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Sintered Sorbent Utilization for H₂S Removal from Industrial Flue Gas in the Process of Smelter Slag Granulation

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Authors suggest removing hydrogen sulfide from the hot industrial gas at temperatures 200-300 °C and its subsequent interaction with Fe₂O₃. For this purpose the following sorbents have been proposed: a mixture of iron oxide and fly ash; iron oxide and pumice; different samples of red mud (bauxite treatment residues containing iron oxide). To prevent dusting and loss of absorbing capacity, the sorbents were shaped into porous granules with other metallic oxides. Materials utilized in the study were obtained the following way: mixing of Fe₂O₃ with fly ash; sintering of the mixture with red mud. The blend contains aluminum oxide and silica, which can act as matrix shapers, alkali oxides and fluxing agents that reduce the temperature during metal sintering. After the samples had been saturated with sulfur, they were positioned in a venting reservoir, where under the temperature 600-700 °C desorption to the initial state occurred by means of passing an air flow through the sorbent layer. In the process of this operation, sulfur dioxide was released and reactive metal oxides re-emerged. Desorption also generated a small amount of elemental sulfur and sulfuric acid. Absorbing capacity was assessed at higher temperatures, efficiency of H₂S removal reached 95-99.9 %. Proposed technology of air cleaning is recommended to use in metallurgic processes with elevated atmospheric pollution, e.g. granulation of melted blast-furnace slag.

Key words: red mud; industrial flue gas; pumice; absorbing capacity; sorbents; smelter slag

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Introduction. In numerous literary sources on flue gas cleaning in the temperature interval 540-800 °C there is information about flue gas desulfurization in the interval 20-700 °C with iron oxide of fineness –16+100, the same sources contain data on static layers of sorbent pulp in the interval 320-400 °C [18].

Static sorbent layers have been tested at volume speed (100 units of gas volume passing through 1 unit of sorbent volume in an hour). Agentt absorbing capacity accounted for 30 % of sulfur mass. At higher temperatures efficiency of H₂S absorption increased from 95 to 99.9 %. Such production unit can process up to 100 billion liters of coke gas per day.

Iron oxide absorbs sulfur in the layer of sorbent pulp at temperatures between 200 to 300 °C. General functioning of the unit demonstrated satisfactory results due to the fact that large gatherings of finely-dispersed oxide dust were detected in various part of the environment. Authors present their results of study on solid substances that can remove H₂S from hot industrial flue gases generated in the process of slag granulation. The following solid substances have been used: 1) sintered blend of iron oxide (Fe₂O₃) and ash; 2) pumice covered with melted Fe₂O₃; 3) sintered granules of red mud, alumina processing residue, which contains around 50 % Fe₂O₃ [6].

Problem statement. The industry widely applies clean compressed gas, as it perfectly satisfies consumer demands. However, treatment of flue gas is a problematic issue, as it contains sulfur compounds that contaminate the environment, damage the equipment and degrade performance when entering the atmosphere of the plant. One possible solution is to utilize the energy of hot flue gas for a wide range of industrial purposes, which can have a dramatic effect on the economy of smelting [2].

The temperature of industrial flue gases from the slag granulation area with a large share of H₂S equals 150-400 °C. Hence, the use of flue gas heat can carry an economic significance for energy production. For this purpose, the gas must be preliminary cleaned from H₂S. An important factor is whether it is possible to rule out liquid sorbents and limit the application of solid sorbents that can react with H₂S at high temperatures. Sorbent material must be air-regeneratable, so that it could be repeatedly used in several cycles of H₂S absorption [10].

Method. To investigate sorption properties of the materials, samples with preliminary sintered structure have been used in order to facilitate porosity generation. At temperatures 200-300 °C the samples absorbed H₂S from artificially generated flue gas. Sorption samples were represented in three varieties: the first two were iron oxide mixtures with ash and pumice respectively; the third material was a red mud sample (alumina processing residue, contains up to 50 % of Fe₂O₃).

For laboratory conditions a gas mixture was modeled, so that its sulfur-containing component was obtained by means of elemental sulfur combustion and its subsequent addition to the gas under investigation (2 % of the total volume). Gas mixture is fed at a fixed speed to create an imitation of a gas flow, taken from the atmosphere of the granulation area. The gas does not contain ash, its H₂S content equals approximately 1.5 %.

The gas mixture passes through the layer of test sorbent in a burette, positioned in a vertical pusher furnace, where the heating temperature of absorbing agent can be regulated depending on the process (adsorption or desorption) (Fig.1).

The sorbent was preliminary heated to 200, 250 and 300 °C, after which the sulfur-containing gas mixture was fed through it. The flow rate of gas mixture was approximately 500 ml/s. H₂S content was 15-20 mg/l. After sulfur absorption was completed, the temperature became stable in desorption mode. Further tests have been completed for the temperatures of 500, 650 and 800 °C. Experiments continued until H₂S concentration in the flow of effluent gas settled around the mark of 2 mg/l. After that desorption could be considered completed. Agent's absorbing capacity was calculated using the values of H₂S concentration, flow speed and test duration.

H₂S concentration in the gas flow was estimated with Tutwiler method and tested using indication tubes and gas chromatography. An optimal combination of these methods has been identified [1, 5, 8, 17]. Sorbents regenerated by means of passing an air flow through the burette at temperatures 500-800 °C. In the course of first several tests, released SO₂ got absorbed 2.5 times quicker.

In the solution of caustic soda, the liquid was acidized with HCl and titrated with iodine until the starch was fully bleached. A mass of regenerated sulfur was compared to the calculated mass of

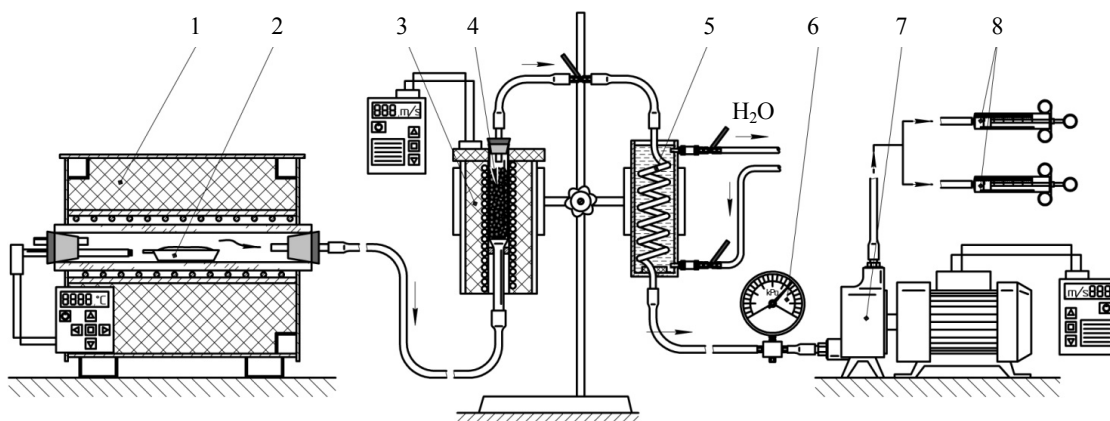


Fig.1. Conceptual chart of regeneration unit

1 – furnace; 2 – sulfur dose; 3 – vertical furnace; 4 – granulated sorbent; 5 – refrigerator;
6 – manometer; 7 – pump; 8 – gas sensor



absorbed sulfur to estimate the error in sulfur balance. Dispersion can be explained by the fact that in the course of regeneration a part of sulfur was emitted in a free state, gathered in the rear end of the reaction tube and therefore was not taken into account. Later SO₂ concentration was measured with silica gel punch tubes.

Research subject. The tests were performed on the following samples: iron oxide promoted with chromium; calcinated granules of dolomite; alkalized granules of aluminum oxide. All of them decomposed in the process of desorption at temperatures 500-800 °C. To obtain satisfactory results several other sorbent samples have been prepared. The first material was composed of fly ash of -4+6 fineness from a bituminous coal power plant (sample 1, see Table) and pure Fe₂O₃.

Chemical composition of sintered ash dust, utilized for H₂S sorption

Sample	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	Other
1 (sintered ash dust)	44.6	23.5	15.1	4.4	1.5	2	2.1	2.5	4.3
2 (granulated pumice)	63.8	13.8	1.4	3.1	2.6	7.3	5.4	0.1	2.5
3 (red mud BAZ)	8.3	18.3	42.5	5.5	2.7	5.7	4.6	0.2	12.2
4 (red mud UAZ)	23.4	6.6	7.6	46.6	2.4	3.8	3.5	0.2	5.9
5 (red mud VAZ)	3.7	12.6	53.3	7.8	2.2	2.3	7.3	1.1	9.7
6 (red mud PAZ)	6.7	13.8	18.4	34.8	5.9	2.8	6.1	1.2	10.3

Fly ash and iron oxide have been thoroughly mixed, blended with water, shaped into granules and sintered at temperature around 980 °C. Beside that, sinter tests on taconite and pure Fe₂O₃ have been performed.

The second sorbent was composed of granulated pumice of fineness -4+8 and Fe₂O₃ content of 99 % (sample 2, see Table). Pumice granules were covered with iron oxide the following way: moistened granules were put into the glass, then dry oxide was added and the contents were subsequently stirred until the granules were uniformly covered. Then for 2 hours they were heated to 950 °C to sinter the materials. Some shrinkage did occur during heating, but the granules remained porous and iron oxide stuck to pumice surface. Excessive shrinkage and loss of porosity occurred at heating temperature of 1030 °C.

The third material consisted of red mud. It is normally dispatched either in powder or in granules, therefore it had to be grinded before use. The powder was moistened with sufficient amounts of water to form a yielding mass, subsequently heated to 260 °C, divided into 8 mm-granules and then soaked for 10-20 minutes at the temperature 1100 °C to get a solid sediment. Chemical analysis of red mud from different plants is presented in the Table (samples from 3 to 6).

Experimental results. All the sorbents were subject to regeneration to the state close to their initial one, air was passed through the sample volume at temperatures 500-800 °C. Sulfide dioxide was released and reactive metal oxides re-emerged. Desorption also generated a small amount of elemental sulfur and sulfuric acid.

Ash (75 %) and Fe₂O₃ (25 %) produced a sediment with a high absorbing capacity of sulfide, which did not decompose under conditions of the experiment. Experiments on one batch of the sorbent confirm absorption capacity of the mixture ash – Fe₂O₃ and contain results of nine consequent regeneration cycles of the air cleaned from H₂S. Obtained data demonstrated that there were no losses in absorbing capacity or visible decomposition of granules. Sorbents with a high Fe₂O₃ content (37 % and higher) were difficult to test because of their decomposition and mutual sintering of granules.

Results of experiment on composite materials, based on pumice covered with iron oxide, are presented in Fig.2. They are decomposition-resistant but have a tendency to sinter together into larger particles [3, 11, 12].

Sample of ash – Fe₂O₃ formed a very resistant structure and had the highest capacity compared to other tested samples of the same base.

Fig.3 demonstrates the capacity of various mixtures to absorb sulfur without decomposition of the grain structure or sintering of several granules into one, which are the main characteristics demanded from materials used as H₂S sorbents.

In the process of regeneration of all sorbents at volume speed 57,000 m³/h, calculated under standard conditions (20 °C, pressure 1 atm), moment concentrations of SO₂ were measured using chemical detector tubes. Regeneration temperature varied between 600 and 700 °C. When the temperature reached 800 °C, the material merged with the mass, which regenerated no longer. Regeneration temperature 650 °C turned out to be optimal for all types of sorbents. Liberation of heat in the process of exothermic regeneration was enough to increase the temperature of the sorbent layer to 200 °C [14, 16, 19].

Full sorbent regeneration is nearly impossible, at the end of the procedure remains a small fraction of SO₂, registered by the measurements after an 80 h holding time. Regeneration (from 6 to 10 % of SO₂) occurs at a high speed in the first 30-50 min, then (after 1 h) drops to 1 % in volume, decreases quickly and slowly reaches zero. Fig.4 demonstrates a dependency of SO₂ concentration on time. Here regeneration temperature equals 500, 650 and 800 °C, sorption temperature is around 250 °C.

Sulfur mass, regenerated in any of the three tests within the first hour, amounted to 80 % of the total mass involved in the reaction. Experiments on the material composed of 63 % ash and 37 % Fe₂O₃ were performed at regeneration temperature of 800 °C, which is enough for quick regeneration of sorbent granules with low sulfur content (around 8 %). However, this temperature did not initiate quick regeneration in granules with high sulfur content (up to 34 %). Apparently, low-sulfur granules (10 % and less), regenerated at a greater speed than the ones with sulfur content 30 % and above. It points to the fact that regeneration should be initiated before the threshold of absorbing capacity is reached.

Result discussion. Mixtures of 75 % ash and 25 % Fe₂O₃ absorbed 8 % of sulfur at 200 °C and 43 % at 300 °C. Granules made of 40 % pumice and 60% Fe₂O₃ demonstrated their sulfur absorbing capacity to be 23 % at 200 °C and 30 % at 300°C. The most efficient sorbent was red mud: from 18 % at 200 °C to 45 % at 300 °C. This substance is a smelting residue and currently recycling of huge masses of red mud is a pressing issue. Obtained results open up an opportunity to use it as a sorbent to capture sulfur compounds in the process of blast furnace slag granulation (Fig.5). Sintered sorbent can substantially lower the costs of preparation and air regeneration [4, 7, 13, 15]. This is possible due to the fact that after thermal treatment the material can restore its properties without decomposition of the grain structure.

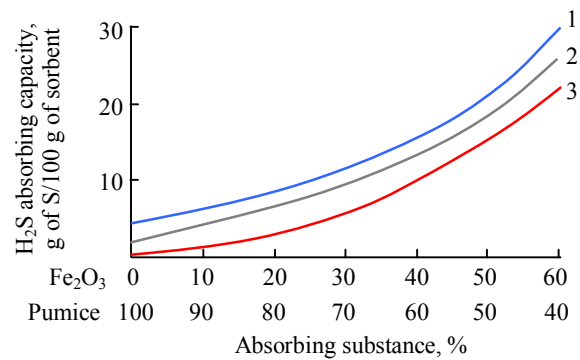


Fig.2. H₂S absorbing capacity of sintered pumice
1 – 200 °C; 2 – 250 °C; 3 – 300 °C

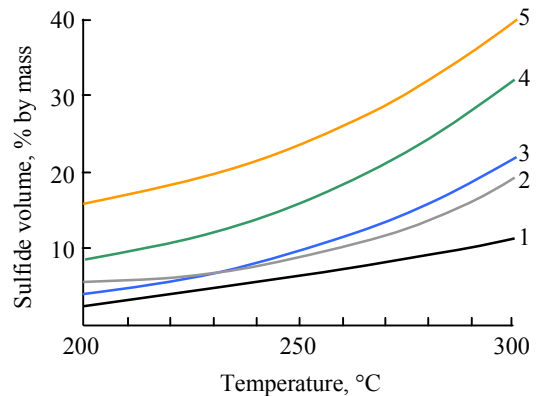


Fig.3. H₂S absorbing capacity of the agents at 200-300 °C
1 – ash; 2 – 37 % Fe₂O₃, 63 % ash; 3 – 13 % Fe₂O₃, 87 % ash;
4 – 25 % Fe₂O₃, 75 % ash; 5– red mud

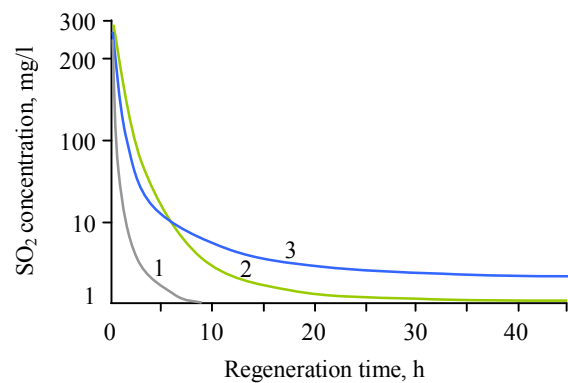


Fig.4. Dependency of SO₂ concentration on regeneration time
1 – 500 °C; 2 – 650 °C; 3 – 800 °C

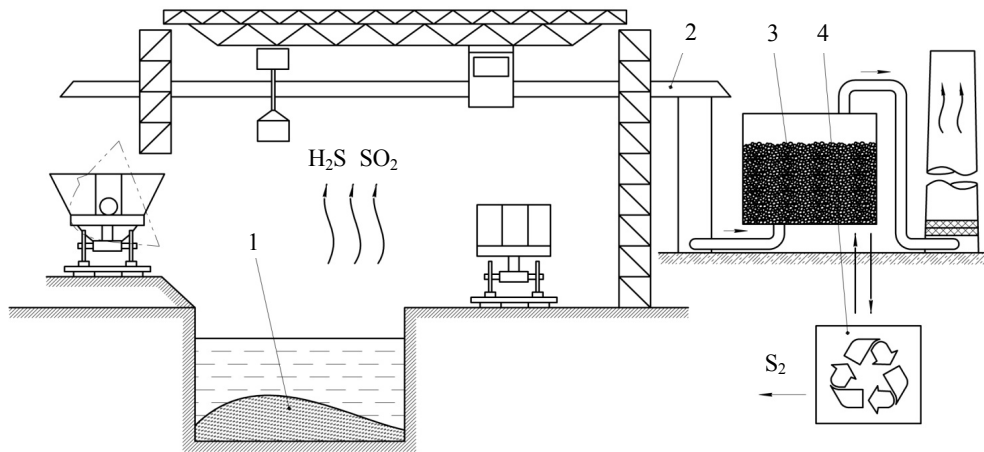


Fig. 5. The graph of air cleaning from sulfur compounds in the granulation area
1 –granulated slag; 2 –gas trap; 3 – sintered sorbent; 4 – regeneration area

Spectrographic analysis of reaction products detected generation of troilite (FeS). Stoichiometric calculations point to generation of iron sulfide (Fe₂S₃) and pyrite (FeS₂) as reaction products. Precise estimation of stoichiometry is impossible due to a variety of forms, in which iron sulfide can occur. Moreover, the reaction is complicated by the presence of other metallic oxides in the sorbent that can have a capacity to absorb H₂S under conditions of the experiment.

Other possible ways of sulfur extraction from SO₂ in the process of regeneration represent catalytic transition to SO₃ with subsequent liberation of sulfuric acid or reaction between SO₂ and a number of gases in the presence of a catalyst with liberation of elemental sulfur.

With the help of gas chromatographic analysis of inlet and flue gases (using sintered mixture of ash and iron oxide), the authors estimated whether reorganization of gas composition occurred and whether the formation of gaseous sulfur compounds took place that could not be detected by H₂S titration. At the temperature of 200 °C water steam with a small concentration of methane (0.4 %) was detected.

Conclusion. All three materials have nearly fully recovered their absorbing characteristics after desorption. A sintered mixture of Fe₂O₃ (25 %) and ash (75 %) have been tested throughout nine cycles of regeneration with a full recovery of H₂S absorbing capacity from the gas flow without visible decomposition of granules. The most efficient sorbent was red mud, which absorbs 18 % of sulfur at 200 °C and 45 % at 300 °C. Hence, it can be repeatedly used in the process of air cleaning in the granulation area.

H₂S, present in the area of smelter slag granulation, can be removed from the residue of flue gases at temperatures 200-300 °C in a reaction with metallic oxides, such as Fe₂O₃. The optimal temperature, identified for sorbent regeneration, is 600-700 °C. However, the material must be included in the granulated porous structure from other metallic oxides to prevent dusting and decomposition of the sorbent grains. The study showed that such substance can be obtained by sintering red mud and be consequently used in the process of air cleaning in the area of blast furnace slag granulation.

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