

In Situ Chemical Oxidation: Performance, Practice, and Pitfalls

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Introduction

In situ chemical oxidation (ISCO) is a rapidly growing area of remediation technology. From its early beginnings in the late 1980's with the use of hydrogen peroxide, ISCO has grown into a multi-faceted technology. There have been two avenues of development that have lead to the growth of ISCO. One has been the development of new oxidant systems. The other avenue of development has been in novel delivery methods. Currently there are ten different commercial oxidant systems, based on five different oxidants. There are at least six different application methods that can be used to apply these different oxidant systems.

As a result of this multiplicity of choices in oxidants and in delivery methods, there is considerable confusion in the industry as to how well ISCO performs. This talk will provide a cogent analysis of the different oxidant systems and the delivery methods. It will provide a basis for comparing relative costs and performance. Finally this talk will provide a decision framework for choosing the best oxidant and delivery method.

Oxidant Systems

There are five oxidants that are currently in use in ISCO. These include ozone, hydrogen peroxide, potassium and sodium permanganate, sodium persulfate, and calcium peroxide. Hydrogen peroxide and potassium permanganate are the two most widely used oxidants. With each of these oxidants there are variations in how they are applied. The following overviews each of these oxidants and the variations in how they are applied:

Hydrogen peroxide is the oldest ISCO oxidant, being first applied in situ in 1986 to treat a formaldehyde spill at a Monsanto Plant in Orchard Park, MA. Prior to that event hydrogen peroxide was, and is still, a widely used oxidant for the treatment of industrial waste waters. Since that early in situ use of peroxide, three different approaches have developed. The oldest, used at the Monsanto plant is the simple addition of a 1-10% peroxide solution with low levels of iron (~50 mg/L). This has been used to treat formaldehydes, phenols and inorganic sulfides. This is a slow-reacting system.

The second peroxide approach, termed Fenton's chemistry, uses a 3-30% hydrogen peroxide with an acid catalyst (usually sulfuric) and an iron II (ferrous sulfate) solution. The intended purpose of this mixture is to generate hydroxyl radicals (HO^\bullet) which are a short-lived but highly reactive oxidant ($E_0 = 2.76\text{V}$). The main drawback with this system is that the peroxide is very unstable and decomposes readily. This decomposition generates heat and oxygen and has lead to fires and explosions on a few occasions. This Fenton's Chemistry has been widely applied, however the long-term success is questionable (1).

The third and most recent approach to using hydrogen peroxide is termed modified Fenton's chemistry. This approach uses a chelated iron catalyst with no pH adjustment. This combination is thought to produce a hydroperoxide anion and super oxide instead of the hydroxyl radical. The reaction mechanism is a combined oxidation and reduction reaction (2). The advantage of this approach is that the milder conditions improve the stability of the peroxide.

A variant of hydrogen peroxide is calcium peroxide (CaO_2). This is added as a slurry since calcium peroxide is only slightly soluble. Calcium peroxide hydrolyzes to produce hydrogen peroxide. The most likely reactive species is the hydroperoxide anion. Calcium peroxide is a "slow-release" oxidant.

Permanganate salts (sodium and potassium) were the second oxidant type developed. Starting in 1990 (3) there has been an increasing interest in permanganate for the treatment of organic contaminants. Much of the work has focused on the oxidation of chlorinated solvents.

Permanganate is available as the potassium form or the sodium form. There is no difference in the chemical reactivity of these two forms. Both have the same electrode potential ($E_0 = 1.7\text{v}$) The only difference is in the solubility and the cost. Potassium permanganate is the less expensive of the two costing about \$1.30 to \$1.50 per pound. It comes as a purple crystalline solid with a solubility of 6.4% at 20°C. Practically speaking it is difficult to get greater than a 3-4% solution without heating. As a result of the limited solubility of potassium permanganate,

sodium permanganate is used to make-up more concentrated solutions. Sodium permanganate is available as a 40% solution and costs about \$6.00 per pound (dry weight).

Permanganate has several advantages over hydrogen peroxide. One is that it is stable. If it doesn't react it will persist in groundwater. This is an advantage in that it allows the permanganate to react with adsorbed phase or NAPL phase organics. A second advantage of permanganate is that it is an intense purple color and is detectable with the human eye at about 50 mg/L. As a result it is easy to monitor the distribution of permanganate.

There are two primary disadvantages of permanganate. First it does not react with all VOCs. In particular it does not react with benzene which limits its application for hydrocarbon fuel spills. Second permanganate reacts readily with naturally occurring soil organic material. This reaction, termed the "soil oxidant demand" or SOD, is often the limiting factor in the economics of permanganate use. In many cases the SOD is greater than the stoichiometric requirements. Not measuring the SOD is a guaranteed means of assuring failure due to under-dosing.

Similar to hydrogen peroxide ozone has been used for a long time for treating industrial waste waters. It was first applied in the early 1990's for in situ treatment (4). Ozone is generated on site and is applied as a 5-10% ozone gas mixture. It reacts both directly with many organics and can also be used in conjunction with hydrogen peroxide to generate hydroxyl radicals. The primary limitation to ozone is its mass delivery rate. A "large" ozone generator will produce 50-100 Lbs./day of ozone. Also ozone has a limited solubility – 600 mg/L. Fortunately ozone appears to react in the gas phase so it is more efficacious than would be true if it reacted only in the aqueous phase.

One of the new and developing application areas for ozone is for the treatment of recalcitrant organics particularly PAHs, pesticides, explosives, and PCBs. Ozone is quite cost effective with these classes of contaminants. For example, in a laboratory study, ozone was able to oxidize 27 wt % PCB 1260 to less than 7,000 mg/kg in 8 weeks (5,6).

The newest oxidant being developed for ISCO is sodium persulfate. Persulfate, similar to hydrogen peroxide, requires a catalyst or activator to be effective. The two most common activators are heat (temperatures above 35-40°C) or a transition metal such as iron. Heated persulfate is able to oxidize all organic contaminants.

Persulfate is available as a crystalline solid and is soluble up to 56%. As result it is possible to deliver high mass loadings of persulfate.

Persulfate reacts through a free radical pathway generating sulfate radicals, which are almost as strong an oxidant as hydroxyl radicals ($E_o = 2.5$ to 2.6 v). The biggest difference between the sulfate radical and the hydroxyl radical is that it is much more stable.

Relative to permanganate persulfate has two advantages. First it reacts readily with benzene so it can be used to treat hydrocarbon fuel spills. Second it does not react readily with soil organics. Having a low SOD makes persulfate more economical than permanganate in soils with high TOC.

Delivery Methods

One of the avenues of development that has led to the growth of ISCO has been the development of new applications technology, particularly direct injection methods. Historically, treatment agents have been added through wells and/or galleries. Distribution has been by groundwater flow. This is a slow and inefficient process especially in low permeable or layer formations.

Recently a number of direct emplacement methods have been developed that allow for the rapid and effective distribution of chemical oxidants. These include geoprobe based injection, pneumatic fracturing, hydraulic fracturing and jet grouting. These methods are based on the injection/mixing of oxidants into the soil matrix. The injection force in some cases can fluidize the soil matrix allowing for effective mixing.

Since many of the oxidants react on contact with the contaminants, effective distribution of the oxidant is the primary factor governing the success of ISCO. Therefore choosing the proper delivery method is an important part of ISCO design.

Decision Matrix for ISCO

With the number of oxidants available and the range of delivery methods there are a plethora of ISCO options. However if one understands the properties and reactivity of the different oxidants it is possible to develop a logical framework for choosing the best ISCO system.

There are a number of factors which need to be evaluated in choosing the best ISCO system. The first is reactivity. Does the oxidant being considered, in fact, react with the contaminants present? The second is either cost or speed. Is quick closure important or is treatment cost? Based on which is most important, cost or speed, there is a logical progression of oxidants to evaluate. The third is the efficiency of the oxidant. How readily does it react with the contaminant(s) of concern versus other reactions. In evaluating each oxidant, therefore, one must consider non-productive reactions such as decomposition or SOD. This consideration may require laboratory testing and/or pilot testing.

Parallel to the selection of an oxidant, is the evaluation of delivery methods. The choice is governed by the oxidant chosen and, again, by whether speed or cost is most important.

It is important to realize that there is a logical framework in which choosing the best ISCO system can be made. With the right information and the proper analysis, one can choose an ISCO approach with the greatest likelihood of success.

References

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