

# Using atomistic simulation techniques to study the adsorption of cations and H<sub>2</sub>O on zeolite surfaces

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Heavy metals and radionuclides are both hazardous cationic species, and their interaction with soils have received increasing attention in recent years. Ion exchange is regarded as one of the key processes that regulate these hazardous species within the environment, but it can also be the process used for the decontamination of polluted soil, (ground)water or effluent. An ion-exchanger, often a zeolite, which is specific to the type of contamination, can be used to selectively remove the pollutant. For example, Clinoptilolite, which is used to remove Cs-137 and Sr-90 from soils and milk, or Phillipsite, which has been used to recover Cd from acid mine drainage.

Due to this selective recovery of the cationic contamination, zeolites concentrate and therefore reduce the waste volume.

For these reasons we decided to model cation-exchange and adsorption behaviour of a range of zeolites with varying structural properties, including ring size and Si/Al ratio. The zeolites studied are; zeolite A (LTA), zeolite RHO, Heulandite and its iso-structure Clinoptilolite. The cationic species used in our calculations were selected for their varying ion size, charge along with their environmental importance (Table 1). Zeolite A was chosen as a model structure to verify our simulation techniques as there is ample experimental crystallo-graphic data available to compare our results with. In addition, atomistic calculations have been used successfully before to study structural and reactivity properties of zeolites, including Na-exchanged zeolite A.

Atomistic simulations could aid the understanding of the ion-exchange properties of zeolites by studying the bulk and surface structures of the different zeolites for; (i) cation adsorption sites, (ii) effect of aluminium distribution, (iii) cation substitution, (iv) cation diffusion pathways and activation energies, (v) effect of water at neutral, acid and basic pH.

## Methodology and potentials

The atomistic simulation methods are based on energy minimisation calculations according to the

Born model of ionic (Born and Huang, 1954) solids in which the forces between the atoms are described by interatomic potentials. The reliability of the potential parameters largely govern the accuracy of our simulations. This is why we use the three-body Shell model potentials derived by Sanders, Leslie and Catlow (1984) because this has been shown to be highly transferable and reduces the need of additional derivation of potential models for each new cation introduced into the zeolite. Moreover, complementary studies on the simulation of water adsorption on rock-salt oxides by de Leeuw *et al.* (1996) provide a transferable set of potentials for the interaction of water molecules with ionic solids and can be readily applied to the simulation of zeolites.

## Results

From the calculation results to date we can make the following observations (Higgins *et al.*, 1997):

Framework relaxation is a very important component in the interaction between cation and framework, and the zeolite lattice cannot be viewed as a rigid structure through which atoms move as has been used in earlier simulations.

In general, the most stable cation sites are located near 6- and 8-membered rings. Some recent experiments have indicated that the metastable adsorption sites identified in our calculations could become important adsorption positions at higher cation loading and when competing cationic species are introduced.

Aluminium addition to the zeolite framework has a pronounced effect on the cation site stability as it reduces the repulsive forces between the exchangeable cation and the zeolite framework. In addition, the introduction of aluminium can change the size and shape of the zeolite ring structures. The cations will either be stabilised or destabilised in their adsorption sites due to the aluminium addition, depending whether it causes an increase or reduction in the number of stabilising bonds possible between cation and framework oxygens.

TABLE 1. Potentially exchangeable cations used in the atomistic calculations along with their environmental importance

Common cations	Exchangeable Cations	
	Heavy-metals	Radionuclides
Ba <sup>2+</sup> , Ca <sup>2+</sup> , K <sup>+</sup> , Na <sup>+</sup>	Cd <sup>2+</sup> , Co <sup>2+</sup> , Ni <sup>2+</sup> , Cr <sup>3+</sup>	Co-60, Cs-137 Sr-90

Upon hydration, the cations were found to move further from the zeolite framework, forming stabilising bonds with the oxygens of the surrounding water molecules in preference to the framework oxygens.

The simulation results to date show good agreement with experimental crystallographic data, which indicates the viability to use our potential model and atomistic simulation methods to probe the structure, stability and diffusivity in zeolites.

### References

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