ENVIRONMENTAL IMPACTS OF CO_2 LEAKAGES FROM STORAGE SITES ON THE QUALITY OF POTABLE GROUNDWATER OF SHALLOW AQUIFERS

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ABSTRACT

Leakages of CO_2 from storage sites to shallow aquifers could have adverse impacts on the groundwater quality. A well-sorted silica sand is modified by the pH-controlled precipitation of eight metals (Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd). Carbon dioxide and water are co-injected in a fixed-bed column packed with the modified sand, and the metal concentration in effluent is measured with atomic absorption spectroscopy (AAS). Mineralogical analysis of sand before and after the flow tests is done by Scanning Electron Microscopy – X-ray Energy Dispersive Spectroscopy (SEM-EDS), X-ray Photoelectron Spectroscopy (XPS), and AAS. Due to continuous CO_2 dissolution, the release of Mn, Ni, Cu, Zn, Co is enhanced profoundly, the release of Cr increases moderately, the Cd dissolution accelerates, whereas Fe is strongly bonded as goethite and does not dissolve almost at all. The inverse modeling of the flow test results with a model coupling the mass-transfer with reactive processes enables us to quantify the dynamics of metal release in terms of equilibrium and kinetic desorption parameters, estimated under realistic flow conditions.

INTRODUCTION

There is always the risk of CO_2 leakages from the deep storage reservoir toward overlying and relatively shallow aquifers of potable groundwater [1]. Results show that elevated CO_2 levels in freshwater aquifers can mobilize trace metals (e.g. Cd, Pb, etc) from the solid phase and increase their concentration in groundwater to undesirable levels [2]. During the last years, significant efforts have been done on elucidating the role of CO_2 leakages from storage sites on the perturbation of subsurface geochemistry and the subsequent release of metal from aquifer minerals [1,3]. Systematic batch experiments have revealed that the CO_2 influx at room temperature and pressure can mobilize significant amounts of metals from a variety of aquifer host rocks [4,5]. Field-scale tests and numerical modeling of CO_2 leakage from storage sites are commonly used to predict

the acidification processes and mineral alterations, and assess the risks associated with the release of contaminants and deterioration of groundwater quality [6,7].

MATERIALS AND METHODS

The mineralogy of a silicate sand was modified uniformly by the pH-controlled precipitation of metal oxides on sand grains. First, an aqueous solution of nitric salts of Cr, Co, Ni, Zn, Cd, Cu, Mn, Fe was prepared. Thereafter, 1L of the aqueous solution was mixed with 700 ml of well-sorted (grain sizes~125-250 μm) commercial silicate sand in a large flask. In order to stimulate the co-precipitation of metal oxides / hydroxides / complexes, the pH was increased slowly by adding dropwise 1M NaOH solution under continuous stirring. Then the system was left to equilibrate and the procedure was repeated for one week until the pH was stabilized in the range 7.7-8.0. Afterwards, the liquid phase overlying the sand was removed and the residual solid phase was placed inside a programmable oven and left to dry for one night at $120^{\circ}C$.

Scanning Electron Microscope equipped with X-ray Energy Dispersive Spectroscopy (SEM-EDS) was used to confirm the presence of the eight (8) metals (Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd) on the surface of sand grains. The chemical state of the metals in the surface of sand grains was identified with X-ray photoelectron spectroscopy (XPS). Accurate measurement of the metal concentration was done by digesting the sand with dense nitric acid and analyzing the liquid phase with atomic absorption spectroscopy (AAS).

The modified sand was packed into two fixed-bed PVC (polyvinyl chloride) columns of diameter D=0.03 m and length L=0.4 m. The columns were evacuated and saturated with distilled and de-aerated water. In the one column, both water and gas CO_2 were co-injected, and in the other one only water was injected (control experiment). A multi-channel peristaltic pump was used to inject water at a constant flow rate q_w=0.3 ml/min, and a gas mass flow controller was used to supply bottled CO_2 at a constant flow rate, q_g=2 ml/min (Fig.1). Water effluent samples were collected periodically to detect the pH, the electrical conductivity and measure precisely the metal cation concentration by atomic absorption spectroscopy (AAS). The release of metals was modeled by a two-site sorption model [8]. It is assumed that the CO_2 dissolution rate is governed by the mass-transfer rate from the gas to the aqueous phase while the reactions are so fast that the concentration of ionic species (e.g. carbonate, bicarbonate, protons) is controlled by the equilibrium constants. Since the flow rate of CO_2 is one order of magnitude higher than that of water we assume that the CO_2 mass-transfer from gas to aqueous phase has negligible effect on the steady-state flow regime so that the gas / water flow velocity and water saturation are assumed constant throughout the porous medium. The mass balance of dissolved CO_2 is formulated for 1-dimensional advective-dispersive flow with mass-transfer at the gas/water interface. The 2-sorption model is incorporated into the transient mass balances for dissolved, and adsorbed metals whereas the various parameters (e.g. longitudinal dispersivity) are obtained from earlier studies [9]. The resulting system of partial differential equations is incorporated into an inverse modeling scheme where the numerically calculated transient response of each metal concentration in the column

outlet matches the experimentally measured ones in effluents so that the metal desorption parameters (partition coefficient, fraction of sites of type 1 for equilibrium desorption, kinetic constant of sites of type 2 for non-equilibrium desorption) are estimated [8].

RESULTS AND DISCUSSION

The CO_2 dissolution in water is reflected in the increase of conductivity (Fig.2a) and the rapid reduction of pH (Fig.2b). The pH tends slowly to an asymptotic value (~3.6) indicating that equilibrium has been established and the concentration of CO_2 has reached its solubility limit (Fig.2b). The reduction of pH stimulates the release of metal cations from solid hydroxides and/or oxides. The concentrations of certain metals (Mn, Ni, Cu, Zn) in the effluents of the 2-phase column (Fig.3a) increases rapidly and may become several orders of magnitude higher than those of the effluents of 1-phase column (Fig.3b). Cd dissolves easily and is the only metal detected at high concentrations in the effluent of the control test (1-phase column, Fig.3b), whereas the reduction of pH results in the increase of its dissolution rate in the CO_2 injection test (2-phase column, Fig.3a). For the majority of the metals (Cr,Mn,Ni,Cu,Zn,Cd) their release rate decreases gradually and their concentration tends to very low values at late times (Fig. 3a), mainly because of the low residual metal concentration in the solid phase. Among the two trivalent heavy metals (Cr^{3+} and Fe^{3+}), only Cr was detected at respectable concentrations (Fig. 3a).

SEM-EDS analyses confirmed the presence of all metals on the surface of sand grains before the experiments (Fig.4a). After the completion of flow tests, only Fe and Cr were detected in the sand of the 2-phase column while, with the exception of Cd, almost all other metals were detected at respectable concentrations in the sand of the 1-phase column (Fig.4b). XPS analysis indicated the presence of metals in the initial sand, primarily as oxides (Cr_2O_3, MnO_2, NiO, CuO, ZnO) but also as hydroxides (FeOOH-goethite, $Cd(OH)_2$) that have precipitated on the surface of sand grains. The observed concentrations of metals in effluents (Fig.3) are consistent with the initial and residual concentrations of metals measured precisely with AAS (Fig.4b). One metal (Cd) vanished from the sand almost totally, one metal (Fe) was geochemically trapped as goethite and was not mobilized almost at all, whereas the CO_2 dissolution and water acidification were responsible of the significant mobilization of certain metals (Cu, Ni, Zn, Mn, Co), and moderate mobilization of another one metal (Cr) (Fig.4b).

The physicochemical properties of the fluid system were obtained from literature, and the transport properties of the sand columns were determined in earlier studies [9]. The sensitivity of partition coefficients to pH was quantified with batch tests. The parameters of the 2-site sorption model (K_{di0}, f_i, a_i) were estimated (Fig.5), separately for each metal with inverse modeling of the transient variation of metal concentration in the effluents of the 2-phase column. The ranking of desorption rate coefficients, a_i, in descending order is Cd>Cu>Ni~Cr>Mn~Zn (Figure 5a) and shows the relative rate of metals release at conditions far from equilibrium. The partition coefficients at neutral conditions, K_{di0}, estimated from continuous flow experiment are in full qualitative agreement with those estimated from batch experiments (Fig.5b). Therefore, the ranking of partition

coefficients (pH=7) in descending order is Co>Cd>Fe>Mn>Ni>Zn>Cr>Cu (Fig.5b) and shows the relative capacity of metals to desorb at neutral conditions. It is evident that the mobilization of Fe was very limited (Fig.4b) and this might be attributed to the strong resistance of goethite to dissolution at acidic conditions.

CONCLUSION

The equilibrium molar concentration of metal cations $[M_{eq}]$ in saturated solutions can be obtained from the solubility product, K_{sp}, of insoluble hydroxides / oxides and pH.[10]. The higher the $[M_{eq}]$ under less acidic conditions (high pH values), the easier the dissolution of metal and the ranking of metal mobility becomes: Mn>Cd>Co>Ni>Zn>Cu>Cr>Fe. This sequence is comparable to that deduced by the values of partition coefficient, K_{di0}, estimated from the continuous flow test (Cd>Mn>Ni>Zn>Cr>Cu, Fig.5b). However, the ranking of metal mobility changes when their non-equilibrium kinetic coefficient, a_i (Cd>Cu>Ni~Cr>Mn~Zn, Fig. 5a), is accounted for. Therefore, the parameters estimated from continuous flow experiments enable us to give a full quantitative interpretation of the observed dynamics of metal release at conditions simulating realistically the flow regime and regional geochemistry.

ACKNOWLEDGEMENTS

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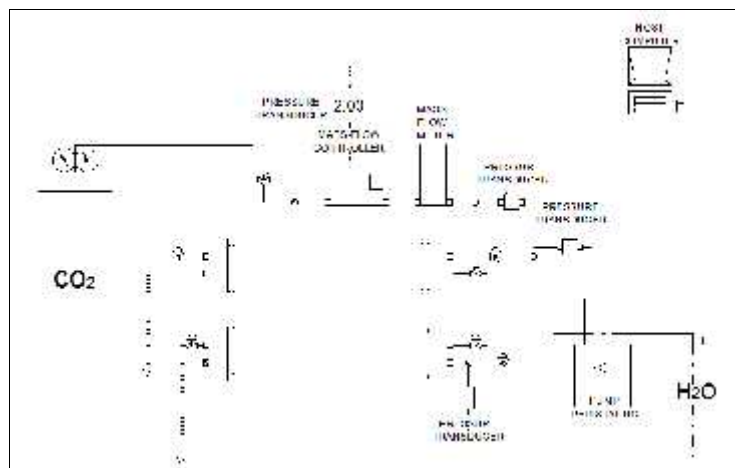10. Bradl, H. *Heavy metals in the environment;* Amsterdam, The Netherlands: *Elsevier* (2005).

Figure 1. Schematic diagram of experimental setup showing the 2-phase (upper) and 1-phase (lower) columns, the pump, the water tank, the bottled CO_2, and the instrumentation and control systems.
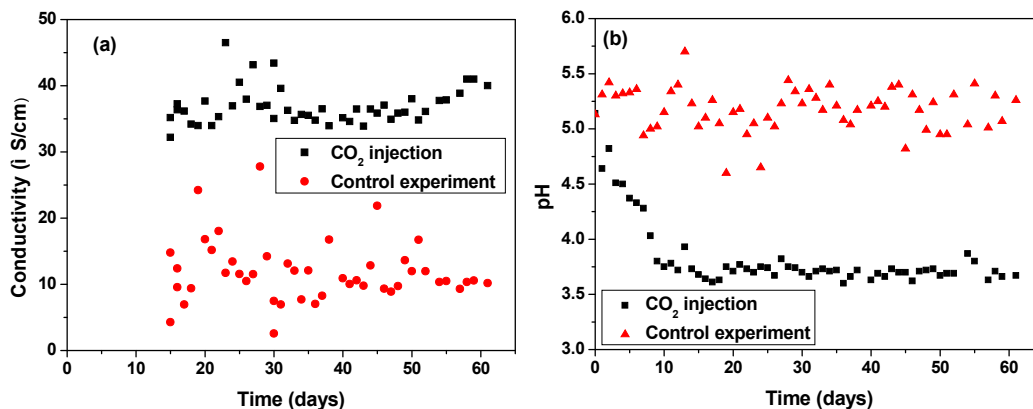

Figure 2. Measurement of the transient variation of (a) conductivity and (b) pH in column effluent.
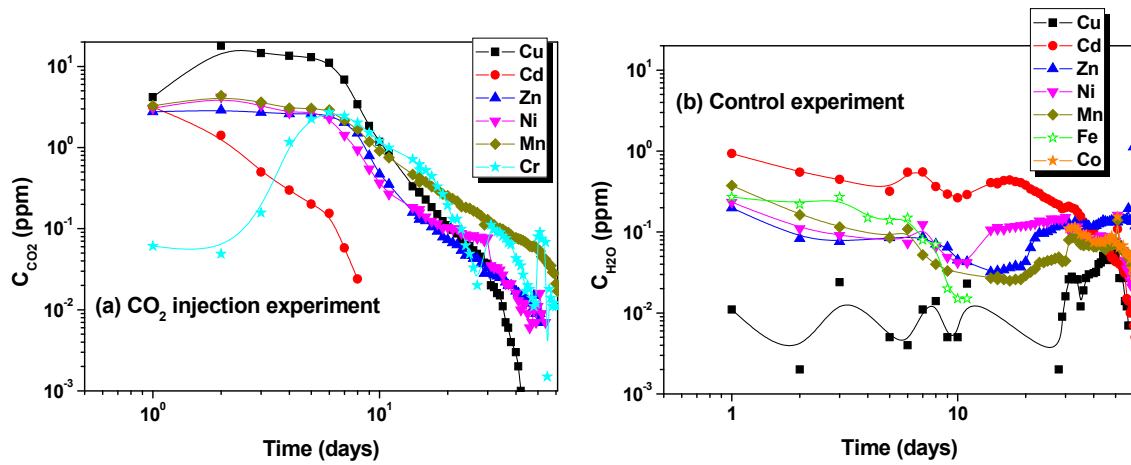
Figure 3. Measurement of the transient response of metal cation concentration in the effluent of (a) 2-phase column, (b) 1-phase column.
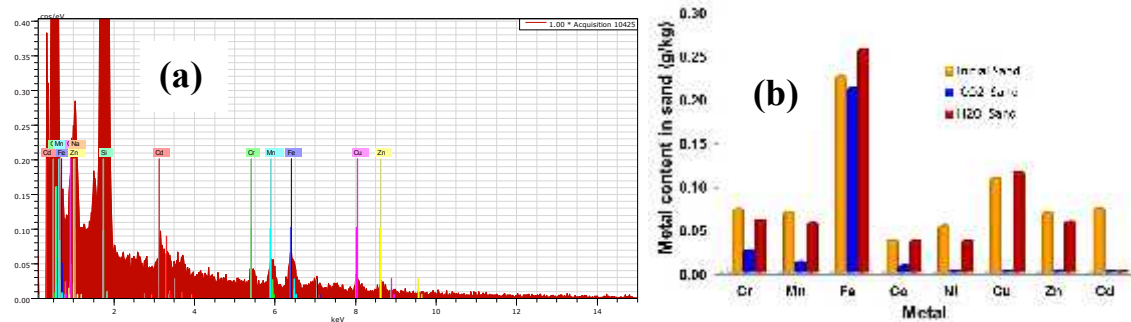

Figure 4. (a) Stoichiometric analysis of the sand surface with energy dispersive x-ray spectroscopy (EDS) showing the coexistence of all metals before the experiment, (b) Comparison of metal concentrations in sand before and after experiment, measured with atomic absorption spectroscopy (AAS).
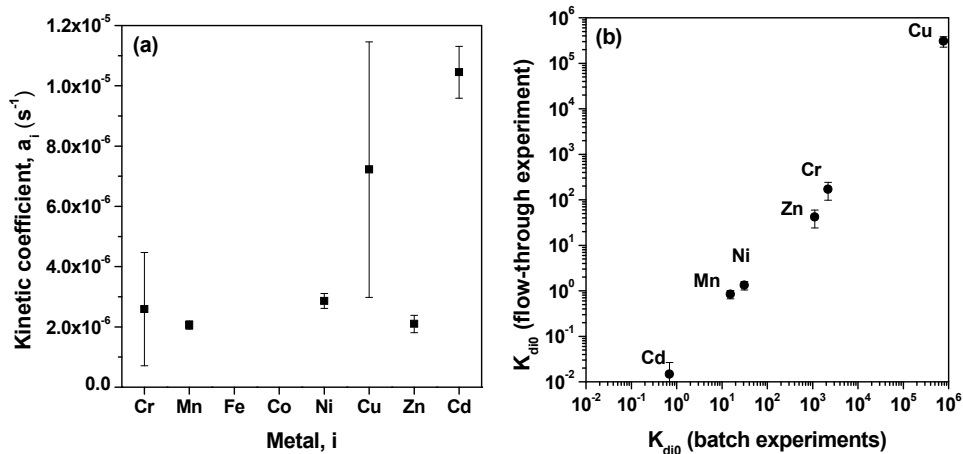

Figure 5. Metal mobilization parameters estimated by inverse modeling of the transient variation of metal concentration in the effluent of 2-phase soil column (Fig. 2): (a) desorption rate coefficient; (b) fraction of equilibrium sites; (c) partition coefficient at neutral conditions.