

## Surface modifications of engineered nanoparticles and their impacts on cytotoxicity

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The interactions of engineered nanoparticles (ENP) with the natural environment will have a deterministic affect on their fate and transport, yet the impacts of environmental transformations of ENP are poorly understood. For example, previous work in our laboratory demonstrated that bare particles of nanosized zero-valent iron exhibited toxicity towards bacterial cells at concentrations as low as a few mg/L, yet oxidation of the iron surfaces or the presence of natural or engineered coatings may eliminate the toxic effects of NZVI. We examined the impact of surface transformations on the bacterial toxicity of ENP through the application of natural and/or engineered coatings on the particles. We selected particles with different mechanisms of expressing cytotoxicity; 1) NZVI- requires direct contact with cells, 2) TiO<sub>2</sub>- produces reactive oxygen species, and 3) AgNP- produce toxic metal cations. Our findings show that both natural and engineered surface coatings on NP may greatly reduce or eliminate the cytotoxicity of NP. However, the ability and mechanism of interference with toxicity is dependent on both the type of particle well as the coating. While engineered coatings of NZVI induced electrostatic or electrosteric repulsion between the NP and cell that prevented toxicity, in the case of TiO<sub>2</sub>, the natural organic matter coatings scavenged reactive oxygen species. Interestingly, engineered polyaspartate coatings did not prevent the toxicity of TiO<sub>2</sub>. The coating of AgNP with engineered and natural polymers has little impact on toxicity, but oxidation of the surface through sulfidation greatly reduced toxicity. Our studies imply that surface modifications may be engineered to minimize cytotoxicity and that the potential for detrimental impacts of ENP in the environment is lessened by coatings on which arise in natural systems.

## Physical versus chemical non-equilibrium model for simulating U(VI) adsorption

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Surface complexation reactions and diffusional mass-transfer between mobile pore water and immobile water associated with the intra-grain pores have been found to play an important role for the overall U(VI) transport behaviour in the US DOE Hanford 300A aquifer. Several laboratory- and field-scale scenario simulations have been carried out to investigate the behaviour of two alternative model approaches for the simulation of coupled intra-grain diffusion and surface complexation of U(VI) under dynamic groundwater flow and hydrochemical conditions.

The physical non-equilibrium approach explicitly calculates aqueous speciation and surface complexation in the intra-grain pore spaces as instantaneous reactions and simulates the diffusional mass-exchange between the mobile and immobile domains by a set of multiple 1<sup>st</sup>-order rates. The chemical non-equilibrium approach approximates the diffusion-limited surface complexation by a multiple 1<sup>st</sup>-order kinetic reactions, which makes it computationally efficient compared to the physical non-equilibrium approach. While for linear sorption scenarios the two model approaches are equivalent, they show differences when the sorption process becomes non-linear, for example as a result of surface complexation reactions under varying hydrochemical conditions.

Under the Hanford 300A field scale hydrological and hydrochemical conditions, the two model approaches predicted largely similar U plume behaviour. In contrast, simulated U(VI) mass discharge into the Columbia River that is adjacent to the 300A was noticeably higher in the physical model due to a higher degree of non-equilibrium in the plume fringe located at the river-groundwater interface. However, compared to other effects, such as that of calcite dissolution on U(VI) mass discharge, the choice of the non-equilibrium model approach appeared to be less important.