Kinetic study of colloidal birnessite formation during oxidation of chlorinated solvent by permanganate

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Introduction

In situ chemical oxidation (ISCO) with permanganate (MnO_4^-) has been developed recently as a technique for cleaning up aquifers contaminated by chlorinated organic solvents. The capability of MnO_4^- to oxidize chlorinated ethylenes in solution quickly has proved to be promising in site remediation. As MnO_4^- oxidizes the chlorinated compound in the subsurface, the reaction produces Mn oxide, a solid precipitate. Unfortunately, this precipitation causes pore plugging and permeability changes, which ultimately can cause the remedial action to fail. A decrease in the flushing efficiency due to the permeability changes is obviously a concern in the practical implementation of this technology

The Mn oxide produced during the oxidation reaction forms initially as colloids before more visible precipitates are evident. A colloid solution can be stabilized if the surface charge of the particles is increased. Change to the surface charge of colloidal particles can be created by adding ions that have large charge and also can adsorb onto the colloids. Studies have shown that the rate of the formation of Mn oxide is slower in phosphate solution. The purpose of this study is to elucidate possible controls on colloid formation by phosphate ion.

Material and Methods

Experiments were to quantify the colloid growth in solutions with and without phosphate ion. A Varian Cary 1 UV-vis spectrophotometer was used with continuous scanning at wavelengths of 418 nm and 525 nm. The reactions were run in a capped cuvette inside the spectrophotometer. All experiments were conducted in an aqueous solution at 22 ^oC. The reactants were $KMnO_4$ and

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trichloroethylene (TCE), with the latter in excess. The concentrations of $KMnO_4$ and TCE were 0.158 mM and 3.8 mM. A buffer, comprised of equal quantities of KH_2PO_4 and K_2HPO_4 was the source of phosphate.

Colloid growth rate was further investigated using photon correlation spectroscopy, which measures the size of submicron particles. The size of colloid particles during the growth process was measured with 90 Plus Particle Sizer (Brookhaven Instrument Co. Holtsville, NY). The concentrations of $KMnO_4$ and TCE were 0.63 mM and 6.09 mM, respectively. The effects of different phosphate ions (KH_2PO_4, K_2HPO_4, and K_3PO_4) were tested in the experiments. KCl was added as necessary to maintain the ionic strength. All chemicals were obtained from Fisher Scientific, and used as received.

Results and Discussion

Spectrometric studies of the colloidal growth with and without phosphate exhibit clear differences In TCE oxidation by MnO_4^- without phosphate, colloids formed immediately, as indicated by an elevated absorbance across all the wavelengths scanned. After reaching a maximum, the spectrum declined to a near zero position. This pattern of behavior indicated that solid Mn oxide formed and precipitated out of solution. With the addition of phosphate, the absorbance spectrum showed a gradual decrease in the MnO_4^- peak until almost all the MnO_4^- was consumed. The spectrum also shows an increase in absorbance at all wavelengths, suggesting the presence of colloids, however at a later time and slower pace.

Colloid size measurements from photon correlation spectroscopy showed a similar result. As expected, the starting point for colloid growth in the solution is delayed by the addition of phosphate, by tens of minutes. The results show that the presence of phosphate ions indeed can slowdown the coagulation process, especially at early times. The result also indicates that ionic strength influences the colloidal growth rate.

The behavior of the Mn oxide colloid growth in phosphate solution can be described in a complexation model. It seems that the Mn oxide from the oxidation first exists as a soluble

Mn(IV) species, which has been reported by other researchers. With phosphate in the solution, a relatively stable Mn(IV)-phosphate complex forms. The complex can keep the Mn(IV) in aqueous phase without forming colloids. Not until a large quantity of Mn(IV) were produced, did colloids and precipitates start to develop. Our study provides scientific background on possibilities of slowing down the formation of colloid during oxidation schemes by chemical additives. With more understanding of this treatment, it should be possible to apply these ideas to mitigate the problem of pore plugging and permeability reduction in ISCO schemes.

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