Corrosion Study for the Effluent Treatment Facility Chrome (VI) Reductant Solution Using 304 and 316L Stainless Steel

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Abstract: The Effluent Treatment Facility has developed a method to regenerate spent resin from the groundwater pump and treat intercepting chrome (VI) plumes (RPP-RPT-32207, Laboratory Study on Regeneration of Spent DOWEX 21K 16-20 Mesh Ion Exchange Resin). Subsequent laboratory studies have shown that the chrome (VI) may be reduced to chrome (III) by titrating with sodium metabisulfite to an oxidation reduction potential (ORP) of +280 mV at a pH of 2. This test plan describes the use of cyclic potentiodynamic polarization and linear polarization techniques to ascertain the electrochemical corrosion and pitting propensity of the 304 and 316L stainless steel in the acidified reducing solution that will be contained in either the secondary waste receiver tank or concentrate tank.

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CPP	cyclic potentiodynamic polarization
ETF	Effluent Treatment Facility
LPR	linear polarization resistance
OCP	open circuit potential
ORP	oxidation reduction potential
SWRT	secondary waste receiving tank

1. INTRODUCTION

The Effluent Treatment Facility (ETF) has developed a method to regenerate spent resin from the groundwater pump and treat intercepting chrome (VI) plumes (RPP-RPT-32207, *Laboratory Study on Regeneration of Spent DOWEX[1] 21K 16-20 Mesh Ion Exchange Resin*). Subsequent laboratory studies have shown that the chrome (VI) may be reduced to chrome (III) by titrating with sodium metabisulfite to an oxidation reduction potential (ORP) of +280 mV at a pH of 2. Equations 1 and 2 give the stoichiometric relationships involved in the reactions (*Pollution Prevention and Control Technology for Plating Operations*, Cushnie 1994).

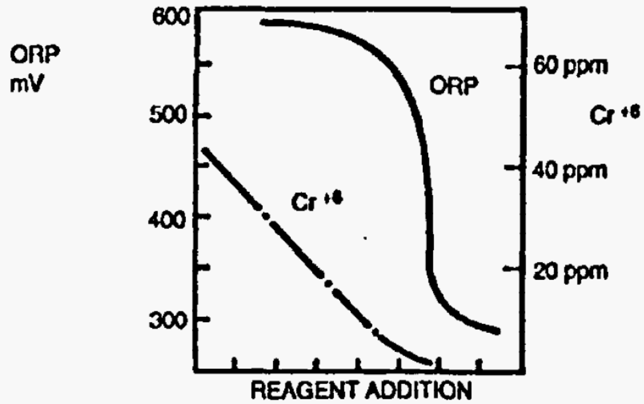
$$Na_2S_2O_5 + H_2O \rightarrow 2NaHSO_3 \quad (1)$$

Then

$$3NaHSO_3 + 2H_2CrO_4 + 3H_2SO_4 \rightarrow Cr_2(SO_4)_3 + 5H_2O + 3NaHSO_4 \quad (2)$$

Figure 1 shows the ORP versus the sodium metabisulfite reagent addition to achieve the reduced chrome (III) species (*pH and ORP Control for Removing Chrome from Plant Effluent*, ADS 3300-02/rev.A).

Figure 1. Oxidation-Reduction Potential mV versus Reagent Addition.



To regenerate the spent ion exchange resin, several bed volumes of 0.5 M sodium sulfate will be used to displace the chrome (VI) from the resin. This will result in a large volume of sodium sulfate and chrome (VI). The chrome (VI) will then be reduced to chrome (III) at a pH of 2 with sodium metabisulfite as described above. The reduction will take place in either the secondary waste receiving tank (SWRT) or the concentrate tank. The materials of construction for the SWRT is 304 stainless steel and the concentrate tank is 316L stainless steel.

[1] DOWEX™ is a registered trademark of Dow Chemical Company, Midland, Michigan.

This test plan describes the use of cyclic potentiodynamic polarization and linear polarization techniques to ascertain the electrochemical corrosion and pitting propensity of the 304 and 316L stainless steel in the acidified reducing solution that will be contained in either the SWRT or concentrate tank.

The customer has made the determination that this effort does not constitute a treatability study and has completed the Treatability Study Determination Worksheet to that effect (Appendix A).

2. PROCEDURE

The electrochemical corrosion testing will encompass allowing the test coupon to equilibrate with the test solution, and the use of both linear polarization resistance (LPR) and cyclic potentiodynamic polarization (CPP) techniques.

2.1 QUALITY CONTROL/QUALITY ASSURANCE

This effort will be conducted under ATS-MP-1032, *222-S Laboratory Quality Assurance Plan.* Before test scans, the instrument response will be tested using ASTM G5-94, *Standard Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements.*

The following discussion of LPR and CPP is extracted from *An Introduction to Electrochemical Corrosion Testing for Practicing Engineers and Scientists* (Tait 1994).

2.2 LINEAR POLARIZATION RESISTANCE

Linear polarization uses a very small spectrum of overpotential from the open circuit potential (OCP) of the material in question. The coupon is scanned ± 20 mV either side of the OCP.

To calculate corrosion currents and therefore corrosion rates from LPR data, a slope is derived that corresponds to the corrosion resistance.

$$R_p = \text{change in potential} / \text{change in current density} = \Delta E / \Delta i \quad (3)$$

The units are volts/amps/cm^2, and volts/amps is ohms, therefore the units are ohms·cm^2.

After the LRP determination is complete, the next calculation is to determine the corrosion current or i_{corr}, which is calculated by:

$$i_{corr} = [1/(2.303R_p)][(\beta_a * \beta_c) / (\beta_a + \beta_c)] \quad (4)$$

where

β_a = the anodic Tafel slope in volts/decade of current density, and
β_c = the cathodic Tafel slope in volts/decade current density.

The quantity $(\beta_a * \beta_c) / (\beta_a + \beta_c)$ is referred to as the Tafel constant.

The units for i_{corr} are mA/cm^2. After calculating the value for i_{corr}, the corrosion rate in mils/year (mpy) is calculated by the following:

$$MPY = i_{corr}(\Lambda)(1/\rho)(\epsilon) \tag{5}$$

where

Λ = a combination of several terms and is 1.2866E05[equivalents·sec·mils]/[coulombs·cm·years]
ρ = metal density in g/cm^3
ϵ = equivalent weight in g/equivalent.

For iron, the density is 7.87 g/cm^3 and the equivalent weight is 27.56 g/equivalent.

The main advantage of using LPR is that it is a nondestructive test and can be repeatedly used on the same test electrode to continuously monitor corrosion for long periods. A limitation of LPR is that the technique can only measure general corrosion rates and thus can not be used to determine if localized corrosion such as pitting or crevice corrosion is present or information around kinetics controlling the rate of corrosion.

2.3 CYCLIC POTENTIODYNAMIC POLARIZATION

Cyclic potentiodynamic polarization curves are an extension of the potentiodynamic polarization scan. The CPP reverses at a given potential or current density as described in the ASTM method ASTM G61-86, *Standard Test Method for Conducting Cyclic Potentiodynamic Polarization Measurements for Localized Corrosion Susceptibility of Iron-, Nickel-, or Cobalt-Based Alloys.*

The CPP curve is a destructive test as opposed to the LPR, in that it will scan from -250 mV versus OCP through a designated potential (or current density) of approximately +1000 mV versus OCP before reversing. The information gathered from the scan includes the following:

a. Electrochemical corrosion (mpy) calculated from the Tafel region of the scan.

b. E_{pp}, the primary passivation potential, which is the potential after which current either decreases or becomes essentially constant over a finite potential range.

c. E_b, the breakdown potential, where the current increases with increasing potential.

d. Positive hysteresis, where the curve reverses at a higher current density indicating pit growth.

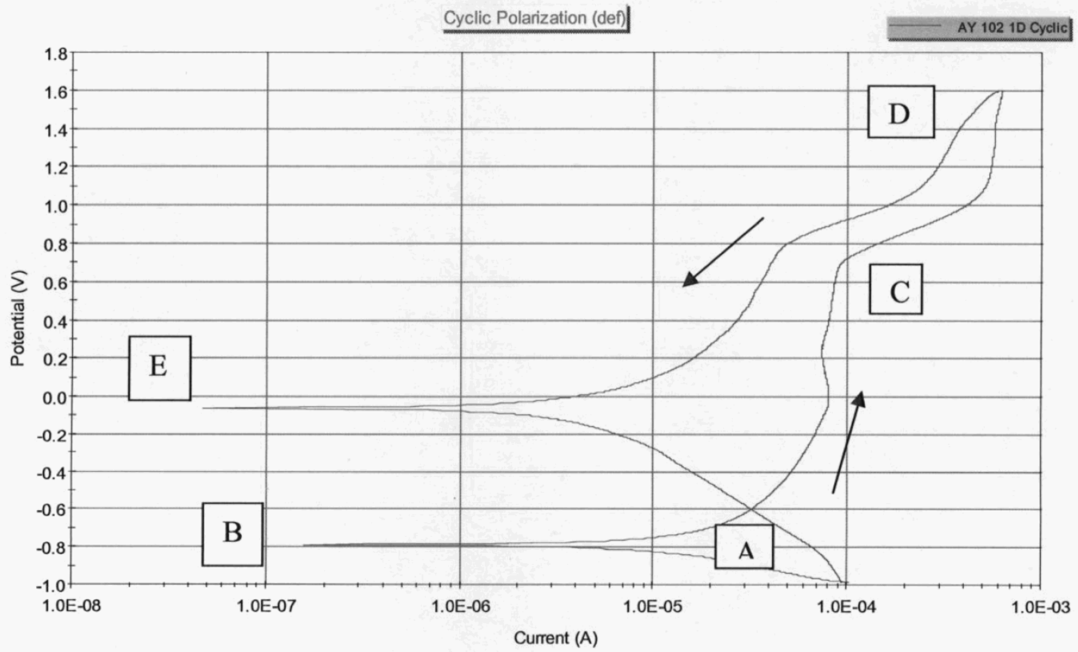
e. Negative hysteresis, where the curve reverses at lower current density indicating no pit growth.

f. E_{rp}, the repassivation potential, essentially a new OCP given the change in potential and the effect on the double layer.

Figure 2 shows an example of a CPP curve that does not indicate pitting propensity. A description of the graph is as follows:

The scan begins at the point below A and goes through the OPC (this is the potential the steel is at electrochemical equilibrium) which is located at B. The curve proceeds to C, which is a breakdown potential (the protective chemical film over the steel has broken apart and the steel is attacked). The curve is reversed at D (this is a predetermined point by the scientist). Because of chemical reactions that occur during scanning, a new OCP is formed, located at E. With this curve, the return scan between D and E is at lower current than from B to C to D. This indicates no pitting propensity for this sample.

Figure 2. Cyclic Potentiodynamic Polarization Curve.



2.4 TEST SOLUTIONS

Table 1 indicates the following test solutions (using deionized water) will be tested against the 304 and 316L stainless steel coupons:

Table 1. Test Solutions

Test Solution (T=140 °F)	Sodium Sulfate	Chrome (VI)[a]	Sulfuric Acid	Sodium Metabisulfite
Test Solution 1	4%	50 ppm	pH 2	300 ppm
Test Solution 2	4%	50 ppm	pH 2	NA
Test Solution 3	NA	NA	pH 2	NA

[a] All weighing/handling of Chrome (VI) will be carried out in a chemical hood.
Also, all Chrome (VI) solutions will be converted to Chrome (III) with sodium metabisulfite.

The test solution concentrations are based on the concentrations found to be associated with the regeneration of DOWEX 21K XLT 16-20 resin. The sodium metabisulfite concentrations were determined during the laboratory effort under the test plan entitled RPP-PLAN-32738, *Test Plan for the Effluent Treatment Facility to Reduce Chrome (VI) to Chrome (III) in the Secondary Waste Stream.*

3. WASTE

Waste will be managed in accordance with ATS-LO-110-129, *ATS Waste Collection of Nonradioactive Materials*. Waste Stream Fact Sheets and Compatibility Reviews are presented in Appendixes A and B, respectively.

4. DELIVERABLES

A CH2M HILL Hanford Group, Inc. supporting document will be issued within 30 days of completion of the test plan.

5. REFERENCES

Application Data Sheet, ADS 3300-02/rev.A, August 2004, *pH and ORP Control for Removing Chrome from Plant Effluent*, in Metals and Mineral Industry, Emerson Process Management, http://www.emersonprocess.com/raihome/documents/Liq_AppData_3300-02.pdf.

ASTM G5–94, 1994 (Reapproved 1999), *Standard Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements*, ASTM International, West Conshohocken, Pennsylvania.

ASTM G61-86, 1986 (Reapproved 2003), *Standard Test Method for Conducting Cyclic Potentiodynamic Polarization Measurements for Localized Corrosion Susceptibility of Iron-, Nickel-, or Cobalt-Based Alloys*, ASTM International, West Conshohocken, Pennsylvania.

ATS-LO-110-129, *ATS Waste Collection of Nonradioactive Materials*, Rev. F-0, CH2M HILL Hanford Group, Inc., Richland, Washington.

ATS-MP-1032, 2007, *222-S Laboratory Quality Assurance Plan*, Rev. 0, CH2M HILL Hanford Group, Inc., Richland, Washington.

Cushnie, G. C., 1994, *Pollution Prevention and Control Technology for Plating Operations*, National Center for Manufacturing Sciences, Ann Arbor, Michigan.

RPP-RPT-32207, 2007, *Laboratory Study on Regeneration of Spent DOWEX 21K 16-20 Mesh Ion Exchange Resin*, Rev. 0, CH2M HILL Hanford Group, Richland, Washington.

Tait, W. S., 1994, *"An Introduction to Electrochemical Corrosion Testing for Practicing Engineers and Scientists,"* PairODocs Publications, Racine, Wisconsin.

APPENDIX A

RCRA Treatability Study Determination Worksheet

RCRA Treatability Study Determination Worksheet

Resource Conservation and Recovery Act of 1976 (RCRA)

1. Document/Work Instruction Title: Corrosion Study for the Effluent Treatment Facility Chrome (VI) Reductant Solution Using 304 and 316L Stainless Steel.

   Document No.: RPP-PLAN-34065, Rev Ø

2. Is the media being submitted for study a dangerous or mixed waste? ☐ Yes ☒ No
   "Dangerous waste" means a waste identified in WAC 173-303-070 through 173-303-100 as dangerous, extremely hazardous or mixed waste.

   If the answer to Question 2 is "yes" then proceed to Question 3 below. If the answer is "no," the study is not a RCRA Treatability Study. Proceed to Question 5 and answer "No."

3. Does the study involve treatment of the dangerous waste? In RCRA, dangerous waste treatment is any physical, chemical, or biological processing of dangerous waste to make it:
   a. nondangerous or less dangerous, ☐ Yes ☐ No
   b. safer for transport ☐ Yes ☐ No
   c. amenable for energy or material resource recovery ☐ Yes ☐ No
   d. amenable for storage, or reduced in volume, with the exception of compacting, repackaging, and sorting as allowed under WAC 173-303-400(2) and 173-303-600(3). ☐ Yes ☐ No

   If the answer is "yes" to any one of the above in Question 3, then the waste is being treated. Continue to Question 4.

   If the answer is "no" to all of the above in Question 3, then the waste is not being treated and the study is not a RCRA Treatability Study. Proceed to Question 5 and answer "No."

4. Is the dangerous waste being subjected to a treatment process to determine one or more of the following:
   a. Whether the waste is amenable to the treatment process? ☐ Yes ☐ No
   b. What pretreatment (if any) is required? ☐ Yes ☐ No
   c. Optimal Process conditions needed to achieve the desired treatment? ☐ Yes ☐ No
   d. Efficiency of a treatment process for a specific waste or wastes? ☐ Yes ☐ No
   e. Characteristics and volumes of residuals from a particular treatment process? ☐ Yes ☐ No

   If all answers to Question 4 are "no," then the study is not a RCRA Treatability Study. Proceed to Question 5 and answer "No."

   If "yes" is answered to any part of Question 4, the study is a RCRA Treatability Study. Proceed to Question 5 and answer "Yes."

5. Based on the answers to Questions 2 – 4, is the study a RCRA treatability study as defined in WAC 173-303-040? ☐ Yes ☒ No

6. If the answer to Question 5 is "yes," has the one-time Ecology notification been made? ☐ Yes ☐ No

   Letter Reference:

K J Lueck (signature)	6-18-07	J Petersen (signature)	6-13-2007
Customer Project Lead	Date	Customer's Environmental Compliance Representative	Date

APPENDIX B

Waste Stream Fact Sheets

222-S LABORATORY DEVELOPMENTAL METHOD WASTE STREAM FACT SHEET

[X] Liquid Waste	[ ] Solid Waste	
CONSTITUENTS OF WASTE GENERATED	**CAS NUMBER***	**APPROXIMATE WEIGHT %**
Sulfuric Acid	7664-93-9	4
Water	7332-18-5	Balance to 100

Waste Codes	Disposal Path	Major Risk	Waste Container	Flash Point	pH
D002	Lab Pack	Corrosive	Glass	NA	<2

Comments:
*May use MSDS number for solid waste.

Intended Use: pH adjust for solutions for electrochemical corrosion scans.

Approvals

Title	Print Name	Signature	Date
Author/Tech Authority	J. B. Duncan	[signature]	6-25-07
Environmental Review	L. E. Borneman	[signature]	6/25/07
Technical Waste Services	R. L. Catlow	[signature]	6-25-07

Waste Stream Labeling Requirements: This label is considered to be an example label, but contains the required information for waste stream identification. Other hazardous waste labeling requirements may apply.

Procedure RPP-PLAN-34065
WSFS 1 of 2
Waste Stream Type: Aqueous Caustic
Container Type: Glass
Waste Codes: D002
Major Risk: Corrosive
Disposal Path: Lab Pack
Hazardous Waste
X Mark if waste has Not been in contact with Tank Farm waste

Waste Stream Type	Waste Stream Number	Page Number
Aqueous Acid	1 of 2	1 of 2

222-S LABORATORY DEVELOPMENTAL METHOD WASTE STREAM FACT SHEET

[X] Liquid Waste	[ ] Solid Waste	
CONSTITUENTS OF WASTE GENERATED	**CAS NUMBER***	**APPROXIMATE WEIGHT %**
Sulfuric Acid	7664-93-9	4
Sodium metabisulfite	7681-57-4	0.03
Chrome (III)	16065-83-1	0.005
Water	7332-18-5	Balance to 100

Waste Codes	Disposal Path	Major Risk	Waste Container	Flash Point	pH
D002	Lab Pack	Corrosive	Glass	NA	<2

LEB 6/26/07

Comments:
*May use MSDS number for solid waste.

Intended Use: Solution to run electrochemical scans against 304 and 316L stainless steel coupons.

Approvals

Title	Print Name	Signature	Date
Author/Tech Authority	J. B. Duncan	[signature]	6-25-07
Environmental Review	L. E. Borneman	[signature]	6/25/07
Technical Waste Services	R. L. Catlow	[signature]	6-25-07

Waste Stream Labeling Requirements: This label is considered to be an example label, but contains the required information for waste stream identification. Other hazardous waste labeling requirements may apply.

Procedure RPP-PLAN-34065
WSFS 1 of 2
Waste Stream Type: Aqueous Caustic
Container Type: Glass
Waste Codes: D002
Major Risk: Corrosive
Disposal Path: Lab Pack
Hazardous Waste
X Mark if waste has Not been in contact with Tank Farm waste

Waste Stream Type	Waste Stream Number	Page Number
Aqueous Acid	2 of 2	2 of 2

APPENDIX C

Compatibility Review

Compatibility Review

Compatibility, in this case, means that two or more substances can be mixed with no adverse effects occurring over an extended period. Incompatibility means contact of two or more substances could result in an explosion, an unexpected rapid evolution of gases, or the emission of substances that are highly toxic and/or flammable.

PROCEDURE NUMBER: RPP-PLAN-34065

CHEMICALS OF CONCERN IN ANALYSIS/WASTE STREAM (WHERE REACTIVITY/CONCENTRATION POSE A POTENTIAL COMPATIBILITY ISSUE)	MAXIMUM CONCENTRATION
Sodium Hydroxide	10%

COMPATIBILITY HAZARDS, INCLUDING SPECIAL STORAGE REQUIREMENTS, POSSIBLE REACTIONS, AND RESULTS OF MIXING INCOMPATIBLE WASTE STREAMS:

Base solution (pH >12.5) and corrosive.

RECOMMENDED WASTE STREAMS:

Aqueous basic corrosive waste

CONTAINER(S) MATERIAL:

Glass

REFERENCE DOCUMENTS USED IN COMPATIBILITY STUDY:

NIOSH Pocket Guide to Chemical Hazards

James B Duncan [signature] 6-26-07
Preparer/Date

Jann M. Frye [signature] 6/26/07
Reviewer/Date

Compatibility Review

Compatibility, in this case, means that two or more substances can be mixed with no adverse effects occurring over an extended period. Incompatibility means contact of two or more substances could result in an explosion, an unexpected rapid evolution of gases, or the emission of substances that are highly toxic and/or flammable.

PROCEDURE NUMBER: RPP-PLAN-34065

CHEMICALS OF CONCERN IN ANALYSIS/WASTE STREAM (WHERE REACTIVITY/CONCENTRATION POSE A POTENTIAL COMPATIBILITY ISSUE)	MAXIMUM CONCENTRATION
Sodium Sulfate	7%

COMPATIBILITY HAZARDS, INCLUDING SPECIAL STORAGE REQUIREMENTS, POSSIBLE REACTIONS, AND RESULTS OF MIXING INCOMPATIBLE WASTE STREAMS:

Sodium sulfate is a hygroscopic solid. The solid is incompatible with strong acids, aluminum, and magnesium. In this procedure it is used as a solution in water and in this form does not have incompatibility issues.

RECOMMENDED WASTE STREAMS:

Collect in a separate waste stream or may be combined with a basic aqueous waste stream of sodium hydroxide.

CONTAINER(S) MATERIAL:

Glass

REFERENCE DOCUMENTS USED IN COMPATIBILITY STUDY:

NIOSH Pocket Guide to Chemical Hazards, Sigma Aldrich MSDS, Hanford #036357.

James B Duncan   James B Duncan   6-26-07
Preparer/Date

Jann M. Frye   Jann M. Frye   6/26/07
Reviewer/Date

Compatibility Review

Compatibility, in this case, means that two or more substances can be mixed with no adverse effects occurring over an extended period. Incompatibility means contact of two or more substances could result in an explosion, an unexpected rapid evolution of gases, or the emission of substances that are highly toxic and/or flammable.

PROCEDURE NUMBER: RPP-PLAN-34065

CHEMICALS OF CONCERN IN ANALYSIS/WASTE STREAM (WHERE REACTIVITY/CONCENTRATION POSE A POTENTIAL COMPATIBILITY ISSUE)	MAXIMUM CONCENTRATION
Sulfuric Acid	1 N

COMPATIBILITY HAZARDS, INCLUDING SPECIAL STORAGE REQUIREMENTS, POSSIBLE REACTIONS, AND RESULTS OF MIXING INCOMPATIBLE WASTE STREAMS:

Acid solution (pH <2) and corrosive. Avoid chlorates, carbides, fulminates, water, powdered metals [Note: Reacts violently with water with evolution of heat. Corrosive to metals.]

RECOMMENDED WASTE STREAMS:

Aqueous acidic corrosive waste

CONTAINER(S) MATERIAL: Glass

REFERENCE DOCUMENTS USED IN COMPATIBILITY STUDY:

NIOSH Pocket Guide to Chemical Hazards

James B Duncan James B. Duncan 6-26-07
Preparer/Date

Jann Frye Jann M. Frye 6/26/07
Reviewer /Date