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Abbreviations

ISCO: in situ chemical oxidation
NAPL: non-aqueous phase liquid
PAHs: polycyclic aromatic hydrocarbons
PHCs: petroleum hydrocarbons

What is ISCO?

ISCO is based on the phenomenon of electron transfer associated with a chemical oxidation–reduction (redox) reaction in order to degrade organic contaminants (PHCs, chlorinated solvents, PAHs, etc.) affecting groundwater, saturated and unsaturated underground soil. Oxidation of contaminants can lead to its complete destruction and therefore to its transformation into water, carbon dioxide and salts. But in most cases, partial oxidation of contaminants leads to the formation of degradation by-products that are generally more biodegradable than initial pollutants. The chemical reactions involved are complex and depend on the species that are present. However, the overall reaction can be divided into two main stages: (1) the transfer of electrons by chemical redox; and (2) the formation of free radicals. During the redox reaction, the oxidant will reduce and the reducing agent will oxidize. Considering n_1 mole of the reducing/oxidant couple (redox) Ox_1/Red_1 and n_2 moles of the redox couple Ox_2/Red_2, the overall reaction and the two half-reactions are as presented in Eqns. 1, 2 and 3:

$$\mathrm{n_2 \times Ox_1 + n_1 \times Red_2 \rightarrow n_2 \times Red_1 + n_1 \times Ox_1} \tag{1}$$

$$\mathrm{Ox_1 + n_1 \times e^- \rightarrow Red_1} \tag{2}$$

$$\mathrm{Ox_2 + n_2 \times e^- \rightarrow Red_2} \tag{3}$$

The capacity of the oxidant to capture electrons is defined by the standard redox potential (E_0) of the redox couple. The higher the E_0, the stronger the oxidizing power of the redox couple considered. The oxidant reduction eventually leads to the formation of chemical species or molecules of which at least one of its atoms has an unpaired electron at the level of the outer electronic shell; these are called free radicals. These species are unstable and therefore particularly reactive and adapted to oxidize organic contaminants. This phenomenon is complex and involves a large number of chemical reactions, depending on the contaminants, porous media characteristics and oxidant type.

Common oxidants

There are four usual oxidants (USEPA 2006b; Watts & Teel 2006; Siegrist et al. 2011; Baciocchi 2013; Ranc 2017) involved in ISCO processes and they all have the capacity to oxidize most common organic compounds: permanganate ions, persulfate ions, hydrogen peroxide and ozone. Nonetheless, they have different properties and their remediation efficiency depends on the contaminant targeted, the oxidation parameters and the underground context. Overall chemical reactions, main advantages and limitations, activation methods if any and recent scientific developments regarding permanganate, hydrogen peroxide and ozone oxidants are presented in the next sections.

Permanganate

Since the early 1990s, permanganate is the oxidant that has been the most widely used to date in wastewater treatment processes, in the chemical industry in general (Dietrich et al. 1995; Singh & Lee, 2001) and in ISCO treatment processes in particular (Thomson et al. 2007; Siegrist et al. 2011). It is still the oxidant most widely used in ISCO today because its reactivity to contaminants as well as the advantages and disadvantages of its use are well known. The chemical reactions involved in the oxidation process depends on the pH and are relatively straightforward since they only involve one step of electron transfer and no radical formation is involved in the process.

Equations 4, 5 and 6 show the reactions of the MnO_4^- species for three different pH ranges:

$$\mathrm{MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_{2(s)} + 4OH^-} \qquad \text{(pH = 3.5-12)} \qquad (4)$$

$$\mathrm{MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O} \qquad \text{(pH <3.5)} \qquad (5)$$

$$\mathrm{MnO_4^- + e^- \rightarrow MnO_4^{2-}} \qquad \text{(pH>12)} \qquad (6)$$

The most common reactions occur with pH values ranging from 3.5 to 12; in this range the reaction is very stable and considered independent of the pH. Unfortunately, permanganate ion is selective with respect to certain contaminants (Singh & Lee 2001; Waldemer & Tratnyek 2006) and reacts with natural organic species present in the subsoil (Mumford et al. 2005). In recent years, scientific works related to its use in ISCO have focused mainly on limiting the clogging of porous media by solid manganese oxides by promoting the dissolution of the latter using different methods (Crimi et al. 2009). Limiting oxidation of natural organic materials in soil has also been a source of interest (De Weert et al. 2014; Dangi et al. 2018).

Hydrogen peroxide and Fenton's reagents

Hydrogen peroxide is a powerful oxidizer widely used in various sectors of the industry (bleaching, water treatment, sterilization, disinfectants, base for aviation and aerospace fuel, etc.). Once catalysed (Fenton 1894) and maintained in an acidic environment (pH <3.5), hydrogen peroxide produces very reactive hydroxyl radicals, which may be able to degrade organic contaminants present in wastewater, for example (Schumb et al. 1955). Since the beginning of the 1990s, scientific (Pignatello 1992; Watts 1992; Pignatello & Baehr 1994) and technical advances have made it possible to better understand the reaction mechanisms involved and applications in the environment have multiplied rapidly. In an ISCO context, even though hydrogen peroxide can be used without an activator, taking advantage of the electron transfer mechanism during oxidation of the targeted contaminant, its oxidation potential is relatively low ($E_0 = 1.8$ V) and its decomposition is rapid and exothermic.

The classic Fenton reagent is widely used for groundwater remediation and consists in catalysing hydrogen peroxide with Fe^{2+} in order to generate highly reactive hydroxyl radicals. Equations 7, 8 and 9 show the three main chemical reactions involved with hydrogen peroxide and iron:

$$\mathrm{H_2O_2 + Fe^{2+} \rightarrow\ Fe^{3+} + OH^{\cdot} + OH^{-}} \tag{7}$$

$$\mathrm{H_2O_2 + Fe^{3+} \rightarrow\ Fe^{2+} + O_2^{-\cdot} + 2H^{+}} \tag{8}$$

$$\mathrm{O_2^{-\cdot} + Fe^{3+} \rightarrow\ Fe^{2+} + O_{2(g)} + 2H^{+}} \tag{9}$$

The chemical reactions are complex and multiple on account of the different phases in which the reagents can be found (liquid, gaseous, NAPL; USEPA 2006b). Furthermore, given the low persistence of oxidizing species after catalysis, it is necessary to bring the hydrogen peroxide, the catalyst and the contaminant into contact simultaneously, to obtain good remediation results (Siegrist et al. 2011). To achieve a proper remediation, a large number of injection wells is necessary depending on the expanse of the contaminant plume. Finally, it is necessary to maintain the pH of the reaction at about 3.5 at any time during the treatment to avoid the precipitation of Fe^{2+}.

In the latest developments, efforts have been made to better understand the reaction mechanisms and optimize the use of Fenton's reagent in the ISCO application context. These studies mainly refer to the use of chelating agents, such as ethylenediaminetetraacetic acid, citric acid, catechol, etc., to maintain Fe^{2+} ions in solution at neutral pH (Kakarla et al. 2002; Gryzenia et al. 2009; Bocos et al. 2015). Improved processes developed thereof are called 'modified Fenton's reagents'. The impact of the presence of these chelating agents in the environment is still being studied and documented. Another emerging technology promising in the ISCO context is called the electro-Fenton process, which allows synthesizing the reagents necessary for the reaction in situ via an electrolytic step involving the use of a sacrificial iron buried anode (Nidheesh & Gandhimathi 2012; Kubo & Kawase 2018). Finally, Lu et al. (2017) studied the use of calcium peroxide as a source of hydrogen peroxide in the context of Fenton's reagents to ensure a gradual release of the reagent

Ozone

Although ozone was first used in drinking water treatment plants in the early 20th century, it was not until the early 1980s that its use became widespread in North America. Over the past 30 years, numerous studies have demonstrated its potential to degrade organic contaminants (Trapido et al. 1994; Siegrist et al. 2011). The oxidation of these pollutants can occur either by direct oxidation or through hydroxyl radicals during the decomposition of O_3. The reaction mechanisms are complex since the reactions can take place in the aqueous phase and in the gas phase by direct contact with the contaminant (Andreozzi et al. 1996; Choi et al. 2002; USEPA 2006b). In the aqueous phase, ozone has to be dissolved by bubbling and its concentration ranges generally between 5 mg/L and 30 mg/L. As the persistence of ozone is very low, it is very difficult to reach its solubility limit of up to 1 g/L at 0° C (Langlais et al. 1991). The direct oxidation takes place following Eqn. 10 (example of trichloroethylene contaminant), the E_0 is relatively low (2.1 V) and the kinetics are relatively slow:

$$\mathrm{O_3 + C_2HCl_3 + H_2O \rightarrow\ 2CO_2 + 3H^+ + 3Cl^-} \tag{10}$$

Radical oxidation occurs via hydroxyl radicals which can be generated naturally during the decomposition of O_3 in water (Langlais et al. 1991) or in the gas phase (Choi et al. 2002), following Eqn. 11:

$$\mathrm{O_3 + H_2O \rightarrow\ O_2 + 2OH^{\cdot}} \tag{11}$$

However, the reaction kinetics are slow and depend on the pH since this reaction is initiated by the hydroxyl anion (Taube & Bray 1940). The presence of hydrogen peroxide with ozone allows the rapid generation of hydroxyl radicals following reactions:

$$\mathrm{2O_3 + 3H_2O_2 \rightarrow\ 4O_2 + 2OH^{\cdot} + 2H_2O} \tag{12}$$

The use of ozone and hydrogen peroxide simultaneously is commonly called peroxone. The advantages of using peroxone over ozone have been highlighted with respect to many contaminants (Mitani et al. 2002). However, its use is less widespread in ISCO than direct ozone injection (Krembs 2008), its implementation being more complex and does not allow treating unsaturated zone of the porous media.

Recent studies related to the use of peroxone and ozone mainly refer to the so-called electro-peroxone (or E-peroxone) processes that directly generate hydrogen peroxide on site by water electrolysis. The main topics of study in relation to this method are the type of electrodes and the conditions of applications (Dinc et al. 2017). Efforts are also being made to deepen our knowledge of the chemical reactions involved in multiphase oxidation processes, and to document oxidation efficiency with respect to emerging contaminants. Finally, alternative activation methods using metal catalysts are also being investigated (Al-Antary et al. 2019; Chen et al. 2018; Ma et al. 2018).

References

Al-Antary T., Shaderma A. & Al-Dabbas M. 2019. Effect of ozonation on spiked chlorfenapyr pesticide on lettuce. *Fresenius Environmental Bulletin 38*, 370–375.

Andreozzi R., Insola A., Caprio V., Marotta R. & Tufano V. 1996. The use of manganese dioxide as a heterogeneous catalyst for oxalic acid ozonation in aqueous solution. *Applied Catalysis A: General 138*, 75–81, doi: 10.1016/0926-860X(95)00247-2.

Baciocchi R. 2013. Principles, developments and design criteria of in situ chemical oxidation. *Water, Air, & Soil Polution 224*, article no. 1717, doi: 10.1007/s11270-013-1717-8.

Bocos E., Fernandez-Costas C., Pazos M. & Sanroman M.A. 2015. Removal of PAHs and pesticides from polluted soils by enhanced electrokinetic-Fenton treatment. *Chemosphere 125*, 168-174, doi: 10.1016/j.chemosphere.2014.12.049.

Chen T., Yavuz B.M., Delgado A.G., Montoya G., Winkle D.V., Zuo Y., Kamath R., Westerhoff P., Krajmalnik-Brown R. & Rittmann B.E. 2018. Impacts of moisture content during ozonation of soils containing residual petroleum. *Journal of Hazardous Materials 34*, 1101–1108, doi: 10.1016/j.jhazmat.2017.11.060.

Choi H., Lim H.N., Kim J., Hwang T.M. & Kang J.W. 2002. Transport characteristics of gas phase ozone in unsaturated porous media for in-situ chemical oxidation. *Journal of Contaminant Hydrology 57*, 81–98, doi: 10.1016/S0169-7722(01)00219-4.

Crimi M.L., Quickel M. & Ko S. 2009. Enhanced permanganate in situ chemical oxidation through MnO_2 particle stabilization: evaluation in 1-D transport systems. *Journal of Contaminant Hydrology 105*, 69–79, doi: 10.1016/j.jconhyd.2008.11.007.

De Weert J.P., Keijzer T.J. & Van Gaans P.F. 2014. Lowering temperature to increase chemical oxidation efficiency: the effect of temperature on permanganate oxidation rates of five types of well defined organic matter, two natural soils, and three pure phase products. *Chemosphere 117*, 94-103, doi: 10.1016/j.chemosphere.2014.05.082.

Dietrich A.M., Hoehn R.C., Dufresne L.C., Buffin L.W., Rashash M.C. & Parker B.C. 1995. Oxidation of odorous and nonodorous algal metabolites by permanganate, chlorine, and chlorine dioxide. *Water Science and Technology 31*, 223–228, doi: 10.2166/wst.1995.0439.

Dinc O., Girgin Z. & Barisci S. 2017. Review—the application of an electro-peroxone in water and wastewater treatment. *Journal of the Electrochemical Society 64*, 16-4546, doi: 10.1149/2.0321706jes.

Fenton H.J.H. 1894. Oxidation of tartaric acid in presence of iron. *Journal of the Chemical Society Transactions 65*, 899–910.

Gryzenia J., Cassidy D. & Hampton D. 2009. Production and accumulation of surfactants during the chemical oxidation of PAH in soil. *Chemosphere 77*, 540-545, doi: 10.1016/j.chemosphere.2009.07.012.

Kakarla P.K., Andrews T., Greenberg R.S. & Zervas D.S. 2002. Modified Fenton's processes for effective in-situ chemical oxidation–laboratory and field evaluation. *Remediation 12*, 23–36, doi: 10.1002/rem.10043.

Krembs F.J. 2008. *Critical analysis of the field-scale application of in situ chemical oxidation for the remediation of contaminated groundwater*. MSc Thesis, Colorado School of Mines.

Kubo D. & Kawase Y. 2018. Hydroxyl radical generation in electro-Fenton process with in situ electro-chemical production of Fenton reagents by gas-diffusion-electrode cathode and sacrificial iron anode. *Journal of Cleaner Production 203*, 685–695, doi: 10.1016/j.jclepro.2018.08.231.

Langlais B., Reckhow D.A. & Brink D.R. (eds.) 1991. *Ozone in water treatment: application and engineering*. New York: American Water Works Association Research Foundation and Compagnie Générale des Eaux.

Lu S., Zhang X. & Xue Y. 2017. Application of calcium peroxide in water and soil treatment: a review. *Journal of hazardous Materials 337*, 163–177, doi: 10.1016/j.jhazmat.2017.04.064.

Ma J., Chen Y., Nie Ma L., Huang Y., Li L., Liu Y. & Guo Z. 2018. Pilot-scale study on catalytic ozonation of bio-treated dyeing and finishing wastewater using recycled waste iron shivings as a catalyst. *Scientific Reports 8*, article no. 7555, doi: 10.1038/s41598-018-25761-6.

Mitani M.M., Keller A.A., Bunton C.A., Rinker R.G. & Sandall O.C. 2002. Kinetics and products of reactions of MTBE with ozone and ozone/hydrogen peroxide in water. *Journal of Hazardous Materials 89*, 197–212, doi: 10.1016/S0304-3894(01)00309-0.

Mumford K.G., Thomson N.R. & Allen-King R.M. 2005. Bench-scale investigation of permanganate natural oxidant demand kinetics. *Environmental Science and Technology 39*, 2835–2840, doi: 10.1021/es049307e.

Nidheesh P.V. & Gandhimathi R. 2012. Trends in electro-Fenton process for water and wastewater treatment: an overview. *Desalination 299*, 1-15, doi: 10.1016/j.desal.2012.05.011.

Pignatello J.J. 1992. Dark and photoassisted Fe^{3+}-catalyzed degradation of chlorophenoxy herbicides by hydrogen peroxide. *Environmental Science and Technology 26*, 944–951, doi: 10.1021/es00029a012.

Pignatello J.J. & Baehr K. 1994. Ferric complexes as catalysts for "Fenton" degradation of 2,4-D and metolachlor in soil. *Journal of Environmental Quality 23*, 365–370, doi: 10.2134/jeq1994.00472425002300020023x.

Ranc B. 2017. *Oxydation chimique in situ de la zone non saturée de sols contaminés par du goudron de houille: du laboratoire au terrain. (In situ chemical oxidation of the unsaturated zone of coal tar contaminated soils: from laboratory to field.)* PhD thesis, University of Lorraine, France.

Schumb W., Satterfield C. & Wentworth R. 1955. *Hydrogen peroxide. A. C. S. Monograph no. 128.* New York: Reinhold Publishing Corporation.

Siegrist R.L., Crimi M. & Simpkin T.J. (eds.) 2011. *In situ chemical oxidation for groundwater remediation*. New York: Springer.

Singh N. & Lee D.G. 2001. Permanganate: a green and versatile industrial oxidant. *Organic Process Research & Devlopment 5*, 599–603, doi: 10.1021/op010015x.

Taube H. & Bray W. 1940. Chain reaction in aqueous solutions containing ozone, hydrogen peroxide, and acid. *Journal of The American Chemical Society 62*, 3357–3373, doi: 10.1021/ja01869a027.

Thomson N.R., Hood E.D. & Farquhar G.J. 2007. Permanganate treatment of and emplaced DNAPL source. *Ground Water Monitoring & Remediation 27*, 74–85, doi: 10.1111/j.1745-6592.2007.00169.x.

Trapido M., Veressinina J. & Munter R. 1994. Ozonation and AOP treatment of phenantrene in aqueous solution. *Ozone Science and Engineering16*, 475-485, doi: 10.1080/01919512.1994.10555755.

USEPA (United States Environmental Protection Agency) 2006b. *In situ chemical oxidation*. Chicago: United States Environmental Protection Agency.

Waldemer R.H. & Tratnyek P.G. 2006. Kinetics of contaminant degradation by permanganate. *Environmental Science and Technology 40*, 1055–1061, doi: 10.1021/es051330s.

Watts RJ. 1992. Hydrogen peroxide for physico-chemically degrading petroleum-contaminated soils. *Remediation 2*, 413–425, doi: 10.1002/rem.3440020407.

Watts R.J. & Teel A.L. 2006. Treatment of contaminated soils and groundwater using ISCO. *Practice Periodical of Hazardous Toxic and Radioactive Waste Management 10*, 2-9, doi: 10.1061/(ASCE)1090-025X(2006)10:1(2).