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Electrolyte Adsorption to Goethite-Water Interfaces

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Overall Goals

❖To ***develop*** a comprehensive model describing goethite (α-FeOOH) protonation and adsorption properties.

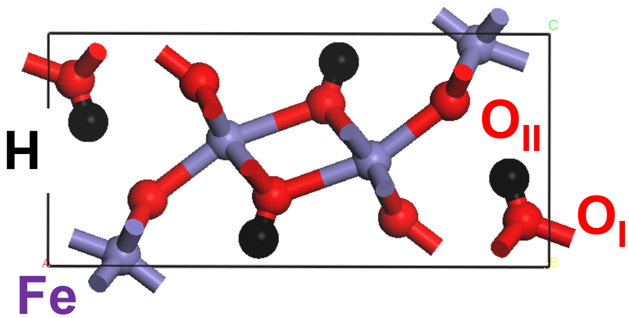
- Examine water structure and hydrogen-bonding on different goethite surfaces.
- Examine the impact of different electrolytes (NaCl, NaF, and $NaSO_4$) on water structure at goethite-water interfaces.
- Examine the impact of surface loading on water structure and electrical potential at goethite surfaces.

➢To ***characterize*** the sites of protonation, cation, and oxyanion adsorption on goethite surfaces.

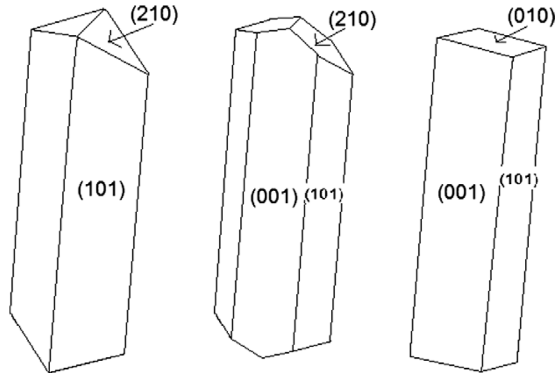
➢To ***characterize*** the structure of oxyanion surface complexes on goethite surfaces as a function of pH and surface coverage.

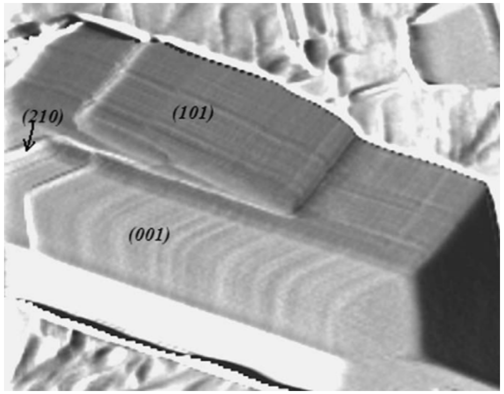
➢To ***incorporate*** molecular observations into thermodynamic models that can predict bulk adsorption data for cation-anion adsorption on goethite.

Goethite: Predominant Surfaces and Surface Sites



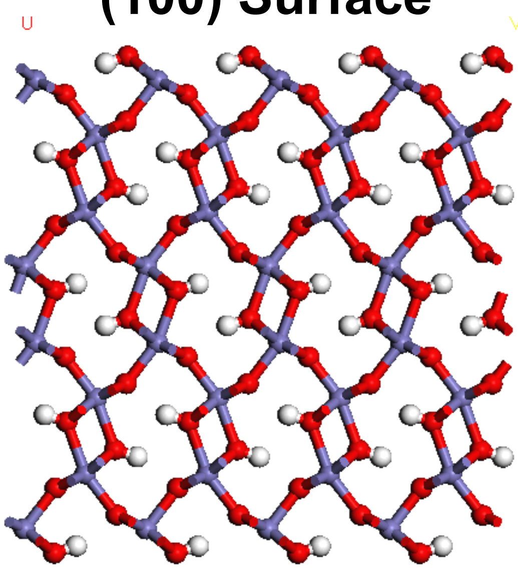
Goethite Unit Cell





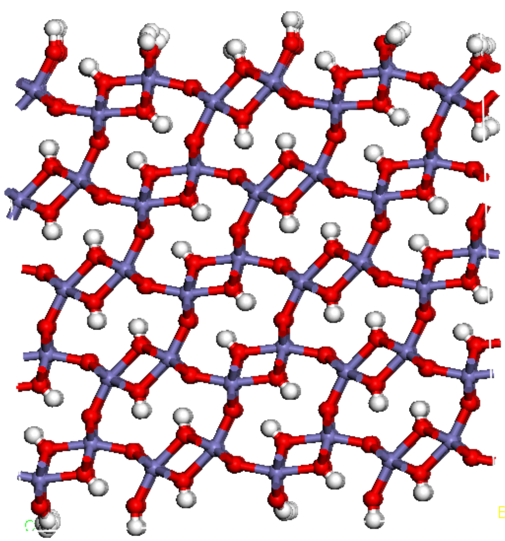
From Villalobos et al. (2009)

(100) Surface



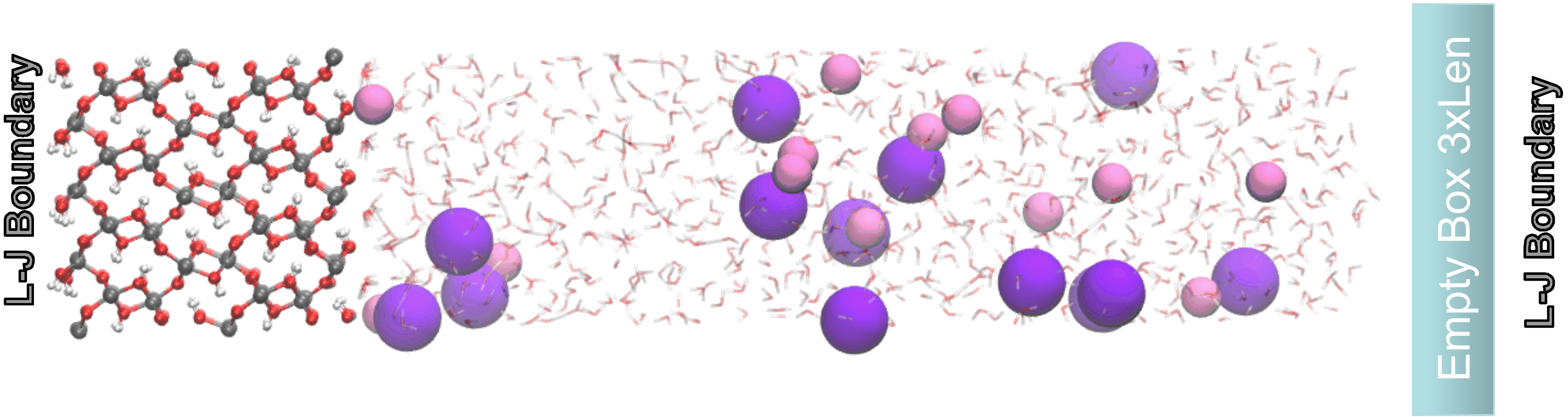
5-fold Fe
Fe_2O_IH
Fe_3O_{II}

(101) Surface



$Fe_1O_{II}H$
$Fe_2O_{II}H$
Fe_3O_{II}
Fe_3O_IH

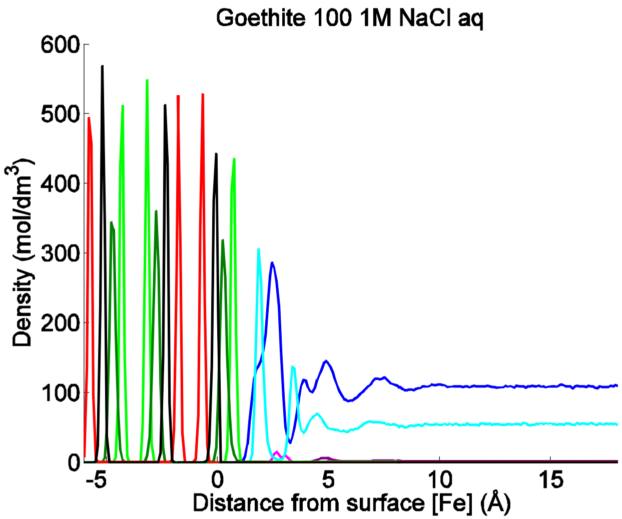
Computational Methods

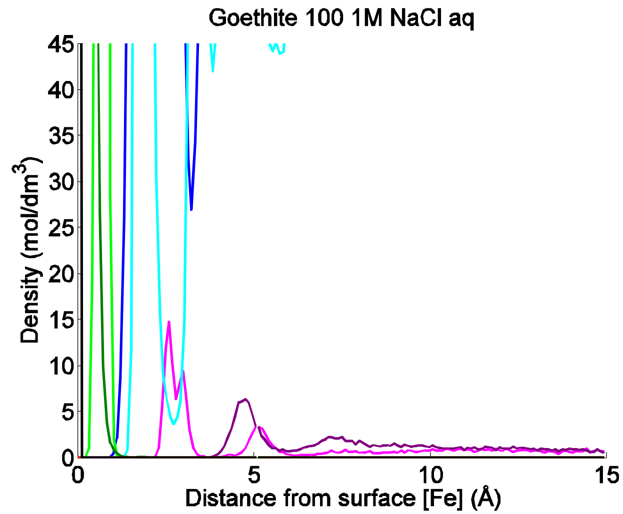


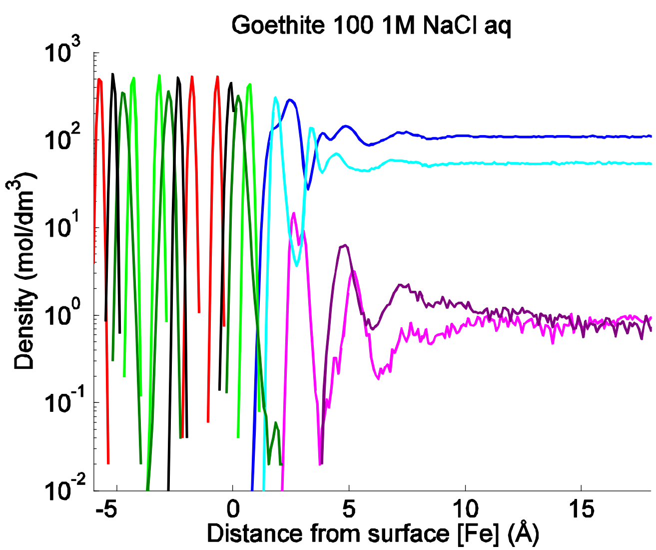
Simulation of 192 FeO(OH) with 720 H2O and 0:1:5M NaCl

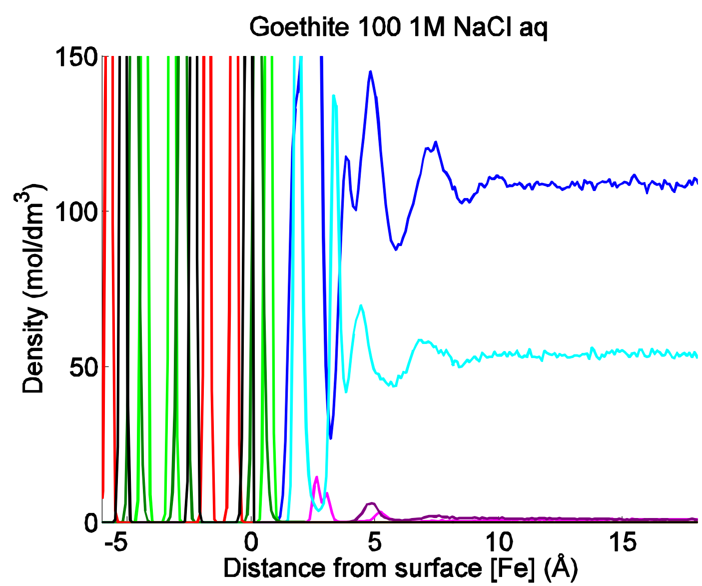
- Two faces: (100) and (101)
- (101) Face required protonation
- clayff force field used with LAMMPS MD simulation
  - NVE (50,000 fs)
  - NVT (200,000 fs)
  - NVT (10,000,000 fs)
- Snapshots every 2,000 fs

Goethite (100) with NaCl Solution

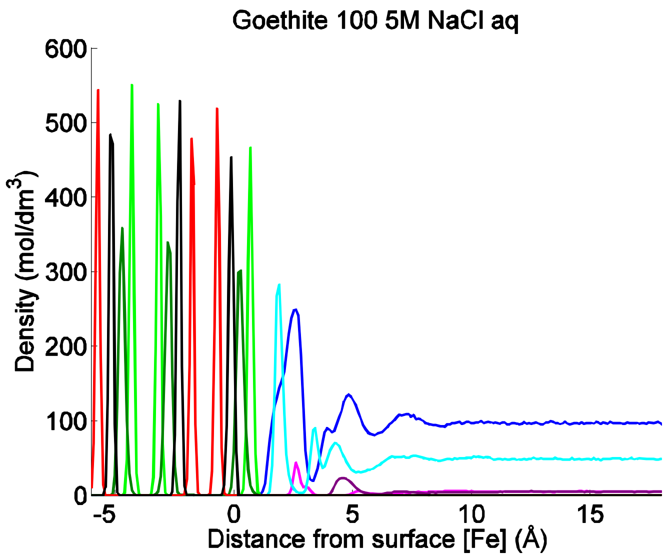


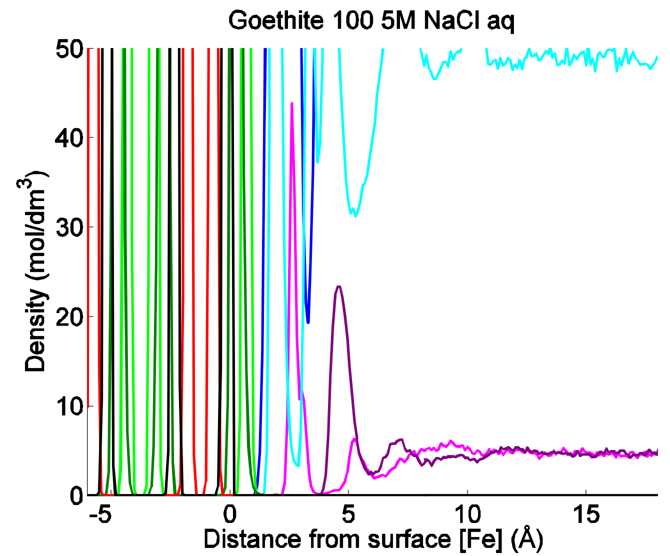


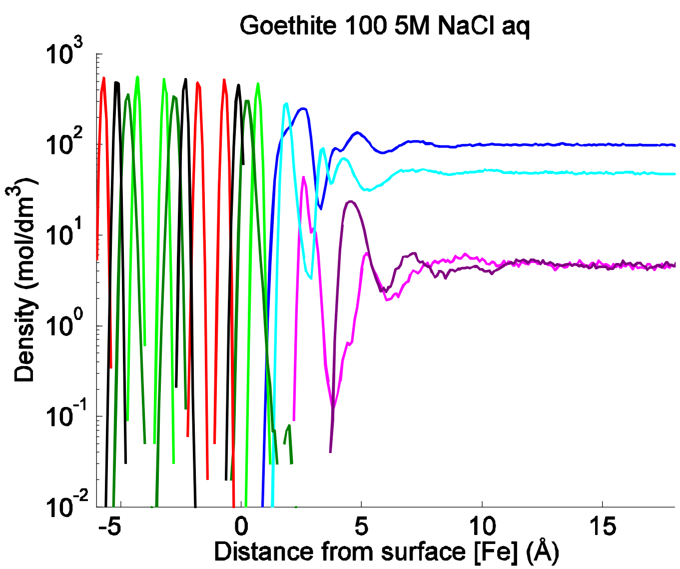


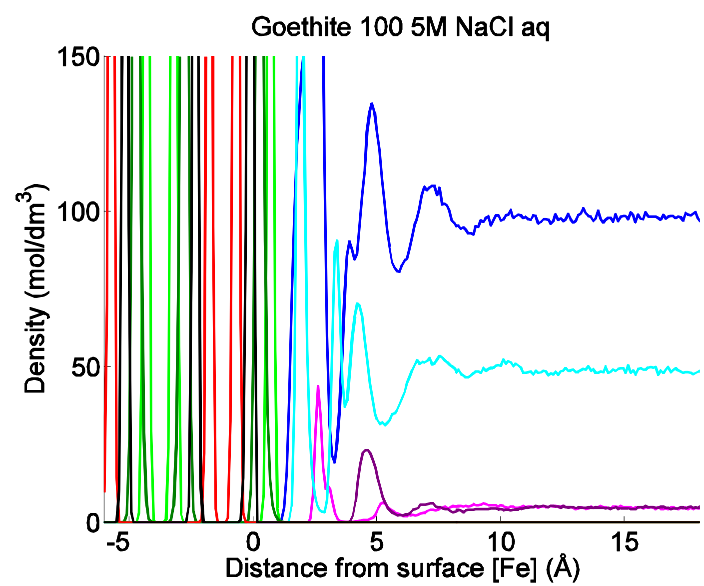


Goethite (100) with 5 M NaCl

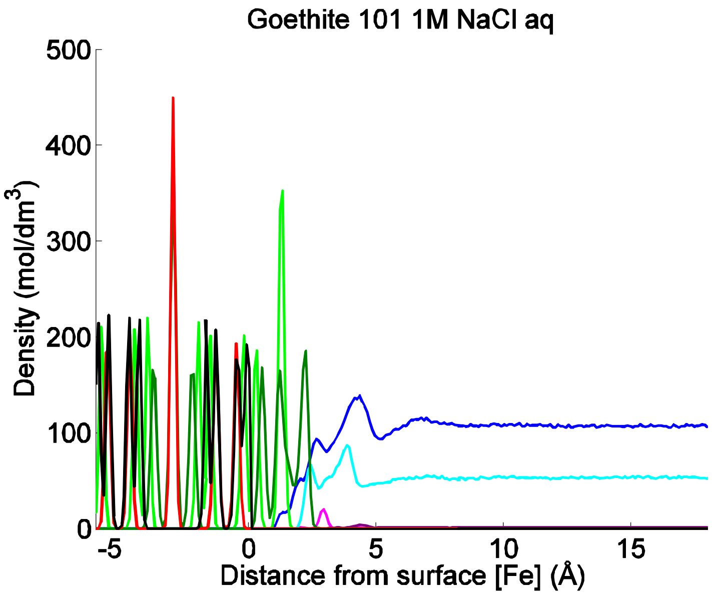


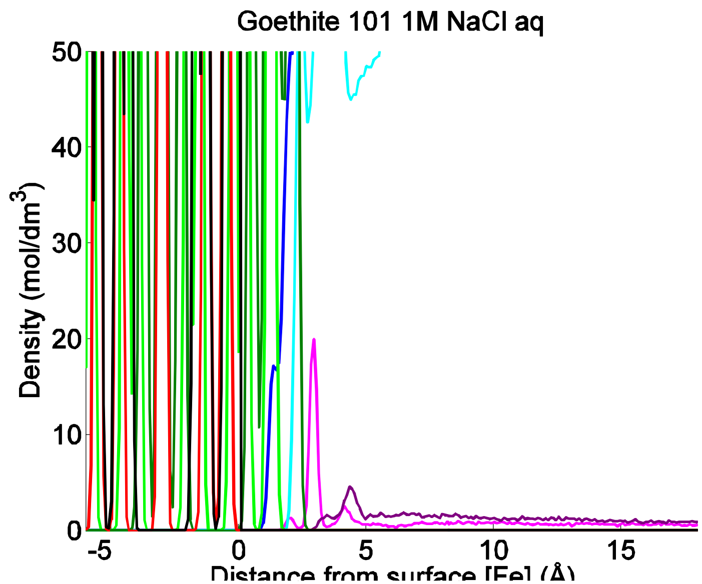


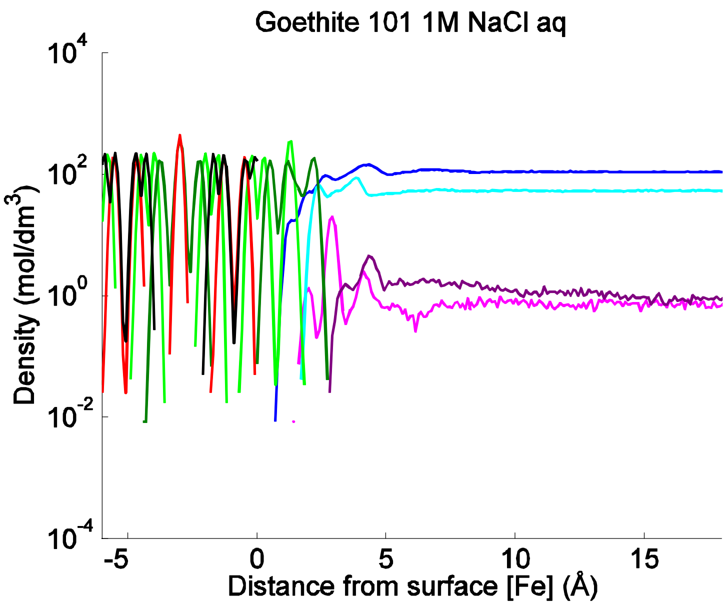


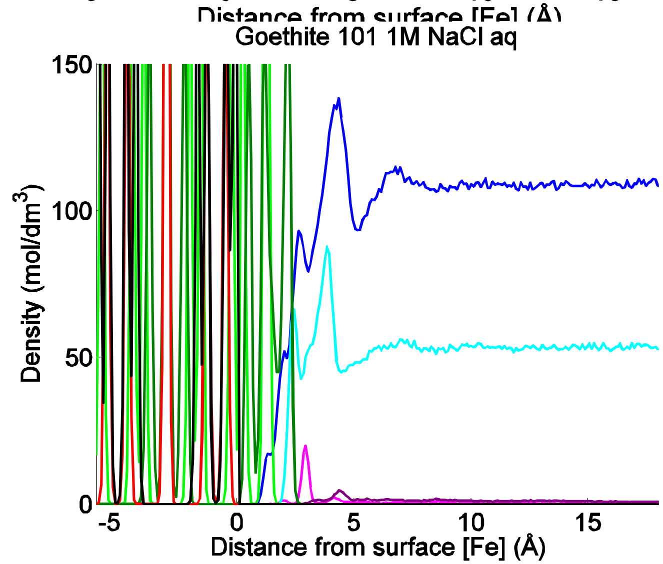


Goethite (101) with 1 M NaCl

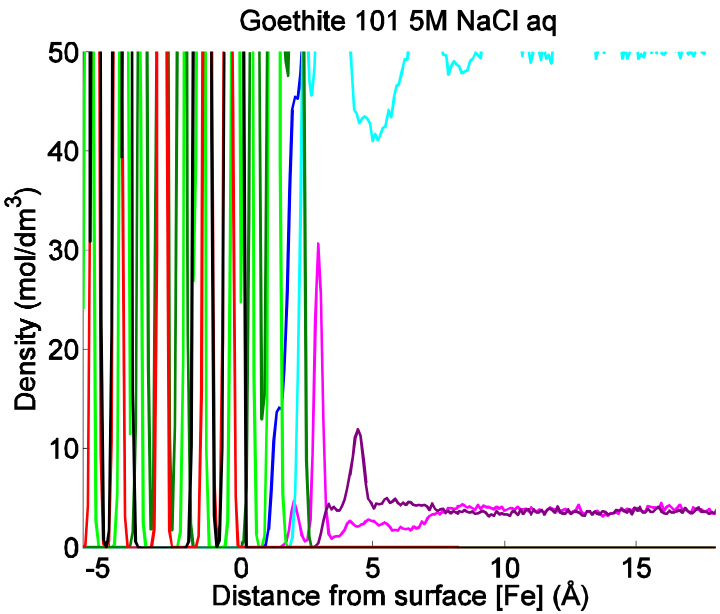


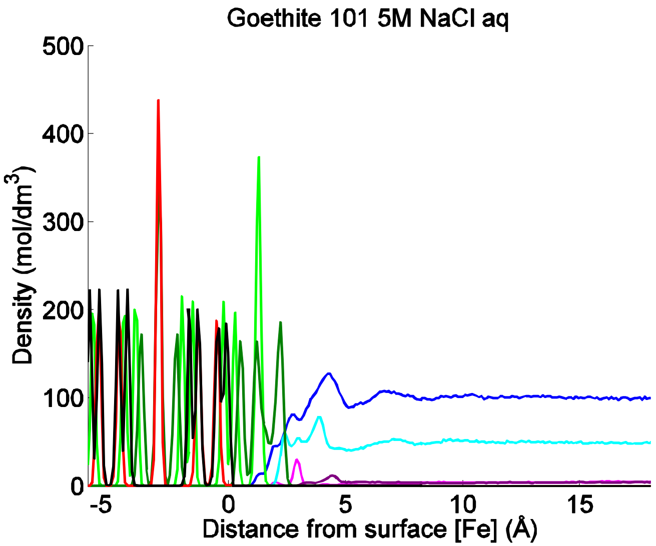


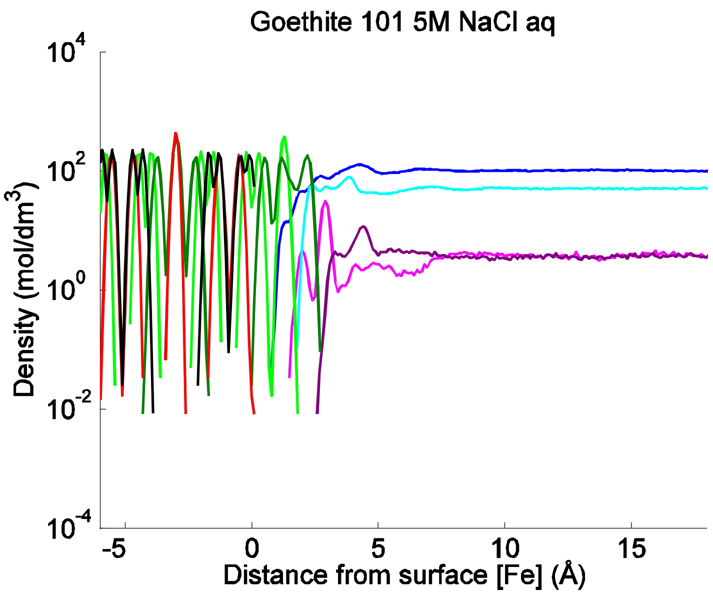


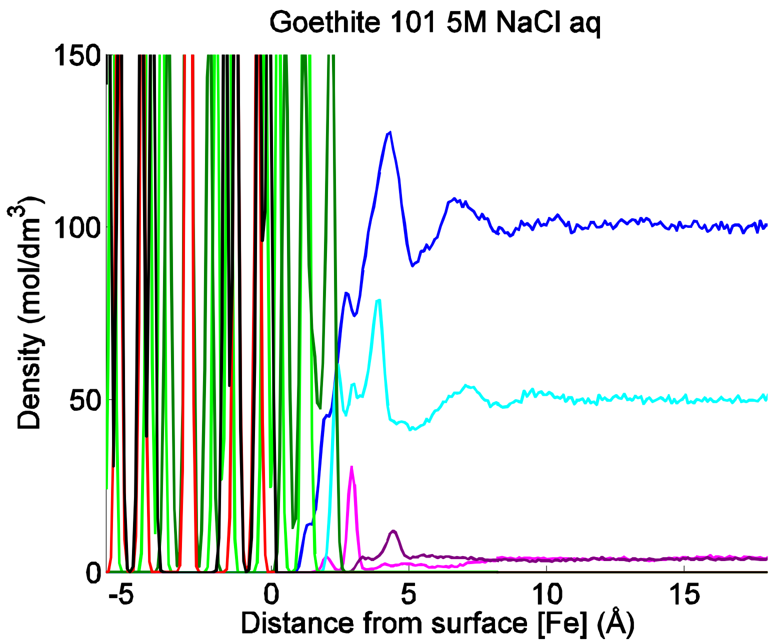


Goethite (101) with 5 M NaCl

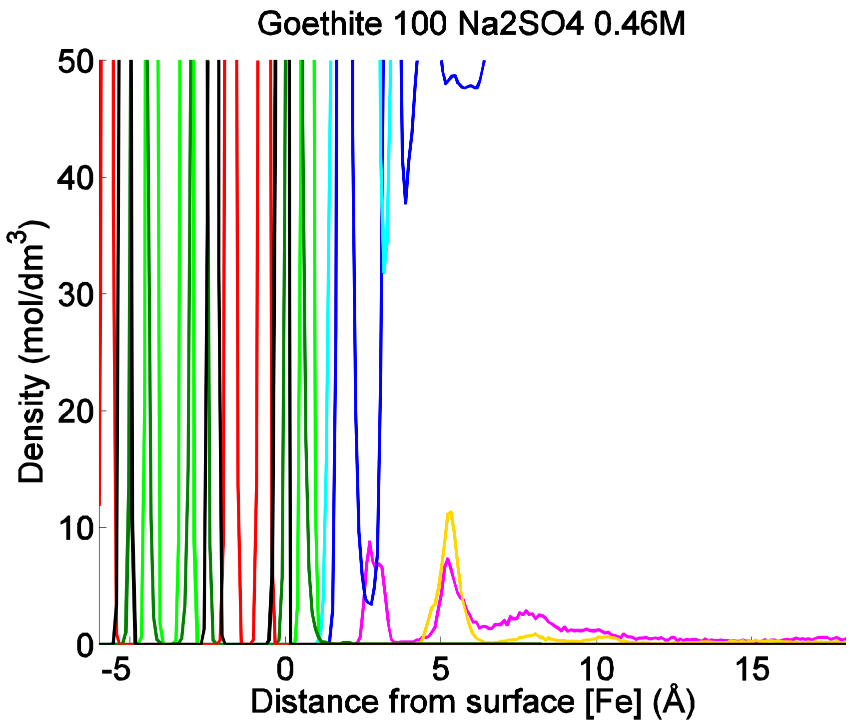


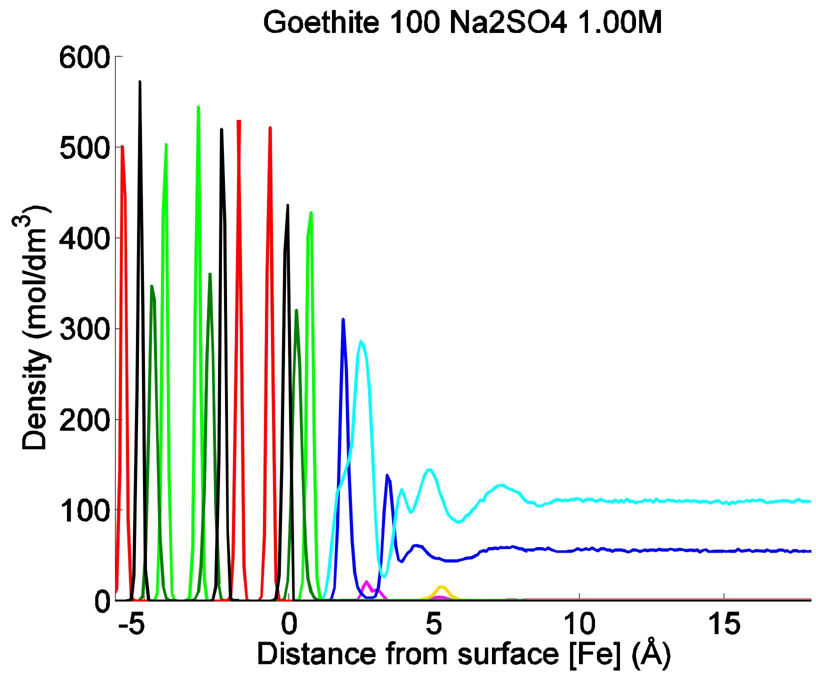




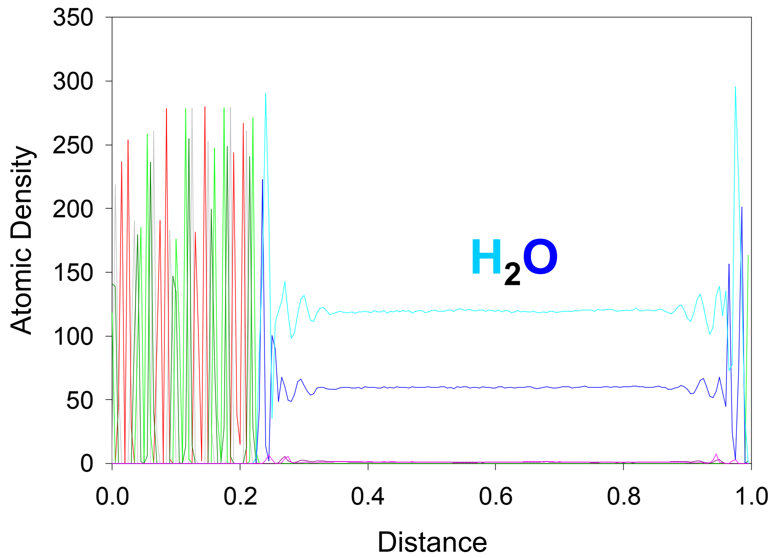


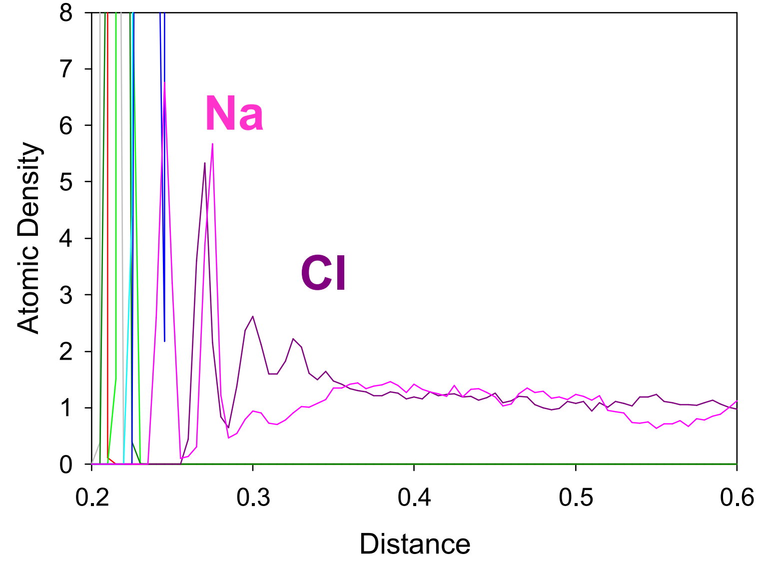
Goethite (100) with $NaSO_4$

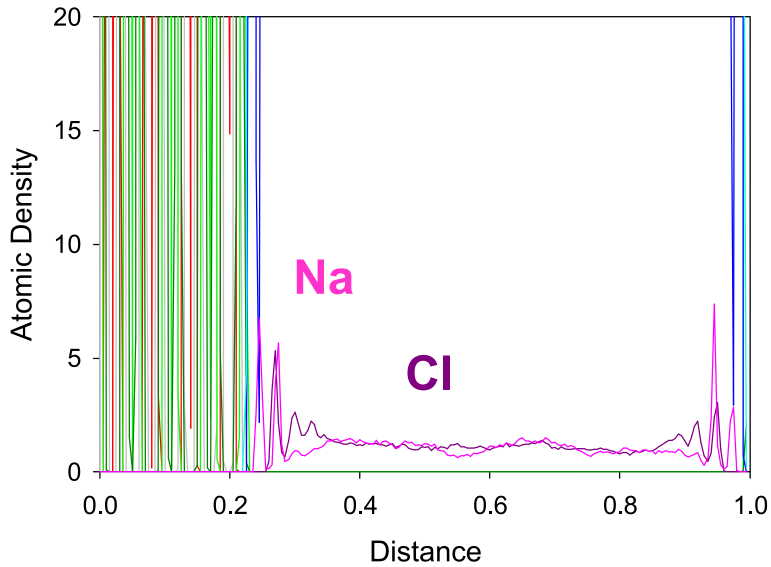


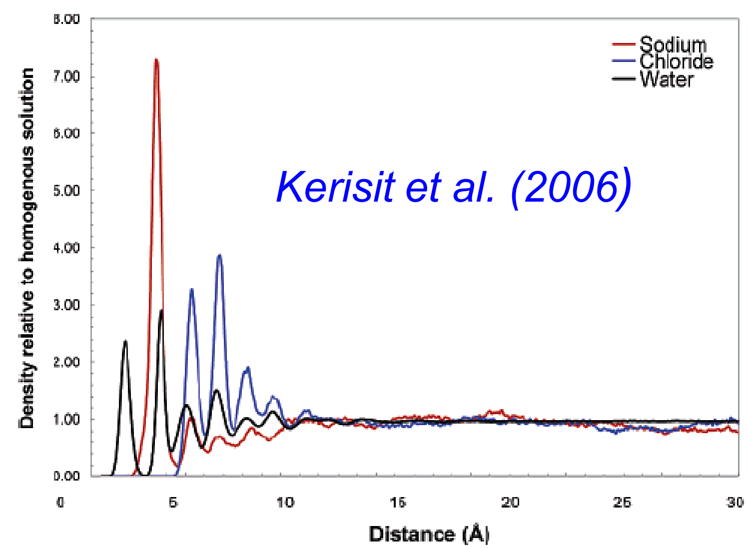


Goethite (100) with NaCl Solution

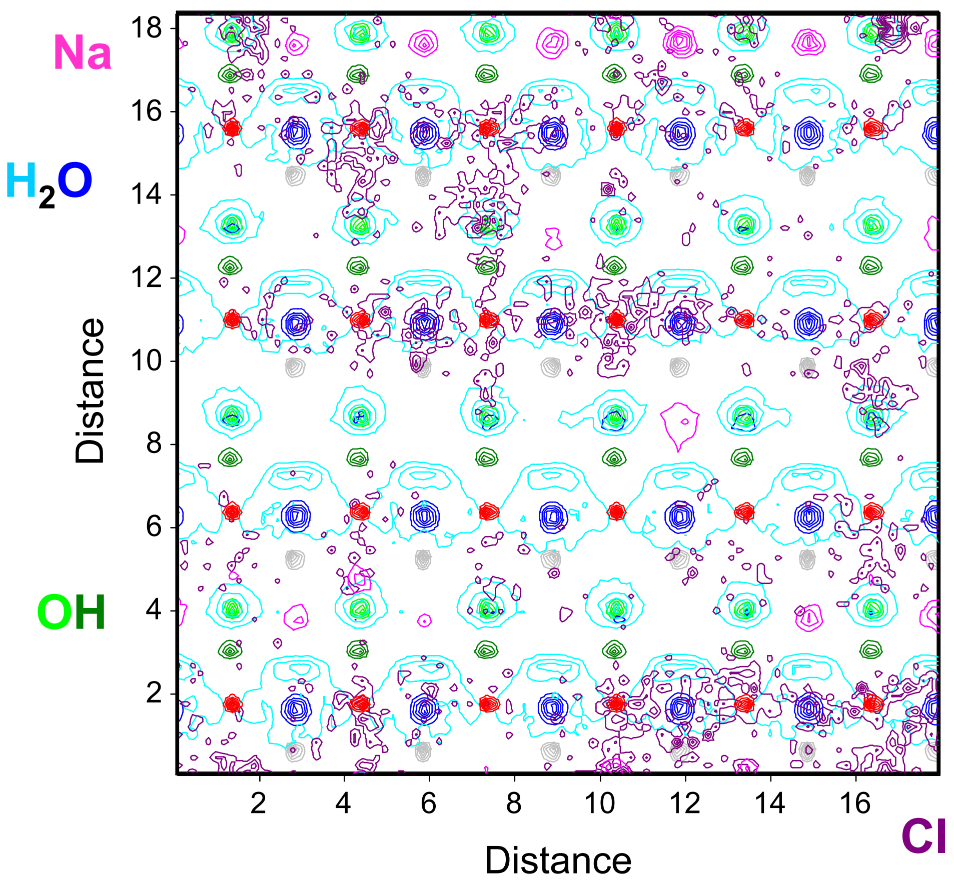






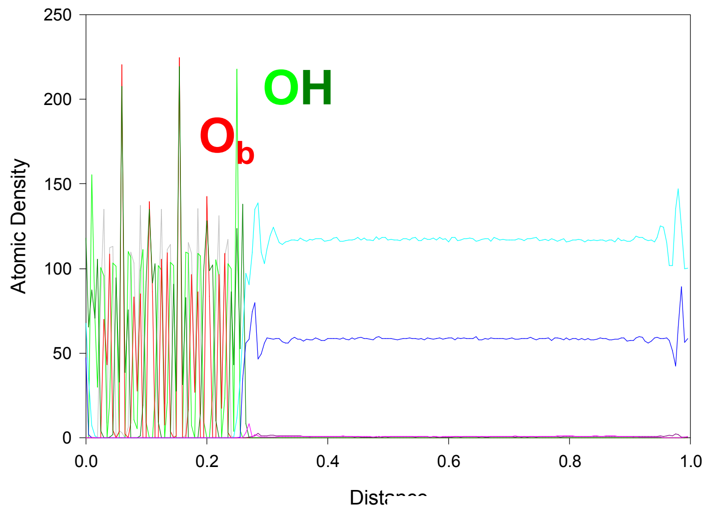


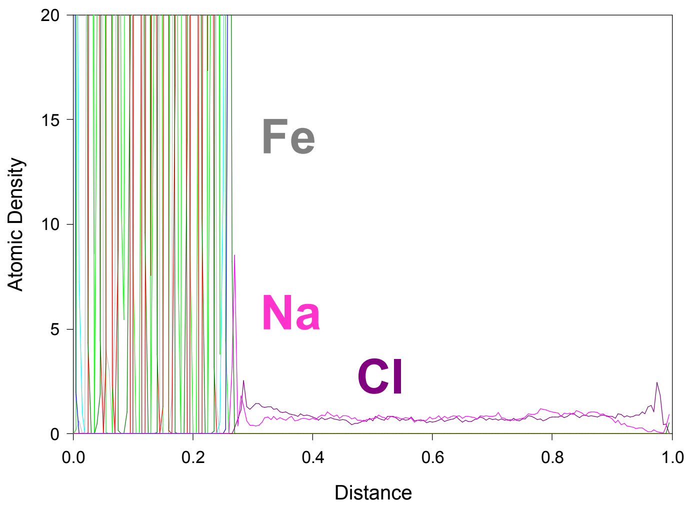
Goethite (100) with NaCl Solution

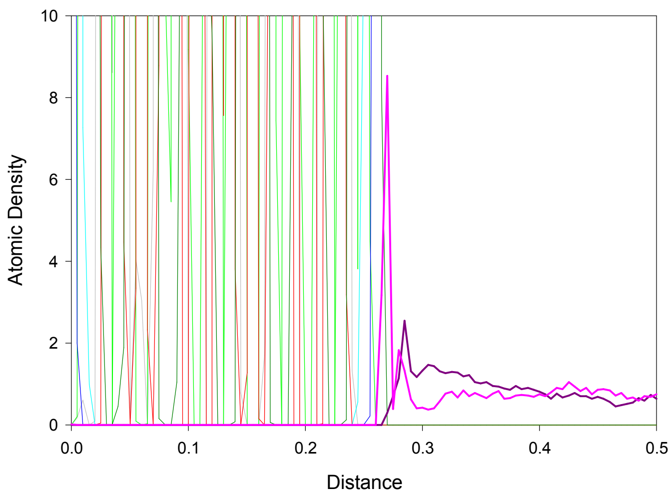


- 10 ns simulation.
- 12 NaCl/192 H_2O molecules.
- Na^+ ions are inner sphere.
- Na^+ always between surface hydroxyl oxygens
- Cl^- ions are outer sphere.

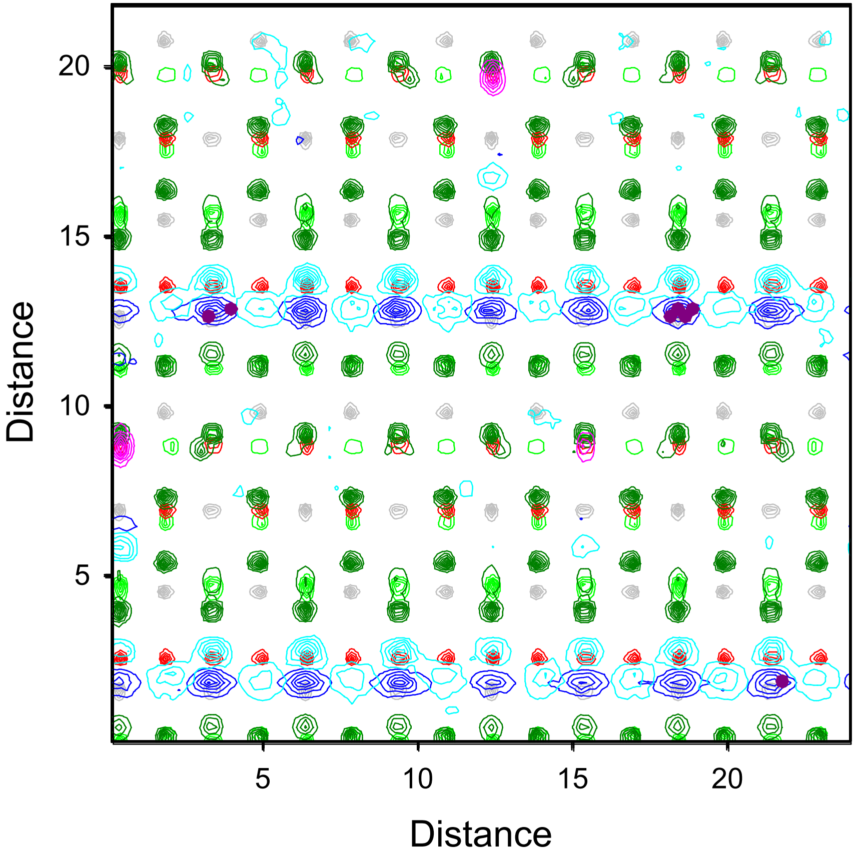
Goethite (101) with NaCl Solution

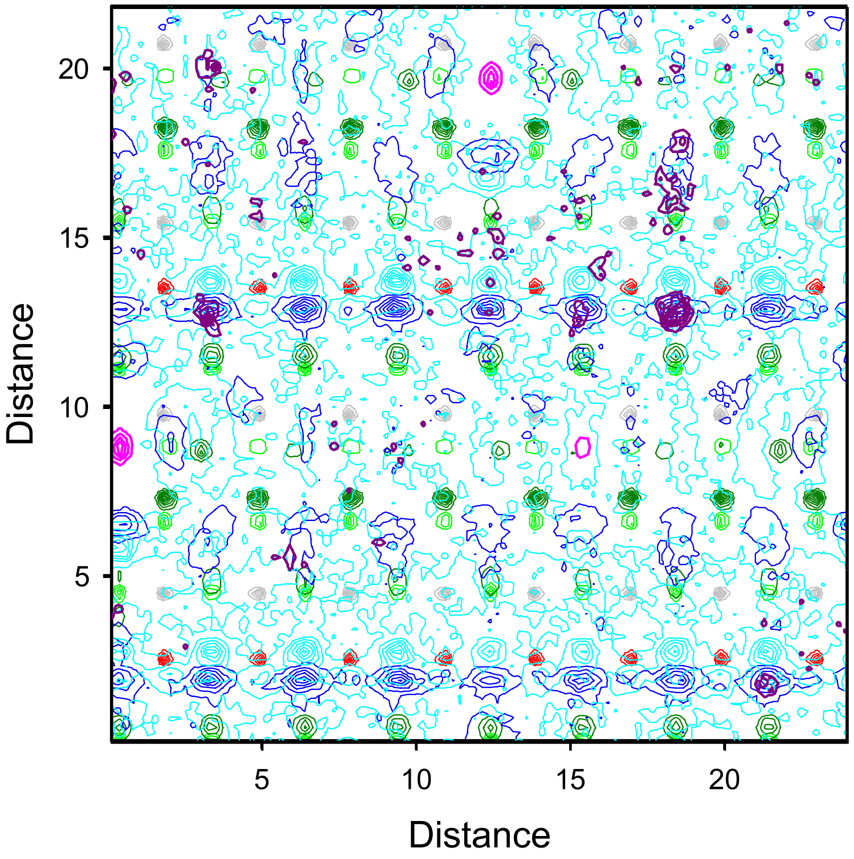






Goethite (101) with NaCl Solution

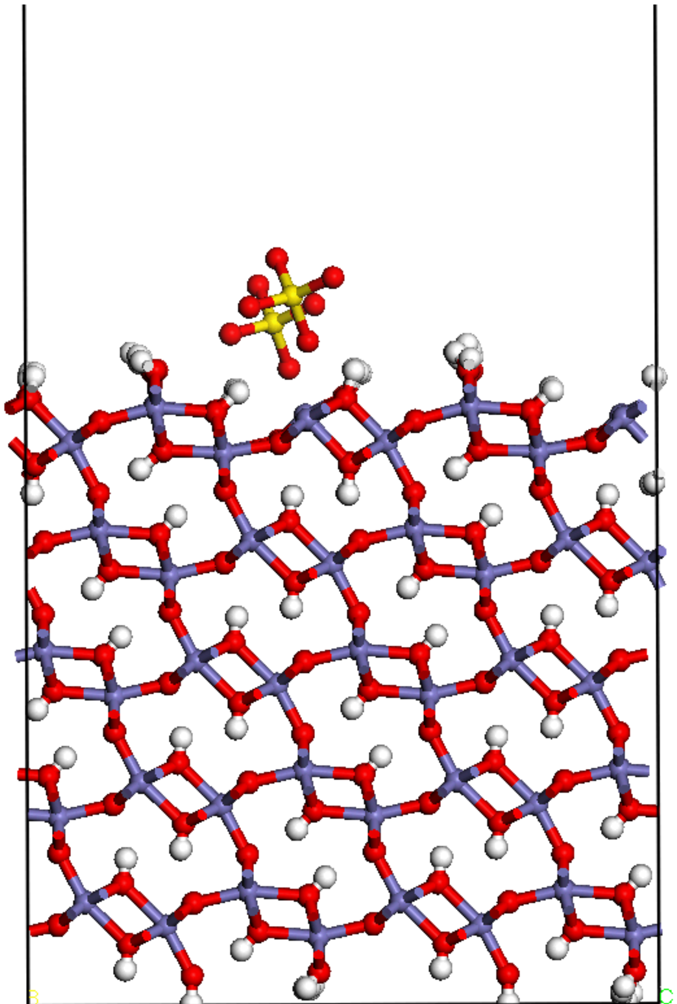




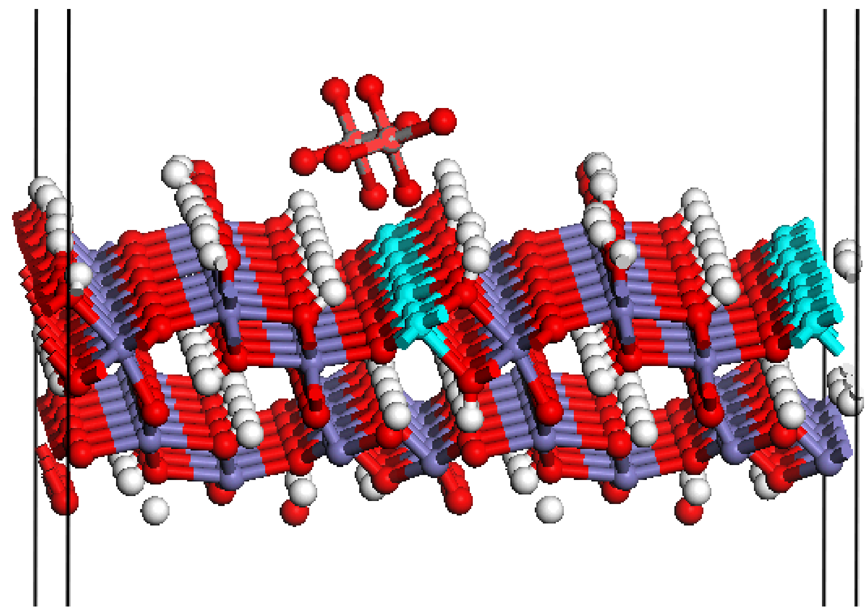
Summary

- Initial results are consistent with other reported results in the literature.
- Na^+ adsorbs as an inner-sphere complex to both the (010) and the (100) surface.
- Cl^- adsorbs as an outer-sphere complex to both surfaces.
- Oscillatory charge distribution from the surface out into solution is developed from H_2O dipole orientations at the surface without the presence of electrolyte.

Future Work



Remove –OH groups from monodentate OH groups



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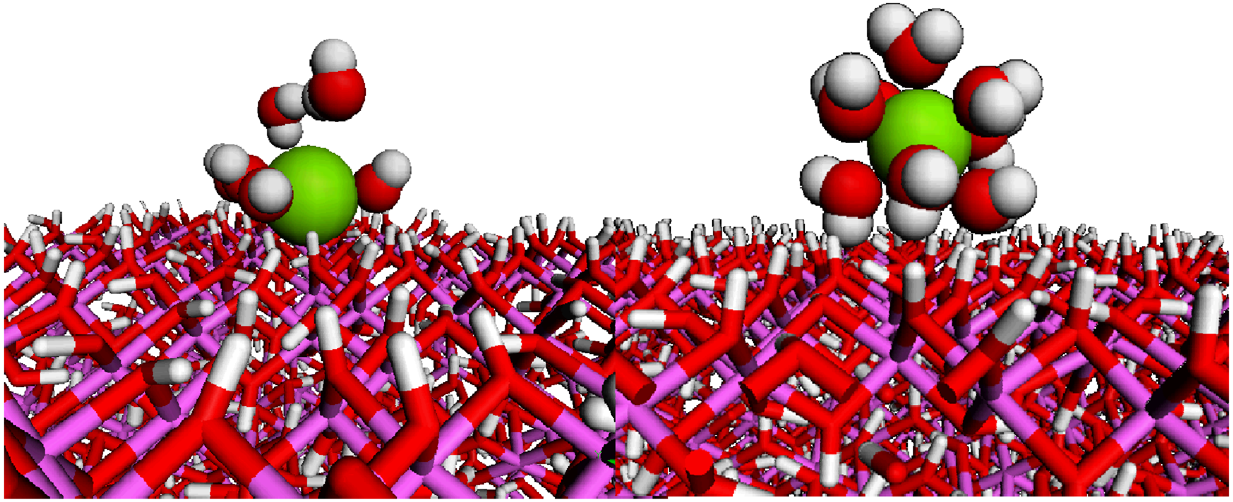
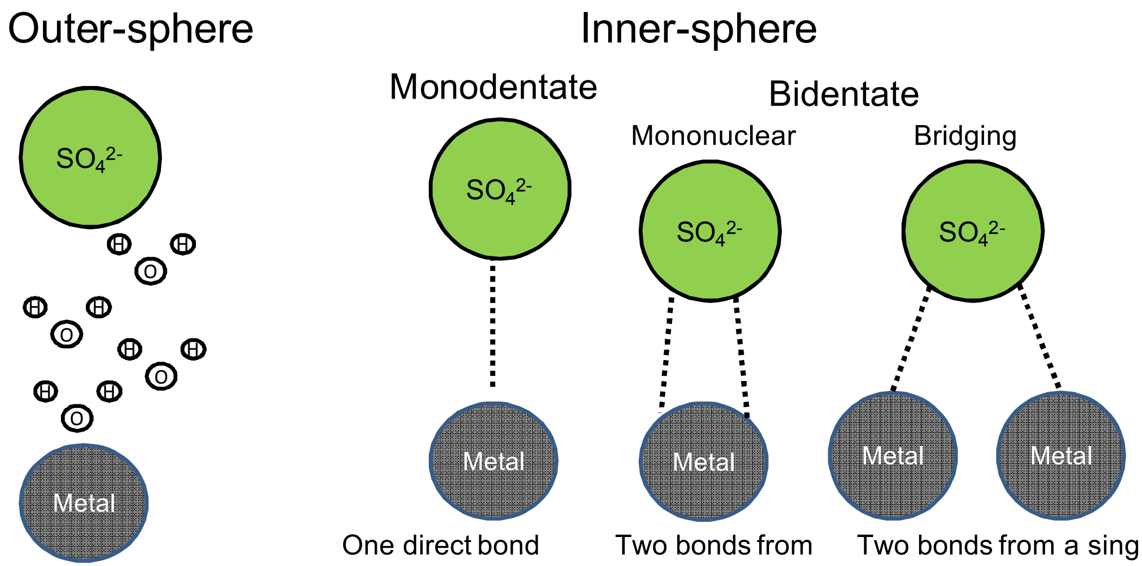


Surface Site Density and Types from Classical Molecular Dynamics

- Compare the adsorption of different electrolytes (e.g., NaCl and Na_2SO_4) on goethite surfaces.
- Characterize the surface species involving Cl^- and SO_4^{2-} as a function of surface site types, inner- vs. outer-sphere, monodentate vs. bidentate, etc.
- Determine the number of reactive surface sites for Cl^- and SO_4^{2-} and compare to SCM model site densities.



No direct bond formation, both metal and sulfate retain all water. Sulfate has T_d symmetry.

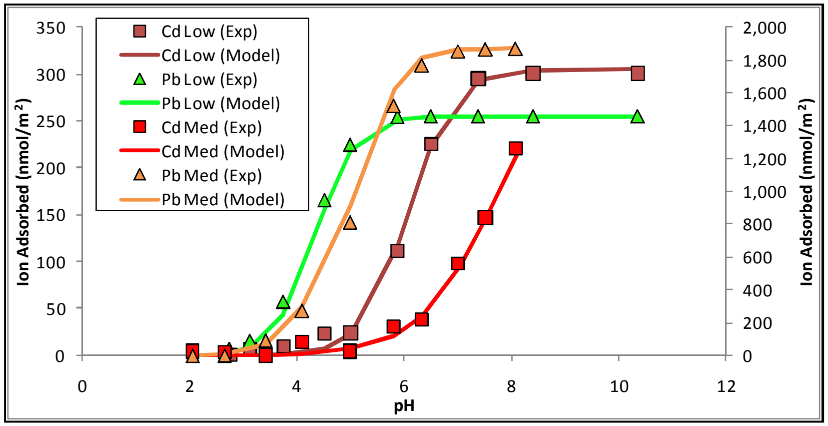
One direct bond formed between oxygen of sulfate and surface metal replacing one water. Sulfate has C_{3v} symmetry.

Two bonds from sulfate oxygens to single metal. Two waters are lost. Sulfate has C_{2v} symmetry.

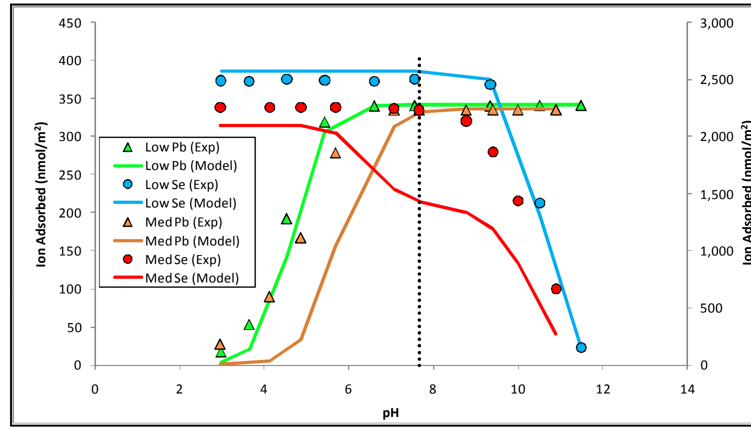
Two bonds from a single sulfate oxygens to two different metals. Two waters lost. Sulfate has C_{2v} symmetry.

Multi-Solute Adsorption Fits using KATZ GROUP Model

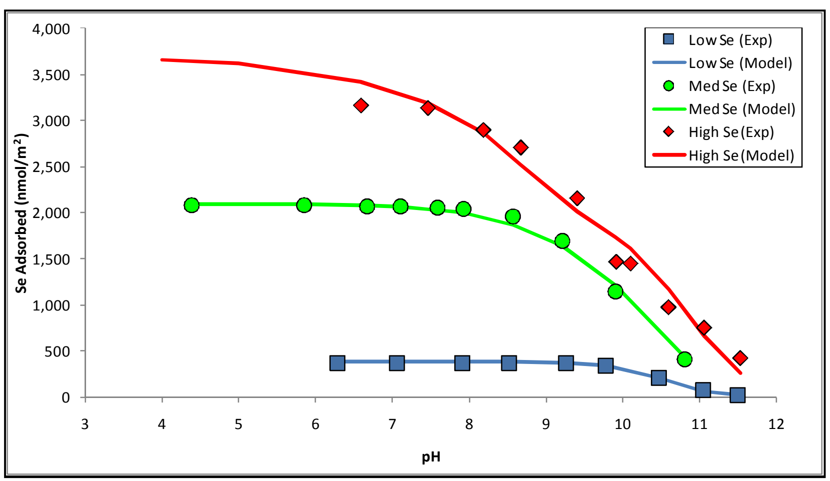
Pb^{+2} and Cd^{+2} Competition



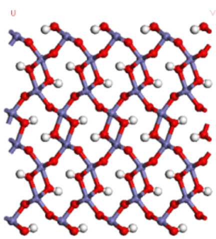
Pb^{+2} and SeO_3^{-2} Competition



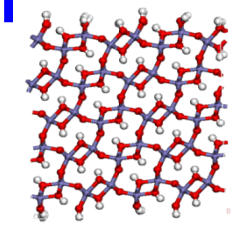
SeO_3^{-2} Adsorption



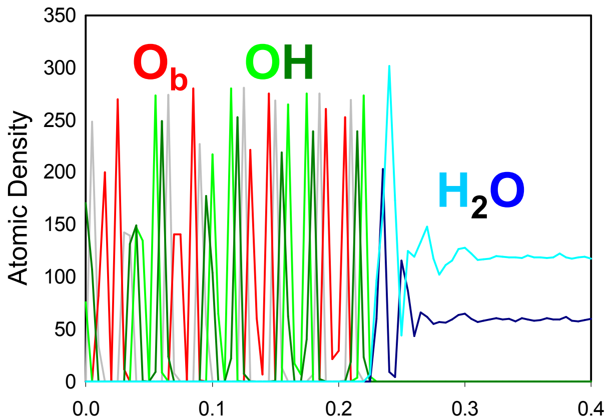
- The model fits Cd^{2+} & Pb^{2+} bi-solute competition
- The model predicts more SeO_3^{2-} adsorption than found in experiment.
- For medium coverage, predicted Pb^{2+} and SeO_3^{2-} adsorbed is low
- These results suggest that different surface site densities (and types) may be involved in cation and anion adsorption

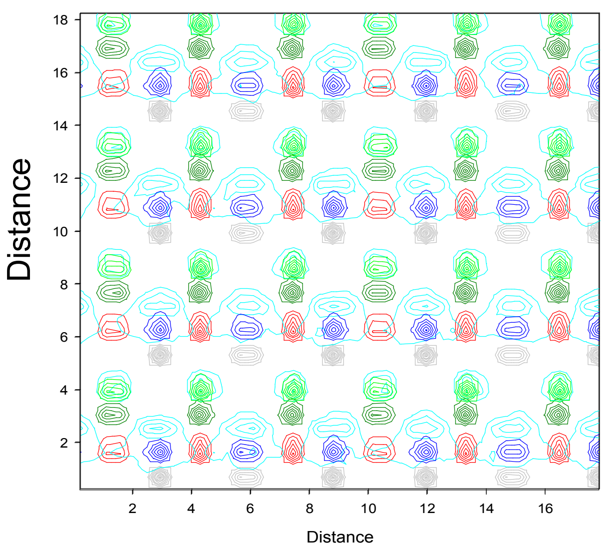


Classical Molecular Dynamics Simulations of Goethite (100) and (101) with H_2O

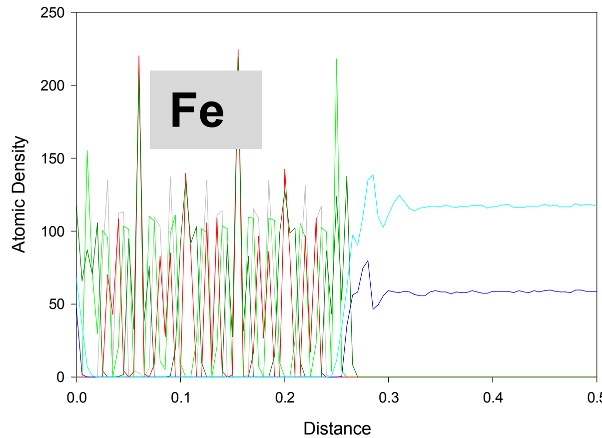


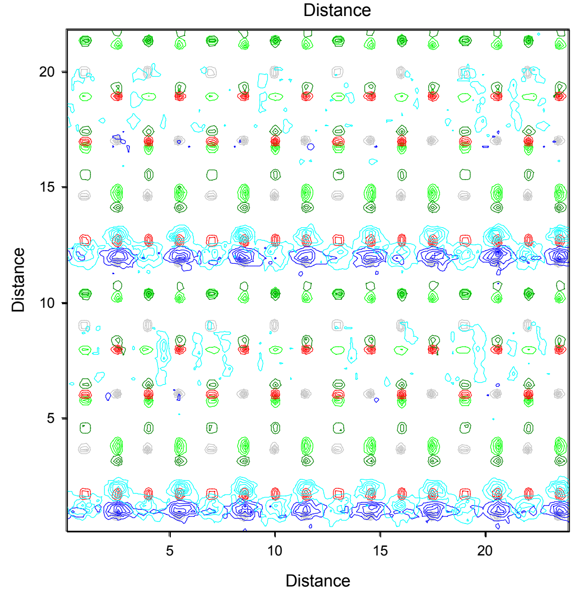
(100) Surface





(101) Surface

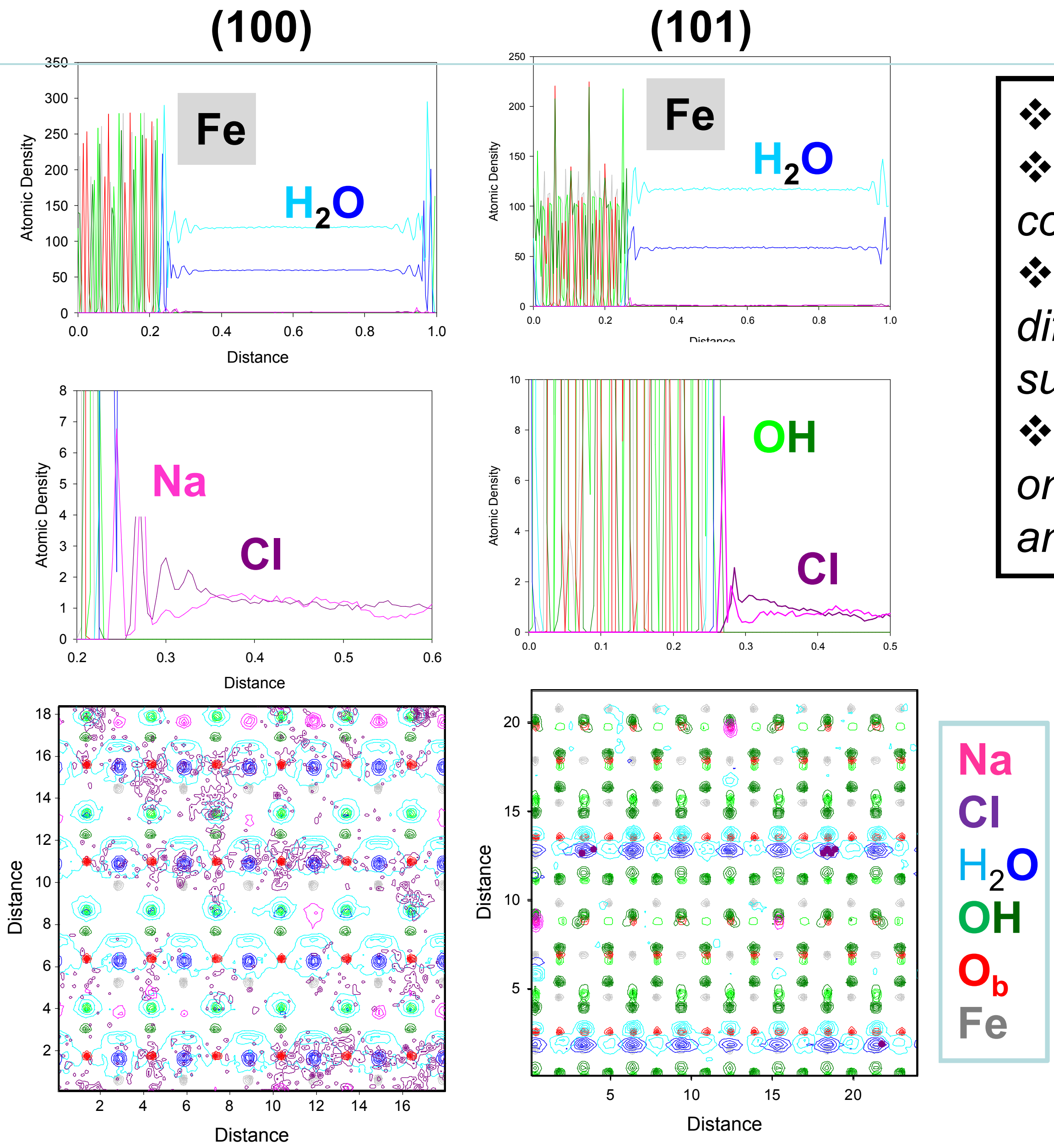




Atomic density profiles and surface maps show more H_2O structure at (100) surface than (101) surface.

1 ns simulation
1 fs timestep

Goethite Surfaces with NaCl Solution



- 10 ns simulations.
- Na^+ forms inner-sphere complexes
- Na^+ surface species are different on (100) and (101) surfaces.
- Cl^- ions are outer-sphere on (100) and both inner- and outer-sphere on (101).