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Experimental assessment of CO$_2$-mineral-toxic ion interactions in a simplified freshwater aquifer: Implications for CO$_2$ leakage from deep geological storage

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Abstract

The possible intrusion of CO_2 into a given freshwater aquifer due to leakage from deep geological storage involves a decrease in pH, which has been directly associated with the remobilization of hazardous trace elements via mineral dissolution and/or via desorption processes. In an effort to evaluate the potential risks to potable water quality, the present study is devoted to experimental investigation of the effects of CO_2 intrusion on the mobility of toxic ions in simplified equilibrated aquifers. We demonstrate that remobilization of trace elements by CO_2 intrusion is not a universal physicochemical effect. In fact goethite and calcite, two minerals frequently found in aquifers, could successfully prevent the remobilization of adsorbed Cu(II), Cd(II), Se(IV) and As(V) if CO_2 is intruded into a drinking water aquifer. Furthermore, a decrease in pH resulting from CO_2 intrusion could reactivate the adsorption of Se(IV) and As(V) if goethite and calcite are sufficiently available in underground layers. Our results also suggest that adsorption of cadmium and copper could be promoted by calcite dissolution. These adsorbed ions on calcite are not remobilized when CO_2 is intruded into the system, but it intensifies calcite dissolution. On the other hand, arsenite As(III) is significantly adsorbed on goethite, but is partially remobilized by CO_2 intrusion.

1   Table of Contents Graphic

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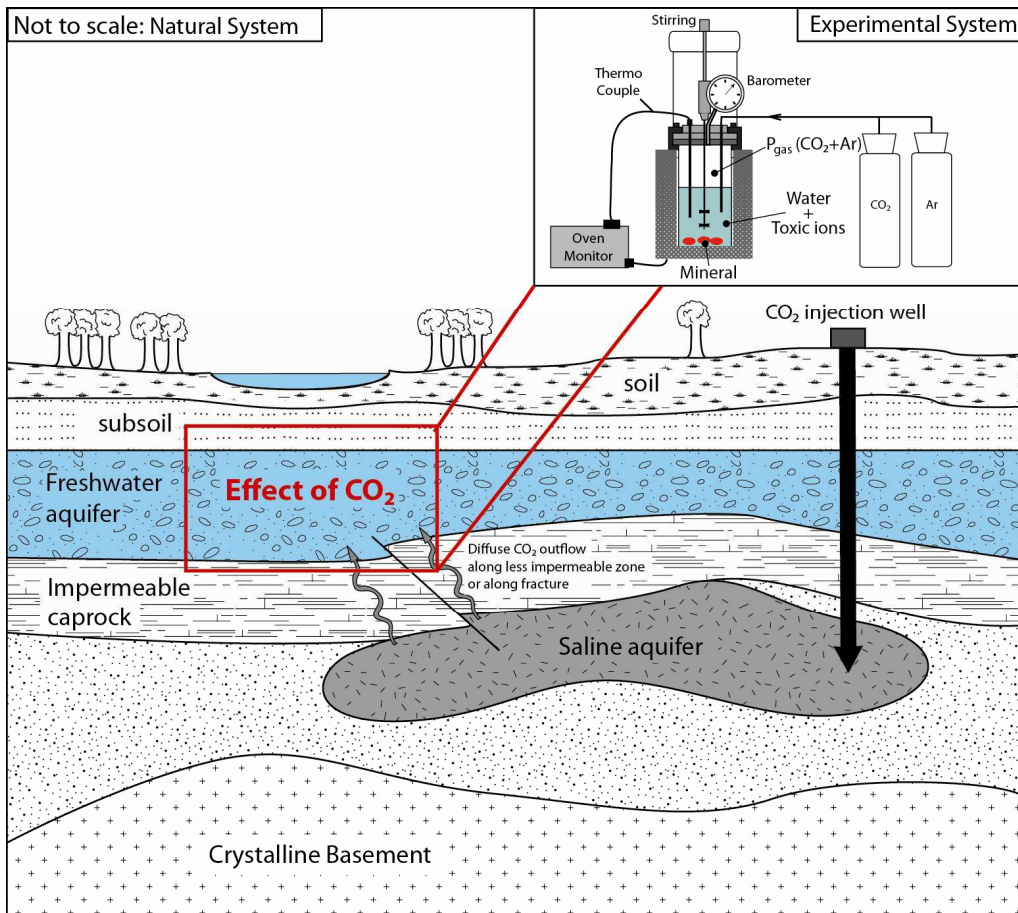
Introduction

Unregulated CO_2 emissions into the Earth's atmosphere (about 22×10^9 ton CO_2/year), caused mainly by fossil fuel combustion, have led to concerns about global warming. To maintain the atmospheric CO_2 level below 500 ppm, CO_2 emissions will have to be stabilized at current levels, although they are forecast to double over the next 50 years (1). Capture from individual industrial sources and long-term geological storage are realistic and available ways of reducing CO_2 emissions because large volumes of this gas can be stored in various deep geological formations (2-5). However, CO_2 injection into porous media (deep geological formations) can significantly modify their storage properties. For example in brine aquifers, nucleation-growth and/or dissolution of minerals are envisaged and these reactions can be enhanced by high in-situ temperatures (80-110°C) and pressures (100-400 bar). Toxic elements (e.g. metalloids or heavy metals) could be liberated or released by native mineral dissolution reactions as measured and/or simulated in some studies (6-8); subsequently, dissolved or released ions could be sequestered by nucleation-growth of secondary mineral phases (9-10). In summary, several physicochemical reactions at fluid-rock interfaces have been envisaged and they need to be studied in detail in the coming years as claimed by various recent studies (5, 8-13).

The deep geological formations considered (e.g. brine aquifer) are always isolated by impermeable layers, so-called caprock formations. Unfortunately, CO_2 leakage from storage sites to higher formations (e.g. drinking water sources) by diffusion through less impermeable zones or transport along (micro-) fractures could be a potential risk in the long term, possibly aggravated by seismic activity and micro-seismicity (14). In this hypothetical case, CO_2 dissolution could influence the mobility and/or retention of hazardous trace elements (e.g. heavy metals and/or metalloids) contained in native aquifer minerals, as recently investigated by reactive transport simulations (7, 15-18), laboratory experiments (19-22) and field tests

(e.g. MSU-ZERT field site) (23-24). In this way, various trace elements such as Cd, Pb, Zn, U and As, which can be toxic to humans or wildlife at µg/L-mg/L concentrations, have been predicted to be released by dissolution reactions of native aquifer minerals (15-18). All simulations in these studies have assumed that the intrusion of CO_2 into drinking water aquifers decreases their pH, enhancing the dissolution reactions of native aquifer minerals and consequently remobilizing trace metal species if such metals are contained in the minerals. Unfortunately, few experimental data are available in the literature in order to challenge or support such predictions. Moreover, the sorption/desorption processes of trace elements (fast or instantaneous processes at the mineral-fluid interfaces) are also rarely simulated because it is difficult to combine them with dissolution-precipitation reactions in reactive transport simulations (16). It should be noted that desorption/adsorption via surface complexation is possibly the most important process controlling the fate of toxic trace elements mobilized by CO_2 leakage (7, 15).

For the above reasons, the present study is devoted to experimental investigation of the effects of CO_2 intrusion on the mobility/retention of toxic ions in simplified equilibrated aquifers (drinking water sources). In our study, "simplified equilibrated aquifer" means a synthetic solution enriched with one or two metal(loid) ions equilibrated for 24h with a single or binary mineral system at 20°C and 10 bar of argon prior to CO_2 injection (8 bar). In this context, six metal(loid) ions ((Cd(II), Cu(II), Se(IV), Se(VI), As(III) and As(V)) and two widespread minerals (goethite, calcite and goethite-calcite composite) were investigated. A schematic illustration of this experimental study with emphasis on CO_2 leakage from deep geological storage is provided in Figure 1. Goethite and calcite were chosen because of their abundance in nature as minerals (abiotic origin) and biominerals (biotic origin). Both minerals can co-exist in several terrestrial environments such as deep geological formations, aquifers (drinking water sources), soils and aerosols, playing an important role in the fate and transport

of several metalloid and heavy metal trace elements and organic molecules at the mineral-fluid interfaces (25-29). Finally, it should be noted that various suspensions were withdrawn from the reactor before and after injection of CO_2 in each experiment or run, in order to monitor the pH and ion concentration ([Ca], [Fe], [Na], [As], [Se], [Cd] and [Cu]) ex-situ as a function of time (up to 48 hours). This allows a simple macroscopic evaluation of element transfer at the mineral-solution interfaces, involving mineral dissolution and/or retention/mobility of adsorbed toxic ions related to the intrusion of CO_2 in the system.

Materials and methods

Minerals

Pure goethite, pure calcite and a goethite-calcite composite were synthesized as mineral analogues for a given simplified potable aquifer. In this experimental study powdered and high-purity minerals were used in order to increase their surface reactivity and also to identify/quantify clearly their physicochemical affinity with investigated toxic ions interacting in CO_2-poor and CO_2-rich solutions as schematically illustrated in Fig. 1. A brief description of these mineral syntheses is provided in the following paragraphs.

Goethite: Low acicular goethite with a high specific surface area ($130m^2/g$) was synthesized by placing 1mol of NaOH and 0.2mol of $FeCl_3.6H_2O$ in a 2L reaction cell and adding 1L of high-purity water. Constant agitation (400rpm) of the solution and a moderate temperature (30°C) for 24h of reaction were required. For more specific details on the synthesis procedure and goethite characterization refer to Montes-Hernandez et al. (30).

Calcite: Nanosized calcite with a moderate specific surface area ($7m^2/g$) was synthesized via gas-solid carbonation of $Ca(OH)_2$ nanoparticles in a static bed reactor. The specific procedure and fine calcite characterization have already been reported by Montes-Hernandez et al. (31). In short, pure calcite was synthesized by placing 74g of $Ca(OH)_2$ in a 2L reaction cell slightly

1 heated to 30°C and by injecting high-purity CO_2 at 20 bar. Complete $Ca(OH)_2$-to-$CaCO_3$

2 (calcite) transformation was reached after about 24h of reaction.

3 Goethite-Calcite composite: Low acicular goethite intimately adhering to sub-micrometric

4 calcite - so-called goethite-calcite composite - with a high specific surface area ($90m^2$/g) was

5 synthesized via three sequential precipitation reactions: (1) Fast precipitation of nanosized

6 acicular goethite (α-FeOOH) using a high OH/Fe molar ratio (=5); (2) Instantaneous

7 precipitation of portlandite ($Ca(OH)_2$) by adding $CaCl_2$ salt into a goethite alkaline

8 suspension, and; (3) Sub-micrometric calcite precipitation by injecting CO_2 into a goethite-

9 portlandite alkaline suspension. These sequential precipitation reactions and textural

10 characterization of goethite-calcite composite have been specifically described by Montes-

11 Hernandez et al. (32).

12

13 *Aqueous solutions*

14 One liter of high-purity water was used to prepare synthetic solutions enriched with

15 single or double metal(loid) ions by using commercial salts of As(III), As(V), Se(IV), Se(VI),

16 Cd(II) and Cu(II). The chemical compositions of all the salts used are summarized in Table 1.

17 For the double metal(loid) ion solutions, two ions were arbitrarily combined as follows:

18 As(III)-Se(IV), As(V)-Se(VI) or Cd(II)-Cu(II). In all cases, a high initial element

19 concentration of about 50mg/L was also arbitrarily considered. This high concentration is not

20 realistic in a given potable water aquifer, but it leads to a high saturation on the surface of the

21 minerals being investigated through a sorption process prior to CO_2 injection. Moreover, it is

22 easy to quantify the release and/or mobilization of adsorbed ion(s) due to CO_2 intrusion into

23 the system.

24

25

Experiments: CO_2-mineral-toxic ion interactions

2   One liter of single or double metal(loid) ion solution and 3g of calcite, goethite or

3   goethite-calcite composite were placed in a 2L reaction cell. This suspension was

4   immediately stirred using constant mechanical agitation (400 rpm) and argon was also

5   immediately injected at 10 bar in order to simulate pressures of the kind relating to potable

6   water aquifers. After 24h of mineral-ion solution equilibration at room temperature ($\approx$20°C),

7   i.e. assuming that adsorption of a given ion takes place during the first 24h, high-purity CO_2

8   was injected at 8 bar into the dispersion in order to assess the release of adsorbed toxic ions

9   and also to quantify the mineral dissolution, both processes being possibly intensified by

10   intrusion of CO_2 into the system. In all experiments, about 15ml of dispersion were

11   withdrawn from the reactor as a function of time before (from 0 to 24h) and after (from 24 to

12   48h) injection of CO_2. The pH of each sample of suspension was measured at room

13   temperature. The suspensions were then filtered through a 0.2 µm Teflon filter. 10 ml of the

14   resulting filtered solutions were acidified for measurement of [Ca], [Fe], [Na], [As], [Se],

15   [Cd] and [Cu] by inductively coupled plasma optical emission spectrometry (ICP-OES).

16

17   **Results and discussion**

18   As predicted and/or measured, the intrusion of CO_2 within a freshwater aquifer decreases the

19   pH, enhancing dissolution reactions of native aquifer minerals and consequently remobilizing

20   trace metal species if such metals are contained in them. Here, various trace elements such as

21   Cd, Pb, Zn, U and As were predicted to be released by dissolution reactions of native aquifer

22   minerals and/or by fast desorption (7, 15-18). In this experimental study, we provide more

23   specific insights into the remobilization of Se(IV), Se(VI), As(III), As(V), Cd(II) and Cu(II)

24   related to CO_2 intrusion into a pre-equilibrated mineral-metal(loid) ion solution system. The

25   chemical speciation of these six ions in solution before and after injection of CO_2 was

1 determined by using the Phreeqc numerical code (33) in order to understand certain observed

2 behaviors more easily (see below). pH data (measured and calculated) and the dominant

3 species in solution are summarized in Table 1.

4   Goethite as an aquifer mineral analogue

5 Figure 2 displays a compilation of five different adsorption experiments using pure goethite

6 as adsorbent. Here, the adsorbed/remobilized amount of a given metal(loid) ion at the

7 mineral-solution interfaces was normalized with respect to the available surface area in the

8 system ($3g*130m^2/g$). In short, Cd(II), Cu(II) and As(III) are significantly adsorbed on the

9 goethite prior to CO_2 intrusion into the system. A lower adsorption capacity was measured for

10 Se(IV) and Se(VI) in the conditions investigated. After CO_2 intrusion, residual dissolved

11 Se(IV) is largely removed from the solution onto the goethite, i.e. the adsorption process is

12 reactivated by CO_2 intrusion. Conversely, adsorbed Cd(II) and Cu(II) are largely removed

13 from the goethite by CO_2 intrusion into the system. Adsorbed arsenite As(III), which is

14 reputed to be a very highly mobile element, was slightly affected by CO_2 intrusion. In general,

15 the so-called oxyanions were re-adsorbed or slightly remobilized (case: As(III)). However, the

16 heavy metals investigated (Cd(II) and Cu(II)) (single cations) were preferentially remobilized

17 from the goethite. This can be explained by a significant change in the surface charge of the

18 goethite after CO_2 intrusion, assuming that surface charge is strongly dependent on pH, as is

19 widely described in the literature (e.g. 27, 34 and references therein) and on the understanding

20 that the Cu and Cd speciation in solution remains unchanged in the presence of goethite when

21 CO_2 is intruded into the system (see Table 1). In our study, the pH (measured ex-situ) changes

22 drastically when CO_2 is intruded into the system (Fig. 2b). In this context, the intrusion of

23 CO_2 could create a positive charge on the goethite, enabling the re-sorption of available

24 dissolved anions in the interacting solution. Finally, a slight release of Fe (<2mg/L) was

25 measured prior to CO_2 intrusion, indicating slight dissolution of the goethite, and Fe was no

1   longer detected in the interacting solution (<0.1 mg/L, "minimum value in our calibrating

2   curve") when CO_2 was intruded into the system (Fig. 2b). This is in agreement with the

3   literature, in the fact that the goethite is stable over a broad range of pH values (from 3 to

4   13.5) at ambient temperature (35, 36) as also verified by equilibrium Phreeqc calculations.

5

6   Calcite as an aquifer mineral analogue

7   In a similar way to the goethite scenario, Figure 3 summarizes five different adsorption

8   experiments now using pure calcite as adsorbent. The respective pH profiles and an average

9   Ca-concentration profile can be also consulted in Figure 3b. The adsorbed/remobilized

10   amounts for all the ions investigated were also normalized with respect to the available

11   surface area in the calcite system ($3g*7m^2/g$). Here, the major result is the fast, strong

12   sorption of Cd(II) and Cu(II) onto/into the calcite. The ex-situ monitoring of pH and Ca

13   concentration in the interacting solution (Fig. 3b) suggests that slight dissolution of calcite

14   enhances the sorption of cadmium and copper (heavy metals) as claimed earlier by Limousin

15   (37) for cadmium in particular. We also note that CO_2 intrusion into the calcite system has no

16   significant effect on the Cd(II) and Cu(II) already sorbed. This means that dissolution of the

17   calcite, i.e. the release of Ca from the calcite into the interacting solution as a result of CO_2

18   intrusion, was dissociated from potential remobilization of sorbed Cd and Cu as might be

19   speculated at first sight. On the other hand, the oxyanions investigated (Se(IV), Se(VI) and

20   As(III)) were only slightly adsorbed on the calcite, if the values are compared with those for

21   the sorbed amounts of Cd(II) and/or Cu(II) (Fig. 3a). We also note that arsenite As(III) and

22   selenate Se(VI) were completely remobilized from the calcite when CO_2 was intruded into the

23   system. Conversely, a more complex behavior was observed in the case of selenite Se(IV); in

24   fact, a given amount of dissolved Se(IV) was re-adsorbed on the calcite by CO_2 intrusion. In

25   this way, the decrease in pH resulting from CO_2 intrusion plays an important role with regard

to the surface charge of a given mineral, the chemical speciation of dissolved elements (partial protonation of selenite from SeO_3^{2-} to $HSeO_3^-$: see Table 1) and possibly the surface complexation process (25). It should be noted that the decrease in pH can be significantly moderated/buffered by the dissolution of carbonate minerals (e.g. calcite) as illustrated in Figures 2a (goethite system) and 3a (calcite system). This pH buffering capacity can be envisaged in freshwater aquifers because these underground layers generally contain carbonate minerals. Numerical simulations have been successfully used to quantify this pH buffering capacity in groundwater in response to CO_2 leakage from deep geological storage (7).

Goethite-calcite composite as an aquifer mineral analogue

Five supplementary adsorption/release experiments are reported in Figure 4, but, in this case, a goethite-calcite composite was used as adsorbent. The pH profile for each adsorption/release experiment and release of Fe and Ca by dissolution of goethite and calcite, respectively, are also reported in Fig. 4b. As indicated in the previous cases, the adsorbed/remobilized amounts of the ions investigated were normalized with respect to the available surface area in the goethite-calcite system ($3g*90m^2/g$). In a similar way to the calcite system, fast, strong adsorption of Cd(II) and Cu(II) onto the goethite-calcite was measured. However, the kinetic behavior was reversed. For example, Cd was adsorbed in the first 10 minutes when pure calcite was used as adsorbent and its adsorption was considerably retarded in the case of the goethite-calcite system (see Fig. 3a and 4a). This was probably due to different textural properties between pure calcite (nanosized) and calcite contained in the composite (sub-micrometric) (31-32). On the basis of the results obtained with the calcite system, we assume that such high adsorption is controlled preferentially by the calcite contained in the composite. Additionally, these two adsorbed heavy metals were scarcely perturbed by CO_2 intrusion into the system; this is in complete agreement with the calcite system (Fig. 3a and 4a). Concerning

the so-called oxyanions, a given proportion of residual dissolved selenite Se(IV) was reabsorbed onto the goethite-calcite composite by CO_2 intrusion. Conversely, adsorbed arsenite As(III) was partially remobilized from the goethite-calcite composite. This is in agreement with the calcite and goethite systems. The selenate Se(VI) ion was slightly adsorbed on the calcite and/or goethite before and/or after CO_2 intrusion into the system (Fig. 2a and 3a). This highly mobile ion had not presented any adsorption affinity with the goethite-calcite composite (Fig. 4a). Finally, mineral dissolution could be intensified by CO_2 intrusion in this way; we assumed that the goethite contained in the composite was extremely stable in the conditions investigated because the Fe concentration measured in the solution was less than 0.1 mg/L, the "minimum value in the calibrating curve". Conversely, significant Ca concentration was measured in the interacting solution and this was intensified by CO_2 intrusion, reaching about 340mg/L at the end of the experiment (48h) (Fig. 4b). As mentioned above, calcite dissolution may moderate the decrease in pH and such dissolution is not related directly to the remobilization of adsorbed heavy metals (e.g. Cd and Cu).

Competitive adsorption/remobilization of binary metal(loid) ions

For competitive adsorption/remobilization of binary metal(loid) ions using goethite-calcite composite as adsorbent, two ions were arbitrarily combined as follows: As(III)-Se(IV), As(V)-Se(VI) or Cd(II)-Cu(II). These three independent experiments are reported in Figure 5. *Cd(II)-Cu(II) competition:* All available copper in the solution (about 50 mg/L) was adsorbed more rapidly than the available cadmium (unfilled circle profiles in Figure 5). The same kinetic behavior was observed in the case of single metal(loid) ion solutions (Fig. 4a). This suggests insignificant competitive adsorption between Cu and Cd using goethite-calcite composite. However, CO_2 intrusion into the system created slight remobilization of adsorbed Cu. This is in disagreement with a single metal(loid) ion solution in the case of the goethite-

calcite system. Such disagreement could be explained if all the adsorption sites on the available calcite were saturated with Cd and Cu, and the liberated Cu therefore comes from the goethite, as observed in the pure goethite system when CO_2 is intruded (Fig. 2a).

Se(IV)-As(III) competition: Clearly, arsenite As(III) is adsorbed on the goethite-calcite composite in preference to the selenite Se(IV) ion (unfilled star profiles in Figure 5). However, CO_2 intrusion into the system reactivates the adsorption of residual dissolved Se(IV). Conversely, adsorbed As(III) is partially remobilized from the goethite-calcite composite. CO_2 intrusion was observed to have a similar effect in the case of single Se(IV) and As(III) ion solutions (Figure 4a).

Se(VI)-As(V) competition: Arsenate As(V) was strongly adsorbed on the goethite-calcite composite. Conversely, insignificant adsorption of selenate Se(VI) was measured in the conditions investigated (unfilled triangle-down profiles in Figure 5). Surprisingly, CO_2 intrusion into the system led to re-adsorption of residual dissolved As(V) on the goethite-calcite composite while As(III) was remobilized in all the other cases investigated. This can be explained in terms of chemical speciation in the solution because arsenate remains partially protonated before and after injection of CO_2 (dominant species $H_2AsO_4^-$: see also Table 1) while arsenite is completely protonated from $H_2AsO_3^{-1}$ to $H_3AsO_3^0$ when CO_2 is intruded into the system.

In conclusion, this simple experimental study provides further specific insights into the remobilization/re-adsorption of Se(IV), Se(VI), Cd(II), Cu(II), As(III) and As(V) caused by CO_2 intrusion into an equilibrated mineral-ion solution system. This has direct implications for CO_2 leakage from deep geological formations and its possible intrusion into freshwater aquifers. CO_2 intrusion into a given aquifer has been directly associated with the release and/or remobilization of trace elements via mineral dissolution and/or desorption. In the present study, we demonstrated that the remobilization of trace elements as a result of CO_2

intrusion is not a universal physicochemical effect. In fact, goethite and calcite, two minerals frequently found in aquifers, can successfully prevent the remobilization of adsorbed Cu(II), Cd(II), Se(IV) and As(V) if CO_2 is intruded into a drinking water aquifer. Moreover, a decrease in pH resulting from CO_2 intrusion can reactivate the adsorption of Se(IV) and As(V) if goethite and calcite are sufficiently available in underground layers. Our results also suggest that the adsorption of cadmium and copper could be promoted by calcite dissolution. In this way, adsorbed Cd(II) and Cu(II) on calcite are not remobilized when CO_2 is intruded into the system, but it intensifies calcite dissolution, which plays a buffering role. On the other hand, arsenite As(III) is significantly adsorbed on goethite, but is partially remobilized by CO_2 intrusion. Finally, our results confirm the low or even insignificant adsorption affinity of selenate Se(VI) with calcite and/or goethite. The latter oxyanion is reputed to be a very highly mobile element in natural oxic environments.

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Table 1. Dominant species and pH in suspensions prior to and after CO_2 injection into the system. These values were determined by using Phreeqc numerical simulations with an element initial concentration of 50 mg/L and 8 bar of CO_2 in the system.

| Soluble Salt	Mineral	pH Phreeqc[1]	Ex-situ[a]	Dominant Species (>98%)		pH Phreeqc[2]	Ex-situ[b]	Dominant Species (>98%)
$NaAsO_2$	Calcite	10.324	9.91	$H_2AsO_3^-$		4.04	6.29	$H_3AsO_3^0$
$NaAsO_2$	Goethite	10.235	9.87	$H_2AsO_3^-$		3.981	5.25	$H_3AsO_3^0$
$Na_2SeO_3.5H_2O$	Calcite	10.06	9.33	SeO_3^{-2}	After CO_2 intrusion within system	4.244	6.25	$HSeO_3^-$
$Na_2SeO_3.5H_2O$	Goethite	9.323	9.25	SeO_3^{-2}		4.196	5.38	SeO_3^{-2}
Na_2SeO_4	Calcite	10.05	8.26	SeO_4^{-2}		3.6	6.28	SeO_4^{-2}
Na_2SeO_4	Goethite	7.035	8.18	SeO_4^{-2}		3.463	5.52	SeO_4^{-2}
$Cd(NO_3)_2.4H_2O$	Calcite	9.678	6.44	Cd^{+2}		3.708	6.25	Cd^{+2}
$Cd(NO_3)_2.4H_2O$	Goethite	6.763	6.40	Cd^{+2}		3.438	6.14	Cd^{+2}
$CuCl_2.2H_2O$	Calcite	7.702	5.72	Cu^{+2}(51%) CuO (49%)		4.357	6.32	Cu^{+2}
$CuCl_2.2H_2O$	Goethite	5.499	5.54	Cu^{+2}		3.439	6.23	Cu^{+2}
$Na_2HAsO_4.7(H_2O)$	Calcite	11.291	8.32	$H_2AsO_4^-$		4.08	6.24	$H_2AsO_4^-$
$Na_2HAsO_4.7(H_2O)$	Goethite	11.291	8.28	$H_2AsO_4^-$		4.038	5.50	$H_2AsO_4^-$

[1] Equilibration between ion solution and mineral prior to CO_2 injection; [a] pH measured ex-situ at 20°C in the mother solution; [2] Equilibration between ion solution and mineral after CO_2 injection; [b] pH measured ex-situ at 20°C at the end of the experiment (after 48h).
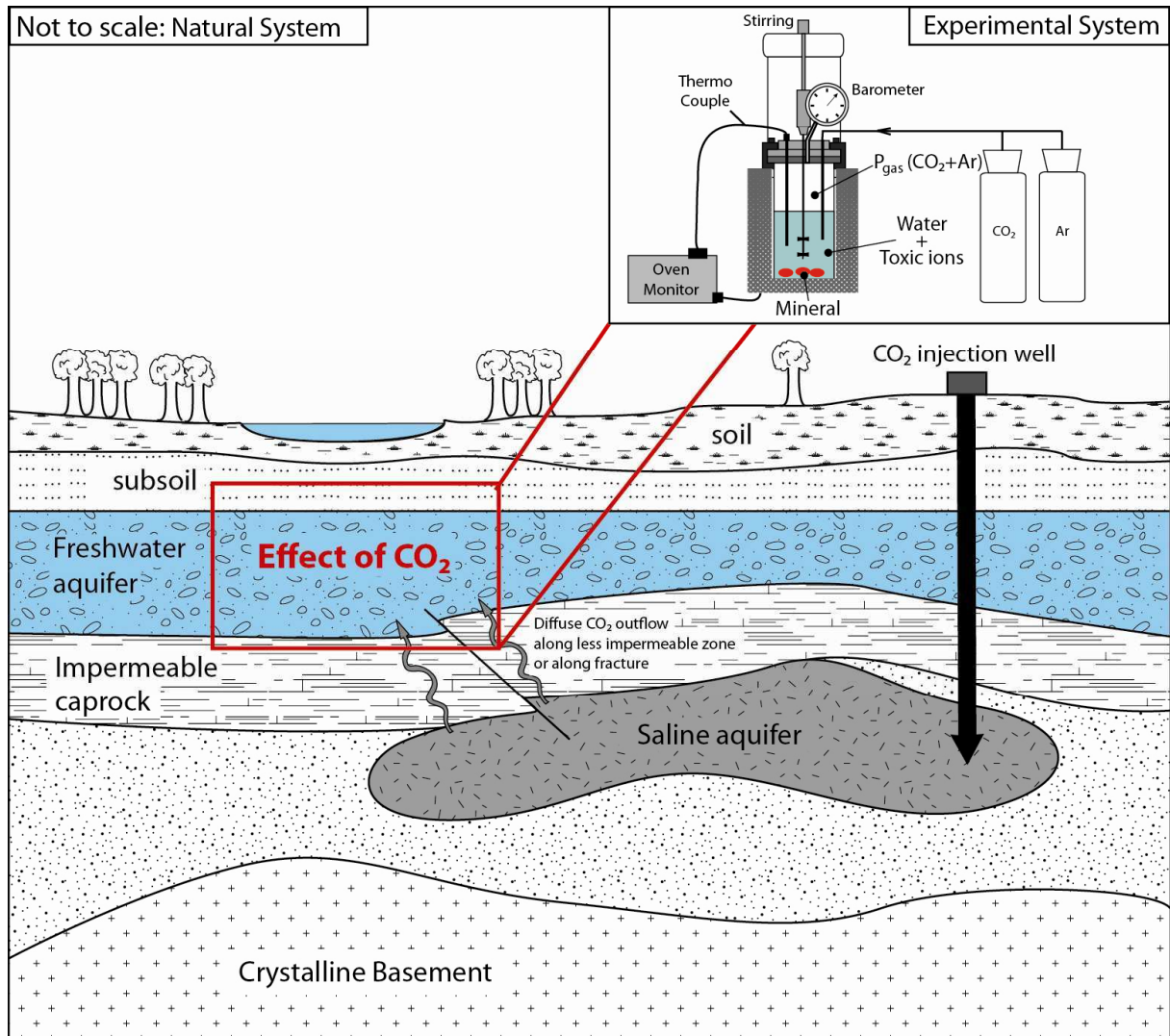
**Figure 1**. Schematic representation of CO_2 leakage from deep geological storage, focusing in red on the present study: "experimental assessment of CO_2-mineral-toxic ions interactions in a simplified potable aquifer".
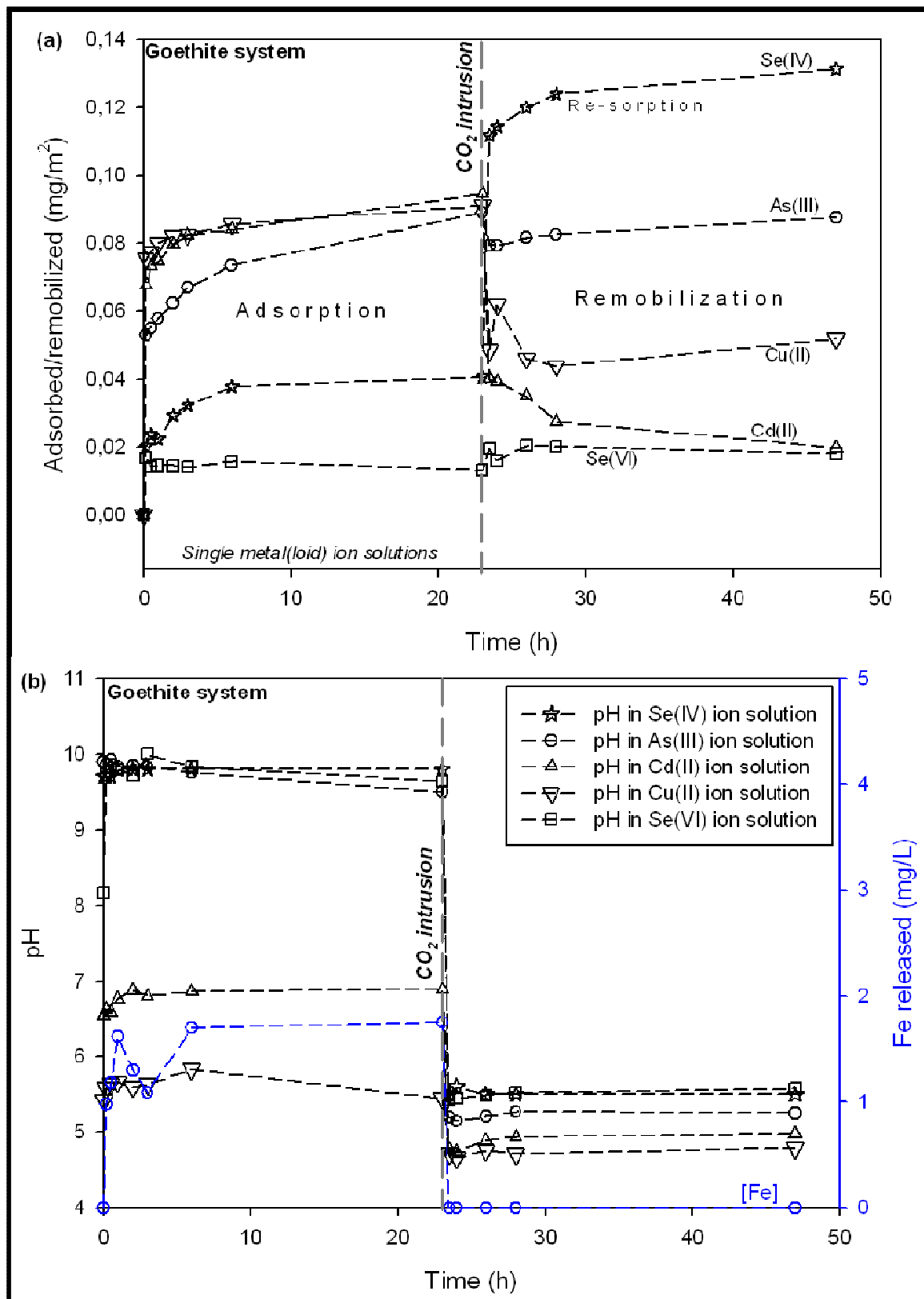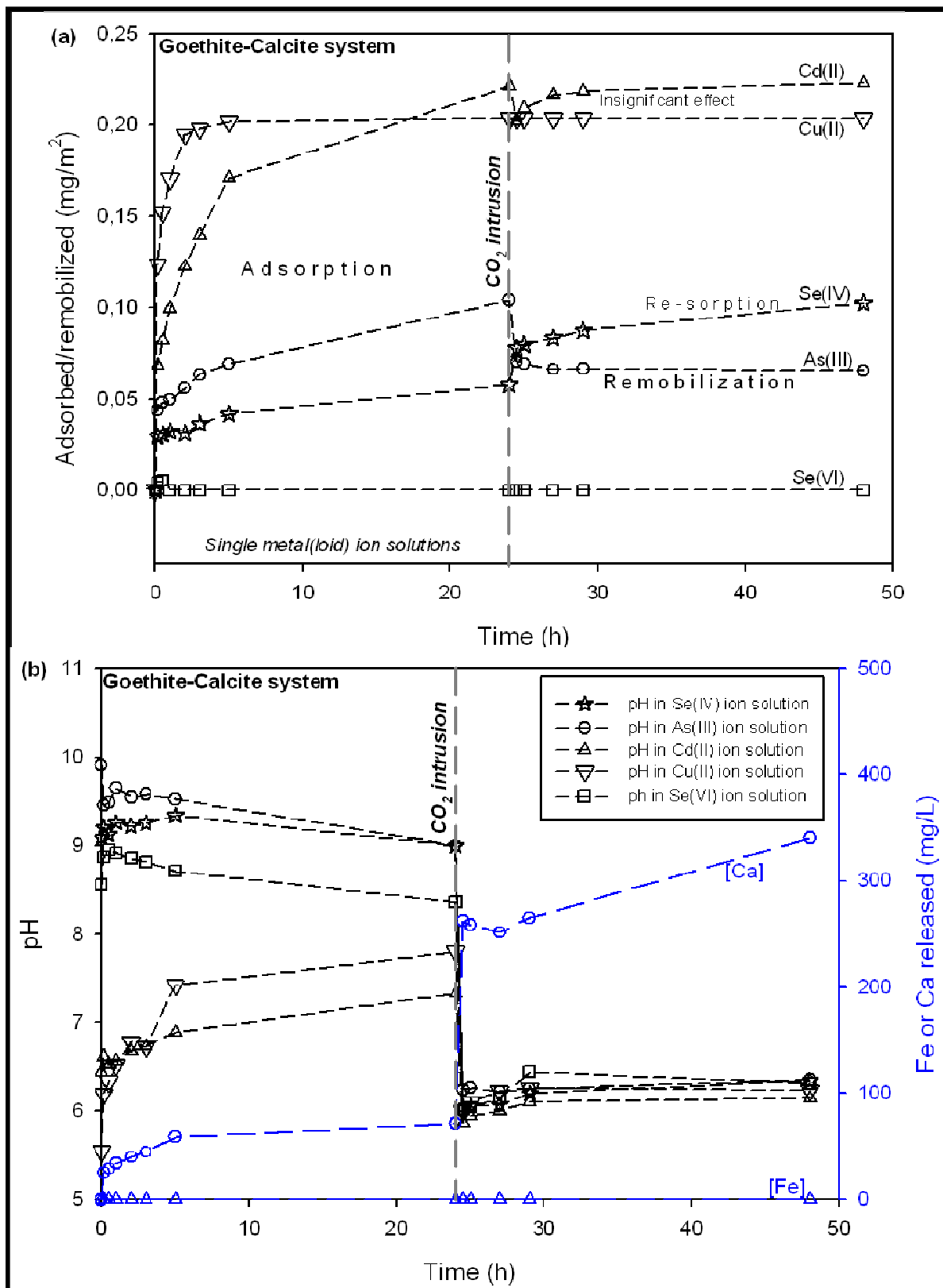
Figure 2. (a) Kinetic adsorption behavior of a single metal(loid) ion on goethite and effect of CO_2 intrusion into the system. (b) pH profiles before and after CO_2 intrusion. In all experiments, a similar initial ion concentration (about 50mg/L) was used and the adsorbed/remobilized amount of each element was normalized with respect to the initial available surface area ($3g*130m^2/g$).
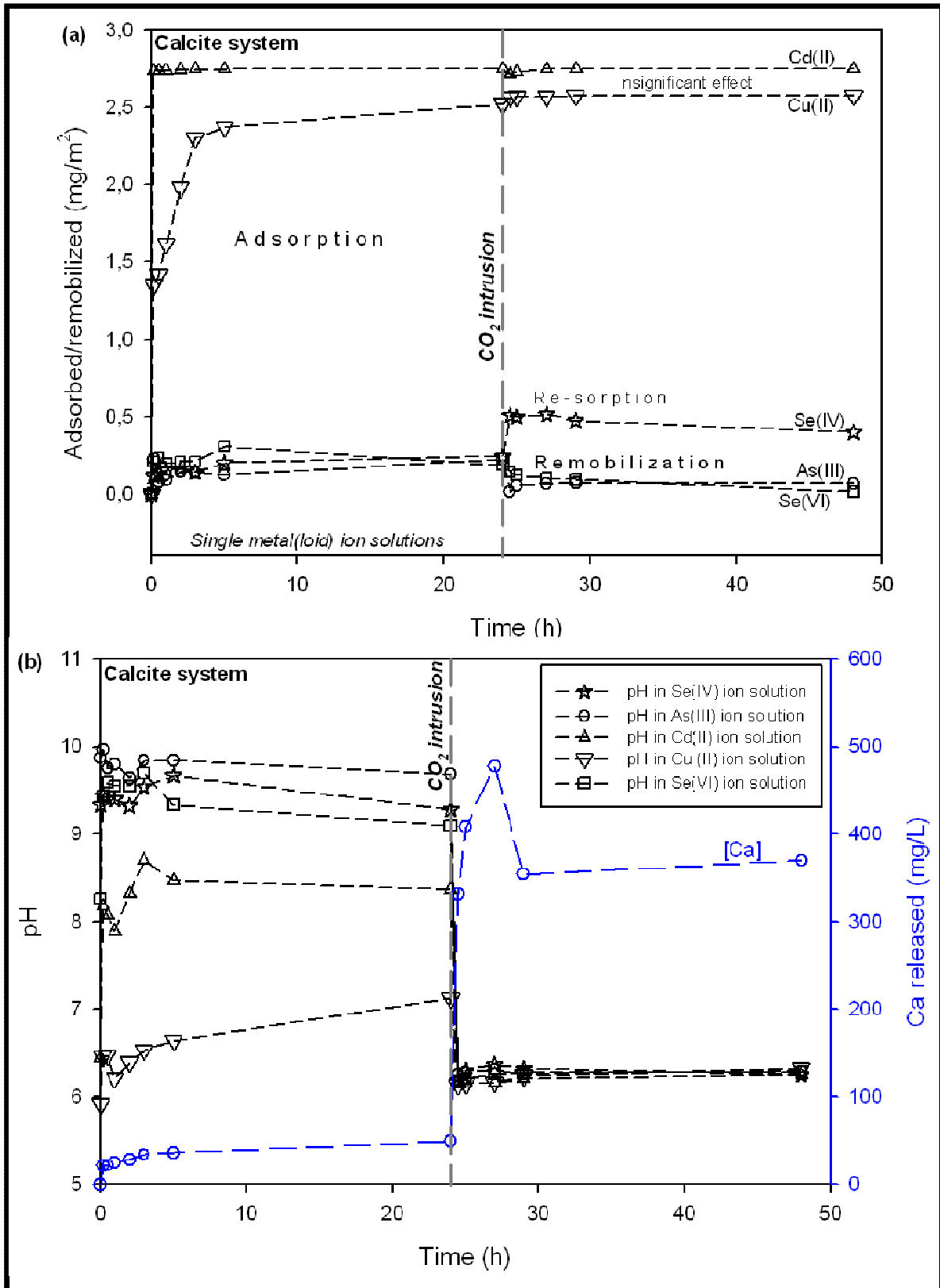
Figure 3. (a) Kinetic adsorption behavior of a single metal(loid) ion on calcite and effect of CO_2 intrusion into the system. (b) pH profiles and average [Ca] profile before and after CO_2 intrusion. In all experiments, a similar initial ion concentration (about 50mg/L) was used and the adsorbed/remobilized amount of each element was normalized with respect to the initial available surface area ($3g*7m^2/g$).

Figure 4. (a) Kinetic adsorption behavior of a single metal(loid) ion on goethite-calcite composite and effect of CO_2 intrusion into the system. (b) pH profiles and average [Fe] and [Ca] profiles before and after CO_2 intrusion. In all experiments, a similar initial ion concentration (about 50mg/L) was used and the adsorbed/remobilized amount of each element was normalized with respect to the initial available surface area ($3g*90m^2$/g).

1
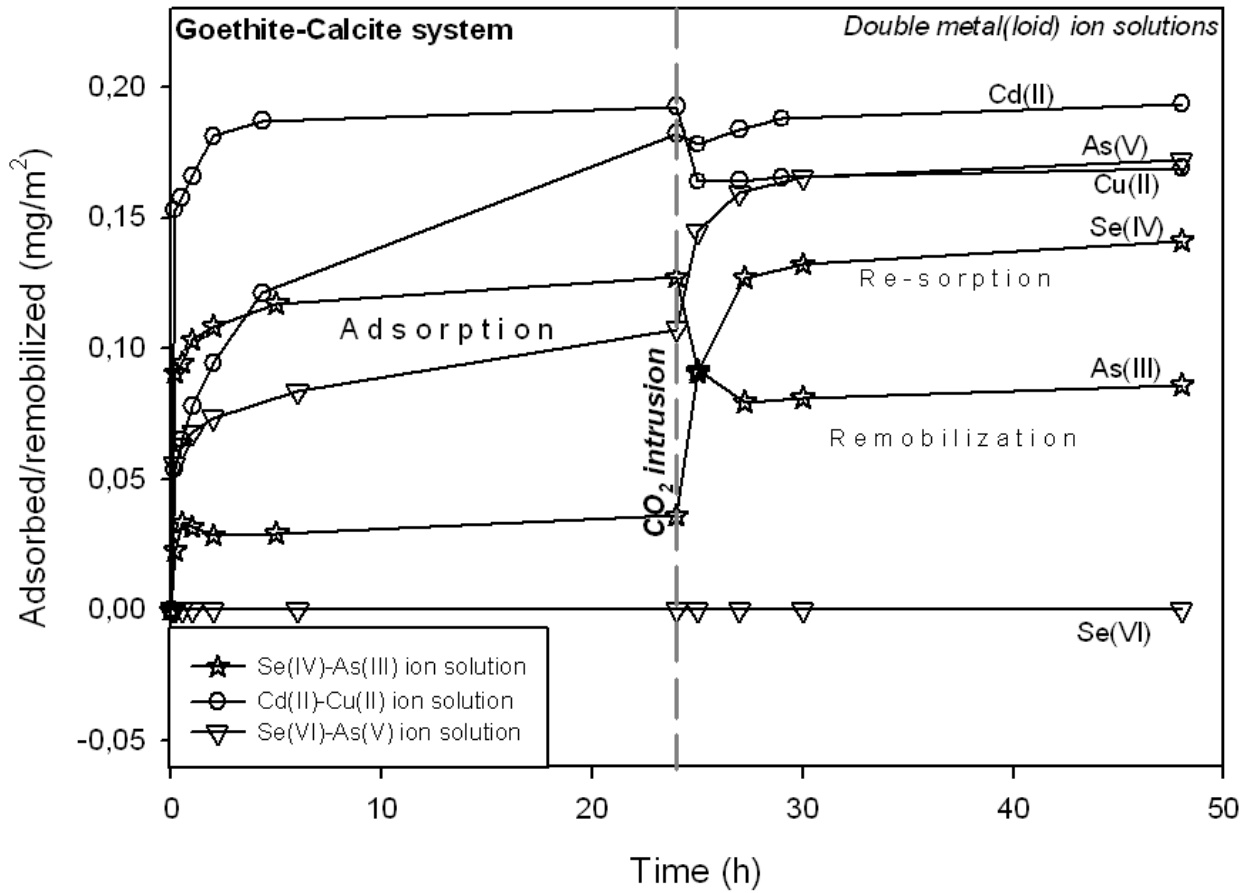
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8 **Figure 5.** Competitive adsorption/remobilization of binary metal(loid) ions by using goethite-

9 calcite composite as adsorbent. Two ions were arbitrarily combined as follows: As(III)-

10 Se(IV), As(V)-Se(VI) or Cd(II)-Cu(II). A similar initial ion concentration (about 50mg/L for

11 each element) was used and the adsorbed/remobilized amount was normalized with respect to

12 the initial available surface area ($3g*90m^2/g$).