Semi-industrial technology tests of the sanitary cleaning of metallurgical enterprises waste gases from sulfur and nitrogen oxides

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Nitrogen emissions in the form of NOx with flue gases from thermal power plants are the most serious pollutants generated during the combustion of coal. The calcium carbonate gas scrubbing process used today is expensive, generates a lot of waste, and leaves a significant amount of SO_2 in the gas. Virtually no NO_x removal.
In this paper, we consider the behavior of nitrogen oxides during the purification of exhaust gases from thermal power plants with a carbonate melt of alkali metals. Based on the thermodynamic analysis of reactions between NO_x and alkali metal carbonates, the possibility of reducing their concentrations in the exhaust gases is shown. It has been established that the process of NO_x absorption in the temperature range of 573...823K is accompanied by the formation of stable potassium nitrite (KNO_2) in the melt, as evidenced by the high negative values of the Gibbs energies of the reactions.
The results of balance experiments fully confirm the established regularities. One can foresee that carbonate melt-based SO_2 removal may become a practical and economical scrubbing method for sulfur-poor flue gases emitted by non-ferrous metal production plants, thereby contributing to the limiting of harmful sulfur and NOx emissions into the atmosphere.

Key words: flue gases, sulfur dioxide, nitric oxide, chemical absorption, carbonate eutectic, potassium carbonate, potassium nitrite, natural gas, Gibbs energy.

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Introduction

Each non-ferrous metallurgy plant annually emits more than 100 thousand tons of sulfur dioxide into the atmosphere. Moreover, most areas of high air pollution coincide with places of concentrated human settlement. Emissions from various sources of the Unified Energy System are dominated by solid particles — 35%, sulfur dioxide — 31%, carbon and nitrogen oxides — 19% and 14%, respectively [1]. The major toxic proponents of flue gas emitted into the atmosphere during fossil fuel combustion and non-ferrous sulfide concentrates treatment are sulfur dioxide (SO_2) and nitrogen oxides (NO_x).

The main problems arise with gases containing low sulfur dioxide and nitrogen oxides content [2–5]. While the majority of sulfur-rich (>3–4 volume % SO_2) flue gases, e.g. from autogenous sulfide ore smelters, are successfully scrubbed to produce sulfuric acid or elemental sulfur [6–8], cleaning of flue gas with lower sulfur content is currently not economically viable. Flue gas scrubbing with calcium carbonate or $Ca(OH)_2$, the desulfurization process most widely in use today, is costly, produces a large amount of waste, and leaves a considerable amount of SO_2 in the gas [3, 9–10]. An alternative method, based on scrubbing SO_2 from flue gas at 450–650 °C with a carbonate eutectic melt ($Na_2CO_3 - K_2CO_3 - Li_2CO_3$), was initially proposed in the 1970s, but despite its efficiency in converting SO_2 to sulfates, it could not be commercially implemented due to the technical complexity of the removal of the sulfates at the melt regeneration stage. Earlier we demonstrated on a laboratory scale (~0.3–0.5 l melt) a relatively simple procedure for regenerating the post-scrubbing carbonate eutectic melt via purging with natural gas [11]:

$$K_2SO_4\ (\text{melt}) + CH_4\ (\text{gas}) \leftrightarrow$$
$$\leftrightarrow K_2CO_3\ (\text{melt}) + H_2O\uparrow + H_2S\uparrow.$$

This reaction lead to the reduction of sulfate to H_2S gas that leaves the melt.

Here, we describe a highly efficient, environmentally friendly technology for the sanitary treatment of waste gases from metallurgical enterprises with the production of marketable products, adapted to the conditions of existing metallurgical plants in Kazakhstan. This goal is achieved in that the exhaust gases are treated with molten alkali metals carbonate salts, followed by regeneration of

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the carbonate-sulfate melt with natural gas for production of the commercial products (elemental sulfur or sulfuric acid).

Materials and Methods

Carbonate eutectic melt. Powdered Li_2CO_3, Na_2CO_3, and K_2CO_3 (Sigma-Aldrich company)(99% purity) were mixed in the ratio (43.5 mole %, 31.5 mole %, 25.0 mole %) and heated to 753–773 K to produce the eutectic melt in a stainless steel container.

Gases. Natural gas (Bukhara Gas Company, Uzbekistan) composition (volume %): CH_4 — 92.6; C_2H_6 — 4.07; C_3H_8 — 1.07; C_4H_{10} — 0.44; C_5N_{12} — 0.42; N_2 — 0.9.

Flue gas scrubbing by carbonate eutectic melt and melt regeneration with natural gas were tested on a semi-industrial scale unit (271.26 kg of the eutectic carbonate melt) with gas collected from the flue damper of a coal-firing boiler in the power plant located in Ust-Kamenogorsk, Kazakhstan **(Fig. 1)**. The two procedures — scrubbing followed by regeneration – were tested in batch mode in the same reactor vessel. In each scrubbing phase, flue gas containing (volume %) 0.15% SO_2, 13 ppm NO, 52 ppm NO_2, 4.7% O_2, 9.3% CO_2, 3.8% H_2O, and rest N_2 with volume 12.87 m^3/min passed through the melt as measured by a SGK-G4 flowmeter (Engels Instrument- Engineering Association “Signal”, Russia). Gas composition was determined using a DAG-510 gas analyzer (Ditan Gaz, Nizhny Novgorod, Russia) with a measurement range of 0–400 ppm and absolute error of ±5 ppm. Duration of the scrubbing stage was 600 min. In addition, 5–10 g samples of the melt were taken on a stainless steel rod for chemical analysis every 60 min. The melt was then purged with natural gas to effect regeneration. Duration of the regeneration stage was 40 min. Then, 5–10 g samples of the melt were then taken, as described above, every 10 min. The amounts of CH_4 and oxygen used for melt regeneration were 0.29 m^3/min and 0.4 m^3/min, respectively. The sulfur and nitrogen content of the melt was determined using an *X*-ray fluorescence energy dispersive spectrometer RLP-21 (Aspageo, Almaty, Kazakhstan). The temperature of the melt was maintained at 883K ± 2K with temperature controller Eurotherm-2416, thermocouple type K.

Results

Thermodynamic Calculations

In previous reports from our group (11, 12), we presented the results of thermodynamic calculations for the sulfur scrubbing by a carbonate melt and regeneration of the carbonate melt with CH_4. Under scrubbing-regeneration process conditions, the Gibbs energy of the reactions of the sulfur scrubbing and melt regeneration is strongly negative. The Gibbs energy of the reactions alkali metal carbonates with SO_2 is equal — (250–300) kJ/mole at 673K and — (220–280) kJ/mole at 873K. The Gibbs energy of the regeneration reactions with CH_4 is equal — (70–80) kJ/mole within a wide temperature range, including the range of interest 673–873K. Calculations of Gibbs energy for the NO_x scrubbing by a carbonate melt in the temperature range 673–973K and for melt regeneration with natural gas were performed. We useda computer program developed by the authors and based on standard values for the pure substances [13]. Results of the Gibbs energy calculations are presented in the **Table 1**. Gibbs energy for the reactions of the K_2CO_3 with NO_2 and NO (reactions 1 and 2 from **Table 1**) is — (40–80) kJ/mole, within a wide temperature range, including the range of interest 673–873K, thereby predicting rapid scrubbing of the NO_2 and NO by a eutectic carbonate melt from the flue gases. In our previous works [11–12], we showed that potassium carbonate is the main reagent for sulfur capturing from flue gases.

The Gibbs energy for the regeneration reactions of the KNO_2 with natural gas (reactions 3 and 4 from **Table 1**) is — (500–550) kJ/mole, thereby predicting rapid extraction of the nitrogen from the eutectic carbonate melt and its regeneration.

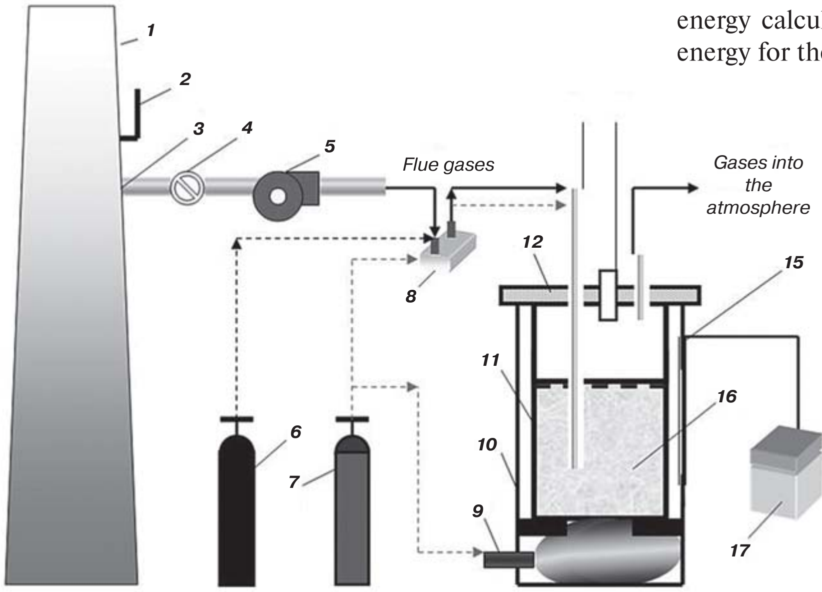

Fig. 1. Semi-industrial scale unit
1 – metal pipe from boiler; *2* – flue gas damper; *3* – gas outlet from pipe to reactor; *4* – bibcock; *5* – compressor; *6* – compressed air; *7* – compressed natural gas (CH_4); *8* – flowmeters; *9* – natural gas burner; *10* – stainless steel casing; *11* – stainless steel reactor; *12* – stainless steel cover; *13* – tube for supply of flue gas to the reactor; *14* – access metal tube for gas and melt sampling; *15* – thermocouple type K; *16* – carbonate melt; *17* – temperature controller

Scrubbing sulfur and nitrogen oxides from industrial flue gas using a carbonate eutectic melt

Our objective in setting up the pilot plant trial described above was

Table 1

Gibbs energy (Δ*G*) calculated NO_x scrubbing by a carbonate melt and melt regeneration

No.	Reaction*	Temperature, K			
		673	773	873	973
		Δ*G*, kJ/mole			
1.	NO_2 (*g*) + 0.5 K_2CO_3 (*l*) + 0.25 O_2 (*g*) = KNO_3 (*l*) + 0.5 CO_2 (*g*)	–70.7	–62.5	–54.7	–47.1
2.	NO (*g*) + 0.5 K_2CO_3 (*l*) + 0.75 O_2 (NO_3 (*l*) + 0.5 CO_2 (*g*)	–77.8	–62.0	–46.5	–31.4
3.	KNO_3 (*l*) + 0.75 CH_4 (*g*) = 0.5 K_2CO_3 (*l*) + 1.5 H_2O (*g*) + 0.25 C (*s*) + 0.5 N_2 (*g*)	–506.7	–521.2	–535.3	–549.2
4.	KNO_3 (*l*) + 5/8CH_4 (*g*) = 0.5K_2CO_3 (*l*) + 10/8 H_2O (*g*) + 1/8 CO_2(*g*) + 0.5 N_2 (*g*)	–505.4	–520.0	–534.2	–548.1

**s* – solid, *l* – liquid, *g* – gas.

Table 2

A complete analysis of off-gases after of Semi-industrial scale unit depending on the duration of gas cleaning process

Duration, min.	SO_2, ppm	NO_x, ppm	O_2, volume %	CO_2, volume %	H_2O, volume %	N_2, volume %
60	64.4	34.9	4.4	9.0	8.8	rest
120	64.4	34.0	4.5	9.0	8.9	rest
180	64.4	36.1	4.5	8.7	8.8	rest
240	63.3	39.1	4.7	8.7	8.8	rest
300	62.7	39.7	4.6	9.2	9.0	rest
360	62.2	38.6	4.5	9.0	8.7	rest
420	61.9	39.1	4.4	9.0	8.8	rest
480	62.2	38.4	4.5	9.1	8.8	rest
540	60.6	38.8	4.3	8.9	9.0	rest
600	59.2	38.2	4.6	8.8	8.7	rest

to determine to what extent a carbonate eutectic is able to efficiently and economically scrub sulfur dioxide and nitrogen oxides from industrial flue gas and then to regenerate the melt by removing sulfur in an industrially useful form. A coal-fired boiler emitting flue gas with 0.15% SO_2, 13 ppm NO, and 52 ppm NO_2 was used as the starting gas. A complete analysis of off-gases depending on the duration of gas cleaning process is presented in **Table 2.**

It is noteworthy that the total content of nitrogen oxides in our gas samples (65 ppm total NO_x) is much less than in gas samples from other coal power stations (400–1000 ppm total NO_x) [2, 14–17]. The sulfur content in the melt was 5.5 weight % and nitrogen contet in the melt was 510 ppm following scrubbing for approximately 600 min.

The dash lines **(Fig. 2)** indicate 100% SO_2 and nitrogen oxides capture from flue gases into the carbonate melt. It can be seen that as the process proceeds and the melt is saturated with sulfate and nitrite, the extraction yield of sulfur and nitrogen decreases. Total sulfur extraction was 96% and nitrogen from nitrogen oxides was 60%. Obviously, this is due to an increase of the total content of the sulfate SO_4^{-2} and nitrite NO_2^{-1} ions in the melt until to 18 mass % **(Fig. 3)**.

In this case, the content of carbonate ion decreases. It is possible that this is related to the incomplete extraction of nitrogen oxides from gases in the final phase of the scrubbing process. Average composition of the flue gases before and after cleaning process is presented in **Table 3**.

Discussion

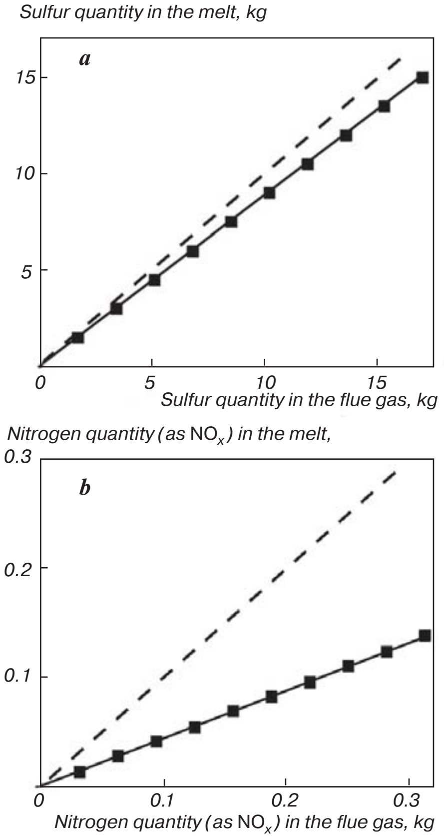

Fig. 2. Scrubbing of sulfur (*a*) and nitrogen oxides (*b*) from industrial flue gas with a carbonate eutectic melt. The dash lines indicate 100% SO_2 and nitrogen oxides capture from flue gases into the carbonate melt

Table 3

Average composition of the flue gases before and after cleaning process

	SO_2, ppm	NO_x, ppm	O_2, volume %	CO_2, volume %	H_2O, volume %	N_2, volume %
Before cleaning	1500 (0.15%)	65	4.7	9.3	3.8	rest
After cleaning	64	39	4.5	9.0	8.8	rest

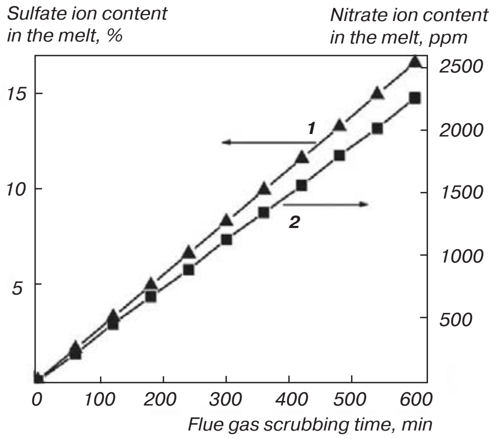

Fig. 3. The sulfate ion (*1*) and nitrite ion (*2*) contents in the melt as a function of time during the scrubbing stage

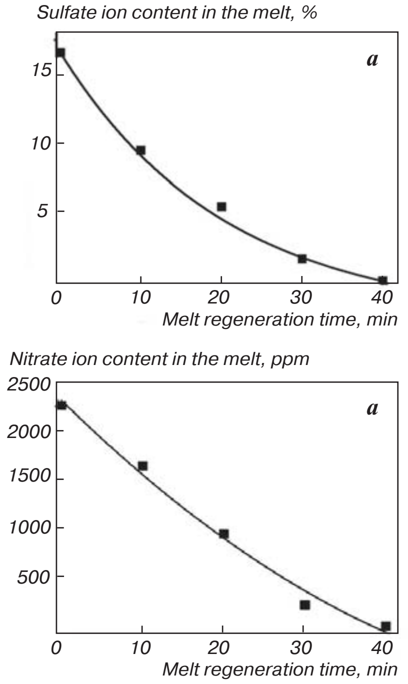

Fig. 4. The sulfate ion (*a*) and nitrite ion (*b*) contents in the melt as a function of time during the regeneration with CH_4

Our proposed modifications to the original concept of [11–12, 18–19], as described above, remove three technical difficulties with respect to commercial implementation of carbonate melt scrubbing/regeneration.

(1) At 550 °C, there is no serious problem of container corrosion; a reaction cell of stainless steel with high chromium content is stable with respect to the carbonate eutectic melt at that temperature.

(2) Removal of sulfur from the carbonate/sulfate melt in the form H_2S provides considerable freedom in choosing a final sulfur-rich product with considerable economic value.

(3) Removal of the nitrogen oxides from flue gases.

Natural gas can be used for melt regeneration. Because of the high reaction rates at all stages [11], the scrubbing and regeneration cells can be made very compact. In many metallurgical plants, dilute sulfur-containing gases (< 0.5–1 volume %) are often emitted to the atmosphere because they are not suitable for sulfuric acid production [20]. We have modified the regeneration process so that natural gas can be used for regeneration because natural gas is the primary energy source **(Fig. 4)**. In this case, sulfur from the melt is extracted as highly concentrated H_2S, which can then be converted into elemental sulfur or to sulfuric acid.

The removal of sulfur in the form of H_2S provides freedom in choosing the final product: either sulfuric acid (by H_2S dry combustion in air) or elemental sulfur (by the Claus process or thermal decomposition), both of which have considerable commercial value.

Conclusions

Removal of sulfate from the carbonate melt *via* bubbling with natural gas can be achieved within the operating temperature range of the flue gas scrubbing tower, i.e. ~823K. At these temperatures, high-temperature corrosion of the sulfate reduction chamber does not pose a problem for industrial implementation of carbonate melt scrubbing.

Removal of sulfur and NO_x from the carbonate melt by natural gas is a relatively simple, one-stage process, which occurs at a rate that is sufficiently high that the small volume of the melt regeneration chamber can be integrated within the scrubbing tower.

One can foresee that carbonate melt-based SO_2 removal may become a practical and economical scrubbing method for sulfur-poor flue gases emitted by non-ferrous metal production plants, thereby contributing to the limiting of harmful sulfur and NO_x emissions into the atmosphere.

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