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SANDIA NATIONAL LABORATORIES
WASTE ISOLATION PILOT PLANT

AP-159

Analysis Plan for Determination of Gas Generation Rates from Iron/Lead Corrosion Experiments

Task 1.4.2.2

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Table of Contents

1 Introduction and Objectives 3
1.1 Introduction 3
1.2 Objectives 3
2 Approach 3
2.1 General Procedure 3
2.2 Determination of Mass-Loss and Corrosion Rates 4
2.3 Calculation of Gas Generation Rates 6
3 Tasks 7
3.1 Task 1 – Mass Loss Determination from Experiments 7
3.2 Task 2 – Determination of Corrosion Products 8
3.3 Task 3 – Determination of Gas Generation Rates 8
3.4 Task 4 – Application of Results 8
4 Software List 8
5 Special Considerations 8
6 Applicable Procedures 8
7 References 9

1 *Introduction and Objectives*

1.1 Introduction

Steel corrosion and organic-material biodegradation have been identified as major gas-generation processes in the Waste Isolation Pilot Plant (WIPP) repository (Brush, 1995). Gas production will affect room closure and chemistry (Butcher, 1990; Brush, 1990). Wang and Brush (1996) provided estimates of gas-generation parameters for the long-term WIPP performance assessment based on experimental work of Telander and Westerman (1993, 1997). These parameters included the rates of gas generation under inundated and humid conditions, the stoichiometric factors of gas generation reactions, and the probability of the occurrence of organic material biodegradation.

Since the analysis of Wang and Brush (1996), a new series of steel and lead corrosion experiments has been conducted under Test Plan TP 06-02, *Iron and Lead Corrosion in WIPP-Relevant Conditions* (Wall and Enos, 2006). The object of these experiments has been to determine steel and lead corrosion rates under WIPP-relevant conditions. Telander and Westerman (1993, 1997) measured both corrosion rates and H_2 generation rates directly. However, the current experiments under Test Plan 06-02 opted to measure only corrosion rates. Thus, the purpose of this AP is to describe the calculations needed to determine new gas generation rates for steel and lead in the WIPP performance assessment. Therefore, this analysis is considered a compliance decision analysis per NP 9-1.

1.2 Objectives

The objective of this Analysis Plan is to derive steel and lead corrosion rates from the mass loss data obtained in the TP 06-02 directed corrosion studies. These corrosion rates and knowledge of the corrosion products formed will be used to determine gas generation rates from the iron and lead corrosion studies.

2 *Approach*

2.1 General Procedure

The purpose of the corrosion experiments was to assess the corrosion behavior of carbon steel and Pb alloys used to contain contact handled (CH) and remote handled (RH) waste under

WIPP-relevant conditions. Specifically, the experiments aim to determine the corrosion rates of these metals and the nature of the corrosion products that will form. At this time all of the corrosion experiments have been completed and analysis of the corrosion products is on-going. The environmental conditions and samples used for this set of experiments were set up to be representative of the conditions expected in the WIPP following its closure. During these experiments steel and lead coupons were immersed in different WIPP-relevant brines or hung in WIPP-relevant atmospheric conditions for a period of two years. Samples were removed from the experiments for analysis at six month intervals. After completion of the corrosion tests, two of the three replicate coupons for each test condition were chemically cleaned in order to remove all of the corrosion products. The mass of the coupons after cleaning was compared to the initial mass and the difference represents the loss of material to corrosion. The mass loss can then be used to calculate a corrosion rate and that rate can be used to determine gas generation rates. A detailed discussion of the methods used and experimental setup of the corrosion studies can be found in Roselle (2009).

2.2 Determination of Mass-Loss and Corrosion Rates

After the corrosion tests were completed, coupons for each test condition were chemically cleaned in order to remove all of the corrosion products. There are numerous standard procedures that outline requirements for the cleaning of corrosion samples: ISO 8407:1991, NACE Standard TM0169-2000 and ASTM G 1 – 03. For the most part, each of these standard procedures outlines nearly identical requirements and all coupons are cleaned per the requirements outlined in these standards. The cleaning process includes multiple cycles of chemical etching, brushing with a nonmetallic soft bristle brush followed by rinsing with deionized water. Following each cleaning cycle the coupons are dried and weighed with the weight for each cycle being recorded in the scientific notebook. A minimum of five cleaning cycles is performed for each coupon.

Because the above cleaning procedures remove some amount of base metal in addition to the corrosion products a procedure needs to be employed that corrects the weight loss measurements for the base metal loss. This study used a procedure of graphical analysis based on multiple cleaning cycles in order to extrapolate the actual weight loss due to corrosion from the total measured weight loss. The graphical analysis method is outlined in ISO 8407:1991 and is shown schematically in Figure 1. The mass of a coupon should have a linear relationship with respect

to the cleaning cycles as long as the duration of each cycle is the same. A plot of the mass versus cleaning cycles ideally results in two lines (AB and BC in Figure 1). Line AB characterizes the removal of corrosion products and possibly base metal, whereas line BC is the result of removal of the base metal substrate after all corrosion products have been removed. Extrapolation of line BC to the 0th cleaning cycle (point D) provides the mass of the coupon at zero cleaning cycles. The true mass of the coupon (minus corrosion products) will be between points B and D. For the purposes of determining mass loss in this study, point D is taken as the final weight.

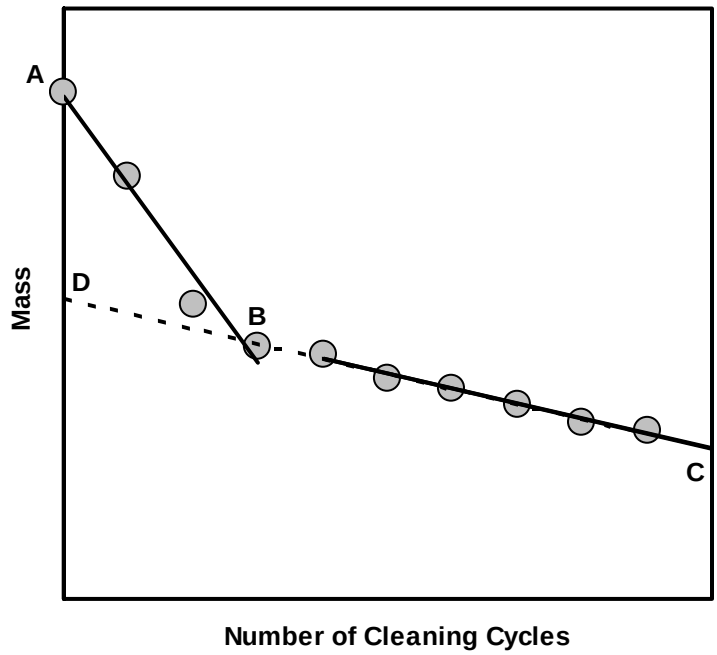

Figure 1 Graphical method used to determine coupon mass loss. True mass of the specimen after removal of the corrosion products will be between points B and D.

Corrosion rates are calculated from the mass loss data according to the following formula (NACE, 2000):

$$rate = \frac{W \times 87.6}{SA \times t \times \rho} \times 1000 \qquad (1)$$

where *rate* is the corrosion rate in μm/yr, *W* the mass loss (mg), *SA* the exposed surface area of the coupon (cm^2), *t* the exposure duration (hours), ρ the metal density (g/cm^3) and 1,000 converts the rate from mm/yr to μm/yr. Metal densities of 7.872 g/cm^3 and 11.340 g/cm^3 were used for steel and lead, respectively (MatWeb, 2009).

2.3 Calculation of Gas Generation Rates

The interaction of steel and lead in the WIPP with repository brines will result in the formation of H_2 gas due to anoxic corrosion of the metals. The rate of H_2 gas generation will depend on the corrosion rate and the type of corrosion products formed. As explained in Brush (1990) two possible anoxic corrosion products of steel in the absence of CO_2 are Fe_3O_4 and $(Fe,Mg)(OH)_2$ via the reactions:

$$3Fe + 4H_2O = Fe_3O_4 + 4H_2 \tag{2}$$

$$Fe + 2H_2O = Fe(OH)_2 + H_2 \tag{3}$$

In the presence of microbially-produced CO_2 steel corrosion can proceed via the reaction:

$$Fe + CO_2 + H_2O = FeCO_3 + H_2 \tag{4}$$

These reactions can be used in conjunction with the experimentally determined corrosion rates to estimate H_2 gas generation rates due to steel corrosion.

Equation (1) results in corrosion rates in terms of μm/year, which must be converted to a mole basis for estimated gas generation rates. Because the corrosion of a 1 m^2 Fe plate to a depth of 1μm results in the consumption of 1 cm^3 of Fe, the linear to molar conversion can be calculated as follows:

$$1\ \mu m/m^2\ Fe \times 7.872\ g/cm^3 \times 0.0179\ mole/g\ Fe = 0.141\ mole/\mu m/\ m^2\ Fe \tag{5}$$

where 7.872 g cm^{-3} is the density of the steel and 0.0179 mol g^{-1} is the inverse molecular weight of Fe. Thus multiplying the corrosion rates obtained from equation (1) by 0.141 mole/μm/m^2 Fe will convert the unit of steel corrosion from μm/year to mole /m^2/year (Telander and Westerman, 1993). This molar corrosion rate can then be used to calculate H_2 gas generation rates based on the molar ratio of Fe to H_2 in the reactions given in equations (2) to (4).

The reactions shown above are based upon observations in the corrosion experiments of Telander and Westerman (1993, 1997). It is possible that other corrosion products (e.g. green

rust, hibbingite, etc.) may also form. If other corrosion products are identified then the appropriate reactions can be written to determine the molar Fe to H_2 ratio. For example, if green rust [$Fe(III)_2Fe(II)_4(OH)_{12}CO_3 \cdot 2H_2O$] were identified as the major corrosion product then the corrosion reaction would be written as:

$$6\ Fe + CO_2 + 15\ H_2O = Fe(III)_2Fe(II)_4(OH)_{12}CO_3 \cdot 2H_2O + 7\ H_2 \qquad (6)$$

The identification of the corrosion products according to TP 06-02 will occur prior to the gas generation analysis.

The anoxic corrosion of Pb could also result in H_2 gas generation via the formation of PbO in the CO_2-free environments and $PbCO_3$ in the presence of CO_2:

$$Pb + H_2O = PbO + H_2 \qquad (7)$$

$$Pb + CO_2 + H_2O = PbCO_3 + H_2 \qquad (8)$$

Conversion of the Pb corrosion rates from μm/year to mole /m^2/year is calculated as follows:

$$1\ \mu m/m^2\ Pb \times 11.340\ g/cm^3 \times 0.0048\ mole/g\ Pb = 0.055\ mole/\mu m/\ m^2\ Pb \qquad (9)$$

Just as in the case of steel corrosion the molar corrosion rate can then be used to calculate H_2 gas generation rates based on the molar ratio of Pb to H_2 in the appropriate reactions.

3 Tasks

There are four tasks associated with this AP. The primary analyst for this AP is Gregory Roselle. Assistance with mass loss determination and corrosion product identification will be provided by current geochemistry lab staff. All tasks associated with this AP should be completed by March 31, 2012.

3.1 Task 1 – Mass Loss Determination from Experiments

At the conclusion of the corrosion experiments two of the three replicate coupons were used to determine corrosion rates based on mass loss, as outlined in Section 2.2. At this time all Task 1 activities are complete and results are documented in Roselle (2009, 2010, 2011a, 2011b).

3.2 Task 2 – Determination of Corrosion Products

Analytical methods such as X-Ray Diffraction Analysis and Scanning Electron Microscopy coupled with Energy Dispersive Spectroscopic Analysis will be used to quantitatively identify the corrosion products that formed during the experiments. This information will then be used to formulate the appropriate corrosion reactions for Fe and Pb.

3.3 Task 3 – Determination of Gas Generation Rates

Once the corrosion rates and corrosion products have been determined the methods outlined in Section 2.3 will be used to calculate gas generation rates for each of the experiments.

3.4 Task 4 – Application of Results

Once the data analysis is completed a summary report will be issued that summarizes all of the results. These results will also be used to formulate new gas generation parameters for use in the WIPP PA.

4 Software List

Commercial off-the-shelf spreadsheet programs, such as Excel, will be used for data manipulation and plotting.

5 Special Considerations

No special considerations have been identified.

6 Applicable Procedures

All applicable WIPP quality-assurance procedures will be followed when conducting these analyses. Training of personnel will be done in accordance with the requirements of NP 2-1, *Qualification and Training*. Analyses will be performed and documented in accordance with the requirements of NP 9-1, *Analyses* and NP 20-2, *Scientific Notebooks*. All software used will meet the requirements of NP 19-1, *Software Requirements* and NP 9-1, as applicable. The analyses will be reviewed following NP 6-1, *Document Review Process*. All required records will be submitted to the WIPP Records Center in accordance with NP 17-1, *Records*.

7 References

ASTM (2003) *Standard Practice for Preparing, Cleaning and Evaluation Corrosion Test Specimens*. ASTM G 1 - 03. West Conshohocken, PA: American Society for Testing and Materials (ASTM) International.

Brush, L.H. (1990) *Test Plan for Laboratory and Modeling Studies of repository and Radionuclide Chemistry for the Waste Isolation Pilot Plant*. SAND90-0266. Albuquerque, NM: Sandia National Laboratories.

Brush, L.H. (1995) *Systems Priority Method – Iteration 2 Baseline Position Paper: Gas Generation in the Waste Isolation Pilot Plant*. Albuquerque, NM: Sandia National Laboratories.

Butcher, B.M. (1990) *Preliminary Evaluation of Potential Engineered Modifications for the Waste Isolation Pilot Plant (WIPP)*. SAND89-3095. Albuquerque, NM: Sandia National Laboratories.

ISO (1991) *Corrosion of Metals and Alloys – Removal of Corrosion Products from Corrosion Test Specimens*. ISO 8407:1991. Geneva, Switzerland: International Organization for Standardization.

MatWeb (2009) *Material Properties for AISI 1008 Steel and Chemical Lead (Pb)*. http://www.matweb.com. ERMS 551896.

NACE (2000) *Standard Test Method - Laboratory Corrosion Testing of Metals*. TM0169-2000. Houston, TX: National Association of Corrosion Engineers (NACE) International.

Roselle, G.T. (2009) *Iron and Lead Corrosion in WIPP-Relevant Conditions: Six Month Results*. Milestone Report, October 7, 2009. Carlsbad, NM: Sandia National Laboratories. ERMS 546084.

Roselle, G.T. (2010) *Iron and Lead Corrosion in WIPP-Relevant Conditions: 12 Month Results*. Milestone report, October 14, 2010, Carlsbad, NM: Sandia National Laboratories. ERMS 554383.

Roselle, G.T. (2011a) *Iron and Lead Corrosion in WIPP-Relevant Conditions: 18 Month Results*. Milestone report, January 5, 2011, Carlsbad, NM: Sandia National Laboratories. ERMS 554715.

Roselle, G.T. (2011b) *Iron and Lead Corrosion in WIPP-Relevant Conditions: 24 Month Results*. Milestone report, May 3, 2011, Carlsbad, NM: Sandia National Laboratories. ERMS 555246.

Telander, M.R., and R.E. Westerman (1993) *Hydrogen Generation by Metal Corrosion in Simulated Waste Isolation Pilot Plant Environments*. SAND92-7347. Albuquerque, NM: Sandia National Laboratories.

Telander, M.R., and R.E. Westerman (1997) *Hydrogen Generation by Metal Corrosion in Simulated Waste Isolation Pilot Plant Environments*. SAND96-2538. Albuquerque, NM: Sandia National Laboratories.

Wall, N.A. and Enos, D. (2006) *Iron and Lead Corrosion in WIPP-Relevant Conditions, TP 06-02, Rev 1*. ERMS 543238. Carlsbad, NM: Sandia National Laboratories.

Wang, Y. and Brush, L.H. (1996) *Estimates of Gas-Generation Parameters for the Long-Term WIPP Performance Assessment*. Memo to Martin S. Tierney, January 26, 1996. ERMS 231943. Carlsbad, NM: Sandia National Laboratories.

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