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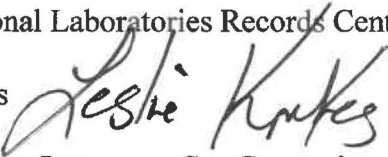
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to: Sandia National Laboratories Records Center

from: Leslie Kirkes

subject: Lead Inventory Impact on Gas Generation

EPA technical discussions regarding the Technical Support Document CRA-2014 section 194.24 sub-section 3.3 (U.S. EPA, 2017) have discussed increases in lead inventory and concerns regarding lead gas generation. EPA has requested that DOE "calculate an approximate lead inventory to justify that lead won't be a big contributor" (Peake, T. 2018. Issue #11). This memo addresses the concerns raised by Issue #11 (Peak, T. 2018).

Gas generation from lead corrosion was assumed by the Performance Assessment Department to be insignificant in the past due to the limited amount of lead in the waste inventory and waste packaging (Bryson, D. 2015). Lead in the waste is accounted for in the category of "Other Metals/Alloys". This category includes all other metals except for iron, so the exact amount of lead in the waste is not tracked. A conservative estimate of lead in the waste is to assume the entirety of the "Other Metals/Alloys" number is lead waste. Lead is also introduced to the WIPP through the Remote Handling (RH) waste packaging via shielded containers and other packaging materials. As of the cut-off date for the Performance Assessment Inventory Report 2012 (PAIR-2012), total projected lead in the waste packing was 8.28E+03 kg (Van Soest, G.D. 2012). After this cut-off date, 9 shielded containers were emplaced in the WIPP and additional shielded containers are expected to be emplaced before WIPP closure. This has led to an increase in lead volumes projected in the 2018 WIPP inventory report, with an estimate of 1.38E+07 kg RH waste packaging (Van Soest, G. D. 2018). While in past PA calculations it was reasonable to assume that gas generation from lead was insignificant, the increase in lead inventory may require a re-evaluation of this assumption. This memo

summarizes the relevant DOE lead experiments, provides a literature review of existing lead corrosion research and proposes a path forward for the lead gas generation subject as it relates to PA calculations.

In the WIPP environment, the anoxic corrosion of lead in the presence of brine, could potentially result in H_2 gas generation via the formation of lead corrosion products. A series of lead corrosion experiments were conducted by DOE under TP 06-02 Rev.1 (Wall, N.A, Enos, D., 2006). These experiments were designed to derive iron in steel and lead corrosion rates from mass loss data and then calculate gas generation rates from steel and lead corrosion using AP-159 (Roselle, G.T. 2011). Details of these experimental set-ups and calculations can be found in the Roselle, G.T. 2013 analysis report: Determination of Corrosion Rates from Iron/Lead Corrosion Experiments to be used for Gas Generation Calculations.

Detailed descriptions regarding the mass loss procedure and cleaning of the corrosion products can be found in Roselle, G.T. 2013 in section 3.5. Three coupons were removed from experimentation at each time interval and for each experimental matrix. Two of the coupons were used for mass loss determination and one of the coupons was used for visual inspection using the Scanning Electron Microscope and Electron Dispersion Spectroscopy (SEM/EDS). Roselle, G.T. 2013, utilized the averages of the partially and fully submerged coupons to calculate corrosion rates for steel and lead at the various time intervals. After further consideration, it was decided that only the fully submerged coupons should have been used for the calculations rather than an average of the partially and fully submerged coupons. Unfortunately, this leaves only 1 or 2 mass loss measurements (negative values are excluded from use) for use in calculating the corrosion rates at each time interval. This is not a large enough sample size to calculate an accurate corrosion rate and follow-on experiments are necessary to determine corrosion rates for lead coupons. In addition, standard deviations of the measured mass loss lead data are somewhat elevated for some of the reported measurements (Table 9 of Roselle, G.T. 2013). Roselle, G.T. (2013) notes, "The porous nature of the lead coupons…is the likely reason for the large variation in the corrosion rate data. The coupon porosity makes it difficult to consistently remove all of the cleaning and rinse solutions used in the weight loss determination. As a result, there is more variation in the measured lead weight losses than observed in the steel experiments." In addition, there has been some concern with use of the mass loss technique for lead. Lead is a much softer metal than steel and it is a concern

that lead mass could have been lost due to physical means rather than chemical means. The loss of lead by physical means (removal of pieces of metal during cleaning) would give a falsely elevated corrosion rate. Removing metal during the cleaning process would falsely elevate corrosion rates when using a mass loss technique, because the metal would be seen as corrosion that wasn't actually present. Although the data may not be adequate for determination of corrosion rates, the data is adequate to demonstrate the effect of passivation. Figure 1 shows the average lead coupon corrosion rates, calculated by Roselle, G.T. 2013, in the various brines plotted as a function of time for 0 and 350 ppm CO_2 atmosphere. As shown in the figures, lead corrosion rates decline as a function of time. The reduction in corrosion rates with time is likely an indication that the samples are beginning to show signs of passivation (Roselle, G.T. 2013). While the corrosion rates have high uncertainty, the data is adequate to demonstrate a trend of diminishing rates over a 24-month time-period. It is likely that the coupons have not reached a final passivation state since the rates are still fluctuating between 18-months and 24-months, however it is evident that passivation is likely occurring.

Figure 1   Average Corrosion rates for lead coupons
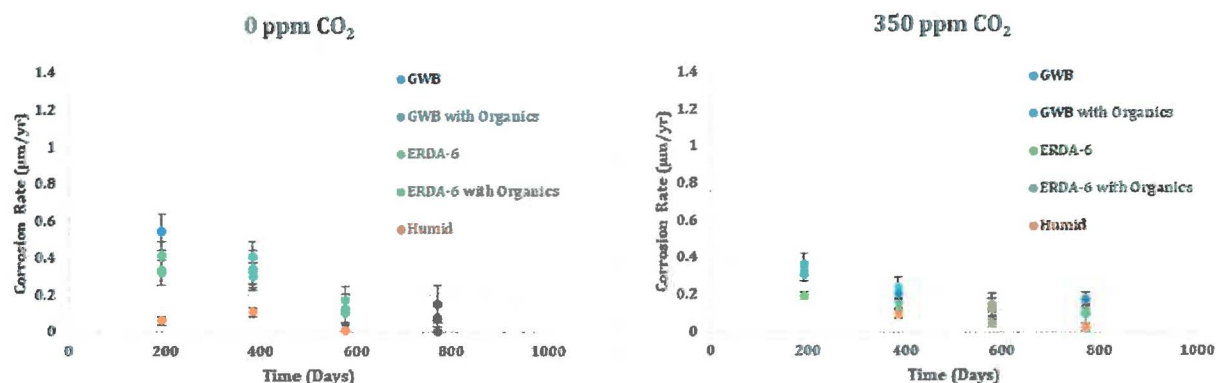
Source of Figure 1: Re-created from Roselle, G. T. 2013

Passivation has been observed in numerous lead corrosion studies, including the work by Azim, A.A. et al., Cassibba R.O. and Fernandez, S., von Fraunhofer, J.A., and others such as Beccaria, A.M. et al. A literature review of current lead corrosion research shows a similar trend. In highly saturated salt conditions, corrosion rates have been shown to reduce compared to tap water and less than WIPP brine saline solutions (Azim, A.A. et al. 1972). Azim, A.A. et al, speculate that this reduction of corrosion rates in saline solutions is likely due to the Cl⁻ ion functioning as an anodic inhibitor. The inhibition is likely due to the ability of the anions to become adsorbed to the metal surface, effectively preventing the entry of Pb^{2+} ions and thus

preventing any further corrosion of the underlying metal. Azim, A.A. et al. observed two types of passivation, with primary passivity being caused by the formation of a salt film and secondary passivity occurring when the surface is covered with lead corrosion products (PbO_2 in this study). Cassibba, R.O. and Fernandez, S. 1989, observed similar passivity occurrence with lead corrosion rates decreasing as salt content increased. Von Fraunhofer, J.A. notes that, lead corrosion rates "fall to a low, almost limiting value at about 35,000 ppm [chloride]". A study conducted by Beccaria, A.M. et al. found the lead corrosion product of $Pb(OH)Cl$ in $NaCl$ solutions and their experiments showed a passivation film developing on the lead coupons in all experimental conditions. The afore mentioned authors disagree slightly on the mechanism of the development of the passivation layer in that they argue whether the passivation layer is being formed by the precipitation of the anions (Cl^- or SO_4^{2-}) or if the passivation layer is being generated by the simultaneous precipitation of the anions (Cl^- or SO_4^{2-}, OH^-) with the Pb^{2+} ions (Beccaria, A.M. et al. 1982). Although disagreeing on the passivation formation mechanism, all afore mentioned authors found that a passivation layer forms in experiments with lead in saline conditions, thus reducing corrosion rates to a minimal rate. The Roselle 2013 research conducted by DOE supports the idea of lead passivation and highly reduced corrosion rates over time in high saline conditions. The effect of the passivation may be amplified further if longer experimental times are employed.

The majority of the studies cited in this memo conducted their research using electrochemical studies, combined with X-Ray Diffraction (XRD), mass loss and visual characterization techniques such as SEM/EDS. Few of the studies used the mass loss technique solely to calculate corrosion rates. This experimental technique has numerous avenues for error, especially for lead experimentation, as cited by Roselle himself in not being able to obtain accurate weights (i.e. high standard deviations between samples) for lead coupon results. While the Roselle 2013 data is useful for demonstrating a trend towards passivation on the lead surface, it is not substantial enough to derive accurate lead gas generation rates.

Due to recent changes in the quantity of lead that may be disposed in the WIPP, assumptions concerning lead corrosion within PA are being reevaluated. In the WIPP lead corrosion studies, issues were identified concerning the lead material properties, experimental methods and sample weight errors. However, the experiments were useful in demonstrating the potential for passivation in lead systems. If passivation eventually leads to a significant

reduction in corrosion, using short-term corrosion rates averaged over a two-year period will overestimate corrosion over the 10,000-year period used in PA calculations. A literature search identifies several saline lead corrosion studies that show passivation.   Additional experimental work is needed to investigate lead corrosion behavior in WIPP relevant conditions using techniques and time-frames appropriate. DOE is planning a series of follow on experiments to the Roselle 2013 research, that include using electrochemical studies and other more modern advanced instruments such as the interferometer as well as the use of specialized techniques to collect and analyze hydrogen gas formation. These follow-up experiments will be designed to provide a more accurate determination of the gas generation and corrosion rates for lead systems under WIPP relevant conditions. DOE does not recommend that an update to the PA calculations model be completed to include lead gas generation. Status on issue #11 from the 2018 docket, has been resolved "as per the September 2018 Technical Exchange, DOE will estimate bounding surface areas for lead for future CRA PAs. If surface areas become significant relative to steel surface areas, lead corrosion rates will be taken into account in PA" (Peake, T. 2018). After additional research is completed, a more accurate evaluation of the lead gas generation and the lead corrosion rates can be proposed, and incorporation of the data into PA calculations can be re-evaluated at that time. Lead inventory increases and its effects on lead gas generation will be addressed in future WIPP certifications after more data has been obtained.

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