

Persulfate Persistence under Thermal Activation Conditions

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Contaminant destruction with in situ chemical oxidation (ISCO) using persulfate (peroxydisulfate) can be enhanced by activation, which increases the rate of persulfate decomposition to sulfate radicals. This step initiates a chain of radical reactions involving species (including sulfate radicals and hydroxyl radicals) that oxidize contaminants more rapidly than persulfate does directly. Among current activation methods, thermal activation is the least sensitive to geochemical conditions (e.g., pH and carbonate concentration) and its temperature dependence is easily predicted with the Arrhenius model. Combining new data for environmentally relevant conditions with previously published data, we have computed three sets of Arrhenius parameters ($\ln A$ and E_{act}) that describe the rate of persulfate decomposition in homogeneous solutions over a wide range of temperatures and pH. The addition of soil increases the decomposition rate of persulfate due to reactions with organic matter and possibly mineral surfaces, but the kinetics are still pseudo-first-order in persulfate and conform to the Arrhenius model. A series of respire experiments with soil at 70°C demonstrate that once the oxidant demand is met, reaction rates return to values near those observed in the homogeneous solution case. However, even after the oxidant demand is met, the relatively short lifetime of the persulfate at elevated temperatures (e.g., >50°C) will limit the delivery time over which persulfate can be effective.

The results presented here have a number of important implications for the application of activated persulfate to contaminant oxidation. First, very high pH's (>11) are needed to significantly increase the rate of persulfate decomposition, suggesting that the apparent success of in situ alkaline activation of persulfate is due, at least in part, to effects other than increased production of sulfate radical. Second, since the thermal decomposition of persulfate follows well-behaved kinetics, it should be possible to quantitatively predict the behavior of persulfate from straightforward laboratory feasibility tests using relevant materials. Third, the presence of soil increases the rate at which persulfate decomposes until the soil oxidant demand has been met. Fourth, once the soil oxidant demand has been met, persulfate continues to degrade via the first-order thermal decomposition reaction. Finally, and perhaps of greatest importance, the lifetime of persulfate (and therefore the availability of sulfate radical) is relatively short at elevated temperatures, which limits the distances over which diffusion of persulfate can be effective and which imposes design constraints on the *in situ* application of thermally-activated persulfate.