

CARBONATE TREATMENT AND SORPTION OF SCANDIUM FROM RED MUD

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Abstract

Known methods for production of scandium compounds are based mainly on the acidic leaching of scandium-containing materials, followed by its isolation as sparingly soluble compounds. However, these schemes have many operations, consume high amounts of reagents and electric power, resulting in a high cost of the final product. The effect of carbonate ions concentration, contact time, temperature, the ratio of S:L, type and amount of sorbent on the degree of scandium separation directly from red mud slurry was studied in this work. It has been shown that the greatest capacity of macroporous adsorbents exhibit scandium acrylic copolymers iminodifosfonic group situated closer to the polymer skeleton

Introduction

The necessity in metal scandium and its compounds is significantly increasing during last decades. This is conditioned by the possibility of scandium compounds use in electronic industry (luminophors, ferrites, garnets) and for production of solar batteries; scandium tantalate has ferroelectric properties.¹

Known methods for production of scandium compounds are based mainly on the acidic leaching of scandium-containing materials, followed by its isolation as sparingly soluble compounds.^{2,3} However, these schemes have many operations, consume high amounts of reagents and electric power, resulting in a high cost of the final product.

These disadvantages are very significant for aluminium production waste treatment, particularly for the red mud treatment. This is conditioned by the fact that concentrations of the main components of the red mud (Fe, Al, Ca, Si, Ti, etc.) are

higher than scandium concentration by an order of several magnitudes. Usually, an elevated amount of an acid is required for the red mud treatment, whereas the leachates contain very low scandium concentration. There are a number of methods for scandium separation from these leachates, including ion exchange.⁴

Non-acidic schemes are also prospective for scandium separation from industrial wastes. Some publications contain information about the possibility of scandium separation from the red mud via its autoclaving at the temperature of 300°C in presence of 300-500 g l⁻¹ of sodium hydroxide.⁵ Unacceptable conditions of scandium leaching and difficulty of its separation from solution are the main disadvantages of this scheme.

A significant research work was done for the development of methods for scandium separation after carbonate treatment of red mud.^{6,7} Certain difficulties, conditioned by transport of carbonate media (gas or salt) as well as by low degrees of scandium leaching, were limited the potential use of this method.

The possibility of intensification of scandium carbonate leaching and further separation from the red mud with simultaneous cost reduction was studied in this work.

Carbonate Treatment

The red mud from the BAZ (RUSAL) aluminium producing plant was used in this work. The content of the main components is given in Table 1.

Table 1: The content of the main components in the red mud from BAZ plant

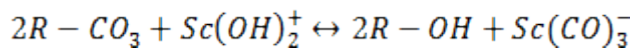
	Al	Ca	Sc	V	Fe	Y	ΣLn	Th	U
Content, %	7.03	8.03	0.01	0.05	26.97	0.02	0.15	0.006	0.005

It is well-known that hydrolysis of scandium occurs in weak acidic solutions; the structure of hydrolysed scandium ion may be described as $[\text{Sc}_4(\text{OH})_m(\text{H}_2\text{O})_{n-m}]^{(12-m)+}$. The gradual addition of CO_3^{2-} ions to the scandium solution results in the total scandium dissolving (at the ratio of $\text{CO}_3^{2-} : \text{Sc}^{3+} = 0.75$), then in its total precipitation as a base carbonate $[\text{Sc}_4(\text{OH})_m(\text{CO}_3)_p]^{(12-2m-p)}$ and finally in the total dissolving of this precipitate at the ratio of $\text{CO}_3^{2-} : \text{Sc}^{3+} = 8.35$.

In practice, carbonation of the red mud is performed using either alkaline metals and ammonium carbonate solutions or carbon dioxide. As a rule, these variants have

such disadvantages as a high salt consumption, accumulation of alkaline metals in the main producing scheme as well as high cost of carbonation by carbon dioxide.

The method of the red mud carbonation via CO_3^{2-} ions introduction using an anion exchange resin was studied in this work. This method allows for saving the cation and volume balance of the producing scheme. Also the suggested RIP-process (Resin In Pulp) is a simple process from the point of view of used apparatus. The ion exchange process with anionite occurs according to the following equation:



Anionites with various basicity, composition and matrix structure were studied. Also, the same anionites in CO_3^{2-} and HCO_3^- forms were studied. Some of the obtained results are shown at Figure 1.

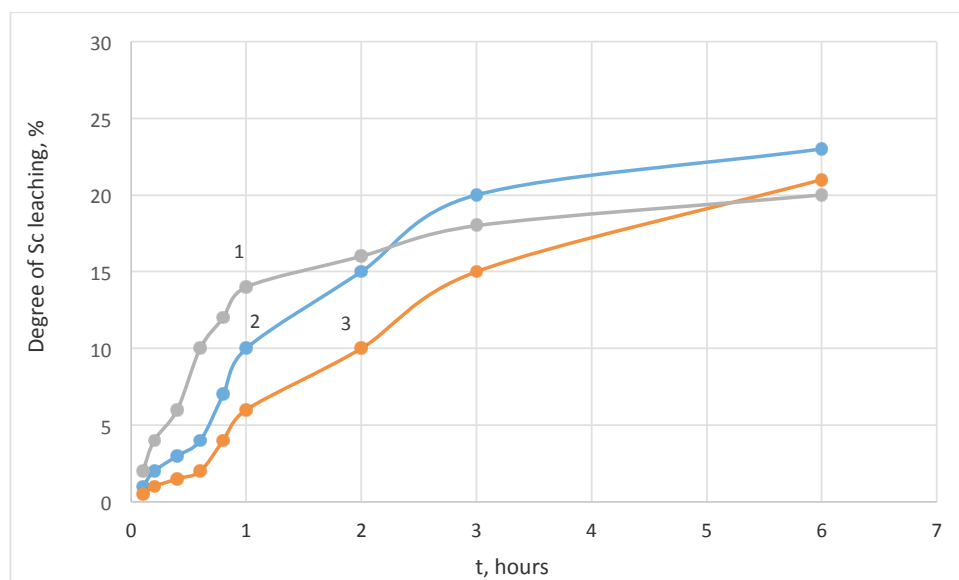


Figure 1: The kinetic curves of Sc leaching from the red mud by $20 \text{ g/l}^{-1} \text{ NaHCO}_3$ solution (1), macroporous-type weak base anion exchange resin (2) and gel-type weak base anion exchange resin (3)

The dependences from Figure 1 have shown that use of anionites for carbonation resulted in the same degrees of Sc leaching as use of sodium carbonate; whereas, significantly lower kinetics of scandium leaching was typical for use of anionites, especially of the gel-type modification.

Scandium Sorption

Our research group was the first one in the former USSR, that developed the technology of scandium sorption separation from the red mud using the RIP method with simultaneous carbonation of the slurry.^{8,9} Phosphate cation exchange resins with phosphonic functional groups and a St-DVB matrix with various DVB content were used for scandium sorption.

Formation of the coordination bond between scandium and oxygen from the phosphonic group results in sorption of scandium carbonate complexes by a phosphate cationite. This coordination bond is stronger than the chemical bond between scandium and carbonate ion. Also, variation of a substituent near phosphorus atom as well as the structure of cationite's matrix results in a change of energy of the chemical bond between scandium and phosphate functional group; this allows obtaining stronger complex compounds.

Several amphoteric based on copolymer of styrene and polyacrylate were studied in this work. The copolymer was aminated by various reagents, that allows regulating the distance between the matrix and phosphate functional group. The structure of functional groups of studied amphoteric is shown at Figure 2.

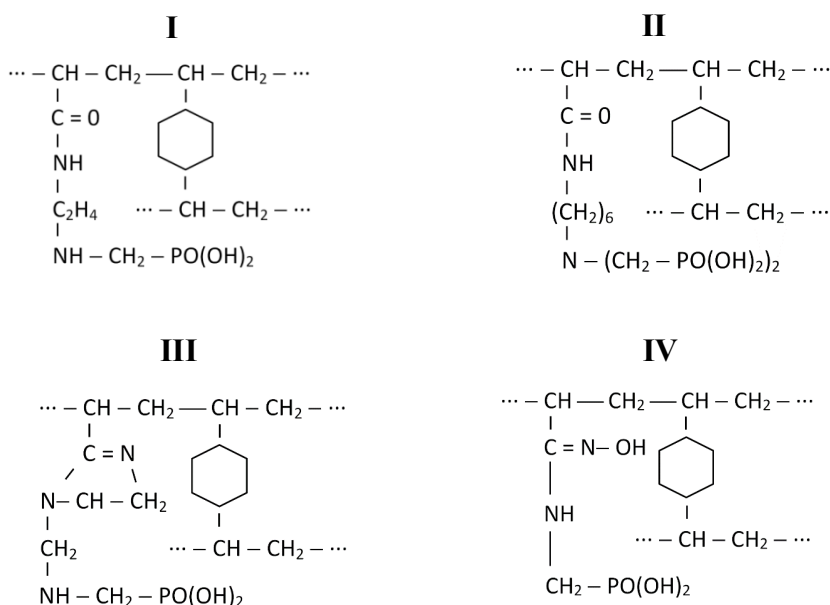


Figure 2: The structure of functional groups of studied amphoteric

The sorption capacity of these amphoteric with respect to scandium was studied in presence of various concentrations of sodium carbonate. The obtained results are summarised at Figure 3.

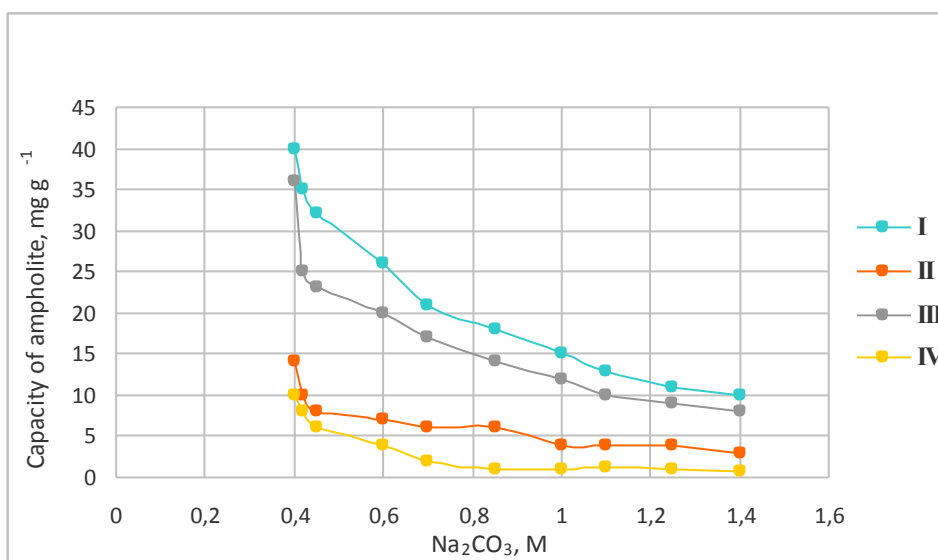


Figure 3: The dependences of amphoteric capacity of Na₂CO₃ concentration in the red mud

Differences of exchange capacity of amphoteric **I-IV** in the process of scandium sorption from the red mud slurry may be explained by various distance between the phosphate functional group and the polymer matrix. Low capacity of the amphoteric **IV** with respect to scandium is probably conditioned by the negative influence of the =N-OH group, presenting in this ion exchange resin.

Acknowledgements

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References

1. C. T. Horowitz (ed.), K. A. Gschneidner, G. A. Melson, D. H. Youngblood and H. H. Schock, “Scandium its Occurrence, Chemistry, Physics, Metallurgy, Biology, and Technology” Academic Press, New York, 1975.
2. S. Xu and S. Li, “Review of the Extractive Metallurgy of Scandium in China”, *Hydrometallurgy*, **42** (3) 337-43 (1996).
3. C. Klauber, M. Gräfe, G. Power, “Bauxite Residue Issues: II. Options for Residue Utilisation” *Hydrometallurgy*, **108** (1-2) 11-32 (2011).
4. M. Ochsenkuhn-Petropoulou, T. Lyberopulu and G. Parissakis “Selective Separation and Determination of Scandium from Yttrium and Lanthanides in Red Mud by a Combined Ion Exchange / Solvent Extraction Method”, *Anal. Chim. Acta.*, **315** (1–2) 231–37 (1995).

5. L. K. Komissariva, V. M. Shackiy and A. I. Zazuban, "Separation of Rare Metals with Similar Properties", *Metalurgizdat*, Moscow, 1962.
6. S. P. Yatsenko, N. A. Sabirzyanov, L. A. Pasechnik et al., "Method for Scandium Production from Red Mud", *Patent 2247788 Russia*, Bulletin No 7, 2005.
7. S. P. Yatsenko, L. A. Pasechnik and I. N. Pyagay, "Production of Concentrates and Pure Scandium Oxide from Dump Mud Using Fuel Gas from Alumina Production", in *Proceeding Of IV International Conference of the Russian Chemical Society named after D. I. Mendeleev*, Moscow, Russia, 2012.
8. V. N. Rychkov, A. L. Zonov, V. N. Onosov et al., "Processing Recovery Scandium from Red Muds from Alumina Production", Patent 1829424, No 4733949, 1992.
9. V. N. Rychkov, A. L. Zonov, S. M. Balakin et al., "Processing Recovery Scandium from Red Muds from Alumina Production", Patent 1839022, No 4777754, 1992.