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Preparation of High-Purity Zirconia from Zircon: An Anion-Exchange Purification Process

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ABSTRACT

This paper describes the preparation of high-purity zirconia involving an anion-exchange purification step. The zirconium wet cake (residue obtained after water-leaching of alkali-fused zircon) is digested with concentrated hydrochloric acid, the slurry is sufficiently aged and filtered, and the residue is leached with a (6 N HCl)–(2 N H_2SO_4) mixture. The slurry is further aged and finally filtered using a filter-aid. The filtrate is passed through an anion-exchange resin. The effluent is treated with 25% (v/v) concentrated sulfuric acid and the resulting zirconium sulfate tetrahydrate is filtered, washed, dried, and calcined at 1000°C for 6–8 hours. A high-purity zirconium dioxide is obtained which has a variety of industrial and scientific applications, especially for the preparation of artificial gems.

INTRODUCTION

Zirconia ceramics have attracted considerable attention in recent years as high technology materials for industrial applications because of their superior mechanical, thermal, electrical, chemical, and optical properties (1). Zirconia has an impressive combination of intrinsic properties including high hardness, strength, high melting point, and biocompatibility. Calcia-, magnesia-, and yttria-stabilized zirconia play important roles as materials of great scientific and technological importance. They are associated with great strength, toughness, and reliability. They compete with metals and alloys in some applications (2) where high temperature performance, erosion resistance, and corrosion resistance are required.

The production of zirconia powders with suitable properties is the first step in the development of zirconia ceramics for industrial applications. The important characteristics required for zirconia powders to be used in the manufacture of ceramics are their purity, particle size, particle morphology, agglomerate strength, surface area, and color.

Zirconia or zirconium dioxide is the most important and stable oxide of zirconium. Pure zirconia is a white powder with a melting point of 2710 ± 35°C and exists in three well-defined crystalline forms: monoclinic, tetragonal, and cubic. Cubic zirconia is widely used as a diamond substitute (3) for both industrial and decorative applications. Chemical purity is essential for either purpose; typically the iron oxide content should be 10 ppm or less and the content of other transition metals should be less than 10 ppm.

The major source of zirconia is the mineral zircon (zirconium silicate, $ZrSiO_4$), and its main occurrence is a constituent of beach sands along with rutile, ilmenite, and monazite. Zircon is separated from other heavy minerals by using wet gravity concentration followed by magnetic and electrostatic processes.

Zircon is a very stable compound chemically. To extract ZrO_2 from zircon requires chemical or thermal dissociation to break the bonds between ZrO_2 and SiO_2. A variety of techniques have been proposed (4) for the extraction of zirconia from zircon. These methods include alkali decomposition (5, 6), chlorination (7), reductive smelting (8), extraction with basic oxides (9, 10), and thermal dissociation of zircon followed by wet chemical treatment (11).

High-purity zirconia can be produced by hydrothermal treatment (12), spray pyrolysis of zirconium-containing solutions (13), crystallization of zirconium oxychloride (14), and precipitation of zirconium as its basic sulfate (15) and hydrate sulfate (16, 17).

A solvent extraction technique has been applied extensively for the purification of zirconium from most of its impurities, including hafnium (18). Because ion-exchange purification is the most powerful technique for purification, both cation- and anion-exchange resins (19, 20) have been utilized for the purification of zirconium solutions, mainly for analytical purposes, by using one type of acid at a time. However, there has been no mention of an $HCl–H_2SO_4$ mixture with an anion-exchange resin for the purification of zirconium solution.

In this paper we report a systematic study undertaken to purify zirconium solutions on a large scale by using an anion-exchange resin with an $HCl–H_2SO_4$ mixture. The drawbacks of using only one acid and the advantages of using an acid mixture are described.

EXPERIMENTAL

Zircon was decomposed by reaction with sodium hydroxide at temperatures above 650°C (Fig. 1). Then it was cooled and leached with water. After filtration, the residue (wet cake) was used for further experiments.

I. Experiments with 6 N HCl

(*a*) *Preparation of Zirconium Feed Solution*

A wet cake (1 kg) was digested at 120–150°C with 4 L commercial grade concentrated hydrochloric acid (~10 N) for about an hour. The slurry was allowed to age at ambient temperature for 4 days. After aging, the slurry was filtered and the residue was washed with 0.5 L concentrated hydrochloric acid. Then the residue was leached with demineralized (DM) water and the slurry was kept for 1 day for further aging. It was then filtered with the aid of a precoat filter. The free acidity (FA) of the filtrate was adjusted to 6 N by using concentrated hydrochloric acid. This final solution was used as a zirconium feed solution (15–18 g ZrO_2/L, FA = 6 N) for the ion-exchange purification step.

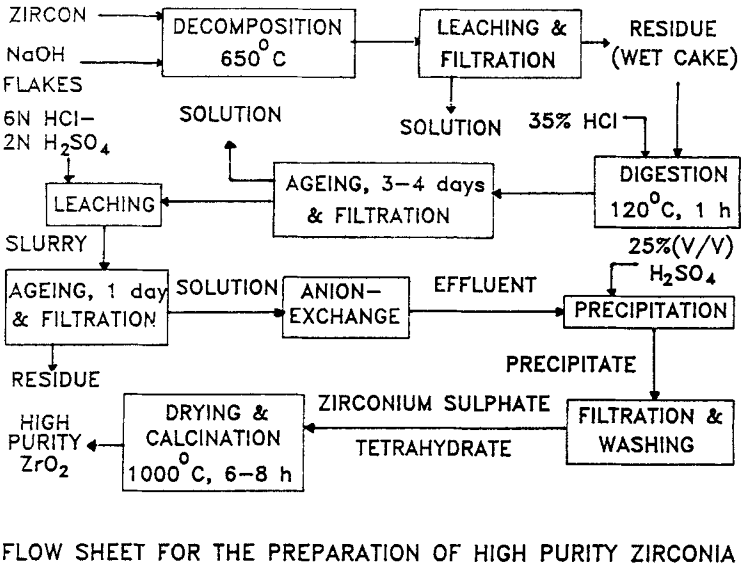

FIG. 1 Flow sheet for the preparation of high purity zirconia.

(*b*) *Conditioning of the Ion-Exchange Column*

A commercial grade anion-exchange resin [DE-ACIDITE FF-IP, −14 to +52 mesh, obtained from Ion-Exchange (India) Ltd., Bombay] in the chloride form was thoroughly washed with DM water. The resin was soaked in 6 N HCl (commercial grade) for 2–3 hours. This resin was then packed in a glass column (1 m long × 8 cm diameter). The resin column was conditioned with 6 N HCl.

(*c*) *Preparation of Zirconium Dioxide*

The zirconium feed solution was passed through the conditioned anion-exchange column at a flow rate of 500 mL/h. The effluent containing the zirconium was distilled. The residue, after cooling to ambient temperature, was dissolved in DM water to make a solution containing 15–20 g ZrO_2/L. Ammonia gas was bubbled through the solution. The precipitate was filtered, dried, and calcined at 850°C for 6 hours. The flow sheet of the process is given in Fig. 1.

II. Experiments with (6 N HCl)–(2 N H_2SO_4) Mixture

(*a*) *Preparation of Zirconium Feed Solution*

In this case also, digestion of the wet cake was done as in Experiment I(a). However, the residue obtained after filtering the digested slurry was leached with 4 L of a (6 N HCl)–(2 N H_2SO_4) solution instead of DM water and then filtered. The final feed solution contained 80–90 g ZrO_2/L.

(*b*) *Conditioning of the Ion-Exchange Column*

The anion-exchange resin and the glass column used for ion-exchange were the same as in Experiment I(b). The resin was conditioned with (6 N HCl)–2 N H_2SO_4).

(*c*) *Preparation of Zirconium Dioxide*

The zirconium feed solution was passed through the conditioned resin column at a flow rate of 1 L/h. The effluent obtained from the ion-exchange column was treated with 25% (v/v) concentrated sulfuric acid (commercial grade). The precipitate was filtered, washed with a mixture of 70 volumes of sulfuric acid, 40 volumes of DM water, and 5 volumes of hydrochloric acid, and finally the precipitate was washed with acetone. The acetone-washed precipitate was dried and then calcined at 1000°C for 6–8 hours.

Determination of Distribution Ratios (K_d)

K_d for iron has been determined in both 6 N HCl and (6 N HCl)–(2 N H_2SO_4) media. The batch equilibrium method was employed for the determination of K_d. For this purpose, an exact volume (100 mL) of the zirconium feed solution was shaken with a weighed amount of the anion-exchange resin (1 g) until equilibrium was reached. Then the mixture was filtered and the amount of iron in the filtrate which was not adsorbed on the resin was determined quantitatively by atomic absorption spectrometry. Based on this determination, the K_d value of iron under the selected experimental conditions was calculated by means of the following equation:

$$K_d = \frac{\text{amount of iron adsorbed in 1 g dry resin}}{\text{amount of iron remaining in 1 mL solution}}$$

Analysis of Zirconium Solutions

The impurities Fe, Ca, Mg, Ti, Al, Na, and Si in the zirconium feed solution were analyzed by atomic absorption spectrometry by using the analytical lines at 248.3, 422.7, 285.2, 365.3, 309.3, 589.2, and 251.6 nm, respectively. Uranium was analyzed by fluorimetry with wavelengths of 365 and 555 nm for excitation and fluorescence, respectively. Zirconium in various solutions was analyzed by gravimetry using mandelic acid as the precipitant. The free acidities of the feed solutions were estimated by volumetry.

DISCUSSION

A typical analysis of the Indian zircon sand used in our experiments is shown in Table 1. As seen from this table, the major impurities are silica, hafnium, aluminum, magnesium, calcium, sodium, iron, and titanium. Zircon is decomposed by sodium hydroxide to produce sodium zirconate and sodium silicate (frit):

$$ZrSiO_4 + 4NaOH \rightarrow Na_2ZrO_3 + Na_2SiO_3 + 2H_2O$$

During leaching of the frit, sodium silicate is removed to a large extent and sodium zirconate hydrolyses to hydrated zirconia:

$$Na_2ZrO_3 + nH_2O \rightarrow ZrO_2\cdot(n - 1)H_2O + 2NaOH$$

Although sodium silicate is highly soluble in water, a considerable quantity of sodium silicate remains in the wet cake due to ineffective leaching

TABLE 1
Analysis of Indian Zircon Sand Used in Our Experiments

Compound	Percent (by weight)
ZrO_2	65.3
HfO_2	1.57
Moisture	0.1
SiO_2	31.8
Fe_2O_3	0.1
Al_2O_3	0.5
K_2O, MgO, CaO, and Na_2O	0.15
P_2O_5	0.1
TiO_2	0.06
Rare earths	0.02
U_3O_8	0.03

of the frit on a large scale. A typical analysis of the wet cake is given in Table 2, which shows that a considerable amount of silica is present.

Silicates are attacked by acids in many different ways. Some are rapidly decomposed by hydrochloric acid, even in the cold, when part of the silicic acid separates as a gel. Others are attacked in the same way but much more slowly. In general, the more electropositive the metal contained in the silicate, more successful is the decomposition. Alkali silicates are easily attacked, alkaline earths less easily, and aluminum and iron silicates still less easily. Because of the complex nature of various silicates in the wet cake, long periods of aging (3–4 days) are required for clear

TABLE 2
Analysis of Wet Cake Obtained after Alkali Fusion

Element/compound	Percent (by weight)
ZrO_2	44.2
HfO_2	1.1
Moisture	47.3
SiO_2	4.7
Fe	0.85
Al	0.6
Ca	0.23
Mg	0.06
Na	0.05
Ti	0.11
U	0.02

separation of silicic acid. Filtration of the slurry and washing of the residue at this stage help in getting rid of the impurities to a considerable extent. This fact is clear from Table 3.

During aging of the digested slurry, the separated silicic acid forms an intimate mixture with the zirconium oxychloride and makes filtration possible without the use of any filter aid such as precoat. In the process of leaching the mixture, zirconium oxychloride dissolves in the solution, leaving behind gelatinous silicic acid. Silicic acid clogs the pores of the filter paper during filtration, thus reducing the flow rate drastically or sometimes completely obstructing the flow. This necessitates the use of a filter aid for filtering the aged silica slurry. The silica content is at a very low level (50 μg/mL) in the final zirconium feed solution, which is essential for loading into the ion-exchange column for the reasons discussed in the following paragraph.

Silica often acts as a type of resin poison, but its effect is more mechanical than chemical. At high acidities, dehydration of silica or its production from dissolved silicic acid leads to its deposition upon the resin beads and, to some extent, into the interior of the beads. This kind of deposition occurs primarily near the point of entry of the zirconium feed solution into the ion-exchange column. This may result in reduction of the flow rate or even complete obstruction to flow if the voids between the beads

TABLE 3
Analysis of Zirconium Solutions Obtained at Various Stages[a]

Element	A	B	C	D
Al	690	1000	217	45
Ca	320	377	93	85
Fe	1090	1780	340	21
Mg	71	76	18	10
Na	1902	2840	4330	4200
Ti	190	294	29	15

[a] A. *Filtrate* (1900 mL). The filtrate obtained after the filtration of the digested slurry after 4 days aging.

B. *Wash solution* (600 mL). The solution obtained by washing the residue in the filtration stage.

C. *Feed solution* (4600 mL). The zirconium feed solution for ion-exchange purification. It contained 87 g ZrO_2/L in (6 N HCl)–(2 N H_2SO_4).

D. *Effluent* (4300 mL). The effluent solution obtained after passing the above zirconium feed solution through an anion-exchange column.

Values are in μg/mL.

become filled. In addition, the silica coating upon the resin beads causes the diffusion rate to be reduced. This gives an apparent reduction in resin capacity.

The limited solubility of zirconium in 6 N HCl restricts the concentration of zirconium in the feed solution to the range of 15–18 ZrO_2/L. This low concentration results in a low throughput of zirconium and the generation of a large volume of effluent, which is normally not desirable for production on a large scale.

In 6 N HCl medium, ferric and uranyl ions are usually present as tetrachloro anionic complexes like $[FeCl_4]^-$ and $[UO_2Cl_4]^{2-}$ which are adsorbed on the anion-exchange resin. The distribution ratio and the capacity of the anion-exchange resin used for iron are 261 and 9.4 mg Fe/g of dry resin, respectively. The adsorbed iron band on the resin bed moves down slowly when the resin column is washed with 6 N HCl. This kind of behavior is not desirable in an ion-exchange purification process. Also, during elution of the impurities with DM water, tailing was observed. Because of this, a large volume of eluant was required for regeneration of the resin column.

HCl–water is azeotropic at 80% water (by mass) and boils at 108.6°C. The distillation of the effluent containing zirconium yields 20% HCl (by mass) which can be reused at the leaching stage of another batch.

The concentration of zirconium in the solution before precipitation with ammonia gas is maintained in the 20–25 g ZrO_2/L range to avoid the formation of a paste-like precipitate which poses problems during filtration and washing.

The hydrated zirconia contains a considerable quantity of ammonium chloride, even after repeated washing with DM water, due to its low solubility. During calcination, ammonium chloride sublimes and deposits in the cooler region of the furnace. This causes a problem in maintaining the exhaust system of the furnace. A fast rate of heating yields granular ZrO_2 which has to be ground to a fine mesh for further applications. The grinding step at this final stage gives scope for external contamination, especially with respect to iron. This is highly undesirable for the preparation of artificial gems from ZrO_2. Calcining zirconium hydroxide in a phased manner while maintaining a slow rate of heating yields a flourlike ZrO_2 powder.

The use of a mixture of (6 N HCl)–(2N H_2SO_4) as a medium for the zirconium feed solution instead of 6 N HCl alone has several advantages.

1. The solubility of zirconium in this acid mixture is about 5–6 times more than in 6 N HCl. Thus, a zirconium feed solution with a large throughput and a lesser volume of effluent generation becomes possi-

ble. The increase in solubility of zirconium in the presence of sulfuric acid can be attributed to complexation of zirconium by sulfate ions at this acidity of sulfuric acid. At higher sulfuric acid concentrations, solubility is reduced and zirconium sulfate precipitates.

2. The distribution ratio, and hence the capacity of the resin, also increase remarkably. The distribution ratio and the capacity of the resin for iron in the acid mixture are 633 and 19.0 mg Fe/g dry resin, respectively. The marked increase in these values may be due to the formation of a mixed ligand complex of ferric ions.
3. The iron band adsorbed on the resin does not move down the column, even on repeated washings of the column with the acid mixture. The adsorbed iron elutes out completely with a small volume of the eluant (DM water) without any tailing. This kind of elution behavior is highly useful for regeneration of the column.
4. There is a distinct color change (dark brownish black to pale brown) in the resin bed after elution with DM water. This color change may

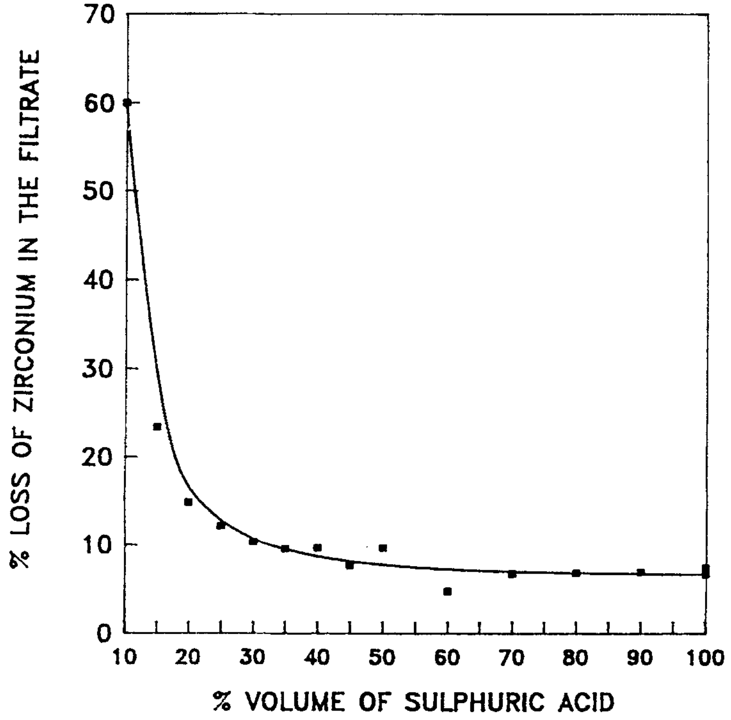

FIG. 2 Plot of percent volume of sulfuric acid vs percent loss of zirconium in the filtrate.

often be used as a quick check (by visual observation) of the status of elution in the resin column.

Zirconium from the effluent is precipitated with concentrated sulfuric acid (commercial grade). The optimum volume of sulfuric acid for precipitation is 25% (v/v). At volumes of sulfuric acid lower than 20% (v/v), the rate of precipitation is slow and the walls of the container have to be scratched to create nucleation centers for the initiation of precipitation. Second, the precipitate forms a hard scaling which is difficult to remove. Finally, zirconium losses in the filtrate are also considerable, as can be seen from Fig. 2.

Precipitation with 25% (v/v) sulfuric acid yields a zirconium sulfate tetrahydrate precipitate in the form of powder which is easily filterable and washable. After a suitable adjustment of acidity, the filtrate can be reused in leaching another batch of wet cake. Upon calcination at 1000°C for 6–8 hours, the zirconium sulfate tetrahydrate precipitate yields a fine, free-flowing ZrO_2 powder with an SO_3 content of less than 150 ppm. The SO_3 gases evolved during calcination can be effectively scrubbed in water with a proper exhaust system. The purity of the zirconia powder obtained through both precipitation routes is given in Table 4. The high calcium content in the ZrO_2 powder is due to the presence of calcium (70 μg/mL) in the commercial-grade hydrochloric acid used in the experiments.

TABLE 4
Purity of Zirconia (values are in parts per million)

Element/compound	6 N HCl, gaseous ammonia precipitation route	(6 N HCl)–(2 N H_2SO_4), sulphuric acid precipitation route
Al	500	490
B	10	33
Bi	<25	<25
Ca	1000	1300
Cr	60	<25
Cu	<25	<25
Mg	780	76
Mn	36	<5
Ni	16	<5
Sb	<25	<25
Sn	<10	<10
Ti	680	140
V	<10	<10
W	<25	<25
U	20	<1
Fe_2O_3	10	<1

However, the presence of calcium in ZrO_2 does not have any deleterious effect on its properties for the various applications cited.

CONCLUSIONS

The present ion-exchange purification process has great potential for adoption in industry for the preparation of high-purity zirconia powders because of its simplicity, economy, and capability to produce high quality powder.

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