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ABSTRACT

REACTIVE MEDIA FOR CHROMIUM REDUCTION UNDER ALKALINE CONDITIONS FOR USE IN PERMEABLE REACTIVE BARRIERS

by
Sachin V. Apte

The purpose of this study was to select the appropriate reactive media for chromate reduction to treat groundwater (high pH) with permeable reactive barriers. The study addresses groundwater contamination for three chromium refining sites located in Hudson County, New Jersey. The use of iron (Fe^0) as a reactive medium was studied and found to be insufficient for use in permeable reactive barriers because of the high pH conditions of groundwater at these sites. Pyrite and iron (Fe^0)-pyrite mixtures were studied as viable reactive media by considering their passivation kinetics, reductive capacities and solubility properties.

Column experiments were carried out with different volumetric ratios of pyrite and iron (Fe^0)-pyrite mixtures with combination of aquifer materials (sand) to calculate the maximal chromium accumulation necessary to accurately estimate the capacities of reactive media. The iron (Fe^0)-pyrite mixture was found to be suitable for treating chromate-contaminated groundwater at the high pH conditions. The reactive media capacities of these mixtures were found to be satisfactory for successful use of permeable reactive barriers to treat the three sites.

We recommend the use of iron (Fe^0)-sand mixture as a reactive medium for the Allied Signal site (#NJL 000005033) and iron (Fe^0)-pyrite-sand mixture as the reactive medium for both the P.P.G (#NJL 000005017) and the Chemical Land Holding sites.

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CONDITIONS FOR USE IN PERMEABLE REACTIVE BARRIERS**

**by
Sachin V. Apte**

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Submitted to the Faculty of
New Jersey Institute of Technology
in Partial Fulfillment of the Requirements for the Degree of
Master of Science in Civil Engineering**

Department of Civil and Environmental Engineering

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APPROVAL PAGE

**REACTIVE MEDIA FOR CHROMIUM REDUCTION UNDER ALKALINE
CONDITIONS FOR USE IN PERMEABLE REACTIVE BARRIERS**

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This thesis is dedicated to
my beloved family

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TABLE OF CONTENTS

Chapter	Page
1 INTRODUCTION.....	1
1.1 Permeable Reactive Barrier.....	1
1.2 Oxidation States of Chromium and Mechanism of Chromate Reduction...	2
1.3 Iron as Reductive Media for Cr (VI) at Different pH.....	3
1.4 Pyrite as a Reductive Media for Cr (VI) at Different pH.....	4
1.5 Chromite Ore Processing Residue (COPR).....	4
1.6 Reactive Media Selection for PRB Application at High Alkaline pH.....	5
1.7 Objective of the Work.....	5
1.8 Organization of Thesis.....	6
2 EXPERIMENTAL PROCEDURES.....	7
2.1 Materials.....	7
2.2 Analytical Procedure.....	8
2.3 Shaken Packed Bed Experiment.....	9
2.4 Column Reactor Experiment.....	10
3 REACTIVE MEDIA CAPACITY AND PREDICTION OF PRB LIFETIME	11
3.1 Passivation of Reactive Media Surface, Reductive Capacity and Surface Area.....	11
3.2 Reduction Rate and Time Dependence.....	12
3.3 Modeling Cr (VI) Removal within PRB at Known Filtration Velocity.....	13
3.4 Different Modes of Passivation Kinetics.....	14
3.5 Prediction of Chromium Distribution as a Function of Time.....	20

TABLE OF CONTENTS
(Continued)

Chapter	Page
3.6 Evaluation of Reactive Media Capacity for Thin Plug Passivation Kinetics	23
3.7 Non Uniform Chromium Distribution across Thin Plug.....	24
3.8 Underevaluation of Reactive Media Capacity in Thin Plug.....	25
3.9 Critical Capacity for PRB for Three Sites in Hudson County.....	26
3.10 Prediction of Maximal Reactive Media Capacity.....	26
3.11 Number of Pore Volumes.....	28
4 RESULTS AND DISCUSSION.....	29
4.1 Shaken Packed Bed Experiment.....	30
4.2 Iron Regeneration as Reductant and Influence of Residence Time on Iron Capacity.....	31
4.3 Column Experiment.....	32
4.4 Iron Assessment as Reactive Media for pH about 12.....	33
4.5 Iron Siderite Mixture.....	34
4.6 Pyrite and Siderite Solubility and its Manifestation in PRB.....	36
4.7 Flow Rate Influence on Reduction and Accumulation of Chromium.....	37
4.8 Two Step Passivation Process and Total Capacity Evaluation.....	40
4.9 Pyrite and Pyrite Sand Mixture.....	40
4.10 Comparison of Iron (Fe ⁰) and Pyrite at pH about 12.....	42
4.11 Iron (Fe ⁰)-Pyrite and Iron (Fe ⁰)-Pyrite-Sand Mixture.....	42
4.12 Influence of pH.....	43

TABLE OF CONTENTS
(Continued)

Chapter	Page
4.13 Discussion of Results.....	44
4.14 Prediction of Barrier Lifetime.....	45
4.15 Barrier Critical Thickness Evaluation for Sites of Hudson County, New Jersey.....	46
4.16 Recommendations for Sites under Investigation.....	46
5 SUMMARY AND RECOMMENDATIONS.....	47
REFERENCES.....	49

LIST OF TABLES

Table		Page
2.1	Groundwater Stream Characteristics for Three Sites of Hudson County....	7
2.2	Information about Different Types of Peerless Iron Used in Experiments..	8
4.1	Groundwater Volume per Gram of Reactive Media for 20 Years Barrier Life	37
4.2	Recommendations for Barrier Thickness and Reactive Media for Sites.....	46

LIST OF FIGURES

Figure	Page
1.1 Permeable Reactive Barrier.....	1
3.1(a) Reduction Rate Coefficient Dependency on Time.....	15
3.1(b) Reduction Rate Coefficient Dependency on Chromium Accumulated.....	15
3.2 Schematic Illustration of Barrier Performance during Time in Years.....	18
3.3 Schematic Distribution of Accumulated Reduced Chromium Distribution..	19
4.1 Result of Shaken Packed Bed Experiment.....	32
4.2 Growth of Effluent Concentration for Iron #3.....	33
4.3 Results of Column Experiments with ISM Volumetric Ratio 50/50.....	36
4.4 Flow Rate Influence on Chromium Accumulation.....	39
4.5 Accumulated Chromium for Pyrite Experiment.....	41
4.6 Accumulated Chromium for Pyrite Sand Experiment.....	41
4.7 Accumulated Chromium for Iron (Fe ⁰)-Pyrite-Sand Experiment.....	43
4.8 Accumulated Chromium for Iron (Fe ⁰)-Pyrite Experiment.....	43
4.9 Comparison of Experimental Results at Neutral and High pH.....	44

CHAPTER 1

INTRODUCTION

1.1 Permeable Reactive Barrier

A permeable reactive barrier (PRB) is a passive treatment zone of reactive material that degrades or immobilizes contaminants as groundwater flows through it Figure 1.1. The contaminants in groundwater react with the reactive media where they are transformed into harmless precipitates within the barrier (1,2). Being passive, the barrier does not require any power or maintenance for a long period of time, possibly years. The application of the permeable reactive barrier technology requires a thorough knowledge of the reactivity of reactive media with the specific contaminant present in the groundwater. In this study, we are concerned with the treatment of chromium-contaminated groundwater, specifically for the case of chromium refining waste sites located in Hudson County, New Jersey.

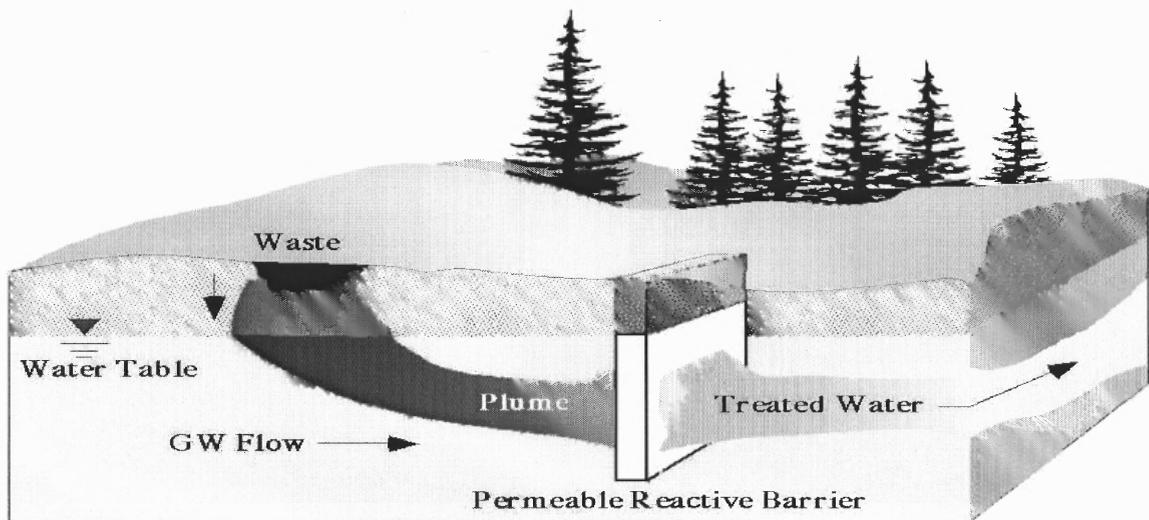


Figure 1.1 Permeable Reactive Barrier

1.2 Oxidation States of Chromium and Mechanism of Chromate Reduction

Chromium is a commonly identified groundwater contaminant. It is present in nature mostly as chromite ore, with a nominal composition of $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ (3). Chromium present in the chromite ore is in the trivalent state, Cr (III). The other most common valence state of chromium is hexavalent, Cr (VI). Oxidation potential and pH of the environment are the two most important factors determining the ratio of the two common valence states (Cr III/Cr VI) in any physical system.

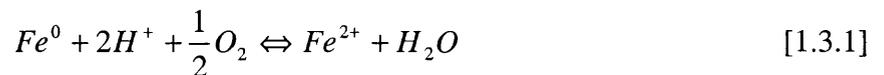
Hexavalent chromium species are stable in an oxidizing atmosphere, whereas the trivalent species dominate in a reducing environment (4). At $\text{pH} > 6$, Cr can exist as chromate ion, CrO_4^{2-} . Despite the strong adsorption affinity of chromate ion to certain mineral surfaces, it is mobile in subsurface systems compared to Cr (III) species (5). Due to its mobility, chromate ion is an environmental concern due to its toxic and carcinogenic properties (4).

Reduction of Cr (VI) by iron, with main focus on ferrous ions in solution, and in the presence of iron bearing minerals are reported in the literature. Gould (6) examined the reduction of Cr (VI) and showed that iron (Fe^0) surfaces are effective in reducing Cr (VI) to Cr (III) under low pH conditions. A corrosion mechanism proposed to explain this reduction process (7). As iron metal corrodes in water, ferrous ion is produced at local anodic sites, and acid is consumed by forming hydrogen gas at local cathodic sites (8). Elemental iron (Fe^0) is also used in permeable reactive processes as a means of enhancing abiotic reductive dechlorination of organic compounds (9,10). Reduction of Cr (VI) to Cr (III) occurs rapidly under acidic conditions (11,12). The reduction rate decreases with increasing the pH of groundwater to be treated (13,14,15). Elemental iron (Fe^0) has the

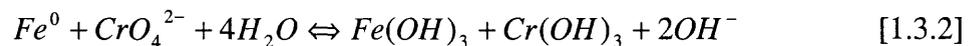
potential to induce rapid reduction to Cr (III) which subsequently precipitates to form a mixed Cr (III)-Fe (III) oxyhydroxide (16).

1.3 Iron as Reductive Media for Cr (VI) at Different pH

Iron, as the reductive media for Cr (VI) reduction at different pH, has been studied for its effectiveness in the treatment of contaminated groundwater. Experimental modeling (16,17), barrier installation and post-installation monitoring (18,19) have confirmed that elemental iron is effective in removing CrO_4^{2-} ion from the aqueous phase at intermediate pH conditions. The systematic investigation for chromium reductions with ferrous ions is well known (20,21,22) and is sufficiently rapid (20) at neutral to alkaline pH (7-10). The precipitation of a mixed Cr (III)-Fe (III) oxyhydroxide occurs at pH values between 5-11 (19,21) which generally lowers the total dissolved concentration of Cr (III) less than the drinking water standards of 0.1 ppm. However formation of the hydroxide complexes results in higher solubilities if the pH is increased above 11 (21). This is often considered as a serious restriction for the treatment of hexavalent chromium at higher pH (>11). Fundamentally the decline in reduced chromium precipitation can occur too at initial pH values lower than 11, because of the oxidation of Fe^0 to Fe^{2+} results in increase in pH (7,15), as follows:



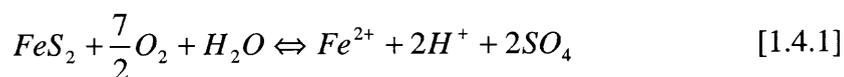
The pH increase due chromium reduction and chromium-iron hydroxide formation is confirmed from the following net reaction (7):



As the moderate pH is more favorable for chromium removal, the application of ferrous (Fe^{2+}) bearing minerals, such as pyrite and siderite, is well known. Prior to this study, there was no systematic investigation of Cr (VI) reduction with the use of elemental iron (Fe^0) at extreme high pH (>11).

1.4 Pyrite as a Reductive Media for Cr (VI) at Different pH

Pyrite is used as reductive media for moderating the pH of contaminated groundwater (23,24). The oxidation of pyrite produces acid, which offsets the acid consumed during the oxidation of Fe^0 . In the presence of oxygen, the net reaction of pyrite oxidation is as follows:



Desai (38) shows that these minerals even under high pH conditions have lowered chromium concentrations. Also the Cr (VI) reduction with pyrites in the absence of oxygen is increased due to the production of acids, as shown in the Equation [1.4.1]. There is no systematic investigation of Cr (VI) reduction with the use of pyrite at high alkaline pH. Reduction of Cr (VI) with pyrite under highly alkaline pH condition is a major part of this research.

1.5 Chromite Ore Processing Residue (COPR)

The industrial conversion of Cr (III) in chromite ore to the soluble hexavalent form is called the chromium refining process. This process is accomplished by roasting the chromite ore in the presence of soda ash, lime and air at about 1100-1150 °C, and thereby converting the trivalent chromium to water-soluble chromate i.e., Cr (VI). The yield of this process is usually between 65 % to 85 %, based on the content of chromium in the

ore (25,26). Mixed Cr (III)-Cr (VI) solid residue waste is generated from this high temperature kiln process. This residue is alkaline in nature since lime and soda ash are used in this process. Earlier in the century, such residue was landfilled in sites near the production facilities. The ratio of Cr (III) to Cr (VI) in refining wastes varied depending on the original nature of the residue, production process, pH and other transformations that may have taken place since landfilling (27,28,29). Because of these reasons, soluble Cr (VI) species from these landfills have been found to significantly contaminate groundwater in the vicinity of these sites (30). That is why it is necessary to develop a technology to treat groundwater with high pH values, > 11 .

1.6 Reactive Media Selection for PRB Application at High Alkaline pH

The selection of reactive media for chromate removal with permeable reactive barriers from groundwater under alkaline conditions (pH about 12) needs to be investigated as most of the chromium-contaminated sites in New Jersey are high pH. The reactivity of reactive media was measured for elemental iron (Fe^0) of different types and for their mixtures with pyrite using groundwater from three COPR sites in Hudson County, New Jersey. The reactive capacity of Fe^0 at high pH is low, and is deemed inefficient for use in permeable reactive barriers. Mixtures of elemental iron (Fe^0) with pyrite mineral has been found to have reactive capacities almost 10 times larger than those of iron alone, and thus making such mixtures as potential candidates for groundwater remediation at $\text{pH} > 11$.

1.7 Objective of the Work

The main objective of this research was to select the best reactive medium to be used in permeable reactive barriers to treat chromate-contaminated groundwater under the high

alkaline conditions present at New Jersey sites. The study was carried out with the following objectives:

1. To study the performance of elemental iron (Fe^0) at $\text{pH} > 11.0$,
2. To assess pyrite and siderite minerals as reduction media under the high pH conditions, > 11.0 ,
3. To determine the reactive capacities of Fe^0 -pyrite and Fe^0 -siderite mixtures, at high pH, > 11.0 ,
4. To experimentally determine the reactive media capacity, and to predict the PRB lifetime by batch experiments,
5. To combine the generated information with existing literature to evaluate models, especially with respect to assessment of long-term performance and passivation of permeable reactive barriers, and
6. To evaluate the barrier critical thickness necessary for 30 years active life for the three COPR sites in New Jersey.

1.8 Organization of Thesis

In Chapter 2, we will discuss the materials, experimental procedures and analytical methods used in this research. In Chapter 3, we will discuss reactive media capacity and prediction of permeable reactive barrier lifetime for the three COPR sites from Hudson County, New Jersey. In Chapter 4, we present and discuss the results of the various experiments for predicting the suitable reactive media for all the sites, and evaluate the critical barrier thickness for each of the sites.

CHAPTER 2

EXPERIMENTAL PROCEDURES

The groundwater samples used in the thesis were obtained from extraction wells present at three sites located in Hudson County, New Jersey, namely: Chemical Land Holding, Allied Signal and P.P.G sites. Table 2.1 summarizes the pH, Eh, and total chromium concentrations of groundwater samples used in this study. The pH of all groundwater of these sites is alkaline and ranges between 11.5 and 12.35. For the evaluation of residence time the Table 2.1 is supplemented with mean values of pore velocity of groundwater within the aquifer at the site, with account for their seasonal variation. Estimation of pore velocity with the use of groundwater velocity is done by assuming the field-cell porosity of 0.65 (31). Residence time refers to the duration of time the contaminated groundwater remains in contact with the reactive media in the permeable reactive barrier, assuming the same hydraulic conductivity of barrier as the aquifer.

Table 2.1: Groundwater Stream Characteristics for Three Sites of Hudson County

Characteristics	Chemical Land Holding	Allied Signal	P.P.G
Total Chromium Concentration (ppm)	55	25	16
pH	12.3	12.2	11.5
Eh (mV)	155	167	240
Groundwater velocity (cm/day)	5-26	1.1-3	15
Residence time (hours)	480-92	2200-800	160

2.1 Materials

Two types of reductive iron media, namely Fisher iron and Peerless iron, were used in our experiments. Peerless iron was supplied by the Peerless Iron Company, while the Fisher iron was purchased from the Fisher Scientific Company. The Peerless iron was

used for the extensive evaluation in this research. Information about the particle dimension of the iron media used in this study is given in Table 2.2. The Peerless iron was used without any pretreatment. Pyrite and siderite minerals used in our experiments were obtained from Chemalloy Company and Scott Resources Company, respectively.

Table 2.2: Information about Different Types of Peerless Iron Used in Experiments

Iron #1		Iron # 2		Iron # 3	
Mesh size	% Retained	Mesh size	% Retained	Mesh size	% Retained
16	0	50	0	60	0
18	0	60	2	80	0.6
25	7	70	20	100	4
40	42	80	17	325	73.2
50	22	100	25	Pan	22
80	19	120	11		
100	4	Pan	25		
Pan	5				

2.2 Analytical Procedure

A microprocessor-based pH meter with a Eh measuring mode (JENCO model 6071) was used. The pH and the corresponding temperature were measured using a 3-in-1 electrode (pH and reference electrode combined with temperature probe JENCO model 6000). The pH meter was calibrated with standard solutions of pH 4, 7 and 10. The pH was regularly calibrated before the measurements.

An oxidation-reduction potential electrode (ORP) electrode was used to measure the Eh of the solution. The electromotive force between the potentials on the standard Ag|AgCl reference and the platinum band, which acts as the second electrode, is measured by the combination ORP electrode. The ORP electrode was routinely tested for with the quinhydrone standard test solution, as per standard methods.

The total chromium concentration in groundwater samples was analyzed by Atomic Adsorption (AA) spectroscopy. The analysis of samples was carried out using Smith-

Heiftje atomic adsorption spectrophotometer. The light source used for the analysis was a hollow cathode lamp with a current of 6.0 mA. The wavelength required is 357.9 nm and with a bandpass of 0.5 nm. The linear range of the instrument was between 0-5 μ g/ml of total chromium. The total chromium measurement was done following the EPA protocols under method #7000 and method # 7191 (32,33). The hexavalent chromium concentrations in the samples were measured by colorimetric analysis based on absorption spectroscopy at 540 nm. The analysis was carried out using the Varian DMS 3000 UV-visible spectrophotometer. The hexavalent chromium was done following the EPA protocols under the method # 7169A (34). Diphenylcarbazide was used as a coloring agent and the sample was acidified for color development using 10% HCl (vol/vol), as per the standard method.

2.3 Shaken Packed Bed Experiment

The evaluation of reductive systems and reduction rate calculations for different types of iron at pH 12 were done by the shaken packed-bed experiment. In this case, a known quantity of reactive media was mixed with the groundwater for a short period of time, normally overnight. The bottles with the measured quantity of mixture were then placed on a shaker. The experiments were carried out for different groundwater characteristics for a definite time, and then the solids were separated from solution by filtration. The final chromate concentrations and pH were measured. The construction set up (7) of shaken bottle experiments almost eliminated oxygen penetration from the atmosphere by the use of sealed bottles. This method enabled us to shorten the time needed to perform a large number of experiments. A large solid to liquid ratio was maintained in these experiments so that the liquid will fill pore volume only. This corresponds to the maximal

rate of reduction. It was found (35,36,37) that the primary factor in determining the rate of reaction is the available specific surface area, i.e. surface area of reactive medium per unit volume. The latter is directly proportional to the volume fraction in the solid-liquid mixture. The aquifer materials or sand were not added to the reactive media even though certain aquifer materials are known to contribute to the reduction rate in experiment (7).

2.4 Column Reactor Experiment

There is a trend in the recent design of column experiment (16), which is aimed to characterize reactive media and to model some significant features of permeable reactive barriers. This is done by the use of rather small (short) columns (about 5-10 cm in length). The use of small columns in our experimental research was admissible because the effluent concentration measurement was sufficient to study the suitability of iron-pyrite mixture for chromate reduction at pH about 12. The short column experiment was necessary to carry out many experiments in parallel in order to determine the long-term performance of different types of reactive media. The column construction used in our experiments almost eliminated the oxygen penetration from the atmosphere.

Different reactive media loosely packed in 100-ml glass columns (cross-section of 5 cm², height 20 cm). The columns were attached to the reservoir bottles that contained the groundwater. The pressure head was adjusted for the flow with two-velocity range. The first range of velocities corresponds to the larger linear velocities of the groundwater stream measured at the sites under investigation. The second range of velocities corresponds to smaller velocities, as needed for the investigation. The column effluent was collected periodically at a designated velocity. The continuous monitoring of effluent chromium concentration and its pH measurements were performed on a regular basis.

CHAPTER 3

REACTIVE MEDIA CAPACITY AND PREDICTION OF PRB LIFETIME

3.1 Passivation of Reductive Media Surface, Reductive Capacity and Surface Area

The study of passivation kinetics (the decrease in reaction rates due to surface effects of reactive media when chromate-contaminated groundwater resides in the barrier), has to be understood, especially for case of high pH conditions when it becomes very important. Two major types of passivation are anticipated. The first type is the passivation in short time duration where a major drop in the reduction rate takes place, which may also lead to a stage where the reduction rate becomes negligible. This type of passivation is significant if the reductive media capacity is large and sufficient for accumulation of all the chromium entering the barrier during some time. The passivation occurring inside the barrier is important; however, the more important parameter is the amount of chromium accumulation per unit volume. The second type of passivation is characterized by an initial drop in reduction rate but then followed by a finite reduction rate lasting for a long time. If total rate of the later stage is large, it may account for additional and possibly significant chromium accumulation during long treatment times.

Reactive media capacity is a function of the linear groundwater velocity and the initial concentration of chromate in the sample. The smaller velocity and the smaller initial chromate concentration, the larger is the reductive media capacity. This regularity also agrees with the assumption that corrosion suppresses the passivation. For a time, T , if the rate of the chromium accumulation is smaller than the rate of corrosion, ability to create defects in the chromium deposits, a condition may arise where the high initial reduction rate is preserved. If during the same time, T , the chromium amount

accumulated is large such that corrosion may not be able to create sufficient number of defects, the reduction rate will decrease. However at larger groundwater linear velocity and high initial chromate concentration, the large amount of chromate is available for reduction and passivation. Increasing the residence time is expected to prevent the passivation of the reductive media. Thus, the reactive media has to be defined by its reactive capacity dependence on groundwater velocity.

Also, the surface area of reactive media exposed to groundwater has to be taken into consideration. Agrawal and Tratnyek (1996) (35) and Matheson and Tratnyek (1994) (36) have found that the primary determinant of reduction rate is the available reactive surface area of the reactive medium. It is clear that the larger the surface area of the reactive medium, the larger chromium amount necessary for effecting passivation. Simple evaluation demonstrates that the passivation caused by the formation of chromium compound on the surface of reactive medium corresponds to a very short passivation time. This means that there is a mechanism, which controls the surface area available for the reduction even at continuous deposition; this is believed to be corrosion. Chromium reduction in a column containing reactive media may be considered a coupling of two processes, with opposite influence on the surface processes, namely: the surface passivation by the chromium deposition and surface activation due to the corrosion of reactive medium surface. The interplay between these two processes depends primarily on the pH.

3.2 Reduction Rate and Time Dependence

For CrO_4^{2-} reduction, the elemental iron is used as a plug (short-column) filled with chromate-contaminated groundwater at $\text{pH} > 11$. The chromium concentration is measured

as a function of time. It was found that the concentration decrease is described by the exponential dependence with rate constant $K = 44 \text{ hour}^{-1}$, according to

$$n = n_i e^{(-Kt)} \quad [3.2.1]$$

where $n_i = 55 \text{ ppm}$ is the initial concentration. The exponential dependence corresponds to the first order kinetics reaction, then

$$\ln \Delta n = -Kn\Delta t \quad [3.2.2]$$

K is the reaction rate constant and t is the time. Its integration yields

$$\frac{dn}{n} = -Kdt \quad [3.2.3]$$

$$\ln \frac{n}{n_i} = -Kt \quad [3.2.4]$$

$$n = n_i e^{(-Kt)} \quad [3.2.5]$$

The first order kinetics simplifies the permeable reactive barrier (PRB) modeling using our batch experiment results.

The first order kinetics arises because Cr (VI) reduction is surface controlled reaction (terminology of Stumm W. " Aquatic Surface Chemistry"). As Cr (VI) ion collides with the iron particle surface, iron donates an electron to Cr (VI) and the reduction rate is proportional to the quantity of collisions of Cr (VI) ions with surface, i.e. proportional to Cr (VI) concentration. The Cr (VI) here refers to the chromate ion.

3.3 Modeling Cr (VI) Removal within PRB at Known Filtration Velocity

At a known filtration velocity, (u), through a barrier with thickness (d), Cr (VI) ion residence time is τ_{res} , is defined by:

$$\tau_{res} = \frac{d}{u} \quad [3.3.1]$$

This residence time for the barrier is analogous to the time, T , for the batch experiments. The difference between batch experiments and Cr (VI) removal by PRB is the hydrodynamic conditions and the influence of this difference with respect to reduction and passivation processes are negligible. Thus the chromium removal in batch experiments and within the PRB can be evaluated by the same set of equations using the same reaction constant K .

$$n = n_i e^{(-Kt)} \quad [3.3.2]$$

$$n_e = n_i e^{(-Kd/u)} \quad [3.3.3]$$

where n_i and n_e are the Cr (VI) influent and effluent concentrations.

3.4 Different Modes of Passivation Kinetics

The interplay between the effects of reduction rate decrease caused by passivation and corrosion, especially over the long-term has to be quantified. As chromium is reduced within the barrier, different modes of passivation kinetics take place (Figure 3.1(a)). Curve 1 corresponds to Mode 1 where high reduction rate preserves for longer duration time as compared to Mode 3. After this, reduction rate decreases rapidly to almost zero. The maximal amount of reduced chromium corresponding to instance at which reduction rate reduces is denoted by Curve 1 in Figure 3.1(b). The stage of rapid reduction for Curve 2 corresponding to Mode 2 coincides with that of Mode 1. The reduction continues even after maximal chromium mass accumulation as seen in Curve 2 of Figure 3.1(b). Curve 3 corresponds to Mode 3 where the stage of rapid reduction is short. Accumulation of chromium mainly occurs during this stage as seen from Curve 3 in Figure 3.1(b).

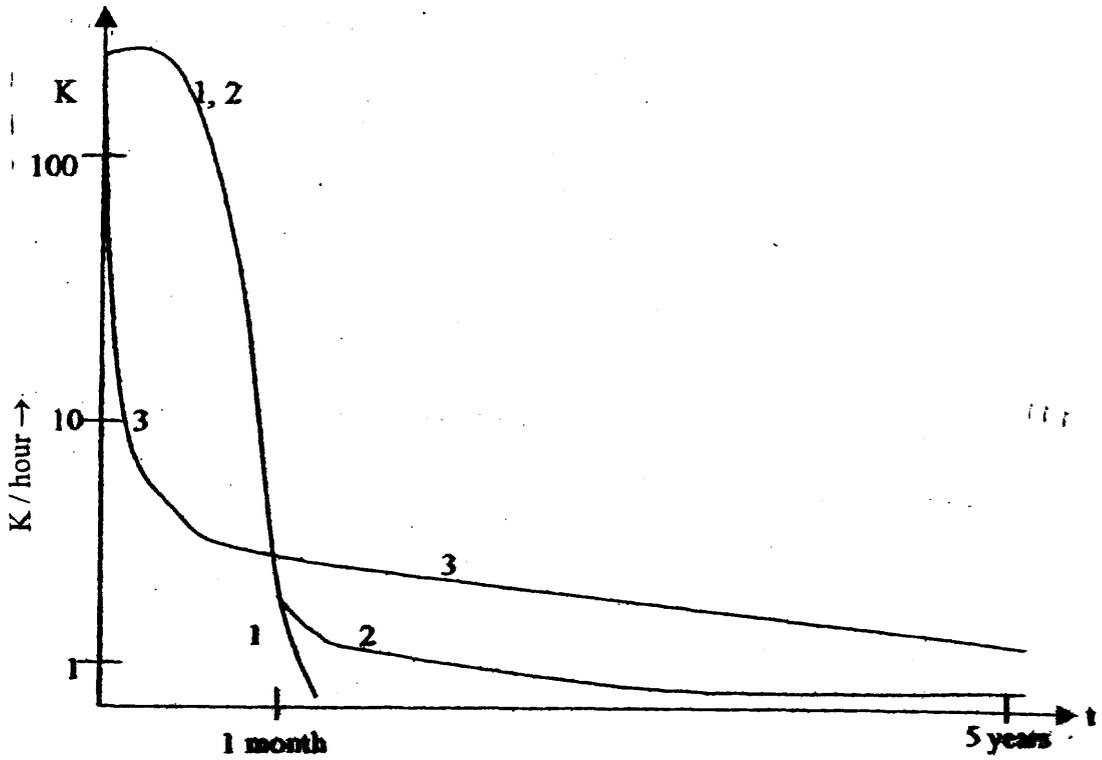


Figure 3.1 (a): Reduction Rate Coefficient Dependency on Time

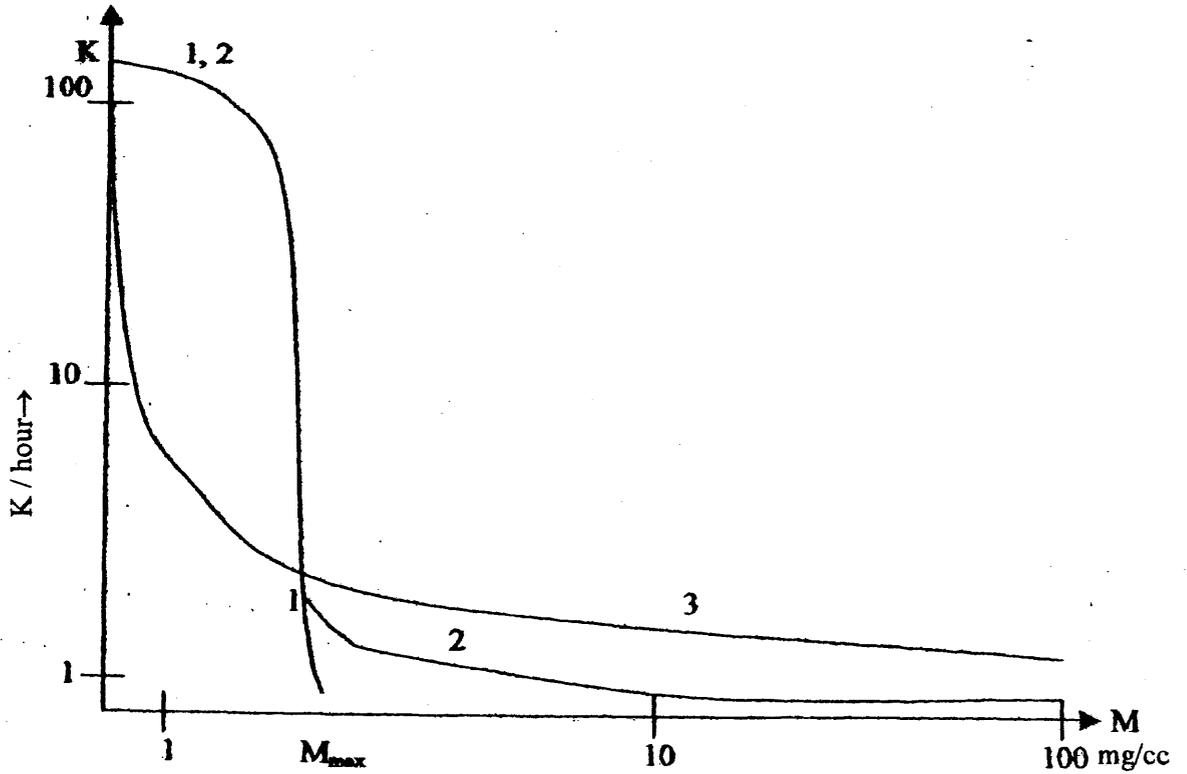


Figure 3.1 (b): Reduction Rate Coefficient Dependency on Chromium Accumulated

The prevailing mode of passivation will thus determine the prediction of barrier's performance. The measurement of the reaction rate constant, K , as shown together with the mass of chromium accumulated $M(t)$ as a function of time is calculated from the thin plug experiments. The development of passivation within the barrier is expected to yield different profiles of K as the mass of accumulated chromium increases in the barrier as shown in Figure 3.1(b).

The above approach is advantageous for the initial investigation of iron passivation accomplished in a short duration of time, i.e. if the first or second mode of passivation is the prevailing mechanism. For these two modes, the reduction will practically cease after the accumulation of maximal chromium amount, M_{\max} .

In the absence of passivation, prediction of the barrier performance is easily solved by the comparison of the residence time in barrier with the measured half-life time for chromate reduction. In contrast with this simple situation, the occurrence of passivation complicates the prediction of barrier performance because the accumulated chromium changes the reduction rate within the barrier. The barrier performance, in terms of chromium distribution at different times is illustrated in Figure 3.2 for the simplest mode of passivation kinetics.

For a simplified mode of reduction, the barrier can be characterized as composed of two parts. Near the barrier's front, there is a completely passivated iron layer, where the maximum chromium amount has already been accumulated and thus can be rendered unreactive, i.e. the chromium concentration in flowing groundwater does not decrease within this layer and remains same as the influent concentration. This means that at any moment of time, t , chromium reduction is provided by a barrier having a smaller

effective thickness $d_{be}(t) = d_b - l(t)$, where $l(t)$ is the thickness of the completely passivated layer which is a linear function of time.

If reduction does not stop such that the rate decreases in the barrier, because of the partial chromium accumulation, the situation of a completely passivated layer does not arise. This implies that a two-zone passivation kinetics model will not be valid for the third mode of passivation kinetics. In this case, the accumulated chromium mass will be maximal at the front section of the barrier, and then decreases in the direction of water flow near the back section of the barrier (Figure 3.3).

In the above case, the barrier can be viewed as consisting of a sequence of thin barriers having different reduction rates. This series will change as a function of time in such a way that their reduction rate will decrease according to an unknown time dependence behavior. The latter model seems to be more realistic than the previous ones.

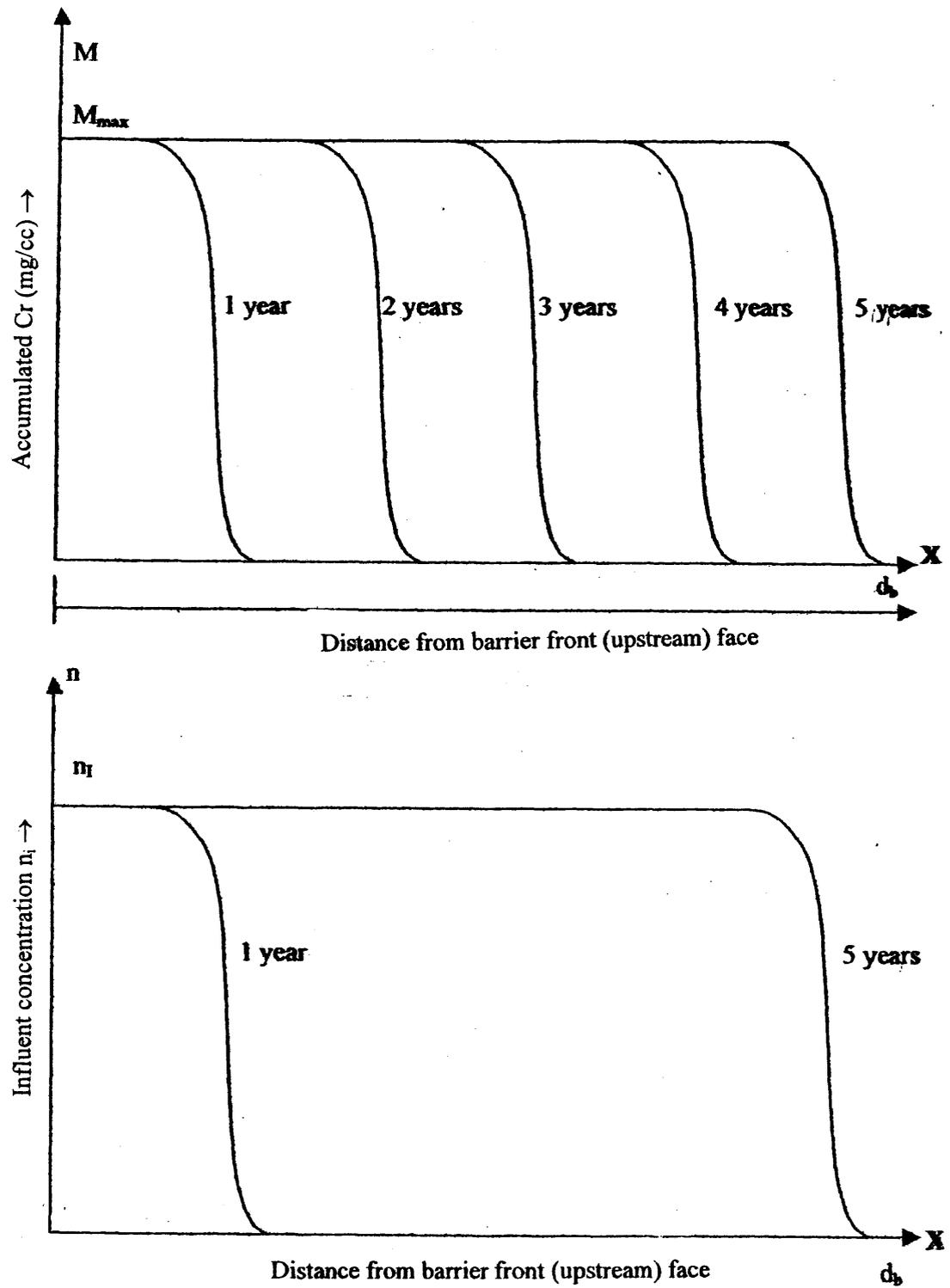


Figure 3.2: Schematic Illustration of Barrier Performance during Time in Years

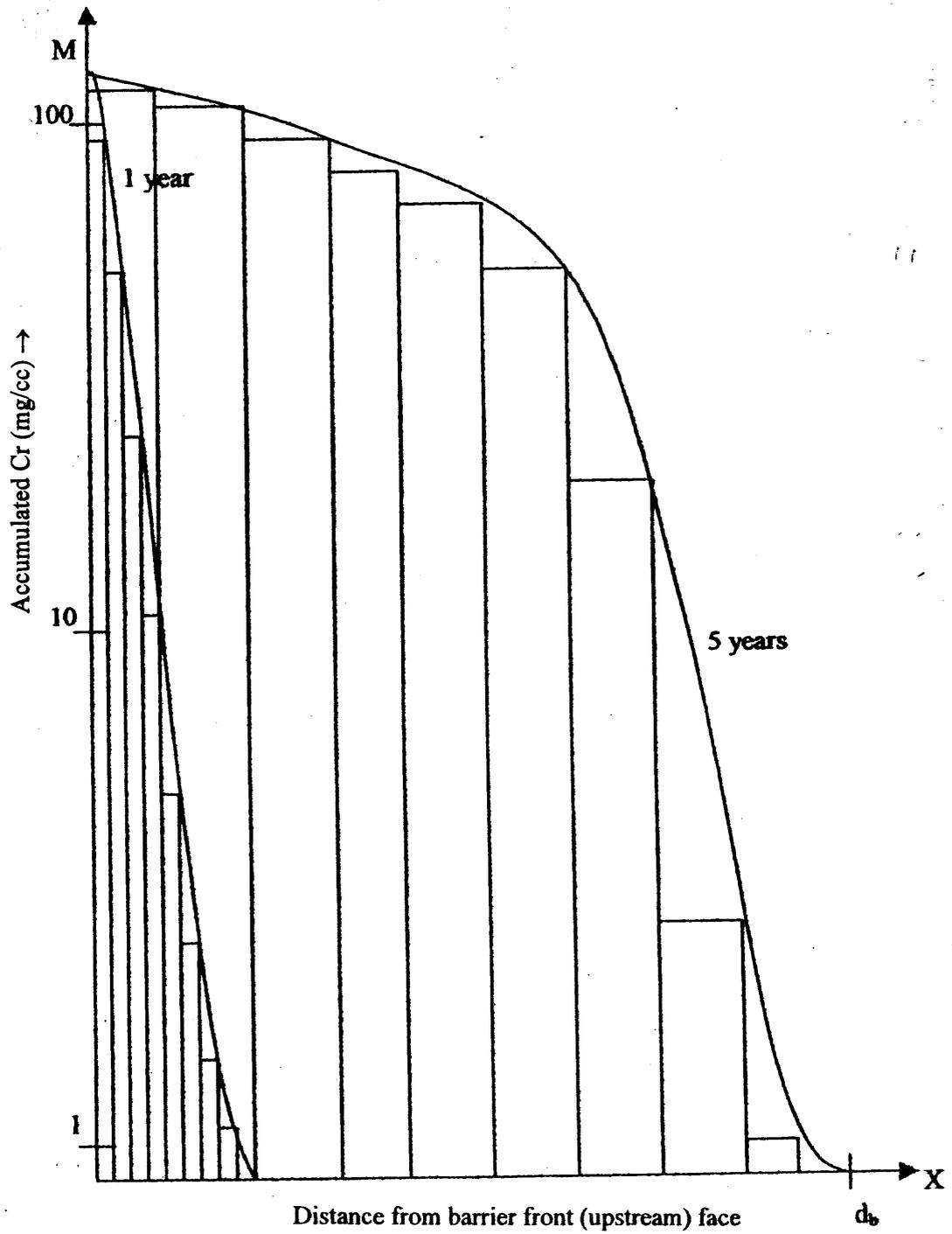


Figure 3.3: Schematic Distribution of Accumulated Reduced Chromium Distribution

3.5 Prediction of Chromium Distribution as a Function of Time

The reactive barrier properties are considered as invariant in time, the steady distribution of chromium accumulation can be of the form

$$n(x) = n_i e^{(-Kx/u)} \quad [3.5.1]$$

arises. Since there is a finite reactive medium capacity with respect to chromate reduction, a layer arises within the barrier consisting of completely passivated (or consumed) reactive media particles. Since the chromium reduction starts at the barrier's entrance a completely passivated layer (CPL) is formed near the entrance. The thickness of the layer $l(t)$ increases with time. Since there is no further reduction possible within the CPL, the chromium concentration would not decrease along this layer, and thus would be equal to that its value before entering the barrier. Thus, the chromium distribution within the reactive barrier can be characterized as consisting of two zones. The first zone will be having length $l(t)$ and the invariant initial concentration, n_i , and a second zone where the chromium concentration decreases from n_i to effluent concentration, n_e . Since the CPL is expanding with time, the rate of this expansion is very small compared to the ground water velocity

$$\frac{dl}{dt} \ll u \quad [3.5.2]$$

Typically, water crosses the entire length of the barrier in a period ranging from 1 to 10 days. When the CPL occupies the entire barrier, chromium leakage will become large, because the effluent concentration will be almost equal to the influent concentration. Therefore, to satisfy the long time requirement of the barrier the left-hand side of Equation [3.5.2] has to be larger than the right hand side by almost 100 to 1000 times.

The above prediction will enable us to formulate the chromate concentration decrease in the second zone of the barrier that is a quasi-steady state, i. e., the boundary condition relates to the mobile boundary,

$$n \Big|_{x=l(t)} = n_i \quad [3.5.3]$$

but its mobility is so low that it can be neglected. Correspondingly, the sought distribution follows Equation [3.5.1] taking into account that $l(t)$ has to be used instead of $x = 0$, gives:

$$n(x) = n_i \exp[-(x-l(t))K/u] \quad [3.5.4]$$

Therefore, CPL extends very slowly, and its extension rate is determined by the chromium transport into this zone. The chromium accumulation in CPL during a time, t , cannot exceed the total chromium amount entering into the barrier during this time. Moreover, it must be even smaller, because the second part of chromium present is second zone, and the third part penetrates the barrier (Figure 3.2).

We need to quantify the conditions needed for the efficient performance of the barrier, i.e., effluent flux must be small in comparison with influent flux. Thus their part can be neglected. As to the second part, let us restrict the consideration by the situation, when the CPL zone occupy the main part of the barrier after a long time, i. e., when

$$[d-l(t)] \ll d \quad [3.5.5]$$

In this case, the chromium amount in the second zone is very small in comparison with that in CPL and can be neglected. Keeping in mind these two conditions, the chromate conservation means, that all chromium is accumulated in CPL

$$n_i u t = l(t) M_{\max} \quad [3.5.6]$$

In this equation the units of n_i and M_{\max} are grams per unit volume. Thus the ratio

$$n = \frac{n_i}{M_{\max}} \quad [3.5.7]$$

is a dimensionless one.

It is easy to generalize Equation [3.5.6] with account for chromium accumulated in the second zone, when the restriction in Equation [3.5.5] is not satisfied. The condition of barrier efficient work is

$$l(T_b) \leq d \quad [3.5.8]$$

where T_b is the necessary time for efficient barrier work, or barrier effective life.

Naturally, the difference between $l(T_b)$ and d has to be not very small. But it can be rather small, that is clarified with the analysis of the condition, following from Equation [3.5.3]

$$\frac{n_e}{n_i} = \exp[-(d - l(T_b))K / u] \quad [3.5.9]$$

where $d - l(T_b)$ is the second zone thickness.

The specification of the condition for $K = 10 \text{ hour}^{-1}$, $d = 100 \text{ cm}$, $u = 100 \text{ cm/day}$ demonstrates, that the condition

$$d - l(T_b) \ll d \quad [3.5.10]$$

is satisfied due to very rapid reduction rate.

The prediction of chromium concentration within the zone

$$d - l(T_b) < x < d \quad [3.5.11]$$

needs further investigation, because the distribution [3.5.9] has to be considered, at first approximation, based on reduction rate identification with its initial value K . In the meantime, as the CPL grows the chromate-contaminated groundwater crosses the second

zone and chromium reduction causes a decrease in the reduction rate. This decreased reduction rate constant $K[M(x,t)]$ has to be used in the equation to be more exact, than the equation $dn = -Kndx$ and M value approaches to M_{\max} in small vicinity of the CPL edge, i.e.

$$0 < M(x) < M_{\max} \quad [3.5.12]$$

This means that $K(M)$ deviation from K is large near the CPL edge only. It enables to apply the method of sequent approximation. The second approximation is

$$\frac{n(x)}{n_i} = \exp[-z - (1 - e^{-z})] \quad [3.5.13]$$

where $z = K/u(x-l(t))$. The essential difference between first i.e. equation [3.5.9] and second Equation [3.5.13] approximations shows that further approximations are necessary. As a result, the zone becomes more wide which calls for using a correction to the evaluation of the second zone thickness.

3.6 Evaluation of Reactive Media Capacity for Thin Plug Passivation Kinetics

The effluent concentration for a thin reactive media plug is measured as a function of time in long term experiments at the definite values of linear groundwater velocity and at its initial chromate concentration. As the effluent concentration increases till value

$$n_e(T) \sim 0.1 n_i \quad [3.6.1]$$

the experiment continues at smaller velocity.

The total volume of liquid entered in the packed bed during time, T , is measured as $V(T_1)$.

The total chromium mass accumulated in permeable barrier equals

$$M(T_1) = n_i V(T_1) \quad [3.6.2]$$

It is assumed that this chromium amount is uniformly distributed within the packed bed with the volume

$$V_p = S_p d_p \quad [3.6.3]$$

Where S_p and d_p are the cross-sectional areas and width of permeable barriers respectively. The chromium amount accumulated with 1 cm³ of permeable barrier is thus:

$$C_{p1} = \frac{n_i V T_1}{S_p d_p} \quad [3.6.4]$$

The measured capacity corresponds to a definite value of linear velocity and initial concentration can be expressed by:

$$C_{p1} = C_{p1}(n_i, u_1) \quad [3.6.5]$$

3.7 Non Uniform Chromium Distribution across Thin Plug

The conventional procedure for the experiments was implemented and the experiments were performed with the condition that the effluent concentration is very small as compared to the influent one.

The opposite situation, i.e.

$$n_e \sim n_i$$

corresponds to the completely passivated plug. As the plug is passivated completely, i.e. the plug as a whole loses its ability to reduce chromium the equation mentioned above is valid. The opposite situation means, that at least the back part of the plug remains partially passivated and this part provides the reduction and the effluent concentration decreases. The non-uniform chromium accumulation within the plug, its decreased

concentration within back part of the plug shows that the notion of reactive media capacity needs some refinement with account for incomplete chromium accumulation.

3.8 Underevaluation of Reactive Media Capacity in Thin Plug

The conventional procedure was followed for carrying out the experiments with the condition that the effluent concentration is very small in comparison with the influent one. This procedure may lead to the underevaluation of the reactive media capacity due to the non-uniform chromium distribution. It is accepted that the reactive media within a barrier accumulates the maximum amount of chromium. This is a valid statement for the main part of a barrier volume with the exception that its smaller part is in the barrier back. A thin layer near the barrier end has to be clean. This is understandable because the chromium effluent concentration will be high, if the barrier as a whole accumulated the chromium amount equal to the reactive media capacity. If the barrier as a whole is strongly passivated then the effluent concentration is high.

Therefore we conclude that the determination of reactive media capacity in the thin plug experiment has to be accomplished in the conditions similar to chromium effluent concentration in the barrier during the years, namely near to plug maximal saturation with chromium. For illustration, let us assume that for one layer:

$$n_e \sim (0.5 - 0.9) n_i$$

for a thin plug and also let us consider that the barrier as a thin plug sequence i.e. 30-35 layers. The effluent concentration after the first layer corresponds to the above condition. But after 10 layers the effluent concentration will be

$$n_e \sim (0.5 - 0.9)^{10} n_i$$

if the degree of passivation is assumed to be same for the first 10 layers.

3.9 Critical Capacity for PRB for Three Sites in Hudson County

The comparison of measured value of reactive media capacity, M_{\max} , with the barrier critical capacity, C_{bcr} , would enable us to formulate the main criteria needed for evaluating reactive media needed for this application. The reactive media can provide the needed efficiency for a successful barrier application, if its capacity to reduce chromium exceeds critical barrier capacity. If this condition is not satisfied, the reactive media under investigation has to be rejected, and another reactive media with larger specific surface area or higher reactivity has to be investigated. The following equation characterizes barrier critical capacity, C_{bcr} .

$$n_i u_b T_b = C_{bcr} d_b$$

i.e. C_{bcr} is a function of barrier thickness d_b , the groundwater velocity u_b and influent concentration n_i .

The left-hand side of the equation yields the total chromium amount entering the barrier during a total period of time T_b . The right hand side shows the total amount of accumulated chromium in the barrier.

3.10 Prediction of Maximal Reactive Media Capacity

The determination of reactive media capacity by determining the maximal chromium amount M_{\max} can be accomplished in a short duration of time compared to barrier passivation time. This is accounted by the equation

$$n_i u_p T_{pcr} = M_{\max} d_p \quad [3.10.1]$$

where d_p is the iron plug thickness, u_p is the flow velocity through the plug, T_{pcr} characterizes the time when the effluent concentration n_e becomes equal to the influent concentration n_i .

To relate between T_{pcr} and the characteristics of the barrier and the chromium solution flow follows comparing the above two equations

$$T_{pcr} = \frac{u_b M_{\max} d_p}{u_p C_{bcr} d_b} \quad [3.10.2]$$

Taking into account that the cases when M_{\max} values equal to C_{bcr} , or larger, is interesting

$$M_{\max} \geq C_{bcr} \quad [3.10.3]$$

and considering that $u_p = u_b$ one obtains,

$$T_{pcr} \sim T_{bcr} \frac{d_p}{d_b} \quad [3.10.4]$$

where T_{bcr} is barrier lifetime and d_b is the barrier thickness.

The physical meaning of this result is very clear, namely the smaller the plug thickness, the smaller is its entire capacity and shorter time T_{pcr} after which the effluent concentration approaches the influent one. Thus, with $d_p = 2$ cm and $d_b = 100$ cm, T_{pcr} can be 50 times smaller than T_{bcr} , i.e. 2 months of plug performance would be equivalent to barrier's T_{bcr} equal to 8 years.

3.11 Number of Pore Volumes

The number of pore volumes in column experiment for reactive media should exceed that of the barrier ($NPV_{RM} \gg NPV_b$) for reactive media suitability at pH equal to 12. The number of pore volumes for the reactive media is calculated by the column experiments.

$$NPV_{RM} = \frac{v_{cr}}{S_c d_c p_c}$$

where NPV_{RM} is the number of pore volumes in column, S_c , d_c and p_c are cross-section area, thickness and porosity of reactive media, respectively.

CHAPTER 4

RESULTS AND DISCUSSION

This chapter presents and discusses the results pertaining to the study of reactive media selection for hexavalent chromium reduction in groundwater, especially at high pH conditions for use in permeable reactive barriers. The groundwater used in the study was obtained from three sites in Hudson County, New Jersey. This chapter discusses the following results:

1. Iron shaken packed bed and column experiments
2. Assessment of using iron (Fe^0) as a reactive medium at the high pH condition
3. Assessment of using pyrite mineral as a reactive medium at the high pH condition
4. Assessment of using iron (Fe^0)-pyrite and iron (Fe^0)-siderite mixtures as reactive media at the high pH condition
5. Influence of hydraulic loading on the reactive capacity of iron (Fe^0)
6. Two step passivation process and total capacity evaluation
7. Barrier critical thickness evaluation for three sites in Hudson county
8. Recommendations for critical barrier thickness and reactive media suitable for sites under investigation.

The main objectives of this study were:

1. To evaluate the suitability of various reactive media for barrier applications at high pH condition, and
2. To recommend application of suitable reactive media for long term performance of treatment of groundwater.

At the end of this chapter, recommendations are given regarding the selection of a reactive media and applicability of permeable reactive barrier technology for treating groundwater of chromium refining waste sites.

4.1 Shaken Packed Bed Experiment

Various types of buffering systems were studied for their acid generating capacities by Desai (38). According to this study (38), silicic acid generating minerals did not exhibit adequate lowering of pH to make them suitable for use as reactive medium. This was attributed to their low dissolution rates in groundwater as discussed by Stumm (8). Phosphoric acid generating materials showed considerable solubility and pH decrease of groundwater; however, these materials were deemed impractical for use in barriers because of their fast dissolution rates. The most promising reductive media among the materials investigated by Desai (38) were H₂S-generating minerals such as iron pyrite and carbonic acid generating minerals such as siderite.

Shaken packed bed experiments were carried out with the peerless iron materials at a residence time of 8 hours and initial chromium concentration of 16 ppm. The final chromate concentrations in the effluent were 0.05-0.1 ppm after 8 hours. The shaken packed bed experiments were accomplished for three peerless iron materials with different particle size distribution namely: Iron #1, Iron #2, Iron #3 (Table 2.2). Iron #3 showed the lowest final chromium concentrations at residence time of 30 minutes when used with groundwater having an initial chromium concentration of 55 ppm.

The reduction rate for Iron #3 at pH = 12 is smaller than that measured at intermediate pH (upto about 9.0). Desai (38) concluded that there is a similarity in pH dependence for chromate ion reduction rate with the use of Fe²⁺ containing solutions and

with the use of elemental iron (Fe^0) because the reduction rate in both cases decreases with increasing pH. In addition, the increase in iron corrosion at $\text{pH} > 12$ appears to be favorable for chromium reduction, as discussed below in Section 4.2.

4.2 Iron Regeneration as Reductant and Influence of Residence Time on Iron Capacity

Due to its large specific surface area, Iron #3 was used to study the reactive media capacity. The information about the deactivation kinetics was obtained by the multiple reuse of the same iron sample. After the first use, the iron was separated from the reduced groundwater. The pore volume of the same sample iron was then filled with groundwater for the second time and allowed to stand for a fixed residence time (8 hours). The number of pore volumes is used as a scaling factor to extrapolate column tests to barrier field time. Increase in effluent concentration starts after the entire volume of used portions of groundwater equals to about 10-12 pore volumes at initial chromium concentration of 16 ppm and residence time 8 hours (Figure 4.1). The reactive media stability is defined as the length of time (or NPV) where the reactive medium maintains its reactivity.

The effluent concentration for first or even second reuse is very small in comparison with the initial influent concentration of 16 ppm. This indicates that the chromium amounts accumulated on the iron particle surface are almost the same for the first and second reuses.

The deactivation of Iron #3 is stronger for short residence time than for longer residence time at the same amount of accumulated chromium. This difference in surface deactivation at the same chromium accumulation is caused by the regeneration of reactive iron surface. There is a longer time available for regeneration at longer residence times.

The regeneration mechanism (16) in this case appears to be related to corrosion whose role is important for chromate reduction. This was verified by varying the residence time for reuses #10 and #20 (shown by the arrows in Figure 4.1). During reuse #10 and #20, we increased the residence time that corresponded to more corrosion (regeneration) and thus resulting in lower effluent concentration.

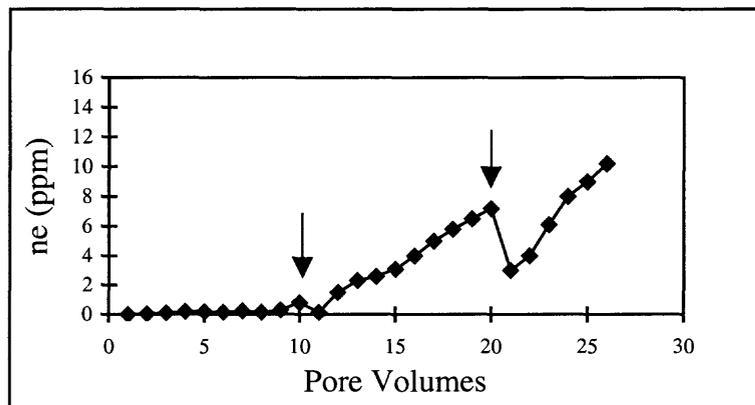


Figure 4.1: Result of Shaken Packed Bed Experiment
(Arrows indicate the increase in residence time for reuse #10 and #20)

4.3 Column Experiment

The effluent concentration for column experiment as a function of time is plotted for Iron #3 and for the initial chromium concentration of 55 ppm. The residence time at pore velocity of 0.3 cm/hour equals to 12 hours because reactive media thickness is 4 cm. At this longer residence time, the effluent concentration measured was 0.05 ppm. The increase in effluent concentration started after 10 pore volumes (Figure 4.2).

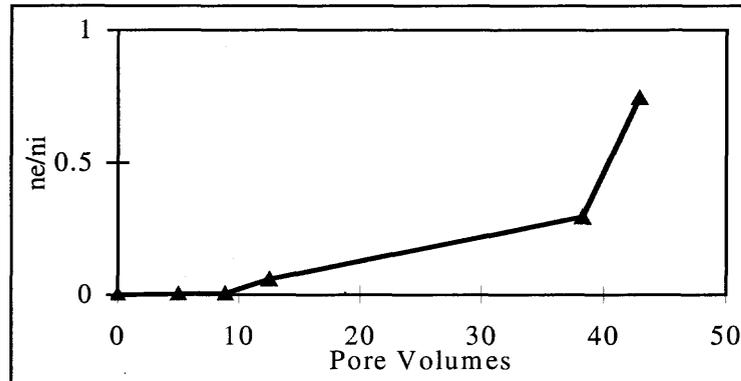


Figure 4.2: Growth of Effluent Concentration for Iron #3

4.4 Iron Assessment as Reactive Media for pH about 12

Iron (Fe^0) as a reactive medium has been used for chromate reduction at intermediate pH conditions. The estimation of iron (Fe^0) as a reactive media for pH about 12 was carried out in this research. When iron (Fe^0) is used as a reactive medium, the increase of chromium concentration in the effluent at $\text{pH} = 6$ to 7 occur at about 80 pore volumes. The latter was the result is of column investigations carried out at influent chromium concentration of 18 ppm and a pore velocity of 40m/year (16). This velocity is comparable to the velocity used in our experiments (Figure 4.2). The stability decrease at pH about 12 can be characterized as large if the difference in the initial concentrations is disregarded. However, because of the difference in the initial chromium concentrations between (16) and us, further analysis was needed as shown below.

This small difference in stability allows us to conclude that peerless Iron #3 as a reactive medium is not worse than the iron used in the important research for intermediate pH (16) and can also be used for further stability modeling at higher pH about 12.

The iron surface specificity does not seem to play a primary role as Sivavec and Horney (1995) (37) studied the degradation rates for chlorinated compounds with 25 types of different commercial iron sources. In addition, Agrawal and Tratnyek (1996) (35) and Matheson and Tratnyek (1994) (36) have found out that the primary determinant of degradation rates is the available specific surface area for reduction. Thus peerless Iron #3 provides the optimal condition because its surface area essentially exceeds the typical values of iron surface area given in literature. This means that the measured stability for Iron #3 can be used to assess of using Fe^0 as a reactive medium at pH about 12. 10 m/year is considered in (16) to be representative of pore velocity typically observed in shallow aquifers. For velocities not very large than this, the measured number of pore volumes is 10-30 is rather small compared to the 80 pore volumes at intermediate pH. These smaller values are due to the high influent chromium concentration of 55 ppm in our case. Therefore, we conclude that the iron (Fe^0) application at high pH will be limited to extreme cases of very low groundwater velocity (less than 10m/year) and to smaller chromium concentrations to achieve sufficient stability.

We conclude that a permeable reactive barrier with Iron #3 reactive medium may be suitable for treating groundwater in the case of Allied Signal site where the pore velocity is less than 10 m/year and chromium concentration is about 25 ppm. The use of iron (Fe^0) alone is not valid for the P.P.G and Chemical Land Holding sites and therefore other reactive media are required, as will be discussed in the following sections.

4.5 Iron Siderite Mixture

Iron (Fe^0) and Siderite (FeCO_3) were mixed at a volumetric ratio of 50/50 and used as reactive media. There is a two-stage process observed in our experiment as a function of

time (Figure 4.3). During the first stage, the effluent concentration values are less than the drinking water standards for chromium (0.1 ppm). The gradual increase of the effluent concentration takes place during the second stage. The chromium amount accumulated within 1 cm³ of reactive media during first stage can be called as the reactive media capacity, regarding chromium accumulation. Two long-term experiments were accomplished with iron (Fe⁰)-siderite mixture (ISM) 50/50 using Iron #2/Siderite and Iron #3/Siderite. The effluent concentration as a function of number of pore volumes is plotted in Figure 4.3.

The large influence of the velocity on NPV is seen in Figure 4.3. Iron #2/Siderite had a flow velocity of 26.5 cm/hr which is very high as compared to actual groundwater velocity, while Iron #3/Siderite had a velocity of 1.9 cm/hr. The results show that Iron #3/Siderite mixture is more effective than Iron #2/Siderite mixture. The advantage of ISM 50/50 at pH = 12 is apparent even at the higher influent chromium concentration of 55 ppm. However, the siderite application can be limited because of its high solubility in water. It may occur that siderite completely dissolve in groundwater stream during time shorter than 20-30 years which makes barrier useless for longer term application with this mixture. It is well known that water samples collected from some iron barriers approaches equilibrium with respect to siderite. Thus these barrier sites have to be classified into two groups namely with quasiequilibrium in the system groundwater siderite and one without quasiequilibrium. The ISM 50/50 is of primary interest in the first group of barrier sites with quasiequilibrium.

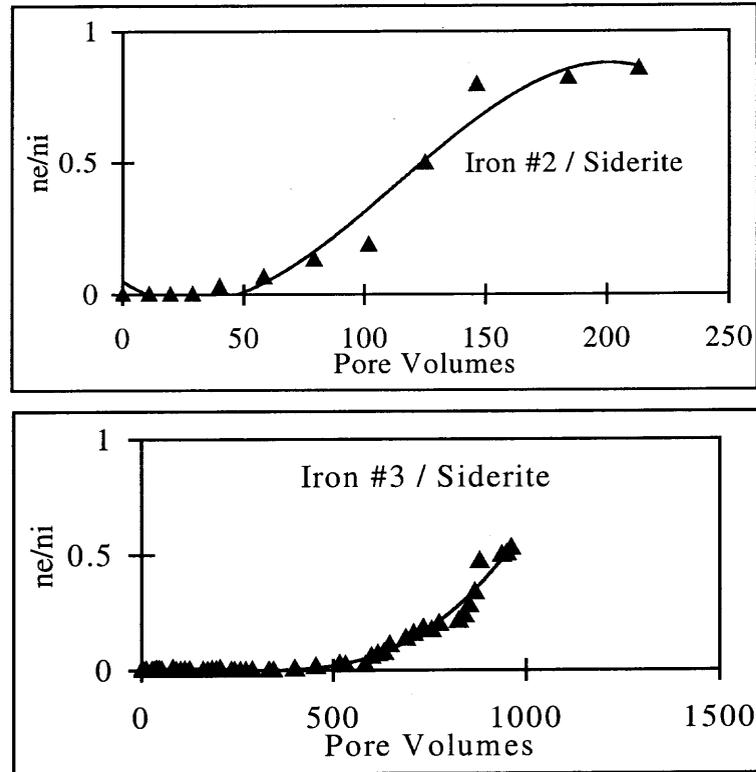


Figure 4.3: Results of Column Experiments with ISM Volumetric Ratio 50/50

4.6 Pyrite and Siderite Solubility and its Manifestation in PRB

The most important examination concerning the pyrite and siderite relates to their solubilities in water over the long term. It is possible that these minerals may dissolve in less than 20 years, which will limit the barrier service life. Handbook data (39) for the solubility of pyrite and siderite is given as:

a) Pyrite: $0.0005 \text{ g}/100 \text{ cm}^3$ (or $1 \text{ g}/2 \times 10^5 \text{ cm}^3$)

b) Siderite: $0.007 \text{ g}/\text{cm}^3$

For the complete dissolution of one gram of pyrite, the critical volume of water v_{cr} necessary is given by

$$v_{cr} = 2 \times 10^5 (\text{cm}^3 / \text{g}) \quad [4.6.1]$$

Let us consider a barrier cross section perpendicular to a stream with area, S and the pyrite volume in barrier, Sdp_p where d is the width of barrier and p_p is the pyrite volume fraction. During time, T_b , the groundwater volume (uT_bS) crosses the cross-section of the barrier, i.e. this volume is available to dissolve the pyrite volume with mass $Sd\rho p_p$ where ρ is the pyrite density. Thus the ratio:

$$v_b = \frac{uT_bS}{d\rho S p_p} = \frac{uT_b}{d\rho p_p} \left(\frac{cm^3}{g} \right) \quad [4.6.2]$$

where u (cm/day) and T_b (day) has to be compared with v_{cr} . With $d = 100$ cm and $T_b = 20$ years, the results are given in the table:

Table 4.1: Groundwater Volume per Gram of Reactive Media for 20 Years Barrier Life

$p_p \rightarrow$	0.5	1.0
u (cm/day) \downarrow		
100	3×10^4	1.5×10^4
10	3×10^3	1.5×10^3

Small pyrite volume fraction corresponds to the reactive media soil mixture with reactive media volume fraction 0.2. It can be seen that pyrite solubility within the barrier in this case is not negligible. Nevertheless, this complication may not arise because groundwater velocity is much smaller. Siderite solubility is five times larger. Siderite application in mixture with soil at large groundwater velocity is not reasonable for the sites of the second type, when equilibrium is absent.

4.7 Flow Rate Influence on Reduction and Accumulation of Chromium

The increase in flow rate of groundwater by approximately 10 times is accompanied by a decrease in reactive media capacity by 15-20 times i.e. $1mg/cm^3$ instead of

20mg/cm³. This can be interpreted if we account for the competition between two processes - passivation and regeneration. In parallel with Cr (III) accumulation on the iron particle surface, which decreases a part of surface available for reduction, an opposite process takes place, which regenerates the reduction ability of such surface. To illustrate these effects, the chromium reduction is accompanied with formation of a surface compound containing Fe³⁺. Beneath this compound, Fe⁰ is present which in turn reduces Fe³⁺ to Fe²⁺. The Fe²⁺ formation enhances the particle ability to reduce chromium because Fe²⁺ is an electron donor. Also, the simultaneous corrosion process occurring during the reaction is expected to be involved in the regeneration process.

The slower the reduction process, the stronger is the regeneration process. At higher Cr (VI) concentration, the reduction rate is higher and the rate of regeneration is lower and hence the latter cannot compete with reduction, i.e. the role of regeneration is minor in this case. At lower Cr (VI) concentration, the reduction rate is lower and the regeneration can compete with reduction i.e. the regeneration is significant.

Two types of iron (namely Iron #2 and Iron #3) were chosen since they achieved high reduction rates. The initial reduction rate of Iron # 2 was higher but the specific surface area for Iron #3 far exceeds that of Iron #2. Iron (Fe⁰)-siderite mixture experiments discussed above can be considered as a representative for the influence of flow rate on reduction and accumulation. The graphs in Figure 4.3 denote that Iron #2/Siderite mixture having flow rate of 26.5 cm/hr had rapid increase in increase in effluent concentration at 50 pore volumes because of higher velocity than that of field conditions. Iron #3/Siderite on the other hand with flow velocity of 1.9 cm/hr showed an increase in effluent concentration at about 550-600 pore volumes which clearly indicates

that higher velocity than field groundwater velocity is not favorable for chromate removal. Also, the accumulated chromium amount per cubic cm of reactive media denotes the flow rate influence on accumulation (Figure 4.4). The chromium accumulation for Iron #2/Siderite is 2 mg/cc while that for Iron #3/Siderite is 17-18 mg/cc which clearly demonstrates the influence of flow rate on chromium accumulation.

The increase in groundwater velocity thus causes the decrease in the number of pore volumes. The accelerated determination of reactive media capacity by means of its measurements at velocities exceeding that of the aquifer is therefore not admissible. This is because reactive media capacity decreases very rapidly with increasing the velocity, which will cause immense underevaluation of the reactive media capacity.

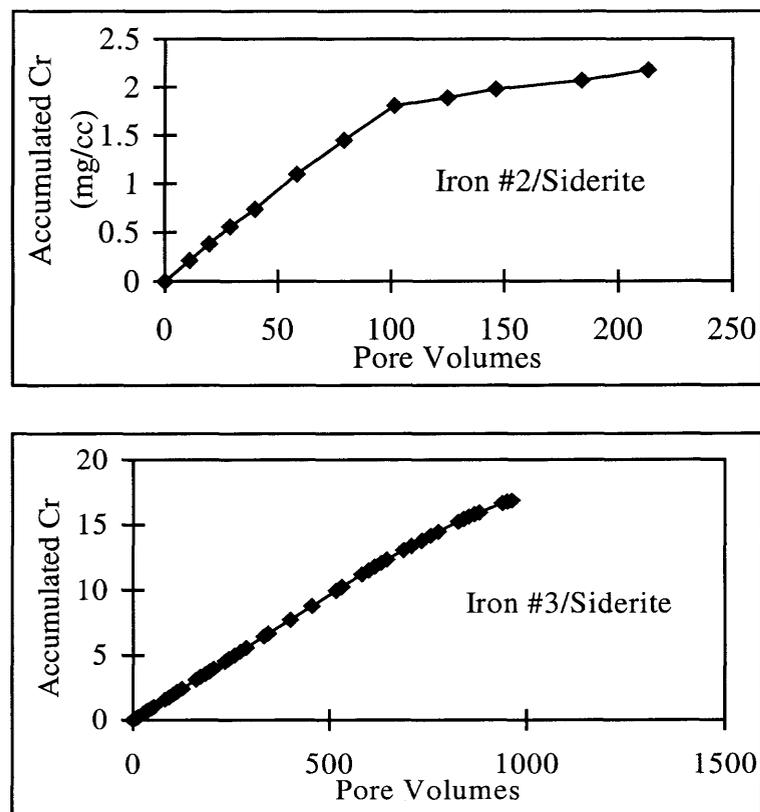


Figure 4.4: Flow Rate Influence on Chromium Accumulation

4.8 Two Step Passivation Process and Total Capacity Evaluation

The two step passivation process has to be discriminated in relation to kinetics of chromium accumulation. The first step is characterized with almost zero effluent concentration where the capacity of the reactive media is calculated in context of the number of pore volumes (NPV). The second step of passivation takes place with continuous increase in the effluent concentration and the reactive media capacity for this step of passivation of reactive media is calculated by the equation:

$$C_{RM} = \frac{M_{\max}}{V_{RM}} \quad [4.8.1]$$

where C_{RM} is reactive media capacity for the second mode of passivation, M_{\max} is the maximal accumulated chromium and V_{RM} is the volume of groundwater cleaned through the reactive media. The total capacity of reactive media is thus based on both first and second step of passivation kinetics.

4.9 Pyrite and Pyrite Sand Mixture

Column experiment with entire volume of pyrite equal to 25 cubic cm was conducted with initial groundwater chromium concentration of 55 ppm. The growth of effluent concentration with respect to time was observed for this reactive medium. The groundwater velocity passing through the column was maintained relatively near that of the actual groundwater velocity. The total chromium accumulation per cubic cm of reactive media was 21 mg/cc, which is the maximal capacity of the barrier for pyrite reactive medium.

Analysis of pyrite alone does not meet the active barrier life requirements so aquifer material sand was added to pyrite to see its effectiveness in treating contaminated groundwater. The addition of aquifer material leads to entire reduction rate decrease due to decrease of reactive media surface area (or volume fraction). Pyrite and sand were mixed together at a volumetric ratio of 30/70. The total chromium accumulation per cubic cm of reactive media was 25 mg/cm^3 , which is the maximal capacity of the barrier. The maximal capacity was calculated considering the volume of pyrite alone. This capacity was sufficient only for five years of active barrier life.

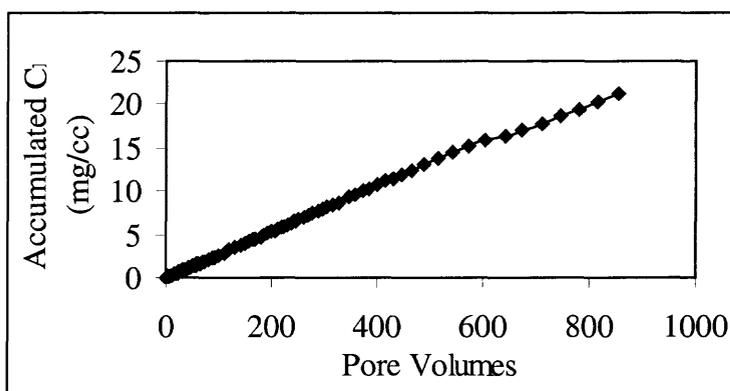


Figure 4.5: Accumulated Chromium for Pyrite Experiment

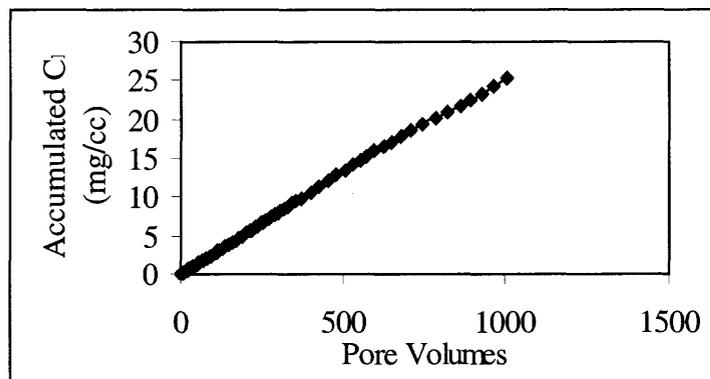


Figure 4.6: Accumulated Chromium for Pyrite Sand Experiment

4.10 Comparison of Iron (Fe^0) and Pyrite at pH about 12

The reactive media capacity of iron (Fe^0) alone at high pH is very low and has been found to be insufficient for use in permeable reactive barriers for two of the three sites. In addition, the reactive media capacities of pyrite alone were insufficient to provide the required barrier active lifetime (30 years). Therefore, a new approach for developing their mixture was investigated, as discussed below.

4.11 Iron (Fe^0)-Pyrite and Iron (Fe^0)-Pyrite-Sand Mixture

The passivation kinetics of iron (Fe^0)-pyrite mixtures (IPM) with and without aquifer material sand were studied. The iron (Fe^0)-pyrite mixtures were used in volumetric ratio of 50/50. The pyrite role is to decrease the pH caused by dissolution. As pyrite fraction in the mixture decreases, the useful pH decrease diminishes. Thus small amount of pyrite in the iron (Fe^0)-pyrite mixture is not favorable. On the other hand, chromium reduction occurs on iron particle surface so that small fraction of iron is not desirable.

The experimental results with iron (Fe^0)-pyrite and iron (Fe^0)-pyrite-sand (IPS) mixtures give us the required reactive media capacity that is sufficient for 20 years of active barrier life. The reactive media capacity of IPSM mixture 50/50 is greater than the required barrier capacities for all the sites. The amount of chromium accumulated per cubic cm of reactive media for iron (Fe^0)-pyrite-sand (IPS) and iron (Fe^0)-pyrite mixtures is shown in Figure 4.7 and Figure 4.8 respectively.

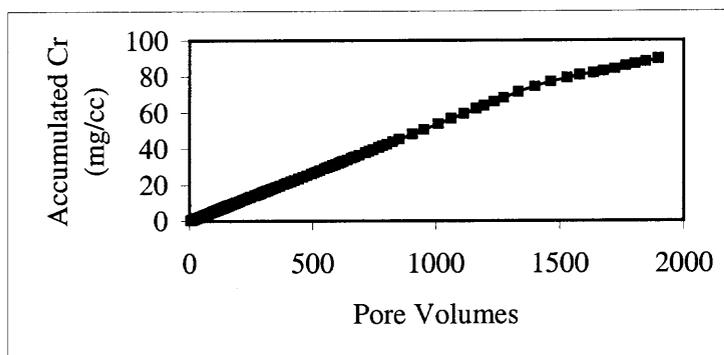


Figure 4.7: Accumulated Chromium for Iron (Fe^0)-Pyrite-Sand Experiment

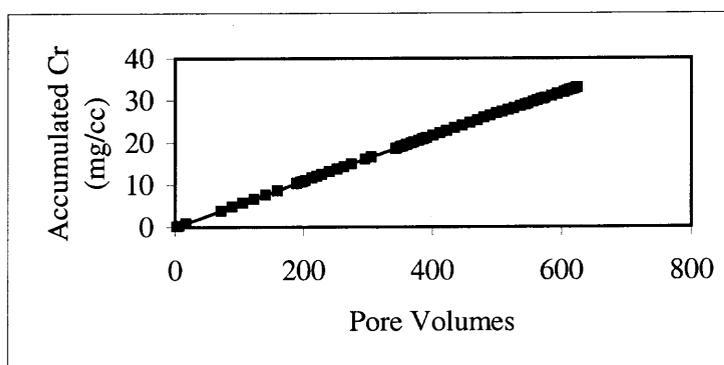


Figure 4.8: Accumulated Chromium for Iron (Fe^0)-Pyrite Experiment

4.12 Influence of pH

The influence of pH on treatment of groundwater was studied by comparing our results with those of Blowes et al (16). 80 pore volumes at intermediate pH were found by Blowes et al (16) shown in Figure 4.9. The same regularity is inherent in our experimental data with iron (Fe^0)-pyrite mixture (IPM) as a reductant. The iron (Fe^0)-pyrite mixture gave 2000 pore volumes with effluent less than the required EPA standards (Figure 4.9).

The results of these experiments show that even at high pH conditions, the iron (Fe^0)-pyrite mixture can be used as an effective reactive medium with significant stability sufficient for long barrier lifetime (more than 30 years).

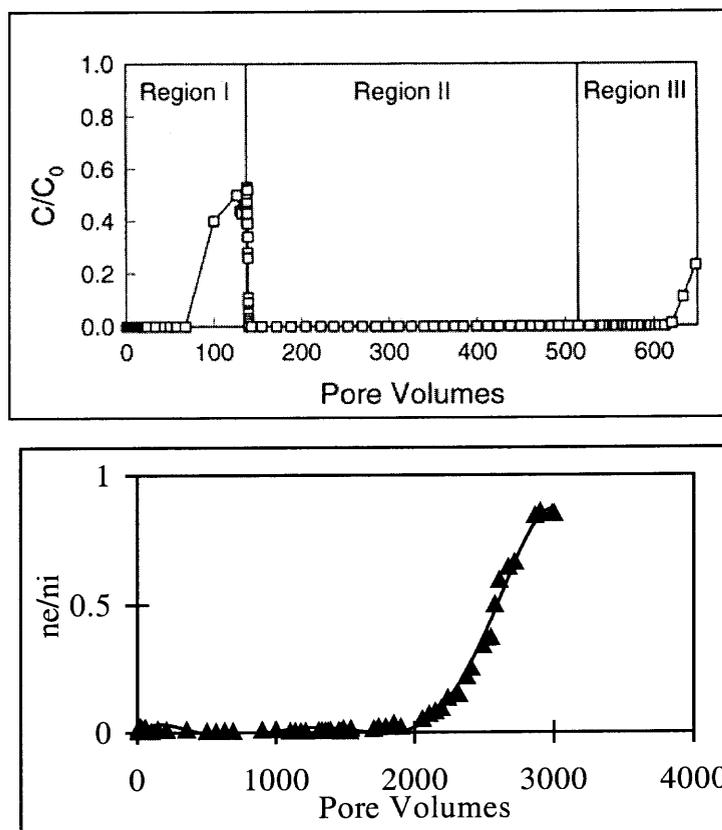


Figure 4.9: Comparison of Experimental Results at Neutral and High pH

4.13 Discussion of Results

The advantage of iron (Fe^0)-pyrite mixture for chromate removal at pH about 12 is interesting to discuss especially with respect to groundwater with high pH. The iron (Fe^0)-pyrite mixture gives better results than that of iron (Fe^0) alone as seen from results of the experiments conducted. The sodium sulfide/ferrous sulfate process is a well-known treatment technology for chromate reduction at neutral pH. The important feature of this process is that metal sulfides tend to be two to three magnitudes less soluble than

corresponding hydroxide. The neutral process developed by the US Air Force utilizes sulfide catalyzed by ferrous iron to reduce chromate and sulfide to precipitate heavy metals at pH 7.4-8.4. The sulfide stoichiometrically improves hexavalent chromium reduction and removal when added concurrently with ferrous iron. Under more alkaline conditions i.e. pH about 10, ferrous iron was found to react stoichiometrically, but sulfide addition contributed little and was not effective by itself. This does not contradict with our result, since the addition of pyrite to iron (Fe^0) at pH 12 results in the production of acid that compensate for acid consumption occurring during chromate reduction.

Iron (Fe^0)-pyrite mixture stability at pH about 12 with initial influent chromium concentration 16 ppm is about 2000 pore volumes at velocity of 54 m/year. This is 30 times better than iron (Fe^0) stability of 80 pore volumes at initial effluent concentration 18 ppm and velocity 40 m/year at intermediate pH (Figure 4.9). IPM mixture is therefore suitable for P.P.G and Chemical Land Holding with barrier life of 30 years, or more.

4.14 Prediction of Barrier Life Time

Our prediction of the active barrier lifetime will be done according to the two step passivation kinetics as discussed in Section 4.8. The equation for first step of passivation kinetics for barrier lifetime T_{bcr} is

$$T_{bcr} = NPV_{RM} \frac{d_b}{u_b} = \frac{C_{RM}(n_i, u_b)d_b}{p_c n_i u_b} \quad [4.14.1]$$

Universally accepted Equation [4.14.1] mentioned above underevaluates a barrier lifetime because the total capacity of reactive media is not accounted for. This underevaluation occurs, because the Equation [4.14.1] is derived in context of NPV and NPV notion is not generalized to account second step of accumulation.

$$T_{bcr}^{tot} = \frac{C_{RM}(n_i, u_b)d_b}{p_c n_i u_b} \quad [4.14.2]$$

The generalized Equation [4.14.2] for barrier lifetime is derived with respect to the proposed model of chromium accumulation in barrier space.

4.15 Barrier Critical Thickness Evaluation for Sites of Hudson County, New Jersey

The reactive media capacities for iron (Fe^0), pyrite, and iron (Fe^0)-pyrite mixture with and without addition of aquifer materials (sand) are evaluated. The barrier critical thickness d_{bcr} should be:

$$d_{bcr} \leq \frac{n_i u_b T_b}{C_{RM}^{tot}} \quad [4.15.1]$$

where n_i is the influent chromium concentration in ppm, u_b is the velocity of groundwater flowing through the barrier in cm/day, T_b is the time for barrier lifetime and C_{RM}^{tot} is the total reactive media capacity for the two modes of passivation kinetics.

4.16 Recommendations for Sites under Investigation

We will now formulate our results in form of recommendations for various sites with respect to the reactive media to be used for treatment as well as the critical barrier thickness needed for achieving the 30 years of active barrier life (Table 4.2).

Table 4.2: Recommendations for Barrier Thickness and Reactive Media for Sites

Site Name	Initial Chromium Concentration	Barrier Thickness	Reactive Media Recommended
Allied Signal	25 ppm	100 cm	Iron(Fe^0)-Sand mixture
P.P.G	16 ppm	100 cm	Iron(Fe^0)-Pyrite-Sand mixture
Chemical Land Holding	55 ppm	300-400 cm	Iron(Fe^0)-Pyrite-Sand mixture

CHAPTER 5

SUMMARY AND RECOMMENDATIONS

The results of this research can be summarized as follows:

1. H₂S-generating minerals such as pyrite and carbonic acid generating minerals were found out to be the most promising reductive media among the materials investigated during our studies.
2. Assessment of iron (Fe⁰) was done in the shaken packed bed and column experiments to assess its suitability for its use as a reactive media for treatment of chromium-contaminated sites at high pH conditions. Shaken packed bed experiments carried out with peerless iron showed that the reduction rate decreases with increasing pH. Different types of peerless iron according with different particle size distribution were analyzed to estimate their kinetics. Iron #3 showed considerable reduction capacity to be used for stability modeling at higher pH about 12.
3. Assessment of siderite mineral mixed with aquifer material sand was done for two peerless iron types (Iron #2 and Iron #3) and their reactivity was measured. The influence of groundwater velocity on the number of pore volumes was analyzed. Chromium accumulation was investigated and proved that the chromium accumulation per cubic cm of reactive media is less at high flow rates. Solubility of siderite and its manifestation in permeable reactive barriers was evaluated; its application with mixture in soil at high groundwater velocities is not reasonable.
4. Pyrite mineral was assessed as a reactive medium with and without aquifer material sand for use in permeable reactive barriers. The total chromium accumulation with the initial groundwater influent concentration 55 ppm was found to be insufficient for 20

years of active barrier life. Therefore, a mixture of iron (Fe^0)-pyrite was investigated and found to be satisfactory.

5. Passivation kinetics of iron (Fe^0)-pyrite mixtures with volumetric ratio 50/50 was studied. Two long-term experiments, one with iron (Fe^0)-pyrite and other with iron (Fe^0)-pyrite-sand mixtures were carried out to determine their reactive media capacities. The results showed that the latter gave capacity sufficient for 20 years of active barrier life.

6. Our results showed that iron (Fe^0)-pyrite mixture stability at high pH was almost 30 times better than at intermediate pH.

Based on the foregoing results, it appears that iron (Fe^0)-pyrite-sand mixtures can be considered as a viable reactive media for treatment of chromium-contaminated sites at high pH. Recommendations are given for three sites of Hudson County, New Jersey for their reactive media and barrier critical thickness.

Future investigation depending on hydraulic conductivity of soil should be carried out to avoid effects of bypassing of contaminated plume of groundwater to be treated. Novel barrier designs for high flow rates and high concentrations need to be developed for the high pH groundwater cases.

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