.9	3.8		5.3
247	"	2.8		2.8		5.3	
248	"	2.8		4.0			

Therefore, a series of runs was processed using $(NH_4)_2SiF_6$ only in both cycles in order to determine whether the required decontamination could be obtained. Results through the decontamination cycles were good (dF = 5.2), however, the factor in the crossover step was the poorest obtained on any of the demonstration runs. Investigation of this contrary behavior of the two cycle runs to the one cycle runs by means of analyses of individual fission products before and after crossover showed that columbium decontaminated quite well, but that zirconium and barium, which quickly grows to lanthanum, decontaminated very poorly. On the one cycle $(NH_4)_2SiF_6$ runs that followed this series, a barium sulfate scavenger was employed to remove this active barium in an attempt to improve decontamination. This was formed along with the LaF_3 by-product precipitation (discussion of the procedure for this is given in the section of the crossover step). The decontamination factor for barium as shown by F.P. analyses was good (see Table 45) and the gross decontamination factor in the crossover step was about 5 times as good as that obtained on a previous series of runs processed under the same conditions, except that no barium scavenger was used.

Because of the improvement affected by use of the barium scavenger, it was felt that possibly the goal factor could be reached with its assistance on two cycle $(NH_4)_2SiF_6$ runs. Therefore, a series of 12 runs were processed in this manner. In order that the scheduled processing of metal would not be delayed, these runs each were made from 2/3 ton of metal instead of 1/2 ton as on previous demonstration runs and the two cycles were obtained by running both a product and a by-product precipitation in each $BiPO_4$ process cell rather than a single precipitation in each cell which required storing a series of runs and re-using cells 6, 4 and 5 for the crossover cycle. The decontamination in the crossover step of these runs was only about twice as good on the previous series of two cycle runs rather than the five times that resulted from using barium sulfate on the one cycle runs.

The reason for the poorer results in the crossover on the two cycle runs than on the one cycle runs was not understood and a thorough investigation of this point could not be made because of the very low activities of the solutions after the crossover step. More active solutions available at Hanford will afford a better opportunity for an investigation of this.

<u>Zr Addition to 10N Product Solution Before the Crossover Step</u> - It was believed that decontamination in the crossover possibly could be improved by adding a small amount of inactive zirconium just before the crossover cycle which would cause an exchange of molecular form, which form might be responsible for rather poor decontamination of this element.

This was tried on four of the 2/3 ton two cycle $(NH_4)_2SiF_6$ runs (286 - 289). On the first two, 1 mg/liter in the 10N product cake solution just prior to the crossover step was used and in the other two 10 mg/liter was used. The concentration was kept low so that, if it carried through to isolation, it would not exceed the amount tolerable in the product solution for isolation. It was estimated that the 1 mg/liter concentration used in the first two runs would not exceed the maximum allowable in isolation if it all remained in the product solution. It was felt that a decontamination factor of 10 on this element could be expected, and therefore for the second two run batch, 10 mg/liter was used.

Apparently the inactive zirconium was effectively removed since the amount of Zr found in the product solution for isolation was "nil" in both batches. The active zirconium, however, showed no improved decontamination as near as could be determined from overall factors.

Product Reprecipitation Process Demonstration - Laboratory studies indicated that a dF of 7.0 could be obtained by making two product reprecipitations in 0.5M $(NH_4)_2SiF_6$ in place of the second decontamination by-product and product precipitation steps. Two runs were made to demonstrate this process using the recommended procedure as outlined below:

1. First decontamination cycle normal using 0.05M $(NH_4)_2SiF_6$, the product cake from this being dissolved and then sent to solution tank.

2. Solution reduced in the solution tank at 60° C. for one hour with 0.1M ferrous ammonium sulfate and with 0.5M $(NH_4)_2SiF_6$ present.

3. Dilution solution in the precipitator prepared during reduction by adding process chemicals so that the concentrations after addition of the reduced product solution would be 0.5M $(NH_4)_2SiF_6$, 0.6M H_3PO_4 and 0.1M ferrous ammonium sulfate.

4. Reduced solution jetted into dilution solution in the precipitator over 30 minute period while maintaining the temperature in the precipitator at 60° C.

5. 24 lbs. 14% Bi solution added over 30 minutes followed by a two hour digestion period.

6. Product slurry centrifuged, cake dissolved and returned to the solution tank.

The above procedure was repeated for the second reprecipitation, after which the normal flowsheet procedure was followed for the crossover $BiPO_4$ by-product precipitation.

Run 292 was processed in this manner with a resulting dF of 4.4 before the crossover step and 5.5 through the crossover. On the normal $(NH_4)_2SiF_6$ two cycle runs, an average dF of 5.0 was obtained before crossover and 6.2 through the crossover step. Also the waste losses for this run were higher than for the previous runs - 4.3% as compared to 1.0%

In the preparation of the dilution solution (step 3 above) for run 293, 60% nitric acid was added instead of the phosphoric acid which resulted in the failure of the $BiPO_4$ precipitate to form. Before this error was discovered additional bismuth solution had been added to rework the effluent. Therefore, when the solution was diluted and made 0.6M in H_3PO_4 a cake too large to handle as a single run resulted. Because of this, the cake was split and each part processed as a separate run.

Product loss from the first reprecipitation with the large cake and high HNO_3 normality (1.4) was 5.1% and the loss for each of the two second reprecipitations was 1.4% and 1.6%. The dF's before crossover on these runs averaged 5.1 and after crossover, 5.8.

While the reprecipitation procedure was not very well demonstrated in this study, indications are that the normal cycle using a by-product and product with 0.05M $(NH_4)_2SiF_6$ is better both with respect to decontamination and waste losses.

First $BiPO_4$ By-Product Waste Losses - On the series of runs 255 - 263 processed with 1/3 ton of metal per run to demonstrate $(NH_4)_2SiF_6$ alone in both cycles, waste losses from the first by-product step were about 1% higher than previous runs with no scavengers used in this step. The only difference was that fission product elements were added to the metal solution for this series of runs. It was also noted that these losses were higher than those obtained on runs made from 1/2 ton of metal, both with and without F.P.E., where the HNO_3 normalities for oxidation and precipitation were necessarily higher because of the limited tank capacities. A comparison of these results together with the known differences in conditions is presented in the table below.

Table 43

	F.P.E. Added	Oxidation Norm. HNO_3	Pptn. Norm. HNO_3	No. of Runs	BP-1 Losses
1/3 Ton runs	Yes	5.4	1.0	9	1.8
1/3 Ton runs	No	5.4	1.0	85	0.7
1/2 Ton runs	Yes	6.9	1.25	4	0.8
1/2 Ton runs	No	6.9	1.25	25	0.5
2/3 Ton runs (20% larger cake but same soln. volumes as on 1/2 ton runs.)	Yes	6.9	1.25	12	1.0

Uranous Sulfate in Place of Ferrous Ammonium Sulfate for Product Reduction - On six of the regular Clinton runs (one decontamination cycle) uranous sulfate was used for reduction in the $BiPO_4$ product precipitation step in place of ferrous ammonium sulfate that is normally used so that the neptunium would not be lost. There were no increases in product waste losses as a result of this change. The reduction was affected by making the solution 0.01M in uranous sulfate, by adding a solution of 0.3M uranous sulfate in 1N sulfuric acid and heating for one hour at 75° C. Upon making up the solution, the solid uranous sulfate was found to contain an insoluble fraction which was removed from the solution by settling.

Increased Centrifugation Feed Rate for $BiPO_4$ Slurries - On the 1/2 ton runs, $BiPO_4$ product and by-product slurries were jetted to the centrifuges at the maximum rate of the jet giving feed rate of 145 - 150 lbs. per minute. There was no noticeable increase in waste losses because of the increased rate.

F. CROSSOVER STEP.

Operations in the crossover step have continued satisfactorily through this period. In general, conditions as discussed in the first section of this report were followed. However, four modifications were made, namely: (1) Supernatants, washes and filter cake leachings from the isolation step were recycled into this step, (2) A 1N HNO_3 wash of the LaF_3 product cake was incorporated as recommended for Hanford, (3) The quantity of La^{+3} solution in the product precipitation step was reduced so that it was possible to combine 3 third ton (or 2 half ton) runs for metathesis in Room D and, (4) A $BaSO_4$ precipitation was formed along with the LaF_3 by-product step to aid in the removal of active barium which decays to active lanthanum, a strong gamma emitter. A rather extensive study was made of the behavior of the principle gamma emitting fission product elements (lanthanum, zirconium and columbium, and barium a beta emitter, which grows to lanthanum) through the separations process with particular emphasis on their behavior in the crossover step on runs where $(NH_4)_2SiF_6$ alone was used to aid decontamination. This study and the above changes are discussed in the following section.

Product Recycled into the Crossover Step - On the first series of runs to demonstrate the Hanford isolation procedure (202 - 217) product was recycled into the LaF_3 product precipitation step of the crossover cycle in order to build up the concentration of product beyond the point where a peroxide precipitation would be formed from the solution of the metathesized LaF_3 slurry from the crossover step. The lanthanum contained in the supernatant from the first peroxide precipitation went to form the LaF_3 precipitate in the cell, one quarter of the recycle solution being added for each strike of a two run batch. Since additional product was introduced during the second strike, full effectiveness of the dual precipitation was not obtained on this product. Therefore, it was necessary to make an additional precipitation on the effluent before disposing of it. After this series, in order to avoid the necessity of reworking the effluent wastes on each run and also to avoid the possibility of accumulation of some impurities in the process, recycle solutions were introduced in the LaF_3 by-product precipitation step. Since about twice as much lanthanum was used for this step, the recycled product could be introduced in the first strike only, fresh lanthanum solution being used for the second strike.

Because the recycle solutions contained considerable H_2O_2 which would complicate the re-oxidation of the product prior to the by-product precipitation, it was necessary to decompose the H_2O_2 before the recycle was added to the run. This was done in Room D equipment using $NaNO_2$ as the reactant followed by treatment with $KMnO_4$ to destroy any excess $NaNO_2$ and to oxidize the product. Further discussion of this decomposition treatment is given in the discussion of Room D operations. As an additional assurance that all

of the product was oxidized, the recycle solution was added to the run before the re-oxidation step. Since the lanthanum for the first strike was of necessity present before the HF was added, a co-formed precipitate resulted rather than a pre-formed precipitate as used previously. The second strike, of course, was pre-formed as before.

No operational difficulties were experienced with this procedure. The reaction between the H_2O_2 and $NaNO_2$ was easily controlled and the completeness of oxidation of the product before precipitation was as complete (percentage-wise) as on runs with no recycled product as evidenced by no increase in waste losses. No loss in decontamination efficiency resulted from the change to a co-formed precipitate for the first strike.

1N HNO_3 Wash on the LaF_3 Product Cake - Starting with run 202, all LaF_3 product cakes were washed twice with 1N HNO_3 before removal from the centrifuge and transfer to Room D in order to more closely duplicate the conditions to be experienced at Hanford with the recommended flowsheet. No increase in waste losses was experienced because of this change.

Reduction in La^{+3} Concentration in the LaF_3 Product Step - The lanthanum concentration in the product precipitation step was decreased two more times after the first change from 225 mg/liter to 125 mg/liter on run 186. On runs 202 - 217, processed to study the Hanford isolation procedure, the amount of lanthanum salt used to form the cake from each two run batch was reduced from 10.8 lbs. to 10 lbs. which is equal to the amount to be used on each run at Hanford. This resulted in a concentration of 110 mg/liter in the product precipitation step. Again, starting with run 218, in order to allow the combination of three 1/3 ton runs to make a batch for metathesis and isolation, the 10 lbs. of lanthanum salt were divided between the three runs, resulting in a concentration of about 90 mg/liter for each run. This concentration is equal to that recommended for Hanford. On the 1/2 ton runs, the same amount (10 lbs.) was used on each two run batch, and since the solution volumes were increased one third, the concentration was still 90 mg/liter. No effect on the waste losses was noted as a result of changing to the lower concentrations.

$BaSO_4$ Scavenger with the LaF_3 By-Product Precipitation - From the studies of the behavior of specific fission product elements on runs using $(NH_4)_2SiF_6$ and no Ce-Zr scavengers, it was indicated that the removal of active barium was poor. Removal of this element is important, especially on runs processed with metal of short cooling time, since it rapidly grows to the gamma emitter, lanthanum. Therefore, in order to improve decontamination at this point, a $BaSO_4$ scavenger precipitation was formed along with the first strike of the LaF_3 by-product precipitation starting with run 264. Later, starting with run 282, $BaSO_4$ was formed with both strikes. The procedure is as follows:

First Strike -

1. After re-oxidation and just prior to the addition of HF, add 84 lbs. of 8% $Ba(NO_3)_2$ solution.

2. Add 46 lbs. of 93% H_2SO_4 uniformly over 15 minutes.

3. Digest 15 minutes.

Second Strike -

1. Add 84 lbs. of 8% $Ba(NO_3)_2$ solution to scale tank containing the La salt solution to be added for the second strike and air sparge to mix.

2. Add the mixed solutions to the precipitator uniformly over 20 minutes. (Normal addition time for La salt solution.)

No clearcut comparison of overall decontamination factors could be made to determine the effectiveness of this treatment, but analyses for active Ba and La showed that these elements were decreased as shown in Table 46. There were no operational difficulties with this procedure and no indication that the precipitated barium sulfate did not follow the lanthanum fluoride into the waste tank.

Behavior of Specific Fission Product Elements - A tabulation of data obtained in the study of the behavior of specific fission product elements through the separations process is presented in Tables 44, 45, and 46.

In the studies of the process using no scavengers, but with ammonium fluosilicate in both cycles attention was centered on what elements are important at the end of the decontamination cycle and at the end of the crossover cycle, and what factor is obtained in the crossover for each of these. The data which were obtained at these points are given in Table 46 These results also show the effect of making a barium sulfate precipitation along with the lanthanum fluoride precipitation in the crossover. (This point is discussed in the next section.) Note that in this table many of the runs were made with only one decontamination cycle.

From this table it can be seen that gross beta decontamination was lower than gamma in the crossover step. In order to determine which beta emitting elements remained in the final solution, an analysis was run on the $La(OH)_3$ product cake solution of run 286 - 287. The results are given in the table below.

Table 44

Percent Beta Distribution in DIP - Run 286 - 87

Ce	Sr	Ba	Zr	Cb	Te & Se	La & Pr	Total
6.3	12.8	.12	.03	.01	6.5	26.2	52.0

In view of the consistency of the results of the fission product analyses from run to run (Table 46) and the fact that the individual components add up to roughly 100%, it would appear that the analyses must represent a true picture of what is taking place for the individual elements. However, the activity in the various solutions is so low that in spite of these consistencies the results may be misleading. Because of the low counts satisfactory decay and absorption characteristics cannot be obtained for separated fractions in order to determine with any degree of certainty that some other element is not actually responsible for the activity.

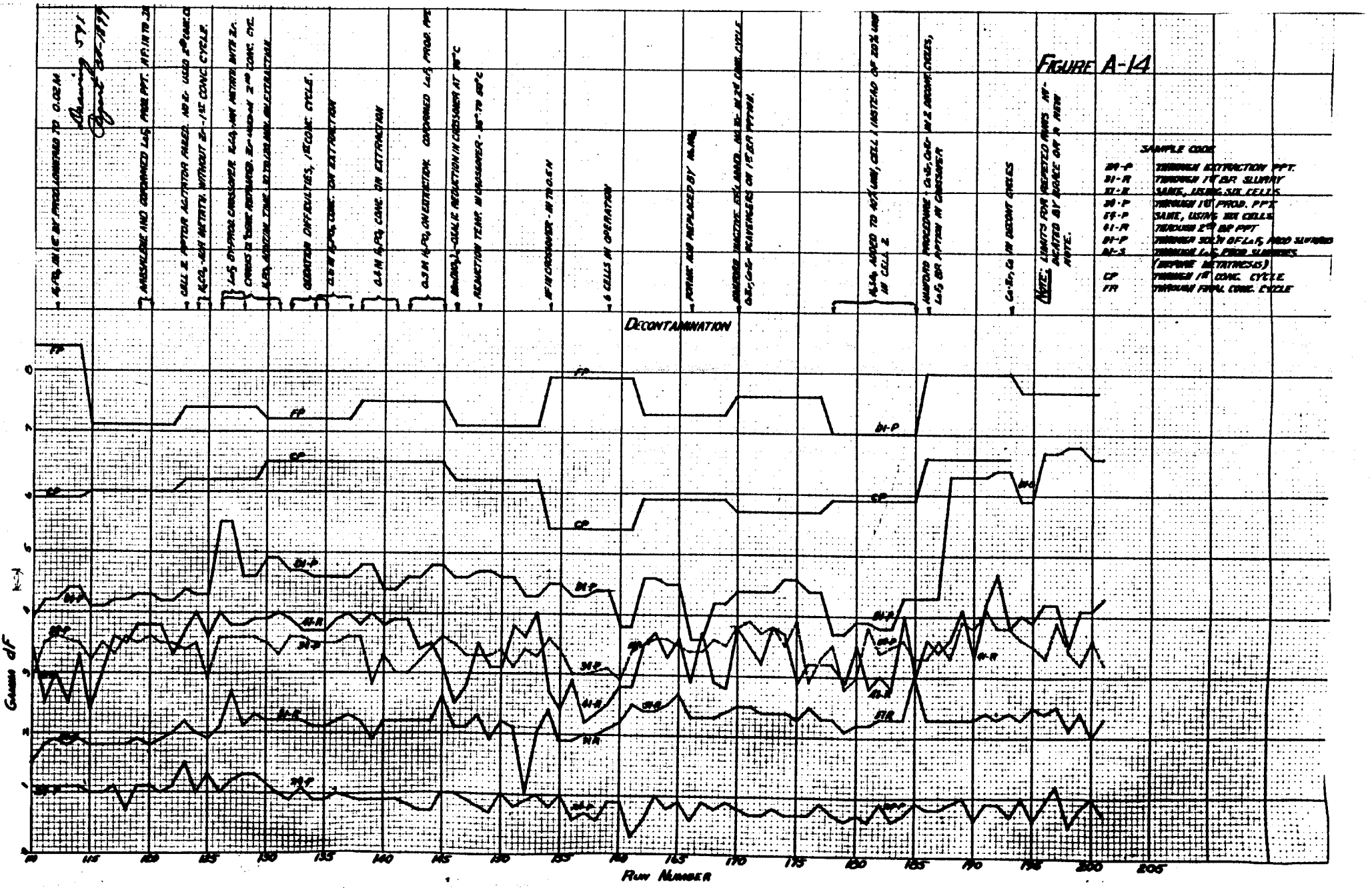


FIGURE A-14

[redacted]

TABLE 45

GAMMA DECONTAMINATION DATA FOR INDIVIDUAL FISSION SPECIES

Dr-1005
CN-2021 + CN-1879 (Supp)

Fission Element	Process	Run	EXTRACTION CYCLE: Metal Solution, % of Constituent Act'y	EXTRACTION CYCLE: Metal Solution, Cumul've Decon. Fctr.	EXTRACTION CYCLE: Solution of Extraction ppt. in 5N HNO_3, % of Constituent Act'y	FIRST DECONTAMINATION CYCLE: Effluent from First By-Product Centrifugation, % of Constituent Act'y	FIRST DECONTAMINATION CYCLE: Effluent from First By-Product Centrifugation, Cumul've Decon. Fctr.	FIRST DECONTAMINATION CYCLE: Solution of First Cycle Product ppt. 5N HNO_3, % of Constituent Act'y	FIRST DECONTAMINATION CYCLE: Solution of First Cycle Product ppt. 5N HNO_3, Cumul've Decon. Fctr.	SECOND DECONTAMINATION CYCLE: Effluent from Second By-Product Centrifugation, % of Constituent Act'y	SECOND DECONTAMINATION CYCLE: Effluent from Second By-Product Centrifugation, Cumul've Decon. Fctr.	SECOND DECONTAMINATION CYCLE: Solution of Second Cycle Product ppt. 5N HNO_3, % of Constituent Act'y	SECOND DECONTAMINATION CYCLE: Solution of Second Cycle Product ppt. 5N HNO_3, Cumul've Decon. Fctr.
La (Gamma)	C	205	40	47	7.9	97	61	33	5.6×10^3	72	6.5×10^3	50	1.75×10^5
		208	34	40	9.0	98	58	34	3.6×10^3	58	5.3×10^3	39	1.58×10^5
	A	212	54	35	7.3	99	58	64	5.27×10^2	89	6.0×10^3	78	5.58×10^5
		215	15	27	2.3	93	24	58	2.7×10^3	109	2.0×10^3	87	1.50×10^5
	D	220	33	32	3.8	79	46	47	1.7×10^3	99	1.6×10^3	52	1.10×10^5
		223	38	41	3.5	98	48	98	1.5×10^3	110	1.63×10^3	64	7.24×10^4
	A	228	18	29	3.3	88	32	15	3.43×10^3	61	4.27×10^3	32	3.25×10^5
		231	23	61	1.0	96	61	35	7.24×10^3	53	1.14×10^4	57	6.00×10^5
Zr (Gamma)	C	205	26	3.8	58	2.8	1.8×10^3	46	2.5×10^3	23	1.38×10^4	50	1.75×10^5
		208	23	4.5	56	1.0	4.1×10^3	40	2.2×10^3	31	6.7×10^3	52	8.13×10^4
	A	212	32	2.5	51	0.3	1.4×10^4	12	1.66×10^4	3.1	2.92×10^5	13	1.64×10^6
		215	35	2.6	55	0.9	1.32×10^4	11	3.43×10^4	0.8	7.52×10^5	6.2	7.21×10^6
	D	220	30	2.2	51	13	3.45×10^2	5.2	3.2×10^4	2.5	1.00×10^5	29	2.40×10^6
		223	25	1.9	49	0.5	6.56×10^3	1.8	8.12×10^4	1.7	7.02×10^4	36	8.56×10^5
	A	228	35	4.0	45	1.2	4.53×10^3	42	2.39×10^3	13	3.81×10^4	53	3.77×10^5
		231	28	1.3	55	1.1	5.80×10^3	33	9.36×10^3	15	5.10×10^4	38	1.12×10^6
Cb (Gamma)	C	205	21	5.1	38	2.1	1.60×10^3	41	2.6×10^3	7	3.93×10^4	50	2.49×10^5
		208	33	9.6	37	1.0	5.70×10^3	32	3.8×10^3	11	2.71×10^4	16	3.68×10^5
	A	212	23	2.3	43	0.7	4.80×10^3	25	6.3×10^3	2.8	2.51×10^5	2.2	7.66×10^6
		215	43	4.1	43	0.7	2.43×10^4	33	1.34×10^4	0.8	8.42×10^5	7.3	7.26×10^6
	D	220	31	3.2	46	0.9	4.5×10^3	56	4.3×10^3	0.2	1.80×10^5	29	4.30×10^6
		223	38	3.0	49	0.1	4.68×10^4	2.5	6.8×10^4	1.0	1.49×10^5	4.8	9.77×10^5
	A	228	45	6.6	36	0.4	1.54×10^4	44	2.94×10^3	38	1.70×10^4	23	1.11×10^6
		231	41	2.7	36	1.4	7.67×10^3	36	1.24×10^4	14	7.69×10^4	23	4.29×10^6
Ba (Beta)	C	205	4.9	162	1.0	2.6	122	1.7	2.03×10^4	1.2	2.85×10^4	0.1	3.68×10^5
		208	6.4	191	1.3	3.2	211	1.8	2.34×10^4	1.3	4.08×10^4	0.2	3.78×10^6
	A	212	3.8	73	1.1	1.7	120	0.8	1.98×10^4	0.2	2.27×10^4	0.2	3.23×10^6
		215	1.7	68	0.3	0.2	95	0.8	1.25×10^4	0.8	1.25×10^4	0.2	1.88×10^6
	D	220	3.0	35	2.0	3.8	79	0.5	1.2×10^4	0.6	1.40×10^4	0.7	1.80×10^6
		223	3.0	45	1.2	2.6	94	0.5	1.28×10^4	0.5	1.27×10^4	0.7	1.65×10^6
	A	228	3.2	74	0.9	1.6	147	1.0	1.83×10^4	1.2	1.55×10^4	0.4	2.02×10^6
		231	3.3	56	0.7	1.3	193	1.0	2.71×10^4	0.9	2.98×10^4	0.4	4.29×10^6
Gross Gamma	C	205	--	9.1	--	--	252	--	4.0×10^3	--	1.16×10^4	--	2.17×10^5
		208	--	10	--	--	168	--	2.34×10^4	--	9.1×10^3	--	1.83×10^5
	A	212	--	4.9	--	--	106	--	6.3×10^3	--	9.8×10^3	--	8.31×10^5
		215	--	4.4	--	--	157	--	1.11×10^4	--	1.63×10^4	--	9.41×10^5
	D	220	--	3.7	--	--	108	--	2.4×10^3	--	4.6×10^3	--	1.78×10^5
		223	--	3.8	--	--	125	--	3.89×10^3	--	4.97×10^3	--	1.22×10^5
	A	228	--	5.2	--	--	153	--	2.87×10^3	--	1.43×10^4	--	5.77×10^5
		231	--	2.4	--	--	254	--	1.10×10^4	--	2.63×10^4	--	1.47×10^6
Gross Beta	C	205	--	34	--	--	68	--	6.4×10^3	--	6.5×10^3	--	1.13×10^5
		208	--	31	--	--	91	--	3.7×10^3	--	6.5×10^3	--	1.17×10^5
	A	212	--	22	--	--	54	--	4.2×10^3	--	5.0×10^3	--	1.73×10^5
		215	--	11	--	--	83	--	5.5×10^3	--	5.3×10^3	--	2.21×10^5
	D	220	--	24	--	--	70	--	2.2×10^3	--	3.0×10^3	--	4.46×10^4
		223	--	18	--	--	81	--	2.18×10^3	--	2.08×10^3	--	3.94×10^4
	A	228	--	21	--	--	75	--	5.73×10^3	--	6.07×10^3	--	2.56×10^5
		231	--	12	--	--	74	--	8.00×10^3	--	7.88×10^3	--	4.35×10^5

PROCESS A: Two shot Ce-Zr/Ce-Zr, both cycles.

PROCESS C: Two shot Ce-Zr/Ce, first cycle, ammonium fluosilicate only in second cycle.

PROCESS D: Two shot Ce-Zr/Ce-Zr, and ammonium fluosilicate first cycle, ammonium fluosilicate only in second cycle.

[redacted]

Table 46

Behavior Of Fission Product Elements in Crossover Step
($(NH_4)_2SiF_6$ and F.P.E.'s used Except Where Noted)

Run Numbers	Soln. of Prod. Cake Before Crossover - % Gamma					Soln. of Prod. Cake After Crossover & Metath. - % gamma					Gamma Factor in Crossover						Cycles	No. of $BaSO_4$ Scavengers*	
	La	Zr	Cb	Ba (% Beta)	La+Zr+Cb	La	Zr	Cb	Ba (% Beta)	La+Zr+Cb	La	Zr	Cb	Ba (Beta)	Gross Gamma	Gross Beta			
243	21	50	23	.5	94												1		
243-244						85	10	2.4	4.9	97	68.	1380.	2630	9.	275.	92	1		
247	67	6	26	.9	99												1		***
247-248						88	10	1.1	3.3	99	45.	33.	1375	8.	58.	49	1		***
255-263	12	13	75	.3	99												2		
255-257						18	55	10.	4.8	83	1.7	0.7	21	0.4	2.7	7	2		
258-260						78	22	1.6	4.8	102	0.9	3.5	356	0.5	5.7	7	2		
261-263						18	74	60.	4.0	98	0.6	1.7	122	1.6	9.8	21	2		
270-271						92	6	2.5	0.1	103							1	1	**
272-273	87	6	7	.2	100	89	7	1.1	0.03	98	197.	165.	1210	252.	195.	34	1	1	**
274-275	83	5	7	.2	95	96	5	1.4	0.1	102	236.	293.	1260	136.	271.	68	1	1	**
276-277	86	4	4	.2	94	102	2	0.4	0.6	104	184.	438.	2395	19.	218	56	1	1	**
278-279	82	6	17	.4	105												1	1	**
282-283	66	7	25	.5	98	45	24	3.4	0.1	72	117.	23.	588	74.	80	16	2	2	
284-285	75	9	17	.2	101	59	27	4.5	0.05	91	91.	25.	249	85.	72	21	2	2	
286-287						82	27	4.5	0.2	114							2	2	

* 1 = $BaSO_4$ scavenger in first LaF_3 by-product strike.
2 = $BaSO_4$ scavengers in both LaF_3 by-product strikes.

**No F.P.E.'s added.
***Process: Ce-Zr, Ce-Zr.

G. ROOM D OPERATION.

Since the start of the demonstration runs of the Hanford isolation procedure (run 202) which involves precipitation of the product peroxide directly from a solution of the metathesized LaF_3 product slurry from the crossover step, and continuing through the completion of operations, Room D operations have been reduced to the running of the metathesis and solution of the resultant $La(OH)_3$ cake except in a few special cases. For this isolation process, it was recommended that a K_2CO_3 assisted metathesis be used. Metathesis waste losses with K_2CO_3 were high and each waste therefore had to be reworked. Later, however, a normal Clinton metathesis, that is, without K_2CO_3 was tried with good results and its use was continued through the completion of operations.

On the first series of runs (202 - 217) all of the product sent to isolation was recycled into the LaF_3 product precipitation step of the crossover in order to build up the concentration of product beyond where a precipitate would form. After this series, isolation supernatants, washes and leachings were returned to the process in the LaF_3 by-product step which necessitated the decomposition of the peroxide remaining in the recycle solution. This operation was performed in Room D since suitable equipment was available there.

During this period it was necessary to run a LaF_3 concentration cycle on several solutions for special purposes. For the by-product step, $KMnO_4$ was used in place of $Na_2Cr_2O_7$ and zirconium was omitted. Results were good, indicating that the $KMnO_4$ may in some manner perform the same function as did the zirconium.

These changes are discussed below.

Reworking of K_2CO_3 - KOH Metathesis Wastes - The amount of product remaining in the effluent after centrifugation of the $La(OH)_3$ cakes formed by the metathesis procedure using 10% K_2CO_3 - 15% KOH was high on all runs as predicted from laboratory studies of the method (average of all runs = 2.7%). In order to recover some of this product, the effluents were reworked. At first recentrifugation was tried with some recovery, and the addition of 25 lbs. of 1% lanthanum salt solution was tried. This latter treatment gave good results and was made standard procedure. Table 47 shows the results of the tests made to develop the rework procedure. The average amount of product lost to waste after reworking on all runs was 1%.

Table 47

Reworking of Metathesis Caustic Wastes

Run No.	Operations Performed	Results after Each*
202-203	Centrifuged 4 times	4.4, 1.4, 0.3, 1.0
204	Centrifuged 3 times	2.4, 1.9, 1.1
205-206	Cent., 25# La soln. added and cent.	2.5, 1.3
207	Centrifuged 2 times	1.8, 1.6
208-209	Centrifuged 3 times	2.0, 1.4, 1.2
210-211	Cent. 2 times, added 25# La soln. and cent.	2.1, 0.9, 0.006
212	Cent., added 25# La soln. and cent.	2.4, 0.5
213-214	Cent., added 25# La soln. and cent. 2 times	1.4, 0.9, 0.6
216-217	Cent. 2 times, added 25# La and cent. 2 times	2.2, 1.9, 0.6, 0.6

*Percent of product in the effluent is based on the actual amount of product in the LaF_3 slurry before metathesis.

Elimination of K_2CO_3 from the Metathesis Step - The recommended metathesis procedure for converting the fluorides of lanthanum and product to the corresponding hydroxides, so that these elements may be taken into solution in nitric acid, calls for the use of 15% KOH and 10% K_2CO_3. The reason for not using KOH alone was that HNO_3 insolubles are formed which hold considerable product and there is no reason to believe this is not valid for the particular slurries which were studied. However, a number of Clinton plant slurries were metathesized without K_2CO_3, and the resulting hydroxides dissolved successfully in the flowsheet quantity of nitric acid (equal to the Hanford quantity). The Clinton plant equipment is very similar to the Hanford equipment and so it is believed that this procedure would be entirely satisfactory there.

The losses when using the carbonate assisted metathesis range from 2 to 5% unless the wastes are reworked. Earlier and also very recent experience with the straight KOH metathesis indicate that the corresponding losses average about 1%. Table 48 presents some of the recent data on the two procedures including data on the product removed by filtration of the nitric acid solution of the hydroxides. The losses in all cases with the insoluble material was very low. The metathesis waste liquors from the straight KOH metathesis were reworked since the time was available; but, even before reworking, they contained, on an average of these runs, less product than the carbonate assisted metathesis wastes after reworking.

Table 48

Effect of K_2CO_3 on KOH Metathesis

Run Numbers	K_2CO_3 Assisted	% Metathesis Waste Losses (Caustic and Water Wash)		% Filter Cake Losses (After HNO_3 Leaching)
		Before Rework	After Rework	
268 - 269	Yes	1.4	0.9	0.1
270 - 271	Yes	2.5	2.1	0.1
272 - 273	Yes	1.4	0.6	0.05
274 - 275	Yes	3.8	1.2	0.06
276 - 277	Yes	2.4	1.1	0.4*
278 - 279	Yes	1.4	0.4	0.07
280 - 281	No	0.8	0.6**	0.3*
282 - 283	No	0.9	0.4	0.2*
284 - 285	No	0.6	0.3	0.1*
286 - 287	No	0.8	0.8**	0.1*
288 - 291	No	1.2	0.3	0.1*
292 - 293	No	1.5	0.5	

Note: Caustic wastes were reworked by adding 25 lbs. of 1% La salt solution, digesting and centrifuging, except on runs marked (**), which were recentrifuged only.

*The indicated product loss was decreased further (on an average, 57%) by slurrying the cake in water, decanting and returning the water to the process.

Decomposition of Hydrogen Peroxide in Recycle Solutions - Starting with run 218, the supernatants, washes and leachings from filter cakes were recycled into the first strike of the LaF_3 by-product step of the crossover cycle. Therefore, it was necessary to decompose the hydrogen peroxide remaining in the solution, since this holds the product in the reduced state. A procedure was developed whereby the peroxide was decomposed with sodium nitrite in a Room D tank provided with ventilation and a cooling coil. The procedure is as follows:

To 100 volumes of supernatant (in Tank D-8) cooled as low as possible (about 19° C.) add 15 volumes of 60% HNO_3 (to make at least 1N) and then 17% $NaNO_2$ solution at a rate such that the temperature does not exceed 30° C. When about 65% of the $NaNO_2$ necessary to decompose the peroxide (peroxide content previously determined by analysis) has been added, remove a sample to ascertain if the peroxide has been all decomposed. If not, add more nitrite and resample. After the end-point has been passed, add a small amount of $KMnO_4$ solution until a permanent pink color appears.

No difficulties were experienced with control of the reaction and about two hours was necessary for the addition of the nitrite while maintaining the temperature below the upper limit of 30° C. An average of about 80% of the stoichiometric amount of nitrite was required to complete the reaction.

After the solution is returned to a slight pink, it is made 0.15M in $KMnO_4$ and heated for one hour at 75° C. in order to pre-oxidize the product. While the recycled product is present during the reoxidation of the product in the run immediately prior to precipitating the LaF_3 by-product, it was felt that this pre-oxidation would give added certainty that the recycled product was in the oxidized state. Although no indications can be found that it was beneficial no abnormally high waste losses were obtained in this step.

$KMnO_4$ Oxidation for LaF_3 Concentration Cycle By-Product Step - On several occasions, it was necessary to run a concentration cycle in Room D. Since good oxidation has been obtained in the crossover LaF_3 by-product step with $KMnO_4$, this was used in place of the $Na_2Cr_2O_7$ and zirconium ion which was formerly used. Zirconium could not be used on these runs because this element interferes with the product peroxide precipitation in the isolation step. As shown in the table below, losses were about as low as on those runs where $Na_2Cr_2O_7$ and zirconium were used and better than those using $Na_2Cr_2O_7$ and no zirconium.

Number of Runs	Conditions	Waste Losses	
		Avg.	Range
40	$Na_2Cr_2O_7 + ZrO^{+2}$	.6	.2 - 1.1
4	$Na_2Cr_2O_7$ alone	5.4	3.7 - 6.4
8	$KMnO_4$ (0.15%)	0.9	0.5 - 1.7

H. PRODUCT ISOLATION.

The original Clinton procedure for isolation of the plutonium after decontamination in the canyon was to run two LaF_3 concentration cycles in Room D which affected a decrease in LaF_3 carrier by a factor of 400. The final LaF_3 slurry was then delivered to another group where the product was isolated in laboratory scale equipment.

However, at Hanford the product content of each run is high enough so that the concentration cycles are not necessary and the product can be precipitated as a peroxide directly from the solution of the LaF_3 cake from the crossover step.

In order to demonstrate this process at Clinton, equipment suitable to handle the solutions was installed in Building 204. This first installation was of stainless steel for the tanks used for the first precipitation step and with tygon tubing for connections. For the final precipitation (considerably less volume of solution) laboratory glass equipment was used. Later, a unit for the first precipitation was constructed entirely of stainless steel and for the final precipitation, a unit with stainless steel head tanks and tubing. Only the precipitator flask, the product dissolving flask and the filter were of glass. All equipment was installed in well-ventilated hoods and operated as much as possible by remote control to minimize any possibility of ingesting or inhaling even small amounts of product.

The recommended Hanford procedure for isolation of product directly from the solution of the metathesized LaF_3 cake from the crossover step was demonstrated for the first time on runs from the series 202 - 217. In order to build up the concentration of product to the point where a precipitate was formed, it was necessary to return all of the product delivered to isolation to runs of the next batch to be processed. This was introduced in the crossover step. A precipitate first formed from the third batch was thus treated. The solubilities obtained on the batches of this series were quite low (72 mg/liter average) and no difficulties were experienced with operation except on the first batch where it was found necessary to decrease the precipitation temperature from 60° to 20° because of decomposition of the H_2O_2. Because of the good results obtained with this process and since considerably higher product concentrations in each batch were to be obtained because of higher operating level of the pile as well as the fact that three 1/3 ton runs were to be combined for metathesis instead of two runs, it was felt that this method of isolation was more advantageous for Clinton operations than the former method of two concentration cycles in Room D followed by isolation from a small volume. This method was therefore used on all runs (with the exception of a few runs processed for special purposes) and with only a few modifications as discussed later in this section.

The procedure as used on the final runs at Clinton is outlined in the appendix. This includes several modifications of the original procedure which developed as studies progressed. However, a brief outline of the original procedure is given below to aid in understanding the discussion which follows.

(A) First filtration and precipitation.

1. $La(OH)_3$ cake formed by a K_2CO_3 assisted KOH metathesis dissolved in HNO_3 and delivered to the 204 Building.

2. Product cake solution filtered.

3. HNO_3 acidity adjusted to about 1N and H_2SO_4 added to make solution 0.2N.

4. Solution heated to 60° C. and H_2O_2 added in four portions, each portion over 30 minutes then digesting ten minutes, to make the total concentration 10%.

5. Solution cooled to 0° - 5° C. and the precipitate allowed to settle.

6. Supernatant decanted by means of a filter stick and saved for recycling.

7. Precipitate washed with 1N HNO_3.

(B) Final precipitation.

1. Precipitate dissolved in HNO_3 (10.6 cc. 60% HNO_3 per gram of product) and solution filtered.

2. Solution adjusted to 1N HNO_3 and H_2SO_4 added to make 0.2N.

3. Solution heated to 60° C. and H_2O_2 added in four portions as before to make solution 10%.

4. Solution cooled to 0° - 5° C. and precipitate allowed to settle.

5. Supernatant decanted and saved for recycling.

6. Precipitate washed with 1N HNO_3, washings saved for recycling.

(C) Final filtration and drying.

1. Precipitate dissolved in HNO_3 (10.6 cc. 60% HNO_3 per gm. of product).

2. Solution filtered and then dried in the tube in which it is to be shipped.

Note: All filter cakes are leached with HNO_3 and the leachings are saved for recycling.

Decrease of Precipitation Temperature - The first batch that was processed according to the procedure (202 - 203) was treated with 1/4 of the total amount of H_2O_2, according to the proposed procedure, at 60° C. over a period of 30 minutes. During this period, vigorous evolution of gas occurred, caused by the decomposition of the peroxide, probably catalyzed by the iron present. Since this occurrence made the process inoperable, laboratory investigations were conducted to find a procedure with which the decomposition of the H_2O_2 was less likely to occur. It was found that a satisfactory precipitation could be made at 20° C. by adding the peroxide slowly and continuously over a period of one hour followed by digestion at 20° C. for one hour. At this temperature the peroxide is much more stable and requires considerably more iron to catalyze the decomposition. The precipitate formed in this manner was found to settle sufficiently in 6 to 9 hours to allow separation by decantation, provided the solution is cooled to 0° - 10° C. in order to decrease gas evolution.

Variable Peroxide Precipitation Solubilities - The amount of product remaining in solution after precipitation with H_2O_2 varied considerably and showed no particular trend and no correlation, under the conditions encountered, with the concentrations of substances that were known to affect the solubility such as Fe, Zr, Bi, H_2O_2, and acidity. Laboratory invesitgations indicated that some of the product was oxidized to the plus 6 state during solution of the $La(OH)_3$ and that it was not reduced completely by the H_2O_2 during the precipitation settling time, because of the low temperature during precipitation (20° C.) and settling (0° - 5° C.). Therefore, in an attempt to prevent the oxidation during dissolving of the cake, part of the sulfuric acid normally added just before peroxide precipitation was used along with the HNO_3 to dissolve the cake, with the expectation that this H_2SO_4 might hold the product in the plus 4 state. However, no improvement in the situation resulted.

Further laboratory studies indicated that treatment of the cake solution with 1% H_2O_2 at 50° C. for 1 hour after addition of the H_2SO_4 then cooling to 20° C. and adding more H_2O_2 to make a total of 10% as previously would give lower and more consistent results. This was demonstrated on the last four plant batches processed and the results were good. No difficulty was experienced from decomposition of the peroxide at the elevated temperature although some gas evolution did occur.

Later, it was indicated in laboratory studies that treatment with 0.1M hydroxylamine at 20° C. for 1 hour would result in lower solubilities than the 1% H_2O_2 treatment, besides being the preferable method from the operational point of view (no concern over a violent evolution of gas and less operating time because of the elimination of the heating and cooling operation). Since the isolation of all regular plant runs had been completed by the time this method was devised, a demonstration could not be made on a regular plant solution. However, it was possible to demonstrate the operability of this treatment on the last batch of product picked up in flushes through the process equipment made as part of the final clean-up program. Although this batch was concentrated in Room D so that it could be processed through the small equipment in isolation, the concentration of lanthanum in the cake solution was about the same as on a normal batch. It was felt, therefore, that from the standpoint of operability at least, a fairly good demonstration could be made on this solution. The solution was run in two parts, one part being treated with 1% H_2O_2 and the other with 0.1M hydroxylamine. The solubilities were 60 - 70 mg/liter for the H_2O_2 pretreated solution and 49 mg/liter for the hydroxylamine pretreated solution.

Table 49 shows a comparison of recent results obtained with the different procedures together with some laboratory results on samples of plant batches.

Table 49

Effect of Prereduction on Peroxide Solubilities

Run Numbers	Fe (M)	Procedure	Solubility - mg/liter		
			204	Lab.-No Prered.	Lab-Prered.
268-269	0.0061	Normal	130	162	42
270-271	0.0117	"	207	203	109
272-273	0.0208	"	165	-	-
274-275	0.0064	"	68	-	-
276-277	0.0066	"	44	-	-
278-279	0.0078	H_2SO_4 with dissolving acid	141	-	-
280-281	0.0155	"	172	215	77
282-283	0.0107	"	92	75	80
284-285	0.0078	"	158	103	56
286-287	0.0094	1% H_2O_2 @ 50° C.	56	110	65
288-291	0.0061	"	55	89	74
292-293	0.0083	"	77	191	127
298-299	0.0078	"	82	-	-

Run	Prereduction Treatment	Solubility mg/liter
Lab. sample of 286-287	0.1M hydroxylamine @ 20° C.	29-39
Lab. sample of 286-287	0.25M	47-48
Lab. sample of 286-287	0.25N hydrazine	42
Lab. sample of 286-287	1% H_2O_2 @ 50° C.	86
1st half of flush - batch	0.1M hydroxylamine @ 20° C.	49
2nd half of flush - batch	1% H_2O_2 @ 50° C.	60-70

Note: Zirconium $<0.00002M$ in all of the above runs.

Decrease in $La(OH)_3$ Cake Solution Volume - A 33% decrease in volume of the $La(OH)_3$ cake solution was affected (starting with run 227) by not including the final Room D centrifuge bowl wash in the solution, but rather recycling the wash into the LaF_3 slurry of the next batch. A decrease in the amount of product remaining in the supernatant from the first precipitation and consequently a decrease in amount of product to be recycled was thus affected.

0.2M H_2SO_4 Wash on First Peroxide Precipitate - High waste losses were found in the wash of the first product precipitate. Because some indications of peptization were observed when 1N HNO_3 was used for this purpose (as evidenced by cloudiness of the wash solution), 0.2M H_2SO_4 was tried, resulting in much lower losses at this point. (Product in this wash was not actually lost since it was recycled as was the case with all other product solutions in isolation that remained after processing a batch. However, it was desirable to keep the amount of product to be recycled at a minimum for Clinton operations.)

Development of a Method of Drying the Final Product Solution for Shipment - After the final peroxide precipitate has been converted to the nitrate, by dissolving in HNO_3, it is necessary to concentrate the salt for shipment. This is done by evaporating the excess nitric acid from the solution in the container in which the product is to be shipped. The apparatus that was used for the first several batches at the start of operations in the 204 Building is shown in Figure I-3. The glass shipping tube containing the product nitrate solution was heated by means of a water bath and the vapors were removed from the tube by drawing air, previously scrubbed with concentrated H_2SO_4, through the vapor space of the tube. This method was very slow, requiring several days to dry each batch.

The drying process was speeded up considerably, by preheating the air used to sweep away the vapors. This was done by passing the air through a coil of small stainless steel tubing set in the water bath. However, the time necessary for drying still was greater than desired.

Therefore, a new apparatus was devised which allowed higher temperatures to be used on the drying tube. This employed an electric furnace instead of a water bath for heating the tube. A separate furnace was used to preheat the air. (See Figure I-4.) Also, it will be noted from the diagram that the glass assembly at the top of the drying tube was so arranged as to allow additions to solution to be added by sucking portions from another container without the necessity of opening the tube and pouring the solution in as was previously done.

Using temperatures of 130° - 140° C. on the inlet air, 120° - 125° C. at the top of the stainless steel cup and 100° - 110° C. at the base of the cup, evaporation rates of 15 - 20 cc. per hour were obtained, during the major portion of the drying period. The use of higher temperatures than these, particularly at the end of the drying period, are likely to cause foaming of the material. Total drying time was thus reduced to 30 - 40 hours. It was noted on several batches that crystallization of the product salt occurred during drying and in these cases the final stages of the drying was more rapid than when crystallization did not occur.

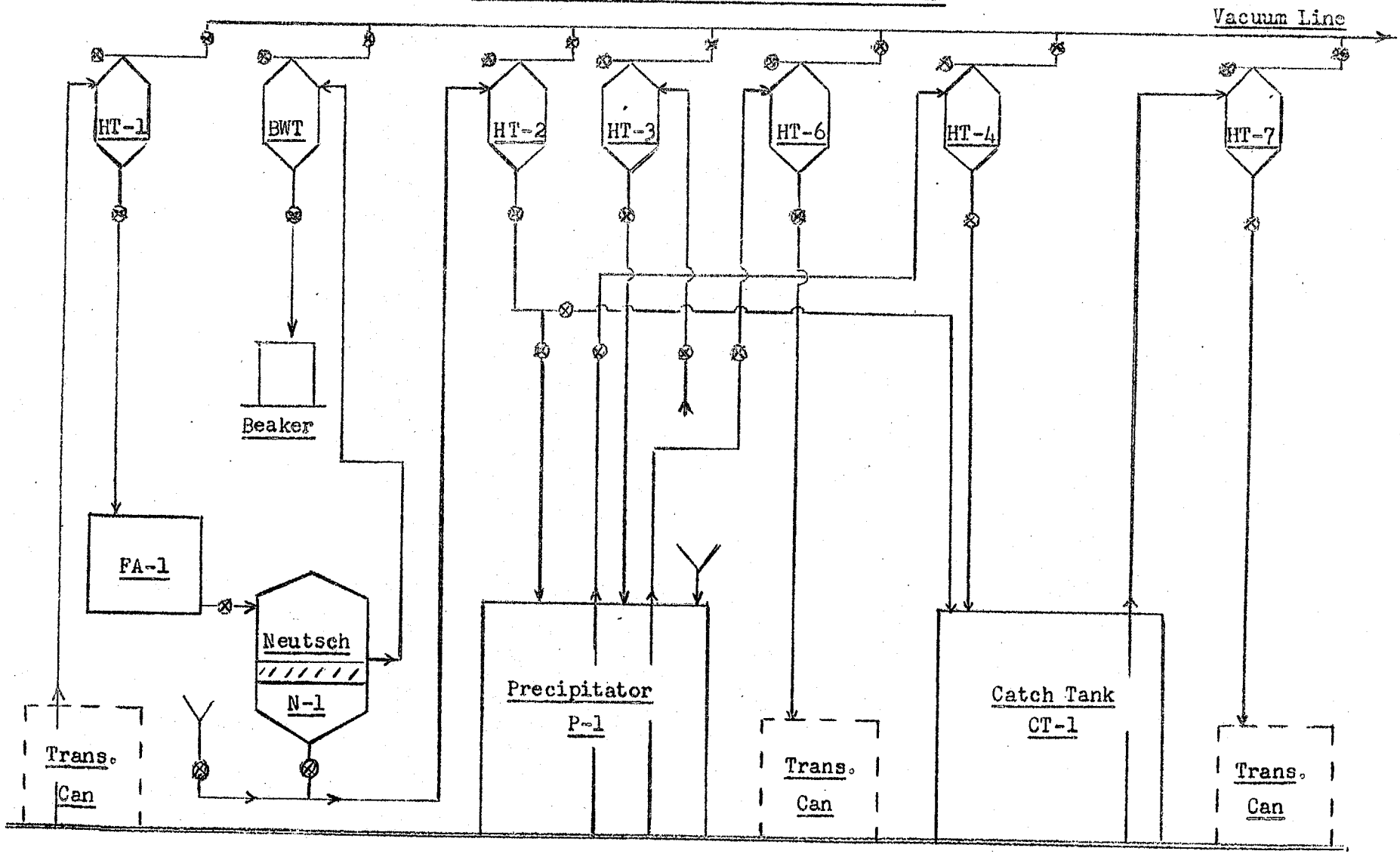
Product Hold-Up in Isolation Equipment - It was found that with stainless steel equipment considerable amounts of product were held up on the first few runs, probably adhering to the surfaces. After the surfaces had become "saturated", good recovery was obtained on an average, although occasionally on individual runs, considerable amounts might be held back or picked up which cause considerable variation in material balances for these batches.

It was found that this product held up could be easily removed by 60% HNO_3 flushes.

Product was also left in the large precipitator in variable amounts, because of the difficulty of washing under the disk-type agitator in this tank. This situation was improved considerably by replacing the disk-type agitator with an agitator having four vertical blades.

Figure I-1

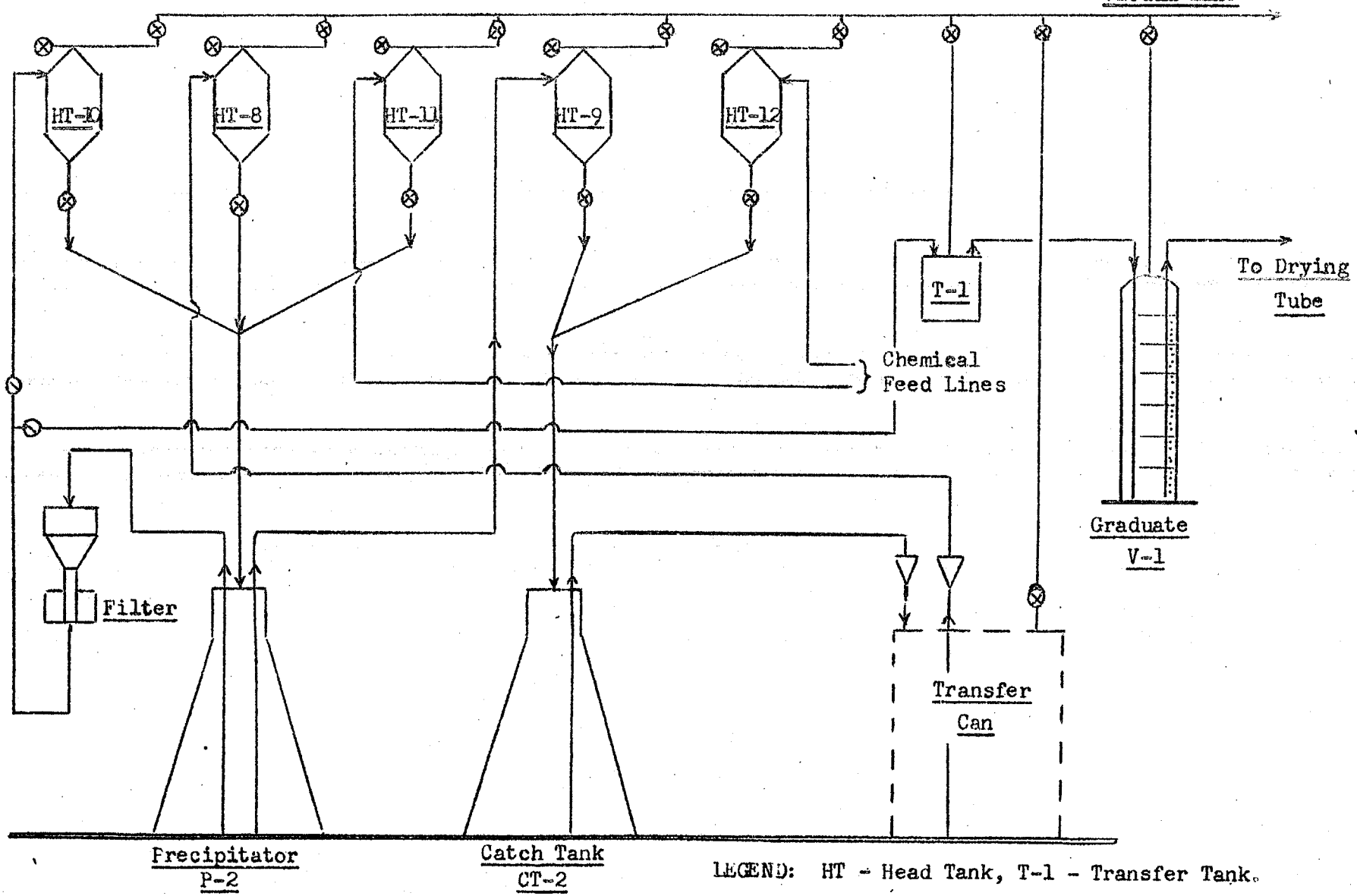
ISOLATION - FIRST PRODUCT PRECIPITATION



LEGEND: HT - Head Tank, FA - Filter Aid Tank, BWT - Backwash Tank.

Figure I-2

ISOLATION - SECOND PRODUCT PRECIPITATION



LEGEND: HT - Head Tank, T-1 - Transfer Tank.

Figure I-3

DRYING APPARATUS
BLDG. 204

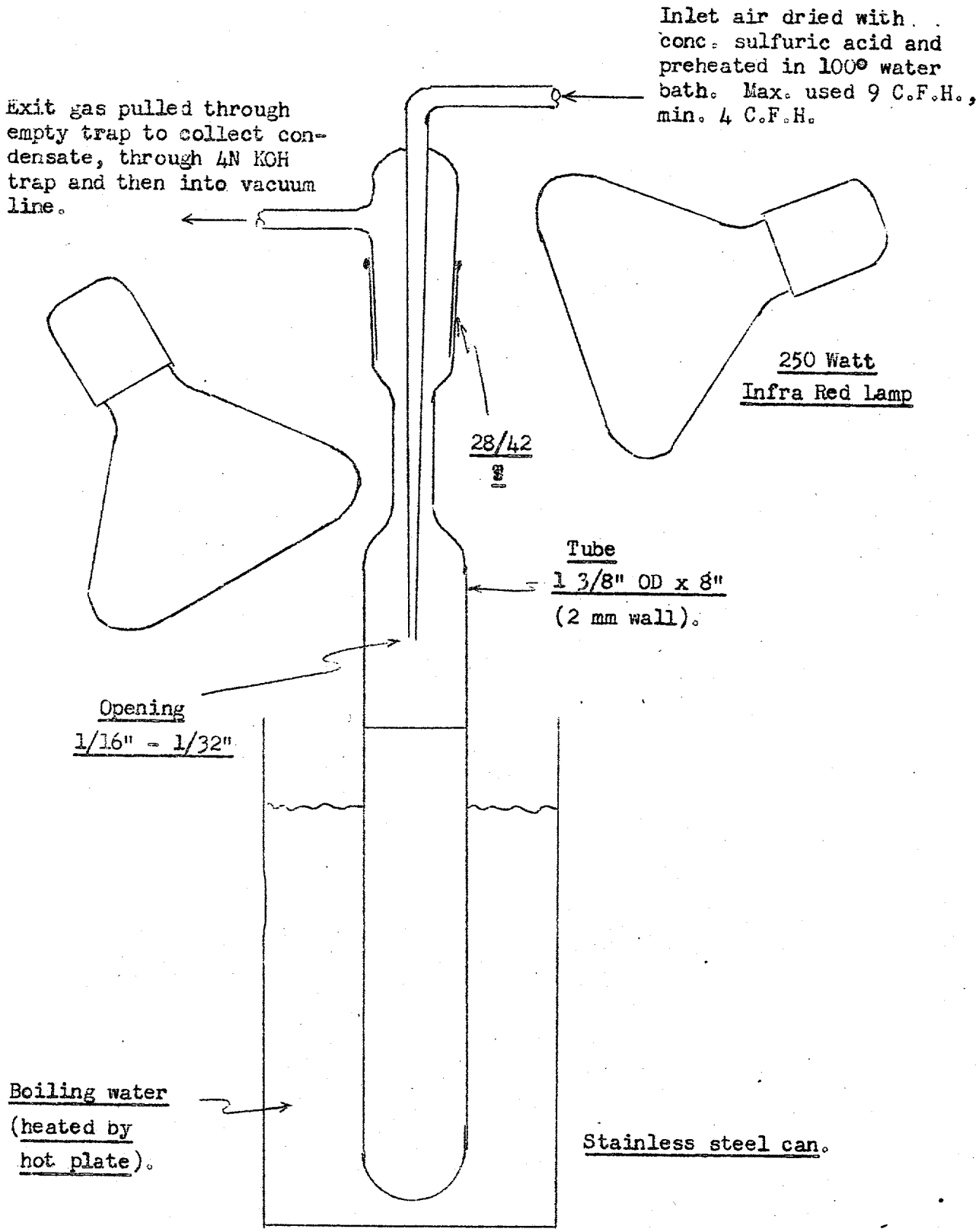
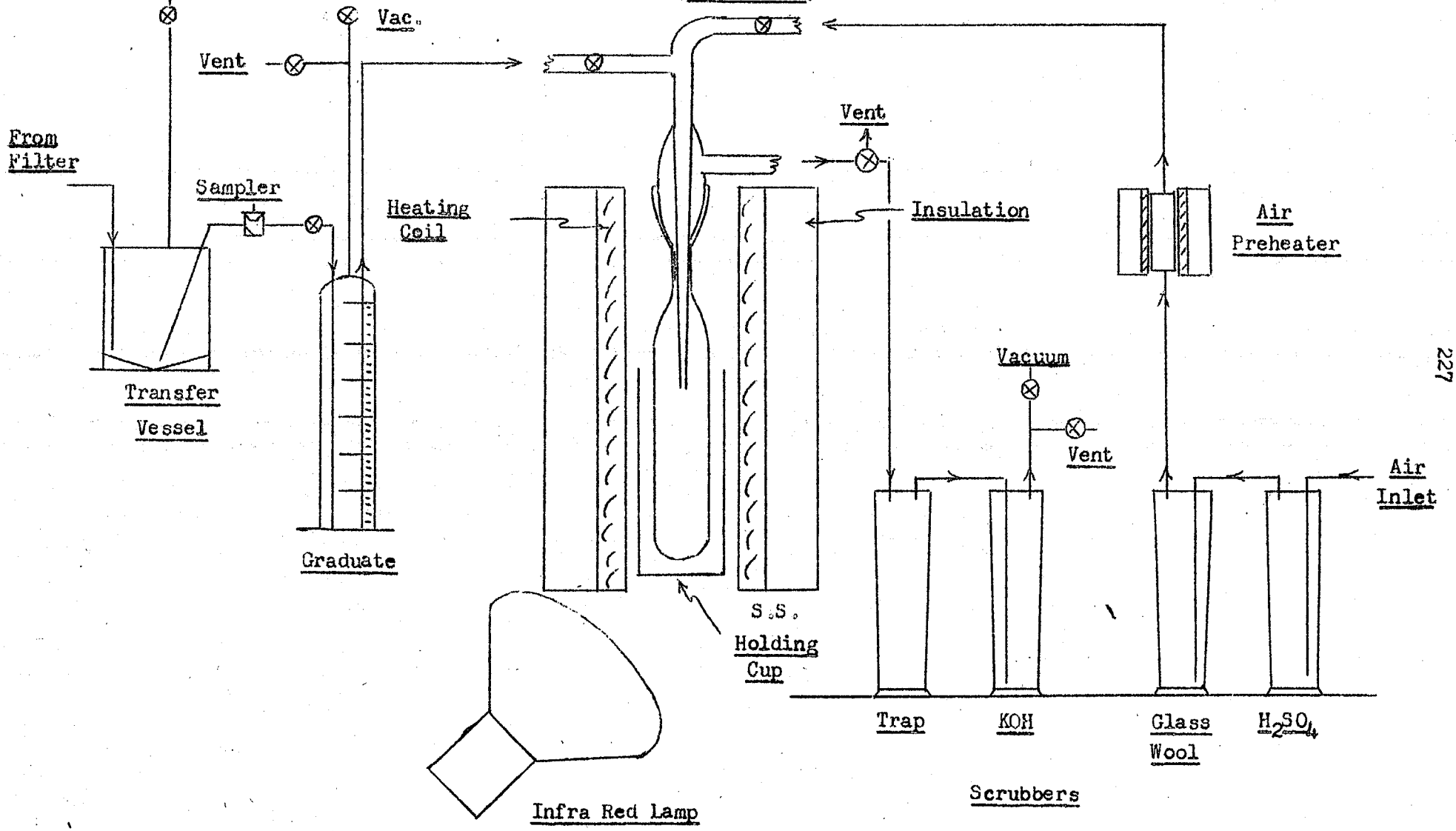


Figure I-4

DRYING APPARATUS - BLDG. 204

(ELECTRICAL)



V. RADIATION HAZARDS AND DISPOSAL OF RADIO-ACTIVE WASTES

The problems involved in handling radio-active chemicals in the separations plant during the last months of operation are discussed below. A review of chemical hazards is not made since the original report covers this subject and no real additional problems were met. Ammonium fluosilicate, a new chemical to the process, was handled safely in the dry and solution states using rubber gloves and goggles where deemed necessary.

A. RADIATION HAZARDS.

A summary of the radiation hazards encountered during the first nine months of 200 Area separations processing, as well as the detection equipment used and steps taken to minimize exposure of personnel, are discussed in the original section of this report devoted to Radiation Hazards. The last few months of operation found increasing emphasis being placed upon prevention of personnel exposure to alpha radioactivity emanating from product. During this period the product isolation steps were carried out in the 204 Building under 200 Area supervision and the process to be used at Hanford was developed and adequately demonstrated. The additional processing steps required for product isolation deserved and received the development of more sensitive detection instruments for product activity, as well as the adoption of the most rigid operating techniques and evolution of safe processing hoods and equipment. Further refinements were also incorporated into Room D equipment to minimize product hazard potentially present during the metathesis operation and the decomposition step carried out on supernatant returned from the hydrogen peroxide precipitation steps.

Discussion of radiation hazards in this supplementary report is accordingly largely confined to the major efforts made to protect personnel from product during the operating period. Further and more detailed review of the numerous steps taken to decontaminate all processing equipment and rooms of all forms of radioactivity following cessation of operations, will be found in the section dealing with this work.

Protective Measures in Room D - The completion of adequate ventilating facilities and equipment for remote operating control of the Room D process behind a full barricade resulted in essentially complete protection of personnel. Numerous air tests made on the operating side of the barricade revealed practically no product in the air and tests made on the equipment side of the barricade were in most cases less than 5% of tolerance.

Shortly after the additional protective facilities were installed in Room D, the process was changed to demonstrate Hanford procedure. This eliminated the concentration cycle in Room D in all but a few special runs, and permitted delivery of product to the Isolation Building direct from the larger equipment following metathesis. Beta and gamma radiation were held well below tolerance limits during the metathesis operation in spite of higher operating levels by virtue of improvements in decontamination obtained prior to delivery to Room D. High electroscope readings were obtained, however,

against the stainless steel carrier used for movement of nitric solutions from Room D to the isolation room. The readings varied from 3 mr/hr. for runs made from metal discharged from the pile 38 days before and decontaminated with two $BiPO_4$ cycles, to 180 mr/hr. for runs subjected to only 26 days metal cooling and one $BiPO_4$ cycle treatment. This source of radiation was recognized at all times, exposure times were kept short, and there were no cases of meter discharge attributable to the handling of these solutions. As great care was exercised by isolation personnel and ring film meters worn on the fingers of the men disclosed no cases of overexposure.

The use of one of the 55 gallon tanks in Room D for decomposition of the product peroxide supernatant prior to being recycled to the cell process, required further improvements to prevent the spreading of alpha activity behind the barricade. Pouring from the 5 gallon transfer cans with attendant spill possibility was eliminated by installing an air jet to permit jetting directly into the tank. Air tests during the jetting operation proved to be above tolerance and were reduced to less than 10% of tolerance by increasing ventilation on the Room D tank to maintain negative pressure at all times. The additional precaution was taken of requiring the operator to wear an Army assault type gas mask equipped with a special dust filter while behind the barricade during the jetting process.

The protective measures described above were accompanied by frequent Pluto surveys made by the Health-Physics Group and operating supervision. Whenever external surface contamination was observed immediate steps were taken to remove it by wet methods. When scrubbing with soap and water failed, the use of chemicals was resorted to. Ucilon paint was successfully applied to the floor to cover alpha activity at times when cleaning methods failed.

Protective Measures in Product Isolation Work - Preventative measures taken to avert exposure of operating personnel to product are presented below in detail. In general, the information is not intended to include equipment development work which is discussed in Section III of this report, but is confined to a review of survey work and other measures taken to assure safe operation.

1. Product surveys and hand counter checks.

The Health-Physics representative stationed in 204 Building made frequent air tests in the room as well as in the hoods using precipitrons. These showed that alpha activity in the building air did not increase in general over background from the time that the building was put into operation. Some high results recorded from time to time have been traceable to minor spills or handling of product contaminated equipment without adequate precautions. High readings were obtained near the hooded sink used for washing equipment although these rarely were above 25% of tolerance (5×10^{-10} micrograms of product/cc of air being considered tolerance when breathed 40 hrs./week for 1 year. See CH-1433.). Readings of 30% above tolerance were obtained at a time when inadequate draft was maintained for a short length of time on the hoods, however,

no other similar occurrence was observed.

As soon as isolation processing became routine and the men gathered experience in the work involved, an improvement in air samples, smear tests and Pluto surveys was noted. Positive smear tests outside of the operating hoods became rare and were confined to the immediate vicinity of locations where small spills occurred. These were successfully cleaned up in all cases using sulfuric acid on glass wool followed by water as soon as possible following detection. Frequent Pluto surveys, combined with extreme care in work habits were essential factors in preventing contaminating spills.

The new type alpha hand counter with about 15% geometry assisted materially in reducing the activity level on gloves and hands. The benefit was gained in being able to make frequent and reliable hand checks with an instrument showing high counting rates for even slight alpha contamination. With this as an important factor the records show a decided downward trend in total counts on operators' hands and gloves even as the amount of product processed in succeeding batches increased. The hand checks made showed uniformity between the various men in relation to the particular operations performed prior to counting. Glove counts were higher following sampling or transfer of liquids into or from the Room D transfer cans as well as when cleaning operations were performed. Work with peroxide solutions also resulted in alpha contamination whenever uncovered containers were used. In any event, during the final weeks of operation most of the hand counts showing activity above background were between 0 - 700 disintegrations/minute, with less than 10% showing 1500 - 3000 d/m and none above 4000 d/m. Between 75 - 100 checks were made each week, normally following a thorough scrubbing using surgeon's technique and Lanokleen soap.

The hand counter also proved extremely useful in checking wearing apparel and movable equipment since it was much more sensitive than Pluto in detecting slight activities (0 - 1000 d/m).

During the final clean-up operations (discussed in Section VI of this report) the added advantage was gained of having the recently developed portable proportional counter alpha probe. This instrument had several important features not found in Pluto as enumerated below:

a. It was more sensitive and had approximately twice the range of Pluto.

b. It was not affected by ventilating drafts and was insensitive to mechanical vibrations and sound.

c. Being small in size (about the size of a 2-cell flashlight) and attached to an extension cord, it could cover areas inaccessible to Pluto. Large areas could be rapidly monitored.

d. The voltage could be lowered to detect alpha particles alone, or at higher voltages within the Geiger region it would pick up beta activity.

e. It was insensitive to external electrostatic fields.

2. Protective clothing for personnel.

Coveralls and rubber gloves were standard apparel for isolation operators, in addition shoes were changed when entering and leaving the building. Light weight rubber gloves, surgical or post-mortem, were found most suitable for the work; however, extreme care had to be taken to keep the gloves free from alpha contamination and to prevent wearing them inside out. The stamped size numbers and lettering was used to determine the outside of the glove and when these were worn or washed off, the glove was discarded rather than risk the possibility of reversal.

Whenever it was necessary for an operator to do work involving the breathing of air within a hood an air line hood was used. The hoods resembled the full vision rubber hoods usually provided in acid work, permitting free discharge of air around the shoulders. A satisfactory filter-reducing valve setup was devised to permit use of regular plant air for the purpose. Respirators, and perferably chemical warfare assault masks were used at times when workwas done in front of open hoods.

Work with product was not permitted whenever an operator had an open cut on his hands. All such injuries were treated at first aid and the Medical Department decision was respected on whether or not further work could be undertaken with proper dressing on the wound. Only two wounds occurred that could have been contaminated. Both were superficial and could be thoroughly cleaned to eliminate the possibility of buried product.

3. Cleaning of hoods and equipment.

a. Cleaning of contaminated glassware used in the process was a problem. Using a combination of chromic acid and soap washes reduced this potential hazard. In cleaning glassware to a counter background to permit work by the glass blower, it was found that a series of caustic and acid washes was the best. No method for decontaminating rubber tubing stoppers or plastic tubing was successfully developed. After prolonged contact with product solutions these materials were discarded rather than attempt to recover them. With the most stringent of cleansing operations it was not possible to decontaminate to a safe point. Under such treatment it was felt that the equipment was rendered unsafe to use. After cleaning glassware, it was found that a static charge developed on the surface of the glass which affected Pluto. Equipment showing a very low activity level on the hand counter would throw Pluto off scale in one direction or the other.

b. Hoods and stainless equipment.

All air taken into the 204 Building passed through two glass wool filters placed in series. However, in spite of the precautions taken to remove dust particles from the air, considerable dust accumulated in the various hoods. Some of this undoubtedly was brought into the building by personnel and through leaks, since the building was maintained under a slight negative pressure.

Removal of the dust presented a problem since it was found to carry varying amounts of product. Some efforts were made to reduce dust accumulation within hoods by weekly cleaning using cloths wetted with soap and water, however, this practice was discouraged as a routine procedure. The hoods in 204 Building were not suitably constructed to permit water hosing, however, Spindle oil (Prorex Oil C-Socony Vacuum) sprayed on all surfaces and subsequently removed using oiled cheesecloth proved quite effective in laying the dust and in removing product. 50 to 80% of the contamination was usually removed by the initial oil treatment and subsequent cleanings effected similar reductions, paving the way for final safe use of soap and water for removal of residual oil film and small amounts of product. One drawback found in the use of oil for cleaning was the fact that alpha counts were picked up by the hands even when protected by heavy gauntlet type rubber gloves, hence extreme care was required when wiping the surfaces. Hand contamination was greatly reduced when the practice was adopted of covering the hands with a generous layer of talcum powder prior to donning gloves.

During the final clean-up operation the use of a glycerin-liquid soap mixture was tried in place of Spindle oil with marked success. This mixture appeared to be as entirely effective in removing alpha contamination and had the additional advantage of being easily removed from surfaces with a wet cloth.

It is of interest to note that a thorough smear test survey made during the last runs and prior to any extensive clean-up work showed that probably 250 milligrams of product was spread over the total areas within the ten hoods. Contamination was greatest in those hoods in which work had been done using open vessels or where repeated sampling had been carried on.

4. Sampling technique.

Hand and hood contamination was found to result from sampling of the precipitation vessel equipped with the "W" type spoon. No real solution was found, however, the use of an ordinary eye dropper resulted in less contamination than micropipettes and was easier to use when drawing solution from sampling cups limited in capacity to less than that of the dropper tube.

B. DISPOSAL OF RADIO-ACTIVE WASTES.

In general the handling of radio-active wastes continued uneventfully during the last few months of separations plant operation. All metal or uranium containing waste from the extraction step was accumulated in the underground gunite storage, utilizing the additional facilities made available previously by removal of chemical wastes from W-7 and W-8. Discharge of by-product or chemical wastes from W-5 and W-6 into the settling basin and thence into White Oak Creek followed the pattern established earlier. No real

difficulty was encountered in maintaining the settling basin effluent well below the tolerance limit of 400 beta counts per minute per cc of water established by the Health Group on October 25, 1944 following discussion with Dr. J. G. Hamilton. Previous to this time a tolerance limit of 270 beta counts/min./cc of water had been adhered to and the increase in allowable activity permitted more rapid discharge of chemical wastes into the settling basin. Actually, calculations of the amount of activity previously discharged into White Oak Creek, monitoring of the mud, water and debris throughout the creek and the Clinch River had shown that a five-fold increase would have been permissible.

A flash flood on September 29, 1944 caused White Oak Creek to overflow the stream bed and for two hours a heavy flow of water surged over the north-east corner of the settling basin dyke. This rapidly filled the basin and caused overflow at the south-west corner; however, the numerous samples taken at the time of overflow and following return to normal conditions showed no significant increase in radioactivity outside of the basin proper. Shortly after this occurance the White Oak Creek bed was straightened and deepened to prevent future flooding of the settling basin.

Volatile Wastes - Periodic monitoring of the dissolver off-gas was continued, however, no significant increase in active zenon or idodine was shown in spite of the larger batches processed. The reliability of the monitoring equipment was not felt to be too great. Atmospheric surveys made by the Health Group showed a slight increase in radio-active content in the air while 200 Area dissolvings were in progress, still all readings did not increase to more than about twice background for natural radioactivity revealing no real cause for concern.

Metal Wastes - The filling of Gunite storage tanks W-9 and W-10 with metal waste made it necessary to utilize W-7 and W-8 for additional capacity. An attempt was made to "date" the age of waste stored in the respective tanks as an aid for sampling purposes in connection with metal recovery development work. W-9 was used for intermediate storage, receiving waste from W-4, and steam syphons and lines were installed for transfer to W-7 and W-8, W-10 being filled by overflow from W-9. The various tanks became full as follows:

W-10 - August 27, 1944 (11'-8")

W-7 - October 1, 1944 (11'-10")

W-8 - December 10, 1944 (10'-4")

A tank inventory taken on January 21, 1945 showed that in addition to the above storage, W-9 contained 4'-5" of waste, W-4 held 2'-10" of waste, largely consisting of sludge, and W-3 was empty.

Chemical Wastes - Gunite tanks W-5 and W-6 remained in service as treatment and settling tanks for chemical wastes prior to discharge at a uniform rate into the settling basin. The addition of 300 - 400 lbs. per day of $CaCl_2$ to W-5 was continued in order to precipitate a considerable amount of the radio-active constituents. The rate of discharge from W-6 was controlled to maintain reasonable outage in the storage tanks coincident with the greater waste volumes resulting from the processing of larger batches in the 205 Building.

Late in October, 1944 a steam syphon and line was installed to empty W-5 via W-6, however, water samples taken from the lower dam in January, 1945 by the Health Group and assayed by the Analytical Group showed a perceptible rise in the barium and strontium content of the radio-active components. Since the possibility existed that sludge from both tanks might be entrained with supernatant when low levels existed in the tanks, final efforts were not made to leave both tanks empty. The syphon and line between W-5 and W-6 was dismantled and in any future operations W-5 will normally overflow into W-6 to minimize forward movement of the sludge.

In further explanation of the chemical analyses made on dam waters during January, 1945, it should be stated that although these showed the radio-active constituents to contain 20% barium and 60% strontium as opposed to 10% - 30% for both elements in previous analyses, the total radioactivity was so low as to cast considerable doubt on the analytical accuracy. The tolerance value of $3.3 \times 10^{-3}\mu$ curies/cc of water for strontium (when the water is consumed regularly for one year) established by the Health Group was usually bettered by a factor of 10 to 100 and was approached only for short periods where flood conditions were extant and activity absorbed in the creek bed clay tended to wash downstream.

The latter condition led finally to adoption of the more conservative operation of waste tanks W-5 and W-6, although it was also recognized that overflow of the W-11 holding tank onto the surrounding terrain late in November, 1944 resulted in gradual seepage into White Oak Creek. The contents of the tank, used by the Research Group, no doubt originated in 706-C and consisted of radio-active chemicals subjected to only short decay periods following discharge from the pile.

The growth of algae within the settling basin presented a problem since it formed on the floor of the basin and in rising to the surface entrained considerable radio-active material. This created local areas of high radiation levels (50 - 100 mr/hr.) where the algae floated and in addition resulted in the presence of active precipitate in the discharge waters. Turbulence caused rapid breakdown of the growth and settling of the precipitates in the creek bed, however, it was felt best to minimize this contamination and baffles were installed at all of the outlet weirs to prevent escape of algae. Early in November, 1944, the algae growth was effectively destroyed and additional growth did not occur during the remainder of the operating period. 200 gallons of 37% formaldehyde was added to the basin inlet water over a period of eight hours to give a concentration of about 30 p.p.m. and the flow of water was diverted around the basin for three days to permit effective killing.

Table 18 tabulates representative data showing the activity present at various times in the settling basin inlets and outlets, as well as at the White Oak Dam. The higher radiation readings recorded on the settling basins are due in part to surface algae, but largely to accumulation of sludge in the adjacent weir. No known instances of personnel exposure resulted from these sources, however, when operations were completed the sludge was removed from the inlet weirs, dropping the activities on the walkway to tolerance ranges.

Table 19 presents additional information on mud activity surveys made along White Oak Creek. It will be noted that samples of accumulated scum and algae from the White Oak Dam were 150 - 210 times higher in activity than corresponding mud samples.

Table 18

Activity of Water at the Settling Basin and White Oak Dam

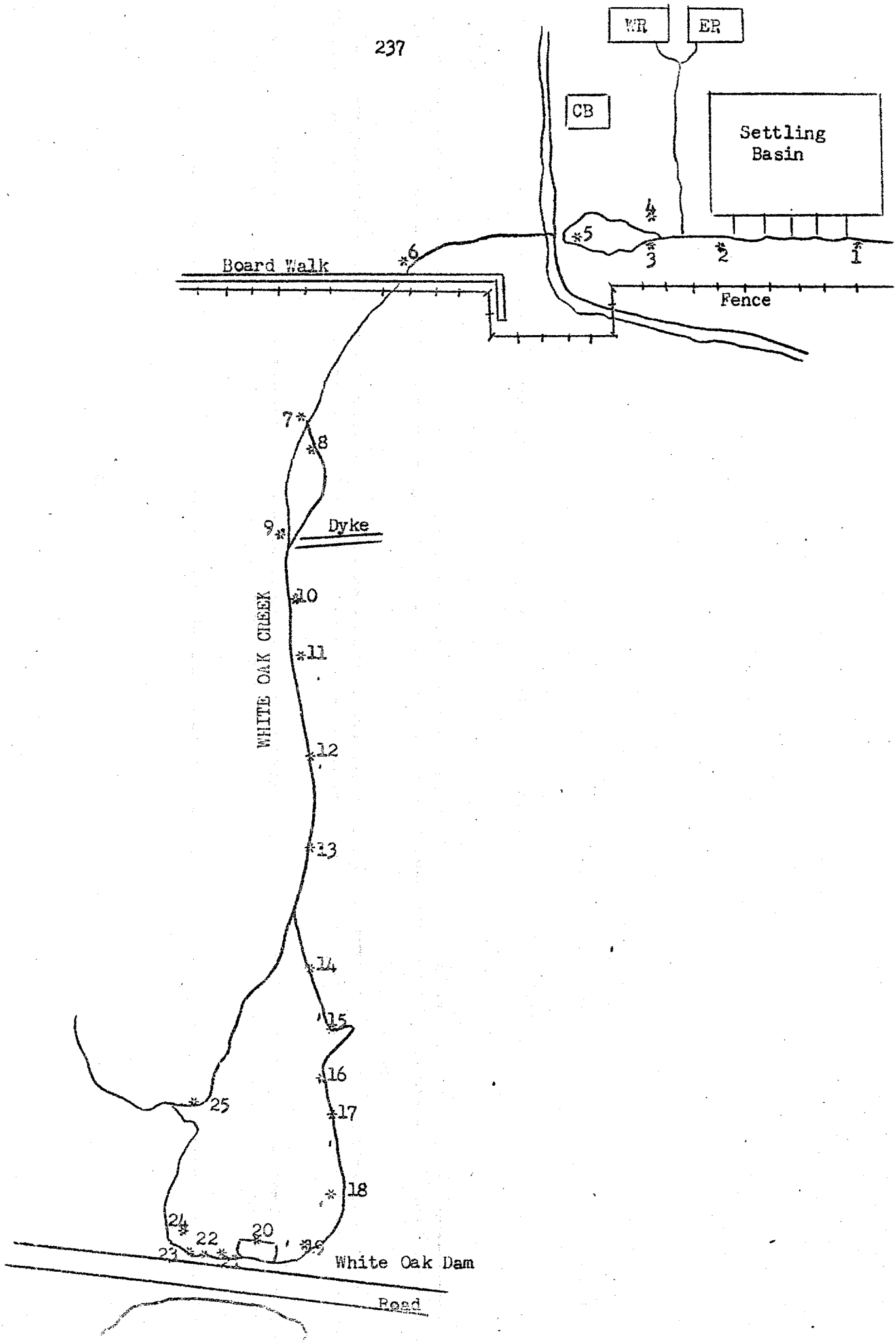
Date	Sample Source	Settling Basin - mr/hr. Water	Settling Basin - mr/hr. Radiation to Walkway	Dam Water mr/hr.
9-1-44	Inlet		6	
	Outlet		3	
9-15-44	Inlet		11	
	Outlet		12	
9-29-44	Flood covered and flushed settling basin			
10-2-44	Inlet	0.76	20	0.004
	Outlet	.30	7	.004
10-28-44	Inlet	.03	90	
	Outlet	.87	15	
11-6-44	Inlet	4.36	171	
	Outlet	.47	39	
11-11-44	200 Gals. of formaldehyde added to basin			
11-15-44	Inlet	12.27	136	
	Outlet	.84	33	.02
12-26-44	Inlet	.99	155	
	Outlet	.36	15	.01
1-26-45	Stopped $CaCl_2$ addition			
1-27-45	Stopped W-6 jet to basin			
1-27-45	Inlet	.02		
	Outlet	.08		.04
1-28-45	Inlet		166	
	Outlet		14	.06
1-30-45	Inlet	.06	185	
	Outlet	.05	16	
2-3-45	Inlet	.07	213	
	Outlet	.04	16	
2-7-45	Inlet	0.00		
	Outlet	0.00		
2-13-45	Heavy rain - 2.93 inches			
2-14-45	Inlet	.08		
	Outlet	.01		.05

Table 19

Activity of Mud From White Oak Creek - $\mu c/gm$ of Dry Mud

Key to Sampling Spots	8-25-44 $\mu c/gm$	9-29-44	11-3-44	11-11-44	11-20-44	12-27-44	1-19-45	1-26-45	1-27-45	2-13-45	2-15-45
1	1.5×10^{-1}	Flash flood described in the text occurred on this date.		200 gals. of formaldehyde added to the settling basin.				End of addition of $CaCl_2$ to W-5.	W-6 jet to settling basin off.	Rainfall of 2.93 inches.	
2					7.8×10^{-4}		1.9×10^{-3}				
3	1.1×10^{-2}										
4	2.7×10^{-2}										
5	-						3.4×10^{-3}				2.9×10^{-3}
6	3.7×10^{-3}				8.0×10^{-3}		2.3×10^{-3}				1.0×10^{-2}
7	1.3×10^{-3}		1.3×10^{-1}		4.9×10^{-2}	3.3×10^{-2}	5.4×10^{-3}				8.4×10^{-3}
8	5.6×10^{-2}				1.4×10^{-1}	2.9×10^{-2}	9.3×10^{-3}				
9			3.6×10^{-1}		2.8×10^{-1}	5.9×10^{-3}	5.0×10^{-3}				7.9×10^{-3}
10	5.9×10^{-2}										8.4×10^{-3}
11											2.6×10^{-2}
12	2.5×10^{-2}										
13	9.0×10^{-3}										
14							1.2×10^{-4}				
15	1.2×10^{-5}		5.1×10^{-4}								
16											
17	3.1×10^{-4}						2.8×10^{-4}				7.8×10^{-4}
18	2.8×10^{-4}		9.9×10^{-5}			9.3×10^{-2}*					
19					1.1×10^{-2}*	7.1×10^{-4}	1.7×10^{-5}				8.1×10^{-4}
20											
21	1.1×10^{-4}		5.9×10^{-4}		8.0×10^{-3}*	3.8×10^{-5}					
22							1.3×10^{-4}				1.2×10^{-4}
23											
24	5.4×10^{-5}		9.7×10^{-5}		1.1×10^{-4}	7.4×10^{-4}					
25	1.8×10^{-4}		2.6×10^{-4}		4.3×10^{-4}	9.2×10^{-4}					4.7×10^{-4}

*Scum and algae samples.


WR
ER
CB
Settling Basin
Board Walk
Fence
Dyke
WHITE OAK CREEK
White Oak Dam
Road
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2
3
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VI. CLEAN-UP AND DECONTAMINATION OF 200 AREA AFTER SHUTDOWN

A. CELLS AND PIPE TUNNEL.

Preliminary Clean-Up - Following the last processing of material through the area an extensive clean-up program was undertaken, the aim being to get activity levels from both product and fission products down to as low a figure as possible without going into too extensive and involved clean-up procedures. Tentative maximum levels for outside surfaces were set as 0.1 r/8 hours on beta and gamma radiation and 50,000 disintegrations per minute on product contamination as determined by Pluto or smear tests. Air contamination due to product was reduced to as near an absolute zero as possible throughout the operating area, including cells, pipe tunnels, operating galleries, isolation room and hoods.

The first step taken toward the clean-up was to remove any residual active material from the internal surfaces of the equipment. When dissolving the last regularly scheduled run, the heel of metal normally left in the dissolver was removed by adding additional increments of nitric acid until no further reaction was indicated by a rise in the specific gravity of the solution in the vessel.

Following this run the vessels and pipe line in the canyon were cleaned by flushing the equipment with a total of twenty washes using the following solutions: 60% HNO_3, 60% HNO_3 + 2% $(NH_4)_2SiF_6$, 25% caustic soda, and 25% potassium carbonate. Five of these flushes picked up enough product to warrant processing through Room D and product isolation. Readings taken at the approach to the doorways in Cells 1 and 2 were greater than 1000 mr/hour at the start of the clean-up procedure. Readings in the other cells were considerably lower. After flushing, the activity inside the cells was reduced to a level low enough to permit removal of the cell blocks and entrance into the cells for external cleaning and flushing. The acid flushes using $(NH_4)_2SiF_6$ proved most effective in cleaning equipment handling the $BiPO_4$ precipitates while the K_2CO_3 solution was the best cleansing agent for LaF_3 precipitates. Temperature of the solutions during the flushing procedure was maintained at 50° - 75° C. The usual program followed was to pass the solution continuously from the precipitator, through the centrifuge and catch tank and back to the precipitator, at the same time jetting intermittently from the centrifuge to the solution and oxidation tank and then back into the precipitator.

Table 1 lists the gross gamma counts in each flush just prior to its removal to the next cell or to waste.

In Table 2 are the electroscope readings in mr/hour in the doorway and at the base of each tank within the respective cells at the completion of each flush through the cell.

Table 1

Cell Flushes
Total Gamma Counts and Percent Product Recovery in Each Flush
(Percent Based on Normal Run)

Flush Number	Flushing Material	Cell 1		Cell 2		Cell 3		Cell 6		Cell 4		Cell 5	
		G's	%	G's	%	G's	%	G's	%	G's	%	G's	%
1	A		1.4	-	-	-	-	-	-	-	-		
2	B	1.5×10^8	2.8	2.5×10^{10}	17.3	2.7×10^{10}	21.0	*2.5×10^{10}	22.0	2.0×10^8			
3	B	2.8×10^8	.6	9.1×10^8	2.5	1.0×10^9	3.4	1.0×10^9	4.8				
4	B	1.2×10^8	.1	8.4×10^7		1.1×10^8	.1	1.0×10^8	1.0				
5	B	-	-	7.5×10^7	.2	8.9×10^8	3.5	8.5×10^8	3.0				
6	C	8.1×10^7	-	-									
7	A	-		3.5×10^7	0.0	2.2×10^7		2.3×10^7	.3				
8	B	9.7×10^7		1.2×10^8		4.3×10^7		5.3×10^7	.1				
9	D	-		-						*	10.0	8.8×10^6	15.4
10	B	5.8×10^7		6.0×10^7		1.3×10^8			.2				
11	D			-						*1.1×10^7		2.4×10^6	20.4
12	B	No samples taken											
13	D			-						*9.2×10^5	.2	6.4×10^6	4.4
14	B			1.5×10^7		3.5×10^7		8.4×10^6	.1				
15	A			2.2×10^7		5.9×10^6		6.4×10^6	.0				
16	A			-						2.3×10^6	.3	*1.4×10^7	10.3
17	B			1.5×10^7		4.9×10^6		5.0×10^7	.0				1.5
18	D							7.0×10^7				3.9×10^6	2.3
19	B			6.4×10^6									
20	C			3.9×10^6		7.1×10^6							

Process A - 60% HNO_3
B - 60% HNO_3 - 1.8% $(NH_4)_2SiF_6$
C - 25% NaOH
D - 25% K_2CO_3

*Cell in which processing for product recovery was started.

Table 2

Electroscope Surveys
mr/hr.

After Flush Number	Flushing Material	Cell 1		Cell 2					Cell 3					Cell 6				
		Drwy.	11	Drwy.	21	22	23	24	Drwy.	31	32	33	34	Drwy.	61	62	63	64
1	A	605	-															
2	B	160							46	60		83						
3	B	51	690							23		44						
4	B	15	122	34	58	70	275		8	10	11	60	18					
5	B							68		18		30		9	12	7	23	11
6	C	15	145															
7	A			31			165	37	5	48	48	100	48	6	2	4	13	6
8	B	7	100	25			350	39	7	8	9	53	15	3	14	3	16	10
9	D																	
10	B	9	62	30			400	34	7	9	8	52	22	<1	2	2	11	6
11	D																	
12	B	6	38															
13	D																	
14	B			43	52	76	780	36	6	8	9	47	16	2	2	3	10	5
15	A			27	40	285	165	36	4	7	8	41	12	2	2	2	10	5
16	A																	
17	B				41	48	185	35	6	6	6	29	9					
18	D								2	4	3	18	3					
19	B			12	18	27	105	33										
20	C			11	24	14	25	16										

Flush Number	Flushing Material	Cell 4					Cell 5				
		Drwy.	41	42	43	44	Drwy.	51	52	53	54
9	D	<1	6	6	15	5	<1	<1	<1	<1	<1
11	D	<1	3	4	12	3					
13	D	<1	3	3	16	3					

Flush Number	Flushing Material	Cell 7			
		Drwy.	71	72	73
1	A	78			
2	B	47			
3	B	41			
4	B	34			
16	A		22	32	27
18	D		24	31	48

Final Clean-Up and Decontamination of Cells and Pipe Tunnel - After the twenty flushes were sent through the cells, neutralized and sent to waste, or processed for product recovery if the product content was sufficient; the entire system from Cell 1 through Cell 7 was water flushed thoroughly. The cell blocks were removed and external clean-up of equipment, walls, floors, etc. was undertaken.

However, before any external cleaning was undertaken a set of B and G smear tests were taken amounting to 10 and 25 smear samples from each cell, each smear having covered approximately 2 sq. ft. of area on what appeared to be the most highly contaminated portions of the vessels, motors, walls and floors. A tabulation of these tests will be found in the accompanying B and G Smear Test summary (Table 3) which lists only the highest reading found in any particular cell from any one set of samples.

Table 3

B & G Smear - Summary

	Initial			Final
Cell 1	>50,000 c/m	27,136 c/m	7,020 c/m	384 c/m
Cell 2	>50,000	23,300	9,188	2,176
Cell 3	-	20,100	17,536	896
Cell 4	21,504	1,025	1,152	384
Cell 5	5,120	-	1,152	128
Cell 6	24,960	-	4,680	384
Cell 7	43,520	-	4,480	256
Pipe Tunnel	10,624	-	-	0

Note: All readings shown are the highest on any one survey. Each survey consisted of from 10 to 25 samples, each sample of 2" x 4" paper towel having been smeared over an area of two square feet, with heavy pressure. Smears were counted on a B and G foot counter.

Prior to entering the cells, except for survey purposes, each cell was given a hosing with a fire hose for periods which would correspond to more than eight hours constant hosing of any one cell.

Following the initial hosing operation, the cells were entered, while wet, and sprinkled with dry sodium carbonate. With the exception of the motors, which had been covered with tarpaulin, previous to the hosing operation, all exposed surfaces of vessels, walls and floors were sprinkled and permitted to stand overnight. Since at this point the condition of the cell air, with respect

te product, had not been determined; full protective equipment, including respirators, was required of those entering the cells. After several such treatments as described above, the cells were sprayed with a water solution of ammonium fluosilicate, allowed to stand overnight and rehosed the following day. In addition Cell 1 was sprinkled with flake potassium hydroxide and hosed intensely. During the course of the actions briefed above, every effort was made to complete a maximum of clean-up with a minimum of exposure time in the cells. It is difficult to say just which of these agents was most effective in removing B and G activity; although some further good was accomplished with the ammonium fluosilicate after the soda ash treatments appeared to have reached a point of leveling off. Thus, the major quantity of external contamination was removed before any considerable portion of the clean-up work, requiring entry of the cells, was undertaken. In fact all cells and the pipe tunnel, with the exceptions of Cells 1, 2 and 3, were below the arbitrarily specified tolerance of 5000 c/m, on B and G smear samples, at the conclusion of this phase of the work.

At this point a complete set of precipitron air tests were made in which the highest result of 5.86% of the accepted tolerance of 5×10^{-10} gms/cc of air was obtained in Cell 4.

On the basis of the data obtained following the clean-up procedure described above, it was felt safe to enter the cells for purposes of a more intensive clean-up, since by this time the air tests, B and G smear tests and electroscope surveys indicated that the allowable time ranged from 2 hours in Cell 2 to 4 to 8 hrs. in all other cells and the pipe tunnel. Each cell was then given a complete B and G survey, by means of a B and G walkie-talkie and a Lauritsen electroscope. These tests indicated that the majority of localized hot spots were contained in the badly corroded concrete drains; corroded concrete from tank overflows to drains; all tank overflow lines; other tank nozzles which could not be flushed internally either by normal or flush procedures; and the black iron couplings below the "Philly Gear Reducers" on the precipitators and solution tanks. The greater portion of these hot spots were reduced to a minimum through the use of alternate floor washes of Na_2CO_3 and HNO_3, soap and water scouring and repeated fire hosing. When no further progress was forthcoming on the reduction of contamination around floor drains, all badly corroded spots were resurfaced with fresh concrete. In the case of Cell 2 this reduced a reading of 100 mr/hr. to 35 mr/hr. Overflow lines in Cell 2 were sufficiently hot to warrant dismantling, blanking off and soaking internally, alternately with ammonium fluosilicate, nitric and caustic flushes. In the cases of Cells 1 and 2 it was found necessary to completely coat the exterior of all vessels with a paste of Na_2CO_3 and water. This was permitted to dry and upon hosing off, the B and G smear counts were reduced to a high of $<$2500 c/m in Cell 2. (See Table 3.)

During the initial stages of the clean-up, most emphasis was placed on the B and G decontamination. It was felt that in most cases product contamination would be accompanied by by-product contamination and hence a major portion of the product clean-up would be accomplished along with this clean-up. As each cell reached a point where all B and G readings were below an 8 hour working tolerance, or it was felt that further decontamination was impractical, the

cells were given a complete survey to identify the points of high product concentrations. The initial objective, so far as product contamination was concerned, was to accomplish a clean-up, such that no area covered by Pluto would give a reading of greater than 50,000 disintegrations per minute. The use of the newly constructed portable alpha probe was found to be quite helpful in locating areas which were rather generally contaminated, although at present the instrument itself is quite bulky and requires considerable time to move from cell to cell.

Prior to the cessation of operations in the 205 Building, it was pretty generally felt that the major product hazard was contained in the fluoride by-product and product Cells 4 and 5. Surveys taken during the clean-up indicated, however, that this was not the case. Although Cell 4 was found to be the most highly product contaminated cell, with one spot originally reading > 600,000 d/m (maximum Pluto detection), all the high spots were easily attributable to previous centrifuge outer spray gasket leaks. Cell 5, on the other hand, was, with the exception of Cell 1, found to be least contaminated with product.

The initial alpha survey of Cell 2 indicated that the entire area, including walls, ceiling, concrete piers, etc. in the vicinity of the centrifuge and precipitator was highly and very generally contaminated. The general area gave readings of about 50,000 d/m on the average, with localized points running as high as 135,000 d/m. In order to reduce this high contamination on walls and ceiling of Cell 2, it was necessary to hose the cell for approximately an eight hour shift from the lower cell doorway. On the isolated spots, the alternate use of nitric acid, sodium carbonate, soap and water and hosing brought all points down to < 30,000 d/m in all cells except Cell 4.

In the case of Cell 4, where the areas beside and beneath the centrifuge has been highly contaminated, hydrochloric acid was employed as a last resort. By this means, the high spot of > 600,000 d/m was lowered to approximately 250,000 c/m after which two heavy coats of paint were applied to an area at the base of the centrifuge A-Frame. This procedure made possible the reduction of product to where only three isolated spots in Cell 4 read approximately 50,000 d/m while all other areas in all cells were then < 30,000 d/m. More detailed information on product decontamination will be found in the accompanying Table 4 of Cell Pluto Surveys. Also a table showing alpha smear results of a smear survey made in conjunction with the original Pluto survey is included. It is readily noticeable that the alpha smear survey is indicative only of that contamination which is loosely adhered to the surface, while the Pluto and alpha probe surveys also pick up counts from material which is more deeply imbedded in corroded surfaces.

Table 4

Pluto Survey - Summary
(Including alpha smear samples vs. original Pluto survey)

	Initial Survey		2nd - Pluto & Alpha Probe	Final Pluto
	Smears	Pluto		
Cell 1	500 d/m	15,000 d/m	-	< 10,000 d/m
Cell 2	1,000	135,000	100,000 d/m	< 30,000
Cell 3	339	80,000	50,000	< 20,000
Cell 4	3,280	> 600,000	250,000	< 50,000*
Cell 5	1,680	26,000	< 10,000	< 10,000
Cell 6	1,117	50,000	< 20,000	< 20,000
Cell 7	452	185,000	70,000	< 30,000
Pipe Tunnel	-	> 600,000	< 20,000	< 20,000

The initial Pluto survey was accompanied by an alpha smear survey which failed to indicate more than about 5% of the activity picked up by Pluto.

*It was necessary to paint over an area of approximately 2 to 3 sq. ft. at the base of Cell 4 centrifuge A-Frame in order to reduce it to tolerance.

All readings are representative of the highest point of contamination located within the cell.

Upon completion of the product clean-up in each cell and with by-product contamination reduced to a minimum, the cell process line gaskets were removed. Several precipitron tests were made during the flange breaking operation, with the precipitron tube placed six inches from the broken flange. In no case did the air tests show greater than 10% of tolerance. Nevertheless the entire gasket removal job was completed with all personnel utilizing the Army assault type masks in order to insure against any possible product hazard. In addition to this precaution, the flanges were wetted frequently to prevent any dusting. As far as possible, gaskets were removed directly to a container which was sent to the burial ground. In view of the fact that, after completion of gasket removal and rehosing, the cell decontamination was equally as good as at the beginning of this phase of the work; it was felt that above procedure had proven worthwhile. Several of the gaskets which were removed, were checked with Pluto and found to contain product activity ranging as high as 50,000 d/m. No attempt whatever was made to decontaminate these as they were removed immediately to the burial ground.

At the conclusion of the decontamination work, all cell motors and centrifuge drive heads were removed and stored in the solution make-up room. The external surfaces of the motors were cleaned by operations and left in storage with no B and G smear tests showing > 5,000 c/m and no Pluto checks indicating > 10,000 d/m alpha activity. Indications are that, internally, the cell motors are quite contaminated; especially with product evidenced at the vent slots and motor fans. The responsibility for removing the internal contamination from all cell motors was placed with Maintenance and, with the assistance of the Health-Physics Group, will be accomplished along with the reconditioning of this equipment.

Tabulated below in Table 5 is a brief summary of the cell and pipe tunnel contamination as left in its final condition. The Lauritsen Electroscope readings shown are the highest readings found anywhere in that particular cell, and were taken with the scope window open in order to read as much soft beta activity as possible. The high reading of 170 mr/hr. in Cell 7 was found to be localized at a point on the chemical waste neutralization tank where precipitate had become deposited on the inner surface of a horizontal pipe used to brace the tank baffle. All other points in Cell 7 were < 60 mr/hr.

Table 5

	Lauritsen Readings - mr/hr.				
	Max. Point	Other Points	Maximum B & G Smears	Maximum Pluto Reading	Results of Last Precipitron
Cell 1	42	< 12½	384 c/m	< 10,000 d/m	.0 %
Cell 2	60	< 25	2176	< 30,000	1.82%
Cell 3	65	< 12½	896	< 20,000	4.38%
Cell 4	6	< 6	384	< 50,000	5.86%
Cell 5	12	< 12	128	< 10,000	2.37%
Cell 6	6	< 6	384	< 20,000	2.27%
Cell 7	170	< 60	256	< 30,000	3.41%
Pipe Tunnel	100	< 56	0	< 20,000	4.0%

All cells and the pipe tunnel were cleaned to a point where an eight hour working tolerance - 12½ mr/hr. - was attained or bettered, with the exception of a few isolated spots indicated below:

a. One spot on side of the dissolver.
b. Area above and around Cell 2 precipitator.
c. Cell 2 drain.
d. Cell 3 precipitator coupling.
e. Large chemical wastes neutralization tank in Cell 7.
f. Three floor drains in the pipe tunnel.

B. FINAL CLEAN-UP AND PRODUCT DECONTAMINATION OF ROOM D.

Tank Flushes - The entire system in Room D was given two 20% K_2CO_3 flushes followed by one 60% HNO_3 flush. The first flush warranted product recovery, while the second K_2CO_3 and the HNO_3 flush were discarded. Following these flushes the system was water flushed.

Tank Exteriors, Piping, Walls, Floor, etc. - Initial surveys of the room, prior to any external cleaning, indicated that no B and G hazard was involved and that the general area behind the barricade was contaminated with product to the extent of approximately 50,000 d/m on most points, this being 5 times the desired tolerance level in Room D.

This area was sprayed with 30% sodium carbonate solution, allowed to stand from 3 to 16 hours, neutralized with 60% nitric acid, and hosed down with water. The entire equipment side of the barricade was treated with a second Na_2CO_3 - HNO_3 application after which another product survey was made. With the exception of the area around the small equipment, practically all contamination was removed.

Further work was done on isolated spots on the concrete in the vicinity of the small equipment, employing several treatments of dry sodium carbonate followed by concentrated hydrochloric acid and hosing down. In spite of all efforts it was found impossible to reduce contamination in this area to the goal of 10,000 d/m. It was necessary to paint the concrete floor in this area with two coats of "Ucilon" in order to cover the remaining hot spots, of approximately 50,000 d/m, sufficiently to give tolerance readings of < 10,000 d/m throughout.

Tank Vents and Air Ducts - The section of 4" black iron pipe, constituting the Room D tank duct header, was dismantled, sprayed internally with Spindle oil and buried. Alpha smear samples taken from the ends of this section ran as high as 342,000 d/m. The remainder of the tank duct work, consisting of a 2" stainless line from each tank cover through the roof and formerly flanging into the 4" black iron duct mentioned above, was cleaned, blanked off at the roof outlets and left in position. These sections were alternately flushed with 30% Na_2CO_3 and 60% HNO_3 solutions. Since it was difficult to determine to just what extent the interiors of these ducts were contaminated, they are to be presumed dirty and shall be considered in a like category with the inner surfaces of the process vessels themselves.

Masonite air duct work, which provides room ventilation to that section of Room D which is enclosed by the barricade, was painted externally and left in position to provide a constant suction to Room D.

Miscellaneous Loose Equipment - All transfer cans, valves, jets, short lengths of piping and other processing equipment which could readily be dismantled, were digested for 16 hours in 60% HNO_3, then hosed with water. Contamination, on all such material, was readily reduced well below 10,000 d/m.

Motors and Gear Reducers - Exteriors of all motors and gear reducers were cleaned below tolerance. Oil was drained from the gear reducers and followed with a Cosmolene flush. The motor fans and interiors were left contaminated as it was not feasible to remove them from behind the barricade without considerable dismantling of the barricade itself.

Gaskets - Process gaskets were removed and buried. Flange faces were decontaminated by digesting in 60% nitric acid where possible or by the alternate application of Na_2CO_3 and HCl. Army assault masks were worn throughout the flange breaking phase of the clean-up. Precipitron tests made during this operation indicated the air ran as high as 365% of the allowable tolerance.

Portable "Lightnin" Mixers - The shafts were badly contaminated, but were readily cleaned with HCl. Exterior surfaces of the motors and gear reduction units were cleaned below tolerance and repainted. The interior of the motors must be considered as contaminated equipment and as such will remain a permanent part of Room D equipment.

Painting - At the conclusion of the final clean-up, all black iron pipe braces, safety guards and the like were painted. The operating platform as well as the panel board at the barricade was also painted.

Final surveys of Room D indicated there was no contamination exposed, which gave more than 10,000 d/m. Inner surfaces of process lines and vessels as well as motor interiors are, however, contaminated.

C. ISOLATION BUILDING CLEAN-UP.

Processing Equipment - The initial decontamination steps taken in the product isolation room consisted of internal flushing of all equipment with nitric acid solutions at 35° - 50° C., recovering product where practicable. Two to four flushes were made with the last solutions picking up only negligible amounts of product in each case. 60% and 70% nitric acid were used followed by a solution of 10% nitric - 10% ammonium fluosilicate flush which removed only minor amounts of product. Since the equipment used in both peroxide steps was to be left intact, only a few internal checks were made for product, however, these tests showed that considerable residual alpha activity remained. It is estimated on the basis of probing within the larger precipitation vessel that about 2 to 3 milligrams of product may remain in the entire equipment.

The equipment formerly used for metathesis received two successive flushes using 60% nitric. Checks of the inside surfaces of open vessels with the new alpha probe showed sufficient contamination remaining to warrant dismantling of all the obsolete equipment. This was done, following external cleaning with Spindle oil, using assault masks and air line hoods, the individual pieces being wrapped in paper and then sent to the burial ground.

Hoods and Equipment Exteriors - Alpha smear tests made before decontamination work was started showed that about 250 mg of product had spread over the entire integrated surface of all hoods. It has been demonstrated, however,

that smears will not remove all of the alpha activity deposited upon even moderately rough surfaces; in addition hood surfaces had been painted from time to time to cover partial areas so it is felt that product contamination was somewhat greater than shown by the tests. Considerable dust had accumulated behind and above the transite ventilating panels as well as in the vertical transite ducts immediately above the hoods. This dust was shown to be rather heavily contaminated with alpha activity.

The following pattern of protective procedure was adhered to in all work carried on in hood decontamination:

1. Operators wore either air line hoods or Army type assault masks. Nose type respirators had not been adequately tested for radio-active work involving dust, hence were not used except as an extra precaution when no respiratory protection was deemed necessary.

2. Coveralls, caps and rubber gloves were worn.

3. All equipment and hood portions removed for burial were first wetted with Spindle oil and then wrapped with heavy paper either within or near the hood.

Following internal flushing of equipment vessels and lines, the transite top panels were carefully sprayed with Spindle oil and removed. At this point the upper hood region, including the vertical ducts, were covered with Spindle oil. Waste was placed in the duct openings and the upper hood given several treatments with Spindle oil followed by wiping with lightly oiled cloths. Wherever possible the false rear panels were similarly removed, and in hoods where equipment remained intact, oiled waste was forced through the inner compartments several times in succession to remove all active dust.

The remainder of the hoods as well as the equipment remaining in place were then cleaned with two, or at the most three, treatments of Spindle oil. Soap and water cleaning followed to remove residual oil films and dust. Readings below 1000 disintegrations/minute were sought at all points. A few spots remained and acetone was used successfully to lower all but a few spots to the established tolerance.

A number of the stainless trays in hoods 1 through 6 as well as the exterior of the neutsch did not respond to the standard treatments given to the hoods. Further decontamination work was carried out using H_2SO_4 and then K_2CO_3 followed by water washing, and in one instance chromic acid was also used when the other chemicals failed to reduce alpha activity.

When decontamination work became complete within all of the hoods, the transite duct work to the main stack was removed. As each section was removed, the ends were immediately closed with waste and then masked with paper prior to burial. As the initial vertical ducts above the hoods were removed the waste fell out of two pipes, scattering some active dust around the room. Pluto surveys failed to reveal any active dust in any of the piping beyond this point, hence Spindle oil treatments were not felt necessary, however, assault masks were worn. Alpha counter and probe checks subsequently made, failed to reveal any contamination on the workmen's hands or coveralls.

Final Clean-Up and Painting - During the removal of duct work from the building proper several precipitron air tests were made for alpha activity and showed readings varying from 25% to 60% and 490% of tolerance (tolerance being considered 5 x 10^{-10} micrograms of product per cc of air). These concentrations were considerably higher than others taken near hoods during clean-up operations when 12% to 32% resulted, and entry to the building was permitted only with assault masks. After thorough wet cleaning of the floor the air samples showed 4 - 14% of tolerance. Seven additional samples averaged 24% of tolerance. The interior and exterior surfaces of all hoods and other parts of the building showing alpha activity even in slight concentrations were sprayed with a glycerin-liquid soap mixture. This application proved highly effective in removing contamination and had the advantage over Spindle oil of being easily removed with wetted cloths.

A complete survey at this point with the sensitive alpha probe revealed slight contamination on only a few local areas within hoods. The floor and all other exterior surfaces were found to be clean and ready for final painting. Further efforts lowered all readings within hoods to 500 - 1000 d/m maximum with the exception of a few isolated spots including the strip across the back wall of hood 1A where 10,000 d/m remained (the probe used covered a field of 5.6 sq. in.). In addition, one process line elbow outside of hood 5 as well as one valve in hood 6 were disclosed to have leaked slightly during operation and could not be decontaminated. Both were left tagged, although two coats of paint lowered the elbow contamination from 50,000 d/m to 300 d/m.

Two coats of paint were finally applied to all interior and exterior hood surfaces and the floor was covered with one layer of Amercoat.

Final alpha surveys:

Following painting only three spots in the building showed readings above background on the alpha probe. These were:

1. The floor tray in hood 1 where the highest reading was 400 d/m.

2. The elbow outside of hood 5 referred to above - 300 d/m.

3. The valve in hood 6 also explained above - 10,000 to 20,000 d/m.

Final precipitron tests:

After completion of the final painting and just prior to locking the building for standby, three precipitron air tests indicated 22%, 8% and 8% of tolerance respectively. While these readings were not alarming, it does indicate the presence of contamination and for that reason full protective equipment, including an Army assault mask, will be required for personnel entering the 204 Building, until such time as the building is adequately equipped with a ventilation system.

D. STEPS TAKEN TO PLACE THE 200 AREA IN STANDBY CONDITION.

General - At the conclusion of operations in the separations plant, the area was placed in standby condition. Primary consideration was given to the possibility of starting up the area, at an indefinite date, on a process which might conceivably utilize all or any portion thereof. For this reason, in so far as was practical all equipment was left intact and in place. However, it was recognized that, in all probability, certain critical equipment would, out of the overall project expediency, be relocated at other more pressing locations.

Several portions of the area were left in operable condition, in order to afford facilities for other groups on the site. The 205 laboratory was left intact, including all necessary services, to provide facilities for the Research Group. The fan and stack area was continued in operable condition in order to provide adequate continued ventilation for the cells and Room D as well as to dilute volatile off-gases from Building 706-C. The 206 Waste Area was delegated to the supervision of the Technical Division, and operations continued in order that waste disposals from the 100 Area, 706-A and 706-C might continue uninterrupted.

Utilities - The 150 lbs./sq. in. steam supply header to the 205 Building was left on the main header in order that the supply to the 4" off-gas line jet might function as required by Building 706-C. The header valves were closed and tagged out, (1) at the individual operating boards, (2) ahead of the 18 lbs./sq. in. reducer which supplies jacket steam to the operating vessels, and (3) ahead of the reducer to the supply line for the cell and pipe tunnel heaters.

All radiator steam was left on the building with individual adjustments made to the radiators in order that the temperature of the building might be regulated. A steam tracer line was tied into the radiator steam and traced the supply line to the process water head tank.

The air supply to the 205 Building was left on in order to provide services for the control laboratory. All the individual header valves, other than those on the lines running to the laboratory, were closed and tagged out. The auxiliary compressor unit which was tied into the plant air system was left intact. It, however, was shutdown and tagged out at the discharge valve and starter switch, as it was no longer essential to the operation.

A filtered water supply to the building was left intact. The process water supply was shut off and the header blanked. In order that the process water head tank on the roof of the 205 Building might be kept filled at all times to prevent drying of the wood, a filtered water line was installed above one of the process water measuring tanks. This made possible the filling of the head tank whenever it was deemed necessary. With this installation it was necessary to by-pass the Solenoid valve in the head tank supply line, therefore the circuit to the Solenoid valve was broken.

It was necessary to continue the supply of raw water to the air-conditioning unit in Room G. However, the header valves to the lines supplying all outside safety showers were closed and tagged out to reduce the possibility of freeze-up's. Adequate signs were posted at each of these safety showers denoting that they were out of service. The header which supplied water to the cell hose oibb outlets was closed and tagged out to prevent freeze-up's of the lines in the cells.

Briefly, the 200 Area electrical shutdown consisted of de-energizing the 440 volt, 3 phase power circuit No. 2 feeding the 205 Building, tapping into the No. 1 circuit feeding Building 105 (in order to supply 440 volt, 3 phase power to those units which were to continue operating) and the cutting loose of the 440 volt, 3 phase power service to the 204 Building at the service drop line. These changes permitted the opening of the 440 volt circuit at 501-A Sub-Station in the interest of safety and at the same time made possible continued services to the units enumerated below:

1. 200 Area stack fan.

2. All facilities in Room G including the air-conditioning equipment, vacuum pump and auxiliary air compressor.

3. The emergency light plant, which also supplies power to Room F instruments in the event of power failure.

4. The 110 volt building lighting circuit was continued in operation, by disconnecting the lighting circuit to Cells 6 and 7 as well as various instrument receptacles from a No. 2 circuit 440/110 volt transformer and placing them on the 110 volt lighting circuit.

More detailed information on these changes was covered in the March 1, 1945 letter of B. C. Nylen to L. B. Emlet - "200 Area Electrical Shutdown". It was felt wise to caution that should in the future more lights and/or instruments be placed in service, the load on the 110 lighting circuit must be closely checked. Decisions should be reached on the desirability of retaining the Room G facilities and the fan motor on the No. 1 circuit.

Outside Area - The 4" off-gas line from the dissolver to the 200 Area stack was blanked at a point just above the 205 roof. This line was teed into the 2" off-gas line from the 706-C Building and, hence operations of this building could proceed without fear of interference from the stand-by equipment.

All miscellaneous material and equipment such as 5-gallon stainless steel small chemicals cans, sampler drip pans, measuring rods, and other devices which facilitated the operation of the 205 Building were cleaned and stored in the pipe tunnel. Those items which showed any indications of contamination were placed within a roped area marked, "Contaminated - Stay Out". However, all these items showed much less than the 8 hour tolerance of 12½ mr/hr. Each of the 3" stainless steel waste lines which led from the cells to either the metal waste or chemical waste storage tanks was blanked off at the cell outlets. This insured that no active solutions or gases

would inadvertently enter the cells. The line running from the chemical waste diversion box to W-7 was cut, flanged and blanked off in order to insure that the metal and chemical wastes were isolated.

Operations of the fan and stack area was placed under the immediate supervision of the 100 Area. It was felt that ventilation should continue on the cells and Room D at all times in view of the possibility of an increased product hazard. Should the ventilation of these areas be terminated for any considerable extent of time it was advised that frequent precipitron tests be made in order to determine the extent of the known to be existent hazard.

The roof of the 205 Building was thoroughly cleaned and indicated that all points were well below the specified 12½ mr/hr. However, since contamination was known to be existent, the entire surface of the roof was retarred with two applications. The stairways leading to either end of the roof were blocked with a 2 x 4 railing upon which was posted a sign reading, "No Entry Without Permission Of 100 Area Supervision".

Solution Make-Up and Operating Gallery - On completion of the cell clean-up, all scale tanks, make-up tanks, etc. in the solution make-up room, and operating gallery were water flushed. All lines were broken, gaskets removed, and flanges left bolted with two bolts. Excess stainless steel nuts and bolts, valve and flange guards, were nailed up in properly identified box and stored in the pipe tunnel. The surfaces of water and steam lines, and any other corrosive lines were painted.

Fuses were removed from all starter boxes and each starter was adequately labeled to facilitate accurate and ready replacement.

Cells and Pipe Tunnels - The interior of all processing equipment and lines throughout the cells and pipe tunnel were internally cleaned with the twenty flushes as described in Section VI-A of this report. Following this work, an extensive external clean-up of equipment, cell walls, floors, etc. was conducted as outlined in the detailed Clean-Up Procedure of Section VI-A of this report. A complete water flush then followed in order to remove any corrosive chemicals from both the interior and exterior of the vessels and cells. Gaskets throughout the entire area which had any contact with processing materials were removed and buried.

All lines were left loosely bolted with two nuts and bolts. Excess stainless steel nuts and bolts and other miscellaneous parts are stored in their respective cells in wooden boxes.

The Philadelphia gear reducer units were drained of oil, flushed with light Cosmolene and left filled with Cosmolene. No evidence was found which pointed toward contamination of the oil in these units, however, as an added precaution all the oil thus removed was buried. All motors were removed from the cells after external cleaning and placed in storage in the solution make-up room. These were known to be contaminated internally and as such were turned over to the Maintenance Department to be cleaned. The Maintenance Department was advised that as clean-up of these motors proceeds, extreme care must be exercised and additional health surveys made in conjunction with this work.

The centrifuge drive head units after cleaning were likewise removed, dismantled, cleaned by Maintenance and stored in the solution make-up room. To eliminate the possibility of damaging the jackets to the processing vessels which would occur through freeze-up's, at least one flange at the lowest point of the water supply to these jackets was broken for drainage.

It was necessary to dismantle the dissolver column during the cleaning operation. This was left dismantled and lashed to pipe lines in the corner of Cell 1.

During the inspection of equipment in Cells 3 and 4, it was necessary to remove all lines adjoining these centrifuges. After inspection these two centrifuges were left as such.

Final information relating to the Health surveys was posted behind each of the cells and pipe tunnel doors.

Concentration Room - The standby condition of the equipment in Room D very nearly parallels that of the cells. However, due to the impracticability of removing the motors from Room D (this would entail considerable dismantling of the Room D barricade) all motors were left in place. As pointed out in Section VI-B of this report these motors are known to be internally contaminated and must be respected accordingly.

The duct work which ties the barricade side of Room D into the main 200 Area cell duct was cleaned, painted, and left intact in order to provide constant ventilation of Room D. However, the black iron duct work formerly on the roof of Room D and servicing the ventilating system to the individual tanks was removed and buried. Those sections of this latter duct work, that is, stainless steel leads directly from the tanks, which were left blanked and adjoining tank covers were cleaned similarly to the interior of the Room D vessels themselves. It was felt that any work pertaining to these lines should be respected in the same light as the tank interiors, in so far as contamination is concerned. The room, both barricade and operating side, was padlocked with information relative to final health surveys having been posted behind the barricade door.

Isolation Building - 204 - Following the final clean-up of the 204 Building as detailed in Section VI-C of this report, the steam, air and water supplies to the building were closed and tagged out. The 440 volt circuit to the building was cut at the service drop line and the 110 volt lighting circuit was left intact with the switches thrown at the building. The building was padlocked and information relative to the final health surveys was posted on the bulletin board within the room.

VII. APPENDIX

A. FLOWSHEET OF SEPARATIONS PROCESSES AT CLINTON.

A flowsheet for run 286 is presented to show in detail the procedure followed in the demonstration of the two cycle runs. Although run 286 was made using ammonium fluosilicate alone in both decontamination cycles and barium sulfate scavengers in the crossover cycle, it was selected because it demonstrated well, both the 2/3 ton batch size operation and the processing of double cycle runs without the necessity for storing charges prior to the crossover step.

PREPARATION OF METAL SOLUTION

Cell #1

	Average Time in Minutes
A. Coating Removal (Basis - 2 charges of 2/3 ton each).	
1. Add 280 lbs. 50% NaOH and 533 lbs. water to dissolver (tank 11).	
2. Sparge with air and cool; add 358 lbs. 60% HNO_3 to dissolver at a controlled rate such that 11 temperature does not exceed 70° C.	
3. Cool to 30° C. and leave cooling water on; sparger off.	
4. Charge four buckets metal to dissolver.	
5. Control reaction rate by use of coil cooling water. Add 280 lbs. 50% NaOH at a rate such that maximum column pressure drop does not exceed 5" water. When column pressure and temperature in 11 start to drop, cut water off coils allowing temperature to reach 100° C., using 20 lbs. steam on coil as necessary. Digest at 100° C. for one hour.	127
6. Cool to 35° C. or below with coil water while sparging with air.	150
7. Jet coating removal solution to waste.	
8. Add 400 lbs. water to dissolver, air sparge for 10 min. and jet to waste.	
9. Add 400 lbs. water and 40 lbs. 60% HNO_3, air sparge for 10 min. and jet to waste.	68
	5 hrs. 45 min.

Solution Composition
(Coating Removal Solution)

NaOH	10%
$NaNO_3$	20%

B. Metal Solution (Basis - 2/3 ton metal).

1. Drop 800 lbs. 60% HNO_3 to dissolver, followed by 1/2 gallon line flush of water.
2. Add 534 cc. F.P. stock solution #4, followed by 1/2 gallon water flush.*
3. Drop 400 lbs. 60% HNO_3 to dissolver.
4. Add F.P. stock solutions (534 cc. each) to dissolver in this order: #1, 2, 3, 5, 6, and follow with 5 lbs. 60% HNO_3 flush.
5. Drop remaining 2060 lbs. 60% HNO_3 to dissolver and air sparge for 15 minutes.
6. Heat dissolver contents with 20 p.s.i. steam on coil and maintain steam unless column pressure drop exceeds 5" of water. If necessary, hold below 5" by water on coil. 92

*See page 140 for composition of each inactive fission product element stock solution. Amounts given in this table are for 1/3 ton charges. Therefore, quantities must be doubled for the 2/3 ton charges.

Run 286

	Average Time in Minutes
7. Hold 1850 lbs. of water in C-11 for drowning charge in event of necessity.	
8. Digest until Sp. Gr. of 1.79 is obtained, or for a total digestion time of 15 hours.	669 (11 hrs. 9 min
9. At end of digestion period, drop 1850 lbs. of water to dissolver and air sparge with 30 lbs. air while cooling with water on coil to 40° C. Air sparge for 40 more minutes.	
10. Jet 11 to 21.	120
	14 hrs. 41 min

Solution Composition

HNO_3	approx. 2.0%
UNH	50.0%

C. Dilution and Pre-Extraction Treatment.

1. Add 2000 lbs. water to dissolver and sparge.	
2. Dissolve 16 lbs. $NaNO_2$ in 10 gal. water and add to dissolver.	
3. Drop 1650 lbs. water to dissolver and air sparge 10 minutes.	
4. Jet 11 to 21.	42
	42 min.

PRODUCT EXTRACTION

Run 286

Cell #2

Average Time in Minutes

A. Product Precipitation.

1. Receive metal solution and dilution water from 11 to precipitator 21.
2. Add 1510 lbs. of water to 21. Adjust 21 temperature to 40° C., and agitate 1/2 hour. 135

$NaNO_2$	.026M	.14%

3. Adjust 21 temperature to 75° C. and add 540 lbs. 93% H_2SO_4 followed by 5 lbs. 60% HNO_3 line flush.
4. Add 259 lbs. 14% Bi solution.

14%	$BiONO_3$
52%	HNO_3

Add this solution rapidly and follow with 5 lbs. 60% HNO_3 flush.

5. Agitate 21 tank contents for 15 minutes and add 805 lbs. 75% H_3PO_4 uniformly over two hours.

H_3PO_4	73.5%
HNO_3	1.2%

6. Add 150 lbs. water to 21 tank and digest one hour at 75° C. after addition of all H_3PO_4.
7. Cool to 50° C. and leave cooling water on during the centrifugation. 305

7 hrs. 20 min.

Slurry Composition

HNO_3	0.24M	1.19%
UNH	.547M	22.0%
H_2SO_4	.50M	3.89%
H_3PO_4	.60M	4.66%
Bi	2.58	.21%

B. Product Separation and Washing.

1. Centrifuge at 870 RPM at full steam pressure. 95
2. When jet 21 to 22 gasses, recycle from 23 to 21 for period of 10 to 30 second and repeat four times. Finally recycle 1000 lbs.
3. After 5 min., skim 22.
4. Add 250 lbs. water to 21, jetting to 22 as it is added to 21.
5. Five minutes after completing (4), skim 22 and plug 22 to stop. 54

Average Time in Minutes

6. With 22 turning at 10 RPM, add 250 lbs. water through sprays at 70 lbs. pressure or higher. Bring 22 to 110 RPM, hold 2 min., and plug to stop. Repeat the latter operation twice.
7. Bring 22 to 870 RPM, hold 5 min. and skim. Plug to stop.
8. With 22 turning at 10 RPM, add 250 lbs. water through sprays at 70 lbs. pressure or higher. Bring 22 to 110 RPM, hold 2 min., plug to stop. Repeat the latter operation twice. 57

3 hrs. 26 min.

C. Product Cake Solution.

(NOTE: 1183 lbs. 60% HNO_3 for cake solution added to 24 immediately after oxidation of previous charge in order to dissolve any product that might have been left.)

1. Agitate 24 tank for one hour, transfer dissolving acid to 21. With 21 agitator running jet through 21 distributor for 30 min. with cooling water on jacket.
2. With 22 stopped, jet 350 lbs. acid from 21 to 22.
3. Bring 22 to 110 RPM, hold 2 min., plug to stop. Repeat twice.
4. With 22 stopped, jet 22 to 24 and start 24 agitator.
5. Jet 350 lbs. acid from 21 to 22.
6. Bring 22 to 110 RPM, hold 2 min., plug to stop. Repeat twice.
7. With 22 stopped, jet 22 to 24.
8. Jet remaining acid to 22. (If 22 weight exceeds 400 lbs., immediately jet excess acid to 24.)
9. Bring 22 to 110 RPM, hold 2 min., plug to stop. Repeat twice.
10. With 22 stopped, jet 22 to 24. 84
11. Air sparge 23 for 40 min., sample, jet to waste.

1 hr. 24 min.

D. Oxidation of Product Cake.

1. Agitate 24 for 2 hours at 50° C. (Do not exceed 50° C.)

HNO_3	9.44N	45.7%
$BiPO_4$	0.105M	2.45%

2. With cooling water on jacket add 300 lbs. water to 21 and distribute through spray for 15 min., holding temperature below 35° C.
3. Upon completion of 2 hour agitation of 24 and with 22 stopped jet 21 to 22, and 22 to 24 simultaneously. 145
4. Adjust 24 temperature to 50° C. and add 50 lbs. 10% $NaBiO_3$ followed by 80 lbs. process water.

Run 286

Average Time in Minutes
92
3 hrs. 57 min.

5. Agitate 24 at 50° C. for one hour and add 24 lbs. 10% $Na_2Cr_2O_7$.
6. Cool 24 to 35° C.

Solution Composition (in 24)

HNO_3	6.83M	34.6%
$BiPO_4$	—	1.93%
$NaBiO_3$	0.0108M	.244%
$Na_2Cr_2O_7$	0.0056M	.117%

DECONTAMINATION

First By-Product Precipitation - Cell 2

Average Time in Minutes

A. By-Product Precipitation and Cake Washing.

1. Add 6700 lbs. water to 21 and heat to 40° C. Receive oxidized solution from 24, and rinse 24 with 500 lbs. of water.
2. Heat 21 to 75° C. Add 25 lbs. 75% H_3PO_4 to 21 and follow with 10 lbs. water rinse. — 112

HNO_3	1.27N	7.6%
H_3PO_4	0.0214M	0.20%
$BiPO_4$		.425%

3. Digest 21 at 75° C. for one hour.
4. Cool 21 to 50° C. and leave cooling water on during the centrifugation. — 125

3 hrs. 57 min.

B. By-Product Separation and Washing of By-Product Cake.

1. With centrifuge at 870 RPM transfer slurry from 21 to 22 at full steam pressure.
2. When jet from 21 to 22 first gases, jet from 23 to 21 for 10 to 30 seconds. Repeat four times. Finally recycle 1000 lbs. Jet 23 to 31. — 70
3. Add 250 lbs. water to 21 and jet from 21 to 22.
4. Five minutes after Item 3, skim 22, and plug 22 to stop. Jet 23 to 31.
5. With 22 at 10 RPM add 250 lbs. water through sprays at 70 lbs. pressure or higher. Bring 22 to 110 RPM, hold 2 min. and plug to a stop. Repeat twice.
6. Bring 22 to 870 RPM, hold 5 min., skim and plug 22 to a stop.
7. Jet from 23 to 31. — 125

3 hrs. 15 min.

C. By-Product Cake Solution.

1. Add 1183 lbs. 60% HNO_3 to 21. With cooling water on the jacket distribute this acid through the spray, holding temperature below 35° C.
2. Jet 340 lbs. from 21 to 22.
3. Plug 22 to 110 RPM, hold 2 min., plug to stop. Repeat twice.
4. With 22 stopped, jet 22 to 71.
5. Repeat Items 2, 3, and 4.
6. Jet the remaining acid from 21 to 22. If 22 weight exceeds 400 lbs., immediately jet the excess acid above 400 lbs. to 71.

Run 286

		Average Time in Minutes
7.	Bring 22 to 110 RPM, hold 2 min., plug to stop. Repeat twice.	
8.	With 22 stopped, jet 22 to 71.	
9.	Add 125 lbs. water to 21 and distribute for 5 min. through spray.	
10.	Jet 21 to 22. Bring 22 to 110 RPM and plug to stop.	
11.	Jet from 22 to 71.	81
		1 hr. 21 min.

DECONTAMINATION

First Product Precipitation - Cell 3

Average Time in Minutes

A. Reduction in Precipitator.

1. Receive product solution and washes from 23 to 31.
2. Add 625 lbs. 17.6% $(NH_4)_2SiF_6$ to 31.
3. Add 650 lbs. 20.0% ferrous ammonium sulphate to 31.
4. Heat to 75° C. and digest for one hour. — 150

2 hrs. 30 min.

B. Product Precipitation.

1. With temperature at 75° C. add 215 lbs. 14% bismuth solution to 31 uniformly over 30 min., and follow with 5 lbs. 60% HNO_3 flush. Digest for 30 minutes at 75° C.
2. Add 950 lbs. 75% H_3PO_4 to 31. Digest for two hours at 75° C.
3. Cool to 50° C., leaving cooling water on during the centrifugation. — 265

4 hrs. 25 min.

Slurry Composition (in 31)

HNO_3	1.1N	6.5%
H_3PO_4	.62M	5.70%
$(NH_4)_2SiF_6$	.052M	0.87%
Bi	10N	.179%
$BiPO_4$	1.9 g./l.	.260%
Fe	2.77 g./l.	.146%
	.028M	.146%

C. Product Separation.

1. With centrifuge at 870 RPM transfer slurry from 31 to 32 at full jet pressure. — 103
2. When jet from 31 to 32 first gases, jet from 33 to 31 for 10 to 30 seconds. Repeat 4 times. Finally, recycle 1000 lbs.
3. Five minutes after Item 2, skim 32.
4. Add 250 lbs. water to 31 and jet to 32.
5. Five minutes after Item 4, skim 32 and plug to a step. — 53

2 hrs. 36 min.

D. Product Cake Washing.

1. With 32 at 10 RPM add 250 lbs. water through sprays at 70 lbs. pressure or higher.
2. Bring 32 to 110 RPM, hold 2 min. and plug to a step. Repeat twice.
3. Bring 32 to 870 RPM, hold 5 min. and skim. Plug to a stop.
4. Repeat Items 1, 2 and 3. — 44

44 min.

Average Time in Minutes

E. Product Cake Solution.

(NOTE: 1183 lbs. 60% HNO_3 added to 34 immediately after oxidation of previous charge.)

1. Jet dissolving acid from 34 to 31. With cooling water on 31 jacket jet 31 to 31 distributor for 30 minutes, holding temperature of 31 below 35° C.
2. Jet 350 lbs. acid from 31 to 32.
3. Bring 32 to 110 RPM, hold 2 minutes and plug to stop. Repeat twice.
4. With 32 stopped jet 32 to 34.
5. Repeat Items 2, 3 and 4.
6. Jet remaining acid from 32. If 32 weight exceeds 400 lbs., immediately jet the excess acid above 400 lbs. to 34.
7. Bring 32 to 110 RPM, hold 2 min., plug to stop. Repeat twice.
8. With 32 stopped, jet 32 to 34. 71
9. Air sparge 33 for 40 minutes, sample and jet to waste.

1 hr. 11 min.

F. Oxidation of Product Cake.

1. Agitate 34 for 2 hours at 50° C.

Solution Composition

HNO_3	9.44N	45.7%
$BiPO_4$	.091M	2.12%

2. Add 300 lbs. water to 31 and distribute through spray with cooling water on 31 jacket to keep temperature below 35° C.
3. Jet 31 to 32 and from 32 to 34. Adjust 34 to 50° C. 136
4. Add 50 lbs. 10% $NaBiO_3$ to 34 and follow with 80 lbs. water flush.
5. Agitate 34 at 50° C. for one hour.
6. Add 24 lbs. 10% $Na_2Cr_2O_7$ to 34.
7. Cool 34 to 35° C. 117

4 hrs. 13 min.

Solution Composition

HNO_3	6.83N	34.6%
$BiPO_4$	0.066M	1.61%
$NaBiO_3$	0.0108M	0.244%
$Na_2Cr_2O_7$	0.0056M	0.117%

DECONTAMINATION

Second By-Product Precipitation - Cell #3

Average Time in Minutes

A. By-Product Precipitation.

1. Add 6700 lbs. water to 31 and heat to 40° C. with jacket steam.
2. Jet from 34 to 31.
3. Add 500 lbs. water to 34 for a rinse and jet to 31.
4. Heat 31 to 75° C. — 89
5. Add 25 lbs. 75% H_3PO_4 to 31 and follow with a 10 lbs. water flush. Digest at 75° C. for one hour.
6. Cool 31 to 30° C. and leave cooling water on during the centrifugation. — 120

3 hrs. 29 min.

Solution Composition

HNO_3	1.27N	7.6%
H_3PO_4	.0216M	0.2%
$BiPO_4$	3.39 g./l.	0.321%

B. By-Product Separation.

1. With centrifuge at 870 RPM jet 31 to 32 at full steam pressure. — 83
2. When jet from 31 to 32 first gases, jet from 33 to 31 for 10 to 30 seconds. Repeat four times. Finally recycle 1000 lbs.
3. Five minutes after Item 2, skim 32.
4. Jet 33 to 61.
5. Add 250 lbs. water to 31 and jet to 32 at the same time.
6. Five minutes after Item 5, skim 32 and plug to a stop.
7. Jet 33 to 61. — 65

2 hrs. 28 min.

C. By-Product Cake Washing.

1. With 32 at 10 RPM add 250 lbs. water to 32 through sprays at 70 lbs. pressure or higher.
2. Bring 32 to 110 RPM, hold 2 min., plug to a stop. Repeat twice.
3. Bring 32 to 870 RPM, hold 5 min., skim and plug to a stop.
4. Jet 33 to 61. — 36

36 min.

D. By-Product Cake Solution.

1. Add 1183 lbs. 60% HNO_3 to 31 and jet to distributor for 15 min. with cooling water on 31 jacket so as to keep the temperature below 35° C.

Run 286

		Average Time in Minutes
2.	Jet 340 lbs. acid from 31 to 32.	
3.	Bring 32 to 110 RPM, hold 2 min., plug to a stop. Repeat twice.	
4.	With 32 stopped, jet 32 to 71.	
5.	Repeat Items 2, 3, and 4.	
6.	Jet the remaining acid from 31 to 32. If 32 weight exceeds 400 lbs., immediately jet the excess acid to 71.	
7.	Bring 32 to 110 RPM, hold 2 min., plug to a stop. Repeat twice.	
8.	With 32 stopped, jet 32 to 71.	
9.	Add 125 lbs. water to 31 and jet to 31 distributor for 5 min.	
10.	Bring 32 to 10 RPM, jet 31 to 32, bring 32 to 110 RPM, and plug to a stop. Jet 32 to 71.	102
		1 hr. 42 min.

DECONTAMINATION

Second Product Precipitation - Cell #6

Average Time in Minutes

A. Reduction in Precipitator.

1. Receive product solution and cake washes from 33 in 61.
2. Add 625 lbs. 17.6% $(NH_4)_2SiF_6$ solution to 61.
3. Add 650 lbs. 20.0% ferrous ammonium sulfate solution to 61.
4. Heat 61 to 75° C. and digest for one hour. 143

2 hrs. 23 min.

B. Product Precipitation.

1. Add 215 lbs. 14% Bi solution to 61 at 75° C. uniformly over 30 minutes. Follow with 5 lbs. 60% HNO_3.

Solution Composition (in 61)

$BiONO_2$	14%
HNO_3	52%

2. Digest for 30 min. at 75° C.
3. Add 950 lbs. 75% H_3PO_4 to 61 and digest at 75° C. for 2 hours.
4. Cool 61 to 50° C. and leave cooling water on during the centrifugation. 262

4 hrs. 42 min.

Slurry Composition

HNO_3	1.1N	6.5%
H_3PO_4	.62M	5.7%
$(NH_4)_2SiF_6$	.052M	0.87%
Bi	1.9 g./l.	0.179%
Fe	.028M	0.146%

C. Product Separation.

1. With centrifuge at 870 RPM jet 61 to 62 at full jet pressure. 88
2. When jet from 61 to 62 first gases, jet from 63 to 61 for 10 to 30 seconds. Repeat four times. Finally recycle 1000 lbs.
3. Five minutes after Item 2, skim 62.
4. Add 250 lbs. water to 61 and jet to 62 at the same time.
5. Five minutes after Item 4, skim 62 and plug to a stop. 46

2 hrs. 14 min.

Average Time in Minutes

D. Product Cake Washing.

1. With 62 at 10 RPM add 250 lbs. water through sprays at 70 lbs. pressure or higher.
2. Bring 62 to 110 RPM, hold 2 min. and plug to a stop. Repeat twice.
3. Bring 62 to 870 RPM, hold 5 min., skim and plug to a stop.
4. Repeat Items 1, 2 and 3. — 53

53 min.

E. Product Cake Solution.

(NOTE: 1183 lbs. 60% HNO_3 added to 64 immediately after oxidation of previous charge.)

1. Jet dissolving acid from 64 to 61. With cooling water on 61 jacket jet to 61 distributor for 10 min., holding temperature below 35° C.
2. Jet 350 lbs. acid from 61 to 62.
3. Bring 62 to 110 RPM, hold 2 min., and plug to a stop. Repeat twice.
4. With 62 stopped, jet 62 to 64.
5. Repeat Items 2, 3, and 4.
6. Jet remaining acid from 61 to 62. If 62 weight exceeds 400 lbs., immediately jet the excess acid above 400 lbs. to 64.
7. Bring 62 to 110 RPM, hold 2 min., and plug to a stop. Repeat twice.
8. With 62 stopped, jet 62 to 64. — 77
9. Air sparge 63 for 40 min., sample and jet to waste.

1 hr. 17 min.

Solution Composition (in 64)

HNO_3	9.44N	45.7%
$BiPO_4$	.091M	2.12%

F. Oxidation of Product Cake.

1. Agitate 64 for 2 hours at 50° C.
2. Add 300 lbs. water to 61. With cooling water on 61 jacket jet to 61 distributor for 5 minutes holding 61 temperature below 35° C. Jet 61 to 62, and upon completion of two hour agitation in 64, jet 62 to 64. — 135
3. Add 50 lbs. 10% $NaBiO_3$ to 64 and follow with 80 lbs. water flush.
4. Agitate 64 at 50° C. for one hour.
5. Add 24 lbs. 10% $Na_2Cr_2O_7$ to 64.
6. Cool 64 to 35° C. — 107

4 hrs. 2 min.

Run 286

Average Time in Minutes

Solution Composition

HNO_3	6.83M	34.6%
$BiPO_4$	.066M	1.61%
$NaBiO_3$	.0108M	.244%
$Na_2Cr_2O_7$	.0056M	.117%

Run 286

CROSSOVER

$BiPO_4$ By-Product Precipitation - Cell #6

Average Time in Minutes

A. By-Product Precipitation.

1. Add 5600 lbs. water to 61 and heat to 40° C. with jacket steam.
2. Jet 64 to 61 and rinse 64 to 61 with 500 lbs. of water.
3. Heat 61 to 75° C.
4. Add 105 lbs. 75% H_3PO_4 to 61, and follow with 95 lbs. water flush. — 100
5. Digest 61 at 75° C. for one hour.
6. Cool 61 to 50° C. and leave cooling water on the jacket during centrifugation. — 125

3 hrs. 45 min.

Slurry Composition (in 61)

HNO_3	1.41N	8.45%
H_3PO_4	0.10M	0.938%
$BiPO_4$	4.1 g./l.	0.392%

B. By-Product Separation.

1. With centrifuge at 870 RPM jet 61 to 62 at full steam pressure.
2. When jet from 61 to 62 first gases, jet 63 to 61 for 10 to 30 seconds. Repeat four times. Finally recycle 1000 lbs. — 66
3. Five minutes after Item 2, skim 62. Jet 63 to 41.
4. Add 250 lbs. water to 61, and jet 61 to 62 at the same time.
5. Five minutes after Item 4, skim 62 and plug to a stop. Jet 63 to 41. — 61

2 hrs. 7 min.

C. By-Product Cake Washing.

1. With 62 at 10 RPM add 250 lbs. water through sprays at 70 lbs. pressure or higher.
2. Bring 62 to 110 RPM, hold 2 min. and plug to a stop. Repeat twice.
3. Bring 62 to 870 RPM, hold 5 min., skim and plug to a stop.
4. Jet 63 to 41. — 25

25 min.

Run 286

Average Time in Minutes

D. By-Product Cake Solution.

1. Add 1183 lbs. 60% HNO_3 to 61 and with cooling water on jacket jet to distributor for 5 min. holding temperature below 35° C.
2. Jet 340 lbs. acid from 61 to 62.
3. Bring 62 to 110 RPM, hold 2 min., and plug to a stop. Repeat twice.
4. With 62 stopped jet 62 to 71.
5. Repeat Items 2, 3, and 4.
6. Jet remaining acid from 61 to 62. If 62 weight exceeds 400 lbs., immediately jet the excess acid above 400 lbs. to 71.
7. Bring 62 to 110 RPM, hold 2 min. and plug to a stop. Repeat twice.
8. With 62 stopped, jet 62 to 71.
9. Add 125 lbs. water to 61, and jet to 61 distributor for one minute. With 62 at 18 RPM, jet 61 to 62. Bring 62 to 110 RPM and plug to a stop. Jet 62 to 71. 77

1 hr. 17 min.

PEROXIDE SUPERNATANT DECOMPOSITION

Room D

Average Time in Minutes

(Peroxide supernatant is returned by Isolation to Room D where the H_2O_2 in the supernatant is decomposed with $NaNO_2$ solution.)

A. Decomposition.

1. Solution received in D-8, sampled and analyzed for % H_2O_2. 20
2. Solution cooled and made 1N HNO_3. Add 17% $NaNO_2$ solution slowly so as not to exceed temperature of 30° C. Volume of solution to be used based on one mole of $NaNO_2$ solution per one mole of H_2O_2 as determined by the analysis. When approximately 60% of $NaNO_2$ has been added mole spot tests with ammonium vanadate (1) and continue addition until a neutral solution is indicated. 100
3. Make final check on H_2O_2 with a nitrite indicator (2) to insure end-point.

(1) 1.5 gms. ammonium vanadate per 25 ml. of 8N H_2SO_4. Color change: blood red to colorless.
(2) 0.1 gm. benzidene di-hydrochloride in 30 ml. of 6N acetic acid and 0.25 ml. of Di-methyl aniline. Excess nitrite gives light pink color.

B. Oxidation.

1. When decomposition is complete, make 0.15% in $KMnO_4$ and hold at 75° C. for thirty minutes. Cool to 50° C. and hold until required for Cell 4. 45

2 hrs. 45 min.

Run 286

CROSSOVER

LaF_3 By-Product Precipitation - Cell #4

Average Time in Minutes

A. First By-Product Precipitation.

1. Receive product solution and washes from 63 in 41.
2. Add to 41 one-half (122 lbs.) of the peroxide supernatant from two previous runs in order to recycle product not recovered by the Isolation Group. While heating to 75° C., also add 300 lbs. 5% $KMnO_4$ solution followed by a water flush of 5 gallons.
3. Adjust temperature to 75° C. and agitate 1/2 hour. — 94
4. Cool 41 to 40° C., and leave cooling water on.
5. Add 84 lbs. 8% $Ba(NO_3)_2$ solution to 41.
6. Add 46 lbs. 93% H_2SO_4 to 41 uniformly over 15 minutes.
7. Digest 15 minutes.
8. Add 40 lbs. anhydrous HF to 41 over 30 min. period.
9. Digest for one hour with cooling water on 41 jacket. — 278

6 hrs. 12 min.

Slurry Composition

HNO_3	1.24N	7.31%
HF	.22N	.412%
$KMnO_4$	0.0106M	.157%
$BaSO_4$	660 mg/l.	.0617%
H_2SO_4	.0454M	.415%
LaF_3	186 mg/l.	.0174%
La	132 mg/l.	.0124%

B. First By-Product Separation.

1. With 42 at 1740 RPM jet 41 to 42 at a rate of 70 lbs. per min. using steam as necessary for a constant rate. — 148
2. When jet from 41 to 42 gases, cut off steam and reduce 42 to 870 RPM.
3. Five minutes after completing Item 2, skim 42. Leave 42 running at 870 RPM. — 17

2 hrs. 45 min.

C. Second By-Product Precipitation.

1. Jet 43 to 41 and start cooling solution in 41.
2. Add uniformly over a period of one hour a mixture of 500 lbs. of 1% La salt solution and 84 lbs. 8% $Ba(NO_3)_2$ solution.
3. Cool 41 to 40° C. or lower, and leave cooling water on. — 160

2 hrs. 40 min.

Run 286

Average Time in Minutes

Slurry Composition (in 41)

LaF_3	171 mg/l.	.0161%
La	121 mg/l.	.0114%

D. Second By-Product Separation.

1. Bring 42 to 1740 RPM, and jet 41 to 42 at rate of 70 lbs. per min. using steam as necessary to maintain a constant rate. 152
2. As jet from 41 to 42 gases, cut off steam and reduce 42 to 870 RPM.
3. Five minutes after completing Item 2, skim 42 and plug to 10 RPM.
4. Jet 43 to 51. 35

3 hrs. 7 min.

E. By-Product Cake Washing and Removal.

1. With 42 at 10 RPM add 225 lbs. water to 42 through sprays at 70 lbs. pressure or higher. Add 25 lbs. 60% HNO_3 to 42.
2. Bring 42 to 110 RPM, hold 2 min., and plug to a stop. Repeat twice.
3. Bring 42 to 1740 RPM, hold 10 min., slow 42 to 870, hold 5 min., skim and plug to 10 RPM. Jet 43 to 51. 40
4. Start water to sprays in 42 at 70 lbs. pressure or higher and jet 42 to 71. Stop water to sprays intermittently so as to keep bowl empty. Continue spraying until 71 weight equals 1500 lbs.
5. Agitate 71 for two hours, sample, and send to waste.

40 min.

Run 286

CROSSOVER

LaF_3 Product Precipitation - Cell #5

Average Time in Minutes

A. Product Reduction.

1. Receive product solution and washes from 43 in 51.
2. Add 950 lbs. 9.2% oxalic acid solution to 51.
3. Digest at 35° C. to 50° C. for one hour.
4. Cool 51 to 30° C.

127

2 hrs. 7 min.

B. Product Precipitation.

1. Add 85 lbs. anhydrous HF to 51.
2. Add 250 lbs. 1% La salt solution to 51 uniformly over 20 minutes.
3. Digest 51 for one hour at 40° C. or below.
4. Cool to 30° C. or below, and leave cooling water on.

82

3 hrs. 40 min.

Slurry Composition

HNO_3	0.93N	5.62%
HF	0.51N	0.98%
$H_2C_2O_4$	0.0567M	0.688%
La	49 mg/l.	0.0047%

C. First Product Separation.

1. With 52 at 1740 RPM, jet 51 to 52 at rate of 70 lbs. per min. using steam as necessary for a constant rate.
2. When jet from 51 to 52 gases, cut off steam and reduce 52 to 870 RPM.
3. After completion of Item 2, skim 52, leave 52 running at 870 RPM.

187

14

3 hrs. 21 min.

D. Second Product Precipitation.

1. With cooling water on 51 jacket jet 53 to 51.
2. Add 250 lbs. 1% La salt solution to 51 uniformly over 20 minutes.
3. Digest for one hour at 40° C. or lower.
4. Cool 51 to 30° C. or lower, and leave cooling water on.

113

1 hr. 53 min.

Slurry Composition

La	44.5 mg/l.	.00426%

Run 286

	Average Time in Minutes
E. Second Product Centrifugation.	
1. With 52 at 1740 RPM jet 51 to 52 at rate of 70 lbs. per min. using steam as necessary for a constant rate.	215
2. When jet from 51 to 52 gases, cut off steam and reduce 52 to 870 RPM.	
3. Five minutes after completing Item 2, skim 52 and plug to stop.	17
	3 hrs. 52 min.
F. Product Cake Washing.	
1. With 52 at 10 RPM add 225 lbs. water through sprays at 70 lbs. pressure or higher. Add 25 lbs. 60% HNO_3 to 52.	
2. Bring 52 to 110 RPM, hold 2 min. and plug to stop. Repeat twice.	
3. Bring 52 to 1740 and hold 10 minutes. Slow 52 to 870 RPM, hold 5 min. and skim.	
4. Repeat Items 1, 2 and 3.	101
	1 hr. 41 min.
G. Cake Removal.	
1. With 52 at 10 RPM start water to 52 sprays at 70 lbs. pressure or higher. To keep bowl empty stop water to sprays intermittently. Spray and jet from 52 to 44 until 44 weight reaches 700 lbs.	18
2. Hold this LaF_3 slurry in 44 until the next charge is combined with this one whereupon the two charges are transferred to Room D, and 52 and 44 are consecutively rinsed with 150 lbs. water which is also sent to Room D.	26
3. Agitate 53 for 40 min., sample, and jet to waste.	
	44 min.

METATHESIS

Room D

Average Time in Minutes

A. KOH Treatment.

1. Receive slurry of two runs from 44 in D-1.
2. Add 444 lbs. 85% KOH (solid).
3. Make volume up to 2370 lbs.
4. Heat to 80° C. and hold for 90 minutes.
5. Cool D-1 to 35° C. and leave cooling water on. 160

2 hrs. 40 min.

Slurry Composition

KOH	3.07N	15.0%
La	1.165 g./l.	.1012%

B. $La(OH)_3$ Separation.

1. With D-2 centrifuge at 1800 RPM jet D-1 to D-2 at such a rate that the effluent is not cloudy by visual observation. 290
2. Five minutes after completion of Item 1, skim D-2 and plug to a stop.
3. Agitate D-3 for 10 min., sample and jet to waste.

4 hrs. 50 min.

C. $La(OH)_3$ Cake Removal and Wash.

1. Scrape cake from D-2 bowl wall with plows. Add water to D-2 sprays at 70 lbs. pressure or higher and jet D-1 to D-2 Repeat washing until bowl is clean.
2. Add water to D-1 until weight is 2081 lbs.
3. Add 49 lbs. 85% KOH (solid) to D-1.
4. Agitate for one hour at 25° C. or lower. 119

1 hr. 59 min.

Slurry Composition (in D-1)

KOH	0.37N	2.0%
La	1.165 g./l.	0.115%

D. $La(OH)_3$ Centrifugation.

1. With D-2 centrifuge at 1800 RPM jet D-1 to D-2 at a rate such that by visual observation the effluent is not cloudy. 263
2. Recycle three 10 gallon washes from D-3 to D-1 and jet to D-2.
3. Five minutes after completing Item 2, skim D-2 at 1800 RPM and plug to a stop.
4. Agitate D-3 for 10 min., sample, and jet to waste.

4 hrs. 41 min.

Run 286

Average Time in Minutes

E. Product Cake Solution.

1. Add 14.3 lbs. 60% HNO_3 to D-2.
2. Dissolve cake by swinging acid up sides of bowl and plugging down. Slurry for 20 minutes.
3. Syphon dissolved cake to D-11.
4. Add 20 lbs. water to D-2. Swing up and down sides of bowl, and slurry for 10 minutes.
5. Syphon wash to D-11. Drain contents of D-11 into two stainless steel cans, and deliver the cans to 204 Building.
6. Add 100 lbs. water to D-2 through sprays at 70 lbs. pressure or higher. Slurry 20 minutes and jet to D-1. 91

1 hr. 31 min.

Solution Composition

HNO_3	2.08N	12.25%
La	35.7 g./l.	3.43%

ISOLATION - 204 BUILDING

Clarification

Average Time in Minutes

NOTE: Transfers between reaction vessels are made by way of head tanks which operate by vacuum. Additions of chemicals are also made via head tanks.

A. Transfer and Filtration.

1. Transfer contents of one stainless steel can from Room D to tank FA-1 via head tank.
2. Add 4 grams Hyflo-Super-Cel per liter of solution to FA-1, and agitate 2 minutes.
3. Apply vacuum to HT-2, and filter from FA-1 to HT-2. Drop filtrate from HT-2 to P-1.
4. Repeat Items 1, 2 and 3 again on the other Room D can.

B. Washing and Sampling.

1. Add one liter of one normal nitric to the two Room D cans and flush to HT-1. Drop this wash to FA-1 and suck through the filter to HT-2, and then drop to P-1.
2. Agitate P-1 for 10 minutes and sample. If HNO_3 concentration is less than 0.95 normal, add sufficient nitric to make solution one normal. 136

2 hrs. 16 min.

C. Filter Cake Leaching.

1. Add 200 cc. 60% HNO_3 to FA-1 and drop to N-1 filter. Draw the wash to HT-2 and suck from HT-2 to HT-4 and drop it to CT-1 which holds wastes to be returned to Room D.
2. Repeat Item 1 six times, using 200 cc. of one normal nitric each time.

D. Backwashing Filter N-1.

1. Apply vacuum to BWT tank and add 3 liters water through chemical inlet of N-1 filter.
2. Drop slurry from BWT tank to 4 liter beaker and sample.

ISOLATION - 204 BUILDING

First Peroxide Precipitation

	Average Time in Minutes
A. Reduction.	
1. Make solution in P-1 0.2N in H_2SO_4 by adding with agitation 5.6 cc. 94% H_2SO_4 per liter of solution in P-1.	20
2. Add slowly with agitation 28 - 30 percent concentrated peroxide to make the solution in P-1 one percent in H_2O_2.	

Solution Composition

HNO_3	1N	6.3%
H_2SO_4	0.2N	0.98%
H_2O_2		1.0%
La	37 g./l.	

3. Raise temperature of P-1 to 50° C. and hold for one hour.	83
4. Cool to 20° C.	40
	2 hrs. 33 min.

B. Precipitation.	
1. Add with agitation and continuously over a period of one hour to P-1 via HT-3 enough 30% peroxide to make the final solution 10% in H_2O_2. Maintain temperature at 20° C.	49

Solution Composition

HNO_3	.67N	4.22%
H_2SO_4	.13N	.87%
H^+	.8N	
H_2O_2		10.0%
La	24 g./l.	

2. Agitate P-1 at 20° C. for one hour.	60
3. Cool P-1 to 5 - 8° C.	56
4. Stop agitation and allow P-1 to settle 9 hours with cooling water on jacket.	540
	11 hrs. 45 min

C. Decantation.	
1. Put vacuum on HT-4 and draw supernatant from P-1 to HT-4.	50
2. Drop supernatant from HT-4 to CT-1. Keep temperature at 20° C. or lower.	15
3. Draw supernatant from CT-1 into stainless steel cans and deliver to Room D.	
	1 hr. 5 min.

Run 286

	Average Time in Minutes
D. Slurry Washing.	
1. With suction on HT-6 add 1500 cc. of 0.2 normal H_2SO_4 to P-1, washing the product precipitate toward the draw-off line to HT-6. Repeat washing with an additional 1500 cc. 0.2N H_2SO_4.	
2. Drop slurry from HT-6 to transfer can for transportation to Hood 1 for further processing.	35
	35 min.

ISOLATION - 204 BUILDING

Second Peroxide Precipitation

	Average Time in Minutes
A. Transfer.	
1. Transfer E-1 transfer can containing product slurry from Hood 6 to Hood 1.	
2. Suck product slurry from E-1 to HT-8, and drop to P-2.	
3. Add 200 cc. 0.2N H_2SO_4 wash solution to transfer can. Suck this wash to HT-8 and drop to P-2.	
4. Let settle 30 minutes or longer if necessary.	92
5. With vacuum on HT-9 decant supernatant to a volume of 15 cc. per unit of product present.	
6. Drop supernatant from HT-9 to CT-2, draw off supernatant from CT-2 to transfer can and transfer from transfer can to CT-1 where the supernatant can be combined with other wastes and sent to Room D for product recovery.	
	1 hr. 50 min.
B. Nitric Acid Solution and Filtration.	
1. To the product slurry in P-2 add 9 cc. 70% HNO_3 per unit product.	
2. Agitate and bring to 40° - 50° C. over a period of 30 minutes.	65
3. If the precipitate is not in solution, agitate at 40° - 50° C. for one hour or until the precipitate dissolves.	
4. Add 4 g./l. Hyflo-Super-Cel as a water slurry.	
5. Filter through 3 inch sintered glass filter to HT-10.	243
6. Drop product solution from HT-10 to P-2.	
7. Adjust final solution volume to one liter, or two liters if necessary. Add 5.6 cc. 96% H_2SO_4 per liter of solution.	
8. Cool P-2 to 20° C.	56
	6 hrs. 4 min.

Solution Composition

HNO_3	1N	6.3%
H_2SO_4	0.2N	0.98%
Product	8 g./l.	

C. Precipitation.

1. Through HT-11 add to P-2 continuously over a period of one hour enough 28 - 30% H_2O_2 to make final solution 10% in H_2O_2. Maintain temperature at 20° C.

Slurry Composition

HNO_3	.67N	4.22%
H_2SO_4	.13N	0.87%
Product	5.33 g./l.	
H_2O_2		10%

Run 286

		Average Time in Minutes
2.	Agitate for one hour at 20° C.	60
3.	Cool to 5° - 8° C.	30
4.	Stop agitation and allow to settle nine hours with cooling water on.	540
5.	Suck supernatant to HT-9 and drop to CT-2.	
6.	Wash precipitate with 100 cc. of 0.2N H_2SO_4 for 15 minutes.	
7.	Settle 30 minutes or longer if necessary.	60
8.	Decant P-2 to 15 cc. per unit product to HT-9, and drop to CT-2.	
9.	Draw off HT-9 to transfer can and return to CT-1 to be held for Room D.	
10.	Using 10 cc. shots, leach the IR-2 cake caught during the filtration through the 3 inch sintered glass funnel. Use 50 cc. 70% HNO_3 in all.	
11.	Wash IR-2 cake with 200 cc. water.	
12.	Return acid and water washes of IR-2 cake to CT-1.	
		11 hrs. 30 min.

ISOLATION - 204 BUILDING

Final Nitric Solution, Filtration and Drying

	Average Time in Minutes
A. Solution and Filtration.	
1. To the product slurry in P-2 add 9 cc. 70% HNO_3 per unit product.	
2. Agitate and bring to 40° - 50° C.	
3. Hold at 40° - 50° C. until precipitate is dissolved.	95
4. Cool and filter through one inch sintered glass filter (no filter-aid used). Draw to graduated vessel in Hood 2 by vacuum.	
5. Rinse P-2 through glass filter with four 20 cc. water washes.	200
6. Leach IR-3 cake with 20 cc. 70% HNO_3 and then wash cake with 200 cc. water. Return washings to CT-1. Sample CT-1 and hold combined wastes in CT-1 for Room D.	
	4 hrs. 55 min.
B. Drying.	
Transfer the product solution from the graduate to the shipping tube, which can be sealed off at the capillary filling tube after the final drying. Pass preheated air through the capillary onto the surface of the solution until it is evaporated to dryness. The drying operation will require 35 hours, including the transfer time and the actual drying.	35 hrs.
	35 hrs.

B. YIELD AND MATERIAL BALANCES.

Tables showing yields and material balances for the runs processed since run 201, shown on Page 171 of this report, are included on the following page. Because of the changes in Concentration and Isolation procedures during this period the tabulation does not conform to the previous tabulations which were based on batches of eight runs each.

Yields and Material Balance - Single Cycle Runs

Run Numbers	236-246	247-254	264-265	266-279	280-291	292-293	294-299
Material Balance							
Thru 2nd by-prod. pptn. (410S)	105.2	107.5	102.9	108.2	104.6	109.8	108.4
Overall* (IFP corrected)	87.6	122.1	54.8	113.5	99.3	163.6	146.4
Overall Yield* (IFP corrected)	99.1	109.0	41.2	103.7	89.3	146.9	134.6

Yields - Two Cycles

Run Numbers	202-209	210-217	218-226	227-235	255-263
% Orig. prod. in extr. ppt.	93.7	98.2	95.3	87.1	95.5
% Orig. prod. after 1st by-prod. ppt.	97.4	108.5	100.6	100.2	102.7
% Orig. prod. in 1st prod. ppt.	94.0	93.6	92.1	88.8	98.2
% Orig. prod. after 2nd by-prox. ppt.	94.8	96.0	97.1	89.6	101.6
% Orig. prod. in 2nd prod. ppt.	94.6	91.7	92.9	88.8	95.5
% Orig. (aver.) prod. in 2nd prod. ppt.	92.1	93.3	95.3	85.5	98.3
Basis after return of recycle	187.0	425.5	153.2	200.0	193.0
% Prod. after LaF_3 by-prod., recycle basis**	85.8	105.7	94.2	88.1	94.8
% Prod. in sol. of LaF_3 pr. slurry**	95.9	76.3	89.2	89.2	87.2
% Orig. prod. in final peroxide ppt.	71.1		87.6	70.9	82.4

Material Balance - Two Cycles

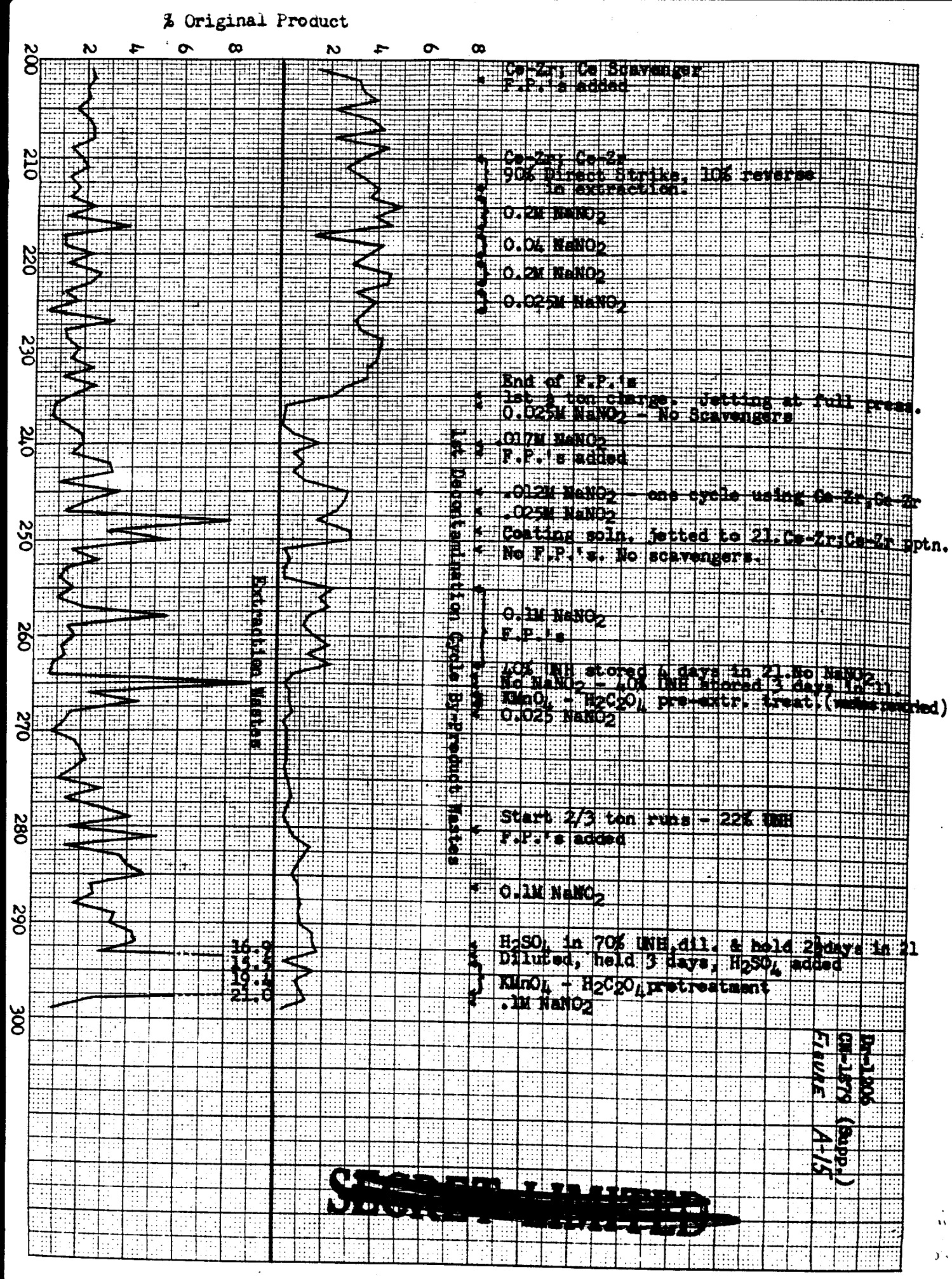
Run Numbers	202-209	210-217	218-226	227-235	255-263
Through 1st by-prod. ppt.	102.7	114.1	105.6	105.5	106.4
Through 2nd by-prod. ppt.	101.5	108.8	104.0	101.3	106.8
Through Decont. Cycles	101.6	105.2	100.5	101.4	101.0
Through final peroxide 1 FP*	100.8		101.4	92.5	96.7

*Corrected for gain or loss in product content of recycle solution on hand and based on 11M.

**Based on 11M plus amount of recycled product.

C. GRAPHS OF WASTE LOSSES FOR INDIVIDUAL RUNS.

The following graphs are continuations of the data given following Page 172 of this report.



Dr-1206
CM-1879 (Supp.)
FIGURE A-15

NO. 329-C. MILLIMETERS. 180 BY 250 DIVISIONS.
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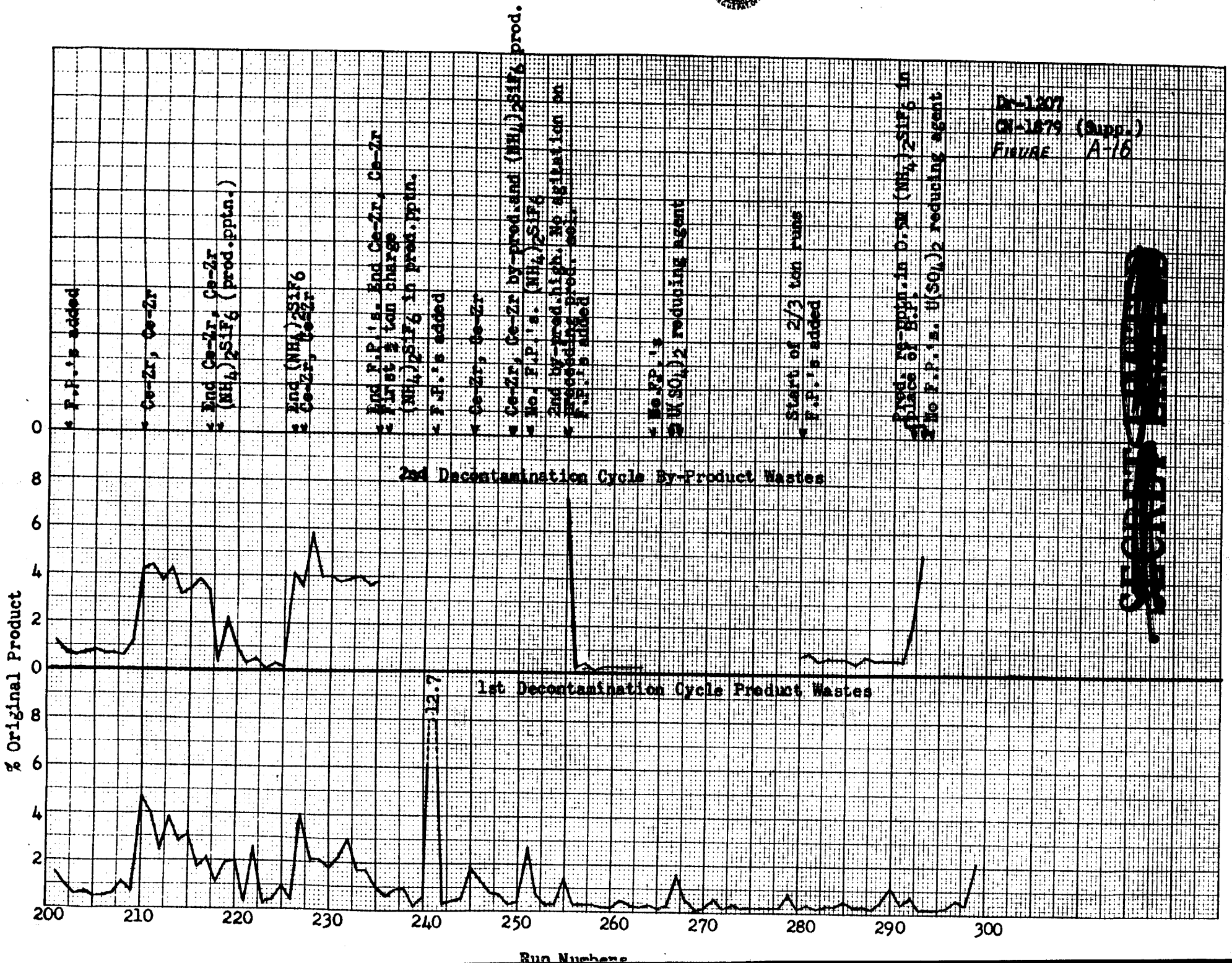

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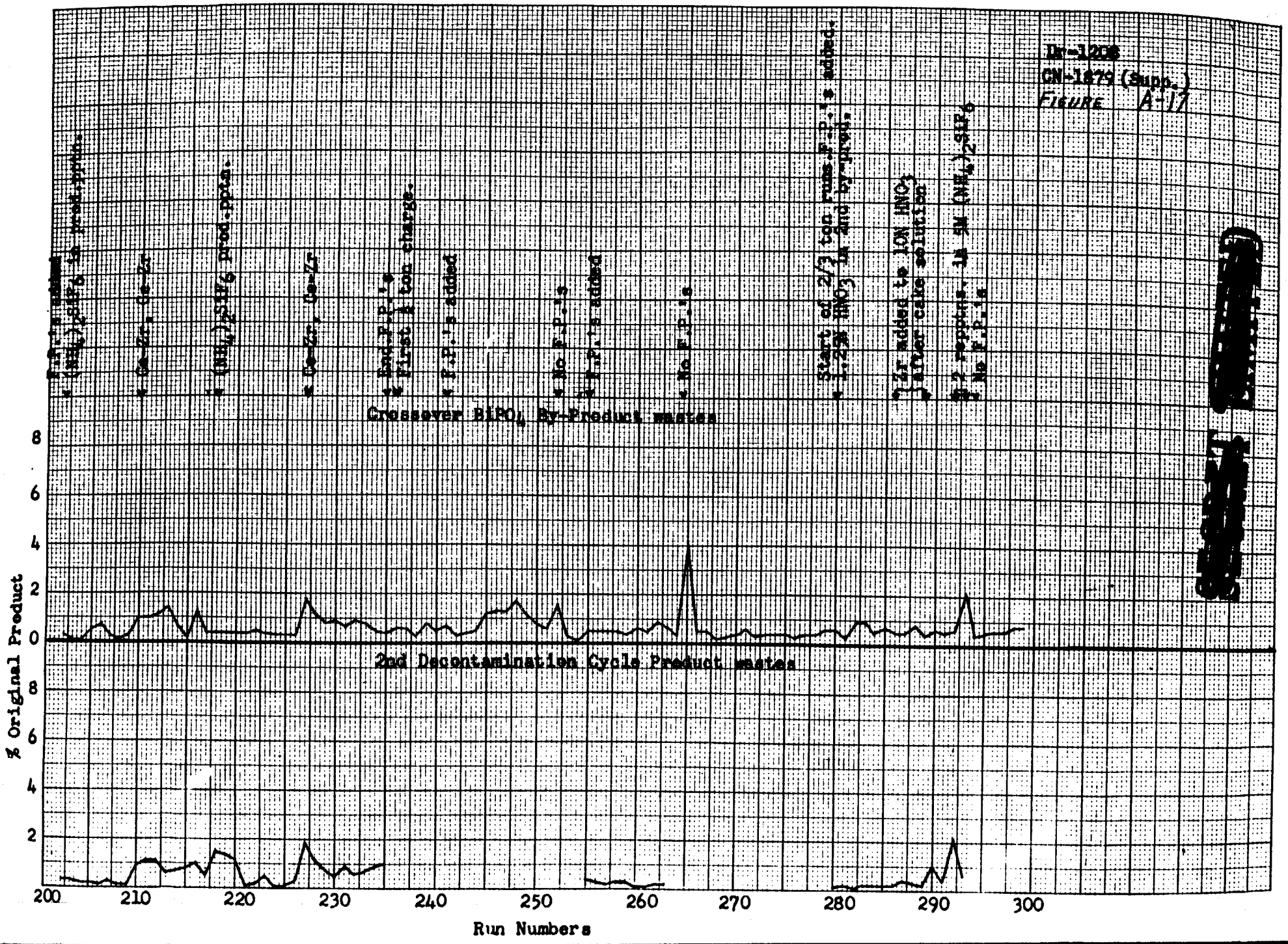

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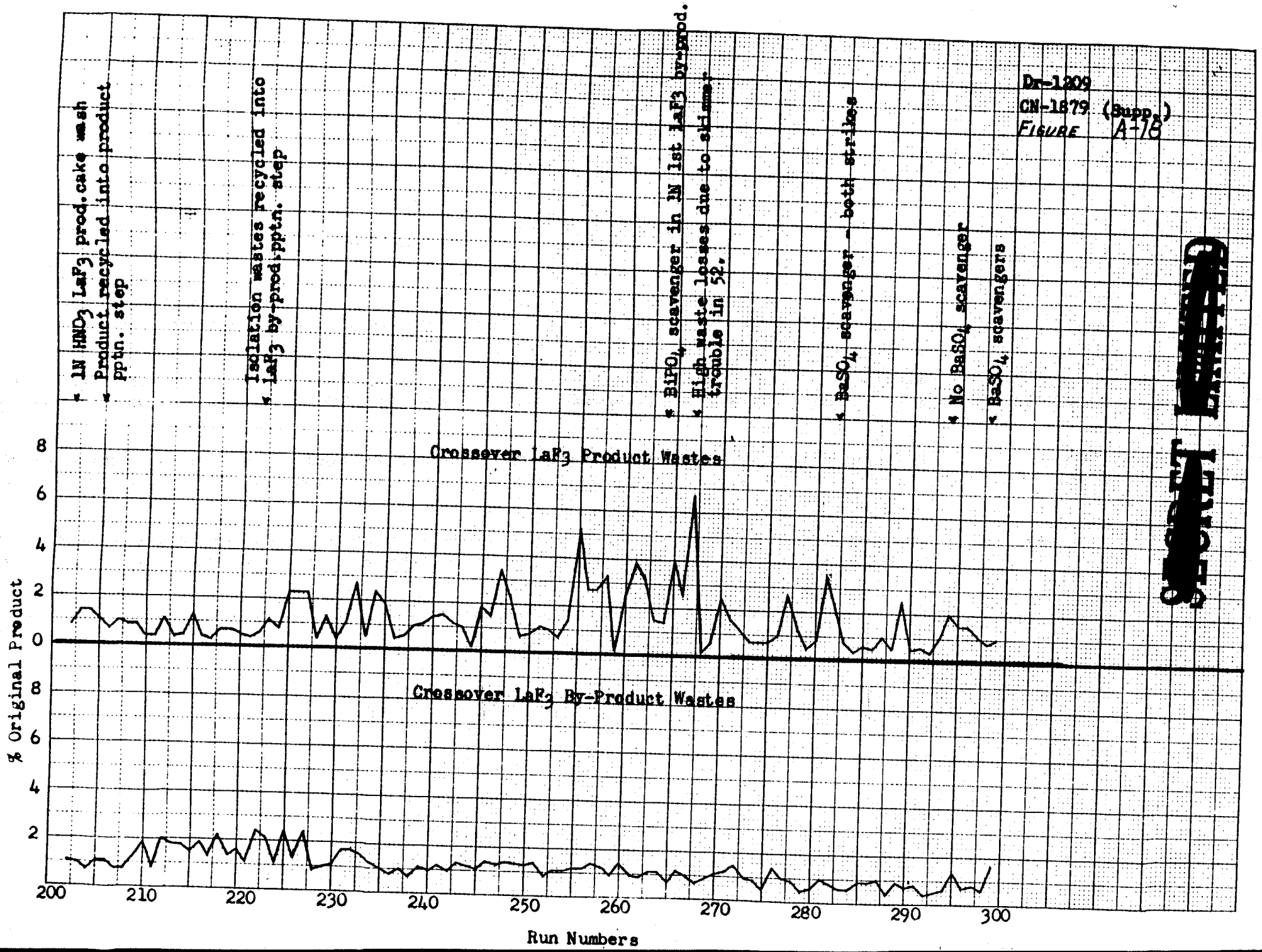
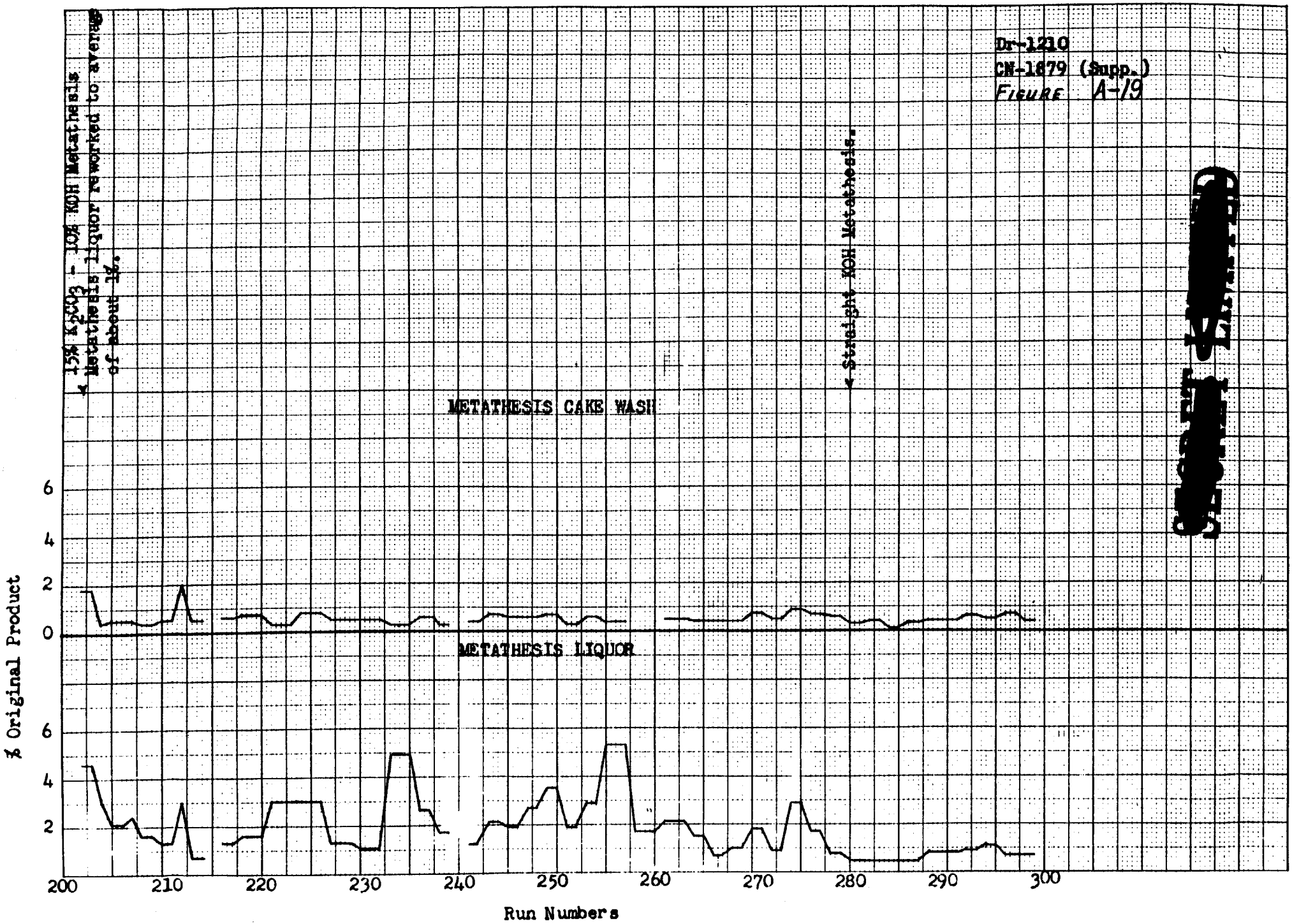


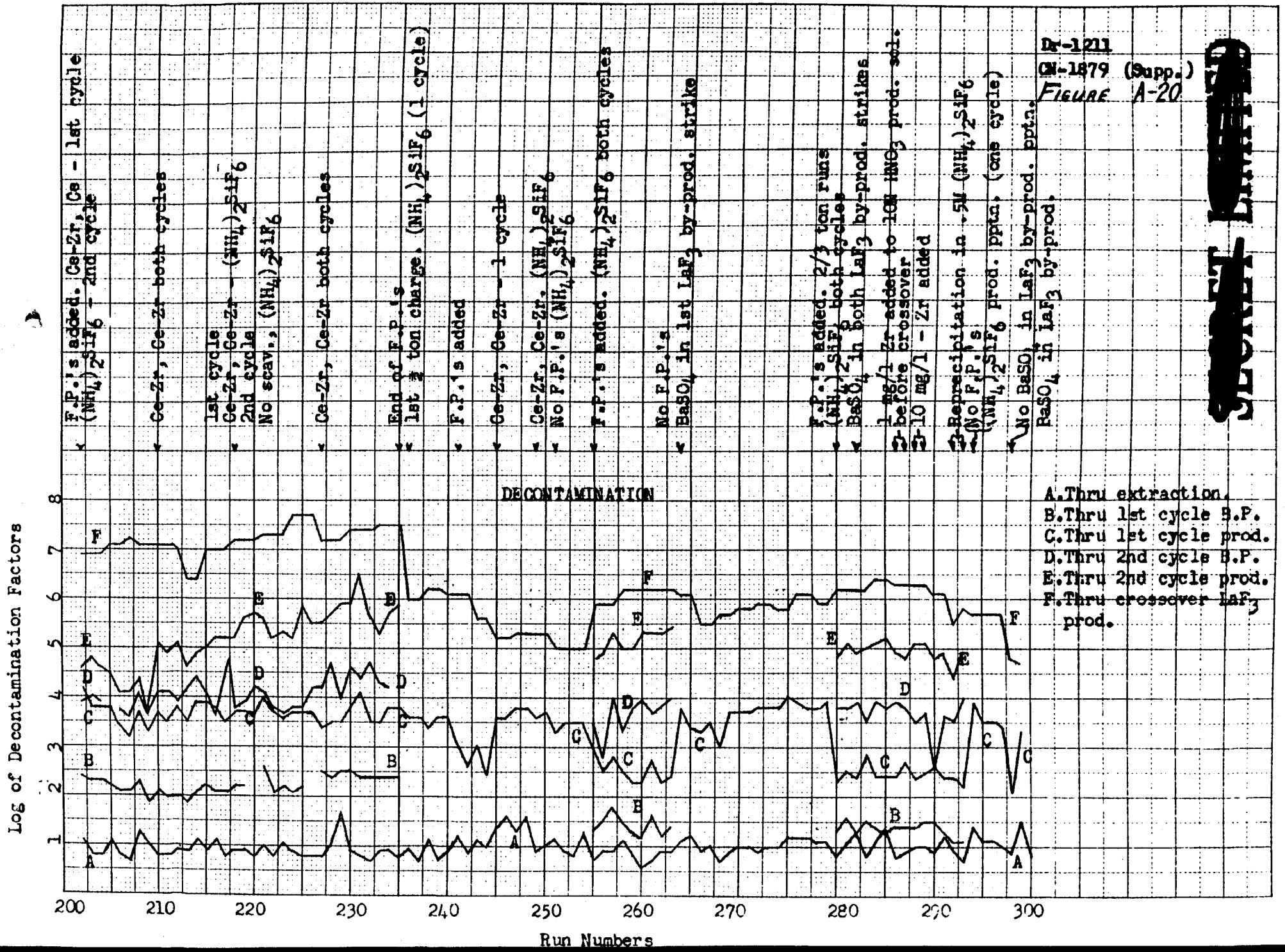
Dr-1210
CN-1879 (Supp.)
FIGURE A-19



[redacted]

D. GRAPHS OF DECONTAMINATIONS FOR INDIVIDUAL RUNS.

The following graphs are continuations of the data given following Page 173 of this report.


Dr-1211
CN-1879 (Supp.)
FIGURE A-20
[redacted]
F.P.'s added. Ce-Zr, Ce - 1st cycle
$(NH_4)_2SiF_6$ - 2nd cycle
Ce-Zr, Ce-Zr both cycles
1st cycle
Ce-Zr, Ce-Zr - $(NH_4)_2SiF_6$
2nd cycle
No scav., $(NH_4)_2SiF_6$
Ce-Zr, Ce-Zr both cycles
End of F.P.'s
1st ⅔ ton charge. $(NH_4)_2SiF_6$ (1 cycle)
F.P.'s added
Ce-Zr, Ce-Zr - 1 cycle
Ce-Zr, Ce-Zr, $(NH_4)_2SiF_6$
No F.P.'s $(NH_4)_2SiF_6$
F.P.'s added. $(NH_4)_2SiF_6$ both cycles
No F.P.'s
$BaSO_4$ in 1st LaF_3 by-prod. strike
F.P.'s added. 2/3 ton runs
$(NH_4)_2SiF_6$ both cycles
$BaSO_4$ in both LaF_3 by-prod. strikes
1 mg/l Zr added to 10N HNO_3 prod. sol.
before crossover
10 mg/l - Zr added
Reprecipitation in -5N $(NH_4)_2SiF_6$
(No F.P.'s
$(NH_4)_2SiF_6$ prod. ppta. (one cycle)
No $BaSO_4$ in LaF_3 by-prod. ppt.
$BaSO_4$ in LaF_3 by-prod.
DECONTAMINATION
A.Thru extraction.
B.Thru 1st cycle B.P.
C.Thru 1st cycle prod.
D.Thru 2nd cycle B.P.
E.Thru 2nd cycle prod.
F.Thru crossover LaF_3 prod.
Log of Decontamination Factors
Run Numbers
200
210
220
230
240
250
260
270
280
290
300
1
2
3
4
5
6
7
8
A
B
C
D
E
F