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PRODUCTION OF HAFNIUM BY CARBOCHLORINATION AND FLUOROSILICATION OF ZIRCON CRYSTALS.

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Abstract: Over decades of research, it has been observed and concluded that, if this planet is to attain a zero-carbon emission in the years to come, nuclear energy is going to play an indispensable role in that process. Having said that, there's still a lot of untapped potential when it comes to commercial usage and applications of nuclear energy. The most critical challenge faced by the researchers and the scientists today, is the dearth of information available on the potential elements which are capable of making nuclear energy, a part of the main stream. The main focus of this study is to research, explain and check feasibility of two major methods of production of Hafnium from zircon and then separation from zirconium using liquid-liquid extraction or Kroll process, an element which has a gargantuan potential when it comes to controlling the rate of nuclear fission reactions. This paper also covers the Nonetheless, the gospel truth is that, there's a long way to go when it comes to producing something like hafnium on a commercial basis. When it comes to methods of production of hafnium or be it refining, separating or storing it; new strides are being made on a diurnal basis, with paradigm shifting discoveries and small but incremental change every day.

Keywords— Nuclear, Zircon, Zirconium, Liquid-liquid Extraction, Kroll Process

I. INTRODUCTION

Hafnium was one of those elements that the chemists knew existed, but could not find. The only evidence, that hafnium actually existed; before it was discovered by Coster and Hevesy on 1923, was the empty space in the periodic table itself. Hafnium is a lustrous, silvery metal, which is corrosion resistant and is chemically similar to zirconium. One of the main reasons that the discovery of hafnium took so long was in fact the similarity between hafnium and zirconium. Hafnium is a metal that is not so abundant in nature, when in abundance it is estimated to be about 5 parts per million of the earth's crust.

Hafnium is known to have only a few applications, one of the most important use being in the nuclear power plants. But what interests the scientists throughout the planet is how hafnium reacts to neutrons. Hafnium has a unique ability of absorbing the incident neutrons very easily which makes it an ideal candidate to be used in rods that control the rate of a nuclear fission reaction.

This ability not only makes hafnium a key in the production of nuclear energy but also this trait is what separates hafnium from zirconium. While most of the neutrons pass right through zirconium; hafnium absorbs most of the neutrons. The only challenge that scientists are facing today is finding a way to separate hafnium from zirconium, since; in nature hafnium always occurs in combination with zirconium. As of now there hasn't been a single method which has been put forth which could produce pure hafnium on a large scale, and as far as the information that has been read, researched and rectified; there is no pure hafnium that is available on the commercial market. This research paper mainly focuses on the production of pure hafnium from zircon dust, which can in turn lead to a paradigm shift in the field of nuclear energy, as with the help of pure hafnium, that too on the commercial scale, would lead to a more controlled state of the nuclear reactions that are occurring as of now, and would assist in leading to reach the maximum potential of the nuclear industry and at the same time would also help in minimizing the accidents. Natural hafnium is a mixture of six stable isotopes:

hafnium-174 (0.2 percent), hafnium-176 (5.2 percent), hafnium-177 (18.6 percent), hafnium-178 (27.1 percent), hafnium-179 (13.7 percent), and hafnium-180 (35.2 percent).

Property	Value
Atomic number	72
Atomic weight	178.49
Density, at 298K, kq/m3	13.31 10
melting point, K	2504
boiling point, K	2504 4903
specific heat, at 298 K, J/(kg-K))"	144
latent heat of fusion, J/kg	1.53 10
electrical resistivity, at 298 K, f-m Hall coefficient, at 298 K, V-m/(A-T)	3.37 x 107
work function, J	-1.62 x 10-12
thermal conductivity, W/(mK)	6.25 x 10-1
at 273 K	23.3
at 1273 K	20.9
Young's modulus, at 293 K, GPa shear modulus, at 293 K, GPa Poisson's ratio, at 293 K thermal expansion coefficient, linear, from 293 to 1273 K, 10/K	141
shear modulus, at 293 K, GPa	56
Poisson's ratio, at 293 K	0.26
thermal expansion coefficient, linear, from 293 to 1273 K, 10/K	6.1

Table 1. Properties of Hafnium

II. RAW MATERIAL AVAILABILITY

Industry-graded Hafnium is produced from Zircon dust(a zirconium silicate mineral) which is found naturally in the earth's crust and is extracted by mining processes. Zircon consists of hafnium and zirconium which have abundant chemical similarities due to its similar atomic radii (1.45 Å and 1.44 Å respectively) and similar valence electronic configuration of 2 electrons in the valence d orbital. Zirconium is antagonistic towards a large variety of rock-constituting minerals and so its concentration rises when there is fractional crystallization during a melt whereas the solubility of Zr in that melt decreases exponentially. Correspondingly the zircon from most magma will precipitate due to cooling down to a temperature below which it can be saturated with zircon, as a result of which zircons are found in a wide range of igneous rocks. This happens universally except in conditions where the magma has

1. Lower zirconium concentration
2. Lower SiO_2 concentration (which leads to formation of Baddeleyite in greater quantities instead of Zircon)
3. High alkalinity in which instead of zircon formation, zirconosilicate minerals can form.

Zircon availability is generally restricted by the available amount of zirconium which is around 82 μg/g in oceanic crust (Jenner and O'Neill, 2012); and higher concentrations of 193

μg/g in the continental crust (Rudnick and Gao, 2014).

III. ZIRCON MINING:

Zircon is also a co or by-product in the mining or processing of the sands of heavy-minerals for titanium or tin minerals or ilmenite or rutile. It is usually obtained by dry mining methods if the deposit is shallow or has harder base materials in it. Heavy machinery like scrapers and excavators are used to dig the ore from its base which is then in turn transported to the initial processing plant. The ore is then shifted to a wet concentrator by overland conveyor or slurry pipeline.

Around 1400 thousand metric weight of zircon was excavated globally of which, Australia is the biggest supplier as it has around 35% of the world's zircon which comes from the heavy mineral sand deposits from Victoria and western Australia. The 3 major exporters of Zircon are Australia, South Africa and China.

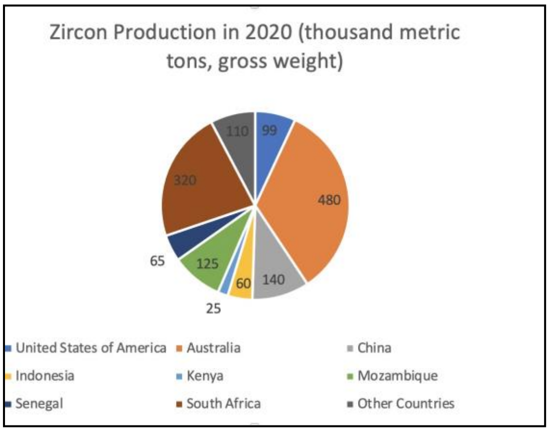

Fig. 1. Zircon Production in 2020 (usgs)

IV. PROCESS DESCRIPTION

Zircon constitutes of various elements in the oxide form. Empirically zircon consists of about 43% of Zirconium, 14.5% of silicon, 34% of oxygen, 4.7% of hafnium. The rest is made up of oxides of Lanthanum, Cerium, Praseodymium, Neodymium and Samarium which make up to around 4% of its composition. Due to the abundance of Zirconium, Silicon and Oxygen, it naturally occurs as $ZrSiO_4$. In general, the commercial nuclear reactor grade hafnium production involves ore cracking, zirconium separation, calcination, pure chlorination and then reduction to the pure method. The decomposition of zircon is a high temperature process which can take place only with the use of aggressive chemicals.

The most commonly used method when it comes to Hf synthesis is carbochlorination which uses carbon and chlorine for reduction of the Zirconium silicate crystals. The process includes the heating of zircon sand and carbon in a fluidized bed to 1200°C under fluidizing gas of chlorine. Milled Zircon and coke are reacted with hot chlorine with chlorine acting as the fluidizing medium. The reaction occurring in the Fluidizing bed is:

$$(ZrHf)SiO_4 + 4\,C + 4\,Cl_2 \xrightarrow{1200^{\circ}C} (ZrHf)Cl_4 + SiCl_4 + 4\,CO$$

The reaction is endothermic and requires an additional energy in order to sustain it which is usually done by induction heating or by adding silicon carbide grain which on chlorination gives out energy which can be used for the reaction. The product gases are cooled to a temperature below 200°C to condense and collect the zirconium-hafnium as powders and Silicon tetrachloride exists in the liquid form at a much lower temperature.

In order to increase the conversion efficiency, we can also consider the fluorosilicate fusion in which we add milled zircon and potassium hexa-fluorosilicate are heated to give potassium hexa-fluorozirconate [$K_2(ZrHf)F_6$] and silicon dioxide.

$$(ZrHf)SiO_4 + K_2SiF_6 \xrightarrow{700\ ^{\circ}C} K_2(ZrHf)F_6 + 2\,SiO_2$$

The addition of potassium chloride or carbonate reduces the loss of volatile silicon tetrafluoride which in turn helps in improving the conversion efficiency which then on cooling, crushing and leaching with acidified hot water, the resulting solution of hexafluoro zirconate- hafnate is filtered to remove silica to allow crystallization of the potassium hexafluorozirconate-hafnate. Despite filtering many of the impurities still remain in the solution itself.

V. SEPARATION OF HAFNIUM FROM ZIRCONIUM

Hafnium is extremely suitable for nuclear applications due to its low neutron-absorption cross-section and excellent corrosion-resistance properties. Hafnium is always found in combination with zirconium, this is due to lanthanoid contraction which causes almost similar radii of both of them. The two metals can remain unseparated for all uses except for nuclear applications due to their extremely opposite absorption characteristics for thermal neutrons. For using as nuclear reactor material, zirconium should have a very low hafnium content of less than 100 ppm, but separating hafnium from zirconium is a challenging issue because of their great chemical similarities. Most of the commercial separation methods are hydrometallurgical routes, including fractional crystallization, methyl isobutyl ketone (MmK) extraction and tributyl phosphate (TBP) extraction. However, for nuclear grade hafnium production, the combination of pyrometallurgical ore cracking, hydrometallurgical Zr-Hf separation and pyrometallurgical zirconium compounds reduction always results in high production cost, intensive labor and heavy environmental burden. In order to enhance the whole production process, a number of investigations have been focused using pyrometallurgical route for the separation of zirconium and hafnium during the past decades.

The current dominant zirconium-hafnium separation route involves:

- Pyrometallurgical ore cracking
- Multi-step hydrometallurgical liquid-liquid extraction for zirconium removal
- Reduction of hafnium tetrachloride to the pure metal (Kroll process).

But furthermore, we are going to discuss about two of the methods only which have a greater relevance according to today's industry and commercial standards, owing to every aspect taken into consideration for example: labor cost; price of resources; machinery etc.

1) Kroll process- It is a pyrometallurgical industrial process used to produce metallic titanium from titanium tetrachloride since a long period of time. It has been developed for seven decades and is operated on an industrial scale in which hafnium tetrachloride vapor is reduced by liquid magnesium in an inert atmosphere in a batch operation. The reaction is initiated by heating the upper zone to slowly sublime the hafnium tetrachloride which vapors into the lower chamber and reacts with magnesium to form 3 micrometer sized small spheres of hafnium metal which settle to the bottom of the chamber as hafnium-magnesium mud. The rate of this exothermic reaction is controlled by adjusting the upper zone temperature thereby controlling the rate of tetrachloride sublimation. Furthermore, distillation of magnesium begins allowing the hafnium micro-sized spheres to slowly sinter into a porous sponge. The entire process is complete after several hours at 980ºC. After the furnace is cooled, the sponge is broken by a hydraulic chisel operating in an argon atmosphere box which gives us hafnium. The whole process takes place by the thermal decomposition of tetraiodide.
2) Liquid-Liquid Extraction: In this process Ammonium thiocyanate is added to an acidic solution of Zirconium-hafnium hydroxide chloride. This solution is then treated with an immiscible methyl isobutyl ketone solution. Both hafnium and zirconium thiocyanate complexes mix well in both phases, but hafnium is preferred to be distributed in the ketone phase. Hafnium is recovered from the ketonic phase with dilute sulphuric acid which is then neutralized to precipitate hydrous hafnium which is then passed

through a calcination process to hafnium oxide. The reaction of calcined hafnium oxide with carbon and chlorine in a fluidized bed at 900-1000°C produces hafnium tetrachloride. Which is then purified by sublimation in a nitrogen-hydrogen atmosphere.

VI. BLOCK DIAGRAM

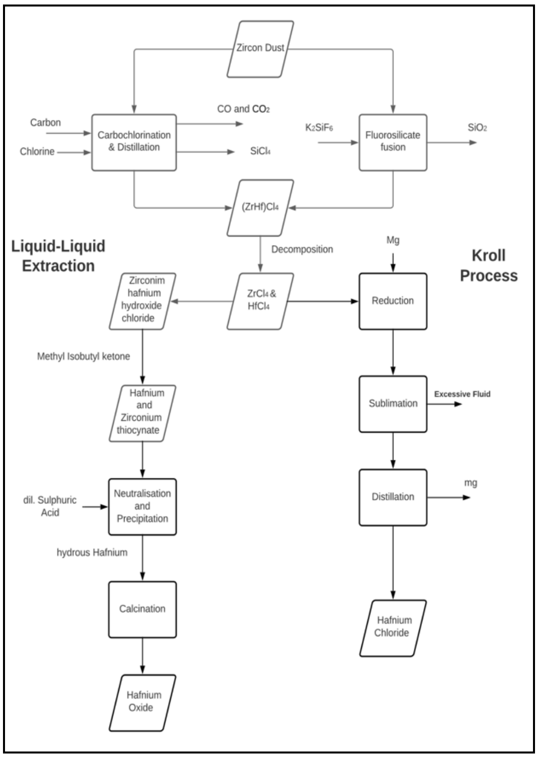

Fig 2. Production of hafnium chloride and oxide by undergoing numerous chemical processes.

Uses of Hafnium

- Nuclear**-** The first and primary market for many years has been for control rods in pressurized light water reactors which power naval vessels such as submarines and destroyers. It excels in this field because of its excellent hot water corrosion resistance; good ductility and large neutron absorption cross section. The ability of hafnium to absorb neutrons above thermal energies makes it more effective as an absorbing material
- Alloying -Hafnium is used as an alloy in high temperature application alloys such as superalloys and refractory metal alloys where hafnium additions improve the high temperature tensile and creep strength. Hafnium reacts with carbon, nitrogen or oxygen in these alloys to form a fine dispersion of hafnium carbide, nitride or oxide respectively. This effect is maintained at high temperature because of the high melting points thermodynamic stability of these components. The largest use of hafnium is in micro quantities in superalloys for cast vanes and turbine blades following the combustion zone of jet aircraft engines.
- Other uses- It is an effectively strengthens solid solution at high temperatures for other alloys such as nickel aluminides. Very pure hafnium forms effective diffusion barrier for multilevel integrated circuits. It has also been proposed as an ingredient in permanent magnets.

VII. CONCLUSION

Producing clean energy is the pathway to a sustainable future. With fewer carbon emissions, and clean sources of generation, nuclear energy can create a paradigm shift. The methods of production, of hafnium by carbochlorination and fluorosilication of Zircon crystals have been studied and explained so as to gain a thorough insight on how the methods of preparation differ under different aspect and in turn learn the dynamics behind it. It has been observed that both the methods discussed in this paper are effective in theory but, only when they are commercially applied, we would know the further implications that are associated with these processes. Which as of now is still a subject for further study.

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