

Article

Scandium Recovery from an Ammonium Fluoride Strip Liquor by Anti-Solvent Crystallization

Şerif Kaya ^{1,*}, Edward Michael Peters ^{2,*}, Kerstin Forsberg ^{2,*}, Carsten Ditttrich ³, Srečko Stopic ⁴ and Bernd Friedrich ⁴

¹ Mining Engineering Department, Middle East Technical University, Ankara 06800, Turkey

² KTH Royal Institute of Technology, Department of Chemical Engineering, Teknikringen 42, SE-100 44 Stockholm, Sweden

³ MEAB Chemie Technik GmbH, 52068 Aachen, Germany; carsten@meab-mx.com

⁴ IME Institute of Process Metallurgy and Metal Recycling, RWTH Aachen University, 52056 Aachen, Germany; sstopic@ime-aachen.de (S.S.); bfriedrich@ime-aachen.de (B.F.)

* Corresponding author: serifikaya@gmail.com (Ş.K.); edwpet@kth.se (E.M.P.); kerstino@ket.kth.se (K.F.); Tel.: +90-537-513-0949 (Ş.K.); +46-72-565-9653 (E.M.P.); +46-8-790-6404 (K.F.)

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Abstract: In this study, the crystallization of scandium from ammonium fluoride strip liquor, obtained by solvent extraction, was investigated using an anti-solvent crystallization technique. Acetone, ethanol, methanol and isopropanol were added individually to the strip liquor as the anti-solvent and scandium was precipitated and obtained in the form of $(\text{NH}_4)_3\text{ScF}_6$ crystals. The results show that scandium can be effectively crystallized from the strip liquor to obtain an intermediate, marketable scandium product. Yields greater than 98% were obtained using an anti-solvent to strip liquor volumetric ratio of 0.8. Acetone had the least performance at lower anti-solvent to strip liquor volumetric ratios, possibly due to its limited H bonding capability with water molecules when compared to alcohols.

Keywords: scandium; anti-solvent crystallization; solvent extraction; precipitation; ammonium scandium hexafluoride; chemical equilibrium diagram

1. Introduction—Previous Studies and State of the Art

Scandium was identified as a critical raw material (CRM) to the European Union in 2017 and in the US draft list of critical minerals in 2018 [1,2]. Scandium is used in solid oxide fuel cells (SOFCs), which is a rapidly growing market [3,4]. Currently more than 90% of the annual global production of Sc is used for the production of SOFCs [3]. Scandium also finds use in, e.g., laser garnets, as phosphors for light emitting diodes and as an alloying element for aluminium [5–7]. The aluminium scandium alloys have high strength, are corrosion resistant and allow welding without loss in strength, which makes them attractive for the aerospace and automotive industries [3,7]. Viable sources of scandium include nickel-cobalt laterites, uranium processing wastes, residues from titanium oxide production and bauxite residues (so called red mud) [8–13]. Scandium is produced in a few countries worldwide with 66% of the production in China, 26% in Russia and 7% in Ukraine [1].

In the conventional processing to extract scandium, the last steps often consist of the precipitation of scandium oxalate or scandium hydroxide from a purified solution [8]. The scandium salts can then be calcined to obtain pure scandium oxide [14]. The scandium oxide can then be fluorinated with HF (Hydrofluoric acid) to produce ScF_3 [15]. The latter is the precursor used in scandium metal production. This is a long procedure with many stages, driving the cost and environmental footprint of scandium fluoride and scandium metal. According to sale statistics in the US, the estimated price

of Sc_2O_3 (99.99% purity) is 4.60 US dollars/g, that of ScF_3 (99.9% purity) is 277 US dollars/g, whilst that of Sc metal ingot is 132 US dollars/g in 2018 [16]. An alternative approach is to pre-concentrate scandium from waste streams by leaching, solvent extraction, and then stripping scandium from the organic phase using ammonium fluoride. A pure scandium ammonium fluoride solid phase can then be obtained by crystallization. Anti-solvent crystallization is a technique that involves adding a solvent that is soluble in a solution so as to lower the solubility of the desired salt, thereby generating supersaturation in the resultant mixture [17].

There is information about the crystallization of scandium fluoride phases in literature. Scandium can be precipitated from an ammonium fluoride solution as $\text{ScF}_3 \cdot (0-0.25)\text{H}_2\text{O}$, NH_4ScF_4 , $(\text{NH}_4)_3\text{ScF}_6$, $(\text{NH}_4)_5\text{Sc}_3\text{F}_{14}$, $\text{NH}_4\text{Sc}_3\text{F}_{10}$ or $(\text{NH}_4)_2\text{Sc}_3\text{F}_{11}$, depending on the composition of the solution and temperature [18–20]. Scandium could also be precipitated as sodium or potassium fluoride and ammonium fluoride salts [19]. Scandium has been crystallized as scandium trifluoride on an industrial scale after the stripping of Ti(IV), Th(IV) and Sc(III) from dodecyl phosphoric acid in kerosene using hydrofluoric acid in uranium processing [13]. Scandium and thorium were precipitated while titanium was left in the solution. The solids were further processed after dissolution in a sodium hydroxide solution. Scandium has also been stripped from loaded organic phases of D2EHPA by using sodium fluoride solution from which Na_3ScF_6 has been obtained [14]. The precipitate, $(\text{NH}_4)_2\text{NaScF}_6$, has also been reported to form from a Sc containing strip liquor using NaOH solution at pH 9. After calcination of this intermediate product, a cryolite type phase ($\text{NaScF}_4\text{-Na}_3\text{ScF}_6$) can be obtained for use in Al electrolysis in place of Na_3AlF_6 to obtain Al-Sc alloys [10].

In the present work, a novel approach is suggested where scandium is precipitated as an ammonium scandium hexafluoride $(\text{NH}_4)_3\text{ScF}_6$ salt by addition of an alcohol to an NH_4F strip liquor containing Sc. The alcohol acts as an anti-solvent, which effectively reduces the solubility of the scandium salt in the resultant mixture. The precipitated ammonium scandium hexafluoride salt can directly be used for scandium metal production by eliminating the use of environmentally undesirable hydrofluoric acid during the conversion of Sc_2O_3 into ScF_3 .

2. Experimental Procedure

2.1. Thermodynamic Modeling

A thermodynamic model of the Sc-F system was constructed using MEDUSA (Make Equilibrium Diagrams Using Sophisticated Algorithms) software, version 2017-Jan-27, developed at KTH Royal Institute of Technology, Stockholm, Sweden [21]. The software is based on algorithms for the computation of multicomponent, multiphase solution equilibrium [22–24]. The pH was varied between 1 and 12, and the logarithmic total fluoride concentration, $\log[\text{F}^-]_{\text{TOT}}$, was varied between -2 and 2 , corresponding to a total F^- concentration of 0.01 to 100 mol/L at 25 °C. All models were conducted for a total Sc concentration of 67 mmol/L (3000 mg/L) at 25 °C. The software predicts the solution speciation based on the stability constants and solubility products of various complexes and salts, respectively. The overall stability constants of the Sc-F and Sc-OH complexes used as well as the solubility products of the respective solids are shown in Table 1. The overall stability constant of ScF_6^{3-} was extrapolated and approximated from the constants of the lower Sc-F complexes, since they had a perfect quadratic fit. The existence of the pentafluoride complex, ScF_5^{2-} , was only mentioned briefly [20] with no adequate information available in other sources. There is also evidence of the polynuclear complex, $\text{Sc}_2\text{F}_3^{3+}$ [25]. The software computed the ionic strength as the fluoride concentration, and the pH was varied. The first thermodynamic model was conducted by considering soluble complexes only, without considering the formation of any solids; the second model considered the formation of solids; and the third model was conducted by varying the fluoride activity, $\log\{\text{F}^-\}$, between -8 and 2 , instead of the total fluoride concentration, as was the case in the first and second models.

Table 1. Stability constants of Sc complexes and solubility products of Sc salts.

Complex	pK _n	Ref.	Complex	pK _n	Ref.
ScF ²⁺ (aq)	7.08		ScO(OH)	−9.4	
ScF ₂ ⁺ (aq)	12.89		Sc(OH) ₃	−29.7	
ScF ₃ ⁰ (aq)	17.36	[26]	Sc(OH) ₂ ²⁺ (aq)	−4.3	
ScF ₄ [−] (aq)	20.21		Sc(OH) ₂ ⁺ (aq)	−9.7	[27]
ScF ₆ ^{3−} (aq)	22.00 *		Sc(OH) ₃ (aq)	−16.1	
Sc ₂ F ₃ ³⁺ (aq)	20.7	[28]	Sc(OH) ₄ [−] (aq)	−26	
ScF ₃ (s)	−11.5	[29]	Sc ₂ (OH) ₂ ⁴⁺ (aq)	−6	
Sc ₂ O ₃ (s)	−36.3	[27]	Sc ₃ (OH) ₅ ⁴⁺ (aq)	−16.34	

* denotes extrapolated.

The model served to determine the dominant Sc-F complexes under the experimental conditions.

2.2. Experimental Procedure

The scandium containing strip liquor was prepared through the solvent extraction of a synthetic scandium sulphate solution followed by stripping since this procedure mimics that employed to recover scandium by the envisaged process. The organic solvent that was used contained D2EHPA purchased from Lanxess, Germany; the actual composition is withheld for proprietary reasons. This solvent was mixed with a scandium sulphate solution containing 3671 mg/L Sc at room temperature in a beaker for 10 min at an organic to aqueous phase volumetric ratio of O/A: 1/1. The synthetic scandium sulphate solution was prepared by dissolving 99.9% scandium sulphate pentahydrate obtained from Richest Group, China. After mixing the organic extractant and the scandium-containing aqueous phase, the loaded organic was separated from the raffinate via a separation funnel, and the raffinate phase was analyzed for scandium content to calculate the % extraction. No purification steps were conducted on the reagents used during the solvent extraction tests. The stripping of scandium from the loaded organic phase was conducted at room temperature by using a 3 mol/L reagent grade ammonium fluoride solution with an aqueous to organic phase ratio of A/O: 1/1. After stripping, the stripped organic phase was separated from the scandium-containing strip liquor via a separation funnel and the scandium content of the ammonium scandium fluoride strip liquor was analyzed to determine the stripping efficiency. A synthetic strip liquor was then obtained for use in the anti-solvent crystallization experiments.

After stripping, reagent grade acetone, ethanol, methanol and isopropanol were added to the ammonium scandium hexafluoride strip liquor separately at room temperature as anti-solvents. The solutions were mixed for 10 min whereby precipitation occurred. The precipitated crystals were separated from the solution by means of filtration using a 0.22 µm membrane. The obtained crystals were then washed with the same anti-solvent, dried overnight at 60 °C, and analyzed by a “Rigaku Ultima-IV” model powder X-ray diffractometer (Rigaku, San Antonio, TX, USA) with a Cu-Kα X-ray tube working under 40 kV and 40 mA to identify the crystal structure of the precipitates. A Spectro Arcos ICP-OES analyzer (SPECTRO Analytical Instruments GmbH, Kleve, North Rhine-Westphalia, Germany) capable of true-axial and true-radial plasma observations was used to analyze the total concentration of the liquid samples. The samples were diluted by a factor of 100, such that the organic concentration in the samples analyzed was below 0.5% v/v. A JEOL JSM-6490LV SEM (Scanning Electron Microscope) (JEOL USA, Peabody, MA, USA) was used to determine the crystal morphology and size of the precipitates.

3. Results and Discussion

3.1. Thermodynamic Model

Figure 1A,B shows the thermodynamic models conducted for a total Sc concentration of 67 mmol/L (3000 mg/L) at 25 °C to determine the stability of soluble complexes with varying pH and total fluoride concentration, as well as a consideration of solids precipitation, respectively. Figure 1C shows the model (67 mmol/L Sc at 25 °C) with variation of fluoride activity and pH.

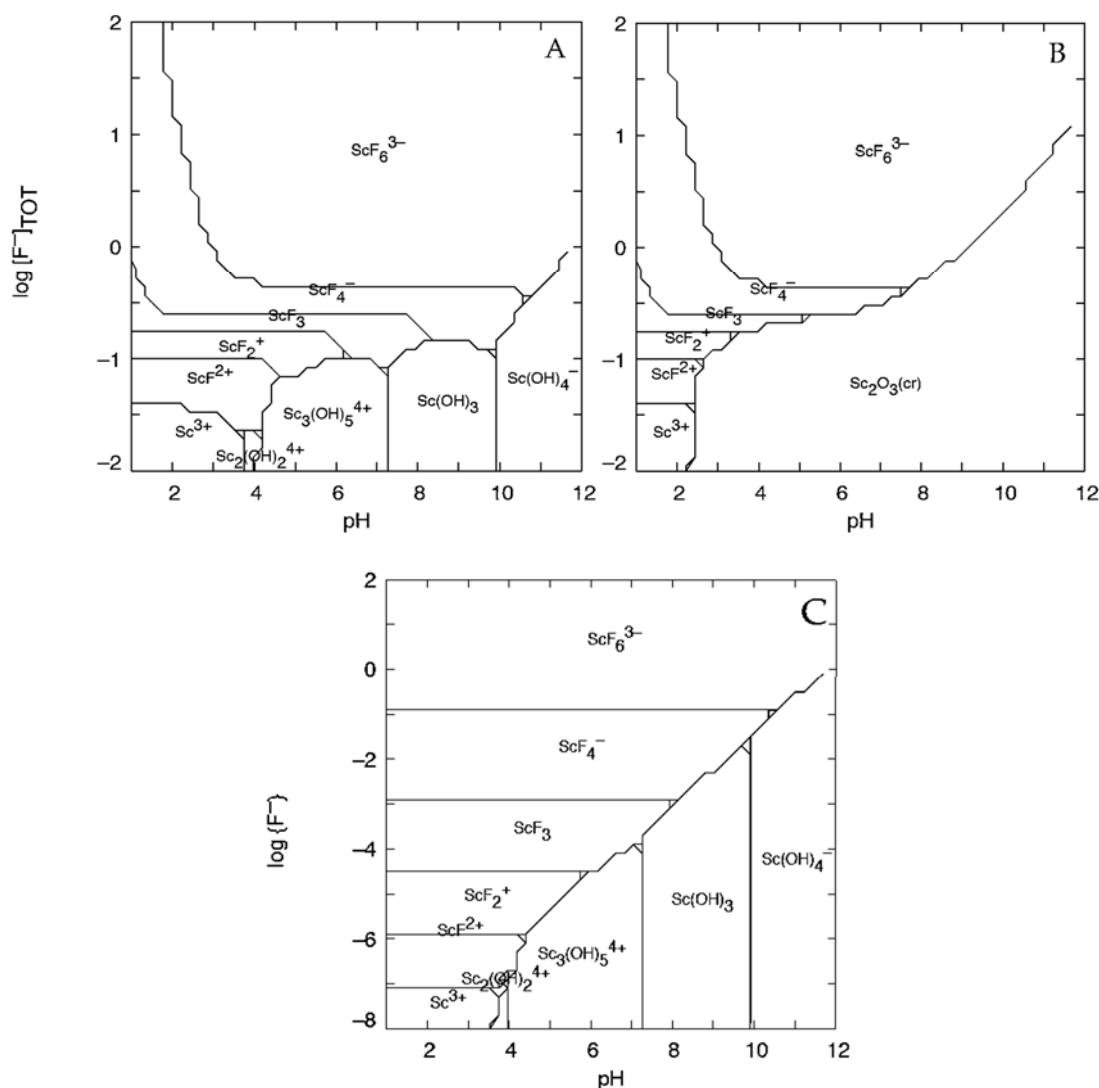


Figure 1. Predominance area diagram of Sc species in fluoride medium at 67 mmol/L (3000 mg/L) Sc at 25 °C. (A) Soluble complexes only with respect to logarithm of total fluoride ion concentration and pH; (B) Soluble complexes and solids formation with respect to logarithm of total fluoride concentration and pH; (C) Soluble complexes only with respect to logarithm of fluoride activity and pH.

The diagrams show that higher Sc-F complexes become more stable with an increase in the F^- ion concentration. The fluoride complexes, $[ScF_n]^{3-n}$, for values of $n = 0$ to 4, are more stable at a total fluoride concentration below 0.5 mol/L, corresponding to $\log [F^-]_{TOT}$ of -0.3 ; above that, the ScF_6^{3-} complex becomes more dominant. The Sc-OH complexes are more dominant in alkaline media at low fluoride concentrations. The tetra- and hexafluoride complexes are also stable over the entire range of pH values at fluoride concentrations above $\log [F^-]_{TOT} -0.6$. The strip liquor used in this study had a pH of about 5.6 and a fluoride concentration of about 3 mol/L, corresponding to $\log [F^-]_{TOT}$ of

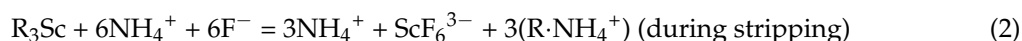
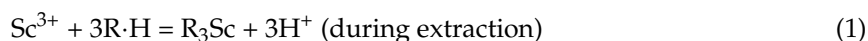
0.48 mol/L. The region of operation is the one in which ScF_6^{3-} is more stable; therefore $(\text{NH}_4)_3\text{ScF}_6$ is likely to be precipitated under the experimental conditions. However, Figure 1B shows that Sc_2O_3 is likely to precipitate out as the pH increases above 2.5 within a certain region of lower fluoride concentrations; dominated by hydroxide complexes in Figure 1A and extending to higher fluoride concentrations above pH 8. Presumably, it is actually the hydroxide, $\text{Sc}(\text{OH})_3$, that precipitates as the pH increases, but the software most certainly predicts the oxide since it is the most insoluble. The results of this model are not universal and should be used with care; otherwise a new model is required for each different system.

A similar model, depicted in Figure 1C, was conducted by varying the logarithm of fluoride activities; the result matched the one in the literature [30] up to $\log\{\text{F}^-\}$ of -3 over the entire range of pH 1–12. The difference between the two models is that the new model considers higher scandium fluoride complexes (ScF_4^- and ScF_6^{3-}) at higher activities $\log\{\text{F}^-\}$ between -3 and 2 , as well as some polynuclear Sc-OH complexes. Note that $\log\{\text{F}^-\}$ is used herein to refer to logarithm of activity and $\log[\text{F}^-]_{\text{TOT}}$ refers to logarithm of total concentration as shown in Figure 1A–C.

3.2. Strip Liquor Preparation

The chemical analysis of the raffinate phase with O/A: 1/1 showed that after mixing scandium sulphate solution containing 3671 mg/L Sc with the organic phase, almost all of the scandium present in the aqueous phase was extracted to the organic phase with a raffinate scandium concentration of <1 mg/L and an extraction efficiency of $>99.9\%$. The extracted scandium was then stripped from the organic phase by 3 mol/L NH_4F solution. The chemical analysis result of the strip liquor obtained with A/O: 1/1 ratio showed that the strip liquor contained 3660 mg/L scandium with a 98% stripping efficiency.

The high stripping efficiency of scandium with 3 mol/L NH_4F solution is due to the complexation of scandium and fluoride ions in high concentration of ammonium fluoride media [20,31–34] according to the following extraction and stripping reactions Equations (1) and (2), in which the organic extractant is represented as R:



The scandium will exist with fluoride and ammonium ions in complexes with different stoichiometry, as shown in Figure 1 with the ScF_6^{3-} complex being dominant at F^- concentrations above 0.5 mol/L.

3.3. Anti-Solvent Crystallization

After the stripping of scandium during the solvent extraction step, a synthetic stock solution of 3660 mg/L scandium-containing ammonium fluoride strip liquor was obtained and was used for anti-solvent crystallization experiments. In order to decrease the solubility of scandium, the direct addition of ethanol, methanol, isopropanol and acetone was tested. The results from these experiments are presented in Figure 2. Figure 3 shows the results from another experiment conducted using ethanol as the anti-solvent at higher ethanol to strip liquor ratios. In these figures, the vol.% reagent added is expressed as a fraction of the strip liquor volume, not the total solution mixture volume. It can be seen that the solubility of scandium decreases as the volume of anti-solvent added to the initial strip liquor increases. This is attributed to the reduction in the solubility of $(\text{NH}_4)_3\text{ScF}_6$ in the resultant solvent mixture.

According to the information given in Figure 2, acetone was found to be the least effective anti-solvent in precipitating out a Sc phase from the strip liquor, compared to the other solvents. This could be due to differences in the molecular structure between a ketone and an alcohol. The ketone has a limited hydrogen-bonding capability compared with the alcohols, implying that it interacts weakly with water molecules in solution. The lower molecular weight ketones are capable of forming

hydrogen bonds with water as hydrogen acceptors due to the lone pair of electrons on the oxygen atom [35], whereas alcohols and water are both hydrogen acceptors and donors. To further understand the degree of interaction of solvents, the solubility parameters of various solvents were computed [36] taking into account the contributions of the dispersion (London) forces, polar forces and hydrogen bonding. This parameter is used to determine the degree of interaction of solvents; the closer the values of the solubility parameters of two solvents, the greater the level of interaction. The solubility parameters of water, methanol, ethanol and acetone have been reported as 23.5, 14.28, 12.92 and 9.77 $\text{cal}^{1/2} \cdot \text{cm}^{-3/2}$, implying the decreasing solubility of the organic solvents in water in that order. By using 25 vol.% and 50 vol.% of ethanol, methanol or isopropanol, >88% and >98% of Sc present in the strip liquor can be precipitated and separated out from the strip liquor, respectively.

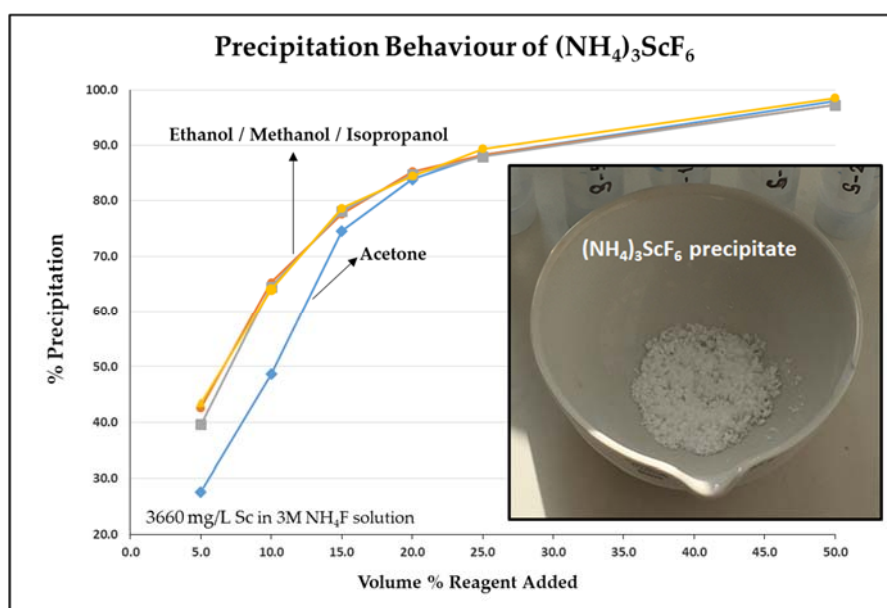


Figure 2. Effect of different anti-solvent addition on the crystallization behavior of scandium.

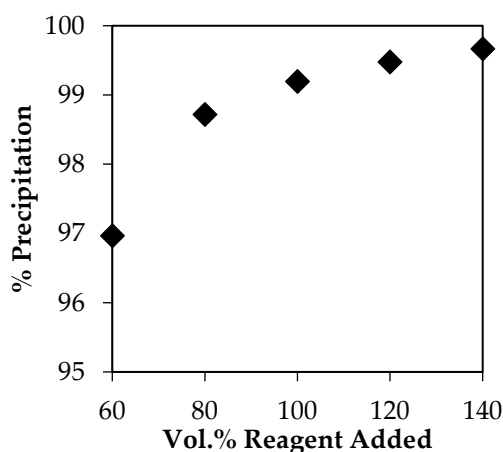


Figure 3. Effect of ethanol addition at higher ratios (Adopted from [37]).

Figures 2 and 3 are in close agreement and the latter shows that the extent of the precipitation becomes asymptotical at a ratio of 0.8 with yields greater than 98.5%. This means that the amount of anti-solvent added could be optimised within the ratio 0.8–1.0 since the further addition of anti-solvent has a minor precipitation effect, hence unnecessary cost and process overloading. After adding the anti-solvent, scandium immediately started to precipitate from the strip liquor in the form of fine crystals, which settled down to the bottom of the beaker when stirring was stopped. The crystals were

easily separated by filtration and analysed by powder XRD (X-Ray Diffraction), the result of which is given in Figure 4. According to the XRD data, the precipitated crystals were found to be in the form of $(\text{NH}_4)_3\text{ScF}_6$ [18].

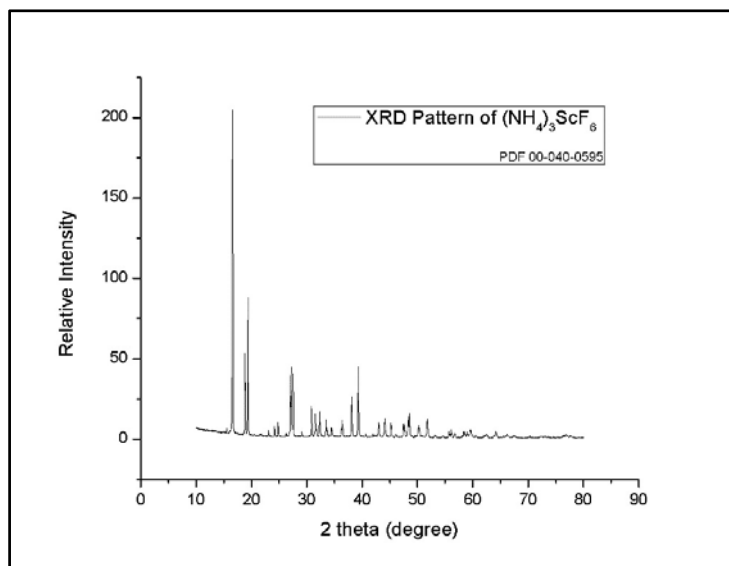
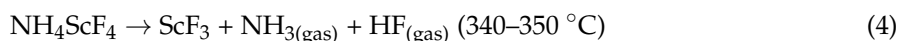
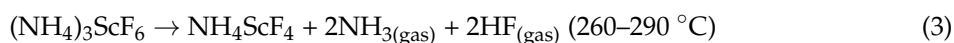


Figure 4. XRD pattern of the obtained $(\text{NH}_4)_3\text{ScF}_6$ crystals.

At the end, fine $(\text{NH}_4)_3\text{ScF}_6$ crystals can be obtained, and since this compound is a water soluble form of scandium, it may be marketed to the industry in this form for various applications. Alternatively, the obtained $(\text{NH}_4)_3\text{ScF}_6$ crystals may be calcined in an atmosphere controlled furnace (to capture HF gas) according to the following chemical reactions Equations (3) and (4) [38] to obtain ScF_3 , which is the precursor for the production of Sc metal or alloys by metallothermic or electrometallurgical processing techniques.



A detailed techno-economic viability study would be required in the future for a comparison of this process with the traditional fluorination route. In the traditional process, scandium was crystallized as the hydroxide or oxalate which were then calcined at temperatures of about 700–800 °C to obtain scandium oxide [13] followed by fluorination using HF acid to obtain ScF_3 . In the current processing route, scandium is precipitated as $(\text{NH}_4)_3\text{ScF}_6$ from an NH_4F solution. This precipitate is then calcined at 350 °C to obtain ScF_3 . Whilst large alcohol quantities are required for this process, it is possible to recover the alcohol by distillation for re-use in the crystallization process. This implies higher equipment costs, but a substantial reduction in operating costs could be realised since the alcohol can be re-used, the calcination temperature is much lower and the process eliminates the use of HF acid. On the other hand, the main disadvantage of the envisaged process is the use of alcohols, which are highly flammable and pose a safety hazard in an industrial scale operation. However, using equipment that minimizes the risk of fire, along with adherence to safety standards and regulations can minimize this risk.

The morphology of the $(\text{NH}_4)_3\text{ScF}_6$ crystals was analysed by SEM as shown in Figure 5. Discrete regular shaped crystals were obtained and the bulk of the crystals had sizes in the range ca. 1–3 µm. There were no significant discrepancies in morphology and crystal sizes observed amongst the different anti-solvents used. All experiments were conducted by the addition of the anti-solvent in

bulk without control of supersaturation. It is expected that a better crystal product quality could be obtained by controlling the supersaturation through the controlled addition of the anti-solvent.

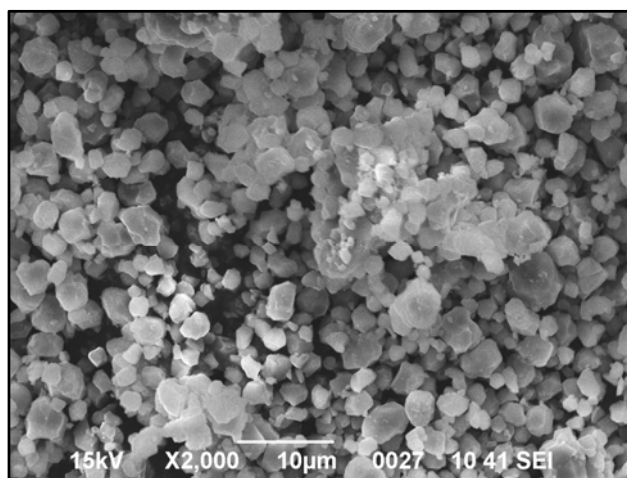


Figure 5. SEM image of $(\text{NH}_4)_3\text{ScF}_6$ crystals obtained using ethanol at a ratio of 0.2.

4. Conclusions

In this study, scandium was successfully crystallized and recovered from ammonium fluoride strip liquor in the form of fine $(\text{NH}_4)_3\text{ScF}_6$ crystals by means of an anti-solvent crystallization technique. The use of acetone, ethanol, methanol and isopropanol was predicted to decrease the solubility of $(\text{NH}_4)_3\text{ScF}_6$, and it was proven that upon adding the above-mentioned anti-solvent reagents, scandium immediately started to crystallize out of the solution in the form of fine $(\text{NH}_4)_3\text{ScF}_6$ within just 10 min of mixing. Very high precipitate yields above 98% could be obtained with an anti-solvent to strip liquor ratio of 0.8, after which it levelled off. The crystal product was regular shaped with sizes in the range of ca. 1–3 μm , and no discrepancies were observed in the product quality amongst the different anti-solvents employed. Acetone had the least effectiveness at very low ratios, which was ascribed to its limited H-bonding capability in comparison to the alcohols, and hence its weaker solvent-solvent molecular interactions in solution.

Author Contributions: Ş.K. and E.M.P. conceived, designed and performed the experiments; all of the authors analysed the data; C.D. contributed reagents/materials; S.S. and B.F. contributed analysis tools; Ş.K., E.M.P. and K.F. wrote the paper.

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

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