

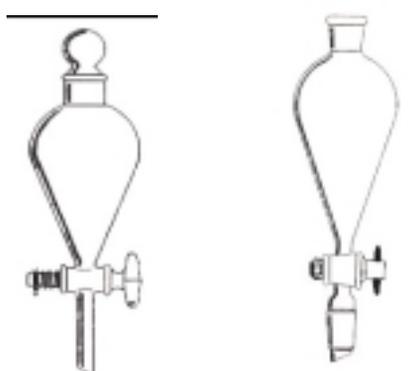


The role of liquid-liquid extraction on separation/recovery of zirconium and hafnium—A general study

JYOTHI Rajesh Kumar

*Minerals & Materials Processing Division,
Korea Institute of Geoscience & Mineral Resources (KIGAM),
Yuesong-gu, Daejeon 305-350, South Korea
E-mailaddress: rajeshkumarphd@rediffmail.com*

Liquid-liquid extraction (LLE) is a process of transferring a chemical compound from one liquid phase to a second liquid phase, immiscible with the first. For the separation and purification of metal ions, this method is known since 1842^[1]. In LLE, a solute distributes itself between two immiscible liquids. The distribution of a solute between two immiscible solvents is univariant at constant temperature and pressure. That is, if we choose the concentration of the solute in one phase, its concentration in the other phase is fixed. In analytical chemistry, this method enjoys a favored position among separation techniques because of its simplicity, speed and wide scope. By utilizing simple apparatus no more complicated than a separatory funnel and requiring several minutes at most to perform, extraction procedures offer much to the analytical chemist.



Models of separating funnels

In chemical technology, the LLE of metal chelates play an important role in the purification of chemical reagents. This method is also frequently used in nuclear chemistry and technology for the separation of various radioisotopes and for the reprocessing of nuclear fuels.

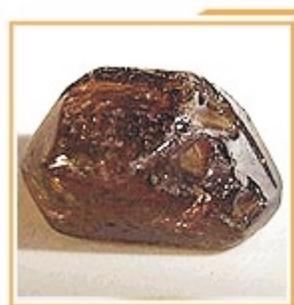
Zirconium metal basically finds application in the nuclear power program due to the combination of variety of properties such as (i) low thermal neutron absorption cross section, (ii) adequate strength and ductility at reactor operating temperatures, (iii) good corrosion resistance at high temperatures in aqueous environments, (iv) reasonable dimensional stability under irradiation and (v) good compatibility with the fuel material. Zirconium and hafnium co-exist in nature and are difficult to separate because of similar chemical properties due to the lanthanide contraction. To produce high pure zirconium, the processing involves production of ZrO_2 free of hafnium.



Hafnium metal



Zirconium rod



Zirconium Silicate ($Zr.SiO_4$)

Klaproth^[2] had previously isolated the oxide of zirconium from a sample of zircon



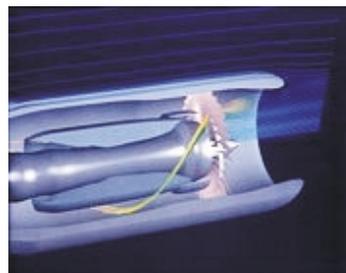
$ZrSiO_4$. Zirconium's main minerals are zircon ($ZrSiO_4$) and baddeleyite (ZrO_2) found in the USA, Australian and Brazil and invariably containing hafnium, most commonly in quantities around 2% of the zirconium content. Only in a few minerals, such as alvite, $MSiO_4 \cdot X H_2O$ ($M=Hf, Th, Zr$), hafnium content occasionally exceed that of zirconium. As a result of the lanthanide contraction the ionic radii of zirconium and hafnium are virtually identical and their association in nature parallels their very close chemical similarity.

Hafnium, a co-genitor of zirconium, occurs to the extent of 1–2 % in the mineral zircon, which is an important constituent of the beach sands of south– west and east–coasts of India, representing about 8 % of the Global reserves. Indian Rare Earths operates three plants of mining and beneficiation of beach sand minerals and their current production of zircon is about 20,000 turns per year. In order to achieve these objectives, the zirconium and hafnium metals industry and the need to separate zirconium and hafnium from other associated metals like Ti, Fe, Si and Al etc are indispensable.

The major uses of hafnium involve the metal as an alloying additive (1-2%) in the preparation of nickel-based super alloys. These alloys are used in turbine vanes in the combustion zone of jet aircraft engines. The second major use of hafnium is as control-rod material in nuclear reactors. Hafnium tetrachloride has been used to prepare hafnium metallocene Ziegler–Natta type catalysts, which were the first catalysts to provide high yields of high molecular mass isotactic polypropylene^[3] and in some heavy – metal fluoride glass cladding^[4].



Pratt & Whitney F100 turbo fan engine



Low bypass turbo fan's airflow

Nuclear power plants in India

Initially, two different LLE^[5] techniques were used to promote zirconium and hafnium separation: the MIBK (Methyl-isobutyl ketone) – thiocyanic- hydrochloric acid process and the TBP (Tri-butyl-phosphate)–nitric acid process. The former began to be developed at the Oak Ridge National Laboratory in 1949 and was optimized in a pilot plant at the US Bureau of Mines. The second process was developed in France 1954 by the French Nuclear Agency and was improved at Iowa State University. In 1978, a French state company, CEZUS began to operate using a new pyrometallurgical process.

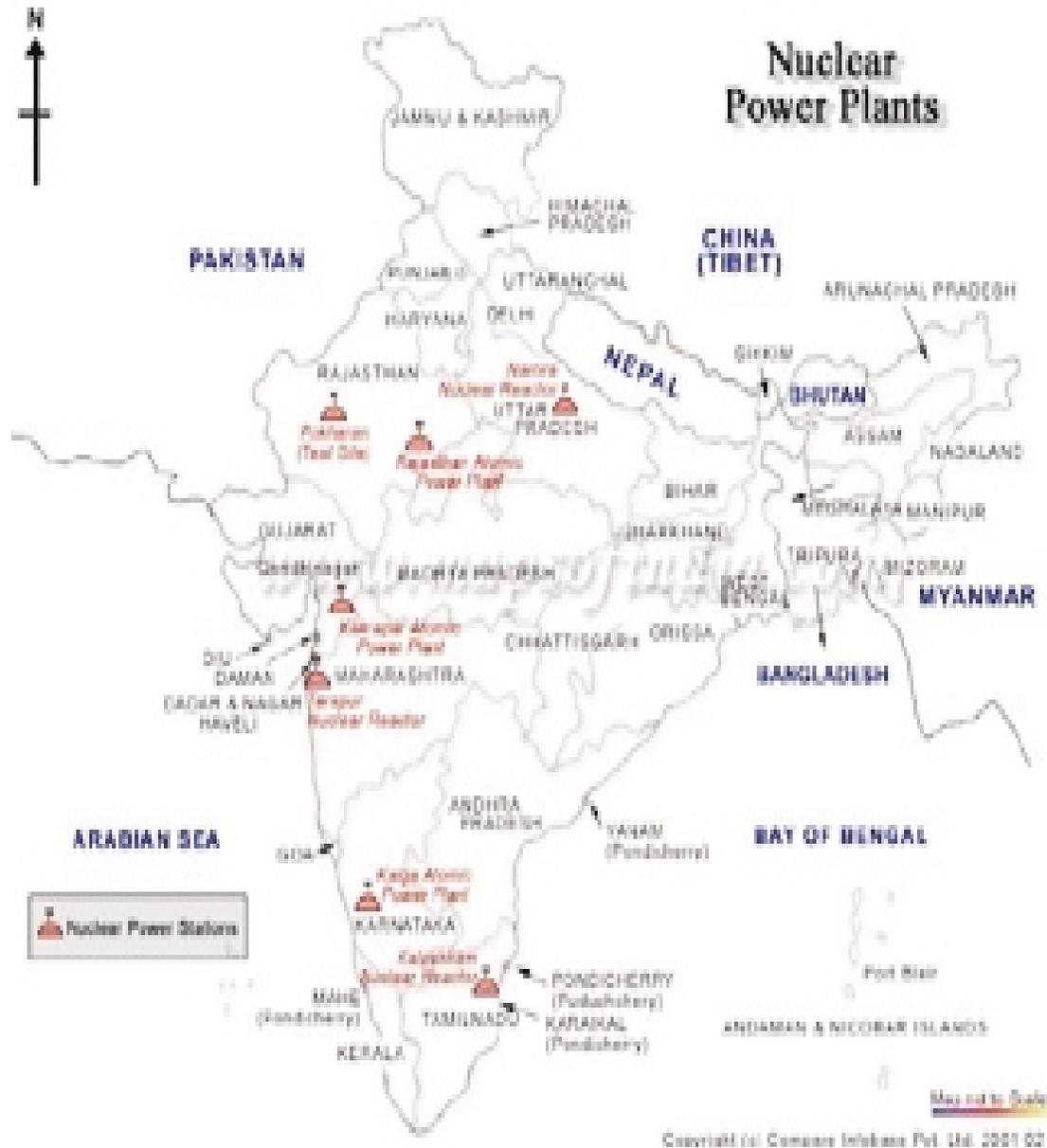
In the MIBK process, the thiocyanate complexes of zirconium and hafnium formed in HCl medium (2 mol.dm^{-3}) exhibit different solubility in MIBK. In this process, it is hafnium, the minor component that is concentrated in the organic phase and exhibits a separation factor ($\beta = D_{Hf} / D_{Zr}$) of seven. Nevertheless, the generated waste streams contain high concentrations of ammonium



Manthan

cyanides; the solvent itself is highly volatile and exhibits about two percent solubility in the aqueous phase. In the TBP process, the organic phase containing TBP diluted in kerosene is contacted with aqueous phase containing below 30 gpl metals (Zr + Hf) and about 3 mol.dm⁻³ HNO₃ and NaNO₃. This

process is selective for zirconium and exhibits a separation factor ($\beta = D_{Zr} / D_{Hf}$) of ten. Presently, this process is used in India. The drawback of this process is its inability to produce nuclear grade hafnium. In spite of the commercial metal separation processes available based on LLE, there has been a



Nuclear power plants in India



continuous effort worldwide in the development of new reagents and their applications as reagents for metal determination, metals separation in analytical chemistry and ultimate use in commercial separation of metals if possible.

In this endeavour, the development of organophosphorus based extractants such as D2EHPA or TOPS 99 an equivalent of D2EHPA produced in India (Di-2-ethylhexyl phosphoric acid), PC 88A (2-ethyl hexyl phosphonic acid mono-2-ethyl hexyl ester) marketed by Daihachi Chemical Industry, Japan, Cyanex 272 (bis (2,4,4-trimethylpentyl) phosphinic acid) marketed by Cytec Canada, which are commercially applied for impurities removal from feed solutions, separation and recovery of cobalt from nickel, separation of rare earths etc., and oxime based extractants such as LIX reagents with different combinations (LIX 84-IC (2-hydroxy-5-nonylacetophenoneoxime) and LIX 860N-IC (2-hydroxy-5-nonylsalicylaldehydeoxime)) supplied by Cognis Corporation, USA, which are commercially applied for the separation and recovery of copper from highly acidic lean leach liquors obtained by the dump leaching of inferior quality copper sources, achieved a breakthrough in separation science and technology.

A study related to LLE of zirconium and hafnium would be helpful to the advancement of existing knowledge in this field. This information would be useful in carrying out further studies in the extraction and separation methods.

With this objective, our ongoing research we were established the LLE of tetravalent zirconium and hafnium from acidic chloride solutions, the organophosphorus, thioorgano phosphorus, oximes and isoxazolones have been used as extraction reagents^[6-17].

Organophosphorus and thioorgano phosphorus extractants have some particular advantages such as chemical stability, generally good kinetics of extraction, good

loading and stripping characteristics, low solubility in the aqueous phase and availability in commercial quantities. Recently there have been increased interests in the potential applications of phosphonic and phosphinic acids. Oximes are designed specifically for the selective extraction of copper from dilute copper dump leach liquors by solvent extraction. These extractants are being investigated mainly for the extraction of copper, however other metals are also extracted by the oximes depending on the aqueous pH and metal oxidation state. Several types of oximes have been used for metal extraction to study due to their extraction abilities, loading capacities and kinetics of extraction. The oximes as extraction reagents offer immense possibilities for chemical separations in view of the numerous combinations of long chain oximes, the wide array of diluents available and the many anionic aqueous systems that can be readily produced. Isoxazolone group based extractants, have low acid dissociation constant due to electron delocalisation, and this property makes the isoxazolones an interesting class of β -diketones with potential application as reagents for extraction of metal ions from strong complexing in acid media.

References

- [1] E. Peligot, *Ann. Chim.*, **5**, 7, **1842**.
- [2] N. N. Green and A. Earnshaw, *Chemistry of the Elements*, First Ed, Maxwell Macmillan International Editions, **1984**.
- [3] J. A. Ewen, L. Haspeslagh, J. L. Atwood and H. Zhang, *J. Am. Chem. Soc.*, **109**, 6544, **1987**.
- [4] D. C. Tran, *Halide Glasses I. Material Science Forum*, Trans. Tech. Pub. Switzerland, **5**, 339, **1985**.
- [5] A. B. V. Da Silva and P. A. Distin, *Canadian Institute of Mines Metallurgy & Petroleum Bulletin*, **91**, 221, **1998**.



- [6] B. Ramachandra Reddy, J. Rajesh Kumar, A. Varada Reddy, D. Neela Priya, *Hydrometallurgy*, **72**, 303 **2004**.
- [7] B. Ramachandra Reddy, J. Rajesh Kumar, A. Varada Reddy, *Minerals Engineering*, **17**, 553, **2004**.
- [8] B. Ramachandra Reddy, J. Rajesh Kumar, A. Varada Reddy, *Analytical Sciences*, **20**, 501, **2004**.
- [9] B. Ramachandra Reddy, J. Rajesh Kumar, A. Varada Reddy, *Hydrometallurgy*, **74**, 173, **2004**.
- [10] B. Ramachandra Reddy, J. Rajesh Kumar, K. Phani Raja, A. Varada Reddy, *Minerals Engineering*, **17**, 939, **2004**.
- [11] B. Ramachandra Reddy, J. Rajesh Kumar, A. Varada Reddy, *J Chemical Technology & Biotechnology*, **79**, 1301, **2004**.
- [12] B. Ramachandra Reddy, J. Rajesh Kumar, *Separation Purification Technology*, **42**, 169, **2005**.
- [13] B. Ramachandra Reddy, J. Rajesh Kumar, S. V. Rao *Solvent Extraction Research & Development, Japan*, **12**, 47, **2005**.
- [14] B. Ramachandra Reddy, J. Rajesh Kumar *Solvent Extraction Research & Development, Japan*, **13**, 37, **2006**.
- [15] B. Ramachandra Reddy, J. Rajesh Kumar, A. Varada Reddy, *J Brazilian Chemical Society*, **17**, 780, **2006**.
- [16] K. Janardhan Reddy, J. Rajesh Kumar, M. L. P. Reddy, A. Varada Reddy, *Solvent Extraction and Ion Exchange*, **24**, 419, **2006**.
- [17] J. Rajesh Kumar, B. Ramachandra Reddy, K. J. Reddy, A. Varada Reddy, *Separation Science and Technology*, **42**, 865, **2007**.

