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# VALORIZATION OF INORGANIC SOLID WASTES FROM INDUSTRIAL ACTIVITIES INTO ACTIVE MATERIALS FOR REMOVAL OF HYDROGEN SULFIDE IN GAS PHASE

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## ABSTRACT

Hydrogen sulfide ( $H_2S$ ), which was formed from both natural and anthropogenic processes, is one of the most toxic contaminants affecting machine, people health, and ecosystem. Activated carbon and its derivatives (with metal oxides) are conventionally for  $H_2S$  removal. However, they are expensive. Besides, the worldwide production of soda ash bases mostly on the Solvay Process<sup>®</sup> (59% in 2000), which generates a large amounts of inorganic solid wastes with the main composition of  $CaCO_3$ . This study aims to investigate the use of this calcified solid wastes from the Solvay Process<sup>®</sup> for removal of  $H_2S$  in gas phase in order to limit the environmental impacts and enhance the economic benefits. The solid wastes, after some pretreatments, were tested for the removal of  $H_2S$  in a glass fixed-bed reactor at ambient condition. Different parameters such as the influence of the calcination, contact time, iron-doping were investigated. Physico-chemical characterizations by TG-DSC, SEM-EDX were applied. Results showed that these solid wastes are promising for  $H_2S$  treatment. The presence of inorganic impurities played an important role. The pretreatment by calcination and modification by iron-doping strongly improved the reactivity of the initial sorbents. The sorption of  $H_2S$  on calcified sorbent was partially reversible.

**Keywords:** hydrogen sulfide, solid wastes, sorbent, reactivity, iron impregnation, Solvay Process<sup>®</sup>

## 1. INTRODUCTION

With the increasing reliance on coal-fired power plants, air pollution is quickly increasing in Vietnam. Many countries in a similar economic development situation have experienced acid rains, which is a known threat to soils, water, vegetation, aquatic ecosystems, and historical buildings and monuments [1]. The majority of acid rains usually result from the pollution by sulfur compounds, due to sulfur's high-water solubility [2]. This is why every year in the world, billions of dollars are spend in desulfurization technology.

$H_2S$  is also known as momosulfide which is colorless, heavier than air, and has a characteristic rotten-egg odor. It dissolves in water forming a weak acid solution.  $H_2S$  is a strong reducing agent, easily reacts with numerous oxidizing agents to form sulfur compounds with varying degrees of oxidation in normal conditions. Therefore, it causes metal corrosion, seriously affecting the mechanical equipment. Moreover,  $H_2S$  is a toxic gas to human health. When people are directly

exposed at low concentrations (3-5 ppm) it causes unpleasantness by dint of its strong odor and can accumulate in our body and leads to some diseases later; at higher concentrations (10-300ppm) it is responsible for loss of smell and exposure over 4 hours is considered dangerous; higher concentrations (> 300ppm) results in serious respiratory trouble and death [3].

There are a variety of methods for removal of hydrogen sulfide. They include: biological, absorption, adsorption, catalytic oxidation, scrubbing, scavenger, membrane separation. A chosen method is based on the end-use of the gas, the gas composition, and the amount of gas needing to be treated. Activated carbon and its modifications by metal oxides are the best sorbents for the treatment of H<sub>2</sub>S [4], but their costs are high.

This study aims to investigate the use of solid inorganic co-products from Solvay Process<sup>®</sup>, which produces sodium carbonate and sodium bicarbonate from brine and limestone [5], for the treatment of H<sub>2</sub>S in gas phase. Those solid co-products, rich in calcium carbonate, are generated at high quantities which may be valorized into useful materials instead of its simple disposal. So the gain is double: the valorization of a co-product (solid waste) for the abatement of a gaseous pollutant. The removal of H<sub>2</sub>S is carried out by adsorption process.

## 2. MATERIALS AND METHODS

### 2.1. Materials

A mixture of the solid wastes named as CaCO<sub>3</sub>-S, which has composition of CaCO<sub>3</sub> (98%) and other inorganic impurities such as: magnesium, potassium, iron, aluminium,...from Soda company was used in this study. After a thermal pre-treatment at temperature from ambient to 850<sup>o</sup>C, It was used as a H<sub>2</sub>S sorbents at ambient condition. Iron impregnation was also applied to improve the reactivity of the sorbents. Pure Calcite CaCO<sub>3</sub> from (Fisher Scientific) and activated carbon (L3S, CECA) were used as references.

### 2.2 Methods

#### 2.2.1 H<sub>2</sub>S sorption test

The dynamic tests were carried out at ambient temperature (20<sup>o</sup>C). The sorbent was packed into a glass laboratory-designed fixed-bed reactor (length 60 mm, internal diameter 11 mm). The bed volume (or the media volume) varied in a range of 1.5 to 3.2 cm<sup>3</sup> (depending on the amount of sorbent used, 0.5g or 1.0 g, and the density of the studied sorbents). A synthetic waste gas, basing on dried air and containing 50ppm of H<sub>2</sub>S passed through the reactor with a flow rate of 50 mL/min and was controlled by a flow meter. The output H<sub>2</sub>S concentration was monitored using an analyser named BW Gas Alert QUATTRO with a recording period of 5 seconds. The amount of input H<sub>2</sub>S and the accumulated H<sub>2</sub>S on the sorbents in milligram (mH<sub>2</sub>S, mg) was calculated from the data of the analyser with Eqs. (1) and (2), respectively:

$$m_{\text{Input}} = \frac{P \cdot Q \cdot M}{10^6 \cdot R \cdot T} c_0 t_s \quad (1)$$

$$m_{\text{Accumulated}} = \frac{P \cdot Q \cdot M}{10^6 \cdot R \cdot T} (c_0 t_s - \int_0^{t_s} c(t) dt) \quad (2)$$

Where: P is the atmospheric pressure (P=1 atm); Q is the inlet flow rate (Q=50 mL/min); T is the temperature (T=293 K); M is the molecular weight of H<sub>2</sub>S (M= 34 g/mol); R is the universal gas constant (R=8.3145 J/mol.K) c<sub>0</sub> and c(t) are the input and output concentrations of H<sub>2</sub>S (ppm); t<sub>s</sub> the reaction time (min).

The term “zero time or t<sub>100%</sub>”, is also defined as the duration of the complete removal of H<sub>2</sub>S from the gas phase by a sorbent.

2.2.2. Physico-chemical analysis and characterizations

Thermogravimetry (TG) was performed in a SDTQ600 analyzer (TA Instruments) with a heating rate of 5°C/min under air flux (100 mL/min). Scanning electron microscopy (SEM) was carried out on a Philips XL30 ESEM apparatus (FEI Company) which was coupled with an energy-dispersive X-ray spectroscopy (EDX analysis).

3. RESULTS AND DISCUSSION

3.1. Determine the suitable temperature for the wastes pre-treatment

With expecting to improve the reactivity of the solid wastes, iron impregnation was applied. After impregnating the support (CaCO<sub>3</sub>-S or pure calcite) with an aqueous solution of Fe(NO<sub>3</sub>)<sub>3</sub>, the mixture was dried at room temperature. The dried solids were then analysed by TG in order to determinate the temperature for complete decomposition of iron precursor to form iron oxide.

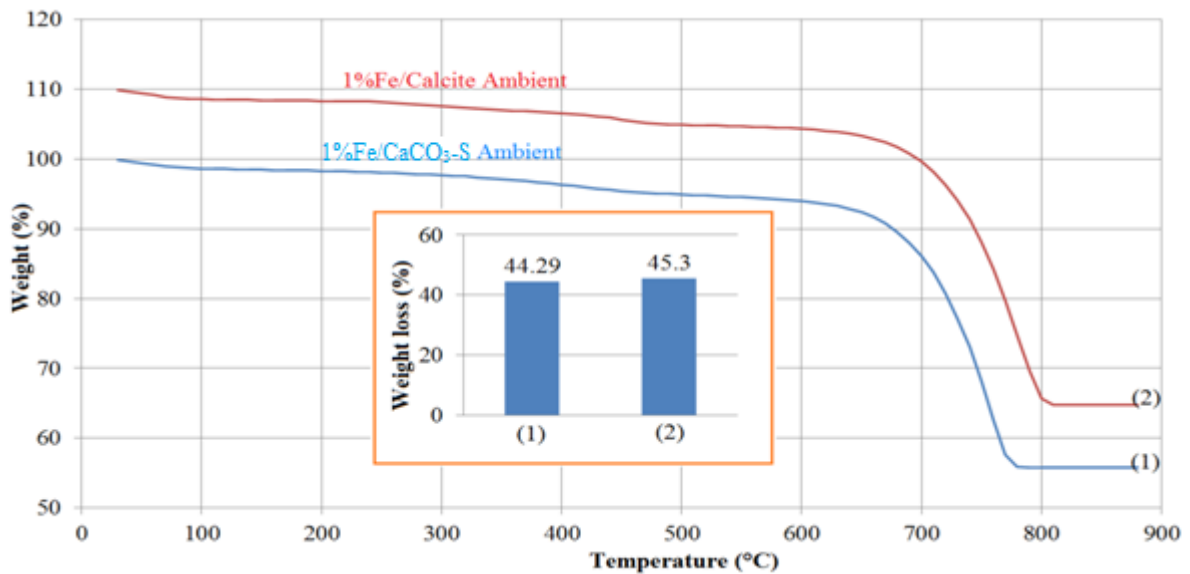


Figure 1. TG curves of CaCO<sub>3</sub>-S and pure calcite impregnated with Fe(NO<sub>3</sub>)<sub>3</sub> and dried at room temperature

From the results in Figure 1, we can see that Fe(NO<sub>3</sub>)<sub>3</sub> decomposed totally at 500°C. So this temperature was chosen for converting iron precursor to iron oxides. It was confirmed by previous study [6]

3.2. Using solid waste as a H<sub>2</sub>S promising sorbent

As can be seen in Figure 2, CaCO<sub>3</sub>-S with 1 wt.% of iron (1%Fe/CaCO<sub>3</sub>-S) calcined at 500°C and activated carbon (L3S from CECA, France) had a similar reactivity with *t*<sub>100%</sub> of about 70 min when 0.5g of sorbents were used.

The addition of 1 wt.% of iron on CaCO<sub>3</sub>-S resulted to increasing *t*<sub>100%</sub> from about 40 min to 150 min when 1 g of sorbent was used (Figure 2). As expected, *t*<sub>100%</sub> decreased when the quantity of the sorbent decreased. Using the same iron-doped CaCO<sub>3</sub>-S, *t*<sub>100%</sub> reached only about 70 min for 0.5 g of sorbent, compared with 150 min for 1 g of sorbent.

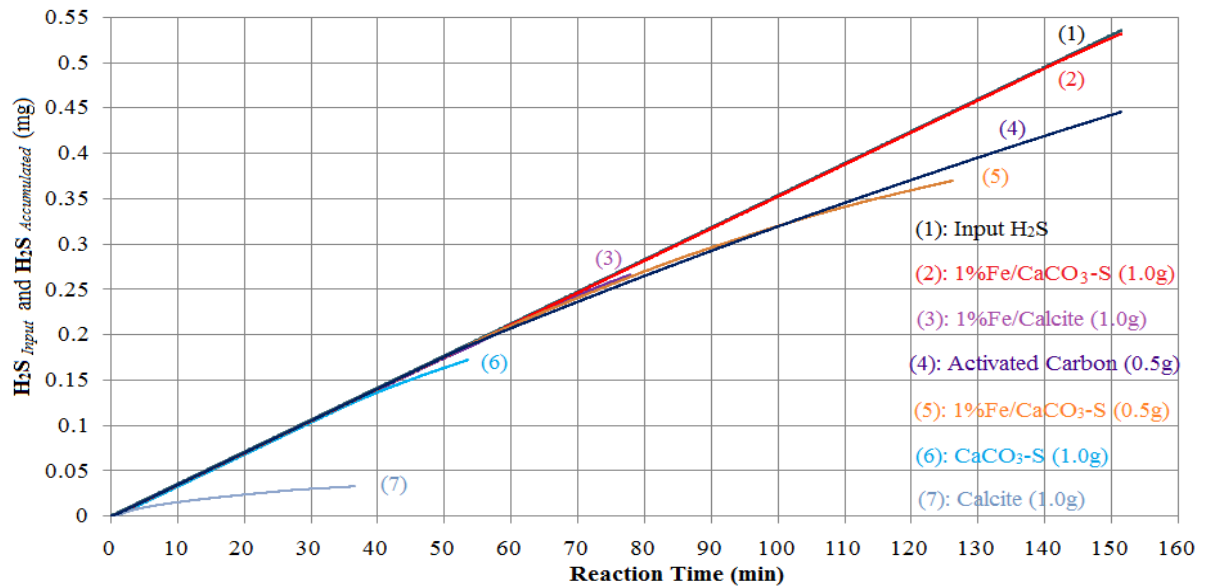


Figure 2. Reactivity of initial CaCO<sub>3</sub>-S, commercial calcite, iron-doped CaCO<sub>3</sub>-S, iron-doped calcite and activated carbon L3S CECA. 50 ppmv of H<sub>2</sub>S in dried air, 50 mL/min, 0.5 ou 1.0 g of sorbent, room T and P.

In general, CaCO<sub>3</sub>-S had better reactivity than commercial calcite. This was also true when iron impregnation was applied. The initial calcified matrix played also important role for the dispersion of iron particles, and therefore for the reactivity of the sorbents doped with iron. Containing the same iron content, iron-doped CaCO<sub>3</sub>-S was found to be more active than iron-doped commercial calcite, with  $t_{100\%}$  of 150 min and 70 min, respectively (Figure 2). This can be explained by SEM results (Figure 3). Smaller iron particles could be observed on CaCO<sub>3</sub>-S than on commercial calcite. And there were fewer agglomerations in CaCO<sub>3</sub>-S than in commercial calcite. In the other words, there were more iron atoms on the surface of CaCO<sub>3</sub>-S than on the surface of commercial calcite. Metallic surface atoms are responsible for the fixation of H<sub>2</sub>S in gas phase.

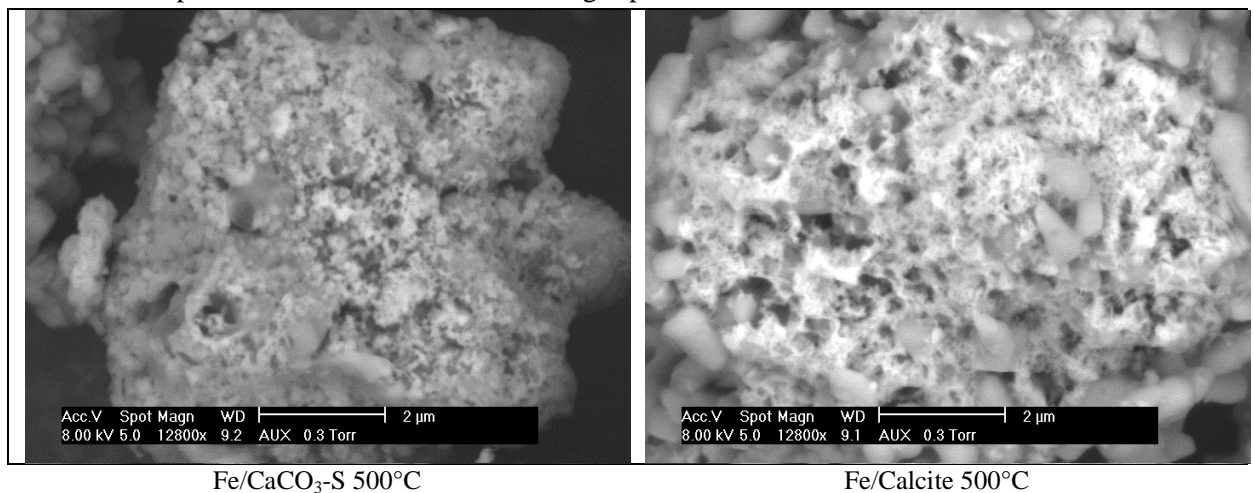


Figure 3. SEM images of Fe/CaCO<sub>3</sub>-S 500°C and Fe/Calcite 500°C.

### 3.3. Recycling test

The recycling test was carried out with the iron-doped CaCO<sub>3</sub>-S (Figure 4). After the first test with 1 g of the sorbent, the solid was recovered and calcined at 500°C before using for the first

recycling (second test). This procedure was repeated for the second recycling. The results shown that there was a strong loss of reactivity at the second test.  $t_{100\%}$  decreased from 150 min to 45min for the second use, and to 25 min for the third use. Probably,  $H_2S$  forms strong chemical bonds with metallic active sites present in the initial  $CaCO_3$ -S sorbent. These bonds are not reversible in the regeneration conditions applied (calcination at  $500^\circ C$ ).

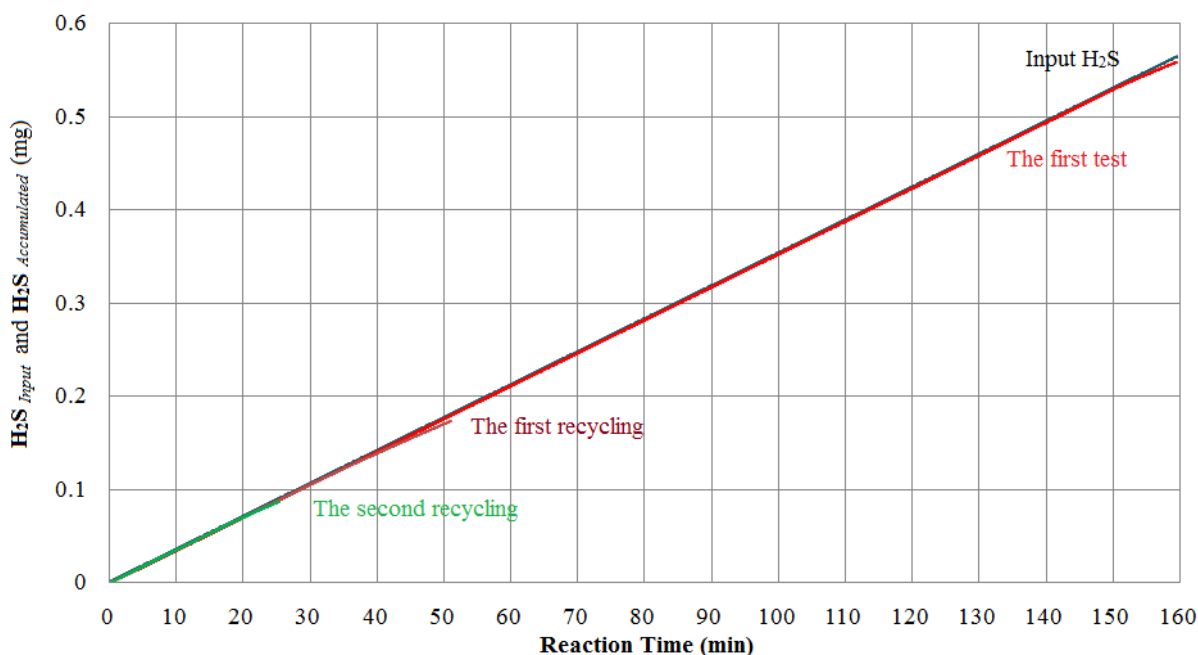


Figure 4. Regeneration capacity of the iron-doped  $CaCO_3$ -S, pre-treated at  $500^\circ C$ . 50 ppmv of  $H_2S$  in dried air, 50 mL/min, 1.0 g of sorbent, room T and P.

#### 4. CONCLUSIONS

Sorbents based on the solid wastes generated from Solvay process® were prepared and investigated in the removal of  $H_2S$  from a synthetic gas effluent. The solids wastes were more active than pure calcium carbonate (calcite). It was probably due to the presence of different metals in the solid wastes. The reactivity of the solid wastes could be improved by simple calcination, and  $500^\circ C$  was found as the best calcination temperature.

Adding a small amount (1 wt.%) of iron to the  $CaCO_3$ -S solid waste improved strongly the reactivity of this material. The reactivity of this iron-doped  $CaCO_3$ -S was similar to that of a commercial activated carbon L3S from CECA, France .

The fixation of  $H_2S$  was partially reversible. The thermal treatment by calcination under air allowed recovering only partially the reactivity of these sorbents.

Nevertheless, these results were very promising by dint of the solid wastes of Solvay Process® are very available, which could be used as useful materials for the treatment of another pertinent waste.

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