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Extraction Chromatography and Fractional Precipitation Procedures for Production Various Zirconium Grades for Industrial and Nuclear Interest from Egyptian Zircon Ore

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ABSTRACT

The present study describes purification of zirconium from hafnium from the Egyptian zircon ore, by selective leaching, successive precipitations and two analytical techniques. The obtained results indicated that three fractions of Zr-concentrates were obtained by selective precipitation of the leached solution, namely: PPt-A, PPt-B and PPt-C. In the precipitation process, the PPt-B fraction, Zr exists with actinides (U and Th) and less than 0.002% of the original hafnium in the mother solution. This zirconium fraction, PPt-B, was further purified by fractional precipitation or anion exchange chromatography. The purity of Zr obtained by both methods reached 99%. Meanwhile, recoveries were varied between 64% by fractional precipitation and 95% by anion exchange chromatography. The ratio of Hafnium to zirconium was 24×10^{-3} in original Egyptian zircon concentrate. This ratio decreased to 17×10^{-3} , 2.17×10^{-3} , and 3.52×10^{-3} for PPt-A, PPt-B and PPt-C fractions respectively. Further decrease in ratio of hafnium to zirconium to 0.18×10^{-3} and 0.15×10^{-3} occurred for anion exchange chromatography and fractional precipitation techniques.

1. INTRODUCTION

Zirconium (Zr) has a concentration of ~ 130 mg/kg within the Earth's crust and ~ 0.026 $\mu\text{g/L}$ in sea water [1]. The main mineral sources of Zr are zircon (ZrSiO_4) and baddelyite (ZrO_2) [2], which are found primarily in Australia, Brazil, India, Russia, South Africa and the United States as well as in smaller deposits around the world. In Egypt, zircon occurs as a main constituent of beach sands along with ilmenite and monazite. This mineral is a main source for zirconium important raw material for producing metallic Zr, its alloys, and compounds [3-5].

Domestically, the major end uses of the mineral zircon are in refractories, foundry sands, and ceramic industry [6]. Zircon is also marketed as a natural gemstone, and its oxide is processed to produce cubic zirconia, a diamond, and colored gemstone simulant. Zircon has been identified as a potentially useful material for the production of thermo luminescence (TL) dosimeters. In addition, zircon finds application in the glass and iron

industry, in abrasives and in the manufacture of Zr chemicals as well as in ceramics [7]. In Nuclear technology, zirconium and its alloy play a main role in uranium fuel clade materials as well as equipment used in reprocessing of spent nuclear fuel. Uranium used for such purposes should be almost free from hafnium. This is due to the high neutron absorption cross section of Hf which affect the efficiency of the neutron flux of nuclear reactors. Further, zircon is proposed as a host phase for the disposal of radioactive actinides such as weapon grade plutonium [8-13], due to its high chemical durability.

The hydrometallurgical methods used for processing of zircon concentrate include fusion with caustic soda with the formation of acid soluble zirconate, sintering with lime or chalk and formation of calcium zirconate [14]. Thermal dissociation by plasma are used for the production of technical and pure grade ZrO_2 in addition to the chlorination of a mixture of zircon and carbon to produce ZrCl_4 and become the most popular method for producing ZrCl_4 [15].

Egyptian zircon concentrate was analyzed by Attallah et al. [16], they found that, Egyptian zircon concentrate contains mainly 57.26% zirconium, 1.42% hafnium, and traces of rare earth elements (REEs) together with traces of uranium and thorium, **Table .1**. The activity concentration and associated radiological hazard indices of this concentrate due to the presence of natural radionuclides was also estimated and evaluated [17]. This mineral can be considered a good candidate for chemical processing to produce different grades of zirconium provided that the different impurities are removed, specially hafnium which is around 1.42% in Egyptian zircon concentrate [16].

Within these merits, the present work is conducted for separation of various high grades of Zr-concentrates solutions with low hafnium concentration from the Egyptian zircon concentrate. To attain this goal, some chemical procedures based on selective fractional precipitation and anion exchange chromatography are investigated.

2. EXPERIMENTAL

2.1 Samples

The zircon ore was provided by the Egyptian nuclear materials authority. The zircon concentrate samples were separated from the black sand deposits on the Rosetta beach (N:31°24'16", E:30°24'59"), Elbehaira Gov., Egypt. Before use, the zircon sample was dried, homogenized and sieved to grain size <0.05 mm.

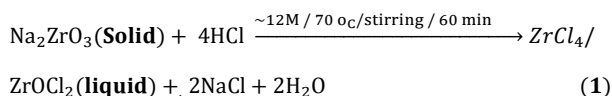
2.2 Chemicals and Reagents

All chemicals used were of high analytical grade with purity > 99%, which used without further purifications. The working solutions were prepared using double distilled water (DDW). The ion exchange resin used herein was Dowex-1×2 resin (50-100 mesh, Chloride form) provided by the Dow Chemical Company (Michigan, USA).

2.3 Digestion of Egyptian Zircon

The zircon concentrate sample was digested by caustic method using NaOH pellets (1:1.25) by weight, 1 Kg zircon concentrate with 1.25 Kg sodium hydroxide. The mixture was homogenized in a 2 liters stainless-steel container and fed into an electric furnace where the fusion reaction took place at 650 °C and continued for 2 hours [18]. The fused product was washed with 4-folds of its weight with hot DDW. The mixture was mechanically stirred for 2 hours to dissolve sodium silicate (Na₂SiO₃). The remained hydrolyzed sodium zirconate (Na₂ZrO₃) was separated from the sodium silicates by decantation.

The residual is dried and leached with 2-folds of its weight of hot conc. HCl at 70 °C with stirring to produce Zr-tetrachloride (ZrCl₄) and/or Zr-oxy-chloride (ZrOCl₂) mixture as simplified by the following chemical equation [18]:



After complete dissolution of the cake of the obtained, the zirconium chloride liquor (ZrCl₄ and ZrOCl₂), leach liquor, was filtered off to remove the dissolved matters and analyzed.

2.4 Selective Precipitation of Zr Fractions

The clear chloride liquor containing hydrolyzed ZrCl₄ / ZrOCl₂ mixture together with dissolved zircon impurities, was used for the selective successive precipitation steps at different three pH's values of 2.5, 5.0 and 9.0 to produce three fractions of zirconium concentrates, namely: PPt-A, PPt-B and PPt-C, respectively. In this concern, the initial chloride liquor was stirred and slowly neutralized using drops of ammonia solution (26%) till pH 2.5. The mixture was stirred for 15 minutes, then, left overnight for aging. The precipitated zircon filtered and separated to give PPt-A fraction. The filtrate was stirred and neutralized again to pH 5.0 to produce zirconium of fraction PPt-B. After filtration, the filtrate was neutralized to pH 9.0 to produce zirconium of PPt-C fraction. The formed precipitates were separated by centrifugation (15 min, 4000 rpm) and washed twice using DDW. The different precipitate materials of Zr fractions were dried in an oven at 110±2 °C for 24 hours, cooled at room temperature; grinded and homogenized in manual porcelain mortar to fine particle sizes less than 0.1 mm.

Analysis of different precipitates indicated that fraction of PPt-B contains the least amount of hafnium, as seen in Table 2, it was chosen for further purification. On the other hand, Zr concentrate in PPt-D grade was produced from the PPt-B fraction by the fractional precipitation at pH 3.0.

2.5 Purification of Zr from Fraction PPt-B

Removal of minor actinides and REEs associated with Zr in PPt-B fraction was done by column anion chromatography and fractional precipitation procedures. The anion exchange chromatography was carried out by using a glass column (6×100 mm, ended by glass wool) and packed with the strongly basic anion exchange resin (Dowex[®]-1X2, 50-100 mesh, Cl⁻ form).

The resin length in the column was adjusted at 10 mm, washed by DDW and conditioned by 50 ml 9.0 M HCl with constant flow rate of 1.0 ml/min. Solution of Zr-concentrate was prepared by dissolving 0.5 g of PPT-B fraction in concentrated HCl with stirring and heating for 15 minutes. The solution was diluted by DDW till 25.0 mL. Before loading into the column resin, the elemental analysis of this solution by the ICP-OES was reported, Table 3. The solution was homogenized, then, 1.0 mL of this liquor is loaded onto the pre-conditioned column. To learn about re-distribution of the metals associated with Zr in the PPT-B fraction, column bed was sequentially washed with 50 mL of 9.0M HCl.

Fractional precipitation of 5.0 mL of the prepared leach liquor of PPT-B fraction was again diluted by DDW to about 50 mL using DDW. The solution is heated at 65 °C with stirring and neutralized using diluted ammonia solution till pH 3.0. The turbid solution was stirred for 10 minutes and left overnight. Then, a precipitate of PPT-D fraction was separated by centrifugation, washed twice DDW and re-dissolved in 9.0M HCl for elemental analysis by ICP-OES.

2.6. Elemental Analysis

Concentration of the major, minor and trace constituents in the different solid materials included original zircon concentrate and Zr-concentrates (PPT-A, PPT-B and PPT-C fractions) were identified and quantified non-destructively by the X-ray fluorescence technique (Philipps-2400, Netherlands). Moreover, the concentration of the metal in aqueous samples was determined by high dispersion prism inductively coupled plasma optical emission spectrometry (ICP-OES). The instrument was provided from the Teledyne Technologies Company (USA) and calibrated using certified reference solutions [19].

3. RESULTS AND DISCUSSION

3.1 Chemical Analysis of Zircon Concentrate

The XRF measurement exhibits presence of three categories included major, minor and trace constituents in zircon concentrate, **Table 1**. It is revealed that, zirconium, silica and hafnium represent the main constituents in the zircon concentrate, with concentration percent of 57.26, 21.35 and 1.42%, respectively. As a minor concentration, the elements Ti, Ca, Fe and Al are present with a concentration between 0.1% and below 0.3%. Moreover, trace amounts of REEs, U, Th, and Mn are found within the concentration below 0.1%.

Table (1): Main chemical composition of the Egyptian zircon concentrate measured by the X-ray fluorescence [16].

i) Major constituents (>1%)		ii) Minor constituents (>0.1%)		iii) Trace constituents (>0.01) ¹	
Metal	Concentration, %	Metal	Concentration, %	Metal	Concentration, %
Zr	57.26	Ti	0.26	REEs	0.094
Si	21.35	Ca	0.20	U	0.034
Hf	1.42	Fe	0.14	Th	0.022
--	--	Al	0.13	Mn	0.020

¹: Concentrations of Na and K were less than 0.01

3.2 Fractionation of Zr in Zircon Concentrate

As mentioned in the experimental and after caustic digestion, the chemical compositions of the zircon concentrate together with that of the three fractions obtained are given in **Table 2**.

In this respect, fraction PPT-A of Zr-concentrated was obtained initially in acidic solution at pH 2.5, the second fraction PPT-B was formed in slight acidic solution at pH 5.0. The third fraction of PPT-C was produced in alkaline solution at pH 9.0. It is observed that, Zr in Egyptian zircon concentrate was redistributed between the three fractions obtained, depending on hydrogen ion concentration. In **Table 2**, the chemical analysis of the three different precipitated fractions at pH's 2.5, 5.0, and 9.0 together with that of zircon chloride sample are given. Zirconium concentrations obtained in the different fractions can be mostly attributed to loss of Si as soluble sodium silicates [20]. Moreover, some of the remained silica was also lost as volatile silicon tetrachloride (SiCl₄, b.p. 56.7 °C) [20-22].

Chemical analysis of PPT-A obtained at pH 2.5 as compared to the original composition of zircon solution indicated that zirconium concentration in PPT-A decreased to 54.1% compared to 57.26% in the original zircon matrix. This indicates that more than 94% of zirconium is precipitated at pH 2.5. This can be supported by the speciation diagram, was calculated and represented in **Fig.1**, obtained by the computer programs HYDRA and MEDUSA [23].

At this hydrogen ion concentration, zirconium is mainly hydrolyzed with the formation of ZrO₂ as given simply by Eq. 2. At pH 2.3, hafnium is less hydrolyzed than zirconium, **Fig. 2**. This was reflected by the release of about 33% of Hf in the filtered solution and bring only about 66% of Hf to precipitate.

Table (2): Comparison for the chemical composition of original zircon concentrate and the obtained concentrates in (PpT-A, PpT-B, PpT-C fractions) at different pH values.

Element	Concentrations						
	Original Zircon concentrate solution	PpT-A, pH = 2.5	Precipitation, %	PpT-B, pH = 5.0	Precipitation, %	PpT-C, pH = 9.0	Precipitation, %
Zr(IV)	57.26 %	54.100 %	94.4	1.29 %	2.3	0.71 %	1.24
Hf(IV)	1.42 %	9360 ppm	66	28 ppm	1.9x10 ⁻³	25 ppm	1.7x10 ⁻³
Ti(IV)	0.25 %	1090 ppm	4.3	2 ppm	8x10 ⁻⁴	1 ppm	4x10 ⁻⁴
Actinides ¹	560 ppm	ND ²	0	490 ppm	87.5	ND ²	0
REEs	720 ppm	ND ²	0	ND ²	0	490	68
Fe(III)	1400 ppm	810 ppm	58	280 ppm	20	20	1.4
Si	21.35 %	0.82 %	3.8	0.45 %	2	ND ²	0
Ca	0.2 %	ND ²	0	580 ppm	29	290 ppm	14.5
Total purity of Zirconium		96.5%		68.6%		89.5%	

¹: U, Th.

²: Not Detected.

At pH 5.0 and 9.0 around 2.3 and 1.24 % of zirconium is precipitated, respectively. From this information, PpT-B fraction contain minimum amount of hafnium representing 1.9x10⁻³% of hafnium in the original leach solution. This fraction was taken for further purifications.

However, each fraction has specific characteristics differ than the others. It is clear that separation of different amounts of Zr, Ti, and Hf can be based on the formation of very insoluble hydrolyzed metal (IV) hydroxide/oxide compounds of these metal ions. It is reported that solubility product of these tetravalent ions follow the sequence of the K_{sp} values. In this concern, the solubility product (K_{sp}) of $ZrO(OH)_2$, 6.3×10^{-49} is much lower than that of titanium as $TiO(OH)_2$, 1.0×10^{-29} and that of hafnium as $Hf(OH)_4$, 4.0×10^{-26} [20].

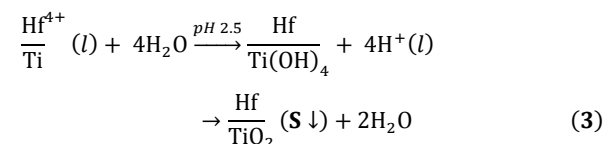
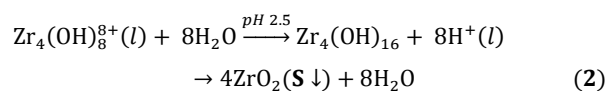
To explain the different compositions of the different precipitated fraction, the speciation diagrams of the metal ions if interest where displayed in figures 1-4.

This agrees with speciation diagrams for Zr, Ti and Hf at the studied conditions of pH and chloride medium depicted in Fig. 2 [23].

This indicates that recovery of the metals is largely dependent on its concentration and solution acidity. For instance, at pH 2.5, the PpT-A fraction is produced as a result of conversion of the soluble cationic species of zirconium as different hydrolysed polymeric products such as $Zr_4(OH)_8^{8+} > Zr_3(OH)_5^{7+} > ZrOH^{3+}$. For hafnium as $Hf^{4+} > HfOH^{3+} > Hf(OH)_2^{2+}$, while for titanium the

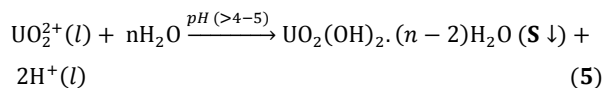
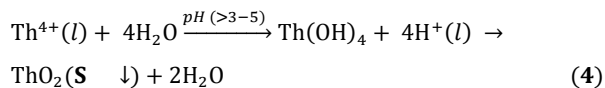
species $Ti^{4+} > TiO^{2+} > TiO(OH)^+$ into an insoluble metal hydroxide. Then, the formed metal hydroxides are hydrolyzed finally to the corresponded hydrolyzed metal oxide (e.g., ZrO_2 , HfO_2 and TiO_2) as simply represented in equations 2 and 3. Iron was interfered with Zr in all fractions of Zr-concentrates (A-C).

Calcium was not detected in PpT-A, while it was appeared in PpT-B and PpT-C fractions. In contrast, actinides such as U(VI) and Th(IV), and REEs are not detected in PpT-A fraction, since they are still soluble at pH 2.5 till pH 4.5, Fig. 2. Thus, Zr and its analogue elements Ti and Hf in PpT-A fraction is selectively formed without uranium, thorium, or REEs according to the following [18];



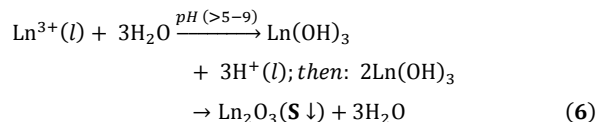
At the pH 5.0, the PpT-B fraction was formed and contain mostly Zr and its analogues as $Zr \gg Hf > Ti$, Table 2. Also, actinide species of U and Th are precipitated as $UO_2(OH)_2 \cdot H_2O$ and ThO_2 (Eqs. 4 and 5), respectively. Moreover, some of the Fe is co-precipitated after pH 1.0 as $10Fe(OH)_{27}Cl_3$ [24], meanwhile some of Ca existing in this concentrate due to sorption process

onto the formed hydrolyzed metal oxides at pH 5.0 remained soluble, **Fig. 4**. In contrast, metal ions of the REEs as Y or La remained soluble in leach solution at pH 5.0, **Fig. 3**.



In PPt-C fraction precipitated from the alkaline solution at pH 9.0, mainly constitutes of Zr and its homologue elements Ti and Hf. Moreover, REEs and

residues of Fe and Ca are co-precipitated as metal oxides. The trivalent REEs as Ln(III), Y(III), or La(III) are beginning to be precipitate at pH > 5 (Eq. 7). This agrees with speciation diagrams designated in **Figs. 3, 4**.



As seen above, the tetravalent zirconium in Zr-concentrate in PPt-B fraction formed at pH 5.0 exists with its homologues, i.e., Ti^{4+} and Hf^{4+} , actinide elements, i.e., UO_2^{2+} and Th^{4+} , interfering metal ions as Fe^{3+} and Ca^{2+}

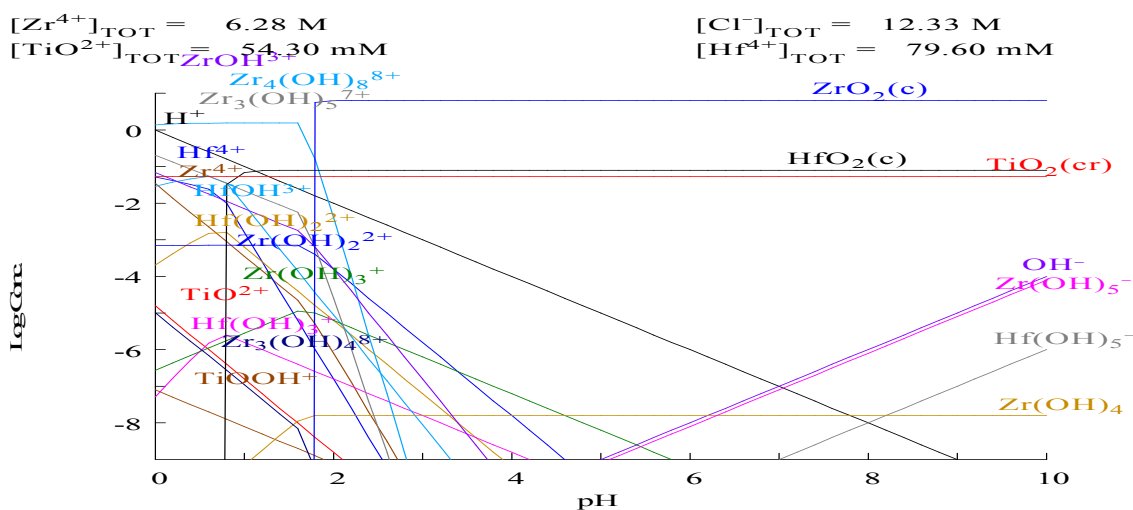


Fig. (1): Speciation diagram of Zr(IV), Ti(IV) and Hf(IV) in chloride liquor within pH range 0-10, calculated by Hydra/Medusa.

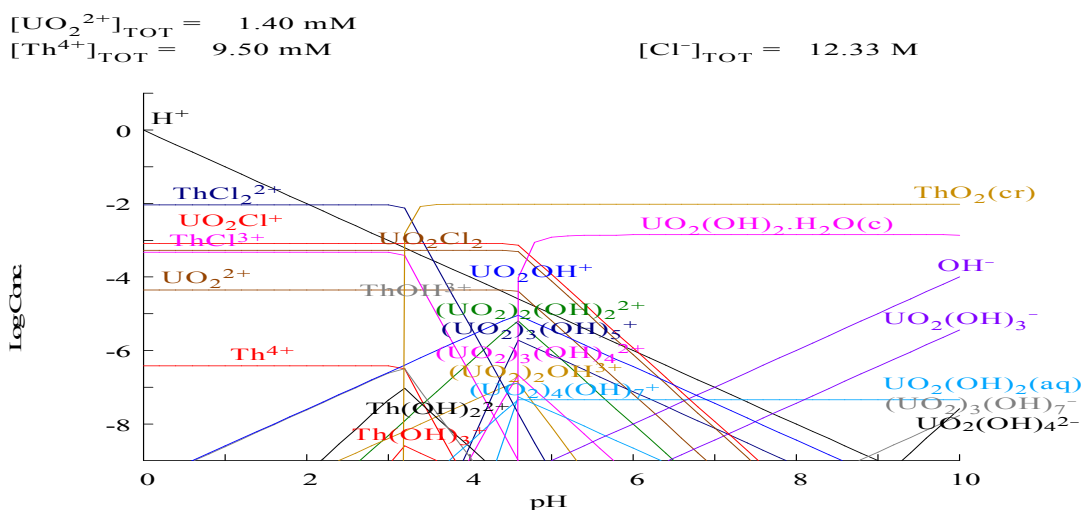


Fig. (2): Speciation diagram of U(VI) and Th(IV) in chloride liquor within pH range 0-10, calculated by Hydra/Medusa.

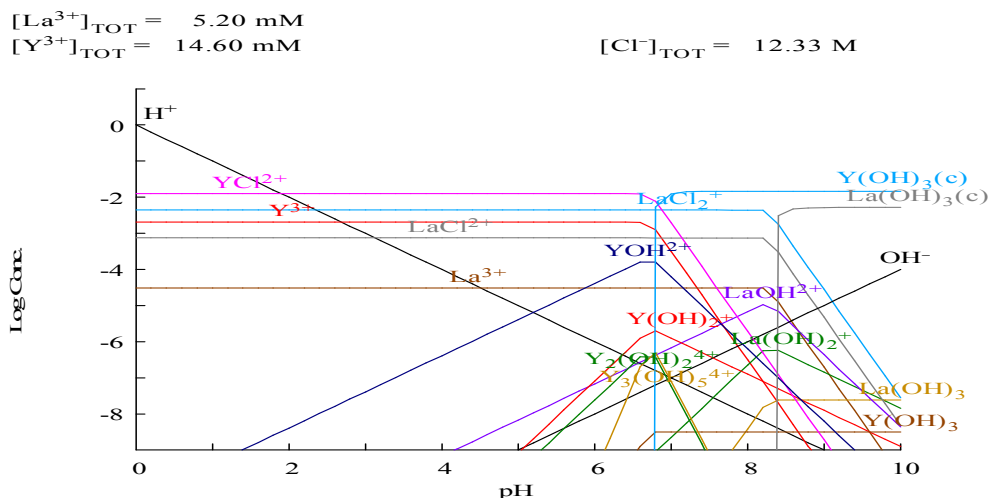


Fig. (3): Speciation diagram of La(III) and Y(III) in chloride liquor within pH range 0-10, calculated by Hydra/Medusa.

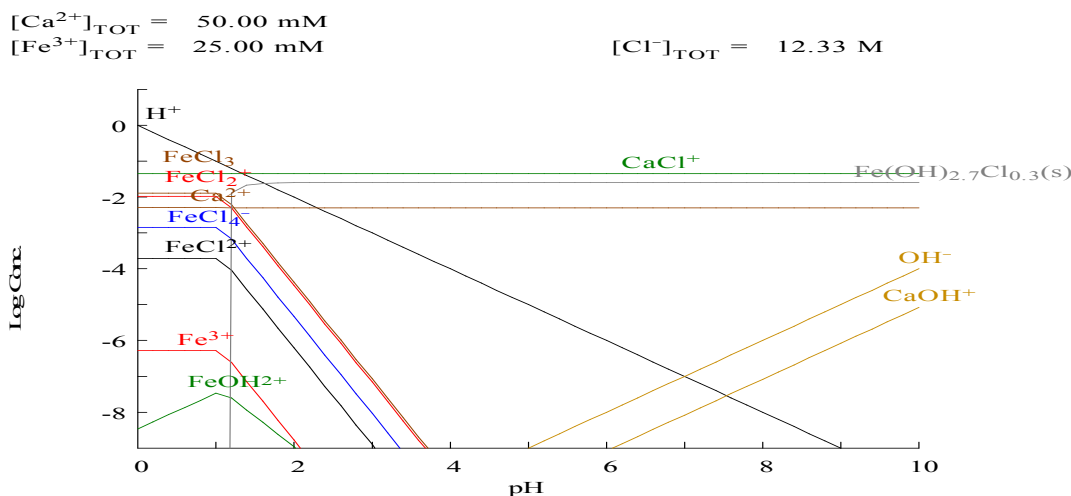


Fig. (4): Speciation diagram of Ca(II) and Fe(III) in chloride liquor within pH range 0-10, calculated by Hydra/Medusa.

Due to the nuclear interest of zirconium and its homologous, e.g., Ti(IV) and Hf(IV), and actinide, e.g. Th(IV); the next section discusses two analytical routes to purify and enhance Zr as possible, as given in the following section.

3.3 Purification of Zr from PPT-B fraction

3.3.1 Anion Exchange Chromatography

To eliminate the non-desired elements associated with Zr(IV) specially Hf from PPT-B fraction, anion exchange chromatography using Dowex-1 \times 2 resin is employed. It is observed that 50 ml 9.0 M HCl is efficient to elute Zr from the interfering metal ions. As given in **Table 3**, the anion exchange resin showed a good redistribution for metal admixture loaded onto the column resin. However, 2685 ppm of Zr was eluted while the amount of all other metals interfered with Zr

was below 2 ppm. Also, recovery of Zr relative to the loaded amount was high and reached to ~95%. Thus, 50 ml 9.0M HCl solution can be considered as an efficient and promising eluent for recovery of ~95% of Zr loaded onto the column resin. However, Zr concentration in the eluted HCl fraction represents 99.9%, while the total interfered metals with Zr loaded onto the column resin were insignificant with concentration value below 0.1%. Furthermore, the extraction chromatography (Dowex-1 \times 2) used herein is comparable with that used for separation of Zr in allanite sample contain Th(IV) and U(VI) [25].

3.3.2 Fractional Precipitation

Separation by fractional precipitation is generally faster and more efficient than other methods. It is known that Zr(OH)₄ hydroxide precipitates at a low pH than the

Hf(OH)₄. Therefore, Zr concentrates in the precipitate, leaving the Hf in solution [26]. The difference in the pH of precipitation is most marked in nitrate and chloride solution and the order of precipitation is reversed in sulfate solution [27]. In this study, concentrations of Zr and associated metals in PPt-B fraction have been distributed by the fractional precipitation at pH 3.0, **Table 4**. The precipitate obtained at pH 3.0 in PPt-D was largely enriched in zirconium than the corresponded filtrate. However, the concentration of Zr in PPt-D fraction was 2280 ppm, while the overall concentration of impurities does not exceed 3 ppm. Although, the concentration of Zr in the PPt-D was high, i.e., 99.9%, its recovery from the main PPt-D was low, i.e., 64%. This means that 36% of Zr was lost or remained soluble in the filtrate.

Now, it is necessary to construct a comparison between the analytical tools used therein to purify Zr in PPt-B concentrate. From the data of concentrations of Zr and the interfered metals detected in the eluted acid solution from the anionic column resin and PPt-D concentrate.

Table (3): Distribution of Zr and other metals in PPt-B grade by anion exchange chromatography method.

Element	Loaded solution ¹ , ppm	Eluted ² by 9M HCl, ppm	Effluent ³ , ppm
Zr	2830.4	2685.8	124.6
Hf	0.699	0.574	0.108
Ti	0.553	0.455	0.084
Actinides	0.924	0.711	0.134
Si	0.731	ND ⁴	0.620
Fe	0.257	0.076	0.151
Ca	0.692	0.100	0.485
Σ Total	2834.3	2687.7	126.2

¹:Loaded from 1ml leach solution, ²:Elution by 50ml 9M HCl, ³: washing by double distilled water, ⁴: not detected

Table (4): Distribution of Zr and other metals in PPt-B in chloride solution by fractional precipitation at pH 3.0.

Metal ion	Concentration, ppm		
	Before precipitation	PPt-D, pH =3.0	Filtrate
Zr	3562	2280	1082
Hf	0.61	0.394	0.116
Ti	0.529	0.365	0.104
Actinides	1.001	0.691	0.225
Si	1.268	0.735	0.433
Fe	0.154	0.148	0.037
Ca	0.5235	0.388	0.1155
Σ Total	/	2282.7	/

It is observed that Zr obtained by the both analytical tools have high purity, since Zr concentration 99.9%, while the other metals contribute less than 0.1%. However, recovery of Zr by the both methods were varied. The recoveries of Zr by anion exchange chromatography and fractional precipitation were ~95 and 64%, respectively. Thus, anion exchange chromatography is more efficient and promising analytical tool to purify Zr from its concentrates such as PPt-B, with a minor of interfering metal ions and without Si (**Table 3**).

Based on the obtained results, it is necessary to evaluate the progress in separation and concentration of Zr as a result of different chemical processes included conversion of zircon concentrate by alkali caustic method, dissolution in concentrated hot HCl, selective precipitations, and purification by anion exchange chromatography and fractional precipitation. From data, to measure the progress in the purity of Zr by the mentioned processes of the Zr % in zircon concentrate and all produced fractions and grades, it can be said that concentration of Zr% in PPt-B concentrate (~70%) is larger than its original concentration in zircon concentrate (~57.3%). Furthermore, Zr % was also enhanced and increased to high concentrations (~99%) when the PPt-B concentrate was again purified by anion exchange chromatography or fractional precipitation. To confirm purification of Zr in zircon and due to selective separation in PPt-B concentrate and after purification, the ratios between Hf and Zr have been calculated. It is clear that Hf/Zr ratio was 24×10^{-3} in original zircon concentrate, while it is decreased to 17×10^{-3} , 2.17×10^{-3} , and 3.52×10^{-3} for PPt-A, PPt-B and PPt-C fractions respectively.

After choosing the fraction of PPt-B to have the lowest Hf/Zr ratio for further refining. Further decrease in ratio of hafnium to zirconium to 0.18×10^{-3} and 0.15×10^{-3} occurred for anion exchange chromatography and in PPt-D by fractional precipitation at pH 3.0 respectively. This agrees with those reported by others [25,26].

Set-up of the experimental procedure is given in **Fig. 5**.

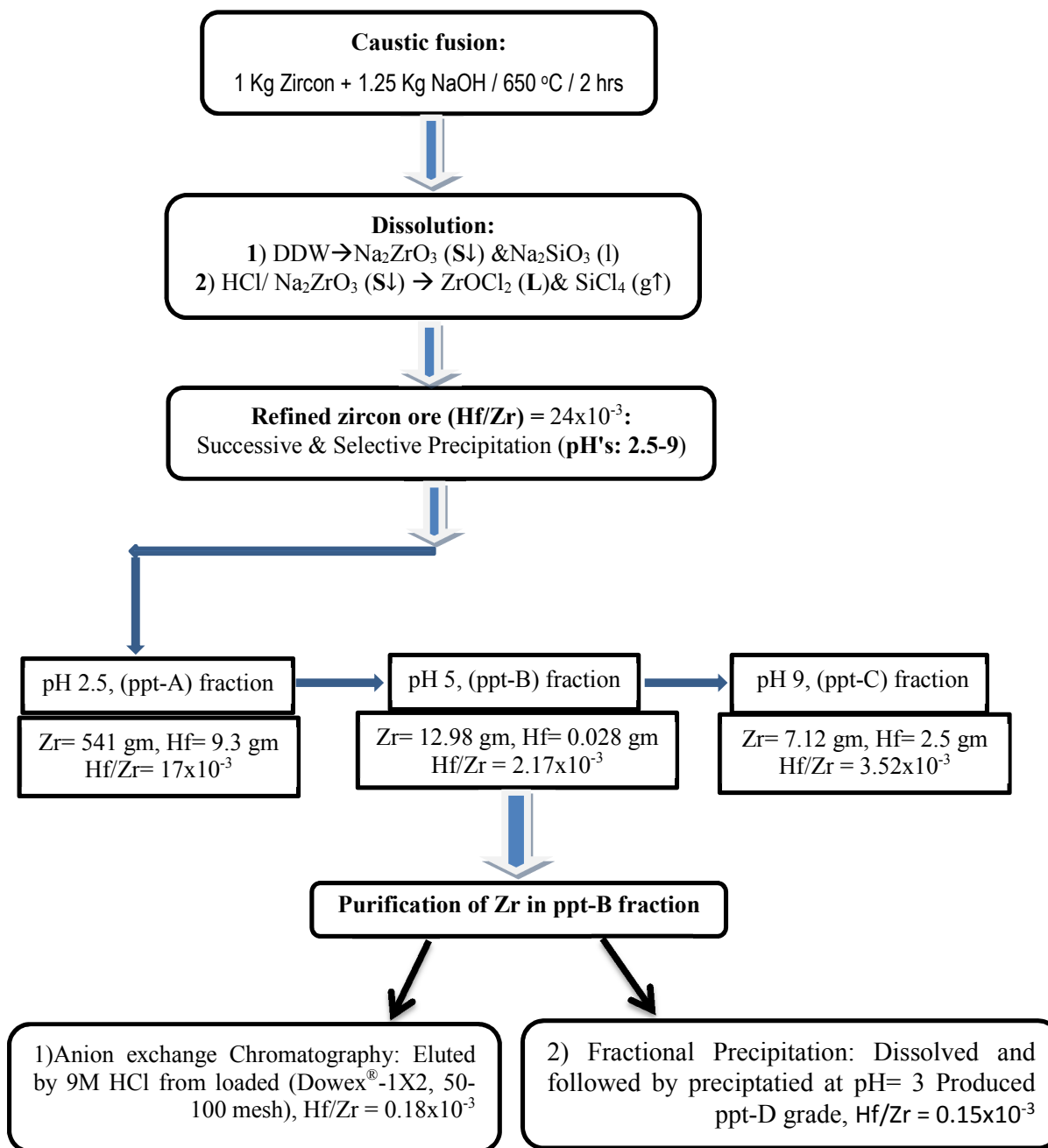


Fig. (5): Flowchart represents refined Zr and its homologues in the Egyptian zircon concentrate.

4. CONCLUSION

In this work, zirconium in zircon (~57.3%) was refined by caustic fusion and selective precipitation. It was purified by two analytical roots. It is summarized that ~98% of Zr was totally fractionated by selective precipitation in three different concentrates (PPt-A, PPt-B and PPt-C) with undesired impurities. Since Zr exists with actinides (U and Th), Zr was purified by anion

exchange chromatography and fractional precipitation. By both methods, Zr was separated with high purity reached to more than 99%. Meanwhile, recoveries were varied between 64% by fraction precipitation and 95% by anion exchange chromatography.

It is obvious that Hf/Zr ratio was $\sim 24 \times 10^{-3}$ in original zircon concentrate. The ratio in PPt-A became slightly decreased to 17×10^{-3} and clear widely decreased

to 2.17×10^{-3} and 3.52×10^{-3} PPt-B and PPt-C respectively. PPt-B fraction obtained by selective precipitation at pH 5.0. Furthermore, the Hf/Zr ratio is again decreased to 0.15×10^{-3} in PPt-D by fractional precipitation at pH 3.0. and to 0.18×10^{-3} in the PPt-B concentrate is purified using anion Exchange chromatography method.

It can be recommended that the anion exchange chromatography or fraction precipitation method are efficient for recovering and purifying Zr from its associated impurities. However, the efficiency for separation of total zirconium is rather limited.

For other non-nuclear purpose PPt-A and PPt-C fractions can be used with zirconium purity 96.5 and 89.5%, respectively but with a higher percent of hafnium.

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