

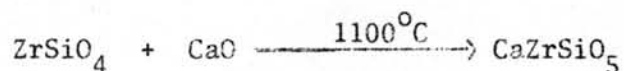
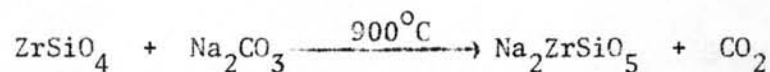
CHAPTER II

EXTRACTION OF ZIRCONIUM FROM ZIRCON



The process employed in the extraction of zirconium from the native silicates depends on the degree of purity desired. If a high degree of purity is desired, or silica is to be removed, it is necessary to open up the mineral by fusion with suitable fluxes.

Zircon reacts with alkalis and alkaline earths at high temperatures forming metal zirconium silicates. (3)

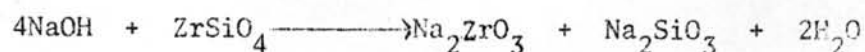


The mineral is generally unreactive to acids but is attacked by concentrated sulphuric acids at high temperature and pressure.

2.1 Alkali Fusion

The first step in recovering zirconium is to decompose the ore which is difficult in the case of silicates. Generally the most commonly used methods are volatilization, acid attack, alkali fusion, hydrofluoric acid treatment and fluoride fusion, chlorination and sintering with alkali double fluoride. (2, 4) Of these methods, the fusion with alkali is used on a commercial scale because it requires a lower temperature and less time. (5, 6) Although it is not appreciably attacked by aqueous alkalis, it responds readily to

breakdown by fused sodium hydroxide at temperature of 550 to 650°C. The reaction varies according to the proportion of the reactants and other conditions but can be represented approximately by the equation. (7).



Stainless-steel vessels are normally used, although this is not essential. Cast iron is satisfactory if it is not subjected to undue thermal shock.

Leaching is then carried out with water to remove sodium silicate, excess sodium hydroxide and to convert sodium zirconate to zirconium hydroxide. The succeeding dissolution of hydrous metal oxide cake in nitric acid is not always successful because of the presence of large quantities of hydrated silica which causes the entire mass to become gelatinous. This gelatinous silica could be eliminated by evaporating the solution to dryness and redissolving in nitric acid. This apparently dehydrates the gel to insoluble silicates that can be filtered from the nitric acid solution. However, difficulty is again encountered when extraction is attempted. Even no gel appeared in the aqueous feed solution, a heavy gelatinous mass could be formed in several stages of the extraction. (8) The dissolution with sulphuric acid introduces sulphate ion which may interfere with subsequent purification. The zirconium distribution is decreased about 100 fold by 0.1 mol/l phosphate, tenfold by 0.01 mol/l fluosilicate, and sixfold by

0.1 mol/l sulphate.⁽⁹⁾ The dissolution of hydrous metal oxide in hot concentrated hydrochloric acid, followed by the addition of a small amount of gelatin causes a mutual flocculation between the colloidal silica and the gelatin. The precipitation of this silica floc markedly lowered the content of silica in the product. The silica content of the compound is now less than 100 ppm., which is low enough for the tri-n-butyl phosphate (TBP) extraction.⁽¹⁰⁾ The insoluble residue is filtered from the hot solution. When the acid solution is cooled to room temperature, most of the zirconium oxychloride octahydrate crystallizes out. This salt is easily purified by recrystallization in 8 to 10 mol/l hydrochloric acid.⁽¹¹⁾ The zirconium oxychloride octahydrate is dissolved in water and zirconium can be selectively precipitated from the solution by adjusting the pH of the solution to 4.5 using sodium hydroxide solution. The zirconium hydroxide precipitate is subjected to further purification by solvent extraction.

2.2 Solvent Extraction

Hafnium is usually present in zircon to the extent of 2 per cent and its chemical properties are so similar to those of zirconium that the two elements remain together through the ore breakdown and the preliminary chemical processing steps. Other impurities, including uranium, thorium, silicon and iron are fairly readily removed.

Many methods have been developed for the separation of

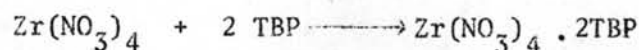
zirconium and hafnium, including fractional crystallization, selective precipitation, fractional distillation and solvent extraction. (2, 4, 12) Of all these processes, solvent extraction seems to be the one most easily applied on large-scale production. It has been found that the extraction of zirconium from nitric acid solution using tri-n-butyl phosphate diluted with xylene or kerosene (8, 13, 14, 15) provides the most satisfactory results. Tri-n-butyl phosphate is a rather viscous solvent, density of which (0.975 g/cm^3 at 20°C) is near that of water. It must be diluted in order to make decantation easier. Kerosene is chosen as the diluent because it is cheap, chemically inert to nitric acid and insoluble in water. (9) Several inorganic nitrates, including those of aluminium, ammonia, calcium, magnesium and sodium, have been used to increase the nitrate ion concentration in the aqueous phase. (16, 17, 18)

The purification of zirconium by tri-n-butyl phosphate extraction is performed in three stages.

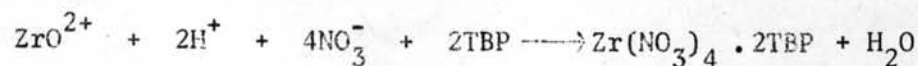
2.2.1 Extraction

Zirconium is extracted from the aqueous feed solution into the organic solvent phase whereas most of the impurities remain in the aqueous phase. The distribution coefficient for a single-stage extraction of uranium, thorium and rare earths from 5 mol/l nitric acid solution using 50 per cent TBP/kerosene were found to be 5.5, 2.5 and 0.046 respectively. (19)

The chemical mechanism of the TBP extraction may be represented as follows (14, 20)



or



This equation has not been quantitatively confirmed but it serves adequate to give a qualitative picture of the observed behavior.

Writing the equilibrium constant in mass term, the following equation is obtained.

$$K_{\text{Zr}} = \frac{K}{G} [\text{H}^+]^2 [\text{NO}_3^-]^4 [\text{TBP}]^2$$

where

K_{Zr}	=	distribution constant
K	=	equilibrium constant
G	=	Gibbs free energy

Thus, ignoring any variation with concentration of the activity coefficient term (G), extraction is favored by the increase of acidity, total nitrate and TBP concentration.

2.2.2 Scrubbing

Scrubbing is operated to remove hafnium from the organic phase. A mixture of sodium nitrate-nitric acid is normally used.

2.2.3 Stripping

Zirconium is recovered by backwashing the loaded solvent with an equal volume of water.

The schematic process flow diagram for the alkali fusion and TBP extraction of zirconium is shown in Figure 2.1.

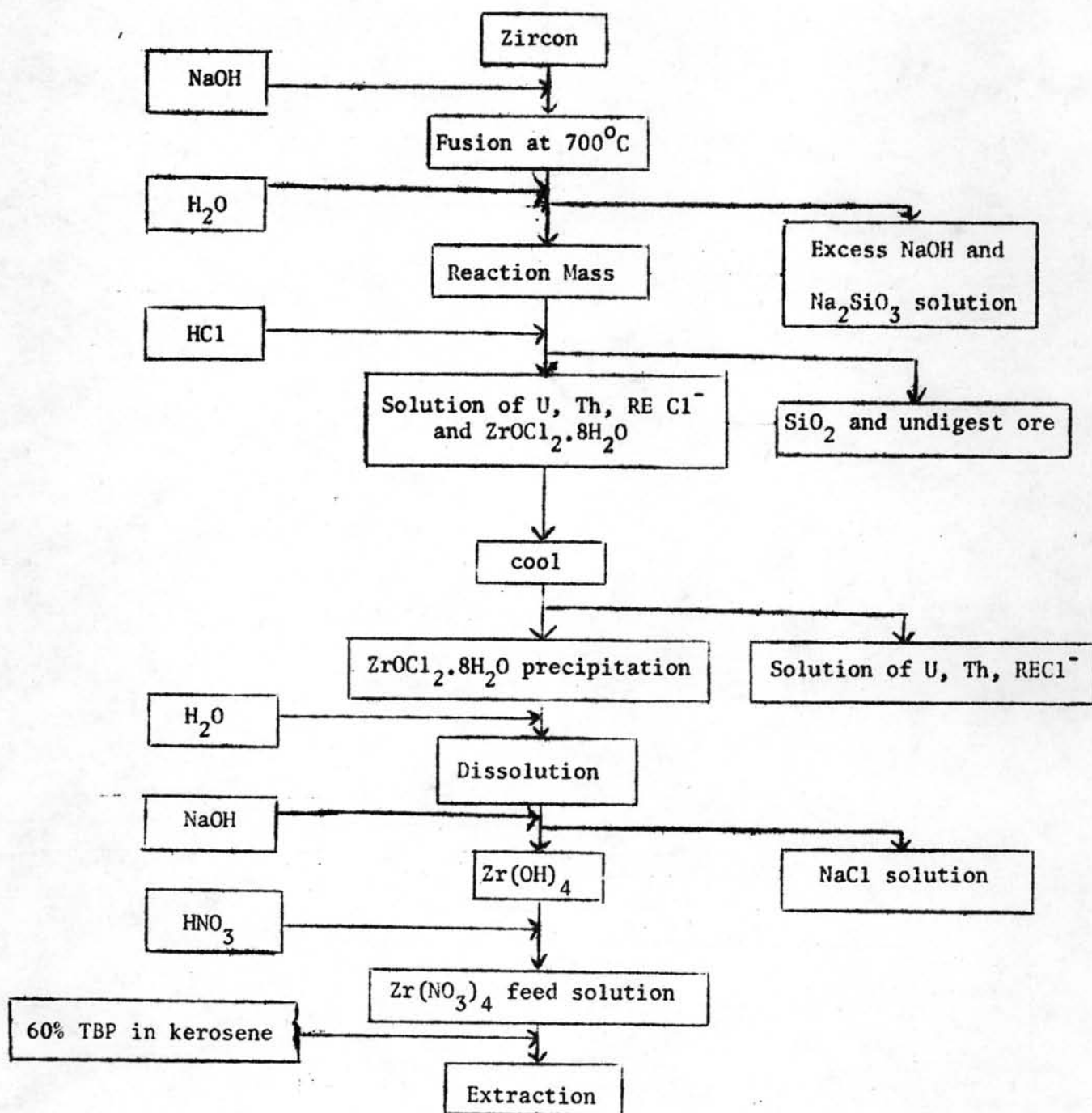


Figure 2.1 Simplified flow diagram of alkali fusion of zircon and purification of zirconium

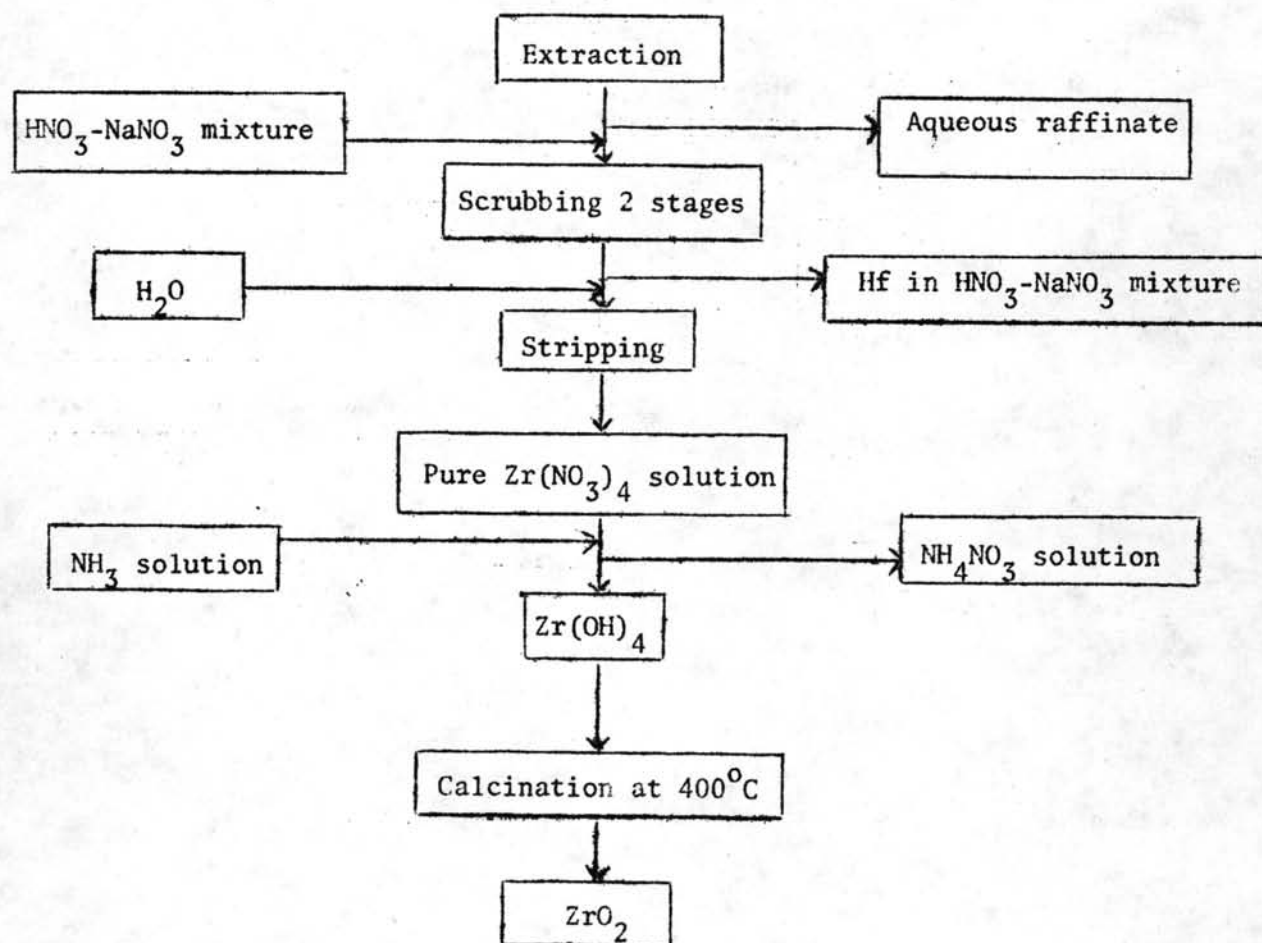


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