

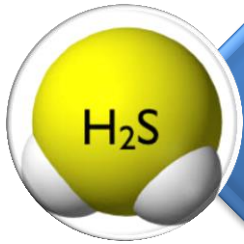
Valorization Of Inorganic Solid Wastes From Industrial Activities Into Active Materials For Removal Of Hydrogen Sulfide In Gas Phase

Hoạt hóa chất thải rắn vô cơ từ hoạt động công nghiệp tạo thành vật liệu loại bỏ Hydro Sunfua ở pha khí

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Outline



Introduction



Materials and Methods



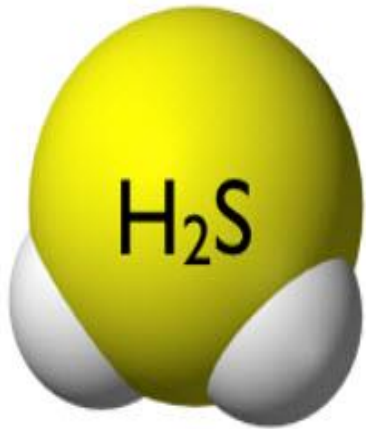
Results and Discussion



Conclusions

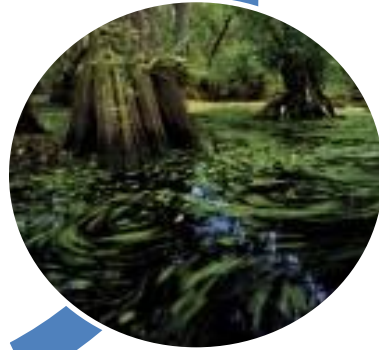
Introduction

Sources of Hydrogen Sulfide (H₂S)?



Anthropogenic:

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



Nature:

- Volcanoes
- Wet-land
- Biological processes

Introduction

Harmful effects of Hydrogen Sulfide



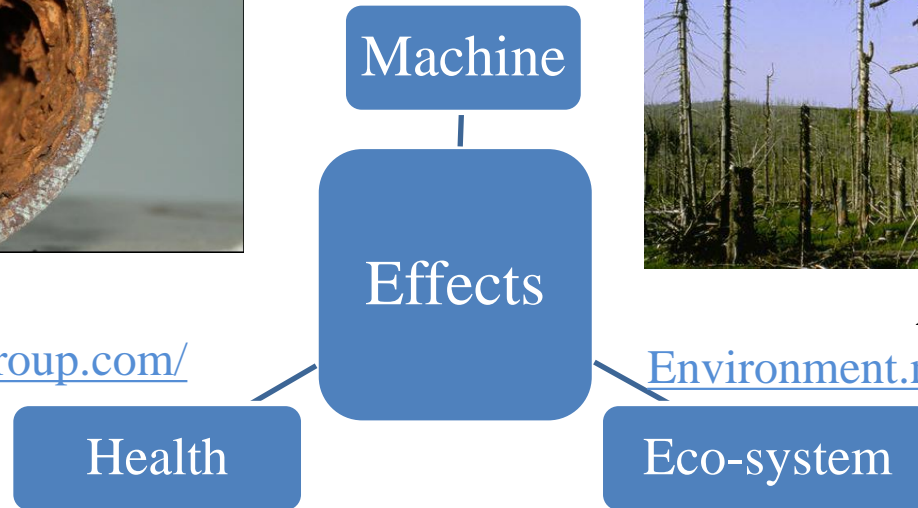
Corrosion

<http://www.legend-group.com/>



Acid Rain

Environment.nationalgeographic.com



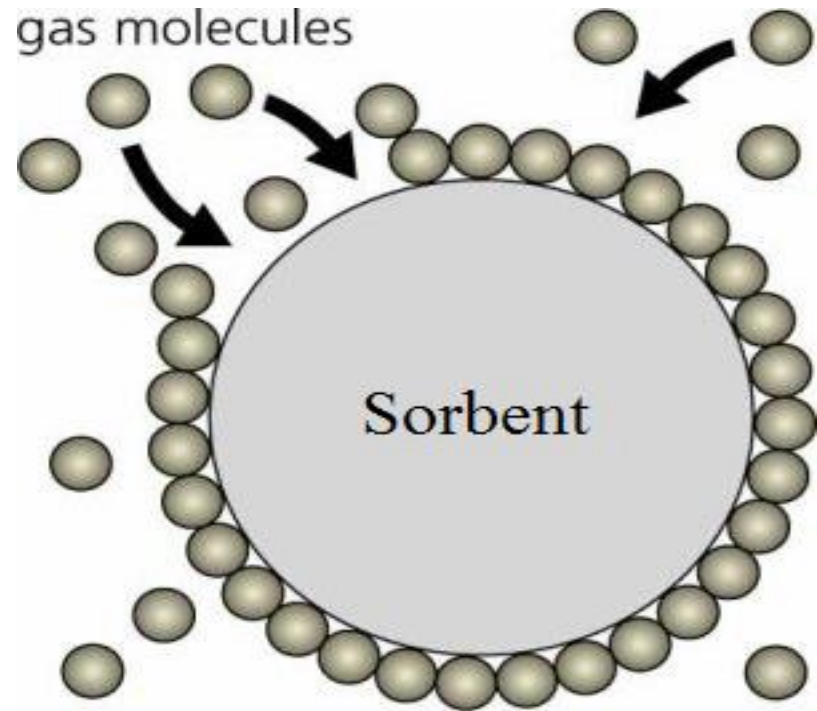
3-5 ppm	Strong Odor
300-500 ppm	Serious Respiratory Trouble (15 min)
>1000 ppm	Immediate death

Introduction

Treatment of H₂S:

1. Methods:

- Biological Desulfurization
- Adsorption
- Absorption
- Catalytic Oxidation
- Scrubbing
- Membrane Separation



Academy Artworks

Adsorption

2. Sorbents

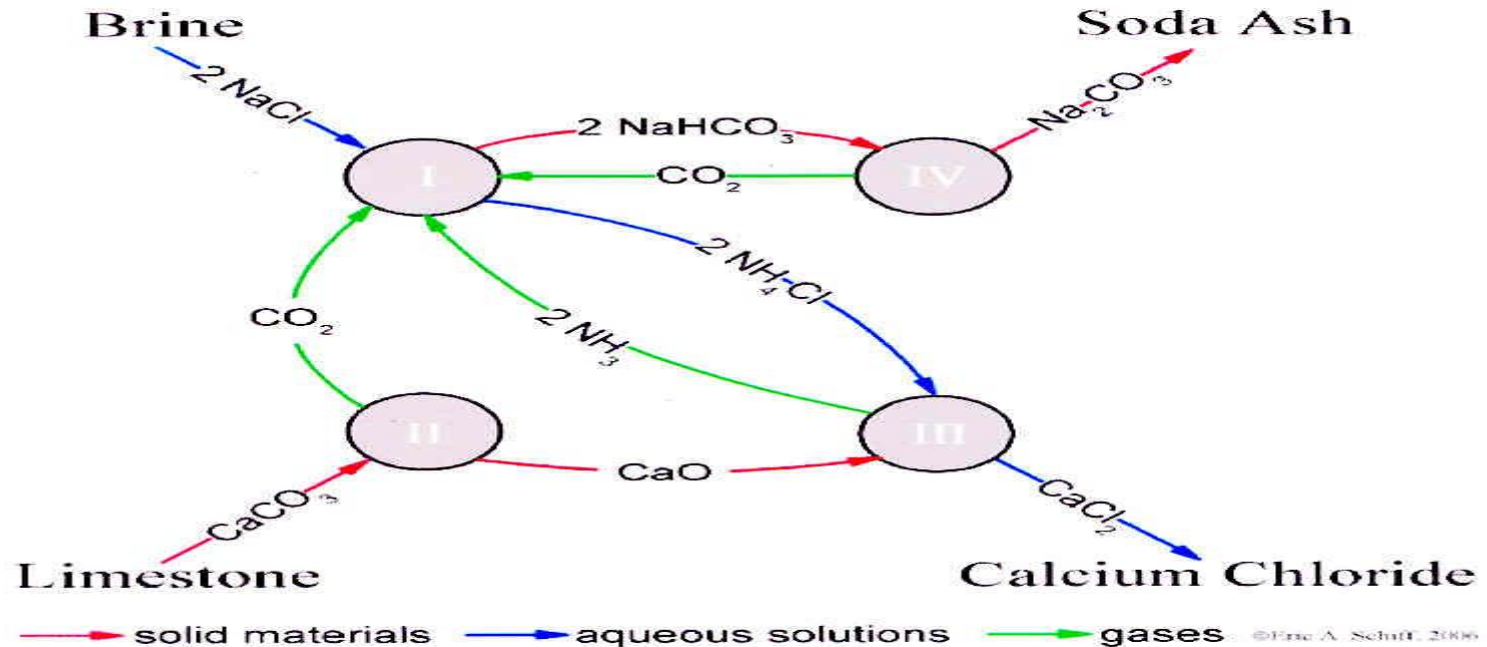
- Activated Carbon, COST↑
- Calcium Carbonat (CaCO₃).



Activated Carbon

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 CaCO_3

=> Impact on environment and economic

Objectives: Valorization of solid wastes from Solvay Process[®] for treatment H_2S in gas phase to limit environmental impacts and enhance economic benefit.

Material and Methods

Equipment



Fix bed
Reactor



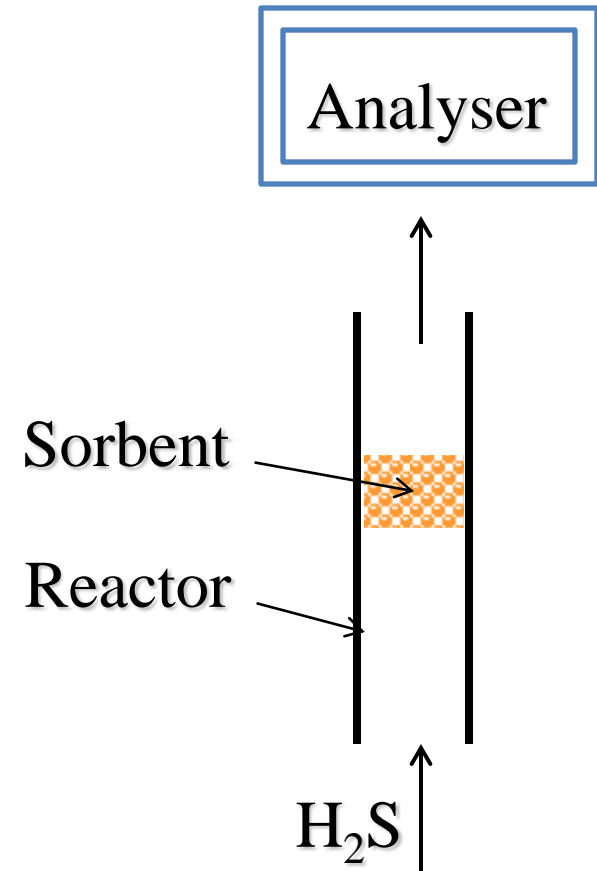
Analyser



Flow
meter



H₂S tank



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 K α (1.543 Å) radiation source.

3. X-ray Fluorescence (XRF)

4. Fourier transform infrared (FTIR) spectroscopy

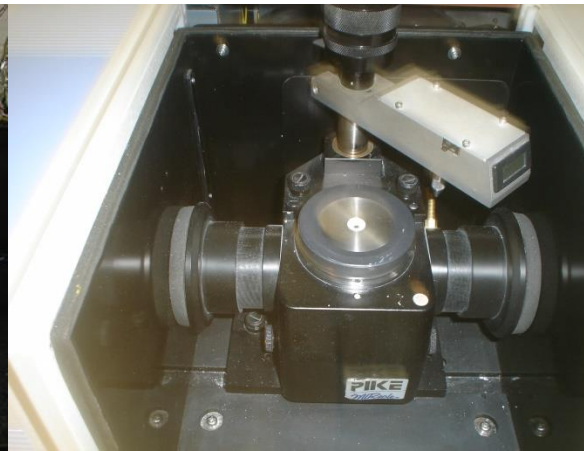
Shimadzu 8400S spectrometer.

5. Scanning electron microscopy (SEM)

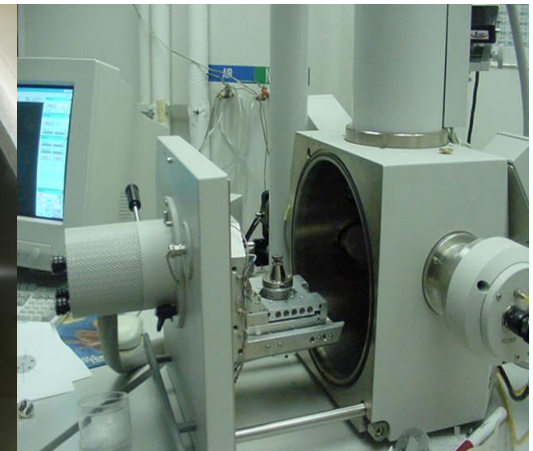
Philips XL30 ESEM apparatus (FEI Company) + X-ray spectroscopy (EDX analysis).



TGA



FTIR



SEM

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

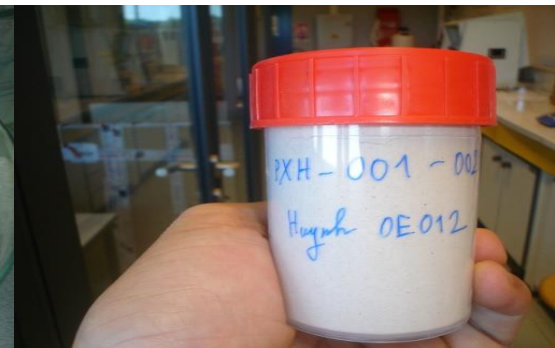
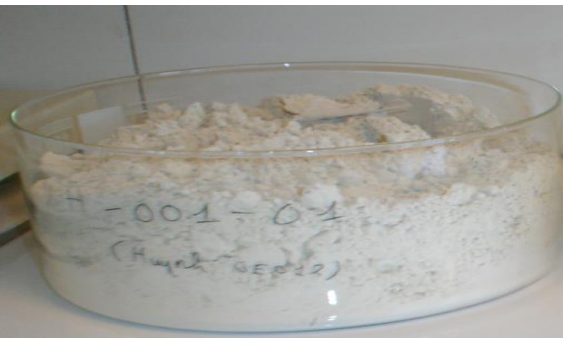
- **Pre-treatment:** sieve ($< 315 \mu\text{m}$), dry 2 days at ambient temperature (T)
- **Thermal treatment:** calcine at different T ($105 \text{ }^\circ\text{C}$ to $850 \text{ }^\circ\text{C}$)

3. Chemical modification: Doping with iron by impregnation

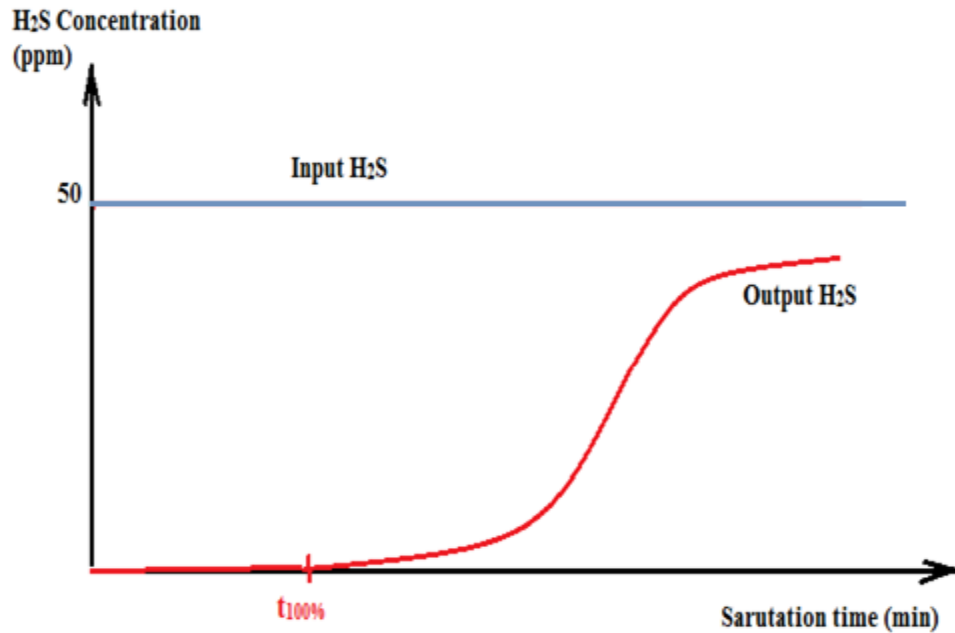
$\text{Fe}(\text{NO}_3)_3$ + powder → Dried 105°C → calcined in air at 500°C
(Fe: Available, low cost)

Table1: Composition of Solid wastes (XRF results)

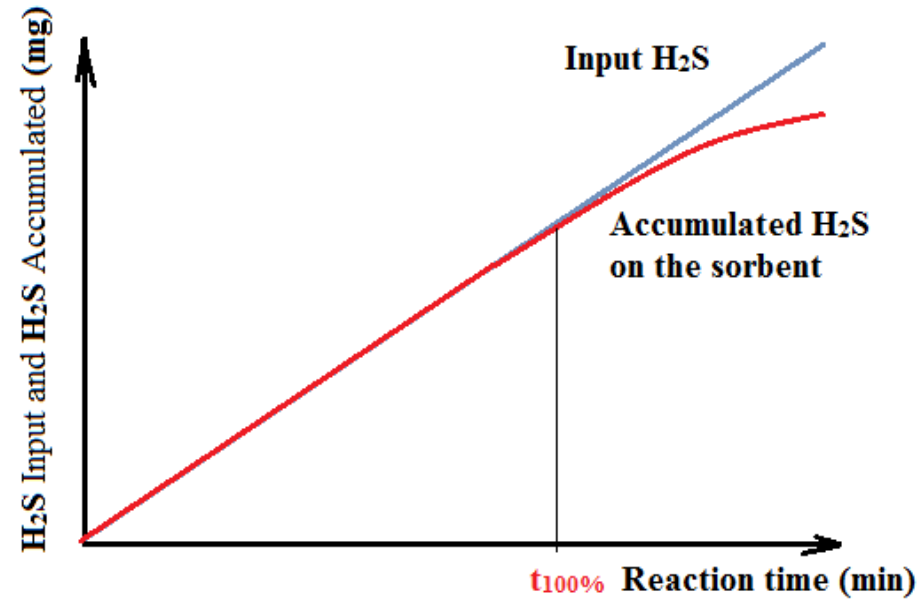
Compositions	CaCO_3	Mg	Al	Si	Fe	S	Cl	Na	P, Cu, Mn, Zn, Sn
Ca-STAR (% wt)	97.63	0.55	0.19	0.47	0.47	0.15	0.1	0.38	0.467



Results and Discussion



Saturation curve



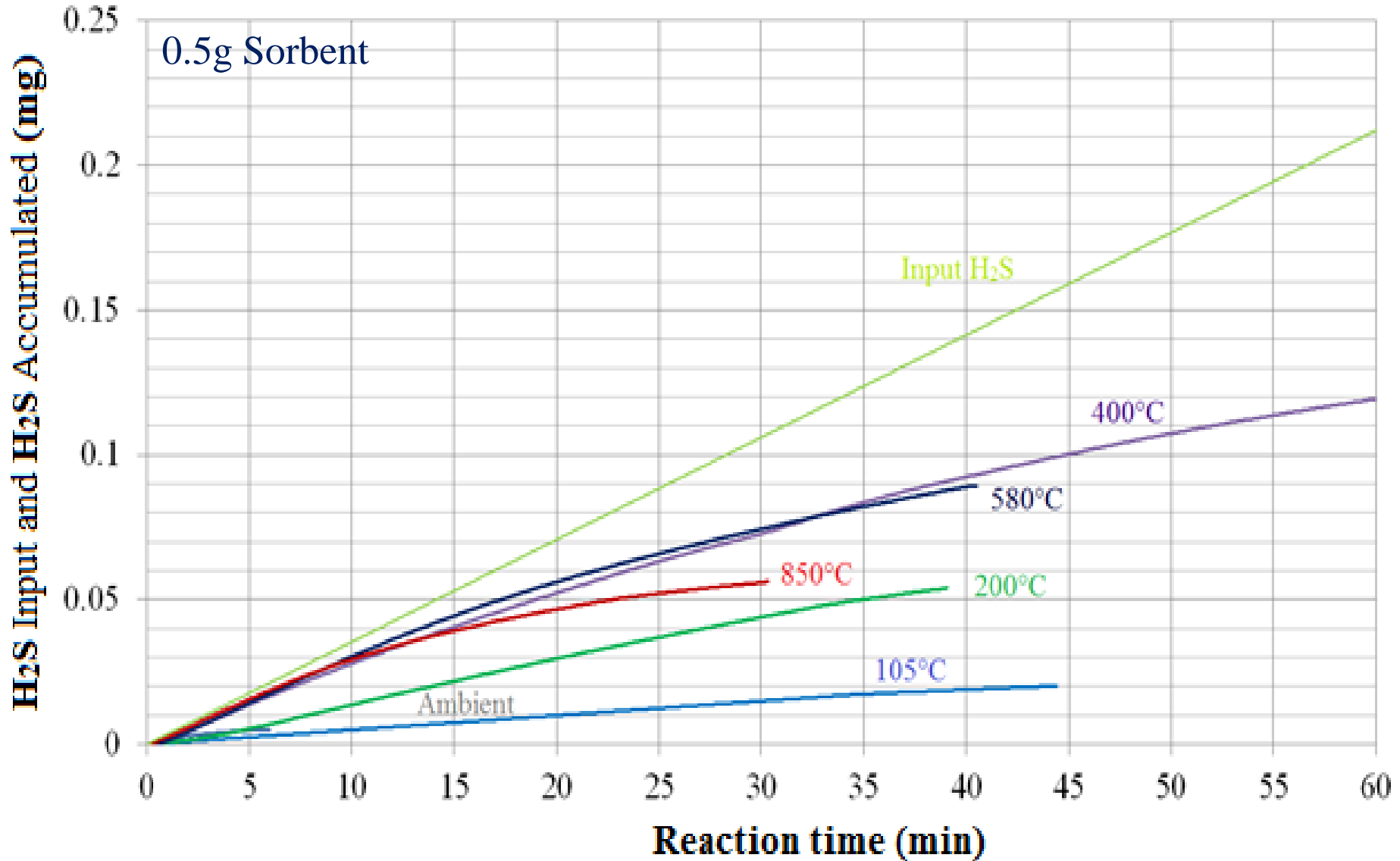
Accumulation curve

$t_{100\%}$: Duration that H₂S is totally absorbed by the sorbent

$$m_{\text{H}_2\text{S}} = \frac{P.Q.M}{10^6.R.T} (c_0 \times t_s - \int_0^{t_s} c(t) dt)$$

- Atmospheric Pressure: P=1 (atm)
- Molar mass of H₂S: M= 34 (g/mol)
- Constant of ideal gas: R=8.3145 (J/mol.K)
- Input and Output H₂S concentration: Co, C(t) (ppm)
- Reaction time: t_s (min)

Effect of pre-treatment temperature with Ca-STAR



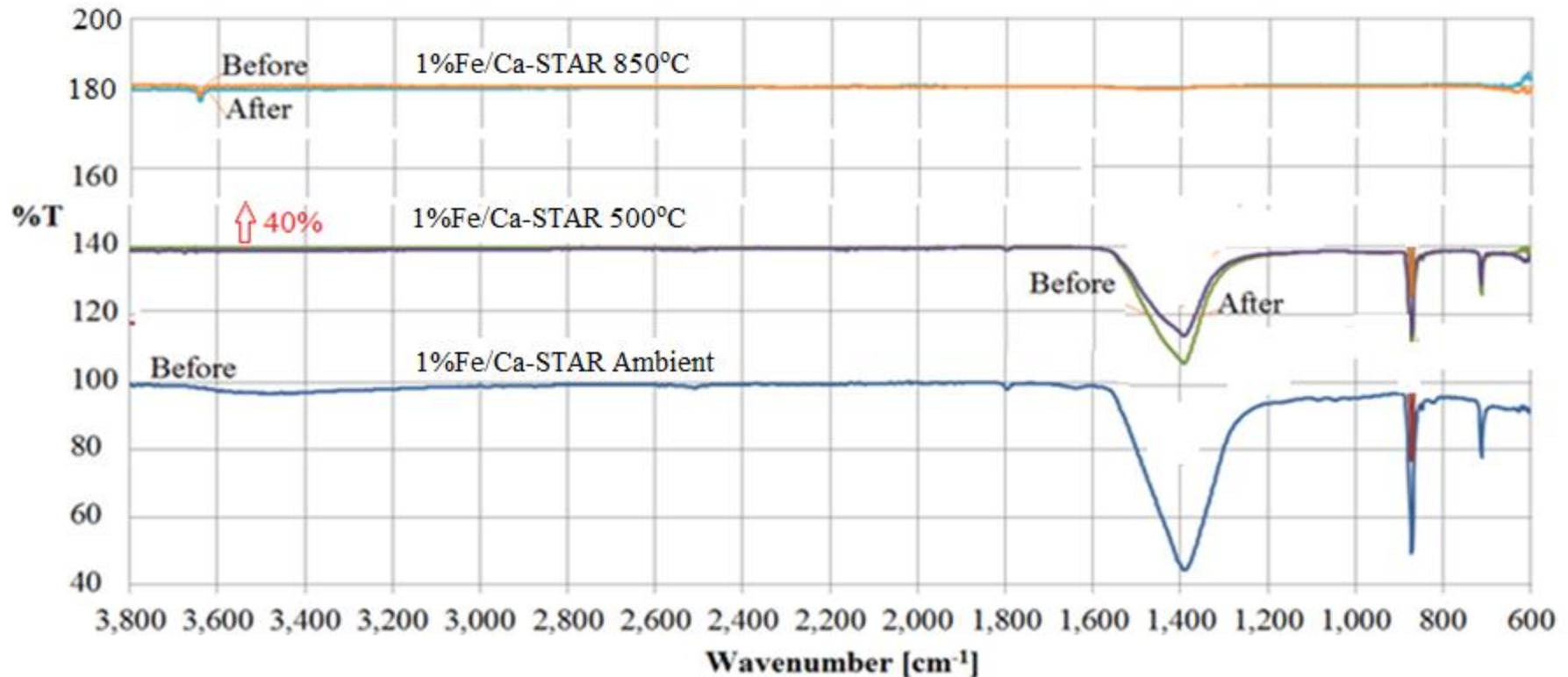
T (400°C - 580°C) – the best pre-treatment temperature

Characterizations

FTIR, TGA, DRX :

Up to 580°C: there is no decomposition of CaCO_3

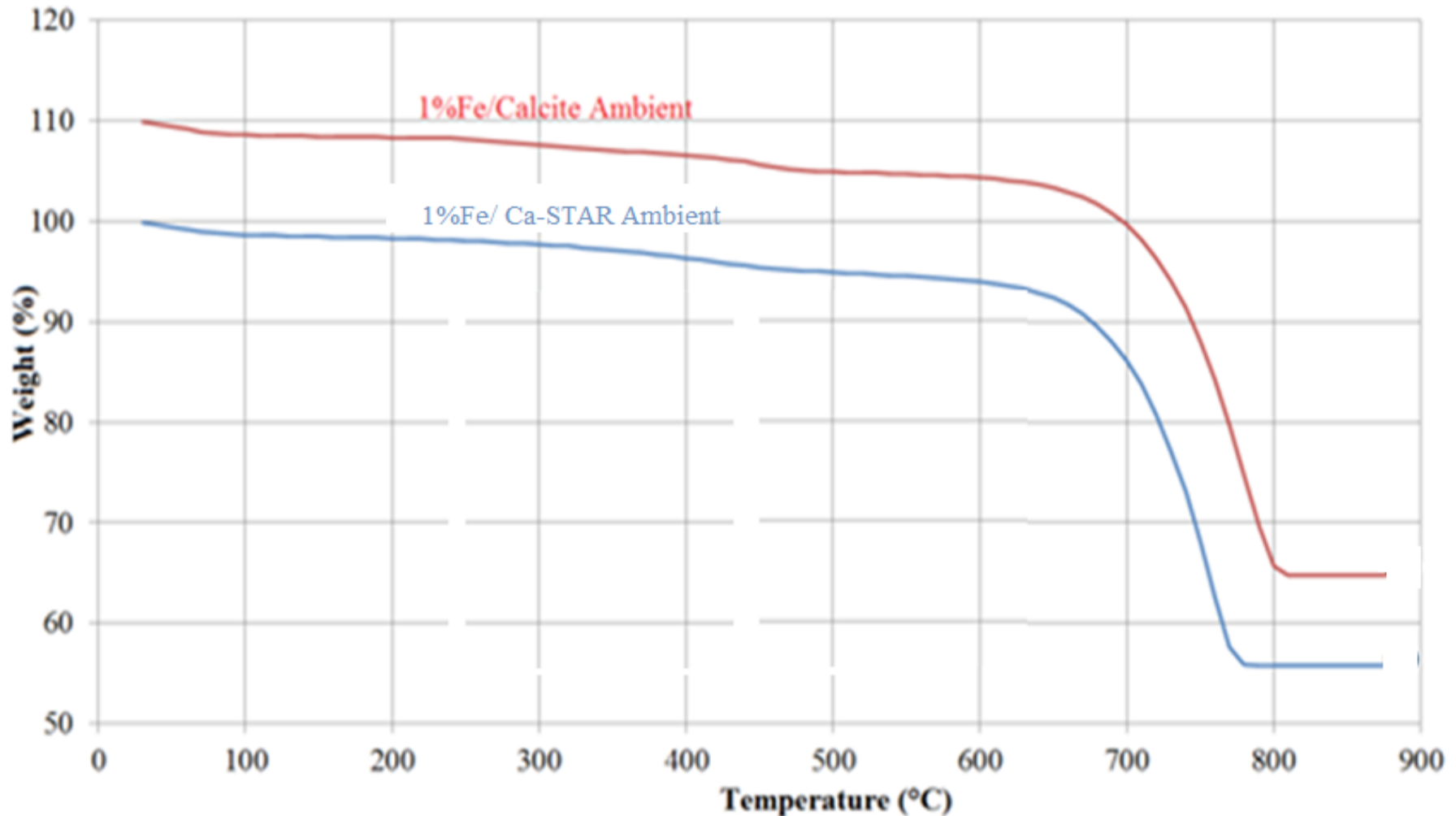
At 850°C: decomposition is complete: CaCO_3 into $\text{CaO} \Leftrightarrow \uparrow$ the basicity for fixation of H_2S .



→ 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



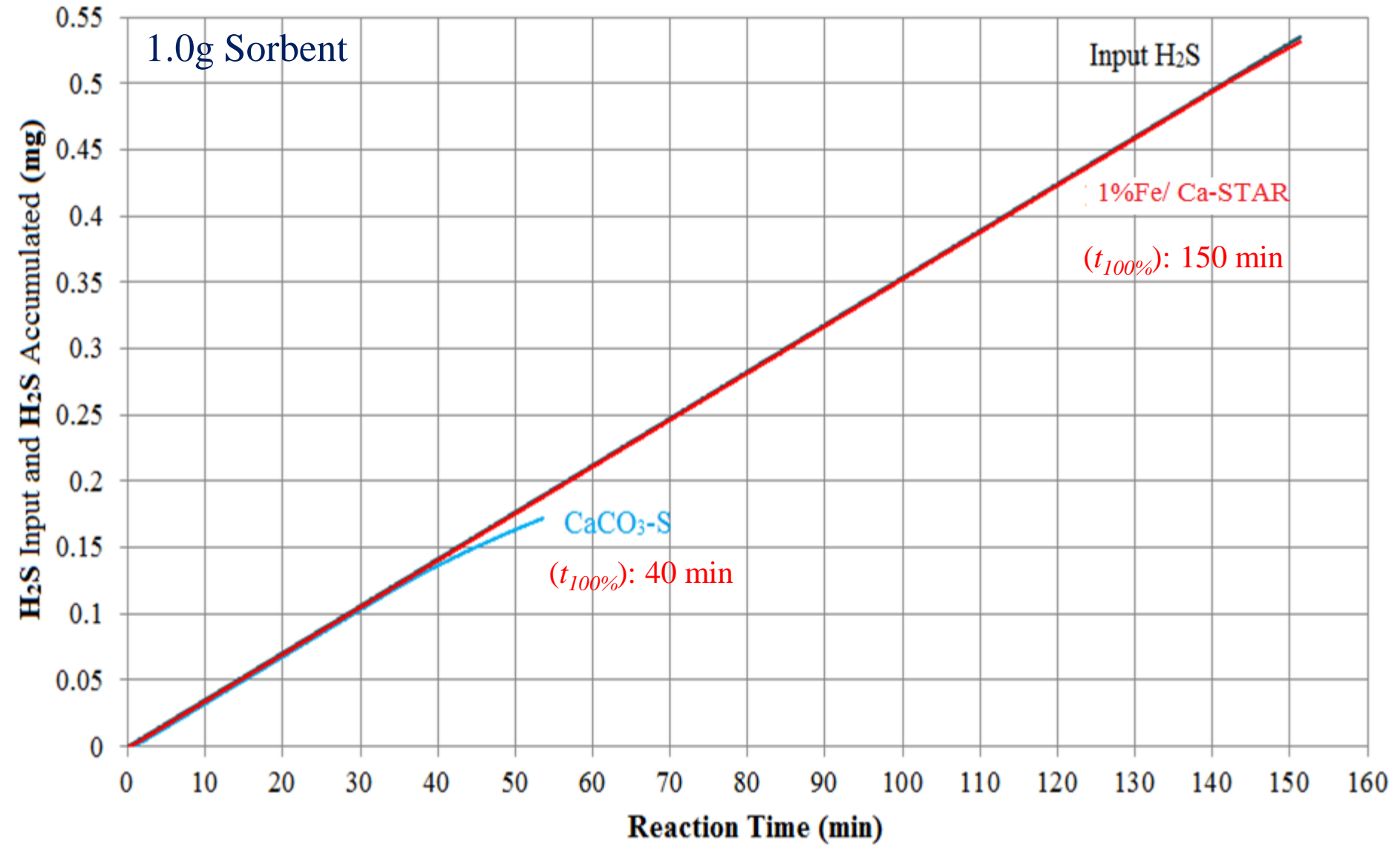
TGA results

$\text{Fe}(\text{NO}_3)_3$ is decomposed totally at 500°C



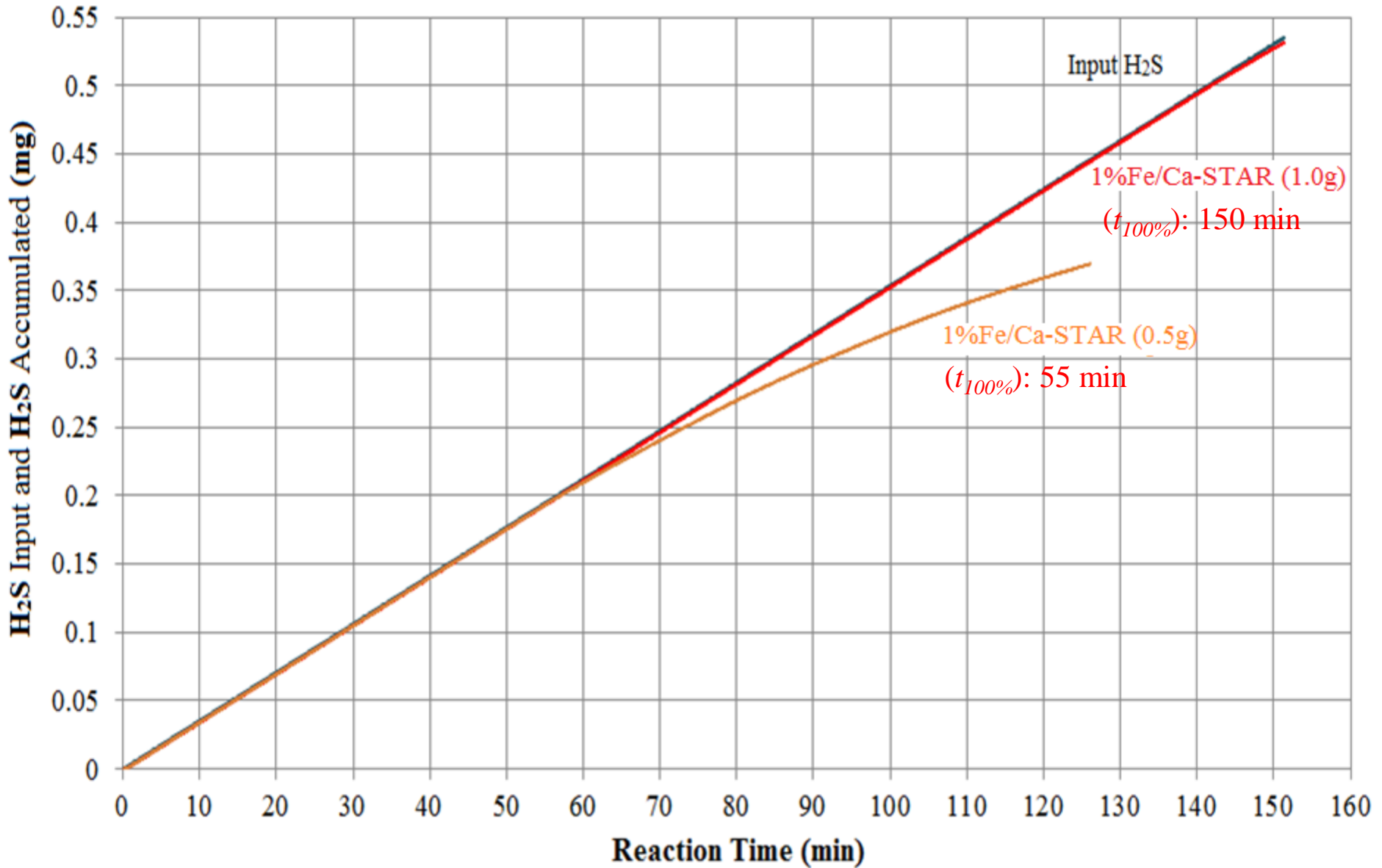
500°C is suitable for for the solid wastes pre-treatment

Effect of Iron Impregnation



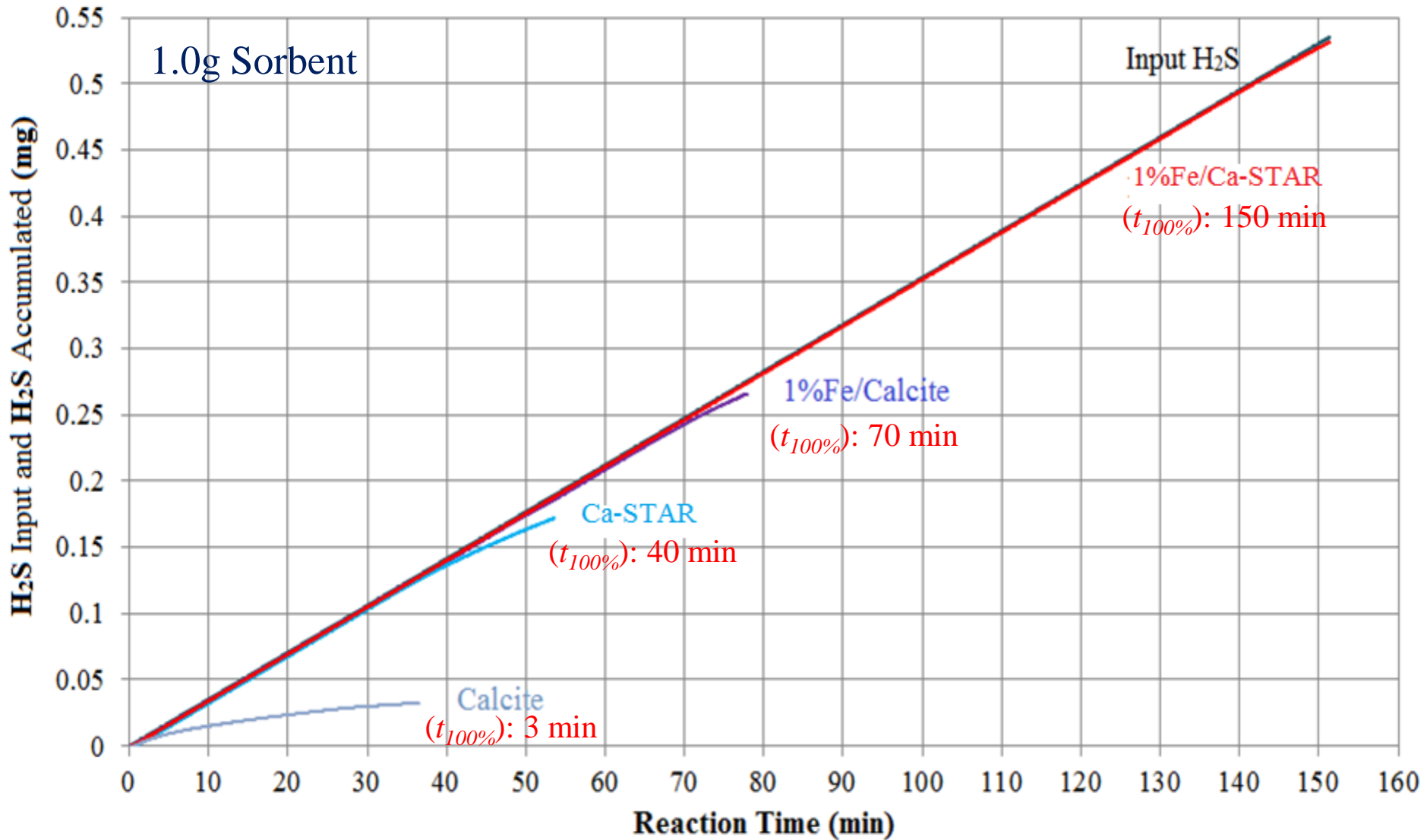
➡ Iron Impregnation => Reactivity ↗

Effect of quantity of the sorbent



➔ Quantity of sorbent ↑ => $t_{100\%}$ or Reactivity ↑

Compare reactivity of the sorbent with Calcite



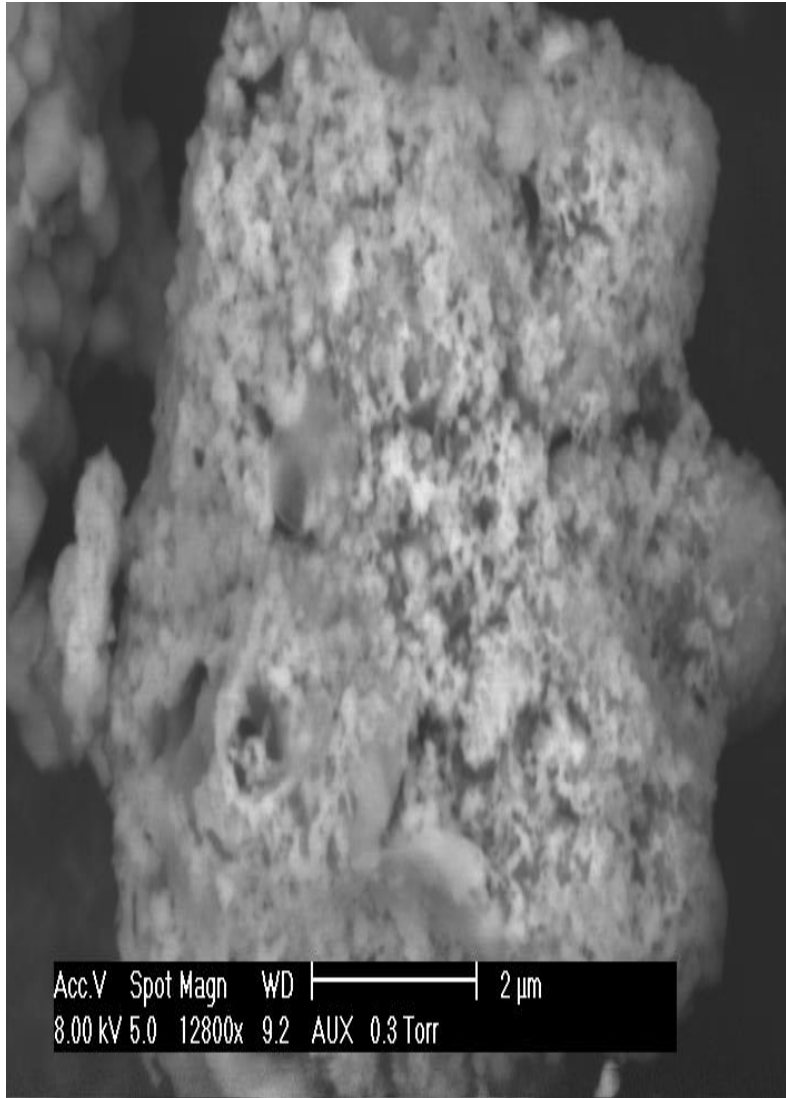
- Reactivity:



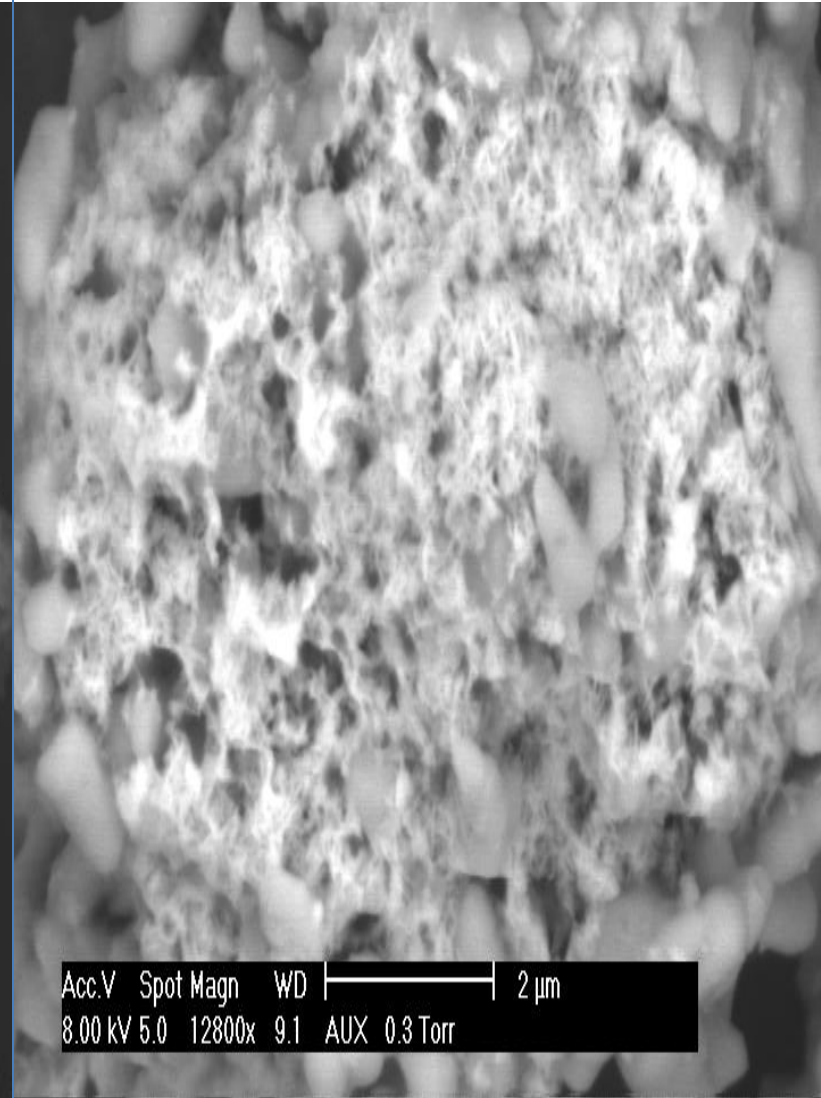
+ Raw Material: Ca-STAR > Calcite

+ Iron Impregnation: Ca-STAR > Calcite

SEM: 1%Fe/Ca-STAR

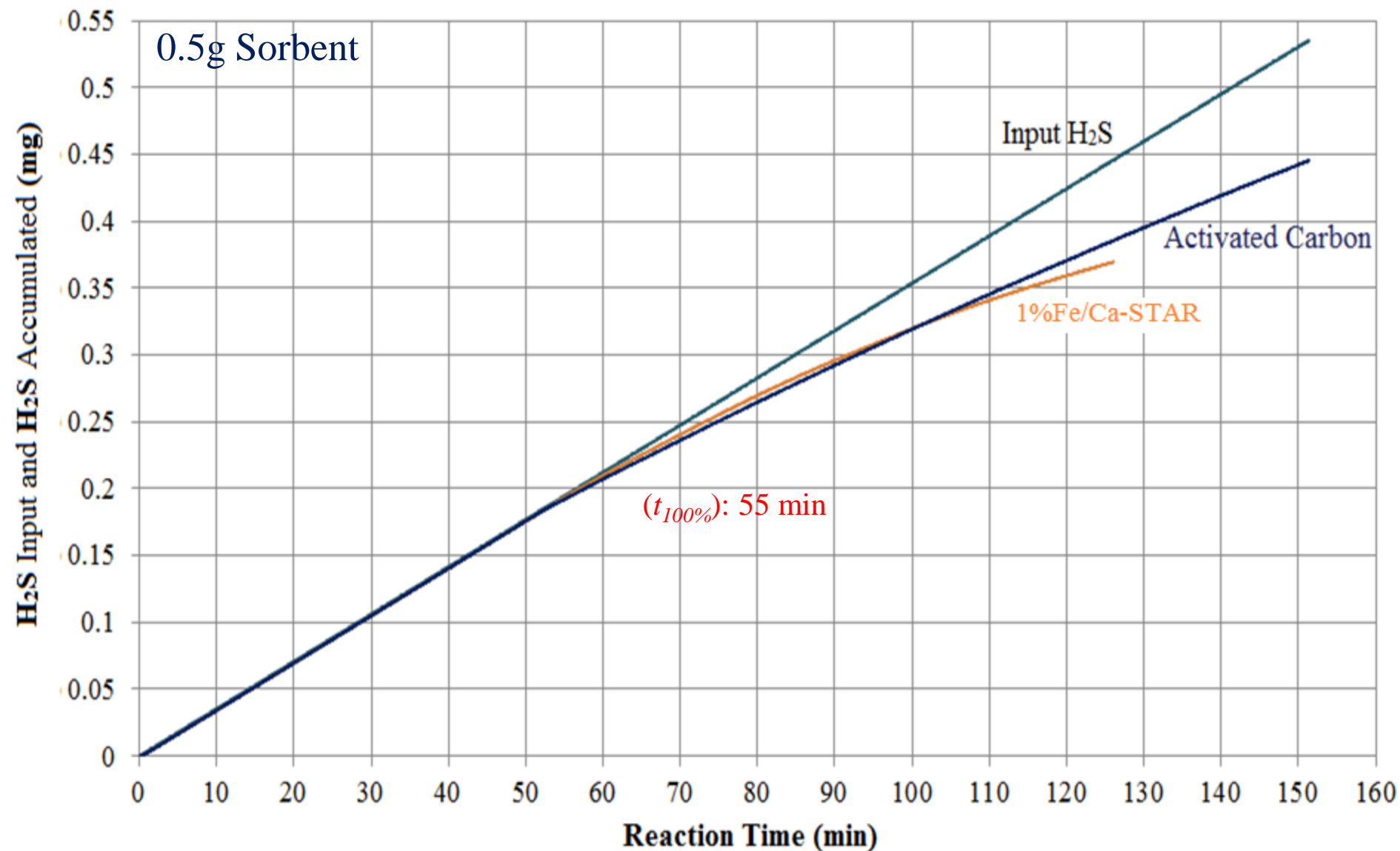


SEM: 1%Fe/Calcite



Ca-STAR : Impurities of metals, good dispersion of Fe
Smaller Fe particle ⇔ Better Reactivity

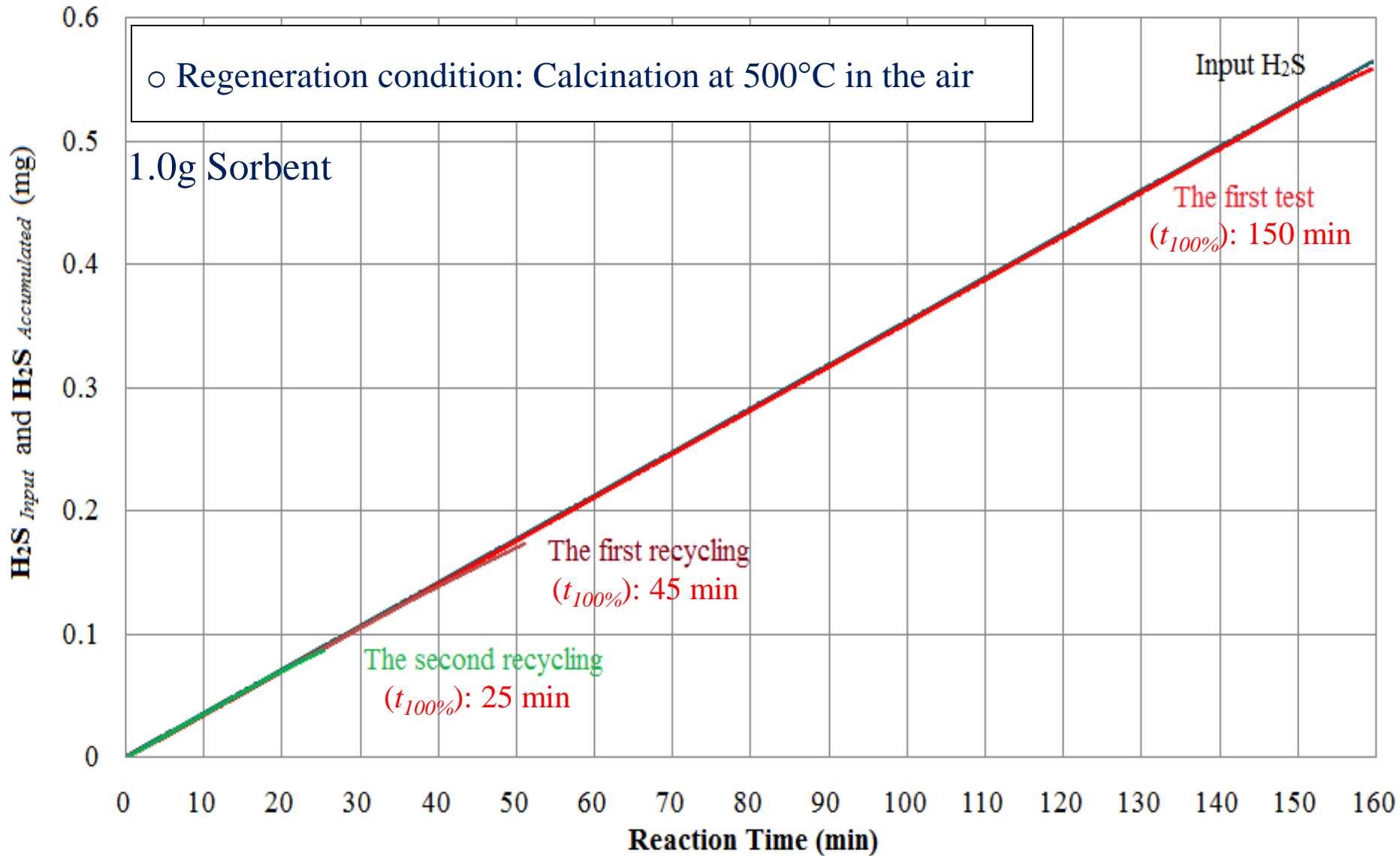
Compare reactivity of the sorbent with Activated Carbon



➔ Reactivity:

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

Recycling test



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 H₂S treatment.
- 500°C 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 H₂S: partially reversible

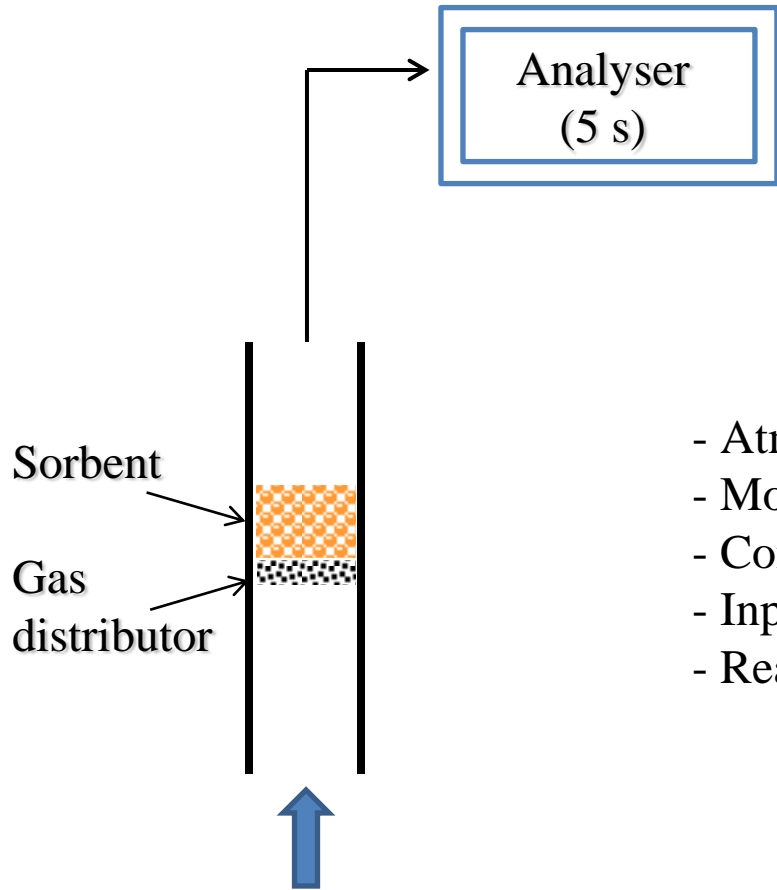


Thank for your attention!

Hydrogen Sulfide Treatment



Other data of the experiments



Calculation of accumulated H_2S (mg)

$$m_{\text{H}_2\text{S}} = \frac{P \cdot Q \cdot M}{10^6 \cdot R \cdot T} (c_0 \times t_s - \int_0^{t_s} c(t) dt)$$

- 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)

- 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