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Reactor-Grade Zirconium Oxide
From a Zirconium-Bearing
Chloride-Sulfate Strip Liquor Solution**

By D. J. MacDonald, C. E. Defilippi, and H. G. Henry



UNITED STATES DEPARTMENT OF THE INTERIOR

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UNIT OF MEASURE ABBREVIATIONS USED IN THIS REPORT

°C	degree Celsius	mg	milligram
°C/min	degree Celsius per minute	min	minute
g	gram	mm	millimeter
gal/min	gallon per minute	pct	percent
g/L	gram per liter	ppm	part per million
L	liter	psi	pound per square inch
lb/h	pound per hour	torr	mm Hg pressure
L/(min·m ²)	liter per minute per square meter		

INVESTIGATION OF METHODS FOR PRODUCING REACTOR-GRADE ZIRCONIUM OXIDE FROM A ZIRCONIUM-BEARING CHLORIDE-SULFATE STRIP LIQUOR SOLUTION

By D. J. MacDonald,¹ C. E. Defilippi,² and H. G. Henry¹

ABSTRACT

The Bureau of Mines investigated two alternative methods for treating a zirconium-bearing chloride-sulfate strip liquor to obtain reactor-grade ZrO_2 . One method involves neutralization with NH_3 and the other hydrothermal precipitation. The strip liquor was derived from zircon sand by a Bureau of Mines method for separating zirconium and hafnium via solvent extraction with a tertiary amine. Neutralization with NH_3 to precipitate hydrous zirconium oxide required 0.9 to 1.1 g NH_3 per gram of zirconium. The NH_3 can be recovered for recycle. ZrO_2 that met reactor-grade specifications was produced by precipitation with NH_3 . Hydrothermal precipitation of ZrO_2 from strip liquor required that the solution be maintained at 260° C and 680 psi for 10 min and in a non-corrodible pressure vessel. In bench-scale experiments both methods gave zirconium recoveries greater than 99 pct.

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INTRODUCTION

The Bureau of Mines performed bench-scale investigations leading to the design of an integrated process for producing reactor-grade zirconium oxide from zircon sand. Reactor-grade zirconium oxide is the precursor for zirconium alloys used in pressurized-water and boiling-water nuclear power reactors. The process avoids the air pollution, water pollution, and fire hazard associated with the conventional hexone-thiocyanate process. The Bureau of Mines process includes preparation of crude hafnium-bearing zirconyl sulfate solution from zircon sand (1),³ and purification by liquid-liquid extraction with Alamine 336⁴ to transfer zirconium values from the crude solution to a purified zirconium-bearing strip liquor (2). Figure 1 is a simplified flowsheet for producing strip liquor with the following composition:

	g/L
Zr.....	15
SO ₄ ²⁻	75
Na.....	92
H ⁺49
Cl.....	159

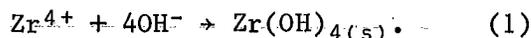
In the hexone-thiocyanate process (the conventional industrial zirconium extraction process), zirconium is precipitated as Zr₅O₈(SO₄)₂ from a purified raffinate by neutralization with ammonia, but that method is not applicable to a strip liquor of the above composition because the solution does not have the required 5:2 mole ratio of zirconium to sulfate. This report describes two methods for treating strip liquor from the Bureau of Mines amine extraction process to obtain reactor-grade ZrO₂, involving (1) neutralization with NH₃ or (2) hydrothermal precipitation.

³Underlined numbers in parentheses refer to items in the list of references at the end of this report.

⁴Reference to specific products does not imply endorsement by the Bureau of Mines.

In carrying out the precipitation, it is desirable to avoid introducing adventitious impurities, as from corrosion of equipment or from reagents, and to minimize retention of sulfate. Sulfate in the product would cause an air pollution problem when the ZrO₂ is chlorinated to make ZrCl₄ to be used in the Kroll reduction process.

Hydrous zirconium oxide precipitates from zirconium-bearing solutions at pH greater than 2. The chemical reaction for the freshly precipitated α form of hydrous zirconium oxide is



The apparent solubility product was reported to be 10⁻⁵² (3) and implies that precipitation of zirconium is complete at pH >2.

Precipitation of hydrous zirconium oxide from zirconium-bearing solutions occurs spontaneously without addition of any neutralizing reagent and regardless of acidity if the temperature is high enough. This is the basis for the hydrothermal precipitation method.

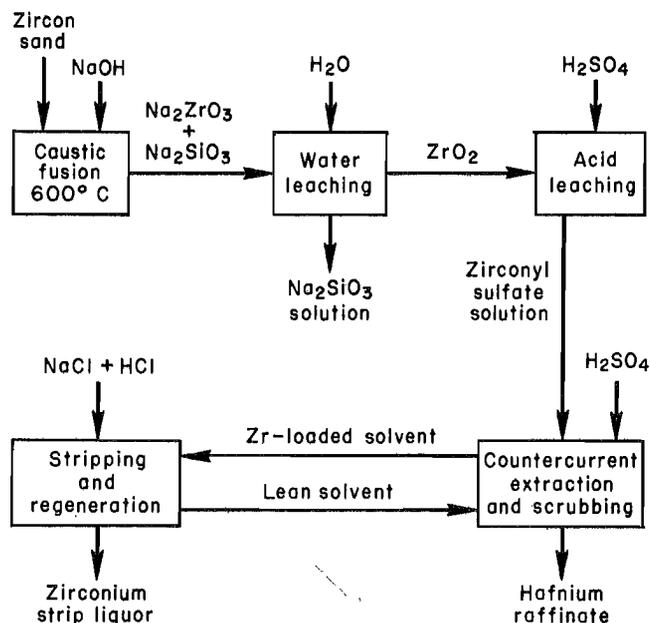


FIGURE 1. - Simplified flowsheet for production of strip liquor.

MATERIALS AND EQUIPMENT

Strip liquor samples used were produced in bench-scale extraction runs and had the following compositions:

	<u>g/L</u>
Zr.....	6.4- 21.5
SO ₄ ²⁻	60 - 75
Na.....	92
H ⁺49
Cl.....	159

Concentrations of Zr and SO₄²⁻ depended on flow rates used in the liquid-liquid extraction step in which the strip liquor was produced. Use of a range of compositions demonstrated that applicability of the methods described is not restricted to a single strip liquor composition.

Impurities present in the strip liquor and capable of influencing the purity of a ZrO₂ product follow:

	<u>mg/L</u>			<u>mg/L</u>
Al.....	10		Hf.....	0.2- 1.0
B.....	<3		Ni.....	<.1
Cr.....	<.1		Ti.....	<2
Fe.....	.1		U.....	.03

Other impurities, such as Na, Si, and entrained organic matter, although present, would not affect the purity of the product.

Reagents used included 99.99-pct anhydrous ammonia and reagent grade calcium oxide powder.

Coors high-alumina ceramic boats (99.8 pct recrystallized Al₂O₃) were used for roasting the precipitated zirconium oxide. A Globar tube furnace with an Alundum tube having a hot zone 75 mm in diameter and 500 mm long provided heat.

METHODS

Two alternative techniques of strip liquor treatment, neutralization with NH₃ and hydrothermal precipitation, were investigated.

NEUTRALIZATION WITH AMMONIA

Ammonia is a suitable neutralizing reagent because it can be recovered for recycle and does not contribute impurities to the precipitated zirconium oxide. Sodium hydroxide would be unsuitable because excessive impurities, such as boron, phosphorus, and aluminum, would be precipitated with the zirconium oxide. Especially undesirable in a neutralizing reagent would be anionic impurities such as borate and phosphate, because precipitated zirconium oxide has a strong ion-exchange affinity for multivalent anions (4).

Precipitation was carried out by sparging anhydrous ammonia gas into batches of strip liquor in a stirred 1-L, three-neck flask fitted with a glass-electrode pH probe. Precipitation did not begin with

the first addition of ammonia, but began at pH less than 2 and was complete before pH 4 was attained. Using a slight excess of ammonia, enough to give pH 9, resulted in faster filtration. Proceeding to pH 9 for this purpose is also described in a patent (5).

The slurry of precipitated hydrous zirconium oxide and mother liquor was filtered with vacuum on a Buchner funnel. Vacuum was continued until the flow of filtrate ceased. The filter cake was washed without agitation and with a volume of water equal to twice the volume of the filter cake. The filtrate and washings were set aside for subsequent ammonia recovery, and the filter cake was dried at 100° to 120° C. Although freshly precipitated hydrous zirconium oxide was partially soluble and subject to peptization on washing, careful drying made the zirconium oxide insoluble and immune to peptization while leaving most of the chloride and sulfate leachable. The dried filter cake was pulverized, washed by agitation with water, filtered,

dried, and roasted for at least 15 min at 1,000° C in high-alumina ceramic boats. Five to ten liters of wash water per kilogram of solids was satisfactory. The resulting filtrate need not be processed for recycle of ammonia value since its ammonia content is insignificant. Washing the carefully dried precipitate had the beneficial effect of decreasing its sulfate content and the amount of SO₃ evolved in the subsequent high-temperature roasting step. Sulfate in the final ZrO₂ product should be as low as possible, to minimize production of air polluting byproducts, such as SOCl₂ and S₂Cl₂, during chlorination.

The initial filtrate with excess Ca(OH)₂ was heated to about 90° C in a stirred three-neck flask to regenerate ammonia as in a standard ammonia still. The resulting vapor of H₂O and NH₃ was passed into a tubular water-cooled glass condenser to form an aqueous ammonia solution. In a larger scale operation, the vapor or condensate would be recycled to the precipitation step. The slurry from ammonia regeneration was filtered on a Buchner funnel and yielded a CaSO₄·2H₂O filter cake and an NaCl-CaCl₂ filtrate. In a larger scale operation, the filtrate, after addition of makeup NaCl and HCl, could be recycled to the solvent extraction step of the overall process,

but the feasibility of recycling that filtrate was not verified.

HYDROTHERMAL PRECIPITATION

Precipitation of hydrous zirconium oxide from strip liquor can be accomplished by maintaining the solution at elevated temperature in a pressure vessel and not adding neutralizing reagents. The procedure is called hydrothermal precipitation and was investigated by Battelle Columbus Laboratories, Columbus, OH, under a Bureau of Mines contract (6).

Samples of strip liquor provided to Battelle by the Bureau were heated in a stirred 1-L stainless steel autoclave. The extent of precipitation of zirconium-bearing solids was determined as a function of time and temperature. Temperatures up to 300° C were used. Corresponding pressures, which were assumed equal to the vapor pressure of water, were up to 1,246 psi.

Thermogravimetric analysis was used to measure the loss of H₂O and SO₃ from dried precipitate. The measurements were made on ZrO₂ precipitate that had been dried to constant weight at 110° C before being heated in vacuum (pressure 0.1 torr) at a constant rate of temperature increase (10° C/min).

RESULTS

NEUTRALIZATION WITH AMMONIA

Neutralizing samples of strip liquor that contained approximately 15 g/L Zr to pH 9 with NH₃ required 13 to 16 g NH₃ per liter of solution. A typical neutralization curve is shown in figure 2. Several precipitation tests were stopped at lower pH values to permit measurement of the rate of filtration as a function of pH. Table 1 shows results of filtration tests made at about 600 torr vacuum and with a wet filter cake thickness of 5 to 6 mm. Fastest filtration was obtained when final pH during precipitation was 8 to 9. In this pH range, filtration rates for filter cakes 5 to 6 mm thick were 3 to 4

L/(min·m²). At pH 7 or less, the precipitate was gelatinous and difficult to filter. Filtration through thicker filter cakes was slower. The cake had a high water content of about 85 pct. A representative sample of wet filter cake had a specific mass of 7.9 g per gram of contained zirconium.

About 97 pct of the NH₃ used was recoverable from the filtrate and could be recycled.

Precipitation of zirconium values was complete and rapid. Concentration of zirconium in the filtrate after precipitation was less than 0.008 g/L. Residence

time during precipitation was not critical. Five minutes was adequate because precipitation was complete at pH <9. Heat was generated predominantly from neutralization of excess acidity, which raised the temperature about 20° C above the initial temperature. Increase in temperature is desirable because it speeds filtration.

TABLE 1. - Range of filtration rates as a function of pH¹

pH	Filtration rate, L/(min·m ²)
6.....	1.9-2.1
7.....	2.5-3.4
8.....	3.2-4.1
9.....	3.2-3.4

¹For 5- to 6-mm filter cake thickness, room temperature, and 600-torr vacuum.

A representative sample of wet filter cake contained the following constituents in addition to NH₃ and H₂O:

	pct
Zr.....	8.0
SO ₄7
Cl.....	.3
Na.....	.2

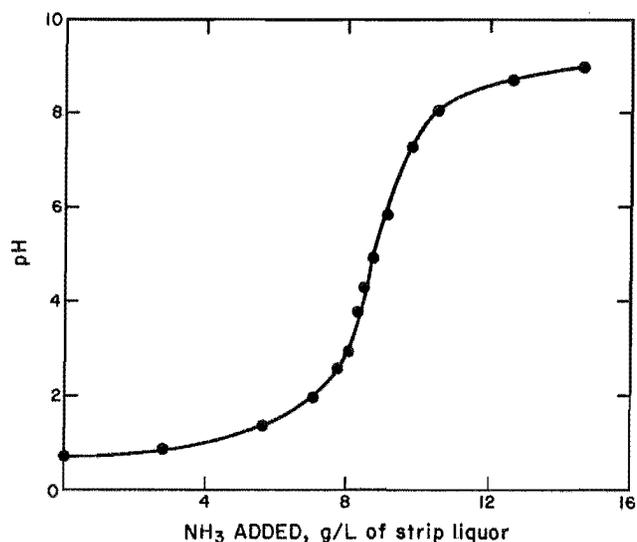


FIGURE 2. - Neutralization of strip liquor with NH₃: pH versus NH₃ added, beginning at 25° C and 15 g/L Zr.

Corresponding filtrate contained in addition to NH₃ and H₂O:

	g/L
Zr.....	<0.008
SO ₄	70
Cl.....	72
Na.....	68

A conceptual flowsheet for recovery of ZrO₂ by neutralizing strip liquor with NH₃ is shown in figure 3.

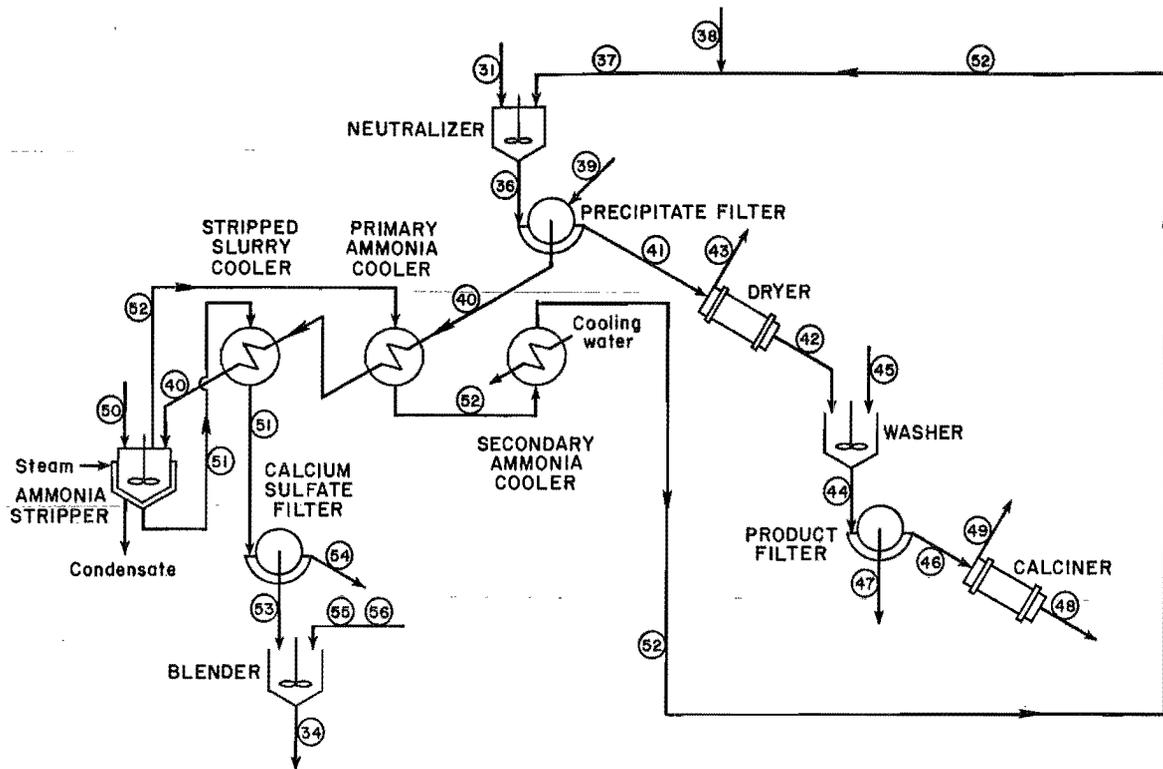
Table 2 gives results of a spectrographic and chemical analysis of a 100-g sample of calcined ZrO₂ produced through ammonia precipitation. ZrO₂ produced by the Bureau's process was purer than representative ZrO₂ from the hexone-thiocyanate process and had extremely low levels of Cr, U, and P--less than half those of ZrO₂ by the hexone-thiocyanate process. The Bureau's process would be superior for use with zircon sand having higher than usual amounts of these elements. The Bureau's ZrO₂ is higher in Sn, B, Al, and Na than ZrO₂ made by the hexone-thiocyanate process, but because these elements are eliminated during chlorination their presence is not deleterious.

TABLE 2. - Impurity content of roasted ZrO₂ from ammonia precipitation¹

	Conc, ppm		Conc, ppm
Al.....	87	Na.....	90
B.....	² >5	Ni.....	<10
Ca.....	27	P.....	<25
Cb(Nb)..	<50	Si.....	555
Cd.....	<.2	Sn.....	25
Co.....	<5	SO ₄018
Cr.....	<10	Th.....	<100
Cu.....	<10	Ti.....	<25
Fe.....	<25	U.....	<2.0
Hf.....	<25	V.....	<5
Mg.....	10	W.....	<10
Mn.....	<5	Zn.....	<50
Mo.....	<5		

¹Analysis performed by Teledyne Wah Chang Albany Corp.

²Boron content was more than the upper limit of the analytical method used.



Stream ¹	Stream name	Flow rate, lb/h							Total	Volume flow, gal/min
		ZrO ₂	H ₂ O	SO ₃	Na ₂ O	HCl	NH ₃	CaO		
31	Strip liquor.....	433.7	28,702	1,918	4,044	4,899	0	0	39,996.7	64.8
34	Stripping agent solution.....	0	27,442	² 1,043	4,044	5,353	0	² 24	37,906	64.8
36	Precipitate slurry.....	433.7	38,010	1,918	4,044	4,899	394.6	0	49,699.3	84.5
37	Ammonia solution...	0	9,308	0	0	0	394.6	0	9,702.6	19.7
38	Ammonia makeup.....	0	0	0	0	0	10	0	10	NAp
39	Wash water No. 1...	0	3,710	0	0	0	0	0	3,710	7.4
40	Spent liquor.....	0	36,759	1,780	3,810	4,593	384.5	0	47,326.5	81.4
41	Wet precipitate ZrO ₂	433.7	4,961	138	233.8	305.6	10	0	6,082.1	10.5
42	Dry precipitate ZrO ₂	433.7	778	138	233.8	305.6	0	0	1,889.1	³ 25
43	Water vapor.....	0	4,183	0	0	0	10	0	4,193	NAp
44	Washed precipitate ZrO ₂ slurry..	433.7	5,702	138	233.8	305.6	0	0	6,813.1	12
45	Wash water No. 2...	0	4,924	0	0	0	0	0	4,924	9.85
46	Washed precipitate ZrO ₂	433.7	607	76	171.8	276.6	0	0	1,565.1	³ 20
47	Waste wash solution.....	0	5,095	62	62	30	0	0	5,249	10.5
48	Reactor-grade ZrO ₂	433.7	0	.07	.05	NAp	0	0	433.8	³ 20
49	Calciner vapor.....	0	607	76	171.8	276	NA	0	1,130.8	NAp
50	Lime.....	0	0	0	0	0	0	541	541	4
51	Stripped slurry....	0	27,451	1,780	3,810	4,593	0	541	38,175	64.2
52	Ammonia vapor.....	0	9,308	0	0	0	384.6	0	9,692.6	NAp
53	Stripped filtrate.....	0	25,094	1,043	3,810	4,593	0	24	34,564	³ 66
54	Calcium sulfate....	0	2,357	737	0	0	0	517	3,611	³ 25
55	NaCl makeup.....	0	-68	0	234	275	0	0	441	³ 4.8
56	HCl makeup.....	0	2,416	0	0	485	0	0	2,901	5.4

NAp Not applicable. NA Not available.

¹Stream name and number correlate with figure 9 of reference 2.

²Reference 2 did not recognize the presence of a minor amount of CaSO₄ that would be dissolved in reconstituted stripping agent solution.

³Cubic feet per hour; as solids.

FIGURE 3. - Flowsheet for recovery of ZrO₂ by neutralizing strip liquor with NH₃. Flow rates correspond to plant capacity of 10 tons zircon sand per day.

HYDROTHERMAL PRECIPITATION

Investigations by Battelle Columbus Laboratories determined the extent of hydrous zirconium oxide precipitation as a function of time and temperature. Different strip liquor samples having zirconium concentrations ranging from 6.4 to 13.0 g/L were used, but initial zirconium concentration had no effect on completeness of precipitation. Experimental data given in table 3 show that almost complete precipitation occurred at $\geq 260^\circ\text{C}$ and that 10 min at or above 260°C was sufficient. Because of the time required to heat the autoclave and its contents to temperature, a time-at-temperature of less than 10-min duration was not feasible to investigate.

The precipitate was finely divided, but was more easily filtered than the precipitate from ammonia neutralization. Filtration to produce filter cakes from 5 to 12 mm thick was accomplished at rates ranging from 75 to 1.5 L/(min·m²). Filtration of the solids was approximately twice as rapid following precipitation at 260°C as it was after precipitation at 250°C .

Washing the precipitate with water impaired its filterability and caused partial loss of zirconium values due to peptization, but washing with 10-pct ammonia solution preserved or enhanced the filterability. Washing with 10-pct HCl solution impaired filtration but did not cause a loss of zirconium values. Washing with 10-pct-ammonia solution was effective in removing chloride and sulfate, but did not remove sodium. Washing with 10-pct-HCl solution removed sodium but not chloride or sulfate.

The stainless steel autoclave was corroded by contact with strip liquor, resulting in increased impurities in the precipitate and spent liquor. Zirconium metal would probably be a suitable material of construction for pressure vessels or liners for use in hydrothermal precipitation of zirconium oxide. Glass-lined pressure vessels would not be suitable because the required combination of temperature and pressure (260°C and 680 psi) is too near the upper limits for a glass lining.

TABLE 3. - Extent of hydrothermal precipitation from zirconium-bearing strip liquor as a function of time and temperature

Strip liquor [Zr], g/L	Time, min	Temp, °C	Spent liquor [Zr], g/L	Extent of Zr precipitation, pct
6.4	90	260	0.13	98.0
9.2	15	220	1.36	85.2
9.2	30	220	1.28	86.1
9.2	60	220	1.16	87.4
9.2	20	260	.07	99.2
9.2	30	260	.04	99.6
9.2	40	260	.04	99.6
9.2	60	260	.02	99.8
9.2	10	300	.04	99.6
9.2	20	300	.03	99.7
13	10	180	3.03	76.7
13	20	180	2.95	77.3
13	40	180	2.83	78.2
13	10	260	.04	99.7
13	20	260	.05	99.6

Thermogravimetric analysis of dried precipitate (fig. 4) showed a gradual loss of water vapor in the temperature range 100° to 500° C that amounted to 13 pct of the original mass of dried precipitate. Heating from 500° to 900° C caused a loss of water vapor and SO₃ that totaled 25 pct of the original mass of precipitate.

A conceptual flowsheet for hydrothermal precipitation is shown in figure 5. The spent liquor (stream 33) could probably be recycled for use as stripping agent solution.

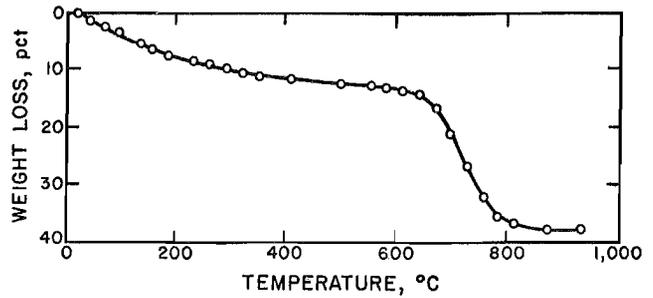
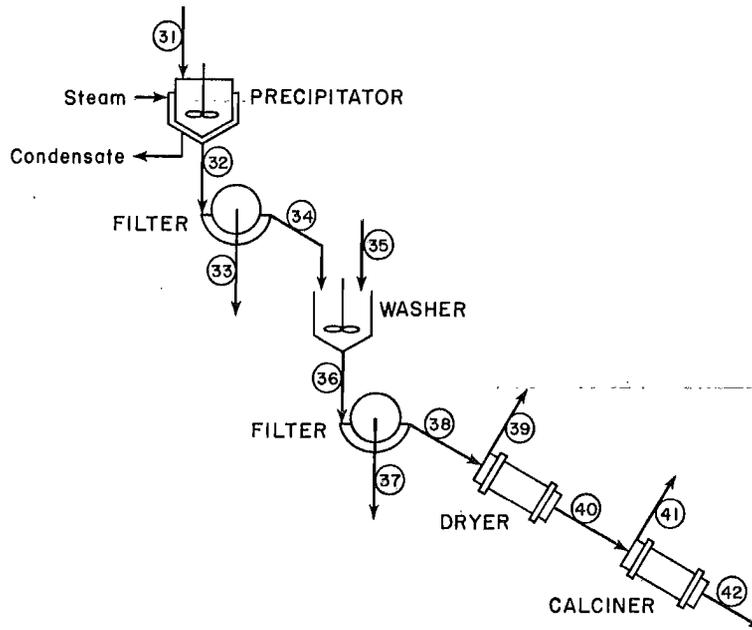


FIGURE 4. - Weight loss from dried precipitate ZrO₂ as a function of temperature during roasting. Vacuum was 0.1 torr, and rate of heating was 10° C/min.



Stream ¹	Stream name	Flow rate, lb/h					Total	Volume flow, gal/min
		ZrO ₂	H ₂ O	SO ₃	Na ₂ O	HCl		
31	Strip liquor.....	433.7	28,702	1,918	4,044	4,899	39,996.7	64.8
32	Precipitate slurry.....	433.7	28,702	1,918	4,044	4,899	39,996.7	64.8
33	Spent liquor.....	0	23,915	1,832	4,035	4,888	34,670	63.9
34	Wet precipitate.....	433.7	4,787	86	9.4	11	5,263.1	² 20
35	Wash solution....	0	2,748	0	0	275	3,023	5.8
36	Washed slurry....	433.7	2,856	86	9.4	286	3,607.1	6.8
37	Wash filtrate....	0	2,748	10	4.3	281	3,043.3	5.8
38	Washed precipitate.....	433.7	4,787	76	NA	NA	5,297	² 20
39	Water vapor.....	0	4,180	0	0	0	4,180	NAp
40	Dried precipitate.....	433.7	607	76	NA	NA	1,117	² 20
41	Calciner vapor...	0	607	76	0	0	683	NAp
42	Zirconium oxide..	433.7	0	NA	NA	NA	434	² 20

¹NAp Not applicable. NA Not available.

²Stream name and number correlate with figure 9 of reference 2.

²Cubic feet per hour; as solids.

FIGURE 5. - Flowsheet for recovery of ZrO₂ by hydrothermal precipitation from strip liquor. Flow rates correspond to plant capacity of 10 tons zircon sand per day.

SUMMARY

Recovery of ZrO_2 from zirconium-bearing chloride-sulfate strip liquor was demonstrated in bench-scale experiments by two methods, neutralization to pH 9 with NH_3 and hydrothermal precipitation with no added reagents. Neutralization required 13 to 16 g NH_3 per liter of strip liquor that contained initially 15 g/L Zr. About 97 pct of the NH_3 was recoverable for recycle. Hydrothermal precipitation required a temperature of 260° C for 10 min. Each method gave more than 99-pct recovery.

By the NH_3 neutralization method, 100 g of ZrO_2 suitable for making reactor-grade zirconium was produced. In hydrothermal precipitation experiments, conditions needed for >99-pct recovery were determined, but quantities of ZrO_2 produced were not large enough to demonstrate reactor-grade purity. Although both methods are feasible, investigations on a larger scale would be needed to decide which method is better.

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