SAND2018-13223C

Lead/Lead-based Alloy Materials For High Level Nuclear Waste Disposal: Insight From Advances In Lead Solution Chemistry

Material Research Society (MRS) Fall Meeting, November 25-29, 2018, Boston, MA

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This research is funded by the Spent Fuel Waste Science and Technology (SFWST) programs administered by the Office of Nuclear Energy (NE) of the U.S Department of Energy. SAND2018-xxxxC

OUTLINE OF PRESENTATION

- Introduction
- Advances in Lead Solution Chemistry Including Lead Corrosion in Harsh Environments
- Objective of This Work
- Solubility of Lead Corrosion Product, Cerussite, $PbCO_3(cr)$ in A Reference Clay Repository for HLW & SNF
- Solubility of Lead Corrosion Product, Cerussite, $PbCO_3(cr)$ in A Reference Crystalline Rock (metamorphic rock) Repository for HLW & SNF
- Solubility of Lead Corrosion Product, Cerussite, $PbCO_3(cr)$ in Reference Granite Repositories for HLW & SNF
- Summary

INTRODUCTION

- In multiple component engineered barrier system (EBS) for high level nuclear waste (HLW) and spent nuclear fuel (SNF), a canister/overpack is the key component satisfying eight requirements:
  - Ensuring there is no release of radionuclides at least for 1,000 years in the performance period of up to one million years for a repository, meeting the regulatory requirements.
  - Avoidance of detrimental impacts on other barriers
  - Retrievability during the operational phase
  - Good radiation shielding ability
    - 150 mm thickness required for carbon steel (Asono and Aritomi, 2005)
    - 5 mm thickness required for lead
    - Not specified for copper, see the design report for disposal canister in Finnish design concept (Raiko, 2005)
      - May largely rely on cast iron insert for radiation shielding

Asano, H. and Aritomi, M., 2005. Long-term integrity of waste package final closure for HLW geological disposal,(I) Points at issue concerning 1,000 years containment capability of overpack. *Journal of nuclear science and technology*, *42*(5), pp.470-479.

Raiko, H., 2005. Disposal canister for spent nuclear fuel-Design report. *Posiva report*, *2*, p.61.

INTRODUCTION (Cont.)

- Key requirements for canisters/overpacks (continued):
  - Availability of raw material
  - Reasonable cost associated with raw material, fabrication, and handling (i.e., precious metals and others such as Ti, W, Nb, Ta, etc., are excluded from consideration)
  - Ease of sealing and inspection
  - Reasonable structural strength/robustness

INTRODUCTION (Cont.)

- Copper has been the canister/overpack material of choice for the following countries' nuclear waste disposal programs:
  - Sweden, Finland
  - Canada partially uses copper as a coating material for carbon steel
  - Copper is a good material for canister because of its resistance to corrosion, but is relatively expensive and the availability is limited, in comparison with carbon steel and lead (see following slides).
    - $3.29/lb (http://www.infomine.com/investment/metal-prices), accessed on November 6, 2018.
  - Serious questions over the economics of use of Cu, especially in view of the limited availability of copper minerals (Landolt et al., 2009).
  - Not suitable for the repository design concepts in unsaturated zones, as the corrosion product, malachite, $Cu_2CO_3(OH)_2(cr)$, is rather high (Wersin et al., 1994).

Wersin, P., Spahiu, K. and Bruno, J., 1994. *Kinetic modelling of bentonite-canister interaction. Long-term predictions of copper canister corrosion under oxic and anoxic conditions* (No. SKB-TR--94-25). Swedish Nuclear Fuel and Waste Management Co.

INTRODUCTION (Cont.)

- Carbon steel has been the canister/overpack material of choice for the following countries' nuclear waste disposal programs:
  - Belgium, France, Japan, Switzerland
  - Carbon steel is relatively cheap in comparison with copper.
    - $0.50/lb (https://agmetalminer.com/metal-prices/carbon-steel/), accessed on November 7, 2018.
  - Good mechanical strength
  - A major concern for use of carbon steel: Hydrogen generated by corrosion may damage barrier properties in EBS and rock formations (Landolt et al., 2009).
  - Iron may promote microbial activity that could degrade bentonite buffer (e.g., Liu et al., 2012; Stone et al., 2016; Haynes et al., 2018), as iron is a nutrient for microbes.
  - Not suitable for the repository design concepts in unsaturated zones, as the corrosion rates of iron are too high under oxidized conditions.

Haynes, H.M., Pearce, C.I., Boothman, C. and Lloyd, J.R., 2018. Response of bentonite microbial communities to stresses relevant to geodisposal of radioactive waste. *Chemical Geology*.

Landolt, D., Davenport, A., Payer, J., Shoesmith, D., 2009. A Review of Materials and Corrosion Issues Regarding Canisters for Disposal of Spent Fuel and High-level Waste in Opalinus Clay. Technical Report 09-02. NAGRA, Hardstrasse 73, CH-5430 Wettingen, Switzerland.

Liu, D., Dong, H., Bishop, M.E., Zhang, J., Wang, H., Xie, S., Wang, S., Huang, L. and Eberl, D.D., 2012. Microbial reduction of structural iron in interstratified illite-smectite minerals by a sulfate-reducing bacterium. *Geobiology*, *10*(2), pp.150-162.

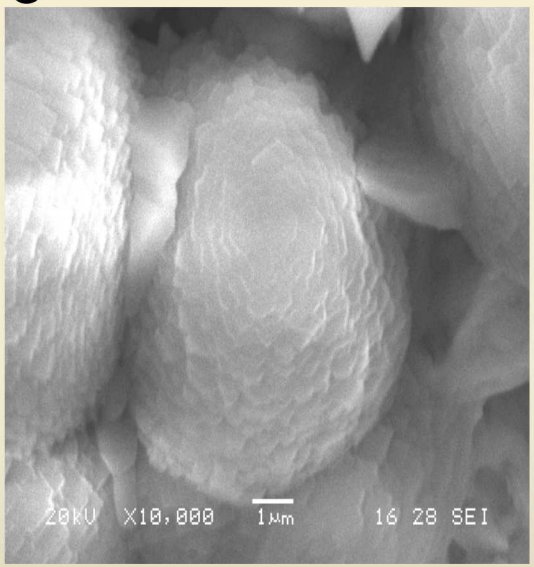
Stone, W., Kroukamp, O., Moes, A., McKelvie, J., Korber, D.R. and Wolfaardt, G.M., 2016. Measuring microbial metabolism in atypical environments: Bentonite in used nuclear fuel storage. *Journal of microbiological methods*, *120*, pp.79-90.

INTRODUCTION (Cont.)

- Lead/lead-based alloys have been the canister/overpack material of choice for the following countries' nuclear waste disposal programs:
  - Argentina, Brazil, Russia
  - The price of lead is between copper and carbon steel.
    - Copper, $3.29/lb
    - Lead, $0.87/lb (http://www.infomine.com/investment/metal-prices), accessed on November 6, 2018
    - Carbon steel, $0.50/lb
  - Excellent resistance to corrosion, as evidenced by archaeological studies on ancient lead artificial products, survived for thousands of years
  - Excellent radiation shielding ability
  - Lead is not a nutrient for microbes.
  - Suitable for the repository design concepts in unsaturated zones, as canisters are protected by the passivative corrosion product(s) from further corrosion
  - Mechanical strength is weaker in comparison with copper and carbon steel, but its mechanical properties can be significantly strengthened by alloying with other elements.

RECENT ADVANCES IN LEAD SOLUTION CHEMISTRY

- Recent Advances in Lead Corrosion in Harsh Environments (Roselle, 2013):
  - Long-term corrosion experiments up to ~800 days in high ionic strength solutions with high concentrations of chloride up to 6.3 mol•kg^{-1} at 26^{o}C
  - P_{CO_2} ranging from $10^{-3.46}$ to $10^{-2.46}$ atm
  - New findings:
    - Passivation of Pb at all P_{CO_2}, including experiments without imposing P_{CO_2} , as indicated by decrease in corrosion rate with time
    - Observed corrosion products at $P_{CO_2} = 10^{-2.82}$ atm or higher: cerussite, $PbCO_3$, and tarnowitzite, (Ca, Pb)CO_3
    - Lead subjected to humid conditions show no evidence of corrosion



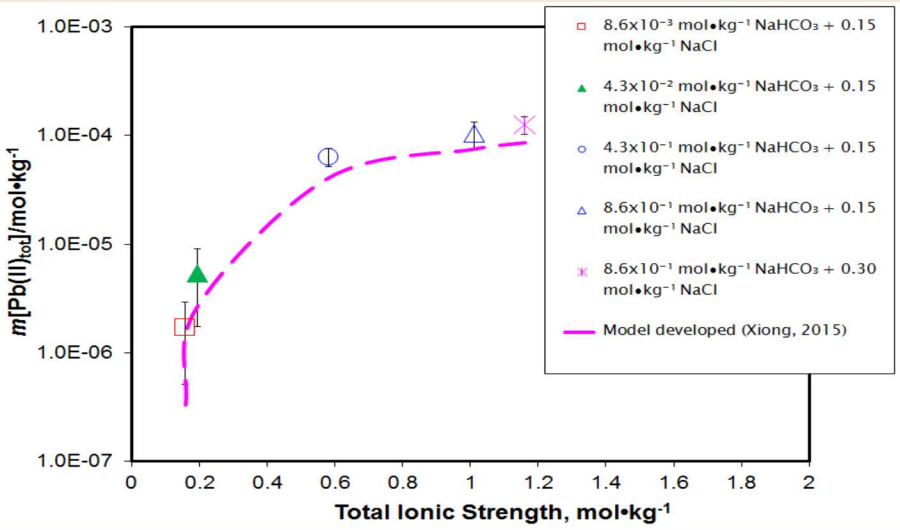
Roselle, G.T., 2013. Anoxic Corrosion of Steel and Lead in Na-Cl +/- Mg Dominated Brines. Sandia National Laboratories, Albuquerque, NM, SAND2013-3509C.

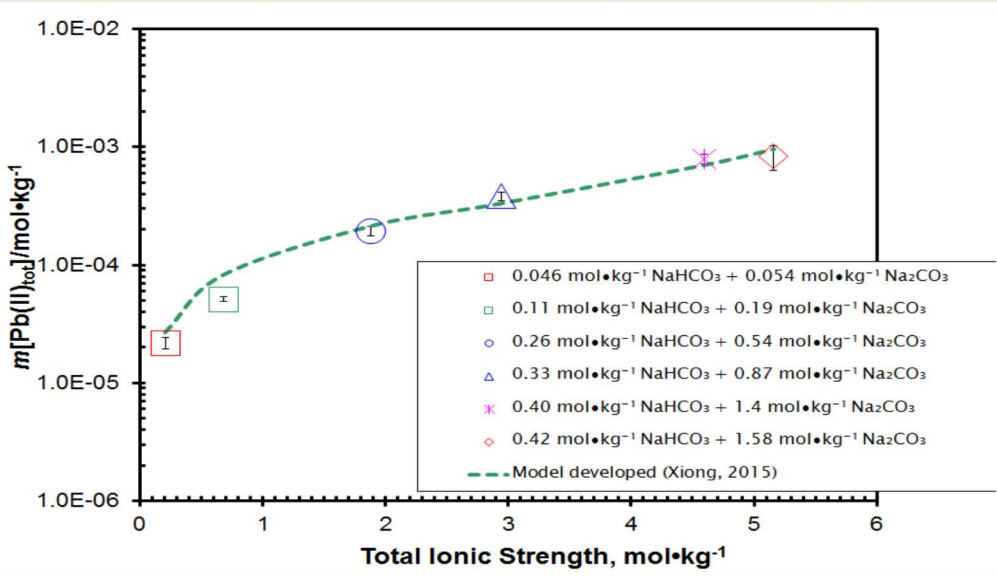
RECENT ADVANCES IN LEAD SOLUTION CHEMISTRY (Cont.)

- Recent Advances in Lead Solution Chemistry to High Ionic Strengths (Xiong et al., 2014; Xiong, 2015):
  - We have developed a thermodynamic model that can describe solubilities of cerussite with high precision to high ionic strengths up to 5.4 mol•kg^{-1}.

Xiong, Y.-L., Kirkes, L., and Westfall, T., 2014. Experimental and Thermodynamic Modeling Solubility of Lead in the Carbonate System to High Ionic Strengths. Goldschmidt Conference 2014, June 8 through 13, 2014, Sacramento, California. Sandia National Laboratories, Albuquerque, NM: SAND2014-4668C.

Xiong, Y., 2015. Experimental determination of lead carbonate solubility at high ionic strengths: a Pitzer model description. *Monatshefte für Chemie-Chemical Monthly*, *146*(9), pp.1433-1443.





OBJECTIVE OF THIS STUDY

- Cerussite is the most likely passivative corrosion product when lead is corroded in carbonate-bearing groundwater:
  - Further corrosion of a lead canister will not occur until total soluble lead (ΣPb) in equilibrium with cerussite is diffused into bentonite buffer to produce a thermodynamic force for the dissolution of cerussite.
  - Solubility of cerussite plays a key role in the further corrosion of lead/lead-based alloy canisters.
- We predict solubilities of cerussite in various disposal designs for HLW & SNF.
  - Solubility predictions are performed at 25°C.
    - Results are expected to be conservative because cerussite has retrograde solubility, meaning that its solubility decreases with temperature.
- We use EQ3/6 Version 8.0a (Wolery et al., 2010; Xiong, 2011) with the database that incorporates the updated lead chemistry including cerussite (Domski, 2015; Xiong and Domski, 2016) for solubility predictions.

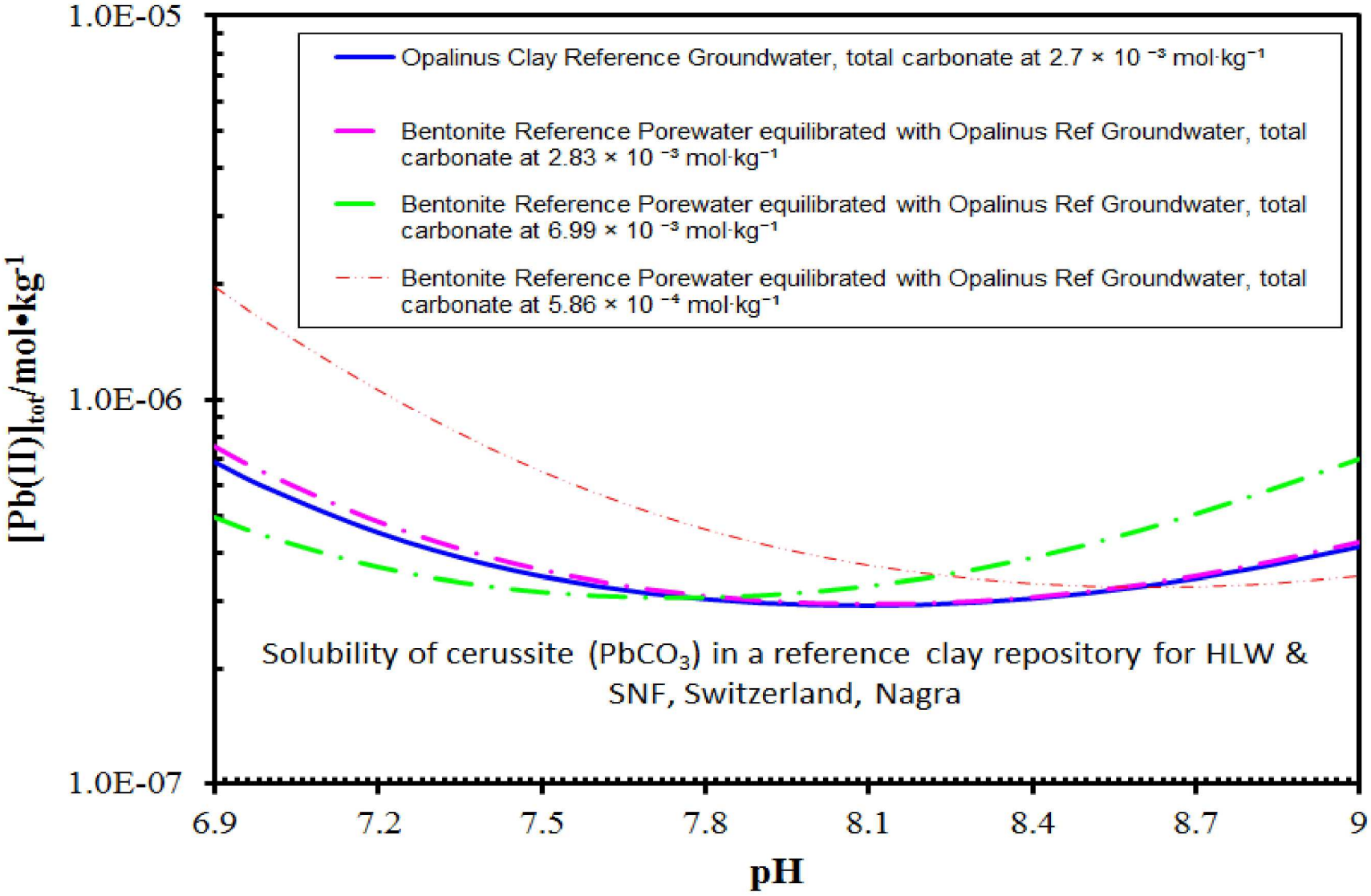
Domski, P.S. 2015. "Memo AP-173, EQ3/6 Database Update: DATA0.FM2" Memorandum to WIPP Records, October 27, 2015. Carlsbad, NM: Sandia National Laboratories. ERMS 564914.

Wolery, T.J., Xiong, Y.-L., and Long, J. (2010) Verification and Validation Plan/Validation Document for EQ3/6 Version 8.0a for Actinide Chemistry, Document Version 8.10. Carlsbad, NM: Sandia National laboratories. ERMS 550239.

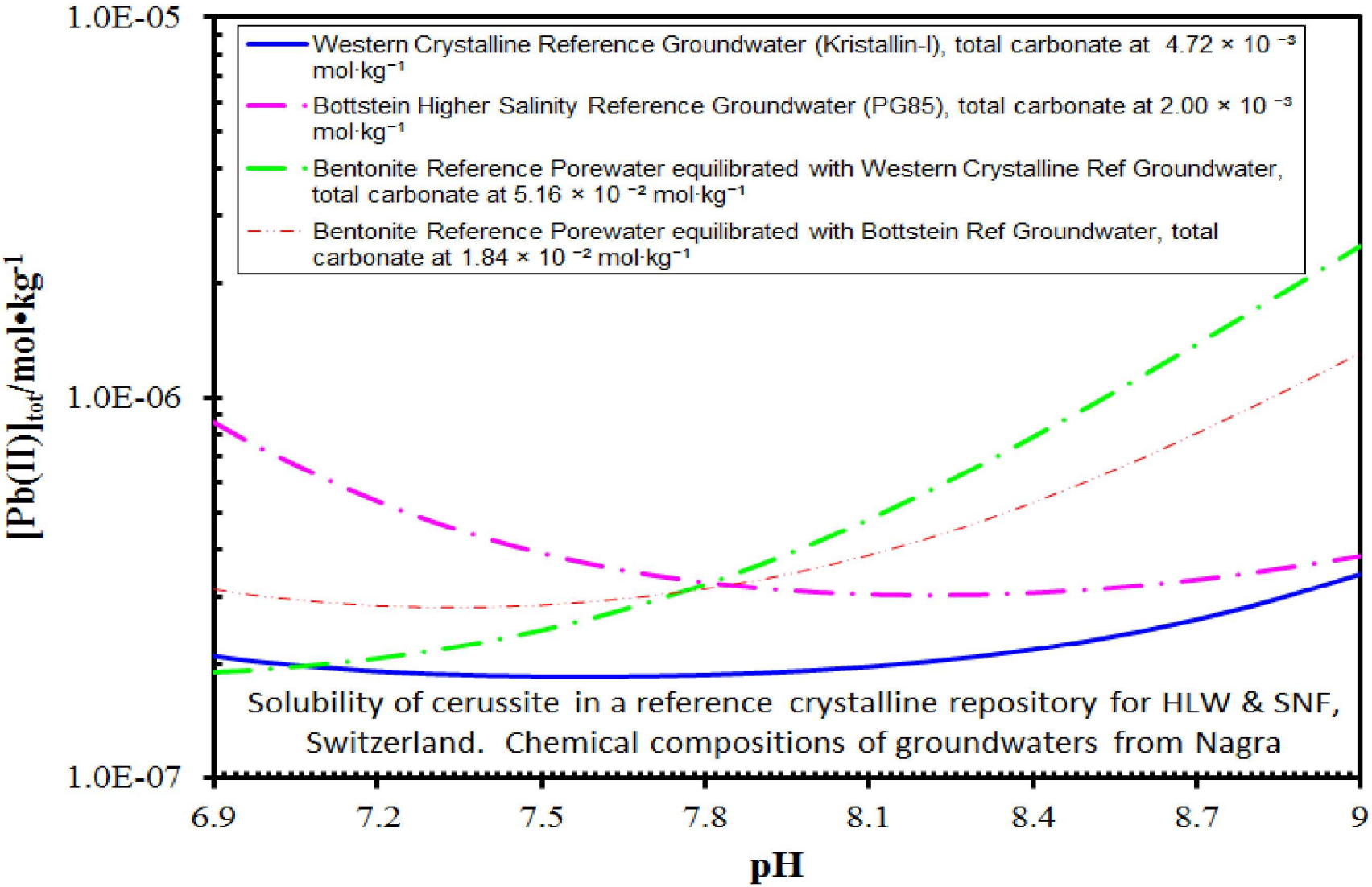
Xiong, Y.-L. (2011) WIPP Verification and Validation Plan/Validation Document for EQ3/6 Version 8.0a for Actinide Chemistry, Revision 1, Document Version 8.20. Supersedes ERMS 550239. Carlsbad, NM. Sandia National Laboratories. ERMS 555358

Xiong, Y.-L., Domski, P.S.: (2016) Updating the WIPP Thermodynamic Database, Revision 1, Supersedes ERMS 565730. Carlsbad, NM: Sandia National Laboratories. ERMS 566047

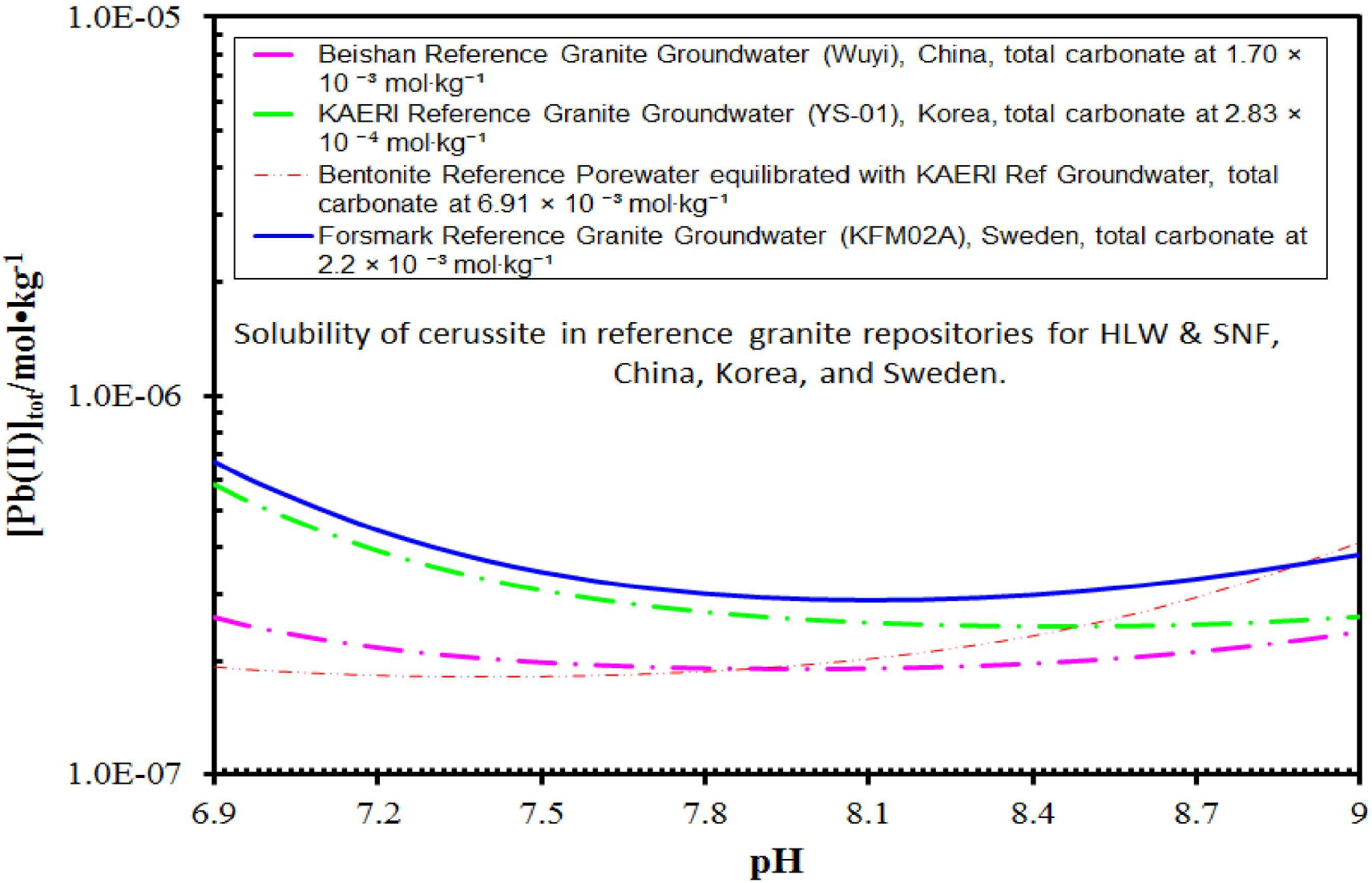
Solubility of Lead Corrosion Product—Cerussite in Reference Repositories for HWL & SNF



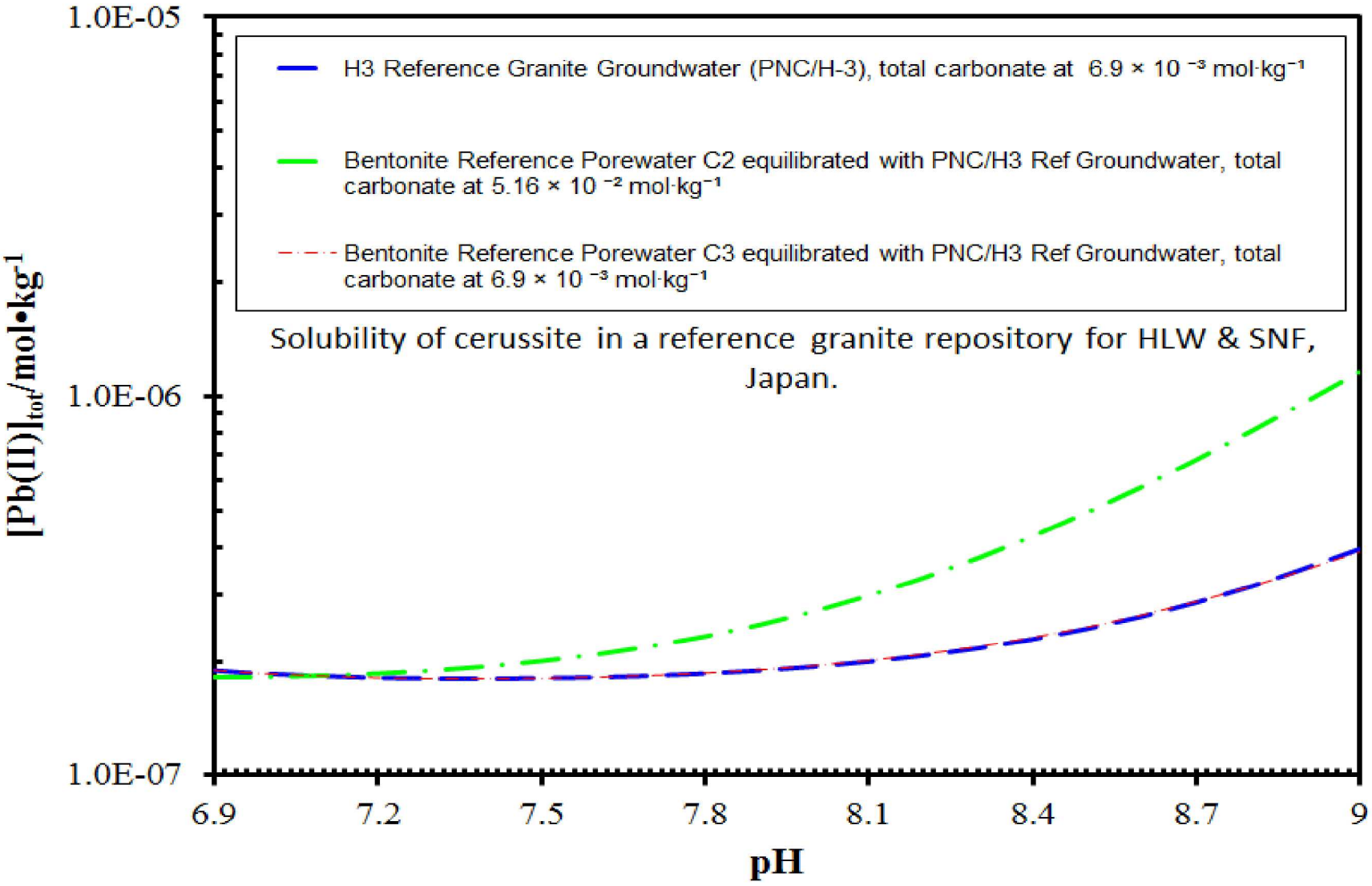
Solubility of Lead Corrosion Product—Cerussite in Reference Repositories for HWL & SNF



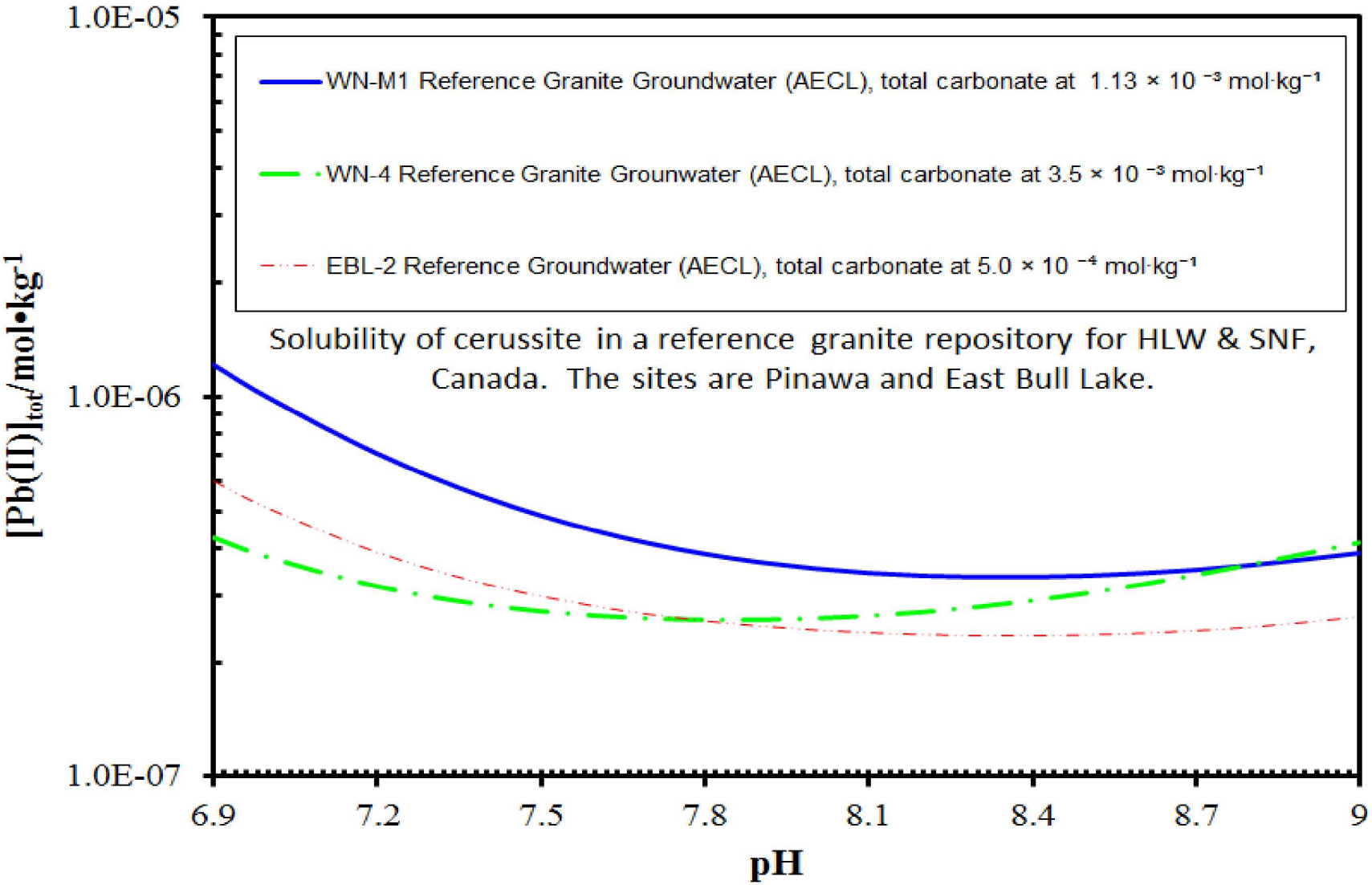
Solubility of Lead Corrosion Product—Cerussite in Reference Repositories for HWL & SNF



Solubility of Lead Corrosion Product—Cerussite in Reference Repositories for HWL & SNF



Solubility of Lead Corrosion Product—Cerussite in Reference Repositories for HWL & SNF



Summary

- Our recent studies indicated the passivation of Pb at all P_{CO_2}, including experiments without imposing P_{CO_2}.
- The corrosion product(s) in carbonate-bearing groundwaters is cerussite, $PbCO_3$, or the solid solutions between $CaCO_3$ and $PbCO_3$, i.e., tarnowitzite, $(Ca,Pb)CO_3$, in groundwaters containing calcium .
- The solubility of cerussite in various design concepts for HLW & SNF is very low, generally below 10^{-6} mol•kg^{-1}.
- In a multiple-barrier system, the further corrosion of a lead/lead-based alloy canister/overpack will be governed by diffusion of Pb2+ ion in equilibrium with cerussite into the buffer (e.g., bentonite buffer) immediately in contact with the canister, owing to the Pb chemical potential gradient.
  - At such low concentrations of lead, diffusion will be a very slow process.
- Lead/Lead-based alloy canisters/overpacks are expected to perform well in various design concepts for HLW & SNF, including the design concept for disposal in oxidized, unsaturated zones,
  - Copper, carbon steel, are certainly not suitable for such a design concept.

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