

Laboratory Study for the Reduction of Chrome(VI) to Chrome(III) Using Sodium Metabisulfite under Acidic Conditions

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Richland, WA 99352

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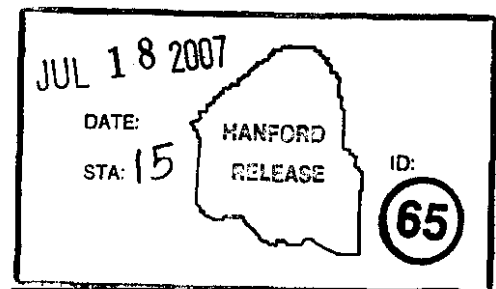
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Abstract: This report describes the results from RPP-PLAN-32738, "Test Plan for the Effluent Treatment Facility to Reduce Chrome(VI) to Chrome(III) in the Secondary Waste Stream," using sodium metabisulfite. Appendix A presents the report as submitted by the Center for Laboratory Sciences (CLS) to CH2M HILL Hanford Group, Inc. The CLS carried out the laboratory effort under Contract Number 21065, release Number 30. This report extracts the more pertinent aspects of the laboratory effort.

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LABORATORY STUDY FOR THE REDUCTION OF CHROME(VI) TO CHROME(III) USING SODIUM METABISULFITE UNDER ACIDIC CONDITIONS

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Table of Contents

1. INTRODUCTION..... 1

2. PROCEDURE AND RESULTS 2

 2.1 SCOUTING TEST..... 2

 2.2 SIMULATED GROUNDWATER..... 4

 2.2 TOXICITY CHARACTERISTIC LEACHING PROCEDURE RESULTS..... 6

3. CONCLUSIONS..... 6

4. REFERENCES..... 6

Appendix A..... A-i

List of Figures

Figure 1. ORP mV versus Reagent Addition..... 2

Figure 2. Cumulative Volume of 0.5 M Sodium Metabisulfite to Achieve an Oxidation
Reduction Potential of 279 at pH 2 in 20 Wt% Sodium Sulfate and 80 mg/L Cr(VI)... 3

Figure 3. Cumulative Volume of 10N Sodium Hydroxide to Achieve a pH Greater than 10.5... 3

Figure 4. Cumulative Volume of 0.5 M Sodium Metabisulfite to Achieve an ORP of 280
at pH 2 in Basin 43 Simulant at 110 mg/L Cr(VI). 5

Figure 5. Cumulative Volume of 10N Sodium Hydroxide to Achieve a pH Greater than 10.5... 5

List of Tables

Table 1. Liquid Effluent Retention Facility Basin 43 Groundwater Simulant. 4

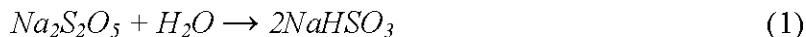
Table 2. Toxicity Characteristic Leaching Procedure Results..... 6

1. INTRODUCTION

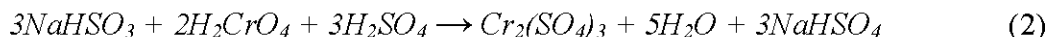
This report describes the results from RPP-PLAN-32738, *Test Plan for the Effluent Treatment Facility to Reduce Chrome(VI) to Chrome(III) in the Secondary Waste Stream*, using sodium metabisulfite. Appendix A presents the report as submitted by the Center for Laboratory Sciences (CLS) to CH2M HILL Hanford Group, Inc. The CLS carried out the laboratory effort under Contract Number 21065, release Number 30. This report extracts the more pertinent aspects of the laboratory effort.

The reduction of hexavalent chromium [Cr(VI)] to trivalent chromium [Cr(III)] will decrease the mobility of chromium in the environment, allowing the waste stream from the Effluent Treatment Facility (ETF) Thin Film Dryer to pass the Method 1311, "Toxicity Characteristic Leaching Procedure" (TCLP), for final disposal in the Environmental Restoration Disposal Facility landfill.

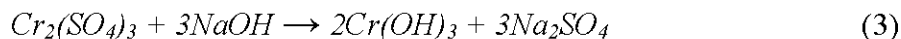
The effort used sodium metabisulfite as the reducing agent. Sodium metabisulfite, when added to water, forms sodium bisulfite (Equation 1). In the presence of acid and Cr(VI), the sodium bisulfite has the following reaction as shown in Equations 2 and 3 (*Pollution Prevention and Control Technology for Plating Operations*, Cushnie 1994):



Then

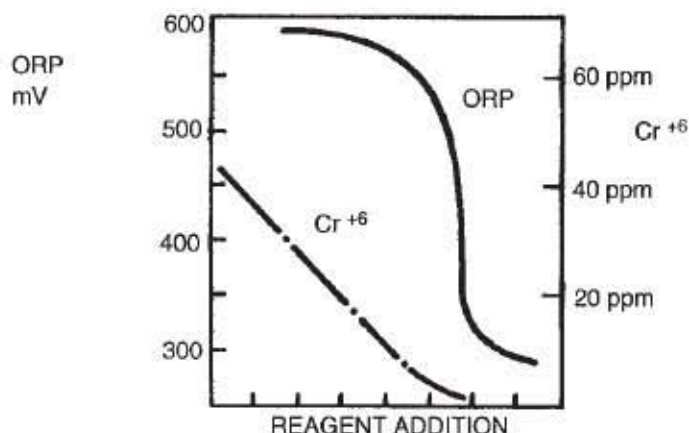


After the hexavalent chromium is reduced to the trivalent state, it is then reacted with caustic to precipitate chromium hydroxide [Cr(OH)₃] as shown in Equation 3.



During the course of the experiments, Cr(VI) and total Cr were determined using ion chromatography and inductively coupled plasma-mass spectroscopy, respectively. Since there is no laboratory method for Cr(III), the difference between Cr(VI) and total Cr is assumed to be Cr(III) due to the reduction reaction (Equation 2).

The sodium metabisulfite was successful at the lower pH ranges and at an oxidation reduction potential (ORP) of approximately +280 mV, Figure 1 (ADS 3300-02/rev.A).

Figure 1. ORP mV versus Reagent Addition.

2. PROCEDURE AND RESULTS

2.1 SCOUTING TEST

To test the efficacy of Cr(VI) reduction using sodium metabisulfite, a solution of 100 ppm sodium chromate was formulated in tap water containing 20 wt% of sodium sulfate. Two levels of pH were tested, pH 2 and pH 4. As will be shown, the pH 4 solution was not as efficacious as was the more acidic solution.

A scouting test was performed at pH 2 using tap water, 20 wt% sodium sulfate, and a calculated (unconfirmed) concentration of Cr(VI), reported as Table 1 and 2 in Appendix A. Table 3 of Appendix A indicates the amount of sodium hydroxide used to raise the pH to greater than 10.5.

The tests were considered successful and a second experiment was conducted using the same conditions. The tabular results are presented in Tables 4 and 5 of Appendix A. Figure 2 shows the cumulative milliliters used to adjust the solution to an ORP value of 279, a total of 13 mL/L. The pH was maintained as close to pH 2 by addition of sulfuric acid during the experiment. Figure 3 shows the amount of 10 N sodium hydroxide per liter consumed to attain a pH of 10.78.

Another solution was prepared as above and titrated with sodium metabisulfite at pH 4 (Table 6 in Appendix A). The Cr(VI) was reduced from 110 mg/L to 28 mg/L. It was decided not to continue the titration and not pursue the reduction of Cr(VI) to Cr(III) in solutions greater than a pH of 2.

After the sodium metabisulfite titration, the solution pH was raised to 10.5 or greater to precipitate Cr(OH)₃. The solution was then dried at 180° C to simulate ETF Thin Film Dryer conditions and a TCLP was performed. The results from the pH 2 solution (Table 8 in Appendix A) are the following:

pH	Total Cr (ppm)	Cr(VI) (ppm)
2→10	0.32575	0.00254

Figure 2. Cumulative Volume of 0.5 M Sodium Metabisulfite to Achieve an Oxidation Reduction Potential of 279 at pH 2 in 20 Wt% Sodium Sulfate and 80 mg/L Cr(VI).

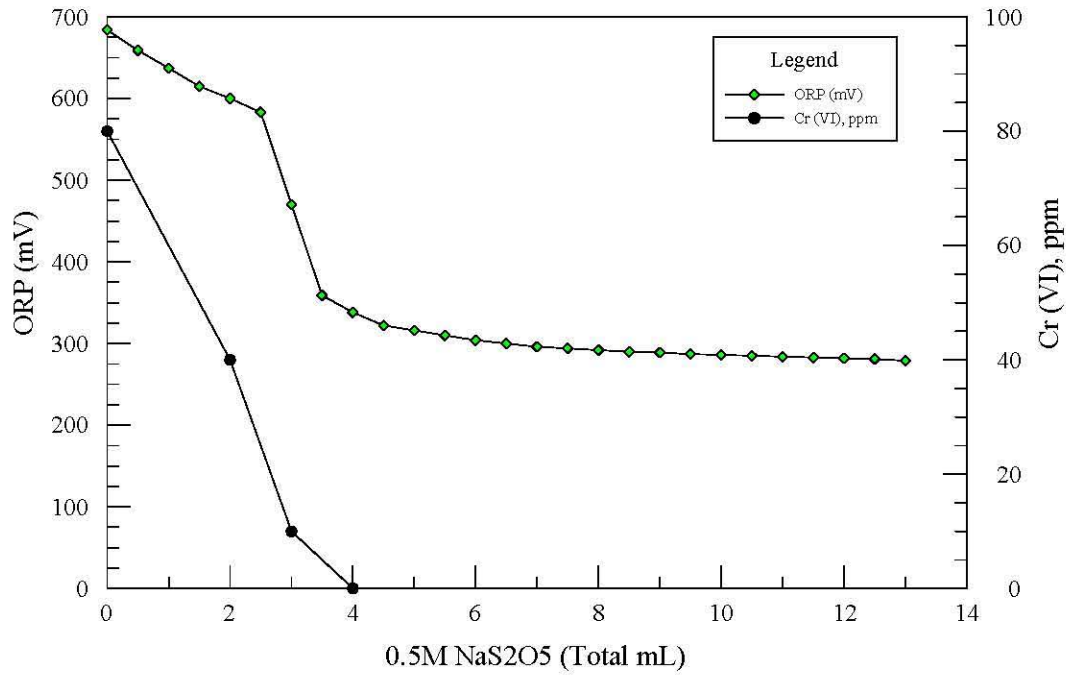
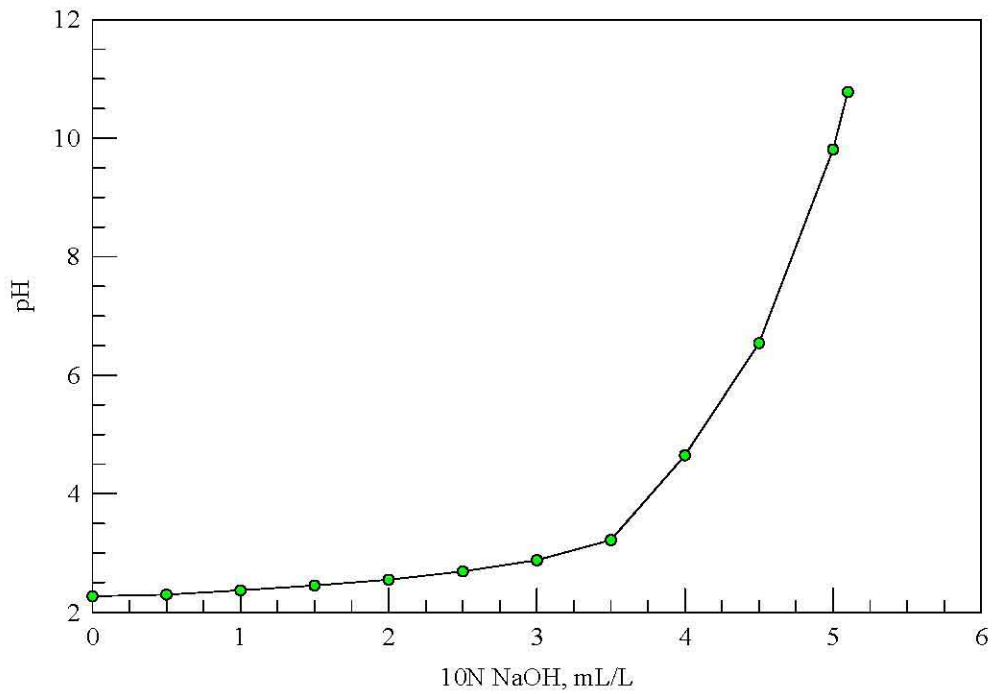


Figure 3. Cumulative Volume of 10N Sodium Hydroxide to Achieve a pH Greater than 10.5.



2.2 SIMULATED GROUNDWATER

Once efficacy was established with a tap water matrix, simulated groundwater from Liquid Effluent Retention Facility Basin 43 was formulated. Table 1 shows the composition of the simulated groundwater (Table 11 in Appendix A).

**Table 1. Liquid Effluent Retention Facility
Basin 43 Groundwater Simulant.**

Component	Formula	g/L
Deionized water	H ₂ O	740.4
Sodium sulfate	Na ₂ SO ₄	38.7
Calcium sulfate	CaSO ₄ *2H ₂ O	126.1
Calcium nitrate	Ca(NO ₃) ₂ * 4H ₂ O	85.7
Magnesium nitrate	Mg(NO ₃) ₂ * 6H ₂ O	127.4
Magnesium chloride	MgCl ₂ * 6H ₂ O	15.9
Potassium chloride	KCl	5.9

The simulant (referred to hereafter as Basin 43) was titrated with 0.5 M sodium metabisulfite. During the first titration, the pH was not controlled and drifted to a final pH of 3.25, requiring 41 mL of sodium metabisulfite to reach an ORP end point of 270 mV (Table 12 in Appendix A).

The experiment was re-run maintaining tight control of the pH level, which required 30 mL of sodium metabisulfite to reach an end point of 280 mV (Table 14 in Appendix A).

Figure 4 shows the titration curve obtained from the data presented in Table 14 of Appendix A. The concentration of Cr(VI) is not plotted on this figure, as the initial value was 110 mg/L; at an ORP of 550 mV, Cr(VI) was 10 mg/L; and at an ORP of 307 mV, Cr(VI) is less than 0.01 mg/L.

Figure 5 shows the titration curve to obtain a pH greater than 10.5 for Basin 43 (Table 15 in Appendix A).

Figure 4. Cumulative Volume of 0.5 M Sodium Metabisulfite to Achieve an ORP of 280 at pH 2 in Basin 43 Simulant at 110 mg/L Cr(VI).

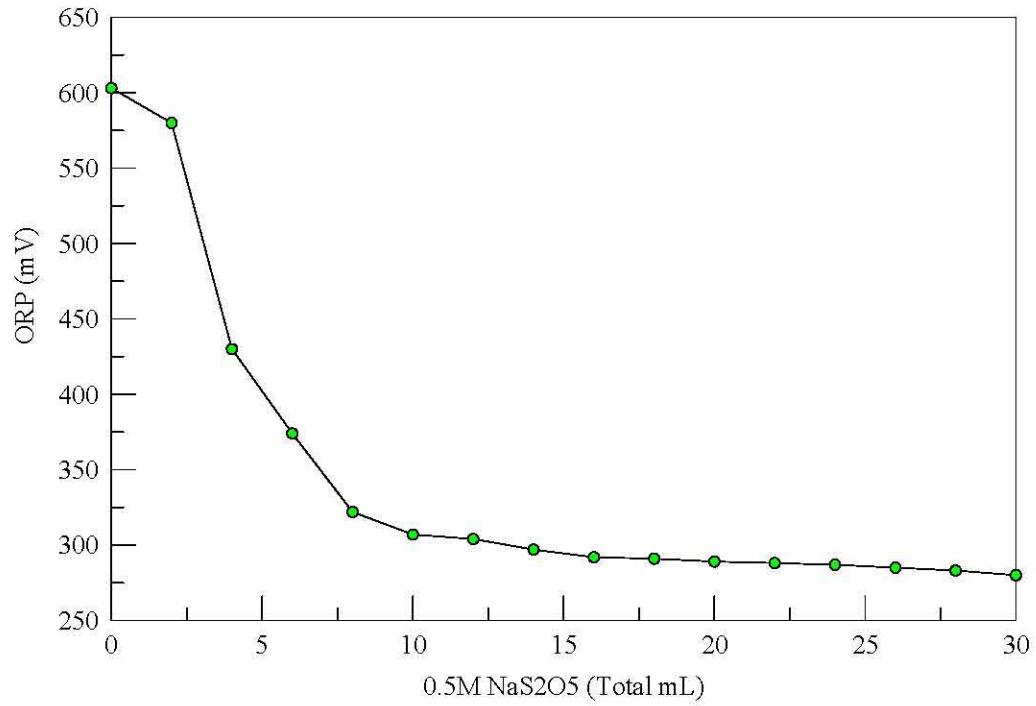
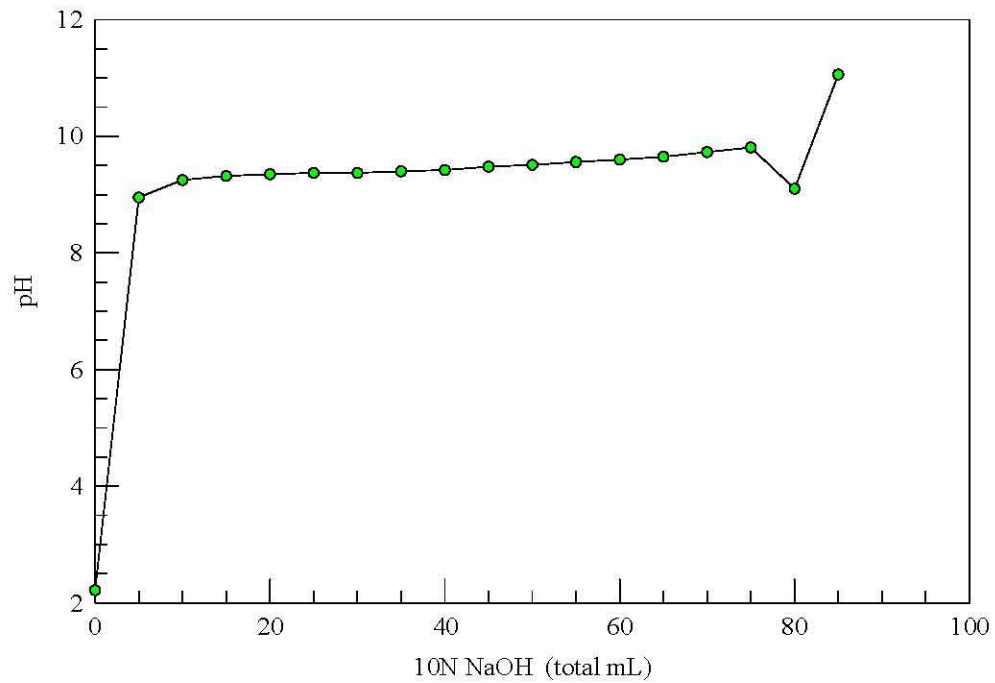


Figure 5. Cumulative Volume of 10N Sodium Hydroxide to Achieve a pH Greater than 10.5.



2.3 TOXICITY CHARACTERISTIC LEACHING PROCEDURE RESULTS

The results from the TCLP are presented in Table 2 (Table 18 of Appendix A).

Table 2. Toxicity Characteristic Leaching Procedure Results.

Reference Table in Appendix A	pH	Total Cr (ppm)
Table 15	9.10	17.65
Table 15	11.06	0.085
Table 17	10.6	2.79
Table 17	11.5	3.4

As shown in Table 2, the higher pH samples were successful in yielding a successful TCLP. The sample at the pH level of 11.5 yielded a higher total ppm Cr than the 11.06 pH. This may be because the laboratory ran the 11.06 pH sample in a shorter time frame, and the 11.5 pH sample was allowed to sit stagnant for several weeks. During this time enough carbon dioxide may have been taken up to lower the pH from the initially measured pH of 11.5.

3. CONCLUSIONS

The use of sodium metabisulfite to reduce Cr(VI) to Cr(III) is an efficacious method if the solution is maintained at close to pH 2. When precipitating Cr(OH)₃ by the addition of NaOH, it is best to attain a pH of 11 to 11.5 to ensure a TCLP of less than 5 ppm.

4. REFERENCES

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Appendix A

Center for Laboratory Sciences Report



Effluent Treatment Facility Secondary Waste Stream Chrome Reduction Study

Laboratory Report

Report Date: June 28, 2007

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Table of Contents

1.0	Objective	1
2.0	Introduction.....	1
3.0	Experimental Procedures	2
3.1	Phase I, Sodium Sulfate Solution, Hexavalent Chrome, Sodium Metabisulfite Addition	2
3.1.1	Phase I, Case 1a– pH 2 Sodium sulfate/Sodium chromate Solution Titration with Sodium Metabisulfite.....	3
3.1.2	Phase I, Case 1b– pH 4 Sodium sulfate/Sodium chromate Solution Titration with Sodium Metabisulfite.....	6
3.2	Phase I, Case 1 Experimental Results.....	7
3.3	Phase I, Case 2 – Trisodium Phosphate to bind Chromium (III)	8
3.4	Phase I, Case 2 Experimental Results.....	9
3.5	Phase II, Case 1 – Basin 43 Groundwater Matrix	9
3.5.1	Phase II, Case 1 – pH 2 Basin 43/Sodium Chromate Solution Titration with Sodium Metabisulfite.....	10
3.6	Phase II, Case 1 Experimental Results	15
4.0	Summary	15

List of Tables

Table 1 – Calculation for 100 ppm of Hexavalent Chrome	3
Table 2– pH 2 sodium sulfate/sodium chromate solution titration to 300mV–Trial #1	3
Table 3– pH 2 reduced chrome solution titrated to pH 10–Trial #1	4
Table 4– pH 2 sodium sulfate/sodium chromate solution titrated to 280 mV– Trial #2	5
Table 5– pH 2 reduced chrome solution titrated to pH 10.5–Trial #2.....	6
Table 6 – pH 4 sodium sulfate/sodium chromate solution titrated to 258 mV.....	7
Table 7 – pH 4 reduced chrome solution titrated to pH 10.9	7
Table 8 – TCLP results for pH 2 and pH 4 reduced chrome experiments	7
Table 9 – pH 2 solution titration to reduce Cr (VI) to Cr (III).....	8
Table 10 – Titration with 0.5M Trisodium phosphate to bind Cr (III).....	9
Table 11– Basin 43 Groundwater.....	10
Table 12 – pH 2 Basin 43 Groundwater/sodium chromate solutions titrated to 270 mV– Trial #110	
Table 13– pH 2 reduced Basin 43 chrome solution titrated to pH 10.9 Trial #1.....	11
Table 14– pH 2 Basin 43 Groundwater/sodium chromate solutions titrated to 270 mV– Trial #212	
Table 15– pH 2 reduced Basin 43 chrome solution titrated to pH 11.06 Trial #2.....	13
Table 16– pH 2 Basin 43 Groundwater/sodium chromate solutions titrated to 270 mV– Trial #313	
Table 17– pH 2 reduced Basin 43 chrome solution titrated to pH 11.5–Trial #3.....	14
Table 18– TCLP and Cr ⁶⁺ results for pH 2 Basin 43 reduced chrome experiments.....	15

List of Figures

Figure 1 – ORP (mv) versus Reagent Addition	2
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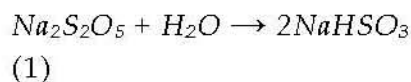
1.0 Objective

The Center for Laboratory Sciences (CLS) was sought out to perform a series of laboratory experimental activities in support of Fluor Hanford's demonstration of the use of sodium metabisulfite to reduce hexavalent chromium to its more stable trivalent form. Under the direction of Fluor Hanford and CH2M Hill's technical personnel, the laboratory tasks in Phase 1 and Phase 2 of this demonstration were performed as follows: sodium metabisulfite titrations using tap water and Basin 43 groundwater as matrices, Toxicity Characteristic Leaching Procedure (TCLP) method of the final titrated solutions at various pH targets, and analytical testing using inductively coupled plasma-mass spectrometry and ion chromatography for chromium concentrations. The experimental procedures and results are presented in this report.

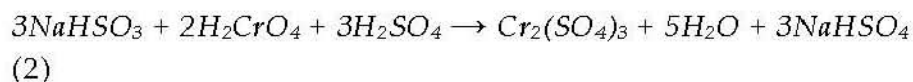
2.0 Introduction

At present time the Effluent Treatment Facility (ETF) has several waste streams which are processed through their Thin Film Dryer. As part of this process, the waste has to pass final disposal restrictions in order to be disposed of in the Environmental Restoration Disposal Facility (ERDF) landfill. One of the major setbacks for disposal has been the inability to decrease the mobility of chrome in the environment. Therefore, it has been proposed to test the efficiency of using sodium metabisulfite to reduce hexavalent chromium (Cr (VI)) to the more stable trivalent form of chromium (Cr (III)). The reduction of Cr (VI) to Cr (III) will decrease the mobility of chromium in the environment, allowing the waste streams from the ETF Thin Film Dryer to pass the Method 1311, "Toxicity Characteristic Leaching Procedure" (TCLP).

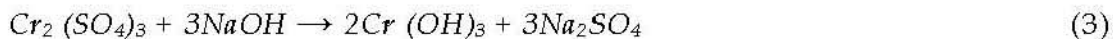
It has been determined elsewhere, that sodium metabisulfite, when added to water, forms sodium bisulfite. In the presence of acid, the sodium bisulfite has the following reaction (*Pollution Prevention and Control Technology for Plating Operations*, Cushnie, 1994):



Then



After the hexavalent chromium is reduced to the trivalent state, it is then reacted with caustic to precipitate chromium hydroxide [Cr (OH)₃].



During the course of the experiments, Cr (VI) and total Cr will be determined using ion chromatography and inductively coupled plasma-mass spectroscopy, respectively.

*Reduction from Chrome (VI) to Chrome (III)**Laboratory Report*

Since there is no laboratory method for Cr (III), the difference between Cr (VI) and total Cr is assumed to be Cr (III) due to the above reduction reaction (Equation 2).

It is expected that sodium metabisulfite will be successful at the lower pH ranges and at an oxidation reduction potential (ORP) of approximately +280 mV, Figure 1 (ADS 3300-02/rev. A).

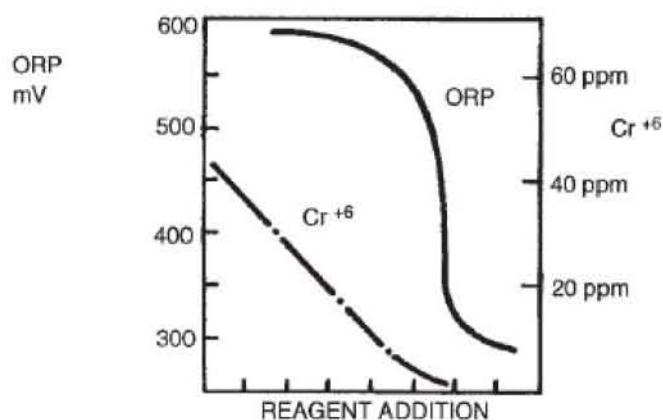


Figure 1-IORP (mV) versus Reagent Addition

3.0 Experimental Procedures

The testing for this effort was divided into two phases. Phase one consisted of case experiments in which the matrix was tap water. Case 1 was used to determine the baseline with 20 wt% sodium sulfate (Na_2SO_4) and hexavalent chrome. Sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$) was incorporated to establish its effectiveness at reducing the oxidation-reduction potential (ORP) as a function of pH. Case 2 used trisodium phosphate as a method to bind the trivalent chromium from the most promising experiment from Case 1. Those experiments which provided promising results based on initial analysis were prepared for TCLP testing.

Phase two of the procedures utilized Basin 43 Groundwater as the matrix, which is an ETF waste stream at this time. The most successful parameters in Phase one, which yielded the most reduction of chrome (VI) from the TLCP, was used to prepare the mixture for this particular phase. Those experiments which provided promising results based on initial analysis were prepared for TCLP testing.

3.1 Phase I, Sodium Sulfate Solution, Hexavalent Chrome, Sodium Metabisulfite Addition

For all the Phase 1 experiments, a 1-Liter 20wt% sodium sulfate (Na_2SO_4) solution was prepared in a volumetric flask. Approximately 100 ppm of chrome in the form of sodium chromate ($\text{Na}_2\text{CrO}_4 \cdot 4\text{H}_2\text{O}$) was added to the solution. The calculation for 100ppm is provided in Table 1. The solution was then adjusted to a designated pH of

*Reduction from Chrome (VI) to Chrome (III)**Laboratory Report*

either 2 or 4. This solution was then titrated with 0.5M sodium metabisulfite ($\text{Na}_2\text{S}_2\text{O}_5$) to achieve an ORP reading close to 280 mV. Aliquots during the titration were removed at different intervals and tested with a HACH test meter for Chrome (VI). After the completion of the titration to a reduced pH, a titration was performed to increase the pH to >10. Samples were retrieved and dried at 180°C for TLCP analysis for total Cr.

Table 1 – Calculation for 100 ppm of Hexavalent Chrome

Component	FW (gram/mole)	Cr ⁶⁺ (100 ppm)
Na ₂ CrO ₄ ·4H ₂ O	234.04	0.4501 grams
Cr (metal)	52.00	N/A

3.1.1 Phase I, Case 1a– pH 2 Sodium sulfate/Sodium chromate Solution Titration with Sodium Metabisulfite

A 1-Liter batch of the sodium sulfate and sodium chromate mixture was prepared. The mixture appeared dark yellow in color, with a milky consistency. The solution was adjusted to pH 2 with an initial addition of 1mL of 0.1 N sulfuric acid, and then 0.8 mL of 2N sulfuric acid and a final addition of 2 mL of concentrated 92% sulfuric acid to achieve a pH of 2.05. The corresponding ORP was 658 mV. The mixture was then titrated with sodium metabisulfite to attain an ORP of at least 300 mV to provide the most reduction of chrome. The actual amounts used for this experiment are provided in Table 2.

Table 2– pH 2 sodium sulfate/sodium chromate solution titration to 300mV–Trial #1

Color of solution	0.5M Na ₂ S ₂ O ₅ (Total mL)	ORP (mV)	pH	aliquots taken	HACH Cr(VI) reading
yellow	0.0	669	2.05	N/A	N/A
yellow	0.5	671	2.05	N/A	N/A
yellow	1.0	657	2.05	N/A	N/A
yellow	1.5	651	2.05	N/A	N/A
yellow	2.0	650	2.05	N/A	N/A
yellow to light green	2.5	634	2.05	N/A	N/A
light green	3.0	615	2.05	N/A	N/A
medium green	3.5	603	2.05	1st	18 ppm
medium to blue green	4.0	448	2.05	2nd	N/A
light blue/pale green	4.5	355	2.05	3rd	N/A
light blue	5.0	327	2.05	4th	N/A
light blue	5.5	319	2.05	5th	N/A
light blue	6.0	315	2.05	6th	N/A
light blue	6.5	313	2.05	7th	0.11ppm

*Reduction from Chrome (VI) to Chrome (III)**Laboratory Report*

As shown in Table 1, the chrome (VI) reduction is evident due to the color change from yellow to green to blue. A Hach test meter was used to do intermediate readings from aliquots pulled throughout the titration. The chrome (VI) initially should be close to 100 ppm and based on the readings dropped to 0.11ppm after titration. This solution was then titrated to a pH greater than 10 with 10N sodium hydroxide. The results from that experiment are provided in Table 3.

Table 3– pH 2 reduced chrome solution titrated to pH 10–Trial #1

10N NaOH (total mL)	pH	Color change
0.0	2.05	Light blue
0.5	2.15	Light blue
1.0	2.22	Light blue
1.5	2.3	Light blue
2.0	2.4	Light blue
2.5	2.53	Light blue
3.0	2.71	Light blue
3.5	3.02	Light blue
4.0	4.35	Light blue
4.5	9.46	Cloudy blue color
4.6	10.81	Cloudy blue color

An observation from this titration was an increase in the amount of solids precipitated from the solution as the pH increased to 10. These solids are thought to be mainly Cr (III).

This experiment was repeated to validate the results. The working solution of sodium sulfate and sodium chromate had an initial pH of 7.73 with an ORP of 260mV. 1.78 mL of concentrated sulfuric acid was used to reduce the pH to 2.01. The results of the titration with 0.5M sodium metabisulfite are provided in Table 4.

*Reduction from Chrome (VI) to Chrome (III)**Laboratory Report***Table 4– pH 2 sodium sulfate/sodium chromate solution titrated to 280 mV– Trial #2**

Color of solution	0.5M Na ₂ S ₂ O ₅ (Total mL)	ORP (mV)	pH	aliquots taken	HACH Cr(VI) reading (ppm)
bright yellow	0.0	684	2.04	1st	80
slight color change	0.5	659	2.05	N/A	N/A
hint of green	1.0	637	2.05	N/A	N/A
slightly more green	1.5	615	2.06	N/A	N/A
lime green	2.0	600	2.07	2nd	40
green	2.5	583	2.07	N/A	N/A
touch of blue	3.0	470	2.08	N/A	10
light blue	3.5	359	2.08	N/A	N/A
light blue	4.0	338	2.07	3rd	0.02
light blue	4.5	322	2.08	N/A	N/A
light blue	5.0	316	2.08	N/A	N/A
light blue	5.5	310	20.6	N/A	N/A
light blue	6.0	304	2.06	N/A	N/A
light blue	6.5	300	2.08	4th	No reading
light blue	7.0	296	2.09	N/A	N/A
light blue	7.5	294	2.09	N/A	N/A
light blue	8.0	292	2.09	N/A	N/A
light blue	8.5	290	2.10	N/A	N/A
light blue	9.0	289	2.10	N/A	N/A
light blue	9.5	287	2.10	N/A	N/A
light blue	10.0	286	2.10	N/A	N/A
light blue	10.5	285	2.10	N/A	N/A
light blue	11.0	284	2.10	N/A	N/A
light blue	11.5	283	2.11	N/A	N/A
light blue	12.0	282	2.11	N/A	N/A
light blue	12.5	281	2.11	N/A	N/A
light blue	13.0	279	2.11	5th	No reading

The solution was then titrated to a pH of 10.5 or greater with 10N NaOH. The results are provided in Table 5.

*Reduction from Chrome (VI) to Chrome (III)**Laboratory Report***Table 5– pH 2 reduced chrome solution titrated to pH 10.5–Trial #2**

10N NaOH (total mL)	pH	Color change
0.0	2.27	Light blue
0.5	2.3	Light blue
1.0	2.37	Light blue
1.5	2.45	Light blue
2.0	2.55	Light blue
2.5	2.69	Light blue
3.0	2.88	Light blue
3.5	3.22	Light blue
4.0	4.65	Light blue
4.5	6.54	Light blue
5.0	9.81	Cloudy blue color
5.1	10.78	Cloudy blue color**

**A sample of this final batch was put aside and dried for total Cr and Cr⁶⁺ analysis.

As seen previously in Case 1a Trial #1, the titration with caustic caused solids to precipitate from the solution as the pH increased to 10. These solids are thought to be mainly Cr (III). A sample was retrieved for TCLP analysis of total Cr and hexavalent Cr. These results will be discussed later in this report in Section 3.1.2.1. .

3.1.2 Phase I, Case 1b– pH 4 Sodium sulfate/Sodium chromate Solution Titration with Sodium Metabisulfite

A 1-Liter batch of the sodium sulfate and sodium chromate mixture was prepared. The mixture appeared dark yellow in color, with a milky consistency. The solution had an initial pH of 7.71 and was adjusted to pH 4.00 with an initial addition of 0.1mL of concentrated 92% sulfuric acid followed by an addition of 1.25 mL of 0.1N sulfuric acid. The corresponding ORP was 457 mV. The mixture was then titrated with sodium metabisulfite to attain an ORP of at least 300 mV to provide the most reduction of chrome. The actual amounts used for this experiment are provided in Table 6.

*Reduction from Chrome (VI) to Chrome (III)**Laboratory Report***Table 6 – pH 4 sodium sulfate/sodium chromate solution titrated to 258 mV**

Color of solution	0.5M Na ₂ S ₂ O ₅ (mL)	ORP (mV)	pH	aliquots taken	HACH Cr(VI) reading (ppm)
bright yellow	0.0	457	4.01	1st	110
darker yellow	0.5	377	4.13	N/A	N/A
very slight hint of green/yellow	1.0	339	4.45	N/A	N/A
very slight hint of green/yellow	1.5	313	4.75	2nd	70
slight green	2.0	296	4.88	N/A	40
light green	2.5	280	5.03	N/A	45
green	3.0	267	5.16	N/A	27
green	3.5	258	5.2	N/A	28

The solution was then titrated to a pH of 10.5 or greater with 10N NaOH. The results are provided in Table 7.

Table 7 – pH 4 reduced chrome solution titrated to pH 10.9

10N NaOH (total mL)	pH	Color Change
0.0	4.75	N/A
0.5	10.94	no visible color change**

**A sample of this final batch was put aside and dried for total Cr and Cr⁶⁺ analysis.

As seen previously in Case 1a, the titration with caustic caused solids to precipitate from the solution as the pH increased to 10. However, the amount of solids appeared to be less than the experiments at pH 2. These solids are thought to be mainly Cr (III). A sample was retrieved for TCLP analysis of total Cr and hexavalent Cr. These results will be discussed in Section 3.1.2.1.

3.2 Phase I, Case 1 Experimental Results

After completion of Case 1, all of the data regarding TCLP analysis for total Cr and Cr⁶⁺ were compiled and reviewed to determine the most promising mixture of the two pH endpoints to proceed further testing. Total chrome analysis was performed using a Perkin-Elmer ICP/MS. The hexavalent chrome was quantified using ion chromatography. The TCLP results for the pH 2 and pH 4 mixtures denoted by an asterisk (*) in Tables 4 and 6 are provided in Table 8.

Table 8 – TCLP results for pH 2 and pH 4 reduced chrome experiments

pH	Total Cr (ppm)	Cr ⁶⁺ (ppm)
2→10	0.32575	0.00254
4→10	0.32394	1.704

*Reduction from Chrome (VI) to Chrome (III)**Laboratory Report*

As shown in Table 8, the pH 2 solution more effectively reduced the Cr⁶⁺ content although the total Cr quantity remained similar for both. Based on this observation, pH 2 is the most promising pH to use for these experiments. An increase in pH would only decrease the effectiveness of the chrome reduction.

3.3 Phase I, Case 2 – Trisodium Phosphate to bind Chromium (III)

For Case 2, a working solution of the pH 2 sodium sulfate/sodium chromate mixture was prepared, based on the results from the TCLP. The solution had an initial pH of 7.81 with an ORP of 230mV. It was adjusted to pH 2.05 with an addition of 2.2mL of concentrated 92% sulfuric acid. The corresponding ORP was 658 mV. The mixture was then titrated with sodium metabisulfite to attain an ORP of at least 300 mV to provide the most reduction of chrome. The actual amounts used for this experiment are provided in Table 9.

Table 9 – pH 2 solution titration to reduce Cr (VI) to Cr (III)

Color of solution	0.5M Na ₂ S ₂ O ₅ (Total mL)	ORP (mV)	pH	HACH Cr(VI) reading (ppm)
dark yellow	0.0	607	2.01	100
slightly cloudy	0.5	599	2.02	N/A
very slight green	1.0	588	2.02	N/A
light green	1.5	578	2.02	N/A
green	2.0	582	2.01	N/A
green	2.5	579	1.97	N/A
blue green	3.0	531	1.98	N/A
blue	3.5	347	1.98	N/A
blue	4.0	334	1.98	N/A
blue	4.5	324	1.98	N/A
blue	5.0	317	1.99	N/A
blue	5.5	309	1.99	N/A
blue	6.0	304	1.99	N/A
blue	6.5	301	1.99	N/A
blue	7.5	295	1.99	N/A
blue	8.5	291	1.99	N/A
blue	9.5	288	1.99	N/A
blue	10.5	284	2.00	N/A
blue	11.5	280	2.00	0.08

This reduced chrome solution was then titrated with a 0.5M trisodium phosphate solution in an effort to bind the remaining Cr (III), Table 10.

*Reduction from Chrome (VI) to Chrome (III)**Laboratory Report***Table 10 – Titration with 0.5M Trisodium phosphate to bind Cr (III)**

0.5 M Na ₃ PO ₄ (Total mL)	ORP (mV)	pH	HACH Cr(VI) reading (ppm)
0.0	280	2.15	0.07
0.5	310	2.15	N/A
1.0	309	2.16	N/A
1.5	308	2.16	N/A
2.0	308	2.16	N/A
2.5	308	2.17	N/A
3.0	307	1.17	N/A
3.5	307	2.18	N/A
4.0	307	2.19	N/A
5.0	306	2.2	N/A
6.0	306	2.21	N/A
7.0	305	2.24	N/A
8.0	305	2.24	N/A
9.0	305	2.24	N/A
10.0	305	2.24	No reading

During the titration with trisodium phosphate, there were no solids coming out of solution. A 15-mL sample of 0.5M trisodium phosphate was added to 10-mL of the ending solution in Table 10 above. The pH changed to 12.18 and no solids appeared. A titration with 10N sodium hydroxide was not necessary.

3.4 Phase I, Case 2 Experimental Results

Based on the observations from the experiment, it didn't appear that the trisodium phosphate was useful in binding the Cr (III) from the solution. This experiment was not continued any further.

3.5 Phase II, Case 1 – Basin 43 Groundwater Matrix

For all the Phase 2 experiments, there were at total of three trial mixtures. All of them were consisted of a 1-Liter solution of Basin 43 groundwater prepared according to the recipe in Table 11. Approximately 100 ppm of chrome in the form of sodium chromate (Na₂CrO₄*4H₂O) was added to the solution, as provided in Table 1. The solution was then adjusted to a pH of 2 based on the success of this pH endpoint for the tap water matrix. This solution was then titrated with 0.5M sodium metabisulfite (Na₂S₂O₅) to achieve an ORP reading close to 280 mV. Aliquots during the titration were removed at different intervals and tested with a HACH test meter for Chrome (VI). After the completion of the titration to a reduced pH, a titration with 10N NaOH was performed to increase the pH to >10. Samples were retrieved and dried at 180°C for TLCP analysis for total Cr.

*Reduction from Chrome (VI) to Chrome (III)**Laboratory Report***Table 11 – Basin 43 Groundwater**

Component	Formula	gram/Liter
Deionized Water	H ₂ O	740.4
Sodium Sulfate	Na ₂ SO ₄	38.7
Calcium Sulfate	CaSO ₄ *2H ₂ O	126.1
Calcium Nitrate	Ca(NO ₃) ₂ * 4H ₂ O	85.7
Magnesium Nitrate	Mg(NO ₃) ₂ *6H ₂ O	127.4
Magnesium Chloride	MgCl ₂ * 6H ₂ O	15.9
Potassium Chloride	KCl	5.9

3.5.1 Phase II, Case 1 – pH 2 Basin 43/Sodium Chromate Solution Titration with Sodium Metabisulfite

For Case 1, Trial #1, a working solution of the pH 2 Basin 43/sodium chromate mixture was prepared. The solution had an initial pH of 8.20. It was adjusted to pH 2.06 with an addition of 0.350 mL of concentrated 92% sulfuric acid. The corresponding ORP was 636 mV. The mixture was then titrated with sodium metabisulfite to attain an ORP of at least 300 mV to provide the most reduction of chrome. The actual amounts used for this experiment are provided in Table 12. During the titration, the pH kept rising well beyond the 2.0 range. AT one point during the titration, concentrated sulfuric acid was added to adjust the pH back down to about 2.0. As a result, a large amount of sodium metabisulfite needed to be added to the solution in order to achieve an ORP of 280mV.

Table 12 – pH 2 Basin 43 Groundwater/sodium chromate solutions titrated to 270 mV– Trial #1

Color of solution	0.5M NaS ₂ O ₅ (Total mL)	ORP (mV)	pH	aliquots taken	HACH Cr(VI) reading (ppm)
milky yellow	0.0	657	2.06	N/A	110
yellow	2.0	655	2.06	N/A	N/A
yellow	6.0	646	2.38	N/A	N/A
yellow	8.0	635	2.69	N/A	N/A
yellow	10.0	585	3.86	N/A	N/A
yellow	12.0	556	4.67	N/A	N/A
yellow	14.0	539	5.00	N/A	N/A
yellow	16.0	523	5.28	N/A	N/A
yellow	18.0	513	5.47	N/A	N/A
yellow	20.0	503	5.64	N/A	N/A
yellow	22.0	488	5.89	N/A	N/A
<i>Conc. acid addition</i>	<i>700μL</i>	652	2.06	N/A	N/A

*Reduction from Chrome (VI) to Chrome (III)**Laboratory Report*

yellow	24.0	653	2.13	N/A	N/A
yellow	26.0	651	2.24	N/A	N/A
toothpaste pale blue	31.0	349	2.68	1st	<0.01
pale blue	36.0	302	2.93	N/A	N/A
pale blue	41.0	270	3.25	2nd	N/A

The solution was then titrated to a pH of 10.5 or greater with 10N NaOH. The results are provided in Table 13.

Table 13- pH 2 reduced Basin 43 chrome solution titrated to pH 10.9 Trial #1

10N NaOH (total mL)	pH	Color Change
0.0	2.27	N/A
0.5	2.30	N/A
1.0	2.37	N/A
1.5	2.45	N/A
2.0	2.55	N/A
2.5	2.69	N/A
3.0	2.88	N/A
3.5	3.22	N/A
4.0	4.65	N/A
4.5	6.54	N/A
5.0	9.81	Cloudy blue color
5.1	10.78	N/A

For Case 1, Trial #2, a working solution of the pH 2 Basin 43/sodium chromate mixture was prepared. The solution had an initial pH of 8.09. It was adjusted to pH 1.99 with an addition of 0.250mL of concentrated 92% sulfuric acid. The corresponding ORP was 603 mV. The mixture was then titrated with sodium metabisulfite to attain an ORP of at least 300 mV to provide the most reduction of chrome. The actual amounts used for this experiment are provided in Table 14. During the titration with sodium metabisulfite, the pH was adjusted with concentrated sulfuric acid to keep it within the 2.0 range unlike what was done in Trial #1 above. This allowed for the addition of less sodium metabisulfite to the solution to achieve an ORP at about 280 mV.

Reduction from Chrome (VI) to Chrome (III)

Laboratory Report

Table 14- pH 2 Basin 43 Groundwater/sodium chromate solutions titrated to 270 mV- Trial #2

Color of solution	0.5M NaS ₂ O ₅ (Total mL)	ORP (mV)	pH	aliquots taken	HACH Cr(VI) reading (ppm)
milky yellow	0.0	603	1.99	1 ^{st**}	110
yellow	2.0	580	2.14	N/A	N/A
hint of blue	4.0	430	2.5	N/A	N/A
<i>conc. acid addition</i>	<i>100 µL</i>	553	2.03	N/A	10
lime	6.0	374	2.21	N/A	N/A
<i>conc. acid addition</i>	<i>40 µL</i>	366	2.04	N/A	N/A
blue green	8.0	322	2.07	N/A	N/A
light blue	10.0	307	2.10	N/A	<0.01
light blue	12.0	304	2.14	N/A	N/A
<i>conc. acid addition</i>	<i>20 µL</i>	302	2.06	N/A	N/A
light blue	14	297	2.10	N/A	N/A
light blue	16	292	2.13	N/A	N/A
<i>conc. acid addition</i>	<i>20 µL</i>	294	2.06	N/A	N/A
Added 700mL of concentrated sulfuric	18.0	291	2.10	N/A	N/A
light blue	20.0	289	2.13	N/A	N/A
<i>conc. acid addition</i>	<i>20 µL</i>	290	2.07	N/A	N/A
toothpaste pale blue	22.0	288	2.12	2 ^{nd**}	BDL
<i>conc. acid addition</i>	<i>20 µL</i>	290	2.06	N/A	N/A
pale blue	24.0	287	2.09	N/A	N/A
pale blue	26.0	285	2.12	N/A	N/A
pale blue	28.0	283	2.15	N/A	N/A
pale blue	30.0	280	2.18	3 ^{rd**}	BDL

**Aliquots were taken for Cr6+ analysis using Ion Chromatography

BDL=Below Detection Limit

The solution was then titrated to a pH of 10.5 or greater with 10N NaOH. The results are provided in Table 15. A large volume of sodium hydroxide was necessary to adjust the pH to 10.5. At the end of the titration, samples were removed for drying at 180°C and TCLP preparation for the analysis of Total Chrome.

*Reduction from Chrome (VI) to Chrome (III)**Laboratory Report***Table 15– pH 2 reduced Basin 43 chrome solution titrated to pH 11.06 Trial #2**

10N NaOH (total mL)	pH
0	2.22
5	8.95
10	9.25
15	9.32
20	9.35
25	9.37
30	9.37
35	9.4
40	9.42
45	9.48
50	9.51
55	9.56
60	9.6
65	9.65
70	9.73
75	9.81
80	9.10*
85	11.06*

**A sample of this final batch was put aside and dried for total Cr and Cr⁶⁺ analysis.

For Case 1, Trial #3, a working solution of the pH 2 Basin 43/ sodium chromate mixture was prepared. The solution had an initial pH of 7.45. It was adjusted to pH 1.92 with an addition of 0.2 mL of concentrated 92% sulfuric acid. The corresponding ORP was 609 mV. The mixture was then titrated with sodium metabisulfite to attain an ORP of at least 300 mV to provide the most reduction of chrome. The actual amounts used for this experiment are provided in Table 16. During the titration with sodium metabisulfite, the pH was adjusted with concentrated sulfuric acid to keep it within the 2.0 range as was done with the Trial #2.

Table 16– pH 2 Basin 43 Groundwater/sodium chromate solutions titrated to 270 mV– Trial #3

Color of solution	0.5M NaS ₂ O ₅ (Total mL)	ORP (mV)	pH
Yellow	0.0	N/A	N/A
yellow	1.0	N/A	N/A
<i>conc. acid addition</i>	<i>50 μL</i>	390	2.03
yellow	2.0	N/A	N/A
<i>conc. acid addition</i>	<i>50 μL</i>	415	1.95

*Reduction from Chrome (VI) to Chrome (III)**Laboratory Report*

hint of blue	3.0	347	2.05
lime	4.0	341	2.08
lime	5.0	337	2.1
lime	10.0	326	2.22
lime	15.0	320	2.28
lime	20.0	N/A	N/A
<i>conc. acid addition</i>	<i>20 μL</i>	316	2.03
lime	25.0	N/A	N/A
<i>conc. acid addition</i>	<i>20 μL</i>	319	2.07
lime	30.0	N/A	N/A
<i>conc. acid addition</i>	<i>20 μL</i>	317	2.07
lime	35.0	N/A	N/A
<i>conc. acid addition</i>	<i>60 μL</i>	316	2.04
lime	40.0	N/A	N/A
<i>conc. acid addition</i>	<i>20 μL</i>	314	2.07
blue green	45.0	311	2.11
light blue	50.0	309	2.14
light blue	55.0	307	2.18
light blue	60	305	2.22
light blue	70	302	2.29
light blue	80.0	299	2.34
light blue	130.0	283	2.58

The solution was then titrated to a pH greater than 10.5 with 10N NaOH. The results are provided in Table 17. A large volume of sodium hydroxide was necessary to adjust the pH to 10.5. At the end of the titration, two samples were removed for drying at 180°C and TCLP preparation for the analysis of Total Chrome.

Table 17- pH 2 reduced Basin 43 chrome solution titrated to pH 11.5-Trial #3

10N NaOH (total mL)	pH
0.0	2.59
10.0	5.4
20.0	8.88
330.0	9.08
40.0	9.12
50.0	9.16
60.0	9.21
70.0	9.31
80.0	9.41

*Reduction from Chrome (VI) to Chrome (III)**Laboratory Report*

90.0	9.55
100.0	9.8
109.0	10.6**
118.0	11.5**

**A sample of this final batch was put aside and dried for total Cr and Cr⁶⁺ analysis.

3.6 Phase II, Case I Experimental Results

After completion of Phase II, all of the data regarding TCLP analysis for total Cr and Cr⁶⁺ were compiled and reviewed to determine success of using Basin 43 Groundwater as a matrix. Total chrome analysis was performed using a Perkin-Elmer ICP/MS. The hexavalent chrome was quantified using ion chromatography. The TCLP results for the Trial #2 and 3 mixtures denoted by an asterisk (*) in Tables 15 and 17 are provided in Table 8.

Table 18– TCLP and Cr⁶⁺ results for pH 2 Basin 43 reduced chrome experiments

Trial #	pH	ORP (mV)	HACH (ppm)	Cr ⁶⁺ (ppm)	Total Cr (ppm)
Prior and during titration with 0.5M Sodium Metabisulfite					
2-Aliquot #1	1.99	603	110	105.1	N/A
2-Aliquot #2	2.12	288	BDL	BDL	N/A
2-Aliquot #3	2.18	280	BDL	BDL	N/A
After titration with 10N Sodium Hydroxide					
2-Aliquot #1	9.1	N/A	N/A	N/A	17.65
2-Aliquot #2	11.06	N/A	N/A	N/A	0.08494
3-Aliquot #1	10.6	N/A	N/A	N/A	2.79
3-Aliquot #2	11.5	N/A	N/A	N/A	3.4

As shown in Table 18, the Cr⁶⁺ content in the Basin 43 groundwater was effectively reduced from 100ppm with the use of sodium metabisulfite.

4.0 Summary

Based on all of the data regarding the hexavalent chrome and trivalent chrome concentrations, it appears that the addition of sodium metabisulfite is a useful means of reducing chrome in sodium sulfate and Basin 43 waste waters at a pH of 2. The concentration of Cr⁶⁺ was drastically reduced with this method, which promotes the success of immobilizing the chrome in the environment, aiding in ERDF's land disposal requirements.