

Laboratory Evaluation of the Potential for In Situ Treatment of Chromate- Contaminated Groundwater by Chemical Precipitation

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Abstract - A995

LABORATORY EVALUATION OF THE POTENTIAL FOR IN SITU TREATMENT OF CHROMATE-CONTAMINATED GROUNDWATER BY CHEMICAL PRECIPITATION

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Laboratory testing activities have been undertaken to evaluate the potential of in situ remediation of chromate-contaminated groundwater through the introduction of ferrous and sulfide ions. Initial tests with chromate-solutions indicated that ferrous sulfate can quantitatively reduce and precipitate hexavalent chromium if applied at a Fe(II):Cr(VI) mole ratio of 9 under slightly alkaline conditions. Verification tests were also conducted with chromate-contaminated Hanford Site groundwater and soil from the Hanford Site. Ferrous sulfate and combinations of ferrous sulfate and sodium sulfide were reacted with groundwater/soil mixtures in this set of experiments to assess the capability of removal of chromium from groundwater through reduction and precipitation. The application of 7 equivalents of reductant per equivalent of chromium was found to provide satisfactory treatment results. A ferrous sulfate solution or ferrous/sulfide solution with a concentration of about 10 equivalents (i.e., a Fe(II):Cr(VI) mole ratio of 30), however, is recommended for the system associated with this study since the soil exhibited a tendency to react with the reductants to a moderate extent. This corresponds to the injection of about 1200 μ moles of Fe^{2+} per liter of treatment solution (67 ppm Fe^{2+}) for remediation of groundwater containing 2100 ppb hexavalent chromium.

The results of these tests suggest that in situ remediation of chromate-contaminated groundwater by injection of solutions containing ferrous or ferrous/sulfide ions is feasible. This approach should be considered as a method that could enhance the efficiency of pump and treat operations.

Laboratory Evaluation of the Potential for In Situ Treatment of
Chromate-Contaminated Groundwater by Chemical Precipitation

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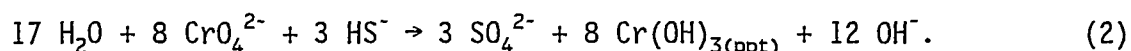
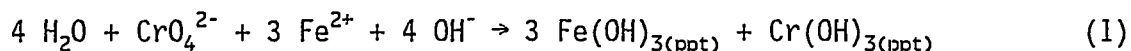
INTRODUCTION

The current technology commonly utilized for remediation of contaminated groundwater systems consists primarily of the pump and treat method. In this approach, groundwater is pumped to the surface, contaminants removed, and the treated water returned to the aquifer or otherwise disposed of. While generally effective for removing contamination in the early stages of operation, an extended period of pumping may be required to reduce contamination to acceptable levels.¹ This may be attributed to contaminant sorption/desorption processes and the heterogeneous nature of aquifer systems.

In situ chemical treatment of metal or radionuclide contaminants within groundwater systems has been recognized as a potential remediation approach that warrants development and may provide a viable alternative to the pump and treat method.^{2,3} The objective of in situ chemical treatment is to immobilize contaminants within the aquifer by precipitation as a relatively insoluble compound. Precipitation of chromium or uranium, for example, may be achieved by lowering the oxidation potential of the system, thus causing the valence of the metal to drop to a lower oxidation state. The reduced metal species are less soluble and, consequently, the metal is precipitated as a component of a solid phase.

The objective of this paper is to present the results of a series of small-scale batch tests performed to assess the effectiveness of chemical precipitation in the remediation of chromate-contaminated groundwater. These tests involved treatment of chromate solutions with ferrous and sulfide ions. In addition, tests were conducted that involved treatment of mixtures of chromate-contaminated groundwater and uncontaminated soil with the ferrous ion. A combination of ferrous sulfate and sodium sulfide was also tested in the groundwater treatment tests, since this approach has been shown to be an efficient method for treating electroplating wastewaters.⁴

The chemical reactions that govern the redox level of this system can be presented as follows:



The above have been written as basic solution reactions since groundwater systems are commonly somewhat alkaline in nature (pH ~8).

The reduction of hexavalent chromium, as indicated in reaction 1, requires a mole ratio of Fe(II):Cr(VI) of at least 3 to completely reduce chromium. Reaction 2 requires a minimum ratio of S(-II):Cr(VI) of only 3:8.

Solution samples obtained during these tests were analyzed for hexavalent chromium spectrophotometrically using diphenylcarbazide. Solution samples were filtered or centrifuged to remove sediment or precipitates, and analyzed for total chromium by inductively coupled plasma atomic emission spectroscopy (ICP). Measurement of pH was also performed on most of the solution test samples.

FERROUS SULFATE TESTS

To evaluate the effectiveness of ferrous iron in reducing and precipitating chromium, ferrous sulfate was added to solutions containing 500 ppb hexavalent chromium. The results of these tests are summarized in Figure 1, which illustrates the rate of decrease in the concentration of hexavalent chromium remaining in solution during treatment. Data from tests 1A, 2A, and 4A, which were all conducted at a mole ratio of Fe(II):Cr(VI) of 3, indicate that the extent of reduction increases as solution pH is lowered. Thus in test 1A, which was conducted under acidic conditions, hexavalent chromium decreased to less than 50 ppb within the first several hours. In test 2A, which was almost neutral, hexavalent chromium was approximately 100 ppb throughout the test. In test 4A, which was conducted at a pH of about 8, Cr(VI) concentrations declined to only 381 ppb after 120 hours of reaction.

Comparison of the results of tests 2A and 3A indicates that the extent of hexavalent chromium reduction increases as the mole ratio of Fe(II):Cr(VI) increases. Thus, at a mole ratio of 3 in test 2A, Cr(VI) decreased to about 100 ppb while in test 3A, which was conducted at a mole ratio of 9, Cr(VI) was quantitatively reduced. Tests 5A and 6A were conducted with soil at a soil to water mass ratio of 0.1. Comparison of the results from these two tests further illustrates that an increase in the mole ratio of Fe(II):Cr(VI) greatly enhances reduction of hexavalent chromium.

Comparison of the data from tests 2A, 4A, and 5A illustrates that introduction of soil results in less chromium reduction. Note that a pH value of 8 for the reacted solution was measured in test 5A, while the pH of the reacted solution of test 2A was 5.8. The higher pH of test 5A may be attributed to interaction of the solution with the calcareous component of the soil used in the test. The higher pH of this test appears to have resulted in less reduction of hexavalent chromium. This conclusion is supported by the similarity of the results of test 5A with those of test 4A, in which the solution pH was adjusted to 8. In addition, a portion of the reducing agent may have been consumed in test 5A by interaction of the ferrous ion with oxide coatings associated with the soil.

The data collected in these tests generally indicate that equilibrium is attained within the first 24 hours, as evidenced by the approach of Cr(VI) concentrations to constant values. Tests 4A and 5A, however, indicate that higher pH values and soil interaction effects may lengthen required reaction time somewhat. Reaction time can be minimized by increasing the mole ratio of Fe(II):Cr(VI), as demonstrated by the results of tests 3A and 6A.

Solutions from a portion of these tests were also analyzed for total chromium. Comparison of the difference between total chromium and hexavalent chromium provides a measure of the trivalent chromium remaining in solution after treatment. This data indicated that even though most of the hexavalent chromium was reduced to trivalent chromium during the tests, relatively little of the trivalent chromium was precipitated under neutral to acidic conditions or in the tests conducted at a Fe(II):Cr(VI) mole ratio of 3.

The effect of using a mole ratio of Fe(II):Cr(VI) of 9 on chromium reduction and precipitation was evaluated further in two additional tests. These tests were also conducted at a somewhat higher pH (8 to 8.5). In the first test, which was conducted without soil, essentially complete reduction and precipitation took place. In the second test, which included soil, 96% reduction and 80% precipitation of

chromium was achieved. These results suggest that ferrous ion in excess of the stoichiometric amount is required to achieve quantitative reduction of hexavalent chromium under alkaline conditions. Once reduction occurs, however, the reduced chromium readily precipitates as a hydroxide solid phase. The high degree of immobilization observed is probably related to the precipitation of ferric hydroxide generated by oxidation of the ferrous sulfate during the reaction. This precipitate may have enhanced removal of chromium by coprecipitation of iron and chromium, and by adsorption of chromium ionic species by the hydroxide precipitate.^{5,6}

SODIUM SULFIDE TESTS

Sodium sulfide was added to 500 ppb hexavalent chromium solutions to assess the potential of using sulfide to reduce and precipitate chromium. In one series of tests conducted under near neutral pH conditions (2D-1, 2D-2, 2D-3, and 2D-5), the solutions were treated with sodium sulfide at mole ratios of S(-II): Cr(VI) of 6, 9, and 12. This corresponds to 16, 24, and 32 stoichiometric equivalents according to reaction 2. The results of these tests are presented in Figure 2. Note that increasing the mole ratio used resulted in only a limited improvement in the reduction of hexavalent chromium in the solutions. Test 2D-5 also contained soil at a soil to water mass ratio of 0.1 and was treated at a mole ratio of 12. The degree of Cr(VI) reduction that occurred in the first 24 hours was similar to the other tests in this series. An apparent reversal, however, was observed at 48 hours. The cause of the reversal is uncertain but may be due to oxidation of the sulfide by the soil or, alternatively, to a gradual increase in solution pH in response to dissolution of the calcareous fraction of the soil.

An additional test was conducted to obtain data related to the degree of treatment and immobilization of hexavalent chromium that would occur in groundwater treated with sodium sulfide at a moderately high mole ratio. A mole ratio of 50 was employed in this test and solution pH was adjusted to 10 by addition of NaOH. The results of this test were relatively favorable, achieving 97% reduction and 20% precipitation of chromium.

GROUNDWATER TREATMENT TESTS

The results of the tests presented above indicate that ferrous sulfate should be effective in remediating groundwater systems contaminated with hexavalent chromium. Additional tests were undertaken to further verify this by treating contaminated groundwater and soil mixtures with ferrous ion. In addition, tests were run with combinations of ferrous and sulfide ions to assess the effectiveness of ferrous/sulfide in situ treatment of groundwater. All tests were run in duplicate during separate weeks. The analytical results presented below represent averaged values of corresponding solution samples collected at 168 hours from these duplicate tests.

Chromate-contaminated groundwater from the Hanford unconfined aquifer was obtained from well D5-15 of the 100-D Area for use in these tests. Analysis of the groundwater indicated a total chromium content of about 2100 ppb, with essentially all of the dissolved chromium in the hexavalent oxidation state (Table 1). Uncontaminated soil was also collected from the 100-D Area of the Hanford Site for testing purposes. Table 1 presents the results obtained by combining the soil and groundwater at several soil/water mass ratios. These data indicate that the soil has a relatively oxidized character since little or no reduction of hexavalent chromium occurred during the 168 hours associated with the tests.

Ferrous treatment tests were performed at three levels in terms of soil amount and two levels of ferrous iron concentration. The objective of this portion of the testing was to verify that remediation of chromate-contaminated groundwater can be achieved by the addition of ferrous ion and to determine the oxidizing capacity of the soil relative to the ferrous ion. These tests were conducted by combining ferrous iron, groundwater, and soil in the amounts shown in Table 2, where soil/water is a mass ratio and Fe/Cr is a mole ratio.

Tests A, B, and C were conducted at a Fe/Cr mole ratio of 2.64, which is slightly less than the stoichiometric ratio required for reduction (Fe/Cr = 3). The results of these tests indicate that the soil is oxidizing relative to ferrous ion, with an oxidizing capacity of about 0.17 μ equivalents per gram of soil.

The results of tests D, E, and F indicate that essentially complete reduction and precipitation of hexavalent occurred when a Fe/Cr mole ratio of 21.16 was employed (i.e., about 7 stoichiometric equivalents of reductant). Furthermore, the addition of soil up to a soil/water mass ratio of 0.2 did not significantly affect the treatment results.

Ferrous/sulfide treatment tests were performed at two levels in terms of soil amount and three levels of ferrous and sulfide concentrations. The primary objective of this portion of the testing was to determine if remediation of chromate-contaminated groundwater can be more readily achieved by the addition of both ferrous and sulfide ions than by the use of the ferrous treatment alone. These tests were conducted by combining ferrous iron, sulfide, groundwater, and soil in the amounts shown in Table 2, where soil/water is a mass ratio and Fe/Cr and S/Cr are mole ratios. Components were added in the order ferrous sulfate, sodium sulfide, and soil to the groundwater sample.

Tests G and H were conducted with a total of 0.55 stoichiometric equivalents of reductants at a Fe/S mole ratio of about 2. Minimal reduction of hexavalent chromium was observed. In tests I and J, a total of 7 stoichiometric equivalents of reductants was added at a Fe/S mole ratio of about 0.5. Significant reduction occurred, although the addition of soil interfered with treatment. The results of Tests K and L indicate that essentially complete reduction and precipitation of hexavalent occurred when 7 stoichiometric equivalents of reductants was applied at a Fe/S mole ratio of 2. The addition of soil up to a soil/water mass ratio of 0.2 did not significantly affect the treatment results.

DISCUSSION

The results of the ferrous and sulfide treatment tests conducted with chromate solutions clearly indicate that ferrous treatment is superior to sulfide treatment in the reduction of hexavalent chromium. The treatment of chromate-contaminated groundwater with ferrous ions during this study further demonstrated that the application of ferrous ion at a sufficiently high ratio of Fe/Cr may be a feasible remediation approach. It is suggested that an elevated molar ratio serves to overcome the lower reaction rates associated with the moderately alkaline character of the groundwater. Once reduced, the chromium readily precipitates as a hydroxide phase under these conditions. It also appears that combined ferrous/sulfide treatment should be effective if applied at a moderately elevated value of total reductant to chromate ratio and a mole ratio of Fe/S of 2.

The soil sample utilized in this study has a generally oxidizing character, as demonstrated by the interaction with ferrous ion. Thus, a somewhat higher total reductant ratio of applied ferrous ion or ferrous/sulfide to chromate would be required to achieve quantitative reduction of chromium if treatment solutions were injected into the groundwater system being considered. The results of these tests indicate that the soil sample has an oxidizing capacity of about 0.17 μ equivalents per gram of soil relative to the ferrous ion. If we assume that the soil/water mass ratio of the aquifer is 5 and one pore volume of treatment solution is injected, a ferrous sulfate solution with a concentration of 870 μ moles/L (49 ppm Fe^{2+}) would be required to overcome the inherent oxidizing capacity of the aquifer. Additional ferrous iron must also be added to reduce the hexavalent chromium present. The results of this study suggest that a Fe/Cr mole ratio of 9 is adequate for efficient reduction of chromate (three times the stoichiometric ratio). Since the hexavalent chromium concentration of the aquifer is about 2100 ppb in this case, an additional 363 μ moles/L of ferrous ion would be needed. Thus, injection of a ferrous sulfate solution at a concentration of about 1200 μ moles/L (67 ppm Fe^{2+}) should be sufficient to achieve complete reduction and immobilization of chromate present in the groundwater system.

Application of the in situ chemical precipitation approach to aquifer remediation could be conducted in conjunction with a pump and treat program. That is, pumped groundwater could be treated in ex situ facilities to remove contamination, the treatment agent added, and the groundwater reinjected in an upgradient position within the aquifer. Subsequent movement of the treatment agent through the zone of contamination would serve to reduce and precipitate hexavalent chromium within the aquifer. This approach could potentially provide significant cost savings by reducing the amount of time required to achieve cleanup goals.

CONCLUSIONS

The results of a series of small-scale batch tests indicate that injection of ferrous or ferrous/sulfide solutions may be a viable approach to remediation of many chromate-contaminated groundwater systems. The application of diluted solutions amended with ferrous iron is particularly attractive since the solutions would be nonhazardous in nature and should be simple to prepare and inject. The use of ferrous/sulfide combinations may also be effective in some situations, but may require negotiations with regulatory staff owing to the potentially hazardous nature of sulfide.

The test results presented in this study indicate that application of a solution with a Fe/Cr mole ratio of 9 or greater is required to achieve quantitative reduction and precipitation of hexavalent chromium. This ratio may need to be increased somewhat, however, depending on the capacity of associated aquifer sediments to oxidize the treatment agent. It is recommended that bench-scale tests similar to those presented here be conducted as a means of determining appropriate treatment solution concentrations for remediation of other chromate-contaminated groundwater systems.

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REFERENCES

1. C.C. Travis and C.B. Doty, "Can contaminated aquifers at Superfund sites be remediated?" Environ. Sci. Technol., 24(10):1464-1466 (1990).
2. D.E. Sanning and M.I. Black, Protecting the Environment at Superfund Sites through Chemistry, EPA/600/D-87/222, U.S. Environmental Protection Agency, Hazardous Waste Engineering Research Laboratory, Cincinnati, 1987, pp 5-11.
3. E.C. Thornton, C.A. Jurgensmeier, and M.A. Baechler, Laboratory Evaluation of the In Situ Chemical Treatment Approach for Remediation of Cr(VI)-Contaminated Soils and Groundwater, WHC-SP-0704, Westinghouse Hanford Company, Richland, WA, 1991, pp 1-33.
4. J.M. Beller, G.S. Carpenter, R.E. McAtee, et al., Full-scale Implementation of the Sodium Sulfide/Ferrous Sulfate Treatment Process, ESL-TR-89-08, Engineering and Services Laboratory, Air Force Engineering and Services Center, Tyndall AFB, FL, 1989, pp 1-30.
5. L.E. Eary and D. Rai, "Chromate removal from aqueous wastes by reduction with ferrous ion," Environ. Sci. Technol., 22(8):972-977 (1988).
6. T.E. Higgins and V.E. Satar, Treatment of Electroplating Wastewaters by Alkaline Ferrous Reduction of Chromium and Sulfide Precipitation, ESL-TR-83-21, Engineering and Services Laboratory, Air Force Engineering and Services Center, Tyndall AFB, FL, 1983, pp 3-8.

Table 1. Groundwater analysis and soil/groundwater test results.

Test ID	Soil/Water	Cr(VI), ppb	Cr(total), ppb	pH
D5-15	0	2114	2118	8.2
Soilblank-1	0.1	2148	2113	8.0
Soilblank-2	0.2	2078	2063	8.2

Table 2. Ferrous treatment of chromate-contaminated groundwater and soil/groundwater mixtures.

Test ID	Soil/Water	Fe/Cr	Cr(VI), ppb	Cr(total), ppb	pH
A	0	2.64	232	232	8.3
B	0.1	2.64	574	569	8.0
C	0.2	2.64	834	777	8.0
D	0	21.16	<50	10	6.9
E	0.1	21.16	<50	15	8.1
F	0.2	21.16	<50	25	8.1

Table 3. Ferrous/sulfide treatment of chromate-contaminated groundwater and soil/groundwater mixtures.

Test ID	Soil/Water	Fe/Cr	S/Cr	Cr(VI), ppb	Cr(total), ppb	pH
G	0	0.31	0.17	1871	1873	8.2
H	0.2	0.31	0.17	1874	1790	7.9
I	0	1.23	2.47	113	144	8.1
J	0.2	1.23	2.47	367	432	7.9
K	0	4.23	2.12	<50	10	8.2
L	0.2	4.23	2.12	<50	17	7.8

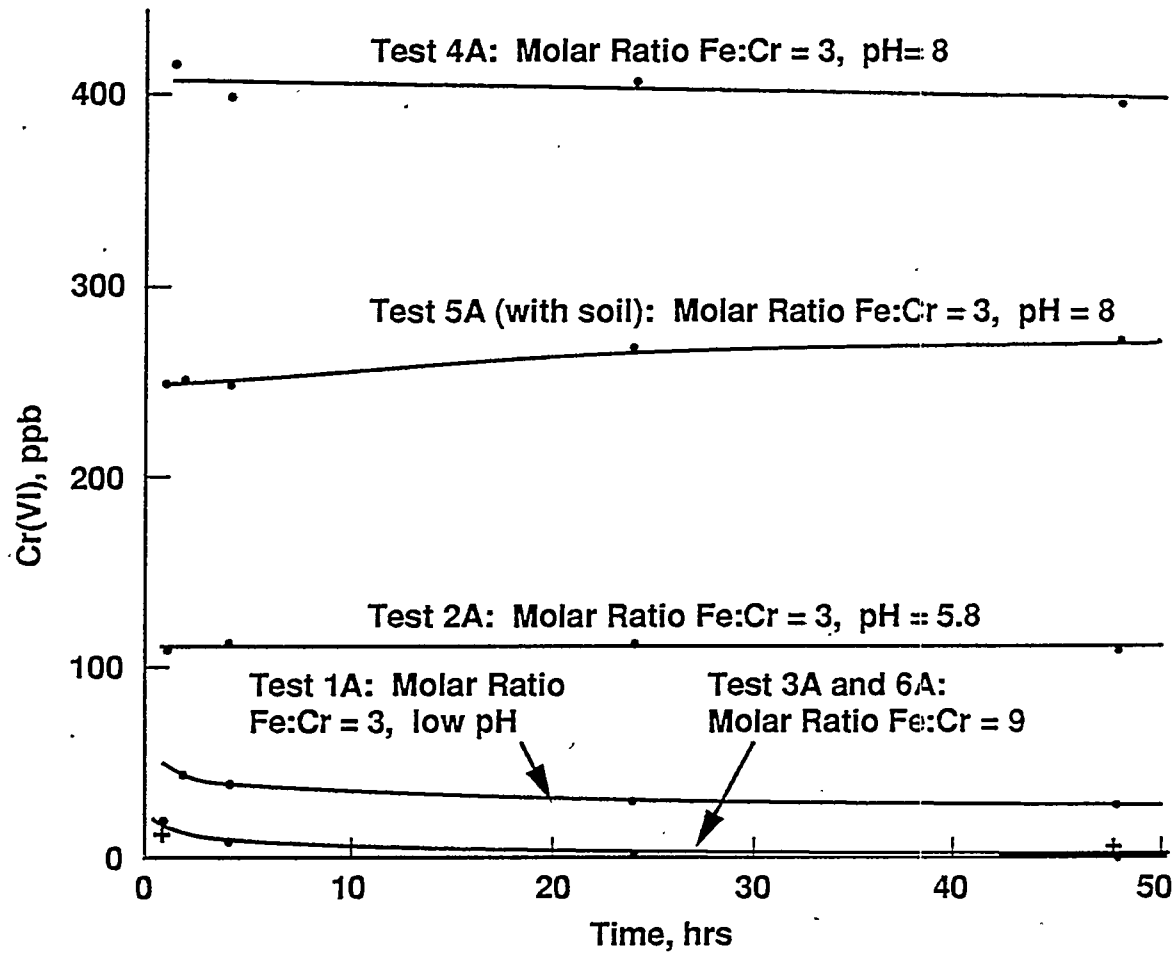


Figure 1. Change in concentration of hexavalent chromium with time following treatment of a 500 ppb solution of Cr(VI) with ferrous sulfate.

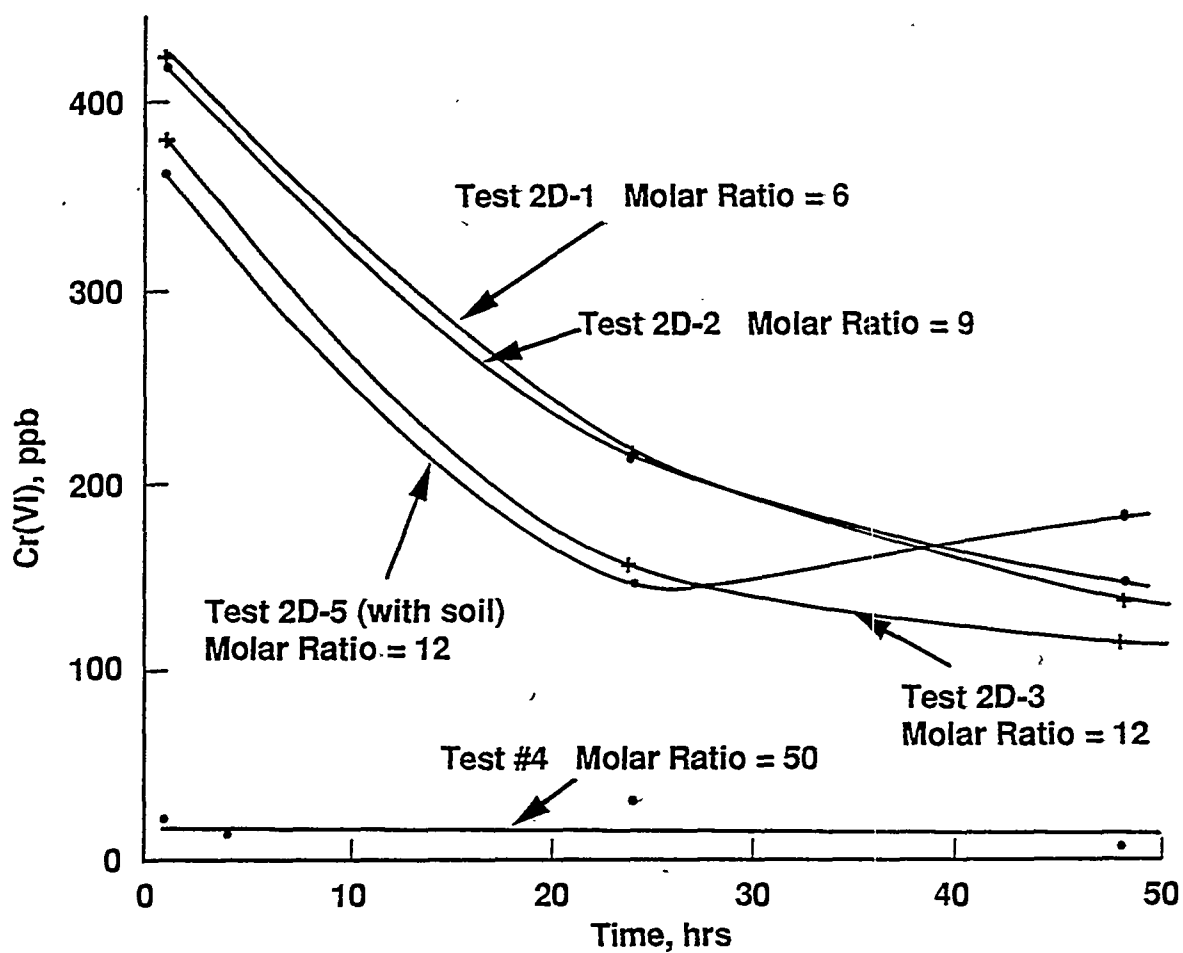


Figure 2. Change in concentration of hexavalent chromium with time following treatment of a 500 ppb Cr(VI) solution with sodium sulfide.