

# Kinetic behaviour of iron oxide sorbent in hot gas desulfurization

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## Abstract

Although a number of reports on sorbents containing ZnO for H<sub>2</sub>S removal from coal-derived gases can be found in the literature, it is shown in our study that a special sorbent containing Fe<sub>2</sub>O<sub>3</sub>·FeO (SFO) with minor promoters (Al<sub>2</sub>O<sub>3</sub>, K<sub>2</sub>O, and CaO) as the main active species is more attractive for both sulfidation and regeneration stages, also under economic considerations. This paper presents the kinetic behaviour of SFO in a hot gas desulfurization process using a thermogravimetric analysis under isothermal condition in the operating range between 500 and 800 °C. The gas stream was N<sub>2</sub> with a 2% wt of H<sub>2</sub>S. Experiences carried out on sorbent sulfidation with SFO (particle sizes in the range of 0.042–0.12 mm) indicate that the sorbent sulfidation capacity sharply increases with temperature in the range of 500–600 °C. It is also shown that the sample weight reaches its maximum absorption capacity, near saturation, at 600 °C so that it makes no sense to increase the sulfidation temperature from this point. To make a comparison between SFO and a zinc titanate based sorbent, a set of sulfidation tests was carried out at 600 °C during 7200 s using the same sieve range for both sorbents between 42 and 90 μm. Results show that the sulfidation capacity of SFO is 1.9 times higher than that of zinc titanate.

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## 1. Introduction

High-temperature desulfurization of coal-derived fuel gases improves the thermal efficiency of modern integrated gasification combined-cycle power generation processes that employ gas turbines or gasifier-molten carbonate fuel cell power plants. In both cases, highly-efficient sulfur removal processes are needed to remove the H<sub>2</sub>S contents from several thousand parts per million down to about 100 ppm for fuel cell power plants, or down to about 1 ppm for gas turbines. Traditionally, commercial desulfurization processes have been based on liquid scrubbing at room temperature, resulting in considerable thermal efficiency losses and requiring costly wastewater treatment facilities. In addition, the sulfur removal efficiency of these traditional liquid scrubbing plants is only about 98%. This means (assuming a 1% sulfur content in the inlet fuel gas) that the sulfur content in the outlet gas should be about 1000 ppm.

However, city gas and chemical industries have used iron oxide or zinc oxide as non-regenerable sorbents in ‘guard beds’, ensuring less than 20 ppm of sulfur in the gas and protecting catalyst beds from traces of sulfur impurities.

Several pure and mixed solid oxides such as MnO, V<sub>2</sub>O<sub>3</sub>, CaO, Fe<sub>2</sub>O<sub>3</sub>, ZnO, CuO, Fe<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>, ZnO–Fe<sub>2</sub>O<sub>3</sub>, CuO–Fe<sub>2</sub>O<sub>3</sub>, ZnO–TiO<sub>2</sub> and CuO–Fe<sub>2</sub>O<sub>3</sub>–Al<sub>2</sub>O<sub>3</sub>, have been researched [1–6] as desulfurization and regenerable sorbents for the direct removal of H<sub>2</sub>S at high temperatures. Among the oxides, some studies have indicated that Fe<sub>2</sub>O<sub>3</sub> has the greatest capacity for sulfur removal per gram of sorbent, followed by CaO and ZnO<sub>2</sub>. It has also been shown that, in gases mainly consisting of carbon monoxide and hydrogen, almost all the Fe<sub>2</sub>O<sub>3</sub> is first converted to metallic iron at 600–900 °C before it reacts with H<sub>2</sub>S, and that the subsequent sulfidation of Fe is the main step. The SFO with active species was considered to be the most suitable sorbent based on the following criteria: good absorption capacity, physical strength and regenerability. Furthermore, the regeneration of the sulfide iron oxide sorbent is particularly attractive in terms of sulfur recovery [4]. It is also shown in our study that a sorbent containing Fe<sub>2</sub>O<sub>3</sub>·FeO (SFO) as the main active species is more

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attractive in terms of both sulfidation and economic considerations. Hot gas desulfurization was carried out in thermogravimetric analysis equipment under isothermal conditions in the range 500–800 °C, using a gas stream with 70 ml/min of N<sub>2</sub> and 2 wt% of H<sub>2</sub>S. Experiences indicate that sulfidation capacity sharply increases with temperature from 500 to 600 °C, and that the sample weight reaches its maximum absorption capacity, almost reaching saturation, above 600 °C.

## 2. Experimental

### 2.1. Materials

#### 2.1.1. Preparation of the SFO

The first step consists in melting F<sub>3</sub>O<sub>4</sub> bars in a furnace at 1600 °C. After that, minor promoters, which will stabilize the iron oxide microstructure at high temperatures (see Section 2.1.3), are added to the melted bars of F<sub>3</sub>O<sub>4</sub>. The homogeneous melted body is cooled. After solidification, the SFO bars are crushed and sieved in the 40–120 μm range. The sieved material is used as sample in the experimental apparatus.

#### 2.1.2. Physical properties of the SFO

Apparent density (g/ml) 2.7–2.9  
 BET surface area (m<sup>2</sup>/g) 16–18  
 Porosity (%) 48–52

Zinc titanate (mixture of Zn<sub>2</sub>TiO<sub>4</sub>+ZnTiO<sub>3</sub>) bought from the Research Triangle Institute (RTI) was used for comparison with the SFO as a sorbent. Zinc titanate was sieved in the 40–90 μm range.

#### 2.1.3. Chemical composition of the SFO

Chemical composition of the SFO is given in Table 1.

### 2.2. Apparatus and operative procedure

The tests were performed on a Setaram TG 85 thermobalance. The main structure of this equipment was described in a previous work [7]. Both the sample weight loss (TG) and the rate of weight loss (D.T.G.) were recorded continuously under isothermal conditions as functions of time. Isothermal runs were performed in both sulfidation and regeneration steps.

Table 1  
 Chemical composition of the SFO

Material	F <sub>3</sub> O <sub>4</sub>	Al <sub>2</sub> O <sub>3</sub>	K <sub>2</sub> O	CaO
wt%	96.2	1.8	1.0	1.0

#### 2.2.1. Sulfidation runs

Firstly, 100 mg of the SFO sample was taken. Then, the heating speed was set at 100 °C/min. A nitrogen flow of 70 ml/min was passed through the sample during the temperature raising step. When the sample had reached the desired temperature, the pure nitrogen stream was replaced by a nitrogen stream containing 2 wt% of H<sub>2</sub>S. The stream flow was also 70 ml/min.

#### 2.2.2. Regeneration runs

Firstly, 100 mg of the sulfidated sample was taken. Then the heating speed was set at 100 °C/min. A nitrogen flow of 70 ml/min was passed through the sample during the temperature raising step. When the sample had reached the desired temperature, the pure nitrogen stream was replaced by a nitrogen stream containing 2 wt% of H<sub>2</sub>S. The stream flow was also 70 ml/min.

#### 2.2.3. Single complete cycle for sulfidation–regeneration

Firstly, the operations described in Section 2.2.1 were repeated. After completion of the sulfidation test, a purge stream consisting of a 70 ml/min nitrogen flow was kept running for 30 min through the sorbent. In the meantime, the desired regeneration temperature was adjusted. The operations described in Section 2.2.2 were then repeated.

## 3. Results

### 3.1. Sulfidation tests

In order to compare the performance of the two sorbents (the SFO and the zinc titanate-based sorbent), sulfidation tests were carried out for 180 min at 600 °C using the same sieving range. Typical sulfidation test results are shown in Figs. 1 and 2 for the SFO and zinc titanate-based sorbents, respectively.

As can be seen in Figs. 1 and 2, a bulk mass increment of 17.2% was reached for SFO at 600 °C after 120 min, when

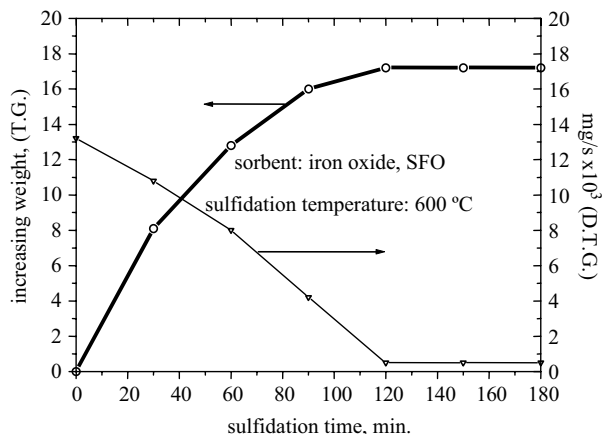


Fig. 1. Mass increment and mass increment rate for SFO sorbent.

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