

# Estimating the Total Oxidant Demand for *In Situ* Chemical Oxidation Design

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*Analytical techniques for designing of in situ chemical oxidation (ISCO) to treat organics in soil and groundwater are emerging. There are several issues that need to be resolved prior to adopting a standard analytical technique. Some of the more salient issues are discussed. In addition, currently practiced analytical techniques for estimating the oxidant demand for the oxidants permanganate and persulfate are provided. In the absence of analytical measurements, rules of thumb can be used with caution to estimate the overall oxidant demand. © 2003 Wiley Periodicals, Inc.*

## INTRODUCTION

*In situ* chemical oxidation (ISCO) is becoming increasingly popular for remediating organics in soil and groundwater (Vella & Veronda, 1994; Gates et al., 1995; Schnarr et al., 1998; West et al., 1998; Huang et al., 1999; Siegrist et al., 1999; Gates-Anderson et al., 2001; Lowe et al., 2002; Struse et al., 2002). Proper design of a field-scale implementation of ISCO requires data on target contaminant levels as well as quantitative estimates of other oxidant sinks. If all of the reactions that consume oxidant are not properly estimated, the amount of oxidant that needs to be injected will be underestimated, and it is likely that the ISCO effort will fail. Additionally, the demand for the oxidant exerted by subsurface materials may make ISCO economically infeasible for particular sites.

There are a number of chemical and physical factors that contribute to the total oxidant demand (TOD) of a subsurface environment. These include: 1) dissolved phase contaminant, 2) sorbed phase contaminant, 3) free phase contaminant, 4) dissolved phase reduced minerals, 4) solid phase (or sorbed phase) reduced minerals, 5) dissolved and sorbed phase natural organic matter (NOM), and 6) thermal and chemical decomposition. Obviously, the mass of oxidant cannot be reliably estimated from the target contaminant levels alone.

Dissolved phase and sorbed phase contaminant levels can be estimated by widely accepted analytical techniques. Estimating the oxidant required for contaminant treatment is just a simple stoichiometric calculation thereafter. The estimation of free phase contaminants (or dense nonaqueous phase liquids [DNAPL]) is very difficult. In fact, free phase product is seldom seen with chlorinated solvents. Rather, there is often indirect evidence of DNAPL, such as contaminant concentrations above 10 percent of solubility. In addition, sampling techniques may be so disruptive that they inhibit capture of chlorinated solvents.

Besides the target contaminant, other subsurface components will consume oxidant, such as reduced minerals and NOM, as mentioned. The amount of reduced minerals that will deplete oxidant depends on the present oxidation-reduction potential (ORP) of

the subsurface environment, as well as the chemical composition of the soil matrix (percentage of iron, for example). Rough estimates of the oxidant demand for reduced minerals can be made based on soil description and semi-qualitative descriptions of the ORP of the aquifer (for example, iron- or sulfate-reducing conditions). However, this type of estimate can easily be in error as much as an order of magnitude and result in under- or over-injection of oxidants. The reduced minerals are typically the largest oxidant sink, but in some instances the NOM demand can be overwhelming. Obviously, not all NOM will consume oxidant (Struse et al., 1999, Siegrist et al., 1999), and the level of NOM oxidation depends on the oxidant. Therefore, a simple analytical measurement such as total organic carbon may not provide an accurate estimate of the oxidant required for NOM. Oxidants may also be consumed through thermal decomposition, such as the conversion of hydrogen peroxide to water and oxygen.

With the exception of thermal or chemical decomposition of the oxidant, all oxidant sinks can be quantitatively estimated using fairly simple analytical techniques. The tests are currently being conducted by many practitioners in the ISCO field. There is not even a common terminology for the test—some of the more common terms are soil oxidant demand (SOD), natural oxidant demand (NOD), or total oxidant demand (TOD). The term TOD is utilized herein because SOD may not capture the oxidant demand that may occur in the aqueous phase. NOD may imply that all of the oxidant demand is natural, when in fact, significant oxidant demand may result from non-natural reasons. Nonetheless, there is not an accepted terminology and TOD is merely a suggested term that will be used in this article.

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There is also not concurrence on methods for completing a TOD test. There are several issues that must be considered. The ISCO science is relatively immature in broad practice. There may eventually be common acceptance. The ultimate goal is for an established procedure that the scientific community will accept. This will facilitate consistent implementation of ISCO. Many of the issues that must be considered are presented here. To our knowledge, this is the first paper on this narrow topic in ISCO. However, the opinions presented herein are merely meant to initiate some technical discussion of the TOD test. The opinions herein may not all be accepted eventually. It is hoped that it will eventually lead to a common and well-accepted standardized analytical technique.

Much of the TOD discussion centers on the use of permanganate as an oxidizing agent. Obviously, there are many other oxidizing agents that are used for soil and groundwater remediation (Siegrist et al., 2001). There is a discussion of TOD testing with sodium persulfate (Hoag et al., 2002) and with hydrogen peroxide (and Fenton's reagent). TOD testing can be an important part of any oxidation program. There may be more oxidants that emerge for remediation, and TOD tests may need to be developed for those oxidants. This article presents methods currently employed for estimated TOD, as well as the issues that must be considered with respect to TOD testing, including: 1) sample size; 2) sample location and number; 3) sample preservation, 4) sample location; 4) DNAPL type, mass, and distribution; 5) contaminant location (i.e., vadose zone, fractured bedrock, etc.); and 6) oxidant concentration.

## METHODS FOR ESTIMATING TOD

Simple colorimetric techniques can be used to estimate the TOD of the aquifer or soil material. The colorimetric technique uses varying ratios of oxidant mass to soil mass prepared in separate vials. The TOD tests are typically conducted in 250-ml translucent

polyethylene bottles with lined screw caps. Groundwater from the site or deionized water is added to field soils (about 125 ml). Controls are prepared in similar containers with deionized water. Oxidant is added, the bottles are sealed and shaken vigorously for about 15 seconds, then allowed to stand at room temperature for a period of 48 to 72 hours. Samples can be acquired from the bottles and measured throughout this time period if it is desirable to characterize the kinetics of oxidant depletion. If the oxidant is permanganate, no color indicator is necessary because of the strong purple color from permanganate (measured spectrophotometrically at 525 nm [APHA, 1998]). If the oxidant is persulfate or others, a starch-iodide or other red-ox indicator is necessary. The varying ratios of oxidant/soil mixtures are allowed to react, and the resulting color is measured. The TOD can be narrowed down to the mixture ratio where color remains and the mixture ratio where color is depleted. Based on numerous TOD tests, the TOD can be as little as 0.05 grams of oxidant per kilogram of saturated soil (for carbonate aquifers, for example) or as high as 15 grams of oxidant per kilogram of saturated soil (for organic-rich sediments under sulfate-reducing conditions, for example).

Siegrist et al. (2001) present a summary of oxidant demand test results, with the oxidant permanganate, from various experimental and field studies. The results of the 10 to 15 studies they presented suggest the permanganate demand by natural media varies from 2 to over 100 mg  $\text{MnO}_4^-$  per mg of organic carbon measured in the natural media. It is important to note that this demand is comparable to that of targeted contaminants such as trichloroethylene (TCE) and tetrachloroethylene (PCE).

Another variation of the colorimetric technique utilizes a single aquifer or soil sample and excess oxidant (and color indicator, if necessary). The oxidant is allowed to react and the excess oxidant is "titrated" back with a reductant, such as sodium bisulfite or sodium thiosulfate. This colorimetric technique has the advantage that it only requires one sample, but it does require the additional titration step at the end of the reaction time.

The permanganate colorimetric technique uses a selected maximum ratio of oxidant mass to soil mass (10 g/kg), using soil samples that have been collected from different soil borings or different depths within the same boring. The oxidant/soil mixtures are mixed and allowed to react for a select period—typically 48 hours. Following the reaction period, the TOD is determined by titrating the mixture with a solution of a reducing compound (sodium thiosulfate) until the purple color of the permanganate ion disappears:



The governing reaction shows that 3 moles of sodium thiosulfate are required to reduce 8 moles of potassium permanganate. When multiplied by the appropriate molecular weights, a required mass ratio of 0.375 grams of sodium thiosulfate to potassium permanganate is required. The mass of excess oxidant is calculated in one of two ways. A known (standardized) solution of thiosulfate can be used and the excess oxidant calculated from the required volume of titrating solution, its molar concentration, and the required (stoichiometric) mass ratio. Alternatively, a control solution of permanganate (containing about the same mass as was added to the soil water mixture) can be titrated with an unstandardized thiosulfate solution. This titration (essentially a standardization step) gives the volume of solution required per unit mass of permanganate added. The same thiosulfate solution is also used to titrate the soil water mixtures. The mass of excess oxidant is then the volume required for titrating a given sample divided by the volume-to-mass ratio required for the control. The TOD is then the difference between

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the mass of original oxidant and excess oxidant divided by the mass of soil. Titrations are typically prepared using about 0.1 to 0.2 M sodium thiosulfate solutions. These reductant concentrations are used to ensure that there is adequate sensitivity in the titration volume to measure TOD differences on the order of or less than 0.1 g/kg.

Depending on the soil characteristics—most notably, the soil color—titrations can require slow, step-wise additions of reductant followed by a short settling period to observe the color in the water phase. In addition, some cohesive soil can absorb permanganate and release it slowly; therefore, the stepwise procedure with vigorous mixing may also be required under these conditions.

Another method that can be employed is direct measurement (i.e., no titration) of permanganate concentration (initial and at selected time points). No indicator is necessary as the deep purple color of the permanganate ion is used. Direct spectrophotometric measurements are made of the samples, and translated to concentration using a standard calibration curve (APHA, 1998). The demand then equals the difference between the initial and final permanganate concentrations for the mass of sample examined. It is important to note that when applying this method,  $\text{MnO}_2$  by-product and other solids must be pre-filtered (0.2  $\mu\text{m}$ ) from the aqueous phase sample as they interfere with permanganate absorption measurements at 525 nm, and the concentration of the resulting permanganate solution must fall within the calibration range (i.e., samples may require dilution).

In the absence of a test, TOD can be estimated by examining the current biogeochemical state of the aquifer.

### *Inferring TOD from Other Data*

In the absence of a test, TOD can be estimated by examining the current biogeochemical state of the aquifer. For example, if the geochemical state of the subsurface system is highly reducing (or biologically anaerobic), it will require injecting significant quantities of chemical oxidant in order to bring the aquifer sufficiently oxic for oxidation of the target contaminants. As a second example, if there is elevated dissolved oxygen (DO), then ISCO may be applicable because there may not be significant quantities of reduced metals.

Fortunately, the analytical measurements of the groundwater that indicate the biogeochemical state of the aquifer are often collected as part of an overall assessment program. These results can be used in the absence of a TOD test to infer the magnitude of the oxidant sinks. These parameters include: pH, ORP, dissolved oxygen, alkalinity, dissolved iron and manganese, sulfate, nitrate (or ammonium), and dissolved hydrocarbons such as methane, ethene, and ethane. Ethene and ethane are important when the target contaminant is chlorinated alkenes, such as TCE plus daughters. ORP measurements must be interpreted in conjunction with the other parameters. In a number of instances, conflicting ORP measurements have been observed (e.g., a large negative ORP reading for a system that has elevated dissolved oxygen).

In general, the biogeochemical state of the aquifer changes from background conditions in response to microbiological activity associated with the released contaminants and other materials. Typically, for sites with some petroleum contaminant released, oxygen is the first element that is consumed during microbial processes. Microbes gain energy from the consumption (oxidation) of electron donors coupled with the utilization (reduction) of electron acceptors. For example, a common biodegradation activity is the aerobic metabolism of fuel contaminants. In this case, oxygen is the electron acceptor, while the fuel hydrocarbon is the electron donor, which may be oxidized completely to  $\text{CO}_2$  by this process. After the oxygen is consumed, alternative electron acceptors, such as nitrate and sulfate, may be utilized in contaminant oxidation in the

absence of oxygen. In general, the electron acceptor will be used in the following order:  $O_2 > Mn^{+4} > NO_3^- > Fe^{+3} > SO_4^{2-} > CO_2$ . Thus, the presence or absence of these parameters will indicate the ORP range of the groundwater. For example, if nitrate was depleted and sulfate was present at high levels, it may be concluded that the system is moderately reducing (somewhere around iron-reducing conditions). If sulfate was not present at elevated levels and methane was present, the system would be even more reducing, past sulfate-reducing conditions and onto methanogenic conditions. Methanogenic is generally the most reducing that an aquifer can naturally sustain.

As previously stated, the presence or absence of these parameters in comparison to background levels can be used to infer the geochemical state of the subsurface environment. Absence of DO (less than 2–3 ppm) indicates anaerobic or anoxic conditions. The presence of dissolved manganese (greater than 10 ppm) may indicate manganese-reducing conditions. As the manganese (+4) accepts electrons, it is converted to the generally more soluble manganese (+2). Nitrate depletion may indicate denitrification (the reduction of nitrate to  $N_2$ ) or nitrate reduction. Nitrite, an intermediate in denitrification, may also be an indicator of this process. Elevated ammonia/ammonium measurements can also indicate nitrogen-reducing conditions. The presence of dissolved iron (greater than 10 ppm or so) may indicate iron-reducing conditions where generally insoluble ferric iron has been reduced to more soluble ferrous iron. However, under sulfate-reducing conditions, hydrogen sulfide is produced that readily precipitates ferrous iron. Sulfate depletion (relative to background) or the presence of sulfide gas may indicate sulfate-reducing activity. The presence of dissolved methane gas (10 to 100 ppb or so) in groundwater indicates methanogenic conditions. Elevated concentrations of these gases will also indicate microbial activity in groundwater samples. Chapelle et al. (2002) have recently shown that sulfate may be present at 10s of ppm and methanogenic conditions may still be present.

Based on hundreds of TOD tests and comparing those data to standard geochemical parameters, we have noted some trends for TOD. These estimates should only be used in the absence of a TOD test and should be considered order-of-magnitude estimates at best. There are wide ranges that can be expected for TOD. In general, the lesser the amount of minerals (iron or manganese compounds, for example) or NOM in the soil, the lower the TOD. However, even moderate amounts of minerals and/or NOM under highly reducing conditions can result in TOD values that may preclude ISCO as a viable remedial alternative. At the same time, moderately strong reducing conditions have been observed along with a low TOD for limestone aquifers. Exhibit 1 summarizes the various inferences on TOD.

Geochemical Condition	Occurrence	Range of TOD
Low metals content	Limestone or clean sand	<0.1 to 0.5 g/kg
Low NOM	Limestone or clean sand	<0.1 to 0.5 g/kg
Oxic conditions	Elevated dissolved oxygen	<0.1 to 1 g/kg
Mildly reducing conditions	Elevated ferrous iron	<0.1 to 2 g/kg
Moderately reducing conditions	Depressed nitrate but elevated sulfate	<0.1 to 5 g/kg
Strongly reducing conditions	Elevated methane or ethene (for chlorinated volatile organic compounds)	<0.1 to 15 g/kg

**Exhibit 1.** Inferences on TOD

## CONSIDERATIONS FOR TOD

There are many factors to consider when completing a TOD test. It is desirable but not always practical to complete the test in the field under ORP conditions that mimic the current aquifer conditions. The test should be completed in the target treatment area, but the level of contamination may affect the ORP conditions. As a result, the test results may need to be corrected for large variations in contaminant concentration. The TOD test should be viewed as an analytical and quantitative estimate of the oxidant required to overcome reduced minerals and NOM. It is not an exact measurement, but it is significantly better than an estimate based on semi-qualitative or even indirect quantitative measurements (e.g., total organic carbon). Estimates of TOD are crucial to a successful ISCO remedial approach because the oxidant demand for reduced minerals and NOM can be significantly greater than the oxidant demand for target contaminants.

The TOD test should be viewed as an analytical and quantitative estimate of the oxidant required to overcome reduced minerals and NOM.

### SAMPLE SIZE

The sample size can obviously affect the TOD test results. Given the variability in subsurface geochemistry, a consistent sample size and several TOD tests for the site are recommended. For numerous TOD tests, a 100g sample has proved to be sufficient. With this sample size, we add about 1g of potassium permanganate, which is almost always sufficient. In the cases where it is not sufficient, it would generally indicate that chemical oxidation may not be a cost-effective remedial alternative for the site. The TOD tests are typically conducted in 500-ml translucent polyethylene bottles with lined screw caps.

### SAMPLE LOCATION AND NUMBER

The location of the soil sample requires some thought. When confronted with a soil sample in a clear liner, there are often large visible variations in the soil composition. There may be areas with clear indications of iron-staining, while other areas may have visibly greater levels of NOM. When there are large natural variations, it is recommended to take a greater number of soil samples from the core rather than try to produce a more homogeneous sample by mixing soil samples from different portions of the core. The mixing process (especially in open air) could result in mineral oxidation and inadvertently bias TOD toward a lower result.

Obviously, there can be large variations in the ORP over the aquifer. This can translate to large variations in TOD. For example, chlorinated solvents often were used as degreasing agents prior to disposal. At the point of disposal, the grease may result in biological activity that produces highly reducing conditions. Because the grease may not be as mobile with the groundwater (as compared to the chlorinated solvent), the subsurface environment may become less reducing farther away from the original disposal point. Therefore, it is desirable to complete TOD tests over the entire portion of the aquifer so that the range in TOD is captured. This is, of course, if ISCO is being considered for the entire plume. Sometimes, ISCO is used for the source area, and other less aggressive approaches are used for the remaining portion of the aquifer.

There are many factors that will determine the sample location. These may include the current characterization of the plume, access to sampling locations, etc. In all cases, the sample for the TOD must be collected within the plume and preferably within the area where ISCO will be applied. The contaminants targeted for treatment (or their co-

contaminants) will almost always affect the ORP state of the subsurface environment. The only exception is if the sample absolutely cannot be collected from the treatment area (for let's say, high radioactivity or some other reason). In this case, it may be worthwhile to consider an injection pilot test rather than a TOD test, if there are not other implementable and viable options.

## SAMPLE PRESERVATION

In a perfect situation, the TOD test would be initiated in the field so that the ORP conditions of the test are maintained. However, from a practical point of view, this is not always cost-effective or viable. Also, given that the ORP varies dramatically over the site, there is a question of how to maintain the sample. A nitrogen glove box may make the conditions more anoxic than they were in the field, while working in open-air may be too oxic. It is impossible to know and mimic the entire range of ORP conditions that are encountered in the field. The most effective approach is to minimize the exposure of the sample to another environmental condition.

Typically, the soil sample is collected in an acetate liner using direct push technology. The liner is sealed on both ends as quickly as possible with plastic caps. The soil sample is stored on ice until it is prepared for analysis. Analysis should be initiated as soon as possible—preferably within 24 hours.

If the TOD test is being completed in the saturated zone, it is preferable to collect a groundwater sample at the same location of the soil sample. However, it is not entirely necessary, in our opinion, to use a groundwater sample in the TOD test. After having completed numerous oxidant tests on groundwater alone, the oxidant demand from the water phase is often negligible (less than 1 percent) compared to the soil phase. So if the aquifer will not yield sufficient water for the TOD test, distilled water can be used without compromising the estimate of the test. If groundwater is collected, transfer the groundwater to a 250- to 500-ml amber jar with zero headspace. Store the sample on ice as quickly as possible. Do not use any preservatives for the groundwater because it will alter the natural geochemical conditions and the TOD test results.

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## PRESENCE OF DNAPL

The presence of DNAPL may result in very high TOD levels. However, visible free phase product is seldom encountered. In highly contaminated areas, it may be necessary to correct the TOD for the contaminant concentrations in order to get a true picture of the background oxidant demand. This may only be warranted for sites where a few number of samples have been collected and analyzed for TOD. In this case, the soil and groundwater should be analyzed for the target contaminants. Thereafter, the reaction stoichiometry should be determined, and the load of oxidant for the contaminant only should be calculated. In this manner, the oxidant demand can be extrapolated over a large portion of the site without it being completely biased toward the portion of the oxidant demand that is from the target contaminant.

As an example, consider a hypothetical TOD test completed with potassium permanganate on a saturated soil sample with high levels of trichloroethene. For illustrative purposes, assume the contaminant concentration in the soil was 110 milligrams per kilogram (mg/kg), and the groundwater concentration was 150 milligrams per liter (mg/l). The TOD test results were 3.2 grams per kilogram (g/kg) of saturated soil. Assume the

treated area is 10 m × 10 m × 10 m, the effective porosity is 30 percent, and the soil density is 1.7 grams per ml. The permanganate required for just the soil contaminant is 0.297 g/kg of dry soil, the permanganate required for the aqueous phase contaminant is 0.406 grams per liter of groundwater. For the hypothetical aquifer, this translates to 122 kg of permanganate for the aqueous phase contamination, 505 kg of permanganate for the soil phase contamination, and 6,400 kg of permanganate to overcome TOD. In this example, the contamination is biasing TOD to be greater than the background oxidant demand. Interestingly though, even with very high levels of contamination, the mass of permanganate required to overcome TOD is significantly more than the contaminant oxidant demand.

Proper implementation of ISCO in the vadose zone will require saturating or nearly saturating the soil.

## CONTAMINANT LOCATION

The TOD test for the vadose zone differs slightly from saturated conditions. For the vadose zone, the test uses distilled water to saturate the soil sample. For saturated conditions, groundwater should be used to saturate the soil sample. However, as previously discussed, distilled water can be substituted for groundwater if sufficient groundwater is not available for the saturated zone test. Proper implementation of ISCO in the vadose zone will require saturating or nearly saturating the soil. The water for mixing the oxidant will likely come from the nearest potable water source. If the water source is known for the potential implementation, that water can be used to saturate the soil sample for the TOD. However, oxidant demand on potable water is typically negligible, so it may not be necessary to use the potable water source.

### *Fractured Bedrock*

The value of a TOD test in fractured bedrock environments is questionable. It is extremely difficult to determine the surface area of rock that will be exposed to the oxidant during an injection into fractured rock. If the sample is pulverized in the laboratory prior to the TOD test, this substantially increases the available surface area available for reaction. The surface area will be much greater than that contacted in the actual ISCO field implementation and, as a result, the TOD test results will lead to overinjection. There also can be geochemical alterations (change in oxidation state) when the sample is pulverized if extreme care is not taken to make sure the atmospheric environment does not alter the minerals. If the sample is not pulverized, the ambient pressures typically associated with a TOD test may not be sufficient to mimic the reaction area that will occur in the field. In this instance, TOD would be underestimated. More expensive flow-through cell measurements could be made for fractured bedrock, but it is feasible to forego a TOD analysis. A small-scale injection test may be more suitable for fractured bedrock environments.

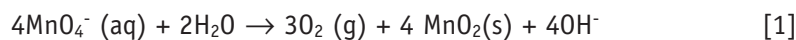
## OXIDANT CONCENTRATION

### *Permanganate Decomposition*

It has been demonstrated in several instances that the initial concentration of permanganate applied in a TOD test will influence the ultimate TOD measured for a sample. A higher initial permanganate concentration will result in a higher oxidant demand



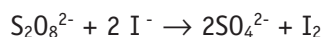
(Siegrist et al., 2001; Siegrist et al., 2002). It is possible this effect is due to autocatalyzed decomposition of permanganate by the by-product  $\text{MnO}_2$ .



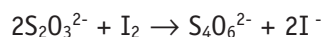
Due to this potential for additional permanganate consumption, TOD testing should be conducted at several permanganate concentrations at the site. It is not advisable to extrapolate results of tests conducted at one oxidant concentration to another, especially to a higher range. In lieu of conducting the tests at multiple concentrations, the test should be completed at concentrations that are expected for the actual implementation. Often, the goal in the implementation of the ISCO is to get as much permanganate in per pound of fluid injected. This may necessitate working at near permanganate solubility limits for the TOD testing.

### Sodium Persulfate TOD

The TOD test for persulfate is very similar to the titration test for TOD for permanganate. The main exception is that sodium persulfate solutions do not have visible color under normal reaction conditions. As a result, a starch-iodide indicator is used to visually determine the ORP change. The colorimetric technique uses a selected maximum ratio of oxidant mass to soil mass (10 g/kg) that has been collected from different soil borings or different depths within the same boring. The oxidant/soil mixtures are mixed and allowed to react for a period of 48 hours. TOD is determined by first adding potassium iodide to produce iodine from unreacted persulfate:



The potassium iodide is typically added in excess (approximately 10 times the molar concentration of the original persulfate added). Excess iodide is used because the reaction kinetics are relatively slow and the solution is allowed to react for 1/2 to 1 hour. The orange-red colored iodine solution is then back-titrated with a solution of a reducing compound, sodium thiosulfate:



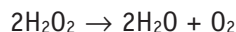
Starch indicator is added near the end of the titration (when the solution becomes pale yellow) to produce an intensely blue-colored starch-iodine complex. The indicator is not added until this point because the complex formation can yield irreversible products when iodine concentrations are high. The titration is then continued until the blue complex color has dissipated. The governing reactions show that two moles of sodium thiosulfate are required to reduce one mole of iodine, which, in turn, was produced from one mole of excess persulfate. When multiplied by the appropriate molecular weights, a required mass ratio of 1.33 grams of sodium thiosulfate to sodium persulfate is required. The mass of excess oxidant is calculated in one of two ways. A known (standardized) solution of thiosulfate can be used and the excess oxidant calculated from the required volume of titrating solution, its molar concentration, and the required (stoichiometric) mass ratio. Alternatively, a control solution of persulfate (containing about the same mass as was added to the soil water mixture) can be titrated with an unstandardized thiosulfate

In lieu of conducting the tests at multiple concentrations, the test should be completed at concentrations that are expected for the actual implementation.

solution. This titration (essentially a standardization step) gives the volume of solution required per unit mass of persulfate added. The same thiosulfate solution is also used for titrating the soil water mixtures. The mass of excess oxidant is then the volume required for titrating a given sample divided by the volume-to-mass ratio required for the control. TOD is then the difference between the mass of original oxidant and excess oxidant divided by the mass of soil.

### *Hydrogen Peroxide and/or Fenton's Chemistry*

A TOD test can be completed in a similar manner to sodium persulfate for ISCO that is planned with hydrogen peroxide and/or Fenton's chemistry. There are some additional considerations with these oxidants because hydrogen peroxide will undergo autocatalytic decomposition. That is, the hydrogen peroxide will decompose as follows:



If the oxygen is not utilized to oxidize the minerals, it can result in a higher than actual TOD. The autodecomposition of peroxide is accelerated by heat. So, depending upon how ISCO is implemented in the field, there may be greater losses of peroxide in the field. A TOD test for peroxide or Fenton's chemistry should only be viewed as a minimum requirement for the oxidant load.

If ISCO is going to be completed with hydrogen peroxide, it may be acceptable to use the actual oxidant. However, it may be worthwhile to consider utilizing other oxidants in the TOD laboratory test so that the minimum oxidant demand can be estimated. The actual implementation will likely require additional quantities of oxidant that can best be determined through field implementation.

## CONCLUSIONS

There are many considerations for implementing ISCO. Proper estimation of TOD is just one part of a successful ISCO implementation. Even if the dose is properly calculated, there are many other factors that can hinder ISCO. Thus, proper delivery of the oxidant is also a key component to successfully implement ISCO. The oxidant must also be brought in contact with the target contaminant for the reaction to occur. The methods presented here help with properly designing an ISCO program. It is just one component of an overall program.

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