Arsenic Mobilization in Shallow Aquifers due to CO_2 and Brine Intrusion from Storage Reservoirs

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Abstract

Carbon dioxide (CO_2) or brine leakage from deep sequestration reservoirs to overlying underground sources of drinking water (USDW) is a major concern for geologic CO_2 sequestration (GCS). In this study, we developed an integrated framework of combined batch experiments and reactive transport simulations to quantify water-rock-CO_2 interactions and arsenic (As) mobilization responses to CO_2 and/or saline water leakage into USDWs. Both experimental and simulation results suggest that when CO_2 is introduced, pH drops immediately that initiates release of As from clay minerals. The buffering effect of calcite during dissolution can increase pH slightly and cause As to re-adsorb onto clay minerals. Thus, the mineralogy of the USDW is ultimately a determining factor of As and other such risks. A genetic field-scale reactive transport model was also created with the kinetic parameters obtained from the integrated framework to forecast As leakage pathways. Salient results suggest that: (1) As desorption/adsorption from/onto clay minerals is the major reaction controlling its mobilization, and clay minerals could mitigate As mobilization with surface complexation reactions; (2) dissolution of available calcite plays a critical role in buffering pH; (3) high salinity in general hinders As release from minerals; (4) the magnitude and quantitative uncertainty of As mobilization are predicated on the values of reaction rates and surface area of calcite, adsorption surface areas and equilibrium constants of clay minerals, and cation exchange capacity; and (5) within 1,000-year simulation time, the aquifer sediments stabilize almost 100% leaked As. Results of this study are intended to improve ability to quantify risks associated with potential leakage of reservoir fluids into shallow aquifers, in particular the possible environmental impacts of As mobilization at carbon sequestration sites.

Methods

☐ Batch experiments

Two sets of experiments were conducted, with "background" (BG, TDS ~ 200 mg/L) and "saline" (S, TDS ~ 4000 mg/L) synthetic groundwater, to represent the conditions with/without saline water intrusion. Before CO_2 injection, the sediment samples were exposed to the synthetic groundwater for ~3 days to reach a steady state. Water samples were then collected over a 26-day experimental period: 14 days for CO_2 injection and 12 days for post injection.
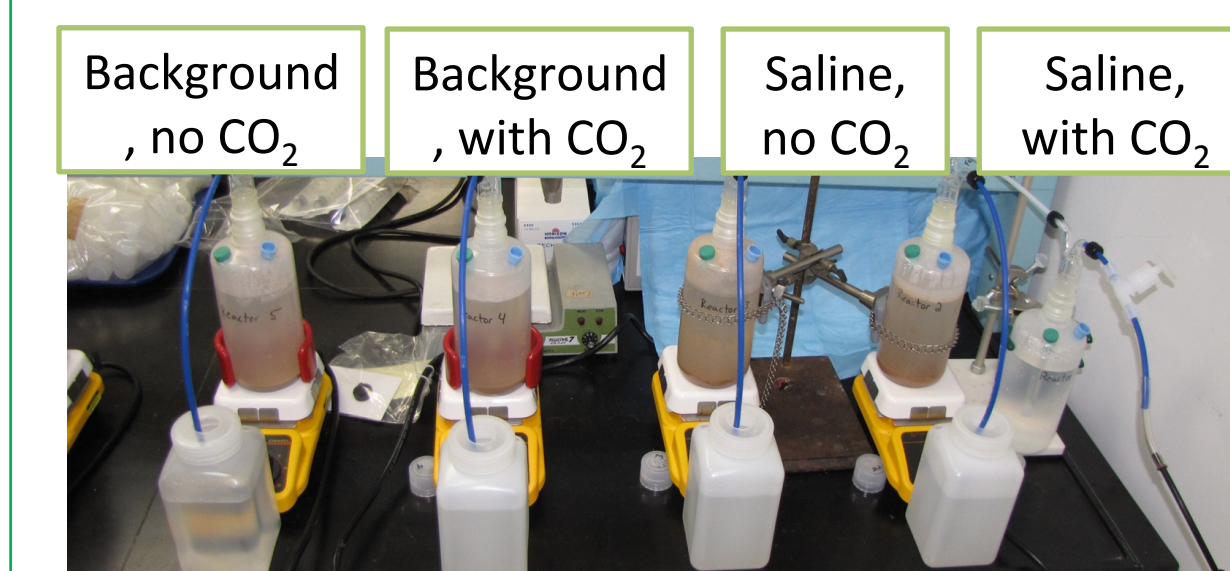
Concentrations for major ions (mg/L)

Element	Background	Saline
Ca	5.2	222.1
K	0.7	38.6
Mg	2.8	220.4
Na	73.9	783.9
Cl	28.0	2050.0
SO4	56.0	333.0
As	< DL	1.5×10^{-4}
pH (unitless)	8.5	6.4

☐ Estimations of uncertainty parameters

Uncertainty parameters were estimated via inversion by minimizing the objective function J with PEST program:

$$J = min \sum_{i=1}^{N} E_i(p) \; ; \; E_i(p) = \sum_{l=1}^{L_i} w_{li}^2 \left(u_l^i(p) - \tilde{u}_l^i\right)^2$$

where $E_i(p)$ is the sub-objective function from chemical species i, N is the number of chemical species, w_{ii} is the weighting coefficient for the lth measurement of the ith species, which is computed with the inverse of the standard deviation of the experimental data, and u_l^i and $\tilde{u}_l^i$ are the simulated and observed concentrations.

☐ Reactive transport simulations

TOUGHREACT models were conducted considering aqueous species complexation, mineral dissolution/precipitation, adsorption/desorption, and cation exchanges.

The initial mineralogy: 26% quartz, 3.6% K-feldspar, 2.4% albite, 2.4% anorthite, 0.4% calcite, 0.4% hematite, 29.5% illite, 1.5% kaolinite, and 20.2% smectite.

Hydrogeologic parameters for the 2-D field scale model

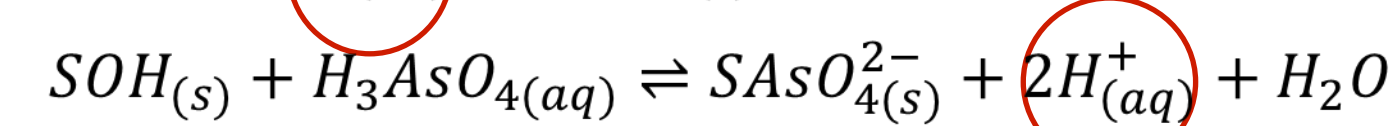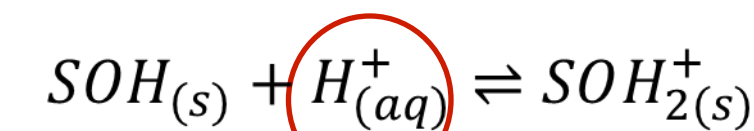|	
Aquifer domain size	$6,000 \times 100 \times 10 \text{ m}^3$
Permeability	10^{-13} m^2 (aquifer), 10^{-12} m^2 (fault)
Porosity	0.3 (aquifer), 0.8 (fault)
Temperature	25 °C
Pressure	1 atm at the top boundary
CO_2 leakage rate	1.14×10^{-3} kg/s
Brine leakage rate	4.28×10^{-2} kg/s
Simulation time	1,000 years
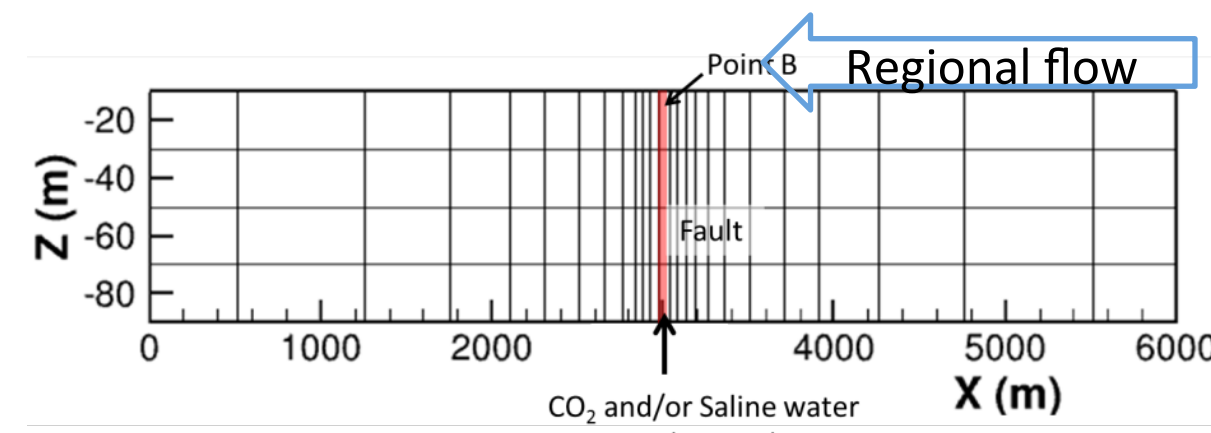
Model set-up and numerical mesh

Results and Discussion

☐ Arsenic mobilization mechanisms
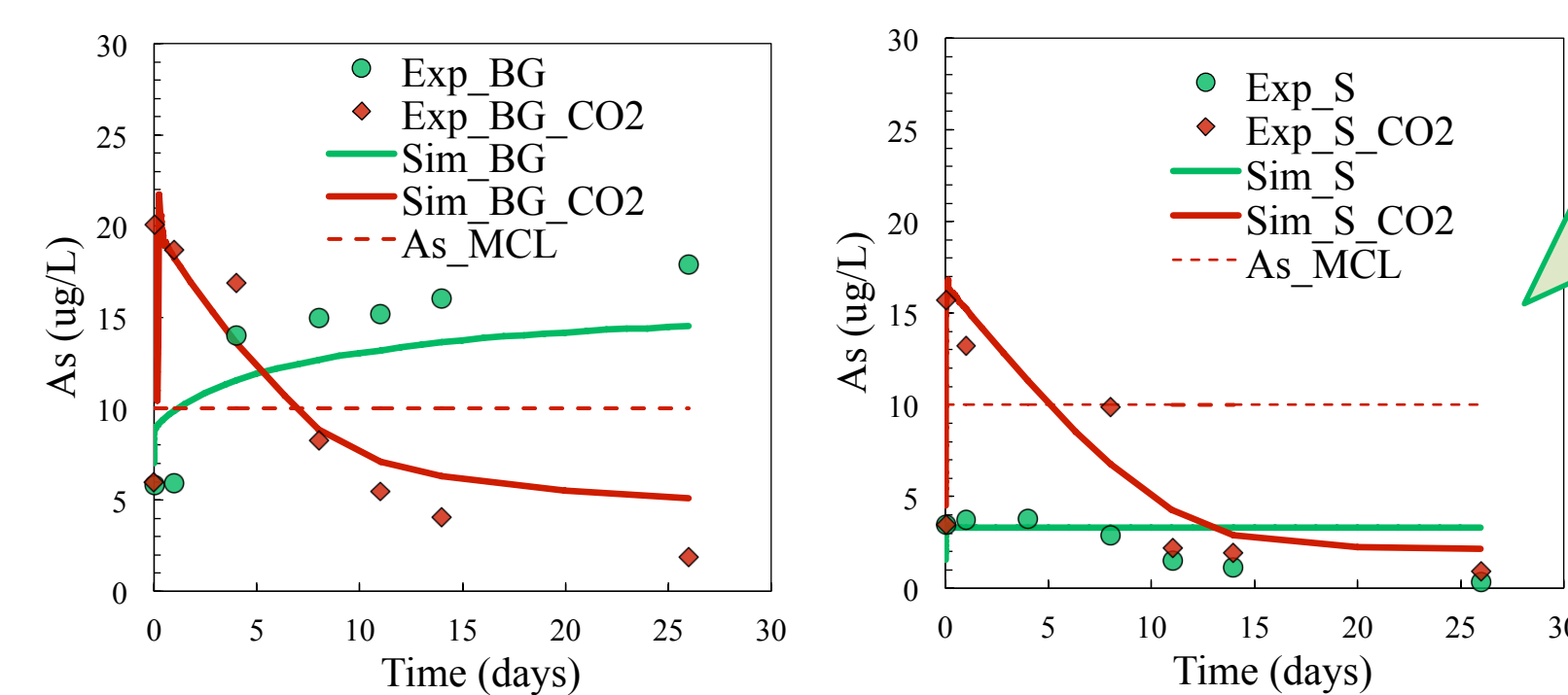
Measured (symbols) and calculated (lines) water chemistry of the batch experiments

- Simulation results match with the experimental measurements.
- Without CO_2 intrusion, As concentrations increase.
- With CO_2 intrusion, As concentrations increase at the initial time and decrease slowly afterwards.

Adsorption/desorption onto/from the surfaces of clays controls As mobilization with water-rock-CO_2 interactions. The surface complexation reactions of the clay minerals (S represents mineral sites) could be written as:

$$SOH_{(s)} + H_{(aq)}^+ \rightleftharpoons SOH_{2(s)}^+$$
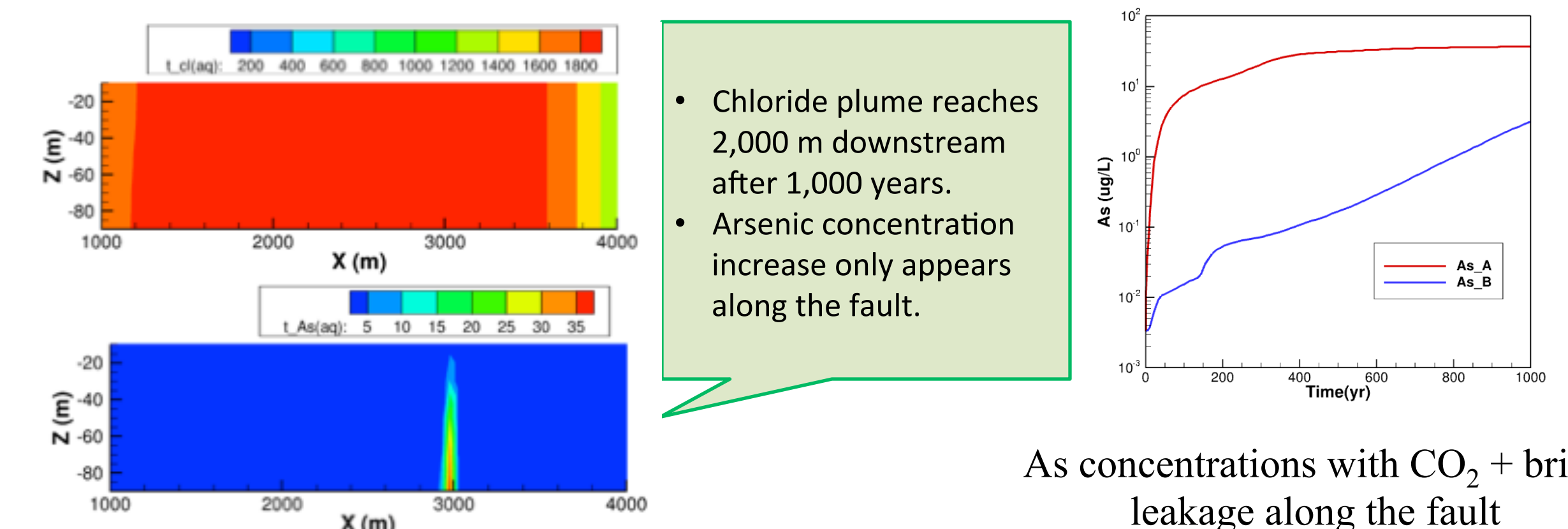$$SOH_{(s)} + H_3AsO_{4(aq)} \rightleftharpoons SAsO_{4(s)}^{2-} + 2H_{(aq)}^+ + H_2O$$

- Arsenic and H ions compete for mineral sites.
- With calcite dissolution, it consumes H+ for gradual As adsorption onto clay minerals.

☐ Sensitivity of key parameters
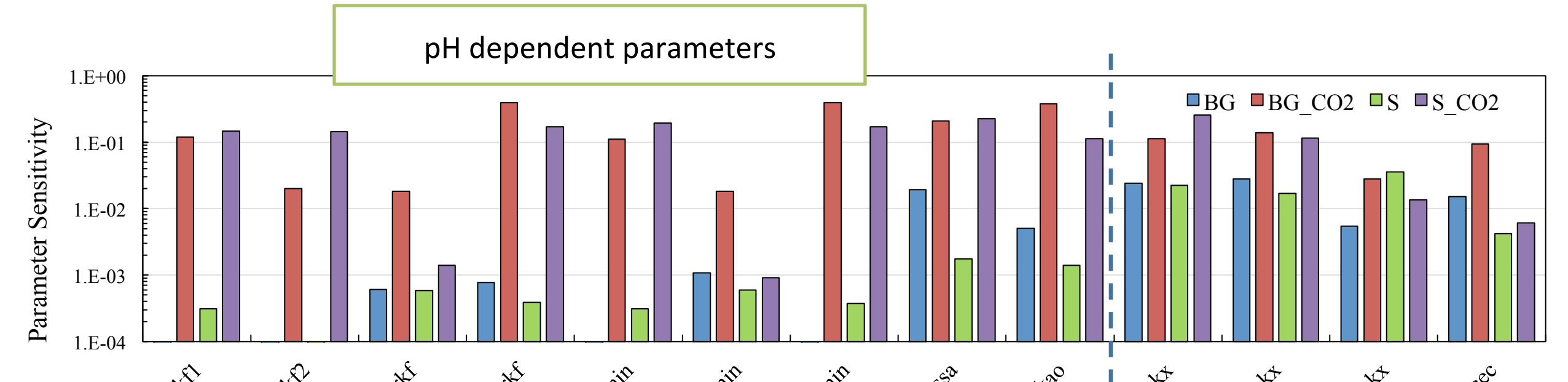
Sensitivity analysis of the geochemical reactive parameters

☐ 2-D simulation results

Cl and As concentrations with CO_2 + brine leakage after 1,000 years

- Chloride plume reaches 2,000 m downstream after 1,000 years.
- Arsenic concentration increase only appears along the fault.

As concentrations with CO_2 + brine leakage along the fault

Acknowledgement

Environmental Implications

✓ Arsenic may be considered an insignificant long-term concern in a CO_2 rich USDW environment because of clay adsorption.

✓ Increased salinity of USDW via the leaked saline water may likely be a larger concern than associated released trace metals.

✓ The integrated framework of this study provides an example for risk assessments of potential reservoir fluids leakage into USDWs with site-specific information.

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