

HYDROGEN PEROXIDE EFFICIENCY IN In-SITU CHEMICAL OXIDATION

The following is a discussion of the nature of the hydrogen peroxide efficiency in in-situ chemical oxidation.

It is well established that the decomposition of hydrogen peroxide in the Fenton reaction can be approximated by a first order decay rate:

$$C = C_0 e^{-kt} \quad \text{Eqn. 1}$$

where: C = concentration at any given time (%)
 C_0 = initial concentration (%)
 k = first order decay rate constant (min^{-1})
 t = elapsed time (min)

The pattern for such a decay is shown in Figure 1 for two initial starting concentrations, 2% and 4%, and a decay rate constant of 0.1 min^{-1} .

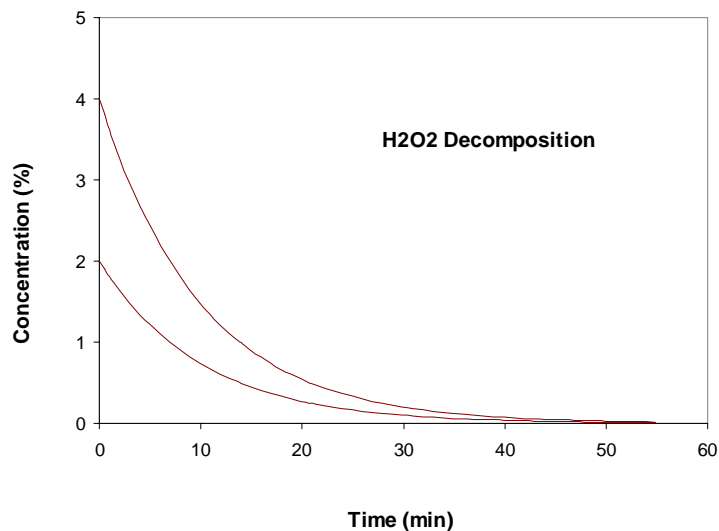


Figure 1. The decomposition of hydrogen peroxide in the Fenton reaction for initial peroxide concentrations of 2% and 4%.

Note that the decay rate constant, k , is the same for both curves in Figure 1, and that the concentration at any given time is doubled when the starting concentration is doubled.

Site specific values of k are affected by catalyst strength and soil and groundwater conditions, but are commonly on the order 0.05 to 0.5 min^{-1} and can be determined by bench testing. Figure 2 depicts hydrogen peroxide decomposition for three different decay rate constants.

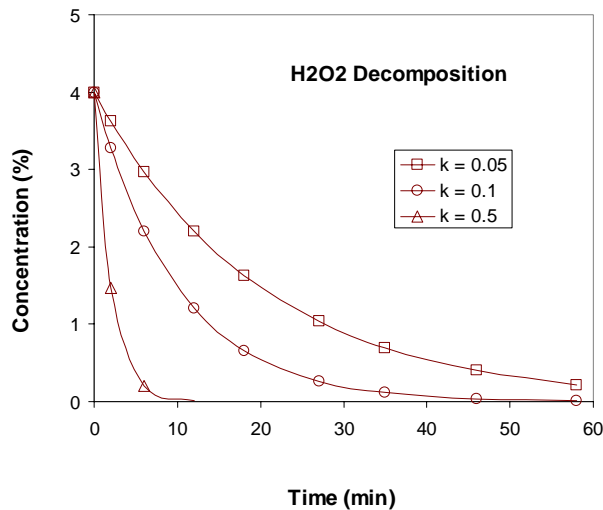


Figure 2. Hydrogen peroxide decomposition according to first order model for three different decay rate constants.

Note that after approximately 60 minutes the concentration of peroxide has diminished to less than 5% of its initial value in all cases. This is consistent with field observations and lab studies of heterogeneous systems, and can be easily verified by pouring common household peroxide onto soil and observing the rate of decomposition as indicated by release of oxygen (bubbling).

Chelates have been shown to decrease the rate of decomposition and improve the efficiency of hydrogen peroxide in homogeneous (aqueous only) systems. However, in heterogeneous systems (systems in which both soil and water are present) this benefit may not be gained. In heterogeneous systems, decomposition of the peroxide will be catalyzed by both soil and added ferrous iron. If the ferrous iron is sequestered by a chelating agent, the peroxide may preferentially decompose via soil-catalyzed reaction pathways. These pathways yield less oxidizing potential than the Fenton reaction and thus, use of chelates in field applications may reduce the effectiveness of Fenton's reagent.

When Fenton's reagent is injected into the subsurface, optimum distribution can be modeled on the assumption that uniform flow occurs, with reagent filling a cylinder of aquifer surrounding the injection well. The radius of such a cylinder is described by:

$$r = \left(\frac{Qt}{\phi\pi H} \right)^{\frac{1}{2}} \quad \text{Eqn. 2}$$

where r = radius of the treated soil cylinder (ft)
 Q = volumetric injection rate (ft³/min)
 t = elapsed time (min)
 ϕ = soil porosity
 H = height of treated soil column (ft)

In practice, uniform reagent flow is not observed, with reagent often detected at substantially greater distances than would be predicted by Eqn. 2. This deviation can be used as a measure of performance efficiency. For example, assume that a 4-foot tall soil column with a porosity of 0.33 is treated by injecting 100 gallons (13.4 ft³) of reagent at a single point. If reagent is then observed at a monitoring point 12 feet away, it could be estimated that 7% efficiency was achieved: either 7% of the targeted volume was contacted by reagent, or reagent was diluted to 7% of its original strength. This estimate is determined using Eqn. 2, which assumes perfectly uniform distribution and indicates that 100 gallons of reagent would reach a radius of 1.8 feet in the given soil column, treating an aquifer volume of 41 ft³. Uniform distribution over a 12 foot radius, however, would indicate treatment of 602 ft³, and result in 15:1 dilution of reagent, 7% of its original strength. A determination of the extent to which dilution is responsible for accelerating reagent movement relative to short-circuiting can be made using a non-reactive tracer. If the tracer is measured at the monitoring point at 7% of its original strength, uniform distribution would be indicated. If it is measured at full strength, short-circuiting would be indicated.

The above example does not account for reagent degradation. Knowing the decay rate of reagent (Eqn. 1) and the distance reagent travels as a function of time (Eqn. 2), it is possible to calculate reagent strength at various distances at various times. If a target minimum reagent strength is selected below which it is assumed satisfactory contaminant destruction will not occur, then the given relations can be used to predict a satisfactory radius of influence.

Figure 3 has been prepared from Eqn. 1 based on a decay rate constant of 0.1 min^{-1} and initial peroxide concentrations of 2% and 4%. A concentration of 0.5% peroxide, shown by a horizontal line, has been arbitrarily selected as the minimum concentration required for successful contaminant degradation in the treated zone.

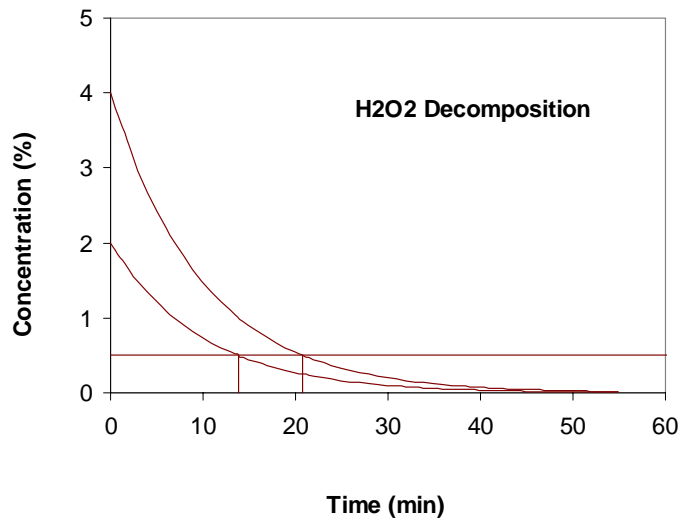


Figure 3. Hydrogen peroxide concentration as a function of time for two different initial starting concentrations. Volumetric flow rate and decay rates are identical in both cases.

It can be seen that the target minimum is reached after approximately 14 minutes in the low initial concentration case, and after 21 minutes in the high initial concentration case.

The distance traveled by reagent at various times is presented in Figure 4, prepared from Eqn. 2 and based on a reagent injection rate of $0.5 \text{ ft}^3/\text{min}$, a soil column height of 5 feet, and a porosity of 0.3.

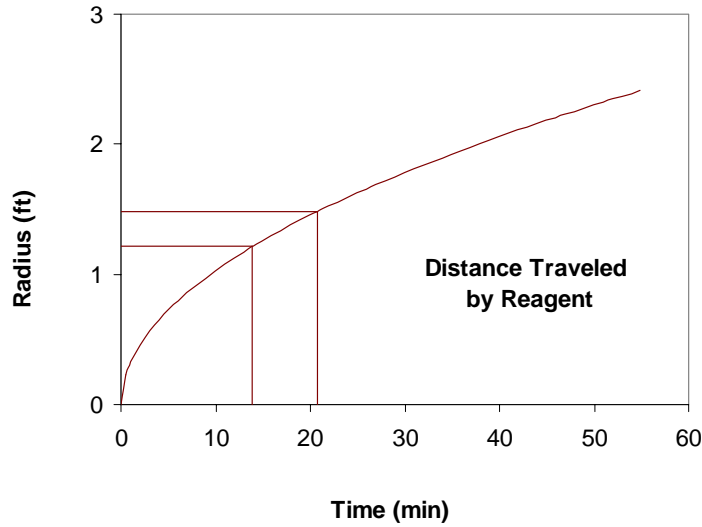


Figure 4. The distance traveled by reagent is a function of time, porosity, volumetric injection rate and soil column height. It is independent of reagent strength.

It can be seen that for the given conditions, reagent will have traveled approximately 1.2 feet after 14 minutes, and 1.5 feet after 21 minutes. These values translate to areal coverages of 1.1 and 1.8 square feet, respectively. Thus, a 100% increase in reagent strength results in a 63% increase in the amount of soil treated. Figure 5 depicts this trend for initial peroxide concentrations ranging from 0.2% to 50%.

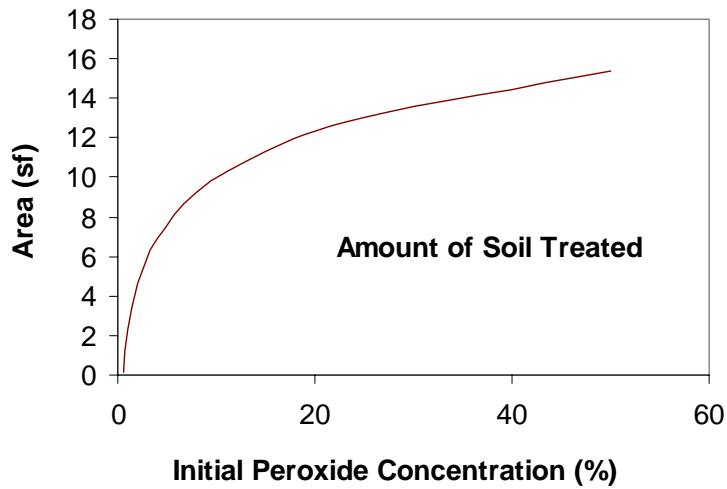


Figure 5. Treated area as a function of initial reagent strength.

Thus it is seen that due to the nature of hydrogen peroxide decomposition in the subsurface, as well as geometric considerations governing the movement of injected reagent, the area over which reagent can be expected to be effective is limited, and reagent efficiency diminishes as the initial reagent concentration increases.