



# Recovery of Zr from a leach solution of eudialyte residue using basic sulfate precipitation

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## Abstract

Following the initial hydrometallurgical extraction of rare earth elements from eudialyte concentrate, the residue was known to contain Zr, and H<sub>2</sub>SO<sub>4</sub> was ensured to be the best candidate for Zr leaching from the eudialyte residue. The resulting sulfate leach solution contained some common impurities such as Al<sup>3+</sup> and Fe<sup>3+</sup>. In this reported study, a selective precipitation method was investigated to recover Zr from the leach solution. The objective was to obtain Zr enriched precipitate with low impurities for further treatment. It was found that ordinary metal hydroxide precipitation was infeasible to obtain a relatively pure product due to the co-precipitation of Al<sup>3+</sup> and Fe<sup>3+</sup>, but precipitation by basic sulfate salt would be selective. After partial removal of SO<sub>4</sub><sup>2-</sup> through calcium sulfate precipitation, basic zirconium sulfate precipitate could be obtained using a suitable combination of parameters including time, temperature, pH. Zr and Hf loss during the SO<sub>4</sub><sup>2-</sup> removal step was only 0.11 %, and the yield in basic sulfate salts precipitation step was 96.18 % under optimum conditions. During the process, pH of the solution was maintained at low value so that Al<sup>3+</sup> and Fe<sup>3+</sup> remained in the leach solution. Finally, a product with high Zr content (33.77 %) was obtained with low amount of Al and Fe.

## 1 Introduction

Zirconium is widely used as a structural and container material of nuclear reactor due to its low thermal neutron capture cross-section and strong resistance to corrosion [1 – 2]. Zirconium is also an important alloying element in steel industry [3]. The major source of zirconium is zircon



(ZrSiO<sub>4</sub>), but it is highly stable, thus requiring extremely drastic conditions to be decomposed [4]. Eudialyte is a complex Na-Ca-zirconosilicate mineral that is generally rich in Fe, Al, Mn, Ti, K, Nb and contains attractive quantities of rare earth elements (REE) [5]. The typical empirical chemical formula for eudialyte is Na<sub>4</sub>(Ca, Ce, Fe)<sub>2</sub>ZrSi<sub>6</sub>O<sub>17</sub>(OH, Cl)<sub>2</sub>, but it displays a wide range of chemical compositions [6]. It is another source for zirconium. The content of Zr (5 – 10%) in eudialyte is much lower than that in zircon, but it can be decomposed by acid easily [6 – 7]. Another issue is that REE extraction from eudialyte sometimes takes priority as they have a higher value [8 – 9]. However, the residual Zr after REE extraction from eudialyte should not be overlooked if Zr has not been recovered simultaneously.

H<sub>2</sub>SO<sub>4</sub> is ensured to be the best candidate for Zr leaching from the eudialyte or eudialyte residue, but the leaching process is not selective so that there are many impurities like sodium, iron and aluminum in the resulting leach solution [10 – 11]. Few researches have studied the Zr recovery from the sulfate system with impurities [12].

Ionic precipitation can be defined as a process in which the metal ion is allowed to react with other compounds and form a product with low solubility, and precipitation method is widely used for selective recovery of metals or impurity removal in the hydrometallurgical processing. In this paper, the aqueous chemistry of zirconium was firstly studied to reveal the properties of the Zr-bearing sulfate leach solution. Then, zirconium basic sulfate salt precipitation was investigated to recover Zr from the solution, expecting to obtain a precipitate with low impurities for further treatment.

## 2 Experimental

### 2.1 Materials and Analysis

As a resource for REE in EURARE project, eudialyte ore was mined in South Greenland and eudialyte concentrate after beneficiation was the initial material for REE extraction. After REE extraction, the eudialyte residue was known to bear Zr, Hf and Nb. H<sub>2</sub>SO<sub>4</sub> had been used to leach Zr from the eudialyte residue, detailed description of leaching process was given in literature [10]. The resulting sulfate leach solution was the initial material used in this study, and the composition of the leach solution is shown in Table 1. The CaCl<sub>2</sub>, Na<sub>2</sub>CO<sub>3</sub> used were of analytical grade, and all aqueous solutions were prepared using distilled water.



Table 1: Chemical composition of the leach solution of eudialyte residue

Al	Fe	Zr	Hf	Nb	Si	Ca	SO <sub>4</sub> <sup>2-</sup>
g/L	g/L	g/L	mg/L	g/L	mg/L	g/L	g/L
15.75	2.99	19.1	357	1.15	< 5	1.1	112

The contents of elements in the solution were measured by inductively coupled plasma emission spectroscopy (ICP) with a PS-6 PLASMA SPECTROVAC, BAIRD (USA). The composition of the precipitate was determined by XRF analysis (X-ray fluorescence), Zr in the solid sample was analyzed by solution after dissolving.

## 2.2 Thermodynamic analysis and methods

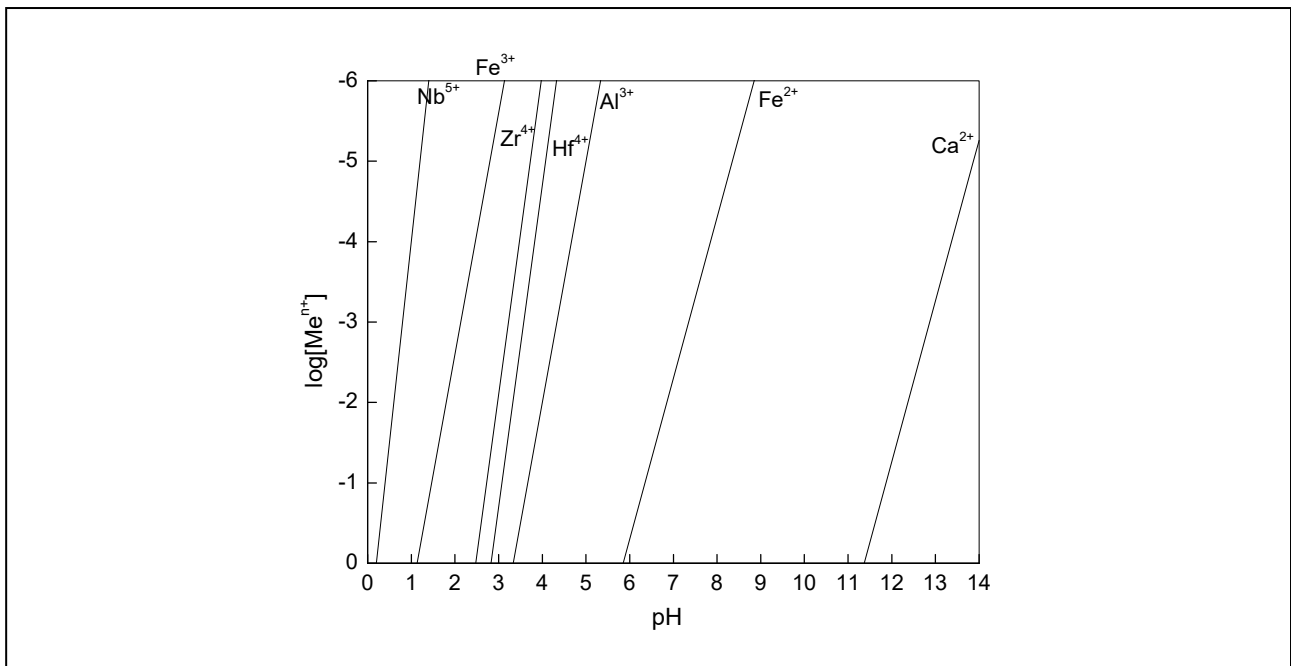


Figure 1: log[Me<sup>n+</sup>]-pH diagram based on the solubility product constants ( $K_{sp}$ ) of metals hydroxide at 298.15 K

The log[Me<sup>n+</sup>]-pH diagram based on the solubility product constants of metals hydroxide at 298.15 K is shown in Fig. 1. As shown, the pH range of hydrolysis of Zr<sup>4+</sup> is 2.5 – 3.5, between the pH ranges of hydrolysis of Fe<sup>3+</sup> and Al<sup>3+</sup>. Fig. 2 shows the E-pH diagram of Zr-SO<sub>4</sub><sup>2-</sup>-H<sub>2</sub>O at 298.15 K and low pH. As can be seen, the formation of complexes with SO<sub>4</sub><sup>2-</sup> can expand the stable region of dissolved Zr. It also increases the pH range for the hydrolysis of Zr<sup>4+</sup> to obtain zirconium hydroxide (Zr(OH)<sub>4</sub>), so precipitation of Zr via Zr(OH)<sub>4</sub> over Fe<sup>3+</sup> and Al<sup>3+</sup> cannot be achieved. The preliminary experiments verified that selective precipitation of Zr via Zr(OH)<sub>4</sub> was not feasible, obtain-



ing  $Zr(OH)_4$  when pH above 3.5 with much  $Fe(OH)_3$  and  $Al(OH)_3$ . Precipitation via zirconium basic sulfate ( $Zr_5O_8(SO_4)_2 \cdot x H_2O$ ) instead of  $Zr(OH)_4$  would be another choice. According to the literature [13 – 14], zirconium basic sulfate could be obtained when zirconium chloride solution was mixed with sulfuric acid solution at a certain temperature (60 – 90 °C) and pH (1.2 – 2) for a certain time with zirconium ( $Zr^{4+}$ ) to sulfate ( $SO_4^{2-}$ ) ratio of 5 : 2. For our solution, the excessive  $SO_4^{2-}$  should be removed firstly and then zirconium could selectively precipitate via zirconium basic sulfate at low pH without co-precipitation of  $Al^{3+}$  and  $Fe^{3+}$ . The flowchart of the process is shown in Fig. 3.

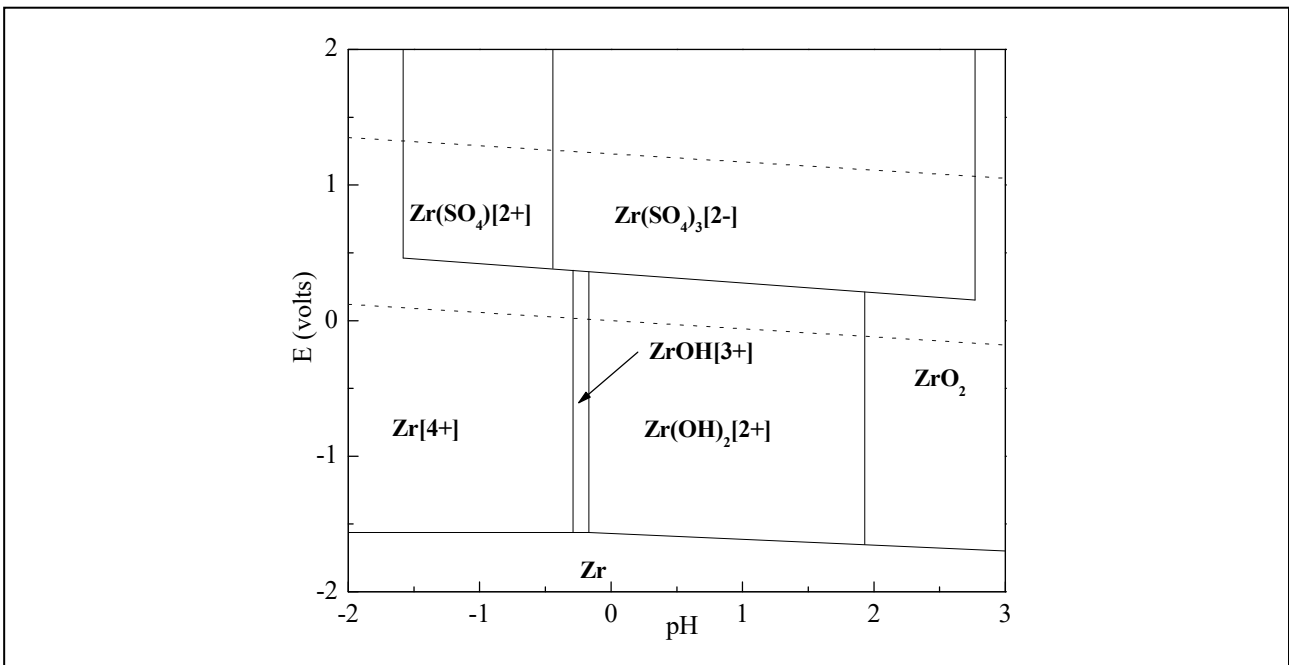


Figure 2: E-pH diagram of  $Zr-SO_4^{2-} H_2O$  at 298.15 K and low pH

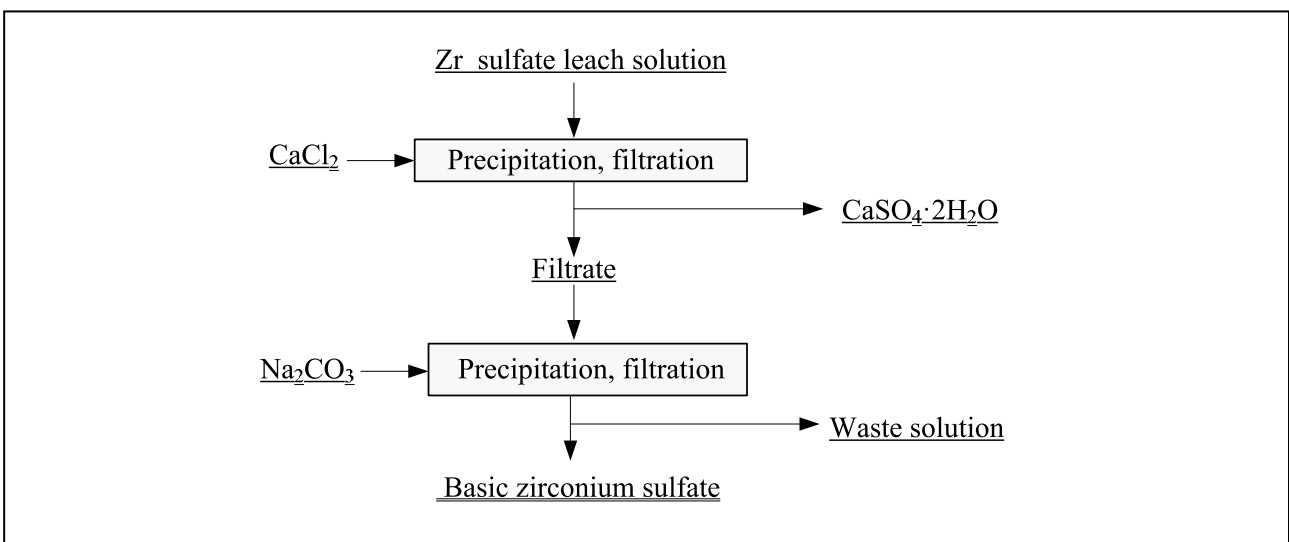


Figure 3: Proposed flowchart for recovery of Zr using a basic sulfate precipitation



### 3 Results and Discussion

The effects of different parameters such as the amount of  $\text{CaCl}_2$  for controlling  $\text{SO}_4^{2-}$ , temperature and time for basic sulfate precipitation were preciously studied and they were consistent with the conditions in literature. The optimum conditions were adding 120 g/L  $\text{CaCl}_2$  for  $\text{SO}_4^{2-}$  removal step, 75 °C, time 60 min, pH ~ 1.6 for Zr basic sulfate precipitation step. The Zr precipitation yield was 96.18 % under these conditions. Fig. 4 shows the effect of pH on the Zr precipitation yield. As seen, the Zr precipitation yield increased with an increase in pH from 1.2 to 1.6, then kept constant. However, if pH is increased above the value of 1.6, removal of main impurities such as Al and Fe became difficult due to co-precipitation.

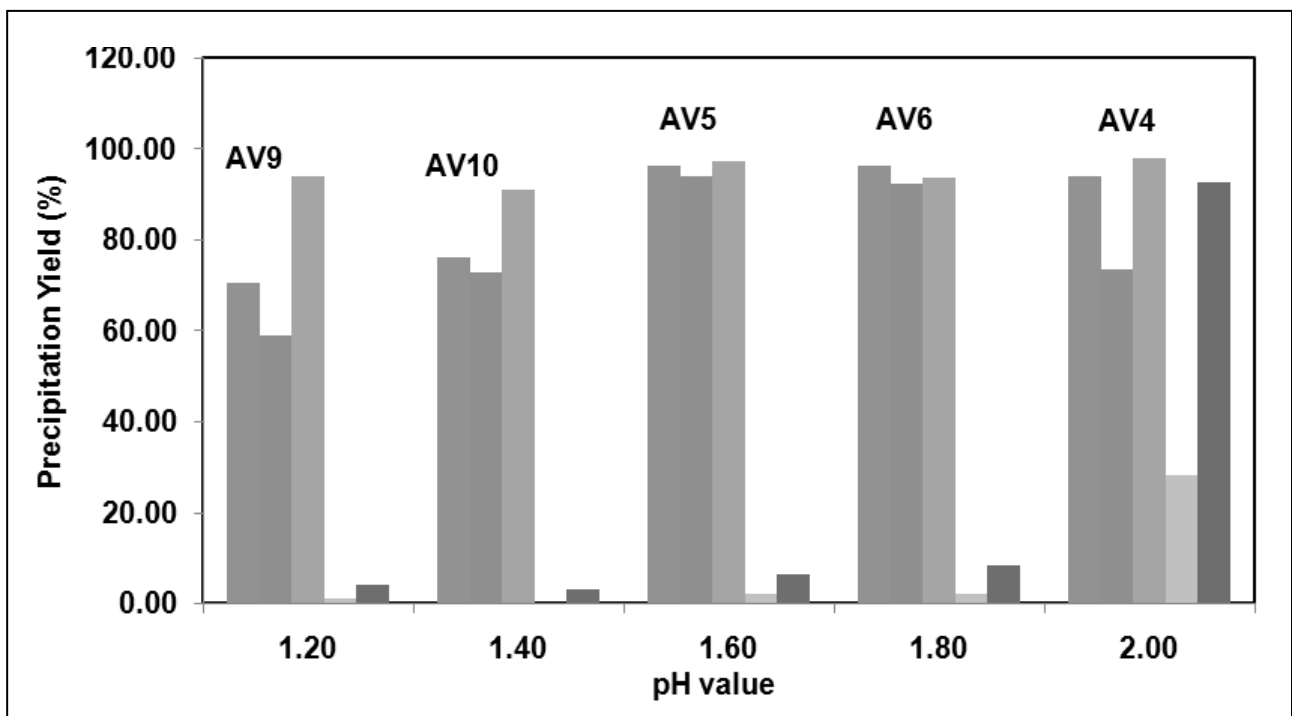


Figure 4: Effect of pH on the Zr precipitation yield

Table 2 shows the chemical composition of calcium sulfate precipitation by adding 120 g/L  $\text{CaCl}_2$ . The loss of Zr in the  $\text{SO}_4^{2-}$  removal step was low. After washing, the calcium sulfate could be a by-product.

Table 2: Chemical composition of calcium sulfate precipitation

Element	Al	Fe	Hf	Nb	Zr	Ca	O	S
Content [wt.-%]	0.09	0.10	0.05	0.08	0.11	23.26	55.7	19.1

Table 3 shows the chemical composition of the basic zirconium sulfate precipitation prepared under the optimum conditions. As can be seen, the content of iron and aluminium were very low. The Zr



basic sulfate prepared by this method was easily dissolved in acids, thus it could be transferred to conventional techniques to produce final product, like  $ZrOCl_2$  and  $ZrO_2$ .

Table 3: Chemical composition of the basic zirconium sulfate precipitation

Element	Al	Fe	Hf	Nb	Zr	Ca	O	S
Content [wt.-%]	0.33	0.11	0.59	1.94	33.77	6.28	31.30	10.30

## 4 Summary

In this reported study, zirconium basic sulfate precipitation from a leach solution of eudialyte residue, which achieved removal of aluminum and iron, was investigated. Thermodynamic analysis and experimental results showed that ordinary metal hydroxide precipitation was infeasible to obtain a relatively pure product due to the co-precipitation of  $Al^{3+}$  and  $Fe^{3+}$ . After partial removal of  $SO_4^{2-}$  by adding 120 g  $CaCl_2$  per 1 L solution, 96.18 % Zr precipitation yield was obtained by adjusting the pH to  $\sim 1.6$ , keeping at 75 °C for 60 min. The resulting precipitation contained 33.77 % Zr with low Fe and Al. There were few other impurities like Ca in the precipitation, further purification was necessary to get pure Zr product. Nevertheless, this method achieved removal of main impurities and enrichment of Zr from the sulfate leach solution.

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