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CONVERSION OF ZIRCONIUM SULFATES TO
ANHYDROUS ZIRCONIUM TETRAFLUORIDE

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Conversion of Zirconium Sulfates to Anhydrous
Zirconium Tetrafluoride*

by

G. H. Beyer, E. L. Koerner and E. H. Olson

Abstract

Increased interest in zirconium metal has resulted in attempts to develop cheaper processes for winning zirconium from its domestic ore zircon. One such process, now under development at the Ames Laboratory, consists of opening up zircon sand by caustic fusion and dehydrating the silica by sulfuric acid dissolution. Crystals of zirconium sulfate are then reacted with 70 per cent hydrofluoric acid to form hydrated zirconium fluoride, which is dried at elevated temperatures under an atmosphere of anhydrous hydrogen fluoride. Anhydrous zirconium tetrafluoride can be bomb-reduced with calcium to yield ductile zirconium metal.

This report discusses production of zirconium tetrafluoride suitable for making soft zirconium metal. The quality of the zirconium metal was dependent upon the purity of the fluoride employed in the reduction. Particular emphasis was placed upon the preparation of zirconium sulfate and pentazirconium disulfate, since the major portion of the impurities had to be removed in this step in order to produce a high-purity fluoride.

The dehydration of zirconium tetrafluoride monohydrate was studied. Satisfactory dehydration conditions resulted when the fluoride was heated at 400°C. for four hours under an anhydrous hydrogen fluoride atmosphere. Sulfate contamination in the form of unconverted zirconium sulfate caused caking in the dehydration step and increased conversion time. Hydrated zirconium tetrafluoride free from

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sulfate contamination was prepared from pentazirconium disulfate. Because the disulfate also resulted in a granular fluoride, it was the preferred sulfate for making the fluoride. Sodium fluoride contamination was found in zirconium tetrafluoride prepared from pentazirconium disulfate. However, this sodium fluoride was not detrimental to the quality of the metal because it was removed in the slag of the bomb reduction.

The investigation showed that zirconium sulfate tetrahydrate and pentazirconium disulfate can be satisfactorily converted to zirconium tetrafluoride. The quality of the zirconium metal produced was sufficiently soft (Rockwell A hardness 43-46) to indicate that sulfate contamination can be controlled.

Introduction

During the last decade many attempts have been made to develop a cheaper process for making zirconium metal. Such a process would yield zirconium metal of sufficient purity and ductility at costs of less than ten dollars per pound. At present, the Van Arkel-deBoer Iodide Process (12) yields excellent metal but the cost is high. The Kroll Process (6) yields a less pure but high-quality ductile zirconium.

The present commercial process for opening up zircon involves the electric furnace smelting of zircon with carbon to form an impure carbide. The carbide is then chlorinated in an electric furnace to form zirconium tetrachloride, or burned in air to form the oxide (2).

An alternate method for opening up zircon uses a caustic decomposition (1,10,13). One part zircon and 1.1 parts caustic soda are reacted in a furnace at 650°C. By subsequent water leaching and treatment with hydrochloric acid, pure zirconyl chloride results, from which sulfate, nitrate, or fluoride can be made.

Preliminary work by R. P. Cox (4) showed that zirconium tetrafluoride could be produced by sulfuric acid treatment of the leached zircon-caustic soda reaction product, followed by crystallization of zirconium sulfate tetrahydrate to remove impurities. Reaction with hydrofluoric acid then formed hydrated zirconium tetrafluoride.

Proposed processes for making zirconium metal are shown in Figure 1. When calcium is used as the reductant for zirconium tetrafluoride, the cost of the zirconium is about the same as for the Kroll process. A cheaper reductant such as magnesium might appreciably reduce the cost of the zirconium metal.

Zirconium sulfate tetrahydrate was found to be the cheapest salt of zirconium that could be made from the leached zircon-caustic soda reaction product (washed frit) (5,8). Reaction with sulfuric acid also permitted efficient silica removal by a simple filtration. However, hydrofluorination of zirconium sulfate tetrahydrate produced a powdery fluoride which was difficult to wash and dehydrate. Fluoride prepared from pentazirconium disulfate was a fine granular material which was easily washed and dehydrated. Hydrated zirconium tetrafluoride was made by reaction of zirconium sulfates with 70 per cent hydrofluoric acid. Water content above 0.5 per cent interfered with the calcium reduction, requiring drying at elevated temperatures in an anhydrous hydrogen fluoride atmosphere.

It was the objective of this investigation to develop a process for the production of zirconium tetrafluoride suitable for bomb reduction to zirconium metal. The process was divided into four sections for the purpose of investigation: (1) preparation of zirconium sulfates, (2) hydrofluorination of zirconium sulfates, (3) dehydration of zirconium tetrafluoride, and (4) bomb reduction of zirconium tetrafluoride.

Preparation of Zirconium Sulfates

The reaction product of the caustic treatment of zircon has been termed "frit" because of its friable nature. The material was porous and easily broken into fine particles; however, it had no glassy properties as do the frits spoken of in the glass industry. The reaction product probably contains sodium silicates, sodium zirconate, some sodium silicozirconate, unreacted sand and sodium hydroxide. Soluble sodium silicates and excess sodium hydroxide were removed by water leaching. The efficient removal of the insoluble silicates as dehydrated silica was necessary to reduce the hydrofluoric acid requirements and to eliminate filtration difficulties in subsequent operations.

The washed reaction product can be dissolved in nitric, hydrochloric, hydrofluoric, or sulfuric acids. Cox (4)

FIGURE 1 PROCESSES FOR CONVERTING ZIRCON SAND TO ZIRCONIUM METAL

showed that zirconium sulfate was the simplest and cheapest compound to prepare. His criteria were based on cost and adequate silica removal. The direct utilization of hydrofluoric acid to produce zirconium tetrafluoride was not used because of excessive hydrofluoric acid requirements for the conversion of silica to silicon tetrafluoride. In general, acid dissolution left a residue of unreacted sands and silica hydrates. It was necessary to filter these undissolved solids from the solution before further processing.

Preparation of zirconium sulfate tetrahydrate

The conversion of the zirconium in the reaction product to a soluble sulfate was carried out as shown in Figure 2. Washed reaction product was added to sulfuric acid in an agitated vessel and allowed to react for about 30 minutes, forming a heavy slurry of zirconium sulfate. After dissolution in water a residue of unreacted sands and dehydrated silica remained. The zirconium sulfate solution was filtered in a centrifuge to remove the solids.

When 85 per cent sulfuric acid was added to the washed reaction product, the highly exothermic reaction caused violent boiling of the liquid. The combination of high temperatures with the dehydrating action of the sulfuric acid caused sufficient removal of the water of hydration from the silica so that no evaporation of the solution was necessary. Even though agitation was used during the reaction, unreacted lumps of material formed.

However, when washed reaction product was slowly added to 85 per cent sulfuric acid no unreacted lumps remained. Violent boiling of the liquid did not occur even though the final reaction temperature was the same. Final silica content was about the same in both cases. Ten-pound quantities of washed reaction product were added to 17 pounds of 85 per cent sulfuric acid at a rate of one pound per minute. The reaction produced a heavy slurry of zirconium sulfate which was water-soluble. This slurry was allowed to stand for 30 minutes and then was dissolved in 18 pounds of water.

Addition of stoichiometric amounts of acid followed by water dissolution yielded a solution which was difficult to filter. The nature of the cake was that of a gel, indicating incomplete dehydration of the silica. A 25 per cent excess of acid was found necessary to obtain a reasonably fast-filtering cake. The discharged residue had

FIGURE 2 FLOW DIAGRAM FOR PRODUCTION OF ZIRCONIUM SULFATE TETRAHYDRATE FROM WASHED FRIT

the appearance of a granular mud. Eighty-five per cent sulfuric acid was used for dissolution because it yielded the fastest-filtering cake.

The sulfuric acid and reaction product mass was allowed to stand for 30 minutes to complete the dehydration and then dissolved in 0.216 gallons of water per pound of washed reaction product used, producing a 3.4 normal sulfuric acid solution containing about 130 grams of zirconium per liter. The unreacted sands and dehydrated silica residue were removed in a centrifuge using a precoat of pulped filter paper. The cake was washed with a minimum of water to displace the entrained liquor.

The filtration of the unreacted sands and dehydrated silica residue was found to be a time-consuming operation. The use of various filter aids as a precoat on the centrifuge was not effective. The best filter aid was pulped paper, as mentioned previously. It was found, by chance, that the addition of calcium carbonate or calcium hydroxide precipitated calcium sulfate which speeded up filtration. The addition of one mole of calcium per mole of zirconium reduced the filtration time by one-third.

Material balances of zirconium for the acid dissolution showed yields of about 95 per cent from the washed reaction product. The zirconium sulfate solution resulting from the acid dissolution step was 1.3 molar in zirconium and 3.4 normal to sulfuric acid.

The solubility of zirconium sulfate in different strengths of sulfuric acid as determined by Masteller (7) is shown in Figure 3. As the concentration of sulfuric acid was increased, the solubility of zirconium sulfate decreased quite markedly. In order to decrease the impurities present in the sulfuric acid-zirconium sulfate solution, it was desired to separate zirconium sulfate crystals from the solution. The choice of final sulfuric acid concentration was based upon two factors. The first was the cost of obtaining the desired sulfuric acid concentration and the second was the recovery of zirconium from the solution. As can be seen from Figure 3, the solubility of zirconium decreased rapidly until the solution was 14 normal sulfuric acid. Further increase of acid concentration beyond this point had little effect on zirconium recovery. A sulfuric acid concentration of 14 normal could be obtained in two ways. The solution could be evaporated, or concentrated acid could be added until the solution was 14 normal.

FIGURE 3 SOLUBILITY OF ZIRCONIUM SULFATE TETRAHYDRATE IN SULFURIC ACID SOLUTIONS AT ROOM TEMPERATURE

The first attempt at producing zirconium tetrafluoride was made by adding 70 per cent hydrofluoric acid directly to the 3.4 normal sulfuric acid solution of zirconium sulfate. Zirconium tetrafluoride yields of only 25 per cent were obtained. In addition, the fluoride retained high residual sulfate-contamination. It was then decided to increase the sulfuric acid concentration in order to decrease the zirconium solubility. Evaporation of the 3.4 normal sulfuric acid solution was attempted. When the solution was evaporated to 14 normal sulfuric acid and cooled, zirconium sulfate crystals precipitated as a heavy paste. The addition of 70 per cent hydrofluoric acid to this mass resulted in a slurry which was difficult to filter and wash. High sulfate contamination was also retained.

The best method for crystallizing zirconium sulfate was found to involve adding 95-98 per cent sulfuric acid until the solution was 14-16 normal. Approximately 2.25 lbs. of 95-98 per cent sulfuric acid per pound of washed reaction product used was added to the 3.4 normal sulfuric acid solution of zirconium sulfate. Continuous stirring was necessary to dissipate the heat. The temperature of solution usually reached 90-95°C. The optimum conditions for crystallization were a controlled cooling rate of 0.4°C per minute down to 45°C. Crystals usually started forming at about 70°C. If the cooling rate of 0.4°C per minute were exceeded, a large number of very small slow-settling crystals were formed. Agitation was stopped when the temperature reached 45°C and the crystals were allowed to settle. Thirty minutes settling time was usually sufficient to assure maximum recovery of the crystallized zirconium sulfate when the mother liquor of sulfuric acid was decanted. Between 65 and 70 per cent of the liquid was removed by decantation. The utilization of a false-bottom container would reduce the time requirements. The decanted liquor could be evaporated to concentrated sulfuric acid and recycled, provided some method of separating the impurities could be found. The impurities present in the decanted liquor were probably sodium silicates, sodium sulfate, and iron sulfates. Zirconium tetrafluoride was prepared directly from wet sulfate crystals. Material balances showed 90 per cent recovery of the zirconium by the decantation process.

An alternate procedure was to filter the crystals in a centrifuge, followed by an acetone wash. In this manner very pure zirconium sulfate free from occluded sulfuric acid could be made. The zirconium sulfate crystals were very fine even though controlled crystallization was used. Efforts to prepare a granular precipitate were unsuccessful. A

granular precipitate was desired so that more occluded mother liquor could be removed by decantation.

Sulfuric acid dissolution offered important advantages over either hydrochloric or nitric acid dissolution. Sulfuric acid was lower in initial cost, had lower weight requirements, gave more efficient silica removal by its greater dehydrating action, and gave better yields of zirconium from the washed reaction product.

Preparation of pentazirconium disulfate

Pentazirconium disulfate, $\text{Zr}_5\text{O}_8(\text{SO}_4)_2 \cdot 14\text{H}_2\text{O}$ (also written $5\text{ZrO}_2 \cdot 2\text{SO}_3 \cdot 14\text{H}_2\text{O}$), was prepared from the washed reaction product to determine if this compound offered any advantages over zirconium sulfate. One known advantage was that it contained 44.3 per cent zirconium (hafnium-free basis) as compared to 25.65 per cent zirconium in zirconium sulfate. It was also reported to be a fast-filtering compound (11).

Sulfuric acid dissolution was not used in this case because the excess sulfate concentration caused the precipitation of basic sulfates instead of the desired product. Pentazirconium disulfate was prepared from washed frit as shown in Figure 4. A seven per cent excess of concentrated hydrochloric acid was added to the washed reaction product. The solution was evaporated to two-thirds of its original volume to aid in silica dehydration. After adding enough water to make the solution one molar in zirconyl chloride, the solution was decanted from the silica residue.

Silica analysis of the decanted solution showed that only about one-half of the silica was removed by acid dissolution. More silica could be removed by crystallization of zirconyl chloride. This step was not warranted since the final silica content of the zirconium tetrafluoride compared favorably with the silica content of fluorides made from zirconium sulfate or zirconium tetrachloride.

The one molar zirconyl chloride solution was heated to 80°C and five normal sulfuric acid was added to obtain a zirconium to sulfate mole ratio of five to two. The pH was then adjusted to 1.5 with 10 normal sodium hydroxide. As a pH of 1.5 was approached, precipitation of pentazirconium disulfate occurred rapidly. The precipitate formed was granular but very fine and attempts at controlling the precipitation to obtain larger granular crystals were unsuccessful. After allowing the precipitate to digest at 80°C for

FIGURE 4 FLOW DIAGRAM FOR PRODUCTION OF PENTAZIRCONIUM DISULFATE FROM WASHED FRIT.

15 minutes, the pH was readjusted to 1.5 and the crystals were filtered. A wash solution of water adjusted to a pH of 1.5 with hydrochloric acid was used. Washing with ordinary water caused the crystals to gel and made complete washing impossible.

The pentazirconium disulfate thus formed usually contained 126 waters of hydration. Controlled drying at 80°C resulted in a compound with 14-16 waters of hydration. To make zirconium tetrafluoride, the material as obtained from the filter was hydrofluorinated directly with 70 per cent hydrofluoric acid.

Hydrofluorination of Zirconium Sulfates

The purified zirconium sulfates were hydrofluorinated directly with 70 per cent hydrofluoric acid to produce hydrated zirconium tetrafluorides. When zirconium sulfate tetrahydrate was hydrofluorinated, zirconium tetrafluoride monohydrate resulted, while hydrofluorination of pentazirconium disulfate yielded zirconium tetrafluoride trihydrate.

Zirconium tetrafluoride monohydrate from zirconium sulfate tetrahydrate

Crystals of zirconium sulfate, wet with 14-16 normal sulfuric acid, were added directly to 70 per cent hydrofluoric acid. The probable reaction was:

The solubility of zirconium tetrafluoride monohydrate in various strengths of sulfuric acid is shown in Figure 5. It can be seen that the solubility of zirconium tetrafluoride monohydrate is very low in 14 to 16 normal sulfuric acid. Attempts to produce the fluorides in lower concentrations of sulfuric acid caused large losses in the mother liquor.

Both 48 and 70 per cent aqueous hydrofluoric acid were used. The 48 per cent acid was more pure, but it was decided to employ 70 per cent acid because of lower cost, higher reaction temperatures and decreased zirconium solubility.

When 70 per cent hydrofluoric acid was added to the wet zirconium sulfate crystals, volatility losses of hydrofluoric

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FIGURE 5 SOLUBILITY OF ZIRCONIUM TETRAFLUORIDE MONOHYDRATE IN SULFURIC ACID SOLUTIONS. AT ROOM TEMPERATURE

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acid were high. Lumps of unreacted zirconium sulfate were formed even though agitation was used. Sulfate concentrations as high as 25 per cent were found in the fluoride cake after thoroughly washing with acetone. The addition of a large excess of hydrofluoric acid resulted in appreciable zirconium losses; possibly caused by the following reaction:

When the wet crystals of zirconium sulfate were slowly added to 70 per cent hydrofluoric acid, the volatility losses of the acid were low--approximately 4 per cent. No lumps of unreacted zirconium sulfate were visible in the reaction mass. However, some zirconium sulfate was found in the fluoride cake unless the wet crystals were added very slowly with constant stirring. A very slow addition of the wet crystals to the acid usually resulted in higher hydrofluoric acid losses because of the longer time involved. A five per cent excess of hydrofluoric acid was used to provide for the acid loss by vaporization. The maximum temperature of 55-60°C was reached as soon as all of the wet crystals had been added to the acid. The precipitation of the fluoride occurred rapidly but the reaction mass was agitated for 10 minutes to insure complete precipitation.

Zirconium tetrafluoride monohydrate crystals were recovered from the reaction mass by centrifuging. About 25 per cent of the mother liquor was retained in the cake. At this point the cake was usually light brown in appearance. When the mother liquor was removed by washing the cake with acetone, the zirconium tetrafluoride monohydrate crystals were white. The zirconium tetrafluoride monohydrate formed was powdery in nature. The effectiveness of the acetone wash was reduced since the cake became tightly packed on the filter and made removal of the last traces of the occluded sulfuric acid impossible. The best washing was obtained by removing the cake from the filter and mixing into a slurry with acetone. Filtration of this slurry followed by another acetone wash was sufficient to remove the last traces of occluded sulfuric acid. The white color of the cake was usually sufficient to determine the end of the washing step. Material balances showed a zirconium recovery of 92 per cent for the hydrofluorination process.

Zirconium tetrafluoride trihydrate from pentazirconium disulfate

A slurry of the washed cake of pentazirconium disulfate with 126 waters of hydration was made by adding 50 moles of water

per mole of washed cake. This slurry was added slowly to a 15 per cent excess of 70 per cent hydrofluoric acid. Approximately 10 per cent of the excess hydrofluoric acid was consumed by the residual silica. The probable reaction was:

The solution was evaporated to one-third its original volume. Upon cooling, spontaneous precipitation of tiny granular crystals occurred. Slower cooling of the evaporated solution increased the crystal size somewhat but a screen analysis showed that approximately 65 per cent of the crystals passed 120 mesh. The crystals were vacuum filtered on a Buchner funnel and washed with acetone. The crystals thus obtained were zirconium tetrafluoride trihydrate. The monohydrate resulted when the crystals were air dried at 80°C.

No sulfate contamination was found in the hydrated zirconium tetrafluoride prepared in the previously described manner. The absence of sulfate and the granular nature of the tetrafluoride were distinct advantages in the dehydration process. The granular nature of the precipitate made possible efficient washing with acetone directly on the filter. Both the sulfate and fluoride formed by this method were fast-filtering, exceptionally pure compounds.

From spectrographic analyses of tetrafluoride samples prepared by the different methods, it was evident that the removal of the impurities titanium, iron and aluminum depended upon the extent of sulfate removal. These data are presented in Table I. Spectrographic analyses of the mother liquor from which the pentazirconium disulfate crystals were obtained showed that the bulk of the impurities were removed at this point. Because of its high purity and also its granular nature, the fluoride prepared from pentazirconium disulfate was the preferred product.

Preparation of Anhydrous Zirconium Tetrafluoride

Anhydrous zirconium tetrafluoride was prepared by drying the hydrated fluorides at elevated temperatures in an anhydrous hydrogen fluoride atmosphere. Drying by conventional means or under an inert gas atmosphere caused the liberation of hydrogen fluoride gas with the probable formation of zirconium oxyfluoride:

Table I

Spectrographic Analyses of Zirconium Tetrafluoride Monohydrates

Source of $\text{ZrF}_4 \cdot \text{H}_2\text{O}$	% Sulfate Present as $\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$	Major Impurities Parts Per Million			
		Si	Fe	Ti	Al
$\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$	none	1000	250	39	1000
$\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$	~5	900	460	27	>1000
$\text{Zr}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$	~10	>1100	600	58	>1000
$\text{Zr}_5\text{O}_8(\text{SO}_4)_2 \cdot 14\text{H}_2\text{O}$	none	850	140	25	76

Further decomposition of the oxyfluoride in the presence of water vapor might also occur:

However, these reactions were not verified. The material obtained from runs using helium as the carrier gas for the water vapor gave erratic zirconium and fluorine analyses.

The operating variables studied were temperature and time of drying. The effects of sulfate, both as occluded sulfuric acid and unreacted zirconium sulfate in the initial charge of zirconium tetrafluoride monohydrate, were also studied.

A diagram showing the essential features of the drying furnace is shown in Figure 6. In order to obtain drying data, a three-quarter inch sampling hole was drilled in the side of the charge tube. A plug fabricated from Hasteloy

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FIGURE 6 DEHYDRATION FURNACE

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metal sheet was fit snugly into the hole. A 1-1/4 inch hole in the outer nickel pipe made it possible to obtain samples at various times by opening the furnace, stopping the rotation of the tubes at a point where the sample hole was accessible, removing the plug, and dipping into the charge with a spatula. The entire sampling operation was performed in less than one minute. The temperature of the furnace dropped only a few degrees when the furnace was opened for sampling.

Effect of temperature on zirconium tetrafluoride dehydration

Zirconium tetrafluoride monohydrate was apparently unaffected by temperatures below 140°C. Above this temperature, however, the compound began to hydrolyze, yielding hydrogen fluoride and zirconyl fluoride. The amount of hydrolysis increased slowly as the temperature was raised to 230°C. At higher temperatures the presence of hydrogen fluoride became evident.

When zirconium tetrafluoride monohydrate was dried in an atmosphere of anhydrous hydrogen fluoride, the water of hydration was effectively removed without excessive hydrolysis occurring. The mechanism of drying is not fully understood. Schmidt (9) reported that the bulk of the water was removed in less than two hours at 258°C. He reported time-composition data for various temperatures. In each instance the charge was heated to the desired temperature for a specified length of time, the furnace shut off, and the charge allowed to cool before a sample was taken. It was felt that this method of obtaining time-composition data might not give a true indication of the actual drying; therefore, the sampling procedure previously described was adopted for this investigation.

Schmidt heated the fluoride for three hours at 250°C and five hours at 400°C. The final temperature of 400°C was thought necessary to remove the last traces of water. The first drying run was made under the conditions used by Schmidt. The fluoride used in this run was made from purified zirconium oxychloride octahydrate. Samples of the fluoride were taken every one-half hour from one hour to four hours and then every hour. The data obtained are shown in Figure 7.

It can be seen that the bulk of the water was removed in the first hour while the furnace temperature was climbing to 250°C. It should be pointed out that the temperatures reported were "indicated" temperatures. Gas flow cooled

FIGURE 7 EFFECT OF DRYING TIME ON ZIRCONIUM
TETRAFLUORIDE WITHOUT SULFATE IN INITIAL CHARGE.

the thermocouple as much as 20°C when the furnace temperature was 250°C, and as much as 50°C when the furnace temperature was 500°C. A better indication of the temperature of the charge was obtained by shutting off the HF gas flow and noting the temperature on the recorder after a few minutes.

The dotted lines in Figure 7 represent the theoretical values for pure zirconium tetrafluoride. The zirconium content appeared to increase more rapidly than the fluorine content, although the fluorine analyses scatter considerably. The zirconium and fluorine analyses were obtained by a pyrohydrolysis method.

The theoretical zirconium-to-fluorine ratio is 54.5 per cent zirconium divided by 45.5 per cent fluorine or 1.20. A better method of presenting these data might have been to plot Zr/F_4 versus time, but this ratio was very erratic. The final dehydrated fluoride was not considered for bomb reduction unless this ratio was reasonably close to 1.20.

After five hours the zirconium concentration appeared to increase above the theoretical 54.5 per cent. This was interpreted as an indication of the presence of oxide. Since the fluoride concentrations dropped at the same point, oxide formation was probably occurring. Oxide formation could have occurred because of air leakage into the charge tube around the loose fit at the gas entrance line.

When the zirconium tetrafluoride had been dried for three hours at 250°C and one half hour at 400°C, analyses showed a high-quality fluoride. Longer drying times than three and one-half hours apparently decreased the effectiveness of the dehydration. A run at 250°C for three and one half hours was made to determine if higher temperatures were necessary to get final dehydration. It was found that both the zirconium and fluorine analyses were low and hence it was concluded that a temperature higher than 250°C was essential.

Some bomb reductions were successful even though the zirconium and fluorine content totaled only 98.5 per cent. However, soft metal was not always obtained when the total was this low.

Attempts to further decrease the dehydration time were made by drying the fluoride at temperatures as high as 550°C. Oxide or oxyfluoride started forming at temperatures as low as 440°C. It was concluded from these experiments that dehydration of the fluoride should be completed at 400°C.

Effect of sulfate on zirconium tetrafluoride dehydration

Zirconium tetrafluoride monohydrate prepared from zirconium sulfate was the charge material for a series of runs. Eleven per cent sulfate as zirconium sulfate was present. Time-composition data were obtained, with the temperature varying from 40°C to 510°C in five hours. These data are shown in Figure 8.

In each of these runs it was necessary to start with a cold furnace. Attempts at preheating the furnace before the charge tube was inserted failed because excessive caking occurred on the sides of the tube before rotation could be started. About 5 minutes were required to assemble the rotation mechanism and the gas feed line. In most cases the desired furnace temperature could be reached in about one hour after starting the run.

Sulfate in the furnace charge increased the time of dehydration. The sulfate also caused caking on the walls of the tube, making dehydration difficult. As long as any sulfate was present in the charge copious amounts of dense sulfuric acid fumes were evolved. This sulfuric acid attacked the monel charge tube and contaminated the zirconium tetrafluoride with a black scale which was found to consist of principally copper and nickel.

The significance of Figure 8 is obscured by the use of excessive drying temperatures for sulfate-contaminated fluoride. It seems likely that considerable oxide was formed, either by hydrolyzing the sulfate in the charge or by overheating the anhydrous zirconium tetrafluoride. With charges containing five per cent or less sulfate contamination, however, zirconium tetrafluoride which yielded soft zirconium metal was produced. Even though caking occurred when sulfate-contaminated fluoride was used as the charge, no residual sulfate was found in the final dried product. To test whether sulfate was totally converted to fluoride, a charge of zirconium sulfate and another charge of pentazirconium disulfate were fluorinated directly in the furnace. No residual sulfate was found in either charge after eight hours of fluorination.

The physical form of hydrated zirconium tetrafluoride varied from a granular crystal to a free-flowing powder. Fluoride from oxychloride or pentazirconium disulfate was granular; fluoride from zirconium sulfate was very fine and powdery. When the material was tumbled in the furnace, the

FIGURE 8 EFFECT OF DRYING TIME ON ZIRCONIUM
TETRAFLUORIDE WITH SULFATE IN INITIAL CHARGE.

granular fluoride tended to grind itself finer while the powdered fluoride agglomerated into lumps. Because the presence of lumps in the fluoride hindered drying, and powdery fluoride limited the size of the charge, the granular fluoride was preferred.

Bomb Reduction of Zirconium Tetrafluoride

The sole criterion used for evaluating the dehydration procedure was product metal hardness. Specifications of zirconium metal hardness from 40-50 on the Rockwell A scale have been set by the Atomic Energy Commission. Corrosion resistance is an important metal property which was not tested.

The bomb-reduction charge used in this investigation was extensively tested by Carlson and Schmidt (3). The following materials were intimately mixed prior to reduction:

ZrF ₄	350 grams
Ca	221 grams (25 per cent excess)
Zn	64 grams (25 per cent alloying addition)
I ₂	56 grams (booster)

From the biscuit obtained, zinc was quantitatively removed by vacuum distillation at 1500°C leaving a zirconium sponge. This sponge was then melted in graphite to form a button of zirconium metal.

The first reductions were made using zirconium tetrafluoride prepared from the tetrachloride. Zirconium metal produced from this tetrafluoride had a hardness of 49. One thousand grams of this fluoride was redried at 500°C for one hour. Two samples of metal produced from the redried fluoride had hardness values of 43.5 and 44.4. These reductions were made to determine the best quality of metal that could be expected.

When zirconium tetrafluoride made from zirconium sulfate dried for four hours at 400°C was reduced, the hardness of the metal was 43.5 and 45.6. Ordinarily, reduction of the same sample in larger batches would lower the hardness. It

was therefore concluded that fluoride produced from zirconium sulfate could yield metal which would meet hardness specifications.

One charge of fluoride prepared from pentazirconium disulfate was dehydrated for three hours at 400°C. Some sodium fluoride was found in the dried zirconium tetrafluoride. Since it was believed that the sodium fluoride might be removed in the slag, the material was bomb-reduced. Zirconium metal with a hardness of 46.0 resulted. It was concluded that zirconium tetrafluoride produced from pentazirconium disulfate could also yield soft zirconium metal, and that some sodium fluoride contamination was not detrimental.

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