

SELECTIVE RECOVERY OF SCANDIUM(III) FROM BAUXITE RESIDUE LEACHATES BY SOLVENT EXTRACTION WITH A CARBOXYL-FUNCTIONALISED IONIC LIQUID

Bieke ONGHENA¹, Chenna Rao BORRA², Tom VAN GERVEN², Koen BINNEMANS¹

¹ Department of Chemistry, KU Leuven, 3001 Heverlee, Belgium

² Department of Chemical Engineering, KU Leuven, 3001 Heverlee, Belgium

bieke.onghena@chem.kuleuven.be

Abstract

Bauxite residue is an interesting potential secondary scandium (Sc) source because it contains relatively high concentrations of scandium and because huge, easily accessible amounts have been stockpiled over the years. Hydrometallurgical processes such as leaching and solvent extraction (SX) are most commonly used for the recovery of Sc(III). In our work we examined the selective recovery of Sc(III) from acidic leachates of bauxite residue by solvent extraction with the ionic liquid betainium bis(trifluoromethylsulfonyl)imide, [Hbet][Tf₂N]. This ionic liquid shows a high affinity for Sc(III), but a much lower affinity for the other metal ions present in red mud, with the exception of Fe(III), which shows a very similar extraction behavior to Sc(III). Separation of Sc(III) and Fe(III) was improved by selective precipitation stripping with oxalic acid.

Introduction

After the Rare-Earth Crisis of 2011, the price of scandium (Sc) did not drop like the other rare-earths elements, but remained high (5000 USD/kg in 2013).¹ This was a result of the increasing demand for scandium, which is used in solid oxide fuel cells (SOFCs) and scandium-reinforced aluminium alloys, in combination with limited supply rates.¹⁻³

Bauxite residue (BR), also called *red mud* is an interesting potential scandium source because of its relatively high scandium levels and the high, easily accessible amounts that have been stockpiled since the start of the Al₂O₃ production in the beginning of the 20th century.⁴ As described in the literature, the recovery and purification of scandium from bauxite residue is mostly performed using leaching with mineral acids, followed by solvent extraction or ion exchange.⁵⁻¹³

Our work focusses on the selective recovery of scandium(III) by solvent extraction with the ionic liquid betainium bis(trifluoromethylsulfonyl)imide, [Hbet][Tf₂N] (Figure 1). Ionic liquids consist entirely of ions and generally have a low melting point, resulting in a low volatility and flammability.¹⁴⁻¹⁵ Because of these properties, ionic liquids are considered safer and greener alternatives for traditional organic solvents. In previous work on extractions with synthetic solutions, [Hbet][Tf₂N] was already proven valuable for the separation of Sc(III) from the other rare-earth ions and the most important major elements present in red mud, namely Al(III), Ca(II), Na(I) and Ti(IV).¹⁶ Fe(III), on the other hand, showed very similar extraction behaviour to Sc(III), indicating that the separation of Sc(III) and Fe(III) by extraction with [Hbet][Tf₂N] is a challenge. Thus, to validate the potential of [Hbet][Tf₂N] for the recovery of Sc(III) from red mud, first the separation of Sc(III) and Fe(III) was further investigated and discussed in this paper, after which the extraction system was applied to real red mud leachates.

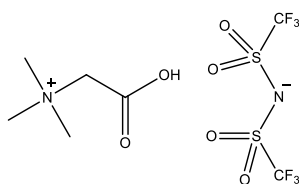


Figure 1: Chemical structure of betainium bis(trifluoromethylsulfonyl)imide or betainium bistriflimide, abbreviated by [Hbet][Tf₂N]

Experimental

The extractions concerning the influence of chloride on the separation of Sc(III) and Fe(III) were performed by first pre-equilibrating 2 g of water-saturated [Hbet][Tf₂N] with 2 g of aqueous solution containing varying concentrations of HClO₄ to adjust the pH and NaCl to adjust the chloride concentration. Next, 1 g of both the pre-equilibrated aqueous phase and ionic liquid phase were isolated and mixed together with 10 mg of solid mixture of ScCl₃ and FeCl₃. After extraction, the aqueous and ionic liquid phase of the extraction mixture were separated and their metal content was determined using *total reflection X-ray fluorescence* (TXRF) spectroscopy with a Bruker S2 Picofox TXRF spectrometer.

Stripping with oxalic acid was performed by mixing an ionic liquid phase loaded with Sc(III) and Fe(III) with an aqueous oxalic acid solution of varying concentration, which was saturated with ionic liquid to prevent phase changes during extraction. After shaking for 30 min, the mixtures were centrifuged to induce settling of the

precipitate, after which the ionic liquid phase and aqueous phase were separated from the precipitate and analysed by TXRF.

Direct leaching of red mud was performed using the method of Borra et al.¹⁷ Two leaching experiments were performed, one using HCl and the other using HNO₃. For both experiments, 0.2 N of acid was used in a 50:1 liquid-to-solid ratio and the mixture was shaken at room temperature for 24 h. The type of red mud sample was the same as used in the work of Borra et al. and was of Greek origin.¹⁷

The extraction experiments on the real red mud leachates were performed by contacting the red mud leachates with water-saturated [Hbet][Tf₂N]. Both the influence of O/A phase ratio, defined as the ratio of the mass of the ionic liquid phase to the mass of the aqueous phase, and pH were investigated. The pH was adjusted by addition of varying amounts of NaOH to the leachates.

Results and Discussion

The ionic liquid [Hbet][Tf₂N] is a carboxyl-functionalised protic ionic liquid, which forms a two-phase system with water at room temperature (Figure 1).¹⁸ The water-[Hbet][Tf₂N] mixture shows UCST-type of phase behaviour with an upper critical solution temperature (UCST) of 55 °C. Moreover, the phase behaviour of [Hbet][Tf₂N] and water is pH-dependent, i.e. the solubility of the ionic liquid in the aqueous phase increases by increasing the pH. This can be explained by the presence of the carboxyl function which is deprotonated upon addition of a base, creating a zwitterion which is highly soluble in water. The presence of this carboxyl function and the fact that the [Hbet][Tf₂N]–water mixture is biphasic at room temperature without pH adjustment, leads to the presence of a pH buffer system in the aqueous phase with a pH around 1.2–1.5.

To improve the separation of Sc(III) and Fe(III) in the [Hbet][Tf₂N] extraction system two options were considered: (1) enhancement of the separation of Sc(III) and Fe(III) during the extraction step itself, and (2) separation of Sc(III) and Fe(III) in an additional process step. The first option involved the addition of chloride to the aqueous phase, which forms stronger coordination bonds with Fe(III) than Sc(III). The formed Fe(III) chloro complexes had a preference for the aqueous phase and thus were almost not extracted to the ionic liquid phase. The experimental results showed an increase in the separation of Sc(III) from Fe(III) during extraction upon increasing the chloride concentration. However, the effect was only small since the highest separation factors obtained at 4 M of chloride in the aqueous phase were still below 5 and many additional extraction steps would be required to fully separate Sc(III) from Fe(III).

The second option was the separation of Sc(III) from Fe(III) using one of the most pronounced differences in chemical behaviour between Sc(III) and Fe(III), namely the solubility of their oxalate complexes. Scandium(III) oxalate precipitates almost completely in neutral media, while Fe(III) forms highly soluble oxalate complexes.¹⁹ Thus, ideally, Sc(III) can be separated from Fe(III) in solution by reaction with oxalic acid. It is important to include this selective precipitation step only at the end of the process, when a pure Sc(III)-Fe(III) mixture is obtained, to prevent co-precipitation of other metal ions, contaminating the scandium(III) oxalate precipitate. Therefore, the selective precipitation was applied to strip the loaded ionic liquid phase obtained after extraction and stripping, thus containing only Sc(III) and Fe(III). To examine the oxalate precipitation stripping, an ionic liquid phase loaded with Sc(III) and Fe(III) by extraction from a synthetic solution, was contacted with different solutions containing varying amounts of oxalic acid. It was observed that stripping of Fe(III) occurred by back-extraction only, with almost 100 % stripping, at 2.25 equivalents of oxalic acid to total metal ion content (expressed as the molar ratio of oxalic acid to total metal ion content). Sc(III), on the other hand, was stripped by back-extraction only at low oxalic acid concentrations (dark grey area in Figure 2), but starting from 0.5 equivalents of oxalic acid also precipitation stripping occurred (light grey area in Figure 2). At 2.25 equivalents of oxalic acid, almost all Sc(III) is stripped by precipitation. Thus, by stripping with 2.25 equivalents of oxalic acid, Sc(III) and Fe(III) can be separated almost completely from each other. Fe(III) is transferred to the aqueous phase as the highly soluble oxalate complex and Sc(III) oxalate is precipitated.

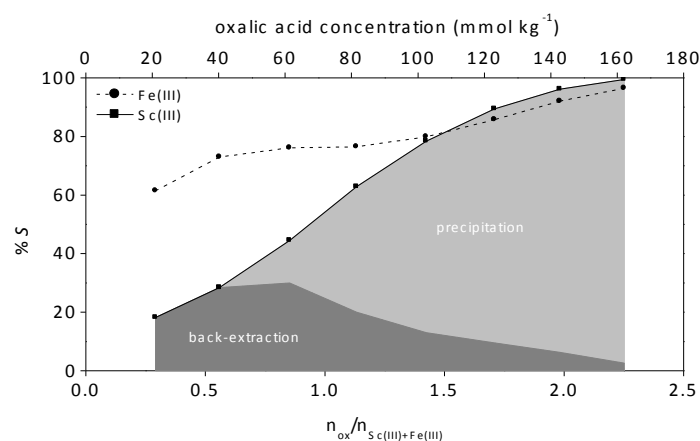


Figure 2: Selective stripping of an ionic liquid phase loaded with Sc(III) (41 mmol·kg⁻¹) and Fe(III) (31 mmol·kg⁻¹) by contacting with an oxalic acid solution (20–160 kg⁻¹) as a function of the ratio of the oxalic acid content to the total metal ion content (1:1 phase ratio).

The results discussed above indicate that the [Hbet][Tf₂N] ionic liquid might be suitable for the recovery of Sc(III) from real red mud samples by a combination of extraction, scrubbing and stripping with oxalic acid. To validate this, it was tried to selectively recover Sc(III) from real red mud leachates. Both the influence of the phase ratio of the extraction mixture (Figure 3) and the influence of the pH was examined. Lowering the phase ratio resulted in a large decrease in extraction but only a small increase in the Sc(III) and Fe(III) concentration in the ionic liquid phase. Thus, lowering the phase ratio is not beneficial for the processing of red mud leachates and extraction should be performed preferably at a phase ratio of 1. Similar results were obtained for both the HCl and the HNO₃ leachates, but the extraction of Fe(III) is lower in the case of the HCl leachates. This might be explained by the relatively high chloride concentration in the aqueous phase which inhibits Fe(III) extraction by the formation of anionic chloro complexes.

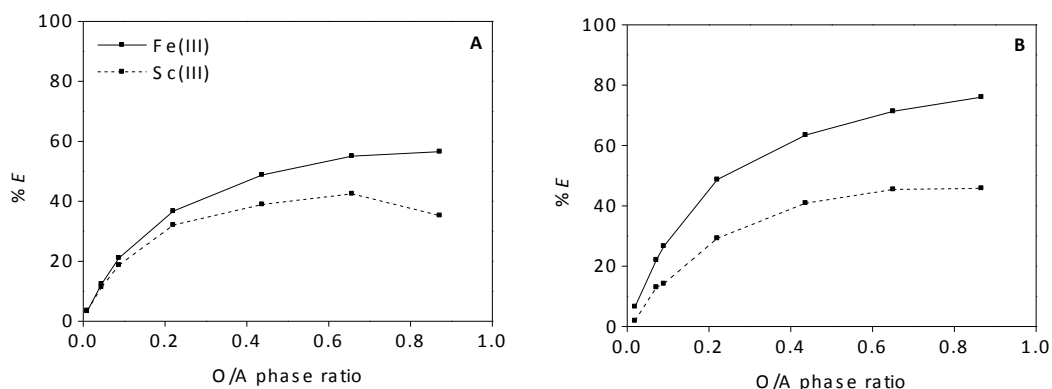


Figure 3: Extraction of Sc(III) (dashed line) and Fe(III) (solid line) from red mud leachates as a function of the O/A phase ratio. **A:** %E for the extraction from the HCl leachate. **B:** %E for the extraction from the HNO₃ leachate.

The influence of the pH was examined by addition of NaOH to the extraction mixture. The equilibrium pH of a 1:1 extraction mixture of red mud leachate and [Hbet][Tf₂N] without any pH adjustment was equal to approximately 1. Since the extracting ionic liquid is an acidic extractant, extraction should be improved by increasing the pH, for instance by addition of NaOH. However, as described earlier, [Hbet][Tf₂N] forms a pH buffer when contacted with an aqueous solution, making it hard to significantly increase the pH. Furthermore, precipitation was observed when increasing the equilibrium pH above 1.2. The results of the experiments showed that an increase of the pH from 1 to 1.2 led to a very small increase in extraction of Sc(III) and Fe(III), but an almost doubling of the undesirable co-extraction of the trivalent lanthanide ions.

Conclusions

The ionic liquid [Hbet][Tf₂N] is a promising solvent for the selective recovery of Sc(III) from red mud leachates by solvent extraction. Sc(III) is efficiently separated from most of the ions present in red mud leachates, namely Y(III), the trivalent lanthanide ions, Al(III), Ti(IV), Ca(II) and Na(I), during the extraction itself. However, Fe(III) is co-extracted to a large extent. Full separation of Sc(III) and Fe(III) was obtained by precipitation stripping using oxalic acid, based on the differences in solubility of scandium(III) and iron(III) oxalate. By contacting the loaded ionic liquid phase with an oxalic acid solution, scandium(III) oxalate precipitated out of solution while Fe(III) was back-extracted to the aqueous phase as a highly soluble iron(III) oxalate complex.

Acknowledgements

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