

# Influence of $\text{Na}_2\text{CO}_3$ and $\text{CaCO}_3$ additions on the aluminate slag formation during a single-stage reducing roasting of red mud

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Red mud is an alumina production waste. Due to the absence of effective recycling technologies, red mud is practically not used and is stored in special sludge deposits, representing a serious technogenic threat for the environment and neighboring settlements. Tens of millions tons of red mud are sent to the dumps every year. More than 100 million tons of red mud has been piled up in Russia. High content of iron and aluminium in red mud requires a processing which provides an effective separation of these components and obtaining iron- and aluminium-containing products.

The present paper contains the results of the investigations focused on developing a single-stage reducing roasting process with simultaneous production of cast iron and aluminate slag, the main aluminium-containing component of which is a water-soluble sodium aluminate. Forming of required slag composition is achieved by adding  $\text{Na}_2\text{CO}_3$  and  $\text{CaCO}_3$  to a furnace charge in definite proportions. It was studied the influence of these additions on degree of aluminium extraction into solution during the aluminate slag leaching in an alkalescent aqueous medium. It has been determined that adding of 15%  $\text{Na}_2\text{CO}_3$  and 20%  $\text{CaCO}_3$  provides the most complete aluminium extraction into solution during leaching the product of the red mud reducing roasting.

At the same time, an incomplete aluminium extraction is associated with formation in the system of complex calcium aluminosilicates (helenite predominantly). The carried out study has showed a principle possibility of aluminate slag obtaining in the process of a red mud single-stage reducing roasting and subsequent aluminium extraction into solution by water leaching in an alkalescent aqueous medium.

**Key words:** red mud, alumina production, reducing roasting, cast iron, aluminate slag.

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## Introduction

**R**ed mud is the main waste of alumina production. This is a fine-dispersed material forming at a leaching stage. Red mud mainly consists of ferric oxides and various aluminosilicates of sodium and calcium. The chemical composition of red mud is determined by that of the processed bauxite as well as by treatment conditions. Thus, the content of red mud components in the process of alumina manufacturing by the Bayer process varies in a wide range as follows, %: 25–60 of  $\text{Fe}_2\text{O}_3$ , 8–20 of  $\text{Al}_2\text{O}_3$ , 4–15 of  $\text{SiO}_2$ , 5–15 of  $\text{CaO}$ , 2–5 of  $\text{Na}_2\text{O}$ , 2–5 of  $\text{TiO}_2$ , etc. [1]. Bauxites with high silica

content are processed by sintering. Depending on their processing technique, a volume of red mud may amount to 2.5 tons for each ton of the alumina produced. Since the effective technologies of red mud processing are absent, these waste products are being accumulated in special sludge deposits attached to alumina factories representing a serious technogenic threat to the environment and neighboring settlements [2]. On a global scale, tens of millions of tons of red mud are sent to the dumps every year [3]. In Russia, there is also amassed great volume of such waste products.

Many scientific institutions worldwide are attacking the problem of red mud processing. The suggested tech-

nological approaches may be subdivided into two lines: hydro- and pyrometallurgical ones. The hydrometallurgical processing supposes, for the most part, acid technologies with subsequent application of extraction or sorption [4–5]. Taking into account the fact that red mud is also a potential raw material for obtaining scandium, a part of investigations is devoted to the questions of its extraction [6–9]. The pyrometallurgical processing supposes the recovery of ferric oxides, the content of which in red mud may come to a half of its mass. Thus, cast iron and aluminium-containing slag are obtained. There also exist the studies on obtaining the slag with predetermined composition meeting the requirements of cement manufacturing [10–14]. However, the methods of aluminium afterextract from red mud may be considered as the most effective solution of the red mud processing problem. A series of papers propose to process the mud in two stages: reducing roasting with cast iron obtaining as the first one and sintering with soda for aluminate slag obtaining as the second one. A necessity to carry out two roastings is the shortcoming of such a method, since material costs are increasing and profitability of the red mud utilization process is decreasing.

The aim of the paper is to develop a single-stage reducing roasting process which allows one to produce simultaneously both cast iron (for steel industry) and aluminate slag (for alumina production) and to eliminate the need for additional sintering operation. The ferric oxides reduction to metal takes place within the frame of one process along with obtaining the aluminate slag, the main aluminium-containing phase in slag.

In the previous researches we have ascertained the general regularities of the processes which proceed during red mud reducing roasting and have studied an influence of different factors on forming the aluminate slag phase composition and on separation of the metal and slag phases [15].

It was also determined optimal parameters of red mud reducing roasting, which provide the most complete iron conversion into cast iron as follows: the coke rate of 8.5–9.0%, the temperature range of 1350–1375 °C. The composition of the obtained cast iron has been studied. The fulfilled experiments have showed a principle possibility of sodium aluminate formation as a part of aluminate slag in the process of a red mud single-stage reducing roasting. The present paper shows how specific amount of  $\text{Na}_2\text{CO}_3$  and  $\text{CaCO}_3$  additions affects both phase composition of aluminate slag, obtained under the optimum conditions of a single-stage reducing roasting, and degree of aluminium extraction into solution during this slag leaching in an alkaline aqueous medium.

## Experimental

The sample of red mud has been dried at 105 °C for 2 hours before implementing

reducing roasting. The reducing roasting has been carried out in a laboratory vertical electric-tube furnace at 1375 °C without additional holding in order to minimize sodium losses with sublimes [15]. Duration of heating from 1000 °C up to the predetermined temperature was 6 min. Coke with ash content of 14% has been used as a reducing agent. This ash has the following chemical composition, %: 5.47 of  $\text{Fe}_2\text{O}_3$ ; 48.64 of  $\text{SiO}_2$ ; 31.93 of  $\text{Al}_2\text{O}_3$ ; 4.58 of  $\text{CaO}$ ; 1.72 of  $\text{MgO}$ ; 0.42 of  $\text{P}_2\text{O}_5$ ; 0.36 of  $\text{Na}_2\text{O}$ ; 0.67 of  $\text{K}_2\text{O}$ . The prepared charge of predetermined composition has been compacted to a tablet, which has been placed to a graphite crucible. To create an inert atmosphere, argon has been fed to a reaction zone of the furnace. After cooling, the product has been crushed and subjected to magnetic separation for separating metal and slag phases. Degree of iron reduction to a metal phase has been determined by the residual iron content in slag. Phase composition of the slag has been defined by X-ray diffraction (XRD) and microscopic analysis (a Carl Zeiss Axio Scope A1 microscope). The residual iron content in the slag has been determined by chemical analysis. The resulting slag has been grinded up to the coarseness of  $-0.05$  mm and leached by soda-and-carbonate solution (0.33%  $\text{NaOH}$  + 1.53%  $\text{Na}_2\text{CO}_3$ ) at 80 °C for 45 min. The solution has been separated from the residuum by filtration. Degree of aluminum extraction into solution was determined by its content in the unleached residue.

## Results and Discussions

Content of main components in a sample of red mud is represented in Table 1. According to XRD, the principal phases with aluminium in their composition are cancrinite, hydrogranat and other aluminosilicates of sodium and calcium. About a half of the slag mass is represented by ferric oxides in the form of hematite and magnetite. Perovskite is a titanium-containing mineral.

Formation of sodium aluminate and dicalcium silicate in the process of reducing roasting is guaranteed in the presence of the fixed amount of added to the charge. Concentrations of sodium and calcium oxides in the obtained aluminate slag must comply the following mass ratios:  $\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 = 0.6$ ;  $\text{CaO} : \text{TiO}_2 = 0.7$ ;  $\text{CaO} : \text{SiO}_2 = 1.87$ . Table 2 contains calculated compositions of the slag, obtained at different quantities of additions in the form of sodium and calcium carbonates taking into account complete iron reduction to metal. Computations have shown that optimum slag composition may be obtained at addition of 5%  $\text{Na}_2\text{CO}_3$  and 20%  $\text{CaCO}_3$ .

Table 1  
Chemical composition of red mud, %

$\text{Fe}_2\text{O}_3$	$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	$\text{TiO}_2$	$\text{CaO}$	$\text{Na}_2\text{O}$	Others	LOI
47.56	9.36	8.51	4.93	9.40	2.99	4.76	12.49

Table 2

**Calculated compositions of the red mud roasting products with  $\text{Na}_2\text{CO}_3$  and  $\text{CaCO}_3$  additions**

Addition, %			Mass loss	Metal output of red mud, %	Slag output, of red mud, %	Slag composition, %				
Coke	$\text{Na}_2\text{CO}_3$	$\text{CaCO}_3$				$\text{SiO}_2$	$\text{TiO}_2$	$\text{Al}_2\text{O}_3$	CaO	$\text{Na}_2\text{O}$
9	5	20	33.9	33.8	54.7	16.7	9.0	17.8	37.8	10.9
9	10	20	34.1		57.7	15.8	8.5	16.9	35.8	15.6
9	15	20	34.3		60.7	15.0	8.1	16.1	34.0	19.7
9	15	15	34.0		57.9	15.7	8.5	16.9	30.6	20.7
9	15	10	33.7		55.1	16.6	8.9	17.7	28.3	21.8
9	15	5	33.3		52.9	17.2	9.3	18.4	24.2	22.7

In order to investigate an influence of additions of sodium and calcium carbonates on the aluminate slag phase composition as well as on degree of aluminium conversion into a water-soluble sodium aluminate, the mixtures of red mud with additions of sodium and calcium carbonates have been prepared according to Table 2. The results of the reducing roasting of such mixtures are listed in Table 3.

The experiments evidence that additions 5%  $\text{Na}_2\text{CO}_3$  and 20%  $\text{CaCO}_3$  of the mud mass results in incomplete iron metallization. At such a composition of initial charge, an enlargement of metallic shots doesn't take place which is connected with high slag viscosity. In Fig. 1, *a* one can see that small metallic granules are placed on the surface of a reduced sample. Output of a metal phase increases up to 33% as quantity of  $\text{Na}_2\text{CO}_3$  grows and enlargement of metal granules also takes place (Fig. 1, *b*). In these conditions, the slag's output is 55.3% initial red mud. Decreasing of quantity of  $\text{CaCO}_3$  addition doesn't lead to significant decrease of the metal phase output (Table 3, Fig. 1, *c, d*).

Following the magnetic separation, the aluminate slags have been leached by soda-and-carbonate solution. Their solubility and degree of aluminum conversion into solution have been determined (Table 4).

According to the obtained data, a degree of aluminum extraction into solution significantly rises as consumption of  $\text{Na}_2\text{CO}_3$  grows from 5 to 15%. In a way, a  $\text{CaCO}_3$  addition also influences an increase of degree of aluminum extraction. Consumption of 15%  $\text{Na}_2\text{CO}_3$  and 20%  $\text{CaCO}_3$  under optimal conditions of reducing roasting provides conversion of about 72% of aluminum into a soluble sodi-

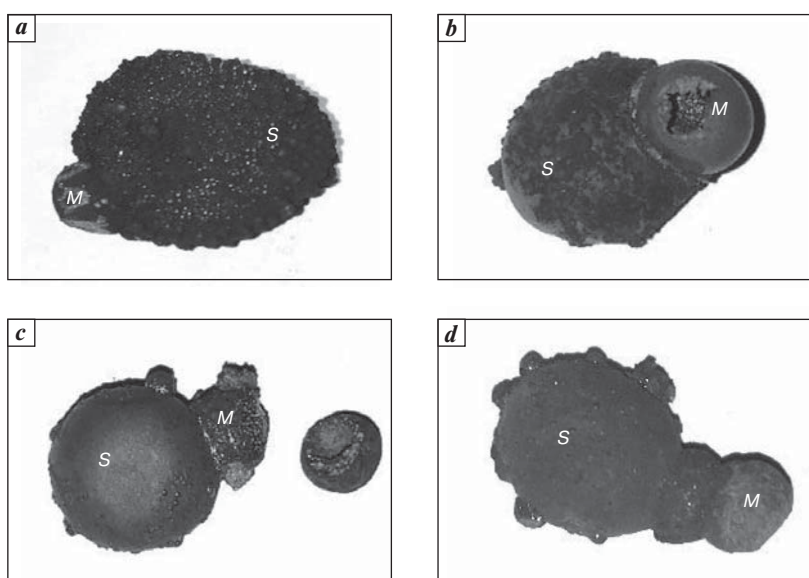
um aluminate. Decreasing the quantity of  $\text{CaCO}_3$  addition from 20 to 6 causes deterioration of the slag solubility from 24.8 to 12%, which have an effect on aluminum extraction into solution. This is explained by the fact that in such a process  $\text{SiO}_2$  doesn't get bounded completely into dicalcium silicate and binds a part of aluminum into insoluble aluminosilicates.

Table 3

**The results of red mud reducing roasting**

Sample	Addition, %			Mass loss, %	Product output, from initial red mud, %	
	Coke	$\text{Na}_2\text{CO}_3$	$\text{CaCO}_3$		Metal	Slag
SRM-5-20*	9	5	20	33.7	20.8	53.3
SRM-10-20	9	10	20	34.2	32.9	54.2
SRM-15-20	9	15	20	35.2	33.0	55.3
SRM-15-15	9	15	15	34.9	32.1	53.6
SRM-15-10	9	15	10	34.7	31.8	52.0
SRM-15-6	9	15	6	33.65	31.7	51.4

\* SRM = Sample of Red Mud



**Fig. 1.** Appearance of the products of red mud reducing roasting:  
*a* – SRM-5-20; *b* – SRM-15-20; *c* – SRM-15-10; *d* – SRM-15-6

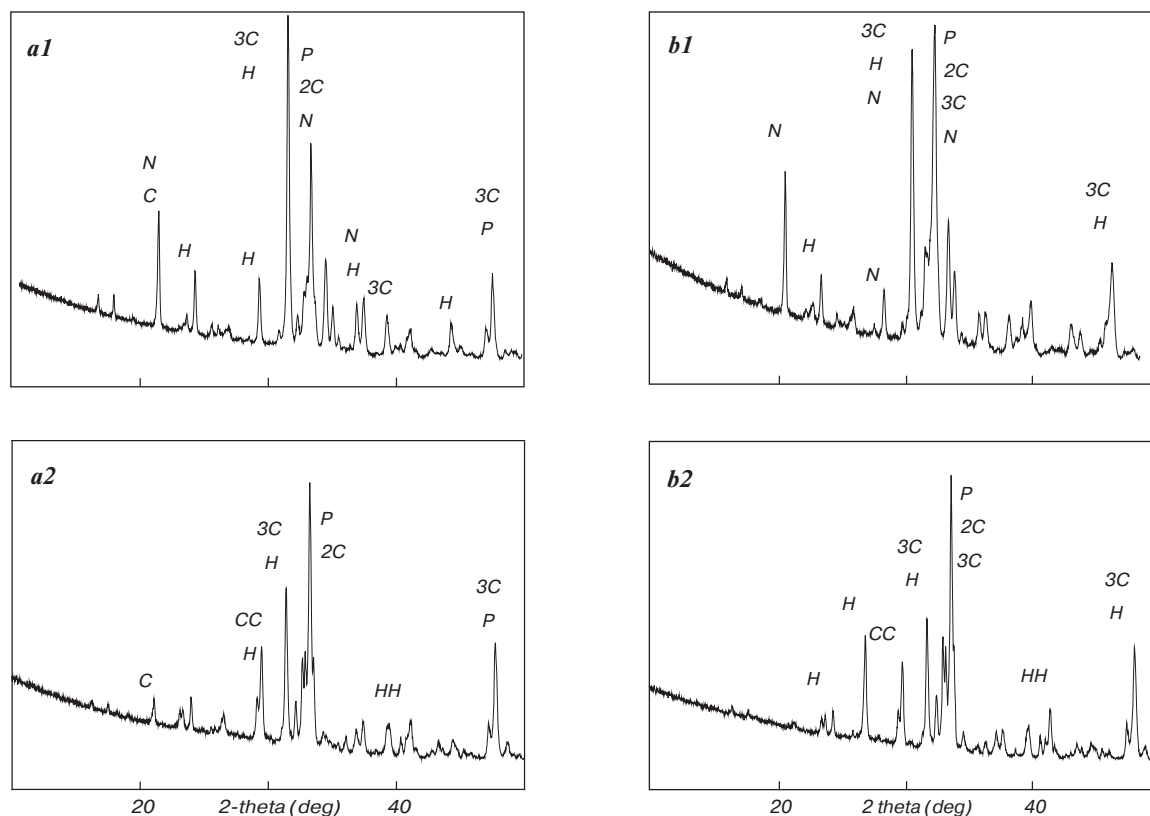


Fig. 2. Diffractograms of the aluminite slags (*a1*, *b1*) and their residues after leaching (*a2*, *b2*):

*a* – 15%  $\text{Na}_2\text{CO}_3$ , 15%  $\text{CaCO}_3$ ; *b* – 15%  $\text{Na}_2\text{CO}_3$ , 20%  $\text{CaCO}_3$ .

H – helenite, N –  $\text{NaAlO}_2$ , P – perovskite, C – carnegieite, 2C –  $\text{Ca}_3\text{Al}_2\text{O}_6$ , 3C –  $\text{Ca}_2\text{SiO}_4$ , HH – hydrogranat, CC – calcium carbonate

Table 4

**The results of leaching of aluminite slags**

Number of experiment	Degree of slag dilution, %	Content of $\text{Al}_2\text{O}_3$ in a leaching residue, %	Degree of Al extraction, %
SRM-5-20	12.9	13.2	34.5
SRM-10-20	20.6	9.2	57.7
SRM-15-20	24.8	6.31	71.9
SRM-15-15	22.1	8.10	63.9
SRM-15-10	18.6	10.89	50.8
SRM-15-6	12.0	12.51	39.5

According to the XRD data (Fig. 2), not only  $\text{NaAlO}_2$  and  $\text{Ca}_2\text{SiO}_4$  are presented in aluminite slag, but small amounts of calcium aluminosilicate helenite  $\text{CaAl}(\text{SiAlO}_6)$ ,  $\text{Na}_2\text{Ca}_3\text{Al}_2\text{O}_6$  and  $\text{Ca}_3\text{Al}_2\text{O}_8$  too, which lowers a degree of aluminum extraction into solution. The required residue after aluminum extraction contains not only  $\text{Ca}_2\text{SiO}_4$  and other insoluble phases, but also hydrogranat  $\text{Ca}_3\text{Al}_2(\text{SiO}_4)_2(\text{OH})_4$  and  $\text{CaCO}_3$ , which are formed on leaching the aluminite slags. Moreover, up to 10%  $\text{TiO}_2$  in the composition of perovskite ( $\text{CaTiO}_3$ ) is also presented in the residue.

The insoluble residue after aluminum extraction consists mainly of dicalcium silicate ( $\text{Ca}_2\text{SiO}_4$ ) and serves

as a high-grade raw material for production of cement clinker. Chemical analysis has shown that content of primary components in the insoluble residue is as follows, %: 6.31  $\text{Al}_2\text{O}_3$ ; 0.82  $\text{Fe}_2\text{O}_3$ ; 18.83  $\text{SiO}_2$ ; 8.35  $\text{TiO}_2$ ; 37.54  $\text{CaO}$ ; 2.0  $\text{Na}_2\text{O}$ . An aluminite solution is supposed to be sent to carbonization with successive precipitation of aluminum hydroxide and sodium carbonate. Consequently, some part of soda may be removed out of the system for recycling.

### Conclusions

An influence of additions in the form of sodium and calcium carbonates on the phase composition of aluminite slag and on separation of the metal and slag phases during the process of red mud residual roasting is studied. The most complete aluminium extraction into solution on soda-and-carbonate leaching of the red mud reducing roasting products is achieved in case of adding 15%  $\text{Na}_2\text{CO}_3$  and 20%  $\text{CaCO}_3$  is determined. Consequently, the aluminum extraction degree is about 72%. An incomplete aluminium extraction is associated with formation of compound calcium aluminosilicates (helenite predominantly) in the system. The carried out

study has showed a principle possibility of aluminate slag obtaining in the process of a red mud single-stage reducing roasting and subsequent aluminium recovery into solution during water leaching in an alkaline aqueous medium.

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