

1 %Effect of Aqueous Media on Recovery of Scandium by Selective Precipitation (Article)

## 2 Effect of Aqueous Media on Recovery of Scandium 3 by Selective Precipitation

4 Bengi Yagmurlu<sup>1,2,\*</sup>, Carsten Dittrich<sup>1</sup> and Bernd Friedrich<sup>2</sup>

5 <sup>1</sup> MEAB Chemie Technik GmbH

6 <sup>2</sup> RWTH Aachen, IME Institute of Process Metallurgy and Metal Recycling

7 \* Correspondence: [bengi@meab-mx.com](mailto:bengi@meab-mx.com); Tel.: +49-1575/4954583

8 Received: date; Accepted: date; Published: date

9 **Abstract:** This research presents a novel precipitation method for scandium concentrate refining  
10 from bauxite residue leachates and the effect of aqueous media on this triple-stage successive  
11 precipitation process. The precipitation pattern and the precipitation behavior of the constituent  
12 elements was investigated using different precipitation agents in three major mineral acid media,  
13 H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub> and HCl in a comparative manner. Experimental investigations showed that there are  
14 behavioral similarities between HNO<sub>3</sub> and HCl media while H<sub>2</sub>SO<sub>4</sub> media differentiate from them  
15 because of its complex forming nature. NH<sub>4</sub>OH was found to be the best precipitation agent in every  
16 leaching media to remove Fe(III) with low Sc co-precipitation. To limit the Sc loss from the system,  
17 Fe(III) removal step was divided into two, reaching more than 90% Fe(III) removal in the final Fe-  
18 removal step. Phosphate concentrates are produced in the final step of the precipitation process with  
19 dibasic phosphates which have a strong affinity towards Sc. Concentrates containing more than 50%  
20 ScPO<sub>4</sub> were produced in each case from the solutions where Fe(III) was removed as described. The  
21 flow diagram of the selective precipitation process was proposed for these three mineral acid media  
22 with characteristic parameters.

23  
24 **Keywords:** bauxite residue; red mud; hydrometallurgy; recovery; scandium; precipitation  
25

---

### 26 27 1. Introduction

28 Recent agreements and climate accords in reducing carbon emission and specified deadlines for  
29 automotive industries has placed light metals and alloys under spotlight [1]. One of this reasons is  
30 due to the direct relation between vehicle weight and its energy consumption. Scandium (Sc) is used  
31 as a tuning metal especially for aluminum alloys making it one of the promising candidates for light-  
32 weight alloys [2]. It is, however, an extremely expensive element for widespread application in  
33 industrial usage at the moment [3]. As aluminum alloys with improved strength, thermal resistance  
34 and weldability can be achieved with minor additions of Sc, improved oxygen-ion conductivity can  
35 also be attained in solid-oxide fuel cells [4-6]. Hence, this metal was classified recently as a critical  
36 metal for future, owing to the steep increase in demand despite its price [7].

37 Unfortunately, Sc is widely dispersed in nature instead of a direct mineral and generally has to  
38 be extracted from secondary raw materials or as a by-product of uranium, nickel-laterite or titanium  
39 pigment processing. Bauxite residue (i.e. red mud) is the by-product obtained throughout the Bayer  
40 Process, having approximately four billion tones with previously reported 160 million tonnes annual  
41 production [8,9]. This alkaline waste can be considered as a valuable resource because of its metal  
42 content (Fe, Al, Ti, Sc, REEs, etc.). Therefore, complete or partial valorization of bauxite residue (BR)  
43 has been in the focus of great interest [10-13].

44 Previously, complete or partial recovery of Sc from bauxite residue was reported to be achieved  
45 mainly by solvent extraction, ion exchange or the combination of these two techniques as a result of  
46 the low concentration in the leachates [14-20]. Zhang et. al. recovered 91% of Sc from bauxite residue  
47 leachates by inorganic metal(IV) phosphate ion-exchangers, although Fe(III) found to be as an  
48 interfering ion in this process [20]. In another study, a newly developed supported ionic liquid phase  
49 (SILP) had almost complete Sc extraction, while having a decrease in efficiency in the presence of  
50 Fe(III) [14]. In all of these hydrometallurgical operations, co-extraction of Fe, Al and Ti became a  
51 problem and intensive purification was required to produce a high quality product.

52 In our previous work, a three-staged precipitation process was designed using a sulfuric acid  
53 media based on selective Fe removal step by  $\text{NH}_4\text{OH}$ , since Fe is the most problematic element during  
54 Sc processing [21,22]. This is successively followed by selective Sc phosphate precipitation by  
55  $(\text{NH}_4)_2\text{HPO}_4$ . As a result of this precipitation route, the Sc phosphate concentrate containing 65% Sc  
56 was synthesized from impure synthetic bauxite residue leach solutions. Nevertheless, the processing  
57 route must be tailored in a relation to the geological presence of the bauxite residue as a consequence  
58 of different mineralogy and association of the phases. Hence, different mineral acids other than  
59  $\text{H}_2\text{SO}_4$ , such as  $\text{HNO}_3$  and  $\text{HCl}$ , were also tried for leaching bauxite residue.

60 In order to cover wider range bauxite residues as well as other recoverable waste generating  
61 processes such as Ti-pigment and Ni laterite production, the design of selective Sc precipitation route  
62 for bauxite residue has to be flexed into different mineral acid media. Thus, this paper investigates  
63 the effect of aqueous media on the recovery of Sc by a selective precipitation method.  
64

## 65 2. Materials and Methods

66 Bauxite residue sample was obtained from Aluminium of Greece, subject to lithium borate  
67 fusion, and analyzed using ICP-MS/AAS, as shown in Table 1.  
68  
69  
70  
71  
72  
73

74

**Table 1.** Chemical composition of the bauxite residue

Major Compounds	wt. %	Minor Compounds	ppm
Fe	29.6	La	110
Al	8.6	Ce	380
Ca	8.3	Sc	120
Si	3.3	Nd	100
Ti	2.6	Y	80
Na	2.8		
Others	32.1		
LOI	12.7		

75

76 Synthetic leach solutions were prepared with a consideration of pre-treatments before the  
 77 selective precipitation route. This leachate is the expected pregnant leach solutions (PLS) after the  
 78 major part of Fe, Al and Ti are recovered from the solution by both pyrometallurgical and  
 79 hydrometallurgical methods. Hence, the synthetic solution mentioned in this study is the predictive  
 80 of the speciation of real PLS in cooperation with the linked studies. The Sc and REEs concentrations  
 81 were arranged to be higher than real PLS cases to observe the precipitation behaviors of those  
 82 elements clearly. Additionally, the selective precipitation process was also tested directly on the real  
 83 solutions which had similar results as it was observed in this study [21,23].

84 In addition to the major impurities present in bauxite residue (e.g. Fe and Al), Nd and Y are also  
 85 used as the representative elements of light and heavy group of REEs within the synthetic PLS, since  
 86 the sub-groups of REEs distinguishes similar chemical properties.

87 Synthetic solutions in chloride media were prepared by adding the required amount of reagent  
 88 grade  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{AlCl}_3$ ,  $\text{Sc}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$ . In a similar manner, reagent  
 89 grade  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ ,  $\text{Sc}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{NdCl}_3 \cdot 6\text{H}_2\text{O}$  and  $\text{YCl}_3 \cdot 6\text{H}_2\text{O}$  were used to  
 90 synthesize the solution in nitrate media. Sulfate and chloride salts were first precipitated as  
 91 hydroxides and washed before converting into necessary forms before addition to avoid unwanted  
 92 sulfate or chloride ions which can affect the precipitation yields with complex formations in the  
 93 aqueous solution. All precipitation solutions were prepared from reagent grade salts. The  
 94 concentrations of the precipitation agents were 12.5 wt.% for  $\text{CaCO}_3$  (limestone) slurry, 1 mol/L for  
 95  $\text{NaOH}$ ,  $\text{NH}_4\text{OH}$  and  $\text{KOH}$ , and 1mol/L for  $\text{K}_2\text{HPO}_4$ ,  $(\text{NH}_4)_2\text{HPO}_4$ ,  $\text{Na}_2\text{HPO}_4$ .

96 In order to have a comparative precipitation results, a composition similar to the one that is used  
 97 in sulfate media was chosen. The pH of both systems was set between 1.2-1.4 with the addition of the  
 98 necessary amounts of  $\text{HCl}$  or  $\text{HNO}_3$ . The composition of the synthetic solutions are presented in Table  
 99 2.

100

101

102

103

**Table 2.** Composition of the synthetic solutions in HNO<sub>3</sub> and HCl media

	Composition in HNO <sub>3</sub> media (mg/L)	Composition in HCl media (mg/L)
Al	340	348
Fe (III)	312	290
Sc	86	78
Y	108	96
Nd	101	105

104

105 The precipitation agents mentioned were carefully added using a precision burette into 50 mL  
106 of the synthetic PLS while monitoring pH and temperature. All experiments presented in this study  
107 were done at room temperature. For hydroxide precipitation; agents were added until the target pH  
108 was attained under mild agitation to reach homogeneity in the solution and to prevent local pH  
109 differences.

110 Precipitation solutions containing dibasic phosphates were prepared as 1 mol/L and added into  
111 the leach solutions starting with stoichiometric amount considering only scandium precipitation. In  
112 each step, the amount added was doubled until reaching 20 times of the stoichiometric amount.

113 The resulted suspension for each case is then stabilized and homogenized at a given pH and  
114 temperature for 2 hours and subsequently filtered through fine filter paper via suction filtration. The  
115 separated solid residue was washed with distilled water and dried at 110°C for 24h. Both filtered  
116 solutions and the solid residues were assayed.

117 The concentrations of the constituent ions of iron (Fe), aluminum (Al), scandium (Sc), yttrium  
118 (Y) and neodymium (Nd) were determined by microwave plasma optical emission spectroscopy  
119 (Agilent MP-AES 4100). Each sample was prepared by adding 100 µL of caesium ionization buffer  
120 and 500 µL of ultrapure concentrated HNO<sub>3</sub> to 10 mL of sampled solution. Quantitative analyses  
121 were performed at 371.993 nm, 396.152 nm, 361.383 nm, 371.029 nm and 430.358 nm spectral emission  
122 lines for Fe, Al, Sc, Y and Nd respectively.

123 The measurements for pH were performed using WTW ProfiLine pH 197 series pH-meter with  
124 Sentix 81 precision electrode. The pH meter was calibrated with standard technical buffering  
125 solutions at pH 2.00, 4.01 and 7.00 to achieve maximum sensitivity in pH measurements.

126

### 127 3. Results

128 We previously reported that more than 90% of the Fe can be removed with negligible amount of  
129 Sc loss from sulfuric acid based solutions by simply adding NH<sub>4</sub>OH in a dual-staged precipitation  
130 process [22]. Furthermore, with a successive precipitation route which combines both hydroxide  
131 precipitation route and phosphate precipitation route, a Sc phosphate concentrate which is easier to

132 process, can be synthesized from sulfate based aqueous solutions. Since Sc-containing liquors can  
133 also be exist in both chloride or nitrate media, the effect of those aqueous media on precipitation  
134 should also be investigated. By this way, the successive precipitation process can be adapted and  
135 flexed into other major mineral acid media.  
136

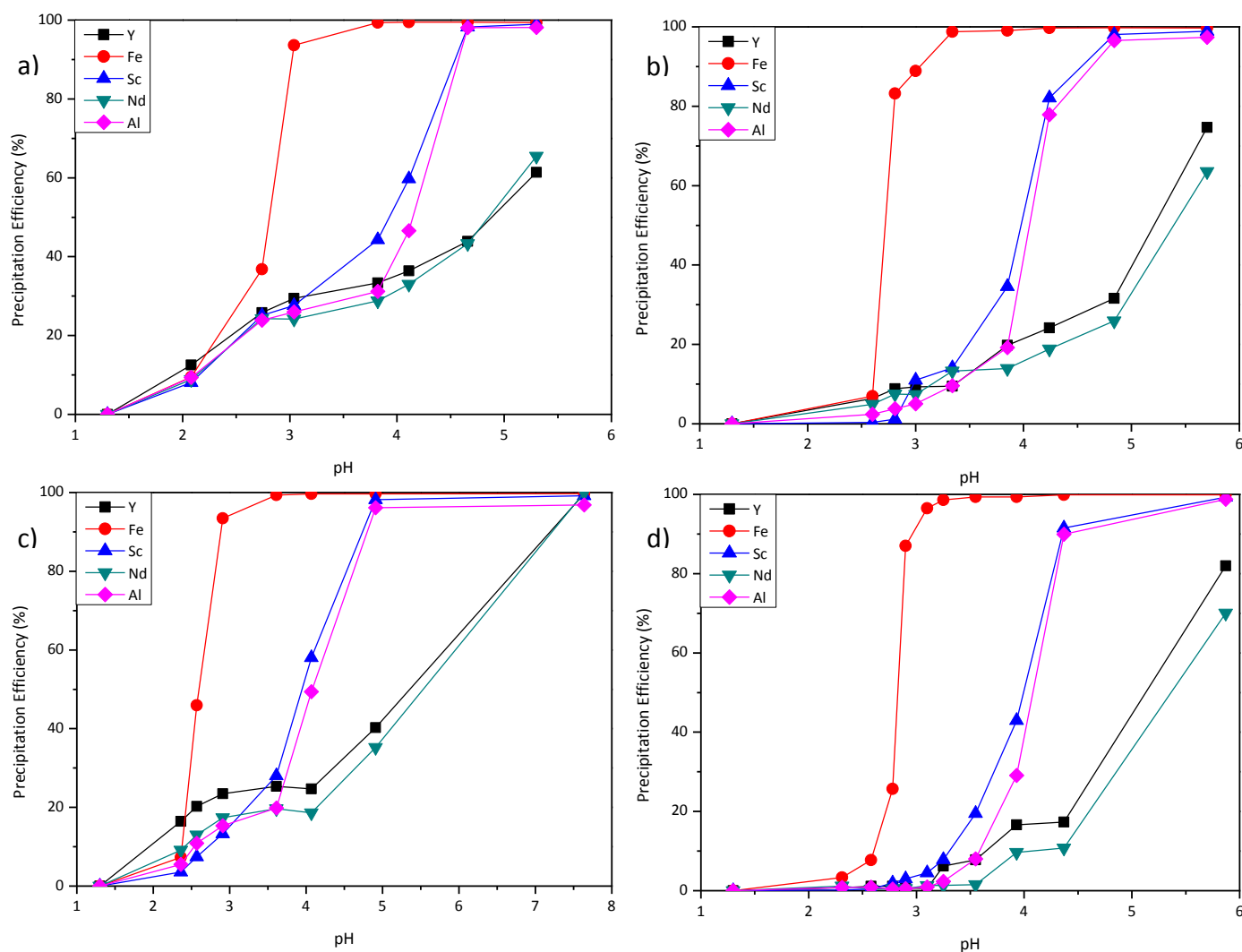
### 137 3.1. Precipitation in $HNO_3$ Media

#### 138 3.1.1. Fe Removal Step

139 In all recovery and purification operations regarding scandium, iron reported to be one of the  
140 most problematic elements. Thus, to propose an easier route to process scandium, iron content should  
141 be minimized in the solution beforehand. For this purpose, the easiest route was determined to be  
142 the hydroxide precipitation. Limestone slurry, sodium hydroxide, potassium hydroxide and  
143 ammonium hydroxide were preferred as precipitation solutions and a wide range of pH values was  
144 examined with the addition of those hydroxide donors.

145 The precipitation trends of the constituent elements as hydroxides were shown in Figure 1.  
146 Precipitation of Fe(III) with the addition of limestone slurry took place in the pH range between 2.0-  
147 3.5. As it can be seen from the Figure 1a, when Fe(III) precipitation is triggered, the co-precipitation  
148 of the other components stayed around 25-30%. In the case of NaOH and KOH addition to the system  
149 (Figure 1b and 1c respectively), more distinctive Fe(III) precipitation was observed. Yet, the co-  
150 precipitation levels were relatively high, between 10-20%, when more than 90% of the Fe(III) was  
151 removed. The addition of  $NH_4OH$  had similar results as described in the sulfate system. A distinctive  
152 Fe(III) precipitation resulting low co-precipitation levels of the other components was observed  
153 (Figure 1d). When more than 95% of the Fe was removed from the solution, Sc and the REEs  
154 precipitated less than 5%. In all cases precipitation order was found to be Fe(III)>Sc>Al>Y≈Nd.  
155

156



157

158 **Figure 1.** Precipitation behavior of Fe(III), Al, Sc, Nd and Y in HNO<sub>3</sub> media at different pH values  
 159 with the addition of a) limestone, b) NaOH, c) KOH, d) NH<sub>4</sub>OH

160

161 In this removal step, it is desirable to remove Fe from the system with minimum co-precipitation  
 162 of the recoverable elements; therefore, selectivity was an essential parameter. Selectivity of the  
 163 precipitation is calculated with the Eq. (1) given below:

$$164 \quad D_{A,B} = \frac{C_{prec}}{C_{aq}} \quad \text{and} \quad S_{A/B} = \frac{D_A}{D_B} \quad \text{Eq. (1)}$$

165

166 where,  $D_A$  or  $D_B$  is the distribution coefficient of the mentioned element,  $C_{prec}$  is the concentration of  
 167 the element in the precipitate,  $C_{aq}$  is the concentration of the element in the aqueous solution after  
 168 precipitation,  $S_{A/B}$  is the selectivity coefficient which indicates the selectivity of A over B.

169 The precipitation yields of the elements and selectivity of Fe over Sc can be found in Table 3a  
 170 and 3b when the Fe precipitation reach 70% and 90% respectively. It is found from Table 3a that the  
 171 best candidates to remove Fe in HNO<sub>3</sub> media are NaOH and NH<sub>4</sub>OH since the S<sub>Fe/Sc</sub> are far superior  
 172 to the other hydroxide donors. Nevertheless, co-precipitation levels of all elements had a jump in the  
 173 case of NaOH upon further addition to remove 90% of the Fe(III). Thus, NH<sub>4</sub>OH showed astonishing  
 174 performance considering both co-precipitation and the S<sub>Fe/Sc</sub>. Once more than 95% of all Fe in the  
 175 system was removed, around 4% of Sc and 1% of the others were precipitated with a remarkable S<sub>Fe/Sc</sub>  
 176 of 585. The most logical explanation of this low co-precipitation levels is the occurrence of hexamine  
 177 scandium complex upon addition of NH<sub>4</sub>OH [24,25]. Hence, Fe precipitation is triggered whereas Sc  
 178 stayed as complex form preventing the co-precipitation of Sc between these pH ranges.

179 The main difference of the nitrate-based aqueous solution compared to the sulfate-based is the  
 180 pH ranges of the precipitation. Although it was found that the precipitation of Fe was triggered in  
 181 pH values between 2.5 to 4.0 in sulfate media, similar precipitation was observed in a lower pH,  
 182 between 2.0 to 3.0. It is known that sulfate ion forms in inner sphere complexes, while nitrate  
 183 complexes can be classified as forming outer sphere complexes [26,27]. Consequently, more OH<sup>-</sup> ion  
 184 are needed to be released to disrupt inner sphere complex since it has lower Gibbs Energy ( $\Delta G$ ) in  
 185 that state.

186

187 **Table 3a.** Critical pH values for 70% Fe(III) removal from the system by hydroxide precipitation  
 188 and precipitation % of the constituent ions with selectivity of Fe over Sc

Precipitation Agent	pH	Fe(%)	Sc(%)	Al(%)	Y(%)	Nd(%)	S <sub>Fe/Sc</sub>
Limestone	2.95	76.6	26.8	25.1	28.1	24.2	9
NaOH	2.78	72.3	1.1	3.3	8.1	6.8	235
KOH	2.74	69.7	10.4	13.1	21.9	15.2	20
NH <sub>4</sub> OH(aq)	2.87	71.5	2.4	0.5	0.5	0.5	102

189

190 **Table 3b.** Critical pH values for above 90% Fe(III) removal from the system by hydroxide  
 191 precipitation and precipitation % of the constituent ions with selectivity of Fe over Sc

Precipitation Agent	pH	Fe(%)	Sc(%)	Al(%)	Y(%)	Nd(%)	S <sub>Fe/Sc</sub>
Limestone	3.05	93.6	27.6	25.9	29.4	24.2	38
NaOH	3.00	88.9	11.0	5.1	9.3	7.4	65
KOH	2.91	93.4	13.3	15.3	23.5	17.4	92
NH <sub>4</sub> OH(aq)	3.10	96.5	4.5	0.9	0.6	1.3	585

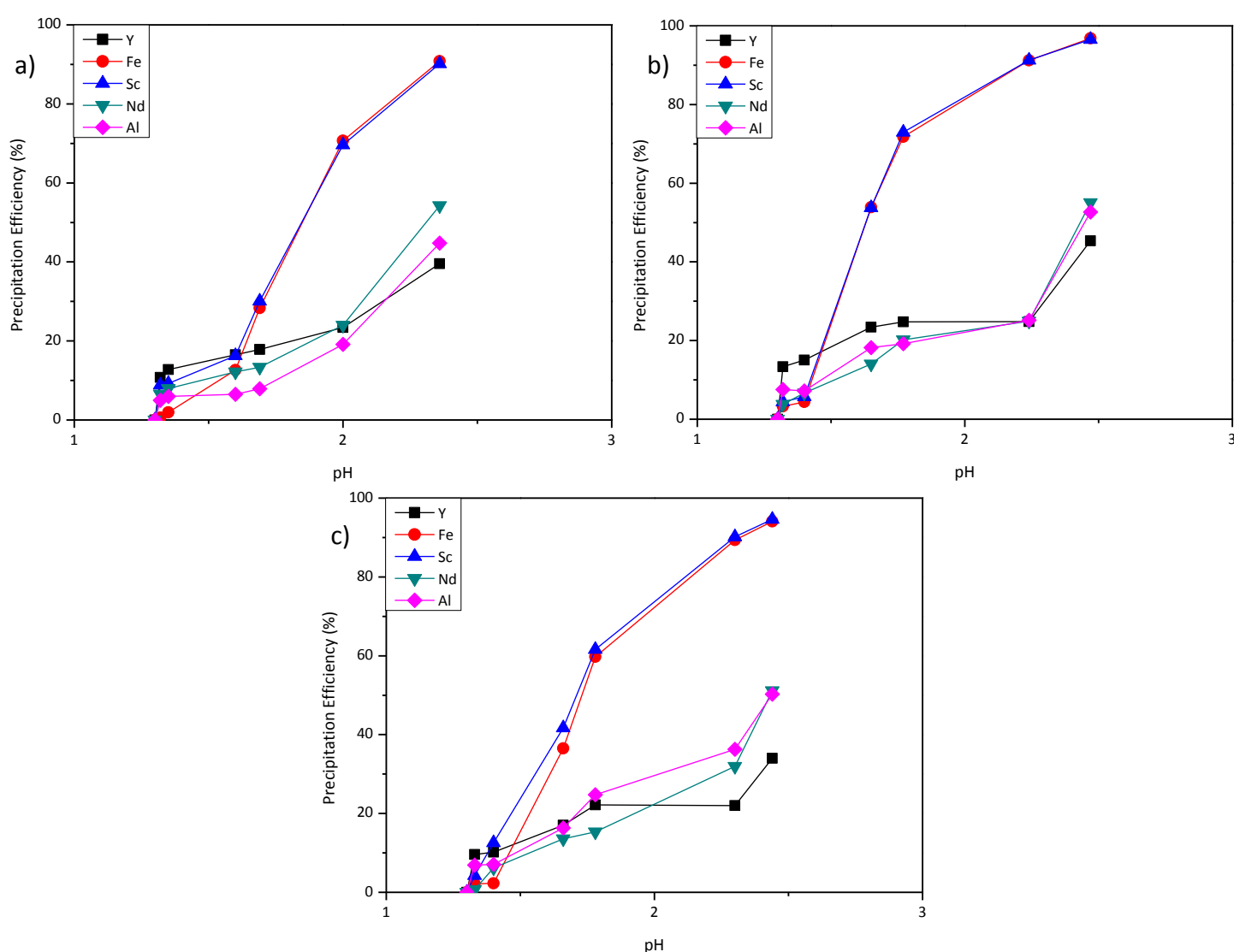
192

193

## 194 3.1.2. Phosphate Precipitation

195 In previous studies, it was shown that there is a strong affinity of Sc and REEs towards  $\text{PO}_4^{3-}$  ion  
 196 [22,28,29]. In leach solutions within sulfate media, addition of dibasic phosphate resulted in a  
 197 selective precipitation of both Fe(III) and Sc from the system. In a similar consideration, dibasic  
 198 phosphate solutions were tested with the intention of recovering Sc from the PLS. Addition of three  
 199 different dibasic phosphate solutions and the resulted precipitation pattern of the constituent  
 200 elements are shown in Figure 2. Precipitation solutions were added starting from the stoichiometric  
 201 amount considering only Sc precipitation and the amount introduced is increased in each step until  
 202 reaching 20 times over stoichiometric value.

203



204 **Figure 2.** Precipitation of the elements in  $\text{HNO}_3$  media with the addition of a)  $\text{Na}_2\text{HPO}_4$ , b)  $\text{K}_2\text{HPO}_4$   
 205 and c)  $(\text{NH}_4)_2\text{HPO}_4$

206

207 In all cases, similar precipitation trends were observed. Upon addition of the precipitant  
 208 solution, immediate precipitation of Fe and Sc was initiated. More than 90% of Sc and Fe precipitation



209 were occurred at pH value around 2.5. Since, dibasic phosphates releases  $\text{OH}^-$  into the system, an  
 210 uncontrolled rise of pH will lead to precipitation of the constituent elements as hydroxides which  
 211 will deteriorate the selectivity towards Sc recovery. It is important to note that, while high levels of  
 212 co-precipitation of the other elements were detected with the of  $\text{Na}_2\text{HPO}_4$  addition, approximately  
 213 40-50%, it was found to be limited -between 20-25%- when  $\text{K}_2\text{HPO}_4$  or  $(\text{NH}_4)_2\text{HPO}_4$  was introduced  
 214 into the solution as phosphate donors. All additions yielded to the precipitation order as  
 215  $\text{Fe(III)}=\text{Sc}>\text{Al}>\text{Y}=\text{Nd}$ . The precipitation efficiencies upon addition of dibasic phosphate precipitation  
 216 solutions can be found in Table 4.

217

218 **Table 4.** Critical pH values for above 90% Sc recovery from the solution system by dibasic  
 219 phosphate precipitation and the precipitation efficiencies of the constituent ions

Precipitation Agent	pH	Fe(III)(%)	Sc(%)	Al(%)	Y(%)	Nd(%)
$\text{Na}_2\text{HPO}_4$	2.36	90.8	90.2	44.8	39.6	54.3
$\text{K}_2\text{HPO}_4$	2.24	91.2	91.3	25.1	24.8	24.9
$(\text{NH}_4)_2\text{HPO}_4$	2.30	89.3	90.2	36.3	22.0	31.2

220

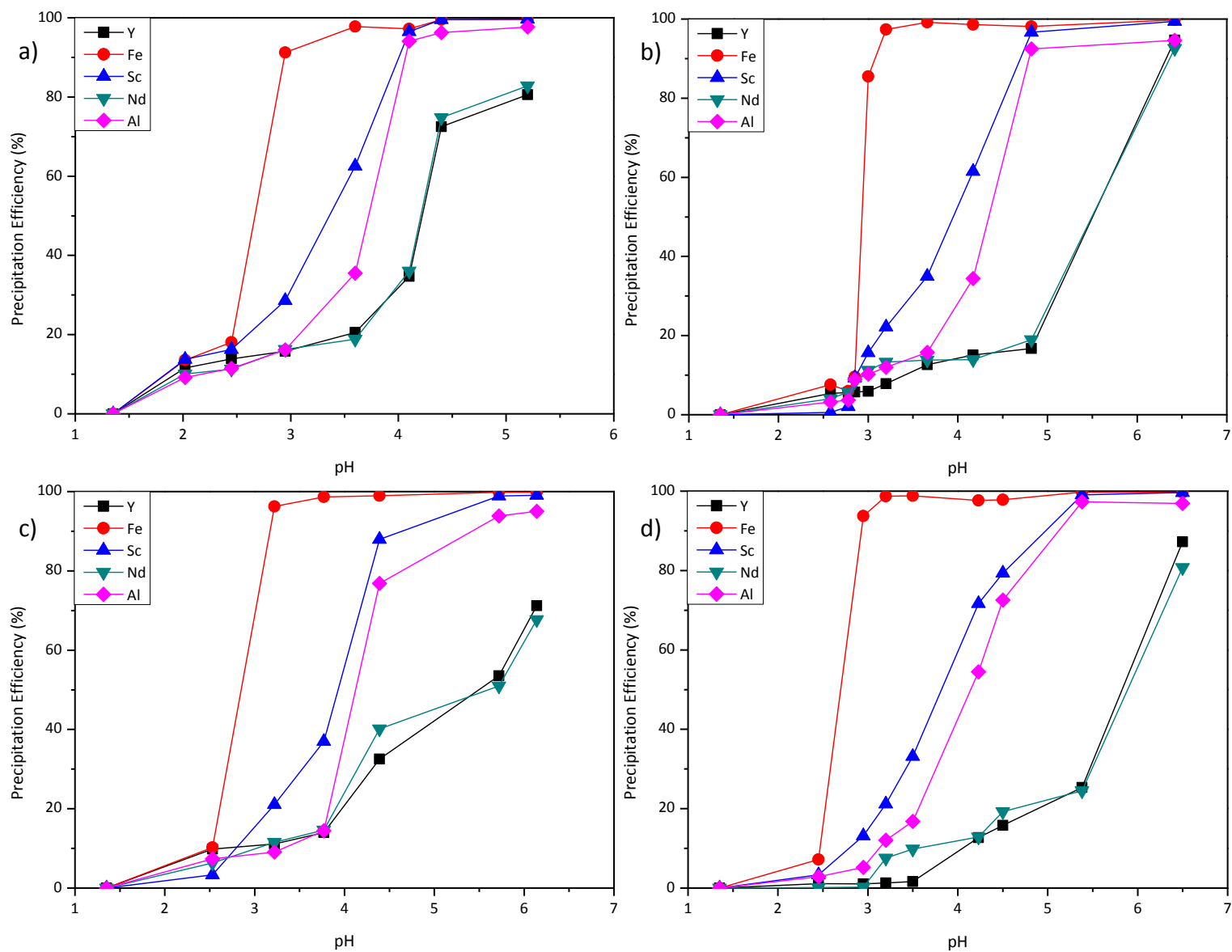
### 221 3.2. Precipitation in HCl Media

#### 222 3.2.1. Fe Removal Step

223 The same precipitation solutions for hydroxide precipitation were further tested in HCl media  
 224 and the results were summarized in Figure 3. Similar precipitation routes and behaviors were  
 225 observed as in the case of  $\text{HNO}_3$  media. While addition of limestone slurry resulted in co-  
 226 precipitation of all other elements with Fe(III), more distinctive cases were achieved when NaOH,  
 227 KOH and  $\text{NH}_4\text{OH}$  were used. As in the previous case, with the addition of  $\text{NH}_4\text{OH}$ , the lowest co-  
 228 precipitation was achieved, yet Sc precipitation observed to be the greatest among the other elements  
 229 when Fe content in the solution was minimized. In all cases the precipitation order was detected as  
 230  $\text{Fe(III)}>\text{Sc}>\text{Al}>\text{Y}=\text{Nd}$ .

231 The precipitation percentages of elements in the solution can be found from Table 5a and 5b,  
 232 when Fe(III) was removed at 70% and 90% respectively. The major difference of the precipitation  
 233 behavior between  $\text{HNO}_3$  media and HCl media is the co-precipitation levels of Sc. It was previously  
 234 discussed that both in nitrate and sulfate media, Sc was remained in the solution while Fe(III) was  
 235 almost completely taken out from the solution. With the addition of  $\text{NH}_4\text{OH}$ , 70% Fe(III) as well as  
 236 9% Sc were precipitated pH levels around 2.8, while Sc precipitation stayed at 13% once 93% of Fe(III)  
 237 was removed from the solution at a pH value around 3.0. The interaction between  $\text{Fe}^{3+}$  and  $\text{Cl}^-$  ions  
 238 was the main reason why the precipitation range is limited and the co-precipitation level of Sc is  
 239 increased when Fe was started to precipitate. This interaction shifted the precipitation range of Fe(III)  
 240 slightly, prompting Sc precipitation in the same range.

241 Still, the precipitation procedure to synthesize a scandium concentrate is applicable even in this  
 242 case. Although the selectivity of Fe over Sc was found to be 24 when precipitation of Fe reached 70%,  
 243 as the precipitation progressed, value of 100 was reached with the addition of  $\text{NH}_4\text{OH}$ .  
 244  
 245



246 **Figure 3.** Precipitation behavior of Fe(III), Al, Sc, Nd and Y in HCl media with the addition of a)  
 247  $\text{CaCO}_3$ , b)  $\text{NaOH}$ , c)  $\text{KOH}$ , d)  $\text{NH}_4\text{OH}$

248  
 249  
 250  
 251  
 252  
 253  
 254

255 **Table 5a.** Critical pH values for 70% Fe(III) removal from the system by hydroxide precipitation  
 256 and precipitation % of the constituent ions with selectivity of Fe over Sc

Precipitation Agent	pH	Fe(%)	Sc(%)	Al(%)	Y(%)	Nd(%)	S <sub>Fe/Sc</sub>
Limestone	2.81	70.7	25.2	15.3	15.1	15.6	7
NaOH	2.97	70.3	14.4	9.9	5.8	10.6	14
KOH	3.05	75.1	16.7	8.2	10.6	8.3	15
NH <sub>4</sub> OH	2.82	71.3	9.6	4.4	1.0	0.2	24

257

258 **Table 5b.** Critical pH values for above 90% Fe(III) removal from the system by hydroxide  
 259 precipitation and precipitation % of the constituent ions with selectivity of Fe over Sc

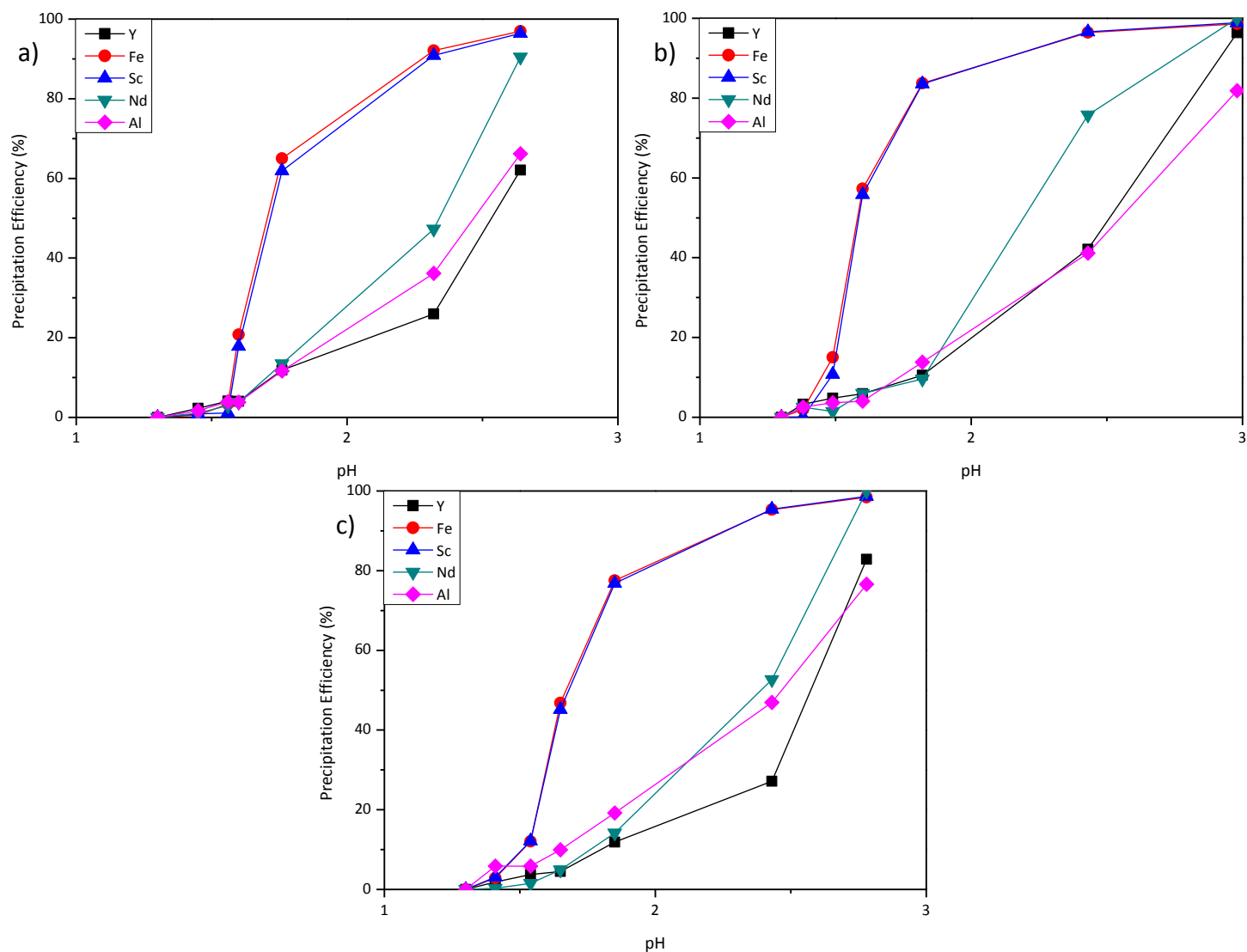
Precipitation Agent	pH	Fe(%)	Sc(%)	Al(%)	Y(%)	Nd(%)	S <sub>Fe/Sc</sub>
Limestone	2.95	91.2	28.6	25.9	29.4	24.2	25
NaOH	3.10	91.4	18.9	11.1	6.9	12.3	46
KOH	3.22	96.3	21.0	9.1	11.1	11.5	98
NH <sub>4</sub> OH	2.95	93.8	13.2	5.2	1.1	0.3	100

260

### 261 3.2.2. Phosphate Precipitation

262 Figure 4 shows precipitation behavior with the addition of different phosphate donors into  
 263 synthetic solution with HCl media. Selective precipitations of scandium and iron were triggered  
 264 immediately with the addition of dibasic phosphate solution and 60% precipitation efficiency was  
 265 attained with below 10% co-precipitation of other elements at pH values around 1.5 in all cases. After  
 266 that point, further addition of phosphate ions resulted in growth of both targeted and non-targeted  
 267 elements. Best selectivity with 90% of Sc precipitation efficiency is reached at pH 2.2 with the addition  
 268 of K<sub>2</sub>HPO<sub>4</sub> with co-precipitation yields of 27%, 26% and 43% for Al, Y and Nd respectively.  
 269 (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> showed similar performance with slightly increased co-precipitation levels as 36% in Al,  
 270 23% in Y and 42% in Nd when Sc precipitation hit 90%. Critical pH values for above 90% Sc recovery  
 271 from the solution system by dibasic phosphate precipitation and the precipitation efficiencies of the  
 272 constituent ions can be found in Table 6.

273 Since, introducing new ions into the system is unwanted throughout the precipitation process,  
 274 (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> is selected as the best precipitation agent for selective precipitation of Sc from bauxite  
 275 residue leachates.



276 **Figure 4.** Precipitation of the elements in HCl media with the addition of a)  $\text{Na}_2\text{HPO}_4$ , b)  $\text{K}_2\text{HPO}_4$   
 277 and c)  $(\text{NH}_4)_2\text{HPO}_4$   
 278

279 **Table 6.** Critical pH values for above 90% Sc recovery from the solution system by dibasic  
 280 phosphate precipitation and the precipitation efficiencies of the constituent ions

Precipitation Agent	pH	Fe(III)(%)	Sc(%)	Al(%)	Y(%)	Nd(%)
$\text{Na}_2\text{HPO}_4$	2.32	92.1	90.9	39.2	26.0	47.3
$\text{K}_2\text{HPO}_4$	2.19	90.1	90.2	27.5	26.3	42.7
$(\text{NH}_4)_2\text{HPO}_4$	2.27	90.4	90.3	36.3	22.9	42.1

281

282 3.3. Successive Precipitation in All Media

283 Taking all the findings into consideration, triple-staged precipitation processes concerning  
 284 synthesizing a scandium concentrate from bauxite residue solutions can be proposed for the possible

285 mineral acid systems. Proposed precipitation processes were summarized in Figure 5 and the  
 286 variation in concentration with the successive addition of the precipitation agents into H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>  
 287 and HCl media can be found in Figure 5a, 5b and 5c respectively. The three precipitation regions  
 288 labelled as regions 1, 2 and 3, are shown in all graphs. Region 1 is the removal of Fe from solution  
 289 with minimum Sc loss by the addition of NH<sub>4</sub>OH until specified pH is reached for each media. The  
 290 residue obtained from this step which is enriched in Fe, is filtered and removed from the solution.  
 291 Critical pH ranges for 1<sup>st</sup> Fe removal step are decided as 3.3-3.4 for H<sub>2</sub>SO<sub>4</sub> and 2.8-2.9 for HNO<sub>3</sub> and  
 292 HCl. Region 2 denoted as 2<sup>nd</sup> Fe removal step by further addition of NH<sub>4</sub>OH that promotes higher Fe  
 293 precipitation with a low amount of Sc co-precipitation. Precipitate is then filtered and can be recycled  
 294 into the initial feed which minimizes the Sc losses during 2<sup>nd</sup> Fe removal step as well as behave as a  
 295 seeding agent for better Fe separation. The pH ranges for this step are in between 3.6-3.7 for H<sub>2</sub>SO<sub>4</sub>,  
 296 3.1-3.2 for HNO<sub>3</sub> and 3.0-3.1 for HCl media.

297 After removing more than 95% of Fe using NH<sub>4</sub>OH with low Sc loss, a phosphate precipitation  
 298 step is applied as the 3<sup>rd</sup> part of this successive precipitation process. It is observed that phosphate  
 299 precipitation with dibasic phosphates showed similar performance regardless of the system. The pH  
 300 of all systems are adjusted to 2.0 in advance with the purpose of avoid unwanted hydroxide  
 301 precipitation which can be triggered in pH levels above 3.0. Dibasic phosphate solutions are added  
 302 into all systems until reaching a pH range between 2.5-2.6 where best selectivity for Sc was reached.  
 303 Since, Fe was removed in previous steps, both the amount of precipitant solution and co-precipitation  
 304 levels of the constituent ions were decreased. For all media, more than 95% of Sc and Fe was  
 305 recovered, while approximately 15% of Al and 10% of Y and Nd were co-precipitated during the  
 306 process. The compositions of the resulted concentrate in the form of mixed phosphates can be found  
 307 in Table 7.

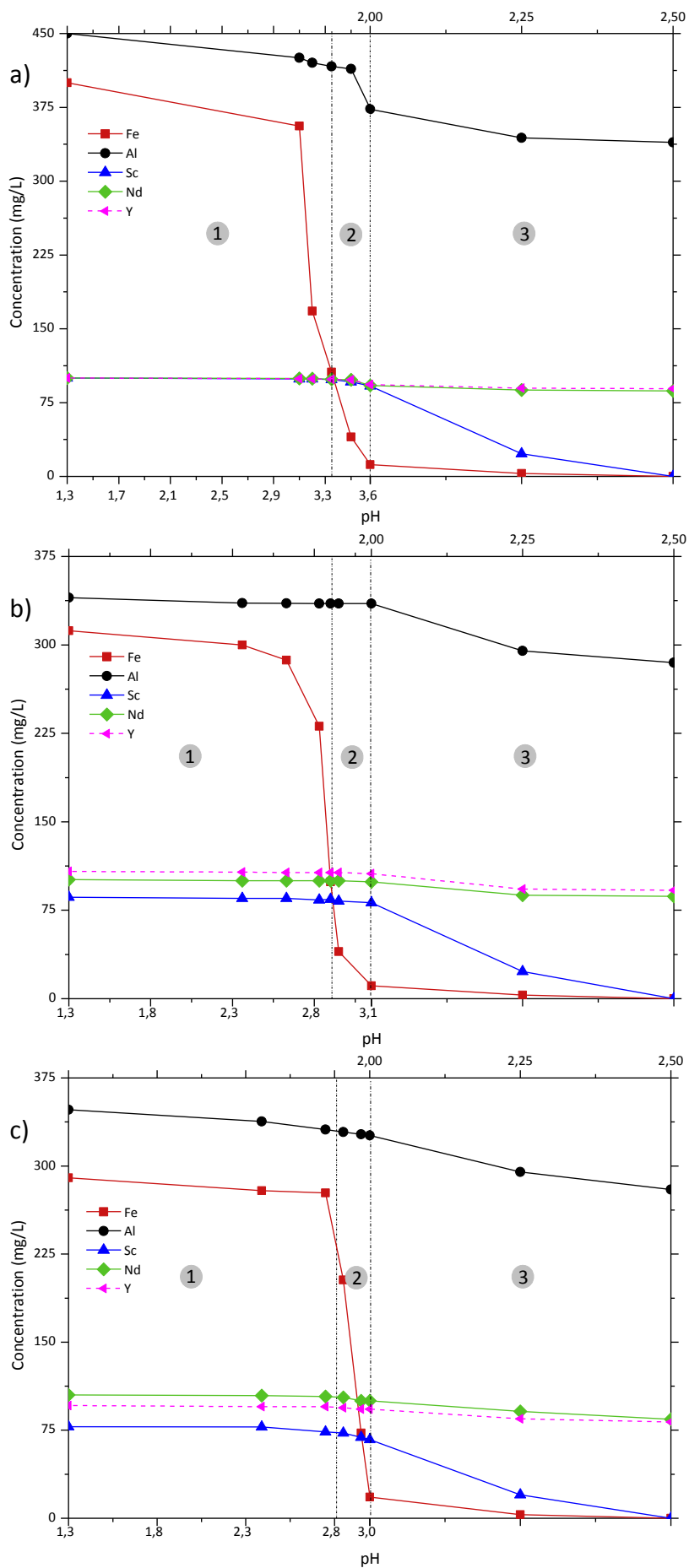
308

309 **Table 7.** Compositions of each concentrate obtained after successive selective precipitation as  
 310 phosphates

	H <sub>2</sub> SO <sub>4</sub>	HNO <sub>3</sub>	HCl
ScPO <sub>4</sub> (%)	66	56	51
FePO <sub>4</sub> (%)	13	12	13
AlPO <sub>4</sub> (%)	19	23	26
YPO <sub>4</sub> (%)	1	3	5
NdPO <sub>4</sub> (%)	1	6	5

311

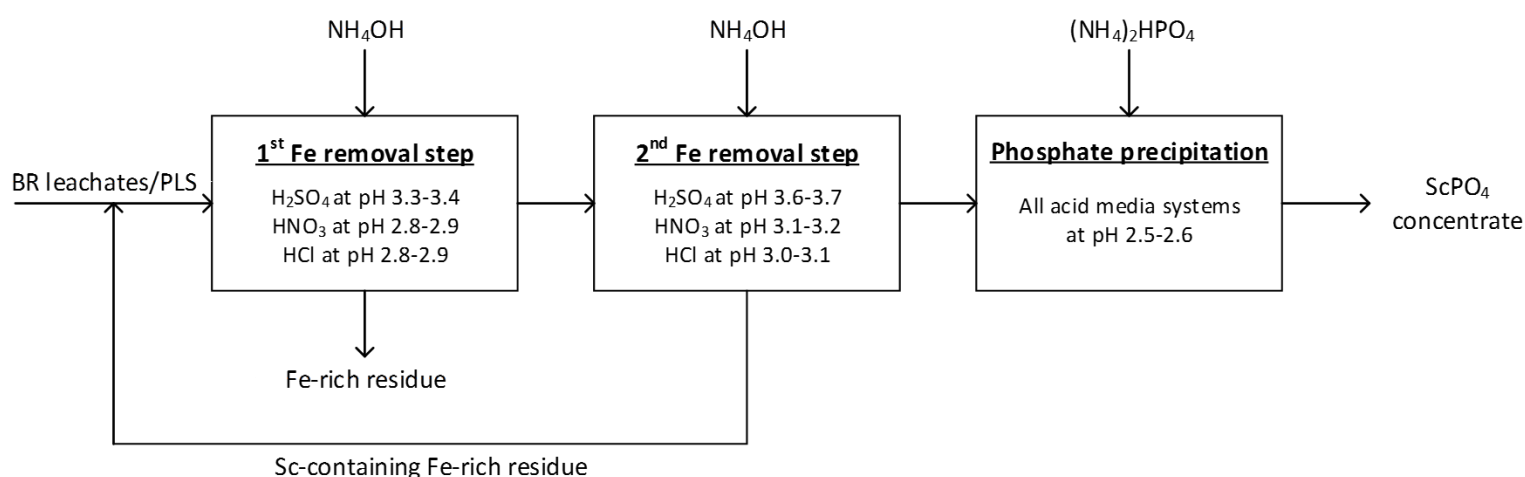
312 In all cases, Sc concentrates containing more than 50% ScPO<sub>4</sub> were synthesized. Since the  
 313 precipitation patterns of the ions are more discrete in the sulfuric acid media, best results were  
 314 obtained in this media with 66% ScPO<sub>4</sub> in its content. The major impurity element was found to be  
 315 Al in the concentrate which can be easily processed and removed with basic purification operations.



317 **Figure 5.** Triple-staged successive precipitation with  $\text{NH}_4\text{OH}$  and  $(\text{NH}_4)_2\text{HPO}_4$  from a)  $\text{H}_2\text{SO}_4$ , b)  
 318  $\text{HNO}_3$  and c)  $\text{HCl}$  media  
 319

#### 320 4. Assessment and Conclusion

321 A triple-step precipitation route is proposed to refine a scandium concentrate from synthetic  
 322 bauxite residue leachates and the effect on aqueous media was investigated. In all media,  $\text{NH}_4\text{OH}$   
 323 showed better selectivity and performance similar to the behavior in  $\text{H}_2\text{SO}_4$  media. While  $\text{HNO}_3$  and  
 324  $\text{HCl}$  media showed quite similar patterns during precipitation, the behavior of precipitation,  
 325 especially within the pH ranges of precipitation, was the main difference compared to the  $\text{H}_2\text{SO}_4$  case  
 326 because of the nature of their complex formation. Although the Sc loss during Fe removal step in  $\text{HCl}$   
 327 media was observed to be relatively higher compared to the others as a result of the interaction  
 328 between  $\text{Fe}^{3+}$  and  $\text{Cl}^-$  ions, still more than 50% Sc content was achieved in the concentrate. The  
 329 proposed selective precipitation route to produce this  $\text{ScPO}_4$  concentrate can be seen from Figure 6.  
 330



331 **Figure 6.** Proposed selective precipitation route to synthesize  $\text{ScPO}_4$  concentrate for three mineral  
 332 acid media  
 333

334 Scandium concentrate containing more than 50%  $\text{ScPO}_4$  in its content was successfully obtained  
 335 with this selective precipitation route from synthetic solutions. Depending on the impurity level,  
 336 aqueous media and the initial composition of the feed solution, the amount of  $\text{ScPO}_4$  in the  
 337 synthesized concentrate can vary between 15-65%. Since it contains more scandium than the other  
 338 elements, the processing and the purification of this concentrate is much easier to handle during  
 339 operations. The removal of the most problematic element for scandium, which is in the presence of  
 340 iron, limits the dependence for advanced processes to obtain a high purity scandium product.  
 341 Furthermore, the remaining solution after precipitation can be treated for further REEs recovery  
 342 through other means.  
 343

344 **Acknowledgments:** The research leading to these results has received funding from the European Community's  
345 Horizon 2020 Programme ([H2020/2014–2019]) under Grant Agreement no. 636876 (MSCA-ETN REDMUD).  
346 This publication reflects only the author's view, exempting the Community from any liability. Project website:  
347 <http://www.etn.redmud.org>. The authors thank Wenzhong Zhang and Dzenita Avdibegovic for their supports  
348 in ICP Measurements.

349

350 **Author Contributions:** B.Y., C.D. and B.F. conceived and designed the experiments; B.Y. performed the  
351 experiments; B.Y. analyzed the data; B.Y. wrote the paper; B.Y., C.D. and B.F. reviewed the paper.

352

353 **Conflicts of Interest:** The authors declare no conflict of interest.

354

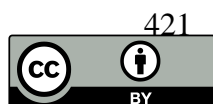
## 355 References

- 356 1. UNFCCC. *Adoption of the paris agreement, report no. Fccc/cp/2015/l.9/rev.1;*  
357 <http://unfccc.int/resource/docs/2015/cop21/eng/l09r01.pdf>, 2015.
- 358 2. Røyset, J.; Ryum, N. Scandium in aluminium alloys. *International Materials Reviews* 2005, 50, 19-44.
- 359 3. Gambogi, J. *USGS minerals information: Scandium*; U.S. Geological Survey: January 2017, 2017; pp 146-  
360 147.
- 361 4. Lathabai, S.; Lloyd, P. The effect of scandium on the microstructure, mechanical properties and  
362 weldability of a cast Al–Mg alloy. *Acta Materialia* 2002, 50, 4275-4292.
- 363 5. Marquis, E.; Seidman, D. Nanoscale structural evolution of Al<sub>3</sub>Sc precipitates in Al-Sc alloys. *Acta*  
364 *materialia* 2001, 49, 1909-1919.
- 365 6. Yamamoto, O. Solid oxide fuel cells: Fundamental aspects and prospects. *Electrochimica Acta* 2000, 45,  
366 2423-2435.
- 367 7. Commission, E. *Study on the review of the list of critical raw materials: Executive summary*; Directorate-  
368 General for Internal Market, Industry, Entrepreneurship and SMEs, 2017; pp 1-93.
- 369 8. Power, G.; Gräfe, M.; Klauber, C. Bauxite residue issues: I. Current management, disposal and storage  
370 practices. *Hydrometallurgy* 2011, 108, 33-45.
- 371 9. Evans, K. The history, challenges, and new developments in the management and use of bauxite  
372 residue. *Journal of Sustainable Metallurgy* 2016, 2, 316-331.
- 373 10. Li, G.; Liu, M.; Rao, M.; Jiang, T.; Zhuang, J.; Zhang, Y. Stepwise extraction of valuable components  
374 from red mud based on reductive roasting with sodium salts. *Journal of hazardous materials* 2014, 280,  
375 774-780.
- 376 11. Liu, Y.; Naidu, R. Hidden values in bauxite residue (red mud): Recovery of metals. *Waste management*  
377 2014, 34, 2662-2673.
- 378 12. Paramguru, R.; Rath, P.; Misra, V. Trends in red mud utilization—a review. *Mineral Processing &*  
379 *Extractive Metall. Rev.* 2004, 26, 1-29.
- 380 13. Alkan, G.; Yagmurlu, B.; Cakmakoglu, S.; Hertel, T.; Kaya, Ş.; Gronen, L.; Stopic, S.; Friedrich, B. Novel  
381 approach for enhanced scandium and titanium leaching efficiency from bauxite residue with  
382 suppressed silica gel formation. *Scientific Reports* 2018, 8, 5676.



- 383 14. Avdibegović, D.; Regadio, M.; Binnemans, K. Recovery of scandium(III) from diluted aqueous solutions  
384 by a supported ionic liquid phase (silp). *RSC Advances* 2017, 7, 49664-49674.
- 385 15. Narayanan, R.P.; Kazantzis, N.K.; Emmert, M.H. Selective process steps for the recovery of scandium  
386 from jamaican bauxite residue (red mud). *ACS Sustainable Chemistry & Engineering* 2017.
- 387 16. Ochsenkühn-Petropulu, M.; Lyberopulu, T.; Parissakis, G. Selective separation and determination of  
388 scandium from yttrium and lanthanides in red mud by a combined ion exchange/solvent extraction  
389 method. *Analytica Chimica Acta* 1995, 315, 231-237.
- 390 17. Onghena, B.; Borra, C.R.; Van Gerven, T.; Binnemans, K. Recovery of scandium from sulfation-roasted  
391 leachates of bauxite residue by solvent extraction with the ionic liquid betainium bis  
392 (trifluoromethylsulfonyl) imide. *Separation and Purification Technology* 2017, 176, 208-219.
- 393 18. Wang, W.; Cheng, C.Y. Separation and purification of scandium by solvent extraction and related  
394 technologies: A review. *Journal of Chemical Technology and Biotechnology* 2011, 86, 1237-1246.
- 395 19. Wang, W.; Pranolo, Y.; Cheng, C.Y. Recovery of scandium from synthetic red mud leach solutions by  
396 solvent extraction with D2HPA. *Separation and Purification Technology* 2013, 108, 96-102.
- 397 20. Zhang, W.; Koivula, R.; Wiikinkoski, E.; Xu, J.; Hietala, S.; Lehto, J.; Harjula, R. Efficient and selective  
398 recovery of trace scandium by inorganic titanium phosphate ion-exchangers from leachates of waste  
399 bauxite residue. *ACS Sustainable Chemistry & Engineering* 2017, 5, 3103-3114.
- 400 21. Yagmurlu, B.; Alkan, G.; Xakalash, B.; Friedrich, B.; Stopic, S.; Dittrich, C. In *Combined safe smelting and  
401 hydrometallurgical treatment of bauxite residue for enhanced valuable metal recovery*, ICSOBA 2017, Germany,  
402 2017; Germany.
- 403 22. Yagmurlu, B.; Dittrich, C.; Friedrich, B. Precipitation trends of scandium in synthetic red mud solutions  
404 with different precipitation agents. *Journal of Sustainable Metallurgy* 2017, 3, 90-98.
- 405 23. Alkan, G.; Xakalash, B.; Yagmurlu, B.; Kaussen, F.; Friedrich, B. Conditioning of red mud for  
406 subsequent titanium and scandium recovery—a conceptual design study. *World of Metallurgy—  
407 ERZMETALL* 2017, 70, 5-12.
- 408 24. Horovitz, C.T. *Scandium its occurrence, chemistry physics, metallurgy, biology and technology*. Elsevier: 2012.
- 409 25. Vickery, R.C. *The chemistry of yttrium and scandium*. Oxford: 1960; Vol. 2.
- 410 26. Ahrland, S. How to distinguish between inner and outer sphere complexes in aqueous solution.  
411 Thermodynamic and other criteria. *Coordination Chemistry Reviews* 1972, 8, 21-29.
- 412 27. Spiro, T.G.; Revesz, A.; Lee, J. Volume changes in ion association reactions. Inner-and outer-sphere  
413 complexes. *Journal of the American Chemical Society* 1968, 90, 4000-4006.
- 414 28. Lucas, S.; Champion, E.; Bregiroux, D.; Bernache-Assollant, D.; Audubert, F. Rare earth phosphate  
415 powders  $REPO_4 \cdot nH_2O$  (Re= La, Ce or Y)—part i. Synthesis and characterization. *Journal of Solid State  
416 Chemistry* 2004, 177, 1302-1311.
- 417 29. Beltrami, D.; Deblonde, G.J.-P.; Bélaïr, S.; Weigel, V. Recovery of yttrium and lanthanides from sulfate  
418 solutions with high concentration of iron and low rare earth content. *Hydrometallurgy* 2015, 157, 356-  
419 362.

420



© 2018 by the authors. Submitted for possible open access publication under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).