

Zero-valent iron for the in situ remediation of selected metals in groundwater

Kirk J. Cantrell*, Daniel I. Kaplan, Thomas W. Wietsma

Pacific Northwest Laboratory, Transport Geochemistry Group, MSIN K6-81, P.O. Box 999, Richland, WA 99352, USA

Received 28 September 1994; accepted 1 March 1995

Abstract

Zero-valent iron (Fe^0), metallic iron, is being evaluated as a permeable reactive barrier material to mitigate the transport of a wide array of highly mobile contaminants in groundwater. Zero-valent iron has previously been shown to destroy effectively numerous chlorinated hydrocarbon compounds via reductive dehalogenation. No references could be found regarding the ability of zero-valent iron to reduce UO_2^{2+} , MoO_4^{2-} , or TcO_4^- .

A series of kinetic-batch studies was conducted to determine the capability of particulate Fe^0 to remove UO_2^{2+} , MoO_4^{2-} , TcO_4^- , and CrO_4^{2-} from groundwater. Particulate Fe^0 effectively removed each of these contaminants from solution; removal rates decreased as follows: $\text{CrO}_4^{2-} > \text{TcO}_4^- > \text{UO}_2^{2+} \gg \text{MoO}_4^{2-}$. The removal mechanism appears to be reductive precipitation. Thermodynamic equilibrium calculations indicated that the rate of removal of the metals from solution increased as the difference in pe (Δpe) increased between the redox half reaction for the redox couple of interest and the $\text{Fe}^0/\text{Fe}^{2+}$ couple. Furthermore, the pe value for a redox couple provided a qualitative indication of the reduction rate by Fe^0 . These results indicate that the rate of removal of CrO_4^{2-} , TcO_4^- , and UO_2^{2+} from groundwater is rapid, permitting an inexpensive barrier of practical dimensions to be used for in situ remediation purposes.

1. Introduction

Zero-valent iron (Fe^0), metallic iron, is being evaluated by a number of laboratories for its potential use as a reactive material to minimize the subsurface migration of chlorinated-hydrocarbon compounds and certain reducible metal ions. The Fe^0 could be placed in a trench [1] or injected as colloids [2, 3] in the flow path of a plume containing reducible contaminants (Fig. 1). The barrier would permit groundwater to

* Corresponding author. Tel.: (509)376-8647. Fax: (509)376-5368.

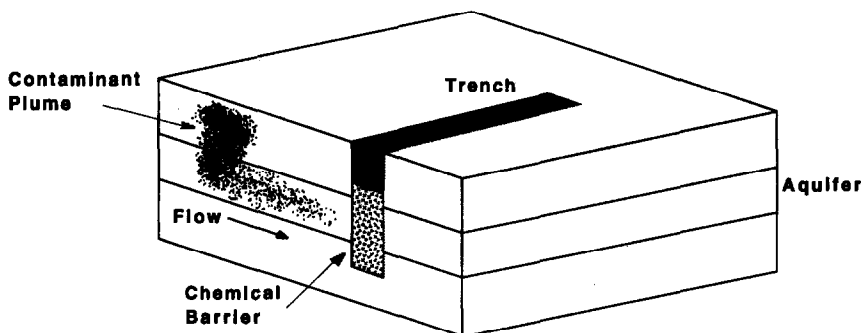


Fig. 1. Trench and fill concept for an in situ permeable reactive barrier for remediation of contaminated groundwater.

pass through while selectively degrading chlorinated hydrocarbons and precipitating reducible metals, thereby eliminating or greatly reducing contaminant migration.

Chemical reactive barriers have a number of advantages over conventional pump-and-treat, dig-and-treat, and containment methods. Pump-and-treat and dig-and-treat technologies tend to be very expensive, while containment methods which attempt to isolate the waste site from infiltration or groundwater penetration typically fail. It is expected that permeable reactive barriers which do not restrict the flow of groundwater, but selectively remove hazardous components will be both technically attractive and cost effective.

Previous work has shown that CrO_4^{2-} is rapidly reduced by Fe^0 to Cr^{3+} [4, 5]. Subsequent precipitation of $\text{Cr}(\text{OH})_3$ or $\text{Cr}_x\text{Fe}_{1-x}(\text{OH})_3$ solid solution causes dramatic reductions in dissolved Cr concentrations. Batch studies have shown that CrO_4^{2-} reduction and subsequent removal is greater in the presence of Fe^0 than pyrite (FeS_2) [5]. Furthermore, both reactions are pH dependent [5]. Reduction of CrO_4^{2-} to Cr^{3+} by Fe^{2+} occurs rapidly in environments where the pH is less than 10 and phosphate concentrations are low [6]. Low concentrations of dissolved oxygen have also been found to improve CrO_4^{2-} reduction by Fe^{2+} , presumably by decreasing competitive oxidation of Fe^{2+} [6]. Zero-valent iron is also known to be capable of reducing Cu^{2+} , Ag^+ , and Hg^+ to their zero-valent metallic form [7, 8]. This process is frequently referred to as cementation in the engineering literature and has been used to extract metals from low-grade ores and purifying electrolytic solutions.

Based on thermodynamic considerations, Fe^0 should also be able to reduce the mobile TcO_4^- , UO_2^{2+} , and MoO_4^{2-} species to their more immobile counterparts. However, a practical requirement for using Fe^0 as a permeable barrier material is that the kinetics of the sequestering reaction must be rapid. A slow reaction rate would require a prohibitively thick Fe^0 barrier to extend the contaminant's residence time within the barrier. The objective of this study was to determine the capability and rate that Fe^0 particles remove UO_2^{2+} , MoO_4^{2-} , and TcO_4^- from groundwater. CrO_4^{2-} was included for comparison. Particular attention was directed at relating these findings to determinations of thermodynamic pe values of the reduction–oxidation (redox)

couples for predicting the effectiveness of Fe^0 as a permeable barrier material to mitigate the transport of reducible contaminants in groundwater.

2. Methods

A series of kinetic-batch studies was conducted in which approximately 50 ml of redox-sensitive-metal solutions was added to polystyrene centrifuge tubes containing 1.00 g of 40-mesh (<0.42 mm) metallic iron (Fisher Scientific, Fair Lawn, NJ). The iron particles had a specific surface area of $2.43 \text{ m}^2/\text{g}$, as determined by gas adsorption (Micromeritics, Gemini 2360) on samples that had been rinsed with methanol and dried under N_2 gas. A sufficient amount of solution was added to eliminate head space in the tubes. The sample tubes were mixed with an end-over-end mixer. For each of five time intervals, three tubes containing Fe^0 and a tube without Fe^0 (control) were sampled. At the end of the experiment, the control and treated solutions were centrifuged; the resulting supernates were passed through a $0.2\text{-}\mu\text{m}$ -syringe filter (Millipore Co., Bedford, MA), and the filtrates were analyzed for the appropriate metal. All experiments were conducted at room temperature (approximately 22°C).

The metal solutions were prepared by adding reagent grade or better salts of UO_2^{2+} (0.45 and $8.7 \text{ mg l}^{-1} \text{U}$), CrO_4^{2-} (0.5 and $10.0 \text{ mg l}^{-1} \text{Cr}$), TcO_4^- (5.4×10^3 and $5.4 \times 10^5 \text{ pCi ml}^{-1} {}^{99}\text{Tc}$: 0.32 and $32 \text{ mg l}^{-1} {}^{99}\text{Tc}$), and MoO_4^{2-} (4.5 and $26 \text{ mg l}^{-1} \text{Mo}$) to uncontaminated groundwater samples collected from the Hanford Site, Richland, WA. Hanford groundwater is dominated by Ca, Na, and bicarbonate (Table 1). The well used to collect the sample (well number 6-0S3-25) is screened in the unconfined aquifer, upgradient of plumes contaminated with a number of chlorinated hydrocarbons, U, Cr, and Tc.

CrO_4^{2-} was determined colorimetrically by the 1,5-diphenylcarbohydrazide method [9]. MoO_4^{2-} was determined colorimetrically by the ternary complex method obtained from the Hach Company (Loveland, CO). Technetium-99 activity was determined by liquid scintillation. UO_2^{2+} was determined by laser-phosphorimetry (Chemchek Instruments Inc., Richland, WA).

MINTEQA2 [10] calculations were conducted to determine the chemical speciation and equilibrium pe ($\text{pe} = -\log\{e^-\}$, where $\{e^-\}$ represents the electron activity) values for various redox couples of interest in Hanford groundwater. For the purposes of the calculation, it was assumed that the redox couples of interest controlled the pe of the system, the dissolved concentration of each oxidation state was equal and the total dissolved metal concentration was fixed at the measured value in solution at the end of the batch experiments (no precipitation allowed). The major ion data used to model the system are listed in Table 1 (except pH). The pH value used in the calculation was the final pH value measured at the end of the batch experiments ($\text{pH} = 8.4$). Thermodynamic data for Cr were taken from the MINTEQA2 database [10]. Thermodynamic data for U, Tc, Mo, and Fe were obtained from outside sources and added to the MINTEQA2 database. Thermodynamic data for Tc and U were from Refs. [11] and [12], respectively. Most of the Mo data originated from Ref. [13].

Table 1
Chemical composition of groundwater^a

Constituent	Concentration (mg l ⁻¹)
pH	8.14
Eh	309.0 (mV)
B	0.1
Ba	0.08
Ca	48.8
K	9.9
Mg	14.6
Na	32.1
Si	16.4
Sr	0.25
F ⁻	0.5
Cl ⁻	27
SO ₄ ²⁻	75
Total alkalinity (as CO ₃ ²⁻)	67.5
TOC	1
Cations (meq/l)	5.29
Anions (meq/l)	4.60

^a Sample passed through a 0.4- μ m polycarbonate filter. Al (<0.05), Cr (<0.08), Fe (<0.05), Mn (<0.05), Mo (<0.05), P (<0.05), U (0.004), NO₂⁻ (<0.3), and NO₃⁻ (<0.5).

Experimental hydrolysis constants for Mo³⁺ are not available and were estimated using an empirical linear free-energy method [14]. The value for pe⁰ for the Fe²⁺/Fe⁰ redox half reaction was taken from Ref. [15].

3. Results and discussion

3.1. Thermodynamic calculations

Thermodynamic calculations were conducted to determine the feasibility of using Fe⁰ as a reductant for removing CrO₄²⁻, TcO₄⁻, UO₂²⁺, and MoO₂²⁻ from the dissolved phase. Results from these calculations (Table 2) suggest that the equilibrium pe values for separate systems containing Cr, U, Tc, and Mo are above that of Fe²⁺/Fe⁰ couple. This indicates that it is thermodynamically favorable for Fe⁰ to reduce all four metals. In addition to the pe values calculated for these systems, the dominant dissolved species for each redox state is also presented in Table 2. Preliminary simulations in which chemical complexation was not taken into consideration suggested the pe values of UO₂²⁺/U⁴⁺ and MoO₂²⁻/Mo³⁺ were less than that of Fe²⁺/Fe⁰, contrary to our experimental evidence. These calculations emphasize the necessity of taking into consideration complexation when modeling redox chemistry.

Table 2
Equilibrium pe values calculated for Hanford groundwater with equal concentrations of each oxidation state for various redox couples^a

Redox pair	pe	Dominant oxidized species (%)	Dominant reduced species (%)
Cr ⁶⁺ /Cr ³⁺	6.0	CrO ₄ ²⁻ (98%)	Cr(OH) ₃ ⁰ (aq) (94%)
Tc ⁷⁺ /Tc ⁴⁺	- 1.3	TcO ₄ ⁻ (100%)	TcO(OH) ₂ ⁰ (aq) (94%)
U ⁶⁺ /U ⁴⁺	- 1.8	UO ₂ (CO ₃) ₃ ⁴⁻ (71%) + UO ₂ (CO ₃) ₂ ²⁻ (28%)	U(OH) ₄ ⁰ (aq) (57%) + U(OH) ₅ ⁻ (43%)
Mo ⁶⁺ /Mo ³⁺	- 7.6	MoO ₄ ²⁻ (100%)	Mo(OH) ₃ ⁰ (aq) (94%)
Fe ²⁺ /Fe ⁰	- 10.0	Fe ²⁺ (89%)	Fe ⁰ (s) (100%)

^a All species are dissolved except Fe⁰ (s) which is a solid. The major ion composition of the modeled system included the components listed in Table 1 (except pH = 8.4). The total elemental concentrations of dissolved Cr, U, Tc and Mo used in the calculations were fixed at the final concentrations shown in Fig. 2. Fe²⁺ concentration was assumed to be 10⁻⁵ M, and each oxidation state of the redox pair was set at 50% of the total elemental concentration.

3.2. Laboratory results

Results of the batch experiments are presented in Fig. 2 for oxidized metal ions added as CrO₄²⁻, TcO₄⁻, UO₂²⁺, and MoO₄²⁻ to natural groundwater containing Fe⁰ particles (specific surface area of 2.43 m²/g). Blank solutions (tubes without Fe⁰) were analyzed at each sampling period; less than a 7% decrease in metal concentrations of the blanks occurred during the course of these experiments (data not presented). The rate of removal from solution of these ions by Fe⁰ followed the order CrO₄²⁻ > TcO₄⁻ > UO₂²⁺ >> MoO₄²⁻. Zero-valent iron caused CrO₄²⁻ concentrations to decrease from 10 000 µg l⁻¹ Cr and 500 µg l⁻¹ Cr to < 5 µg l⁻¹ Cr in < 1 h (Fig. 2(a)). For the high initial concentration, this is a decrease of more than three orders of magnitude in < 1 h. Beyond 1 h, the concentration of dissolved Cr was less than the detection limit (approximately 5 µg l⁻¹). Similarly, Blowes and Ptacek [5] found that Cr removal from distilled water by Fe⁰ filings was extremely rapid; Cr concentrations decreased from 25 to < 0.05 mg l⁻¹ in less than 3 h.

The mechanism of CrO₄²⁻ removal from solution in these experiments is reduction to Cr³⁺ which readily hydrolyzes and forms the sparingly soluble precipitate Cr(OH)₃ (s). The solubility of Cr(OH)₃ (s) at pH 8.4 is quite low, approximately 5 µg l⁻¹ [16]. Small amounts of iron oxides were observed to form in our batch experiments; thus, it is possible that a (Cr_xFe_{1-x})(OH)₃ solid solution formed [6, 16]. This distinction in solid phases has important ramifications in regard to the use of Fe⁰ as a barrier material. Cr³⁺ concentrations in equilibrium with (Cr_xFe_{1-x})(OH)₃ solid solution are appreciably less than those in equilibrium with Cr(OH)₃(s) [6, 16]. The possibility that CrO₄²⁻ was lost from solution by adsorption onto the iron oxides was ruled out because CrO₄²⁻ adsorption by iron oxides at the pH of this study (pH 8.4) is essentially zero and cannot explain the large decreases in CrO₄²⁻ concentrations observed [16]. Although the primary reductant is believed to be Fe⁰, reduction of CrO₄²⁻ by Fe²⁺ and H₂ (g) are also possible [4, 6]. Reduction of CrO₄²⁻ by Fe²⁺ is also quite fast [6];

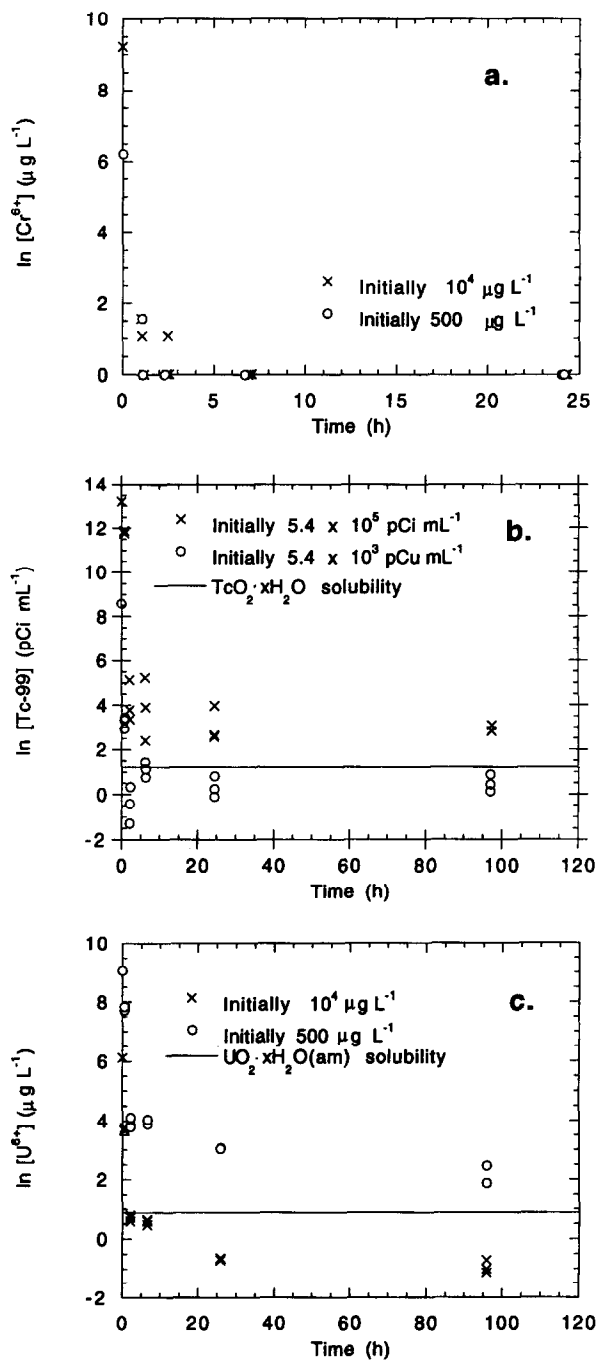


Fig. 2. Removal of metal ions from solution in the presence of Fe⁰ particles during batch experiments: (a) CrO₄²⁻, (b) TcO₄⁻, (c) UO₂²⁺ and (d) MoO₂²⁻.

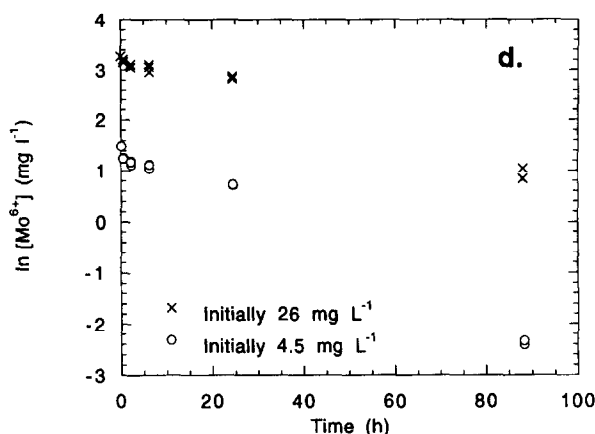


Fig. 2d.

however, reduction by Fe^0 is more favorable from a thermodynamic standpoint and is likely to be faster. Gould [4] suggested that H_2 (g) produced by the oxidation of Fe^0 by water may also participate in CrO_4^{2-} reduction.

In the TcO_4^- experiments (Fig. 2(b)), the high initial concentration of 5.4×10^5 pCi ml^{-1} decreased to an average value of 1.3×10^5 pCi ml^{-1} in approximately 0.6 h and to 80 pCi ml^{-1} after 2 h. In the experiments started at 5.4×10^3 pCi ml^{-1} ^{99}Tc , the concentrations decreased to approximately 30 pCi ml^{-1} after 0.7 h and to 0.8 pCi ml^{-1} after 2 h. As was the case with CrO_4^{2-} , the decrease of Tc in solution was likely the result of reduction of TcO_4^- to Tc^{4+} which was precipitated as a sparingly soluble solid. The Tc concentration at the end of the experiment (Fig. 2(b)) coincided with the equilibrium solubility of $\text{TcO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ [17], providing indirect evidence that this amorphous solid was controlling dissolved Tc concentrations. Adsorption onto ferric oxides is not likely to be an important mechanism for TcO_4^- removal because little adsorption takes place on ferric oxide surfaces, especially at the elevated pH levels of these experiments [18].

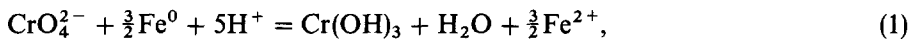
The rate of UO_2^{2+} removal from solution by Fe^0 was somewhat slower than for CrO_4^{2-} and TcO_4^- (Fig. 2(c)). Uranium concentrations decreased from approximately 8700 to 2500 $\mu\text{g l}^{-1}$ and 450 to 40 $\mu\text{g l}^{-1}$ U within 0.6 h. After 2 h, the U concentrations had decreased to 40 and 2 $\mu\text{g l}^{-1}$ in the high and low concentration solutions, respectively. The mechanism of UO_2^{2+} removal from solution is not readily apparent from physicochemical considerations. Three removal mechanisms are conceivable. First, reduction of UO_2^{2+} by Fe^0 to form the sparingly soluble $\text{UO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ phase may have occurred. The equilibrium solubility of $\text{UO}_2 \cdot x\text{H}_2\text{O}(\text{am})$ is indicated in Fig. 2(c) for comparison [19]. Secondly, UO_2^{2+} adsorption onto iron oxides may have occurred under the conditions of the experiments (pH = 8.4 and total $\text{CO}_2 = 2.2 \times 10^{-3}$ M) [20]. Third, it is possible that both reduction/precipitation and adsorption to newly precipitated iron oxides occurred concurrently.

The rate of MoO_2^{2-} removal from solution was significantly slower than for the other ions tested (Fig. 2(d)). After 88 h, initial MoO_2^{2-} concentrations of 26 and $4.5 \text{ mg l}^{-1} \text{ Mo}$ decreased to approximately 2.5 and $0.09 \text{ mg l}^{-1} \text{ Mo}$, respectively. Experimental thermodynamic data involving the reduced forms of Mo are incomplete; however, it has been demonstrated that other zero-valent metals (Zn^0 , Cd^0 and Pb^0) are capable of reducing MoO_2^{2-} to Mo^{3+} which then precipitates as $\text{Mo}(\text{OH})_3$ [21]. Therefore, it was assumed that the MoO_2^{2-} in the system was reduced to Mo^{3+} , which hydrolyzed to form a sparingly soluble $\text{Mo}(\text{OH})_3$ (s) phase. Based on thermodynamic calculations, it appears the reduction of MoO_2^{2-} to Mo^{3+} by Fe^0 is thermodynamically favorable, although to a much lesser extent than CrO_4^{2-} (Table 2).

The Δpe is the difference in pe values between the redox half reaction for the redox couple of interest and the $\text{Fe}^0/\text{Fe}^{2+}$ couple and is proportional to the driving force (Gibbs free energy) of the redox reaction. As the value of Δpe increased (calculated from the data in Table 2), the rate of removal from solution also increased. These results suggest the value of Δpe can be used as a qualitative indicator of the rate of reduction by Fe^0 .

Attempts to model the reductive precipitation process with data presented in Fig. 2 as simple first- or second-order reaction mechanisms were largely unsuccessful. Towards the end of the experiments, numerous reactions were clearly occurring concurrently, such as the reductive precipitation of the dissolved species, Fe-oxide formation, and in some cases surface complexation on Fe-oxides of the dissolved species was possible. Although several semi-empirical kinetic models exist to describe some of these reactions [22, 23], we were unable to find any models in the literature capable of describing the full suit of reactions likely to be occurring in this experiment.

Satisfactory results were obtained for modeling reductive precipitation of the MoO_2^{2-} using a pseudo-first-order kinetic model. In addition, the early stages of the CrO_4^{2-} , TcO_4^- , and UO_2^{2+} experiments (less than 3 h) were successfully modeled using pseudo-first-order kinetic models. For example, the kinetic rate equation for reduction of CrO_4^{2-} :



can be expressed as:

$$-\frac{d[\text{CrO}_4^{2-}]}{dt} = k[\text{CrO}_4^{2-}][\text{Fe}^0]_s^{3/2}[\text{H}^+]^5, \quad (2)$$

where k is the specific rate constant for the reaction. By assuming that the number of reaction sites on the Fe^0 ($[\text{Fe}^0]_s$) remains constant and hydrogen ion concentration remains constant, Eq. (2) can be simplified. The assumption that $[\text{Fe}^0]_s$ remains constant is reasonable because the number of available sites greatly exceeds the quantity of oxidants. The assumption that $[\text{H}^+]$ remained constant is less reasonable because the pH increased from 8.14 to 8.4 during the experiments. With these assumptions, the pseudo-first-order rate constant k' can be defined as $k' = k[\text{Fe}^0]_s^{3/2}$

Table 3
Pseudo-first-order rate constants (h^{-1}) and half-life (h) for reduction of metal ions by zero-valent iron

Metal	High concentration		Low concentration	
	k' (h^{-1})	$t_{1/2}$ (h)	k' (h^{-1})	$t_{1/2}$ (h)
CrO_4^{2-}	7.7	5.3	6.5	0.11
TcO_4^-	4.5	4.4	4.5	0.15
UO_2^{2+}	2.5	2.5	2.5	0.28
MoO_2^{2-}	0.026	0.042	0.034	20

$[\text{H}^+]^5$. Eq. (2) can then be rewritten as

$$-\frac{d[\text{CrO}_4^{2-}]}{dt} = k'[\text{CrO}_4^{2-}]. \quad (3)$$

After integration and rearrangement, this equation becomes

$$\ln[\text{CrO}_4^{2-}] - \ln[\text{CrO}_4^{2-}]_0 = -k't, \quad (4)$$

where $[\text{CrO}_4^{2-}]_0$ is the initial CrO_4^{2-} concentration. If a plot of $\ln[\text{CrO}_4^{2-}] - \ln[\text{CrO}_4^{2-}]_0$ versus time is linear then the model is appropriate. Similar equations can be derived for the other redox reactions studied.

Table 3 shows the values determined for k' and the half-lives. Rate constants were determined separately for both the high and low concentration experiments. The half-life $t_{1/2}$ of a reaction is the time required for the disappearance of the oxidized species. In the case of a pseudo-first-order reactions, the half-life is independent of the initial concentration and is calculated with

$$t_{1/2} = \frac{0.693}{k'}. \quad (5)$$

Note that the rate constants shown in Table 3 are essentially empirical constants applicable only to the conditions of our experiments. Generally good agreement is observed for the results determined between the high and low concentration experiments. Significant differences are apparent between the different metals.

In Fig. 3, the pseudo-first-order rate constants are plotted against Δpe from Table 2. The results suggest that a significant correlation ($R^2 = 0.94$, $P \leq 0.01$, d.f. = 7) exists between these parameters. Linear regression of the data in Fig. 3 forced to a zero intercept results in the following equation:

$$k' = 0.40 \Delta\text{pe}. \quad (6)$$

This equation may be useful as a means to provide qualitative estimates of pseudo-first-order rate constants for other reducible metals of interest. It must be emphasized that Eq. 6 is applicable only in the early stages of the reduction process for most of the metals studied here and for the conditions of our experiments. It also neglects the effects of processes other than reductive precipitation which could effect the kinetics of

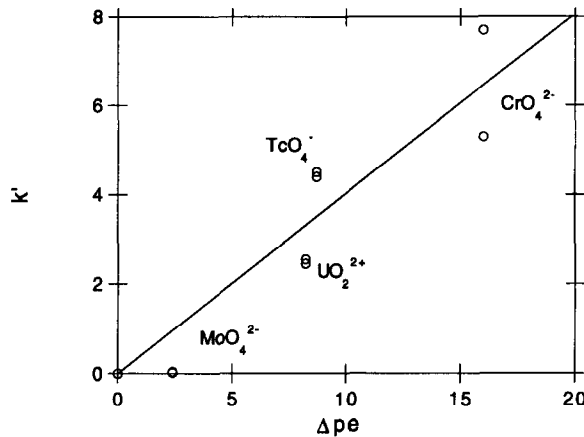


Fig. 3. Pseudo-first-order rate constant k' for reductive precipitation of CrO_4^{2-} , TcO_4^- , UO_2^{2+} and MoO_4^{2-} as a function of Δpe .

the systems including changes in pH, Fe-oxide formation which could affect the available surface area of Fe^0 , and in some cases surface complexation of the dissolved species on Fe-oxides.

4. Conclusions

There are three primary conclusions from this study. First, the list of mobile contaminants that can be precipitated through reduction by Fe^0 was extended to include TcO_4^- , UO_2^{2+} , and MoO_4^{2-} . Numerous halogenated-hydrocarbon compounds [1] and CrO_4^{2-} [4] have been reported to be removed effectively from groundwater. The identification of an inexpensive material which can immobilize both Tc and U, two highly mobile radioactive materials, is especially important because no such materials are presently available for in situ remediation purposes. Second, the rate of removal of CrO_4^{2-} , TcO_4^- , and UO_2^{2+} from the dissolved phase is rapid, permitting an inexpensive barrier of practical dimensions to be used for in situ remediation purposes. Many halogenated hydrocarbon compounds have also been reported to have rapid degradation kinetics when exposed to Fe^0 [24]. Third, the rate of removal of these dissolved species is correlated with their Δpe values. This latter point has significant ramifications with regard to predicting the effectiveness of removal from solution of dissolved oxidizable contaminants by Fe^0 . Plans for a potential field demonstration are currently being developed to apply the Fe^0 permeable barrier concept to a mixed waste plume at the 100-Area on the Hanford Site containing carbon tetrachloride, TCE, PCE, CrO_4^{2-} , TcO_4^- , and UO_2^{2+} , all highly mobile contaminants that can be degraded or precipitated by this process.

Acknowledgements

Pacific Northwest Laboratory is operated for the US Department Energy by Battelle Memorial Institute under Contract DE-AC06-76RLO 1830. This work is funded by the Office of Technology Development, within the Department of Energy's Office of Environmental Management, under the In Situ Remediation Integrated Program, Jef Walker HQ Program Manager. The authors wish to thank Kenneth Krupka of Battelle, Pacific Northwest Laboratory for his assistance in the equilibrium speciation modeling, Tim Johnson and Paul Tratnyek, Oregon Graduate Institute of Science and Technology for surface area data and Calvin Ainsworth of Battelle, Pacific Northwest Laboratory for reviewing an earlier version of this manuscript.

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