Supplementary materials for atomistic and mesoscale simulation of sodium and potassium adsorption in cement paste

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I. MESOSCALE MODEL

Ioannidou's *et al.* mesoscale C-S-H model [1, 2] was used to calculate granular adsorption/desorption by DFT simulations. The precipitation of C-S-H nano-grains and settings was simulated using the approach recently proposed in Ref. [3]. In this approach, a free energy gain drives the precipitation of particles of few nanometers (C-S-H nanoscale hydrates) which also interact and aggregate. The simulations consisted of a Grand-Canonical Monte Carlo (GCMC) scheme, where the chemical potential corresponds to the free energy gain just mentioned, coupled to a Molecular Dynamics (MD) scheme.

The effective interparticle forces between cement hydrates depends on the concentration of calcium ions in the solution and changes during the hydration [4, 5]. In precious works, the microstructure of C-S-H gels at early hydration stages was investigated using attracto-repulsive potential arising from ion-ion correlation forces [3, 6].

Differently from [3] here we consider only effective interactions that would correspond to the hardened cement paste and can be well modeled [2] with a short-range attractive Mie potential

$$V(r) = \alpha \epsilon \left[\left(\frac{\sigma}{r}\right)^{2\gamma} - \left(\frac{\sigma}{r}\right)^{\gamma} \right] , \qquad (1)$$

where r is the inter-particle distance, α is the well depth (with ϵ the unit energy) between two particles with size diameter σ and we have fixed the exponent to $\gamma = 12$. We have set $\alpha = 6$ and the temperature to T = 0.15 (typically measured in units ϵ/k_BT), while time is measured in usual MD units $\sqrt{m\sigma^2/\epsilon}$, all in reduced units.

II. CSHFF PARAMETERS

The CSHFF parameters are presented in Table I. This parametrization is an extension of the parametrization reported in Ref. [7].

III. VALIDATION OF THE INTER-ATOMIC INTERACTION POTENTIAL

Configurations for the molecular dynamics (MD) simulations were created using the reported crystallographic databases (in the case of combeite, the low-temperature combeite structure was chosen). The configurations were relaxed using molecular statics. Atomic displacements before and after relaxation are reported. 300K MD runs were performed, and confirmed that the structures were stable. We the simulation box size was also optimized. The results are illustrated in Fig. 1. As for lattice parameters, the model predicts a correct value for combeite, a value 3% too large for senkevichite, and a value 2% too large for hydroxyapophyllite. The largest discrepancies between the model and experiments are observed for hydrogen. Note that the CSH-FF model was not designed for accuracy in non-CSH systems, such as the alkali-rich minerals used for this validation. Given this limitation, these results are reassuring and show that extending CSHFF by importing the original ClayFF alkali parametrization leads to physically meaningful results.

IV. SAMPLE LAMMPS PARAMETERS

In the LAMMPS data file, bond and angle coefficients are set:

Bond Coeffs # harmonic

1 554.135 1

#log

Angle Coeffs # harmonic

1 45.7696 109.47

A sample LAMMPS input file:

log.lammps # if you want to see output of lammps

Specie	Si	Ca	(Cw		Ob		0	0	h
Role	Si	Oxide Ca	Hydra	ated Ca	Brid	ging silica	O non-br	ridging silica O	Hydrox	cide O
Charge	1.722357	1.435466	1.70	05529	-	1.076687	-	1.217782	-0.996	6444
Specie	Ow	Hw		Н		Na		Κ	С	s
Role	Water O	Water H	Hydr	oxide H		Na		Κ	С	s
Charge	-0.82	0.41	0.	.425	0	.8527645	0	0.8527645	0.852	7645
Elemen	t_i Elemen	$\operatorname{nt}_j \epsilon$ (Kcal	/mol)	σ (Å	1)	$\operatorname{Element}_i$	Element _j	$\epsilon \; (\rm Kcal/mol)$	σ (2	Å)
Ca	Ob	7.05E	2-04	5.45230	0155	Ob	Ow	8.72E-01	2.89542	20834
Ca	Ο	8.69E	2-04	4.36540	3719	0	Ow	5.26E-03	4.24067	77898
Ca	Oh	8.69E	2-04	4.36540	3719	Oh	Ow	8.72E-01	2.89542	20834
Cw	Ob	1.04E	2-03	4.44558	4604	Ow	Ow	1.54E-01	3.16269	90449
Cw	О	1.46E	2-03	4.36540	3719	Ob	\mathbf{Na}	8.97E-02	2.89674	82730
Cw	Oh	1.04E	2-03	4.44558	4604	0	\mathbf{Na}	4.02E-01	2.54195	67675
Si	Ob	$5.95\mathrm{E}$	2-04	3.26068	9308	Oh	\mathbf{Na}	8.97E-02	2.89674	82730
Si	О	5.60E	2-04	3.26959	8296	Ow	\mathbf{Na}	1.42E-01	2.75777	69820
Si	Oh	$5.95\mathrm{E}$	2-04	3.26068	9308	Ob	Κ	7.87E-02	3.388	738
Ob	Ob	6.18E	2-02	3.44777	8039	0	Κ	3.53E-01	3.033	956
0	О	$1.24\mathrm{E}$	+00	2.73505	9065	Oh	Κ	7.87E-02	3.388	738
Oh	Oh	6.18E	2-02	3.44777	8039	Ow	Κ	1.24E-01	3.249	776
Ob	О	$4.54\mathrm{E}$	2-02	3.62595	7783	Ob	\mathbf{Cs}	7.86E-02	3.63952	21334
Ob	Oh	6.18E	2-02	3.44777	8039	0	\mathbf{Cs}	3.53E-01	3.28302	21334
0	Oh	$4.54\mathrm{E}$	2-02	3.62595	7783	Oh	\mathbf{Cs}	7.86E-02	3.63952	21334
Ca	Ow	8.76E	2-04	4.36540	3719	Ow	\mathbf{Cs}	1.24E-01	3.49702	21334
Cw	Ow	6.02E	2-04	4.47231	1565					
Element _i Element _j Element _k $k_r(Kcal/mol/Å^2) k_{\Theta}(Kcal/mol/\Theta^2) r_0(Å) \Theta_0$										
Γ	Hw	Ow	_		554.	13		1	_	
	Η	Oh	_		554.	135	—	1	-	
	Hw	Ow	Hw		—		45.7	7 –	109.47	

TABLE I. Top table: Partial charges used in CSH-FF, adapted for Na-K-Cs. Middle table: Lennard-Jones coefficients, adapted for Na-K-Cs. Bottom table: Bond and angle spring constants for water and hydroxide in CSH-FF. This is an extension of the parametrization reported in Ref. [7].

units	real #metal
atom_style	full #atomic
boundary p p p atom_modify	map array
bond_style	harmonic
angle_style	harmonic

read_data lammpsdata.lmp

pair_style hybrid/overlay lj/cut 12 coul/wolf 0.25 12.0 pair_coeff * * lj/cut 0 0 pair_coeff 2 4 lj/cut 7.05E-04 5.452300155 pair_coeff 2 5 lj/cut 8.69E-04 4.365403719 pair_coeff 2 6 lj/cut 8.69E-04 4.365403719 pair_coeff 3 4 lj/cut 1.04E-03 4.445584604 5 lj/cut pair_coeff 3 1.46E-03 4.365403719 pair_coeff 3 6 lj/cut 4.445584604 1.04E-03 pair_coeff 1 4 lj/cut 5.95E-04 3.260689308



FIG. 1. The distance between the equilibrium positions predicted using CSHFF and crystallographic data. The experimental data is for combetite [8], hydroxyapophyllite [9] and senkevichite [10]. The displacements for each atomic element is plotted separately. The computational data were first reported in Ref [11].

<pre>pair_coeff</pre>	1	5 lj/cut	5.60E-04	3.269598296
pair_coeff	1	6 lj/cut	5.95E-04	3.260689308
<pre>pair_coeff</pre>	4	4 lj/cut	6.18E-02	3.447778039
pair_coeff	5	5 lj/cut	1.24E+00	2.735059065
<pre>pair_coeff</pre>	6	6 lj/cut	6.18E-02	3.447778039
<pre>pair_coeff</pre>	4	5 lj/cut	4.54E-02	3.625957783
pair_coeff	4	6 lj/cut	6.18E-02	3.447778039
pair_coeff	5	6 lj/cut	4.54E-02	3.625957783
pair_coeff	2	7 lj/cut	8.76E-04	4.365403719
<pre>pair_coeff</pre>	3	7 lj/cut	6.02E-04	4.472311565
pair_coeff	4	7 lj/cut	8.72E-01	2.895420834
<pre>pair_coeff</pre>	5	7 lj/cut	5.26E-03	4.240677898
pair_coeff	6	7 lj/cut	8.72E-01	2.895420834
<pre>pair_coeff</pre>	7	7 lj/cut	1.54E-01	3.162690449
<pre>pair_coeff</pre>	4	10 lj/cut	8.97E-02	2.8967482730
pair_coeff	5	10 lj/cut	4.02E-01	2.5419567675
<pre>pair_coeff</pre>	6	10 lj/cut	8.97E-02	2.8967482730
<pre>pair_coeff</pre>	7	10 lj/cut	1.42E-01	2.7577769820
pair_coeff	4	11 lj/cut	7.87E-02	3.388738

pair_coeff	5	11 lj/cut	3.53E-01	3.033956
pair_coeff	6	11 lj/cut	7.87E-02	3.388738
pair_coeff	7	11 lj/cut	1.24E-01	3.249776
pair_coeff	4	12 lj/cut	7.86E-02	3.639521334
pair_coeff	5	12 lj/cut	3.53E-01	3.283021334
pair_coeff	6	12 lj/cut	7.86E-02	3.639521334
pair_coeff	7	12 lj/cut	1.24E-01	3.497021334

pair_coeff * * coul/wolf

Lablel Dictionary : n1 (lammps) : n2 (gulp)
1 : Si
2 : Ca
3 : Cw
4 : Ob
5 : O
6 : Oh
7 : Ow
8 : Hw
9 : H
##10 : Na
##11 : K
##12 : Cs

neighbor 1.0 bin neigh_modify delay 0 every 1 check no

special_bonds coul 0 0 0 1j 1 1 1
run 0
write_data init.lmp

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