

INVESTIGATIONS ON ZIRCONIUM¹

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I—PREPARATION OF ZIRCONIUM OXIDE

In the past two years much interest has been shown in zirconia as a refractory and in zirconium alloys. The demand for purified zirconium oxide has exceeded the very limited production. The following material is an abstract of a portion of a report² submitted on this subject.

Although there is some supply of zircon sand to be had in this country, most of the experimental work recorded below has been done on the Brazilian ore (zirkite). The American zircon sand is relatively impure (40 to 60 per cent ZrO_2), and is much more difficult to get into solution than the Brazilian ore which consists of a mixture of zircon ($ZrSiO_4$) and baddeleyite (ZrO_2), having about 73 to 75 per cent ZrO_2 .³

The following methods have been employed in decomposing zirconium ores:

- 1—Fusion with $NaHSO_4$, commercial niter cake, etc.⁴
- 2—Fusion with caustic soda or soda ash together with sodium peroxide.⁵
- 3—Fusion with $NaHF_2$ or treatment with hydrofluoric acid.⁶
- 4—Ignition with charcoal and subsequent chloridizing.⁷
- 5—Electric arc fusions of zircon, CaO and carbon, leaching with water and chloridizing of the residue.⁸

TABLE I—EFFICIENCIES OF VARIOUS FUSION AGENTS ON ZIRKITE

Fusion Mixture	Ratio of Fusion Mixture to Ore	Time of Fusion	Per cent Decomposed
Na_2CO_3	5	: 1 1 hr. Clear liquid fusion	50
KNO_3	1		
Conc. H_2SO_4 , 180°–90° C.	10 : 1	Digested 0.5 hr.	15
Conc. H_2SO_4 , boiling....	4 : 1	Digested 5 hrs. and heated to dryness	80
Conc. HF.....	10 : 1	Boiled to dryness twice	70
$Na_2S_2O_7$	10 : 1	1 hr. Clear liquid fusion	60
			Incomplete
$NaOH$	3	: 1 20 min. Clear fusion	100
Na_2O_2	1		
$NaCl$	10 : 1	1 hr. Clear fusion	Very Incomplete
Na_2CO_3	1	: 1 0.5 hr. Clear fusion	90
$NaOH$	2		
Na_2CO_3	1	: 1 1 hr. Clear fusion	100
$NaOH$	2		
Na_2CO_3	4	: 1 High temperature and continued fusion necessary for complete decomposition	...
$Na_2B_4O_7 \cdot 10H_2O$ (borax)	1		
NaF	5 : 1	0.5 hr.	100

After the ore is decomposed (with one exception) the zirconium is brought into solution and the hydroxide precipitated and converted into the oxide by ignition. The oxide is further purified by dissolving in

acids and reprecipitating, or by recrystallization of a salt such as the oxychloride. Many trials of these methods were made on quantities of ore varying from one gram up to 10 lbs. (See Table I.)

These trials were made on small samples. On larger samples a longer time of fusion was necessary and in some cases stirring hastened decomposition.

On a commercial scale, the use of fluorides and salt-peter is expensive. The treatment of the ore with lime and coke and subsequent treatment with chlorine was attended with poor results, due partly to the small amounts of zirconium made soluble and partly to the difficulty of finding apparatus which would withstand the chlorine at the high temperature required for satisfactory chlorination.

The results of several trials in which zirkite ore has been fused and ZrO_2 subsequently produced with some success are described below.

(1) CAUSTIC SODA, SODA ASH FUSION AND PRECIPITATION WITH SO_2 —One pound of zirkite (100 mesh) was sifted into a thoroughly fused mixture of 3 parts of Na_2CO_3 and 3 parts of $NaOH$. The fusion was continued for 1 hr., the mass cooled, crushed, and lixiviated three times with hot water. The filtered, washed residue was digested with 1 : 1 HCl , the solution filtered and diluted. The acid was neutralized as nearly as possible with soda ash without incurring precipitation and SO_2 passed into the hot solution. The precipitate yielded 0.5 lb. of nearly white oxide containing 98 per cent ZrO_2 , about 70 per cent of the theoretical quantity. The total cost for this production, exclusive of labor and equipment, is about forty cents a pound.

(2) PHOSPHATE METHOD OF PRODUCTION OF ZrO_2 —Ten pounds of niter cake were fused and one pound of zirkite (100 mesh) was sifted into the liquid melt. The fusion was continued for 1 hr., the mass cooled, crushed, and extracted with hot water. The liquid was filtered, some sodium peroxide and a small calculated excess of sodium phosphate added. The zirconium phosphate was filtered in a filter press, dried, and fused with 3 parts of caustic soda, crushed, leached with water, filtered, and the residue treated with diluted HCl to remove the iron and aluminum. The residue was dried and ignited. It gave a white oxide of 98 per cent purity at a cost of about forty cents a pound. A 60 per cent yield was realized.

(3) BASIC SULFATE METHOD—One pound or a larger quantity of ore was slowly heated with four parts of concentrated H_2SO_4 until free of fumes and the temperature gradually raised to 650° C. After cooling the flour-like residue was extracted with 50 parts of cold water, filtered, and sodium carbonate added to neutralize any free acid until the zirconium hydroxide just began to form. The solution was allowed to stand for 3 or 4 days, during which time the basic sulfate $4ZrO_2 \cdot 3SO_3 \cdot 14H_2O$ gradually separated out. When this was ignited a very high-grade ZrO_2 was obtained, which in one case contained 99.84 per cent ZrO_2 and was free from any determinable trace of SiO_2 . Exclusive of labor and equipment the cost for the production

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² The full report will be published by the U. S. Bureau of Mines in the near future. Thanks are due to Dr. R. B. Moore and Dr. S. C. Lind for their aid and advice during this work.

³ For a discussion of the mining and concentration of the Brazilian ore see Meyer, *Footnote Mineral Notes*, November 29, 1916.

⁴ Franz, *Ber.*, 3 (1870), 58.

⁵ Berzelius, *Ann. Mines*, [1] 12 (1826), 297; Schiøtz ("Suggested Use of Na_2O_2 for Analytical Work"), *Tidskrift. Kem. Farm. Terapi*, 14 (1917), 256.

⁶ Rose, *Ann. chim. phys.*, [3] 60 (1860), 260; Marignac, *Ibid.*, [3] 60 (1860), 257.

⁷ Troost, *Compt. rend.*, 116 (1893), 1227, 1428; Moisson and Lengfeld, *Ibid.*, 122 (1896), 651.

⁸ Troost, *Loc. cit.*

of 1 lb. of oxide by this method was about twenty cents.

(4) OXYCHLORIDE CRYSTALLIZATION METHOD—This method was tried in several cases for the purification of zirconium compounds but it was found to be both too tedious and expensive for commercial work.

II—PREPARATION OF PURE POTASSIUM FLUORZIRCONATE AND THE CRYSTALLINE ZIRCONIUM ALUMINUM ALLOYS

Before pure metal can be prepared, the principal object of the investigations, pure zirconium oxide or zirconium salts, must first be obtained. Even the oxide prepared by the basic sulfate method of crystallization contains various impurities. The quickest and most satisfactory method of purification is by means of successive crystallization of K_2ZrF_6 , previously described by Marignac¹ and others.

The K_2ZrF_6 is prepared by dissolving ZrO_2 in hydrofluoric acid. This was done in the present work in lead vessels made for the purpose having a capacity of one to two gallons.

After heating, the oxide gradually dissolves and a clear solution is obtained. This is diluted and filtered (using a rubber funnel) into a clean lead dish. It should not come in contact with glass on account of the formation of fluorsilicates.

A filtered solution of C. P. potassium carbonate is added in sufficient quantity for the complete formation of all the K_2ZrF_6 , but not enough to neutralize all of the free acid. If too much K_2CO_3 is added the zirconium is precipitated as the hydroxide, and more hydrofluoric acid is needed. Potassium carbonate should be used in place of potassium hydroxide because of its greater freedom from sodium salts. The sodium fluorzirconate is very insoluble and cannot be easily recrystallized.

The solubility of the potassium salt varies considerably with the temperature, as is shown from the following figures:

Temp. ° C.	G. in 100 cc. H_2O	
	K_2ZrF_6	Na_2ZrF_6
100	25.0	1.67
20	15.0	
18		0.38
0	0.78	

After cooling the hydrofluoric acid solution prepared above, the crystals of K_2ZrF_6 are filtered off. The crystals are redissolved in hot water containing a little hydrofluoric acid, filtered while hot, and allowed to cool. The crystals of K_2ZrF_6 again separate.

Starting with 98 per cent ZrO_2 , three crystallizations yield a perfectly white crystalline salt which analyzed 32.10 per cent (theoretical: 32 per cent) Zr. A one-gram sample did not contain enough of either iron or titanium to give distinguishable colorimetric reactions after the fluorides had been removed and the salt was considered to be of at least 99.99 per cent purity.

In the production of zirconium metal the so-called "crystalline zirconium" alloy has also been used. This alloy has often been mistaken for zirconium metal on account of its great stability toward chemical

agents and oxidation. It has been prepared by the method of Weiss and Newman.¹

Recrystallized K_2ZrF_6 is fused in a graphite dish, in a gas furnace. In this investigation bored-out graphite sticks in the shape of deep cylindrical vessels were used. A temperature of about 900° C. is necessary to get a clear liquid. When the fusion is complete 1.5 times its weight of aluminum are added, a little at a time. During these additions a vigorous reaction takes place. When the reaction is finished the heating is continued for 10 to 20 min., the whole mass covered with a layer of sodium and potassium chlorides, and allowed to cool. When the dish is broken the aluminum alloy is found collected free of salt in the bottom of the dish. Flat plate-like, apparently monoclinic, crystals are to be seen on the surface. The alloy is carefully cleaned off, broken up with a chisel and treated with strong solutions of caustic soda until no more aluminum will dissolve. The residue is separated by decantation and filtration, then boiled with successive portions of 1 : 1 hydrochloric acid to remove the zirconium hydroxide which forms.

On filtering and drying the residue it is found to consist of silver-white crystals about 0.5 to 1 mm. across, and about as resistive to chemical action as zirconium metal itself. The more silicon impurity present the larger the crystals. The following is an analysis of this material:

	Per cent
Al.....	30
Zr.....	68
Fe, Si, small amts. Ti, etc.....	1.0
TOTAL.....	99.0

A much purer product showed the following analysis:

	Per cent
Al.....	29.9
Zr.....	70.00
Fe.....	0.03
Si.....	0.05
Ti, not enough to determine	
TOTAL.....	99.98

Since the K_2ZrF_6 can be prepared in very pure condition, the purity of the crystals is governed very largely by the purity of the aluminum metal used. The so-called C. P. aluminum metal rarely runs over 99.5 per cent Al, the principal impurities being iron and silicon.

This aluminide (Zr_3Al_4) may be prepared in impure condition directly from zirkite by fusing the ore with sodium fluoride and then adding the aluminum. The treatment of the alloy (with caustic soda) after cooling is as above. Following is an analysis of this product, where a part of the aluminum is replaced by silicon:

	Per cent
Al.....	13.10
Zr.....	74.47
Fe.....	0.84
Si.....	11.15
Ti, not determined	
TOTAL.....	99.76

A crystalline silver zirconium alloy may also be prepared by the aluminothermal reduction.

¹ Loc. cit.

¹ Z. anorg. Chem., 65 (1910), 248.

III—PREPARATION OF ZIRCONIUM METAL

The literature refers to four varieties of zirconium metal: amorphous, crystalline, graphitoidal, and sintered. The properties given for these varieties of metal by various authors differ widely. The historical references have been omitted for the most part for the sake of brevity.

The following methods have been employed for the production of this metal:

A. AMORPHOUS—(1) Reduction of K_2ZrF_6 with sodium metal in an iron tube;¹ (2) Passing $ZrCl_4$ over heated sodium metal;² (3) Reduction of ZrO_2 with calcium metal.³

B. CRYSTALLINE⁴—Reduction of K_2ZrF_6 with large excess aluminum metal in a graphite dish. This so-called crystalline zirconium has been shown to be an alloy of aluminum and zirconium.

C. GRAPHITOIDAL—The interaction of sodium zirconate and iron is said to yield this variety⁵ of the metal. After repeated failures in attempting to prepare it the conclusion is drawn that there is no such variety.

D. SINTERED⁶—In most cases the authors have introduced the word "coherent" for this variety of metal.

1—Alumino-thermic reductions produce coherent metal.

2—Heating the amorphous product obtained in A-3 yields small lumps or granules of partly coherent metal.

3—Reduction of ZrO_2 with carbon yields Zr metal mixed with carbide.

In the experimental work, all of these methods have been tried in the production of the amorphous and coherent varieties of zirconium.

The amorphous metal has been prepared by the following methods:

1—Reduction of K_2ZrF_6 in an evacuated iron tube with a small excess of sodium. This takes place on heating the tube to a dull red heat. The mass is cooled and extracted with dilute hydrochloric acid until all the salts are removed. Samples were prepared containing 98 per cent zirconium.

2—Reduction of K_2ZrF_6 with aluminum in the Arsem vacuum furnace, in which the excess salts were distilled away, yielded a good grade of amorphous zirconium contaminated with some aluminum.

3—Reduction of ZrO_2 with aluminum will under certain conditions yield an impure amorphous metal.

PROPERTIES OF AMORPHOUS ZIRCONIUM

PHYSICAL

Atomic weight: 90.6 (taken from literature).

Alloys: With one exception does not form alloys under ordinary conditions. Can be alloyed by heating with aluminum. Does not form amalgams.

Boiling point: Very high.

Corrosion: Remains unchanged at ordinary temperatures although when suspended in water it apparently reacts slowly to form the hydroxide.

Color: Black; heated above 1000° C. gray, metallic.

Electrical conductivity: Very low: black amorphous non-conductor.

Fusibility: According to Wedekind, it partly sinters at 1000° C. although we have never observed fusion at any such low temperature. The material apparently runs together to

¹ Berzelius, *Ann. Phys. Chem.* (Pogg.), **4** (1825), 124; **8** (1826), 186.

² Troost, *Compt. rend.*, **61** (1865), 109.

³ Wedekind, *Ann.*, **395** (1913), 149.

⁴ Weiss and Newman, *Z. anorg. Chem.*, **65** (1910), 248; *Am. J. Sci.*, [4] **29**, 457; *J. Soc. Chem. Ind.*, **29**, 218.

⁵ Troost, *Loc. cit.*

⁶ Kuzel and Wedekind, U. S. Patent 1,088,909 (1914).

form the white coherent metal, looking like iron steel, a little above 1600° in a high vacuum in an atmosphere of exceedingly dry and pure hydrogen. If a small amount of air or oxygen is present, this fusion does not take place. The melting point of the zirconium is in the neighborhood of 1600° . When heated to 1000° C. the amorphous black metal changes to gray-colored material, taking a metallic polish.

Hardness: Soft, velvety. Ignited above 1000° C. granular.

Luster: Metallic when polished. When pressed into sticks at a high pressure and polished it has the appearance of a solid gray metal.

Melting point: About 1600° C.

Oclusion of gases: This material absorbs or occludes gases very readily. It also seems to have much affinity for moisture.

Specific gravity: About 4.0. The specific gravity varies with the amount of heating. The amorphous metal when heated in the high vacuum furnace gradually shrinks and the specific gravity increases until coherent metal is obtained, which has a specific gravity of more than 6.0. The amorphous metal as ordinarily prepared has a specific gravity of about 4.0.

Volatility: Does not volatilize at 2000° C. in a vacuum of 1 to 2 mm.

CHEMICAL

Combines readily with chlorine at low red heat; in nitrogen it burns to nitride at dull red heat. When heated in the air to a dull red heat, it burns to the oxide with a white incandescence. It is readily soluble in hydrofluoric acid even when dilute. It is slowly soluble in 1 : 1 hydrochloric acid. It is slowly soluble in nitric acid but more readily soluble in sulfuric acid. It dissolves in the ordinary fusion agents such as potassium bisulfate, caustic soda, etc. Amorphous zirconium formed by the reduction of K_2ZrF_6 with sodium will dissolve in water, forming bluish colloidal solutions which readily pass through the filter paper.

The coherent metal was prepared alumino-thermically in small beads which showed the following analyses:

	Per cent	
Zr.....	99.40	99.50
Ti.....	0.45	0.40
Fe.....	0.01	0.02
Al and Si, by difference...	0.14	0.08
TOTAL.....	100.00	100.00

A typical charge for this alumino-thermic reduction was made as follows:

ZrO_2	90 g.
$KClO_3$	30 g.
Al.....	40 g.

All the materials were first purified, thoroughly mixed and finally fired in a fire-clay crucible.

The coherent metal was also prepared in the Arsem furnace in an evacuated atmosphere of very pure, very dry hydrogen by the reduction of K_2ZrF_6 with aluminum. This method is that used in the reduction to the amorphous, but this amorphous metal cannot be made to cohere unless the evacuated atmosphere in the furnace is entirely free from moisture and air. The following is an analysis of this metal:

	Per cent
Fe and Si.....	0.2
Al.....	Absent
Zr.....	99.5
TOTAL.....	99.7

Coherent metal was also prepared by arcing pressed sticks of the crystalline zirconium-aluminum alloy in an evacuated atmosphere of hydrogen.

PROPERTIES OF COHERENT ZIRCONIUM

PHYSICAL

Alloys: Does not dissolve in lead, tin, or silver by simply heating above the melting point of the respective metal.

Will alloy with silver, aluminum, and iron when heated above the melting point of zirconium in the Arsem furnace. Alloys of silver, iron, nickel, or aluminum are easily made by simultaneous reductions at high temperatures (Goldschmidt's process). Does not form amalgams.

Corrosion: Does not rust or tarnish on long standing in the laboratory but when polished remains bright white like polished nickel.

Color: White metallic.

Electrical conductivity: Fairly good conductor. Probably less than that of iron.

Fusibility: Can be readily fused under the proper conditions away from the air at about 1600° C.

Hardness: About 6-7 on the Mohs scale. The hardness varies with the method of preparation and purity of samples. The pure samples were less hard than the more impure metal. In all cases the metal would readily scratch glass. As would be expected with a metal of this degree of hardness it is also quite brittle and can easily be broken by lightly pounding with a small hammer. The metal is still very hard although less brittle at a red heat. The hardness on the Shore scleroscope is 40 to 45.

Luster: White metallic. Takes a fine polish like nickel.

Melting point: About 1600° C. The U. S. Bureau of Standards has found the melting point of the metal from 1400° to 2200° C. as it was prepared by various authors. In recent trials the metal prepared appears to melt very close to 1600° C. in an atmosphere of pure dry hydrogen.

Occlusion of gases: When samples of zirconium are fused in pure dry hydrogen and rapidly cooled, a phenomenon similar to the so-called "spitting" of silver is observed. When silver is fused it dissolves oxygen and on cooling the oxygen is evolved, causing the "spitting" and leaving the metallic mass porous. The zirconium, when similarly treated in hydrogen, shows the same porous appearance. This porosity is not observed in samples prepared by the Goldschmidt process.

Specific Gravity: Partially sintered amorphous zirconium shows a specific gravity of 4.39. The specific gravity of the aluminothermic, 99.5 per cent zirconium is 5.55, while the specific gravity of 99.5 per cent coherent metal prepared by the reduction of K_2ZrF_6 with aluminum was found to be 6.06. The specific gravity of zirconium, as with other metals, varies with the method of treatment.

CHEMICAL

The white metal is much less chemically active than the amorphous metal. It does not react with chemical reagents readily at ordinary temperatures. This variety of the metal in a solid piece can be heated to a bright red heat in the blast flame with no more than a very thin bluish superficial surface oxidation. It can be burned in the air by heating to a white heat in the finely divided condition. It is insoluble in all acids except aqua regia and hydrofluoric acid. The metal dissolves easily in hydrofluoric acid (1 : 1) but it takes at least 5 hrs. to dissolve one gram of the solid metal by digesting in an excess of aqua regia. The metal is not readily dissolved by fusion with bisulfates, caustic soda, etc.

IV—COMPARISON OF THE METHODS OF ANALYSIS

On attempting the analysis of zirconium ores by the different methods in the literature very conflicting results were obtained. For example, a sample of zirkite ore gave the following percentages of ZrO_2 by different methods:

TABLE II—ANALYSIS OF ZIRKITE ORE BY DIFFERENT METHODS

Method Employed	Weight of Ore (or Aliquot) G.	Weight of Phosphate G.	Weight of ZrO_2 G.	ZrO_2 Per cent
Phosphate.....	0.0853	0.1215	0.0626	73.3
	0.0707	0.1010	0.0520	73.5
Sodium thiosulfate.....	0.2000	0.1740	87.0
	0.2000	0.1700	85.0
Sodium iodate.....	0.2000	0.0947	47.35

The results obtained by the phosphate method are very nearly the correct ones but an inexperienced

worker would have trouble in deciding just what percentage of ZrO_2 the ore should have. The thiosulfate precipitate is high, due to occlusion of large amounts of sodium salts, while the iodate results are low due to too strong acidity of the solution for precipitation.

The following methods in more common use are listed and comparisons are made as to their relative merits. The more important methods for the estimation of zirconium are as follows.

- 1—The phosphate precipitation. Hillebrand, U. S. Geol. Survey, *Bull.* 73 (1900); Lundell and Knowles, *J. Am. Chem. Soc.*, 41 (1919), 1801; Nicolardot and Reglade, *Compt. rend.*, 166 (1919), 348.
- 2—The thiosulfate or SO_2 precipitation. Baskerville, *J. Am. Chem. Soc.*, 16 (1894), 475; Ferguson, *Eng. Min. J.*, 106 (1918), 356, 793.
- 3—The iodate separation. Davis, *Am. Chem. J.*, 11 (1889), 25.
- 4—The peroxide precipitation. Bailey, *J. Chem. Soc.*, 149 (1886), 481; Walker, *J. Am. Chem. Soc.*, 20 (1898), 513.
- 5—The phenylhydrazine precipitation. Allen, *J. Am. Chem. Soc.*, 25 (1903), 421.
- 6—The cupferron precipitation. Ferrari, *Atti. Ist. Veneta Scienze Lettere ed arti*, 73 (1914), 445; Brown, *J. Am. Chem. Soc.*, 39 (1917), 2358.
- 7—The fluoride separation. Headden, *Proc. Colo. Sci. Soc.*, 11 (1917), 185.

In a study of these methods it was found that the fluoride separation is incomplete and the peroxide precipitation takes place only when the concentration of the peroxide is very high in the solution. Methods 4 and 7 were therefore given but scant attention.

TABLE III—COMPARISON OF RESULTS BY DIFFERENT METHODS

Weight of ZrO_2 Taken Grams	Weight of ZrO_2 Found	Variation
Phosphate Method:		
0.0865 ZrO_2	0.0875	+0.0011
0.0357 Fe_2O_3	0.0877	
0.0471 Al_2O_3		
Av., 0.0876		
Sodium Thiosulfate Method:		
0.0865 ZrO_2	0.0845	-0.0018
No Fe_2O_3 or Al_2O_3	0.0850	
Av., 0.0847		
0.0865 ZrO_2	0.0988	No check; large amts. iron and alum in precipitate
0.0643 Al_2O_3	0.1873	
0.1514 Fe_2O_3		
Phenylhydrazine Method:		
0.0865 ZrO_2	0.1370	ZrO_2 , 0.0865 Al_2O_3 , 0.0471
0.0357 Fe_2O_3	0.1388	
0.0471 Al_2O_3		
Av., 0.1380		
Cupferron Method:		
0.0865 ZrO_2	0.1213	ZrO_2 , 0.0865 Fe_2O_3 , 0.0357
0.0357 Fe_2O_3	0.1219	
0.0471 Al_2O_3	0.1213	
Av., 0.1215		0.1222 - 0.0007

The phosphate is best precipitated from about 10 per cent sulfuric acid to which H_2O_2 is added to retain the titanium in solution. An excess of disodium phosphate should be used, the solution heated to boiling and allowed to stand, before filtration. Due to the gelatinous nature of the precipitate and difficulties in washing no larger quantity than 0.05 to 0.1 g. of ZrO_2 should be precipitated from 200 cc. of solution at one time.

It has been found from Table III and similar tables that:

(1) The phosphate gives fairly good results in the presence of iron and aluminum but a 50 per cent excess of ammonium phosphate should be used when the acidity lies between 10 and 20 per cent H_2SO_4 .

(2) The sodium thiosulfate method cannot be used in the presence of much iron and aluminum salts.

(3) Phenylhydrazine precipitates the zirconium together with the aluminum, away from the iron, but this precipitate is slimy and difficult to wash free of impurities. The results by this method should equal the weight of ZrO_2 + the weight Al_2O_3 but are too high *for this reason*. If done in dilute solution the phenylhydrazine separates the Zr and Al from the iron.

(4) Cupferron serves to separate Zr and Fe from aluminum with a fair degree of exactness. The cupferron precipitate is a desirable one to handle.

(5) Although not shown here, the sodium iodate method can be used with accuracy in carefully neutralized solutions. It is subject, however, to somewhat the same limitations as the sodium thiosulfate method.

A method of analysis for zirconium which could be applied to alloys must be such as to include separation from Fe, Al, V, Cr, Ni, Co, Ti, Si(?), and perhaps other elements. The method of analysis of ores is not complicated, as elements such as V, Cr, Ni, and Co are not usually found in zircon ores.

RECOMMENDED METHOD OF ANALYSIS

PREPARATION OF SAMPLE—The alloys, which are for the most part brittle, are pulverized as far as possible in a steel mortar, while the ores are pulverized to pass a 100- to 200-mesh sieve before analysis is undertaken. The thorough grinding of samples of the ore is very important as much of the ease with which the samples go into solution in various fusion agents depends on the fineness of subdivision of the sample.

METHOD OF SOLUTION AND SEPARATION OF THE SILICA—Alloys should be dissolved in aqua regia using about 0.5 to 1 g. of the alloy and, after the solution has been made, diluting it up to 500 cc. or a liter so that a suitable aliquot of 100 cc. would represent about 0.05 g. of ZrO_2 for analysis.

If the percentage of zirconium and silicon in the alloy is high, the process of dissolving it in aqua regia will be slow. It is occasionally necessary to use hydrofluoric acid in a platinum dish in preparing the solution. The use of this is objectionable when the percentage of silicon is desired and the following procedure is to be preferred:

After treatment with aqua regia and evaporating the solution nearly to dryness to separate the silica, if there is an insoluble residue other than silica remaining, the solution is diluted, filtered, and the residue ignited in a platinum crucible. This is then fused with sodium or potassium bisulfate, the fused mass cooled, dissolved in water, and the insoluble silica again filtered and washed. The filtrate is combined with the filtrate from the aqua regia treatment in a 500-cc. volumetric flask. The silica is determined by the usual method of volatilization with HF and H_2SO_4 , and if there is any weighable residue remaining after this treatment, this must be brought into solution by means of a second fusion with bisulfate, the solution from this fusion being combined with the other filtrates in the volumetric flask. Suitable aliquots of this solution, made up to 500 cc. and containing 5 per cent H_2SO_4 , are taken for the zirconium determina-

tion. In no case should more than 0.1 g. of ZrO_2 be taken.

In the case of ores, 1 g. of the ore is fused with four parts of NaOH and one part of Na_2O_2 in a nickel crucible to a clear, dull red liquid fusion for 15 or 20 min. The fused mass is cooled and dissolved out from the crucible with warm water to make a volume of about 100 cc. The zirconium and most of the titanium are in the form of insoluble sodium zirconate and sodium titanate suspended in the solution. The solution is then made about 10 per cent acid with sulfuric acid and heated to dissolve all the zirconium and titanium. After boiling down nearly to dryness the solution is again made up to about 200 cc. and the silica filtered off, together with any insoluble residue. The filtrate is reserved in a 500 cc. volumetric flask, while the silica is determined in the residue by the customary H_2SO_4 and HF treatment. If there is a residue left after the hydrofluoric-sulfuric acid treatment this must be again fused with caustic soda and sodium peroxide and the solution obtained by the subsequent acid treatment combined with the filtrate in the volumetric flask for the analysis.

It is frequently the case that two and even three fusions are necessary in order to obtain a complete solution. It might be further suggested in the determination of the silica that the residues for this purpose be first ignited with a little sulfuric acid and weighed before the hydrofluoric acid treatment is attempted. If this is not done even where there is a small percentage of silica sometimes the weight will be found to increase instead of decrease as it should.

ANALYSIS OF SOLUTION CONTAINING Fe, Al, Cr, Ni, Mo, W, Ni, Co, Zr, Ti, AND P—The acid solution which is now free of silica and has been drawn off in a suitable aliquot to contain about 0.05 g. ZrO_2 is heated nearly to boiling (about 90° C.) and ammonium hydroxide added until a slight permanent precipitate is formed. Dilute HCl (1 : 1) is added from a burette drop by drop until the precipitate which has formed just redissolves and the solution is perfectly clear. About five drops more of the HCl are added to the solution, which should now have a volume of about 200 cc. Three cc. of phenylhydrazine which have previously been dissolved in 10 cc. of hot water are added, and the solution stirred vigorously and filtered immediately through quantitative paper. After washing thoroughly with hot water, the paper and precipitate are dried and ignited in a platinum crucible. This procedure separates practically all of the iron from the zirconium, titanium, and aluminum. In order to separate further the zirconium and titanium from the aluminum the following method is employed: Fuse the residue in the platinum crucible with 5 to 10 g. of Na_2CO_3 and one g. KNO_3 ; after cooling disintegrate the fused mass with hot water, filter, and wash. The residue on the paper now contains zirconium and titanium free from all interfering substances such as aluminum, vanadium, etc., with the possible exception of traces of iron. The paper containing the sodium zirconate and titanate is dried and ignited in a platinum crucible and the titanium and zirconium obtained

in solution by cautiously fusing with 5 to 10 g. of KHSO_4 , bringing the temperature up to a dull red heat for about one-half hour and using a cover on the crucible to avoid spattering during the process of fusion. The zirconium may be determined by practically any of the methods mentioned above, using this solution, provided that the quantity of zirconium in the solution is not greater than 0.1 g. calculated as ZrO_2 . Most precipitates of zirconium are more or less gelatinous, bulky, and difficult to filter and wash, and therefore if larger quantities are taken, accurate results cannot be attained.

If the zirconium alone is desired and there is no need of separating the iron, aluminum, etc., from the solution, the phosphate method is the only one which gives accurate results and a clean separation from both the above-mentioned elements.

The solution which has been freed from silica, containing not over and preferably less than 0.05 g. ZrO_2 , is diluted to 200 cc. volume, made 10 per cent acid with H_2SO_4 , 2 cc. hydrogen peroxide added, heated nearly to boiling and a slight excess of disodium phosphate solution added. The zirconium precipitate is a white or greenish white flocculent, gelatinous precipitate. After allowing to stand for about 2 hrs. or longer the precipitate is filtered onto an 11 cm. filter paper and thoroughly washed with hot dilute sulfuric acid. The paper and contents are then transferred to a platinum crucible, ignited, and finally blasted to remove as much of the carbonaceous matter as possible. The proper ignition of this precipitate is one of the most difficult steps of the whole procedure. The weight of zirconium pyrophosphate, ZrP_2O_7 , multiplied by the factor 0.4632 yields the weight of ZrO_2 .

Iron is determined in the solution from the silica filtration by the method of precipitation as the sulfide from ammonium tartrate solution. This method is well known. To 100 cc. portions of the silica-free solution 0.5 g. of tartaric acid is added, the solution heated to boiling, made strongly alkaline with NH_4OH , and H_2S added. The iron precipitates as the sulfide, is filtered out, washed, and weighed as Fe_2O_3 .

The titanium may also be determined on a separated portion of the original solution (if all HF or HNO_3 has been first removed) by Weller's colorimetric method with H_2O_2 or by titration with methylene blue.

Aluminum is usually determined by difference, the aluminum, zirconium and titanium being precipitated with sodium thiosulfate, SO_2 , or phenylhydrazine practically free from iron, if the percentage of iron in the original is not high. In certain cases it is necessary first to remove the iron by the above-mentioned method and destroy the ammonium tartrate by the ordinary methods of wet combustion with nitric and sulfuric acids before the precipitation of the others is attempted.

V—BIBLIOGRAPHY

Before much work on zirconium was attempted, all of the methods for the production of the metal, etc., described in the literature were reviewed and tried. At the start there were many conflicting data regarding the properties and reactions of zirconium and its

compounds. A complete bibliography of the subject contained about five hundred references, from some forty-one different journals.

It has been arranged in alphabetical order with regard to names of authors under the following headings:

- 1—Zirconium Minerals
- 2—Preparation, Properties, and Uses of Zirconium Salts
- 3—Analytical Chemistry of Zirconium
- 4—Zirconium Metal
- 5—Zirconium Alloys

The bibliography also includes references on the use of ZrO_2 as a refractory and as an opaquing agent in enamels, etc. All of the technical uses have been faithfully included. Section 5 has been devoted to the preparation and properties of zirconium alloys.

A CHEMICAL STUDY OF FROZEN FISH IN STORAGE FOR SHORT AND LONG PERIODS

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The present investigations upon fish commercially frozen and stored were undertaken in the hope of furnishing exact information upon which the public could base its opinion concerning the wholesomeness of frozen fish as food. The part of these investigations of practical interest to the trade has already been published in *Departmental Bulletin* 635 of the U. S. Department of Agriculture, and entitled "The Commercial Freezing and Storing of Fish."

The magnitude of the frozen fish industry of this country is indicated by the fact that over 120,000,000 lbs. of food fish,¹ valued at more than \$12,500,000 to the wholesaler, entered cold storage in 1918. Depending upon the locality, the amount of frozen fish in storage during a year represents from 4 to 15 per cent of the annual catch.² Furthermore, there are over 190 fish-freezing and storage plants in the United States, and the number is increasing. These statistics show that the practical advantage and economic necessity of cold-stored fish have long been realized by those familiar with the industry. Until recently, however, no chemical investigation has been made of the effect upon the food value of the freezing and storing of fish.

HISTORICAL

In 1913 several Dutch scientists³ made experiments with ice-chilled and frozen fish to see what changes in microscopical appearance occurred under refrigeration and what part bacteria played in the process of deterioration. This commission found that certain changes take place in the reaction of the tissues to litmus, the flesh of some species being acid, and, of

¹ Estimate based on U. S. Dept. of Agriculture, Bureau of Markets, Report of Stocks of Frozen and Cured Fish, December 15, 1918; issued December 28, 1918.

² Hearings before the Committee on Agriculture, House of Representatives, on Cold Storage Legislation, August 14, 1919, p. 203.

³ J. M. Bottemaine, "Notes on the Investigation of Preserving Fish by Artificial Cold." (a) Preliminary Report, 48 pages; (b) Preprint, 3 pages; 3rd International Congress of Refrigeration, 3rd Section (The Netherlands), Washington-Chicago (1913).