

RECOVERY OF SCANDIUM FROM BAUXITE RESIDUE BY SELECTIVE PRECIPITATION FROM LEACH SOLUTIONS

By

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ABSTRACT

As a member of EU H2020 ETN Red Mud Project which aims to recover all constituents of bauxite residue (BR) and adopts a zero-waste valorisation point of view, this study focuses on maximized recovery of Scandium in the BR. The red mud investigated was obtained from Aluminium of Greece and contains 130ppm of Sc in its composition which makes it a valuable Sc resource. Previous studies showed that a remarkable amount of Sc (~90%) could be extracted by direct acidic leaching of BR and in this study selective precipitation was investigated on obtained pregnant leach solution (PLS) from BR. Three different approaches; (a) direct precipitation with selected agents from highly impure PLS obtained directly from red mud, (b) pre-purified and enriched PLS in terms of Sc by solvent extraction and (c) cascade type continuous precipitation process to reach various Sc products will be compared and assessed. Advantages and drawbacks of those mentioned approaches will be discussed in cooperation with experimental results.

Keywords: Scandium, Bauxite Residue, Precipitation, Recovery

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INTRODUCTION

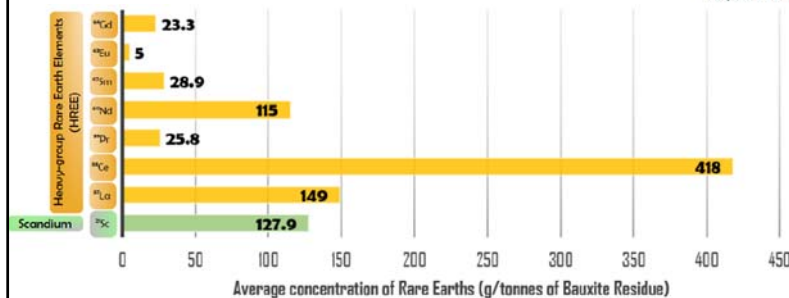
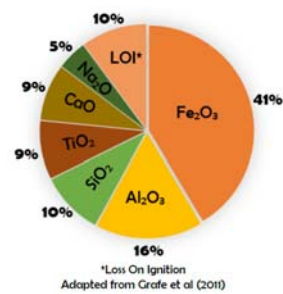
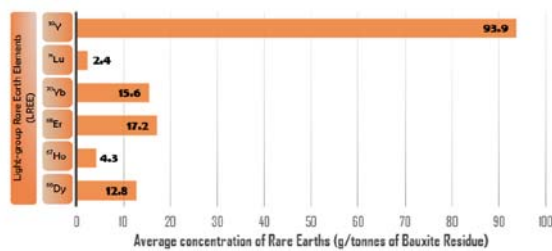
- Despite scandium (Sc) being extremely expensive, the demand of Sc is increasing worldwide owing to recent developments in promising applications in a wide range.
- Due to very limited and rare direct sources of Sc ores, it can be extracted as a by-product which will lead complex metallurgical processes and high production and purification expenses.
- Bauxite residue (BR) is a by-product and the waste obtained from the Bayer Process and stockpiled in huge amounts all over the world.
- Estimated amount of red mud stocks are around four billion tonnes and it is growing unceasingly.

INTRODUCTION (CONT.)

- Producing 1 tonne of Aluminum results in 1 to 1.5 tonnes of bauxite residue.
- Depositing this amount of heavily alkaline waste affects both production costs and the environment.
- However, it can also be considered as a valuable resource for metals.
- BR contains numerous valuable elements such as Ti, Sc, Y, Nd, Ce, etc., it can also be counted as a significant resource.
- The low concentration of Sc in leachates, extraction studies have mainly focused on solvent extraction and ion-exchange processes.

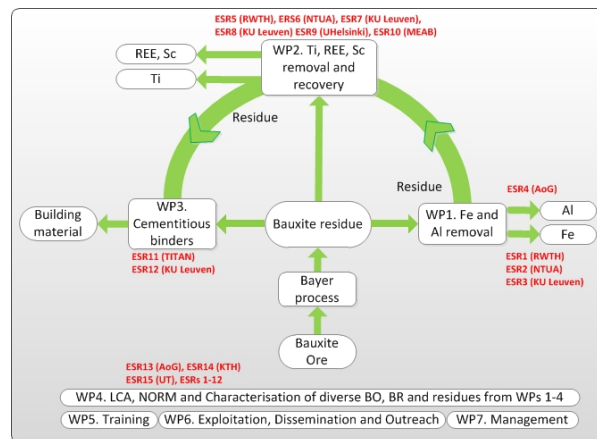
INTRODUCTION (CONT.)

- Chemical composition of BR can be seen here:



INTRODUCTION (CONT.)

- EU H2020 ETN Red Mud Project aims to recover all constituents of BR and adopts a zero-waste valorisation point of view.



AIMS

- The main aim of this study is to develop a continuous process of chemical precipitation.
- Obtaining high purity Sc complexes with >90% precipitation efficiency.
- Investigating the behaviours of different precipitation agents for Sc and comparing their selectivities and the co-precipitation behaviours.
- Comparing different processes for Sc extraction and achieving a low cost high efficiency Sc process.

EXPERIMENTAL

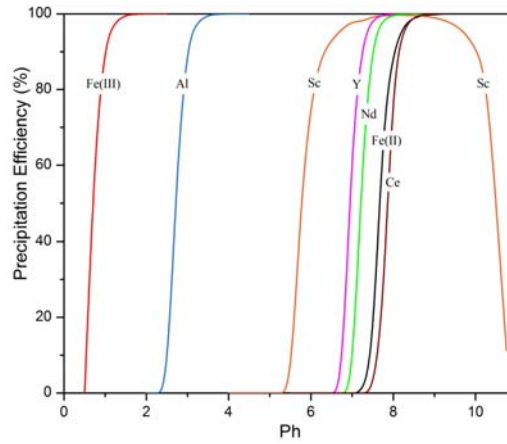
- All experiments were carried out using solutions prepared from analytical grade reagents and de-ionized water.
- The concentrations of the constituent ions were determined by microwave plasma optical emission spectroscopy (Agilent MP-AES 4100).
- The precipitation agents was carefully dripped by sensitive burette into 50ml of the synthetic PLS while controlling pH and temperature.
- The resulting suspension in each case, stabilized and homogenized at given pH and temperature for 2h and filtered via suction filtration.

RESULTS – SYNTHETIC PLS

- This study considers the expected pregnant leach solutions (PLS) obtained by sulfuric acid leaching after recovering Fe, Al and Ti according to recent developments by linked studies in the project.
- Predicted values were used to synthesize the PLS.

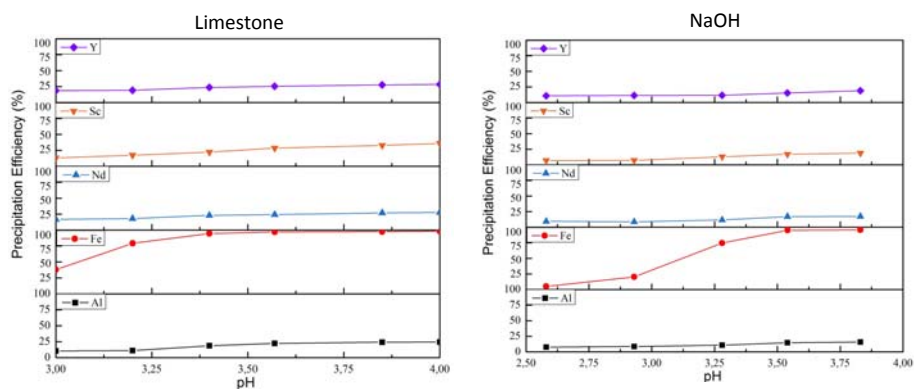
Constituent Ions	Concentration (mg/L)
Al	450
Fe (III)	400
Ca	250
Sc	100
Y	100
Nd	100

RESULTS – HYDROXIDE PRECIPITATION



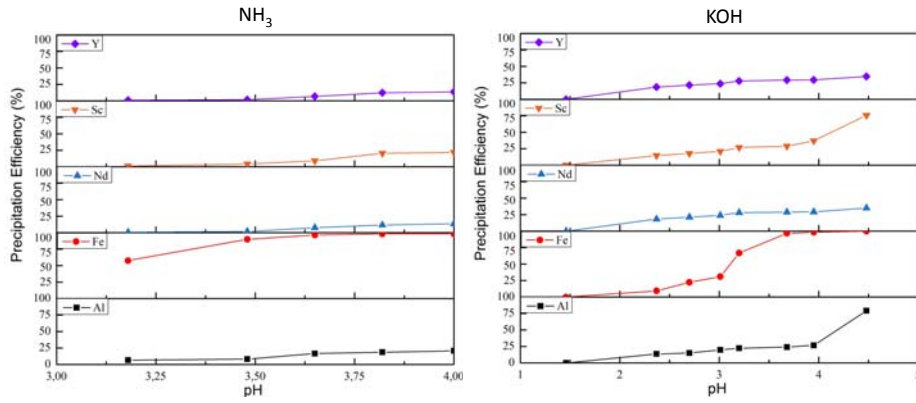
Theoretical precipitation behaviour of the constituent ions according to thermodynamical calculations

RESULTS – HYDROXIDE PRECIPITATION



Addition of Limestone and NaOH to the synthetic solution

RESULTS – HYDROXIDE PRECIPITATION



Addition of NH₃ and KOH to the synthetic solution

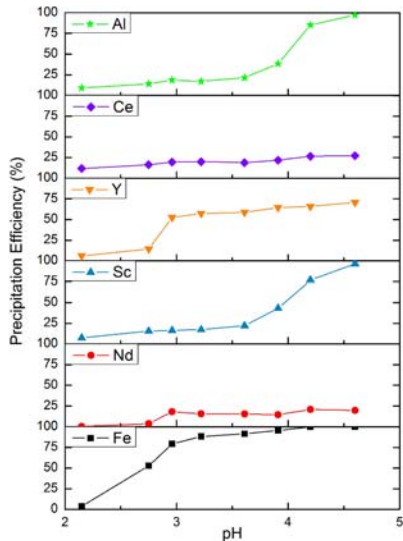
RESULTS – HYDROXIDE PRECIPITATION

Precipitation Agent	pH	Fe (%)	Sc (%)	Al (%)	Y (%)	Nd (%)
Limestone	3.5	95	17	15	15	17
NaOH	3.4	95	22	19	24	23
NH ₃	3.5	90	4	8	2	2

- The selectivity of a agent for two different metals M_1 and M_2 is represented by the separation factors S . This is calculated as quotient of the distribution coefficients D of the two metals. Selectivity of Fe/Sc was compared among different precipitation agents to determine which is performed best.

Precipitation Agent	pH	Selectivity of Fe/Sc
KOH	3.7	70
NaOH	3.6	85
Limestone	3.5	95
NH ₃	3.6	291

RESULTS – HYDROXIDE PRECIPITATION

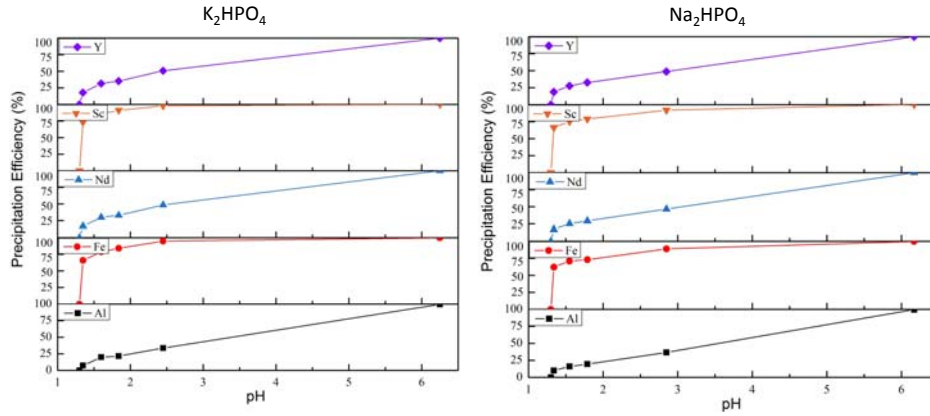


- Precipitation by NH_3 from directly simulated leachate can be seen.
- Similar trend was observed in highly impure solution.
- High co-precipitation with Y is observed.
- Sc loss is approx. 20% while Fe precipitated around 96% as hydroxide.
- NH_3 can be used as a precipitation agent for pre-purification step.

RESULTS – PHOSPHATE PRECIPITATION

- This part of study investigates the precipitation of Sc and REEs by the addition of 1mol/L dibasic phosphate solutions.
- Previous studies showed that, Y^{3+} and REE ions showed strong affinity towards PO_4^{3-} compared to SO_4^{2-} with the addition of phosphate salts to sulphate solution of Y and REEs.
- As the behavioural similarities between Sc and REEs, it was expected to trigger the precipitation with the addition of dibasic salts.
- Dibasic salts, K_2HPO_4 , $(\text{NH}_4)_2\text{HPO}_4$ and Na_2HPO_4 , were tested for Sc precipitation according to the expected Eq:
- $\text{REE}(\text{SO}_4)_n^{3-2n}(\text{aq}) + \text{PO}_4^{3-}(\text{aq}) = \text{REEPO}_4(\text{s}) + n\text{SO}_4^{2-}(\text{aq})$

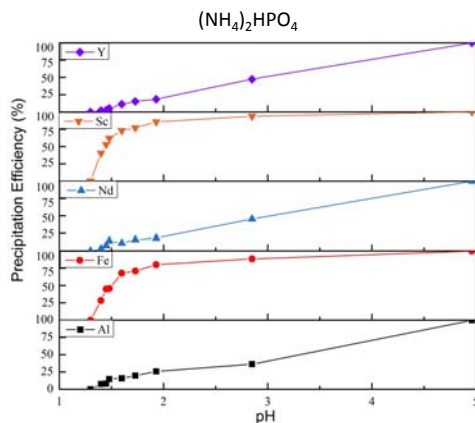
RESULTS – PHOSPHATE PRECIPITATION



Addition of K_2HPO_4 and Na_2HPO_4 to the synthetic solution [1]

[1] Yagmurlu B. et al. (2016), Precipitation trends of scandium in synthetic red mud solutions with different precipitation agents, (submitted to Journal of Sustainable Metallurgy)

RESULTS – PHOSPHATE PRECIPITATION

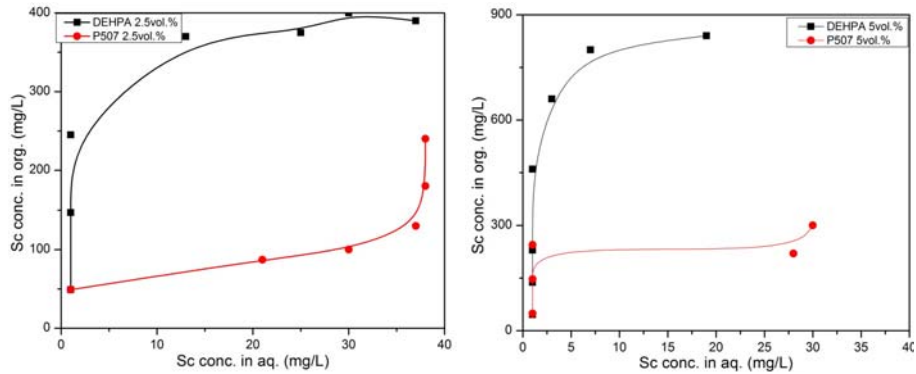


- Highly selective precipitation for Fe and Sc between 1-3 pH
- Rate of precipitation changes with pH
- Reacting constituents changes with pH

Addition of $(NH_4)_2HPO_4$ to the synthetic solution [1]

[1] Yagmurlu B. et al. (2016), Precipitation trends of scandium in synthetic red mud solutions with different precipitation agents, (submitted to Journal of Sustainable Metallurgy)

RESULTS – SOLVENT EXTRACTION

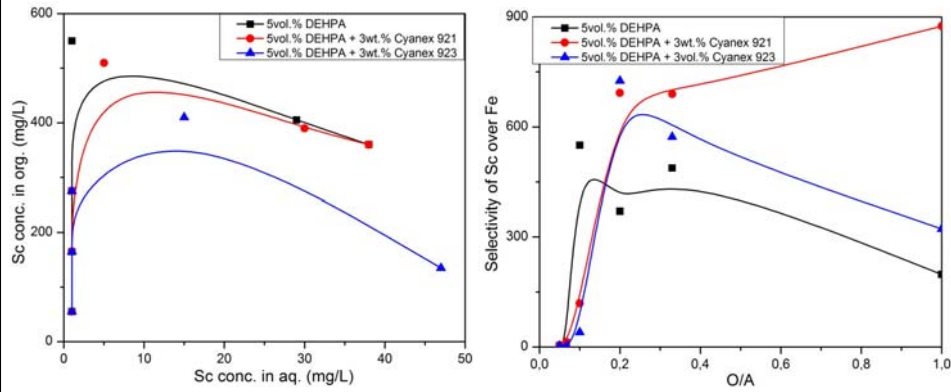


Solvent Extraction of BR Leachate with Di-(2-ethylhexyl)phosphoric acid (DEHPA) and (2-Ethylhexyl)phosphonic acid (P507)

RESULTS – SOLVENT EXTRACTION

- Fe is one of the most problematic elements for Sc extraction.
- While DEHPA extracts approx.15%, P507 extract 15-25% Fe in the solution.
- In all O/A ratios, DEHPA showed better selectivity than P507.
- 5vol.% in D60 of both organics performed better than 2.5vol.%.
- DEHPA performed superior in all concentrations and O/A ratios compared to P507.
- To solve the co-extraction problem of DEHPA, blended organics were tried.

RESULTS – SOLVENT EXTRACTION



Comparison of selectivities of fresh DEHPA, blended DEHPA+Cyanex 921 and blended DEHPA+Cyanex923

RESULTS – SOLVENT EXTRACTION

- To reduce Fe co-extraction, Cyanex 921 & 923 added to 5vol.% DEHPA.
- Extraction behaviour of Sc remained almost the same.
- Fe co-extraction decreased from 10-15% to 5-6% when both Cyanex organics added to fresh DEHPA.
- Selectivity of Sc over Fe increased noticeably.

CONCLUSIONS

- Synthetic solutions was prepared considering the leachates of BR.
- Limestone, NaOH, NH₃ and KOH was compared to remove Fe(III) from the solution.
- Fe in the system was removed selectively and achieved low co-precipitation levels by the help of ammonia.
- Dibasic phosphates showed high selectivity towards Fe and Sc while other constituents had low co-precipitations.
- DEHPA showed superior performance for Sc extraction compared to P507.
- To solve Fe co-extraction problem of DEHPA, blended organics were tried and co-extraction was decreased to 5-10%.