CRYSTALLIZATION OF A SCANDIUM PHASE IN THE VALORIZATION OF METALLURGICAL WASTE STREAMS

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Abstract

Scandium can be recovered from metallurgical waste streams such as bauxite residue by a process comprising various operations including leaching, solvent extraction, crystallization and metallothermic reduction of ScF_3. The focus of this study is to investigate the crystallization of scandium as ammonium scandium hexafluoride from solvent extraction strip liquors in which the scandium content has been elevated to concentrations of about 2000 mg/L in an NH_4F solution. The technical feasibility of anti-solvent crystallization of $(NH_4)_3ScF_6$ from both synthetic and real strip liquors has been proven with recoveries greater than 98% and product purities greater than 98.3%. The impurity metals such as Fe and Zr were also present in the final solid product since their phases have comparable or lower solubilities.

Introduction

Scandium, a highly valued metal with a cost estimate of USD132 per gram ingot as of 2018 [1], can be recovered from waste streams of other metallurgical processes such as bauxite residue and titanium dioxide acid waste. The overall process comprises various stages including acid leaching of the bauxite residue, followed by solvent extraction of the pregnant leach solution using suitable organic solvents and stripping of metals from the organic phase using NH_4F solution to increase the concentration of scandium to levels suitable for crystallization [2-9]. Typical strip liquors used in this study contained > 2000 mg/L scandium and some metal impurities including Fe, Ti, Zr, Al, V, U and Th in varying concentrations in a 3 mol/L NH_4F solution. The technical feasibility of cooling and anti-solvent crystallization to recover scandium as $(NH_4)_3ScF_6$ has been investigated using synthetic strip liquors. Anti-solvent crystallization using ethanol and methanol solvents gave higher recoveries exceeding 98% with respect to Sc using a strip liquor to alcohol volumetric ratio of 1:1, while the recovery obtained by cooling crystallization was below 50% at the lowest investigated crystallization temperature of 1°C [9]. Anti-solvent

crystallization was then investigated in detail using real strip liquors to study the uptake of impurity metals in the final product.

Results

Anti-solvent crystallization was carried out using real strip liquors containing low to high impurity metal : scandium concentration ratios. The composition of one strip liquor with high levels of Ti and Zr in comparison to Sc is shown in Table 1.

Table 1: Strip liquor composition

Sc (mg/L)	Fe (mg/L)	Ti (mg/L)	Th (mg/L)	Zr (mg/L)
924.27	65.95	2707.90	54.37	1295.15

Figure 1 shows the concentration of metals remaining in solution after crystallization against the added alcohol content, as determined by ICP-OES. It was observed that the metal concentrations decrease with increasing alcohol content, except for Ti which remains in solution.

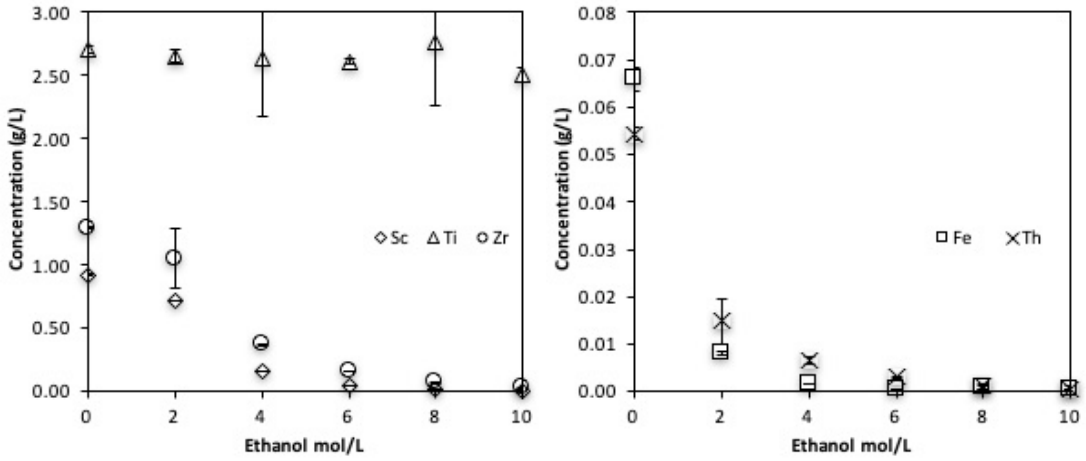

Figure 1: Metal concentrations after crystallization *v*. ethanol concentration. (A solvent to anti-solvent volumetric ratio of 1:1 corresponds to an ethanol concentration of 8.6 mol/L.)

The solid product was analyzed by ICP-OES after dissolution, and was shown to contain almost all metal impurities in concentrations reflective of their relative abundances in the initial strip liquor. However, Ti was only present in the solid product in minute quantities despite having the highest concentration in the initial strip liquor. The highest product purity was obtained using strip liquors containing low impurity metal concentrations, viz. exceeding 98.3 % $(NH_4)_3ScF_6$, and in some cases where Zr was present at very high concentrations the Zr phase, $(NH_4)_3ZrF_7$, was the main product. It is therefore concluded that the purity of the final $(NH_4)_3ScF_6$ product is strongly dependent on the composition of the initial strip liquor, most

likely due to lower or comparable solubilities of the solid phases of the impurities. Preliminary results from experiments where supersaturation is controlled by dosing the alcohol at lower flow rates and by seeding with $(NH_4)_3ScF_6$ crystals indicate that the product purity can be increased. Based on these results, a stage-wise crystallization process can be designed to allow selective crystallization of a purer Sc product from the first crystallizer operating at lower supersaturation and an impure product to crystallize in subsequent crystallizers.

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