

# Supporting information for “Transport Properties of Sulfate and Chloride Ions Confined between Calcium Silicate Hydrate Surfaces: A Molecular Dynamics Study”

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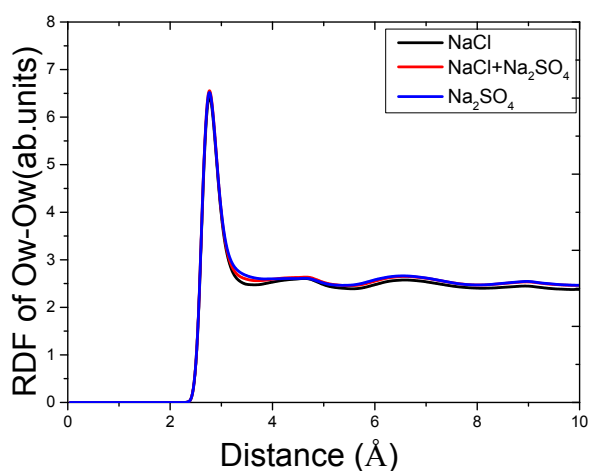
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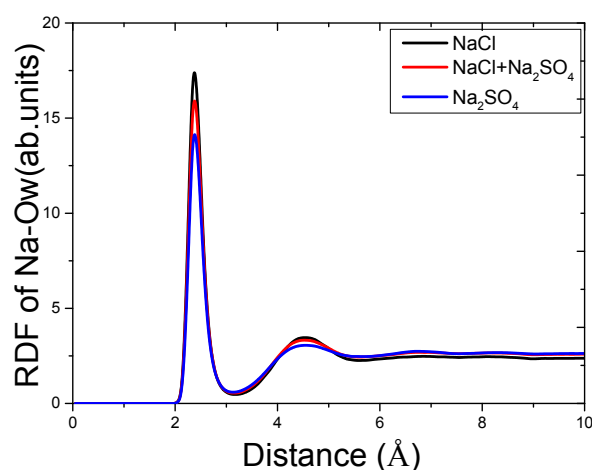
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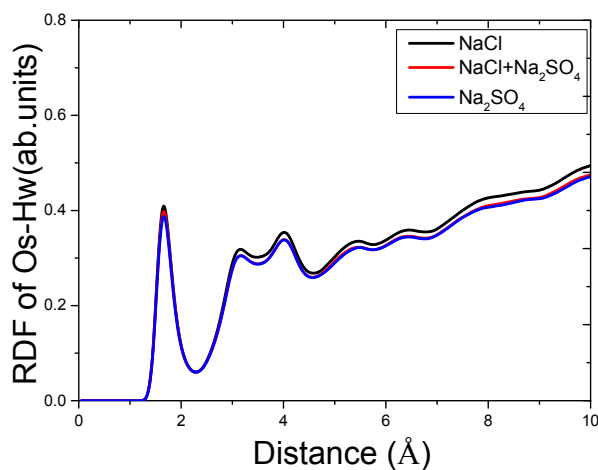
## S1 Radial Distribution Function (RDF)



(a)



(b)



(c)

**FigureS1 Radial distribution function (RDF) of(a)Ow-Ow (b)Na-Ow(c)Os-Ow.**

As shown in Figure S1a, the RDF of  $O_w-O_w$  has the first peak located at 2.76 Å, indicating the nearest neighbor of water molecule connected by the H-bonds. In S1b, the first and second peak of  $Na-O_w$  is positioned at 2.35 and 4.55 Å, respectively, represent the water molecule in the first and second shell of hydrated central sodium ions. Additionally, RDF of ions-water shows no pronounced difference in pure solution and mixed solution, implying that coupled ions interaction in the mix solution has little influence on the ionic hydration structure. As shown in Figure S1c, there are three pronounced peaks of  $O_s-H_w$  located at 1.65, 3.15 and 4.05 Å. It implies that the oxygen sites in the silicate chains can

connect with the water molecules by the H-bonds.

## S2. Coordinate number analysis

Table S1 the coordinate number of sodium ion

	<b>Na-Ow</b>	<b>Na-Cl</b>	<b>Na-S</b>	<b>Na-Os</b>	<b>Total</b>
<b>NaCl</b>	5.34	0.11	0	0.24	5.68
<b>NaCl+ Na<sub>2</sub>SO<sub>4</sub></b>	4.80	0.04	0.58	0.18	5.60
<b>Na<sub>2</sub>SO<sub>4</sub></b>	4.473	0	0.90	0.12	5.49

Table S2 the coordinate number of chloride and sulfate ion

	<b>Cl-Ow</b>	<b>Cl-Na</b>	<b>Cl-Os</b>	<b>Cl-Ca</b>	<b>Cl-S</b>	<b>Total</b>
<b>NaCl</b>	7.42	0.10	0.01	0.01	0	7.60
<b>NaCl +Na<sub>2</sub>SO<sub>4</sub></b>	7.30	0.13	0	0	0.17	7.60
	<b>S-Ow</b>	<b>S-Na</b>	<b>S-Os</b>	<b>S-Ca</b>	<b>S-Cl</b>	<b>Total</b>
<b>NaCl +Na<sub>2</sub>SO<sub>4</sub></b>	11.87	1.64	0.02	0.05	0.15	13.73
<b>Na<sub>2</sub>SO</b>	11.62	1.82	0	0.05	0	13.49

To quantitatively study the nearest neighbors of different solution species confined in the gel pore, the coordination number of ions and water is calculated by accounting the number of the atoms surrounding the central atom within the cutoff distance of the first valley position in the corresponding RDF. As listed in Table S1, the nearest neighbors of confined sodium ions are composed of water molecules, oxygen atoms in silicate chains, chloride ions and sulfate ions in the solution. On average, the total CN of sodium ions ranges from 5.5 to 5.7, consistent with the results from neutron diffraction experiment<sup>1</sup>. In the NaCl solution, on average, the sodium ion coordinates with only around 0.1 chloride ion and 0.24 oxygen atoms in the C-S-H substrate. In the pure Na<sub>2</sub>SO<sub>4</sub> solution, the

sodium ion can connect with around 0.9 sulfate ions and 0.12 oxygen atoms in silicate chains. Hence, in the capillary transport process, the small number of solid oxygen atoms near the sodium ions indicates that the interaction between  $O_s$  and Na plays weak role in resisting the fluid ingress in the nanometer channel of C-S-H gel.

In the mixed solution containing sulfate and chloride ions, the sodium ions are more likely to associate with sulfate ions (0.58) to form the ionic pair, as compared with the chloride ions (0.04). This is partly due to large charge negativity of sulfate ions attracting cations, and partly due to the slow diffusivity of sulfate cluster immobilizing ions. Because of the strong interaction between sulfate and sodium ions, the water molecules and oxygen atoms in silicate chains near the central sodium ions are substituted by the oxygen sites in the sulfate ions, reducing the CN of Na-O<sub>w</sub> and Na-O<sub>s</sub>.

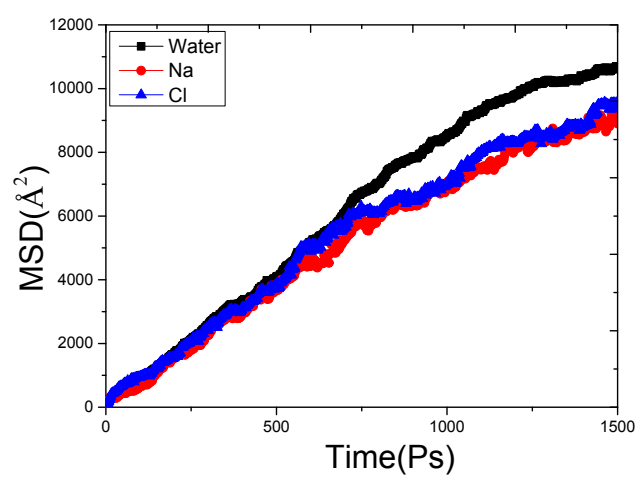
As compared with sodium ions, the local chemical environment of chloride and sulfate ions is more complicated in Table S2. The chloride ions are surrounded by neighboring water molecules by H-bond, sodium ions and surface ions by ionic pairs, and surface oxygen atoms and neighboring sulfate ions. In the pure NaCl solution, the average CN of Cl-O<sub>s</sub> and Cl-Ca is around 0.02. It is consistent with that the few chloride ions are adsorbed on the C-S-H surface as observed in the intensity profile. On average, only less than 0.1 Na ions can form ionic pair with Cl ions in NaCl solution, indicating relative weak Na-Cl connection. Hence, in the pure NaCl solution, neither sodium nor chloride ion is restricted firmly by the C-S-H surface with stable chemical bonds, and there are few ionic pairs and cluster accumulation. This is why the Na and Cl ions can follow closely with water molecules in the gel pore during the capillary transport process.

On the other hand, in the pure  $Na_2SO_4$  solution, each sulfate ion, on average, can associate with 1.82 sodium ions and 0.05 surface calcium ions. It means that the

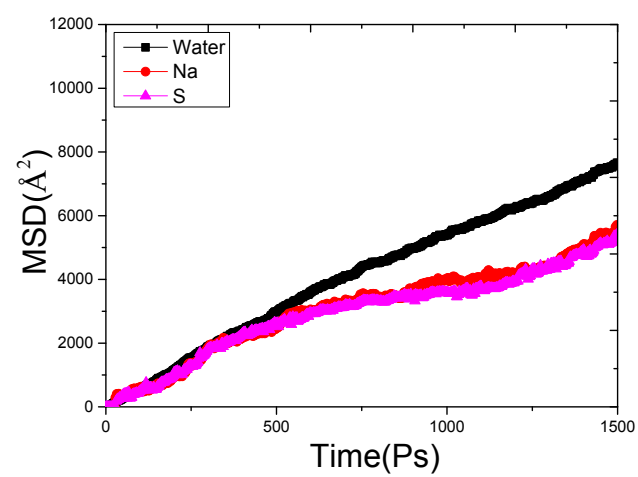
sodium ions take predominated percentage in the anion-cation clusters. Considering that nearly 36% of the sodium ions in  $\text{Na}_2\text{SO}_4$  solution are adsorbed on surface of C-S-H gel, the majority of the  $\text{Na-SO}_4$  clusters remain  $10\text{\AA}$  within the surface region. The C-S-H surface immobilizes the sulfate ions by indirect connection of  $\text{Os-Na-SO}_4$ .

In the mixed solution, the local environment of chloride and sulfate ions is slightly changed due to the influence from interaction between different ions, as compared with the local structure of ions in pure solution. For the chloride ions, both CN of  $\text{Cl-Os}$  and  $\text{Cl-Ca}$  reduces to zero in mixed solution. It implies that the sulfate ions, secondary adsorbed on the C-S-H substrate, enhance the surface charge negativity, further repulsing the chloride ions. More importantly, each chloride ion, on average, has 0.17 sulfate ion surrounding it. It means that the sulfate cluster, associated with sodium ions, can also immobilize part of the free chloride ions in the solution. The spatial correlation between S and Cl is consistent with the  $\text{SO}_4\text{-Na-Cl}$  cluster observed in the mixed solution in gel pore. Hence, the incorporation of the sulfate ions inhibits the transport process of chloride ions in two reasons: the large sulfate cluster can attract part of chloride ions, and the ions accumulation blocks the nanometer channel and prevents the chloride ion from penetrating.

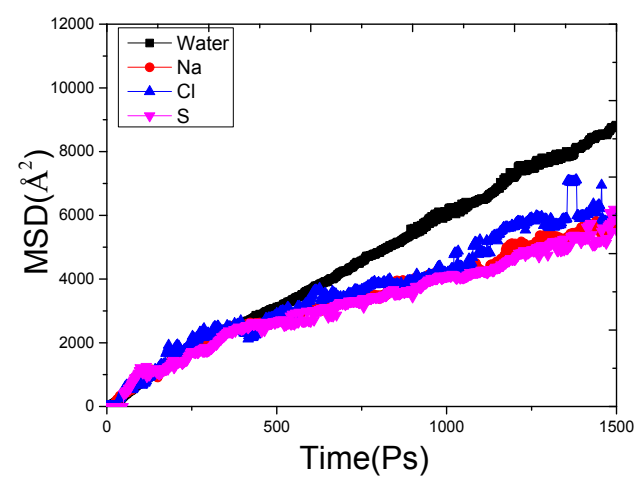
### **S3. Mean square displacement**



(a)



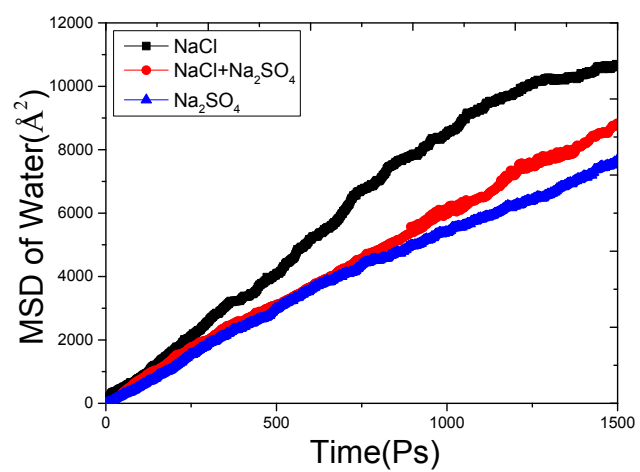
(b)



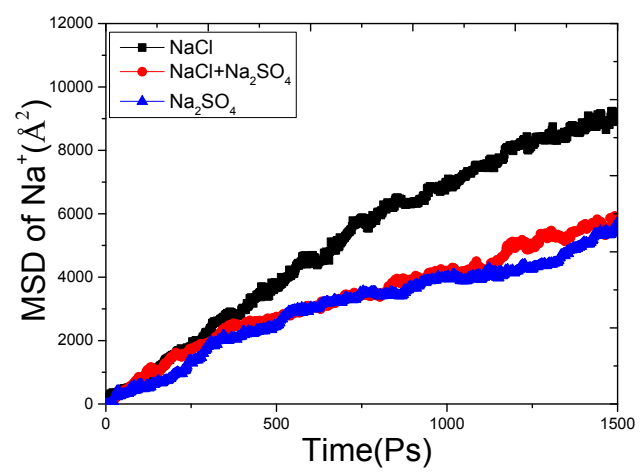
(c)

Figure S2 MSD evolution during 2000ps for water and ions (a) NaCl(b)  $\text{Na}_2\text{SO}_4$

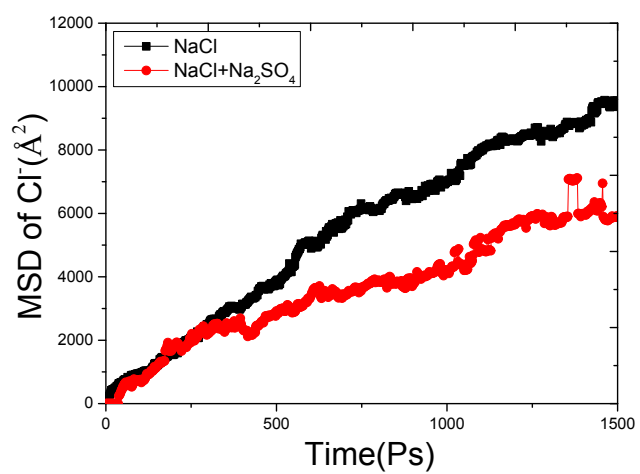
(c)  $\text{NaCl} + \text{Na}_2\text{SO}_4$



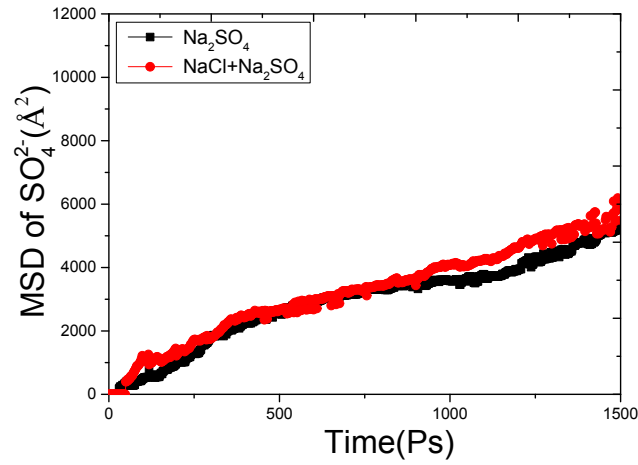
(a)



(b)



(c)



(d)

Figure S3 MSD evolution during 2000ps for water and ions (a) water (b) sodium ions(c) chloride (d)sulfate ions.

The mean square displacement (MSD)<sup>2</sup> and diffusion coefficient (D) are utilized to characterize the dynamics properties of the solution species. MSD (t) is commonly used to characterize the diffusion behavior for liquid by describing the deviation of an atom from its initial position.

$$MSD(t) = \langle |r_i(t) - r_i(0)|^2 \rangle \quad (1)$$

$r_i(t)$  is the coordinate of atom  $i$  at time  $t$ ,  $r_i(0)$  is the original coordinate for atom  $i$ . As shown in FigureS2, the MSD evolution as the function of time indicates that the water molecules move more rapidly than sodium, chloride and sulfate ions both in NaCl and Na<sub>2</sub>SO<sub>4</sub> solutions. As shown in Figure S3a, the time dependent MSD curves exhibit different mobility of water molecules in three solutions: MSD (NaCl) > MSD (mixed solution) > MSD (Na<sub>2</sub>SO<sub>4</sub>). Correspondingly, the diffusion coefficients for water molecules is  $10.17 \times 10^{-9} \text{m}^2 \text{s}^{-1}$ ,  $9.05 \times 10^{-9} \text{m}^2 \text{s}^{-1}$ , and  $7.45 \times 10^{-9} \text{m}^2 \text{s}^{-1}$ , in NaCl solution, mixed solution and Na<sub>2</sub>SO<sub>4</sub> solution, respectively. The slowest mobility of water in Na<sub>2</sub>SO<sub>4</sub> solution is mainly attributed to two reasons. The concentration of Na ions in Na<sub>2</sub>SO<sub>4</sub> solution is higher than that in NaCl and mixed solution. More water molecules form the hydration shell of



sodium and sulfate ions, which restricts the movement of water molecules. Additionally, the ionic cluster, confined in the gel pore, retards the capillary adsorption of water. In Figure S3b, the MSD of Na in three solutions indicates the sodium ions in NaCl solution move dramatically faster than those in NaSO<sub>4</sub> and mixed solution. As discussed in previous section, the sodium ions in NaSO<sub>4</sub> solutions confined in gel pore are immobilized by sulfate ions, forming ionic pair and cluster. The reduction of ionic mobility in NaSO<sub>4</sub> solution reflects the significant discrepancy of diffusivity of sodium ions in free state and cluster state. Similarly, as shown in Figure S3c, the MSD of chloride ions in mixed solution during the simulation time is reduced by 24%, as compared with that in pure solution. Consistent with the finding in transport section, the incorporation of sulfate ions also inhibits the ingress process of chloride ions. On the other hand, it can be observed in Figure S3d that there are no pronounced differences of MSD for sulfate ions in pure solution and in mixed solution. It means that the chloride ions have little influence on the sulfate cluster formation and cluster mobility.

## References

1. (a) Ohtomo, N.; Arakawa, K., Neutron diffraction study of aqueous ionic solutions. II. Aqueous solutions of sodium chloride and potassium chloride. *Bulletin of the Chemical Society of Japan* 1980, 53 (7), 1789-1794; (b) Ohtaki, H.; Radnai, T., Structure and dynamics of hydrated ions. *Cheminform* 1993, 24 (31), 1157-1204.
2. Hou, D.; Li, Z.; Zhao, T.; Zhang, P., Water transport in the nano-pore of the calcium silicate phase: reactivity, structure and dynamics. *Physical Chemistry Chemical Physics Pccp* 2015, 17 (2), 1411-23.