UTILIZAÇÃO DA LAMA VERMELHA DA INDÚSTRIA DE ALUMINA NA GRANULAÇÃO DA ESCÓRIA FUNDIDA DE ALTO FORNO CONTENDO ENXOFRE

USE OF DUMPED RED MUD OF ALUMINA INDUSTRY AT GRANULATION OF THE MOLTEN SULFUR-CONTAINING BLAST FURNACE SLAG

ИСПОЛЬЗОВАНИЕ ОТВАЛЬНЫХ КРАСНЫХ ШЛАМОВ ГЛИНОЗЕМНОГО ПРОИЗВОДСТВА ПРИ ГРАНУЛЯЦИИ РАСПЛАВЛЕННЫХ СЕРОСОДЕРЖАЩИХ ПРОМЫШЛЕННЫХ ШЛАКОВ

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RESUMO

Há um problema no uso de resíduos da produção de alumina da lama vermelha de bauxita. O armazenamento é repleto de catástrofes ecológicas. As lamas vermelhas pioram constantemente o ambiente devido ao pó e à poluição das águas naturais. A lama vermelha é um produto do processamento de bauxita. Uma tonelada de alumina é responsável por 1 a 2,5 toneladas de lama vermelha. Atualmente, não está sendo processado, apesar da disponibilidade de 3.000 publicações e patentes sobre este tema. Um deles é justificado pela ambiguidade na eficácia econômica de seu uso pelos consumidores. Neste artigo, as opções de eficiência econômica e ambiental do uso de lama vermelha são apresentadas como substitutas da cal e calcário usados na purificação de gases industriais emitidos para a atmosfera em grandes quantidades com compostos tóxicos de enxofre. Testes laboratoriais e industriais revelaram as propriedades de sorção das lamas vermelhas. Ao limpar gases do enxofre emitido para a atmosfera por gases de fornos, usinas térmicas, máquinas de sinterização e fornos siderúrgicos. Além disso, é mostrada a eficiência ecológica e tecnológica da purificação de gases contendo enxofre liberados nas áreas de granulação de escórias fundidas de alto forno.

Palavras-chave: *processamento de escória, melhoria ambiental, escória granulada, características de fabricação, redução de emissões de enxofre e gases de efeito estufa.*

ABSTRACT

There is a problem of using waste of alumina production from bauxite red mud. Warehousing of it is fraught with ecological catastrophes. Red muds constantly worsen the environment due to dusting and pollution of natural waters. Red mud is a product of bauxite processing. One ton of alumina accounts for 1 to 2.5 tons of red mud. Currently, it is not being processed, despite the availability of 3,000 publications and patents on this topic. One of them is justified by the ambiguity in the economic effectiveness of its use by consumers. In this

paper, the options for economic and environmental efficiency of RM use are presented as substitutes for expensive lime and limestone used for purification of industrial gases emitted to the atmosphere in large quantities with toxic sulfur compounds. Laboratory and industrial tests revealed the sorption properties of red muds. When cleaning gases from sulfur emitted into the atmosphere by furnace gases, thermal power plants, sinter machines, and steelmaking furnaces. In addition, the ecological and technological efficiency of purification of sulfur-containing gases released in the areas of granulation of molten blast-furnace slags is shown.

Keywords: *slag processing, environmental improvement, granulated slag, fabrication characteristics, reducing emissions of sulfur and greenhouse gases.*

АННОТАЦИЯ

Существует проблема использования отхода производства глинозема из бокситов красного шлама. Складирование его чревато экологическими катастрофами. Красные шламы постоянно ухудшают окружающую среду из-за пыления и загрязнения природных вод. Красный шлам является продуктом переработки бокситов. На одну тонну глинозема приходится от 1 до 2,5 т красных шламов. В настоящее время он не перерабатывается, несмотря на наличие 3000 публикации и патенты по этой теме. Одна из них обоснована неясностью по экономической эффективности его использования потребителями. В данной работе представлены варианты экономической и экологической эффективности использования красных шламов, как заменителей дорогостоящих извести и известняка, используемых для очистки выбрасываемых в атмосферу в больших количествах промышленных газов с токсичными соединениями серы. Лабораторными и промышленными испытаниями выявлены сорбционные свойства красных шламов при очистке газов от серы выбрасываемых в атмосферу печными газами теплоэлектроцентралей, агломерационных машин и сталеплавильных печей. Кроме этого показана экологическая и технологическая эффективность очистки серосодержащих газов, выделяющихся на участках грануляции расплавленных доменных шлаков.

Ключевые слова: *переработка, улучшение экологии, граншлак, технологические свойства, сокращение выбросов сернистых и парниковых газов.*

INTRODUCTION

The most urgent task of modern non-ferrous metallurgy is the processing of alumina waste from bauxite – red mud. Their traditional storage not only constantly worsens the environment due to dusting and pollution of natural waters but also leads to an environmental disaster (Korneev *et al.*, 1991). Per 1 ton of alumina accounts for from 1 to 2.5 tons of red mud. Currently, there are more than 3,000 publications and patents on their processing. The most recent works are listed in the attached bibliography (Trushko *et al.*, 2017; Utkov and Meshin, 1999; Utkov, 2006; Liu *et al.*, 2009; Thakur and Sant, 1983; Klauber *et al.*, 2011; Júnior *et al.*, 2013; Venancio *et al.*, 2010). The search for new industrial technologies continues. One of them is the use of red muds to reduce the emission of gases into the atmosphere by combined heat and power plants (CHP) and industrial furnaces of sulfur compounds. Waste-free use of red muds is especially effective when granulating molten slags. Granulated slag is sustainably used in large quantities in cement production, in road

construction, agriculture, and in other areas of engineering and technology (Sorokin and Demin, 2003; Sennik *et al.*, 2008; Memoli and Guzzon, 2007; Li *et al.*, 2004; Shkolnik *et al.*, 2011; Kuhn *et al.*, 2000; Aleshin *et al.*, 2008; Kravchenko, 2015; Arbuzov *et al.*, 2009; Grospich *et al.*, 2004; Voskoboinikov *et al.*, 2002). When granulating slags, usually containing sulfur, a large amount of harmful substances are released into the atmosphere: sulfur oxides and mainly hydrogen sulfide (Sorokin and Demin, 2003). Its concentration on the working sites of the granulation areas is many times higher than the maximum permissible concentration. The composition of the coolant often injected fine lime or limestone to combat this phenomenon, but it is costly.

In this paper, we studied the possibility of replacing these materials with a fine dumped red mud. Laboratory and industrial tests were conducted. It was found that with the help of red mud, the concentration of sulfur-containing gases at the granulation work sites can be reduced by two orders of magnitude. At the same time, the technological properties of the granulated slag

can be improved in terms of the main technological properties.

CHEMICAL COMPOSITION OF TESTED RED MUD INDUSTRIAL SAMPLES:

Laboratory and industrial tests revealed the sorption properties of red muds when cleaning gases from sulfur emitted to the atmosphere by furnace gases of combined heat and power plants, sintering machines and steelmaking furnaces. In addition, the ecological and technological efficiency of purification of sulfur-containing gases released at the sites of the granulation by molten blast furnace slags is shown.

According to the chemical composition of red muds (Table 1), almost all components of red mud can chemically interact with sulfur compounds according to the reactions (Eq. 1-7)

The calculations of the potential capacity of red muds components by their interactions taking into account the joint technological efficiency of the complex of oxides contained in red mud. The results are shown in Table 2.

RESULTS OF LABORATORY RESEARCH:

Laboratory studies were carried out using the test facility shown in Figure 1. It was also used to determine the sorption properties of red mud with respect to sulfur oxide. Sulfur oxide was obtained in a furnace and in specified dosage quantities (proportions) mixed with air. The mixture was sucked through a tank with slurry pulp using a water jet or vacuum pump. The gas mixture, bubbled through a mixture of pulp, was sent to another absorption tank filled with a solution of NaOH.

During work with sulfur dioxide SO_2 , an additional 3% hydrogen peroxide was introduced into the alkali solution to oxidize it to SO_3 , which reliably bound by caustic alkali to sulfates and nitrates. The amount of absorbed gas was determined by changing the concentration of NaOH by simple titration or by changing the color of the indicator when the caustic solution was completely neutralized. Knowing the total amount of oxide produced in the furnace and the amount of oxide absorbed in the control tank, the amount of gas absorbed by the sludge slurry in the working tank was determined.

As a source of sulfur oxides, an alunite roasting reaction $\text{K}_2\text{SO}_4 \cdot \text{Al}_2(\text{SO}_4)_3 \cdot 2\text{Al}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$

was used. The choice of this reaction was determined by the fact that, depending on the firing conditions, it allows to obtain either SO_2 or SO_3 . Under oxidizing conditions (with an excess of air), the decomposition of alunite proceeds with the formation of sulfuric gas SO_3 (Eq. 8). SO_3 is reduced to sulfur dioxide SO_2 with the reducing agent (ground coal) (Eq. 9). Thus, it was possible to get different sulfur oxides on the same equipment with a slight change in the firing mode.

The above equations made it possible to calculate the amount of gases produced during the firing of a specific sample of alunite, taking into account the content of SO_3 and $\text{K}_2\text{O} + \text{Na}_2\text{O}$ in real alunite rock.

The average concentration of sulfur oxides in the gas-air mixture was set at 0.1% of the total volume. This value was chosen to simulate the composition of industrial gas emissions. For the preparation of the sorbent slurry under study, eleven parallel samples of industrial waste sludge from real alumina production were prepared.

The laboratory studies have studied the effect of the solid to liquid ratio of red muds in the wet scrubbing of gases from sulfur. Since red mud is a fine material, it was used as pulp with a solid to liquid ratio from 3:1 to 8:1. The optimum ratio is 5:1. The results are shown in Figure 2

This result was used to the practical use of red mud in wet granulation of molten blast furnace slag (Aleshin *et al.*, 2008). Granulation plot is one of the most dangerous emissions of hydrogen sulfide and sulfur dioxide into the atmosphere (Kravchenko, 2015).

Since, in practice, lime ($\text{Ca}(\text{OH})_2$) is used in most cases for the removal of sulfur dioxide, experimental studies on pulps have shown that red mud has not worse sorption properties than lime. Fig. 3 shows the data of the use of ground lime and red mud in terms of their efficiency, they are almost equal, but red mud is more technological and cheaper (more than 5 times).

RESULTS OF INDUSTRIAL TESTS:

The technology of using red muds during granulation of sulfur-containing molten slags was tested in industrial conditions. One of the most common sulfur-containing slags is blast furnace slags.

Industrial tests on the use of red mud for the removal of sulfur from industrial gases emitted into the atmosphere were carried out at

the “Severstal” enterprise. The results of industrial tests are shown in table 3. Tests have shown that the degree of purification from these gases in the atmosphere can reach as high as 97-100% using red mud.

The disadvantage of using red mud for the purification of industrial gases from sulfur is a problem with the use of a saturated sorbent, which is poured into a sludge depository. More advantageous is the use of red mud instead of lime in granulation blast furnace slags. The waste-free technology is provided by the proposed granast blast furnace slags method. It seems to use red muds when blast furnace slags are granulated. This process suffers from the release of large amounts of hydrogen sulfide to the work site of granulation, much higher than the maximum permissible concentration (0.008 mg/m^3) (Arbuzov *et al.*, 2009). Industrial tests were carried out, showing that using red slugs in the form of pulp, solid to liquid ratio = 5:1. The content of sulfur dioxide can be reduced by two orders of magnitude. The content of sulfur dioxide decreased by more than 10 times and reached the level of maximum permissible concentration (table 4).

It is important to note that the technology of using red mud granulation blast furnace slags is a waste-free technology. Red mud as a part of the granulated slag improves its technological properties. The rate of drying of this material increases to reduce transportation costs (Figure 4). Also, the power consumption for grinding the granulated slag is reduced before being added to the blast-furnace cement (Figure 5).

About 200 tons of red mud were used in industrial tests. When determining the content of SO_2 in gas-vapor emissions test has shown a positive result. The hydrogen sulfide content of $7.0\text{-}8.0 \text{ mg/m}^3$ is significantly lower than its content with other methods of granulation.

CONCLUSIONS:

1. Storage of red mud alumina production wastes in sludge collectors is harmful to the environment and carries the risks of an ecological catastrophe. These risks increase due to the increasing number of natural disasters (earthquakes, hurricanes, heavy rains, etc.). Therefore, it is necessary to develop technologies that ensure the processing of red muds instead of storage.

2. It has been established experimentally

that the proposed options for using red muds to clean sulfur compounds emitted into the atmosphere give an economic effect by replacing expensive lime and limestone and reducing the cost of operating sludge collectors. The double ecological effect is in reducing the risk of storing sludge in sludge collectors and improving the ecology of red mud consumers.

3. Industrial tests have shown that the hydrogen sulfide content during granulation of slags with the participation of red mud decreases in 10 times. Technological properties of the granulated slag are improved: increases the speed of drying and reduces the cost of its grinding.

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Figure 1. Test facility for sulfur oxides: 1 – silicon furnace; 2 – thermocouple; 3 – millivoltmeter; 4 – material boat; 5 – Drexel flask with pulp; 6 – burette with NaOH solution; 7 – calculating counter; 8 – sulfur-containing water jet pump

Figure 2. The optimal ratio of solid to liquid ratio pulp of red mud

Figure 3. Comparison of sorption capacity for capturing SO_2 : 1 – pulps with $\text{Ca}(\text{OH})_2$; 2 – pulps with red muds; A – pulp sorption capacity; t – interaction time

Figure 4. Comparative material drying speed

Figure 5. Kinetic grinding curves

Table 1. The chemical composition of the most representative components and size of industrial red muds

Method for the production of alumina from bauxite	Chemical composition, %					Loss on ignition	Average size, mm
	Fe ₂ O ₃	SiO ₂	Al ₂ O ₃	CaO	R ₂ O		
Bayer's method	42-55	5-8	12-17	8-13	4-9	6-10	0-0,05
Sintering method	20-25	16-20	8-10	37-42	2-3	4-5	0-10,0

Table 2. The chemical composition of industrial samples tested dump muds of alumina production

No	Al ₂ O ₃	Fe ₂ O ₃	CaO	Na ₂ O
1	11-13	50-57	8-10	1,5-2
2	17-20	47-52	-	2,5-3,8
3	16-19	45-49	8-11	4-5
4	14-15	37-39	11-13	3-4
5	14-16	32-35	13-15	4-6
6	14-15	32-39	11-13	3-4,5
7	13-14	36-42	11-13	3-4
8	12-13	30-32	22-26	4-6
9	12-14	38-40	13-15	4-5
10	4-5	22-24	39-41	2-2,5
11	7-9	20-24	35-37	4-5

Table 3. Comparative annual average flue gas treatment data using red muds

Characteristics of gases emitted into the atmosphere	Combined heat and power plant		Siemens-Martin plant		Agloproduction	
	-	Red mud	-	Red mud	-	Red mud
SO ₃ content, mg/m ³	150-400	13-17	100-200	8-11	250-950	12-17
Cleaning degree, %	95-100		97-100		94-100	
Productivity, thousand m ³ /h	2400		200-300		1630-1900	
Temperature, °C	120-150		190-250		125-145	
Dustiness after electrostatic precipitators, g/m ³	0,1-0,14		0,1-0,19		0,1-0,15	

Table 4. Pollution level in waste gases

Admixture name	Contamination level in waste gases mg/m ³			Maximum permissible concentration
	Without admixtures	+ Ca(OH) ₂	+ Red mud	
H ₂ S	110	0,010	0,008	0,008
SO ₂	150	0,045	0,045	0,050
SO ₃	75	0,008	0,008	0,100