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Recovery of Al_2O_3, Fe_2O_3 and TiO_2 from Bauxite Processing Waste (Red Mud) by Using Combination of Different Acids

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ABSTRACT

Aluminum industries generate red mud as a by-product, which recently has found many applications. Red mud characterizes to be of high alkalinity, so it can cause serious environment problems. The use of red mud as secondary resource to recovery of valuable metals such as titanium, iron and aluminum can be one of the solutions to these problems. Hydrometallurgy methods are simple and inexpensive relatively for extraction of metals. In this study, first, red mud leached by using single acids and then combination of different acids. In order to obtain compounds percentage of red mud X-ray fluorescence (XRF) used and metals content in solution after leaching was measured by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). The use of combination of asides for first time tested and shows highest amounts of extraction and also simultaneous determination of 3 elements (titanium, iron and aluminum) was done. The highest amounts of extraction were obtained from combination of concentrated sulfuric acid and hydrochloric acid with 3 to 1 ratio. Although the experimentations were carried out in lab-scale but the results give this possibility to industrial executor to choose best parameters for extraction of valuable metals from red mud as for economic conditions.

KEYWORDS: Red mud, Bayer process, Leaching, Extraction, Combination of acids

1. INTRODUCTION

Red mud (RM) is a fine-textured residue from bauxite refining by the Bayer process that therein using from bauxite digestion with sodium hydroxide at elevated temperature and pressure for alumina production. Under normal conditionsabout 1–2 tons of red mud residues (dry weight) are generated for a ton of alumina produced. At present, over 90 millions tons of caustic red mud must be disposed of annually all around the world [1]. Red mud is a complex material whose chemical and mineralogical composition varies widely, depending upon the bauxite source and the technological process. The disposal of such a large quantity of this alkaline waste is expensive (up to 1–2% of the alumina price), as it requires a large disposal area (approximately 1 km^2 per 5 years for a 1 Mtpyalumina plant) [2].On the other hand because of high alkalinity characteristic (pH 10-12.5), it can cause serious environment problems. Alkaline solution and red mud slurry usually seep from the red mud landfill site or pipelines into ground or underground water [3].

Also red mud has been used as building materials [3], catalyst [4], inorganic substrate [5], removal agents [6-8] and absorbent [9-11], but all these applications use low amounts of generated red mud.

The use of red mud as secondary resource to recovery of valuable metals can be one of the solutions to these problems. Several methods can be applied to extraction of metals such as hydrometallurgy methods [11-12], leaching after roasting [13], reduction sintering [14], cation exchange membranes [15] and direct magnetic separation [1]. Hydrometallurgy is the method wherein metals from ore extracted into an aqueous solution by liquid processes, such as leaching and digestion subsequently are recovered by a variety of methods such as concentration and precipitation. Hydrometallurgy methods are simple and inexpensive relatively, while other methods are processes with high energy consumption and expensive. Up to now, many researchers have carried out a lot of studies on the effective or comprehensive utilization of red mud.

Red mud mixed with dolomite and coke, and sintered at 1100˚C, and finally smelted at 1550˚C to produce pig iron and a slag containing titanium. The slag was then leached with 30% H_2SO_4 at 90˚C. The titanium recovery on the basis of slag weight was 84.7% [16]. Extraction of titanium from red mud studied by statistically designed experiments with leaching 4N sulfuric acid at 90˚C, that finally recovery amount obtained 70%. [17].

A process was proposed to extraction of Al_2O_3 and Na_2O from red mud. For this purpose red mud was leached with different amounts of 40–60% NaOH solution and milk of lime at 170–210 ˚C for 3.5 h. Overall, 87.8% of Al_2O_3 and 96.4% of Na_2O in red mud could be recovered [18].

In this study, designed experiments were performed to investigate the extraction amount of valuable metalsfrom red mud. First, red mud leached by using single acids and then combination of different acids. The factors such as acids ratio and normality was studied and some others were kept constant during experimentation.

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2. MATERIALS AND METHODS

2.1. Red mud

Used red mud was received from Jajarm alumina plant (Iranian Alumina Co.). For all experiments, samples of red mud were dried in an oven at 110° C for 48 h, then cooled and stored in a desiccator prior to use.

2.2. Method of analysis

In order to obtain the percentage of metal compounds of red mud, Qualitative and semi quantitative analysis was carried out by X-ray fluorescence (XRF). Metal contents in red mud were measured by Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES) after leaching with combination of different acids.

2.3. Leaching method

The red mud leaching procedure was carried out under atmospheric pressure. Test tube was selected as an experiment reactor to the digestion is well done. Heating was provided by an electrical heater and the temperature of digestion was about 100˚Cfor 2h.During experimentation the parameters were kept constant such as solid to liquid ratio and stirring speed in 750 rpm. The cap of test tube completely closed with aluminum foil and parafilm to prevent evaporation of the acid.

3. RESULTS AND DISCUSSIONS

3.1. XRF analysis

The major constituents of the red mud used in experiments were(mass fraction, %): Fe_2O_3, 28.41; Al_2O_3, 17.27; TiO_2, 7.36; SiO_2, 19.29 and CaO, 21.35. Meanwhile, the all mineral compositions of the red mud are listed in Table 1.

Table 1. All mineral compositions of red mud (mass fraction, %)

Composition	% by wt	Composition	% by wt
Na_2O	1.79	Sc_2O_3	600*
MgO	1.75	TiO_2	7.36
Al_2O_3	17.25	Cr_2O_3	0.40
SiO_2	19.29	Fe_2O_3	28.41
SO_3	1.20	Sr	0.11
Cl	0.14	Zn	300*
K_2O	0.37	ZrO_2	0.19
CaO	21.35	Nb_2O_5	300*

*Scale in ppm unit

3.2. XRD analysis

According to the XRD data (Fig. 1), the red mud contains mainly hematite [Fe_2O_3], calcite [$CaCO_3$],katoite [$Ca_3Al_2(SiO_4)(OH)_8$].Anatase [TiO_2], kaolinite [$Al_2Si_2O_5(OH)_4$] and cancrinite [$Na_6Ca_2Al_6Si_6O_{24}(CO_3)_2.2H_2O$] are also present as minor constituents.

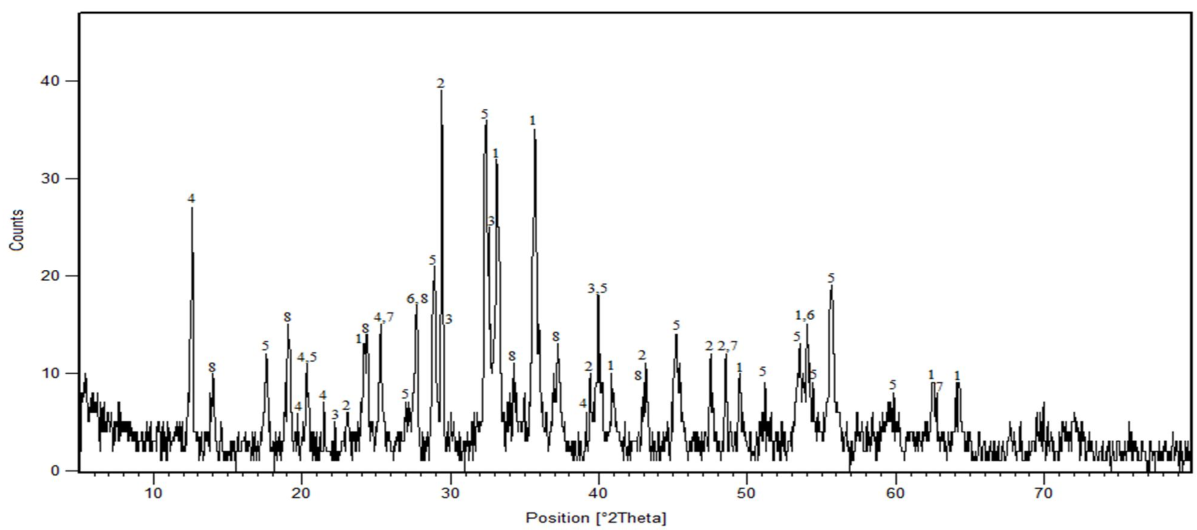

Fig. 1.XRD diagram of red mud used.1, hematite; 2, calcite; 3, sodium calcium silicon oxide; 4, kaolinite; 5, katoite; 6, rutile; 7, Anatase 8, cancrinite.

3.3. Leaching by single acids

In order to find efficacy of combination of acids on extraction amount, first red mud leached with single acids. For this, three acids sulfuric, hydrochloric and nitric with two different normality (concentrated and 6*N*) were used. As shown in Table 2, maximum of extraction percentage for iron, aluminum and titanium were 81%, 89.1% and 71% respectively and minimum of extraction percentage 25%, 40.7% and 50.6% respectively.

Table 2.% Extraction of metals after leaching with single acids

Experiment code	Acid	Acid normality	Iron (%)	Aluminum (%)	Titanium (%)
1′	H_2SO_4	Conc.	50	53	71
2′		6 *N*	35	40.7	62
3′	HCl	Conc.	81	56.5	69.5
4′		6 *N*	81	47.4	50.6
5′	HNO_3	Conc.	25	84.8	59
6′		6 *N*	27	89.1	63.6

Considering the results in Table 2, it can realize that under equal conditions such as temperature, normality acid and leaching time, each of acids extracts the metal more than other metals selectively. For example, iron better extracted by hydrochloric acid, aluminum by nitric acid and titanium with sulfuric acid (See Figure 2).

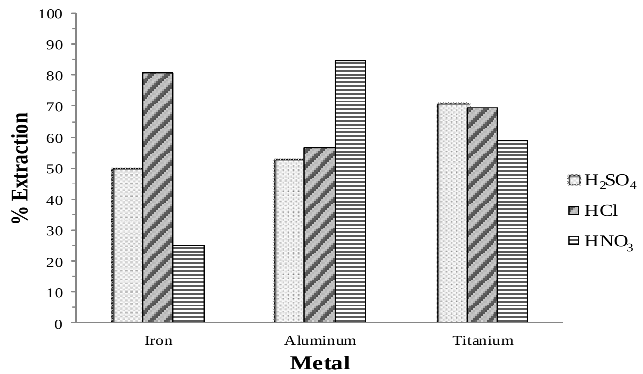

Fig. 2. The metals extraction by single acid selectively

3.4. Leaching by combined acids

The extraction percentage of iron, aluminum and titanium from red mud after leaching by four acids that were binary combined, are given in Table 3.As can be seen, extraction percentage of titanium varied from 4.5% to 97.7%. This amount for iron varied from 20% to 92% and for aluminum from 73.9% to 91.3%. The highest amounts were obtained with using the concentrated sulfuric acid and hydrochloric acid with 3 to 1 ratio.

Table 3 . Extraction percentage of metals after leaching with combined acids

part	Experiment code	Combined acids		Variables studied		Iron (%)	Aluminum (%)	Titanium (%)
				Acids ratio	Acid normality			
	1	H_2SO_4	HCl	3:1	Conc.	92	91.3	97.7
	2			1:1	Conc.	83	82.6	86.1
	3			3:1	6 *N*	68	84.8	77.2
A	4			1:1	6 *N*	77	82.6	72.8
	5			3:1	3 *N*	23	78.3	4.5
	6			1:1	3 *N*	25.5	78	4.5
	7	H_2SO_4	HNO_3	3:1	Conc.	81.5	85	86.7
	8			1:1	Conc.	81	84.8	86.4
	9			3:1	6 *N*	36	87	72.7
B	10			1:1	6 *N*	37	84.8	75
	11			3:1	3 *N*	22.2	76.5	5
	12			1:1	3 *N*	21	75	9.1
	13	H_2SO_4	$HClO_4$	3:1	Conc.	69	76.1	77.2
	14			1:1	Conc.	73.4	79	81.8
	15			3:1	6 *N*	62	78.3	73.1
C	16			1:1	6 *N*	56.3	77.4	68.2
	17			3:1	3 *N*	20	74.2	6
	18			1:1	3 *N*	22.7	75	8.2
	19	HCl	HNO_3	3:1	Conc.	79	78.6	68.2
	20			1:1	Conc.	77.2	78.5	67.8
D	21			3:1	6 *N*	79	80.4	63.6
	22			1:1	6 *N*	78.5	78.3	62.5
	23			3:1	3 *N*	24	78	45.5
	24			1:1	3 *N*	23	73.9	41

Comparison between combined acid son extraction ability of metals with using sulfuric acid as main acid under similar conditions (Codes: 1, 7 and 13), is shown in (Fig. 3).

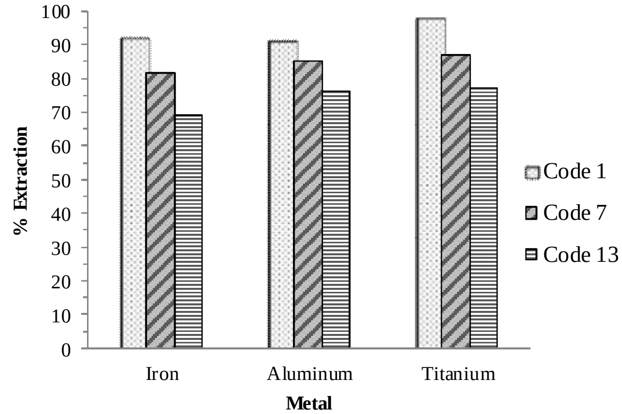

Fig. 3. Comparison between combined acids in extraction ability of metals

Unlike titanium andiron in all experiments with variant conditions, the extraction percentage of aluminum hadn't so change. For example, this case for part A has been investigated in (Fig.4).

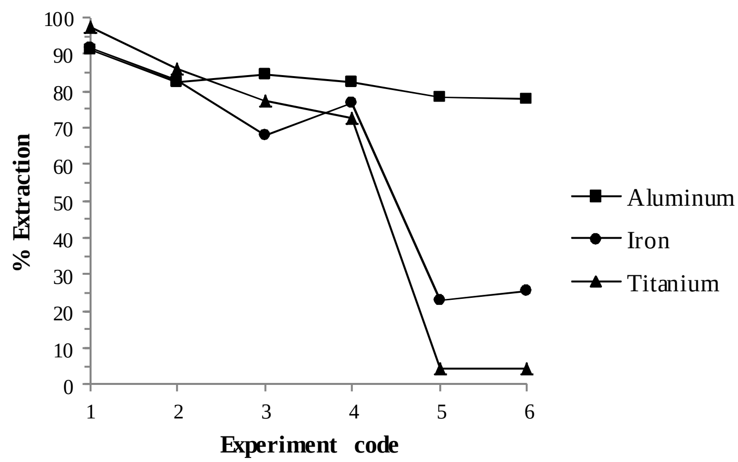

Fig. 4. Theextraction percentage for experiments of part A

When hydrochloric acid and nitric acid were combined (part D), with decreasing acid normality from concentrated to 6N,wasn't seen significant differences in the extraction amount. When even normality arrived to 3N, variation of extraction percentage was negligible for aluminum and acceptable for titanium(see Figure 5).

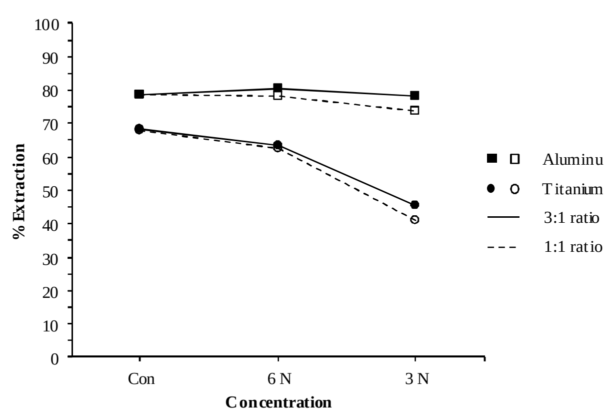

Fig. 5. Extraction amount with decreasing the normality in 3:1 and 1:1 ratio

4. Conclusion

This study, with comparison between the results obtained from leaching by single acids proved that each acid extract sametal more than other metals selectively. Therefore, we used combined acids for extraction of valuable metals of red mud. The results indicate that valuable metals of red mud could be completely extracted with combination of concentrated sulfuric acid and hydrochloric acid with 3 to 1 ratio. Percentages were obtained as the follows: iron 92%, aluminum 91.3% and titanium 97.7%. The range of extraction percentage of aluminum was between73.9% (code 24) and 91.3% (code 1) that shows the parameters such as type of combined acid, acids ratio and normality have no much efficacy on the extraction amount. In the experimentations that carried out with dilute acids (3*N*), combination of hydrochloric acid and nitric acid in 3 to 1 ratio, acceptable amount of titanium obtained. Finally, although the experimentations were carried out in lab-scale but the results of Table 3give this possibility to industrial executor to choose best parameters for extraction of valuable metals from red mud as for economic conditions.

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