

## Zeolites as ion exchanger in harsh ultra-alkaline conditions

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Cement based waste disposal is among the more important options to provide safe storage of non-recyclable often highly toxic waste.[1] Despite all engineering efforts, potentially contaminated ultra-alkaline concrete derived pore waters (pH 12 – 14) will always remain associated with cement based waste disposal. To avoid contamination of the environment due to slow leaching of the metals from these waste forms, engineered barriers are built around the waste disposal sites in order to provide containment. Such engineered barriers, needed to increase the safety level of the waste disposal sites, always incorporate a sorption sink capable of reducing the concentration levels of the toxic metals below specified safety limits.

Zeolites typically crystallize in alkaline, Na/Si/Al rich aqueous conditions and exhibit cation exchange properties.[2, 3] Therefore this family of crystalline porous materials has a significant potential as sorption sink in engineered barriers optimized to function in ultra-alkaline concrete derived pore waters

Cs<sup>+</sup> sorption was evaluated as function of Cs<sup>+</sup> concentration (10<sup>-11</sup> up to 10<sup>-5</sup> mole L<sup>-1</sup>) and time (up to 180 days). The sorption results obtained in ultra-alkaline concrete pore water were compared with data obtained in electrolyte solutions at pH 8 containing identical Na<sup>+</sup>, K<sup>+</sup> and Ca<sup>2+</sup> concentrations.

The isotherms demonstrated an unexpected increased Cs<sup>+</sup> sorption in pH 13 solutions as compared to pH 8 solutions with similar cation content. Sorption results in ultra-alkaline concrete pore water as function of time indicate chabasite and clinoptilolite as two zeolite frameworks stable in these conditions. This confirms results obtained in zeolite formation/transformation studies that indicated a strong stabilizing effect of the alkali cations on specific zeolite frameworks. Binary sorption isotherms confirmed that the selectivity series and calculated selectivity coefficients expected for chabasite and clinoptilolite at trace concentrations (<10<sup>-4</sup> M Cs<sup>+</sup>) are also valid in ultra-alkaline aqueous conditions.

[1] Cote & Bridle (1987) *WM&R* **5**, 55–66. [2] Grutzeck *et al.* (2004) *Cem. Concr. Res.* **34**, 949–55. [3] Barrer (1985) *Surf. Sci. Catal.* **24**, 1–26.

## Determination of sources and flowpaths of nitrate in a karstic watershed

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The Marseillon spring is a strategic resource for the drinking water supply of the Aquitaine region (SW of France). Fed by deep Cretaceous limestone aquifer and local infiltration (favored by karstic limestone outcrop), it is threatened by increasing nitrate concentrations (from 10 to 25 mg/L in 20 years).

Measurement of  $\delta^{15}\text{N-NO}_3^-$  and  $\delta^{18}\text{O-NO}_3^-$  coupled with  $\delta^{11}\text{B}$  allows a good discrimination between the multiple potential sources of nitrate in the area [1]. Additional microbiological markers (bacteriophages, bacteroidales) can offer better precision over the origin of fecal contamination [2].

This work presents a dynamic approach based on these natural isotopic and microbiological tracers measured over samples of Marseillon's groundwater and local surface waters collected from October 2010 to January 2013. Their evolutions within each compartment allow a better understanding of nitrate origin and flow paths in the studied watershed.

[1] Bronders *et al.* (2012), *Environ. Forensics* **13**, 32-38. [2] Briand *et al. Environ. Chem* (in press).