Valorization of Calcium Carbonate-Based Solid Wastes for the Treatment of Hydrogen Sulfide from the Gas Phase

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Valorization of calcium carbonate-based solid wastes for the treatment of hydrogen sulfide from gas phase

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KEYWORDS: Solvay process®, solid waste, calcium carbonate, H_2S removal, regeneration

ABSTRACT:

This paper focuses on the valorization of calcium carbonate-based solid wastes for the removal of hydrogen sulfide from gas phase. Two solid wastes taken from industrial sites for the production of sodium carbonate and sodium bicarbonate by the Solvay process® were analyzed by different physico-chemical methods. Calcium carbonate was found as the main component of both the solid wastes. Trace amounts of other elements such as Mg, Al, Fe, Si, Cl, Na etc. were

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also present in these wastes. These solid wastes showed higher sorption activity for the removal of H_2S, compared to a pure commercial calcium carbonate. The contact time was found as an important parameter for the complete H_2S uptake. The addition of well-dispersed iron-based particles could be carried out by the standard incipient wetness impregnation method. Sorbent containing 1 wt.% of spiked iron had the similar sorption behavior compared to a commercial activated carbon, in terms of reactivity and reactivation possibility.

1. Introduction

Sodium bicarbonate ($NaHCO_3$) and sodium carbonate (Na_2CO_3) are widely used in different applications.[1] They can be used as melting agent in glass and metallurgy industries. They can be used as alkaline reactant in different processes, for the neutralization of acid gas, or for the synthesis of sodium salts such as sodium phosphates, sodium nitrate, sodium chromate, sodium citrate. Other fields of application of sodium carbonate and sodium bicarbonate may be listed as follows: detergence, steel industry, pharmaceutical, paper mill, water softening, food industry, and many others. Discovered and developed by Ernest Solvay during the 1860s, the Solvay process® became the main process for the fabrication of sodium carbonate and sodium bicarbonate from limestone ($CaCO_3$) and salt brine ($NaCl$) as the starting materials.[2] This process can be summarized by the following steps:[1]

- Step 1: Preparation of a saturated aqueous solution of $NaCl$ (brine).

- Step 2: Saturation of this brine with NH_3 to form an ammoniated brine (H_2O, $NaCl$ and $NH_{3(aq)}$).

- Step 3: Calcination of limestone :

$$CaCO_3 \rightarrow CaO + CO_2 \qquad\qquad (1)$$

- Step 4: Preparation of lime milk :

$$CaO + H_2O \rightarrow Ca(OH)_2 \qquad (2)$$

- Step 5: Carbonation of the ammoniated brine with CO_2 recovered from Step 3. Ammonium bicarbonate is formed (Eq. 3), followed by the double decomposition of sodium chloride and ammonium bicarbonate to form sodium bicarbonate (Eq. 4)

$$NH_{3(aq)} + H_2O + CO_2 \rightarrow NH_4HCO_3 \qquad (3)$$

$$NH_4HCO_3 + NaCl \rightarrow NH_4Cl + NaHCO_3 \qquad (4)$$

- Step 6: Sodium bicarbonate, which is less soluble, is filtered from the solution.

- Step 7: Thermal decomposition of sodium bicarbonate to form sodium carbonate at about 150-200°C:

$$2NaHCO_3 \rightarrow CO_2 + Na_2CO_3 + H_2O \qquad (5)$$

- Step 8: Regeneration of NH_3 from lime milk (Step 4) and NH_4Cl (Step 5):

$$2NH_4Cl + Ca(OH)_2 \rightarrow 2\ NH_4OH + CaCl_2 \qquad (6)$$

The global equation of this process is the following:

$$2NaCl + CaCO_3 \rightarrow Na_2CO_3 + CaCl_2 \qquad (7)$$

The key step of this process is the carbonation of the ammoniated brine and the crystallization of $NaHCO_3$, where the yield reaches generally about 70-75% for the transformation from NaCl to $NaHCO_3$. The liquid phase (filtrate) generated from Step 6 contains large amounts of NH_4HCO_3, $(NH_4)_2CO_3$, $NaHCO_3$, NH_4Cl and NaCl, which are soluble in water.[3] Thus, during the generation of NH_3 using lime milk (Step 8), a precipitate which contains mainly calcium carbonate (called hereafter PCC) is formed. Taking into account the annual production of sodium carbonate and sodium bicarbonate by the Solvay process® of about 55 millions of tons worldwide (in 2011),[4] large quantities of PCC are generated annually. Up-to-date, PCC is considered as a by-product and is directly discharged around the production site

or to the sea. However, environmental preservation and production appear as one of the most important challenge of the XXI century. As indicated by the waste management hierarchy,[5] the most favored option for waste management is its prevention, followed by its minimization, its reuse, its recycling, its energy recovery and its disposal.

This work aims to investigate the reuse of two PCC generated by two different sites of Solvay process® for the development of new and low cost sorbents for the treatment of hydrogen sulfide in the gas phase. As we can see later, PCC contains mainly calcium carbonate, but also significant contents of metals such as iron, magnesium, sodium etc. Calcium carbonate, with its basicity, and with the presence of various metals may be favorable for the fixation of hydrogen sulfide (H_2S).[6-8] H_2S is formed as gas pollutant in different processes such as coal combustion, petrochemical processing, fermentation of biomass or gasification of coal/biomass for generating syngas etc.[9-11] The efficient removal of H_2S usually appears as the crucial step for a given process. For example, syngas produced from gasification of biomass has to be purified and the total amounts of H_2S and COS must be less than 20, 20, 1 and 0.01 mg Nm^{-3} for engine, turbine, methanol synthesis and Fisher-Tropsch synthesis applications, respectively.[12-13]

2. Materials and methods

2.1. Chemical and physico-chemical analyses

Different chemical and physico-chemical techniques were used for analyzing sorbents before test of H_2S removal. Thermogravimetry (TG) was performed with a SDTQ600 analyzer (TA Instruments) at a heating rate of 5°C/min under air flux (100 mL/min). X-ray diffraction (XRD) data of the solids were collected using a Phillips Panalytical X'pert Pro MPD diffractometer with a Cu Kα (1.543 Å) radiation source. 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). Specific surface area was determined by BET method, using a

MICROMERITICS Gemini Vacprep 061). X-ray fluorescence (XRF) was carried out with a

PANanalytical (Epsilon E3 XL). Inductively coupled plasma atomic emission spectroscopy

(ICP-AES) using a HORIBA Jobin–Yvon Ultima 2. The pH_{pzc} was determined according to

Pham Minh et al.[14] Calcination experiments as pretreatment of sorbents were done in a static

muffle-furnace (Nabertherm P320). For each calcination, about 5 g of solid was introduced in a

ceramic open dish. This last one was then placed in the furnace. The furnace was heated by

means of 20°C min^{-1} up to the desired temperature (105 to 850°C), and was kept at this final

temperature for 2 h. Then, the furnace was freely cooled down to room temperature. The

calcined solid was immediately used for all further characterization and tests.

2.2. Sorbents

Two PCC sources were used in this study. The first one was sampled from the Solvay

factory at Dombasle-sur-Meurthe (France), which is designated thereafter *PCC-F*. The second

one was taken from the Solvay factory at Torrelavega (Spain), which is called thereafter *PCC-S*.

Both PCC were in fine powder form. They were firstly dried at room temperature (ca. 20°C) up

to constant weight. Then, they were sieved to eliminate particles bigger than 315 µm. In fact, the

fraction of particles larger than 315 µm represented only less than 1 wt.% of both PCC. The

fraction of particles smaller than 315 µm was thermally treated by calcination at 105-850 °C

before sorption test.

Pure calcite powder ($CaCO_3$, > 98 wt.%) from Fisher Scientific, and commercial activated

carbon (L3S from CECA, France, 900 m^2 g^{-1}) in powder form were used as the reference

sorbents. They are designated thereafter "Calcite" and "AC" for pure calcite and activated

carbon, respectively. This pure calcite was also treated by calcination at 105-850°C before

sorption test in order to compare with calcined PCC-F and PCC-S. AC was used as received, without further pretreatment.

2.3. Sorption test

The tests of H_2S removal were carried out at room temperature (ca. 20°C) and ambient pressure using a glass fixed-bed reactor. Figure 1 shows the scheme of the reactor used. This reactor (length 60 mm, internal diameter 11 mm) was equipped with a porous glass disc which allowed keeping the sorbent bed, and the passage of gas through the sorbent bed. The volume of sorbent bed varied from about 1.5 to 3.2 cm^3, corresponding to the apparent density and the amount of sorbent used for each experiment (0.5 to 1.0 g). A synthetic waste gas, based on dried air and containing 50 ppmv of H_2S passed through the sorbent bed with a flow rate of 50 mL min^{-1} and was controlled by a flow meter. The output H_2S concentration was monitored every 5 seconds using a gas analyser from BW Technologies (Gas Alert QUATTRO). Sorption experiments were stopped when the sorbent was saturated or when the rate of H_2S sorption slowed down.
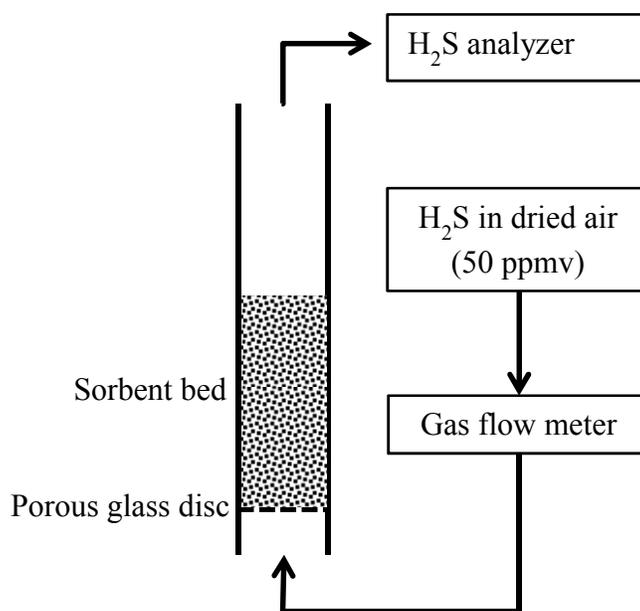

Figure 1. Scheme of the reactor used in this work.

In this paper, the following terms are used in order to compare different sorbents and different experimental conditions:

- H_2S_{Input} (mg): the total accumulated quantity of H_2S injected to the reactor at a given reaction time.

- $Accumulated_{Sorbent}$ (mg): the total accumulated quantity of H_2S fixed on the sorbent at a given reaction time.

- $t_{100\%}$ (min): the reaction time wherein the removal of H_2S was total. So, theoretically H_2S_{Input} is equal to $Accumulated_{Sorbent}$ within $t_{100\%}$.

The amount of H_2S_{Input} and $Accumulated_{Sorbent}$ was calculated with the Eqs. (8) and (9), respectively:

$$H_2S_{Input} = \frac{PQM}{10^6 RT} C_{int} t \qquad (8)$$

$$Accumulated_{Sorbent} = \frac{PQM}{10^6 RT}\left[C_{int} t - \int_0^t C_{out} dt \right] \qquad (9)$$

where Q: inlet flow rate (L min^{-1}), M: the molecular weight of H_2S (34.06 g mol^{-1}), W: mass of sorbent used (g), C_{in}: inlet concentration of H_2S (50 ppmv), C_{out}: outlet concentration of H_2S (ppmv), t: reaction time (min).

3. Results and discussion

3.1. Analysis and characterisation of the sorbents before test

a. Elemental analysis of the initial PCC

Elemental analysis of the initial PCC was carried out by XRF and ICP-AES techniques. Table 1 shows the main elements of both initial PCC-F and PCC-S. Calcium carbonate was found as the main compound of both solid wastes. Other elements were also present, including different metals, sulphur and chlorine. The content of organic compounds was negligible.

Table 1. Elemental analyses of both FCC-F and FCC-S dried at room temperature.

Compounds	$CaCO_3$	Mg	Al	Si	Fe	S	Cl	Na	Others*
FCC-F, wt.%	98	0.6	0.2	0.5	0.5	0.2	0.1	0.4	0.5
FCC-S, wt.%	97	0.7	0.2	0.6	0.3	0.6	0.5	Trace	0.3

(* P, Cu, Mn, Zn, Sn)

b. Thermogravimetric analysis

Figure 2 shows TG curves of different FCC-F solids, which were previously calcined at different temperatures. Small weight losses between 350 and 580 °C were observed for the solids pretreated at 20, 105 and 200 °C. The main weight loss starting at 580-780 °C was due to the decarbonation of calcium carbonate. This weight loss represent 42.8-43.7 wt.% for the solids pretreated at 20-580°C, which means that FCC-F contains mainly calcium carbonate (theoretical weight loss of pure calcium carbonate being 44 wt.%). This confirms again the results of elemental analyses. The calcination at 700 °C for 2 h in a static furnace did not allow the complete decarbonation of calcium carbonate because the weight loss at 580-780 °C of this solid reached again 35.3 wt.% on second thermal treatment in TG analyzer. On the other hand, for the

solid preatreated at 850 °C, the decarbonation was complete after 2 h. Previous studies showed

that the kinetic of calcite calcination depends on the particle size and the atmosphere of

calcination.[15] These results were also found for FCC-S and commercial pure calcite, pretreated

at different temperatures (results not shown here).

Because of the thermal decomposition of calcium carbonate, starting above 580 °C, we

studied only the sorption activity of the sorbents which were thermally treated at 580 °C and
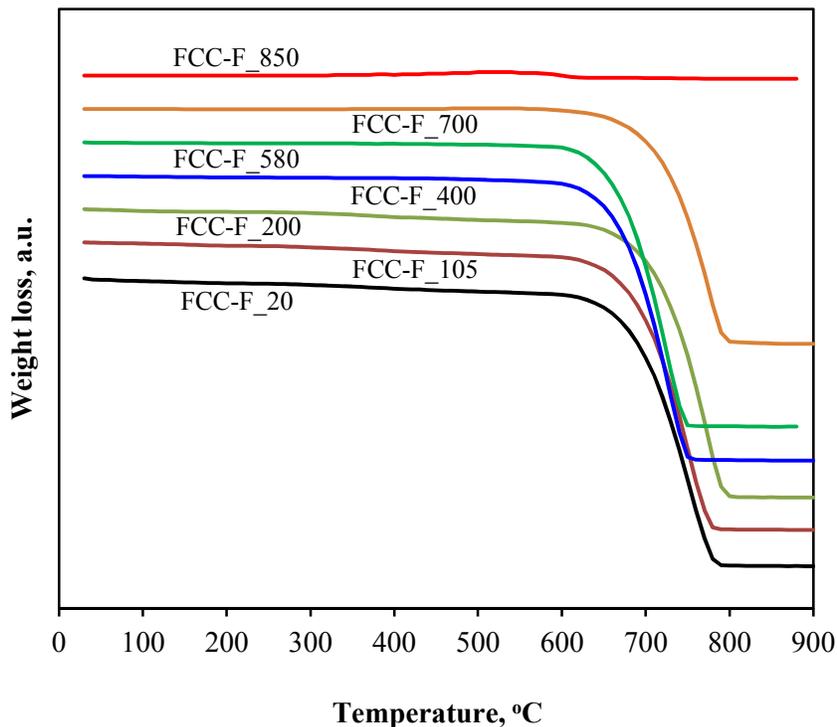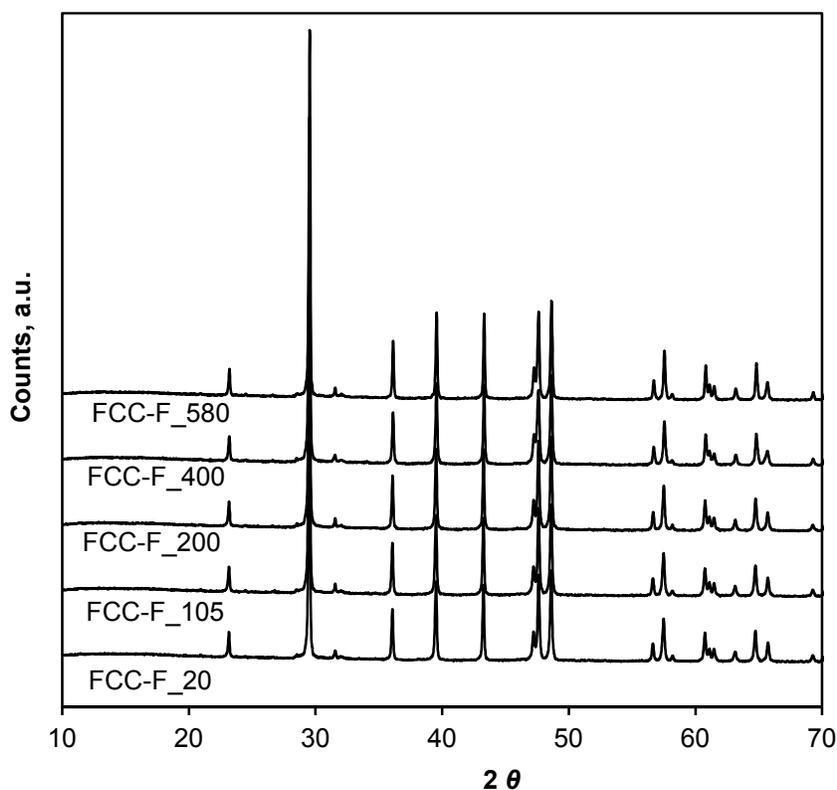
below.

Figure 2. TG curves of the FCC-F after thermal treatment at different temperatures.

c. XRD and specific surface area

Figure 3 shows XRD results of FCC-F after thermal treatment at different temperatures.

All diffraction peaks could be attributed to calcite, which was found as the only main crystalline

phase of this solid waste. The solid powder dried at ambient condition was already highly crystalline. Thus, the calcination step up to 580 °C did not significantly modify its crystallinity. These results confirmed TG analyses above. And the similar results were obtained with FCC-S and commercial pure calcite (results not shown).

All three initial calcite based sorbents (FCC-F, FCC-S, pure calcite) had the specific surface area lower than 3 $m^2\ g^{-1}$.

Figure 3. XRD patterns of the FCC-F after thermal treatment at different temperatures.

3.2. Sorption activity of the sorbents

The reactivity of the different sorbents was investigated at ambient condition. Figures 4-6 show the results obtained with FCC-F, FCC-S and pure calcite based sorbents, respectively. For each figure, the *Input* curve represents the accumulated quantity of H_2S introduced into the

reactor. Other curves represent the accumulated quantity of H_2S, which was fixed by the

sorbents.

Figure 4. Quantity of the accumulated H_2S fed into the reactor (*Input* curve) and remaining after

passing over FCC-F based sorbents. The sorbent were pre-treated by calcination at different

temperatures. Sorption conditions: 50 ppmv of H_2S in dried air, 50 mL min^{-1}, 0.5 g of sorbent,

room temperature and pressure.

For FCC-F based sorbents, the sorption performance increased with the calcination

temperature up to 400 °C (Figure 4). The sorbents calcined at 400 and 580 °C had the similar

reactivity. Thermal treatment is known as an efficient treatment for desorbing molecules

adsorbed on the surface of a given solid, as well as for the combustion of eventual organic

molecules present in the initial sorbents. Thus, calcined solid with clean surface is more

appropriate for the fixation of H_2S. In addition, the thermal treatment allows transforming

carbonates of metals such as iron, sodium, magnesium etc. which were present in this solid waste, into the corresponding metal oxides. These last ones may have higher affinity for H_2S fixation.

When the calcination temperature rose to 580 °C, no further physico-chemical transformation took place, compared to 400 °C, as indicated by TG analysis (Figure 2). This may explain the similar reactivity of the two sorbents calcined at 400 and 580 °C. Taking into account the energy consumed for the calcination step, the pre-treatment at 400 °C was the most efficient.
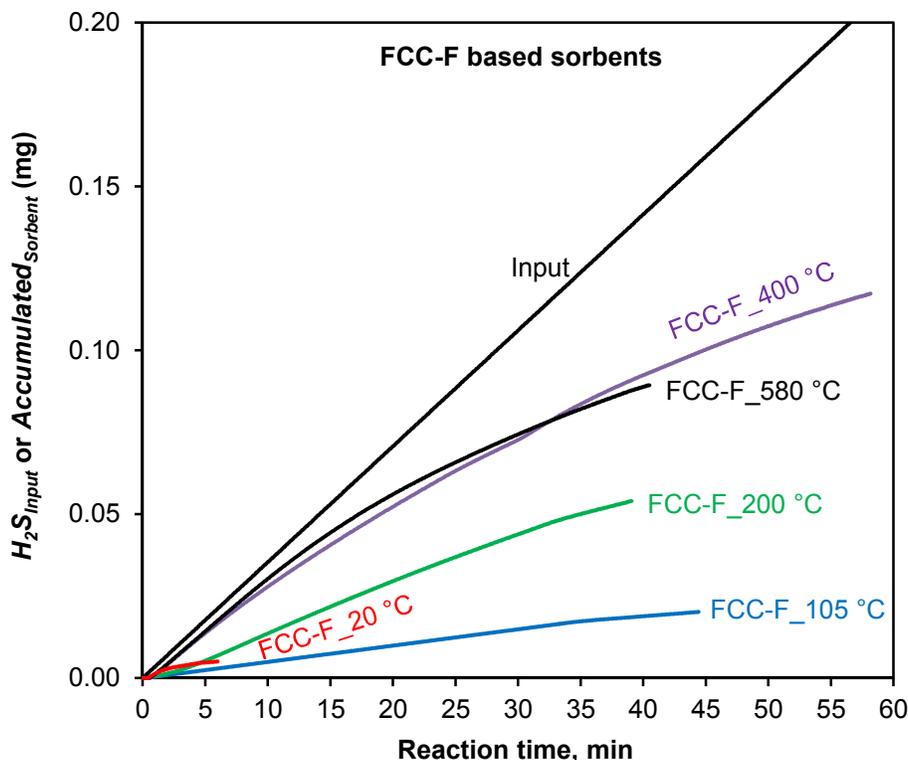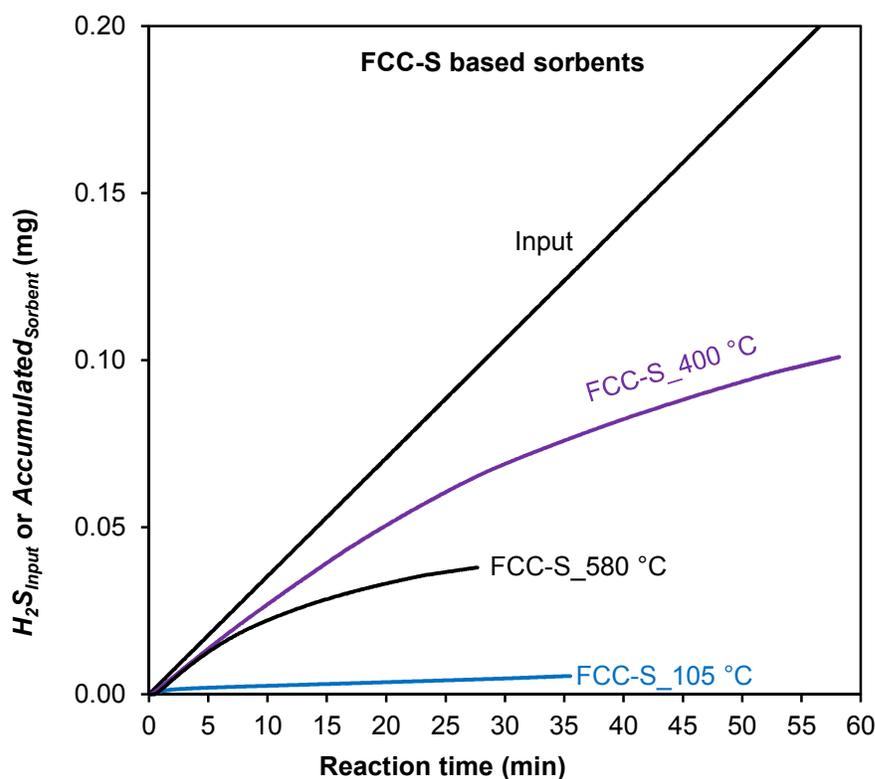

Figure 5. Quantity of the accumulated H_2S fed into the reactor (*Input* curve) and remaining after passing over FCC-S based sorbents. The sorbents were pre-treated by calcination at different temperatures. Sorption conditions: 50 ppmv of H_2S in dried air, 50 mL min^{-1}, 0.5 g of sorbent, room temperature and pressure.

Figure 5 shows the results obtained with FCC-S based sorbents. As previously observed with FCC-F based sorbents, the reactivity of FCC-S treated at 105 °C was smaller than that of the solids treated at 400 and 580 °C. Both the solids calcined at 400 and 580 °C had the similar sorption behaviour during the first 6 min of time-on-stream. Then, the sorbent treated at 580 °C was saturated more quickly than the one treated at 400 °C. This behaviour was also observed for the sorbents starting from pure commercial calcite (Figure 6). Standard characterizations such as TG-DSC, SEM, IR, XRD did not reveal the differences between these calcined solids.
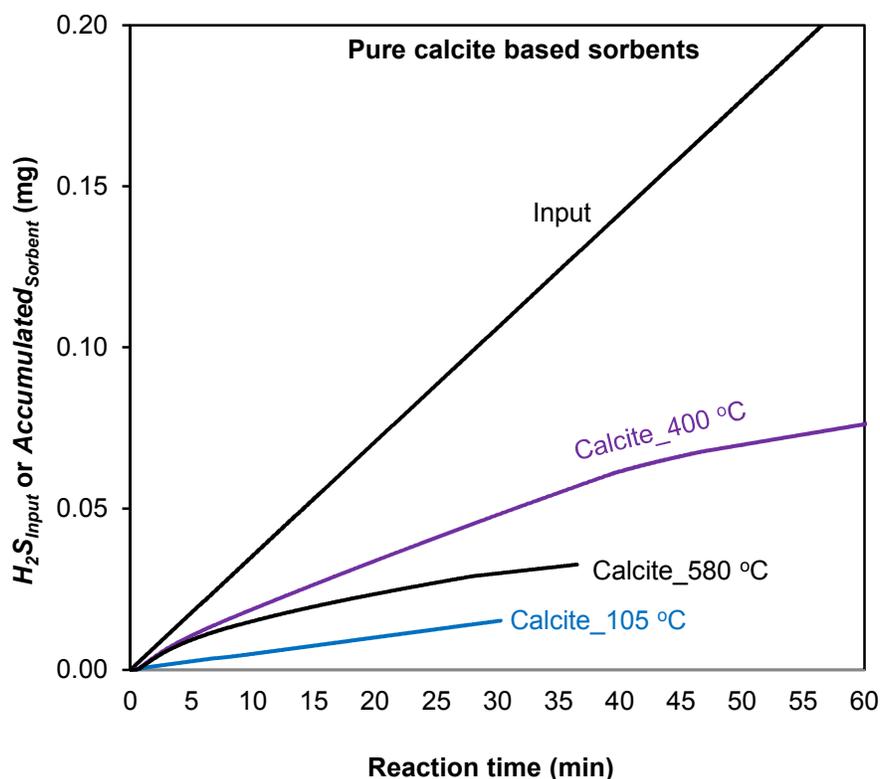

Figure 6. Quantity of the accumulated H_2S fed into the reactor (*Input* curve) and remaining after passing over the pure calcite based sorbents. The sorbents were pre-treated by calcination at different temperatures. Sorption conditions: 50 ppmv of H_2S in dried air, 50 mL min^{-1}, 0.5 g of sorbent, room temperature and pressure.

From the results in Figures 4-6, the calcination at 400 °C seemed to be the most suitable pretreatment of both the solid wastes. The comparison of the reactivity of three sorbents, calcined at 400 °C, shows that both the solid wastes were more active than the pure calcite (Figure 7). This was probably due to the presence of various impurities in the solid wastes, as reported in Table 1. Metals oxides such as iron, copper, zinc oxides, are well known as active phase for H_2S fixation.[16-18] Further study is necessary for understanding the transformation of impurities present in the initial FCC during calcination step, and their role for H_2S removal.
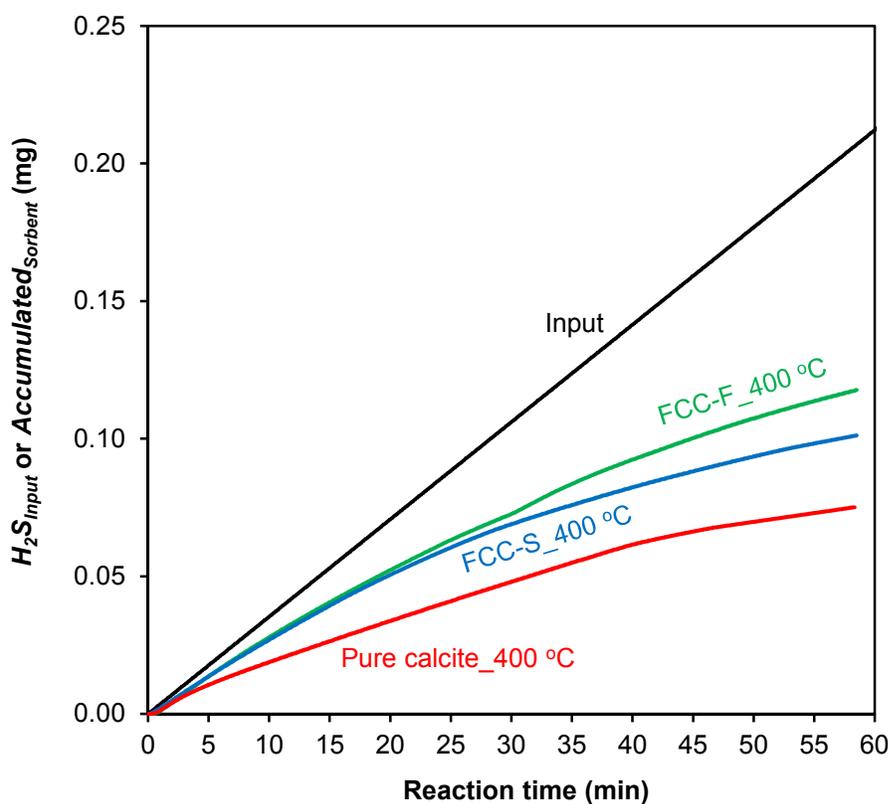

Figure 7. Comparison of three sorbents treated at 400 °C. Sorption conditions: 50 ppmv of H_2S in dried air, 50 mL min^{-1}, 0.5 g of sorbent, room temperature and pressure.
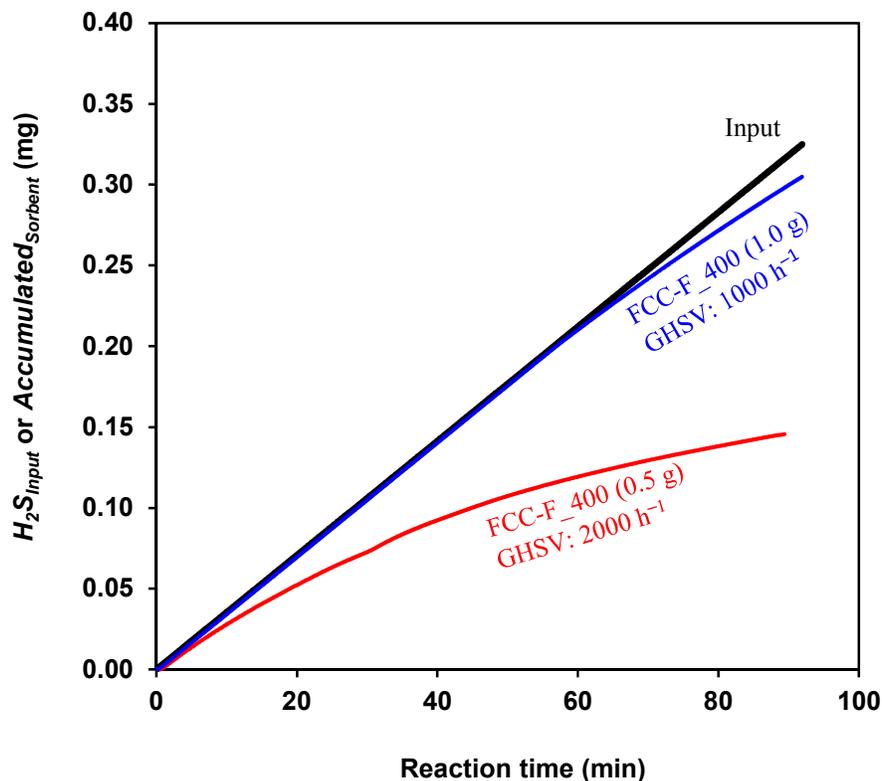
3.3. Influence of the contact time

Figure 8. Influence of the contact time on the performance of the process using FCC-F pre-treated at 400 °C. Sorption conditions: 50 ppmv of H_2S in dried air, 50 mL min^{-1}, 0.5 to 1.0 g of sorbent, room temperature and pressure.

Taking into account the apparent volume of the solid bed of 1.5 mL for 0.5 g of FCC-F or FCC-S, the corresponding gas hourly space velocity used (GHSV) was equal to 2000 h^{-1}. At this GHSV, despite the encouraging results presented above, neither the solid wastes nor pure calcite were good enough for the effective removal of H_2S. In fact, $t_{100\%}$ never exceeded 3 min for all the sorbents treated at various temperatures. In order to enhance the sorption performance, the quantity of the sorbent FCC-F_400 was doubled while keeping unchanged the gas flow rate. Figure 8 show the results obtained. The increase of the sorbent quantity improved strongly the performance of H_2S removal. The value of $t_{100\%}$ reached up to 55 min at the GHSV of 1000 h^{-1}.

So, the contact time was found to be a crucial parameter for the purification of trace amounts of

H_2S in dry air.

3.4. Influence of iron addition
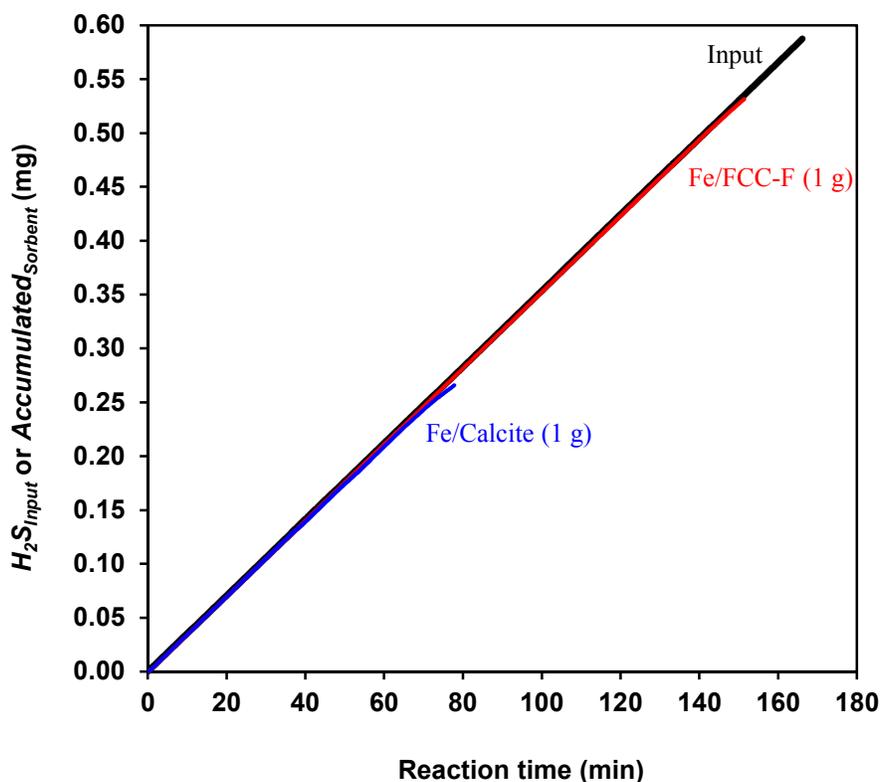
Figure 9. Sorption behavior of iron-doped sorbents. Sorption conditions: 50 ppmv of H_2S in

dried air, 50 mL min^{-1}, 1.0 g of sorbent, room temperature and pressure.

The improvement of the performance of a sorbent can also be realized by the addition of

highly-dispersed metal-based particles, which have high affinity for H_2S immobilization.[19-20] In

this study, we chosen iron as the metal active because of its low cost, its availability and its high

potential reactivity for H_2S removal.[21-22] FCC-F and pure calcite were used as supports for the

dispersion of iron particles. Iron particles deposition was carried out using the standard incipient

wetness impregnation method, as described elsewhere.[23-24] An aqueous solution of $Fe(NO_3)_3$

was added to FCC-F or pure calcite powder in order to wet just enough the outer and pore surfaces of the support material. The concentration of $Fe(NO_3)_3$ solution was calculed to reach finally 1 wt.% of iron in the final solid sorbent, which was either Fe/FCC-F or Fe/Calcite. The iron content was chosen at 1 wt.% according to the low specific surface area of FCC-F and pure calcite. After the impregnation step, the solid was dried overnight at 105 °C and calcined at 500 °C under air before use in H_2S sorption experiment.

Figure 9 shows the sorption behavior of iron-doped sorbents. Firstly, the addition of iron particles to FCC-F solid led to the considerable improvement of its sorption performance. Its $t_{100\%}$ reached 150 min, which was much higher than $t_{100\%}$ of the undoped FCC-F (55 min, Figure 8) under the same sorption conditions. Secondly, using the same preparation method for the deposition of iron particles, FCC-F based sorbent (Fe/FCC-F) was more active than pure calcite based sorbent (Fe/Calcite), which had $t_{100\%}$ equal to 150 and 70 min, respectively. SEM analysis allowed observing the formation of iron-based particles on the surface of these two supports (Figure 10). These particles had higher contrast compared to the surface of the supports, as confirmed by EDX analysis (results not shown). We can see that iron-based particles formed on the surface Fe/FCC-F were smaller than those formed on the surface of Fe/Calcite. In addition, the phenomenon of local agglomeration of iron particles was observed for Fe/Calcite, but was not the case for Fe/FCC-F. In fact, the pH_{pzc} was 8.5 and 9.9 for FCC-F dried at room temperature, and for commercial calcite, respectively. Commercial calcite, with higher pH_{pzc}, led to the local and rapid precipitation of iron oxides during the addition of aqueous solution of $Fe(NO_3)_3$ on its surface. On the other hand, FCC-F solid waste, with lower pH_{pzc}, prevented or limited this local precipitation of iron oxides.
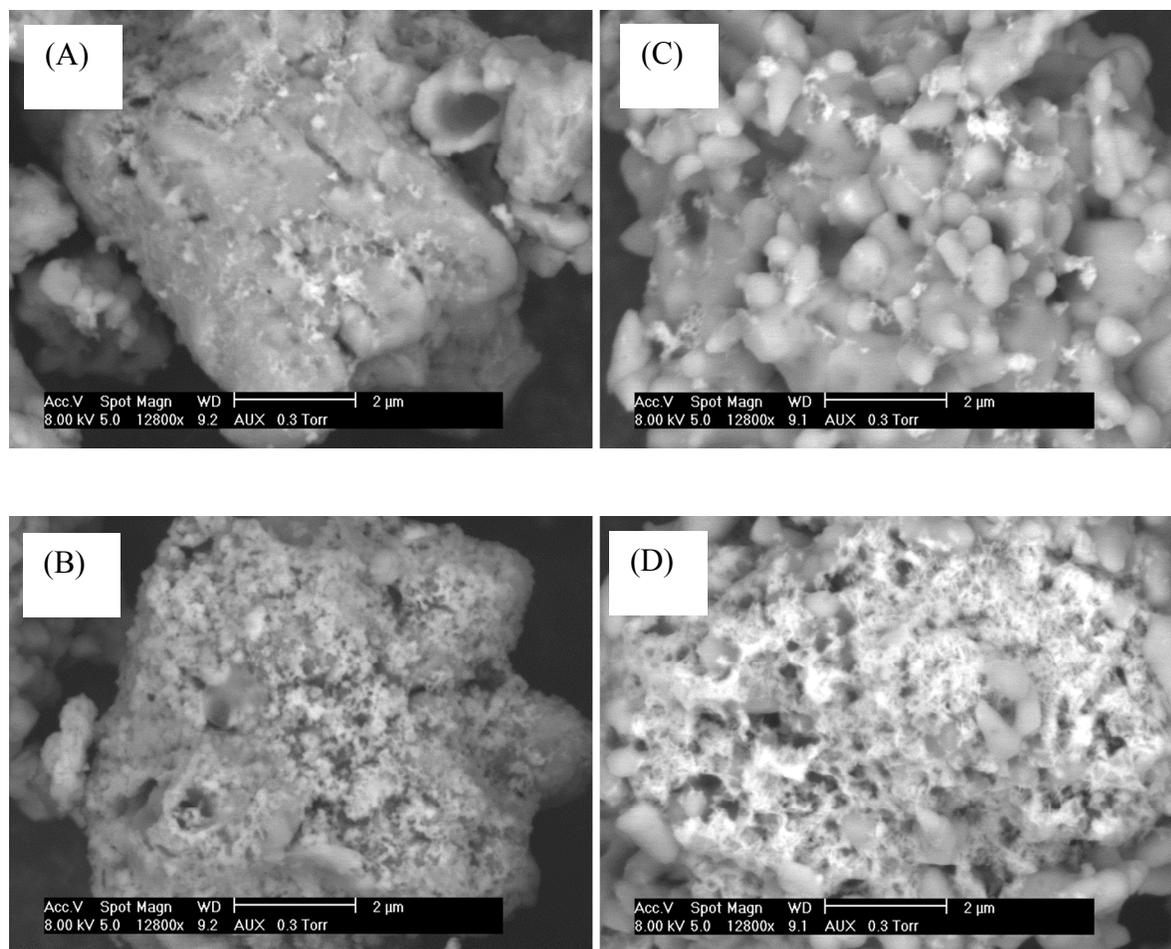
Figure 10. SEM analysis of Fe/FCC-F (A, B) and Fe/Calcite (C, D).

3.5. Comparison with an activated carbon

Activated carbon is considered as the reference sorbent for gas treatment, in particular in the case of H_2S treatment. In this study, the reactivity of the undoped FCC-F_400 and the iron-doped sorbent (Fe/FCC-F) was compared with that of an activated carbon purchased from CECA (France, L3S model), which is specially designed for H_2S treatment. Figure 11 shows the results obtained. FCC-F solid waste doped with 1 wt.% of iron (Fe/FCC-F) was slightly more active than the activated carbon. The value of $t_{100\%}$ reached around 55 and 60 min for the activated carbon and Fe/FCC-F, respectively, when 0.5 g sorbent were used. By doubling the quantity of

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the undoped sorbent FCC-F_400, the equivalent sorption performance compared to Fe/FCC-F or the activated carbon could be also obtained. This observation appeared as a major result because FCC-F and FCC-S are currently considered as solid wastes and need to be treated inside the industrial sites of the Solvay process®.
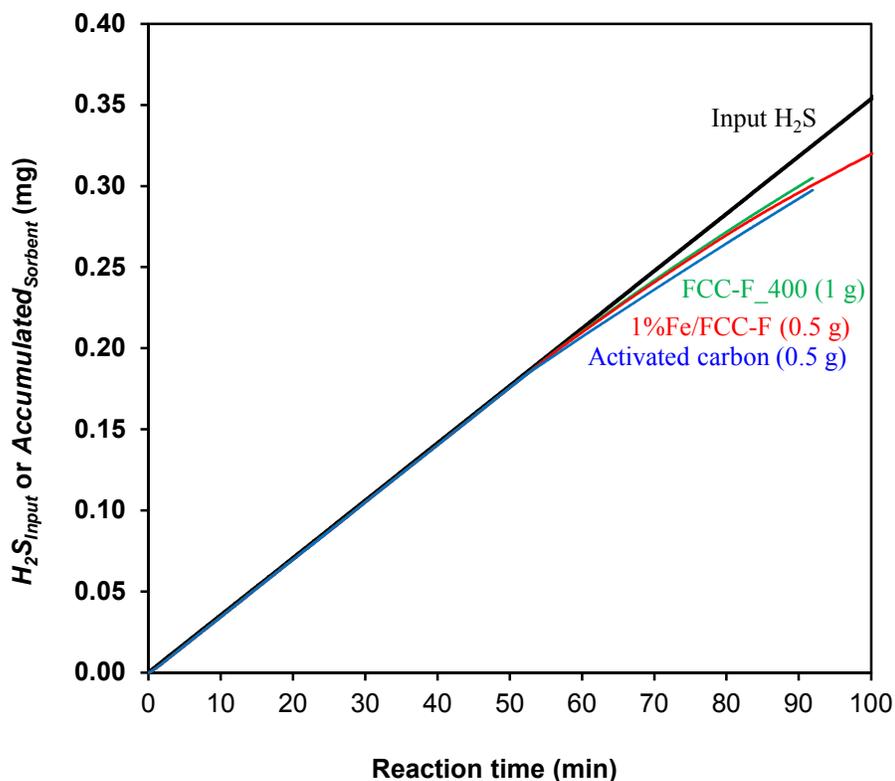

Figure 11. Comparison of the activity of FCC-F based sorbents and an activated carbon as reference. Sorption conditions: 50 ppmv of H_2S in dried air, 50 mL min^{-1}, 0.5 to 1.0 g of sorbent, room temperature and pressure.

3.6. Recycling tests

The higher reactivity of both the solid wastes compared to the pure commercial calcite and the considerable improvement of the reactivity of FCC-F sorbent by adding iron particles on its surface suggest that metals and metal oxides are probably active sites for the fixation of H_2S, in addition to the basicity of calcium carbonate's surface. The fixation of H_2S may relate to the

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adsorption by physisorption interaction, or by chemisorption; this last one is generally not reversible. To verify the reutilization possibility of the used sorbent, desorption test by thermal treatment was tested. The used sorbent was heated at 500 °C for 2 h before the first recycling test. The desorption was repeated again for the second recycling. Figure 12 shows the results obtained with undoped FCC-F, and with iron-doped FCC-F sorbents. For the undoped sorbent (Figure 12 A); $t_{100\%}$ decreased from about 60 min to 30 min at the first recycling, and to 12 min at the second recycling. For the iron-doped sorbent (Figure 12 B), its $t_{100\%}$ decreased from about 150 min to 45 min at the first recycling and to 25 min at the second recycling. The partial loss of reactivity during thermal reactivation of used sorbent has commonly been observed for other kinds of sorbents, such as activated carbon.[25-27] This reactivity loss might be due irreversible interaction between H_2S and metal oxides. This loss might be also due to the oxidation of H_2S to nonvolatile sulfur compounds.[28] This might be also due to the agglomeration of active sites during the regeneration by heating at 500 °C. The agglomeration of active sites is known as irreversible deactivation. Further analysis is needed for determining sulfur compounds formed during H_2S removal and for understanding the reason of this irreversible deactivation.
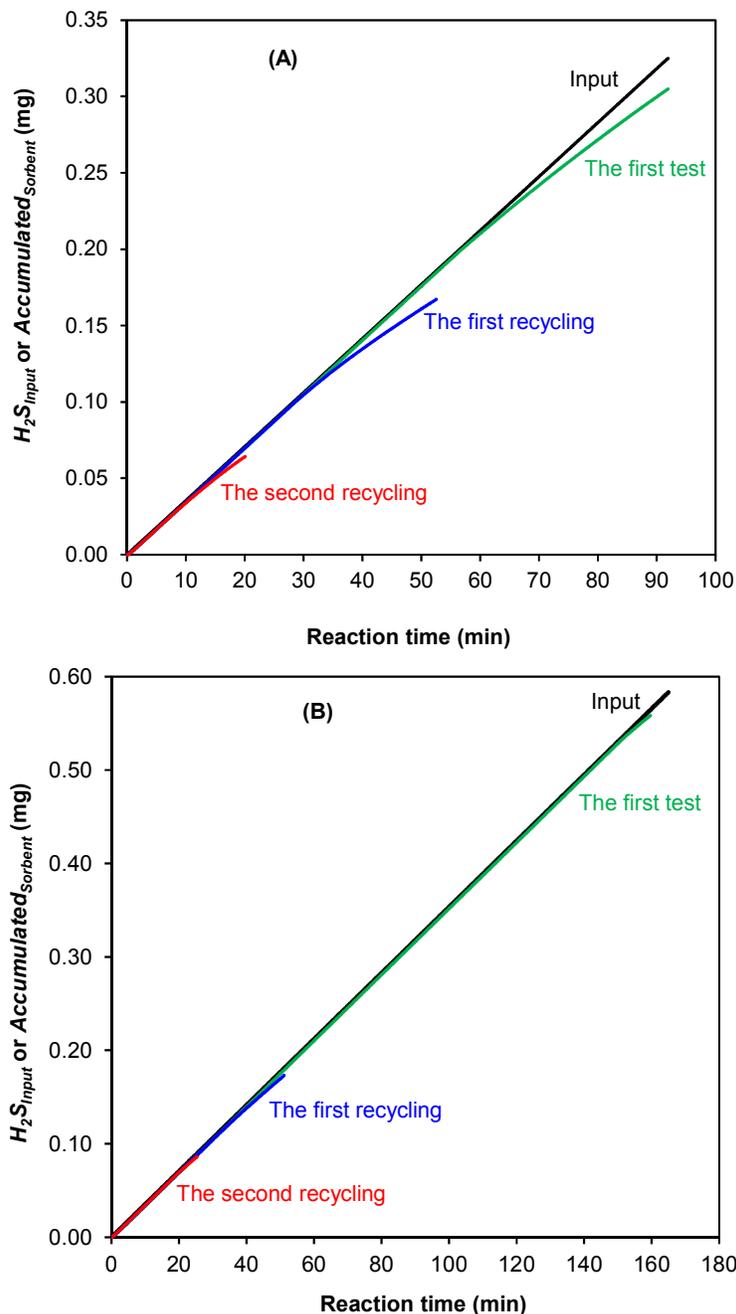
Figure 12. Regeneration of used sorbent; (A) undoped FCC-F_400; (B) iron-doped sorbent

(Fe/FCC-F); Regeneration conditions: heating at 500 °C for 2 h under air atmosphere; Sorption

conditions: 50 ppmv of H_2S in dried air, 50 mL min^{-1}, 1.0 g of sorbent, room temperature and

pressure.

4. Conclusions

Sorption behavior of two calcium carbonate based solid wastes, which were recovered from industrial sites of the Solvay process®, was investigated for the treatment of H_2S in gas phase. The sorbents generated from these solid wastes, by simple thermal pre-treatment or by addition of only 1 wt.% of iron, showed equivalent reactivity compared to an activated carbon. The results open new prospects for the valorization of calcium carbonate-based solid wastes for environmental purposes.

Figure and Table captions

Figure 1. Scheme of the reactor used in this work.

Figure 2. TG curves of the FCC-F after thermal treatment at different temperatures.

Figure 3. XRD patterns of the FCC-F after thermal treatment at different temperatures.

Figure 4. Quantity of the accumulated H_2S fed into the reactor (*Input* curve) and remaining after passing over FCC-F based sorbents. The sorbent were pre-treated by calcination at different temperatures. Sorption conditions: 50 ppmv of H_2S in dried air, 50 mL min^{-1}, 0.5 g of sorbent, room temperature and pressure.

Figure 5. Quantity of the accumulated H_2S fed into the reactor (*Input* curve) and remaining after passing over FCC-S based sorbents. The sorbents were pre-treated by calcination at different temperatures. Sorption conditions: 50 ppmv of H_2S in dried air, 50 mL min^{-1}, 0.5 g of sorbent, room temperature and pressure.

Figure 6. Quantity of the accumulated H_2S fed into the reactor (*Input* curve) and remaining after passing over the pure calcite based sorbents. The sorbents were pre-treated by calcination at different temperatures. Sorption conditions: 50 ppmv of H_2S in dried air, 50 mL min^{-1}, 0.5 g of sorbent, room temperature and pressure.

Figure 7. Comparison of three sorbents treated at 400 °C. Sorption conditions: 50 ppmv of H_2S in dried air, 50 mL min^{-1}, 0.5 g of sorbent, room temperature and pressure.

Figure 8. Influence of the contact time on the performance of the process using FCC-F pre-treated at 400 °C. Sorption conditions: 50 ppmv of H_2S in dried air, 50 mL min^{-1}, 0.5 to 1.0 g of sorbent, room temperature and pressure.

Figure 9. Sorption behavior of iron-doped sorbents. Sorption conditions: 50 ppmv of H_2S in dried air, 50 mL min^{-1}, 1.0 g of sorbent, room temperature and pressure.

Figure 10. SEM analysis of Fe/FCC-F (A, B) and Fe/Calcite (C, D).

Figure 11. Comparison of the activity of FCC-F based sorbents and an activated carbon as reference. Sorption conditions: 50 ppmv of H_2S in dried air, 50 mL min^{-1}, 0.5 to 1.0 g of sorbent, room temperature and pressure.

Figure 12. Regeneration of used sorbent; (A) undoped FCC-F_400; (B) iron-doped sorbent (Fe/FCC-F); Regeneration conditions: heating at 500 °C for 2 h under air atmosphere; Sorption conditions: 50 ppmv of H_2S in dried air, 50 mL min^{-1}, 1.0 g of sorbent, room temperature and pressure.

Table 1. Elemental analyses of both FCC-F and FCC-S dried at room temperature.

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