

An investigation of a single-stage red mud reducing roasting process with the cast iron and aluminate slag production

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Red mud is a technogenic waste product, a result of alumina production. It is a fine-dispersed material containing up to 60% Fe₂O₃ and up to 20% Al₂O₃. For each ton of alumina produced of bauxites there is more than 1 ton of red mud. In the absence of effective recycling technologies, red mud is practically not used and is almost completely stored in special sludge deposits, which negatively affects the environment. Tens of millions of tons of red mud are sent to the dumps every year in the world. 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 original iron- and aluminium-bearing products.

In this connection, the present paper is focused on developing a single-stage reducing roasting process with simultaneous generation of cast iron, a product for steel industry, and the aluminate slag suitable for alumina production. The main stage of the red mud complex processing technology under development is a single-stage reducing roasting process which results in the cast iron and aluminate slag obtaining; the latter is further treated by water leaching for aluminium precipitation from solution. The roast is carried out for the ferric oxides reduction to metal and simultaneous aluminium transfer to water-insoluble sodium aluminate, which is provided by adding Na₂CO₃ and CaCO₃ to a furnace charge in definite proportions. This article considers the manner in which the reducing roasting conditions (temperature, consumption of a reducing agent, composition of the furnace charge) influence over the ferric oxides reduction to metal and obtaining of the aluminate slag with a definite phase composition. As a result, the optimal conditions of the slag and cast iron formation are determined.

Key words: red mud, alumina production, pyrometallurgical processing, reducing roasting, pig iron, aluminate slag, recycling of wastes.

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Introduction

Red mud (RM) is the main by-product of alumina production. This is a fine-dispersed material consisting of ferric oxides and various hydroaluminates of calcium and sodium. Chemical composition of red mud is determined by composition of the processed bauxite and the treatment conditions. Thus, the content of red mud components on alumina producing by the Bayer process varies in a wide range as follows, %: 25–60 of Fe₂O₃, 8–20 of Al₂O₃, 4–15 of SiO₂, 5–15 of CaO, 2–5 of Na₂O, 2–5 of TiO₂, etc. [1]. For each ton of alumina produced by the Bayer process there is formed more than 1 ton of red mud and 2.5 tons in case of production by sintering. At present time, the effective technologies of red mud processing are absent; as a result of this, it practically

is not used and is stored instead in special sludge deposits attached to alumina factories. Tens of millions of tons of red mud are sent to the dumps in the world annually [2]; in Russia, more than 100 million tons of red mud has been sent to the dumps. Meanwhile, permanently accumulating waste products represent serious technogenic threat to the environment and the settlements neighbouring the plants [3]. Application of the effective complex red mud processing will allow to convert it into potential source of aluminium raw material as well as a source of iron and other valuable accompanying components.

Investigations aimed at research of the red mud processing ways are carried out by many scientific institutions worldwide. These methods may be subdivided into hydro- and pyrometallurgical according to the treatment

manner. Hydrometallurgical processing supposes, for the most part, acid technologies with subsequent application of extraction or sorption processes [4–5], but for all that, there takes place formation of the other detrimental wastes, demanding separate sludge storage facilities. Part of the studies concerns the questions of recovery of such a valuable component as scandium, accumulated in slag [6–9]. Since about a half of the slag weight consists of ferric oxides, pyrometallurgical methods are more effective. They are focused on the ferric oxides recovery with cast iron and aluminate slag obtaining. However, the alkali presence in red mud exerts an adverse effect on the processes by creating complications in apparatus equipping of the roast process (destruction of the unit's brick-lining). Moreover, the detrimental impurities presented in the slag (sulphur and phosphorus) may deteriorate the quality of the produced cast iron. Usage of the slag, obtained after iron recovery, for different cement brands manufacturing on appropriate correcting of its composition has been studied in a series of papers [10–14]. Nevertheless, the most prospective are the methods, which guarantee obtaining the slag suitable for alumina production. A disadvantage of such methods is a necessity to fulfil two stages of roasting: the reducing one to get cast iron and sintering with soda in order to obtain aluminate slag. This increases spending on equipment and production price accordingly.

In this connection, the aim of the paper is to develop a single-stage reducing roasting process with simultaneous obtaining cast iron, a product for steel industry, and aluminate slag, suitable for alumina production. It should be noted that both iron reduction and sodium aluminate formation run parallel in one unit, which preclude the need for additional sintering operation. The present paper contains the results of research on the manner in which the reducing roasting conditions (temperature, consumption of a reducing agent and composition of the furnace charge) affect the ferric oxides reduction to metal as well as obtaining aluminate slag with such phase composition that maximizes the rate of aluminium extraction to solution.

Routine of experiments

The sample of the Ural aluminium smelter red mud has been dried at 105 °C before implementing the reducing roasting. The moisture of initial red mud was 15.6%. The reducing roasting has been carried out in a laboratory vertical electric-tube furnace in a temperature range of 1300–1450 °C without additional holding given a 6-min duration of heating from 1000 °C up to the predetermined temperature. Coke with ash content of 14%, moisture of 0.9%, ignition losses of 1.1%, and S content of 0.95% has been used as a reducing agent. Chemical composition of this ash is as follows, %: 5.47 of Fe₂O₃; 48.64 of SiO₂; 31.93 of Al₂O₃; 4.58 of CaO; 1.72 of MgO; 0.42 of P₂O₅; 0.36 of Na₂O; 0.67 of K₂O. The prepared charge of predetermined composition has been compacted to a tablet,

which has been placed to a graphite crucible. To eliminate oxygen presence, argon has been fed to a reaction zone. After cooling, the product has been crushed and subjected to magnetic separation for separating the metal and slag fractions. Degree of iron reduction to a metal phase has been determined by the residual iron content in slag. Thermodynamic estimation of the reducing roasting process has been implemented with the use of the FACT (Facility for the Analysis of Chemical Thermodynamics) software. Phase composition of the slag has been defined by roentgen phase analysis (RPA) and microscopical analysis (a Carl Zeiss Axio Scope A1 microscope). The residual iron content in slag has been determined by chemical analysis and chemical composition of the metal by atomic emission spectral analysis.

Discussion of results

Influence of temperature and amount of reducing agent on cast iron and slag formation

According to RPA data, phase composition of a red mud sample is as follows: hematite α -Fe₂O₃; maghemite γ -Fe₂O₃; cancrinite (Na,Ca,K)_{3–4}(Al,Si)₆O₁₂(CO₃)·2H₂O; hydrogranat Ca₃Al₂(SiO₄)(OH)₈; sodium hydroaluminate Na₂Al₂Si₁₀O₂₄·7H₂O₄; hydroalumination calcium CaAl₂Si₁₀O₂₄·7H₂O and perovskite CaTiO₃ (Fig. 1). Normative substantial composition of red mud has been calculated on the base of chemical and phase composition (it is reported in Table 1). Content calculation for each silica-alumina phase is quite complex because of their variable composition, so cumulative quantity of the slag silicate phases is indicated. Moreover, red mud contains 0.0065 of Th; 0.0022 of U; 0.15 of Sr [15–16].

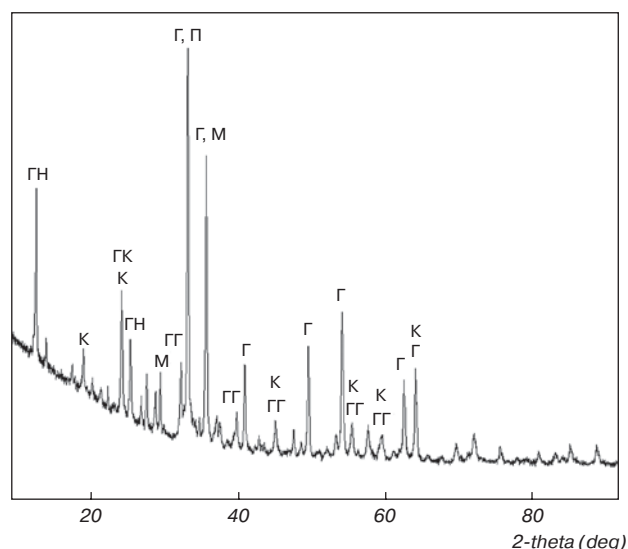


Fig. 1. Diffractogram of red mud: Γ — hematite; M — maghemite; Π — perovskite; K — cancrinite; $\Gamma\Gamma$ — hydrogranat; ΓK — hydroalumination calcium; ΓH — sodium hydroaluminate

Table 1
Normative substantial composition of red mud, %

Phase	Chemical composition, %								The rest	Sum
	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂	TiO ₂	Na ₂ O	CaO	P	S		
Hematite Fe ₂ O ₃	33.00	–	–	–	–	–	–	–	–	33.00
Maghemite γ-Fe ₂ O ₃	11.62	–	–	–	–	–	–	–	–	11.62
Cancrinite (Ca,Na) _{3–4} (Al,Si) ₆ O ₁₂ (CO ₃)·2H ₂ O	–	17.2	8.38	–	–	13.6	–	–	4.96	47.40
Hydrogranat Ca ₃ Al ₂ (SiO ₄)(OH) ₈	–			–	–					
Hydroaluminat calcium CaAl ₂ Si ₁₀ O ₂₄ ·7H ₂ O	–			–	–					
Sodium hydroaluminat Na ₂ Al ₂ Si ₁₀ O ₂₄ ·7H ₂ O ₄	–			–	3.5	–	–	–		
Perovskite CaTiO ₃	–	–	–	4.05	–	2.84	–	–	–	6.89
The rest	–	–	–	–	–	–	0.33	0.76	–	1.09
Sum	44.62	17.2	8.38	4.05	3.5	16.2	0.33	0.76	4.96	100.00

Table 2
Results of the red mud reducing roasting process

Number of experiment	Coke rate, %	T _{max.} , °C	Products output, % of the source mud		Fe _{com} in slag, %
			Metal	Slag	
RM-2-1	7.5	1425	28.8	53.6	6.02
RM-2-2	7.5	1400	28.0	53.8	6.25
RM-2-3	7.5	1350	27.2	54.0	n.d.*
RM-2-4	7.5	1330	26.2	53.5	n.d.
RM-3-4	8.0	1330	26.6	53.1	5.15
RM-5-4	8.5	1330	26.9	52.4	n.d.
RM-6-4	9.0	1330	27.1	51.9	n.d.
RM-5-3	8.5	1350	29.8	49.0	5.2
RM-6-3	9.0	1350	30.3	50.3	4.40
RM-5-2	8.5	1375	30.2	47.5	4.91
RM-6-2	9.0	1375	30.8	47.3	3.57

* n.d. — not detected

In this connection, the red mud samples check on radiation safety has been preliminary fulfilled on a BELLA («БЕЛЛА») dosimeter. Power value of the samples' equivalent dose has amounted not more than 0.12 μSv, which doesn't exceed the natural radioactive background values.

In order to determine optimal conditions of reducing roasting, aimed at the most exhaustive iron transfer to metal phase, a series of the red mud roasts has been implemented at different temperature values with coke consumption from 7.5 to 9.0% (Table 2).

As a result of the experiments, it has been ascertained that the red mud reducing roasting at the coke rate of 8.5–9.0% allows achieving high degree of iron reduction into a metal phase. The residual iron content in slag varies within the limits of 3.5–5.0%. At the same

time almost complete iron metallization and its separation from slag takes place at relatively low temperatures (1350–1375 °C), which results in a carbon metal, or cast iron, obtaining (Fig. 2). The coke rate lowering up to 8.0% and less leads to decrease of the iron metallization degree and a need for the process temperature rise up to 1400–1425 °C. At that, iron content in slag increases up to 6.0%. At the coke rate above 9.0% slag become rather refractory, this negatively affected separation of the metal and slag phases. That's why such charge composition requires the reduction process realization at higher temperatures: 1400–1450 °C and more. Thus, the optimum conditions of the red mud reduction process resulting in the maximum iron transfer to the metal are the following ones: coke rate of 8.5–9.0%, temperature of 1350–1375 °C.

Table 3

Content of Na₂O in aluminium-bearing slag, obtained in the red mud reducing roasting process

Roasting parameters	Slag type						
	RM 1-3	RM 2-1	RM 3-4	RM 5-2	RM 5-3	RM 6-2	RM 6-3
Coke rate, %	7.0	7.5	8.0	8.5	8.5	9.0	9.0
Firing temperature, °C	1350	1425	1330	1375	1350	1375	1350
Fe _{com} in slag, %	8.85	6.02	5.15	4.91	5.2	3.57	4.40
Na ₂ O in slag, %	7.18	6.81	6.98	7.32	7.68	7.44	7.41



Fig. 2. The outward appearance of the product of red mud reducing roasting under optimal conditions
M — metal, Ш — slag

In the slag obtained in the temperature range of 1330–1425 °C, Na₂O content is 6.8–7.5% (Table 3). This suggests that in such conditions an alkali sublimation practically doesn't happen due to a short process period (heating from 1000 to 1425 °C is in progress for 5–7 min only), and sodium remains in a slag phase being a part of nepheline NaAlSiO₄. In addition to nepheline, aluminium forms part of the other aluminosilicate — helenite Ca₃Al₂Si₂O₁₀.

Chemical composition of metal and slag obtained under optimal roasting conditions without additions are listed in Table 4. From this data it is apparent that metal phase is distinguished by heightened content of sulfur and phosphorus, which are extremely foreign material for steel. To raise metal quality, it is necessary to preliminary remove sulfur and phosphorus from red mud; this is the subject of further investigations. At that, the chemical content of slag allows to treat it as a sufficiently high-grade raw material for alumina production by sintering method, which is industrially applied in the nepheline processing.

Influence of temperature and amount of Na₂CO₃ and CaCO₃ additions on the slag phase composition

In order to fulfill the reducing roasting process which results in obtaining the aluminate slag not demanding an additional treatment, it is necessary to adjust composition of the initial charge with Na₂CO₃ and CaCO₃ additions. A thermodynamic simulation of the roasting process has been implemented to determine

Table 4

Chemical compositions of metal and aluminium-bearing slag, obtained under optimal roasting conditions

Metal composition, %					
Fe	C	S	P		
96	3–3.5	0.34	0.33		
Slag composition, %					
Fe _{com}	Al ₂ O ₃	SiO ₂	CaO	TiO ₂	Na ₂ O
3.5–5.2	33–35	15–17	30–33	8–9	7.3–7.7

an amount of these additions and process temperature, required for formation of the wanted slag phase composition. On simulating, the phases generation in a Na₂O – Al₂O₃ – SiO₂ – CaO system has been examined without considering ferric oxides, as iron in initial red mud presents in the form of self-dependent phases: hematite and maghemite. Under the reducing roasting condition, iron is reducing until metal state and separating from a slag phase, in other words, it doesn't essentially affect its formation.

The modelling has allowed to discover an influence of a Na₂CO₃ addition amount on the sodium aluminate formation (Fig. 3), which starts at 1200 °C even without adding Na₂CO₃ at the expense of sodium, presented in initial red mud. Undesirable NaAlSiO₄ and Na₂Ca₃Al₁₆O₂₈

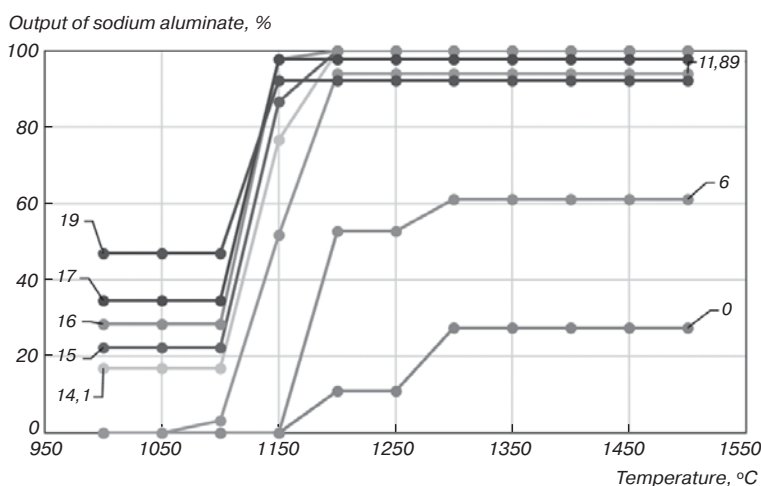


Fig. 3. Influence of Na₂CO₃ addition and temperature on the rated output of sodium aluminate in percentage of theoretically possible

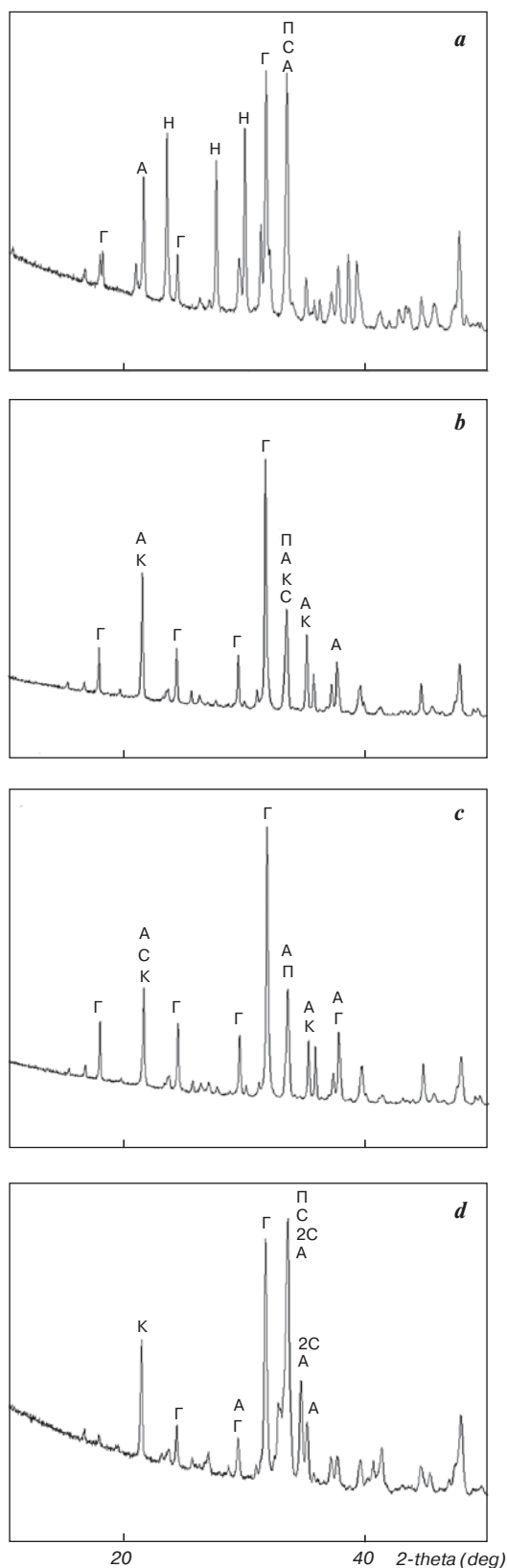


Fig. 4. Diffractograms of the aluminate slag, obtained in the process of red mud reducing roasting with addition of 15% of Na_2CO_3 and various amounts of CaCO_3 :
a – without CaCO_3 ; *b* – 6%; *c* – 9%; *d* – 20%;
 Γ – helenite; H – nepheline; A – NaAlO_2 ; Π – perovskite;
 K – carnegieite; C – $\text{Ca}_3\text{Al}_2\text{O}_6$; 2C – Ca_2SiO_4

phases are forming at 1200–1250 °C. At temperatures above 1300 °C, $\text{Ca}_2\text{Al}_2\text{SiO}_7$ (helenite) becomes the main side phase. These phases are dissolvable and so they lead to decreasing the aluminium extraction to solution on slag leaching. Increase of Na_2CO_3 amount causes quantity growth of the produced sodium aluminate. Yield of sodium aluminate on adding a stoichiometrical quantity of Na_2CO_3 (11.89%) comes to 94%, since a part of aluminium participates in formation of carnegieite. With adding 14.1% of Na_2CO_3 , aluminium is completely converting sodium aluminate. According to thermodynamic calculations, the optimum conditions for sodium aluminate manufacturing are the following ones: addition of Na_2CO_3 in amounts of 14.1–16% of the red mud mass and the reducing roasting temperature above 1200 °C. If content of Na_2CO_3 growth up to 17%, the output of sodium aluminate begins to lessen, which is connected with a $\text{Na}_2\text{Ca}_8\text{Al}_6\text{O}_{18}$ phase formation.

Taking into account the results of thermodynamic modelling, the red mud reducing roasting has been carried out at temperature 1350 °C with adding 9% of coke and 15% of soda. At the same time, the experiments with adding 6, 9 and 20% of CaCO_3 to initial charge has been implemented for studying the CaCO_3 content influence on formation of the slag phase composition. An examination of the phase compositions of obtained slag has shown a small content of helenite $\text{CaAl}(\text{SiAlO}_6)$, $\text{Na}_2\text{Ca}_3\text{Al}_2\text{O}_6$ and $\text{Ca}_3\text{Al}_2\text{O}_6$ (Fig. 4), being presented in the slag along with NaAlO_2 . These aluminium-bearing phases don't dissolve in conditions of leaching, which negatively affected the indicators of aluminium extraction from slag. Quantity of unwanted aluminosilicates in slag may be reduced by decreasing an amount of CaCO_3 . In such a way, dicalcium silicate Ca_2SiO_4 is forming on adding 20% of CaCO_3 ; it binds silica and leads to decrease of helenite amount. At the same time, the residue of aluminate slag leaching may be used in clinker production.

A refinement of the initial charge composition in a single-stage red mud reducing roasting in order to produce the cast iron and aluminate slag with the most complete aluminium transfer into a dissolvable phase requires conducting the research in more detail.

Conclusion

On the base of the fulfilled investigations, ascertained are the general regularities of the processes taking place on the red mud reducing roasting; studied is an influence of different factors on the phase composition of the aluminium-bearing slag and on separation of the metal and slag phases. Determined are the red mud reducing roasting optimal parameters, which provide the most complete iron conversion into cast iron: coke rate of 8.5–9.0%, temperature range of 1350–1375 °C. Influence of the Na_2CO_3 and CaCO_3 additions on the roasting products phase composition has been also studied.

It is determined that adding of 15% Na_2CO_3 and about 20% CaCO_3 is required to form the maximum amount of the water soluble sodium aluminate. The carried out study has showed a principle possibility of the aluminate slag obtaining in the process of a red mud single-stage reducing roasting.

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