

Alteration of carbonates in saline aquifers due to CO₂ and accessory gases at geological storage conditions

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The estimation of an environmentally and economically feasible purity of carbon dioxide for geological storage presumes a comprehensive understanding of the geochemical interactions of CO₂, accessory gas components in the separated gas stream, e.g. H₂O, O₂, N₂, SO_x, NO_x, CO, H₂, H₂S, aqueous highly saline fluids and natural minerals.

The main focus of this geochemical subtask within the project COORAL (= CO₂ - Purity for Capture and Storage) is on experimental work with mineral-H₂O-CO₂-electrolyte- (accessory gas, e.g. SO₂, O₂, NO_x)-systems at *in situ* pressure (p) and temperature (T) conditions and the combination with geochemical modeling applying the numerical code PHREEQC.

A literature survey and systematic parameter evaluation demonstrated that some mineral-fluid-gas systems (shown for calcite-H₂O-CO₂-electrolyte) cannot be adequately described as to a partially simplified incorporation into the model, a lack of data at relevant pT conditions, and/or extrapolation-induced errors of the underlying thermodynamic data sets, confirming the need for additional experimental work at elevated pT conditions.

We show natural mineral and fluid alteration data of dissolution experiments of up to 700 h duration in the system calcite-H₂O-CO₂-(SO₂)-NaCl. Results were obtained with a static batch reactor system equipped with chemically inert and flexible gold-titanium-cells at operating conditions of 200 bars and 120 °C. Dissolution data indicate a stronger release of Ca from calcite in the presence of NaCl or/and CO₂ (and acid generating SO₂) in agreement with published findings. Net dissolution rates of calcite at various calcite-H₂O-CO₂-(SO₂)-NaCl systems will be presented and discussed.

While experimental data without CO₂ are well represented by thermodynamic calculations, rather strong discrepancies from measured data are e.g. observed for simulations of experiments in the presence of CO₂. We discuss reasons for deviations and limitations induced by the databases used.

STXM and XAS study of kaolinite conversion into berthierine-like mineral

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Experiments

In the context of radioactive waste repository in geological formation, kaolinite-Fe⁰ interactions were investigated at the crystallochemical level. Batch experiments were carried out in anoxic conditions at 90°C, for durations of one, three and nine months, by mixing Georgia Kaolinite (KGa2), powder Fe⁰ and aqueous solution (NaCl, CaCl₂). Such parameters were chosen to mimic repository conditions.

Results

First results indicated very fast iron metal consumption, morphological changes and iron-enrichment of clay particles.

X-ray diffraction, Fe K- and L-edges microspectroscopy (μ -XAS, STXM) evidence the rapid formation of an iron-rich 7 Å clay phase, with a structure close to that of berthierine or chamosite. At micrometric and nanometric scales, most iron is ferrous and octahedrally coordinated. However, some of the newly formed iron-rich clay particles display significant amounts of Fe³⁺ with variable Fe²⁺/Fe³⁺ ratio (Figure 1). In order to get further crystallochemical information, iron data were complemented by experiments at both the Si and Al-K edges. Si K-edge spectra display variations mainly due to particles orientation. Al K-edge spectra reveal no change in aluminium status of pristine clay. Although berthierine and chamosite bear both Al^{IV} and Al^{VI}, only Al^{VI} seems to be present in the neoformed iron rich-clays.

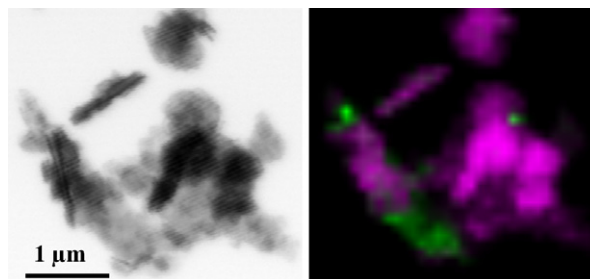


Figure 1: STXM image at 715 eV (Fe L3-edge) and corresponding two components fit (pink Fe²⁺, green Fe³⁺).