

FINAL REPORT OF INVESTIGATION INTO THE CAUSE OF THE FAILURE OF THE
REACTOR AT THE OAK RIDGE Y-12 PLANT, TENNESSEE,
ON APRIL 28, 1954



UNION CARBIDE NUCLEAR COMPANY
A Division of Union Carbide Corporation
P.O. Box 117
Y-12, Oak Ridge, Tennessee

History of Y-12 Zirconium Work

In the year 1949, in response to the needs of the Atomic Energy Commission, Union Carbide Nuclear Company undertook to develop a process for the separation of hafnium and zirconium for use in the reactor program. The method developed by Union Carbide Nuclear Company was a liquid-liquid extraction process which was developed on laboratory scale, pilot-planted, and was put into production in the Y-12 Area in January, 1950. In the production process, the starting material was zirconium chloride which was taken into solution as an aqueous chloride. Ammonium thiocyanate was added and the resultant solution was extracted with methyl iso-butyl ketone. Hafnium was preferentially extracted into the ketone, and the purified zirconium passed out of the extraction plant as zirconium chloride. The zirconium was precipitated from the chloride solution by the use of salicylic acid or alternately, by ammonium phthlate, and the resulting metal-organic compound was calcined to zirconium oxide. The oxide, at one stage of the program, was converted back to zirconium chloride for shipping to the Bureau of Mines in Albany, Oregon, and in the final stages of the program was shipped directly to Albany as the oxide. Some material was also shipped to Foote Mineral Company, in Philadelphia, Pennsylvania.

The Y-12 Plant had not experienced the handling of zirconium in the metal form. However, because of the large amount of scrap material produced in the metallurgical processes attendant to preparing and machining the metal, and because this material had undergone an expensive hafnium removal step, a considerable quantity of the hafnium-free zirconium salvage was shipped back to the Y-12 Plant starting in early 1951. Material shipped into the plant came from Foote Mineral Company, at Philadelphia, Pennsylvania, from the Bureau of Mines, Albany, Oregon, and from Westinghouse Electric Corporation, Homestead, Pennsylvania. The total amount of such material shipped to Y-12 was approximately 15,000 pounds. This salvage material was in various containers, 3-, 5- and 55-gallon steel drums, and 5- and 30-gallon wooden barrels. The material consisted variously of sponge, sponge fines, turnings, machine scrap, and sludge.

Approximately 4,700 pounds of the 15,000 pounds of material which had been received by Y-12 was converted to oxide during 1951 by burning over gas fires. This operation was discontinued because of two factors: (1) during the burning operation it was observed that a serious flash fire hazard attended processing of the material, and (2) it was not economically feasible to build an adequate separate facility for converting material to the

oxide. The unit cost increment became so low because of refinements to the separation process that new material could be processed through the hafnium removal step more economically than this salvage material could be purified and converted back to oxide. As a result of this decision, the material was moved to a point which was at that time in an isolated area west of the Y-12 Plant. The drums were placed on about 30-foot centers scattered over the field. This was done as a precautionary measure against spontaneous firing of one drum starting off others and resulting in a conflagration.

None of the operations carried on with the salvage material in Y-12 revealed any tendency of the material to detonate in a high-order explosion, although it was certainly observed that the material was highly pyrophoric. The Y-12 zirconium-hafnium separation facility was shut down on April 1, 1953, because the Commission no longer needed its output. At approximately the same time the zirconium scrap material was relocated to an area farther west, in order to allow for the reactivation of the 9204-4 Building.

At a later date, December 9, 1954, Union Carbide Nuclear Company requested the Oak Ridge Operations Office of the Atomic Energy Commission to advise them as to the desired disposition of the zirconium scrap material. ORO advised the Pittsburgh Area of the availability of this material by two memoranda and telephone conversations in early 1955. ORO was advised by the Pittsburgh Area on April 29, 1955, that the zirconium salvage material was declared surplus and that public sale was authorized. Union Carbide Nuclear Company made extensive efforts to sell this salvage material through its Salvage Department, and to other government agencies, and also through personal contacts with prospective buyers. These prospective buyers for the most part were brokers who had no facilities for processing the salvage material themselves but who in turn undertook to find industrial customers. Typical of these buyers are the Keystone Metal Company, Pittsburgh, Pennsylvania, (Mr. J. Keefe), and the Colonial Metals Company, Columbia, Pennsylvania, (Mr. J. Richards). No one was interested in accepting this material, even on a gratis basis.

The area adjacent to the storage yard for the zirconium salvage had been activated in 1954 for temporary storage of scrap and salvage materials removed in the stripping operations which preceded the Y-12 Plant expansion. The area containing the zirconium was staked out as a hazardous area and personnel involved in disposing of the scrap metal were advised in Safety Meetings of the hazards attendant to disturbing the zirconium. Routine checks made by members of the Y-12 Safety Department indicated that Salvage Yard Supervision was constantly reminding yard employees with reference to the zirconium hazard and the importance of keeping that area clear of scrap metal.

Prior to January 9, no fires in the zirconium storage area had been reported to the Fire Department. After the explosion of May 14, 1956, the salvage yard supervisor (W. L. Coggins), recalled that on one occasion prior to January 9, 1956, he found evidence of fire in one container and that the container was still warm when he noticed it. Coggins also stated that he had noticed evidence of fire in the form of ashes and scorched wood from wooden containers on several occasions during his tenure of assignments at the Salvage Yard, (1954 to present). This foreman estimated a total of approximately six wooden containers destroyed, and that of these, half were burned prior to his assignment to the Salvage Yard.

No evidence of any fires had been noticed by the Y-12 Fire Chief on infrequent inspections (about two visits per year) of this area, prior to January 9, 1956. No witnesses to any fires in the zirconium storage area prior to January 9, 1956, have been found.

In early January, 1956, the decision was taken to transfer the zirconium salvage to another site for permanent disposal. On January 9, 1956, work was started to re-drum material in rotten drums by a procedure of wetting the material with a water spray, dumping it on a piece of plywood, wetting it again and then shoveling it into a steel drum. In spite of these precautions a flash fire occurred during the filling of the second drum which ignited other drums of zirconium and dry vegetation. In consequence all attempts towards re-drumming and removal were stopped.

Meetings were held between Safety and Fire representatives and supervision which culminated in the Y-12 Safety Department issuing written recommendations to responsible supervision after considerable research and study and in compliance with technical bulletin No. 3, titled "Safety of Zirconium and its Alloys". The recommended procedure consisted of burning the material at its present site to an oxide then disposing of the oxide by burying in approved pits. Supervisory planning for this operation was in close accordance with the Safety recommendations.

In order to carry out these plans it was necessary to clear a roadway into the zirconium area through scrap material, large enough to accommodate a large crane. It was this work that the workmen involved in the explosion were engaged in at the time of the accident.

The final disposal of the zirconium material was effected in a manner similar in essential details to that recommended prior to the accident.

Incidents Involving Zirconium Powder

The technological importance of zirconium metal has increased rapidly over the past few years. Within the Atomic Energy Commission the increase in interest⁽¹⁾ has been due chiefly to need for a metal with the unique combination of physical and nuclear properties which zirconium possesses.

Chief use of the material in Atomic Energy Commission operations has been as massive metal, but the production processes^(2,3) suffer from a lack of efficiency, and there is a sizeable salvage stream of poor grade material produced along with the usable metal.

Powdered zirconium metal is used to some extent in industry, in photoflash bulbs,⁽⁴⁾ and for vacuum tube gettering applications^(5,6). It has also been used in detonators for ammunition elements^(7,8). Each of these applications depends on the reactivity of the finely-divided metal, especially with oxygen or other oxidizing agents, in combination with which it burns rapidly, with considerable heat and light being evolved.

Some work has been done to determine the factors which control the combustion of zirconium powders⁽⁹⁾. This work confirms that the powder has a very low ignition point, and is extremely sensitive to ignition by static

electricity or heat. The work generally defines the dividing line between hazardous and non-hazardous powder as a particle diameter of 10 microns. This statement does not apply to powders nominally coarser than 10 microns but actually consisting of agglomerates of particle size less than 10 microns.

Zirconium powder wet with water is much safer to handle than dry zirconium powder⁽¹⁰⁾ because it is more difficult to ignite. Once ignited, however, the wet powder will burn even more violently than the dry powder, partly because the metal will decompose the water and use the oxygen for its own combustion and partly because the steam formed within the burning mass will scatter the metal. The powder containing about 5 to 10% of water is thought to be the most dangerous.

Another important effect pointed up by the work of Anderson and Belz⁽⁹⁾ is the variation of ignition temperature of the powder with the mass of powder present. Apparently the ignition temperature is significantly decreased as the mass of sample is increased. Thus, the hazards are increased twofold.

During the investigation several instances involving accidents with zirconium powder and zirconium salvage materials have come to the attention of the Committee. An incident involving an explosion of moist zirconium⁽¹¹⁾ took place during grinding operations which were being performed under water. The material being fed was supposedly 16% water by volume. It was being fed to the machine from one-gallon, friction-top cans with polyethylene bag-type liners. From the report it appears that when one of the cans was opened, an explosion was initiated which involved several of the cans and produced a fireball which enveloped the area. Light fixtures were broken and a Transit wall eight feet away was damaged. About 87 pounds of material was involved in this action and two men near the point of initiation of the accident were killed. Two others who were farther away and had their backs to the blast were seriously injured, but survived. It was concluded by the Company involved that the source of initiation must have been static charge from the person opening the can. The cans were darkened and torn apart by the reaction. The Company continued to use the material with 16% water by volume, but all of the particular batch involved in the incident was destroyed as a safety precaution.

In another case,⁽¹¹⁾ a preliminary test by a supervisor had established a sample (believed to contain zirconium, magnesium, and magnesium chloride) as inert. To remove the magnesium chloride the samples were agitated while immersed in several changes of water. The first few operations of this type were performed without incident. On the last attempted operation of this type and without any prior evidence of reaction, the sample exploded while under water. The explosion shattered the laboratory bench on which the work was being done, blew out a window some 25 feet away and permanently disfigured the employee. Particles of material blown into adjacent plaster walls were subsequently found to spontaneously ignite when exposed to the air. No formal report on this incident is yet available.

Another previously unrecorded incident concerning moist zirconium powder⁽¹²⁾ occurred in the Stable Isotope Separation Program which is presently a part of Oak Ridge National Laboratory. This involved only minor damage since

there was a very small amount of material involved, but the incident, which occurred in 1947, could be good evidence. In this particular case a very small amount of zirconium powder was being dried in a flask under vacuum conditions. The drying was proceeding rather slowly, so the flask was placed on a hot plate to hasten the process. A few moments after the material was placed on the hot plate, there was an explosion which shattered the flask and crushed the hot plate. There was blast damage to the hood in which the reaction was being performed. As far as can be determined, there was no access to air, since the vacuum was being maintained by the use of a Cenco-Hyvac pump, which is capable of pulling an excellent vacuum. Of course, the water vapor pressure in the flask before the reaction occurred was not known, but it would appear from this that an explosive reaction can be initiated at very moderate temperatures.

Additional information gained from a Company which shipped part of the salvage material to Y-12⁽¹³⁾ may bear directly on the accident, since it gives evidence as to the reactivity of the actual material involved.

In 1950 and 1951, this Company was preparing crystal-bar zirconium using the de Boer hot-wire process. The sponge metal used as charge material was being prepared by magnesium reduction of zirconium tetrachloride. This reduction process, using tetrachloride which may have been contaminated with quantities of oxide and oxychloride, produced a friable sponge, in contrast to the relatively dense sponge ordinarily used in the hot-wire process. The Company had several incidents with the friable sponge. On some occasions they experienced explosions in the crystal-bar reactors. The practice was to introduce into the units wet sponge, and to evacuate and heat the units in order to dry the sponge before introducing the iodine. In several cases the sponge in the units exploded before drying was completed. There were differences of opinion at the time as to the reason for the explosions. It was considered by some that the fault lay in the fact that several units were on a common header.

In the light of present day information on the subject of the reaction between finely-divided zirconium and water, it might be concluded that these incidents paralleled the others described here. In any case, the operators of the crystal-bar plant made ignition temperature determinations on the friable sponge and found that it was significantly lower than was expected. They found also that it was supersensitive to friction. The salvage materials shipped to Y-12 included sizeable portions of this supersensitive material.

From the various incidents reported here, it appears that there is a region of compositions in the zirconium powder-water system in which there is a possibility of a large fraction of material reacting in a very short time.

As a result of the dispersal of the zirconium powder into the air, an extremely hot fireball is produced which lasts for a much longer time. The amount of water necessary to prevent this type of accident being initiated near room temperature is not known, but it must be on the order of 16% by volume involved in one of the accidents reported above. The amount of material necessary to produce a lethal explosion would seem to be rather small. In addition, an explosive reaction can apparently be generated in an open container.

CONCLUSIONS

The evidence as gathered above indicates quite clearly, and the Committee concludes, that the explosion was caused by a drum of zirconium scrap salvage. The reasons for the elimination of other possibilities as a cause for the explosion and for the determination that it was in fact zirconium are outlined in the paragraphs which follow immediately. The last part of this section, under the heading "Cause of Explosion", will be an assumed reconstruction of the incident, using the evidence to show the events leading up to the accident and the actual explosion itself.

ANALYSIS OF EVIDENCE

Possibilities Other than Zirconium

Since sizeable quantities of alkali metals were known to be used in some of the Oak Ridge Operations, it was considered by the Committee that it was necessary to look for evidence which might indicate an alkali metal as the causative factor in this accident. In order to have such an explosion, however, one must postulate that a quantity of alkali metal would have to be suddenly exposed to a large quantity of water. Such an explosion would, of course, cause tremendous heat along with liberation of copious quantities of hydrogen gas, and it could produce all of the after-effects as seen by witness at the explosion, including the concussion wave, the blast effect, and the fireball. The evidence which indicates that this did not happen, however, is rather extensive. First, in none of the chemical analyses was there found to be any residue of the alkali metals or the alkalinity which might result from such an accident. Second, there was no possibility, in this location, of such a large quantity of water coming into intimate contact with a quantity of alkali metal at one time. Finally, no evidence was found, even though an extensive search was conducted, that any alkali metals were ever placed in the Salvage Yard.

The possibility of a high explosive, such as dynamite, had to be considered because of the high-order explosion and the blast effect. This was considered somewhat unlikely, however, because such an explosion produces no prolonged fireball and it was evident in this case that the fireball produced by the explosion persisted for an extraordinarily long period of time. In addition to this, there was no evidence obtained which would show any of the residual nitric acid one would expect of a high explosive detonation.

The possibility of there having been a large quantity of black powder in the area was investigated, although it was considered unlikely that any black powder had been used in Operations in the Oak Ridge Area. The chief evidence against this having been a black powder detonation was the fact that no alkali metal ash was discovered in the area adjacent to the crater.

Ammonium nitrate is used in large quantities in some of the Oak Ridge Operations functions and there is a slight but remote possibility that through mishandling a quantity of ammonium nitrate could have been moved into the Salvage Area. If this had been the case, it would be the most difficult of any of the materials to definitely determine by means of chemical analyses, because the rain which followed the explosion presumably would have washed away the soluble ammonium salts which might have been left. However, one does not expect a prolonged fireball for an ammonium nitrate detonation. Also, ammonium nitrate is difficult to detonate. For these reasons it is considered by the Committee that ammonium nitrate was not involved in the accident.

Zirconium

The preponderance of the chemical evidence obtained during the investigation after the accident points to zirconium as the causative factor in the incident. All of the materials found adjacent to the explosion were heavily contaminated with zirconium and, while it is recognized that this could have been due to the zirconium ash which was carried into the air by the zirconium fires which were known to have followed the incident, it is also true that the pieces of the drums which were definitely determined to have been involved in the explosion, and which were found at great distances from the zirconium site, were found to be heavily contaminated with zirconium. Scrap metal immediately adjacent, lying side by side with these fragments, had a very low zirconium background. In addition to this, some samples of material that were taken from deep within the head wounds of one of the victims was principally zirconium. There is only a small possibility that this material could have been picked up inside the head wound after the explosion, and it would seem from the appearance and the analysis of this sample that it resulted from a small burning metal aggregate which carbonized the skin layers.

An additional piece of evidence concerns happenings which occurred during the operations taken at a later date to dispose of the material. An explosion which occurred during the disposal operation was very similar in appearance to the fatal explosion. Of course, the disposal operation was conducted in such a way that no hazards were involved, but the explosion was extremely violent and it produced a persistent fireball. The same type blast effect and concussion wave as produced in the fatal accident were observed in the disposal explosion.

CAUSE OF EXPLOSION

It is the conclusion of the Committee that the explosion was caused by finely-divided zirconium metal. The events leading up to the explosion and the mechanism of the explosion are thought to be as outlined below. It should be recognized that this reconstruction of the accident must necessarily use a number of assumptions. The Committee, concludes, however, that the evidence at hand is convincing enough to allow these assumptions.

1. The material in the drum is believed to be the zirconium salvage material which was loaded into the drum during the abortive effort during January 1956, to dispose of the material.

This reasoning accounts for several puzzling factors developed during the investigation. First, it has been definitely determined that the drum containing the material was manufactured during 1955. All of the zirconium salvage material was placed in the Salvage Yard prior to that time and thus the only way the drum could have contained zirconium would have been as a result of the prior attempt to effect disposal. If this assumption is true, and the Committee believes that it is, it also explains why the explosion took place in an area not within the boundary of the known zirconium hazardous area. The drum which exploded was 20 feet outside the boundary of the zirconium storage area. Evidence indicates that this drum contained material transferred from the rotten exposed wooden drum on January 9, 1956, prior to the flash fire. It is assumed that in the excitement attendant to the fire, the drum was shuttled aside and it was not realized that it contained zirconium. Subsequently, this drum was partially covered with material gathered in the spring cleanup.

2. At least part of the material in the drum was the supersensitive sponge shipped to Y-12 by Foote Mineral Company.

The evidence pointing to this assumption is extensive. The January disposal incident concerned transfer of material from rotted wooden barrels to metal drums. The Foote mineral was contained in wooden drums and it is thought that no other shipper used wooden containers. In addition, the description of the material, as obtained from the witnesses' statements, coincides with that expected for the friable sponge from Foote.

3. The material inside the drum was wet with a nominal amount of water.

The January transfer operations included wetting the material with a water spray. It would seem that the percentage of water added was in the dangerous range in the light of present knowledge. Since one of the witnesses has stated that the drum was covered with a lid on the work day prior to the accident, the assumption can be made that the powder in the drum was moist.

4. The powder which was spilled on the ground outside the drum was dry.

It is assumed that the drum was overturned during the afternoon of May 11, in the work on the roadway. This would have spilled some of the moist powder onto the ground. The weather during the week end between May 11 and May 14 was hot and dry, and it can be safely assumed that the moist powder had ample opportunity to become dry and, therefore, more easily ignited.

5. The fire originated in the dry powder and was led into the open end of the drum.

It is concluded that an extremely small amount of energy was required to ignite the dry powder. It is thought that it was the supersensitive sponge and such a simple matter as disturbing it with a stick, or even stepping on it, might have produced enough frictional energy to cause ignition. Once ignited, the fire would have been conducted into the drum before the men could have a chance to move away.

6. The material in the drum was probably in stratified layers, some of which may have been more sensitive than others.

This fact, which must be assumed because of the procedures used in the transfer operation, would have given the flame an opportunity to penetrate deep into the mass of the material. This might have left the effect of a tamp in the open end of the drum.

7. The zirconium metal-water reaction was then initiated by the burning metal.

As has been pointed out, the zirconium-water reaction is much more violent than burning of the metal in air. This is primarily due to the generation of gases. Calculations of the maximum explosion pressure and temperature for a possible water mixture have been made (see appendix). The heat of reaction of zirconium and water, 125 Kcal per gram mole, is greater than the heat of reaction of carbon and oxygen, 94 Kcal per gram mole. The combination of carbon and liquid oxygen is a well known high explosive.

8. The reaction must have proceeded extremely rapidly, without significant loss of heat, under essentially adiabatic conditions.

It is assumed that, because of the tamp, the pressure and temperature rose rapidly and the rate of the reaction increased exponentially. Thus, essentially all of the heat produced could have been used in raising the pressure of the gases in the drum (principally hydrogen and water vapor). The speed of the reaction was, without doubt, enhanced by the finely-divided state of the metal powder.

9. The drum then gave way explosively because of the gas pressure.

It is postulated that this happened in a very short time, probably no more than a few milliseconds after the zirconium-water reaction started. The reaction was so rapid that most of the drum did not get hot enough to burn the paint.

10. Dispersal of the contents into the air gave rise to a large and intensely hot fireball.

The fireball is considered to be the result of the final reactions involved in the accident, zirconium-oxygen and hydrogen-oxygen. Part of the zirconium escaped the fireball without burning.