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RESEARCH ESTABLISHMENT
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REVIEW OF PROCESSES FOR THE PRODUCTION OF HAFNIUM-FREE ZIRCONIUM

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ABSTRACT

The three main industrial processes for the production of hafnium-free zirconium are described in terms of their head-end, zirconium-hafnium separation and zirconium metal forming steps. Possible improvements and alternative processes are outlined.

Zirconium-hafnium separation schemes based on selective reduction of the chlorides or distillation and sublimation techniques show the most promise for future development in competition with the established hexone-thiocyanate and TBP-nitric acid solvent extraction schemes. Head-end steps involving direct chlorination of zircon in fluidised beds or caustic fusion and metal production via electrowinning warrant further development.

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1. INTRODUCTION

Zirconium alloys are mainly used as fuel cladding and structural materials in water-cooled nuclear reactors. In nature, zirconium occurs together with hafnium and the two elements are chemically very similar. In Australian beach sands, a major source of zircon, the zirconium occurs with 2-3 wt.% of hafnium. Zirconium has a low capture cross section for thermal neutrons whereas hafnium is a very efficient absorber of neutrons and consequently only hafnium-free zirconium is used in nuclear reactors. A typical chemical specification for nuclear grade zirconium sponge is shown in Table 1.

Table 2 contains a list of the major producers of hafnium-free zirconium in the free world over the past 20 years. A variety of processes have been used and these, together with some pilot plant operations, are listed in Table 3. In each of these processes, various head-end steps, hafnium-zirconium separation processes and metal production techniques are used. Typical flowsheets illustrating the various steps in three industrial processes are presented in Figures 1, 2 and 3. Flowsheets of earlier processes have been presented by Lustman and Kerze (1955), Jamrack (1963) and Alfredson and Carter (1968).

Figure 1 shows a modern process for zirconium production which includes the hexone-thiocyanate solvent extraction process for the separation of zirconium and hafnium. This is an improvement of the original process developed by the U.S. Bureau of Mines for the production of hafnium-free zirconium. This basic process still accounts for the major part of the zirconium manufactured at the present time.

Figure 2 shows the process developed by Cox et al. (1958) which uses the tributyl - phosphate-nitric acid solvent extraction process for the hafnium-zirconium separation step. This process was used subsequently by the Columbia National Company in the U.S.A. This company is no longer operating this process, but a similar plant has been constructed by Eldorado Nuclear Limited in Canada* and the Department of Atomic Energy in India has operated this process on a pilot plant scale (Department of Atomic Energy, Government of India, 1964-65).

A process used in the U.S.S.R. is presented in Figure 3. It includes a fractional crystallisation process for hafnium-zirconium separation using potassium fluozirconate (K_2ZrF_6) with hafnate (K_2HfZr_6) as the feed material. The flowsheet is constructed from the data of Sajin and Pepelyaeva (1955) and Sundaram et al. (1965), and includes the electrowinning step described by Ogarev et al. (1958).

In this report, the various steps used in the above processes are examined, together with alternative techniques which have been developed or proposed. Comments are also made on the relative efficiencies of these processes and on possible areas in which improvements could be made.

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* Hueston, F. H. (1970). - 10th Ann. Int. Conf. Canadian Nuclear Association Toronto. May 24-27, Paper 70-CNA-663.

2. HEAD-END PROCESS FOR ZIRCON

Zircon, zirconium silicate $ZrSiO_4$, is a stable refractory compound and is not easily decomposed or dissolved readily by any combination of acids. The available head-end processes have been reviewed extensively by Lustman and Kerze (1955), Thomas and Hayes (1960), Jamrack (1963) and Lehr (1963). In the following sections, descriptions are given of the chlorination, caustic fusion and potassium silicofluoride sinter processes. These processes provide feed materials for the three main methods of separating zirconium and hafnium: hexone-thiocyanate solvent extraction, TBP-nitric acid solvent extraction and fractional crystallisation (using K_2ZrF_6).

2.1 Chlorination Processes

2.1.1 Carbide intermediate

Until recently, the preparation of chlorides from zircon on an industrial scale included as an intermediate step the production of zirconium carbide or carbonitride in a graphite lined arc furnace at 1800°C (Kroll et al. 1948).

$$ZrSiO_4 + 4C \rightarrow ZrC + SiO + 3CO$$

The volatile silicon monoxide was liberated in the reaction leaving a solid product which was chlorinated to form zirconium (hafnium) chloride and separated from major impurities (iron and aluminium) by sublimation.

$$ZrC + 2Cl_2 \rightarrow ZrCl_4 + C$$

The intermediate step was used to facilitate the removal of silicon compounds and other impurities which are difficult to separate from the volatile chlorides produced in direct chlorination processes. In addition, the subsequent chlorination of the carbide required a lower temperature (500°C) and was exothermic, whereas direct chlorination requires a temperature of 800-1200°C and is endothermic.

Alternatively, the carbonitride was prepared by admitting air into the arc furnace. The carbonitride so formed contained 82-84 wt.% of zirconium, 3-5 wt.% carbon and 8-10 wt.% nitrogen and gave a more exothermic reaction at 500°C during chlorination (Jamrack 1963) than did the carbide.

2.1.2 Direct chlorination

Several techniques for direct chlorination have been proposed in an attempt to simplify the above route.

$$ZrSiO_4 + 4C + 4Cl_2 \rightarrow ZrCl_4 + 4CO + SiCl_4$$

These have been outlined and discussed by Alfredson and Carter (1968). Recently the Wah Chang Company in the U.S.A. adopted a direct chlorination route. The other major U.S. producer, Amax Specialty Metals, has also investigated direct chlorination methods (Nucleonics Week 1968) and Shumeiko et al. (1968) have described a recent U.S.S.R. development of a zircon chlorination furnace.

In general, reaction temperatures in the range 800 to 1200°C and close contact between the zircon and carbon are required. While a number of patents describe fluidised bed processes, fixed bed reactors appear to be used in industrial plants.

2.2 Fusion Processes

Jamrack (1963) has described the following typical caustic fusion process. Zircon and caustic soda (ratio 1 : 1.1) were fused at 500-650°C to produce a frit of sodium silicate and sodium zirconate.

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

The frit was leached with water to remove sodium silicate and excess alkali using about 7 tons of water per ton of zircon. The final sodium zirconate product contained traces of silica which was thoroughly removed to provide a suitable feed for solvent extraction.

Cox et al. (1958) examined the problem of silica removal in some detail and devised the flowsheet shown in Figure 4. In this process, the washed frit was dissolved in sulphuric acid, the solution filtered and the zirconium precipitated using ammonia. The hydroxide was partially dried and shattered into sand-like grains when water was added, allowing the material to be washed free of silica quite readily. Zirconium nitrate feed material for solvent extraction was prepared by adding nitric acid to the washed hydroxide.

Hyung Sup Choi (1965) described the preparation of pure zirconyl compounds suitable for feed to a TBP-nitric acid solvent extraction process from zircon-caustic frit. The washed frit was dissolved directly in 70 per cent nitric acid at 80°C and acidified gelatin was added to the solution causing mutual precipitation of gelatin and silica as a floc. This floc was readily filtered and the zirconyl nitrate in solution contained less than 50 ppm silicon and less than 20 ppm iron.

Thomas and Hayes (1960) outlined a similar fusion process using sodium carbonate which was patented by Loveman (1918) and has been used by Ugine-Kuhlmann (Alfredson and Carter 1968). Several other alternative processes have been described by Lehr (1963).

2.3 Potassium Silicofluoride Sinter Processes

Sajin and Pepelyaeva (1955) have described this process, which was developed in the U.S.S.R., and a similar Indian development has been described by Sundaram et al.

(1965). Typically a mixture of 200 mesh zircon, potassium silicofluoride and potassium chloride was sintered in a rotary furnace or crucibles at 650-750°C. The sinter product was crushed and leached with dilute 1 vol.% hydrochloric acid to provide the potassium fluozirconate (K_2ZrF_6) product.

3. ZIRCONIUM-HAFNIUM SEPARATION PROCESSES

Owing to the close chemical similarity between zirconium and hafnium, the separation of these two materials is not a simple operation. Reviews of some of the available processes have been given by Thomas and Hayes (1960), and Vinarov (1967). Separation by solvent extraction using either the hexone-thiocyanate process or the TBP-nitric acid process has been applied industrially. These two processes have been reviewed in detail by Royston and Alfredson (1970) and are only briefly summarised here.

Separation by fractional crystallisation has been used industrially in the U.S.S.R. and in pilot plant operations in India and the U.S.A. In the U.S.S.R. and India, potassium fluozirconate with hafnate, $K_2Zr(Hf)F_6$, was used as the feed material. The process examined in the U.S.A. used $(NH_4)_2\,Zr(Hf)F_6$ but an overall flowsheet was not developed.

In the solvent extraction processes, the product from the separation stage is usually converted to an oxide and chlorinated to the tetrachloride for reduction by the Kroll process. Where a chloride head end process is used, it would be advantageous to eliminate this second chlorination step by using a separation process based on the chlorides. However, zirconium tetrachloride reacts readily with water to form the oxychloride and consequently separation methods using chlorides must be non-aqueous. Three important non-aqueous separation techniques - selective partial reduction, distillation and sublimation - are reviewed in this report. Other techniques which have shown limited development potential such as vapour phase dechlorination, electrolysis, ion exchange and fractional precipitation are not considered here.

3.1 Solvent Extraction Separation Processes

3.1.1 Hexone-thiocyanate process

In this process, the thiocyanate complexes of zirconium and hafnium are produced, the hafnium complex being extracted preferentially into the organic (hexone) phase. McClain and Shelton (1960) have described a typical process which is shown in Figure 5. Zirconium tetrachloride was dissolved in water to form an oxychloride solution. Ammonium thiocyanate (NH_4CNS) and hydrochloric acid were added to this solution to give the required feed solution for extraction by hexone also containing NH_4CNS. The resulting organic solution was scrubbed with 3.6 N hydrochloric acid giving an aqueous zirconium stream with less than

50 ppm of hafnium. Zirconium was precipitated from solution as a basic sulphate and calcined to form a pure oxide product. The thiocyanate in the organic stream after hafnium stripping was recovered by contacting with ammonia liquor to form ammonium thiocyanate which was used in feed make-up.

3.1.2 TBP-nitric acid process

Figure 6 shows the TBP-nitric acid solvent extraction process developed by Cox et al. (1958) and used subsequently by the Columbia National Company. A zirconium nitrate feed solution was used, the zirconium nitrate-TBP complex being extracted preferentially into the organic (tributyl phosphate) phase.

The aqueous feed stream contained the nitrate solution and nitric acid. The organic stream was TBP diluted with some inert hydrocarbon such as kerosene or xylene. The zirconium was extracted from the feed solution by the organic stream which was scrubbed with nitric acid, and the zirconium was finally stripped with water. The pure zirconium nitrate solution was processed to provide an oxide product.

3.2 Fractional Crystallisation

Early process studies were based on crystallisation of ammonium fluozirconate and hafnate (Beaver 1950). The unstable nature of the ammonium salt and the corrosive conditions which resulted from the use of highly acidic solutions to suppress this decomposition limited this development. Potassium fluozirconate was used to overcome these problems and was also found to give a higher separation factor and a larger change in solubility between room temperature and 100°C (Sundaram et al, 1965).

Sajin and Pepelyaeva (1955) described briefly the fractional crystallisation process developed and used in the U.S.S.R. with potassium fluozirconate (and hafnate) as the feed material. The crystals were dissolved at 80-90°C to form a 0.5 M solution from which a zirconium-enriched salt recrystallised on cooling, leaving a hafnium-enriched solution. About 16-18 crystallisation steps were required to reduce the Hf/Zr ratio to 0.01. The zirconium fluozirconate was converted to the oxide by precipitation with ammonia, filtration, washing and calcination at 900°C.

3.3 Non-Aqueous Separation Methods Using Chlorides

3.3.1 Selective partial reduction - Newnham process

Figure 7 is a simplified flow diagram of the selective partial reduction process developed at C.S.I.R.O. and described by Newnham (1957a). The process is based on the difference in the rates of reduction of zirconium tetrachloride ($ZrCl_4$) and hafnium tetrachloride ($HfCl_4$) with zirconium metal or zirconium dichloride ($ZrCl_2$). Crude zirconium tetrachloride, containing hafnium tetrachloride was heated with zirconium powder or zirconium dichloride in a vacuum at 400-450°C. Most of the tetrachloride was reduced to the comparatively non-volatile trichloride:

$$3\ ZrCl_4 + Zr \rightarrow 4ZrCl_3$$

or

$$ZrCl_4 + ZrCl_2 \rightarrow 2ZrCl_3$$

The hafnium tetrachloride was not reduced and, together with any unreduced zirconium tetrachloride, was recovered by sublimation. The sublimate contained 10 per cent hafnium in zirconium compared with an original 2 per cent. The trichloride was then disproportionated at 550°C to the di- and tetrachlorides:

$$2ZrCl_3 \rightarrow ZrCl_4 + ZrCl_2$$

The zirconium tetrachloride product sublimed and was recovered. The remaining dichloride was used for the next reduction cycle.

Although this process is capable of producing nuclear grade zirconium tetrachloride, it is not capable of producing a high grade hafnium product owing to dilution by zirconium tetrachloride which does not react in the reduction stage and is sublimed with the hafnium tetrachloride. One other practical limitation of the process lies in the formation of a sinter between products and reactants. The sinter limits the rate and yield of the reaction. Frampton and Feldman (1968) used stirred reactors with $ZrCl_2$ reductant, and found that crust formation, a form of sinter on the surface of the reacting mixture, was not a serious problem, and the reaction proceeded smoothly.

This process has been examined for possible industrial application (Frampton and Feldman 1968) and studies on similar processes have been undertaken in the U.S.S.R. (Vinarov 1967). Frampton and Feldman (1968) described in some detail a proposal for an industrial scale development of the Newnham process. The purification was carried out in two stages using $ZrCl_2$ as the reducing agent in preformed beds operating at atmospheric pressure in horizontal tube screw feed reactors. The first stage produced material containing 0.14 per cent hafnium, and in the second stage the product contained 0.005-0.010 per cent hafnium in zirconium. The $ZrCl_2$ beds were prepared by reacting zirconium sponge and $ZrCl_4$ at 450°C. Once prepared the beds were renewed in the process and impurities were removed via a purge stream of argon. The reduction temperature was 400°C with a contact time between the $ZrCl_4$ and $ZrCl_2$ of 15 minutes. The dissociation step required a temperature of 450°C with a rapid argon purge flow.

In the proposed industrial plant, iron and steel vessels were used with heating by molten tin or sodium to maintain close temperature control. It was suggested that fluidised bed reactors could be used to provide a uniform reactor temperature and bed agitation, thus helping to limit sintering or crust formation.

Newnham (1957b) also patented a separation method using iodides which was similar to that described above for chlorides. The reduction was carried out at 500°C and the unreacted tetraiodides were collected on a cool surface. The zirconium triiodide was disproportionated at 350°C, the tetraiodide being removed by sublimation.

Prakash and Sundaram (1958) used aluminium in place of zirconium and effected some separation on a laboratory scale. However, the separation of the product from the aluminium required wet techniques, thus limiting the value of this process.

3.3.2 Sublimation and distillation methods

3.3.2.1 Sublimation

Gillot and Goldberger (1968) reported the development of a process for the separation of zirconium and hafnium tetrachlorides by thin film sublimation. A bed of inert glass beads moved down a column through which passed sublimed $Zr(Hf)Cl_4$ together with a carrier gas of nitrogen. Differential condensation and resublimation occurred on the surface of the beads, giving some separation between the hafnium and the less volatile zirconium tetrachlorides. Operation was demonstrated both with and without a temperature gradient in the column.

Although the above experiments were conducted on a laboratory scale, a significant degree of separation was achieved and Gillot and Goldberger claimed that the process has potential for development to an industrial scale. However, they also stated that the throughput of material would be lower and the heat requirements higher than in more conventional processes such as distillation and extraction. In addition, throughput could be limited by the thickness of the condensed film. Pluckett et al. (1949) previously encountered the latter problem in sublimation studies using a ten-plate column with mechanical reflux between one plate and another. No significant separation was achieved because the sublimation process took place only at the surface of the transported crystals. This left the interior of the crystals, containing most of the material, unchanged. The same problem could occur with the thin film technique, limiting the film thickness which can be used and consequently the throughput. Also too large a thickness could create blockages or bridging in the bed. Gillot and Goldberger commented that fractional sublimation would offer definite advantages in cases where conventional physical separation methods cannot be used.

3.3.2.2 Distillation of tetrachlorides

Vinarov (1967) described briefly the fractional distillation of zirconium and hafnium tetrachlorides which may be carried out under pressures of 20-30 atm.

at 450°C. In a large scale experiment with a column using metal packing, a zirconium product containing less than 0.05 per cent hafnium was obtained with yields of more than 50 per cent from a feed containing 1.5-2.5 per cent hafnium. A similar process was patented by E. I. du Pont de Nemours (1960). With 30 theoretical plates, a pure $ZrCl_4$ product could be obtained. Fractional distillation of the tetrachlorides in columns irrigated with melts of sodium, potassium and tin chlorides have also been described (Thomas and Hayes 1960, Vinarov 1967). However only a limited degree of separation was obtained with these methods.

In general, the distillation process appears attractive, but development as an industrial process is limited by the necessary use of the highly corrosive tetrachlorides at high temperatures and pressures (Vinarov 1967).

3.3.2.3 Distillation of phosphorus oxychloride complexes

Lustman and Kerze (1955), Thomas and Hayes (1960) and Vinarov (1967) have described the various attempts at separating hafnium and zirconium tetrachlorides by the fractional distillation of their phosphorus oxychloride complexes. However separating the product complex back into the phosphorus and zirconium compounds has proved to be difficult (Thomas and Hayes 1960).

4. CHLORINATION OF ZIRCONIUM OXIDE

Processes used in the chlorination of zirconium dioxide have been reviewed previously by Alfredson and Carter (1968). Fixed bed chlorination of zirconium oxide-carbon briquettes to produce zirconium tetrachloride for reduction to zirconium metal by the Kroll process is used in the U.S.A., France and India. A number of fluidised bed processes have been patented and Spink et al. (1968) suggested that they have the following advantages:

(i) The heat transfer properties of the fluidised bed permit close control of reaction temperature and eliminate problems (such as the formation of a dust) associated with the hot spots generated in a fixed bed operation.

(ii) The excellent gas-solid contact obtained in a fluidised bed promotes a more efficient utilisation of chlorine and better recovery of zirconium.

(iii) A fluidised bed operation offers a more complete utilisation of the feed material in that fine material which is unsuitable for fixed bed use need not be discarded but can be chlorinated directly in a fluidised bed.

5. PREPARATION OF ZIRCONIUM METAL

The most common method of preparing zirconium metal is the Kroll process in which $ZrCl_4$ is reduced by magnesium (in some cases sodium, see Chemical and

Engineering News 1957) to produce zirconium sponge.

$$ZrCl_4 + 2Mg \rightarrow 2MgCl_2 + Zr.$$

An alternative route which has received some attention is the electrolysis of fused salts.

5.1 The Kroll Process

Detailed descriptions of this process have been presented by Lustman and Kerze (1955), Shelton et al. (1955), Jamrack (1963), and a description of the similar process for hafnium by Thomas and Hayes (1960). In consequence only a brief outline is presented here.

Zirconium tetrachloride (containing oxygen and other impurities) was packed in a container in the middle of a vertical tubular furnace and distilled-magnesium ingots were placed in the bottom. The upper part of the furnace was cooled by coils in the lid; the lower parts were heated with the base at 825°C and the central zone at 650°C. The tetrachloride was evaporated at a controlled rate into a helium atmosphere and reacted with the molten magnesium forming zirconium sponge and magnesium chloride. When the reaction was complete the section of the furnace containing the sponge $MgCl_2$ was removed and placed in a second furnace. In this furnace the charge was heated to 825°C under a vacuum as low as 0.05×10^{-3} mm Hg. Under these conditions the chloride evaporated and condensed on the cooled lower part of the equipment. The remaining sponge was cleaned, graded and sized for further processing to a finished metal product.

In early processes, the zirconium sponge required further purification before a product suitable for metal working was produced. The metal was usually purified by the Van Arkel and de Boer iodide decomposition process (Lustman and Kerze 1955). However, subsequent improvements in the Kroll process have made this step unnecessary.

Mauser (1961) described a development of the Kroll process which produced a billet of zirconium on a semi-continuous basis. It was however less pure than that produced in the normal Kroll process and the test buttons from arc melting were considerably harder owing to their high oxygen content (up to 300 ppm). In addition the reactor suffered severely from corrosion, with consequent maintenance problems.

5.2 Fused Salt Electrolysis

Ogarev et al. (1958) described a fused salt electrolysis process used in Russia for the commercial scale production of zirconium. A concentration of K_2ZrF_6 of 25-30 wt.% in KCl was used with a current density of 350-400 amp/dm^2 and a temperature of 750-800°C. The cathode deposit which contained 30 wt.%

zirconium as an accumulation of metal, KCl, KF, K_2ZrF_6 and zirconium fluorides, was crushed to 8-10 mm, milled with a water wash and washed further with 10 per cent HCl, water and acetone respectively. The dried powder was purified from any remaining oxygen by etching with 0.05-5 per cent NH_4HF_2. The zirconium metal powder was melted in a consumable arc furnace to produce metal ingots of 130-140 Brinell hardness suitable for metal working into tubes etc.

Jamrack (1963) described a similar electrolytic process used on a 'near commercial' scale by Horizons Inc. for the U.S.A.E.C. A NaCl-K_2ZrF_6 melt was used at 830-850°C.

5.3 Electrowinning of Hafnium from Hafnium Tetrachloride

Martinez et al. (1969) described an experimental process for the electrowinning of hafnium from hafnium tetrachloride. Owing to the close similarity between hafnium and zirconium, there is reason to believe that this process could be adapted for electrowinning zirconium.

Several electrolytes were examined and KCl-$HfCl_4$ and LiCl-RbCl-$HfCl_4$ were found to be satisfactory. With KCl-$HfCl_4$ containing 10 wt.% $HfCl_4$ at 800°C, hafnium containing 400 ppm of oxygen was produced. In the LiCl-RbCl-$HfCl_4$ system at 700°C with 10 wt.% hafnium, hafnium containing as little as 90 ppm of oxygen was produced.

6. CONCLUDING REMARKS

6.1 Comments on Process Economics

An economic comparison of the established processes can be made only in a general way owing to the lack of detailed information necessary for an accurate cost study. Googin (1958), using 1950-53 data, stated that a process incorporating the hexone-thiocyanate separation stage produced hafnium-free zirconium for $US 14.5/kg, whereas the estimated cost of production for the crystallisation process of Beaver (1950), using $(NH_4)_2ZrF_6$, was $US 19.9/kg. (The fractional crystallisation process using K_2ZrF_6, a simpler process than with $(NH_4)_2ZrF_6$, could be cheaper.) Frampton and Feldman (1968) claimed that hafnium-free zirconium could be produced by the Newnham process for approximately $US 3.3/kg less than by the hexone-thiocyanate process in the period 1957-58.

An indication of present day U.S. costs was given in a review by A. D. Little Inc. (1968). Pure zirconium sponge cost $US 11.55/kg in 1968 compared with $US 13.75/kg in 1959. The current cost (1970) is approximately $US 10.00/kg. A projected reduction to $US 7.7-8.8/kg by the mid-70's was made on the basis of the production of 11,000-13,000 tonne of sponge per year. A. D. Little Inc. (1968) also reported that the economics of zirconium processes are affected by the fluctuating demand for pure hafnium, although Wright (1970 - A.A.E.C. private communication) reports that hafnium production is not considered an important economic factor by some producers. The price of hafnium in 1968 was $US 165/kg.

Assuming 3 wt.% hafnium in zirconium it follows that for every \$100 obtained from zirconium sales, a maximum of \$51 could be gained from the sale of a pure hafnium by-product.

A. D. Little Inc. (1968) gave the market capitalisation for a 910 tonne/year plant as \$US 15 million (most probably a hexone-thiocyanate process). Canadian Chemical Processing (1968) gave the cost of 270 tonne/year plant using the TBP-nitric acid process as \$CAN 8.3 million (\$US 7.7 million in 1968).

6.2 Processes of Interest for Further Development

6.2.1 Separation processes

The choice of a separation process is the first consideration in selecting an overall process for the production of pure zirconium (and hafnium). Vinarov (1967) suggested that the most suitable separation processes should have a high separation factor, high specific throughput, and simplicity of technology, and should offer continuous processing with low cost reagents and materials of construction. Using these criteria, Vinarov selected the following processes as worthy of consideration and further development: solvent extraction, fractional crystallisation using K_2ZrF_6, selective reduction of chlorides (Newnham process), distillation and ion exchange.

Of the separation processes, solvent extraction is most commonly used and satisfies most of the above criteria. The major solvent extraction process, using hexone-thiocyanate, has been developed over many years and possible improvements appear to be limited. The alternative TBP-nitric acid process has a simpler flow-sheet and uses stainless steel equipment, whereas glass or polythene is required with the former process. However, the laboratory performance of the TBP process does not appear to have been reproduced industrially. Low yields of zirconium (less than 80 per cent) have been reported (Keller and Zonis 1959) in plant scale operation and further study of this process seems desirable.

The Newnham process is a very attractive alternative to solvent extraction, giving good separation in one or two stages. The use of an all-chloride system eliminates the intermediate hydrometallurgical stages of other processes. Good temperature control of the dissociation and reduction reactions is necessary. Stirred reactors have been used, but fluidised bed reactors could be an improvement and are suggested as a suitable area for further study. The reduction reactor needs to operate with a low purge gas flow to minimise the dissociation of $ZrCl_3$, and consequently fluidisation using sublimed $ZrCl_4$ and/or inert gas should be considered. The dissociation reactor can be operated with a high purge gas flow and this could be the fluidising medium in this reactor.

Fractional crystallisation with K_2ZrF_6 has received only limited industrial application. It is attractive because cheap materials of construction are used and the one zirconium-containing material, K_2ZrF_6, is used from the head-end to the metal-forming stage. However the process gives low yields of zirconium, and uses batchwise operation, and with the low solubility of K_2ZrF_6 these restrictions result in a low throughput relative to solvent extraction plants. From experience in India, where crystallisation methods were developed but solvent extraction was finally adopted, it appears that the development of this process is not worth while.

Distillation under pressure is inherently attractive but methods have to be found to eliminate or minimise the severe corrosion problems. Ion exchange gives good separation in the laboratory but the cost of an industrial application of this technique could be prohibitive. The sublimation process of Gillot and Goldberger (1968) is also of interest although further laboratory studies are necessary before a proper evaluation can be made.

6.2.2 Head-end and metal forming processes

For the integrated production of metal from ore, head-end and metal forming stages are required in addition to the separation stage. The most common processes use chlorination of zircon and magnesium reduction (Kroll process) respectively. These processes are efficient and have been developed over many years. Any alternative processes would have to offer marked advantages of cost and the possibility of continuous processing.

At present chlorination is carried out in shaft furnaces using zircon-carbon briquettes. Fluidised bed operation should be investigated since it enables continuous operation and better temperature control, leading to better yields of product. An alternative to chlorination is the caustic fusion process, particularly for TBP-nitric acid separation processes. However the elimination of silica is difficult and further studies of this problem using methods similar to that outlined by Hyung Sup Choi (1965) seem desirable.

The development of continuous versions of the Kroll process has met with little success owing to corrosion and purity problems. In the long term lower costs might be achieved using an electrowinning process and the process outlined by Martinez et al. (1969) merits further study.

7. REFERENCES

Alfredson, P. G. and Carter, F. R. (1968). - AAEC/TM431.

ASTM (1964). - B349-64T.

Beaver, W. W. (1950). - BBC54.

Canadian Chemical Processing (1968). - Zirconium route bypasses sponge step, June 1968, p.69.

Chemical and Engineering News (1957). - How USI will make zirconium, March 18, 1957, p.92.

Cox, R. P., Peterson, H. C. and Beyer, C. H. (1958). - Ind. Eng. Chem, 50:141.

Department of Atomic Energy, Government of India, Annual Report (1964-65).

E. I. du Pont de Nemours and Co. (1960). - British Patent 883103 (NSA 14:118805)

Frampton, O. D. and Feldman, J. (1968). - Progress in Separation and Purification (Ed., Perry, E. S.) Interscience Publishers Inc., New York, 1:247.

Gillot, J. and Goldberger, W. M. (1968). - CEP Symp. Series 65(17):36-42.

Googin, J. M. (1958). - Progress in Nuclear Energy Series III, Process Chemistry, Vol. 2 (Eds. - Bruce, F. R., Fletcher, J. N. and Hyman, H. H.), Pergamon Press, Oxford, p.194.

Hyung Sup Choi (1965). - Trans. Can. Inst. Min. Metall. 68:65-70.

Jamrack, W. C. (1963). - Rare Metal Extraction by Chemical Engineering Techniques, Pergamon Press, Oxford.

Keller, W. H. and Zonis, I. S. (1959). - CEP Symp. Series, 55(27):107-112.

Kroll, W. J., Schlechten, A. W., Carmody, W. R., Yerkes, L. A., Holmes, H. P. and Gilbert, H. L. (1948). - Trans. Electrochem. Soc. 92:99-113.

Lehr, P. (1963). - Noveau Traité de Chemie Minérale (Ed. - Pascal, P.), Masson, Paris.

Little Inc., A. D. (1968). - NYO-3853-1.

Loveman, W. R. (1918). - U.S. Patent 1261948 (quoted by Thomas and Hayes (1960), p.44).

Lustman, B. and Kerze, F. (Eds.) (1955). - The Metallurgy of Zirconium, McGraw-Hill Book Co. Inc. New York.

Martinez, G. M., Wong, M. M. and Couch, D. E. (1969). - Trans. Met. Soc. A.I.M.E. 245:2237.

McClain, J. H. and Shelton, S. M. (1960). - The Reactor Handbook, Vol. 1. - Materials, (Ed. - Tipton, C. R.), Interscience, New York, p.64.

Mauser, J. E. (1961). - U.S.B.M. Report 5759.

Newnham, I. E. (1957a). - J. Am. Chem. Soc. 79:5415.

Newnham, I. E. (1957b). - Australian Patent 207410.

Nucleonics Week (1968). - About Industry, 9(48):4

Ogarev, A. M., Shentiakov, V. V., Aksenov, N. G., Shtrapenina, R. B. and Stepina, L. A. (1958). - Proc. 2nd Int. Conf. on the Peaceful Uses of Atomic Energy, 4:280-5.

Pluckett, W. K., Hansen, R. S. and Duke, F. R. (1949). - ISC-51.

Prakash, B. and Sundaram, C. V. (1958). - Proc. 2nd Int. Conf. on the Peaceful Uses of Atomic Energy 4:271-275.

Royston, D. and Alfredson, P. G. (1970). - AAEC/TM538.

Sajin, N. P. and Pepelyaeva, E. A. (1955). - Proc. 1st Int. Conf. on the Peaceful Uses of Atomic Energy, 8:559-562.

Schlechten, A. W. (1968). - CONF-650227, p.347.

Shelton, S. M., Dilling, E. D. and McClain, J. H. (1955). - Proc. 1st Int. Conf. on the Peaceful Uses of Atomic Energy, 8:505-550.

Shumeiko, A. A., Smogorzhevskii, S. I., Kataev, Yu-V., Kozhenyakin, V. A., Orekhov, V. P., Makalkina, A. F., Spevak, N. D., Shapashnikova, S. T. and Polishchuk, S. S. (1968). - Tsvetnye Metally; Soviet Journal of Non-Ferrous Metals g(4), pp.96-9.

Spink, D. R., Cookston, J. W. and Harway, J. E. (1968). - CONF 650227, p.375.

Sundaram, C. V. et al. (1965). - AAET 201.

Thomas, D. E. and Hayes, E. T. (Eds.) (1960). - The Metallurgy of Hafnium, U.S.A.E.C. Washington.

Vinarov, I. V. (1967). - Russian Chem. Rev. 36:522-36.

TABLE 1

PURITY REQUIREMENT FOR ZIRCONIUM SPONGE (ASTM 1964)

Element	Maximum Permissible Impurities (ppm)
Aluminium	75
Boron	0.5
Cadmium	0.5
Carbon	250
Chlorine	1,300
Chromium	200
Cobalt	20
Copper	30
Hafnium	150
Iron	1,500
Manganese	50
Nickel	70
Nitrogen	50
Oxygen	1,400
Silicon	120
Titanium	50
Tungsten	50
Uranium (Total)	3

TABLE 2

FREE WORLD PRODUCTION FACILITIES FOR ZIRCONIUM AND HAFNIUM METAL (PAST AND PRESENT) AFTER SCHLECHTEN (1968)

Company	Plant Location	Capacity (tonne/year)	
		Zr	Hf
Amax Speciality Metals	Parkersburg W.Va. USA	545	10
Columbia-National (ceased production, 1965)	Florida USA	680	-
Reactive Metals Inc. (ceased production, 1965)	Ashtabula Ohio USA	900	18
Wah Chang	Albany Oregon, USA	295 expanding to 1,140	unknown
Murex Ltd. (until 1960)	England	9	-
Ugine Kuhlmann	France	725	unknown
Société Nobel-Bozel	France	100 (1962 production)	2
Toyo Zirconium Co.	Japan	104 (1958 production)	-
Mitsui and Co. Ltd.	Japan	250	-
Eldorado Nuclear Ltd.	Canada	up to 305	unknown

TABLE 3

PROCESSES FOR ZIRCONIUM PRODUCTION (AFTER SCHLECHTEN 1968)

Company	Treatment of Raw Material	Basis of Zr-Hf Separation	Preparation of $ZrCl_4$	Purification of $ZrCl_4$	Reducing Agent	Separation of Sponge and Chloride	Melting of Sponge
Amax Specialty Metals USA	Converted to carbide in arc furnace; then chlorination	Hexone-thiocyanate	Chlorination of oxide plus carbon	Sublimation, then molten salt scrubbing	Mg	Sorting and distillation	Double arc melting in vacuum
Wah Chang USA	As above: Now using direct chlorination	Hexone-thiocyanate	Chlorination of oxide in electric furnace	Sublimation of $ZrCl_4$ from impurities	Mg	Distillation	Consumable electrode
Reactive Metals Inc. USA (ceased production 1965)	Fluid bed chlorination of zircon	Hexone-thiocyanate	Fluid and fixed bed chlorination of oxide	As above	Na	Leaching	Induction melting to 'chunklets'
Ugine Kuhlmann France	Fixed bed chlorination of zircon with carbon	Hexone-thiocyanate	Fixed bed chlorination of oxide	As above in separate vessel	Mg	Distillation	Consumable electrode
Columbia-National USA (ceased production 1965)	Caustic fusion	TBP-nitric acid	-	Sublimation of $ZrCl_4$ from impurities	Mg	Distillation	-
Eldorado Canada	Caustic fusion	TBP-nitric acid	Fluorination of oxide	-	Mg	Bomb reduction to ingot	-
India (proposed small scale production plant)	Caustic fusion	TBP-nitric acid	Chlorination of oxide	Sublimation of $ZrCl_4$ from impurities	Mg	Distillation	-
U.S.S.R.	Sintering zircon with K_2SiF_6 to form K_2ZrF_6	Fractional crystallisation using K_2ZrF_6 (18 stages)	Metal formed by electrolysis of K_2ZrF_6/KCl melt				Consumable electrode
Newnham Process as proposed by Frampton and Feldman (1968)	Fluid bed chlorination of zircon (Reactive Metals)	2 stage reduction/dissociation	Not required	As for Reactive Metals Process			

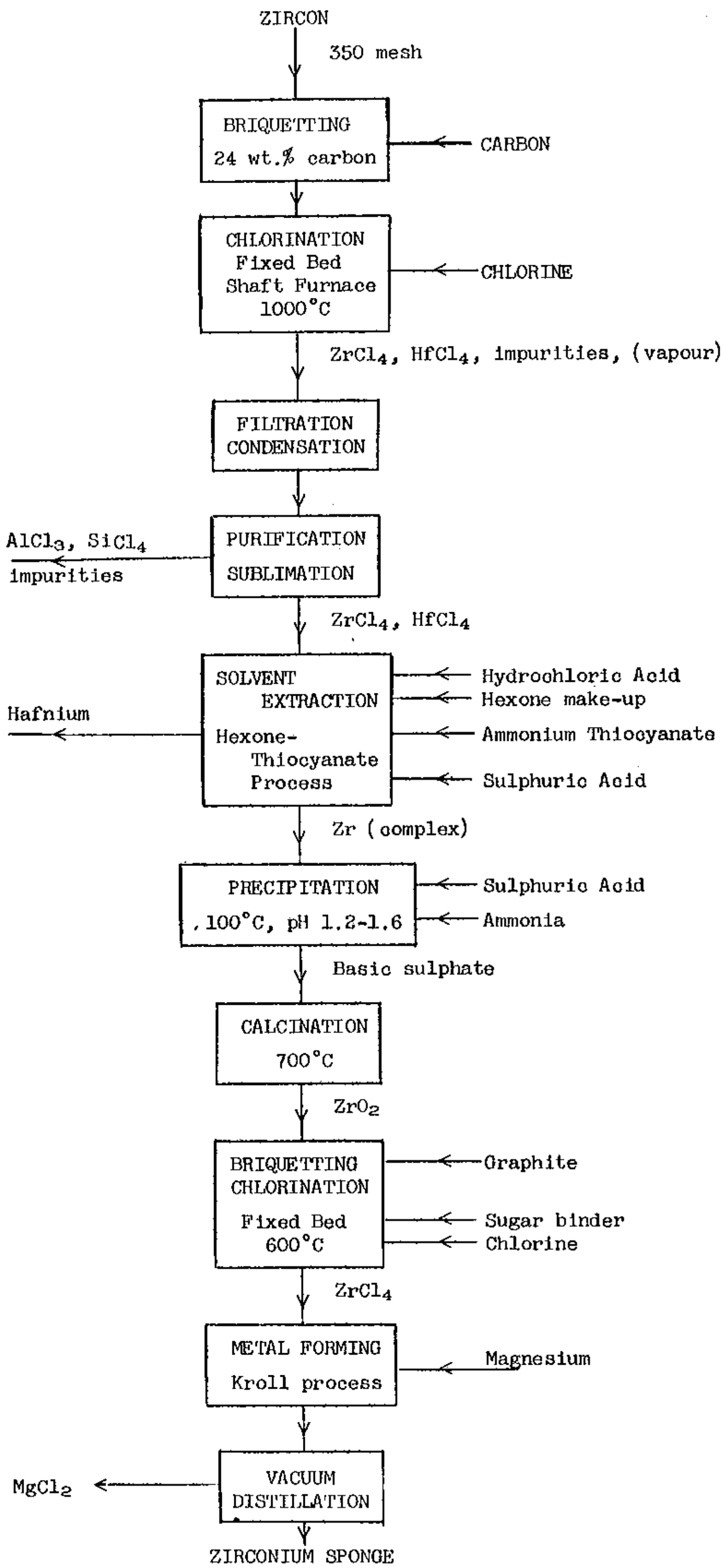

FIGURE 1. HAFNIUM-FREE ZIRCONIUM PRODUCTION, HEXONE-THIOCYANATE PROCESS

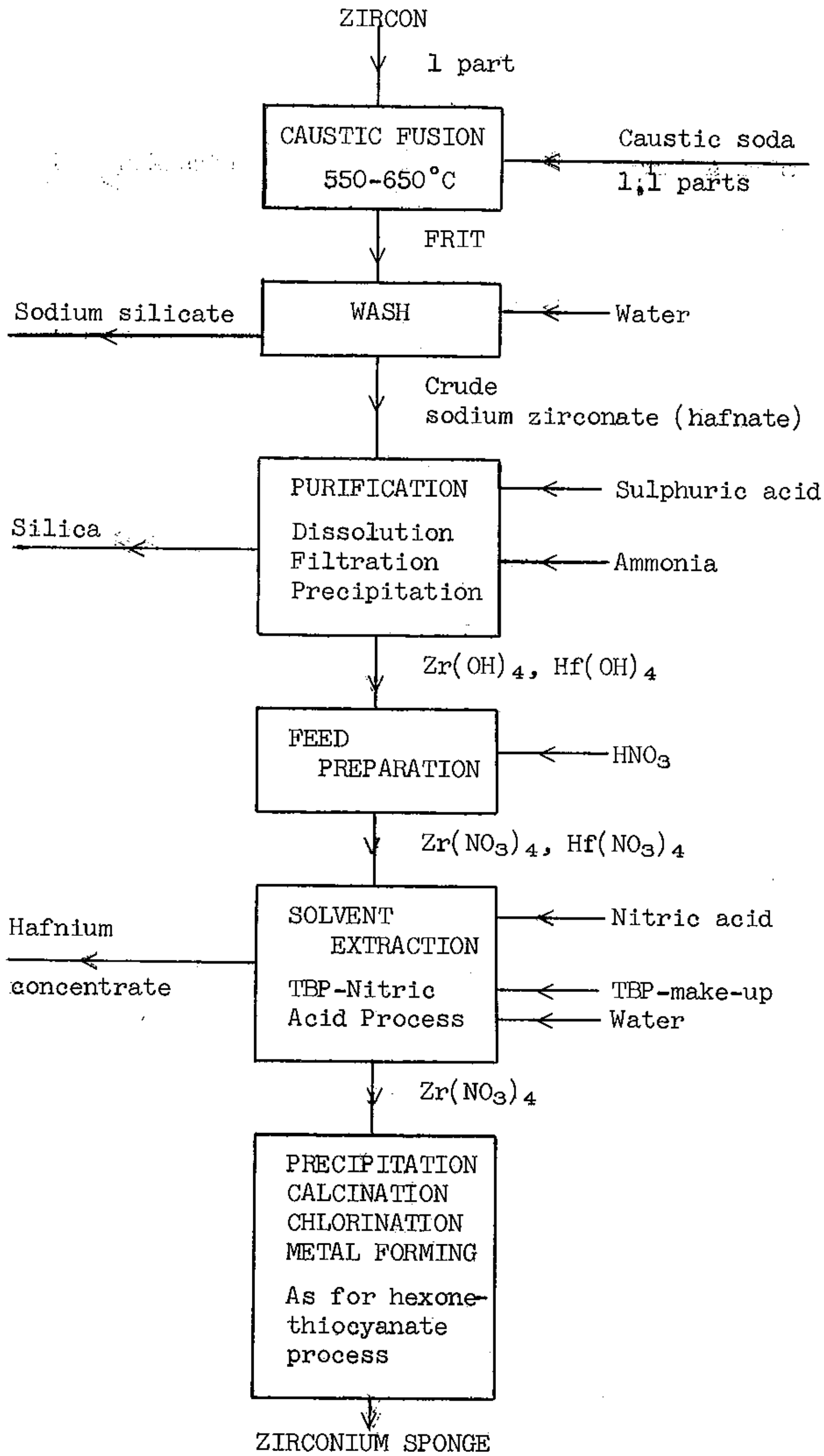

FIGURE 2. HAFNIUM–FREE ZIRCONIUM PRODUCTION, TBP–NITRIC ACID PROCESS
(After Cox et al. 1958)

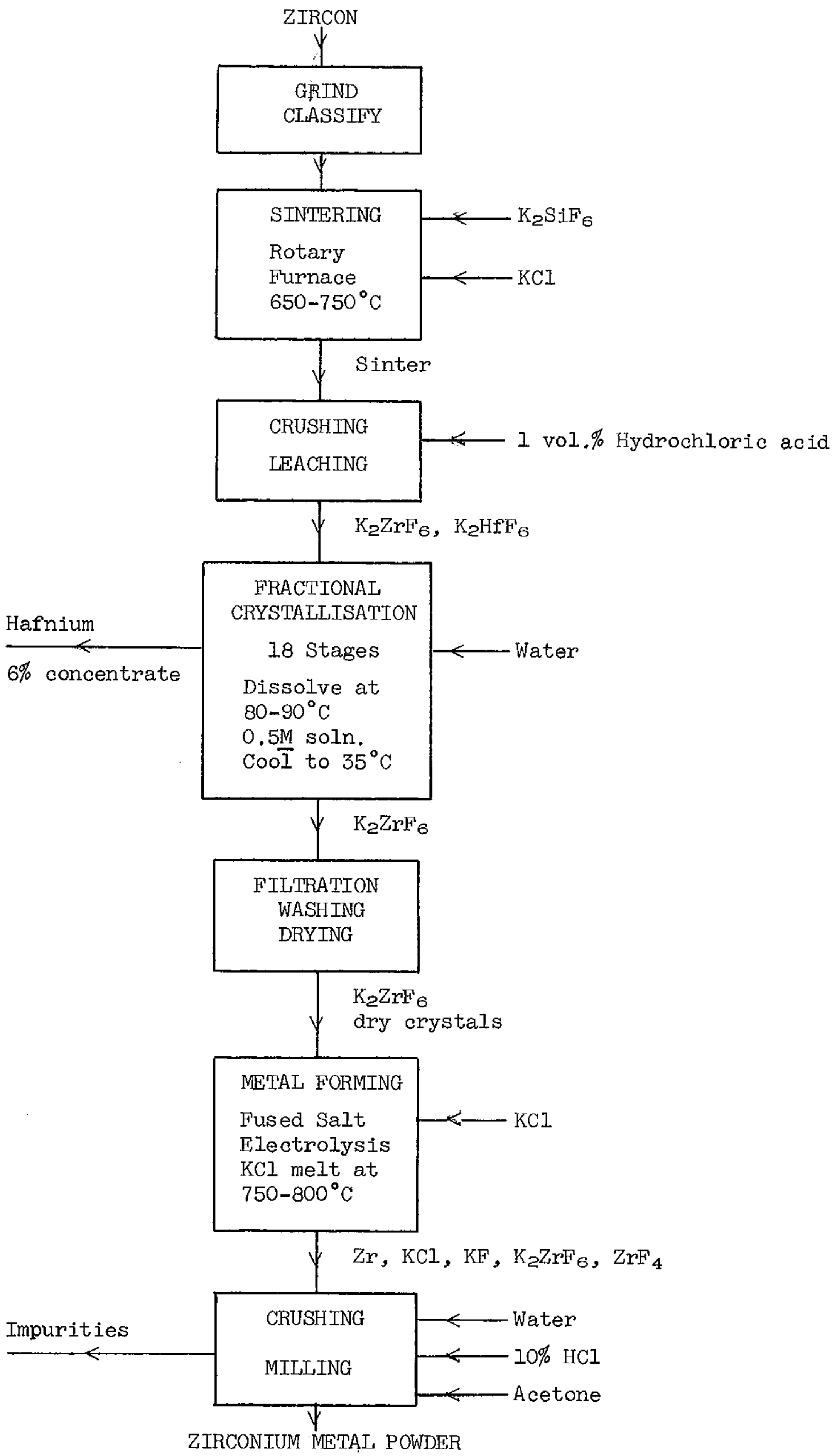

FIGURE 3. HAFNIUM-FREE ZIRCONIUM PRODUCTION, FRACTIONAL CRYSTALLISATION PROCESS (After Sajin and Pepelyaeva 1955 and Ogarev et al. 1958, Sundaram et al. 1965)

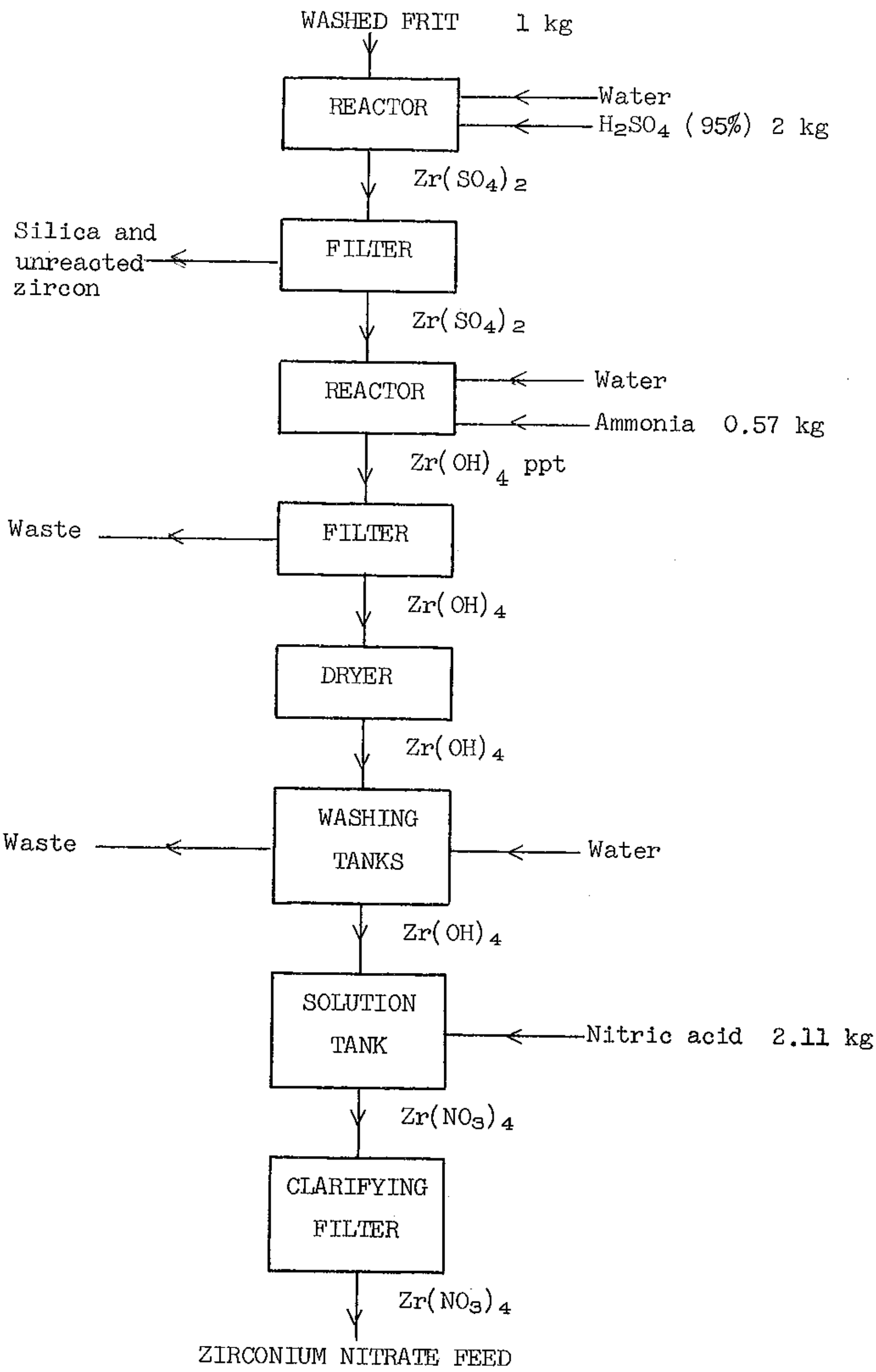

FIGURE 4. ZIRCONIUM NITRATE FEED PREPARATION FROM CAUSTIC FRIT
(After Cox et al. 1958)

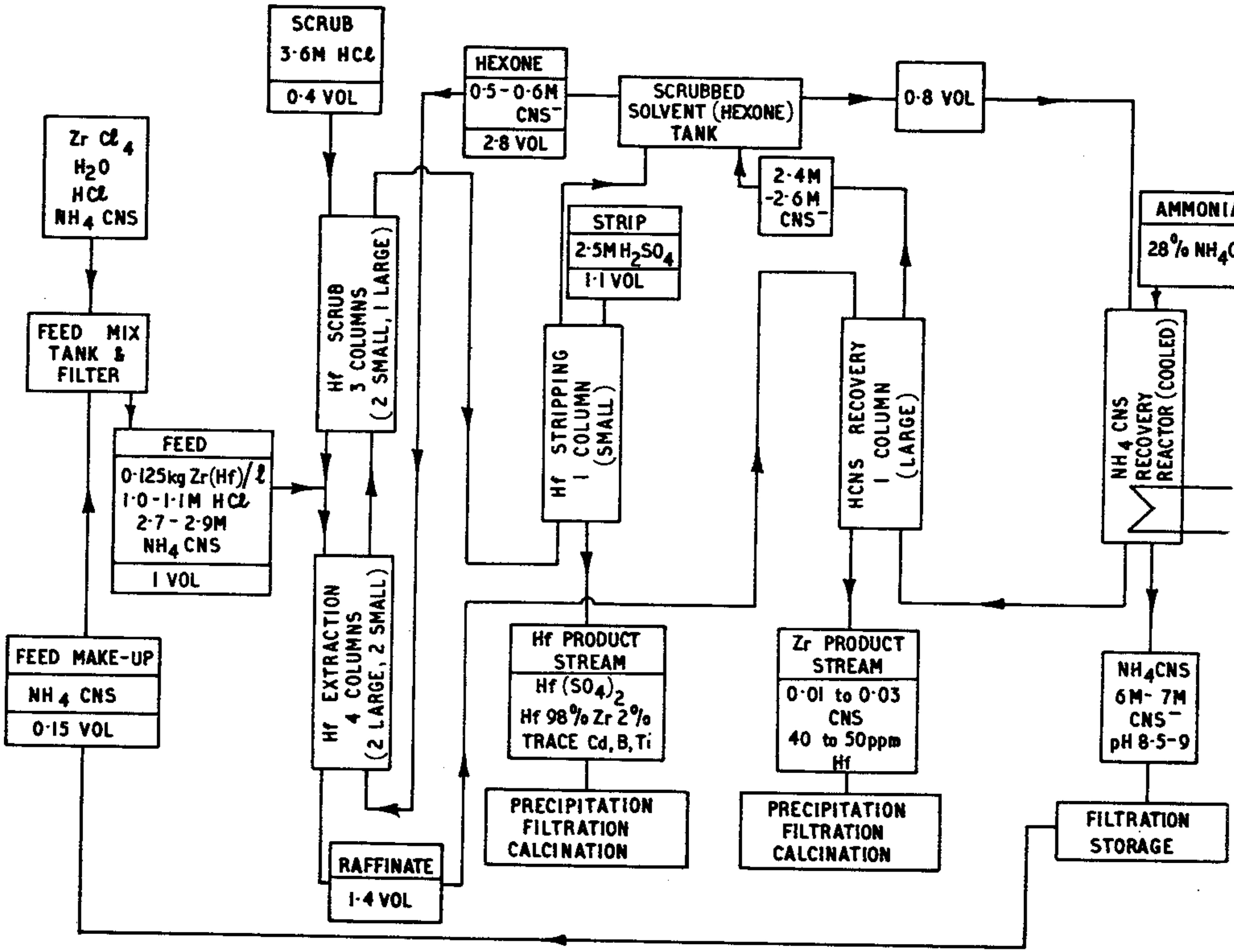

FIGURE 5. HEXONE-THIOCYANATE PROCESS (After McClain and Shelton 1960)

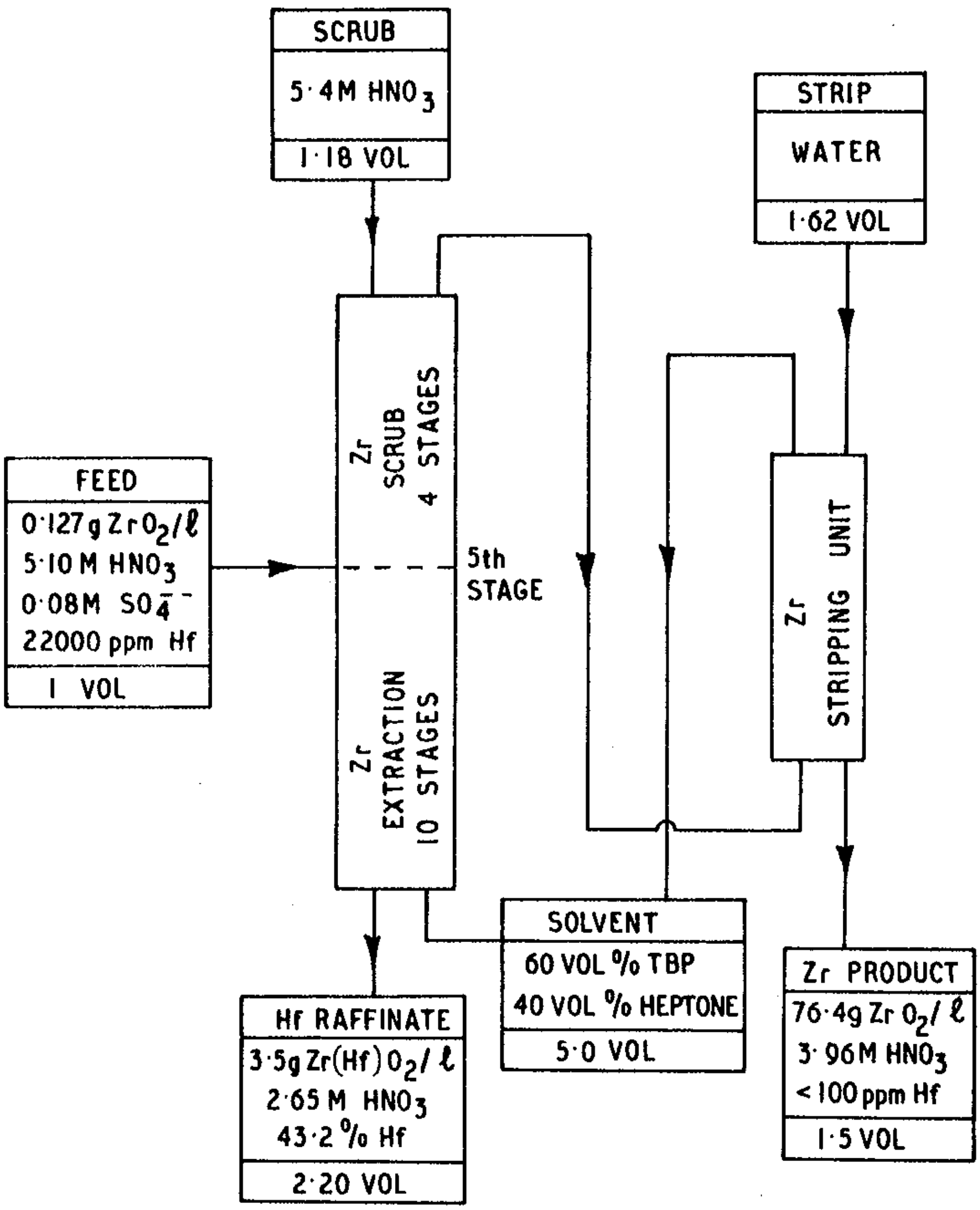

FIGURE 6. TBP-NITRIC ACID PROCESS (After Cox et al. 1958)

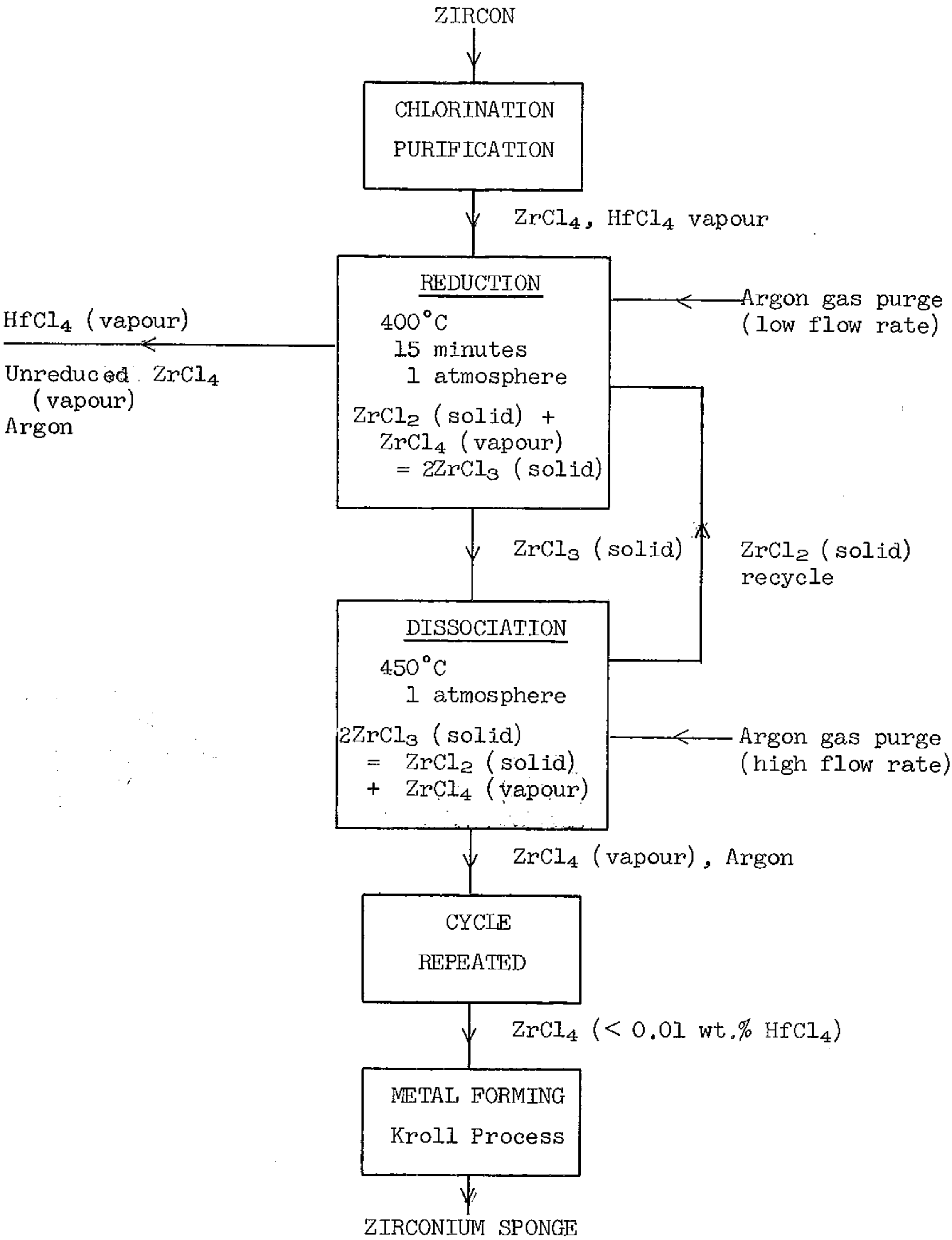

FIGURE 7. NEWNHAM PROCESS
(After Frampton and Feldman 1968)