Trace element mobility during CO₂ storage: application of reactive transport modelling

Dirk Kirste[1,*], *Julie* K. Pearce[2], *Sue* D. Golding[2], and *Grant* K.W. Dawson[2]

[1]Department of Earth Sciences, Simon Fraser University, 8888 University Drive, Burnaby, BC, Canada
[2]School of Earth and Environmental Sciences, University of Queensland, QLD 4072, Australia

Abstract. The geologic storage of CO₂ carries both physical and chemical risks to the environment. In order to reduce those risks, it is necessary to provide predictive capabilities for impacts so that strategies can be developed to monitor, identify and mitigate potential problems. One area of concern is related to water quality both in the reservoir and in overlying aquifers. In this study we report the critical steps required to develop chemically constrained reactive transport models (RTM) that can be used to address risk assessment associated with water quality. The data required to produce the RTM includes identifying the individual hydrostratigraphic units and defining the mineral and chemical composition to sufficient detail for the modelling. This includes detailed mineralogy, bulk chemical composition, reactive mineral phase chemical composition and the identification of the occurrence and mechanisms of mobilisation of any trace elements of interest. Once the required detail is achieved the next step involves conducting experiments to determine the evolution of water chemistry as reaction proceeds preferably under varying elevated CO₂ fugacities with and without impurities. Geochemical modelling of the experiments is then used for characterising the reaction pathways of the different hydrostratigraphic units. The resultant geochemical model inputs can then be used to develop the chemical components of a reactive transport model.

1 Introduction

Carbon capture and storage is one of the most promising technologies available to help reduce point source greenhouse gas emissions [1]. The security of geological storage is a function of the integrity of the reservoir and seal system especially with respect to potential leakage pathways but additionally depends on the migration pathway of the injected CO₂ within the storage system itself [2]. Natural analogue studies and laboratory experiments show that CO₂ saturated solutions in contact with minerals can result in dissolution and precipitation reactions over relatively short periods of time [3]. Impurities such as SO_2, O_2 and NO_x typical for CO₂ captured from coal-fired power plants can significantly increase the reactivity [4-6]. The increase in reactivity has the potential for impacting water quality

---

* Corresponding author: dirk_kirste@sfu.ca

through the release of trace elements commonly identified as contaminants [7-9]. The affect on water quality is of significant concern and understanding the water quality issues arising from the injection in the deep subsurface of CO_2 with impurities is vital for developing strategies to address problems associated with long term storage.

This study focuses on developing an appropriate workflow for conducting geochemical and reactive transport modelling of CO_2 with impurities typical of coal-fired power plant capture streams. The method is demonstrated for a proposed pilot site in the Surat Basin of Queensland, Australia.

2 Methods

The development of the geochemical models was in three parts. The first involved the physical and chemical characterization of the reservoir-seal system targeted for the injection. The second part was conducting experiments at pressure and temperature with varying gas and water compositions. The final part was the generation of geochemical models of the experiments and then scaling those to the reservoir/seal system of the proposed injection site.

2.1 Physical and Chemical Characterisation

Porosity, permeability, relative permeability and capillary pressure were determined for core samples from the West Wandoan-1 well from the Surat Basin, Australia using routine and special core analyses [10]. Using these and the geophysical logs, hydrostratigraphic units (HSU) were determined for the site.

Bulk chemistry was determined using whole rock lithium borate fusion and acid digestion coupled with inductively coupled plasma atomic emission spectrometer (ICP-AES) and inductively coupled plasma mass spectrometer (ICP-MS) analysis for major minor and trace elements and loss on ignition (LOI) analysis. The mineral content of the core samples was determined using X-ray diffraction (XRD), thin section analysis, scanning electron microscopy (SEM), and QEMSCAN™ (Quantitative Evaluation of Materials by Scanning Electron Microscopy). Reservoir pressure and temperature experiments with West Wandoan 1 core, formation water and a CO_2-NO-SO_2-O_2 gas mix (P-T-X experiments) were performed to provide changes in water chemistry including metal concentrations. Geochemical reaction path modelling was carried out on the P-T-X experiments using The Geochemist's Workbench (GWB) software using a thermodynamic database for mineral and aqueous species based on the EQ3/6 database [11] and the published kinetic rate parameters of [12] as described in [13]. Reaction path models were constructed to history match the major, minor and trace element chemical composition of the water samples collected during the P-T-X experiments. The specific chemical compositions of the mineral phases, including the trace element content, were determined using SEM-EDS and synchrotron X-ray fluorescence mapping (XFM) as well as several methods that focussed on trace element content. The first was the use of sequential extraction data, with reference to whole rock geochemistry, to identify the specific phases with which the various trace elements could be associated and the amount mobilised. The sequential extraction procedure was a modified Community Bureau of Reference (BCR) technique using 4 steps including: 1) water soluble; 2) weak acid exchangeable and soluble; 3) reducible; 4) oxidisable with any remaining trace element content considered to be strongly bound. The second method was using the P-T-X (batch) experiments to determine which trace elements were mobilised and the mechanism of mobilisation (e.g. mineral dissolution, desorption).

The major metal element composition (Ca, Fe, Mg, Na) of the individual mineral phases was determined for berthierine/chlorite, plagioclase feldspar, pyrite and the carbonate minerals calcite and siderite using SEM-EDS and XFM. Once a match of the major components was achieved, the trace element chemical compositions of the reacting mineral phases were adjusted based on the relationships determined from the sequential extractions and the mobilization of trace elements during the P-T-X experiments. The incorporation of trace elements in the minerals was carried out by developing regular and ideal mixing models for siderite, calcite and pyrite solid solutions with equivalent carbonate or sulphide minerals containing the trace elements [14] Kinetically controlled reaction path models were constructed using the data produced for each HSU at the T and P of the targeted Surat Basin site. These models were run as 10 year simulations to evaluate the potential impacts of trace element mobilisation on water quality. Simulations were run to determine the effect that the various sources and sinks of trace elements would have on their concentrations. Along with the sources determined above, sinks included the trace element end member carbonate mineral phase (ie. cerrusite, rhodochrosite etc.) and adsorption on iron oxide/oxyhydroxides using the existing database of [15].

3 Results and Discussion

A total of 5 HSU were identified based on the porosity/permeability/bulk chemistry of the core. For each HSU, the reactive minerals that released trace elements during the P-T-X experiments and the sequential extraction method were identified as the carbonates, calcite and /or siderite, and pyrite. A relatively small proportion of the trace elements were related to adsorption on iron oxide/oxyhydroxide or other mineral surfaces. The trace element content for each HSU in the model was limited by the proportion of the total trace metal content mobilised during the different steps of the sequential extraction. Modified calcite, siderite and pyrite compositions and thermodynamic data were generated based on the trace element associations and used in reaction path modelling of the experiments (Figure 1). The chemical composition of the calcite, siderite and pyrite was then adjusted to history match the experiments. For some elements the history match was very close however for others, the relative behaviour was targeted rather than the specific behaviour. In Figure 1 the Cu and As of the models are displaced from the experiment however the pattern of an increase followed by a decrease is achieved. The adsorption data had to give the best results for all of the experiments so some of the individual experiments are not as closely matched.
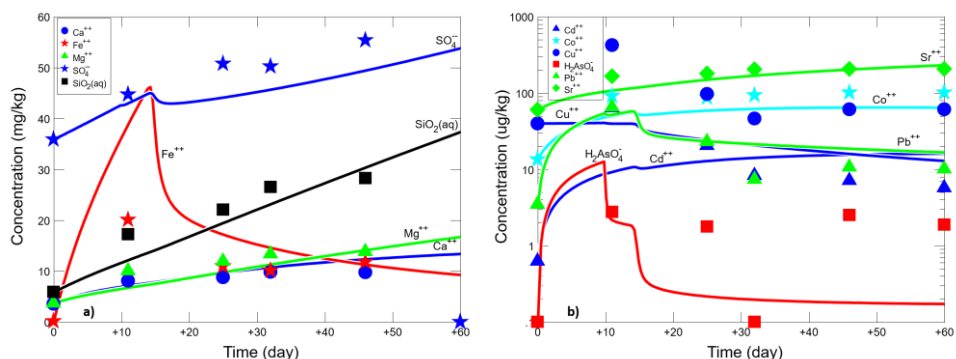

Fig. 1. Reaction path modelling of the P-T-X experiment for sample Precipice 1156 showing the a) major and b) trace element composition through time from the experiments (symbols) and the model (solid lines).

The reaction path models were then scaled to the storage system from the benchtop experiment scale. Models were then run to understand the release of trace elements in the different HSU. Controls on trace element mobility were introduced to generate more comprehensive models of the system behaviour. The main mobility controls included were precipitation of carbonate minerals and adsorption. Figure 2 shows the results for As and Pb under the different modelling scenarios for HSU 1. The models show that with no sinks for the trace elements the concentrations can exceed water quality guidelines (10 µg/kg for As and Pb). With the addition of carbonate precipitation and adsorption the As and Pb concentrations are significantly reduced. Adsorption thermodynamic data derived from the experiments result in even greater reductions of Pb concentrations than when the unmodified Dzombak and Morel (1990) data are used and the As are slightly higher due to the relative increase in other adsorbed constituents (Fig. 2b).
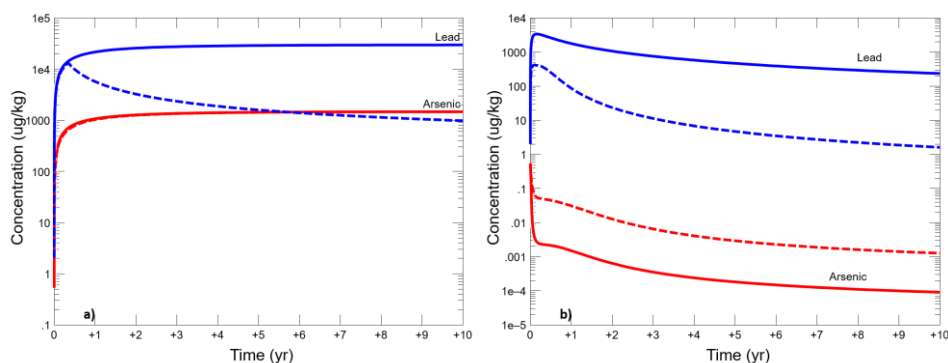

Fig. 2. Reaction path modelling of reservoir scale system for HSU 1 showing Pb and As concentrations for a) models with no sinks for trace metals (solid lines) and with end member carbonate precipitation (dotted lines) and b) with end member carbonate precipitation and adsorption (solid lines) and adsorption data derived from the experiments (dotted line).

4 Conclusions

Reactive transport models are needed in order to be able to predict the geochemical processes that take place during carbon storage. The developing of reactive transport models requires a process of characterization that increases confidence in model outcomes and that can be met by following a detailed workflow. Careful chemical characterisation coupled with experiments is required to generate predictive numerical models of trace element behaviour during carbon storage in deep geological systems. Knowledge of how the trace elements are associated with the mineral phases and the mechanisms of mobilisation allows for the construction of numerical models that increase the confidence the predictive capacity. For the West Wandoan proposed injection site in the Surat Basin of Australia, P-T-X experiments indicate that trace elements can be released in the storage system from all of the proposed HSU. In many cases the concentrations of those trace elements, in particular As and Pb, exceed drinking water guidelines. Geochemical models of the HSU suggest that the elevated concentrations of the trace elements can be attenuated through the process of secondary mineral precipitation and/or adsorption on existing and newly formed mineral surfaces.

References

1. IPCC, *Climate Change 2007: Mitigation of Climate Change. In: Metz, B., Davidson, O.R., Bosch, P.R., Dave, R., Meyer, L.A. (Eds.). Contribution of Working Group III to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change*, Cambridge University, (2007)

2. F.M. Orr, *Science*, **325**, 1656-1658, (2009)

3. I. Gaus, Int. *J. Greenh. Gas Control*, **4**, 73–89, (2010)

4. D.H. Bacon, B. M. Sass, M. Bhargava, J. Sminchak, and N. Gupta, *Greenh. Gas Control Technol. 9, Proc. 9th Int. Conf. Greenh. Gas Control Technol. (GHGT-9), 16–20 Novemb. 2008, Washingt. DC, USA*, **1**, 3283–3290, (2009)

5. J. Wang, D. Ryan, E. J. Anthony, N. Wildgust, and T. Aiken, 10th Int. Conf. Greenh. Gas Control Technol., **4**, 3071–3078, (2011)

6. S. Talman, Int. *J. Greenh. Gas Control*, **40**, 267-291 (2015)

7. A. L. Atchley, R. M. Maxwell, and A. K. Navarre-Sitchler, *Environ. Sci. Technol.*, **47**, 5954-5962 (2013)

8. K. Kirsch, A. K. Navarre-Sitchler, A. Wunsch, and J. E. McCray, *Environ. Sci. Technol.*, **48**, 1436–1442, (2014)

9. A.K. Karamalidis, S. G. Torres, J. A. Hakala, H. Shao, K. J. Cantrell, and S. Carroll, *Environ. Sci. Technol.*, **47**, 322-329 (2013)

10. F. Golab, A., Arena, A., Khor, J., Goodwin, C., Young, B., Carnerup, A. and Hussain, *Report to ANLEC R&D: Milestone 1.4 Final report of RCA and SCAL data on plugs from West Wandoan-1 Well.* (2015). http://anlecrd.com.au/wp-content/uploads/2016/08/SpecialCoreAnalysisfromSuratBasinWestWandoan-1Well.pdf

11. T.J. Wolery, *EQ3/6, A software package for geochemical modeling of aqueous systems: package overview and installation guid (version 7.0)*, Lawerence Livermore National Laboratory Report, Livermore, California, (1992)

12. J.L. Palandri and Y. K. Kharaka, *A compilation of rate parameters of water-mineral interaction kinetics for application to geochemical modeling*. U. S. Geological Survey : Reston, VA, United States, U. S. Geological Survey, Menlo Park, CA, United States, Jan. (2004)

13. J.K. Pearce, D. M. Kirste, G. K. W. Dawson, S. M. Farquhar, D. Biddle, S. D. Golding, and V. Rudolph, *Chem. Geol.,* **399**, 65-86 (2015)

14. P. Glynn, *Rev. Mineral. Geochemistry*, **40**, 481–511, (2000)

15. D.A. Dzombak and F. M. M. Morel, Surface complexation modeling: hydrous ferric oxide. New York: Wiley and Sons, (1990)