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ABSTRACT

STUDY OF REACTIVE MEDIA FOR CHROMIUM REMOVAL FROM GROUNDWATER BY PERMEABLE BARRIERS

by
Hemant S. Desai

The purpose of the study was to select reduction media for application in permeable barriers for removing chromate ions from groundwater emanating from chromium refining sites in New Jersey. The high pH condition of groundwater in such sites is expected to pose limitations on the use of metallic iron (Fe^0) as the sole reductive medium.

Reasonable reduction kinetics was achieved using iron at $\text{pH} < 9.2$. Several pH lowering media were investigated and were found to have either very slow or very fast dissolution kinetics, which rendered them impractical for use in passive permeable barriers. Two other media, namely: pyrite and siderite minerals have shown promising results, but fell short of achieving the required performance. Detailed investigation of interfacial processes in a batch reactor have shown that the addition of a small amount of a neutral salt can significantly improve chromate reduction kinetics, even at high pH conditions around 10.9.

The formation of passivating layers, which can slowdown the reaction significantly, was found to be important at high pH conditions. It is recommended that an injection system be used with the reactive barrier to insure that the pH and salt conditions are adequate to achieving the needed reaction rates while preventing the formation of passivating layers during this long-term application.

**STUDY OF REACTIVE MEDIA FOR CHROMIUM REMOVAL
FROM GROUNDWATER BY PERMEABLE BARRIERS**

by
Hemant S. Desai

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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 Chemical Engineering**

Department of Chemical Engineering, Chemistry and Environmental Science

May 1999

APPROVAL PAGE

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This thesis is dedicated to
my loving parents.

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CHAPTER 1

INTRODUCTION

1.1 History and Source of Heavy Metal Contamination

Industrial activities during the first half of this century resulted in a large scale environmental contamination with heavy metals, especially in the United States. The lack of strict environmental regulations during this period accounts for the majority of existing heavy metal contamination, which is persisting till today. Treatment technologies are therefore needed to remediate waste sites contaminated with heavy metals (1).

Toxic heavy metals in the environment include: cadmium, chromium, lead, nickel, arsenic, zinc and selenium. Major industries that utilize heavy metals in their production processes are listed in Table 1.1(2). Many heavy metals are known to have long-term consequences on human health (2, 3, 4). The acceptable concentration limits for heavy metals in water according to the Federal Water Pollution Control Administration are shown in Table 1.2 (2). Heavy metals' toxicology tolerance levels in animals and humans are given in Table 1.3 (2).

Table 1.1: Source of Heavy Metals Employed in Various Industries (2)

	Zn	Cd	Cr	Cu	Fe	Hg	Pb	Ni	Sn
Organic Chemicals.	X	X	X		X	X	X		X
Fertilizers.	X	X	X	X	X	X	X	X	
Petroleum Refining.	X	X	X	X	X		X	X	
Foundries.	X	X	X	X	X	X	X	X	X
Automobiles.		X	X	X		X		X	
Paper and Pulp.	X		X	X		X	X	X	
Textiles		X							

Table 1.2: Control Limits on the Concentrations of Heavy Metals in Water (2)

	Limit ($\mu\text{g/lit}$)
Arsenic	50
Cadmium	10
Chromium	50
Copper	1000
Iron	300
Lead	50
Manganese	50
Silver	50
Zinc	5000

Table 1.3: Toxicology Tolerance Levels in Animals and Man (2)

	Fish	Mammal	Man
Cr (VI)	0.015 - 0.195 mg / lit	0.45-11 mg / l	0.5-5 g / kg
Fe	0.9 – 152 mg / lit	0.5 – 5 g / kg	0.5 – 5 g / kg
Cd	3 mg / lit	0.07 – 1.5 g / kg	50 – 500 mg / kg
H ₃ BO ₄	1 – 10 g / lit	1 – 5.1 g / kg	5 - 20 g
Co	0.01 – 0.1 mg / lit	0.7 – 1.5 g / kg	50 – 500 mg / kg
As	1 – 23 mg / lit	2 – 15 mg / kg	2 mg / kg
Cu	0.03 – 0.8 mg / lit	8 gm	8 gm
Se - compds	2 – 10.5 mg / lit	5 – 10 mg / lit	0.01 mg / lit

In this research, we are concerned with the treatment of groundwater contaminated with hexavalent chromium, especially for the case of chromium refining waste sites in New Jersey. In order to address this topic, background of the causes of such contamination is given below. This background includes a description of the chromium refining processes that were used in New Jersey, and shows how this heavy metal

contamination took place. Most of the chromium contaminated sites in New Jersey are the result of chromium refining operations, especially in Hudson County.

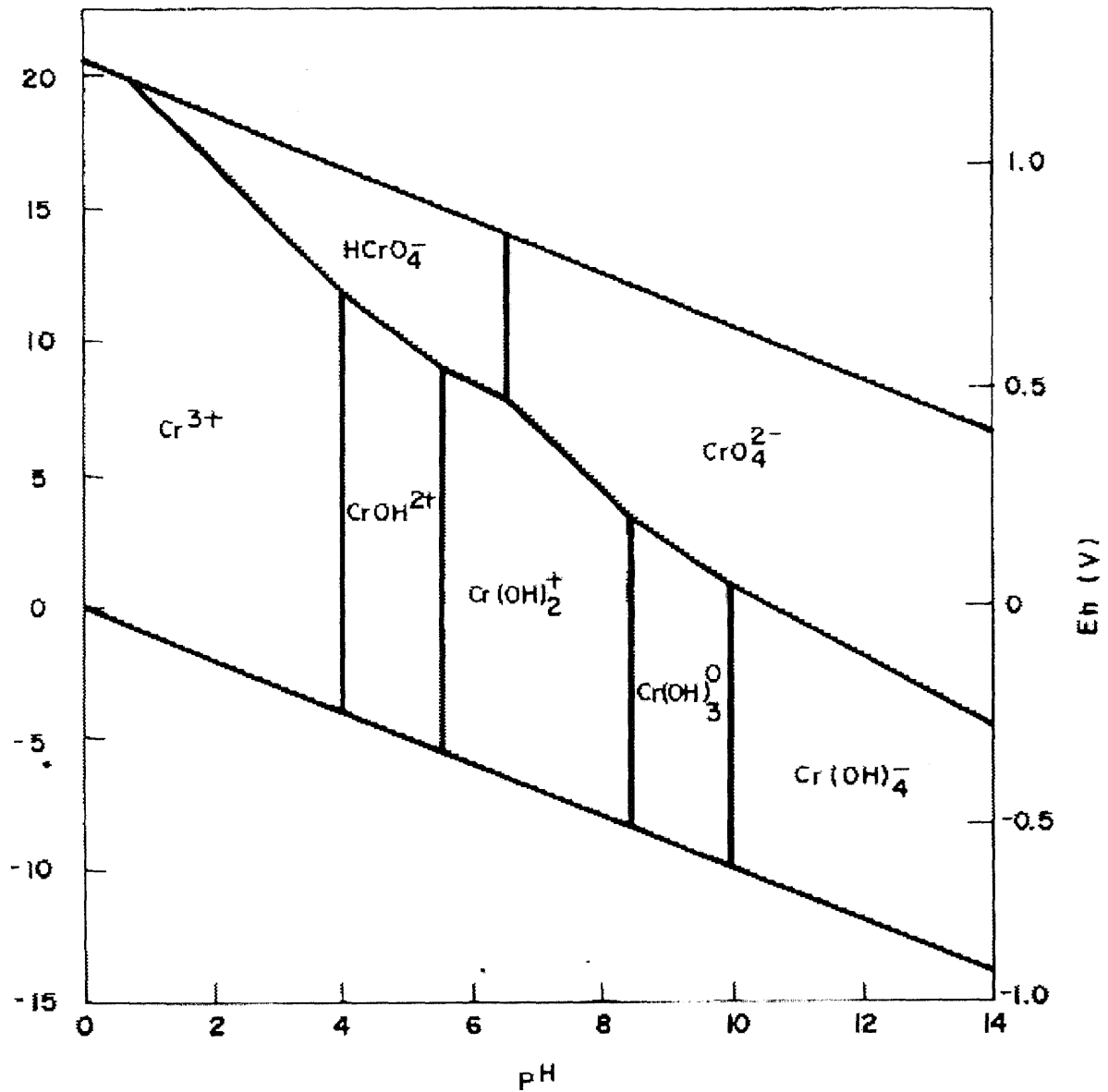
Chromium is present in nature as chromite ore with a nominal composition: $\text{FeO} \cdot \text{Cr}_2\text{O}_3$. The Cr:Fe ratio varies considerably based on the source of the ore. Since the actual ore always contains other elements, the formula of chromite is better represented as $(\text{Fe, Mg})\text{O} \cdot (\text{Cr, Fe, Al})_2\text{O}_3$ (5). Table 1.4 provides a classification of the commonly found chromite ores in nature.

Table 1.4: Classification of Chromite Ores (2)

Class	Geologic Deposit Type	Cr₂O₃ Composition wt %	Cr: Fe Ratio	Principle Use
High chromium	Podiform, Stratiform	46 – 55	> 2 : 1	Metallurgy
High Iron	Stratiform	40 – 46	1.5 – 2 : 1	Metallurgy, Chemistry
High Aluminum	Podiform	33 – 38	2 – 2.5 : 1	Refractory

Chromium present in chromite ore is in the trivalent state, Cr (III). The other most common form of chromium in nature is hexavalent Cr (VI). The ratio of the two valence states (CrIII/CrVI) in any physical system, or in nature, depends mostly on the oxidation potential and the pH of the environment. Hexavalent species are stable in an oxidizing atmosphere, while trivalent species dominate in the reducing environment (3). The various chromium species present under different pH and Eh conditions are best described by the Pourbaix-type diagram, as shown in Figure 1.1 (3).

Figure 1.1: Pourbaix-type Diagram showing the Areas of Dominance of Various Species of Chromium (3).



1.2 Industrial Applications of Chromium

Chromium is used in many industrial applications. In 1992, the combined production of chromate and dichromate salts was about 250,000 tons (6). The two largest sources of chromium contamination are: chemical industries and combustion of natural gas, oil and coal (3, 6). Chromium and its compounds are used in electroplating, metal alloys such as

stainless steel, protective coatings, pigments in paints and in the production of other materials. Other uses include chemical intermediates in wood preservatives, organic chemical synthesis, photochemical processing and industrial water treatment. Chromium compounds are also used in leather tanning, catalytic manufacturing and industrial-cooling water systems - as a corrosion inhibitor. In many of the above applications, chromium needs to be in the hexavalent state (3, 7, 8). To supply chromium for the industry, refining operations have been established in many parts of the world.

1.3 Sources of Chromium Contamination

The chromium refining process is based on converting Cr (III) of the chromite ore to the soluble hexavalent form. This process is accomplished by the roasting of chromite ore in the presence of soda ash, lime and air at about 1100-1150 °C, and thereby converting trivalent chromium to the water-soluble chromate form - i.e., Cr (VI). The yield of this production process is usually between 65% to 85 % - based on the chromium content of the ore (9, 10). The residue generated from this refining process contains both forms of chromium - Cr (III) and Cr (VI). This residue, which needs to be disposed off after the extraction of soluble chromate, is alkaline in nature since lime and soda ash are used in the production process. Early in this century, such residue was disposed off in sites nearby production facilities. The ratio of Cr (III) to Cr (VI) in refining waste sites is known to vary, depending on the original nature of the residue, pH and other transformation that may have taken place since landfilling. (11, 12, 13).

Recently, soluble Cr (VI) species generated from these landfills have been found to significantly contaminate groundwater in their vicinity (8). Also, hexavalent chromium-containing particulates generated by industrial cooling towers, municipal

waste incinerators, cement industry and other sources have been known to cause lung cancer in humans. Therefore hexavalent chromium is considered to be the most important heavy metal posing threat to the environment and public health. According to the Toxics Release Inventory, chromium compounds released to land and water was nearly 200 million pounds from 1987 to 1993 (6).

1.4 Health Hazards Caused by Chromium

Chromium enters the human body via three main pathways: inhalation, diffusion through skin and ingestion. When Cr (VI)-containing particulates are inhaled, they tend to deposit in the lung where they are linked to many incidents of lung cancer. Hexavalent chromium compounds are also known to cause acute injuries to the nasal tissue resulting in mucosal irritation, ulceration and nasal septal perforation.

Chromium is documented as the second most common skin allergen after nickel (3). Skin contact with high concentrations of chromium over prolonged periods is known to cause hypersensitivity. It is also known that hexavalent chromium compounds can penetrate the skin more readily than the trivalent compounds. The most commonly affected areas are wrists, fingers and the backs and sides of hands.

Chromium can be absorbed into the body via the digestive system. Chromium is known to cause damage to liver and to kidney circulatory system. Hexavalent chromium was found to damage human DNA, which is known to lead to cytotoxicity, mutagenicity and carcinogenicity (3). The latter effect is specially relevant to the case of inhalation of hexavalent chromium-containing particulates, and to the incidents of lung cancer in humans (3).

1.5 Regulatory Standards for Chromium

The above stated hazards have forced the authorities concerned with the environmental and health standards to set regulatory limits on the presence of chromium compounds in the environment. The Occupational Safety and Health Administration (OSHA) has established workplace permissible exposure limits (PEL) in air for chromic acid and chromates at $0.1\text{mg}/\text{m}^3$ on an 8-hour time-weighted average (TWA). Chromium metal and other soluble chromium salts have a 8-hour TWA PEL of $1\text{mg}/\text{m}^3$ Cr. NIOSH recommends an exposure limit of $1\text{ micro-g}/\text{m}^3$ for carcinogenic hexavalent chromium compounds while the limits are $25\text{ micro-g}/\text{m}^3$ for non-carcinogenic chromium compounds. The latter limits are on a 10-hour TWA (4). The USEPA has set the Maximum Contaminant Level Goals (MCLG) for chromium at 0.1 ppm in drinking water. It should be noted that these standards are based on total chromium concentration (6). Also the USEPA has established for lifetime exposure an (acceptable intake chronic (AIC)) of $103\text{mg}/\text{day}$ Cr(III) and $0.35\text{ mg}/\text{day}$ Cr(VI) for ingestion. USEPA has also calculated the inhalation cancer potency for Cr(VI) of $42[\text{mg}/(\text{kg}\cdot\text{d})]^{-1}$ risk for a lifetime exposure to $1\text{ micro-g}/\text{m}^3$ hexavalent chromium (4, 5).

1.6 Various Environmental Treatment Technologies

This section provides a brief description of some possible remediation technologies that can be applied to chromium contamination. The technologies discussed in this section include: stabilization, in-situ vitrification, in-situ soil flushing for soil treatment, and pump-and-treat and reactive permeable barriers for groundwater treatment (14).

Stabilization reduces mobility of hazardous contaminants by trapping/immobilizing the contaminants within a host medium (like cement) instead of

removing them by chemical or physical treatments. Some attempts were used to stabilize hexavalent chromium in cement matrices. This process involves the reduction of Cr(VI) with a ferrous ion followed by forming the cement matrix. These attempts were never used in large-scale applications because of the uncertainty of their long-term effectiveness.

In-situ vitrification involves the use of electric current to generate extremely high temperatures in the range of 1600°C to 3600°C to melt and immobilize the contaminants. The products of this vitrification process include water vapor and organic pyrolysis combustion products. The latter are released to the atmosphere after passing them through an off-gas treatment system. This process was found to be expensive for large-scale implementation.

In-situ flushing involves the extraction of contaminants from the soil with an aqueous solution. It is normally accomplished by passing an extraction fluid through in-place soils using an injection system. The extraction fluids must be recovered from the underlying aquifer and recycled, if possible. Another technique that is known to remediate chromate contaminated soil is Electrokinetics. In this technology, the contaminated plume is placed between the positive and negative electrodes of a power supply and the chromate ion is extracted near the anode. Although this technology is simple in principle, it is difficult to apply in the field.

For groundwater treatment, the two commonly used technologies are the pump-and-treat and permeable reactive barriers. The pump-and-treat method involves pumping the groundwater to the surface for treatment followed by back injection into the aquifer. Although this method is effective in the case of chromium, it is costly for large-scale applications requiring close supervision and maintenance over a long period of time.

Permeable reactive barrier technology is considered a viable option for remediating chromium contaminated sites. This technology is being considered for application in New Jersey, and is discussed in details in the next section.

1.7 Permeable Reactive Barrier Technology

This technology has recently been proposed for remediating groundwater in contaminated waste sites. It involves placing a porous reactive wall in the path of the groundwater flow. The contaminants in groundwater react with the reactive media as they pass through the barrier and are transformed into harmless precipitates within such a barrier (15, 16). The barrier, being passive, does not require any power or maintenance for a long period of time, possibly years. The investment in the application of this technology is therefore limited to the cost of placing the barrier and the procurement of suitable reactive media (materials). The application of this technology requires a thorough knowledge of the reactivity of reactive media in the barriers with the specific contaminant present in the groundwater. The effectiveness of the reaction determines the service life of the barrier (17).

A combination of chemical processes can be used to achieve the desired treatment by properly selecting the reactive media. In general, treatment processes taking place in the barrier may be based on the principles of bioremediation (18), sorption (18, 19) and redox reactions (20, 21, 22, 23, 24). The permeable reactive barriers studied in this research are based on the principles of redox reactions. The hazardous component in groundwater (Cr(VI)) reacts with the barrier medium which is mostly reductive material. The contaminant, Cr(VI), forms a half-cell reaction while the barrier material forms the opposite half-cell reaction, where both complete the circuit for a redox electrochemical

cell. The processes in the barrier, thus remove the contaminants from the groundwater and render it harmless to the environment.

Care should be taken so that the barrier would have the same permeability characteristics as the surrounding soil in which it has been erected. This would ensure that the groundwater will pass through the barrier without bypassing it. Also, precautions have to be taken so that the barrier is free of clogging due to the formation of precipitates during the reaction, or due to deposition of colloidal materials in groundwater, which could reduce the permeability of the barrier.

1.8 Selection of Reactive Material for Permeable Barrier Applications

For successful applications, the following conditions need to be satisfied for permeable reactive barriers :

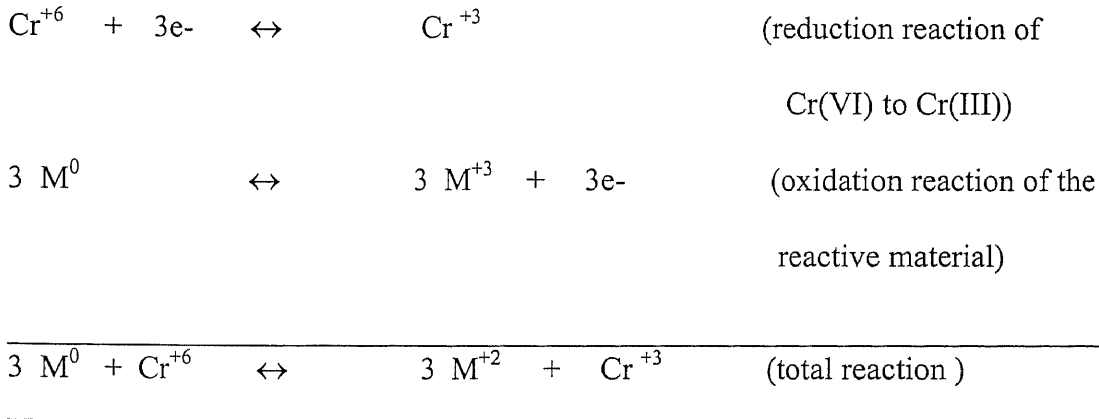
1. Reaction must result in a complete removal of contaminant from groundwater.
2. Reaction rates must be high enough to achieve a complete reduction of contaminant for a given residence time in the barrier. The residence time is a function of the groundwater flowrate.
3. Reaction products or precipitates should not clog the barrier during its service life; These products should not affect groundwater flow parameters of the site.
4. Optimal performance of the barrier must be long (service life should be in years).
5. Cost of reactive media must be reasonable.
6. Placement cost of the barrier must be reasonable.

A key parameter regarding the use of reactive permeable barriers for treating groundwater contaminated with hexavalent chromium is the electrochemical reactions occurring in the barrier. According to Blowes and Ptacek (25), the chromium content in

groundwater could be decreased by a redox reaction of Cr(VI) with reductive media in the barrier (25). The entire process can be expressed as two half cell reactions, as follows:

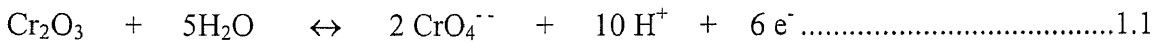
1. Cr (VI) to Cr(III) conversion constitutes one half reduction cell reaction, and
2. Oxidation of the barrier material (M⁰) forms the other half cell reaction.

This can be expressed as:



As a result of this reaction, Cr(III) compounds precipitate within the barrier and thus achieves the decontamination of groundwater (3).

The choice of reductive media for barrier applications is done based on the potential of the electrochemical redox cell that is formed in the reaction. The reduction reactions is believed to follow the following mechanism (26):



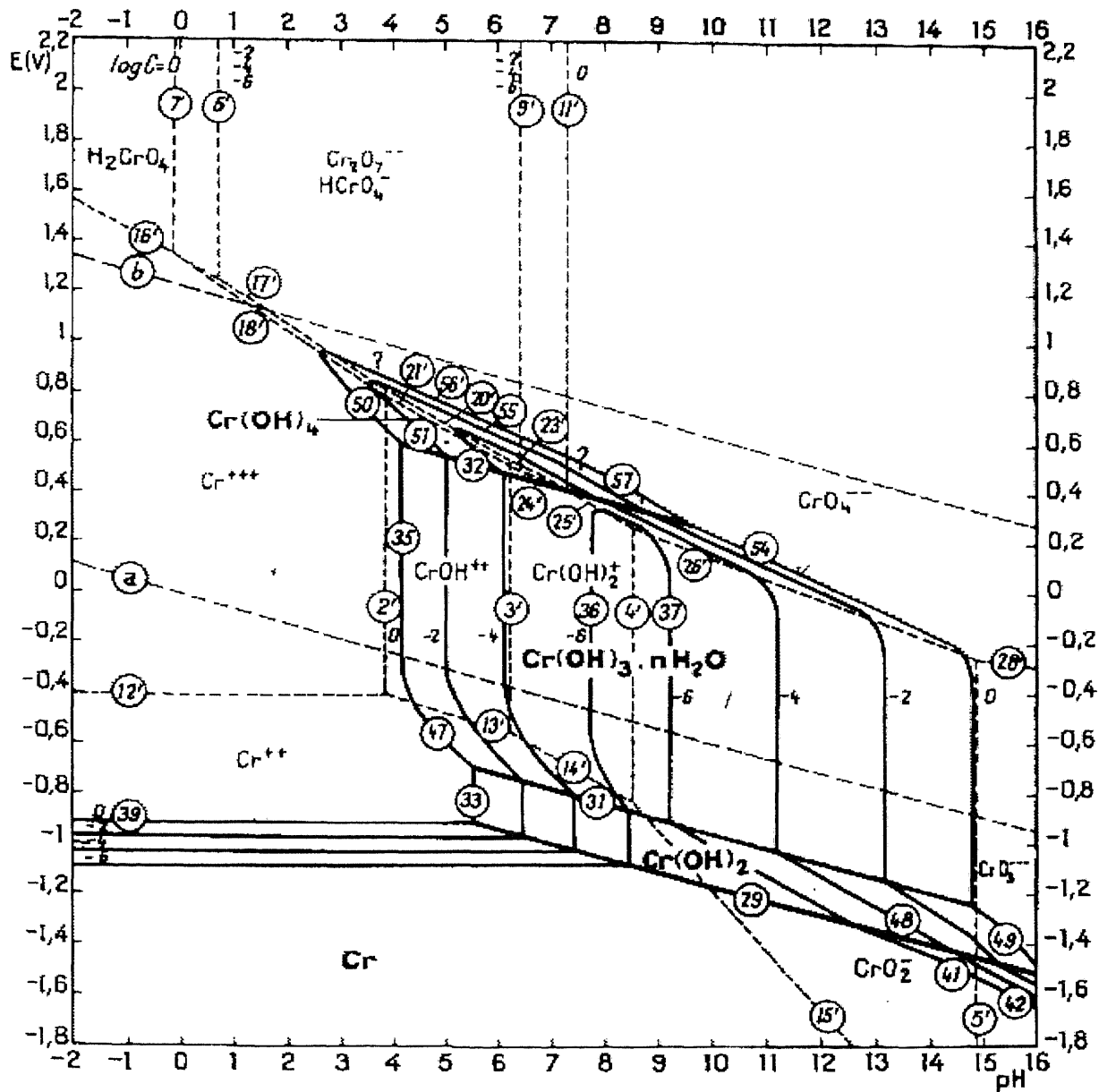
The Eh condition for this half-cell reaction in equation 1.1 is given by equation 1.2 (26).

$$E_o = 1.244 - 0.0985 \text{ pH} \dots\dots\dots 1.2$$

This equation is defined by "line 54" of the Pourbaix diagram shown in Fig 1.2. This line defines the stability regions between the two forms of chromium in nature - Cr(III) and Cr(VI). The region below this line is the stable region for trivalent chromium, while the region above it is the region where hexavalent chromium predominates. To convert

Cr(VI) to Cr(III) in groundwater, we require a reductive media which will accomplish Eh values below the "line 54" in Fig 1.2.

Figure 1.2: Pourbaix Diagram for Chromium (26).



The electrode potential of the metals can be obtained from their respective Eh - pH diagrams (26). The electrode potentials of possible candidate metals for use in the reactive barrier are compiled in Table 1.6. The criterion for successful reduction of

hexavalent chromium by any of the metals should satisfy the following in equation 1.3.

$$\text{Eh of solution} + \text{Eh of metal} < \text{Eh of " Line 54 " } \dots\dots\dots 1.3$$

Table 1.5: Electrochemical Potentials of Different Elements (26).

Element	pH = 12	pH = 11	pH = 10	pH = 9	pH = 8	pH = 7
Line 54	+ 104	+ 202.5	+ 301	+ 400	+ 498	+ 560
Barium	- 2875.2	- 2816.1	- 2757	- 2698	- 2639	- 2580
Magnesium	- 2571.2	- 2512	- 2453	- 2394	- 2335	- 2276
Berilium	- 2529.2	- 2470	- 2411	- 2352	- 2292	- 2233.7
Aluminum	- 2259.2	- 2200	- 2141	- 2082	- 2023	- 1963.7
Titanium	- 2015.2	- 1956.1	- 1897	- 1838	- 1778.8	- 1719.7
Silica	- 1566.2	- 1507.1	- 1448.8	- 1388.9	- 1329.8	- 1270.7
Mangnese	- 1436.2	- 1377.1	- 1318	- 1258.9	- 1200	- 1141
Zinc	- 1148.2	- 1089.1	- 1030	- 970.9	- 911.8	- 852.7
Tugsten	- 828.2	- 769.1	- 710	- 650.9	- 591.8	- 532.7
Molybdenum	- 781.2	- 722.1	- 663	- 604	- 544.8	- 485.7
Iron	- 756.2	- 697.1	- 638	- 578.9	- 519.8	- 460.7
Cadmium	- 704.2	- 645.1	- 586	- 526.9	- 467.8	- 408.7
Cobalt	- 614.2	- 555.1	- 496	- 436.9	- 377.8	- 318.7
Nickel	- 599.2	- 540.1	- 481	- 421.9	- 362.8	- 303.7
Lead	- 461.2	- 402.1	- 343	- 283.9	- 224.8	- 165.7
Bismuth	- 338.2	- 279.1	- 220	- 160.9	- 101.8	- 42.7
Copper	- 139.2	- 80.1	- 21	+ 38.1	+ 97.2	+ 156.3
Lithium	+ 16.8	+ 75.9	+ 135	+ 194	+ 253.2	+ 312.3
Silver	+ 463.8	+ 522.9	+ 582	+ 641.1	+ 700.2	+ 759.3
Gold	+ 747.8	+ 806.9	+ 866	+ 925.1	+ 984.2	+ 1043.3

Iron was chosen as a possible reduction medium due to its reactive properties and low cost. Iron was proven to be an effective reducing agent for chromium in other barrier applications (25, 27, 28, 29). The high pH condition of groundwater in our case is expected to be a limiting factor.

The main problem of this research relates to the applicability of permeable reactive barriers to treat groundwater contamination in chromium refining sites in Hudson County, New Jersey. The main challenges include dealing with the high pH

conditions and the high chromium concentration in the groundwater of these sites. Chromium refining sites are atypical of other sites in the literature, where the chromium concentration is low and the pH is near neutral. The conditions, which need to be satisfied in the case of chromium refining sites, include:

1. Accomplishing high reduction rates at the high pH condition of groundwater, and
2. Using a high buffering capacity medium that can lower the pH and accomplish high reduction rates during long-term application.

1.9 Objective of the Work

The main objective of this research was to define the critical parameters for applying the reactive permeable barrier technology to treat groundwater of the chromium refining sites in New Jersey. The study was carried out to achieve the following objectives:

1. Comparison between different types of iron reduction media,
2. Evaluation of reaction kinetics using groundwater samples collected from three sites as a function of pH,
3. Optimization of iron-to-groundwater ratio on reaction rates,
4. Determination of the effect of oxygen on reaction rates,
5. Assessment of pyrite and sidrite minerals as reduction media under high pH conditions,
6. Understanding the interfacial processes between reaction media and groundwater containing hexavalent chromium

The study was designed to investigate groundwater samples obtained from three different sites in the Hudson county, New Jersey. The plan was to include: determination of reaction rates under various pH conditions and to emphasize the selection of barrier

reactive media. Different types of pH buffering systems, which could be used to achieve the required pH adjustment, were to be investigated in this thesis.

1.10 Organization of the Thesis

In chapter 2, we discuss the procedures and guidelines implemented during the experimentation as well as the use of different analytical methods used in the research. In chapter 3, we discuss the materials, methods and experimental set-ups used to acquire the data presented in this thesis. In chapter 4, we present and discuss the results of the experiments in the laboratory, and provide a general understanding of the processes involved in the reaction between chromate ions and reductive media under different conditions.

CHAPTER 2

ANALYTICAL PROCEDURES

2.1 pH and Eh Measurement

The pH and Eh were measured using a microcomputer-based pH meter with an Eh measuring mode (JENCO model 6071). 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 dual point calibrated with standard solutions of pH 4 and 7. The pH meter was regularly calibrated after every 20 sets of readings, or everyday whichever was early during experimentation.

An oxidation-reduction potential electrode (ORP electrode) was used to measure the Eh of the solution. The ORP electrode is a combination electrode which measures the electromotive force between the potentials on the standard Ag | AgCl reference and the platinum band, which acts as the second electrode. Since the Eh is supposed to be the potential with respect to a standard hydrogen electrode, the Eh of the solution is calculated by adding the measured potential and the standard potential of the Ag | AgCl reference electrode. The standard potential of the standard Ag | AgCl half cell may change slightly with temperature. The additions have been done taking into consideration these temperature variations as shown in the Table 2.1.

The ORP was routinely tested for accuracy with the quinhydrone standard solution test. The ORP of the solution is pH dependant. By saturating pH buffers with quinhydrone, we made a stable mV standard solution to test our ORP electrode. Ideal value for the standard quinhydrone test are given in Table 2.2. For an electrode to be considered working within acceptable limits, the difference between the two readings should be between 169 to 177 mV ($169\text{mV} < \Delta \text{mV} < 177\text{mV}$). As a quality control

measure, it was routinely checked that the ΔmV value was always between these limits.

Table 2.1: Change in the Standard Ag|AgCl Electrode (mV) with Temperature

Temperature (°C)	Eh of the standard Ag AgCl electrode (mV).
15	209
20	206
25	202
30	198

Table 2.2: Limits for the Standard Ag|AgCl Electrode to be Considered Working

Buffer	ORP
4.01 pH	263 mV
7.00 pH	86 mV

2.2 Sample Analysis

2.2.1 Total Chromium Measurement

The total chromium concentration in the groundwater or other liquid samples was analyzed by Atomic Adsorption spectroscopy. The atomic adsorption spectroscopy works on the principle that every element has its own characteristic wavelength and when exposed to it, the element absorb an intensity of radiation corresponding to its concentration in the sample . The sample is atomized into a fine mist by impacting

it's flow with a nebulizer. This mist is introduced into a flame where the drops are heated till they lose their water content and the ion cluster remains, which is further heated till they have enough energy to dissociate to give free atoms. These atoms absorb the characteristic wavelength emitted by a cathode lamp and the amount of absorption can be detected using a photomultiplier. This absorption of the intensity of light gives the concentration of the elemental species to be analyzed. The analysis was carried out using a Smith Hieftje atomic absorption spectrophotometer. The total chromium measurement was done following the E.P.A protocols under method # 7000 and method # 7191 (30, 31). The settings for the measurement of total chromium concentrations on the said instrument were as given in Table 2.3.

The total chromium concentrations measured were analyzed as chromium element. This includes the hexavalent as well as the trivalent forms of chromium. It was assumed that the hexavalent chromium concentration would always be less than the total chromium concentration. So if one can reduce the total chromium concentration below detection limits, the hexavalent chromium concentration will always remain in control.

2.2.2 Hexavalent Chromium Measurement

The hexavalent chromium concentration in the samples was analyzed by a colorimetric analysis based on absorption spectroscopy at 540 nm. A color development reagent is added to the samples. This reagent reacts selectively hexavalent chromium and produces a color. The intensity of the color is proportional to the concentration of hexavalent chromium present in the sample. A reference beam is passed through a blank. The intensity of light is analyzed after it has passed through

the samples and the blank, and the difference in the intensities between the sample and the blank gives the concentration of hexavalent chromium in the sample.

Table 2.3: Setting of the Atomic Absorption Spectrophotometer

Light Source	Hollow Cathode
Lamp current	6.0 mA
Wavelength	357.9 nm
Bandpass	0.5 nm
Burner Head	Nitrous oxide
Flame Description	Nitrous oxide - Acetylene, Fuel rich, Red cone
Sensitivity	0.04 $\mu\text{g} / \text{ml}$
Linear range	0 - 5 $\mu\text{g}/\text{ml}$

The signal received by the detectors can be enhanced by using a photomultiplier. The analysis was carried out using Varian DMS 300 UV-visible spectrophotometer. The hexavalent chromium measurement was done following the E.P.A protocols under method # 7169A (32). Diphenylcarbazide was used as coloring reagent and the sample was acidified for color development using 10% HCl (vol/vol)

2.2.3 Quality Control

The Atomic absorption spectrometer and the absorption spectrophotometer were calibrated after every set of 10 readings. The calibration curve was plotted using one blank and four standards. Checks were carried after every 2 sets of 10 readings to see

that the readings are within 10 % of the value of the standards. Each reading was taken as an average of 3 readings and care was taken to see that the readings have a standard deviation of less than 10 %. The Atomic absorption spectrometer was operated in the range on concentrations between 0 and 5 $\mu\text{g/ml}$ because the linear range for the specific method exists between these concentrations for the wavelength of 357.9 nm. Similarly the absorption spectrophotometer was operated in the range on concentrations between 0 and 2 $\mu\text{g/ml}$ as they have a linear range at the wavelength of 540nm. It should also be noted that the instruments have the maximum sensitivity in the above given range. The samples, which were not in this range, were diluted to within this range, and the dilution factor was taken into consideration when the final results were computed. The groundwater samples were stored at a temperature of 4 °C as specified under the protocols of method # 7000 (30, 31, 32).

The groundwater samples were measured using micropipets with disposable tips. Each tip was used for only one reading so as to reduce possible sources of contamination. The entire glassware used in the experiment were washed with spectragrade certified nitric acid and demineralized water. Also the standards were prepared using demineralized water and Fisher Scientific Company manufactured chromium standards certified for spectroscopy use. These standards were prepared at the beginning of every experimental run. A calibration curve was plotted at the beginning of every experimental run. It was checked that the calibration curve used for the analysis had a correlation coefficient equal to or greater than 0.995.

A post verification spike analysis was carried out during the analysis of the hexavalent chromium, so as to ensure that neither a reducing condition nor chemical

interference is affecting color development. It was verified that the post verification spike recovery was between 85% and 115%.

CHAPTER 3

EXPERIMENTAL PROCEDURES

A batch reactor geometry was used to conduct the experiments in this research. The conducted experiments were always done in triplicates so that the average would reduce the human error in conducting the experiments. In each experiment, the pH of the groundwater was adjusted by addition of HCl, followed by addition of the reduction medium. The bottles were then placed on a wrist action shaker at room temperature for the duration of the experiment. The bottles were also covered with an aluminum foil so as avoid any light induced reactions. The shaking speed was adjusted to get effective mixing of the material during the reaction.

3.1 Selection of Reactive Iron

Two types of reductive iron media were used in our experiments, namely: Peerless and Fisher iron. The Peerless iron was supplied by Peerless Iron Company, while the Fisher iron was purchased from Fisher Scientific Company. The iron was used for more extensive evaluation during this research. Further analysis included the study of reaction rates of the iron when it is used as a reactive material in the barrier. The pH of the samples was varied so as to find the effect of alkalinity on the reaction rates. All the experiments were conducted using 5 grams of iron and 200ml of groundwater per test. The bottles were kept on the shaker for a period of 24 hours. Samples were taken at preset intervals for determining the total chromium content as a function of time.

3.2 Optimization of Iron to Groundwater Ratio

The experiments to optimize the iron-to-groundwater ratio were carried using artificially simulated samples of different chromium concentrations. A 1000 ppm sample was generated by dissolving 2.83 grams of potassium dichromate in one liter of water. A 50ppm total chromium solution was prepared by diluting this sample again with water. Since the pH of the groundwater under investigation ranges between 10 – 12, the samples were adjusted to include this range of pH condition. 1, 2.5, 5, and 7.5 grams of iron were added to 200ml of the above chromium solution. Samples were taken at preset intervals for determining total chromium content as a function of time and the experiments was conducted over a total duration of 24 hours. The results obtained from these experiments were validated by repeating the experiment using actual groundwater samples.

3.3 Study of Pyrite and Sidrite as Reactive Media

Based on previous studies (15, 16), pyrites and sidrite were selected as reductive media because their ferrous cations are the reducing ions. Iron pyrite is FeS and sidrite is FeCO_3 . Iron pyrite and sidrite minerals used in our experiments were obtained from Chemalloy Company and Scott Resources Company, respectively. These materials were investigated as possible reductive media at high pH conditions. The samples were allowed to react with minerals for a period of 24 hours.

3.4 Oxygen Effect on the Reaction Rates

The reactive media in the barrier is expected to react with hexavalent chromium in groundwater in the sub-surface. The oxygen content in the groundwater in the sub-surface is always low at depth of more than 10 feet. In order to simulate these sub-surface conditions, it is necessary that the reactions be carried out under anaerobic conditions, i.e. in the absence of oxygen. A nitrogen blanketing was applied to the reacting mixture by allowing the nitrogen to flow from one reactor to another in a serial manner. The reactions were carried out in aspirator bottles that had opening at their base. A pinch cork was attached to these opening which facilitated sample removal from the reactors without oxygen entry into them. The samples were taken at per-determined intervals to determine the change in chromium concentration as a function of time.

The initial and final samples in all of the above experiments were thoroughly analyzed to determine the Eh-pH conditions and their effect on the total and hexavalent chromium concentrations.

3.5 Effect of Salt Addition on Reaction Rates

The study was conducted using NaCl, which is neutral on dissolution in water. The analysis was carried out using 5 grams Peerless iron and 200 ml of groundwater. The amount of salt added was varied from 0 – 8 grams to check its effects on the reaction rates. The reaction was allowed to proceed for 24 hours. Samples were intermittently drawn at preset intervals to assist in the calculation of reaction rates. An experiment

was also carried out to determine the combined effect of salt and pH on the reaction rates.

The implications of the results obtained in the above experiments and their effects on the applicability of permeable reactive barrier technology for Hudson County sites is discussed in the following chapter.

CHAPTER 4

RESULTS AND DISCUSSION

This chapter summarizes and discusses the results pertaining to the study of reductive media for hexavalent chromium in groundwater, especially those with high pH conditions between 11.5 and 12.35 for application in permeable reactive barriers. The high pH of this groundwater, as described in Chapter 1, is attributed to the high level of soda ash and lime used in the refining processes whose waste was landfilled in the Hudson County sites of New Jersey. This chapter includes six sections as follows:

1. Groundwater Analysis and Characterization
2. Use of Metallic Iron as a Reactive Medium
3. Analysis of Different Buffering Systems.
4. Analysis of other reductive media - pyrites and sidrite
5. Detailed Investigation of Interfacial Processes between Fe^0 and Groundwater containing CrO_4^{-2} ions.
6. General Discussion and Recommendations

The main objectives of this study were:

1. To evaluate the applicability of various reduction media, and
2. To access critical parameters such as lowering the pH and formation of passivating layers on reaction rates especially over long-term use.

At the conclusion of the chapter, a general discussion is given regarding the selection of a reactive media and applicability of permeable barrier technology for treating groundwater of chromium-refining waste sites.

4.1 Groundwater Analysis and Characterization

The groundwater samples used in this thesis were obtained from extraction wells existing at three different sites in the Hudson County in New Jersey. Table 4.1 summarizes the pH, Eh, total and hexavalent chromium concentrations of the groundwater samples used in the study. The pH of all the groundwater samples of these sites is alkaline and ranges between 11.5 and 12.35.

Table 4.1: pH, Eh and Total and Hexavalent Chromium in the Groundwater Samples from the Three Sites in Hudson County, New Jersey *

Source of groundwater samples	pH (± 0.5)	Eh (mV)	Chromium concentration. (ppm)	
			Total	Hexavalent
Site 1	12.25	167	25	19.7
Site 2	12.35	155	55	39.2
Site 3	11.50	241	15	11.5

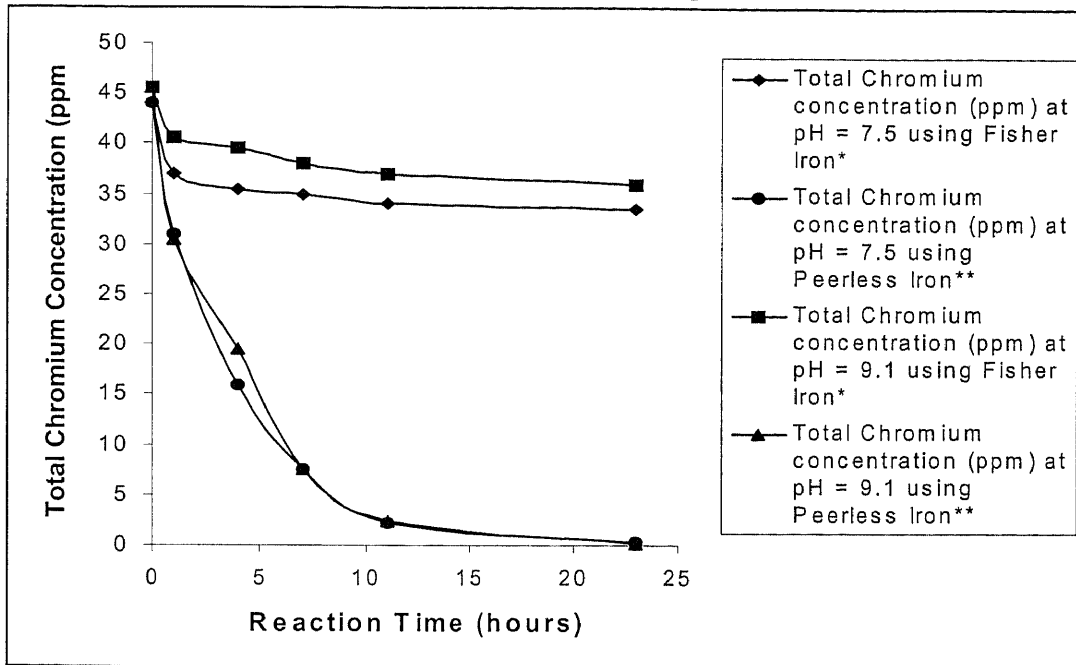
* The values shown in this table are the average of six determinations.

4.2 Use of Metallic Iron as a Reactive Medium

4.2.1 Selection of a Reductive Iron Material

The comparison between two types of iron material when reacted with the same groundwater sample at two pH conditions, 7.5 and 9.1 is given in Figure 4.1. The results of these experiments indicate that the Peerless iron decreases total chromium concentration at rates much higher than the Fisher iron. The reactivity of the Peerless iron may be attributed to the greater number of reactive sites as compared to the Fisher iron. These active sites may be the result of the manufacturing process of the iron; these active sites seem to facilitate the formation of local electrochemical

Figure 4.1: Reduction of Chromium with Two Different Iron Material in Batch Reactor Experiments at pH 7.5 and 9.1



*Fisher iron obtained from Fisher Scientific Co.
 **Peerless iron obtained from Peerless Metal Co.

cells as described by Puls and Powell (29). Based on these results, the Peerless iron was selected for further testing and experimentation during this study.

The groundwater samples from each of the three sites were subjected to reduction (via contacting with the Peerless iron) at different pH conditions. The results summarized in Table 4.2 indicate that a pH condition ≤ 9.0 is needed for an efficient reduction to take place in a reasonable time - a 24-hour period was arbitrary used. The results in Table 4.2 support the initial hypothesis that the solution in contact with Fe^0 should have Eh value under "line 54" of the Pourbaix diagram (Fig1.2) at a given pH for the hexavalent chromium reduction to take place. Therefore, the oxidation potential conditions for the iron can be expressed by the equation 4.1:

$$E_0 = - 0.051 - 0.0591 \text{ pH} \dots\dots\dots 4.1$$

Table 4.2: Effect of pH on Cr Reduction in Batch Reactor Experiments for Three Groundwater Samples*

pH. (±0.25)	Groundwater - 1.			Groundwater - 2.			Groundwater - 3.		
	Initial Cr ppm	Final Cr ppm	Eh (mV)	Initial Cr ppm	Final Cr ppm	Eh (mV)	Initial Cr ppm	Final Cr ppm	Eh (mV)
12.25	25	22	153	47	44	143	-	-	-
11	25	13	233	46	12	277	15	4	254
10	25	5	319	46	6	331	15	1.5	314
9	24	0.23	356	45	0.3	359	14	0.15	360
7.5	23	0.21	367	44	0.26	571	14	0.15	377
4.5	22	0.25	397	44.5	0.3	399	14	0.15	391

(It should be noted that the final chromium concentration in the groundwater was measured after exposure to reductive media).

At pH above 7.0, the redox reaction between hexavalent chromium and Fe^0 produces trivalent chromium possibly in the form of $\text{Fe}_x\text{Cr}_{(1-x)}(\text{OH})_{3x}$.

4.2.2 Reaction Rates and Rate Kinetics

Reaction rates and constants were systematically evaluated for the groundwater samples from the three selected sites at various pH conditions. Table 4.3 and Figure 4.2 summarize these results. Chromium concentrations were carefully plotted for different reaction kinetics mechanisms. The results were subjected to regression analysis. The criterion for selecting the operating mechanism was that the correlation coefficient for the regression model has to be greater than 0.95. The reaction was

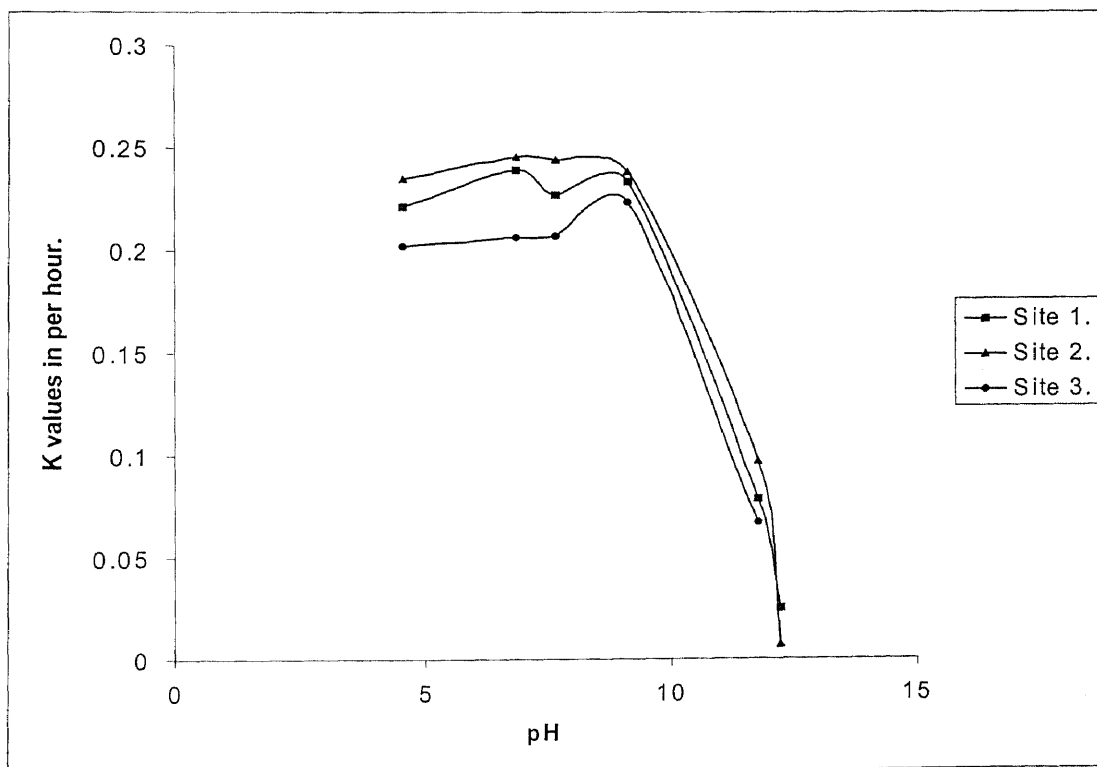
found to follow a first order kinetics. This is in agreement with Puls and Powell (29).

The rate constants seem to flatten as the pH decreases to below 9.2.

Table 4.3: Effect of pH Conditions on the Reaction Rate Constants

pH (± 0.25)	Rate constant 'k' in hour ⁻¹		
	Site 1	Site 2	Site 3
12.25	0.0253	0.0072	-
11	0.0788	0.0727	0.0735
9	0.24	0.24	0.21
7.5	0.23	0.244	0.21
4.5	0.22	0.22	0.2

Figure 4.2: Reaction Rate Constants of Hexavalent Chromium in Groundwater as a function of pH



The rate constants are similar for all groundwater samples obtained from the three sites. This indicates that the pH is the dominant parameter affecting the rate constant for the hexavalent to trivalent reduction reaction, and that the condition needed for reduction is expected to be same irrespective of the source of the groundwater.

It should be noted that the reaction rates generated in this research are not absolute values and that they depend on the design by Puls and Powell are higher than the results shown in Table 4.3 and Figure 4.2. We believe that the mixing efficiency generated in the wrist action shaker can influence the rate constant values. This difference may account for the difference between our results and those obtained by Puls and Powell. For real barrier condition, we believe that measurement procedure simulating the barrier case should be used to determine the actual rate constant needed for such a design.

4.2.3 Optimization of Iron-to-Solution Ratio

The experimental results indicate that 5 grams of Peerless iron per 200 ml of dichromate solution is sufficient to achieve an efficient reduction at pH conditions below 9.2. Lower iron amounts or higher pH did not produce the desired reduction rates as can be seen in Table 4.4. In brief, 5g of Fe⁰/200 ml of groundwater and pH less than 9.2 are needed to achieve fast and efficient reduction in the batch reactor experiments. Table 4.5 and Figure 4.3 summarize the interplay between pH and iron/groundwater ratio.

Table 4.4: Effect of Fe⁰ Amount per 200ml Dicromate Solution on Chromium Reduction at Different pH Conditions

PH	1 gram Peerless iron		2.5 grams Peerless iron		5 grams Peerless iron		7.5 grams Peerless iron	
	Initial Cr ppm	Final Cr ppm	Initial Cr ppm	Final Cr ppm	Initial Cr ppm	Final Cr ppm	Initial Cr ppm	Final Cr ppm
7	51	4.5	53	1.7	51	0.42	53	0.41
8	50	5.3	53	1.9	50	0.83	50	0.83
9	50	3.2	53	1.1	50	0.41	53	0.41
10	55	13.6	51	7	55	3.4	51	3.5

Figure 4.3: Variation of Reaction Rate Constants with Amount of Reactive Media - Dicromate Solution.

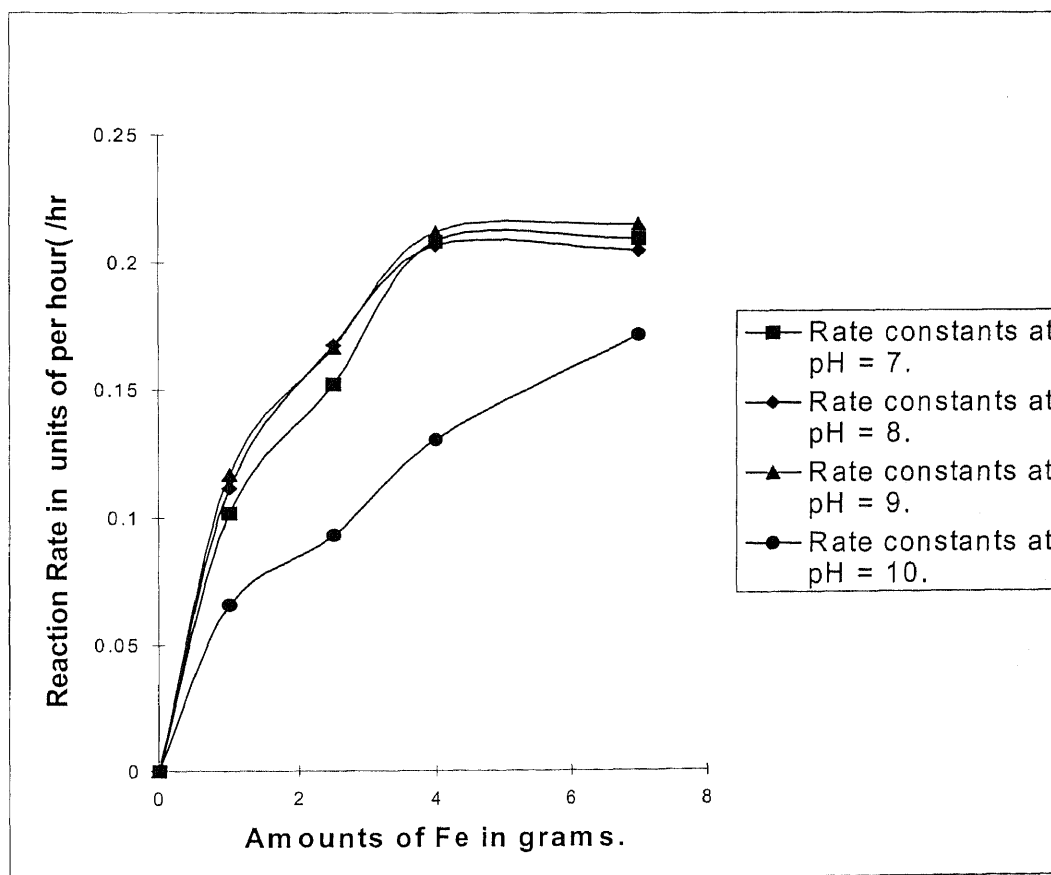


Table 4.5: Effect of Fe⁰ Amount per 200ml Dichromate Solution on Chromium Reduction Reaction Rate Constant

Grams of iron per 200 ml of 50 ppm Cr	Values for the rate constant 'k' in units 'per hour'.			
	pH = 7.0	pH = 8.0	pH = 9.0	pH = 10.0
1	0.1017	0.1116	0.1169	0.0658
2.5	0.1523	0.1678	0.1668	0.0931
5	0.2084	0.2067	0.2122	0.1305
7.5	0.2095	0.2047	0.2151	0.1717

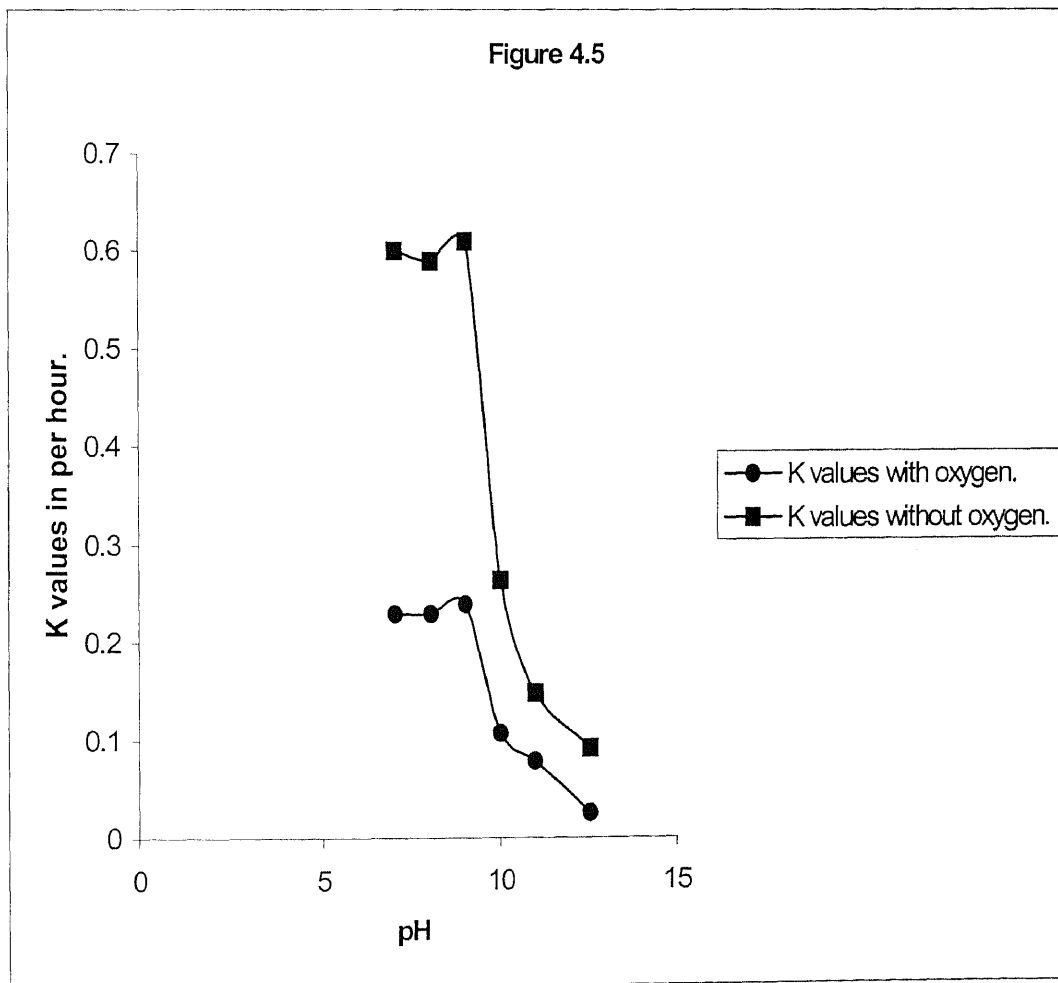
4.2.4 Effect of Oxygen on the Reaction Rates

For permeable reactive barrier application, it is critical to determine the reactions rates under subsurface anearobic conditions. The experimental results show a considerable increase in reaction rates, almost threefold, in the absence of oxygen (Table 4.6 and Figure 4.4).

Since the subsurface has lower oxygen concentration, the reaction rates in Table 4.6 would simulate actual subsurface conditions. This means the reduction of hexavalent deep in the barrier is more favorable than near the surface. The effect of oxygen on increasing the reaction rate constant is expected because Eh conditions are more reducing at lower oxygen concentrations, i.e., conversion of Cr(VI) to Cr(III) is more favourable.

Table 4.6: Effect of Oxygen on the Rate of Reaction

pH	k-values in 'per hour' with Oxygen.	k-values in 'per hour' without Oxygen.
12.53	0.0253	0.0911
11	0.078	0.148
10	0.107	0.264
9	0.24	0.61
8	0.23	0.59
7	0.23	0.6

Figure 4.4: Reaction Rate Constants under Aerobic and Anaerobic conditions

4.3 Analysis of Different Buffering Systems

Several buffering systems were studied in this thesis. The following minerals were analyzed for their acid generating capacities:

1. Silicic acid - generating minerals
2. Carbonic acid - generating minerals
3. H₂S - generating minerals
4. Phosphoric acid - generating minerals

The results of this effort are compiled in Table 4.7. Silicic acid generating materials (1-8 in Table 4.7) did not exhibit beneficial lowering of pH, or substantial buffering capacity. This may be attributed to their low dissolution rates in groundwater as reported by Stumm (33).

Phosphoric acid-generating materials (9-11 in Table 4.7) showed considerable solubility and decrease in the pH of groundwater. However, these materials are deemed impractical for use in barriers because of their fast dissolution rates. This is shown by their diminishing capacity to lower the pH of groundwater during successive exposure cycles, as seen in Table 4.8. The most promising reductive media among the materials investigated were H₂S-generating minerals such as pyrites (12 in Table 4.7), and carbonic acid - generating minerals specifically siderite (FeCO₃) and manganese carbonate (MnCO₃) (13-14 in Table 4.7).

Table 4.7: Effect of Several Potential Buffering Media on the pH of Groundwater*

	S. No.	Material tested.	Initial pH.	pH after 24 hours
	Silicic acid generating	1	Silica	12.73
2		Green sand	12.81	12.43
3		Rock flour	12.56	12.54
4		Kaolinite	12.56	12.51
5		Flint sand	12.56	12.5
6		River sand	12.56	12.5
7		Olivine	12.33	12.22
8		Fly ash	12.56	12.39
Phosphoric acid generating	9	Ammonium phosphate	12.37	6.35
	10	Triple super phosphate	12.37	4.6
	11	Di-ammonium phosphate	12.37	8.77
H ₂ S-generating	12	Iron Pyrite	12.33	12
Carbonic acid generating	13	Manganese carbonate	12.33	10.33
	14	Siderite	12.33	12.17

* Amount of buffering material used was 5 grams for each of the above case.

Table 4.8: Buffering Capacities of Phosphate Minerals

Minerals	First use			Second use		Third use	
	Initial pH	pH after 30 mins.	Final pH	Initial pH	Final pH	Initial pH	Final pH
Ammonium phosphate	12.37	6.35	6.36	12.35	9.85	12.39	11.48
Triple super phosphate	12.37	4.6	3.72	12.35	7.85	12.39	10.95
Di-ammonium phosphate	12.37	8.77	8.67	12.35	9.76	12.39	11.45

4.4 Analysis of Other Reductive Media - Pyrites and Sidrite

Sidrite and pyrite ores have been used as reductive media for other contaminants especially chlorinated hydrocarbons (15, 16). Our results show that chromium concentrations have been lowered by these minerals even under high pH conditions.

Table 4.9: Effect of Pyrite/Groundwater Ratio on decreasing Total Chromium*

Grams of pyrite/250 ml water	Final Cr concentration after 24 hours. (ppm)
2.5 grams	15.9
5 grams	15
7.5 grams	4
10 grams	0.11

* Initial total Chromium concentration in groundwater was 56 ppm.

Table 4.10: Effect of Sidrite/Groundwater Ratio on decreasing Total Chromium*

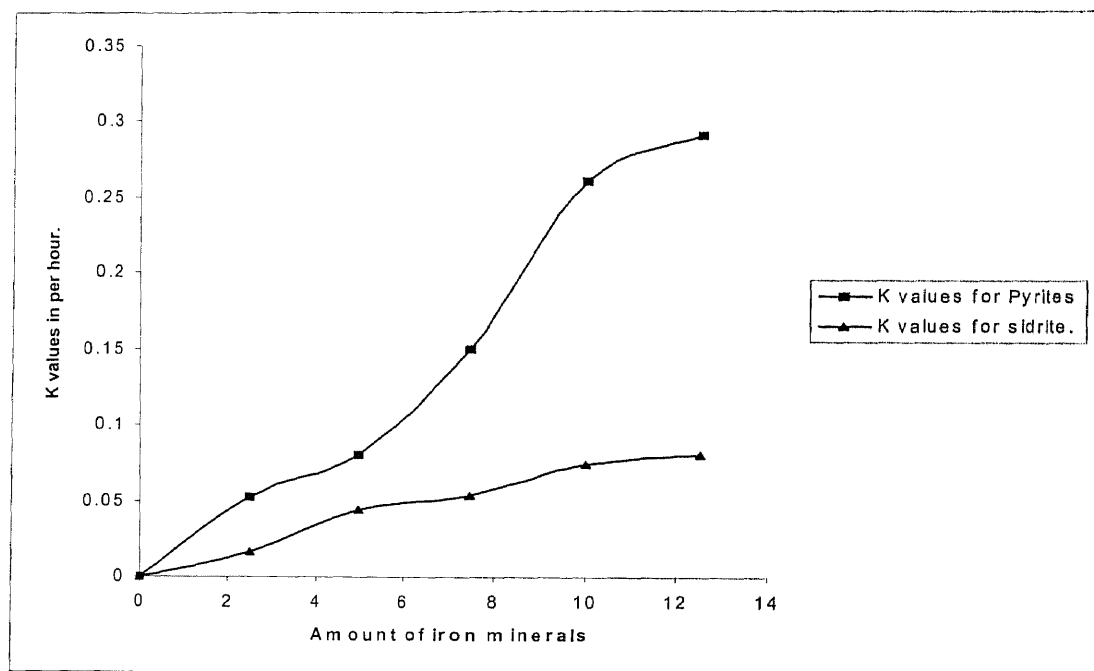
Grams siderite/250 ml of water	Final Cr concentration after 24 hours. (ppm)
2.5 grams	37.4
5 grams	19.5
7.5 grams	15.5
10 grams	9.5

* Initial total Chromium concentration in groundwater was 56 ppm.

Reduction of hexavalent chromium in groundwater samples was evaluated at different mineral/groundwater ratios. The results are shown in Table 4.9 and 4.10 and Figure 4.5. It should be noted that this reduction took place without the addition of the Peerless iron to the reaction vessel. Comparison between the results in Tables 4.9 and 4.10 shows that pyrite is more effective in lowering the chromium concentration than sidrite. The above results pertain to a single exposure of the mineral to the

groundwater sample. The effect of anaerobic and aerobic conditions on the reaction rates using pyrites and sidrite are summarized in Table 4.11 (a, b). Again the absence of oxygen increases the effectiveness of the pyrites and the sidrite in reducing hexavalent chromium to the trivalent form.

Figure 4.5: Effect of Pyrites and Sidrite/ Groundwater Ratio on Reaction Rates*



* 200ml of groundwater was used in each experiment

Table 4.11 (a): Effect of Oxygen on the Reduction Reaction for (a) Pyrites and (b) Sidrite

pH initial	pH Final With O ₂	pH final w/o O ₂	Cr (tot) Initial	Cr(tot) Final With O ₂	Cr (tot) final w/o O ₂	Cr (VI) Initial	Cr (VI) Final with O ₂	Cr (VI) Final w/o O ₂
12.24	11.94	11.9	55.7	3.7	1.1	38.4	1.2	0.15
10.34	4.36	4.26	55.7	0.9	0.25	38.4	0.09	0.09
9.3	4.1	4.04	55.7	0.4	0.18	38.4	0.07	0.07
7.32	4.42	3.79	55.7	0.14	0.13	38.4	0.03	0.02

Table 4.11 (b): (continued)

pH initial	pH Final With O ₂	pH final w/o O ₂	Cr (tot) Initial	Cr(tot) Final With O ₂	Cr (tot) final w/o O ₂	Cr (VI) Initial	Cr (VI) Final with O ₂	Cr (VI) Final w/o O ₂
12.24	11.69	11.32	55.7	40.7	18.9	38.4	22.5	10
10.34	7.94	7.35	55.7	32.4	11.1	38.4	17.8	7.1
9.3	7.42	7.29	55.7	22.2	10.3	38.4	10.2	6.95
7.32	7.23	7.23	55.7	14.6	5.2	38.4	6.5	2.5

4.5 Detailed Investigation of Interfacial Processes between Fe⁰ and Groundwater containing CrO₄⁻² Ions.

The foregoing results showed that pH below 9.2 is needed to achieve reduction of hexavalent chromium at a sufficient rate to be useful for barrier application. In this section we present results pertaining to:

1. Effect salt on surface interaction of Fe⁰ with chromate ions
2. Formation of passivating layers that can affect reaction rates during successive use, which would simulate barrier performance over long term use.

4.5.1 Effect of Salt on Reduction Rates of Chromate Ion at Fe⁰ Surface

The addition of a small amount of neutral salt such as NaCl on the rate of hexavalent chromium reduction was investigated at different pH conditions. When different amounts of NaCl was added to groundwater with initial chromium concentration of 13.5 ppm at a pH of 12.1, a fast reaction kinetics were observed as shown in Table

4.12(a). Almost a complete reduction of hexavalent chromium was achieved at salt concentration more than 0.025 mole/lit of groundwater.

Table 4.12 (a): Effect of NaCl Concentration on Reaction Kinetics

Concentration of salt (moles/lit)	Total Chromium * (ppm)	Reaction rate constant (per hour)
0	10.5	0.01
0.00625	9.4	0.02
0.0125	8.4	0.02
0.025	0.78	0.12
0.075	0.81	0.12

*Groundwater used had a pH=12.1 and total chromium concentration of 13.5ppm.

Table 4.12 (b)

Concentration of salt (moles/lit)	Total Chromium * (ppm)
0	46.5
0.025	41.6
0.05	38.1
0.075	32.4
0.1	34.8

*Groundwater used had a pH=12.2 and total chromium concentration of 55ppm.

When the same condition was applied to groundwater samples containing 56 ppm total chromium, the decrease in chromium concentration was not as considerable

compared to the 13.5 ppm total chromium groundwater as shown in Table 4.12(b). These results prompted us to expand our investigation to cover different salt concentrations. Increasing the salt concentration above 0.5 moles/lit gives no effect on the reaction rate constants (Table 4.13).

Table 4.13: Effect of Salt Addition on Reaction Rates*

Amount of Salt Added (in moles/lit)	Reaction Rate Constants (per hour)
0	-
0.025	0.01
0.05	0.009
0.1	0.01
0.125	0.035
0.5	0.07
1	0.068

*Groundwater has pH = 12.3 and total chromium concentration of 56 ppm.

When we systematically decreased the pH of the groundwater from 12.25 to 7, we found that the addition of salt (0.5 moles/ lit) produced a significant decrease in hexavalent chromium at pH < 10.9. (Table 4.14).

Table 4.14: Effect of Salt on Reaction Kinetics at Different pH Conditions

PH	Final concentration (ppm)	Reaction rate (per hour)
12.3	13.7	0.06
10.9	0.27	0.22
9.6	0.28	0.22
8.9	0.17	0.24
8.1	0.13	0.25
7.7	0.16	0.25

This is further supported by the analysis of reaction kinetics where reaction rate constants under the above condition (with salt) is about the same as that achieved at $\text{pH} < 9.2$ in the absence of salt.

The effects of salt can be best explained by the decrease in repulsion energy between the iron surface and chromate ion. Iron particle is charged and its surface charge produces an electrical field, which attracts electrolyte ions with charge opposite to surface charge (counterions) and repels ions with charge coinciding with the surface charge (coions). As a result of this field, the concentrations of chromate, hydrogen and hydroxide ions near the surface differ from their bulk concentrations, and these differences depend on the sign and the value of the surface charge. Reduction reaction occur near the surface (surface-controlled reaction) and their rate depends on ion concentrations near the surface. Therefore these rates are affected by surface charge which is sensitive to pH and salt concentration. Thus the surface charge and its pH and salt concentration dependence play a significant role in the surface-controlled reduction of chromate ions. The investigation of the surface charge influence on chromate ion reduction rate is a problem of surface electrochemistry and will be elaborated up in future research.

4.5.2 Effect of Passivation Processes at the Surface of Fe^0 Media on the Reduction Kinetics of Chromate Ions

One of the most critical parameters affecting the applicability of a reductive medium for barrier application is the formation of passivating layers that may slow down or even stop the reaction completely. Any development of a reduction media should evaluate this issue in detail. In this study, successive reduction of chromate ions using

the same amount of reaction medium was used to evaluate the formation and effect of such passivating layers. Based on the results shown in Table 4.15, it appears that a small but cumulative degradation in reduction efficiency seems to take place upon the successive use of the Peerless iron. A more significant trend was found for sidrite and pyrite during successive use in chromate reduction (Table 4.16).

Table 4.15: Successive Use of Iron as a Reactive Media with Fresh Groundwater Samples

Use #	Initial Chromium concentration	Final Chromium concentration
1	58	0.02
2	58	0.03
3	58	0.05
4	58	0.08

Table 4.16: Successive Use of Pyrite and Sidrite as a Reactive Media

Initial Cr concentration in ppm	Cr concentration in ppm after 1 st use		Cr concentration in ppm after 2 nd use		Cr concentration in ppm after 3 rd use	
	Pyrite	Sidrite	Pyrite	Sidrite	Pyrite	Sidrite
25	1.8	2.6	4.2	2.9	9.1	4.2
56	15	19.5	23.7	22.6	32.3	28.5

CHAPTER 5

SUMMARY AND RECOMENDATIONS

The results of this research can be summarized as follows:

1. A complete analysis of the groundwater samples obtained from the 3 sites in New Jersey was fully analyzed to determine the total and hexavalent chromium concentration. These samples had chromium concentration ranging between 15-60 ppm and pH condition between 11.5-12.35. These groundwater samples were used to obtain the results generated in this research.
2. Two reductive iron media were compared for their effectiveness in reducing Cr(VI) to Cr(III) in groundwater. The results showed that Peerless iron is more effective than Fisher iron as jugded form the reaction rate constants determined at different pH conditions.
3. The reaction rate constants for reducing Cr(VI) to Cr(VI) by reactive iron was found to be a function of the pH. High reaction rate constants were obtained below pH of 9.3. However, the reaction rate constants decreased very dramatically at pH conditions above 9.3.
4. The two additional reductive media were found to be moderately effective, namely siderite and pyrite minerals. The reductive efficiency of these two minerals was much smaller as compared to Peerless iron.
5. A multitude of buffering material were investigated and found to have limitations for lowering the high pH of groundwater. Only pyrite (H₂S generating minerals) and siderite (Carbonic acid generating minerals) were moderately promising for this application.

6. The effect of oxygen on reaction rate was investigated at a wide pH conditions. At lower oxygen concentration, the reaction rate constants for reducing Cr(VI) to Cr(III) were about three times higher than those generated at atmospheric oxygen saturation.

7. The effect of neutral salts on reaction rate was investigated in details. Salts such as sodium chloride were found to significantly enhance the reductive efficiency of Peerless iron for converting Cr(VI) to Cr(III). We believe that the effect of salt is important at high pH conditions in decreasing repulsive forces between dichromate ions (negatively charged) and reductive iron media (positively charged).

8. The surface passivation of reductive media was observed and studied at high pH condition of the groundwater used in this research. We found that Peerless iron efficiency to reduce chromium decreases with successive use of the same sample of iron. This may be attributed to the formation of reaction precipitate on the surface of iron particles and therefore decreasing the available active surface area of reaction with the groundwater. This effect is extremely important since it will determine the long term efficiency of reactive barriers in this application.

Based on the foregoing results, it appears that permeable barriers based on iron, siderite and pyrite media, for treating the high-pH chromium (VI) contaminated groundwater may have limitations. These limitations may be overcome by simultaneously injecting a solution containing small amount of an appropriate acid and a neutral salt to achieve two major purposes:

1. To lower the pH to the required range for achieving favorable reaction rates, and

2. To dissolve or prevent the formation of any passivating layers that may form on the surface of reactive media during the long-term treatment.

Future investigations should concentrate on optimizing the above processes in column experiments where reduction rate and formation of passivating layers can be assessed under flow conditions simulating the barrier case. Further investigation will also be needed to explore new reductive media that can achieve the required reaction rates without the formation of passivating layers, specially under the high pH conditions of groundwater as in the case of chromium residue sites of New Jersey.

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