Removal of Zinc from Pregnant Liquor by Reductive Sintering

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Abstract

Boehmite-diaspore bauxites deposited in the North of Russia (Middle Timan, the Komi Republic) are characterized by a high content of ZnO (from 120 up to 800 ppm. For a majority of bauxites from all global regions, typical ZnO content amounts to 60 – 70 ppm, which is close to its bulk earth values.), which degrades the quality of smelter grade alumina. The Urals alumina refinery applies several methods of sodium sulfide synthesis with the use of purchased sulfur to bond zinc into insoluble sphalerite (FeS). A method was developed to obtain sodium sulfide from production wastes. Reductive sintering of the alkaline mixture consisting of the bauxite with a low silica ratio, sodium-sulfate mix, and spent potlining, produces a sinter which contains sodium sulfide. Leaching of this sinter generates a sintering aluminate liquor with a concentration of sodium sulfide sufficient to remove zinc from the entire flow of the Bayer pregnant liquor.

Keywords: Zinc sulfide, Reductive sintering, Spent potlining, Sodium-sulfate mix.

1. Introduction

The Urals alumina refinery (UAZ) processes bauxites from the Middle Timan bauxite deposit (STBR) to produce alumina. These bauxites are characterized by a significant content of zinc, which increases the content of sodium zincate (Na_2ZnO_2) in the alkaline-aluminate liquor in the Bayer circuit and degrades the quality of smelter grade alumina. To obtain aluminium hydroxide with a ZnO content of ≤ 0.01 wt. %, as required by the national standard GOST 30558-2017 Smelter Grade Alumina, the concentration of sulfur present as sulfide (S^{2-}) in the alkaline-alumina liquors should be in the range 0.25 to 0.35 in order to remove zinc from the Bayer circuit with the bauxite residue as insoluble ZnS. For this purpose, technical grade sulfur is added to the Bayer process by addition to the STBR bauxite. Notably, ~ 80 % of technical grade sulfur dissolves into the solution [1]. The general flow diagram of zinc removal from the alkaline-aluminate liquors by adding elemental sulfur is as follows:

$$4S + 6NaOH = 2Na_2S + Na_2S_2O_3 + 3H_2O \quad (1)$$

$$Na_2ZnO_2 + Na_2S = ZnS\downarrow + Na_2O_{caust}, \quad (2)$$

The other method of adding sulfide to the aluminate liquor, which is more cost-effective, is reductive sintering of the mixture comprising low-grade bauxites from the North Urals bauxite mine (SUBR) characterized by a higher carbonate content and sodium-sulfate mix from the Bogoslovsk refinery (BAZ) to obtain a higher content of sulfide in the sintering aluminate liquor from the sinter leaching [2–5]. Na_2S allows the removal of zinc as ZnS from the thickener overflow in the hydrochemical circuit. Moreover, it reduces the specific consumption of the calcined soda due to its partial replacement with the production waste, i.e. sodium-sulfate mix (SSM) containing berkeite $Na_2CO_3 \times 2Na_2SO_4$. In course of the reductive sintering of the SSM-containing mixture, sulfate ions reduce to sulfide ions as carbon is added to the mixture as a reducing agent. When the sinters are leached, S^{2-} ions dissolve into the aluminate liquor.

The experiments were carried out to study the behavior of sulfate sulfur, which is a component of the SSM from the BAZ refinery, when sulfate is added to the sinter charge during the reductive sintering (in the presence of the carbon-containing reducing agents in the sinter mixture). Additionally, the most effective reducing agent was determined and the content of sulfate and other forms of sulfur in the aluminate liquor after the sinter leaching were determined.

2. Experiments on the Reductive Sintering

Physical simulation of the reductive sintering is complicated as the atmospheric composition, similar to the atmosphere in the industrial kilns, is difficult to obtain. A lab unit was installed to provide for the reducing atmosphere with an oxygen content of no more than 10 vol. % (see Figure 1 and Table 1).

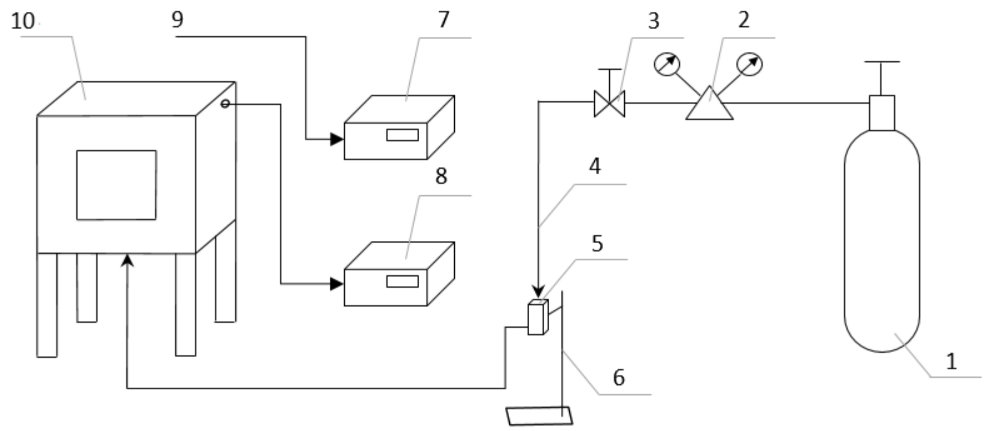

Figure 1. Unit for the adjustment and control of the atmospheric composition during the reductive sintering of bauxite mixtures (see Table 1).

Table 1. Configuration of a unit for mixture sintering in a controlled atmosphere.

No.	Description
1	Nitrogen gas of high purity, grade 1 as per standard GOST 9293-74, cylinder with a volume of 5.7 m^3, at a pressure of 150 atm (at T = 20 °C) with a following composition: Nitrogen min. 99.999 vol. % Oxygen max. 0.0005 vol. % Water vapour max. 0.0007 vol. % Hydrogen max. 0.0002 vol. % Methane max. 0.0003 vol. %
2	Pressure reducer Messer EN ISO 2503
3	Fine control valve
4	PVC tube. 6 * 1.5 mm
5	Flowmeter Bronkhorst MASS-VIEW
6	Stand rod for the flowmeter
7	Gas analyzer POLAR for measuring the gaseous phase of the atmospheric composition

No.	Description
8	Gas analyzer POLAR for measuring the gaseous phase of the exhaust gases from the kiln
9	Intake of the ambient air with a nozzle
10	Batch furnace Nabertherm

3. Reductive Sintering of the UAZ Mixture with Addition of Ekibastuz Coal (from the UAZ's CHP) as a Reducing Agent

If Ekibastuz coal is used as a reducing agent for sintering the UAZ mixture, iron sulfide in the amount of ~ 0.6 % instead of sodium sulfide is formed in the sinter. When sintered material, obtained by adding in the range 4 to 8 % of coal as a reducing agent, is leached, the S^{2-} content in the aluminate liquor amounts to 0.08-0.1 g/dm^3. This amount of sulfide is not sufficient to remove zinc from the aluminate liquor. The absence of sodium sulfide (Na_2S) in the sinter is attributed to the fact that the reaction between sodium sulfate and carbon to form sodium sulfide and carbon oxide (II) proceeds at a temperature of approximately 800 °C:

$$Na_2SO_4 + 4C \rightarrow Na_2S + 4CO\uparrow \quad (3)$$

Under sintering conditions with the use of Ekibastuz coal as a reducing agent, the entire carbon burns at a temperature range of 160–650 °C, as at this temperature iron sulfide FeS is synthesized. To generate sodium sulfate in the sintered material, a reducing agent is required, which burns at higher temperatures.

4. Reductive Sintering of the UAZ Mixture with Addition of Spent Potlining (from the Krasnoyarsk Aluminium Smelter) as a Reducing Agent

Figure 2 shows a thermogram of two coals and spent carbon potlining from the Krasnoyask aluminium smelter (KrAZ), which contains 70.5 % C. The thermogram indicates that carbon in the poltlining burns at higher temperatures (360–840 °C) as compared with coal carbon.

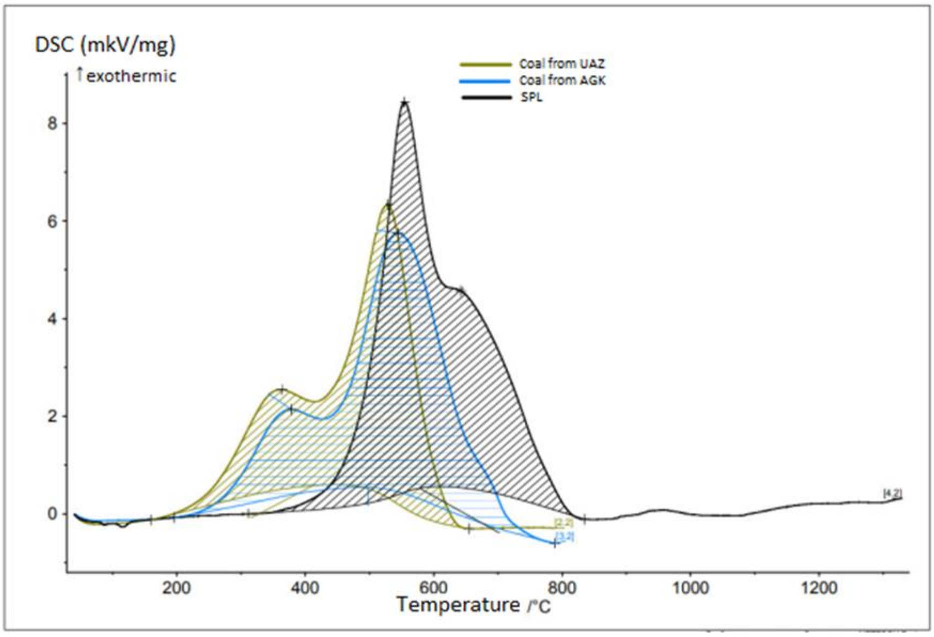

Figure 2. Thermograms of the coals and spent potlining.

When the mixture is sintered with the potlining, carbon monoxide (CO) is emitted within the temperature ranges of 810–1000 °C (Figure 3) which promotes the formation of sodium sulfide.

The X-ray diffraction analysis (XRD) of the sintered material produced, showed that sodium sulfide is not formed, and all the sulfide is in form of iron sulfide (FeS) as its synthesis precedes the generation of sodium sulfide because during the sintering process, CO gas is emitted in small amounts (up to 30 mg/m^3) within the temperature ranges of 240–700 °C.

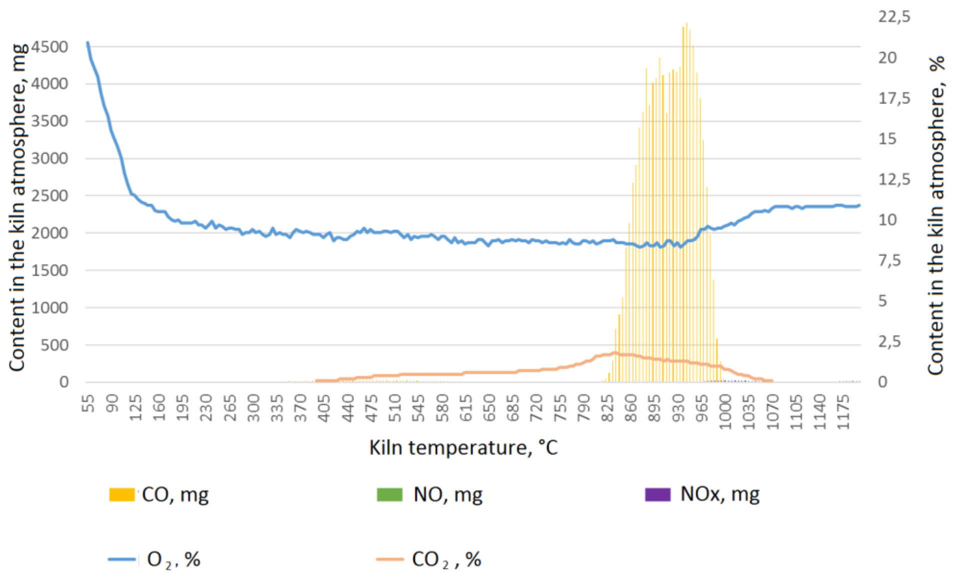

Figure 3. Changes of the composition of the gaseous phase during the mixture sintering; said mixture containing 6 % SSM, 4 % SPL from the KrAZ, the remainder is high-carbonate SUBR bauxites.

As Figure 4 shows, if the amount of the spent potlining in the mixture increases to 6–8 %, the amount of sulfide sulfur in the total sulfur in the sintered materials increases and the amount of oxygen decreases.

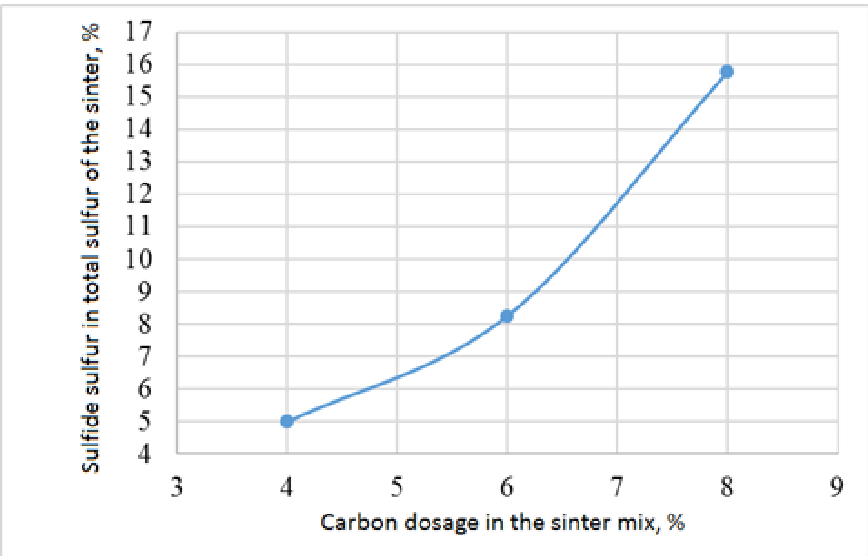

Figure 4. Changes of the percent of sulfide from the total sulfur in the sintered materials depending on the carbon dosage in the sinter mixture.

During the reductive sintering stage, approximately 15 % of sulfate sulfur goes to iron sulfide (FeS). When sinters are leached, ~ 98 % of all the sulfur in the sinter dissolves in the aluminate liquor, as FeS, which is generated during the sintering, is highly soluble in alkaline solutions at high leaching temperatures.

During the sinter leaching, FeS dissolves from the sinters into the alkaline liquor to form sodium sulfide as per the following reaction:

$$FeS + 2NaOH \rightarrow Fe(OH)_2 + Na_2S \quad (4)$$

Table 2. Content of total and sulfide sulfur in the sinters and aluminate liquors with various reducing agents during the sintering process under similar conditions (the UAZ sinter + 8 % C + 6 % SSM).

Component analyzed in the sintered materials and aluminate liquors after the reductive sintering and leaching	Carbon-containing reducing agent for sintering	
	Coal	SPL
S_{total} in the sinter, % (expressed as SO_3)	3.70	3.75
S^{2-} in the sinter, % (expressed as SO_3)	0.53	0.57
S_{total} in the aluminate liquor, g/dm^3 (expressed as S)	2.75	4.03
S^{2-} in the aluminate liquor, g/dm^3 (expressed as S)	0.1	1.06

Therefore, the aluminate liquor, which is obtained from leaching the sinter with SPL, contains enough sulfide-ions to remove zinc from the Bayer aluminate liquor, as the sintering aluminate liquor content reaches up to ~ 25 % of the total flow. When liquors from two circuits get mixed, S^{2-} concentration will be sufficient to remove zinc (i.e. no less than 0.25 g/dm^3 S^{2-}).

5. Conclusions

The paper shows the possibility of removing zinc from the aluminate liquor at the Urals alumina refinery by using reductive sintering by the addition of the production wastes, i.e. spent potlining from the Krasnoyarsk aluminium smelter and soda-sulfate mix (The carbon part of the spent potlining was used after it had been processed to obtain secondary cryolite and degrade cyanides.).

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