



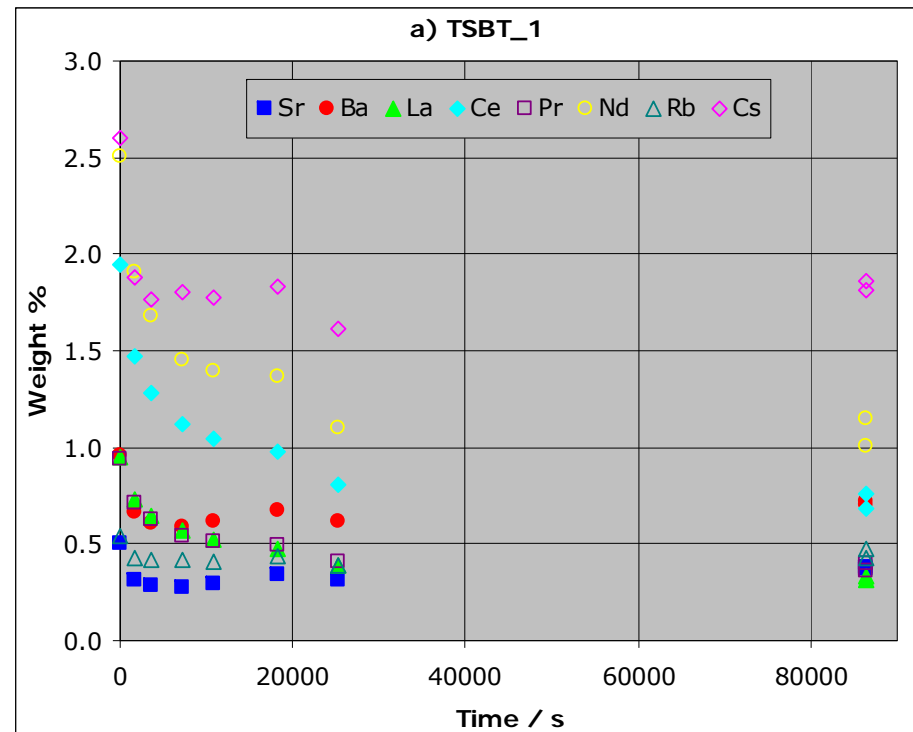
# Optimising fission product extraction from molten salt wastes using zeolite ion exchange

1<sup>st</sup> SACSESS International Workshop

Warsaw, 22-24 April 2015



- Large body of literature on salt decontamination using zeolites
- Effective for lanthanides
- Ineffective for alkali metals and alkaline earths




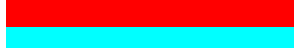



- Conditioning of highly Cs/Sr salt loaded zeolites
- Glass bonding / sintering to maintain high waste loadings
- Optimisation of:
  - Glass bonding matrix (low melting point)
  - Processing conditions (sinter or HIP)
- Avoid conversion of zeolite to sodalite (lower waste loading)
- Viable wasteforms characterised by XRD, SEM and MCC-1 / PCT durability tests

# Cs/Sr Decontamination of salt

- Management of Cs/Sr difficult for salt clean-up
- Zeolite ion-exchange works but with very low efficiency

Salt Decontamination Process	Lanthanides (La, Ce, Nd, Pr)	Alkaline Earths (Sr, Ba)	Alkali Metals (Cs, Rb)
<i>Ion-exchange (zeolites)</i>	Green	Yellow	Orange
<i>Hybrid aqueous closed loop</i>	Cyan	Cyan	Cyan
<i>Precipitation (carbonates/phosphates)</i>	Yellow	Orange	Red
<i>Precipitation (oxygen sparging)</i>	Green	Red	Red
<i>Precipitation (wet argon sparging)</i>	Cyan	Red	Red
<i>Electrolysis</i>	Green	Red	Red
<i>Li-Reduction</i>	Green	Red	Red
<i>Melt crystallisation</i>	Cyan	Yellow	Yellow

	Fully effective, demonstrated at lab-scale (>90% efficient)
	Partially effective, demonstrated at lab-scale (10-90% efficient)
	Slightly effective, demonstrated at lab-scale (<10% efficient)
	Ineffective, demonstrated at lab-scale (0% efficient)
	Assumed effective, but not fully demonstrated

- Safe management of Cs/Sr fission products in pyro-process is essential
- Operation with high degree of uncertainty and few solutions
- KAERI looking melt crystallisation (for  $\text{LiCl-SrCl}_2\text{-CsCl}$ )
- SACSESS approach is to optimise existing process, i.e. zeolite ion-exchange
- Significant long-term advantages:
  - Maximising the salt loading of the zeolite, and
  - Optimising the zeolite for the ion-exchange and capture of Cs and Sr

- Using an iterative modelling/laboratory study approach
  1. Initial construction and testing of model parameters to replicate the experimental system
  2. Sensitivity study to establish optimum variables
  3. Predict loading profiles, decontamination factors.
  4. Perform zeolite ion-exchange experiments in laboratory
  5. Characterise salt-loaded zeolite from (4)
  6. Repeat (1) – (5) above to optimise for chloride and Cs/Sr loading

## Three modelling stages:

- 1) *Create molten salt system and validate model*
- 2) *Create zeolite crystal and validate model*
- 3) *Combine zeolite and molten salt*

## Specific issues:

- Different atomic interactions for different systems
- Methods for inserting (Li,K)Cl molecules into zeolite

## ***Stage 1: Create molten salt system and validate model***

### **Potential:**

- B-H-M, parameters by Matsumiya

$$\Phi_{ij} = \frac{z_i z_j e^2}{4\pi\epsilon_0 r} + A_{ij} b \exp[(\sigma_i + \sigma_j - r)/\rho] - \frac{c_{ij}}{r^6} - \frac{d_{ij}}{r^8}$$

- Checked against simulation results and experimental results of Lantelme & Turq
- (Li, K, Na, Cs):Cl system modelled



# Molten Salt Model Details

600 K

Lantelme & Turq:

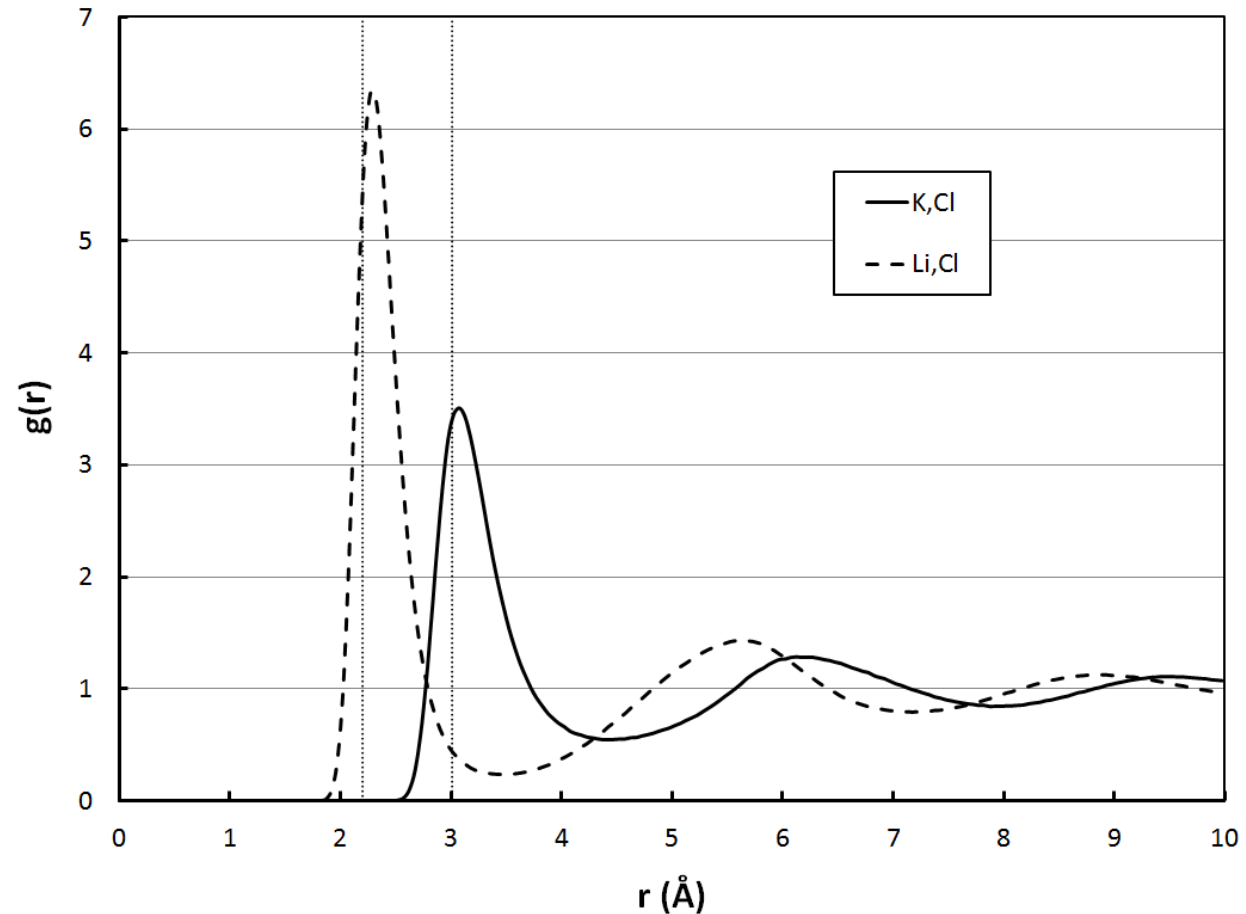
$$r_1 = 2.20 \text{ \AA} (\text{Li,Cl})$$

$$r_1 = 3.01 \text{ \AA} (\text{K,Cl})$$

This Work:

$$r_1 = 2.28 \text{ \AA} (\text{Li,Cl})$$

$$r_1 = 3.08 \text{ \AA} (\text{K,Cl})$$



## Stage 2: Create zeolite crystals and validate model

### LTA

- Common (e.g. Zeolite 4A)
  - Easy to source
  - Well understood

### PHI

- High number of large rings
- Theoretically higher Cs absorption

### MOR

- High Si:Al ratio (mordenite)
  - Abundant in nature
- Large framework cages

### RHO

- Similar to LTA
- Larger central pore due to increased space between  $\beta$ -cages

### FAU

*(In progress)*

- Common and easy to synthesise
- Well understood through petrochemical uses

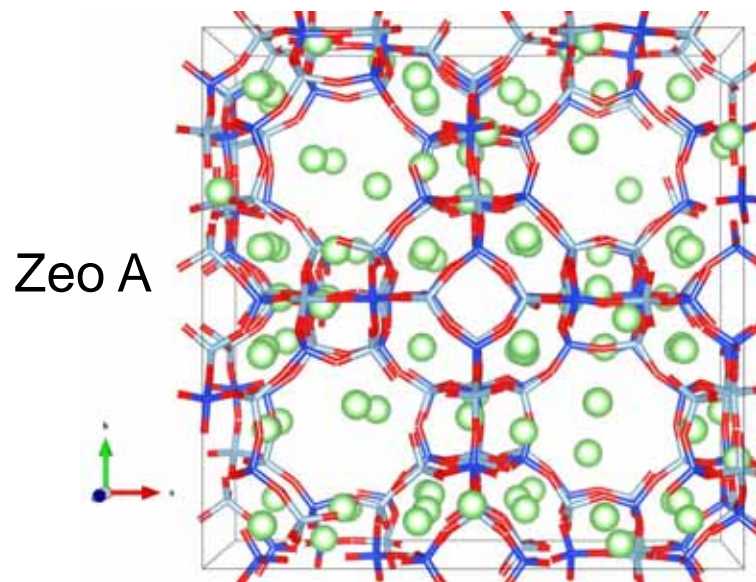
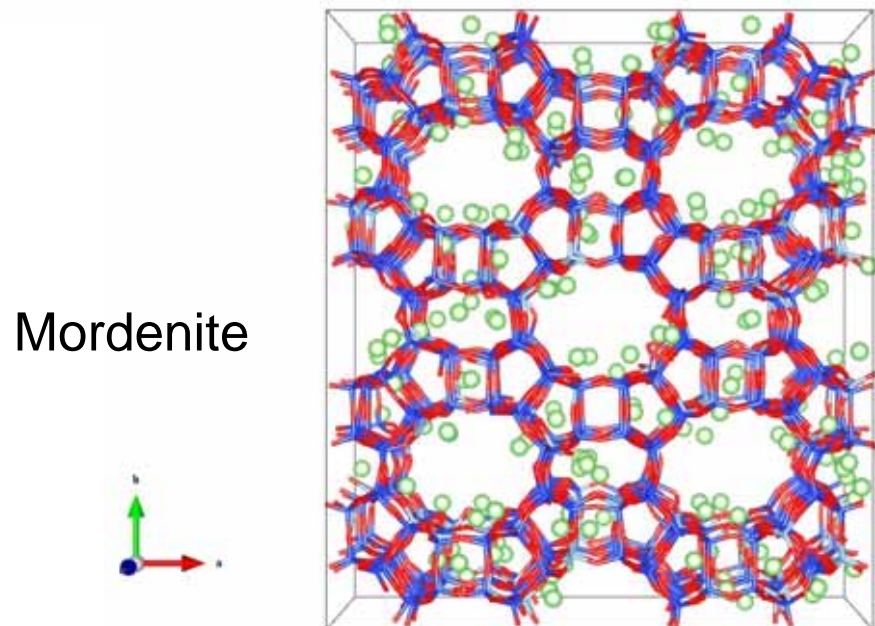
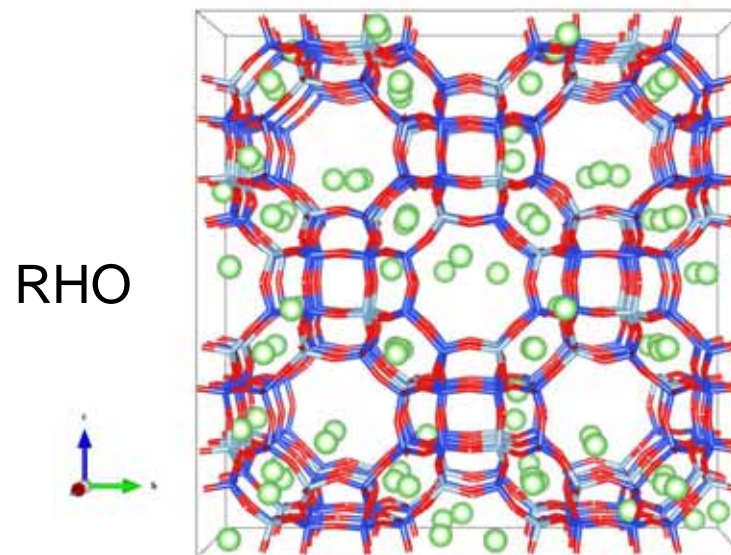
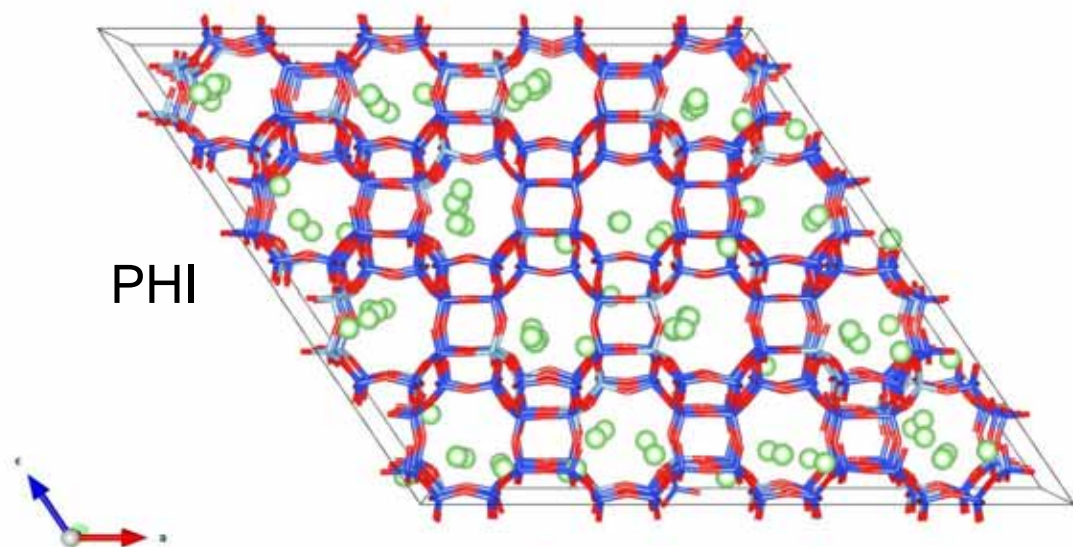
- Lennard-Jones 12-6 potential used for zeolite crystals

$$U(r) = 4\epsilon \left[ \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right]$$

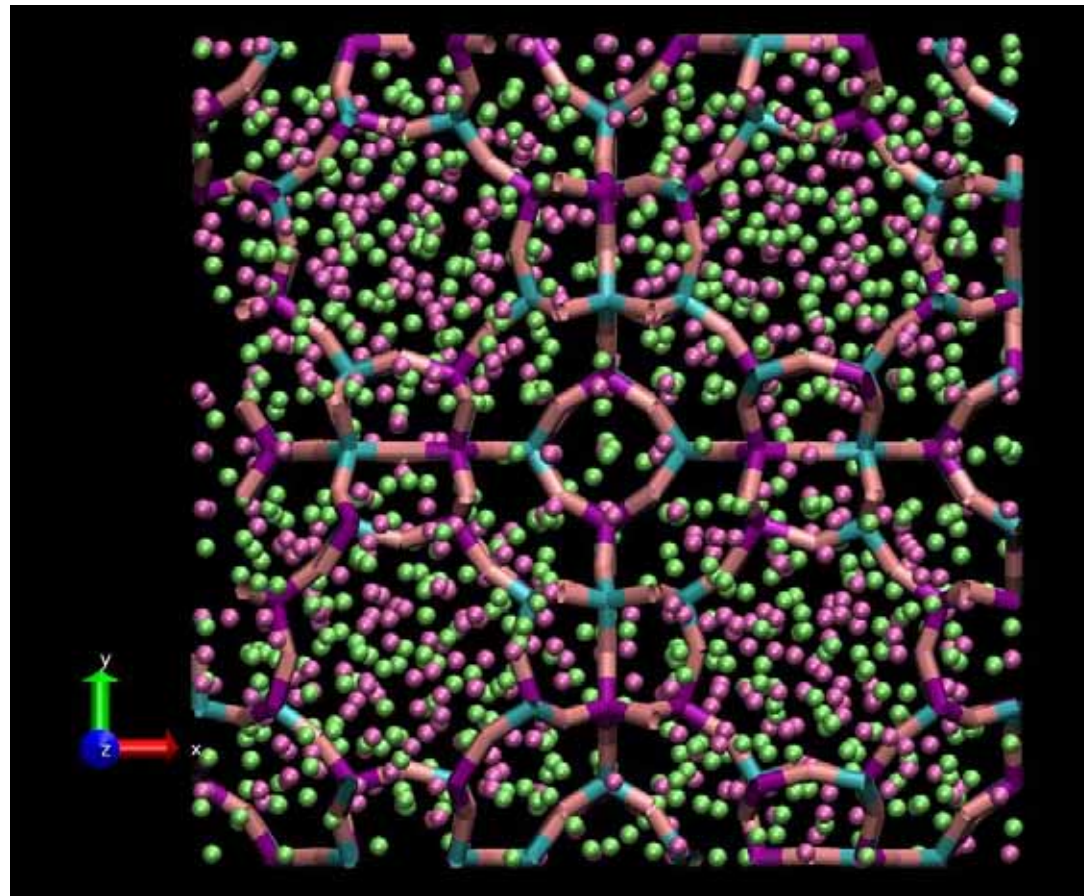
- Parameters from the 'constant valence forcefield' (cvff\_aug)
- Occluded ions assumed to be part of zeolite
  - Salt - Zeolite interactions represented by L-J
  - Salt - Salt interactions represented by B-H-M



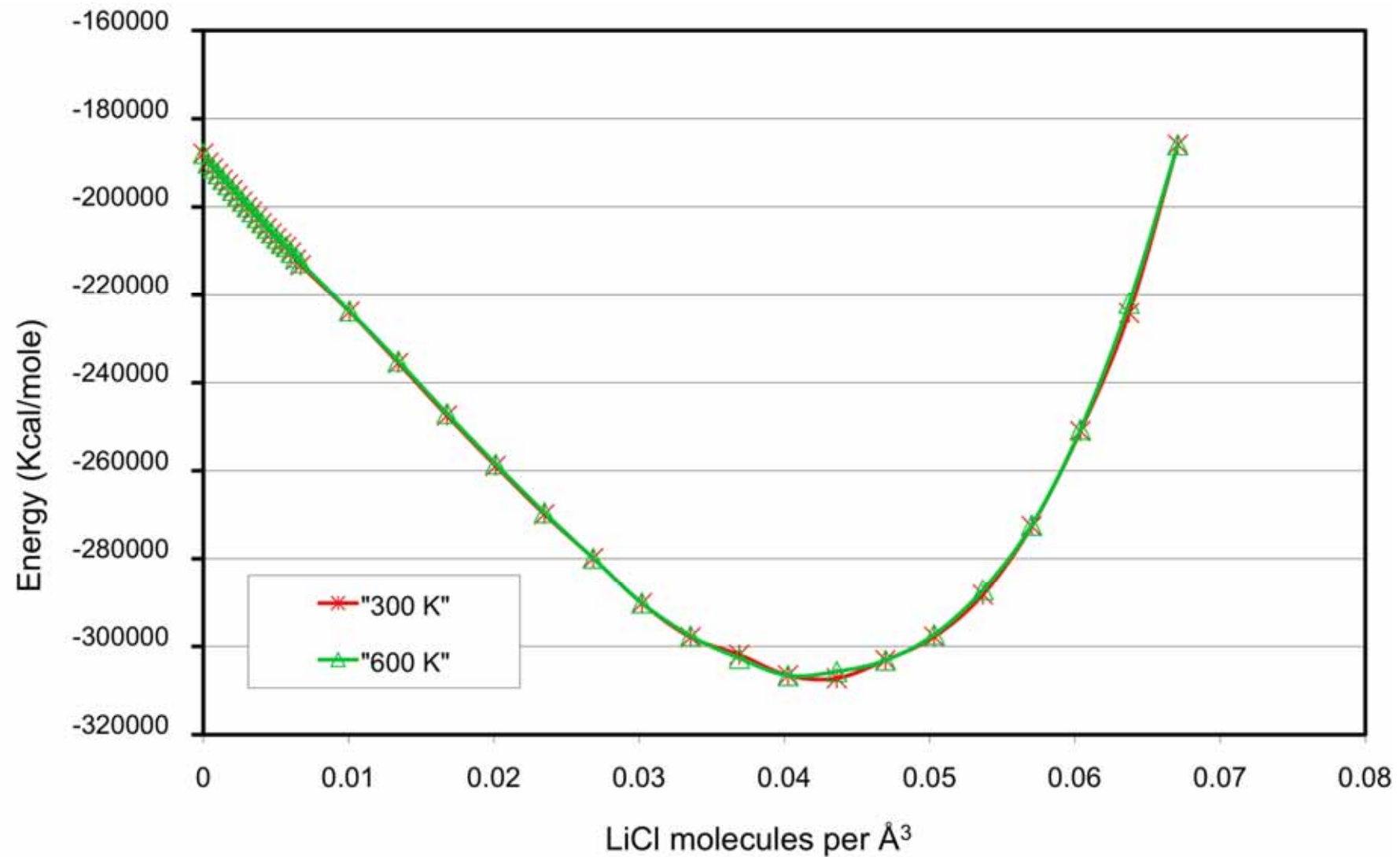
# Occluding framework cations



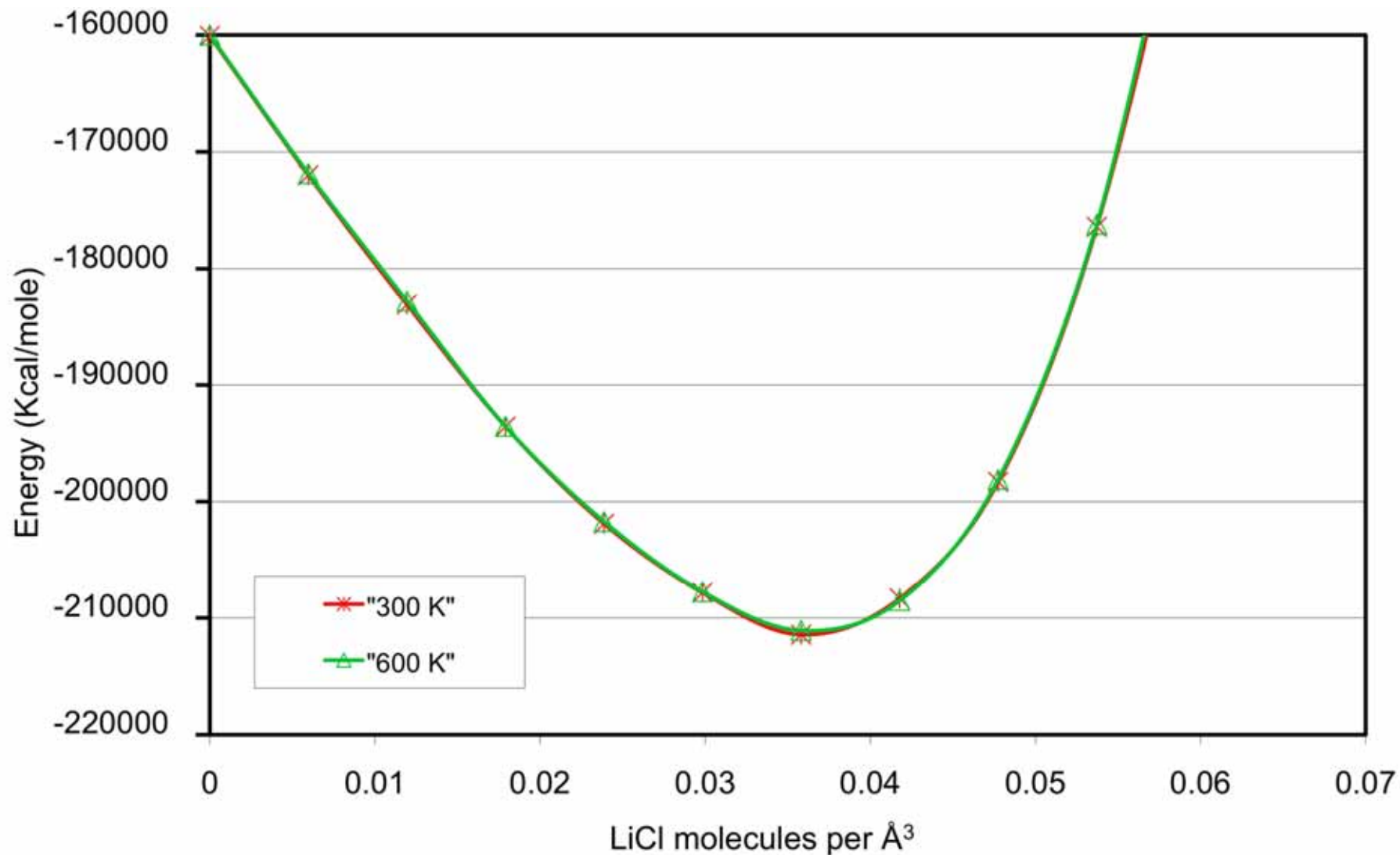
## Stage 3: *Combine zeolite and molten salt system and validate model*



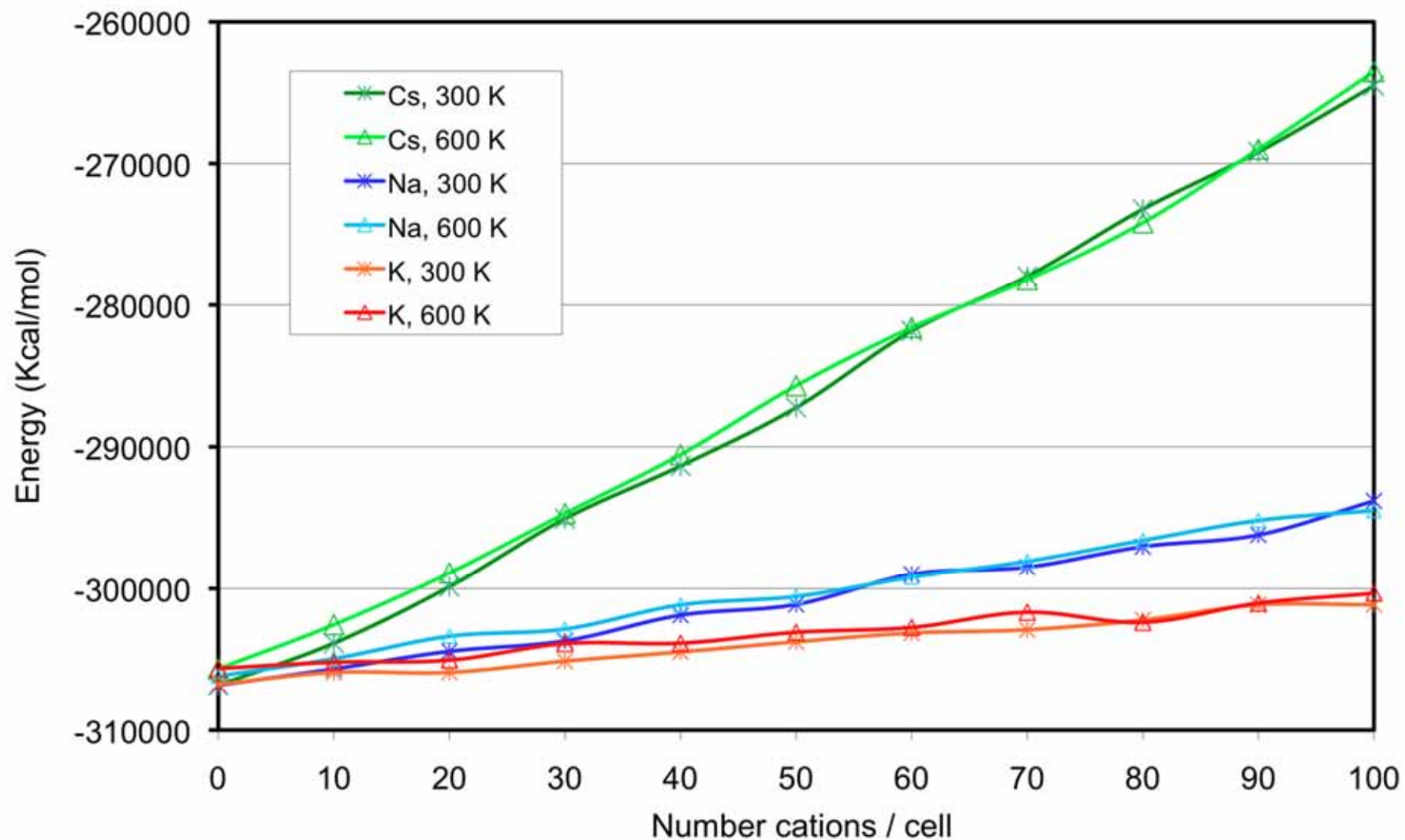
# Adding LiCl Molecules – Zeolite A



# Adding LiCl Molecules – Mordenite

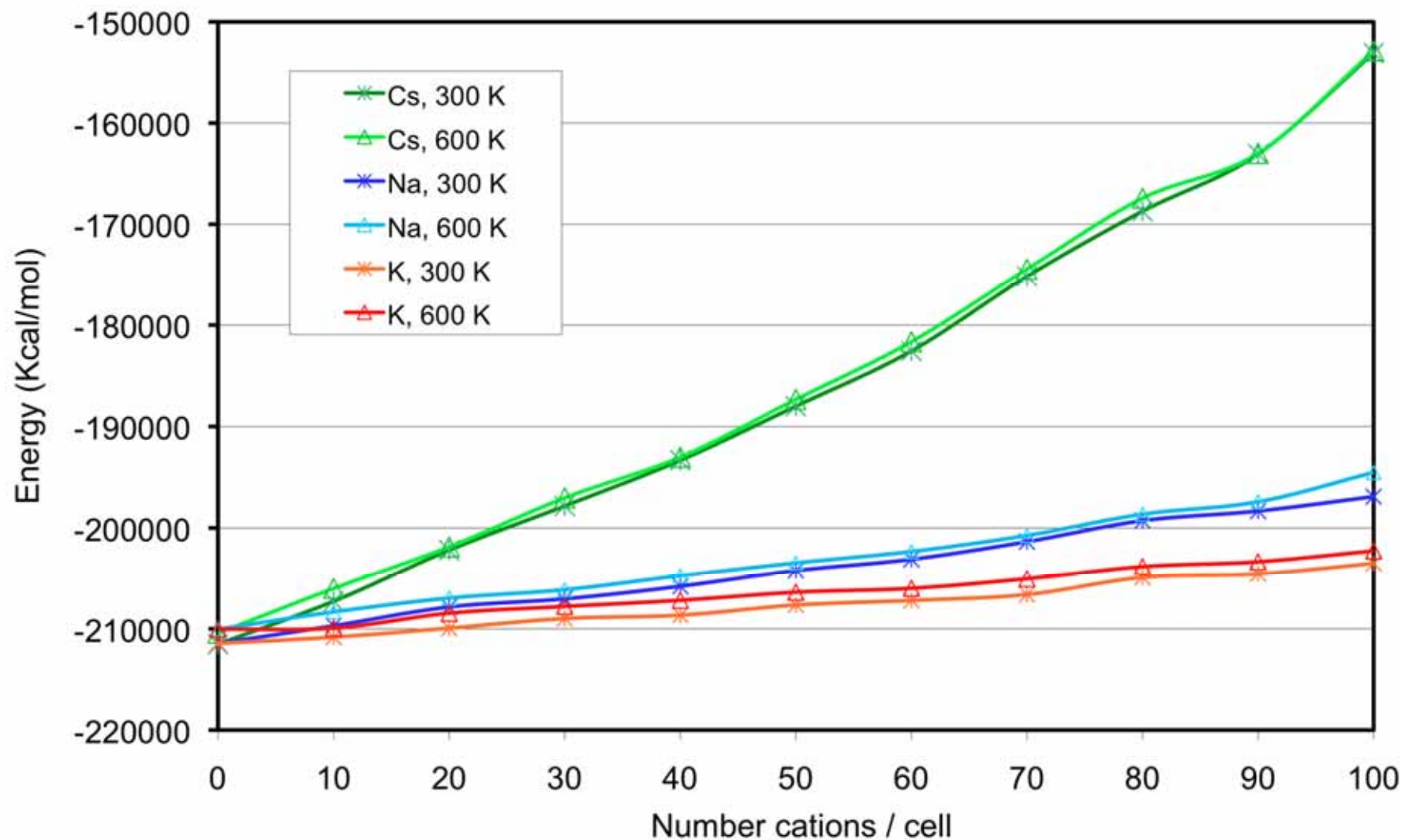


# Including Cs, K, Na – LTA





# Including Cs, K, Na – MOR



# Comparison of Insertion Energies

## LTA

Cation	Insertion Energy (Kcal/mol)	% System energy	% of value for K
K	56.3	$1.9 \times 10^{-4}$	-----
Na	130.4	$4.4 \times 10^{-4}$	231 %
Cs	423.5	$1.6 \times 10^{-3}$	752 %

## MOR

Cation	Insertion Energy (Kcal/mol)	% System energy	% of value for K
K	79.3	$3.9 \times 10^{-4}$	-----
Na	145.3	$7.4 \times 10^{-4}$	183 %
Cs	584.45	$3.8 \times 10^{-3}$	737 %

- Ion exchange of all cations from the salt into the MOR framework is energetically more unfavourable than for LTA
- However, a slight increase in Cs adsorption might be seen for MOR as it is relatively less unfavourable compared with K, Na
- Finalise details of all zeolite frameworks
- Assess self-diffusion coefficients of Na, Li, K and Cs through the salt whilst in the zeolite pores.

