EFFECTS OF CO$_2$ LEAKAGES FROM STORAGE SITES ON THE QUALITY OF POTABLE GROUNDWATER

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SUMMARY
The goal of this work is to study changes caused on the quality of potable groundwater, due to CO$_2$ leakages from underground storage sites. The mineralogy of a well-sorted silica sand is modified by the controlled precipitation of heavy metals (Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd), and flow-through experiments are performed on two sand-packed columns. The first column is co-injected with CO$_2$ and water, while the other column is injected with water. The concentration of heavy metals in effluents is measured with atomic absorption spectroscopy (AAS) and the sand is characterized before and after the experiments by SEM-EDS, XPS and AAS.

INTRODUCTION
To mitigate the greenhouse gas effect due mainly to the combustion of fossil fuels and CO$_2$ emissions in the atmosphere, the storage of CO$_2$ in deep underground reservoirs has been suggested as a long-term and safe solution. Nevertheless, environmental policies and regulations are under development aiming at monitoring eventual changes caused on the groundwater of shallow aquifers by leakages of CO$_2$ from storage sites. Results show that elevated CO$_2$ levels in freshwater aquifers can increase the concentration of trace metals to undesirable levels [1, 2, 3].

MATERIALS AND METHODS
First, the mineralogy of silicate sand was modified by an aqueous solution of nitric salts of metals (Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd). In order to stimulate the co-precipitation of metal oxides/ hydroxides/ complexes on the sand, pH was increased in a controlled manner by adding slowly 1M NaOH under stirring. The identification and quantitative determination of the metal content in the sand was done with Scanning Electron Microscope equipped with X-ray Energy Dispersive Spectroscopy (SEM-EDS), X-ray photoelectron spectroscopy (XPS), and atomic absorption spectroscopy (AAS). The modified sand was packed into two fixed-bed PVC columns. In the one column, gas CO$_2$ and water were co-injected while only water was injected in the other column (control test). The pressure drop across each phase was recorded continuously with a data acquisition card installed in the host computer. Water effluent samples were collected periodically to measure the pH, electrical conductivity and quantify precisely the metal cation concentration by atomic absorption spectroscopy (AAS). The whole experiment lasted for two months.

RESULTS AND DISCUSSION
The fast CO$_2$ dissolution in water is reflected in a rapid reduction of pH which tends asymptotically to stabilize, indicating that equilibrium has been established and CO$_2$ concentration has reached the solubility limit (Figure 1). The rapid decrease of pH (Figure 1) is responsible of the rapid increase of the concentrations of certain metals in the effluent of CO$_2$ column by one order of magnitude compared to those of the effluent of control (H$_2$O column) test (Figure 2). The aforementioned results were also confirmed with mineralogical characterization of the sand surface with SEM-EDS, XPS and AAS. Especially, XPS analysis indicated the presence of metals on sand grains either as oxides/ hydroxides/ complexes chemically bonded to oxygen atoms of SiO$_2$ or as free/hydrated cations. The metal concentration
in sand, before and after the completion of the flow experiments, was measured precisely with AAS (Table 1).

**Table 1.** Metal content (mg/g-sand) in sand before and after flow tests, measured by AAS.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
<th>Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial sand</td>
<td>0.07</td>
<td>0.06</td>
<td>0.22</td>
<td>0.03</td>
<td>0.05</td>
<td>0.10</td>
<td>0.06</td>
<td>0.07</td>
</tr>
<tr>
<td>H₂O sand</td>
<td>0.05</td>
<td>0.05</td>
<td>0.25</td>
<td>0.03</td>
<td>0.03</td>
<td>0.11</td>
<td>0.05</td>
<td>0.0005</td>
</tr>
<tr>
<td>CO₂ sand</td>
<td>0.02</td>
<td>0.01</td>
<td>0.21</td>
<td>0.006</td>
<td>0.001</td>
<td>0.003</td>
<td>0.001</td>
<td>0.00</td>
</tr>
</tbody>
</table>

The residual concentration of most metals in the sand of CO₂ column was negligible (Table 1). Regarding the two trivalent heavy metals (Cr³⁺ and Fe³⁺), a fraction of Cr was mobilized (Figure 2a, Table 1), whereas no mobilization of Fe was detected in the sand of CO₂ column (Table 1). The monitoring of the selective metal mobilization in the groundwater of shallow aquifers might be used as a probe for the early warning of CO₂ leakages from deep storage sites.

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**REFERENCES**

