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Comment to the article "Hydroxyl radical scavenging by solid mineral surfaces in oxidative treatment systems: Rate constants and implications" published by K. Rusevova Crincoli and S. G. Huling in Water Research 169, 2020, 115240.

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Abstract. The fate of radicals in aqueous suspensions can be significantly affected by surfaces scavenging reactions. When short-lived radicals such as •OH are considered, mass-transfer limitation may come into play. Disregarding these limitations may lead to heavy overestimation of surface-mediated reactions. The present comment exposes a potential misinterpretation of experimental data in a recent study with implications for *in-situ* chemical oxidation (ISCO) techniques.

Rusevova Crincoli and Huling (2020) have investigated the impact of suspended solid materials such as silica and alumina on the oxidation rate of rhodamine B by OH-radicals in aqueous suspension. They developed kinetic analysis methods to estimate specific •OH surface scavenging rate constants ($k_{\equiv S}$). These rate constants were applied to *in-situ* chemical oxidation (ISCO) treatment conditions in contaminated aquifers. Based on their experimental results, the authors conclude that mineral surfaces play a key role as radical scavengers in aquifers, thus limiting the overall treatment efficiency in ISCO systems. In a typical model scenario (10 mg L^{-1} trichloroethene as pollutant, 10 g L^{-1} H_2O_2 as oxidant, 30% aquifer porosity) they estimate an efficiency of about 10^{-7} for oxidation of TCE by OH-radicals. More than 99.999% of the generated OH-radicals were consumed by surface scavenging reactions (Figure 2 in the article). These would be very unfavorable conditions for any •OH based ISCO technology.

In our opinion, the presented rate constants are inappropriate and the derived conclusions are ill-founded and potentially misleading.

Let us first consider the derived surface scavenging rate constants $k_{\equiv S}$ which have the units m^{-2} s^{-1} in the article. The corresponding radical quenching rate ($C_{\bullet OH}$ in mol L^{-1} s^{-1}) is described as $C_{\bullet OH} = k_{\equiv S} \times S_A \times m_S \times [\bullet OH]_{SS}$, where S_A is the specific surface area of the solid (in m^2 g^{-1}), m_S the mass of the solid (in g) and $[\bullet OH]_{SS}$ the quasi-stationary concentration of OH-radicals (in mol L^{-1}) in the aqueous phase. $k_{\equiv S}$ has the meaning of a second-order rate constant for the reaction between OH-radicals and surface sites. However, the units are not those of a second-order rate constant. This is a consequence of the factor m_S in the rate equation instead of a solid's concentration. As a consequence, the scavenging rate constants $k_{\equiv S}$ in m^2 s^{-1} presented throughout the article have no general meaning and cannot be applied to other systems.

They could in principle be converted to concentration-related values. This leads us to the second, more important point of critique. In order to be scavenged at a surface, the radicals have to reach this surface. One can, however, easily show that the great majority of OH-radicals cannot reach these surfaces – not in the batch experiments conducted in the study, and even less so under aquifer conditions. In order to demonstrate this, one can first calculate the half-life of •OH in aqueous solution in the presence of 29.4 mM H_2O_2 (as applied in the study): $t_{1/2} = \mathrm{LN}(C_0/½C_0) / (k_{\bullet\mathrm{OH,H2O2}} \times [H_2O_2]) = 0.692 / (2.7 \times 10^7\ \mathrm{M}^{-1}\ \mathrm{s}^{-1} \times 29.4\ \mathrm{mM}) \approx 0.9\ \mu\mathrm{s}$, where $k_{\bullet\mathrm{OH,H2O2}}$ is the second-order rate constant for the reaction of •OH with hydrogen peroxide used in the original article. Other dissolved •OH consumers (such as the used substrate rhodamine B) reduce the life-span of •OH even more. The diffusion distance of •OH in aqueous solution can be derived from the Einstein-Smoluchowski equation (Schwarzenbach et al., 2003) as $L_{\mathrm{diffusion}} = (2 \times D_{\bullet\mathrm{OH}} \times t)^{1/2} \approx (2 \times 2 \times 10^{-9}\ \mathrm{m}^2\ \mathrm{s}^{-1} \times 0.9 \times 10^{-6}\ \mathrm{s})^{1/2} = 60\ \mathrm{nm}$. This means that OH-radicals which are generated in aqueous solution much further than 60 nm from solid surfaces will probably react with dissolved substrates such as H_2O_2 or rhodamine B rather than be scavenged at mineral surfaces. They contribute to the efficiency of the oxidation procedure, regardless of the presence or absence of solids.

Now one has to consider the average distance between solid particles in the reaction systems. This distance is correlated with solid's concentration and particle size. Unfortunately, information on the particle size is missing in the article. When we consider as a reasonable scenario an average particle diameter of 100 µm and the maximum applied solid's concentration of 50 g L^{-1} with a density of α-Al_2O_3 of about 4 g cm^{-3}, we can estimate an average particle-particle distance of 450 µm in the aqueous suspension. Assuming smaller particles, the particle-particle distance would be decreased proportional to the ratio of particle diameters, e.g. 45 µm distance for 10 µm particles. Obviously, this distance is orders of magnitude larger than the travel range of OH-radicals. The mineral suspension was stirred in the batch experiments such that the mass transfer from the aqueous bulk phase onto the particle surface may be controlled by diffusion across the stagnant boundary water layer around the particles (Schwarzenbach et al., 2005). Although the thickness of this layer (δ_{boundary}) depends on the particle size and the agitation intensity, one can estimate the order of magnitude from mass-transfer coefficients $k_L = D / \delta_{\text{boundary}} \approx 10^{-4}$ m s^{-1} (Zhang et al., 2004). This results in $\delta_{\text{boundary}} \approx 20$ µm, which may vary to some extent but is a reasonable estimate. Obviously, this diffusive boundary layer is still some orders of magnitude larger than the predicted •OH travel distance. Hence, even if the mixing of the water bulk phase is assumed to be ideal – i.e. complete and instantaneous – diffusion across the stagnant boundary layer around particles would prevent contact between short-lived OH-radicals and surfaces.

In the last step, one has to check the validity of the batch data for predicting the •OH fate under aquifer conditions. The authors state: „In subsurface systems, the solids to water ratio is much greater than in the dilute suspensions used (≤50 g L^{-1}) during the laboratory testing. This suggests the rate of •OH scavenging by mineral surfaces could be much greater in aquifer and soil systems than in the mineral suspensions used in this study.“ (Rusevova Crincoli and Huling, 2020, p.6). The first sentence of this statement is certainly right, but the second part disregards the quite different hydrodynamic conditions in the batch experiments (stirred suspension) and in an unconsolidated aquifer (stationary pore water). Considering a typical sandy-gravelly aquifer, a reasonable estimate of inter-particle pore sizes may be in the order of 10^1 to 10^3 µm. When OH-radicals are generated in the pore water, e.g. by homogeneous Fenton reaction, the radicals can travel to mineral surfaces exclusively by molecular diffusion. There is no support by convection, such as in the batch experiments. The diffusion process, however, is much too slow to enable any contact between •OH and mineral surfaces, keeping in mind their life-span of ≤1 µs. Hence, OH-radicals are available for oxidative degradation of dissolved pollutants and other dissolved radical scavengers.

Rusevova Crincoli et al. (2020) have published concurrently a related study on the surface scavenching of sulfate radicals in ISCO processes. Although sulfate radicals are less reactive and more long-lived than OH-radicals, the basic issue of disregarded mass-transfer limitations is similar.

Finally, although the interpretation of Rusevova Crincoli and Huling (2020) is flawed, the interesting question remains: which processes are responsible for the observed inhibition of rhodamine B oxidation by suspended minerals and how can they be transferred to aquifer conditions? One hypothesis might be that longer-living radicals others than •OH and $SO_4^{\bullet-}$ contribute significantly to the conversion of reactive substrates such as rhodamine B.

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Graphical Abstract