Scandium extraction from multicomponent systems by crystallization of complex sulfates

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Abstract. Red mud generated from alumina production is one of the most promising scandium resources. Leaching for concentrating scandium and other valuable metals is often performed with the use of acid solutions in specially selected conditions. Different precipitants can be employed for selective precipitation of scandium in the form of poorly soluble compounds. A new method for the crystallization of ammonium scandium sulfates from sulfuric solutions was carried out in this study. Depending on the ammonium cation concentration, precipitation is possible in the form of $\text{NH}_4\text{Sc(SO}_4\text{)}_2$ or $(\text{NH}_4)_3\text{Sc(SO}_4\text{)}_3$. The solubility values for $\text{NH}_4\text{Sc(SO}_4\text{)}_2$ and $(\text{NH}_4)_3\text{Sc(SO}_4\text{)}_3$ in water established by the isothermal saturation method were 9.02 and 12.89 g/l $\text{Sc}_2\text{O}_3$, respectively. Complete precipitation of the most promising gravimetric form of scandium represented by $\text{NH}_4\text{Sc(SO}_4\text{)}_2$ was achieved at 5-6 M $\text{H}_2\text{SO}_4$ and 0.5 M $\text{NH}_4^+$. The product of crystallization from sulfuric solution used for treating poor scandium concentrate produced from red mud is a mixture of polymorphs of the composition $\text{NH}_4\text{Sc(SO}_4\text{)}_2$. Co-precipitated impurities of $\text{Al}$, $\text{Fe}$, $\text{Ti}$, $\text{Zr}$ etc. are separated after repeated dissolution and precipitation of ammonium scandium sulfate under analogous conditions. The recrystallization product after calcination at 1000°C contains 99% $\text{Sc}_2\text{O}_3$.

1. Introduction

About 70 million tons of red mud (RM) – wastes generated after extraction of alumina from bauxites in the Bayer process – are annually disposed into the environment worldwide. These wastes are universally recognized as a promising technogenic feedstock due to a high content of such components as iron, aluminum, titanium, calcium, and rare elements [1,2]. However, technologies for the utilization of red mud with obtaining of valuable products have not been introduced for different reasons including their low efficiency [3]. One of the most valuable components of RM is scandium classified, in spite of its high cost, as a critical metal of the future. Potential application of scandium in metallurgy, chemical and electronic industries is restrained by small volumes of its production in the world and a high price. Thus, the development of effective processes of scandium recovery from cheap secondary and technogenic raw materials is an urgent scientific challenge.

The scandium content in RM does not exceed 120-150 g/t $\text{Sc}_2\text{O}_3$, therefore scandium is recovered by selective extraction or by complete break-down of feedstock with subsequent separation of components [4]. Most often slime and other mineral raw materials are leached with acid solutions, and then scandium is extracted by hydrometallurgical methods – extraction, sorption and precipitation. Earlier we have developed carbonate recovery of scandium from RM pulp with the use of kiln gas emissions [5]. This technique allows mutual neutralization and involvement of two types of industrial waste in the processing – alkaline slime and thermal gases containing acid-forming oxides. A poor scandium concentrate with 2-5% $\text{Sc}_2\text{O}_3$ content was separated from the clarified carbonate solution. In
this paper we propose selective recovery of scandium by crystallization of ammonium scandium sulfates from sulfuric solutions in the presence of impurities of the most abundant metals – Al, Fe, Ti, Zr etc. The structures of ammonium scandium sulfates of two compositions NH₄Sc(SO₄)₂ and (NH₄)₃Sc(SO₄)₃ were first studied by the authors in detail in the works where the conditions of existence of polymorphic modifications were reported [6,7]. These intermediate complex compounds extracted from sulfuric solutions can be calcined at temperatures 550-600°C to produce scandium sulfate and at 950-1000°C to obtain scandium oxide. The information about the solubility of ammonium scandium sulfates in aqueous solutions as a function of acidity was also studied to search for the optimal conditions of complete scandium recovery.

2. Methodology of crystallization from synthetic systems

The individual compounds NH₄Sc(SO₄)₂ and (NH₄)₃Sc(SO₄)₃ were preliminarily synthesized and certified as described earlier. The solubility of the complex sulfates was studied by the isothermal method by keeping the solutions having excessive concentration of the corresponding compound in hermetically sealed vessels at a temperature of 20±0.5°C with constant stirring until equilibrium was reached. The establishment of equilibrium was judged by the constant content of scandium in the solutions. To determine the solubility, it was assumed that the following equilibria are reached in the saturated solutions between the solid substance a and in initial liquid, respectively:

\[
\text{NH}_4\text{Sc(SO}_4\text{)}_2 \leftrightarrow \text{Sc}^{3+} + \text{NH}_4^+ + 2\text{SO}_4^{2-} \quad (1)
\]

\[
(\text{NH}_4)_3\text{Sc(SO}_4\text{)}_3 \leftrightarrow \text{Sc}^{3+} + 3\text{NH}_4^+ + 3\text{SO}_4^{2-} \quad (2)
\]

The thermodynamic constants of these equilibria give the solubility products of the compounds. The solubility values calculated from these constants are presented in Table 1. The obtained values show that NH₄Sc(SO₄)₂ is less soluble and more promising for crystallization from aqueous solutions.

| NH₄Sc(SO₄)₂ | (NH₄)₃Sc(SO₄)₃ |
|-------------|----------------|
| 9.02        | 12.89          |

Table 1. Solubility of scandosulfates at 20±0.5°C, g/l Sc₂O₃

The synthetic solutions of scandium were crystallized to investigate the solubility of NH₄Sc(SO₄)₂ in the presence of 0.5 M NH₄Cl at various acidity using the isothermal solubility method. The solutions with crystallized precipitates were held at 20±0.5°C while stirring for 120 h. The precipitates were filtered, washed with ethanol (95%), dried and weighed, and their composition was monitored. The content of Sc and H₂SO₄ in the solution was determined. The degree of scandium extraction (yield) \( \eta \) (%) in the form of complex scandium ammonium sulfate NH₄Sc(SO₄)₂ was estimated by Eq. (3):

\[
\eta, \% = \frac{m_{\text{Sc}}}{m_{\text{Sc}, I}} \times 100\%, \quad (3)
\]

where \( m_{\text{Sc}, s} \) and \( m_{\text{Sc}, l} \) indicate the quantity (mass) of Sc in precipitate of the complexity scandium-ammonium sulfate and in initial liquid, respectively (mg). Figure 1 shows the solubility in [Sc₂O₃], g/l of the cumulative yield (%) of NH₄Sc(SO₄)₂ phase with increasing concentration acid [H₂SO₄], M.
Figure 1. Solubility and yield of NH$_4$Sc(SO$_4$)$_2$ phase at various acidity.

As expected and shown in Figure 1, the solubility decreased linearly with increasing acidity from 2.5 to 4 M H$_2$SO$_4$, almost approaching a minimum at 5.5 M H$_2$SO$_4$. This means that a high recovery close to 99% of the stable phase of NH$_4$Sc(SO$_4$)$_2$ can be obtained at 5-6 M H$_2$SO$_4$ in the presence of 0.5 M NH$_4$Cl. The equilibrium solid phase in the selected acid concentration interval was the composition NH$_4$Sc(SO$_4$)$_2$ in the form of a mixture of two polymorphous modifications. The quantitative ratio of polymorphs in the precipitate depends on the intensity of mechanical impact in the processes of deposition, washing and preparation for analytical tests. The abrupt reduction of the solubility of the NH$_4$Sc(SO$_4$)$_2$ phase is due to the salting-out effects and the influence of the same ion in the solutions.

3. Crystallization of NH$_4$Sc(SO$_4$)$_2$ from Sc-strip liquor

The results of investigations of the model systems were worked through for the crystallization of scandium from the strip liquor produced by dissolution of poor scandium concentrate from RM. For carbonate recovery and primary concentration of scandium we used red mud from the Bogoslovskii alumina factory located in the Urals (Russia). The main elements contained in the employed red mud are found to be Fe, Al, Si, Ca, Na, Ti, as well as scandium and zirconium, as shown in Table 2. The poor scandium concentrate from RM contained zirconium, iron and titanium as the main impurities, see also Table 2.

Table 2. Compositional matrixes of samples, wt%

| Product               | Fe$_2$O$_3$ | Al$_2$O$_3$ | CaO  | SiO$_2$ | TiO$_2$ | Na$_2$O | MgO  | Sc$_2$O$_3$ | ZrO$_2$ |
|-----------------------|-------------|-------------|------|---------|---------|---------|------|-------------|---------|
| Red mud               | 43.00       | 14.10       | 9.85 | 9.77    | 4.52    | 3.58    | 1.60 | 0.012       | 0.064   |
| I-Sc concentrate      | 1.47        | 0.52        | 1.50 | 0.25    | 2.26    | 2.00    | 0.50 | 3.99        | 20.82   |
| NH$_4$Sc(SO$_4$)$_2$ phase | 0.12       | 0.001       | 0.70 | 0.01    | 0.14    | -       | -    | 13.5        | 2.09    |

Ammonium scandium sulfate was extracted by crystallization from the strip liquor under optimal conditions with 98% yield Figure 2a shows the morphology of crystals obtained by crystallization
from the strip liquor at 5-6 M H$_2$SO$_4$ and 0.5 M NH$_4$Cl. The crystals of the NH$_4$Sc(SO$_4$)$_2$ phase had regular hexagonal prismatic shapes indicating that a highly crystalline product can be obtained. The main microimpurities of Ca and Zr, as well as Fe, Si and Ti in the precipitates of NH$_4$Sc(SO$_4$)$_2$ were determined using ICP-AES (see Table 2) and EDX-analysis (Figure 2b). The impurities were co-precipitated and captured by the precipitate during long-term crystallization to provide complete recovery of scandium and decrease its losses. Repeated crystallization made it possible to completely separate impurity metals with the filtrate. X-ray diffraction analysis of the precipitate showed the simultaneous presence of two polymorphs of the composition NH$_4$Sc(SO$_4$)$_2$, which were detected earlier [6]. The purity of the final product upon calcination of NH$_4$Sc(SO$_4$)$_2$ precipitate at 1000°C was as much as 99.0% Sc$_2$O$_3$.

4. Conclusion
The solubility of the complex sulfates NH$_4$Sc(SO$_4$)$_2$ and (NH$_4$)$_3$Sc(SO$_4$)$_3$ and the conditions of selective precipitation from multi-components industrial liquors by crystallization have been substantiated by modeling the processes on synthetic systems. The solubility values of NH$_4$Sc(SO$_4$)$_2$ and (NH$_4$)$_3$Sc(SO$_4$)$_3$ in water were 9.02 and 12.89 g/l Sc$_2$O$_3$, respectively. A crystalline product corresponding to scandium sulfate NH$_4$Sc(SO$_4$)$_2$ was isolated by crystallization from the sulfuric strip liquor produced by dissolution of scandium concentrate from RM. The main impurities of Ca and Zr, as well as Fe, Si and Ti are co-precipitated or captured by the crystallizing precipitate and can be separated by repeated recrystallization. The technology of crystallization provided a very high yield of the solid product with very high crystallinity, which has a desirable impact on the filtration and washing efficiency.

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References
[1] Mishra B and Gostu S 2017 Materials sustainability for the environment: red-mud treatment. Front. Chem. Sci. Eng. 11 (3) 483–496.
[2] Zinoveev D V, Diubanov V G, Shutova A V et al. 2015 Recycling of red muds with the extraction of metals and special additions to cement Russ. Metall. 2015 (1) 19–21.
[3] Borra C R, Blanpain B, Pontikes Y et al. 2016 Comparative Analysis of Processes for Recovery of Rare Earths from Bauxite Residue JOM 68 (11) 2958–62
[4] Zhang N, Li H X, and Liu X M 2016 Recovery of scandium from bauxite residue—red mud: a
[5] Pasechnik L A, Pigai I N, Skachkov V M, Yatsenko S P 2013 Extraction of Rare Elements from Residual Sludge of Alumina Production with the Use of Flue Gas of Sintering Kilns *Ecology and Industry of Russia*. 2013 (6) 36-38. (In Russ.)

[6] Pasechnik L A, Tyutyunnik A P, Enyashin A N et al. 2017 Synthesis and crystal structure of 3R and 1T’ polytypes of NH$_4$Sc(SO$_4$)$_2$. *J. Solid State Chem.* 255 50-60.

[7] Pasechnik L A, Tyutyunnik A P, Enyashin A N et al. 2018 Polymorphism and properties of ammonium scandium sulfate (NH$_4$)$_3$Sc(SO$_4$)$_3$: new intermediate compound in scandium production *CrystEngComm* 20 3772-83.