OFF-GAS DESULFURIZATION WITH SODIUM BICARBONATE FOR IRON ORE SINTER PLANTS: INVESTIGATION OF THE INFLUENCE OF THE OFF-GAS TEMPERATURE

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Abstract

For dry off-gas desulfurization by chemisorption in iron ore sinter plants hydrated lime is usually used as reactant. In some other off-gas cleaning applications with a gas temperature above 140°C sodium bicarbonate is used instead of hydrated lime. An advantage of sodium bicarbonate is the higher desulfurization efficiency. Additionally, cooling of the off-gas to a temperature below 100°C to achieve satisfactory desulfurization is not required. In sinter plants the off-gas temperature is often below 140°C. Thus, the thermal decomposition of sodium bicarbonate to sodium carbonate, which increases the specific surface area of the reactant, might be too slow. The aim of this study was to investigate the desulfurization gas with sodium bicarbonate in the typical temperature range of sinter plant off-gas of 110-160°C. The experiments were performed in a small pilot system consisting of an entrained flow reactor and a fabric filter. For the experiments a mixture of sulfur dioxide in air was used. The results showed that the efficiency of the desulfurization was only slightly reduced at the lower temperature of 110°C. However, at lower temperatures it takes longer after start-up of the system to reach

stable conditions. At first, the efficiency is lower, but it seems that this is nearly compensated for by reaction in the filter cake, which builds up at the filter. Therefore, sodium bicarbonate is a feasible reactant for the desulfurization of sinter plant off-gas.

Keywords

Dry Desulfurization, Sinter Plant, Sodium Bicarbonate

1. Introduction

Dry chemisorption processes for desulfurization of off-gases are characterized by the absence of any waste water. In these processes the SO_2 reacts with the fine granular solid sorbent, which is usually hydrated lime ($Ca(OH)_2$). The reaction can take place, for example, in a fluidized bed reactor. Another option is entrained flow processes, where the fine dry sorbent is pneumatically injected into the off-gas stream at a point with an appropriate temperature level. The sorbent is re-collected from the off-gas in a de-dusting system, which is usually a fabric filter or an electrostatic precipitator. However, the efficiency of such an entrained flow process using $Ca(OH)_2$ is not very high. Especially the utilization of the sorbent is relatively low, since the SO_2 reacts essentially on the surface of the particles and only slowly diffuses into the solid matter. In order to sustain a higher level of utilization, a portion of the sorbent separated in the subsequent off-gas de-dusting unit is usually re-circulated and re-injected into the off-gas together with fresh sorbent. Additionally, the temperature of the off-gas should be below 100°C to accelerate the chemical reactions for binding and removing SO_2 (Fleischanderl et al., 2006; Kaiser et al., 2000).

In an alternative design of the dry desulfurization process, sodium bicarbonate ($NaHCO_3$) is used as reactant. At higher temperatures the $NaHCO_3$ is converted into Na_2CO_3, which increases the specific surface area of the powder. However, SO_2 can also react directly with $NaHCO_3$ (Keener and Khang, 1993). The dry desulfurization process with sodium bicarbonate usually requires an off-gas temperature above 140°C (Dvořák et al., 2009). In iron ore sinter plants the typical off-gas temperature is in the range of 110 – 160°C (Schuster et al., 2005; Hartig et al., 2007; Bastürk et al., 2009). Thus, the off-gas temperature is often lower than the recommended temperature for desulfurization with sodium bicarbonate.

The aim of this study was to investigate the effect of the gas temperature on the desulfurization efficiency of sodium bicarbonate. The experiments were performed at a small pilot installation using mixtures of ambient air and SO_2.

2. Materials and Methods

The schematic flow diagram of the pilot installation is shown in Figure 1. The entrained flow reactor consists of a horizontal tube with an inner diameter of 72 mm. Ambient air is sucked through the reactor and the subsequent fabric filter for separation of the powder by a speed-controlled fan installed at the end of the system. The temperature of the air in the reactor is controlled by admixture of hot air to the air flowing through the reactor. After the filter the air is cooled in a spray cooler before it enters the fan. At the air inlet of the reactor the sorbent powder is dosed into the air stream by a vibration feeder and dispersed by compressed air at the center of the tube. The dosing rate can be adjusted via the frequency of the vibration feeder.
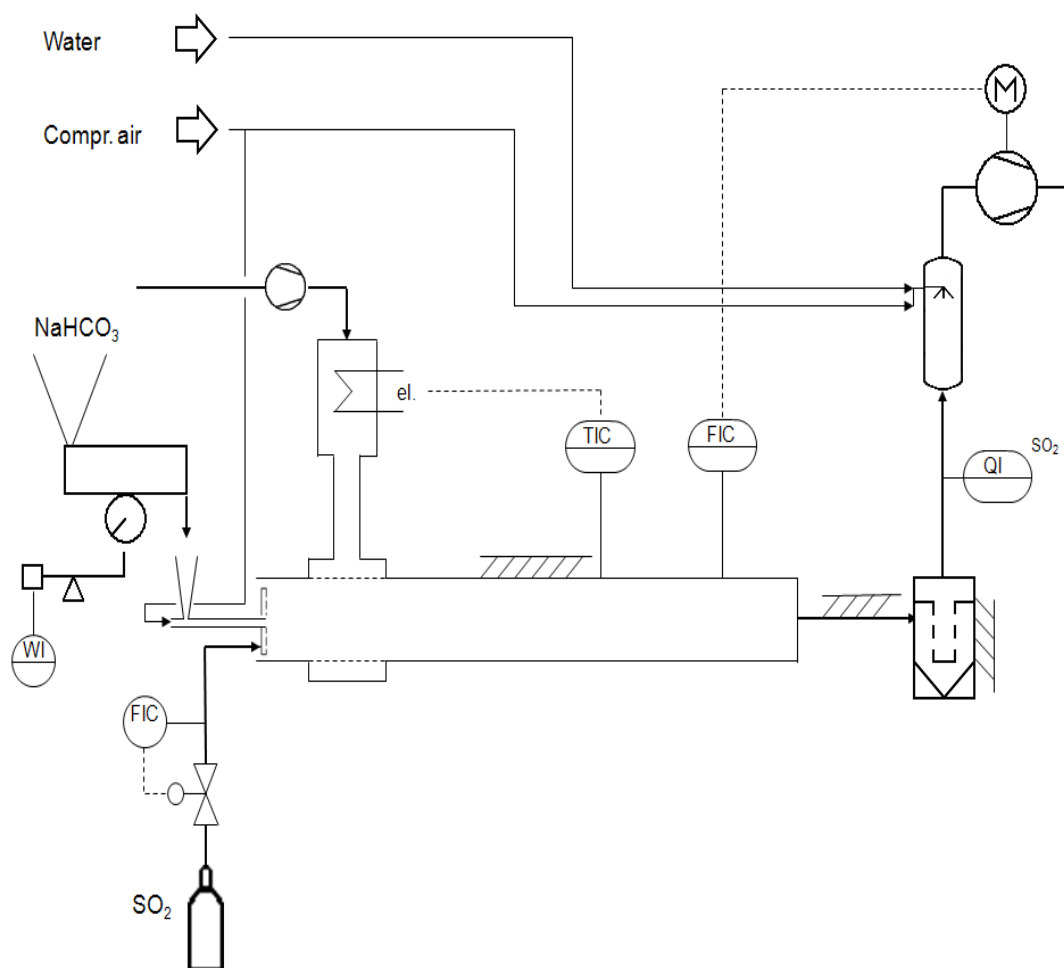

Figure 1: *Schematic flow diagram of the pilot test system*

The actual dosing rate can be calculated from the change in the weight of the stored powder. Through a ring nozzle also installed at the air inlet, SO_2 can be dosed from a gas cylinder at a controlled flow rate. The air flow rate through the entrained flow reactor was approximately 150 m³/h. Thus, the resulting residence time for the gas in the flow reactor was nearly 1.0 s. In the fabric filter GORETEX membrane filter bags with a total filtration area of 3.6 m² were installed. The average residence time of the gas in the filter casing before it passes through the filter bag was approximately 10 s.

The sodium bicarbonate was ground in a laboratory ball mill. The fineness of the material was similar to that of sodium bicarbonate used in full scale gas cleaning applications. The mass median diameter of the ground sodium bicarbonate was 12 μm and the calculated specific surface area was 1.56 m²/cm³. The value of the spread of the particle size distribution (d_{90}/d_{10}) was 68, which was relatively high in comparison to the measured spread of sodium bicarbonate from a full-scale gas cleaning application of approximately 8. The SO_2 concentration was measured with a Leybold-Heraeus Typ BIN 4b.1 instrument, the measuring range was 0 – 3000 ppm SO_2. A two-point calibration of the instrument was performed using ambient air and a certified calibration gas with 981 ppm SO_2.

The experiments were performed in the following way: the fan was started together with the air heating system and the air cooler upstream of the fan. When constant operation at the chosen temperature was reached, the addition of SO_2 at a certain rate was begun. After some time, a constant value of the SO_2 concentration after the filter was reached. This condition requires that all the sodium bicarbonate powder which remains somewhere in the filter after its cleaning has reacted with SO_2. After the constant SO_2 concentration was reached the dosing of sodium bicarbonate at the chosen rate was started. The experiment was continued until a constant SO_2 concentration was obtained in the gas after the filter. After each experiment the filter bags were cleaned with a pulse-jet cleaning system.

The time delay of the measured SO_2 concentration was tested for the starting and stopping of the SO_2 dosing without dosing of sodium bicarbonate. The measured time course of the ratio of the measured SO_2 concentration after the filter to the SO_2 inlet concentration is shown in Figure 2. For both the start of the SO_2 dosing and the cessation of the SO_2 dosing the response of the SO_2 concentration was the same. The time delay for the start of the SO_2 dosing can be described approximately by Equation 1. For description of the cessation the left side of equation (1) has to be changed to (100-x%).

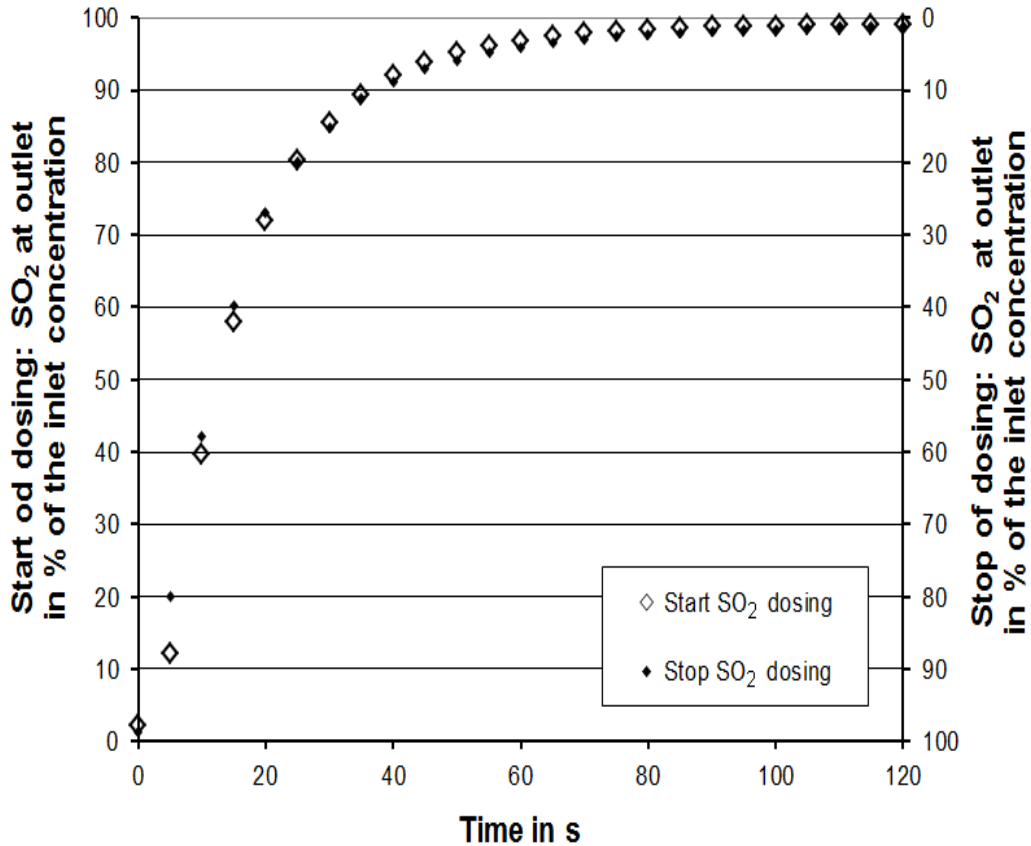$$x\% = 100\% \cdot \left(1 - e^{-\frac{1}{17} \cdot t}\right) \quad \ldots\ldots \text{ (1)}$$

Figure 2: *Time delay of the measured SO₂ concentration*

3. Results and Discussion

The reaction between SO_2 and sodium bicarbonate or sodium carbonate can take place on the one hand during flow of the gas-solid mixture to the filter (entrained flow sorption) and on the other hand when the gas flows through the filter cake which was built up on the surface of the filter material. The amount of SO_2 reacting with the filter cake increases during the build-up of the filter cake until equilibrium is reached between the additional amount of sodium bicarbonate separated by the filter which will react with SO_2 and the amount of sodium bicarbonate in the filter cake which actually reacts with SO_2. This is equivalent to the moment when the sodium bicarbonate separated first on the filter surface does not further react with SO_2.

The experiments were performed at three temperatures: 160°C, 130°C and 110°C. The concentration of SO_2 in the gas was approximately 1,200 ppm and the stoichiometric ratio between the amount of sodium bicarbonate added and the SO_2 contained in the gas (2 Na / S) was between 0.75 and 0.90.

In Table 1.1 the applied dosing rates and further data are summarized. For the experiments at 160°C, 130°C and 110°C the respective stoichiometric ratios were 0.90, 0.78 and 0.75. The course of the SO_2 concentration for the three experiments (a, b and c) is shown in Figure 3. In the diagrams the SO_2 clean gas concentrations of the first 100 seconds were corrected for the time delay. As the available dosing device did not supply the sorbent powder very constantly, the dosing rate had to be adjusted frequently according to the reading of the balance. The effect of the resulting variation of the sorbent addition on the SO_2 concentration was quite evident at 160°C operation temperature, while at 130°C it was less and at the lowest temperature it was nearly not detectable.

For the period where the increasing mass of the filter cake improves the SO_2 separation an approximation function was derived for each experiment. The extrapolation of this function to the start of an experiment was used to determine the separation efficiency of the entrained flow sorption ETA_{ef} only (Table 1).

Table 1: *Test data and results*

Temperature	Dosing rate	ETA_{ef}	ETA_{fc}	ETA_{tot}	t_c	m_{cake} at t_c
160°C	14.4 g/min	21%	13%	34%	500 s	33 g/m²
130°C	13.5 g/min	6%	23%	29%	950 s	60 g/m²
110°C	13.0 g/min	3%	21%	24%	1150 s	70 g/m²

The difference between this efficiency and the constant separation efficiency reached after some time - ETA_{tot} - represents the separation in the filter cake ETA_{fc}. The time after which approximately constant separation efficiency is reached, t_c, increases when the gas temperature is lower. Therefore, the specific mass of the filter cake, m_{cake}, is higher at this time.
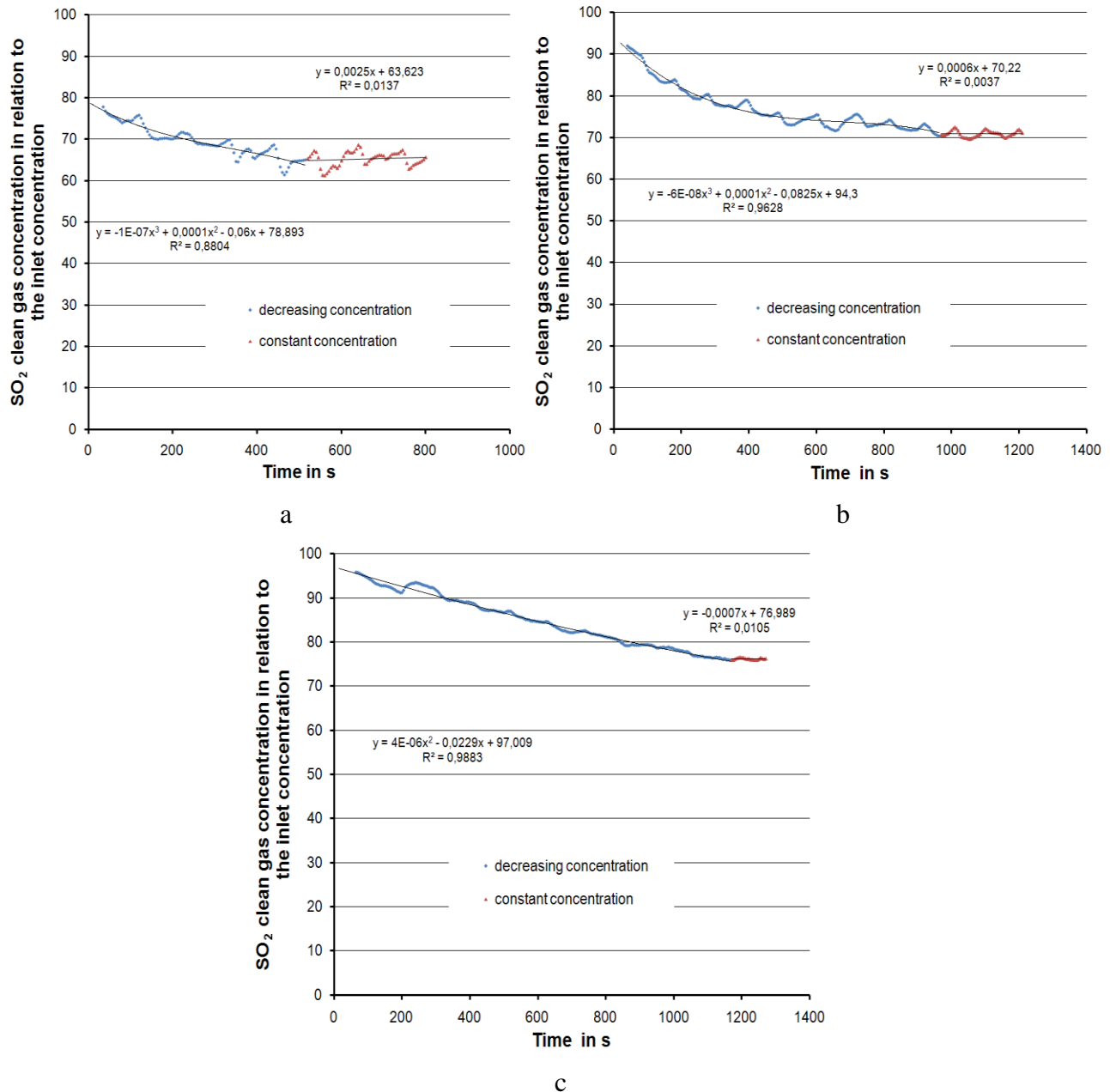
Figure 3: *SO₂ fraction in the clean gas*

As the stoichiometric ratio was not exactly the same in all experiments the separation efficiency was corrected for a stoichiometric ratio of 1.0 using a linear approach (Table 2). The total efficiency was similar for 160°C and 130°C, whereas for 110°C a somewhat lower value resulted. At the same time the efficiency of the entrained flow separation decreased significantly from 160°C to 110°C. However, at 130°C this reduction was compensated by the increase in the separation efficiency of the filter cake. At 110°C the separation efficiency of the filter cake was

nearly the same as at 130°C, which resulted in a somewhat lower total efficiency. This shift from reaction of SO_2 with the sorbent in the entrained flow at higher temperature to reaction with the filter cake at lower temperature might be explained partly by the reduced reaction rate of the Na_2CO_3 formation.

Table 2: *Test result*

Temperature	ETA$_{ef,corr}$	ETA$_{fc,corr}$	ETA$_{tot,corr}$
160°C	23%	15%	38%
130°C	8%	29%	37%
110°C	4%	28%	32%

The reaction of sodium bicarbonate to sodium carbonate is shown in Figure 4. It shows that the reaction is somewhat slower at 130°C than at 160°C, while a reduction of the temperature to 110°C slows the reaction down substantially. Similar results are also available in the literature (Keener and Davis, 1984).
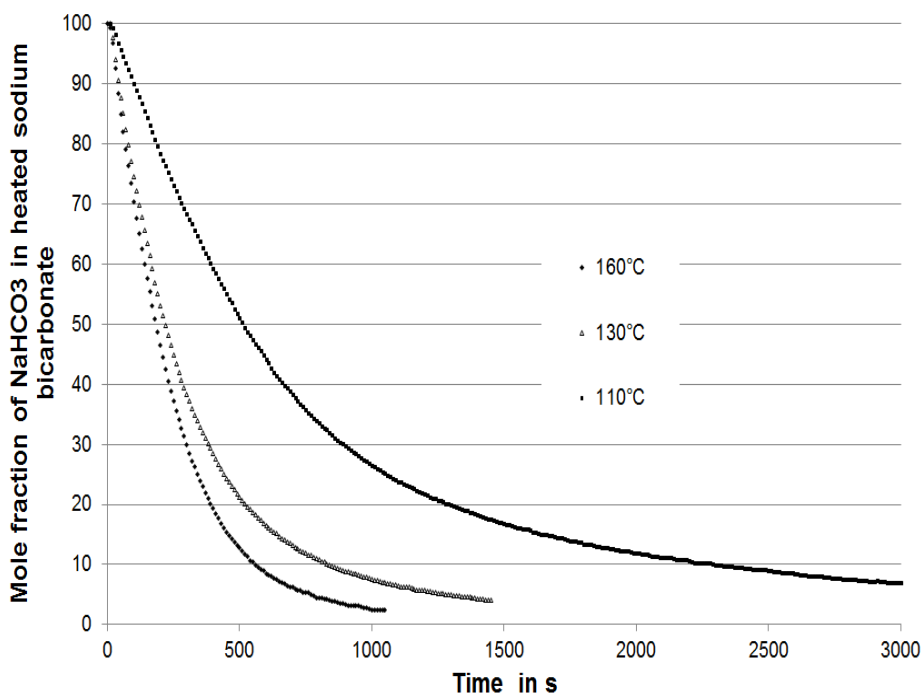

Figure 4: *Time dependence of composition of heated sodium bicarbonate*

In a pilot system with an electrostatic precipitator instead of the fabric filter, an ETA_{tot} of approximately 50% has been reported at a stoichiometric ratio of 1.0 and a gas temperature of 200°C (Pilat and Wilder, 2007). This corresponds well with the results obtained in this study.

Summarizing the results, for off-gas desulphurization at sinter plant off-gas temperatures of 110-160°C sodium bicarbonate can be applied. However, especially at the low end of the temperature range the reduced use of the sorbent would have to be compensated by an increased addition of sodium bicarbonate.

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