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Development of technical guidelines for the application of in-situ chemical oxidation to groundwater remediation

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A B S T R A C T

In-Situ Chemical Oxidation (ISCO) is an effective technology for the remediation of sites contaminated by a wide range of organic contaminants. Despite it is a well-established technology in the United States, the number of full-scale ISCO application in Europe and particularly in Italy is still quite low. The introduction of ISCO in the portfolio of remediation technologies suitable for the Italian market, specifically for national priority contaminated sites, has been facilitated by the issue of technical guidelines for ISCO application in 2005. Although execution of a pilot-scale test was foreseen in the guidelines, no specific indication or requirements on its design, nor indications or suggestions on its monitoring and interpretation, were provided. In order to give an answer to these issues, a new protocol providing more detailed technical indications with specific attention to the inclusion of the key criteria for ISCO application and for the execution of both lab-scale and pilot-scale feasibility test was developed. This paper discusses the main features of the proposed new protocol. The typical site conditions more suitable for ISCO application are discussed first, making reference to the hydro-geological characteristics of the site, the chemical properties of the contaminated matrix and the characteristics of the target contaminants. Besides, the main indications to perform lab-scale and pilot-scale feasibility tests are discussed. Finally, three sites in which the developed feasibility test procedure was applied are presented. For two of the three sites, in situ pilot tests were also carried out and the obtained results are briefly described in the Appendix of the paper.

1. Introduction

In-Situ Chemical Oxidation (ISCO) represents a relevant technological option for the clean-up of groundwater contaminated by organic compounds, such as hydrocarbons, PAHs, PCBs, chlorinated solvents and explosives. The remediation using ISCO involves injecting oxidants into the subsurface to destroy the different organic compounds of concern (ITRC, 2005). Oxidant delivery is commonly accomplished through permeation by vertical direct-push injection probes or flushing by vertical groundwater wells even though other delivery methods, such as horizontal wells, infiltration galleries, soil mixing and hydraulic or pneumatic fracturing, are also employed (Siegrist et al., 2011). There are several different oxidant formulations that are used for ISCO application. The most commonly applied ones are based on hydrogen peroxide, potassium or sodium permanganate, sodium persulfate, ozone or a combination of them. In particular, the application of chemical oxidation in soil and groundwater environments was initially focused on the use of catalyzed hydrogen peroxide using the classic Fenton's process, based on the reaction of hydrogen peroxide with ferrous ions to generate a wide variety of radicals by adding iron sulphate. In their pioneering work, Watts et al. (1990) proposed the application of classic Fenton's reagent for the treatment of soils contaminated by pentachlorophenols, suggesting optimum pH conditions between 2 and 3. Later, this approach was tested by Ravikumar and Gurol (1994) on sand packed columns contaminated again by pentachlorophenol but also trichloroethylene. The application of Fenton-like process, based on the concept of using naturally occurring minerals as iron source was first investigated by Watts et al. (1993), whereas Kakarla and Watts (1997) and more recently Watts and Teel (2005) addressed the issue of H_2O_2 stabilization using phosphate salts. This issue was also investigated

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through batch tests on chlorophenol contaminated soils (Baciocchi et al., 2003), column tests on *Trichloroethylene* (TCE) contaminated soils (Baciocchi et al., 2004) and by Vicente et al. (2011), who also addressed the combined effect derived from the addition of chelating agents, whose application is not expected to increase the mobilization of metals during Fenton's application (Bennedsen et al., 2012). Recently, Pham et al. (2012) gained insight into the main factors affecting hydrogen peroxide stability and hydroxyl radical formation through tests performed in the presence of iron-containing minerals and of a diverse set of aquifer materials; Rahim Pouran et al. (2014) reviewed the substitution of iron in an iron oxide with other transition metals as a mean to improve the properties of the iron oxide towards higher performance for contaminant degradation. As far as potassium permanganate ($KMnO_4$) is concerned, its application for chemical oxidation has been mainly focused on the treatment of chlorinated solvents. The performance of $KMnO_4$ were compared to those achieved by Fenton's reaction by Gates-Anderson et al. (2001), that investigated the effect of the oxidant loading and soil type on the efficiency of the process, showing that higher removal rates of tetrachloroethylene (PCE) could be achieved using potassium permanganate. Potassium permanganate was also shown to be effective in addressing PCE Dense Non Aqueous Phase Liquids (DNAPLs) through lab-scale physical simulation of an in-situ treatment (MacKinnon and Thomson, 2002). The removal efficiency of PCE-DNAPLs could be enhanced using a proper co-solvent, as reported by Zhai et al. (2006). More recently, De Souza e Silva et al. (2009) also demonstrated the effectiveness of $KMnO_4$ in treating Polycyclic Aromatic Hydrocarbons (PAH) contaminated soils, although the performance was lower than the one achieved using the Fenton's process. In order to overcome some of the limitation of Fenton's reagent, whose performances are affected by the high reactivity of hydrogen peroxide leading to typically short lifetime of the oxidant, and those of $KMnO_4$, characterized on the other hand by good reactivity only for chlorinated solvents, activated sodium persulfate was recently proposed as alternative oxidant. Activation of sodium persulfate, that can be achieved in different ways, can lead to the formation of very reactive sulfate radicals, capable of oxidizing a wide range of organic contaminants. Thermally activated persulfate was investigated by Huang et al. (2005) for the degradation of Volatile Organic Compounds (VOCs) in water, showing better performance for unsaturated hydrocarbons and aromatic compound with respect to saturated alkanes. Persulfate activation using soluble Fe(II) was successfully applied for the remediation of a soil contaminated by Diuron (Romero et al., 2010), whereas the effect of iron and manganese minerals on the efficiency of persulfate oxidation was investigated by Ahmad et al. (2010). The mechanisms underlying the base activation of sodium persulfate were elucidated by Furman et al. (2010), that demonstrated the formation of different active species besides sulfate radicals, such as superoxide and hydroperoxide anions. Finally, ozone has been also proposed mainly for the oxidation of petroleum hydrocarbons and chlorinated solvents, specifically in case of contamination of the vadose zone. Namely, Zhang et al. (2005) performed lab-scale column tests for simulating the treatment of anthracene in the vadose zone. More recently, Luster-Teasley et al. (2009) extended this study to pyrene, whereas Javorská et al. (2009) assessed the feasibility of this technique on Polychlorinated Biphenyls (PCBs) contaminated soils, showing the effect of the Soil Organic Matter (SOM) concentration and biphenyl chlorination on the removal efficiencies.

The important research and development (R&D) effort made, prompted in the last decade a rapid development of this technology (Huling and Pivetz, 2006), that led to the application of In-Situ Chemical Oxidation to several clean-up projects, especially in the United States.

For instance, Greenberg et al. (1998) have reported the successful field application of ISCO using catalyzed hydrogen peroxide for the treatment of a gasoline and waste oil contaminated groundwater in a warehousing facility in New Jersey. Nelson et al. (2001) have investigated the geochemical effects resulting from permanganate injection into an unconfined sand aquifer in Ontario (Canada) contaminated by PCE DNAPL. Kakarla et al. (2002) have demonstrated the field effectiveness of a modified Fenton's process for the treatment of a chlorinated solvents contaminated groundwater in a former dry-cleaning facility in Florida. Lowe et al. (2002) have discussed the results of a pilot-scale test conducted at a U.S. Department of Energy site in Midwest (Wyoming) using sodium permanganate for the treatment of a TCE contaminated groundwater. Chapelle et al. (2005) have reported the long-term monitoring carried out in order to evaluate the performances of an ISCO application using a Fenton's process for the treatment of a chlorinated ethane contaminated groundwater located in an abandoned landfill site in Georgia. More recently, McGuire et al. (2006) have investigated the performances of different source depletion technologies for the treatment of chlorinated solvent DNAPL source zones reporting also the results of 23 applications of ISCO using catalyzed hydrogen peroxide and permanganate in different US sites (mainly in Texas and Florida). A review of field-scale ISCO applications in the US, with a critical analysis of more than two hundred sites where ISCO was implemented, is provided by Krembs et al. (2010).

Differently from the US, the development of full-scale ISCO application in Europe and particularly in Italy is surely more limited. This is due to the fact that most of the R&D and patents on ISCO have been developed in the US (Baciocchi, 2013) and as a consequence first tested and applied for some years on US contaminated sites, only. Besides, this technology cannot be applied in other markets by simply transferring the know-how gathered in the US as the different, and typically more tight, legislative framework (e.g. existing EU water/groundwater framework directives) may require modification in the oxidant's formulation as well as in the injection scheme and in the evaluation of all possible side-effects. As a result, so far the experience on ISCO application gathered in the US has not been sufficient to make ISCO convincing enough for the stakeholders involved in the selection or approval of the clean-up options, although its application could allow to increase the sustainability of traditional remediation approaches, such as Pump and Treat (Cappuyns, 2013). This issue has been only very recently tackled within the CityChlor project, co-funded by INTERREG IVB North-West Europe (NWE), a financial instrument of the European Union's Cohesion Policy, that developed a code of good practice dedicated to the application of chemical oxidation to the remediation of sites contaminated by chlorinated solvents (CityChlor, 2013).

As far as the Italian national situation is concerned, the introduction of ISCO in the portfolio of remediation technologies, specifically for national priority contaminated sites, has been initiated by the issue of a protocol for the application of ISCO developed by the Italian environmental agency (now Institute for Environmental Protection and Research-ISPRA, formerly APAT) in 2005 (APAT, 2005). Relying on the 2000/60/CE water framework directive, this document allowed the implementation of ISCO provided that the technology was applied under controlled conditions. Besides, the execution of a lab-scale feasibility test was considered as a prerequisite condition to demonstrate the applicability of ISCO to a given specific site. Although execution of a pilot-scale test was foreseen in the guidelines, no specific indication or requirements on its design, nor indications or suggestions on its monitoring and interpretation, were provided.