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Meeting on Problems of Fluorine Effluents

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2896

K/EM-468

SANITIZED VERSION OF MEETING MINUTES DATED JUNE 14, 1956

(Sanitized Version of Unnumbered CRD Document)

Compiled by
S. G. Thornton
Environmental Management Division
OAK RIDGE K-25 SITE
for the Health Studies Agreement

July 22, 1996

Oak Ridge K-25 Site
Oak Ridge, Tennessee 37831-7314
managed by
LOCKHEED MARTIN ENERGY SYSTEMS, INC.
for the U.S. DEPARTMENT OF ENERGY
under Contract DE-AC05-84OR21400

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MEETING ON PROBLEMS OF FLUORINE EFFLUENTS

June 14, 1956

Present: Chemical Division - E. C. Bollinger and B. H. Thompson; Production Division - J. A. Parsons; Safety and Protection Division - H. F. Henry; Technical Division - J. C. Barton, S. H. Smiley, and P. R. Vanstrum

The subject meeting was held to discuss information which had been obtained subsequent to observations made in the Company-Union Safety Meeting of April 12, 1956, concerning apparent damage to pine trees just outside the plant perimeter fence and roughly east of the plant.

Attached are copies of the pertinent information rather hurriedly obtained and assembled by H. F. Henry and S. H. Smiley and reviewed at the meeting; it was particularly noted that apparently the average fluoride concentration in plant air had neared or exceeded the nationally recommended maximum allowable concentrations for fluorine and fluorides for the past 5 months. Attachment I gives information concerning present plant conditions as well as some general data on the effects of fluorine.

It was agreed by those present that the release of fluorine and hydrogen fluoride did present a plant problem which should be corrected insofar as possible. A review of the locations (see Attachment II) from which significant quantities of these materials are currently released into the air indicated that, currently, about 80%-90% of that released comes from K-311-1, and that significant quantities are otherwise released primarily at K-1131 (including the HF Tank Farm), at K-1420, and during the in-place conditioning of cascade equipment.

It was noted that steps are already underway to control the release at K-311-1, Mr. Thompson agreed to investigate control measures for the K-1131 and K-1420 effluents, and Mr. Parsons agreed to see what could be done about controlling the release during in-place equipment conditioning. For this latter case, the possibility of using smaller quantities of fluorine with a consequent longer conditioning time or building a portable scrubber were briefly mentioned.

Since the air samples and vegetation samples noted (see Attachment I) had been obtained to determine if there were fluorine or fluoride concentrations of concern, Mr. Barton agreed to obtain more definitive vegetation samples, primarily to determine if the year of damage could be determined, and if such damage had been essentially constant over the past few years or could be attributed primarily to releases during any one year. The data thus obtained would be considered basic, and annual rechecks would be made to determine if the effluent controls planned were effective.

Hugh F. Henry

H. F. Henry
Safety, Fire, and Radiation Control

HFH:mh
Attachments
6-20-56

cc: Mr. G. H. Dykes
Mr. A. P. Huber
Mr. D. M. Lang
Mr. W. L. Richardson
Mr. M. F. Schwenn
Those Present

Attachment I

ORGDP Problems of Fluorine and Fluoride Effluents

I. Basic Technical Information

1. Effects of Fluorine* on Vegetation

a. In laboratory type tests[1] where various plants were "repeatedly" exposed to HF for 3-hour periods daily,

1) Many deciduous plants, including common vegetables, showed injury at levels of 1000 ppb or less.

2) Some plants, such as gladiolus, peach, and white pine, were injured in concentrations of 10-100 ppb.

b. In semi-laboratory tests elsewhere[2], it was found that younger plants are injured worse than are older ones and,

1) Young peach trees were damaged when exposed to 200-300 ppb HF on 2 days for a total time of only 8 hours; older trees were also damaged but required exposures for 5 days.

2) Norway Spruce trees showed injury after exposures to 150-300 ppb HF on 2 days for a total of 6 hours.

c. In continuous medium term exposures to HF[3] under field conditions,

1) Five year old Ponderosa Pine trees were injured when exposed for 16 days to HF in average concentrations of 0.5 ppb, and the extent of damage increased as the average HF concentration increased; the maximum concentration encountered was about 2.5 ppb HF.

2) Gladiolus plants showed similar effects at the same concentrations, but only a slight increase in injury with increased HF concentrations.

d. As a result of continuous emission of HF from industrial plants, a high fraction of the Ponderosa Pine trees were killed in a 3 square-mile area and others injured in a 50 square-mile area[4]; the overall average concentration of HF in the "killed" area was probably of the order of 1-5 ppb HF, and the exposures at this level occurred over a period of about 5 years. These concentrations are probably not the minimum ones to produce these effects with continuous exposure since it was noted that meterological conditions were such that there was very little exposure during the time of major leaf growth, the most vulnerable time for injury.

* The word fluorine will be used to indicate both fluorine and hydrogen fluoride.

1 McCabe, Louis, AIR POLLUTION, U.S. Technical Conference on Air Pollution, Chapter 9, The Effect of Fluorine on Plants as Determined by Soil Nutrition and Fumigation Studies, Baines, Robert H., et.al.

2 McCabe, Louis, AIR POLLUTION, U.S. Technical Conference on Air Pollution, Chapter 10, Some Effects of Fluorine Fumes on Vegetation, Griffin, S. W. and Bayles, B. B.

3 AGRICULTURAL AND FOOD CHEMISTRY, Vol. 4, No. 1, January 1956, Relationship of Atmospheric Fluoride Levels and Injury Indexes on Gladiolus and Ponderosa Pine, Adams, Donald F., et.al.

4 INDUSTRIAL AND ENGINEERING CHEMISTRY, Vol. 44, No. 6, June 1952, Atmospheric Pollution in the Ponderosa Pine Blight Area, Adams, Donald F., et.al.

[illegible] of Air Concentration to Vegetation Types

1. In all insect and most of tests, the average natural leaf fluorine content of a variety of plants was in the range of 20-40 ppm.

2. After being in an environment of about 1.0 ppm for a short time, the corresponding leaf concentration varied from about 100-400 ppm fluorine; for white pine, this was 120 ppm as compared with 35 ppm originally.

3. Near Alcoa, the normal fluorine content of caps and grasses is of the order of 10 ppm or less; however, due to exposure, these reached levels up to over 80 ppm and were grazed by cattle which were injured. There is no indication of the average air concentration required to produce these levels.

4. Apparently, the damage due to fluorine and fixation of fluorides in plant leaves occurs promptly, and the time of exposure to air contamination may be determined from the age of injured pine needles.

B. Effects of Fluorine upon Animals

Depending upon the animal, an HF concentration of 30-100 ppm in the feed is about borderline for observable effects during long-term exposures[5]; some will be affected at a level of 10 ppm, and at a level of 500 ppm, cattle refuse to eat after a few days.[6]

II. Plant Conditions (See Attached Map)

1. Effects upon pine trees are noticeable in locations adjacent to the plant, primarily in an east-northeast direction; damage ranges from slight to severe with some trees being apparently actually killed.

2. During the first 5 months of 1956, the average fluorine concentration in the general air at the ORGDP, as measured by routine spot samples, has been 1.7 ppm, with only the powerhouse area showing an average concentration below 1 ppm. More detailed information is given in Table I.

3. Recent day-long samples taken near the plant perimeter fence have shown average air concentrations as high as about 15 ppb; the data are given in Table II, and the actual locations concerned are shown on the map.

4. Pine needles collected at the points indicated on the map have shown the HF concentrations given in Table III.

5. Table IV lists the locations in the ORGDP from which HF or F_2 is more or less routinely purged along with the amounts concerned; these locations are shown on the map.

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5 Merriman, G. M., Moorman, R. P., Jr., and Hobbs, C. S., Survey of the Possible Occurrance and Extent of Fluorosis in Cattle on Selected Farms in Blount County, Page 7, The University of Tennessee Agricultural Experiment Station, April 1956

6 Hobbs, C. S., et.al., Fluorosis in Cattle and Sheep, The University of Tennessee Agricultural Experiment Station, Bulletin No. 285, November 1954, Page 2.

III. Conclusions

1. The ORGDP is actually releasing enough fluorine or hydrogen fluoride to cause damage to vegetation.

2. The air concentrations in some locations are such that, if forage crops were being used, injury to farm animals might occur.

3. Measurements indicate that the average plant air concentration is either exceeding the MAC for persons, or is dangerously close thereto. (MAC for HF is 3 ppm and for F_2 is 1.0 ppm; 0.1 ppm has been recommended by the Industrial Hygiene Association as the MAC for fluorine).

IV. Suggestions

1. Efforts be made to reduce the HF and F_2 effluents from the plant by factors of about 10 or more; this should prevent further vegetation injury near the plant as well as reduce plant air concentrations.

2. Routine sampling systems be set up and the results followed.

   a. A periodic air sampling program be instituted; this could include day-long samples and information on meteorological conditions.

   b. Pine-tree-sampling be established; this could include certain areas where seedlings would be planted annually until a grove with trees of various ages would be available for checking to determine if damage is occurring and if fluorine is concentrating in the needles. Peach trees or some forage crops might also be used for this purpose.

HFH:mh
6-14-56

TABLE I

ROUTINE IN-PLANT SPOT AIR SAMPLES (JAN - MAY, 1956)

LOCATION	AVG. F_2 CONC. (ppm)	MAXIMUM LEVEL (ppm)
K-31 - K-33 Area	1.96	6.6
K-27 Area	2.45	5.9
K-25 Area	1.65	4.6
Administration Area	1.84	5.3
K-1401 Area	2.24	3.6
Barrier Plant Area	1.74	5.0
Power House	0.57	1.0

TABLE II

LONG-TERM AIR STUDIES AT PLANT PERIMETER AREAS (MAY, 1956)

LOCATION	MAP CODE	AVG. F_2 CONC. (ppb)	APPROXIMATE DURATION
East of K-1100	A-1	12.47	2 3/4 Days
West of K-31	A-2	1.0	2 1/2 Days
Southwest of K-27	A-3	2.60	8 Hours
Power House Area	A-4	0.47	2 1/2 Days

TABLE III

FLUORINE CONTENT OF VEGETATION NEAR PLANT PERIMETER AREAS (MAY, 1956)

LOCATION	MAP CODE	NO. SAMPLES TAKEN	AVG. F_2 CONC. (ppb)	MAXIMUM CONC. (ppb)
North of K-1100 Area	V-1	1	56.8	56.8
East of K-1420 Area	V-2	3	21.2	28.4
East of K-1100 Area	V-3	2	330	340
East of K-1400	V-4	1	136	136
Northwest of K-33	V-5	2	10.9	18.0
Northeast of Power House	V-6	2	12.6	12.8

TABLE IV

PLANT FLUORINE EXHAUST SYSTEMS

VENT LOCATION	TYPE EXHAUST	AVG. EFFLUENT
K-1131	Continuous	F_2 - 5-10 lb/day (20% of time) - HF - 5-10 lb/day - UF_6 - 300 ppm/day
K-311-1	Continuous	Unknown
K-312-3	Continuous	Unknown
K-1302	Intermittent	F_2 - 5lb/day (Max. 45 lb/day) - HF - 5 lb/day (may release 5 lb/hr.)
K-402-8	Intermittent	Unknown
K-413	Intermittent	Unknown
K-302-5	Intermittent	Unknown
K-502-2	Intermittent	Unknown
K-602-4	Intermittent	Unknown
K-902-3	Intermittent	Unknown
K-1413	Intermittent	Unknown
K-1004-L Lab.	Intermittent	F_2 - 0.06 lb/day vented through traps and diluted - exact effluent concentration unknown.
K-1004-A, B, C, and D	Intermittent	Unknown
K-1004-J	Intermittent	Unknown
K-1132	Intermittent	Unknown
K-702	Intermittent	Unknown
K-1004-L Pilot Plant	Intermittent	F_2 - 0.06 lb/day UF_6 - Trace amounts (vented through traps)

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Attachment II

INTER-COMPANY CORRESPONDENCE

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D.M.LANG

1956 JUN 21 PM 3:28

UNION CARBIDE NUCLEAR COMPANY

A Divison of Union Carbide and Carbon Corporation

To: Mr. S. H. Smiley (2)

Plant: Oak Ridge Gaseous Diffusion

Date: June 15, 1956

Copies To: Mr. C. R. Schmitt

Subject: Preliminary Air Pollution Survey

The attached tabulation summarizes preliminary information obtained from a recent survey of Oak Ridge Gaseous Diffusion Plant buildings that vent gaseous or particulate contaminants to the atmosphere.

Note: 1) Lab D - Kwasnoski - F_2 used for evaporation studies — < 1 #/mo (F_2) to atmosphere

2) 13# HF from vents / days in cascade due to inleakage — Parsons

3) In-place conditioning 1 cell/week — 457 ft³/cell — Parsons

4) HF in K-1131 - cold traps in hoist.

C. R. Schmitt
Engineering Development Department

/mbc

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WCX-163 (8-55)

This form for Inter-Company Correspondence only

-8-

Building	Type Operation	Contaminant	Amt. of Contaminant	Reference
K-402-8	Cold Trapping	F_2	100 scfm. F_2 at 10% F_2 once a year.	R. H. Dyer
		UF_6	Possible	
K-413	Cold Trapping and Side Withdrawals	F_2	100 scfm. F_2 at 10% F_2 once a year.	R. H. Dyer
		UF_6	Possible.	
K-633	Test Loops	F_2	100 scfm. at 10% F_2 once a month. (Diluted to about 5% thru stack.)	R. H. Dyer
K-631	Tails Withdrawal	UF_6	A release occurs approximately once per year	R. H. Dyer
K-1302	Conditioning of F_2 Cells	F_2	Normally condition ca. 16 F_2 cells per month which requires 1-1/2 hours/cell at 500 - 3500 amps. Equivalent to 4.5 lbs. F_2/cell for each 1.5 hrs. This amount of F_2 is discarded to stack; however, two blowers 15,000 cfm. each are used to dilute F_2 stack effluent.	W. C. Paris
K-1401	Converter Conditioning	F_2 ClF_3 UF_6 poss.	Three stacks are employed for gas discharge. Furnace stands 17 and 19 supply ClF_3 (10 lb./mo. av.) and 5 lb. F_2/mo. to small stack at K-1401 with jet dilution. Remaining furnace stands vent F_2 to K-1302 stack or second small stack at K-1401 depending on load. All gas very dilute after purging and jetting operations. Av. F_2 used for conditioning/mo. = 30 lbs.* Conditioning load variable.	R. G. Nicol and C. M. Preston

* Assume average loss of F_2 per converter; generally treat about converters per month (highest load = converters per month).

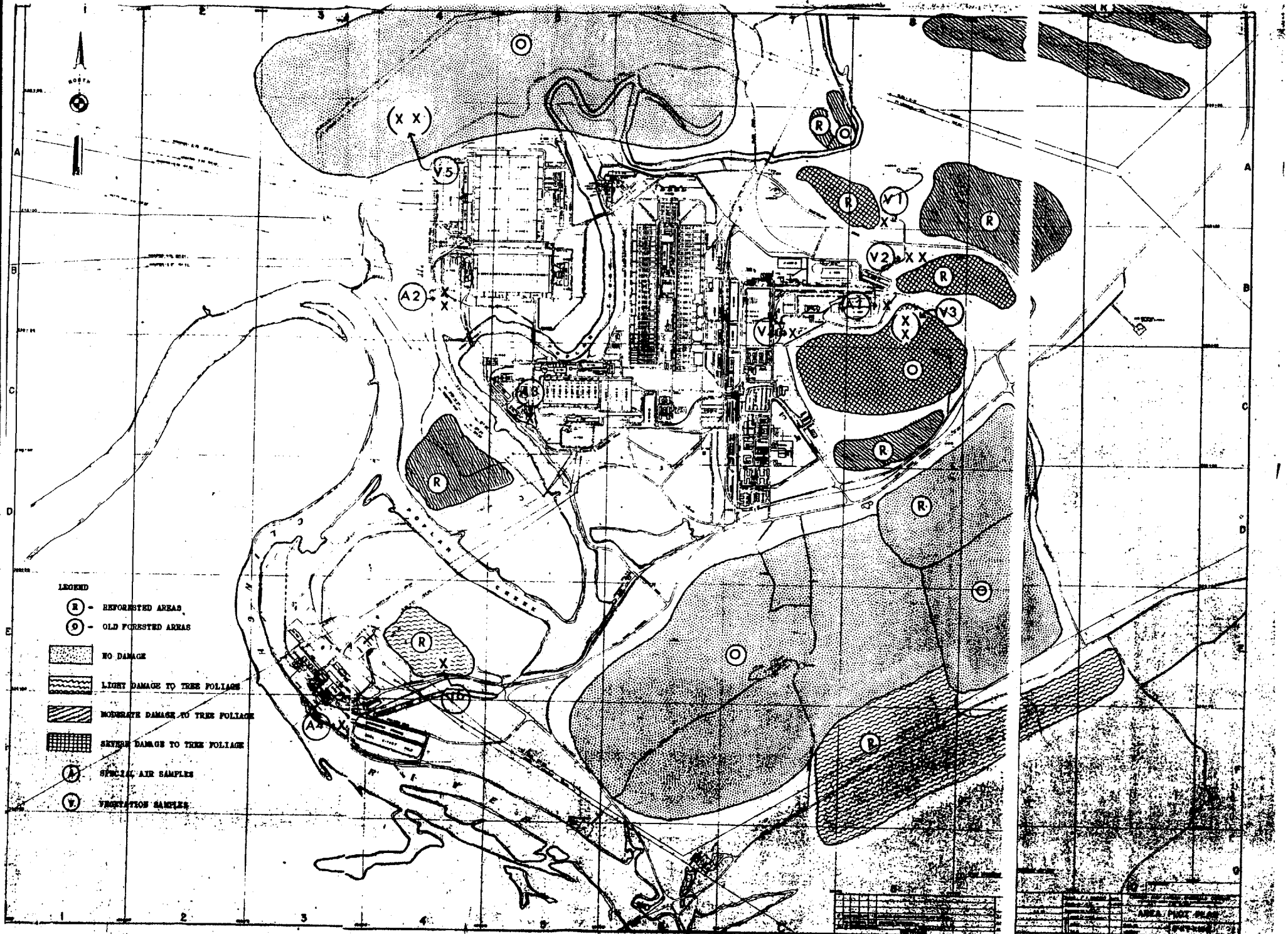
Building	Type Operation	Contaminant	Amount of Contaminant	Reference
K-1420	Nitric Acid Spray Booth	NO_2, NO, N_2O	Intermittent operation. Approx. seven 15-minute periods/day or 2 hrs./ shift, booth analyzes ca. 150 ppm. HNO_3 in 8,000 ft.^{3} in space (20 x 20' x 20') thrown to atmos.	A. L. Allen
K-1420	Furnace Stand Converter Conditioning	F_2	F_2 vented thru K-1302 stack.	J. Dykstra
K-1420	Hg Recovery Room	Hg	Unable to estimate.	J. Dykstra
K-1420	Nickel Recovery	NiF_2	Trace, possibly	J. Dykstra
K-1420	Oxide Fluorination	F_2	Mgg. 30 kgs. UF_6/day 80% F_2 utilization. Normally this F_2 is vented to 1302 stack, but not always; 17 cfm. Kinney pump used to discharge directly to atmos.	J. Dykstra
K-1421	Incineration	Soot	Possibly some traces of UO_2F_2 and UF_4, mostly dust and soot from burning of oily rags, etc.	J. Dykstra
K-1420	Drum Dryer Calciner	NO_2, NO, N_2O	Estimated at 5 lb. HNO_3 max. per day to stack. (Use 120 gal. 3N HNO_3 to make 15 kg. UO_3/day	J. Dykstra
K-1410	Decontamination	F_2 UF_6 possibly	Intermittent operations, maximum of 1 lb. F_2/mo. vented to atmosphere, UF_6 possibly on occasion.	R. E. Shelton
K-1100	Barrier Plant Operation	→ Nickel Carbonyl(?) MAC = 0.001 ppm	Average of 5 lbs. dust/ day discharged to atmos. (amount of dust may be variable, however, occasionally amount may be considerably higher than average.	J. K. Kraszreb

Building	Type Operation	Contaminant	Amount of Contaminant	Reference
K-1131	Cold Trapping	UF_6	Conc. approx. 200 ppm. UF_6. Av. monthly losses range from 35 to 50 lb. UF_6/mo.	L. Nothern, W. D. McCluen (U. control)
K-1131	Feed manufacture	F_2, HF	Approx. 200 lb. F_2 and 1000 lb. HF discharged to stack/mo. The amount of HF may be higher than 1,000 lb./mo. on occasion depending on operation. HF vent tank losses from K-1132, 3, and 4 are included in this estimate.	L. Nothern
K-1413	EDD pilot plant		No fluoride contaminants are vented at present time. Occasionally F_2 may be vented thru stack depending on type of pilot plant operations.	P. J. Marlino R. M. French
K-1004-L	UF_6 pilot plant	UF_6	Occasional seal failure occurs approx. 2 or 3 times a year. These UF_6 losses estimated at 1/2 lb. for each failure.	Flanders and O'Brien.
K-1004-L	UF_6 pilot plant	F_2	Barrier changes approx. twice a month.	Flanders and O'Brien
K-1004-L	UF_6 pilot plant	ClF_3	Trace quantities of ClF_3 are vented thru traps. ClF_3 is extremely dilute. Venting occurs approx. 3 times/mo.	Flanders and O'Brien
K-302-5	Purge and Product	UF_6, F_2	Trace quantites of UF_6 & F_2 lost. Both gases extremely dilute and est. at less than 1 lb./mo.	G. Forseman
K-33 Cooling Towers	K-33 Cooling Water	CrO_4	Loss of chromate in windage calculated at 43.5×10^6 mg. CrO_4/day on basis of 25 ppm. CrO_4 in recirculating water. 230×10^6 gal./day, water recirculating rate, windage at.2% H_2O recirc. rate, 44 fans at 430,000 cfm./fan. Conc. of Cr in windage calculated	

Building	Type Operation	Contaminant	Amount of Contaminant	Reference
			to be 0.49 mg. CrO_3/10 cu. meters of air. According to Amer. Stds. Assn. the max. allowable conc. is 1 mg. CrO_3/10 cu. meters air.	C. R. Schmitt
K-701	Powerhouse		Since some coals contain high fluorides possibly some fluoride contaminant emitted to atm. with stack gases.	J. Gamble
K-1501	Steam Plant	Fly Ash	Flue gases analyze 10-12% CO_2, 2-3% O_2, and remainder @ N_2. Coal has not been analyzed for fluoride content. Some fly ash emitted during winter. Amount of fly ash cannot be estimated.	
K-1004-A, B, C, D	Lab. Area		Some HF, F_2, UF_6 probably vented here. Each lab. room would probably have to be contacted. Fluorides are being used by Kwasnoski and Dr. Bernhardts groups, possibly others.	

Building	Type Operation	Conta	311-1 Vol.%	312-1 Vol.%	312-3 Vol.%	Reference
K-311-1 K-312-1 K-312-3	Cascade Purge	F_2	11.44	3.84	0.41	R. L. Farrar H. L. Goochie
		ClF	0.02	0.42	1.87	
		Cl_2	0.06	0.15	0.55	
		N_2	80.06	86.34	89.19	
		O_2	8.09	8.72	7.87	
		Argon	0.33	0.46	0.37	
		F-114			0.38	
	Total Volume		15,000 to 16,000 scfd.	9,000 scfd.	4,000 scfd.	

K-33 Conditioning & purging



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-13-

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