Valorization Of Inorganic Solid Wastes From Industrial Activities Into Active Materials For Removal Of Hydrogen Sulfide In Gas Phase

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Outline

Introduction

Materials and Methods

Results and Discussion

Conclusions
Introduction

Sources of Hydrogen Sulfide ($\text{H}_2\text{S}$)?

**Anthropogenic:**
- Industrial activities:
  - Petroleum, food, water production…
- Biogas Production (<3%)
- Purification of natural gas

**Nature:**
- Volcanoes
- Wet-land
- Biological processes
Harmful effects of Hydrogen Sulfide

<table>
<thead>
<tr>
<th>Concentration</th>
<th>Effect</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-5 ppm</td>
<td>Strong Odor</td>
</tr>
<tr>
<td>300-500 ppm</td>
<td>Serious Respiratory Trouble (15 min)</td>
</tr>
<tr>
<td>&gt;1000 ppm</td>
<td>Immediate death</td>
</tr>
</tbody>
</table>

**Introduction**

**Corrosion**
http://www.legend-group.com/

**Effects**

**Machine**

**Health**

**Eco-system**

**Acid Rain**
Environment.nationalgeographic.com
Treatment of H$_2$S:

1. Methods:
   - Biological Desulfurization
   - Adsorption
   - Absorption
   - Catalytic Oxidation
   - Scrubbing
   - Membrane Separation

2. Sorbents
   - Activated Carbon, COST
   - Calcium Carbonat (CaCO$_3$).
Introduction

Solvay Process®: (Soda ash- Manufacturing food, glass, chemicals, paper, detergents, etc)

Solvay Process® scheme
- 2000: 59% production of soda ash worldwide (~17 Mt)
- Solid Wastes↑, which have main composition of CaCO₃

=> Impact on environment and economic

Objectives: Valorization of solid wastes from Solvay Process® for treatment H₂S in gas phase to limit environmental impacts and enhance economic benefit.
Material and Methods

**Equipment**

- **Sorbent**
- **Analyser**
- **Material and Methods**
- **H₂S tank**
- **Flow meter**
- **Fix bed Reactor**
- **Reactor**
- **Analyser**
- **H₂S**
Material and Methods

Phisico-Chemical Characterization

1. Thermogravimetry analysis (TGA)
   SDTQ600 analyzer: a heating rate of 5°C/min, air flux (100 mL/min).
2. X-ray diffraction (XRD)
   Phillips Panalytical X’pert Pro MPD diffractometer with a Cu Kα (1.543 Å) radiation source.
3. X-ray Fluorescence (XRF)
4. Fourier transform infrared (FTIR) spectroscopy
   Shimadzu 8400S spectrometer.
5. Scanning electron microscopy (SEM)
   Philips XL30 ESEM apparatus (FEI Company) + X-ray spectroscopy (EDX analysis).
Materials and Methods

1. Reference materials:
- Activated Carbon (CECA L3S, powder)
- Pure Calcium Carbonate CaCO$_3$ (Calcite, Fisher Scientific, powder)

2. Initial materials: Solid wastes Ca-STAR from France
   → Pre-treatment: sieve (< 315 µm), dry 2 days at ambient temperature (T)
   → Thermal treatment: calcine at different T (105 °C to 850 °C)

3. Chemical modification: Doping with iron by impregnation
   Fe(NO$_3$)$_3$ + powder → Dried 105°C → calcined in air at 500°C
   (Fe: Available, low cost)

   Table1: Composition of Solid wastes (XRF results)

<table>
<thead>
<tr>
<th>Compositions</th>
<th>CaCO$_3$</th>
<th>Mg</th>
<th>Al</th>
<th>Si</th>
<th>Fe</th>
<th>S</th>
<th>Cl</th>
<th>Na</th>
<th>P, Cu, Mn, Zn, Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca-STAR (% wt)</td>
<td>97.63</td>
<td>0.55</td>
<td>0.19</td>
<td>0.47</td>
<td>0.47</td>
<td>0.15</td>
<td>0.1</td>
<td>0.38</td>
<td>0.467</td>
</tr>
</tbody>
</table>
Results and Discussion

Saturation curve

$t_{100\%}$: Duration that $H_2S$ is totally absorbed by the sorbent

\[
m_{H_2S} = \frac{P \cdot Q \cdot M}{10^6 \cdot R \cdot T} \left( c_0 \times t_s - \int_0^{t_s} c(t) \, dt \right)
\]

- Atmospheric Pressure: $P=1$ (atm)
- Molar mass of $H_2S$: $M=34$ (g/mol)
- Constant of ideal gas: $R=8.3145$ (J/mol.K)
- Input and Output $H_2S$ concentration: $C_0$, $C(t)$ (ppm)
- Reaction time: $t_s$ (min)
Effect of pre-treatment temperature with Ca-STAR

T (400°C - 580°C) – the best pre-treatment temperature
Characterizations

FTIR, TGA, DRX:
Up to 580°C: there is no decomposition of CaCO₃
At 850°C: decomposition is complete: CaCO₃ into CaO \( \Rightarrow \) the basicity for fixation of H₂S.

→ Impurities play an important role
→ Need other characterization to understand the evolution of impurities during the calcination \( \Leftrightarrow \) related to improve the reactivity of the sorbents.
Determine the best temperature for the solid wastes pre-treatment

Fe(NO₃)₃ is decomposed totally at 500°C
500°C is suitable for the solid wastes pre-treatment
Effect of Iron Impregnation

1.0g Sorbent

Iron Impregnation ➞ Reactivity

Input H₂S

1%Fe/ Ca-STAR

(t₁₀₀%): 150 min

CaCO₃-S

(t₁₀₀%): 40 min
Effect of quantity of the sorbent

Quantity of sorbent $\rightarrow t_{100\%}$ or Reactivity $\uparrow$

1%Fe/Ca-STAR (1.0g) 
$t_{100\%}$: 150 min

1%Fe/Ca-STAR (0.5g) 
$t_{100\%}$: 55 min
Compare reactivity of the sorbent with Calcite

- Reactivity:
  + Raw Material: Ca-STAR > Calcite
  + Iron Impregnation: Ca-STAR > Calcite
Ca-STAR: Impurities of metals, good dispersion of Fe
Smaller Fe particle ⇒ Better Reactivity
Compare reactivity of the sorbent with Activated Carbon

Reactivity:
+Iron Impregnation 1%Fe/Ca-STAR ~ Activated Carbon L3S from CECA, France

(t_{100\%}): 55 min
Recycling test

- Regeneration condition: Calcination at 500°C in the air

1.0g Sorbent

1%Fe/Ca-STAR 500°C: partially reversible

⇒ formation of chemical bonds between Fe and S?
Conclusions

- Calcified solid wastes from Solvay Process® can be valorized for H$_2$S treatment.
- 500ºC is the best pre-treatment temperature
- Iron Impregnation ↔ Reactivity
- Reactivity:
  + solid wastes > pure calcite: role of impurities presenting in solid wastes.
  + 1% Fe/Ca-STAR ~ Commercial Activated Carbon.
- Fixation of H$_2$S: partially reversible
Thank for your attention!

Hydrogen Sulfide Treatment
Other data of the experiments

Calculation of accumulated \( \text{H}_2\text{S} \) (mg)

\[
m_{\text{H}_2\text{S}} = \frac{P \cdot Q \cdot M}{10^6 \cdot R \cdot T} \left( c_o \times t_s - \int_0^{t_s} c(t) \, dt \right)
\]

- Atmospheric Pressure: \( P=1 \) (atm)
- Molar mass of \( \text{H}_2\text{S} \): \( M=34 \) (g/mol)
- Constant of ideal gas: \( R=8.3145 \) (J/mol.K)
- Input and Output \( \text{H}_2\text{S} \) concentration: \( c_o, C(t) \) (ppm)
- Reaction time: \( t_s \) (min)

- \( T, P \) ambient
- 500 to 10000 mg of sorbent (volume 1.5 to 2.3 cm\(^3\))
- Glass fixed-bed reactor: length 60 mm, internal diameter 11 mm
- \([\text{H}_2\text{S}]=50 \) ppm in air; \( Q=50 \) mL/min