PERSULFATE TRANSPORT IN TWO LOW-PERMEABILITY SOILS

BY

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To the Faculty of Washington State University:

The members of the committee appointed to examine the thesis of MARISSA MERKER find it satisfactory and recommend that it be accepted.

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ABSTRACT

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Persulfate is a promising in situ chemical oxidation treatment (ISCO) for the remediation of low-permeability strata because it is more stable in the subsurface and can rapidly degrade recalcitrant contaminants compared to other technologies. ISCO technologies include catalyzed hydrogen peroxide propagations (CHP), ozone, permanganate and persulfate treatments. Persulfate is a strong oxidant similar to CHP; however, it has a wider range of influence due to its longevity in the subsurface. Diffusion is the dominant mechanism of solute transport in fine-grained, or low-permeability, soils and can be estimated mathematically with an analytical solution to Fick's first or second law of diffusion. Knowledge of persulfate diffusion is important the remediation of fine-grained soils. The objective of this research was to use column studies to investigate the transport of persulfate in two low-permeability soils: kaolin and Palouse loess. Persulfate was detected in the kaolin throughout the column length (approximately 4 cm) after an 82 d testing period. For the Palouse loess columns, 1 M solution of persulfate was detected the length of approximately 12 cm over 70 d and the 0.1 M solution reached an approximate depth of 6-7 cm over 85 d. The transport of persulfate generally increased with concentration and time, despite decomposition.

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1. Introduction

1.1 ISCO technologies

Soil and groundwater contamination remains a threat to public health and the environment despite decades of research. Numerous remediation technologies including bioremediation, thermal treatment, soil vapor extraction (SVE), zero-valent iron (ZVI), and in situ chemical oxidation (ISCO) have been developed over the past 30 years. Bioremediation is a cost-effective and simple remediation process for the degradation of contaminants such as benzene, toluene, ethylbenzene, and xylenes (BTEX) (Kao et al., 2010; Nebe et al., 2009). However, bioremediation is constrained by the available microbial community and by its degradation capacity in a given environment (Steliga et al., 2009). Due to the complexities of extending laboratory results to the field (Stenuit et al., 2008), the actual rate of degradation as a result of bioremediation is slow relative to other treatments and often relies on natural attenuation, where no treatment is applied and the contaminant degrades naturally (Kao et al., 2010). Bioremediation, SVE, and ZVI degrade or constrain a narrow range of contaminants and are generally unable to treat sorbed contaminants and dense nonaqueous phase liquids (DNAPLs) due to mass transfer limitations (Watts and Teel, 2006; Watts, 1998).

ISCO has numerous advantages for site remediation including the potential for rapid cleanup and destruction of sorbed contaminants and DNAPLs. The most common ISCO technologies include catalyzed hydrogen peroxide propagations (CHP), ozone, permanganate, and activated persulfate. CHP and ozone rapidly degrade a wide range of contaminants; however, both are unstable in the subsurface and consequently their radius of influence from an injection well is limited (Tsai et al., 2008; Watts and Teel, 2006). Additionally, ozone is less economical due to required on-site generation. Permanganate has greater longevity, but is a

weaker and more selective oxidant (Tsai et al., 2008; Watts and Teel, 2006). Though it does not react as rapidly as CHP, recent results suggest that it is more effective in removing some contaminants such as trichloroethylene and perchloroethylene DNAPLs in certain environments (Crimi and Siegrist, 2005). Persulfate is a strong oxidant and has greater longevity than CHP and ozone; therefore, it has the potential to remediate subsurface contamination (Tsai et al., 2008; Watts and Teel, 2006).

1.2 Persulfate technology

Persulfate is typically activated to promote contaminant degradation (Liang et al., 2004; Waldemer et al., 2007; Furman et al., 2009). The activating agents include: iron-chelated activation (Liang et al., 2004), base activation (Furman et al., 2009), and organic activation (Ahmad, 2010).

A significant difficulty in subsurface remediation is promoting contact between the active remediation agents and the contaminant, particularly in low-permeability strata. Often, contaminants have had decades to diffuse into regions of low permeability and the embedded contaminants act as a source of long-term contaminant release, continually diffusing back into the groundwater. Persulfate, because it is long-lived in the subsurface, has the potential to treat contamination in low-permeability regions. However, the diffusion of persulfate in fine-grained soils has not been studied to date and additional research is required to understand the dynamics of persulfate in the subsurface. The objective of the research was to investigate the transport of persulfate in two low-permeability media in order to determine its potential to destroy embedded contaminants.

1.3 Theoretical background: Diffusion

Diffusion is the dominant mechanism of solute transport in fine-grained soils (Crooks and Quigley, 1984; Rowe et al., 1988). Therefore, a basic understanding of mass transfer theories is necessary for constructing a laboratory experiment and for understanding the analytical solutions used to estimate the diffusion coefficient.

Solutes are transported through the soil by two primary mechanisms: advection and hydrodynamic dispersion (Freeze and Cherry, 1979). Advection describes the transport of the solute due to fluid flow at a rate equal to the seepage (pore-water) velocity. Hydrodynamic dispersion is the combination of two mechanisms, mechanical dispersion and diffusion. Mechanical dispersion is the transport process produced by fluid mixing and diffusion is the movement of molecules due to a concentration gradient.

1.3.1 Mass transport of a non-reactive solute

Assuming saturated conditions in a subsurface porous media and one-dimensional transport, the mass flux of a non-reactive solute in soil can be estimated by (Rowe et al., 1988; Shackelford, 1991):

$$J = n\left(v_s c - D_h \cdot \frac{\partial c}{\partial x}\right) \tag{5}$$

where J is the mass flux [M L^{-2} T^{-1}; where M is mass, L is length, and T is time]; n is the soil porosity [dimensionless]; v_s is the seepage velocity of the fluid [L T^{-1}]; c is the concentration of the solute in pore water [M L^{-3}]; D_h is the hydrodynamic dispersion coefficient [L^2 T^{-1}]; and x is the linear distance through which the solute has traveled in the porous media [L]. Advection is described mathematically by the first term on the right hand side of the equation, $n v_s c$, and the second term, $n D_h \cdot \partial c / \partial x$, represents the effects of hydrodynamic dispersion along a decreasing

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concentration gradient. The hydrodynamic dispersion coefficient is the sum of the mechanical

dispersion coefficient [$L^2 T^{-1}$], D_m, and the effective diffusion coefficient [$L^2 T^{-1}$], $D*$:

$$D_h = D_m + D*$$ (6)

and

$$D* = D_h \tau$$ (7)

where D_0 is the free-solution diffusion coefficient [$L^2 T^{-1}$] and τ is the tortuosity factor

[dimensionless]. The effective diffusion coefficient is commonly used because it includes the

influence of tortuosity, a parameter that is difficult to determine (Shackelford, 1991). However,

Myrand et al. (1992) suggested that porosity, n, is a more accurate parameter for estimating the

increased travel distance caused by the pore structure for undisturbed clay materials. In this case,

D^* may be represented by equation (7) with the substitution of n for τ. Mechanical dispersion

is a function of the dispersivity of the soil, α [L], and the seepage velocity (Rowe et al., 1988):

$$D_m = \alpha v_s$$ (8)

The effects of advection and mechanical dispersion become negligible in fine-grained

soils as the seepage velocity approaches zero due to restricted flow caused by minimal void

space (Rowe et al., 1988). In this case, the first term of equation (5) is neglected and the effective

diffusion coefficient is substituted, which results in Fick's first law for diffusion, given by:

$$J_D = -D^* n \cdot \frac{\partial c}{\partial x}$$ (9)

where J_D is the diffusive flux [M L-2 T-1].

1.3.2 *Mass transport of a reactive solute*

For a reactive solute in an incompressible fluid moving one-dimensionally at steady state through homogenous, isotropic, and non-deformable soil, the equation for advection-dispersion can be written as (Freeze and Cherry, 1979):

$$\frac{\partial c}{\partial t} = \left(\frac{D_h}{R_d}\right) \cdot \frac{\partial^2 c}{\partial x^2} - \left(\frac{v_s}{R_d}\right) \cdot \frac{\partial c}{\partial x} \tag{10}$$

where R_d is the retardation factor [dimensionless]. The retardation factor is the ratio of the transport rate of a non-reactive (non-adsorbed) solute relative to a reactive (adsorbing) solute. The retardation factor has been given by (Myrand et al. 1992; Freeze and Cherry, 1979; Shackelford et al., 1989):

$$R_d = 1 + (\rho_d / n)K_d \tag{11}$$

and

$$K_d = \frac{dq}{dc} \tag{12}$$

where ρ_d is the dry (bulk) density [M L^{-3}], K_d is the partition coefficient [L^3 M^{-1}], and q is the sorbed concentration of the chemical [mass solute sorbed per mass of soil]. The partition coefficient, K_d, can be determined by taking the slope of a q versus c plot, known as a sorption isotherm. In low-permeability soils the seepage velocity becomes negligible and the advection-dispersion equation (eq. 10) is reduced to Fick's second law for diffusion of solutes in soil:

$$\frac{\partial c}{\partial t} = \left(\frac{D^*}{R_d}\right) \cdot \frac{\partial^2 c}{\partial x^2} \tag{13}$$

The diffusion of a remedial agent through low-permeability strata is characterized by the additional complexity of chemical degradation and loss due to side reactions with organic acids. Hong et al. (2009) investigated the diffusion of Cl$^-$ through a 75% sand and 25% attapulgite clay

mixture and calculated diffusion coefficients of 5.86 x 10^{-6} cm^2/s and 7.32 x 10^{-6} cm^2/s for duplicate columns. Diffusion of the chloride ion, a non-reactive species, is essentially the maximum rate of diffusion, which was increased by the addition of sand. Therefore, it was expected that the diffusion of persulfate in clay would be significantly slower.

2. Materials and methods

2.1 Chemicals

Sodium persulfate (≥98%) and iron (III) ethylenediaminetetraacetic acid (Fe(III)EDTA) were purchased from Sigma Aldrich (St. Louis, MO). Sodium hydroxide (98.6%), sodium bicarbonate and potato starch were obtained from J.T. Baker Inc. (Phillipsburg, NJ). Sodium thiosulfate (99%) and potassium iodide were purchased from Fisher Scientific (Fair Lawn, NJ). Double-deionized water (>18MΩ.cm) was generated with a Barnstead NANOpure II Ultrapure system.

2.2 Soils

Two soil types were used in this study. Kaolin was purchased from Dry Branch Kaolin Company (Dry Branch, GA) and Palouse loess was collected from a site near Pullman, WA. The soil characteristics of the Palouse loess are summarized in Table 1.

2.3 Column materials

Polyvinyl chloride (PVC) pipe (ASTM D 3034) with a 10.2-cm inner diameter was purchased from Cresline® (Evansville, IN). Styrene caps were obtained from Genova Products (Davison, MI). PVC couplers were purchased from Savko Plastic Pipe & Fittings (Columbus,

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OH). Polyethylene caps and 5.1-cm tenite butyrate tubing were purchased from U.S. Plastic Corp. (Lima, OH).

2.4 Column preparation

2.4.1 Palouse loess columns

The soil and column preparation was adapted from Cotton et al. (1998). Double deionized water was added to the Palouse loess until a water content of 17% was reached (1.7% below optimum). The soil was stored in double Glad® 4-L bags and allowed to cure for 24 hr. The Palouse loess was then compacted in accordance with ASTM D 698 in 11.6-cm high by 10.2-cm diameter PVC molds. A styrene cap with 5 symmetrically drilled 0.4-cm holes was attached to the column. The holes relieved the pressure created within the column as the cap was attached and allowed for water infiltration during the saturation period. Finally, the columns were submerged in a water bath to saturate the soil and the soil was routinely trimmed to the height of the column. Once the soil swelling was negligible and the columns were saturated, they were removed from the water bath and the cap was sealed with DAP® silicone sealant.

2.4.2 Kaolin columns

Kaolin was mixed with 150% double deionized water (mass/mass) to make a slurry and was poured into two slurry consolidometer apparatuses (Figure 1) (Hammar, 2004; Sheeran and Krizek, 1971). The slurry consolidometer was used to decrease the saturation period, to produce homogenous soil samples, and to control the consolidation pressure (Sheeran and Krizek, 1971). The slurry was allowed to settle for 5 d and then 2 kg, 1 kg, 2 kg, and 4 kg weights were loaded every 48 hr to the loading piston of each consolidometer for a total pressure of 6.36 kPa. The

weight was removed following the final 48 hr of loading and 69 kPa of air pressure was applied for 5 d. A final pressure of 276 kPa was achieved by incrementally increasing the pressure by 34 kPa every 72 hr. The soil was slowly removed from the cylinders with a modified hydraulic jack. Eight-cm high tenite butyrate tubing was pressed into the kaolin and the kaolin was trimmed to a height of 4 cm, which left room for a solution reservoir. Polyethylene caps were attached to the bottoms of the columns. Due to the differences in saturation methods and the necessity to produce 18 columns from the kaolin consolidated in the consolidometer, the kaolin columns were much smaller than the Palouse loess columns.

2.5 Diffusion testing procedure

The single reservoir with a decreasing source concentration method was used (Shackelford, 1991). For testing the persulfate diffusion in Palouse loess, a solution reservoir was created by attaching 11.6-cm high PVC cylinders to the columns with a PVC coupler. The reservoir was filled with solution to a height of 10.3 cm. The solution reservoir was filled to a height of 3 cm for testing diffusion in the kaolin columns.

The diffusion test consisted of 2 solution sets: a 1M persulfate set and a 0.1M persulfate set. Within each set there were 4 treatments: persulfate, persulfate activated by 5mM Fe (III) EDTA, 2:1 molar ratio of NaOH:persulfate, and a persulfate reservoir with no soil column (control). Each treatment was replicated three times. For the Palouse loess columns, two 1 M persulfate and two 0.1 M persulfate sets were made (long and short duration) and the persulfate was allowed to diffuse into the soil for a period of 70-149 days. Due to the smaller size of the kaolin columns, it was estimated that one persulfate diffusion test conducted over 82 d would be sufficient.

2.5.1 Biweekly diffusion test monitoring

Solution sampling was conducted every two weeks; 0.05 ml and 0.1 ml of solution was removed from the kaolin and Palouse loess reservoirs, respectively, and the persulfate concentration was determined by iodometric titration. The solution from the Palouse loess columns was filtered with Millipore 0.22 Millex® GP filters prior to titration in order to prevent the reaction of soil particles with iodide. The pH was also recorded biweekly with a Fisher Accument AB15 pH meter. The solution samples from soil reservoirs were compared to those extracted from the control reservoir as method of quality control. Persulfate degrades naturally over time and degradation is increased with exposure to activators. The control provided a method of tracking the degradation of persulfate that was not exposed to activators and set a standard by which the other treatments could be compared.

2.6 Persulfate analysis in column segments

For the Palouse loess systems, the soil was removed from the PVC columns in 1-cm increments with a hydraulic jack and a 10-g sample was taken from each 1-cm section and placed in 20-ml borosilicate volatile organic analysis (VOA) vials capped with PTFE (polytetrafluoroethylene) lined septa. The same procedure was followed for the kaolin columns with the exception that 0.5-cm sections were collected and 5 g of kaolin was used for persulfate analysis because less soil was available for analysis compared to the Palouse loess columns. The remaining soil from each section was dried at 105° C for 24 hr to determine the water content. For the Palouse loess system, 10 ml of double deionized water was added to the 10-g soil sample, mixed with a Scientific Industries vortex for 15 sec, and centrifuged for 4 min. For the kaolin system, 5 ml of double deionized water was added and the sample was centrifuged for 6

min and was not filtered. A 0.1 ml sample of the supernatant was removed and the Palouse loess samples were filtered with Millipore 0.22 Millex® GP filters. The persulfate concentration was determined by iodometric titration, and concentration versus depth profiles were plotted in order to determine the depth of persulfate diffusion. The pH was also determined for each soil section.

2.7 Statistical analysis

Statistical analyses were performed using Minitab version 15. Tukey's procedure with a 95% confidence level was used to compare treatments.

3. Results and discussion

Three treatments were analyzed for persulfate diffusion: persulfate only, iron (III)-activated persulfate (Fe (III) EDTA), and base-activated persulfate (NaOH). The treatments included two initial persulfate concentrations, 1 M and 0.1 M, which were applied to two soil types, Palouse loess and kaolin. The Palouse loess treatment sets included long and short duration tests. With the exception of the 0.1 M kaolin treatment set, all of the soil columns expanded with the addition of the treatment solution, which increased the length of the columns: the Palouse loess columns expanded 2-3 cm and the 1 M kaolin columns expanded up to approximately 0.75 cm.

3.1 1M persulfate diffusion in Palouse loess

A concentration versus depth profile for the long-duration (149 days), 1 M persulfate treatment set is shown in Figure 2. Persulfate was detected throughout the column length with a minimum concentration of 0.04 M for the base-activated persulfate treatments and 0.16 M for the

iron (III)-activated and persulfate-only treatments. Each treatment had a significantly different average persulfate concentration at the end of the testing period ($p<0.05$): base-activated persulfate had the lowest persulfate concentration and the persulfate-only treatment had the highest persulfate concentration. The concentration measurements taken from the solution reservoir showed identical results, which indicated that the differences in concentration were due to persulfate decomposition caused by the activators in each system rather than the diffusion rate. In other words, persulfate degradation is more rapid in the base-activated system, which results in a lower concentration throughout the column.

The short-duration treatment set (70 d) also showed persulfate diffusion throughout the entire length of each column (Figure 3). However, the concentration of the base-activated treatment approached a concentration of 0.01 M after approximately 9 cm of transport. There was no significant difference in persulfate diffusion in the persulfate-only and iron (III)-activated treatments ($p>0.05$), which reached a minimum concentration of approximately 0.15 M. The base-activated treatment was significantly different than the other treatments ($p<0.05$).

Figures 2 and 3 indicated that there are differences between the short and long-duration treatment sets. The results from the long-duration set showed a more uniform persulfate distribution through the columns, especially for the activated treatments. The uniformity resulted from greater persulfate transport through the columns due to the longer testing period and a decrease in the concentration gradient caused by persulfate decomposition. Furthermore, the minimum concentration of the base-activated treatment was higher in the long-duration set, which indicated that persulfate was transported through the column despite decomposition resulting from activation.

3.2 0.1M persulfate diffusion in Palouse loess

Persulfate was not detected the full length of the Palouse loess columns in the 131-d, 0.1 M persulfate treatment set (Figure 4). The persulfate-only treatment was detected to a depth of approximately 9 cm compared to the iron (III)-activated and base-activated treatments that diffused to approximately 5 cm and 7 cm, respectively. The persulfate concentration for each treatment was significantly different ($p < 0.05$). Due to the difference in concentration gradients, the transport of the 0.1 M persulfate was substantially slower than the 1 M persulfate for comparable test durations.

Similar to the long-duration 0.1 M test, the short-duration diffusion test indicated that the persulfate concentration in the iron (III)-activated treatment was significantly lower than the persulfate-only treatment ($p < 0.05$) at 85 d. There were no significant differences between the persulfate-only and base-activated treatments ($p > 0.05$) or the iron (III)-activated and base-activated persulfate treatments ($p > 0.5$). All treatments were detectable to an approximate depth of 6-7 cm (Figure 5).

For the 0.1 M systems, the iron (III)-activated persulfate had the lowest mass transport into the soil columns. The depth of the iron (III)-activated treatment was greater for the short duration test, which indicated that the transport rate is limited by persulfate decomposition due to iron (III) activation. At the 0.1 M persulfate level, iron (III) activation appears to increase the rate of persulfate decomposition compared to other treatments, which is likely due to the difference in the Fe (III) EDTA:persulfate molar ratio between the 0.1 M and the 1 M treatment sets.

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3.3 1M persulfate diffusion in kaolin

Test results indicated that the 1 M persulfate treatments diffused the entire length of the kaolin columns (Figure 6). The persulfate concentration between treatments was significantly different at the 95% confidence level; the base-activated treatment had the lowest concentration, followed by the persulfate-only treatment, and then the iron (III)-activated persulfate treatment. Similar to the 1 M Palouse loess diffusion tests, the base-activated treatment appears to decompose more rapidly. However, the persulfate was still transported the length of the columns over 81 d, which indicates that there was potential for contaminant destruction.

3.4 0.1M persulfate diffusion in kaolin

All of the 0.1 M persulfate treatments diffused the full length of the kaolin columns and showed no significant difference in persulfate concentration between treatments at the 95% confidence level (Figure 7).

4. Conclusion

The potential for persulfate to diffuse into regions of low permeability was investigated in soil column studies with two soil types: Palouse loess and kaolin. Initial persulfate concentrations of 1 M and 0.1 M where used to examine the difference in diffusion depths resulting from high and low concentrations. Three persulfate treatments, persulfate, iron (III)-activated persulfate, and base-activated persulfate, were tested.

Persulfate diffused into both soil types under each treatment condition. In addition, higher concentrations increased persulfate diffusion; all 1 M persulfate treatments diffused the full length of the columns, approximately 12 cm for the Palouse loess columns and approximately 4-

4.5 cm for the kaolin columns. The 0.1 M treatment diffused the entire length of the kaolin columns and approximately 6 cm in the Palouse loess columns.

Diffusion generally increased with time and was not substantially hindered by persulfate decomposition. The minimum persulfate concentrations were similar for the iron (III)-activated persulfate and persulfate-only treatments at 70 d and 149 d. Furthermore, the minimum persulfate concentration for the base-activated treatment increased between 70 d and 149 d, which indicated that persulfate was able to diffuse into the soil despite decomposition. However, the concentration of base-activated persulfate (1 M) was lower throughout the 1 M column sets compared to the other treatments.

The results of this research indicated that persulfate will diffuse into regions of low permeability, where it can potentially destroy contaminants of concern. Furthermore, persulfate diffusion increased with time and concentration, and was not significantly affected by persulfate decomposition.

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Table 1. Soil characteristics of Palouse loess.

Characteristic	Palouse loess	Standard
Classification	Lean clay	ASTM D 2487
Passing #200 sieve, %	98.2	
Liquid limit, %	33.0	ASTM D 4318
Plastic limit, %	20.7	ASTM D 4318
Plasticity index, %	12.3	ASTM D 4318
Maximum dry unit weight, (KN/m^3)	17.0	ASTM D 698
Optimum water content, %	18.7	ASTM D 698
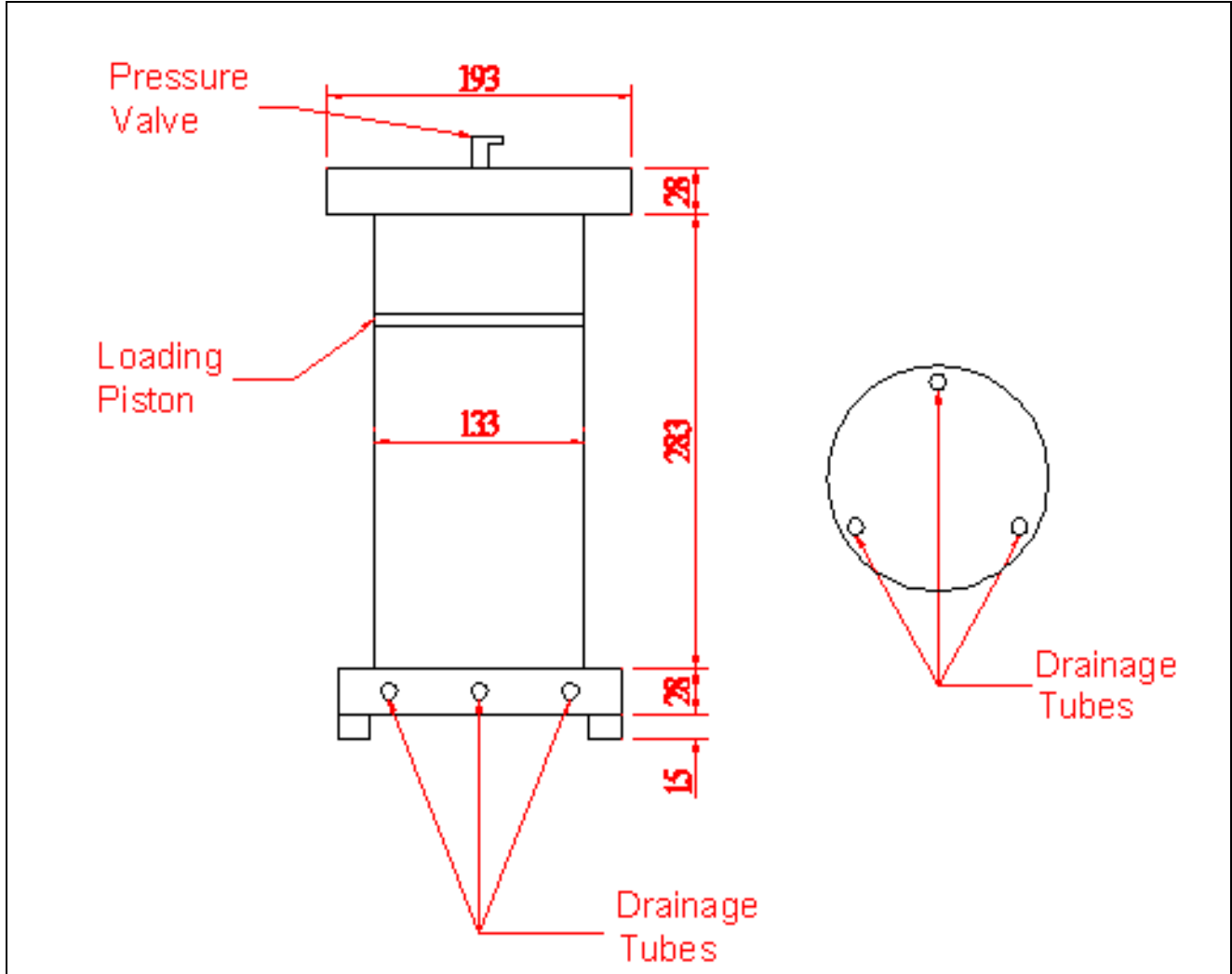
Figure 1. Slurry consolidometer apparatus (adapted from Hammar, 2004).

*All units are in millimeters.
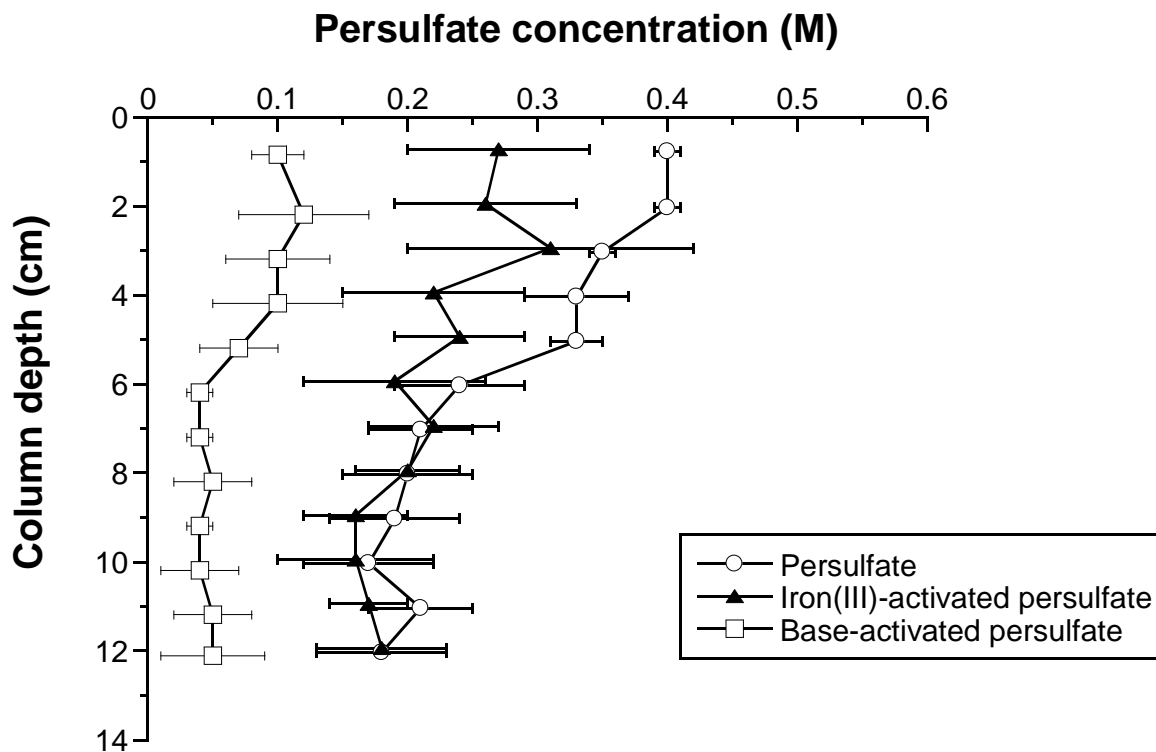
Figure 2. Concentration versus depth profile for diffusion of 1 M persulfate in Palouse loess at 149 days.
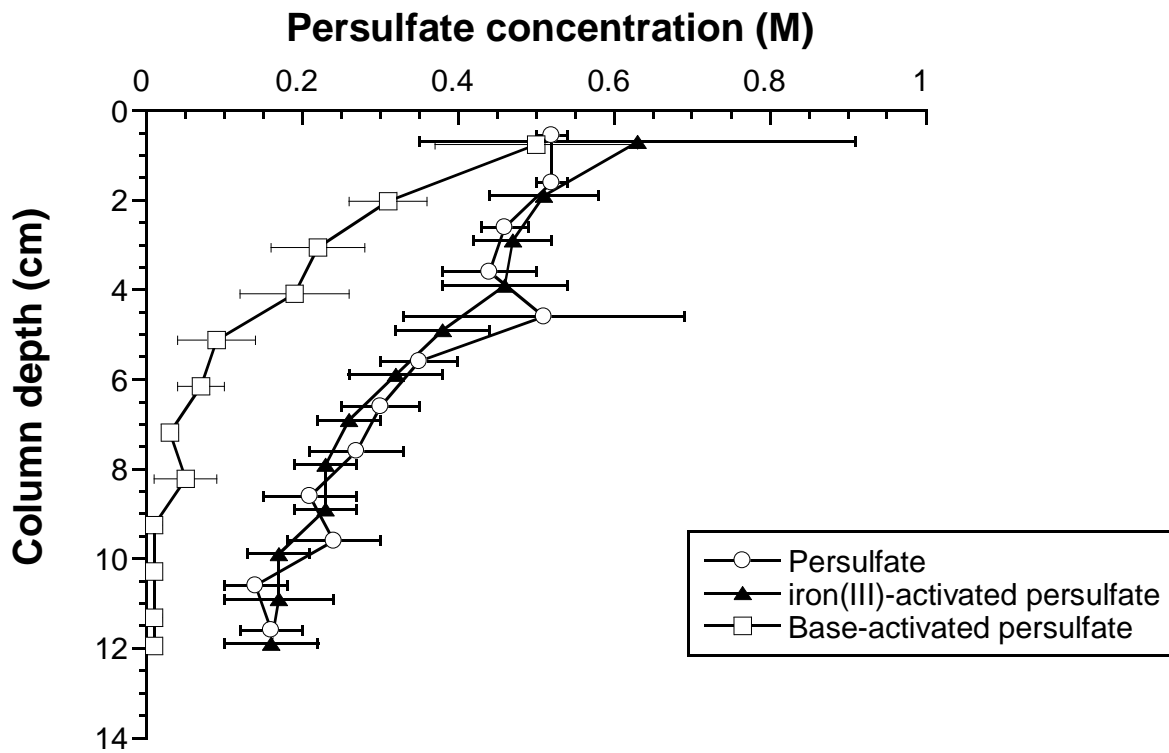
Figure 3. Concentration versus depth profile for diffusion of 1 M persulfate in Palouse loess at 70 days.
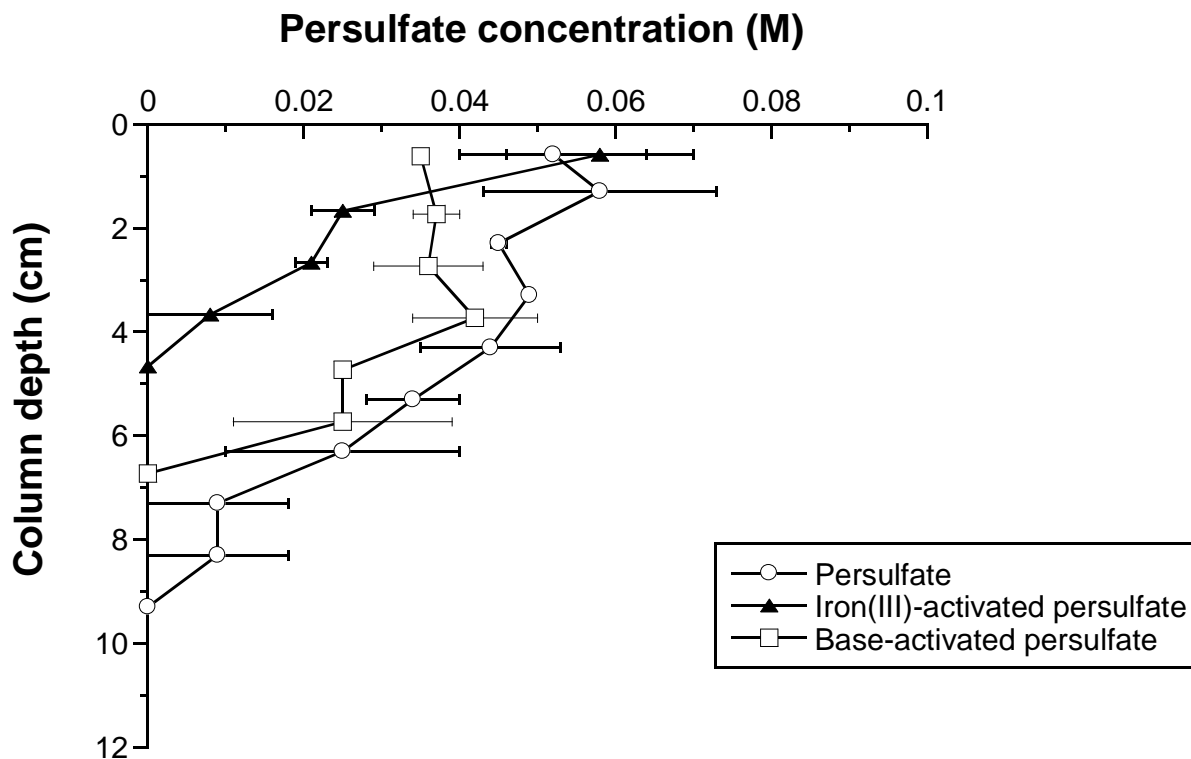
Figure 4. Concentration versus depth profile for diffusion of 0.1 M persulfate in Palouse loess at 131 days.
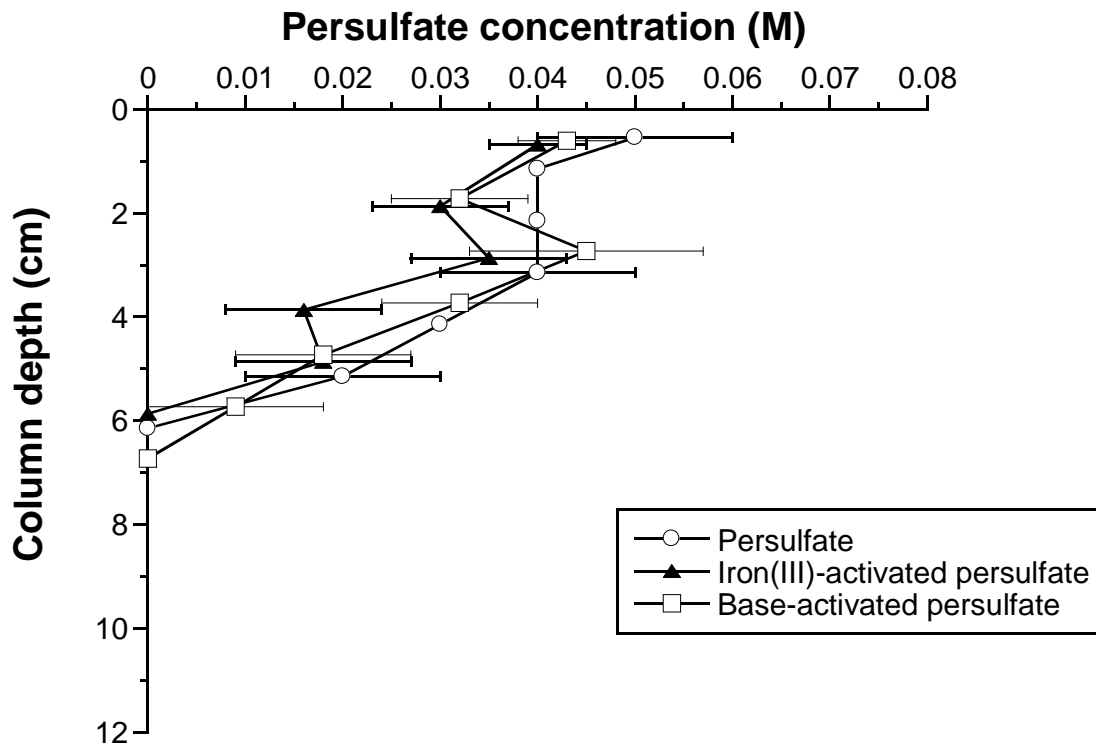
Figure 5. Concentration versus depth profile for diffusion of 0.1 M persulfate in Palouse loess at
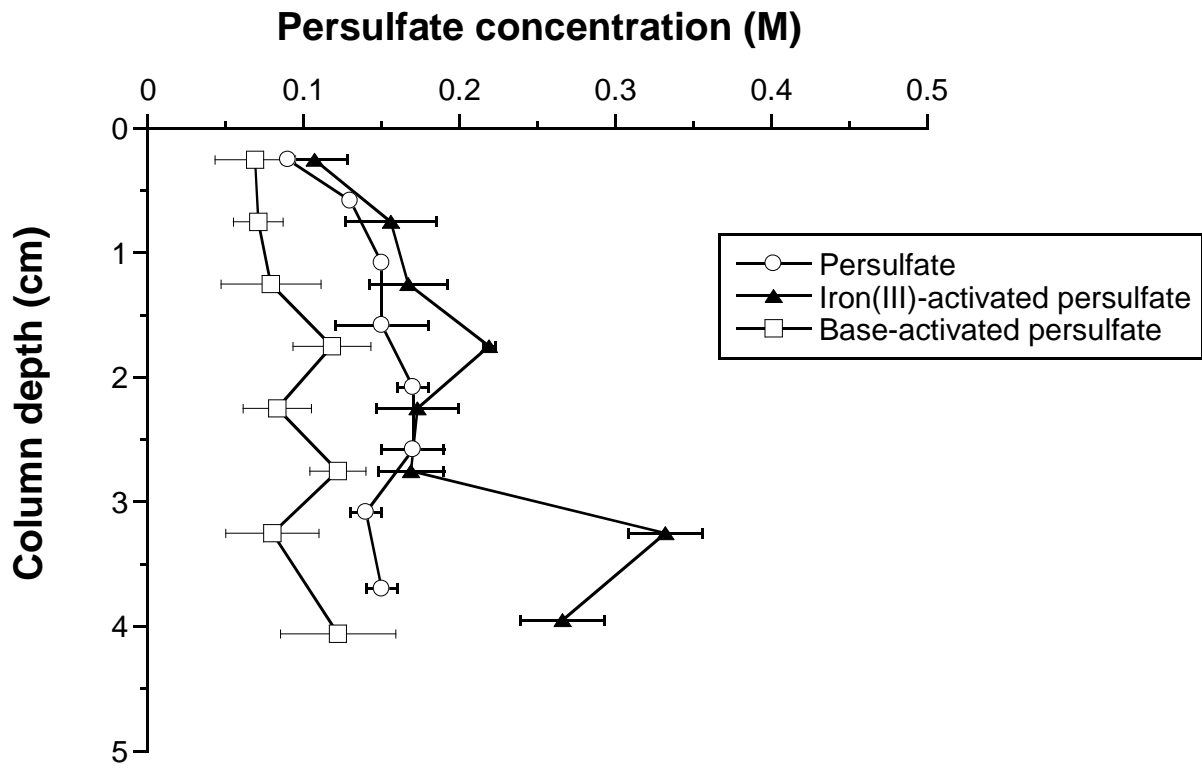
85 days.

Figure 6. Concentration versus depth profile for diffusion of 1 M persulfate in kaolin at 81 days.
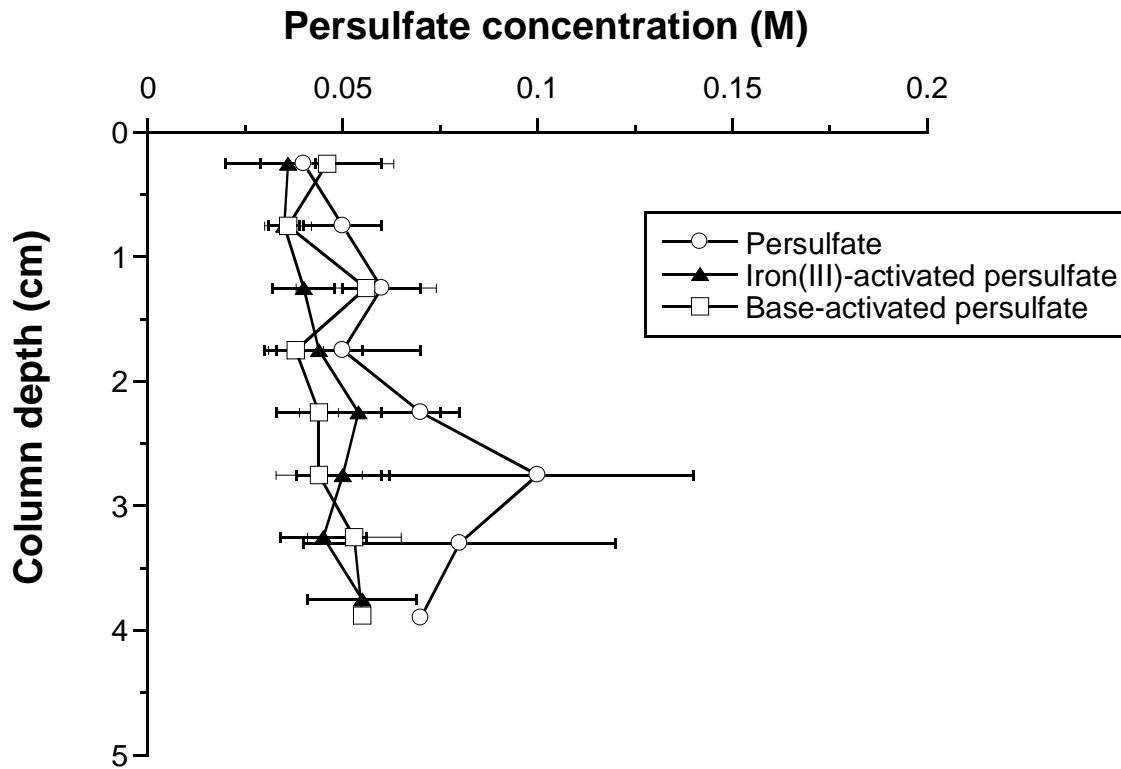
Figure 7. Concentration versus depth profile for diffusion of 0.1 M persulfate in kaolin at 82 days.