

## Ion exchange and dissolution-precipitation in a zeolitic system

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Zeolites are most commonly known for their ion-exchange properties. Previously, much attention has been given to the quantity of, and the necessary conditions for ion exchange. In order to better understand the underlying reaction mechanism, we investigated the reaction between a typical zeolite, scolecite ( $\text{CaAl}_2\text{Si}_3\text{O}_{10}\cdot 3\text{H}_2\text{O}$ ), and a Na-rich fluid, with the expectation that in a solution with high  $\text{Na}^+$  activity natrolite ( $\text{Na}_2\text{Al}_2\text{Si}_3\text{O}_{10}\cdot 2\text{H}_2\text{O}$ ), or, with a lower probability, mesolite ( $\text{Na}_2\text{Ca}_2\text{Al}_6\text{Si}_9\text{O}_{30}\cdot 8\text{H}_2\text{O}$ ) would form. The three minerals have very similar structures and the substitution of 2  $\text{Na}^+$  for  $\text{Ca}^{2+}$  and  $\text{H}_2\text{O}$  can be considered a classical cation exchange.

Against our predictions, mesolite was only observed in longer term experiments. At all reaction times, however, a reaction rim formed consisting of Na,Al-substituted tobermorite ( $\text{Ca}_{4.5}\text{Si}_{5.2}\text{Al}_{1.0}\text{Na}_{1.3}\text{O}_{16}(\text{OH})_2$ ), a zeolite-like mineral that is of special interest because of its high selectivity for Cs.

A strong textural change from scolecite to both tobermorite and mesolite unambiguously shows that the reaction mechanism did not involve solid-state diffusion. The reaction interfaces are sharp, and the product phases form porous pseudomorphs of the original scolecite, strongly suggesting a coupled dissolution-precipitation process as the reaction mechanism. The formation of the comparatively Ca-rich tobermorite instead of the expected natrolite points to the fact that the solution at the reaction interface is not in equilibrium with the bulk solution. Similarly, it has been observed that Cs-Na exchange of the tobermorite did not start simultaneously in the whole, highly porous reaction rim, but only at the outer part.

Our results demonstrate that reaction between scolecite and a fluid with which it is out of equilibrium takes place by coupled dissolution-precipitation, both when the product phase is isostructural with the parent (as is the case for mesolite) and when it is not (as is the case for tobermorite). Moreover, there is much less fluid mobility around separate crystals in a solution than could be expected, which emphasises the importance of interfacial fluids.

## Reactivity of cement and steel interfaces in geological carbon storage

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To some extent, carbon storage in geological environment is always submitted to leakage threats. Among the different possible scenarios, wells in contact with the storage zone are frequently regarded as the best candidates for  $\text{CO}_2$  leakage. Wells materials, namely cement and steel, can both be corroded by the acidity of  $\text{CO}_2$  rich fluids. Moreover, the interfaces between those materials are suggested to be the preferential pathways for fluids progressions. In order to assess this specific reactivity, a series of cement/tubing assemblies were submitted to storage conditions (150 bar of  $\text{CO}_2$  at  $65^\circ\text{C}$ ) during 6 weeks. Beside the assemblies interfaces, the tested parameters were the cement composition (CEM I, III and V), the cement to water ratio (0.14 to 1.24) and the salinity (0 and  $20\text{ g.l}^{-1}$ ). Carbonation of the cements and corrosion of the steel were quantified in each case as well as the resulting porosity, permeability and chemistry of the solid and liquid phases. As expected, the main conclusion of this approach demonstrate the chief role of the interfaces in the corrosion process and a surprisingly good resistance of the portland cement to such attacks.