

Tribochemical studies at the nanometer scale: Synergisms of mechanical and chemical forces

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Bond breaking at surfaces due to stimuli such as exposure of materials to radiation, mechanical stress, or chemical agents are well established. The forces and potentials available to break and reestablish bonds between ions, atoms, and molecules becomes greatly expanded when we consider combining stimuli. Our efforts on combining (mechanical + chemical) or (mechanical+radiative) stimulation aim at understanding the resulting synergisms in, for example, dissolution and/or deposition of material. Here we determine the kinetics of chemical mechanical wear (or polishing) with a single asperity (the tip of an Atomic Force Microscope) on substrates of single crystals, amorphous materials such as silicate glasses, and on polycrystalline oxides controlled chemical media. We find that although the mechanics are relatively straight forward to model using Hertzian mechanics, the *dependence* on the applied normal force (F_N), the applied stress (σ), the solution composition, the solution temperature (T), the duration time of the wear experiment (t), and the relative velocity of the AFM tip and substrate(v) can be complex. In almost all cases studied, we find that simultaneous to modification of the substrate we experience wear of the tip. By using a tip only once for the formation of each observed wear pattern on the substrate for a given set of parameters (e.g., F_N , σ , T, t, and v) and imaging the tip before and after, we are able to model the instantaneous stress (which is dropping) as a function of time during the wearing process. This allows us to unambiguously determine the stress dependence of single asperity wear as well as stress induced dissolution. The latter can also be studied in simple static loading (no sliding); the measured rates are found to be enhanced considerably in the presence of atomic steps on the surface. The minerals of interest include calcite and brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$). We also show that at supersaturation, we can induce crystal growth at rates 10-20 times higher than spontaneous growth with the AFM tip. Evidence is presented to show that the crystallinity of the growth is considerably better for the tip-induced growth compared to spontaneous growth. Finally, we show that combined mechanical and chemical stimuli greatly increase the rate of removal of strongly adhering particles on flat substrates modeled by an environmental crack growth mechanism.

Interaction of Cr, As, and U-containing pollutants with mineral-water interfaces studied by second harmonic and sum frequency generation

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It is now known that mineral-water interfaces can control the transport and chemical transformation of many groundwater pollutants. We present surface-specific, submonolayer-sensitive, real-time second harmonic generation (SHG) studies for monitoring the inorganic priority groundwater pollutants Cr(VI) and U(VI), as well as the organic arsenical Roxarsone, a poultry-feed additive, at silica-water interfaces. Thermodynamic, kinetic, and spectroscopic data are obtained using environmentally representative solute concentrations, and can be used to improve the reliability of existing pollutant transport models. Finally, vibrational sum frequency studies are presented that characterize geochemically important organic functional groups at mineral surfaces. These studies show that nonlinear optical spectroscopies yield important molecular-level information that is complementary to x-ray based techniques, and that they are well-suited for studying heterogeneous processes at mineral-water interfaces in real time, with high sensitivity, and under environmentally representative pH, temperature and concentration conditions.

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