

## Geological carbon storage: Geochemical processes

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Modelling the complex physical and chemical processes that govern retention of CO<sub>2</sub> in geological reservoirs over long time scales present some interesting challenges, although not perhaps as challenging as coping with the consequences of unabated CO<sub>2</sub> emissions.

CO<sub>2</sub> may be held in geological formations by structural, capillary, dissolution and mineralisation trapping. CO<sub>2</sub> or CO<sub>2</sub>-charged brines may corrode reservoir minerals and caprocks. Remote imaging of CO<sub>2</sub> reservoirs, such as at Sleipner [1,2], captures the complex physical behaviour of CO<sub>2</sub> but is unable to completely explain this behaviour or resolve all potential trapping and escape mechanisms. Direct sampling of field small-scale injection experiments offers the best chance to do this [3]. Estimates of capillary trapping can be made by analysis of isotope spikes [4]. Dissolution trapping will be enhanced by the complexities of the flow processes and sampling of brines will be essential to monitor this. Prediction of the reaction rates between CO<sub>2</sub>-charged brines and reservoir minerals or caprocks is even more difficult. Observations on geological analogue sites have recovered the rates of the sluggish reactions between silicate minerals and brines [5]. Curiously the much more rapid rates of dissolution of carbonate, evaporite and oxy-hydroxide minerals in field conditions seen in small scale injection experiments [6] are poorly known. These reactions may also release contaminants.

Modelling of fluid-mineral interactions currently uses averaged fluid properties in pseudo- 1 dimensional models [e.g. 7]. It is not clear if this is an appropriate way to approximate the complex flow paths. What is needed is a method for inverting geochemical data to constrain the key attributes of flow heterogeneities.

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## A bond-valence view of interfacial structure and reactivity

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Studies of interfacial structures will be most useful in cases where we can relate structure to reactivity. However, a quantitative structure-activity relationship (QSAR) requires that structural information be couched in terms that are easily translatable into energy. The bond-valence model (BVM) [1] has proven fairly effective for this purpose, and it has been used to formulate a number of QSARs, including the MUSIC model for predicting surface functional group acidity on oxide surfaces [2]. Such BVM-based QSARs have had varying success, but they are typically applicable under a fairly restricted set of conditions [3].

It is not readily apparent when QSARs like MUSIC should work or fail, however, because nobody has yet worked out a full BVM-based accounting of the relationship between molecular structure and energy. E.g., the most commonly used aspect of the BVM involves summing bond valences calculated from the lengths of bonds to counter-ions surrounding a central ion. The valence sum is then compared to an ideal value, and the difference is taken to be indicative of some aspect of structural energy. But this does not account for directionality in bonding or interactions between co-ions.

We are currently using some lesser-known aspects of the BVM, including vectorial bond valence (VBV) sums [4] and “effective valence” between co-ions [1], combined with some concepts borrowed from the Valence Shell Electron Pair Repulsion (VSEPR) model of molecular geometry, to create a more complete BVM-based model of structure-energy relationships. By analyzing oxide crystal structures and *ab initio* molecular dynamics simulations of aqueous solutions, we have shown that ideal VBV sums have a fairly straightforward relationship with bond character and coordination number. VBV sums also exhibit a strong relationship with deviations from ideal valence sums.

In addition, we will be applying such analyses to simulated interfacial structures to see how our indicators of “structural energy” vary with distance from the interface, salinity, etc. Such information could then be related to double layer theory.

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