Inorganic Geochemical Reactions During In Situ Oxidation of Chlorinated Solvents Using Potassium Permanganate

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ABSTRACT

The potential success of In situ Chemical Oxidation (ISCO) using potassium permanganate as a remediation technology to treat PCE and TCE groundwater impacts was previously demonstrated by several authors, showing that permanganate can completely mineralize chlorinated solvents into neutral by-products soluble ion salts, producing carbon dioxide (CO_2) and manganese oxides, and leading to changes in the groundwater pH. Therefore, the injection of high amounts of oxidants into the aquifer can also change the overall aqueous geochemistry, affecting the concentrations of anions and cations in solution, creating a potential of increasing metals mobility, leading to co-precipitation of some metals species and also increasing adsorptive surfaces due to oxides precipitation. This paper shows the importance of batch experiments and pilot scale remediation field tests in the development of site conceptual geochemical models and how these tools can prevent any significant geochemical modification in the groundwater condition, leading to the potential generation of secondary contaminant plumes during ISCO implementation.

Key words: PCE, TCE, In situ Chemical Oxidation (ISCO), Potassium Permanganate, Remediation Technology.

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1 - INTRODUCTION

The potential success of In situ Chemical Oxidation (ISCO) using potassium permanganate as a remediation technology to treat PCE and TCE groundwater impacts was demonstrated previously (Schnarr *et al*., 1998), showing that permanganate can completely mineralize these chlorinated solvents into neutral by-products soluble ion salts, producing carbon dioxide (CO_2) and manganese oxides, and leading to changes in the groundwater pH (Equations 1 and 2).

$$4KMnO_4 + 3C_2Cl_4 + 4H_2O \rightarrow 6CO_2 + 4MnO_2 + 4K+ + 8H^+ + 12Cl^- \quad (1)$$

$$2KMnO_4 + C_2HCl_3 + 4H_2O \rightarrow 6CO_2 + 2MnO_2 + 2K^+ + H^+ + 3Cl^- \quad (2)$$

At organically contaminated sites, metals can exist naturally in the subsurface or be anthropogenic in a very wide range of concentrations. The addition of high amounts of oxidants into the aquifer and subsequent reactions with TCE and PCE result in profound changes in the redox state and pH. These changes can potentially affect the behavior of trace metals in the subsurface.

In the context of trace metals mobility, the precipitation of MnO_2 solids generated during the reaction may have varied consequences depending upon their genesis and fate in subsurface. These oxides are initially colloidal in size and may either deposit on sediments surfaces providing strong sorbent for aqueous phase metals or become pore filling agents and yield permeability loss. They can also act as a long term source of Mn^{2+} release in the water (Crimi *et al*., 2003).

Additionally, changes in the aquifer redox state and the decrease of pH have also an extensive importance on the solubility of metals. Some authors have shown that chromium and nickel concentrations can be persistent under oxidized and low pH conditions (Crimi *et al*., 2003, Li, 2002) under regulatory concern. These authors have also shown that commercially potassium permanganate can contain heavy metals impurities acting as an additional source of metals concentrations.

Nelson *et al*. (2001) have shown that the dissolution of carbonate minerals can minimize these changes, neutralizing the groundwater pH, increasing the potential of metals co-precipitation and adsorption into solid surfaces. More recently, Al *et al*. (2006) have evaluated the potential of metals partition from solution to precipitated oxides within different pH conditions, showing that pH values within the range of 2.5 to 7 has little effects of metals sequestering.

Case studies are here discussed, showing the results of batch and column experiments and field scale results of how an in situ chemical oxidation (ISCO) remedial

DNAPL treatment using $KMnO_4$ can generally affect the aquifer geochemistry, under the presence of calcite and dolomite buffered aquifer systems (Nelson *et al*. 2001). The effects of changes in pH and redox conditions in the mobility of some metals and their concentration in solution (Lin, 2002; Crimi *et al*., 2003) are presented. Finally, the evaluation of metals partition from solution to precipitated manganese surfaces under different pH conditions (Crimi *et al*., 2004b; Al *et al*., 2006) are also discussed.

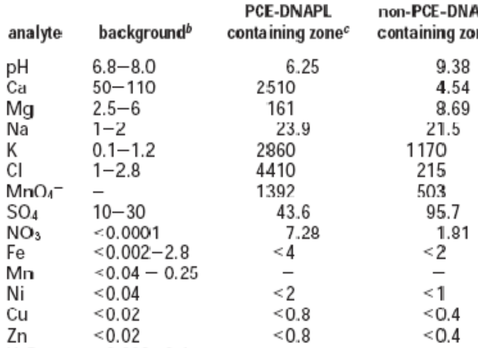
The objective of this paper is to give a general overview, based on the compilation of case studies, of the importance of developing a site conceptual geochemical model, involving batch experiments and site pilot scale tests prior to designing a full-scale ISCO systems, preventing any significant groundwater geochemical impacts, leading to the formation of secondary contaminant plumes.

2 - CASE STUDY - BORDEN AQUIFER, ON, CANADA

Two permanganate injection episodes were conducted in an unconfined carbonate sandy aquifer containing PCE-DNAPL and dissolved PCE impacts. The main objective of this work was to evaluate the geochemical changes within the aquifer associated to the installed treatment system (Nelson *et al*., 2001).

A three dimensional system of sampling points, comprised by thirteen multilevel samplers was used to monitor the groundwater quality over the time. Continuous cores samples were collected at 23 locations to visually evaluate the occurrence of manganese oxides and PCE and to collect samples for optical microscopy analyses (TEM).

According the obtained results, the authors have identified two different geochemical zones in the $KMnO_4$ affected area. One zone, located along the local aquifer-aquitard interface, within the area where DNAPL as present, was characterized by the presence of low pH and the detection of high concentrations of Cl^-, Ca^{2+}, Mg^{2+}, Na^+ and SO_4^{2-} (Table 1 and Figure 1) relative to the background groundwater sample.



analyte	background[b]	PCE-DNAPL containing zone[c]	non-PCE-DNAPL containing zone[d]
pH	6.8–8.0	6.25	9.38
Ca	50–110	2510	4.54
Mg	2.5–6	161	8.69
Na	1–2	23.9	21.5
K	0.1–1.2	2860	1170
Cl	1–2.8	4410	215
MnO_4^-	–	1392	503
SO_4	10–30	43.6	95.7
NO_3	<0.0001	7.28	1.81
Fe	<0.002–2.8	<4	<2
Mn	<0.04 – 0.25	–	–
Ni	<0.04	<2	<1
Cu	<0.02	<0.8	<0.4
Zn	<0.02	<0.8	<0.4
H_2S	<0.002–0.1	–	–

Table 1. Comparison between background groundwater chemistry with PCE and no-PCE containing zones following Permanganate Treatment (mg/L) (Modified from Nelson *et al*., 2001).

The increasing of Cl^- concentration was interpreted as a result of the PCE oxidation. Equilibrium speciation and saturation index simulations using geochemical modeling (PHREEQC), suggested that the local aquifer was saturated with respect to calcite. According to the authors, the trends in Ca^{2+} concentration and the narrow range of pH was explained by the sequential oxidation of PCE, generating acidity, followed by its neutralization by carbonate mineral dissolution, according to the following equation (3):

$3C_2Cl_4 + 5CaCO_3(s) + 4KMnO_4 + 2H^+ \rightarrow 11CO_2 + 4MnO_2 + H_2O + 12Cl^- + 4Ca^{2+} + 4K^+$ (3)

Additionally, the increase of Mg^{2+} concentration was also associated with the dissolution of dolomite. The authors suggested that the increasing of SO_4^{2-} concentrations was related to the oxidation of sulfide minerals by $KMnO_4$.

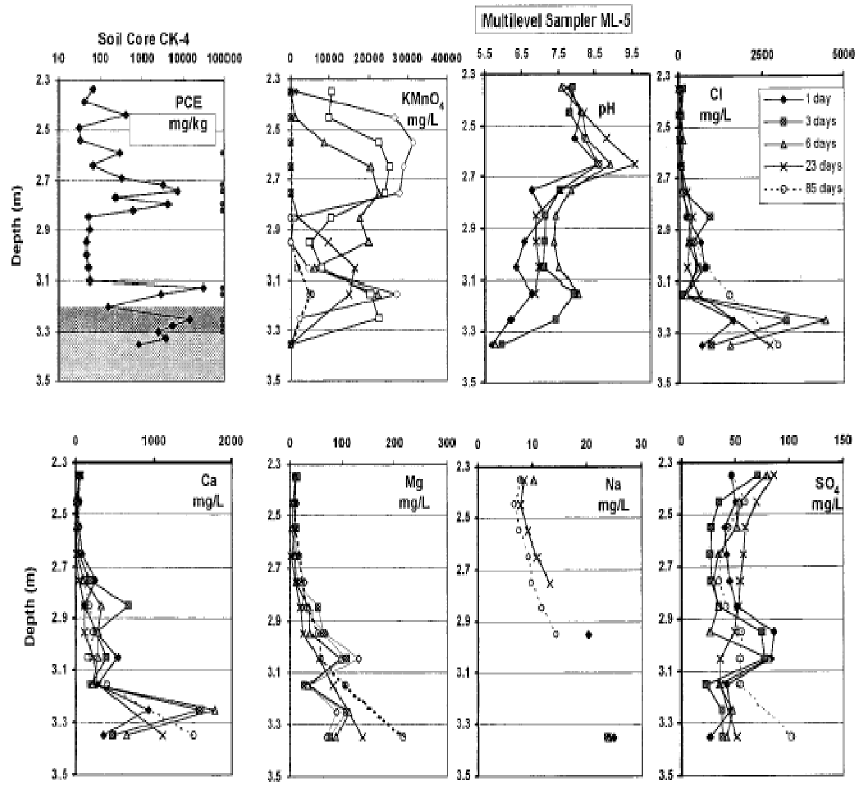


Figure 1. Comparison between initial PCE concentration and aqueous chemical profiles over time from a multilevel sampler device (Modified from Nelson *et al*., 2001).

Another geochemical zone (Table 1) was characterized by relatively high pH and low Cl^-, Ca^{2+}, Mg^{2+} concentrations, where no PCE-DNAPL was found and permanganate was persistent for over 3 months. The increasing of the pH was related to the oxidation of the water by $KMnO_4$, The presence of centimetric sub-horizontal dark brown bands were found in some of the core samples collected as result of the precipitation of manganese oxides (Figure 2).

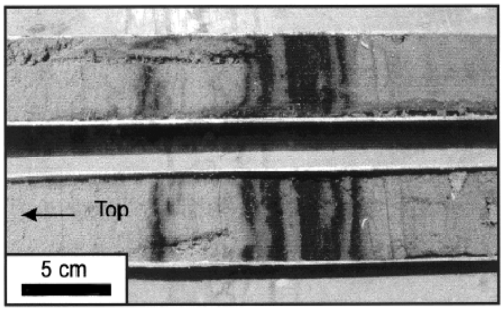


Figure 2. Photograph of a core sample illustrating the manganese oxide precipitation on the aquifer sand (Modified from Nelson *et al*., 2001).

The Energy dispersive X-ray spectroscopy (EDS) analyses indicated an oxide composition dominated by Mn, ubiquitous carbon and oxygen, and traces of Al, Ca, Cl, Pb, P, K, Si, S,Ti, U and Zn. The presence of Cu and the other elements was suggested to be associated with $KMnO_4$ impurities and from minerals within the aquifer (Figure 3).

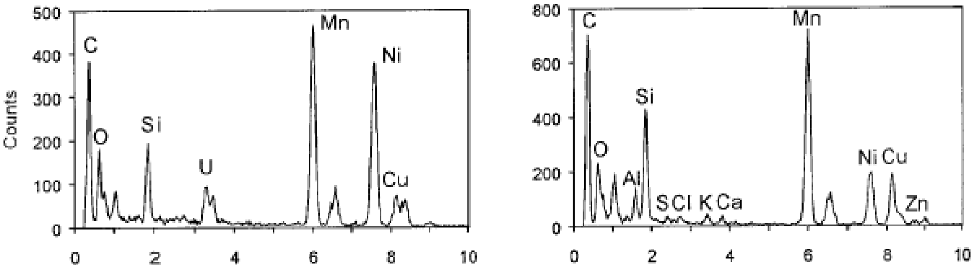


Figure 3. EDS analyses of manganese oxide coatings (Modified from Nelson *et al*., 2001).

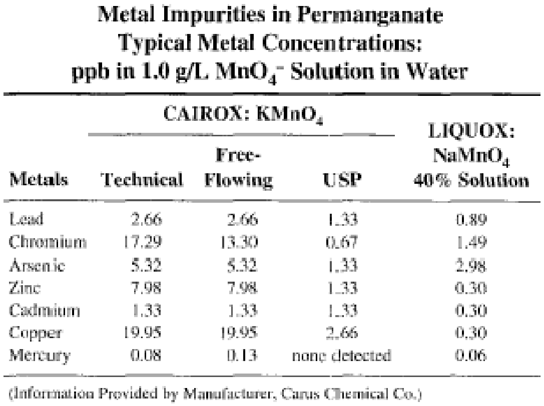
Based on the obtained results, the authors have shown that in carbonate-rich aquifers the oxidation of chlorinated organic solvents by $KMnO_4$ results in pH-buffering reactions, which have important implications for the in situ treatment process and the water quality in the aquifer.

At neutral pH, the reduction of MnO_4^- forms Mn (IV), which is insoluble under oxidized conditions and is favorable to remove trace elements from the aqueous phase by co-precipitation within the manganese oxide. However, in the absence of pH buffering by carbonate minerals, the pH of the groundwater in the DNAPL treatment zone may become acidic and the reduction of MnO_4^- proceeds to Mn (II) which, in groundwater systems with low levels of dissolved O_2, remains soluble in excess of water quality standards. Additionally, the solubility of most of others trace metals, such as Fe, Zn and Pb could increase significantly at low pH conditions, leading to potential effects in the local groundwater quality.

3 - CASE STUDY - CAPE CANAVERAL AIR STATION, FLORIDA, US

This paper describes the results of laboratory sites in support of an in situ chemical oxidation using permanganate for remediation of a DNAPL source at Launch Complex 34 at Cape Canaveral Air Station, Florida (Crimi *et al*., 2003).

According to the authors, the composition of commercially available potassium permanganate could also be relevant to subsurface effects and regulatory criteria. Since $KMnO_4$ solids are derived from mined potassium ores, there are impurities in commercially available $KMnO_4$ crystals, mainly associated to salts and trace metals (Table 2). Depending upon the concentration of $KMnO_4$ used during the remediation and the regulatory criteria that might be applicable, these impurities may be a concern.



Metal Impurities in Permanganate
Typical Metal Concentrations:
ppb in 1.0 g/L MnO_4^- Solution in Water

Metals	CAIROX: $KMnO_4$ Technical	Free-Flowing	USP	LIQUOX: $NaMnO_4$ 40% Solution
Lead	2.66	2.66	1.33	0.89
Chromium	17.29	13.30	0.67	1.49
Arsenic	5.32	5.32	1.33	2.98
Zinc	7.98	7.98	1.33	0.30
Cadmium	1.33	1.33	1.33	0.30
Copper	19.95	19.95	2.66	0.30
Mercury	0.08	0.13	none detected	0.06

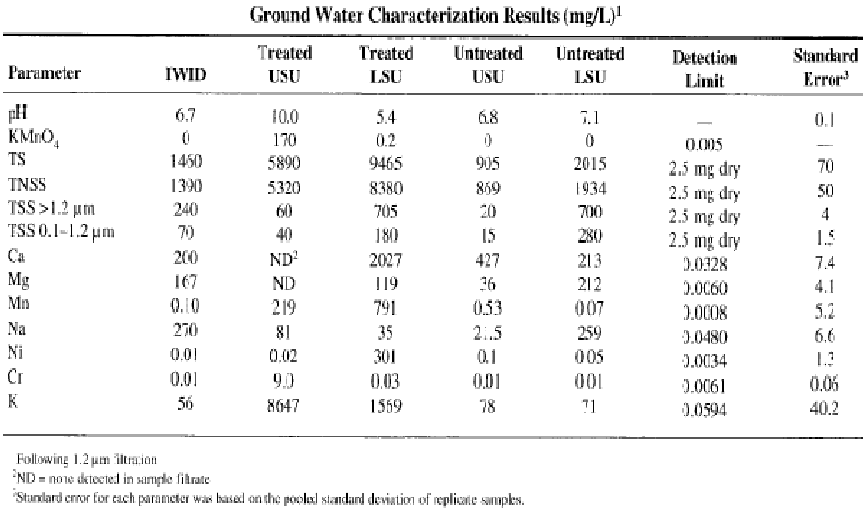
(Information Provided by Manufacturer, Carus Chemical Co.)

Table 2. Metal impurities in commercially available potassium permanganate (Modified from Crimi *et al*., 2003).

Potassium permanganate was delivered to treat a TCE DNAPL impacts in a sandy aquifer classified into three different hydrostratigraphic units: Upper sand unit (USU), Middle fine-grained unit (MFGU) and a Lower sand unit (LSU). During the treatment, 3200 m^3 of 1 to 2 wt% permanganate solution were delivered using a direct-push injection system along the sand units. Site groundwater characterization was performed for both untreated and treated samples (Table 3).

The obtained groundwater results showed that permanganate treated water have much greater potassium and manganese concentrations when compared to the background groundwater. Calcium and nickel were detected in higher concentrations in LSU than USU. Chromium was detected in concentration greater than background and treated LSU.

According to the authors, it was clear that although permanganate impurities may contribute to total metals concentrations in the subsurface, they could not account for all of the observed effects.



Ground Water Characterization Results (mg/L)[1]

Parameter	IWID	Treated USU	Treated LSU	Untreated USU	Untreated LSU	Detection Limit	Standard Error[3]
pH	6.7	10.0	5.4	6.8	7.1	—	0.1
$KMnO_4$	0	170	0.2	0	0	0.005	—
TS	1450	5890	9465	905	2015	2.5 mg dry	70
TNSS	1390	5320	8380	869	1934	2.5 mg dry	50
TSS >1.2 µm	240	60	705	20	700	2.5 mg dry	4
TSS 0.1–1.2 µm	70	40	180	15	280	2.5 mg dry	1.5
Ca	200	ND[2]	2027	427	213	0.0328	7.4
Mg	167	ND	119	36	212	0.0060	4.1
Mn	0.10	219	791	0.53	0.07	0.0008	5.2
Na	270	81	35	21.5	259	0.0480	6.6
Ni	0.01	0.02	301	0.1	0.05	0.0034	1.3
Cr	0.01	9.0	0.03	0.01	0.01	0.0061	0.06
K	56	8647	1569	78	71	0.0594	40.2

Following 1.2 µm filtration

[2]ND = none detected in sample filtrate

[3]Standard error for each parameter was based on the pooled standard deviation of replicate samples.

Table 3. Groundwater results (Modified from Crimi *et al*., 2003).

The increasing of the redox potential provided by permanganate promotes the oxidation of chromium and the increasing of concentrations as Cr (VI), which is more soluble and tends to be dissolved in the groundwater. Once the original conditions are restored and the permanganate is depleted, the mobilized chromium may become associated with the groundwater solids through adsorption or precipitation from solution (as Cr (III)).

Nickel was also oxidized and mobilized upon permanganate treatment. The authors suggested that the high pH of USU groundwater promoted nickel precipitation, while the moderate pH of LSU maintained the compound in solution.

Manganese oxides were also detected in their study and high concentrations of Mn^{2+} were observed within the treated groundwater samples. According to the authors, the MnO_2 solids generated may have consequences based on the oxides genesis and fate. Initially, these oxides are colloidal in size, and may either aggregate, grow and deposit in the sediments, or remain in their colloidal state. As a result, they may become mobile or deposit on sediment surfaces, allowing the adsorption of metals or act as long term source of Mn^{2+} into the groundwater.

4 - CASE STUDY - BATCH EXPERIMENTS

Batch experiments were utilized to investigate the consumption of MnO_{4^-} by sediments and the release of metals into solution (Li, 2002). Twenty-three samples were collected from various geological media, such as, alluvial deposits, carbonate sand and glacial till and placed in 25 ml vials (15 grams of each sediment sample). The sediment samples were mixed with 15 ml of 2.5 g/L $KMnO_4$ solution. Controls solutions were made by a mixture between deionized water and the sediments.

By comparing the differences between metals released from the control experiments and the oxidized materials, the effect of permanganate treatment could be established as described in Figure 4, below.

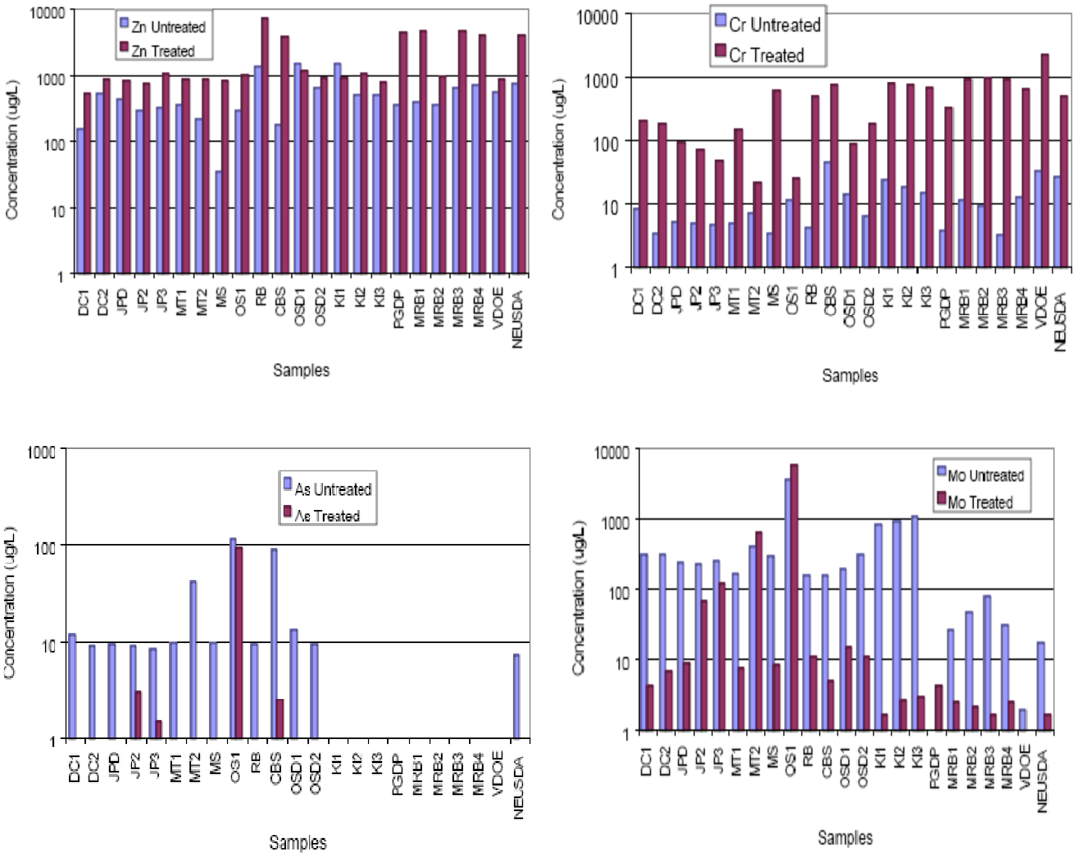


Figure 4. Zn, Cr, As and Mo concentrations (µg/l) (Modified from Li., 2002).

As shown above, Zn concentrations have increased in almost all the treated samples. This increase was interpreted as a result of $KMnO_4$ impurities.

Chromium concentrations have exhibit a large increase due to permanganate oxidation. The author suggests that as the oxidation state changes with the addition of MnO_4^-, the sediments were oxidized releasing Cr (VI) into the water in a mobile form. However, as discussed by the author and previously discussed by others, there is a tendency for Cr (VI) to be converted back to Cr (III) as the redox conditions changes again by the consumption of permanganate or the compound migration beyond the treated area.

Arsenic concentrations have decreased in the treated water samples. The author has shown that As is associated with iron oxide/hydroxide through adsorption or co-precipitation since the binding between As and these oxides is more stronger under oxidizing conditions than in reducing conditions.

Molybdenum concentrations have also declined in al the samples after the MnO_{4-} treatment. The author has suggested that Mo (IV) is oxidized to Mo (VI) forming insoluble salt or co-precipitated by other metals.

5 - CASE STUDY - COLUMN EXPERIMENTS

Sand-column experiments were conducted to simulate the oxidation of TCE by $KMnO_4$ under conditions similar to a flowing groundwater system (Al *et al*., 2006). One column was filled with 100% silica sand (SS) and the second was comprised by a mixture of 75% silica sand and 25% calcite (MSC). The average linear groundwater velocities of the columns varied from 4.1 x 10^{-5} to 4.9 x 10^{-5} m/s in order to simulate an injection-withdraw remediation system. Aqueous solutions of dissolved TCE and dissolved metals (Cu, Pb, Zn, Ni, Mo^- as MoO_4^{2-} and Cr – as CrO_4^{2-}) (1 mg/L of each of the compounds) were pumped from storage reservoirs to the column and mixed at the inlet of column (Figure 5).

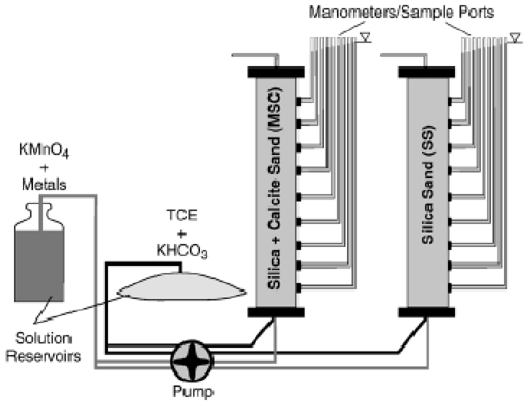
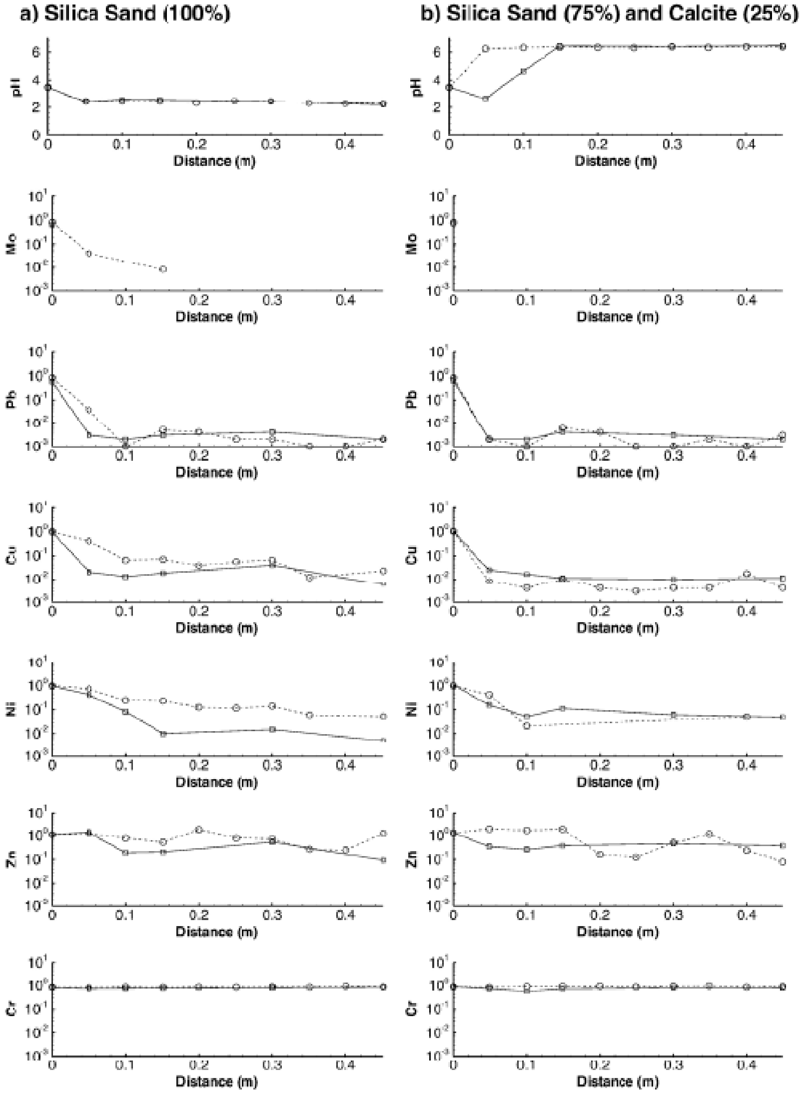


Figure 5. Schematic representation of the column experiments (Modified from Al *et al*., 2006).

The columns operated by 45 days and aqueous solutions were collected in a weekly basis for analyses. When the column experiments were completed, polypropylene threads were removed from the sand in order to conduct TEM analyses of the manganese oxides.

The TCE and $KMnO_4$ concentrations throughout the duration of the experiment have decreased to less than 0.5 mg/L at the first sampling port located 5 cm from the inlet of the and not detectable at greater distances along the flow path in the columns. The reduction of manganese that accompanied the destruction of TCE was evident by the accumulation of a uniformly brown coating on the column sand within hours of starting the experiment. The MSC column, the accumulation of oxides was restricted mostly to the first 15 to 20 cm near the inlet to the column. According to the authors, the enhanced flocculation of oxides within the MSC column were related to pH controlled specific adsorption of calcium ions released by calcite dissolution.


a) Silica Sand (100%)

b) Silica Sand (75%) and Calcite (25%)

Figure 6. Aqueous Geochemical data. Dash lines represent the samples collected at the start of the experiments and the solid lines represents samples collected in the end of the experiment (Modified from Al *et al*., 2006).

As demonstrated by Figure 6, the pH in the SS column decreased from 3.5, in the inlet of the column to a constant value ranging from 2.3 and 2.5 throughout the duration of the experiment. In the MSC column, the pH increased from 3.5 to 6.4 as a result of acid-neutralization that accompanies calcite dissolution.

Molybdenum and lead have strongly decreased to low concentrations or below the detection limit for both column experiments. Similar trends were observed for cooper and nickel. The results obtained have shown that, contrary to the author's expectations, the loss of metals from the aqueous phase was similar in two columns, despite the difference in the pH.

Concentrations of zinc and chromium (VI) showed a different behavior, when compared with the others, remaining constant along the experiment.

Surface complexation was evaluated as a potential mechanism to explain the observed metals behavior. Simulations were conducted with a diffuse-double-layer-surface-complexation model and according to the results obtained, a suggested pattern of metals uptake by manganese oxides were proposed as followed: Cr< Zn< Ni< Cu<Pb<Mo. Co-precipitation was also considered a important role in trace-metal uptake by oxides.

Additionally, similar to previous studies, the authors have conducted mineralogical experiments, showing that the manganese oxides formed during the manganese reduction, contain trace metals in their composition, confirming the hypothesis of metals co-precipitation and the presence of impurities in the used permanganate solution.

6 - GENERAL OVERVIEW AND DISCUSSIONS

The effectiveness In Situ Chemical Oxidation (ISCO) using Potassium Permanganate as remediation method to treat chlorinated solvents groundwater impacts was demonstrated by several authors. Normally, the remediation comprises the injection of a large amount of permanganate solution into the subsurface, and as a function of the natural oxidant demand of the soil, the permanganate solution can persist in the aquifer over a large period of time.

Changes in the aquifer redox conditions by adding a large amount of oxidants into the subsurface and changes in the groundwater pH due to geochemical reactions between the permanganate solution and the contaminants could occur as a result of these injections.

Since the solubility of some inorganic species, such as trace metals are highly dependent of Eh/pH conditions, significant geochemical changes could occur within the aquifer. These changes could also represent risk effects as more toxic species of trace metals, such as Chromium VI, are released into the groundwater and potentially migrate over a large distance.

Trace metals impurities are normally found in the commercially available permanganate composition, representing a potential additional source of metals into the subsurface.

Trace metals concentrations could also be affected by the precipitation of manganese oxides as a result of manganese reduction. As these manganese oxides precipitate, trace-metals could also co-precipitate under specific geochemical conditions. These oxides can also increase the adsorption of trace metals by a variety of mechanisms such as surface complexation and reversible exchange. Additionally, these oxides can potentially act as a long term source of Mn^{2+}.

These effects highlight the importance of the development of a detail site conceptual model of the geochemical conditions of the aquifer prior to the selection of a remediation technology to treat chlorinated solvents groundwater impacts. The success and the time/costs involved in site remediation strategies depend upon the quality of the initial conceptual model of the area.

Following this scenario, complementary tools such as groundwater modeling, batch experiments and pilot remediation tests should be always implemented prior to a full scale system to prevent any significant changes in the subsurface and to guarantee an effective and successful plume remediation.

7 - REFERENCES

Al, .T.A., Banks, V., Loomer, D., Parker, B.L., Mayer, K.U., 2006. Metal mobility during in situ chemical oxidation of TCE by $KMnO_4$. J. Contam. Hydrol. 88 (2006), 137 – 152.

Crimi, M.L Siegrist, R.L. 2003. Geochemical effects on metals following permanganate oxidation of DNAPLs. Ground Water 41 (4), 458-469.

Li, Xuan. PhD. Thesis, The Ohio State University, Ohio, USA, 2002.

Nelson, M.D., Parker, B.L., Al, .T.A., Cherry, J.A, Loomer, D., 2001. Geochemical reactions resulting from in-situ oxidation of PCE DNAPL by $KMnO_4$ in a sandy aquifer. Environ. Sci. Technol. 35 (6), 1266-1275.

Schnarr, M., Truax, C., Farquhar, G.J, Hood, E., Gonullu, T., Stickney, B., 1998. Laboratory and controlled field experiments using potassium permanganate to remediate trichloroethylene and perchloroethylene DNAPLs in porous media. 29, 205-224.