AN AB-INITIO INVESTIGATION OF VARIOUS SULFATES ON A CALCITE SURFACE USING DENSITY FUNTIONAL THEORY

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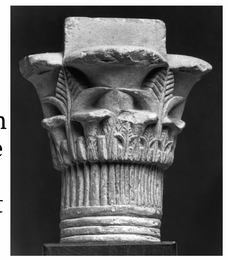
Introduction

Left: Head of a Man, Walters Art Museum



Right: Model of a Composite Capital with Grid on the Top, Walters Art Museum

- In the presence of surface salts, ancient Egyptian limestone artifacts can degrade at faster rates than previously observed.[1]
- Sulfate salts are commonly known pollutants that lead to enhanced surface degradation of limestone.[2]
- Calcite is a stable polymorph of limestone.
- Calcite is prone to protonation and decarboxylation on the surface.
- Plane-wave density functional theory (DFT) can be used to model the interactions between various sulfate salts and differently terminated calcite surfaces.

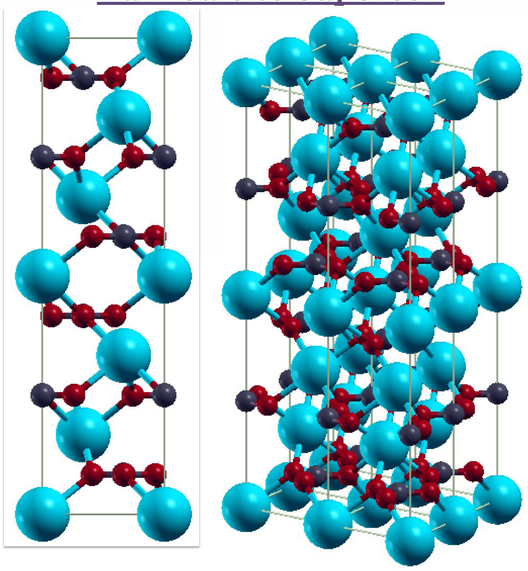
Methodology

All calculations described here employ periodic DFT methods and are carried out using Quantum Espresso, an open source software package.[3-6] All atoms are represented using GBRV-type ultrasoft pseudopotentials.[7,8]A plane-wave cutoff of 40 Ry and charge density cutoff of 320 Ry are employed for all calculations, in line with similar surface studies.[9-11] Bulk structural relaxations use a 6x6x6 k-point grid, and the convergence criteria for self-consistent relaxations is 5x10-6 eV.[12] Geometry optimization of all surface-adsorbate interactions did not include fixing any layers, as detailed in Corum et al. where all atoms are free to relax.[13] All calculations are performed at the GGA level using the Wu-Cohen (WC) modified PBE-GGA exchange correlation functional for solids.[14,15]

References

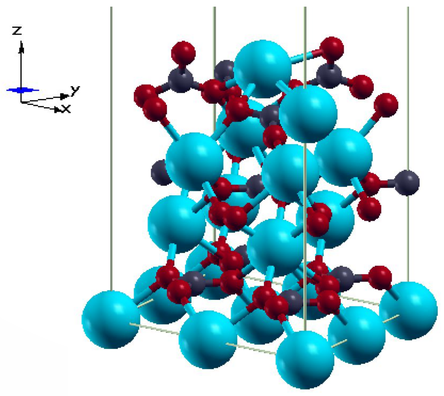
(1) Bradley, S. M.; Middleton, A. P. *J. Am. Inst. Conserv.* **1988**, *27* (2), 64–86.
(2) de la Fuente, D. *et al. J. Cult. Herit.* **2013**, *14* (2), 138–145.
(3) Hohenberg, P.; Kohn, W. *Phys. Rev.* **1964**, *136* (3B), B864–B871.
(4) Kohn, W.; Sham, L. J. *Phys. Rev.* **1965**, *140* (4A), A1133–A1138.
(5) Giannozzi, P. *et al. J. Condens. Matter Phys.* **2017**, *29* (46), 465901.
(6) Giannozzi, P. *et al. J. Condens. Matter Phys.* **2009**, *21* (39), 395502.
(7) Vanderbilt, D. *Phys. Rev. B* **1990**, *41* (11), 7892–7895.
(8) Garrity, K. F. *et al. Comput. Mater. Sci.* **2014**, *81*, 446–452.
(9) Bennett, J. W. *et al. Inorg. Chem.* **2018**, 57 (21), 13300–13311.
(10) Bennett, J. W. *et al. Environ. Sci. Technol.* **2018** 52 (10), 5792–5802.
(11) Bennett, J. W. *et al. Environ. Sci. Nano* **2020**, *7* (6), 1642–1651.
(12) Monkhorst, H. J.; Pack, J. D. *Phys. Rev. B* **1976**, *13* (12), 5188–5192.
(13) Corum, K. W. *et al. Mol. Simulat.* **2017**, 43 (5-6), 406–419.
(14) Perdew, J. P. *et al. Phys. Rev. Lett.* **1996,** 77 (18), 3865–3868.
(15) Wu, Z.; Cohen, R. E. *Phys. Rev. B* **2006**, *73* (23).
(16) A. Kokalj, J. *Comput. Mater. Sci.* **2003**, 28 (2), 155-168.

Bulk Calcite Supercell

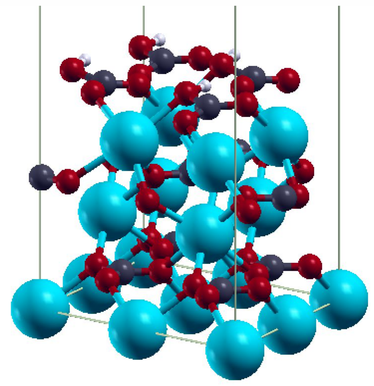


Supercell Surface Slabs We Use

2x2x1 Calcium Terminated Supercell

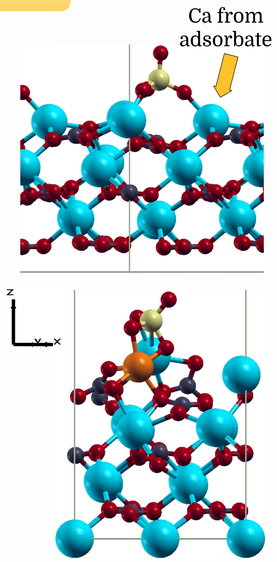


2x2x1 Proton Terminated Supercell



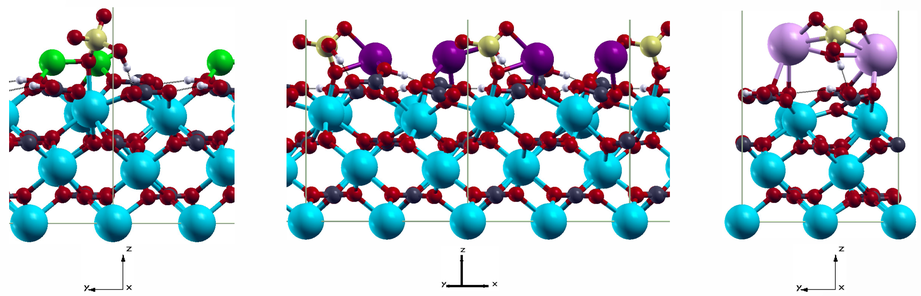
Results and Discussion

Adsorbate	Adsorption Energy (eV)			
	Calcium-Term. Surface		Proton-Term. Surface	
	Config. 1	Config. 2	Config. 1	Config. 2
H_2SO_4	-3.41	-3.04	-0.40	-0.55
Li_2SO_4	-6.05	-3.59	-0.66	-3.49
Na_2SO_4	-5.51	-7.45	-1.23	-4.62
K_2SO_4	-7.72	-7.55	-3.01	-3.13
$LiHSO_4$	-3.34	-5.71	-2.70	-2.69
$NaHSO_4$	-2.96	-4.38	-2.37	-2.34
$KHSO_4$	-3.68	-5.68	-0.58	-2.20
$CaSO_4$	-6.18	-9.95	-5.92	-5.23
$MgSO_4$	-9.21	-7.64	-8.41	-7.15



Above: $CaSO_4$ in config. 2 (**top**) and $MgSO_4$ in config. 1 (**bottom**) on the calcium terminated surface

S H O C Li Na K Mg Ca



Above: Li_2SO_4 (**left**), Na_2SO_4 (**middle**), and K_2SO_4 (**right**) in config. 2 on the proton terminated surface

Future Directions

- Examine the impact of adding explicit water molecules to the calculations
- Use more advanced models (such as DFT + Thermodynamics) to explore the effects of different conditions and environments

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