

# Testing the Reactivity of CO<sub>2</sub>-H<sub>2</sub>S Gas Mixtures with Cd<sup>2+</sup> Aimed at Environmental Remediation Techniques Development

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## INTRODUCTION

The release of dangerous contaminants to the atmosphere due to human activities is an extensively discussed issue (Oelkers & Cole 2008). The economic development often underestimated the consequences of a massive release of substances into the environment. Politic tried to introduce some regulation but in the case of CO<sub>2</sub> emissions, the introduction of the “Carbon Tax” and the other attempts were not successful (Spash 2010).

The possibilities offered by the introduction of a new economic development model such as the circular economy rely on the effort by the academy to assess a public knowledge able to promote the innovation aimed at recycle atoms (Stahel 2016). In this framework, many laboratories and industries all over the world are assessing the effectiveness of different storage options to achieve a mitigation of the CO<sub>2</sub> concentration increase in a realistic scenario where the emissions did not slow (Oelkers & Cole 2008). The common problem between the different strategies is the high cost of the remediation process (Rubin 2008, Ragnheidardottir et al. 2011). In this context, we present an experimental study to determine the reactivity of CO<sub>2</sub>-H<sub>2</sub>S gas mixtures with Cd-bearing aqueous solutions, a dangerous heavy metal. The assessment of a solid kinetic database together with the design of specific catalysts could open new frontiers in the field of the environmental remediation to pollution generated by human activities.

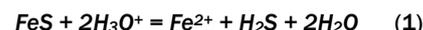
## MATERIALS AND METHODS

The experiments were conducted at room temperature (20-22 °C) using: (i) CdCl<sub>2</sub> and concentrated hydrochloric acid (37% by weight) were provided from

Sigma Aldrich (ACS Reagent), (ii) FeS sticks (also from Sigma Aldrich) were grinded using an agate mortar, (iii) basaltic glass rocks were collected in Iceland near to Eyjafjallajökull volcano (Sólheimajökull: 63°31'48.9" N and 19°22'15.2" W) and finely grinded using an agate mortar, (iv) single natural calcite crystals (Iceland Spar, Mexico) were cleaved to achieve the required mass.

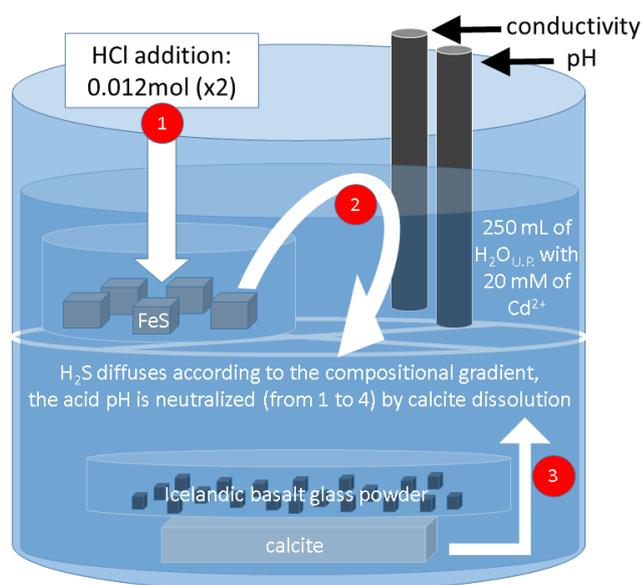
The system was equipped analogously to figure 1, we inserted in a borosilicate glass reactor (500 mL): the calcite crystal on the bottom (0.0375 mol), a glass vessel containing the basalt powder on the top of calcite (2 g), a glass vessel (lifted on the top of the reactor) was used to contain the FeS powder (0.0375 mol) and HCl injections (2 injections, 0.012 mol each) were performed directly in this vessel. The system was filled with 250 mL of

Ultrapure water (18.2 MΩ·cm), where CdCl<sub>2</sub> was previously dissolved with a final concentration of 20 mM. The addition of a strong acid to iron sulfide induces the dissolution of the mineral thus the formation of hydrogen sulfide (as a gaseous phase dissolved in water) according to reaction 1 (Stumm & Lee 1960):



The low pH originated by the addition of HCl induces the dissolution of calcite which produces a neutralization of the system pH as a consequence of the release of carbonate ions.

We continuously monitored the evolution of pH and conductivity in the system using a SevenExcellence S470 system from Mettler Toledo, the first two hour of the experiments we recorded an experimental point every minute after



**fig 1.** Experimental design of the experiments performed to test the reactivity between dissolved H<sub>2</sub>S-CO<sub>2</sub> gas mixtures and Cd-bearing aqueous solutions. The process under study consists of three phases: (1) the addition of HCl triggers the dissolution of FeS and the formation of H<sub>2</sub>S. (2) The chemical gradients of the species allow the reaction of formation of sulfides to take place and (3) the dissolution of calcite produces the neutralization of pH and the supersaturation of the solution with respect to carbonate minerals.

**palabras clave:** H<sub>2</sub>S, CO<sub>2</sub>, Cd, Remediación Medioambiental

**key words:** H<sub>2</sub>S, CO<sub>2</sub>, Cd, Environmental Remediation

this period we started measuring every 20 minutes. Experiments last up to 18 days. After the reaction time, the liquid phase was gently removed and analyzed with visible spectroscopy (Aquamate Vis, ThermoScientific). The solid samples were collected from the different vessels, after they were filtered and washed with 5 mL of ultrapure H<sub>2</sub>O and dried at room temperature before they were analyzed by x-ray diffraction (PANalytical X'Pert Pro, Cu-K $\alpha$ ) and scanning electron microscopy (SEM, JEOL 6610 LV with EDX microanalysis), after metallization with gold (Sputtering Balzers CPD 030).

The hazard induced by using hydrogen sulfide, a dangerous chemical (Reiffenstein et al. 1992), was minimized by carrying out the experiments into a glove box (PlasLabs 850-NB with a total volume of 498 L) where an atmosphere of pure CO<sub>2</sub> was produced.

The effective formation of H<sub>2</sub>S inside the glove box was qualitatively demonstrated using filter paper soaked with a lead acetate solution, Pb(CH<sub>3</sub>COO)<sub>2</sub>, it turns black in presence of hydrogen sulfide (Gilardi & Manganelli 1963).

## RESULTS AND DISCUSSION

The experiments began by injecting twice 1 mL of concentrated HCl into the FeS vessel. The pH and conductivity profiles vs time are reported in figure 2. We can observe the strong pH decrease and conductivity increase produced as a

consequence of these injections. After the initial variation the system reached the boundary values within the first 12 hours (pH= 1.45 and conductivity = 22102  $\mu$ S/cm), these extreme conditions were mitigated by precipitation of greenockite (visually observed by the development of an intense yellow color) and dissolution of calcite to form (Cd,Ca)CO<sub>3</sub> solid solution.

The experiments that we carried out demonstrated that H<sub>2</sub>S and CO<sub>3</sub><sup>2-</sup> can be used to precipitate cadmium ions from an aqueous solution. The XRD analysis on the final products that we isolated from the different vessels showed different phases: (i) in the FeS vessel we observed a mixture of greenockite (CdS), troilite (FeS) and weak signals from goethite (FeOOH), (ii) in the basalt glass vessel we identified greenockite, and signals from the initial substrate, (iii) on the bottom of the reactor we also identified greenockite and otavite-calcite solid solution, (Cd,Ca)CO<sub>3</sub>.

The solubility products of greenockite (Daskalakis & Helz 1992) and (Cd,Ca)CO<sub>3</sub> solid solutions (Prieto et al. 2003) are very low (less than 10<sup>-40</sup>), the precipitation of these phases could constitute an effective reaction to reduce the content of cadmium in contaminated water by using waste gas mixtures produced by geothermal power plants. The concentration of Cd<sup>2+</sup> in solution, after the experiment, was considerably lower (3.3 mM) than the initial value (20 mM) demonstrating that about 85% of the initial amount of Cd<sup>2+</sup> was removed from the aqueous phase

due to the mineralization process.

The combination of different remediation techniques in a unique process could bring to cheaper decontamination systems that could preserve the environment from the release of chemicals due to human activities. In this framework is crucial the development of reliable kinetic and thermodynamic data for processes that could constitute the basis for new and more efficient remediation techniques.

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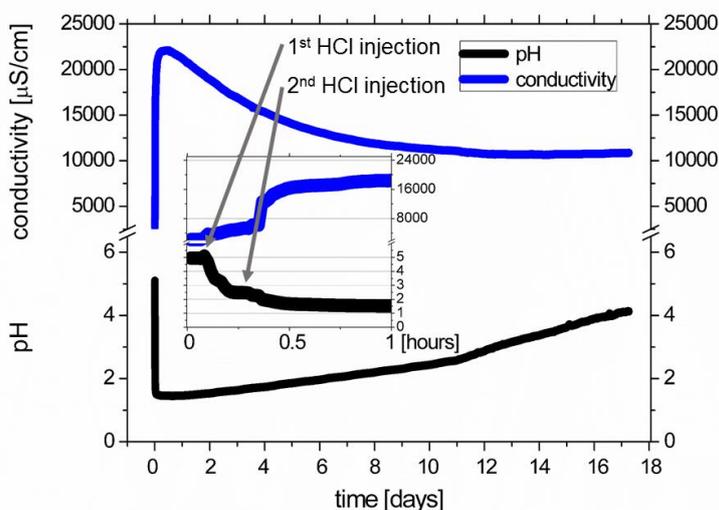


fig 2. Conductivity and pH profiles obtained during the continuous monitoring of the system presented.