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Matrix Studies on Solvent Extraction of Zirconium and Hafnium from Loaded Solvent obtained from Scrub Raffinate

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ABSTRACT: .Solvent extraction technology is separation process for solutes difficult to separate. The extraction of zirconium require separation of hafnium present in GPL (grams per litre). It involves separation of liquid constituents by contact with another insoluble liquid i.e separation of two phases namely aqueous and organic. Zircon is the primary source of Zirconium-Hafnium (50:1).My research paper involves individual effects of different parameters (normality of the feed, load of the sample, number of stages, organic to aqueous ratio)on co-extraction rate. The co–extraction process with varying parameters and study of their combined effects require many experiments and time consuming. Overcoming these difficulties, to get a detailed picture of the effects of the above parameters individually and in combinastion with statistical design of experiment, comparative study with matrix study and solvent extraction Analysis forms my research paper.

KEYWORDS: *Extractant (term for a metal extraction agent), Raffinate (term for the aqueous layer after a solute has been extracted from it), Solvent (term for the organic layer) Scrubbing (term for the back extraction of an unwanted solute from the organic phase), Stripping (term for the back extraction from the organic phase)*

I. INTRODUCTION

Zirconium and hafnium occur in nature as zircon and rarely as baddeleyite. Because of its properties Zircon can be used as a mineral and as an ore of zirconium and hafnium. Zircon is a byproduct from the mining and processing of heavy mineral sands for rutile and illmenite. Zirconium and hafnium occur together in ores at ratios of about 50:1.The extremely opposite absorption characteristics for thermal neutrons in nuclear reactor cores, the zirconium-cladded fuel rods must be hafnium free. The strong absorbing hafnium, if present, would decrease the relative transparency of the zirconium cladding, and the reactors efficiency. For this reason, hafnium is used in reactor control rods to regulate the fission processes via neutron absorption. Hafnium is also used as an additive in super alloys, as refractory and cutting tool coatings, and in oxide and nitride forms. Nuclear fuel rod cladding accounts for most of zirconium's use. Zircon refractory's and foundry sands are used primarily in the production of finished metal glass products. A major use of the metal is in nuclear reactors. It is specially purified to remove hafnium, which absorbs neutrons much more readily. It is usually alloyed with other metals to make it more corrosive resistant for these uses.

1.1 Zirconium

The element Zr has atomic no 40, atomic weight 91.22g.mol^{-1}. Its naturally occurring isotopes are 90, 91, 92, 94 and 96. Zirconium is one of the most abundant elements, and is widely distributed on the Earth's crust. Being very reactive, it is found only in the combined state. Under some conditions, it bonds with oxygen in preference to any other element and it occurs only as oxide, ZrO_2, or as a part of complex of oxide as in zircon. Zircon is commercially the most important ore. Zirconium and hafnium are practically indistinguishable in chemical properties, and occur only together.

Symbol	:	**Zr**
Atomic number	:	**40**
Mass	:	**91.224 g.mol^{-1}**
Melting point	:	**1852^{0}C**
Boiling point	:	**4400^{0}C**
Number of protons/electrons	:	**40**
Number of neutrons	:	**51**
Classification	:	**Transition metal**
Crystal structure	:	**Hexagonal**
Density	:	**6.49**
Color	:	**Grayish**

1.2.Physical properties

1) Zirconium is a very strong, malleable, ductile, lustrous silver- gray metal. At ordinary temperatures it has a hexagonal close–packed crystalline structure. Zirconium is extremely resistant to heat and corrosion. It forms a number of compounds, among them are zirconate (ZrO_3^{-2}) and zirconyl (ZrO^{+2}) salts.
2) The most important property of zirconium is the low value of absorption of cross section of thermal neutrons. The value is 0.15barn per atom that is low capacity for absorbing neutrons when compare with 0.21barn per atom for aluminium and 2.4 for iron.
3) The corrosion resistance of zirconium in water at elevated temperature is better than aluminium.
4) It has good mechanical properties i.e., its strength is good at high temperature and good fabric ability.
5) Zirconium minerals $ZrSiO_4$always contain hafnium to an extent of 1-3%, which is strong neutron absorber. So it is eliminated from Zirconium.
6) It has high resistance to thermal distortion.

1.3. Occurence

In its pure state zirconium exist in two forms: the crystalline form, a soft, white ductile metal; and the amorphous form, a bluish-black powder. Both forms are insoluble in water, slightly soluble in alcohol, and completely soluble in hydrofluoric acid. The metal burns in air at 500^0 C (932^0 F).Zirconium ranks 18th in abundance among the elements in the crust of the earth. Zirconium is never found free in nature; the principle economic source of zirconium is the zirconium silicate mineral, zircon ($ZrSiO_4$),which is found in deposits locate in India, Russia, United States, and the Brazil.

This element is also abundant in S-type stars and has been detected in the sun and meteorites. Lunar rock samples brought back from several Apollo program missions to the moon have very high zirconium oxide content relative to terrestrial rocks.

1.4 characteristics

Zirconium is a grayish-white metal, lustrous and exceptionally corrosion resistant. Zirconium is lighter than steel and its hardness is similar to copper. When it is finely divided, the metal can spontaneously ignite in air, especially at high temperatures (it is much more difficult to ignite the solid metal). Zirconium zinc alloy becomes magnetic at temperature below 35K.

1.5. Applications

The major use of Zirconium is it is used as a refractory material in furnaces and crucibles, foundry sands (including investment casting), and ceramic pacifications, ceramic glazes, in gas mantles. Zircon is also marketed as a natural gemstone (form of a silicate ($ZrSiO_4$)) used in jewelry, it may be clear or colored, and is usually called zircon, and its oxide is processed to produce cubic zirconia, which forms a brilliant clear crystal used as a low-cost substitute for diamond. Zirconium compounds also have minor uses as catalysts, in the dye, textile, plastics, and paint industries, and in pharmaceuticals such as poison ivy lotions. The metal also has many other uses, among them in photographic flashbulbs and surgical instruments, in the removal of residual gases from electronic vacuum tubes, and as a hardening agent in alloys, especially steel. It is employed in tubes for cladding uranium oxide fuel. It is well suited for this purpose because it is corrosion resistant and does not readily absorb thermal neutrons. The most important compound is the oxide zirconia (ZrO_2), used extensively as a refractory material in furnaces and crucibles, in ceramic glazes, and, formerly in gas mantles.

1.6. Hafnium

Chemists knew that an element (Hafnium) could exist in the empty space of periodic table but they could not extract it.

By the twentieth century, nearly all the spaces in the periodic table have been filled except the element 72. There were many unconfirmed reports of finding the element by chemists. But it was not until 1923 that element number 72 was finally discovered.

Hafnium is a shiny, silvery-white metal. It is always found with another chemical element, zirconium. The two elements are very similar. In fact, their similarity is the reason that it took so long to find hafnium.

Symbol	:	**Hf**
Atomic number	:	**72**
Atomic mass	:	**178.49**
Family	:	**Group 4 (IV B) Transition metal**
Melting point	:	**2506 k**
Boiling point	:	**4876 k**
Classification	:	**Transition metal**
Crystal structure	:	**Hexagonal**
Density	:	**13.31 gm/cm^3**
Color	:	**Steel Gray**

1.6. Discovery and Naming:

In the early 1990s, scientists had found a new way to identify elements. This method is called X-ray diffraction analysis. Here is how this method works.

A stream of electron is fired at a metal plate. The electrons can cause the metal plate to emit X rays.

The kind of X ray produced depends on the metal used. Each metal produces its own special X- Ray pattern. In fact, the pattern produced can be used to identify a metal.

In 1923 Dutch physicist Dirk Coaster (1889-1950) and Hungarian chemist George Charles de Hevesy (1889-1966) found an element 72 by X-ray analysis .The element was present in a piece of Norwegian zircon.

Chemist later developed a better understanding about the relationship of zirconium and hafnium. They have nearly identical chemical and physical properties. This explains why it took so long to find hafnium. The difference in the X-ray patterns of the two elements finally proved that hafnium was different from zirconium.

1.7. Physical Properties:

Hafnium is a bright, silvery-white metal that is very ductile. It has high melting point that is 2506 K and its boiling point is about 4876 K. Its density is 13.1 gm/cc. It is a corrosion resistant metal and it has good absorption cross section for thermal neutrons.

The physical property of greatest interest for hafnium is how it responds to neutrons. A neutron is a very small particle found in the nucleus (center) of an atom. Neutrons are used to make nuclear fission reactions occur. The neutron makes the atom break apart. In the process, a large amount of energy is released. That energy can be converted to electricity.

In order to make electricity from nuclear fission, the fission reaction must be carefully controlled. Hence the number of neutrons must be controlled. Hafnium has the ability to absorb (“soak up”) neutrons very easily. It is used in control rods for fission reaction.

This is one of the properties for distinguishing hafnium from zirconium. While hafnium is very good at absorbing neutrons, zirconium hardly absorbs any neutron. Both hafnium and zirconium are used in nuclear power plants.

1.8. Chemical Properties :

Hafnium is not as reactive as Zirconium. It may be more active with hot acids. Hafnium carbide is the most refractory binary compound known and hafnium nitride is the most refractory of all known metal nitrides with a melting point of 3310^0 C. This has led to the notion that hafnium or its carbide might be useful as construction materials when subjected to very high temperatures. The metal is resistant to concentrated alkalis, but halogens react with it to form hafnium tetra halides. At higher temperatures hafnium reacts with oxygen, nitrogen, boron, sulfur, and silicon.

1.9. Occurrence in nature:

Hafnium is a rare element in the Earth’s crust. Its abundance is estimated to be about 5 parts per million. That makes it as abundant as bromine**,** uranium, or tin**.** Hafnium is estimated to make up about 0.00058% of the Earth’s upper crust by weight. It is found combined in natural zirconium compounds but it does not exist as a free element in nature. Minerals that contain zirconium, such as alvite [(Hf, Th, Zr) $Si0_4$ H_2O, thortveitite and zircon ($ZrSio_4$),baddelyite, usually contain between 1 to 5% hafnium with respect to zirconium and is produced as a byproduct of zirconium refinement through solvent extraction. The hafnium hydroxide is calcined to oxide, chlorinated and then reduced to metal from chloride by sodium or magnesium in the Kroll reduction process.

1.10. Extraction:

The vital problem in working with hafnium is to separate it from zirconium. Today, chemists know that compounds of hafnium dissolve more easily in some liquids than do compounds of zirconium. This method can be used to separate compounds of the two elements from each other.

1.11. Uses and compounds:

A nuclear power plant is a facility where energy released from nuclear fission reactions is used to generate electricity.

Nuclear power plant applications account for the largest use of hafnium metal. Hafnium is also used to make binary compounds with interesting properties. A binary compound consists of two elements. These compounds are among the best refractory materials known. A refractory material is one that can withstand very high temperatures. It reflects heat away from itself. Refractory materials are used to line the inside of high temperatures ovens. For example, some alloys are made at temperatures of thousands of degrees in refractory ovens. Some hafnium compounds used to line these furnaces are hafnium boride (HfB_2) and hafnium oxide (HfO_2).

1.12. Health effects:

Both hafnium and its compounds are most dangerous when inhaled. Powdered hafnium metal is also dangerous. It can ignite and explode very easily.

II. CHEMICAL SEPARATION TECHNIQUE

This method is used to purify or to isolate one substance from other substances, for either preparative or analytical purpose. In industrial applications the ultimate goal is the isolation of a product of given purity, whereas in analysis the primary goal is the determination of the amount or concentration of that substance in a sample.

There are three factors of importance to be considered in all separations:

1) The completeness of recovery of the substance being isolated,
2) The extent of separation from associated substances, and
3) The efficiency of the separation.

There are many types of separations based on a variety of properties of materials. Among the most commonly used properties are those involving solubility, volatility, adsorption, and electrical and magnetic effects.The most efficient separation will obviously be obtained under conditions for which the difference in properties between two substances undergoing separation are at a maximum.

The common aspect of all separation methods is the need for two phases. The desired substance will partition or distribute between the two phases in a definite manner, and the separation is completed by physically separating the two phases. The ratio of the concentrations of a substance in the two phases is called its partition or distribution coefficient. If two substances have very similar distribution coefficient, many successive steps may be required for a separation. The resulting process is called a fractionation.

Based on the nature of the second phase, the more commonly used methods of separation are classified as follows:

1) Methods involving a solid second phase include precipitation, electro deposition, chromatography (adsorption), Ion exchange and crystallization.
2) The outstanding method involving a liquid second phase is solvent extraction, in which the original solution is placed in contact with another liquid phase invisible with the first.
3) Methods involving a gaseous second phase include gas evolution, distillation, sublimation and gas chromatography. Mixtures of volatile substances can often be separated by fractional distillation.

III. SOLVENT EXTRACTION

Solvent extraction is widely used commercial technique for separation of Nb, Ta, Zr, Hf, Ga, Mo, U elements. The basic principles of solvent extraction are given below. This method is based on distribution between two liquid phases are particularly valuable for the separation of substances with very similar properties. The advantages of these methods are the ease of multi-stage repetition of individual steps, the possibility of continuous and automatic operation. Since there is no interference due to adsorption, formation of mixed crystals, the efficiency of separation remains essentially constant up to very high purities. The ultimate goal in many rapidly developing new branches of industry, such as extraction and processing of mineral and ore, raw materials metallurgy, nuclear and semi-conductor industries is the production of highly pure substances. Solvent extraction has evolved as a commercial technique for the separation and purification of metals for nuclear applications. Uranium is extracted and purified by solvent extraction process.

Liquid/liquid extraction separates the components of a homogeneous liquid mixture on the basis of differing solubility in another liquid phase because it depends on differences in chemical potential as liquid-liquid extraction is more sensitive to chemical type than to molecular size. This makes it complementary to distillation as a separation technique. One of the first large-scale use was in the petroleum industry for the separation of aromatic from aliphatic compounds. Liquid/liquid extraction also has found application for many years in the coal tar industry. On a smaller scale, extraction is a key process in the pharmaceutical industry for recovery of antibiotics from fermentation broths, in the recovery and separation of vitamins, and for the production of alkaloids from natural products.

The 3 commonly used flow patterns in solvent extraction are as follows:
3.1.1 Co-current/Parallel flow: both feed and solvent flows in the same direction.
3.1.2 Cross-current flow: feed and solvent flows perpendicular to each other.

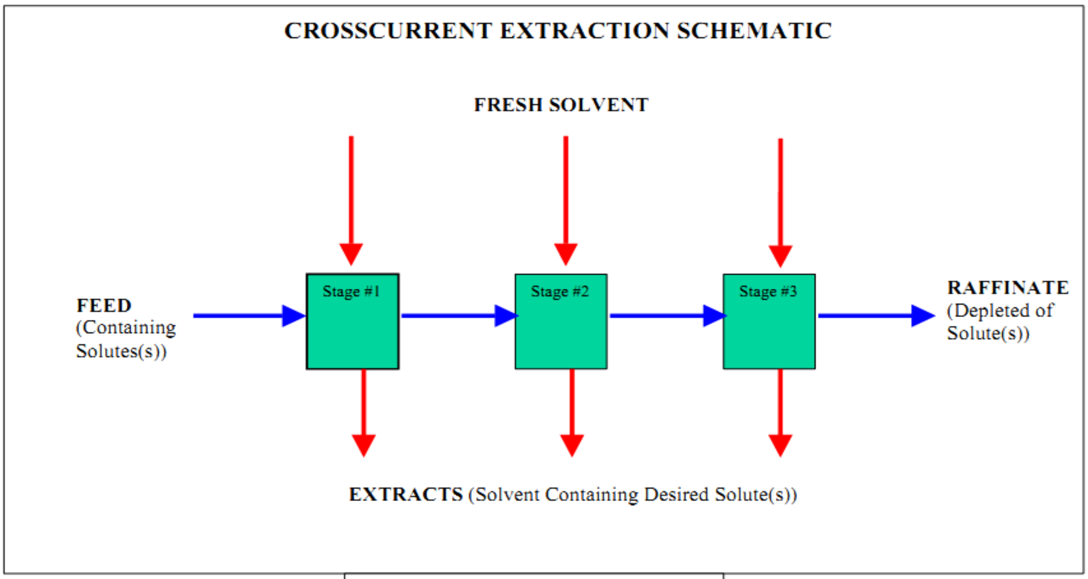

Figure 1: Crosscurrent Extraction

3.1.3CountercurrentFlow:

feed and solvent flows in opposite direction Countercurrent technique is a mechanism used to transfer some property of a fluid from one flowing current of fluid to another across a semi permeable barrier between them. The property transferred could be heat, concentration of a chemical substance, or others. Countercurrent exchange is used extensively in biological systems for a wide variety of purposes. For example fish use it in their gills to transfer oxygen from the surrounding water into their blood, and birds use a countercurrent heat exchanger between blood vessels in their legs to keep heat concentrated within their bodies. In biology this is referred to as Retie Mira bile. Mammalian kidneys use countercurrent exchange to remove water from urine so the body can retain water used to move the nitrogenous waste products. Countercurrent exchange is also a key concept in chemical engineering thermodynamics and manufacturing processes for example in extracting sucrose from sugar beet roots.

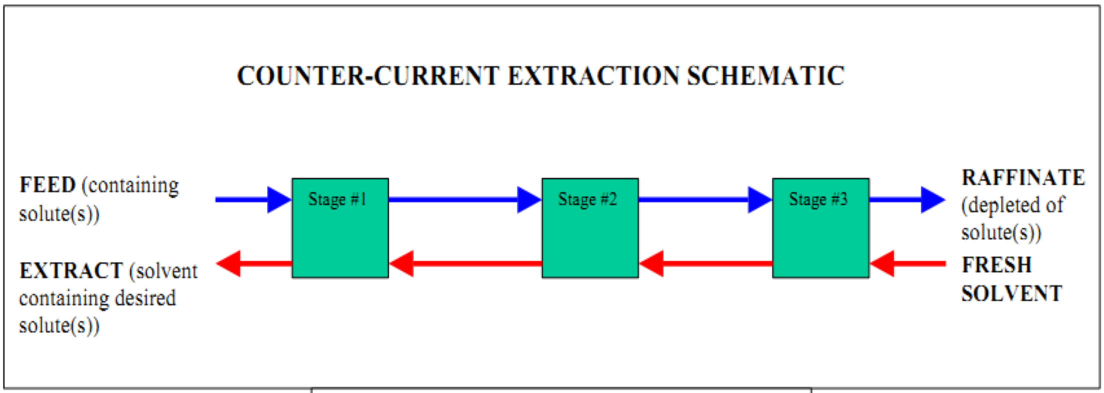

Figure 2: Countercurrent Extraction

The diagram presents a generic representation of a countercurrent exchange, the two flows moving in opposite directions, the countercurrent exchange system maintains a constant gradient between the two flows over their entire length. With a sufficiently long length and a sufficiently low flow rate this can result in almost all of the property being transferred.

We have used countercurrent flow process for the solvent extraction of zirconium.

3.2General description of solvent

Solvent is a substance, usually a liquid, that acts as a dissolving agent or that is capable of dissolving another substance. In solutions of solids or gases in a liquid, the liquid is the solvent. In all other homogeneous mixtures (i.e., liquids, solids, or gases dissolved in liquids; solids; and gases in gases), solvent is of higher proportion. The minor proportion substances are called solutes. The solvent also takes roll of temperature control, either to provide the energy of the colliding particles for speedy reaction or to absorb heat in exothermic reaction.

3.3 Factors Favoring Solvent Extraction

Hydrated inorganic salts tend to be more soluble in water than in organic solvents such as benzene, chloroform, etc whereas organic solvents tend to more soluble in organic solvents than in water unless they incorporate a sufficient number of hydroxyl groups or other hydrophilic groupings.

Ionic compounds are not extracted into the organic solvents from aqueous solutions because of the larger loss in electrostatic salvation energy that would occur. The most effective way to make an aqueous ionic species extractable is to neutralize its charge. This can be done by formation of neutral ion-association. The larger and more hydrophobic the resulting molecule species the better will be its extraction.

Salting out agents like alkali metal nitrates and chlorides, while have pronounced tendency for hydration, are often used to increase the distribution ratio. They bind large number of water molecules thereby lowering the dielectric constant of the solution and favoring ion-association.

There are three terms by means of which the extraction characteristics of any extracting species are characterized. They are distribution ratio, percent extraction and separation factor.

i) Distribution law

The distribution law states that, “The distribution of the extracting species will be such that at equilibrium the ratio of the concentrations of the solute in the two solvents at a particular temperature is constant provided the solute has the same molecular weight in each phase”. For a species ‘X’ distributing between two solvents 1 &2, say $X_{1\ \&}\ X_{2,}$

$K_d = [X_2 / X_1]$ …………………….(3.3.1)

Where K_d is the distribution coefficient, a constant, independent of the total initial concentration. The chemical interactions of the distributing species with the other components in the two phases have profound effect on the distribution constant. This distribution ratio is a stoichiometric ratio including all species of the same component in the respective phases.

$$D = \frac{\text{Total concentration in the organic phase}}{\text{Total concentration in the aqueous phase}}$$

ii) Percent extraction

The percent extraction of any extractable species will be related to the distribution ratio ‘D’ and the initial volume of the aqueous phase and organic phases V_w& V_o respectively as shown below:

$$\% E = \{100\, D / D + (V_w / V_o)\}$$

When the volumes of both phases are equal, the equation reduces to:

$$\% E = \{100\, D / D+1\}$$

iii) Separation factor

The term separation factor gives an idea about the effectiveness of the separation of the metal chelates, which is the main object of solvent extraction. Let A & B be the two metals of forming extractable species with a particular reagent. The distribution ratios for these two species are related as follows:

$$Q = [\,(A)_o / (B)_o\,] / [\,(A)_w / (B)_w\,] = [\,(A)_o / (A)_w\,] / [(B)_o / (B)_w\,] = D_A / D_B$$

Choice of solvent for extraction

A high distribution ratio for desired matrix and low distribution ratio for impurities is the prior requisite for selection of solvent. Other important properties of the solvents for commercial use are as follows.

1) Low solubility in the aqueous phase.
2) Low toxicity and flammability.
3) Sufficiently low viscosity & sufficient density difference from the aqueous phase to avoid the formation of emulsions.

3.4 Extraction of metals

Different types of metals which can be extracted by solvent extraction methods.

Zirconium and hafnium

Zirconium and hafnium can be extracted by using TBP (tri-butyl phosphate) Organic solvent.

Palladium and platinum, Neodymium, Cobalt, Nickel, Copper, Zinc and cadmiumcan also be extracted by using the organic solvent.

3.5 Types of organic solvents used during solvent extraction

3.5.1 Tri-Butyl Phosphate(Tbp)

General properties:

Chemical Formula : $(CH_3CH_2CH_2CH_2O)PO$
Appearance : Colorless to yellowish liquid
Molar Mass : 6.32g/mol
Melting point : 93K
Boiling point : 562K
Density : $0.9727 g/cm^3$
Crystal Structure : Orthorhombic
Solubility : FIXME g/100g of water

3.5.2 Uses

1) TBP is a solvent and plasticizer for cellulose esters (e.g nitrocellulose and cellulose acetate). It forms stable hydrophobic complexes with some metals; these complex are soluble in organic solvents and in supercritical CO2.
2) The major uses of TBP in industry are as a component of aircraft hydraulic fluid and as a solvent for extraction and purification of rare earth metals from their ores.
3) TBP finds its use as a solvent in inks, synthetic resins, gums, adhesives and herbicide and fungicide concentrates.
4) In oil-based lubricants, addition of TBP increases the oil film strength. It is used also in mercerizing liquids, where it improves their wetting properties.
5) It is also used as a heat exchange medium.

3.5.3 Hydrochloric acid – Thiocynate – MIBK

The extraction, scrubbing and stripping operations takes place in open spray column. Feed to the extraction column consist of an aqueous acid – chloride solution, solution containing zirconium and hafnium, present as thiocynate complexes. The aqueous feed, fed in to the top of the first of four open columns flow counter currently to the organic mixture of methyl isobutyl ketone (MIBK) saturated with thiocynate. The organic mixture enters the base of the fourth column is essential hafnium free. The processed aqueous (feed raffinate) is sent to a thiocynate recovery system. The loaded solvent, containing the hafnium and small amount of zirconium, is sent to a scrubbing stage for the removal of zirconium. This operation take place in three column, and the scrub solution is 3.6 to 3.9 N HCL. This aqueous chloride scrub raffinate containing the zirconium is recycled to the feed to the extraction circuit.

General properties of MIBK:

1. Molecular Formula: $C_6H1_2O_6$
2. Appearance : Colorless liquid
3. Molar mass : 100.2 g/mol
4. Melting point : -84.7^0 C
5. Boiling point : $117\text{-}118^0$ C
6. Density : 0.80 g/ml, liquid
7. Viscosity : 0.58 cp at 20.0^0 C
8. Solubility : 1.91 g/100 ml (20^0C)

IV. SOLVENT EXTRACTION (ZIRCONIUM AND HAFNIUM)

1) Co – extraction of Zr and Hf
2) Scrubbing
3) Stripping

4.1 Co – Extraction:

Distribution data can be obtained in two methods. The first method employs variation of the phase ratio of the aqueous and the organic phases. The second method involves re-contacting the organic phase with fresh aqueous phase until the saturation loading of the solvent reaches. 1. In the phase ratio variation method, the ratios employed range from about 1/10 to 10/1. For example, 10 ml of an aqueous phase containing the metal, and 100 ml of an organic phase (Solvent) are contacted until equilibrium is obtained. This is usually done mechanically, such as on a wrist-action shaker. After allowing the phases to disengage, they are separated and analyzed for the metal or aqueous phase, and any aqueous phase from the organic phase, prior toanalysis. This can be accomplished by centrifuging the phases, or by filtering through dry, coarse filter paper. The same procedure is repeated, using phase ratios of, for example 1/5, 1/2, 1/1, 2/1, 5/1 and 10/1. It must be emphasized that the equilibrium pH must be same in all tests. One way of ensuring this is to check the pH of the aqueous phase after equilibrium of the phases, adjust if necessary by the addition of acid or alkali, and then shake the phase again. A distribution isotherm is then constructed by plotting the metal concentration in the organic phase against the concentration in the aqueous phase, as a function of the phase ratio.

The second method of constructing an extraction isotherm is as follows. A suitable phase ratio is decided upon, and the organic and aqueous phases are contacted at ratio until equilibrium is obtained. The phases are followed to separate, and the aqueous phase removed from the separating funnel and analyzed measured portion of the organic phase is also taken for analysis. Fresh aqueous solution is then added to the funnel containing the remainder of the organic phase in an amount to give the same phase ratio as that originally used. The phases are again contacted until equilibrium is obtained. This process is carried on until saturation of this solvent with the metal is obtained. Here again, care must be taken to maintain the same pH throughout the series of shake-outs. One drawback to this method is that a large volume of the organic phase must be used initially to allow for sampling, especially if a large number of contacts are required. Generally, the first method described, employing variation in the phase ratio, is recommended.

The loading capacity of the solvent can be obtained from either of these two methods, for the particular concentration of extractant used. But it cannot be assumed that the loading capacity is linear with increasing extracted concentration. If high concentration (>10 vol %) are to be used, it is advisable to determine the loading capacities at these concentrations. This is readily done either by contacting a solvent several times with fresh aqueous solution, or contacting with a concentrated solution of the metal with high A/O ratio, until maximum loading is achieved.

For most exploratory work, analysis of the organic phase is not necessary, provided no volume change of the phases occur. No third phase or crud is formed, only analysis of the aqueous raffinates is sufficient, since the metal concentration in the solvent can be readily calculated from the initial metal concentration of the feed solution and the phase ratio used.

4.2 Scrubbing

There are many possibilities in accomplishing this end by varying the scrub solution. Normally, however, scrubbing is achieved by water, dilute acid or base, or by an aqueous solution of a salt of the metal of primary interest in the solvent phase. Scrubbing test are carried out in a manner similar to those described above, the loaded solvent is contacted with the scrub solution at the The object of scrubbing is to remove loaded solvent, as much as possible, in any unwanted co-extracted metal. They are appropriate strength, pH, phase ratio, contact time and temperature. After separating the phases, the organic phase is usually analyzed to determine the unwanted metals, and how much of the metal of interest have been removed. The best scrub solution and conditions are determined by varying the various conditions.

The scrub raffinate may contain significance amounts of valuable metals, thus consideration should be given as to where in the process this raffinate should be recycled. Data obtained in scrubbing tests can be presented graphically, such as by plotting the concentration of metals in the organic phase against A/O ratio, salt concentration in the scrub solution, temperature, and so on.

4.3 Stripping

Data required for the construction of stripping isotherms are obtained in a manner similar to those for extraction, except that pH control is usually not required. A general procedure is as follows: the loaded solvent is contacted with a suitable strip solution (acid, base, etc), at an appropriate phase ratio until equilibrium is attained. The aqueous phase is then removed, fresh strip solution is added to the organic phase, and the procedure repeated. This process is continued until all (or as much as possible) of the metal has been stripped from the organic phases. Analysis of the strip liquors, and calculation of the concentration of metal in the organic phase after each strip allows the concentration of a stripping isotherm. This can be used to construct a

McCabe- Thiele diagram the number of theoretical strip stages requires, at the phase ratio and strip solution concentration used.

4.4 Kinetics Of Extraction And Stripping

Unless the extraction and the stripping rates are fast (< 1 min), the time required for equilibrium to be reached in both of these operations will need to be known in order to design a plant.

The time required for a system to reach equilibrium can be determined by shake-out tests. Contact times are varied between say 0.5 to 15 minutes, at suitable intervals, and the extraction coefficient for each contact time plotted as a function of time.

These data will not be directly applicable to a continuous process because the rate of metal extraction is a function, in part, of the type and degree of agitation. However, a good idea of use in a large contactor can be obtained. For example, if equilibrium is attained in less than one minute, almost any type of contactor may be used. Using this method, a lower limit on the contact time of about 0.25 minutes is imposed.

4.5 Chemical Characterization Of Samples

4.5.a. Inductively coupled plasma optical emission spectroscopy (ICP-OES),

Inductively coupled plasma atomic emission spectroscopy (ICP-AES), also referred to as inductively coupled plasma optical emission spectrometry (ICP-OES), and is an analytical technique used for the detection of trace metals. It is a type of emission spectroscopy that uses the inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element. The intensity of this emission is indicative of the concentration of the element within the sample.

Fig: 4.5.1 ICP- OES

V. EXPERIMENTAL PROCEDURE

5.1 Preparation Of Solutions

5.1.1 Feed

The feed for solvent extraction is prepared by dissolving the cakes contacting hafnium and zirconium with other impurities (minor percent of iron, titanium, silicon etc.) with nitric acid. The normality of the feed is adjusted to the required level from experimentation. The studies were conducted with respect to free acidity of the feed determined by titration with standard base. The solid content of the feed is adjusted by dilution with distilled water. After the distilled water dissolution of the cake, with minimal quantity of nitric acid is used for dissolution.

5.1.2 Solvent

TBP (Tri Butyl Phosphate) is more effective organic solvent which can take out Zr from the feed.TBP (Tri Butyl Phosphate) and kerosene is added at a ratio of 1:2, this shows that it will be prepared as per our requirement. If we need about 30 lit of solution for extraction of metal from the raffinate we have to prepare about 10 liters of TBP in 20lt of kerosene. Mixing of this mixture is important; it is done up to 5-10 min till it gets a proper, less- emulsion mixture. This mixture is added with nitric acid to a get require normality.

i) Purpose of adding Nitric acid to TBP – Kerosene

1) For the equilibrium of TBP so as to attain the normality of the feed due to this the extraction is carried out effectively without any change of normality of the feed.
2) Solution should not show any nitride formation.
3) There may be a chance of formation of organic Solvent (TBP) to dibutyl phosphate and monobutyl phosphate.

ii) Purpose of adding kerosene to TBP

1) To get a good liquidity properties to organic solvent.
2) To decrease the viscosity of the organic solvent for free flowing of liquid in funnels.
3) To reduces the emulsification while mixing with feed raffinate.
4) Kerosene is the only solution which can dilute with TBP, in order to get a fine mixer.

5.2 Process Flow Sheet

The general procedure for the process of solvent extraction of Zirconium and Hafnium, fresh Zr scrub raffinate is taken and precipitated with NaOH in the form of cake. The cake is dissolved in nitric acid to prepare feed for the solvent extraction. Using the feed, counter current process is carried out by adding TBP as solvent. This aqueous output solution is re precipitated with NaOH and filtered to get a cake. This cake is re dissolved to obtain a feed to get an aqueous solution which was subjected to co extraction. This is followed by selective stripping to obtain pure hafnium solution. The same is depicted in the flow chart below.

In these cycles the solution flow is carried out in different stages of aqueous to organic solvent ratio. The organic solvent is filled in separating funnels with feed and they are shacked for about 1 minute. The separation between organic solvent and the aqueous feed is carried out in an around 2-3 minutes after separation the Hf and Zr present in the feed will get settled in the organic solvent, and finally feed is collected from the bottom of the funnel. The process is carried out in a counter current method in all the cycles. During co-extraction the elements Hf and Zr which are present in the aqueous feed will transfer to organic solvent (TBP) and the solvent is called loaded solvent. This loaded solvent is then subjected to stripping to operation where the elements from the solvent come to aqueous i.e. acid.

VI. STATISTICAL DESIGN OF EXPERIMENT

The individual effects of different parameters (Ex: normality of the feed, number. of cycles, number of stages to be carried out, organic to aqueous ratio) on the co-extraction rate.
For a complete Matrix the number of experiments to be carried out is given by

$N=2^k$…………………...(6.1)

Where, N is the number of experiments and K is the number of variables.
But purpose can be solved even by half matrix. Hence the system if studies are also called half matrix method.
According to the half matrix method, the number of experiments actually required

$N=2^{k/2}=2^{k-1}$……………(6.2)

Since only four independent variables were to studied for selective stripping of Hf.
The number of sets required was
$N=2^{4-1}=2^3=8$
If the four independent variables of the matrix studies are represented by x_1,x_2, x_3 and x_4 in actual form, and by X_1,X_2,X_3,and X_4 in coded form then the general equation will be

$Y=a_0+a_1.X_1+a_2.X_2+a_3.X_3+a_4.X_4+a_5.(X_1.X_2)+a_6(X_1.X_3)+a_7.(X_2.X_3)$……………………..(6.3)

Where a_0: value of recovery when all the parameters are at base level.
a_1, a_2,a_3: show the effect of corresponding parameters and Y represent the result or recovery obtained for a particular set. The design of matrix and results obtained are shown in table 6.1

The regression coefficients were estimated by
$A_0= Y_i/N$
$Ai = \{(X_{ij}. Y_i)/N\}/N$ and so on.
Where Y_i: value of recovery index in the i^{th} trial shown in i^{th} row
N: total number of trials

X_{ij}: coded value in the ith row and jth column.

Design of matrix for zirconium

Parameters		**: Minimum (-1)**	**Maximum (+1)**
1. Acid (aqueous) Normality	**: X1**	**2**	**6**
2. No. of stages	**: X2**	**2**	**6**
3. No. of cycles	**: X3**	**1**	**3**
4. Aqueous to organic ratio	**: X4**	**3**	**5**

Experiment table 6.1

Exp	X1	X2	X3	X4	X1*X2	X1*X3	X2*X3
1	-1	-1	-1	-1	+1	+1	+1
2	+1	-1	-1	+1	-1	-1	+1
3	+1	+1	-1	-1	+1	-1	-1
4.	+1	+1	+1	+1	+1	+1	+1
5	+1	-1	+1	-1	-1	+1	-1
6	-1	+1	-1	+1	-1	+1	-1
7	-1	+1	+1	-1	-1	-1	+1
8	-1	-1	+1	+1	+1	-1	-1

List of Experiments:

Exp1:Acid Normality = 2N, No. of Stages = 2
No. of cycles = 1, Organic to Aqueous ratio = 1:3
Exp2: Acid Normality = 6 No. stages = 2
No. of cycles = 1 Organic to Aqueous ratio = 1:5
Exp3: Acid Normality = 6 No. of Stages = 6
No. of cycles = 1 Organic to Aqueous ratio = 1:3
Exp4: Acid Normality = 6 , No. of Stages = 6
No. of cycles = 3 , Organic to Aqueous ratio = 1:5
Exp5: Acid Normality = 6, No. of Stages = 2
No. of cycles = 3, Organic to Aqueous ratio = 1:3
Exp6: Acid Normality = 2, No. of Stages = 6
No. of cycles = 1, Organic to Aqueous ratio = 1:5
Exp7: Acid Normality = 2, No. of Stages = 6
No. of cycles = 3, Organic to Aqueous ratio = 1:3
Exp8: Acid Normality = 2, No. of Stages = 2
No. of cycles = 3 Organic to Aqueous ratio = 1:5

Average Experiment:

Exp9: Acid Normality = 4, No. of stages = 4
No. of cycles = 2, Organic to Aqueous ratio = 1:4

Matrix Method for Hafnium

Parameters	:	**Minimum (-1)**	**Maximum (+1)**
1. Acid (aqueous) Normality	**: X1**	**7**	**11**
2. No. of stages	**: X2**	**2**	**6**
3. No. of cycles	**: X3**	**1**	**3**
4. Aqueous to organic ratio	**: X4**	**3**	**5**

Experiment table 5.1

Exp	X1	X2	X3	X4	X1*X2	X1*X3	X2*X3
1	-1	-1	-1	-1	+1	+1	+1
2	+1	-1	-1	+1	-1	-1	+1
3	+1	+1	-1	-1	+1	-1	-1
4.	+1	+1	+1	+1	+1	+1	+1
5	+1	-1	+1	-1	-1	+1	-1
6	-1	+1	-1	+1	-1	+1	-1
7	-1	+1	+1	-1	-1	-1	+1
8	-1	-1	+1	+1	+1	-1	-1

List of Experiments:

Exp1: Acid Normality = 7N, No. of Stages = 2
No. of cycles = 1, Organic to Aqueous ratio = 1:3

Exp2: Acid Normality = 11, No. stages = 2
No. of cycles = 1, Organic to Aqueous ratio = 1:5

Exp3: Acid Normality = 11, No. of Stages = 6
No. of cycles = 1, Organic to Aqueous ratio = 1:3

Exp4: Acid Normality = 11, No. of Stages = 6
No. of cycles = 3, Organic to Aqueous ratio = 1:5

Exp5: Acid Normality = 11, No. of Stages = 2
No. of cycles = 3, Organic to Aqueous ratio = 1:3

Exp6: Acid Normality = 7, No. of Stages = 6
No. of cycles = 1, Organic to Aqueous ratio = 1:5

Exp7: Acid Normality = 7, No. of Stages = 6
No. of cycles = 3, Organic to Aqueous ratio = 1:3

Exp8: Acid Normality = 7, No. of Stages = 2
No. of cycles = 3, Organic to Aqueous ratio = 1:5

Average Experiment:

Exp9: Acid Normality = 9, No. of stages = 4
No. of cycles = 2, Organic to Aqueous ratio = 1:4

VII. RESULTS AND DISCUSSION:

7.1 Practical Results:

Loaded solvent analysis

Experiment table 7.1.1

	Zr ppm	Hf ppm	Ti ppm	Fe ppm
Feed	380550	182600	6560	7120
Feed Raffinate	186200	103050	1601	370
Recovery	194350	79550	4959	6750

Amount of Hf, Zr, Ti, Si recovered by the aqueous solution from the loaded solvent after selective stripping

Experiment table 7.1.2

Exp	Zr	Hf	Ti	Fe
1	83400	16255	1012	1041.5
2	15670	106800	6850	8190
3	79050	101850	6310	7735
4	67050	107000	7095	9340
5	130400	107600	6530	8090
6	69700	62000	4611	5295
7	376700	103150	8390	9695
8	328900	66000	5105	5905
9	297600	112600	7440	8510

Procedure:

To test the utility of the experiment, at the base level, an experimentwas planned, where all the parameters contained were having mean value. The general equation of the experiment is:

$Y=a_0+a_1.x_1+a_2.x_2+a_3.x_3+a_4.X_4+a_5.(X_1X_2)+a_6.(X_1X_3)+a_7.(X_2X_3)$

The parameters are

1. Acid Normality,
2. No.of stages,
3. No.of Cycles,
4. Aqueous To Organic Ratio

According to the half matrix method (statistical design) it is necessary to first calculate the values of a_0, a_1, a_2, a_3, a_4, a_5, a_6, a_7. These values can be calculated with the help of the values in which the recoveries of**Zirconium,Hafnium, Titanium andIron** metals are placed which are obtained by the ICP-OES (Inductively Coupled Plasma-Optical emission Spectroscopy) analysis. The values for a_0, a_2, a_3, a_4, a_5, a_6, a_7 can be obtained by the formula.

$a_0 = (S_1+S_2+S_3+S_4+S_5+S_6+S_7+S_8)/8$
$a_1 = (-S_1+S_2+S_3+S_4+S-S_6-S_7-S_8)/8$
$a_2 = (-S_1-S_2+S_3+S_4-S_5+S_6+S_7-S_8)/8$
$a_3 = (-S_1-S_2-S_3+S_4+S_5-S_6+S_7+S_8)/8$
$a_4 = (-S_1+S_2-S_3+S_4-S_5+S_6-S_7+S_8)/8$
$a_5 = (S_1-S_2+S_3+S_4-S_5-S_6-S_7+S_8)/8$
$a_6 = (S_1-S_2-S_3+S_4+S_5+S_6-S_7-S_8)/8$
$a_7 = (S_1+S_2-S_3+S_4-S_5-S_6+S_7-S_8)/8$

These a_0, a_2, a_3, a_4, a_5, a_6, a_7 values which are calculated will be substituted in the equation,

$Y=a_0+a_1.x_1+a_2.x_2+a_3.x_3+a_4.X_4+a_5.(X_1X_2)+a_6.(X_1X_3)+a_7.(X_2X_3)$

The recovery values calculated theoretically by the standard formula at the given eight different conditions should tally with that of the values got by the ICP-OES analysis.

In this method, an experiment is also done by taking the average of the two extreme values called the base experiment and it should tally with the value of the parameter a_0, which there by acts as a reference to the results obtained from the calculations.

7.3 Theoretical Results

VALUES OBTAINED USING STANDARD FORMULA FROM THE STATISTICAL DESIGN OF EXPERIMENT :

ZIRCONIUM:

a_0 $= (S_1+S_2+S_3+S_4+S_5+S_6+ S_7+S_8)/8$
$=(166.8+313.5+158.1+134.1+260.8+539.4+753.4+657.8) *500/8$
$= 186450$
a_1 $= (-S_1+S_2+S_3+S_4+S_5-S_6- S_7-S_8)/8$
$=(-166.8+313.5+158.1+134.1+260.8-539.4-753.4-657.8) *500/8$
$= -78180$
a_2 $= (-S_1-S_2+S_3+S_4-S_5+S_6+ S_7-S_8)/8$

=(-166.8-313.5+158.1+134.1-260.8+539.4+753.4-657.8) *500/8
= 11630

a_3 = $(-S_1-S_2-S_3+S_4+S_5-S_6+S_7+S_8)/8$
=(-166.8-313.5-158.1+134.1+260.8-539.4+753.4+657.8) *500/8
= 39268.75

a_4 = $(-S_1+S_2-S_3+S_4-S_5+S_6-S_7+S_8)/8$
=(-166.8+313.5-158.1+134.1-260.8+539.4- 753.4+657.8) *500/8
= 19105

a_5 = $(-S_1+S_2+S_3+S_4-S_5-S_6-S_7+S_8)/8$
= (-166.8+313.5+158.1+134.1-260.8-539.4- 753.4+657.8) *500/8
= -46893.5

a_6 = $(S_1-S_2-S_3+S_4+S_5+S_6-S_7-S_8)/8$
=(166.8-313.5-158.1+134.1+260.8+539.4- 753.4-657.8) *500/8
=-48850

a_7 = $(S_1+S_2-S_3+S_4-S_5-S_6+S_7-S_8)/8$
=(166.8+313.5-158.1+134.1-260.8-539.4+ 753.4-657.8)*500/8
= -15518.5

Where
a_1 = Effect of Acid normality,
a_2 = Effect of no. of stages,
a_3 = Effect of no. of cycles,
a_4 = Effect of aqueous to organic ratio,
a_5 = Combined effect of Acid normality & No. of stages,
a_6 = Combined effect of Acid normality & No. of cycles,
a_7 = Combined effect of No of stages & No. of cycles,

EXPLANATION:

✓ Recovery of Zirconium in average experiment =**194350**

a_0 = 186450

✓ **a_1=-78180**is the effect of acid normality,**a_2 = 11630** no. of stages, **a_4= 19105 ,** organic : aqueous ratio,**a_3= 39268.75**No. of cycles, are**POSITIVE** values, directly proportional to the extraction.

STANDARD FORMULA

$Y=a_0+a_1.x_1+a_2.x_2+a_3.x_3+a_4.X_4+a_5.(X_1X_2)+a_6.(X_1X_3)+a_7.(X_2X_3)$

EXPERIMENT-1
Y = 372.9875-(-156.3625)-(23.2625)-(78.5375).(1)-(-38.2125).(1)+ (-93.7875)+(-97.7125)+(-31.0375)]. *500
= 83400

EXPERIMENT-2
Y =372.9875+(-156.3625)-(23.2625)-(78.5375).(1)+(-38.2125).(1)- (-93.7875)-(-97.7125)-(-31.0375)] *500.
= 156750

EXPERIMENT-3
Y =372.9875+(-156.3625)+(23.2625)-(78.5375).(1)-(-38.2125).(1)+ (-93.7875)-(-97.7125)-(-31.0375)] *500.
= 79050

EXPERIMENT-4
Y =372.9875+(-156.3625)+(23.2625)+(78.5375).(1)+(-38.2125).(1)+ (-93.7875)+(-97.7125)+(-31.0375)] *500.
= 67050

EXPERIMENT-5
Y =372.9875+(-156.3625)-(23.2625)+(78.5375).(1)-(-38.2125).(1)- (-93.7875)+(-97.7125)-(-31.0375)] *500.
= 130400

EXPERIMENT-6
Y =372.9875-(-156.3625)+(23.2625)-(78.5375).(1)+(-38.2125).(1)-

(-93.7875)+(-97.7125)-(-31.0375)]*500.
= 69700
EXPERIMENT-7
Y =372.9875-(-156.3625)-(23.2625)+(78.5375).(1)+(-38.2125).(1)+
(-93.7875)-(-97.7125)-(-31.0375)] *500
= 376700
EXPERIMENT-8
Y = (372.9875-(-156.3625)-(23.2625)+(78.5375).(1)+(-38.2125).(1)+
(-93.7875)-(-97.7125)-(-31.0375). *500
=328900

HAFNIUM

a_0 = $(S_1+S_2+S_3+S_4+S_5+S_6+S_7+S_8)/8$
= (124+213.6+203.7+214+215.2+124+206.3+132) *500/8
=83830
a_1 = $(-S_1+S_2+S_3+S_4+S_5-S_6-S_7-S_8)/8$
= (-124+213.6+203.7+214+215.2-124-206.3-132)/8
= 21980
a_2 = $(-S_1-S_2+S_3+S_4-S_5+S_6+S_7-S_8)/8$
=(-124-213.6+203.7+214-215.2+124+206.3-132) *500/8
= 9668
a_3 = $(-S_1-S_2-S_3+S_4+S_5-S_6+S_7+S_8)/8$
= (-124-213.6-203.7+214+215.2-124+206.3+132) *500/8
= 12105.5
a_4 = $(-S_1+S_2-S_3+S_4-S_5+S_6-S_7+S_8)/8$
= (-124+213.6-203.7+214-215.2+124-206.3+132) *500/8
= 1618
a_5 = $(-S_1+S_2+S_3+S_4-S_5-S_6-S_7+S_8)/8$
= (-124+213.6+203.7+214-215.2-124-206.3+132) *500/8
= -11055.5
a_6 = $(S_1-S_2-S_3+S_4+S_5+S_6-S_7-S_8)/8$
= (124-213.6-203.7+214+215.2+124-206.3-132) *500/8
= -10618
a_7 = $(S_1+S_2-S_3+S_4-S_5-S_6+S_7-S_8)/8$
= (124+213.6-203.7+214-215.2-124+206.3-132)*500/8
= -530

Where
a_1 = Effect of Acid normality,
a_2 = Effect of no. of stages,
a_3 = Effect of no. of cycles,
a_4 = Effect of aqueous to organic ratio,
a_5 = Combined effect of Acid normality & No. of stages,
a_6 = Combined effect of Acid normality & No. of cycles,
a_7 = Combined effect of No of stages & No. of cycles,

EXPLANATION:

- ✓ Recovery of Hafnium in average experiment = 79550

a_0 = 83830

- ✓ **a_1=21980** is the effect of **acid normality,** a_2 **= 9668 no. of stages, a_3= 12105.5No. of cycles, a_4= 1618organic: aqueous ratios are POSITIVE,** so they are directly proportional to the extraction.

STANDARD FORMULA
$Y=a_0+a_1.x_1+a_2.x_2+a_3.x_3+a_4.X_4+a_5.(X_1X_2)+a_6.(X_1X_3)+a_7.(X_2X_3)$
EXPERIMENT-1:
Y =(167.66375-43.96125-19.33625-24.21125-3.23625-22.11125-21.23625-1.06125) *500
= 16255

EXPERIMENT-2
Y=(167.66375+43.96125-19.33625-24.21125+3.23625+22.11125+21.23625-1.06125) *500
= 106800

EXPERIMENT-3
Y=(167.66375+43.96125+19.33625-24.21125-3.23625-22.11125+21.23625+1.06125) *500
= 101850

EXPERIMENT-4
Y=(167.66375+43.96125+19.33625+24.21125+3.23625-22.11125-21.23625-1.06125) *500
= 107000

EXPERIMENT-5
Y=167.66375+43.96125-19.33625+24.21125-3.23625+22.11125-21.23625+1.06125) *500
= 107600

EXPERIMENT-6
Y=(167.66375-43.96125+19.33625-24.21125+3.23625+22.11125-21.23625+1.06125) *500
=62000

EXPERIMENT-7
Y=(167.66375-43.96125+19.33625+24.21125-3.23625+22.11125+21.23625-1.06125) *500
= 103150

EXPERIMENT-8
Y=(167.66375-43.96125-19.33625-24.21125+3.23625-22.11125+21.23625+1.06125) *500
= 66000

TITANIUM

a_0 = $(S_1+S_2+S_3+S_4+S_5+S_6+S_7+S_8)/8$
= (2.024+13.7+12.62+14.19+13.06+9.222+16.78+10.21)*500/8
= 5738

a_1 = $(-S_1+S_2+S_3+S_4+S_5-S_6-S_7-S_8)/8$
=(-2.024+13.7+12.62+14.19+13.06-9.222-16.78-10.21)*500/8
=958.5

a_2 = $(-S_1-S_2+S_3+S_4-S_5+S_6+S_7-S_8)/8$
=(-2.024-13.7+12.62+14.19-13.06+9.222+16.78-10.21)*500/8
=863.5

a_3 = $(-S_1-S_2-S_3+S_4+S_5-S_6+S_7+S_8)/8$
= (-2.024-13.7-12.62+14.19+13.06-9.222+16.78+10.21)*500/8
=1042

a_4 = $(-S_1+S_2-S_3+S_4-S_5+S_6-S_7+S_8)/8$
= (-2.024+13.7-12.62+14.19-13.06+9.222-16.78+10.21)*500/8
= 177.5

a_5 = $(-S_1+S_2+S_3+S_4-S_5-S_6-S_7+S_8)/8$
= (-2.024+13.7+12.62+14.19-13.06-9.222-16.78+10.21)*500/8
=-857.5

a_6 = $(S_1-S_2-S_3+S_4+S_5+S_6-S_7-S_8)/8$
= (2.024-13.7-12.62+14.19+13.06+9.222-16.78-10.21)*500/8
= -926

a_7 = $(S_1+S_2-S_3+S_4-S_5-S_6+S_7-S_8)/8$
= (2.024+13.7-12.62+14.19-13.06-9.222+16.78-10.21)*500/8
= 98.875

Where
a_1 = Effect of Acid normality,
a_2 = Effect of no. of stages,
a_3 = Effect of no. of cycles,
a_4 = Effect of aqueous to organic ratio,
a_5 = Combined effect of Acid normality & No. of stages,
a_6 = Combined effect of Acid normality & No. of cycles,
a_7 = Combined effect of No of stages & No. of cycles,

EXPLANATION:

✓ Recovery of Titanium in average experiment = **4959**
a_0= 5738

✓ **a_1=958.4** effect of **acid normality**, **a_2=863.5 effect of no. of stages, a3= 1042 no. of cycles, a4=177.5** Effect of **aqueous to organic ratio,**these values are **POSITIVE**,directly proportional to the extraction.

STANDARD FORMULA
$Y=a_0+a_1.x_1+a_2.x_2+a_3.x_3+a_4.X_4+a_5.(X_1X_2)+a_6.(X_1X_3)+a_7.(X_2X_3)$

EXPERIMENT-1
= (11.47575-1.91675-1.72725-2.08425-0.35475-1.71475-1.85175+0.19775)*500
= 1012

EXPERIMENT-2
=(11.47575+1.91675-1.72725-2.08425+0.35475+1.71475+1.85175+0.19775)*500
= 6850

EXPERIMENT-3
=(11.47575+1.91675+1.72725-2.08425-0.35475-1.71475+1.85175-0.19775)*500
=6310

EXPERIMENT-4
=(11.47575+1.91675+1.72725+2.08425+0.35475-1.71475-1.85175+0.19775)*500
= 7095

EXPERIMENT-5
=(11.47575+1.91675-1.72725+2.08425-0.35475+1.71475-1.85175-0.19775)*500
=6530

EXPERIMENT-6
=(11.47575-1.91675+1.72725-2.08425+0.35475+1.71475-1.85175-0.19775)*500
=4611

EXPERIMENT-7
=(11.47575-1.91675+1.72725+2.08425-0.35475+1.71475+1.85175+0.19775)*500
=8390

EXPERIMENT-8
=(11.47575-1.91675-1.72725+2.08425+0.35475-1.71475+1.85175-0.19775)*500
=5105

IRON:

a_0 = $(S_1+S_2+S_3+S_4+S_5+S_6+S_7+S_8)/8$
=(2.083+16.38+15.47+18.68+16.18+10.59+19.39+11.81)*500/8
= 6911.5

a_1 = $(-S_1+S_2+S_3+S_4+S_5-S_6-S_7-S_8)/8$
=(-2.083+16.38+15.47+18.68+16.18-10.59-19.39-11.81)*500/8
=1427.5

a_2 = $(-S_1-S_2+S_3+S_4-S_5+S_6+ S_7-S_8)/8$
=(-2.083-16.38+15.47+18.68-16.18+10.59+19.39-11.81)*500/8
= 1105

a_3 = $(-S_1-S_2-S_3+S_4+S_5-S_6+ S_7+S_8)/8$
=(-2.083-16.38-15.47+18.68+16.18-10.59+19.39+11.81)*500/8
=1345

a_4 = $(-S_1+S_2-S_3+S_4-S_5+S_6- S_7+S_8)/8$
=(-2.083+16.38-15.47+18.68-16.18+10.59-19.39+11.81)*500/8
=271

a_5 = $(-S_1+S_2+S_3+S_4-S_5-S_6- S_7+S_8)/8$
=(-2.083+16.38+15.47+18.68-16.18-10.59-19.39+11.81)*500/8
= -905

a_6 = $(S_1-S_2-S_3+S_4+S_5+S_6-S_7-S_8)/8$
=(2.083-16.38-15.47+18.68+16.18+10.59-19.39-11.81)*500/8
= -969.5

a_7 = $(S_1+S_2-S_3+S_4-S_5-S_6+S_7-S_8)/8$
=(2.083+16.38-15.47+18.68-16.18-10.59+19.39-11.81)*500/8
=155.2

Where
a_1 = Effect of Acid normality,
a_2 = Effect of no. of stages,
a_3 = Effect of no. of cycles,
a_4 = Effect of aqueous to organic ratio,
a_5 = Combined effect of Acid normality & No. of stages,
a_6 = Combined effect of Acid normality & No. of cycles,
a_7 = Combined effect of No of stages & No. of cycles,

EXPLANATION:

- ✓ Recovery of Ironin average experiment = 6750
  a_0= 6911.5

- ✓ **a_1=1427.5**effect of **acid normality, a_2=1105**effect of **no. of stages**, a_3=1345 effect of cycles,**a_4=271organic to aqueous ratios**, these values are **POSITIVE**, directly proportional to the extraction.

STANDARD FORMULA

$Y=a_0+a_1.x_1+a_2.x_2+a_3.x_3+a_4.X_4+a_5.(X_1X_2)+a_6.(X_1X_3)+a_7.(X_2X_3)$

EXPERIMENT-1

Y=(13.82275-2.854625-2.209625-2.692125-0.542125-1.812125-1.939625+0.310375)*500
=1041.5

EXPERIMENT-2

Y=(13.82275+2.854625-2.209625-2.692125+0.542125+1.812125+1.939625+0.310375)*500
= 8190

EXPERIMENT-3

Y=(13.82275+2.854625+2.209625-2.692125-0.542125-1.812125+1.939625-0.310375)*500
=7735

EXPERIMENT-4

Y=(13.82275+2.854625+2.209625+2.692125+0.542125-1.812125-1.939625+0.310375)*500
= 9340

EXPERIMENT-5

Y=(13.82275+2.854625-2.209625+2.692125-0.542125+1.812125-1.939625-0.310375)*500
=8090

EXPERIMENT-6

Y=(13.82275-2.854625+2.209625-2.692125+0.542125+1.812125-1.939625-0.310375)*500
=5295

EXPERIMENT-7

Y=(13.82275-2.854625+2.209625+2.692125-0.542125+1.812125+1.939625+0.310375)*500
= 9695

EXPERIMENT-8

Y=(13.82275-2.854625-2.209625+2.692125+0.542125-1.812125+1.939625-0.310375)*500
=5905

7.3 Random Experiment

If we want to know the recovery at a condition where the parameters are actually not done in the experiment by using the above formula then

X1=(x1-avg)/(Max-Avg)
X2=(x2-Avg)/(Max-Avg)
X3=(x3-Avg)/(Max-Avg)
X4=(x4-Avg)/(Max-Avg)

We calculate the values of X1, X2, X3, and X4. These calculated values of X1, X2, X3, and X4 are substituted in the above standard equation. The resultant value of "Y" so obtained is the value of recovery at that particular condition.

Example:
Condition: To calculate the recovery of Hafnium at Acid
Normality=5N, No. of stages=2, No. of cycles=2, Organic: Aqueous ratio=1:6
Now

X1=Normality=5, x2=No. of stages=2,
X3=No. of cycles=2, x4=Organic: Aqueous ratio=1:6

X1=(5-4)/(6-4)= 0.5

X2=(2-4)/(6-4)=-1
X3=(2-2)/(3-2)=0
X4=(6-4)/(6-4)=1
$Y=a_0+a_1.x_1+a_2.x_2+a_3.x_3+a_4.X_4+a_5.(X_1X_2)+a_6.(X_1X_3)+a_7.(X_2X_3)$
Y=[167.66375+43.96125(0.5)+19.33625(-1)+24.21125(0)+3.23625(1)-22.11125(-0.5)-21.23625(0)-1.06125(0)] * 500 = 178.5 *500 = 89250

To calculate the recovery of Zirconium at Acid

Y = 372.9875-(78.18125)-(23.2625)-(0)(78.5375)+(38.2125).(1)+ 46.89375+(-97.7125)(0)+(-31.0375)(0)]. *500 = 178325

	Zr ppm	**Hf ppm**	**Ti ppm**	**Fe ppm**
Feed	**380550**	**182600**	**6560**	**7120**
Feed Raffinate	**370330**	**147425**	**3439**	**2270**
Recovery	**10220**	**35175**	**3121**	**4850**

Amount of Hf, Zr, Ti, Si recovered by the aqueous solution from the loaded solvent after selective stripping

Experiment table 7.1.2

Exp	**Hf**	**Zr**	**Ti**	**Fe**
1	**65600**	**29050**	**5280**	**7770**
2	**1167**	**621.75**	**30.5**	**83.55**
3	**198.25**	**1253**	**149.8**	**2370**
4	**403.9**	**2797.5**	**189.3**	**2401**
5	**498**	**3389.5**	**234.35**	**2347**
6	**51500**	**6205**	**5760**	**8560**
7	**52300**	**6735**	**5275**	**8080**
8	**70850**	**26740**	**5970**	**8460**
9	**40870**	**10220**	**4563**	**6630**

7.3 Theoritical Results

7.4 OBTAINED USING STANDARD FORMULA FROM THE STATISTICAL DESIGN OF EXPERIMENT

ZIRCONIUM:

$a_0 = (S_1+S_2+S_3+S_4+S_5+S_6+S_7+S_8)/8$
=(58.1+1.2435+2.506+5.595+6.779+12.41+13.47+53.48)*500/8
= 9598.95
$a_1 = (-S_1+S_2+S_3+S_4+S_5-S_6-S_7-S_8)/8$
=(-58.1+1.2435+2.506+5.595+6.779-12.41-13.47-53.48)*500/8
= -7646
$a_2 = (-S_1-S_2+S_3+S_4-S_5+S_6+S_7-S_8)/8$
=(-58.1-1.2435+2.506+5.595-6.779+12.41+13.47-53.48)*500/8
= -5413.8
$a_3 = (-S_1-S_2-S_3+S_4+S_5-S_6+S_7+S_8)/8$
=(-58.1-1.2435-2.506+5.595+6.779-12.41+13.47+53.48)*500/8
= 379
$a_4 = (-S_1+S_2-S_3+S_4-S_5+S_6-S_7+S_8)/8$
=(-58.1+1.2435-2.506+5.595-6.779+12.41-13.47+53.48)*500/8
= 145.4
$a_5 = (-S_1+S_2+S_3+S_4-S_5-S_6-S_7+S_8)/8$
=(-58.1+1.2435+2.506+5.595-6.779-12.41-13.47+53.48)*500/8
= 5423.65
$a_6 = (S_1-S_2-S_3+S_4+S_5+S_6-S_7-S_8)/8$
=(58.1-1.2435-2.506+5.595+6.779+12.41-13.47-53.48)*500/8
= 699.7

a_7 = $(S_1+S_2-S_3+S_4-S_5-S_6+S_7-S_8)/8$
=(58.1+1.2435-2.506+5.595-6.779-12.41+13.47-53.48)*500/8
= 139.55

Where
a_1 = Effect of Acid normality,
a_2 = Effect of no. of stages,
a_3 = Effect of no. of cycles,
a_4 = Effect of aqueous to organic ratio,
a_5 = Combined effect of Acid normality & No. of stages,
a_6 = Combined effect of Acid normality & No. of cycles,
a_7 = Combined effect of No of stages & No. of cycles,

EXPLANATION:

- ✓ Recovery of Zirconium in average experiment = 10220
  a_0 = 9598.95
- ✓ **a_1= -7646**is the effect of acid normality,**a_2 = -5413.8,** no. of stages, **a_4=-145.4,** organic: aqueous ratios are **NEGATIVE**, so they are inverse effect on the extraction.
- ✓ **a_3= 379**No. of cycles, as it is a **POSITIVE** value, directly proportional to the extraction.

STANDARD FORMULA

$Y=a_0+a_1.x_1+a_2.x_2+a_3.x_3+a_4.X_4+a_5.(X_1X_2)+a_6.(X_1X_3)+a_7.(X_2X_3)$

EXPERIMENT-1
Y = (19.1979 -15.2920-10.8276+0.7580-0.8908+10.8473+1.3994+0.2791) *500
= 57.97 * 500 = 28985

EXPERIMENT-2
Y = (19.1979 -15.2920-10.8276+0.7580-0.8908+10.8473+1.3994+0.2791) *500
= 1.1171 *500 = 558.55

EXPERIMENT-3
Y =(19.1979 -15.2920-10.8276+0.7580-0.8908+10.8473+1.3994+0.2791) * 500
= 1189.95

EXPERIMENT-4
Y =(19.1979 -15.2920-10.8276+0.7580-0.8908+10.8473+1.3994+0.2791) *500
= 2735.65

EXPERIMENT-5
Y =(19.1979 -15.2920 +10.8276+0.7580+0.8908-10.8473+1.3994-0.2791) *500
= 3327.65

EXPERIMENT-6
Y =(19.1979 +15.2920-10.8276-0.7580-0.8908-10.8473+1.3994-0.2791)*500
= 6143.25

EXPERIMENT-7
Y =(19.1979 +15.2920-10.8276+0.7580+0.8908-10.8473-1.3994+0.2791)*500
= 6656.75

EXPERIMENT-8
Y =(19.1979 +15.2920+10.8276+0.7580-0.8908+10.8473-1.3994-0.2791)*500
=27176.75

HAFNIUM

a_0 = $(S_1+S_2+S_3+S_4+S_5+S_6+S_7+S_8)/8$
= 30314.6
a_1 = $(-S_1+S_2+S_3+S_4+S_5-S_6-S_7-S_8)/8$
= -29750
a_2 = $(-S_1-S_2+S_3+S_4-S_5+S_6+S_7-S_8)/8$
= -4214
a_3 = $(-S_1-S_2-S_3+S_4+S_5-S_6+S_7+S_8)/8$
= 696.05
a_4 = $(-S_1+S_2-S_3+S_4-S_5+S_6-S_7+S_8)/8$
= 665.55

a_5 $= (-S_1+S_2+S_3+S_4-S_5-S_6- S_7+S_8)/8$
$= 3948.35$
a_6 $= (S_1-S_2-S_3+S_4+S_5+S_6- S_7-S_8)/8$
$= -814$
a_7 $= (S_1+S_2-S_3+S_4-S_5-S_6+ S_7-S_8)/8$
$= -446.9$

Where

a_1 = Effect of Acid normality,
a_2 = Effect of no. of stages,
a_3 = Effect of no. of cycles,
a_4 = Effect of aqueous to organic ratio,
a_5 = Combined effect of Acid normality & No. of stages,
a_6 = Combined effect of Acid normality & No. of cycles,
a_7 = Combined effect of No of stages & No. of cycles,

EXPLANATION:

- ✓ Recovery of Hafnium in average experiment = 35175

a_0 = 30314.6

- ✓ **a_1**=-29750 is the effect of **acid normality**a_2 **= -4214 no. of stages, are NEGATIVE**
- ✓ **a_3= 696.05 No. of cycles, a_4= 665.55 organic: aqueous ratios are POSITIVE,** so they are directly proportional to the extraction.

STANDARD FORMULA

$Y=a_0+a_1.x_1+a_2.x_2+a_3.x_3+a_4.X_4+a_5.(X_1X_2)+a_6.(X_1X_3)+a_7.(X_2X_3)$

EXPERIMENT-1:
Y= 65604.25
EXPERIMENT-2
Y= 1166.85
EXPERIMENT-3
Y= 198.25
EXPERIMENT-4
Y= 399.65
EXPERIMENT-5
Y= 493.65
EXPERIMENT-6
Y= 51504.65
EXPERIMENT-7
Y= 52299.85
EXPERIMENT-8
Y= 70849.45

TITANIUM

a_0 $= (S_1+S_2+S_3+S_4+S_5+S_6+S_7+S_8)/8$
$= 2861$
a_1 $= (-S_1+S_2+S_3+S_4+S_5-S_6-S_7-S_8)/8$
$= -2707.6$
a_2 $= (-S_1-S_2+S_3+S_4-S_5+S_6+S_7-S_8)/8$
$= -17.59375$
a_3 $= (-S_1-S_2-S_3+S_4+S_5-S_6+S_7+S_8)/8$
$=56.04$
a_4 $= (-S_1+S_2-S_3+S_4-S_5+S_6-S_7+S_8)/8$
$= 126.33125$
a_5 $= (-S_1+S_2+S_3+S_4-S_5-S_6-S_7+S_8)/8$
$= 36.15625$
a_6 $= (S_1-S_2-S_3+S_4+S_5+S_6-S_7-S_8)/8$
$= 4.79375$
a_7 $= (S_1+S_2-S_3+S_4-S_5-S_6+S_7-S_8)/8$
$= -167.41875$

Where

a_1 = Effect of Acid normality,
a_2 = Effect of no. of stages,
a_3 = Effect of no. of cycles,
a_4 = Effect of aqueous to organic ratio,
a_5 = Combined effect of Acid normality & No. of stages,
a_6 = Combined effect of Acid normality & No. of cycles,
a_7 = Combined effect of No of stages & No. of cycles,

EXPLANATION:

- ✓ Recovery of Titanium in average experiment **= 3121**

a_0= 2861

a_1= -2707.6effect of **acid normality**, **a_2=-17.59375 effect of no. of stages, are NEGATIVE ,inversely proportional to the extraction.**

- ✓ **a3= 56.04 no. of cycles, a4=126.33125** Effect of **aqueous to organic ratio,**these values are **POSITIVE**,directly proportional to the extraction.

STANDARD FORMULA

$Y=a_0+a_1.x_1+a_2.x_2+a_3.x_3+a_4.X_4+a_5.(X_1X_2)+a_6.(X_1X_3)+a_7.(X_2X_3)$

EXPERIMENT-1
Y = 5280
EXPERIMENT-2
Y= 30.5
EXPERIMENT-3
Y = 149.8
EXPERIMENT-4
Y= 189.3
EXPERIMENT-5
Y= 234.35
EXPERIMENT-6
Y= 5760
EXPERIMENT-7
Y= 5275
EXPERIMENT-8
Y= 5970

IRON:

a_0 $= (S_1+S_2+S_3+S_4+S_5+S_6+S_7+S_8)/8$
$= 5008.94375$
a_1 $= (-S_1+S_2+S_3+S_4+S_5-S_6-S_7-S_8)/8$
$= -3208.55625$
a_2 $= (-S_1-S_2+S_3+S_4-S_5+S_6+S_7-S_8)/8$
$= 343.80625$
a_3 $= (-S_1-S_2-S_3+S_4+S_5-S_6+S_7+S_8)/8$
$= 313.05625$
a_4 $= (-S_1+S_2-S_3+S_4-S_5+S_6-S_7+S_8)/8$
$= -132.80625$
a_5 $= (-S_1+S_2+S_3+S_4-S_5-S_6-S_7+S_8)/8$
$= 241.30625$
a_6 $= (S_1-S_2-S_3+S_4+S_5+S_6-S_7-S_8)/8$
$= 260.55625$
a_7 $= (S_1+S_2-S_3+S_4-S_5-S_6+S_7-S_8)/8$
$= -425.30625$

Where
a_1 = Effect of Acid normality,
a_2 = Effect of no. of stages,
a_3 = Effect of no. of cycles,
a_4 = Effect of aqueous to organic ratio,
a_5 = Combined effect of Acid normality & No. of stages,
a_6 = Combined effect of Acid normality & No. of cycles,
a_7 = Combined effect of No of stages & No. of cycles,

EXPLANATION:

- ✓ Recovery of Ironin average experiment = 4850

  a_0= 5008.94375

- ✓ **a_1=-3208.55625**effect of **acid normality, a_2=343.80625,** effect of **no. of stages**, **a_3=313.05625, no.of cycles,** these values are **POSITIVE**, directly proportional to the extraction.
- ✓ **a $_4$=-132.80625**effect of**organic to aqueous ratio**, this value is **NEGATIVE** so it is inversely proportional to the extraction.

STANDARD FORMULA

$Y=a_0+a_1.x_1+a_2.x_2+a_3.x_3+a_4.X_4+a_5.(X_1X_2)+a_6.(X_1X_3)+a_7.(X_2X_3)$

EXPERIMENT-1

Y= 7770

EXPERIMENT-2

Y=83.55

EXPERIMENT-3

Y = 2370

EXPERIMENT-4

Y= 2401

EXPERIMENT-5

Y= 2347

EXPERIMENT-6

Y= 8560

EXPERIMENT-7

Y= 8080

EXPERIMENT-8

Y = 8460

Photos : SLURRY EXTRACTOR :

VIII. CONCLUSION

1) By using the eight number matrix experimental set up, we can get the influence of individual and combined parameters,and if the same effect is to be known in a wide range the number of experiments would have crossed hundred.
2) By this mathematical design; we can get optimum values of parameters to get the individual recovery.
3) We can also get the values of recoveries at different parameters without actually performing the experiments.
4) It can be observed that, from the equation theoretically calculated mean values coincide with the experimental values for Hafnium, Titanium and Iron, but there exists difference in the experimental values of Zirconium. This difference in the values for zirconium is because; Zirconium generally has a tendency to stay in the solvent.
5) We observed that the values of $a_0,a_1,a_2,a_3,a_4,a_5,a_6,a_7$ whether positive or negative will show a simultaneous effect on the parameters which were taken into consideration earlier, which implies, the higher and positive values of the parameters, better is the recovery of metals, whereas lower and negative the values of the parameters so is the inverse effect.
6) More the number of stages and more number of cycles, more the organic and aqueous ratio then better will be the recovery of zirconium.
7) Higher the normality of raffinate less will be the recovery of Zirconium.

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