Conference Paper

Red Mud as an Additional Source of Titanium Raw Materials

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Abstract

In this study the extraction of titanium from bauxite residue (red mud) with 2 step acid leaching was proposed. In the first step red mud was leached with diluted hydrochloric acid under stirring to remove the soluble Ca, Na, Al, Si and K at 25°C and pH=3 for 1 hour. The content of iron and titanium in the solid residue increased to 57.7% and 6.4%, respectively. The factors influencing sulfuric acid leaching of the solid residue in the second stage were examined by factorial design. The optimal iron and titanium extraction efficiency was obtained after leaching at 50°C and L:S ration 20:1 for 90 min when 80 g/L sulfuric acid was used. The titanium oxide content in the concentrate obtained under the optimum conditions amounted to 46.7%. The maximum recovery of titanium in the sulfuric acid solution has not exceeded 6%.

Keywords: red mud, acid leaching, TiO2, iron extraction, precipitation, comprehensive utilization

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1. Introduction

To date, red mud (sludge from alumina industry) represent non-recyclable waste generated after processing of bauxite occupying large areas of land, at the same time the red mud contains a big amount of valuable components. The most interesting of them are rare earth metals, aluminium, iron and titanium [1, 2].

Apart from the aluminum industry in the Urals, there is an industry for producing titanium based on imported raw materials from Ukraine and Kazakhstan. However, if it were possible to combine the technologies of these two industries to bind to the Russian titanium raw materials, then there would be a synergistic effect, consisting in the comprehensive processing of minerals and technogenic waste. Such association is especially important because aluminum and titanium belong to the group of light metals, which are actively applied in the same engineering industry – the aircraft.

Currently, the prerequisites of this approach created through the methods, based on joint processing of ore and non-ore raw materials that includes compounds of these light metals.

Much research has been undertaken to extract titanium and other metals from red mud, which can be divided into pyrometallurgical and hydrometallurgical. Pyrometallurgical methods include the process involved adding additives, reduction roasting and subsequent magnetic separation. Acid leaching can be involved in the procedure to recovery Ti [3–5].

Hydrometallurgical techniques include leaching of red mud with various inorganic and organic acids to extract Ti in solution [6, 7] or to obtain titanium-enriched solid residue [8, 9]. Extraction of titanium in the solution does not exceed 70%, and its content in the enriched solid residue - 40%. Therefore, in this work an attempt was made to study the features of using red mud of the Ural alumina refineries for receiving additional source of titanium.

On the Ural alumina refineries for the production of alumina is used a combined method of Bayer-sintering, resulting in two different kinds of red mud: hydrochemical and sintering, that differ significantly in chemical and phase composition. Despite the fact that sintering red mud contains more Ca, Si and H_2O, it is much easier in terms of phase composition. Therefore, in our experiments we used sintering red mud.

2. Experimental

Sintering red mud from Ural alumina refinery, Sverdlovsk region, Russia, was used as the raw material. To determine the phase composition of the red mud and the solid residue after leaching x-ray analysis of a sample was conducted on the RIGAKU Dmax–2200 within the interval of angles of 22-75°, angular scanning speed 1 deg/min in CuKa – radiation (40 kV, 30 mA; A = 1,54056). The obtained results were used for automated JCPDS database searching. Radiograph of sintering red mud is not clear, so unambiguous attribution of lines to certain phases is not possible. The presence of hematite (Fe_2O_3), larnite (calcium silicate – Ca_4SiO_4), hydrogarnets ($Ca_3Al_2(SiO_4)$ 1,25(OH)), the sodium calcium silicate ($Na_2Ca_3Si_2O_8$), tricalcium aluminate ($Ca_3Al_2O_6$) and perovskite ($CaTiO_3$) is assumed.

The chemical composition of the red mud and solid residue after acid leaching were measured by fluorescence X-ray analysis on XRF-1800 SHIMADZU. The chemical composition of the red mud is listed in Table 1.

AR grade hydrochloric (32 wt/v%) and sulfuric (98 wt/v%) acids were used, required concentrations were made from these concentrated solutions along with distilled water through serial dilutions.

There have been some studies on extracting valuable components from red mud with acid leaching, which showed that in the first stage Ca, K and Na can be selectively extracted with the aid of rinsing of raw material with hydrochloric acid [7]. This method

Fe_2O_3	CaO	SiO_2	Al_2O_3	TiO_2	MgO	Na_2O	Sc_2O_3	LOI
47.7	12.2	7.8	7.0	6.0	0.8	2.4	0.01	16.1

Table 1: Chemical composition of the red mud (wt. %).

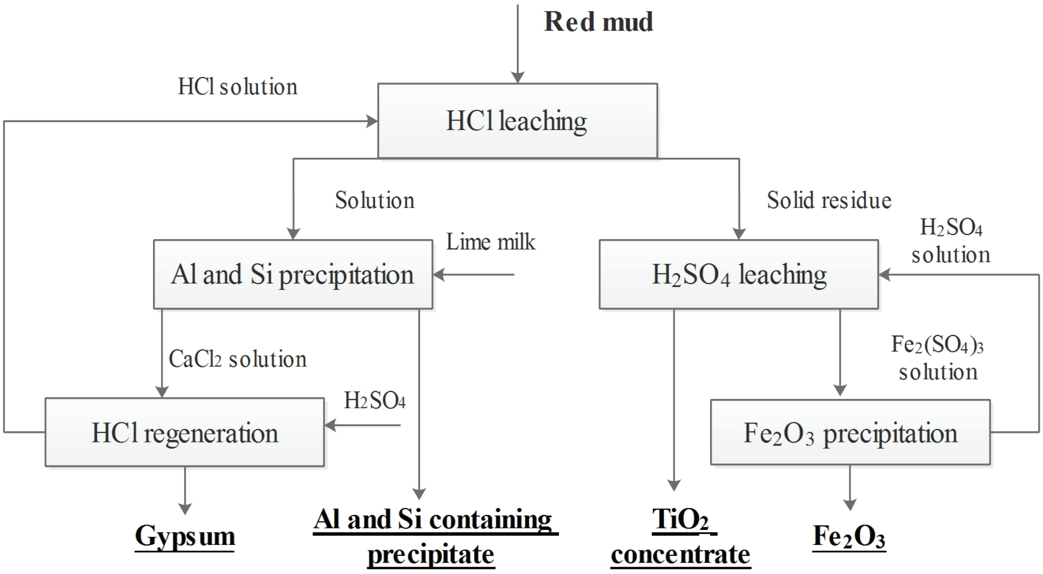

Figure 1: Flowchart for the processing of the red mud and its comprehensive utilization.

allows avoiding unwanted losses of sulfuric acid with the formation of gypsum, which significantly increases the yield of solid residue by sulfuric acid leaching of red mud.

Therefore, the experiments were performed according to the flow sheet as shown in Figure 1. A pre-determined weight of the red mud was leached with diluted hydrochloric acid under stirring to remove the soluble Ca, Na, Al, Si and K at 25°C and pH=3 for 1 hour.

Regeneration of hydrochloric acid can be carried out by deposition of gypsum with help of sulfuric acid. Then the solid residue from first stage was leached with sulfuric acid solution to extract iron. After the required contact time, the supernatant was vacuum filtered, and the leached residue was submitted to successive rinsing with water, before it was dried at 80°C for 24 hours and analyzed for iron and other element contents.

The Fe (III) containing in the filtrate can be effectively precipitated with the jarosite process [10, 11] or the hydrothermal hematite precipitation process. Thus the regenerated sulfuric acid can be reused for leaching of new portions of the solid residue.

3. Results and Discussion

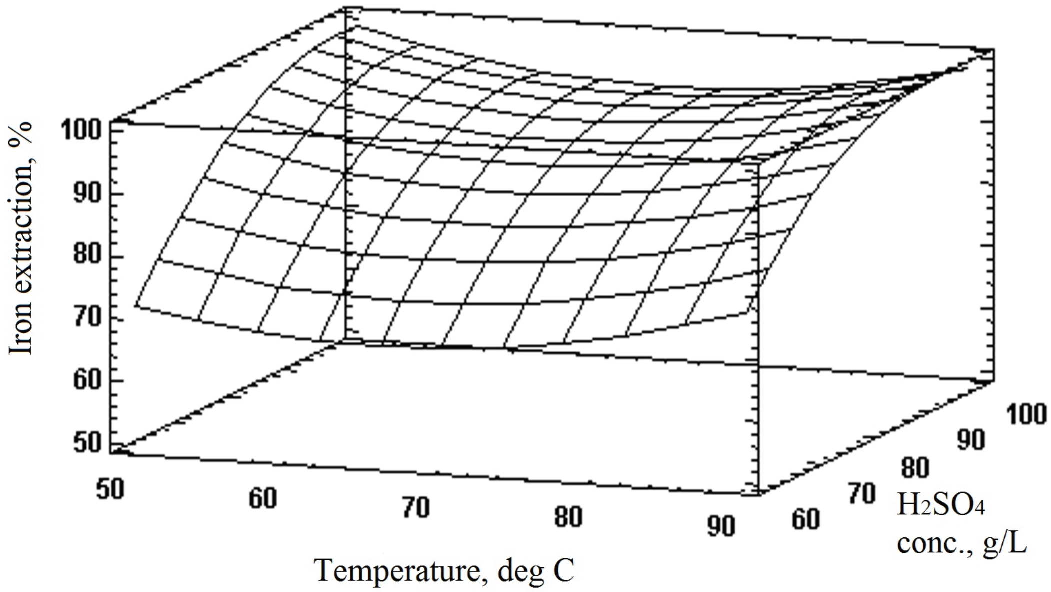

Figure 2: Estimated response surface of multifactor experiment at 90 minute of leaching time.

Fe_2O_3	CaO	SiO_2	Al_2O_3	TiO_2	MgO	Na_2O	Sc_2O_3	LOI
57.9	3.1	2.3	1.7	6.4	0.3	0.5	0.012	23.1

Table 2: Chemical composition of the solid residue obtained after HCl leaching (wt. %).

3.1. Hydrochloric Acid Leaching and Its Regeneration

Table 2 represents the chemical composition of the solid residue obtained after leaching with hydrochloric acid. It is obvious that after the first leaching stage the content of Ca, Na, Al and Si in the residue was considerably reduced. This ultimately leads to higher content of titanium and iron in the solid product. Lime milk is then could be added to the solution containing the extracted components with the aim of deposition of aluminum hydroxide and a gel of silica. Regeneration of expensive hydrochloric acid can be carried out by adding sulfuric acid to the solution, which leads to precipitation of gypsum.

3.2. Sulfuric Acid Leaching of the Solid Residue

To study the leaching of the solid residue with sulfuric acid a multifactorial experiment was carried out. L:S ratio in the all experiments was equal to 20:1.

After the processing of multifactor experiment results the following response surface for the extraction of iron (Figure 2, Figure 3) and titanium (Figure 4) into solution were obtained. The Figure 2 shows that temperature had little effect on the degree of iron extraction into solution. It should however be noted that the iron extraction at a

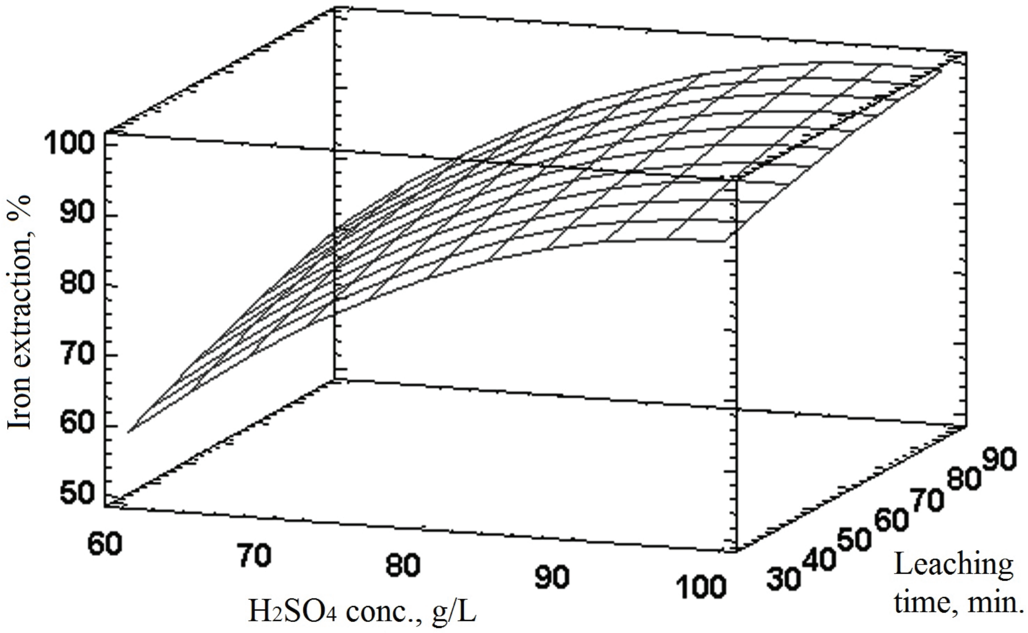

Figure 3: Estimated response surface of multifactor experiment at 50°C.

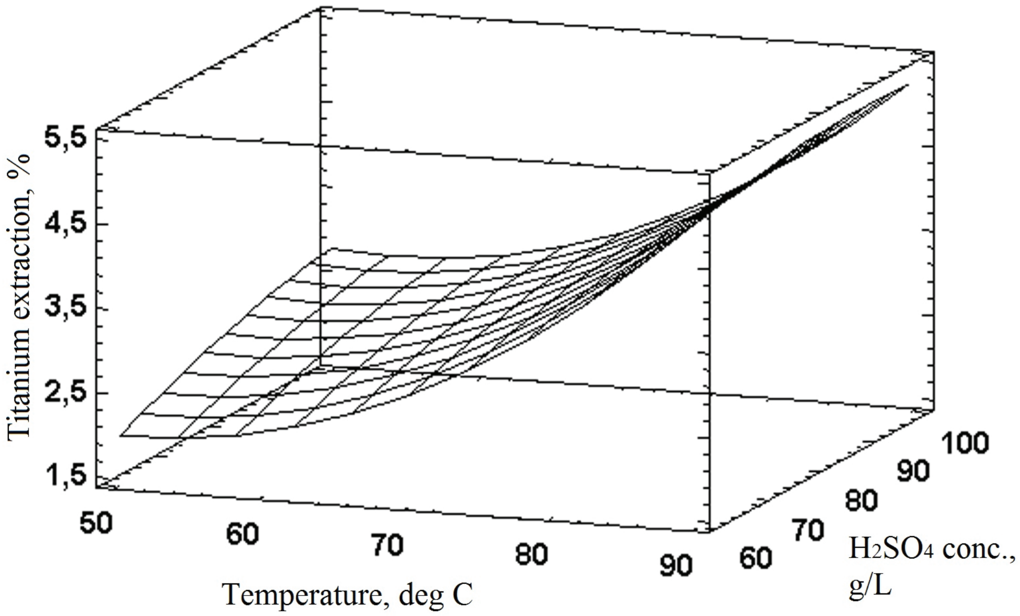

Figure 4: Estimated response surface of multifactor experiment at 90 minute of leaching time.

temperature of 70°C was lower than at 50°C, which appears to be associated with the precipitation of iron sulfate, which was also discovered in [6].

The greatest influence on the extraction of iron had a sulfuric acid concentration (Figure 3). So at the beginning (from 60 to 80 g/L) iron extraction increased sharply, then there was a stage of saturation.

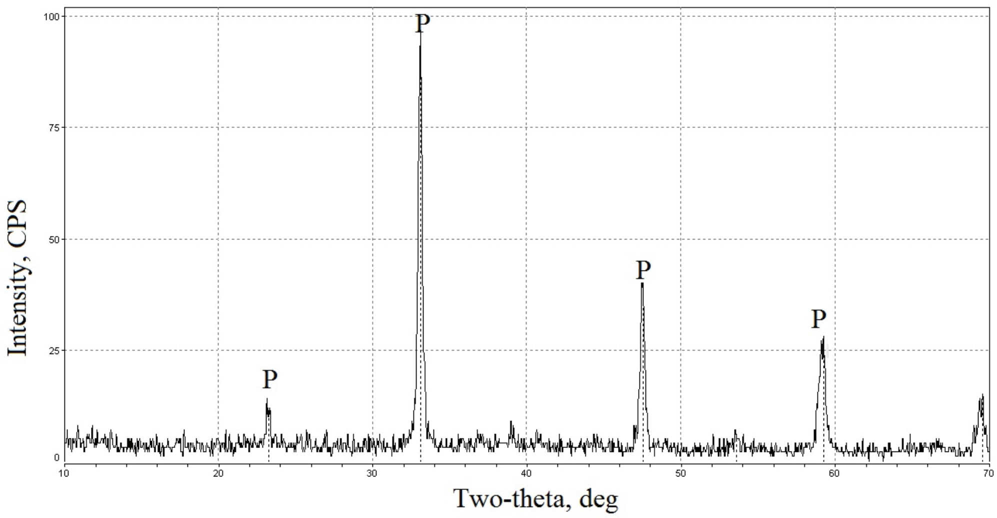

Figure 5: XRD pattern of the titanium concentrate (P, perovskite).

Fe_2O_3	CaO	SiO_2	Al_2O_3	TiO_2	MgO	Na_2O	Sc_2O_3	LOI
16.5	20.3	4.0	3.2	46.7	1.8	0.7	0.018	6.7

Table 3: Chemical composition of the Ti concentrate (wt. %).

In contrast to the iron, extraction of titanium in the solution was most dependent on the process temperature (Figure 4) and the lowest is observed at 50°C, which allows obtaining a richer concentrate. Therefore, the optimal conditions were selected as follows: 50°C acid concentration and 90 minute of leaching.

When these parameters have been adopted titanium concentrate with the following composition (Table 3) was obtained. According to the x-ray analysis the main titanium-containing phase was perovskite (Figure 5).

It should also be noted that the analysis of the solid phase showed that in addition to the main components rare earth metals also extracted in the solution, which increases the complexity of red mud using.

4. Summary

Preliminary hydrochloric acid leaching to extract Ca, Na, Al and Si, sulfuric acid leaching of the solid residue and regeneration of the acid solution were explored using red mud as the raw material. In the first step red mud was leached with diluted hydrochloric acid under stirring to remove the soluble Ca, Na, Al, Si and K at 25°C and pH=3 for 1 hour. The content of iron and titanium in the solid residue increased to 57.7% and 6.4%, respectively. The factors influencing sulfuric acid leaching of the solid residue in the second stage were examined by factorial design. The optimal iron and titanium extraction efficiency was obtained after leaching at 50°C and L:S ration 20:1 for 90 min when 80 g/L sulfuric acid was used. The titanium oxide content in the concentrate obtained under the optimum conditions amounted to 46.7%. The maximum recovery of titanium in the sulfuric acid solution has not exceeded 6%. It can be concluded from the experimental results that the proposed method is efficient and energy-saving. Moreover, it appears to be suitable for the comprehensive utilization of the sintering red mud.

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References

[1] Y. Liu and R. Naidu, "Hidden values in bauxite residue (red mud): Recovery of metals," Waste Management, vol. 34, no. 12, pp. 2662–2673, 2014.

[2] I. V. Loginova, A. A. Shoppert, and L. I. Chaikin, "Extraction of Rare-Earth Metals During the Systematic Processing of Diaspore-Boehmite Bauxites," Metallurgist, pp. 1–6, 2016.

[3] D.-Q. Zhu, T.-J. Chun, J. Pan, and Z. He, "Recovery of Iron From High-Iron Red Mud by Reduction Roasting With Adding Sodium Salt," Journal of Iron and Steel Research International, vol. 19, no. 8, pp. 1–5, 2012.

[4] Y.-H. Guo, J.-J. Gao, H.-J. Xu, K. Zhao, and X.-F. Shi, "Nuggets Production by Direct Reduction of High Iron Red Mud," Journal of Iron and Steel Research International, vol. 20, no. 5, pp. 24–27, 2013.

[5] W. Liu, S. Sun, L. Zhang, S. Jahanshahi, and J. Yang, "Experimental and simulative study on phase transformation in Bayer red mud soda-lime roasting system and recovery of Al, Na and Fe," Minerals Engineering, vol. 39, pp. 213–218, 2012.

[6] R. A. Pepper, S. J. Couperthwaite, and G. J. Millar, "Comprehensive examination of acid leaching behaviour of mineral phases from red mud: Recovery of Fe, Al, Ti, and Si," Minerals Engineering, vol. 99, pp. 8–18, 2016.

[7] Y. Yang, X. Wang, M. Wang, H. Wang, and P. Xian, "Recovery of iron from red mud by selective leach with oxalic acid," Hydrometallurgy, vol. 157, pp. 239–245, 2015.

[8] G. Li, M. Liu, M. Rao, T. Jiang, J. Zhuang, and Y. Zhang, "Stepwise extraction of valuable components from red mud based on reductive roasting with sodium salts," Journal of Hazardous Materials, vol. 280, pp. 774–780, 2014.

[9] Y. Huang, W. Chai, G. Han, W. Wang, S. Yang, and J. Liu, "A perspective of stepwise utilisation of Bayer red mud: Step two-Extracting and recovering Ti from Ti-enriched tailing with acid leaching and precipitate flotation," Journal of Hazardous Materials, vol. 307, pp. 318–327, 2016.

[10] Y. Song, M. Wang, J. Liang, and L. Zhou, “High-rate precipitation of iron as jarosite by using a combination process of electrolytic reduction and biological oxidation,” Hydrometallurgy, vol. 143, pp. 23–27, 2014.

[11] J. E. Dutrizac, “Comparative rates of precipitation of ammonium jarosite and sodium jarosite in ferric sulphate - sulphuric acid media,” Canadian Metallurgical Quarterly, vol. 49, no. 2, pp. 121–130, 2010.