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# Dry gas cleaning in coal gasification systems for fuel cells using composite sorbents

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**Abstract**

Composite sorbents, for the simultaneous removal of sulfur compounds and alkali and heavy metals from coal gasifier products in an integrated gasification fuel cell (IGFC) system, were prepared. Iron oxide and zinc ferrite were selected as desulfurization sorbents and they were synthesized by precipitation from either ferric chloride, ferric nitride, or ferric and zinc nitride solution. In these solutions, fine oxide particles such as kaolinite, sepiolite, and activated clay, which have the capability of alkali and heavy metal absorption, were dispersed. These oxide particles effectively increased the surface area of synthesized iron oxide and zinc ferrite composite particles. In addition, they are expected to avoid the sintering or coking of the sorbents in the desulfurization and regeneration processes. Desulfurization tests were performed in a tube furnace by streaming a model gas containing $H_2S$. The desulfurization performance improved considerably in the case of composite sorbents with a high specific surface area. The desulfurization capacity and crystalline phases before and after desulfurization depended on the type of the oxide particle. The desulfurization rate of a composite sorbent was characterized accurately by the specific surface area.

*Keywords:* Composite sorbent; Desulfurization; Iron oxide; Gel–sol method; Alkali and heavy metal; Integrated gasification fuel cell (IGFC)

## 1. Introduction

Hot gas cleanup is a key technology in an integrated gasification fuel cell (IGFC) system. Fuel gas products from a gasifier contain many contaminants such as sulfur compounds ($H_2S$ and COS) and alkali and heavy metal compounds, which must be removed in order to prevent the corrosion of fuel cell electrodes before synthesized gas is introduced into the fuel cell units. Thus far, wet gas purification processes have been applied in IGFC systems and pilot testing facilities, such as those at the 150 t/d EAGLE Plant in Wakamatsu, Japan [1], were developed. In wet processes, heat loss by water condensation is considerably larger than that in dry processes; in addition, wet processes require plants for waste liquid treatment. When wet processes are used, considerable energy loss results; therefore, the efficiency of the entire system is not sufficiently high as expected. Moreover, because COS cannot be removed directly by wet processes, a COS converter is required to convert COS to $H_2S$.

The focus of the present study is on the dry desulfurization process and the synthesis of new absorbents that can simultaneously remove sulfur compounds, and alkali and heavy metals. So far, calcium, iron, zinc, and copper compounds have been used as major desulfurization sorbents in coal gasification [2]. Because the optimum temperature for desulfurization by iron oxide is lower than that in the case of calcium oxide [3,4], iron oxide type compounds are the most popular sorbents in Japan [5]. Furthermore, the operating temperature for desulfurization is set at 673–773 K from the perspective of using economical materials for reactors and pipelines. Zinc ferrite exhibits a higher desulfurization performance sufficient for reducing the $H_2S$ concentration to the order of 1 ppm in a similar temperature region [6]. In the iron system,

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Table 1
Sorbent preparation conditions

| Sample | Solution A | | | Solution B | |
|---|---|---|---|---|---|
| 1 | 2.0 M $FeCl_3$, 100 ml | | | 6 M NaOH, 100 ml | – |
| 2 | | | | | Kaolinite, 5 g |
| 3 | | | | 12 M NaOH, 100 ml | |
| 4 | 1.5 M $Fe(NO_3)_3$, 100 ml | | | 4.5 M $NH_3$, 100 ml | – |
| 5 | | | | | Kaolinite, 5 g |
| 6 | 1.5 M $Fe(NO_3)_3$, 100 ml | | – | 4.5 M $NH_3$, 100 ml | |
| 7 | | | Sepiolite, 4 g | | |
| 8 | | | Activated clay, 4 g | | |
| 9 | 1.5 M $Fe(NO_3)_3$, 70 ml | 1.5 M $Zn(NO_3)_2$, 35 ml | – | | |
| 10 | | | Sepiolite, 4 g | | |
| 11 | | | Activated clay, 4 g | | |

however, iron carbide is also produced in coal gasification conditions; this causes coking and sintering problems. To avoid these problems, Shirai et al. [7] developed composite sorbents by mixing iron oxide and zinc ferrite particles with ultra-fine silica particles, and they achieved a high desulfurization performance without coking and decomposition of zinc ferrite to ferrite and zinc oxide. The selection of the reaction temperature is also required to avoid the formation of byproducts consisting of iron and silicon compounds, such as $Fe_2SiO_4$ [8]. The dilution of iron oxide or zinc ferrite with an inert third material powder is considered to be advantageous in order to avoid sintering and coking. If such a dilutant has the capability to absorb alkali and heavy metals, which also need to be removed, such composite sorbents are expected to have both desulfurization and metal absorption capacity. The material candidates focused in the present research, which have the capability of alkali and heavy metal absorption, are kaolinite [9–11], sepiolite, and activated clay.

In our series of research, two methods to fabricate composite particles having the capability of both sulfur and metal absorption have been attempted—a dry physical/mechanical method and a wet liquid phase process. In the dry mechanical method, desulfurization sorbent particles and metal absorption particles were mixed using an ellipsoidal type mixer and core metal absorbers were successfully covered with iron oxide or zinc ferrite layers. The composite particles thus obtained have sufficient ability to absorb alkali metal [12]; however, the composition of the desulfurizer component in the composite sorbent was not sufficiently high to expect a high desulfurization performance.

The objective of the present research is the synthesis of such composite sorbents by a wet liquid phase process. Alkali and heavy metal absorbers such as kaolinite, sepiolite, and activated clay were added into the reactant solution. To prepare the iron oxide, a precipitation and long term ripening process–so-called gel–sol process [13]–was chosen. Zinc ferrite and iron oxide were synthesized by coprecipitation and calcinations [7], instead of long term ripening. The synthesized sorbents were tested for their desulfurization performance by investigating $H_2S$ removal from a model gas. In the present study, the target $H_2S$ concentration after desulfurization is set to 20 ppm. It is intended to reduce excess $H_2S$ to the order of 1 ppm, which is an acceptable level for fuel cell units, utilizing additional precise desulfurization units.

## 2. Experimental

### 2.1. Sorbent synthesis and characterization

Sorbents were synthesized by two different patterns, and in this study, they are termed as Pattern 1 and Pattern 2. Table 1 summarizes the composition of the starting solution. Samples 1 to 5 in Table 1 were prepared by Pattern 1 and Samples 6 to 11 were prepared by Pattern 2.

In Pattern 1, solution A was stirred at 500 rpm with an impeller and solution B was added into it over 5 min at room temperature. After addition, the solution was stirred at 800 rpm for 10 min and ripened for 10 days at 100 °C in a capped bottle. The resulting slurry was then cooled from the outside of the bottle by running water at atmospheric pressure; and it was then washed by distilled water and separated from the solution by centrifuging. Washing and centrifugal separation were repeated thrice and the purified slurry was dried at 80 °C for 24 h to obtain the final powdery products.

In Pattern 2, solution A was stirred at 500 rpm at 313 K and solution B was added into it over 5 min and stirred at 500 rpm for 1 h. The obtained slurry was washed and centrifugally separated twice and dried at 100 °C for 24 h. The resulting powder was calcined at 800 °C for 5 h in air.

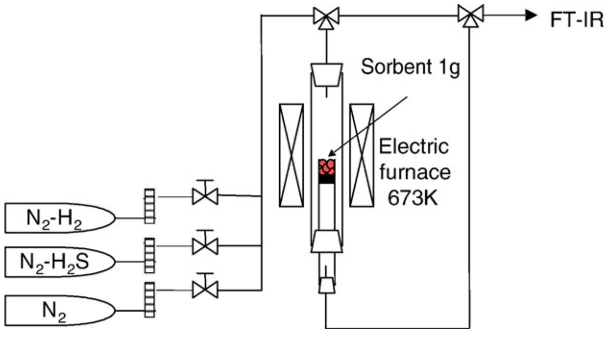

Fig. 1. Apparatus for desulfurization testing.