

**Development of Permeable Reactive Barriers
for
Chromium Residue Sites in New Jersey**

YEAR 1

**Final Report
Submitted to:**

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Executive Summary

The progress made during the past year included: further defining the problems, developing methods and procedures to conduct experiments with groundwater, assessing the pH and chromium concentration of groundwater obtained from the three sites, performing experiments to determine pH limitations on using iron media for decreasing Cr to acceptable levels, screening several sources of reductive iron media, exploring several buffering classes including silicates, sulfides, carbonates, and their mixtures with reductive iron media, determining the applicability of decreasing chromium concentration upon successive use of the same redox and buffering media in the batch reactor, analyzing the data of all experiments and performing preliminary screening of software to model the permeable barrier for use in the field experiment design. The scope of the work performed became wider than that presented in the proposal, mostly because of the limitation of buffering media performance in achieving the needed pH decrease for the case of the highly alkaline NJ groundwater. In spite of such challenges, the program accomplished its objectives and goals.

During this program, we have established a quality control procedure to use the EPA method for measuring total chromium in water samples as the main method for assessing the decrease in chromium concentration as a function of different variables in the study. Based on our results, pH conditions of 9.3 or lower were needed to achieve favorable reduction kinetics with Peerless iron medium - the latter was selected after comparing several iron media. The reaction rate was found to follow a first order kinetics, and the rate constant was found to level off at pHs <9.3. Groundwater obtained from the three sites had similar behavior with respect to the reduction rate constants, as described above. This indicates that the same technology should be applicable to the three sites, with some adjustment of the reductive and buffering capacity of media used in the barrier.

Finding the right buffering medium, or a combination of reductive and buffering media have been the biggest challenge of this study. Silicic acid producing media such as silica, feldspar, olivine and kaolinite were found to be unsatisfactory buffering media. A sulfide-based mineral, iron pyrites, has been promising to some extent. Iron pyrite, either alone or with Peerless iron, has achieved a significant decrease in Cr concentration - even at high pH conditions. Similarly, sidrite, a carbonate-based iron mineral, was able to decrease the Cr level in groundwater, but

to a lesser level compared to iron pyrite. Upon successive Cr reduction with the same reductive-buffering mixture (such as pyrite-Peerless or Sidrite-Peerles), the efficiency of the process decreases. We are in the process of assessing the reductive capacity of the mixtures used in these experiments. The results are, however, encouraging, since the reduction is occurring at the high pH condition, between 11 to 12. It should be noted that sidrite is a very promising medium since it does not suffer from efficiency decline during successive reuse; however, its reductive power is not sufficient by itself - i.e., it cannot be used as a single reductive medium.

Analysis of the results, so far, points to the need to satisfy two conditions to solve this problem:

1. The electrochemical potential must be in the reduction region for chromate, and
2. The oxide/hydroxide layer must be soluble in the surroundings so that a fresh surface is exposed to flowing groundwater at all times.

The above two conditions are satisfied with the Peerless iron at neutral or low pH conditions, but not at the high pH conditions of the NJ-sites' of 11 to 12. At the latter pH, the electrochemical potential condition seems to be satisfied, but the iron forms a hydroxide layer that prevents the reduction of chromate at a reasonable rate. We therefor require an environment that can dissolve the hydroxide layer formed at this high pH condition. The sulfite-based iron pyrite seems to satisfy this condition, but the efficiency, again, drops upon successive use of the same medium. Based on our results, a barrier design based on Peerless, sidrite and pyrite may be attractive to evaluate. We are in the process of conducting column experiments to test the capacity of this design.

Another strategy that promises to deliver a solution to the above problem is to investigate other reductive-buffering media based on bimetallics; again, in combination with sidrite and pyrite. We have recently conducted electrochemical calculations to define such materials. We plan to work with Circona and others in this area. Further screening other buffering system is proceeding. Other suggestions from the RPs are welcomed at this point. Preliminary selection of models for use to design the field experiment is underway. The program is proceeding, as planned.

Introduction / Problem Statement:

Chromium residue sites in New Jersey were generated as the result of the chromium refining operations that took place during the first half of this century. These refining activities were based on converting chromite ore into soluble chromate for use in industrial processes, especially metal plating. This conversion was accomplished by the addition of alkaline additives such as lime or alkalis to chromite ore, and roasting the mixture in air at high temperature - 1300°C or higher. The residue remaining after dissolving the accessible chromate was landfilled in the existing chromium sites. Residues of various chromium sites contain: calcium, iron, aluminum, and a high concentration of hexavalent and trivalent chromium. Because of the addition of lime or alkalis, the waste in these sites is highly alkaline. This is clearly manifested by the high pH conditions of groundwater in such sites. The compositions of chromium residue from the various sites has some variability in composition. This variability is attributed to differences in ore source as well as to the process conditions used by different companies. Several waste treatment processes were proposed in the past, but have proven to be expensive or inappropriate as solutions to the problem. The chromium waste problem has been one of the major environmental issues at the NJ-DEP for about two decades.

Contaminated groundwater associated with chromium sites has many environmental implications. It contains a high concentration of hexavalent chromium, and is expected to adversely affect the environment and the ecology of the local environment. As a solution of this problem, we proposed to investigate the applicability of permeable reactive barriers to intercept and treat groundwater generated from NJ chromium sites. A program was established in 1988 to investigate the feasibility of using such barriers at the laboratory level. This report provides a summary of the results and discussion of the main issues in relation to reactive barriers and their applicability to the present scenario.

Project Design and Methods:

The main objectives of the program were to conduct laboratory experiments to define the critical parameters and screen reactive media for use as barrier materials for treating ground water obtained from three NJ sites. The program was also to determine key parameters that would be used to assess the relative rates of ground water velocity and reaction kinetics in the barrier. Batch experiments and some generic preliminary modeling was planned for the first year's work plan.

The project was designed to investigate three groundwater samples taken from three different sites. The selection of the sites were made by NJ-DEP in collaboration of the Responsible Parties. The plan was to include determination of reaction rates under various pH conditions and to emphasize the selection of barrier reactive media. One of the major challenges of the program was to find ways to overcome the high pH conditions of ground water. As well be seen from the results, the high pH conditions appears to be the most difficult to overcome, especially when considering a long term effectiveness of the proposed barriers.

The main methods used in the study included the use of batch reactor experiments under various conditions. Because the highly demanding needs to find media with high buffering capacity, screening of many more reactive media and their permutations were performed in the present study. Some modeling activities, including those with different barrier geometries were performed as a part of the first year's study.

Quality Assurance:

The main method used to assess the performance of different reactive and buffering media was based on the determination of total chromium by atomic absorption spectroscopy. We followed the basic protocol in method # 7000 and 7190 - both are documented in US-EPA SW-846, Third Edition, 1986. The quality control plan that was submitted for this phase of the program is attached as Appendix I.

Results and Discussion:

Three ground water samples were received from Allied Signal, Chemical Land Holdings and PPG. The samples were immediately stored at 4 °C and used through out the study. For each sample we determined the pH and total chromium

concentration using the AA method. Table .1. summarizes the results of the three samples. The total chromium concentration ranges from 15 to 55 ppm with a pH range between 11.5 and 12.35. The pH of groundwater samples is highly alkaline, and is not suitable for chromium reduction by zero valence iron. In order to accomplish the reduction, a decrease in the pH is required.

A. Initial Studies to Define Reduction Parameters with Iron Media:

In the initial phase of the investigation, a batch reactor geometry was used to conduct the experiments. A known volume of ground water was introduced into a flask and the experiments were done in triplicates. In each experiments, the pH of the groundwater was adjusted by the 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. Samples were taken at preset intervals for determining total chromium as a function of treatment time. The following tasks were accomplished in the initial part of the study:

1. Comparison between different types of iron reduction media..
2. Optimization of the amount of iron-to-groundwater ratio.
3. Measurement of reaction rates and reaction rate constants of groundwater samples collected from the three sites as a function of pH.
4. Determination of the pH and buffering requirements that are needed to accomplished effective chromium reduction at reasonable rates.

In the majority of the experiments, we used 5 grams of iron and 300 ml of groundwater per each test. The bottles were normally kept on the wrist-action shaker for 24 hours (or more) while collecting samples for determining total chromium. The following provides the results and discussion of these initial tasks:

1. **Effect of Iron Reduction Media:** Two types of reductive iron media were used in our experiments, namely: Peerless- and Fisher iron. Peerless iron was supplied by the Peerless Iron Company and is characterized by high porosity and was documented as an effective medium for reductive barriers. Fisher iron consists of solid iron particles and was purchased from Fisher Scientific. The latter has a low surface area and almost no porosity. In order to compare the performance of the two types of iron, they were used as the reductive medium for the same source of groundwater; the Chemical Land Holdings ground water samples were used at two pH conditions, 7.5 and 9.1. The results of these

experiments indicate that the Peerless iron achieves the reduction of hexavalent chromium at high rates compared to the Fisher iron (Table 2). The large surface area of the Peerless iron, which is mostly due to internal porosity, seems to be responsible for the high rates documented in Table 2. It should be noted that the above experiments were done at lower pH conditions (which was achieved by addition of HCl), since the pH of the as-received groundwater is too high for chromium reduction to take place. Based on these results, the Peerless iron was selected for further testing and experimentation during this program.

2. **pH and Buffering Action Needed for a Reactive Barrier Suitable for Groundwater Obtained from the Three NJ Sites:** Groundwater samples from each of the three sites were subjected to reduction (via contacting with the Peerless iron) at different pH conditions. The batch reactor experiments were used for this evaluation and the total chromium was measured after a 24-hour contact with the Peerless iron. The results summarized in Table .3. indicate that a pH condition about 9.0 is needed for an efficient reduction to take place in a reasonable time - a 24-hour period was arbitrary used. In addition, the reaction rates for the three ground water samples appear to be similar, at the same pH conditions. This indicated that condition needed for reduction is expected to be same irrespective of the source of the ground water, and that the pH is the dominant variable for this reduction process. The effect of other parameters such as the colloidal content and other subtle compositional factors will need to be addressed as we proceed with long term evaluation of barrier performance.
3. **Optimization of the Iron-to-Groundwater Ratio:** Batch reactor experiments were used to determine the critical iron-to-groundwater ratio needed to pursue the rest of the study. A 50 ppm total chromium solution was prepared with potassium dichromate and the pH was adjusted at 7,8,9 and 10 in various reaction bottles. 1, 2.5, 5 and 7.5 grams of iron were added to 200 ml of the above chromium solution as shown in Table 4. The experimental results indicates that 5 grams of Peerless iron per 200 ml of chromium solution is sufficient to achieve an efficient reduction at pH conditions up to 9.0. Lower iron amounts or higher pH did not produce the desired reduction rates - See Table .4. and Figure .1-4. The above ratios and conditions were followed for the remainder of the study.

4. **Reaction Rates at Different pH Conditions:** Reaction rates and constants were systematically evaluated for the three groundwater samples using the batch reactor arrangement at various pH conditions. Table 5 and Figures 5-7 summarize the results of this task. The reaction seems to follow a first order kinetics. The rate constants seems to flatten as the pH decreases to less than 9.2. The rate constants are similar for all groundwater samples obtained from the three sites. This again indicates that the pH is the dominant parameter affecting the rate constant of hexavalent to trivalent reduction. Table 6 and Figure 8 summarize the interplay between pH and iron/groundwater ratio. In brief, 5g/200 ml and pH less than 9.2 are needed to achieving fast and efficient reduction in the batch reactor experiments. Since the above results were obtained under aerobic conditions, it is expected that anaerobic conditions to have significantly faster reaction kinetics.

B. Experiments to Define Buffering Systems for Use in the Reactive Barriers.

As discussed in the original proposal, the buffering function of the reactive medium is considered to be the most critical factor for the success of this application. In an intensive effort, we have for the past several months explored many potential buffering systems. In this section, we summarize our results and discuss the implications of our findings.

1. **Buffering Systems Suggested in the Literature:** Early attempts by Puls and Powell (1) suggested that the use of minerals such as feldspar and kaolinite may have buffering functions (plus a decrease in the pH) and that they would assist the reduction of hexavalent chromium in groundwater. The pH range addressed by the Puls and Powell was near neutral. The situation of groundwater obtained from the NJ sites is different, where the pH is about 12, or higher in some cases. Our buffering studies involved the addition of potential buffering media to one of the groundwater samples and determining the pH decrease after exposure for 24 hours. If the addition of a buffering system produced a significant decrease in the pH, we studied the chromium concentration as a function of time with the addition of Peerless iron. Table .7. lists the effect of various potential buffers as suggested by different articles in the literature. Such materials included: silica, green sand, rock flour, kaolinite, flint sand,, fly ash, ferrous sulfide (amorphous), ferrous carbonate and olivine. In all cases the contact of the above minerals and

compounds, all were in the form of fine powders, did not have any measurable decrease of the pH of groundwater. The solubility of the above materials in ground water is very low. The materials listed in Table 7 were based on buffering systems including: silicic acid, hydrogen sulfide and carbonic acid. It is apparent that buffering action produced by these compounds and minerals is too small to lower these high pH values. Therefore, these materials are not expected to assist in chromium reduction - i.e., they are not suitable as buffering media in our application.

- 2. Investigation of Pyrite and Sidrite Minerals as Buffering Systems:** The two mineral systems that hold a high potential are pyrites and sidrite. These two minerals are known to have reasonable solubility in water, and have been cited by others to function as reduction media by themselves. We used two iron pyrites (FeS), and one sidrite (FeCO₃) - both are based on ferrous cations. The two iron pyrites were obtained from Chemalloy Company and Fisher Scientific, respectively. The sidrite mineral used in our experiments was obtained from the Scott Resources Company. Table 8 & 9 shows preliminary results of the effect of mineral -to-ground water ratio on the total chromium remaining after 24 hours exposure in the shaken bottle batch reactors. These experiments were done at the pH of the groundwater sample of about 12.25.

It is interesting to discover that 10 grams of the pyrite mineral is sufficient to achieve a decrease of the chromium level from 56 to 0.11 ppm. Table 8 also shows that sidrite is not as effective as pyrite in decreasing the total chromium of the same groundwater from 56 to 9.5 ppm. It should be noted that this reduction took place without the addition of the Peerless iron to the reaction vessel. The above results pertain to a single exposure of the mineral to the ground water sample.

A major question that needed to be addressed in our study concerns the effectiveness of the above mineral reductive media upon successive exposure to a fresh samples of groundwater. To answer this question we used the same mineral addition to perform the chromium reduction several times, and monitor the effectiveness of the process as function of exposure times. Table 10 shows that trend in Cr concentration decrease upon successive use (three times)of the same amount of pyrite and sidrite. In each experiment, a new sample of the same ground water was used - 250 ml of groundwater and 5 g of mineral was shaken for 24 hours. The results indicate that although pyrite is more effective in first exposure, its efficiency

declines much faster than that of sidrite. This may indicate that the reaction with sidrite may be more predictable. It should also be noted that pyrite is more effective in decreasing the Cr concentration of groundwater samples with initially high Cr (see Table 10). Because of the above observations, we decided to investigate barrier scenarios where the ground water would intercept successive barriers containing mixtures of sidrite plus iron followed by pyrite plus iron. The results of this experiment is summarized below.

Table 11 and Figures 9 summarizes the results of this test with a groundwater sample having 58 ppm total chromium. In Table 11, the first column indicates the number of the experiment/run that was performed, and the second column shows the initial total Cr in the groundwater sample used in each of the runs. These were as follows:

1. Run #1: 250 ml of 58 ppm Cr groundwater was added to 5g Peerless iron and 5 g sidrite and was shaken for 24 hours - column 3 gives the total Cr after this exposure cycle (39.2). Column 4 shows the total chromium after transferring the water from column 3 to a flask containing 5 g of Peerless iron and 5 g of pyrite - the total Cr is now 0.66 ppm.
2. Run #2: After removing all treated water from Flasks 1 and 2, another 250 ml of groundwater (58 ppm Cr) was added to Flask 1 for 24 hrs, and then transferred to Flask 2 for additional 24 hrs. The results are shown in columns 3 and 4, respectively.
3. Run #3: Another 250 ml of the groundwater sample (58ppm) was added to the same reaction media after removing all the water from Run 2.
4. Run #4: The experiment was repeated for the fourth time, following the same procedure described above.

It is apparent from the results shown in Table 11 and Figure 9 that successive use of a mixture of Peerless iron plus sidrite followed by a mixture of Peerless and pyrite exhibit a decrease in efficiency as a function of the number of uses.

The above results indicate that the above two mineral systems are promising, especially if they can be combined with the Peerless iron, other suitable high capacity reduction medium, such as the bimetallic materials developed by Circona. It should be noted here that both pyrite and sidrite has reductive capability as well as buffering capacity.

Further examination of the effectiveness of buffering capability of the sidrite minerals are demonstrated in the results summarized in Table .11. It is indicated that sidrite is most effective in buffering system in the pH range between 10.7 and 8.0.

C. Electrochemical Calculations:

Based on the experimental results of this study, we need to leap beyond the state of the art to further refine reductive media that van operate at the high pH condition of NJ-sites' groundwater. Analysis of the results, so far, points to the need to satisfy two conditions to solve this problem:

1. The electrochemical potential must be in the reduction region for chromate, and
2. The oxide/hydroxide layer must be soluble in the surroundings so that a fresh surface is exposed to flowing groundwater at all times.

For this purpose, we have conducted electrochemical calculations to define what other materials can be reduce chromate at high pH. Table 13 is a list of possible candidates. We are seeking cooperation with Circona to explore the sue bimetallics that may satisfy the above two conditions. The results will be presented in the following report.

Conclusions and Recommendations for Future Work

The following conclusions and plans have been made:

1. In order to use iron as the sole reductive media in a permeable barrier, the pH of groundwater must be at or below 9.3. Although the electrochemical condition for chromate reduction with iron is satisfied at higher pH (>9.3), the formation of a thick passivating layer of iron oxide/hydroxide at the surface of iron media slows the reduction to undetectable level. Therefore, for the iron to be used alone, a buffering system that provide pH <9.3 is needed. This buffering system needs to effective for along period of time - years.
2. The reduction of chromate with the iron medium at pH<9.3 follows first order kinetics. The reaction rate constant levels off at pH conditions <9.3. This result is applicable to groundwater obtained form the three sites selected for the study. Therefore, the technology can be applied to these

sites provided adjustment in buffering and reductive capacity is included in the design of the barrier.

3. Buffering media based on silicic acid-producing minerals such as silica, feldspar, kaolinite and others were not effective in decreasing the pH of groundwater from any of the three sites. This class of buffers will not be used, at least under the current pH conditions - 11 to 12.5.
4. Sulfide-based minerals, specifically iron pyrite, have been found to be effective in the reduction of chromate, even at the high pH of groundwater. However, the efficiency of reduction decreases upon the successive use of the same sample of mineral. This was attributed to be due the formation of a passivating oxide/hydroxide barrier layer slowing the kinetics, or due to the limited reductive capacity of pyrite. We are further assessing the surface mineralogy and chemistry of pyrite as a function of successive use. The addition of Peerless iron to pyrite may have enhanced chromate reduction efficiency, compared to pyrite alone. It appears that the surface dissolution of pyrite at the high pH results in sulfates that may enhance the dissolution of oxide/hydroxide layer formed on the surface of Peerless iron.
5. Carbonate-based minerals, specifically sidrite, have been found to be useful reductive medium by itself, or when used as a mixture with the Peerless iron at the high pH condition of groundwater (11 to 12.5). However, the reductive capacity of sidrite is less than that of pyrite. Sidrite, on the other hand, does not seem to form a passivating surface layer upon successive use. This feature is distinct from that observed for Peerless iron that forms a strong passivating layer when used alone, and for iron pyrite that shows a decreasing reductive ability with successive use. This discovery may allow us to use a composite barrier design where sidrite is an important component. It should be noted the reduction with sidrite still occurs at the high pH condition of 11 to 12.5, and that the product are carbonic acid.
6. Efforts to find practical and economic strong buffering media have not been successful, so far. We are pursuing other materials in this respect. Several systems are under investigation.
7. Our recent efforts are directed to exploring new reductive media that can function at the high pH without the formation of a passivating layer when used for successive reduction. We will be working with Circona to investigate the utility of bimetallic materials.

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8. Efforts to design and model permeable barriers are underway. It appears that a composite barrier consisting of a mixture of reaction media, or a design consisting of more than one barrier may be needed for this application.
9. Column experiments are underway to explore the above design concepts, and to validate the results of the batch reactor experiments.

Details of our future work have been included in the second-year proposal. The study has been proceeding as planned.

Table 1

pH and total chromium of groundwater samples
collected from three sites in New Jersey

Source of groundwater samples	pH (± 0.5)	Chromium* concentration. (ppm)
Allied Signal.	12.25	25
Chemical Land Holdings.	12.35	55
P. P. G.	11.5	15

* Average of six samples

Table 2

Reduction of chromium with two different iron media in batch reactor experiments at pH 7.5 and 9.1

Reaction time (hours)	Initial pH = 7.5		Initial pH = 9.1	
	Cr - ppm concentration Fisher iron.	Cr - ppm concentration Peerless iron.	Cr - ppm concentration Fisher iron.	Cr- ppm concentration Peerless iron.
0	44	44	45.5	45.5
1	37	31	40.5	30.5
4	35.5	16	39.5	19.5
7	35	7.5	38	7.5
11	34	2.25	37	2.4
23	33.5	0.4	36	0.25

Table 3

Effect of pH on Cr reduction in batch reactor experiments

pH. (± 0.25)	Allied Signal.		Chemical Land Holdings.		P. P. G.	
	Initial Cr ppm	Final Cr ppm	Initial Cr ppm	Final Cr ppm	Initial Cr ppm	Final Cr ppm
12.25	25	22	47	44	-	-
11	25	13	46	12	15	4
10	25	5	46	6	15	1.5
9	24	0.23	45	0.3	14	0.15
7.5	23	0.21	44	0.26	14	0.15
4.5	22	0.25	44.5	0.3	14	0.15

Table 4
Effect of groundwater/reactive media ratio 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

Table 5

Effect of pH conditions on the reaction rate constant

pH. (± 0.25)	Rate constant 'k' in units 'per hour'.		
	Allied Signal.	Chemical Land Holdings.	P. P. G.
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

Table 6
Effect of groundwater/reactive media ratio of 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

Table 7

Effect of several potential buffering media on the pH of groundwater

S.No.	Material tested.	Initial pH.	Final pH after 24 hours
1	Silica	12.73	12.71
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	Fly ash	12.56	12.39
8	Iron pyrite	12.33	12
9	Sidrite	12.33	12.17
12	Olivine	12.33	12.22

Table 8

Effect of pyrite/groundwater ratio on reaction rate of chromium reduction

Grams pyrite/250 ml water	Initial Cr concentration (ppm)	Final Cr concentration after 24 hours. (ppm)
2.5 grams	56	15.9
5 grams	56	15
7.5 grams	56	4
10 grams	56	0.11

Table 9

Effect of siderite/groundwater ratio on reaction rates of chromium reduction

Grams siderite per 250 ml of water	Initial Cr concentration (ppm)	Final Cr concentration after 24 hours (ppm)
2.5 grams	56	37.4
5 grams	56	19.5
7.5 grams	56	15.5
10 grams	56	9.5

Table 10.**Successive use of pyrite and sidrite as a reactive media.**

Initial Chromium concentration in ppm	Chromium concentration in ppm after 1 st use		Chromium concentration in ppm after 2 nd use		Chromium 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

Table 11

Results of successive chromium reduction with Peerless iron/sidrite mixture (Flask 1), followed by Peerless iron/pyrite mixture (Flask 2)

Experiment or Run #	Initial Chromium (ppm)	Flask 1*	Flask 2**
1	58	39.2	0.66
2	58	41.5	9.4
3	58	46.3	19.6
4	58	47.5	25.2

* Flask 1 : 5 grams Peerless iron and 5 grams sidrite.

** Flask 2: 5 grams Peerless iron and 5 grams pyrite.

Table 12

Buffering efficiency of sidrite - pH decrease of groundwater with sidrite
(5 grams sidrite/250 ml water)

Experiment Number	Initial pH	pH after 24 hours	pH after 48 hours
1	12.35	12.33	12.32
2	10.77	8.66	8.59
3	8.92	8.02	7.78
4	8.00	7.21	7.51
5	7.00	7.11	7.51

Table 13

Comparison between different elements for use as reactive media based on electrochemical potentials*

Element	pH = 12	pH = 11	pH = 10	pH = 9	pH = 8	pH = 7
Chromate reduction potential	+ 104	+ 202.5	+ 301	+ 400	+ 498	+ 560
Barium	- 2875.2	- 2816.1	- 2757	- 2698	- 2639	- 2580
Magnesium	- 2571.2	- 2512	- 2453	- 2394	- 2335	- 2276
Beryllium	- 2529.2	- 2470	- 2411	- 2352	- 2292	- 2233.7
Aluminium	- 2259.2	- 2200	- 2141	- 2082	- 2023	- 1963.7
Titanium	- 2015.2	- 1956.1	- 1897	- 1838	- 1778.8	- 1719.7
Silicon	- 1566.2	- 1507.1	- 1448.8	- 1388.9	- 1329.8	- 1270.7
Manganese	- 1436.2	- 1377.1	- 1318	- 1258.9	- 1200	- 1141
Zinc	- 1148.2	- 1089.1	- 1030	- 970.9	- 911.8	- 852.7
Tungsten	- 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

* The algebraic addition of chromate reduction potential and oxidation potential of elements shown in the table must be in the chromate reduction region as predicted by Pourbaix diagram. Elements above iron in this table are favorable. The most appropriate ones are those that do not form a strong passivating layer at the high pH. Cost and safety would be other issues that need to be considered.

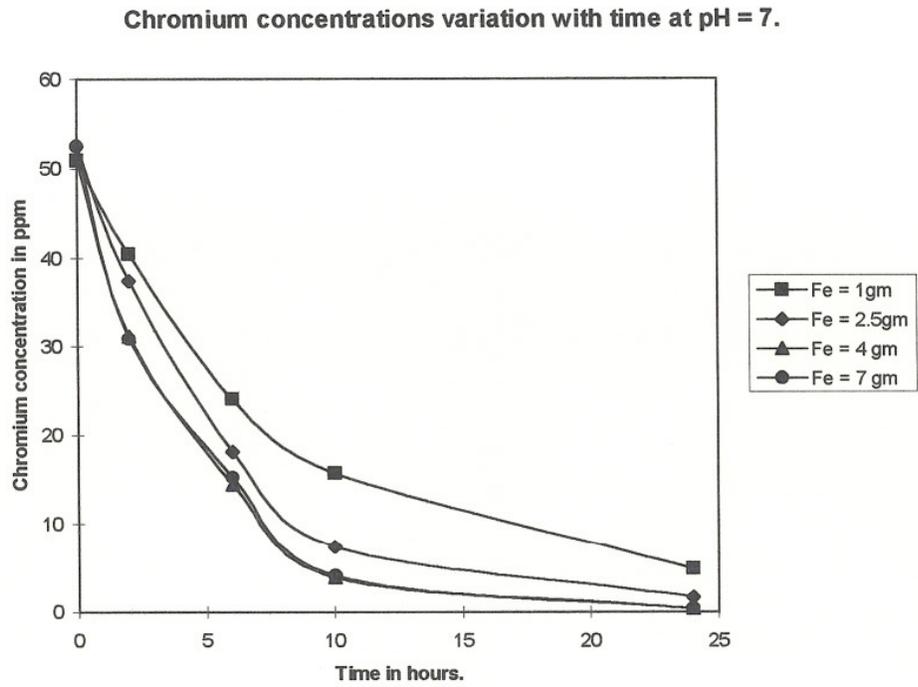


Figure 1: Effect of iron/groundwater ratio on chromium reduction at pH 7.0

Chromium concentration variation with time for pH = 8

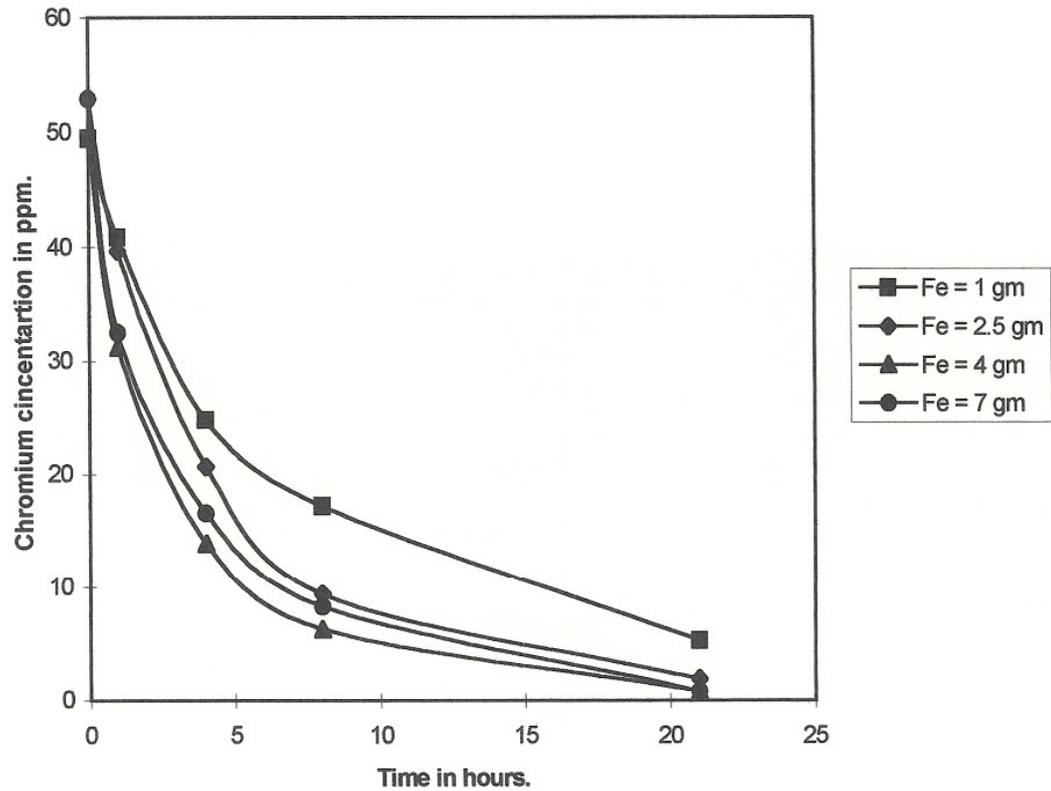


Figure 2: Effect of iron:groundwater ratio on chromium reduction at pH 8.0

Chromium concentration variation with time for pH = 9.

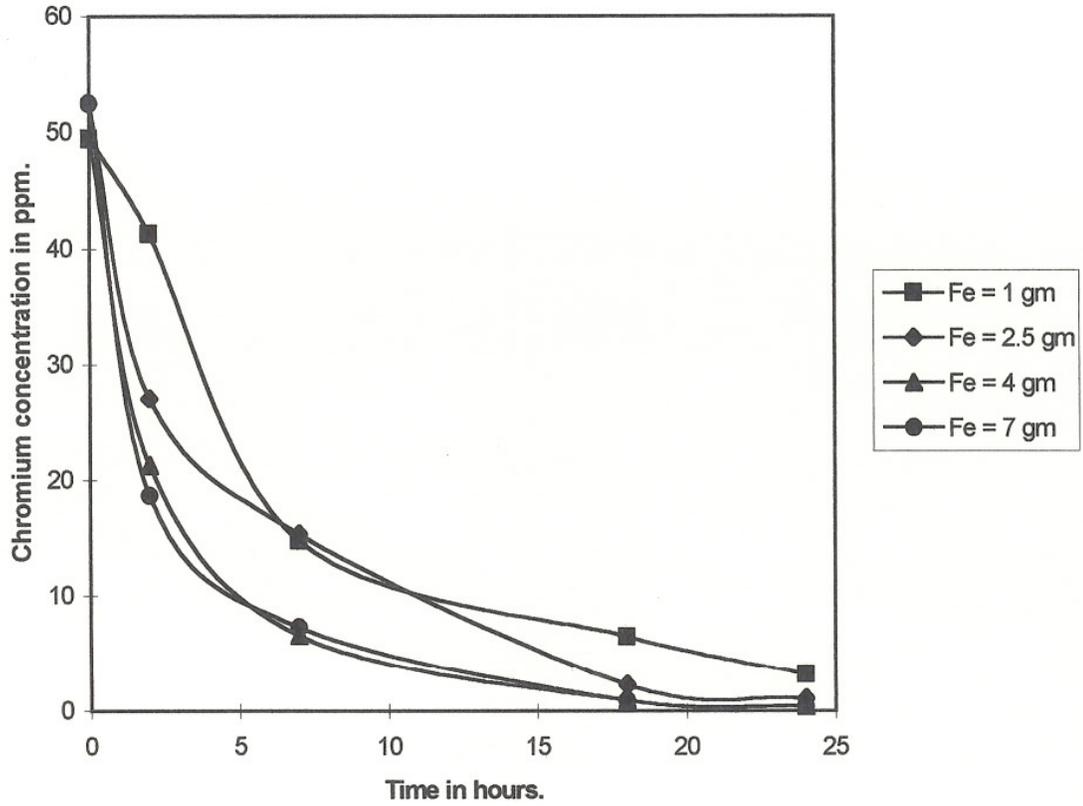


Figure 3: Effect of iron/groundwater ratio on chromium reduction at pH 9.0

Chromium concentration variation with time for pH = 10.

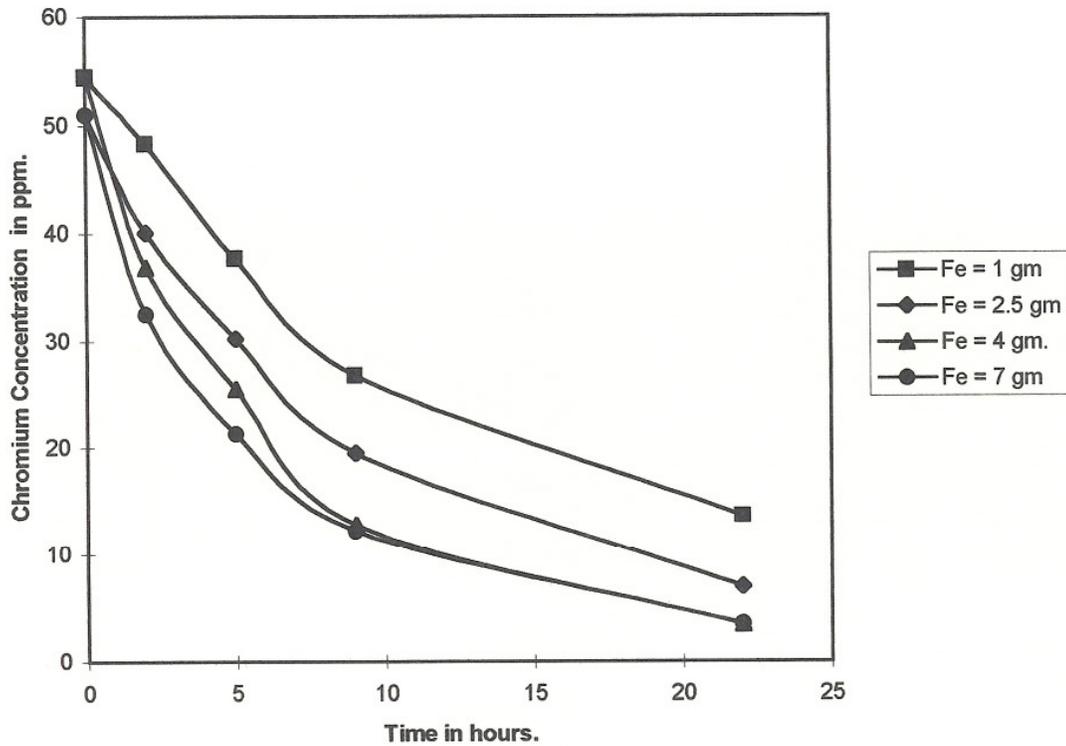


Figure 4: Effect of iron/groundwater ratio on chromium reduction at pH 10.0

Variation in the values of rate constant 'k'
with change in pH for 'Allied Signal'.

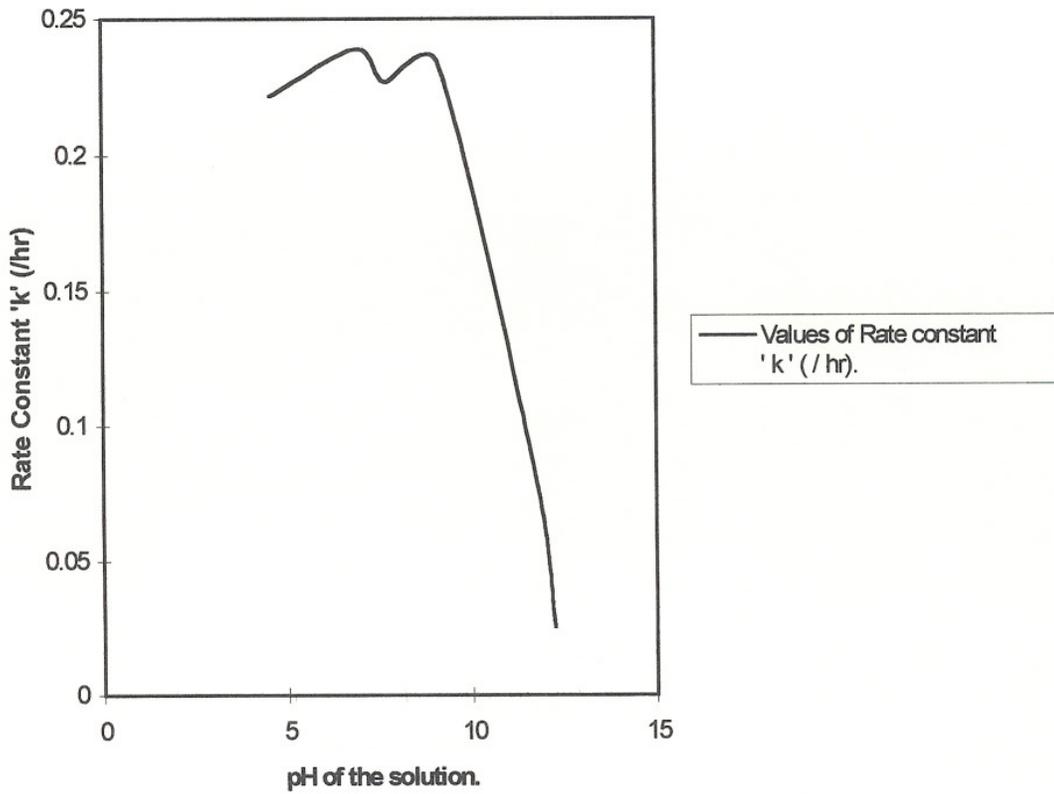


Figure 5: Effect of pH on reaction rate constant for chromium reduction with iron media - Allied Signal site

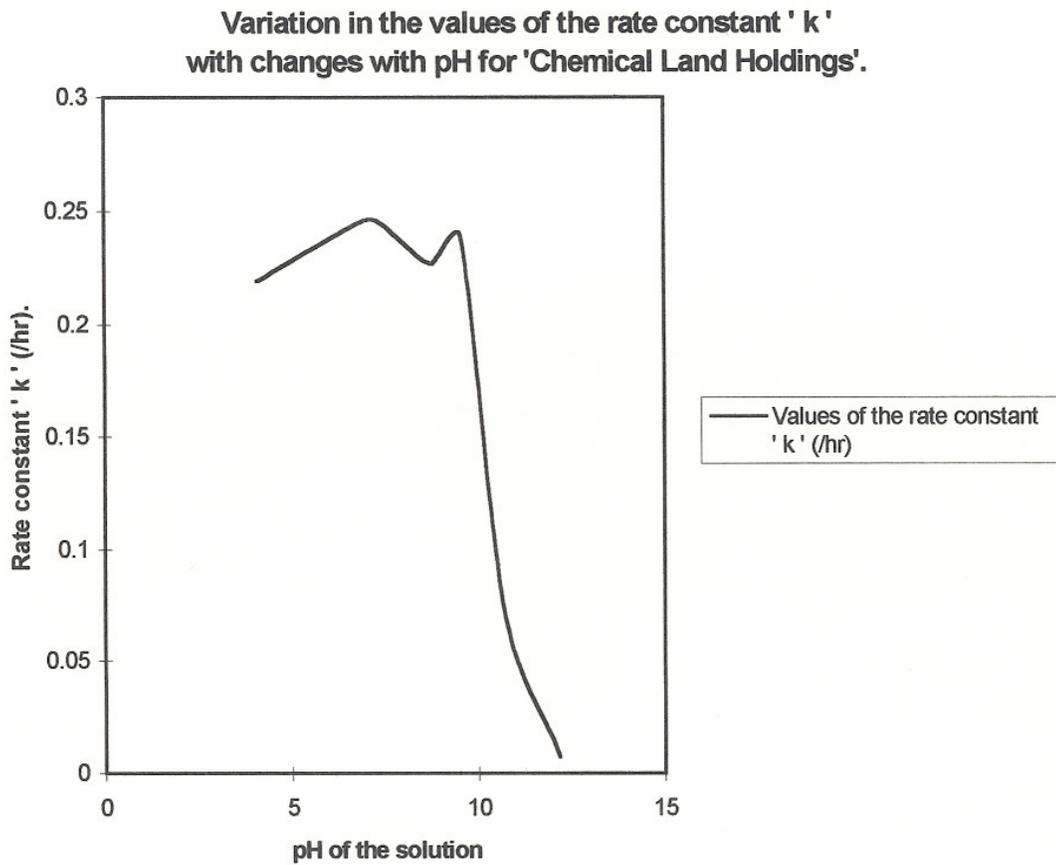


Figure 6: Effect of pH on reaction rate constant for chromium reduction with iron media - Chemical Land Holdings site

Variation of values of the Rate Constant 'k'
with changes in pH for P.P.G.

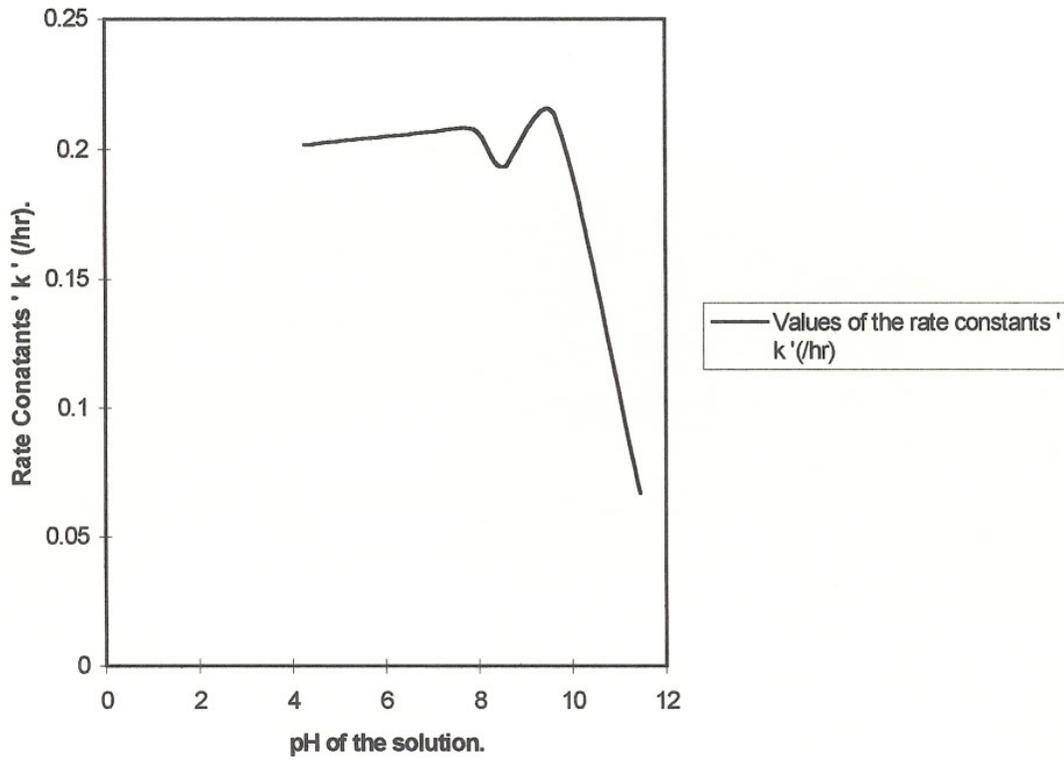


Figure 7: Effect of pH on reaction rate constant for chromium reduction with iron media - PPG site

Change in the reaction rate constants with changes in the pH of the solution and amounts of Fe used.

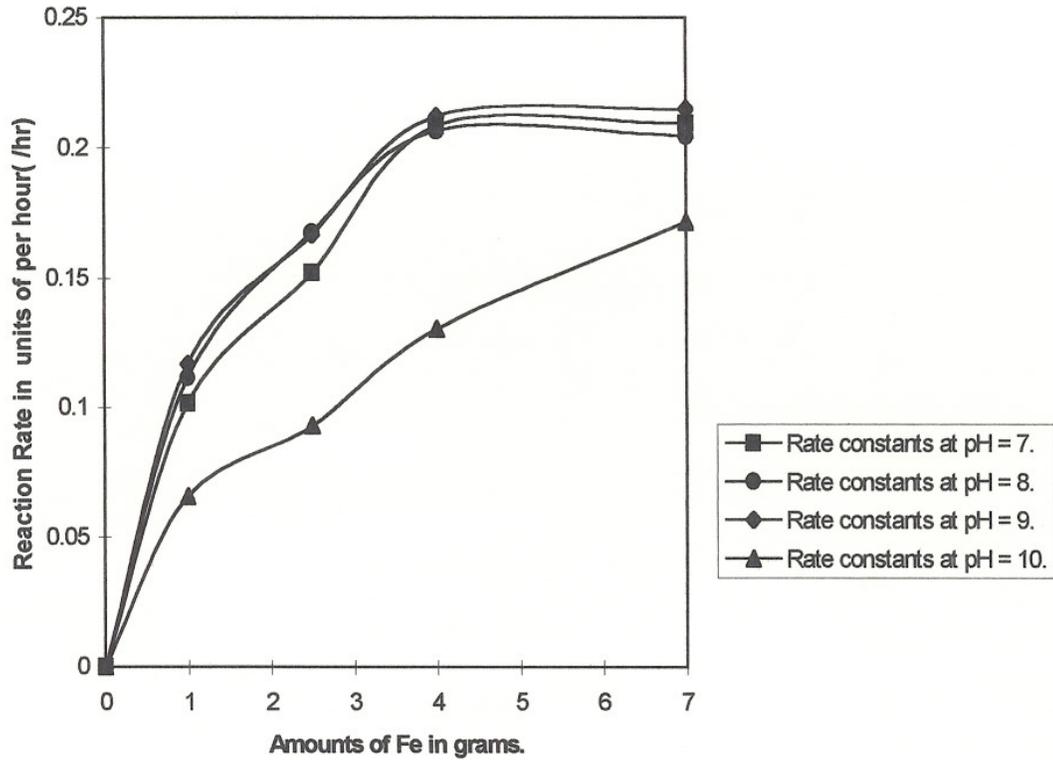


Figure 8: Effect of iron/groundwater ratio on reaction constant at different pH conditions

Graph of Chromium conc. versus no. of reuses

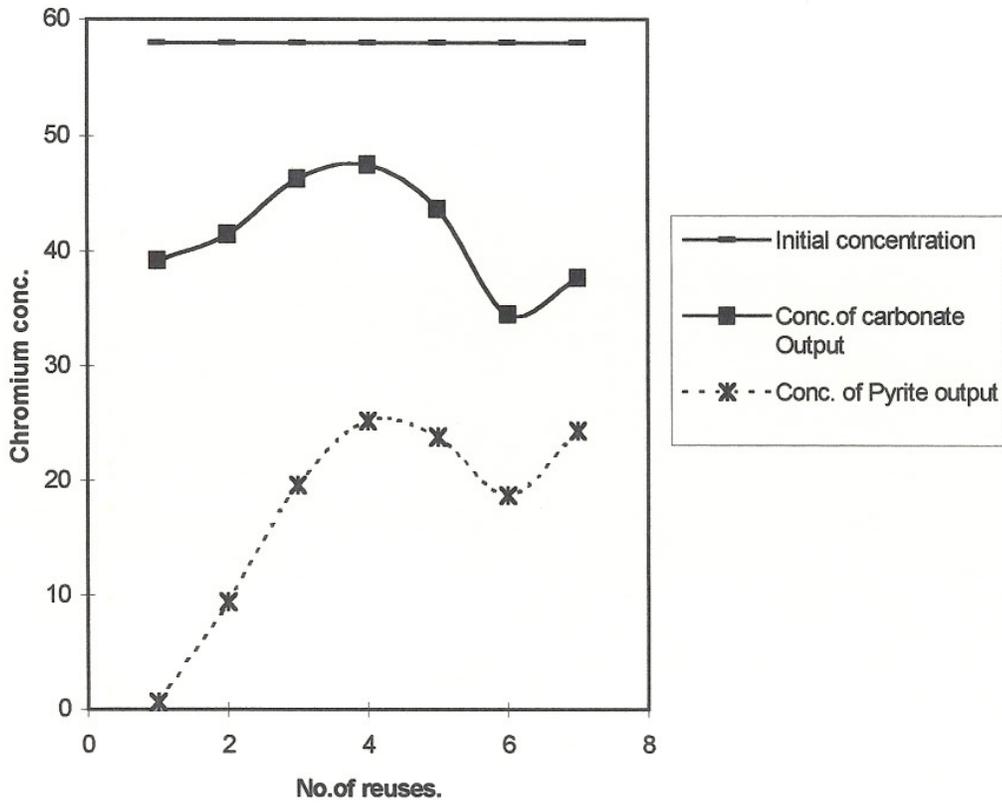


Figure 9: Effect of successive reduction with sidrite-iron mixture followed by pyrite-iron mixture - See Table 11