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Modeling of the Stability of Lead Solid Phases at the WIPP Conditions

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Luzheng Zhang, Leslie Kirkes, Jay J. Jang

Sandia National Laboratories, 4100 National Parks Highway, Carlsbad, NM 88220, USA

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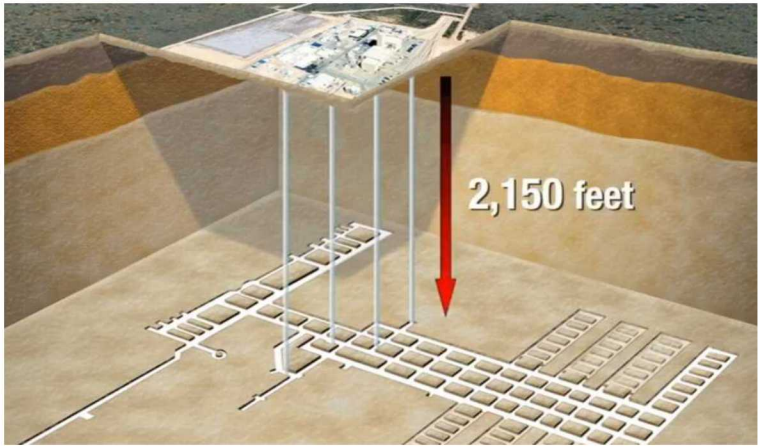
Outline

- Introduction and Motivation
- Observation of Lead Solids
- Current Modeling
- Road to a New WIPP QA Database with Lead Chemistry
  - Chemical model
  - Pitzer parameters fitted to experimental data
- Prediction of Stability of Lead Solids
- Summary

Introduction

- The Waste Isolation Pilot Plan (WIPP)
  - The Nation's only deep geological long-lived radioactive repository.
  - Disposal of defense-generated transuranic (TRU) waste from DOE sites.
  - 26 miles southeast of Carlsbad, NM, USA.
  - 2,150 feet underground in a Salado formation.
  - Geological formation: Bedded salt is free of fresh flowing water, easily mined, impermeable and geological stable.
  - Ideal for permanently isolating TRU waste from the environment.



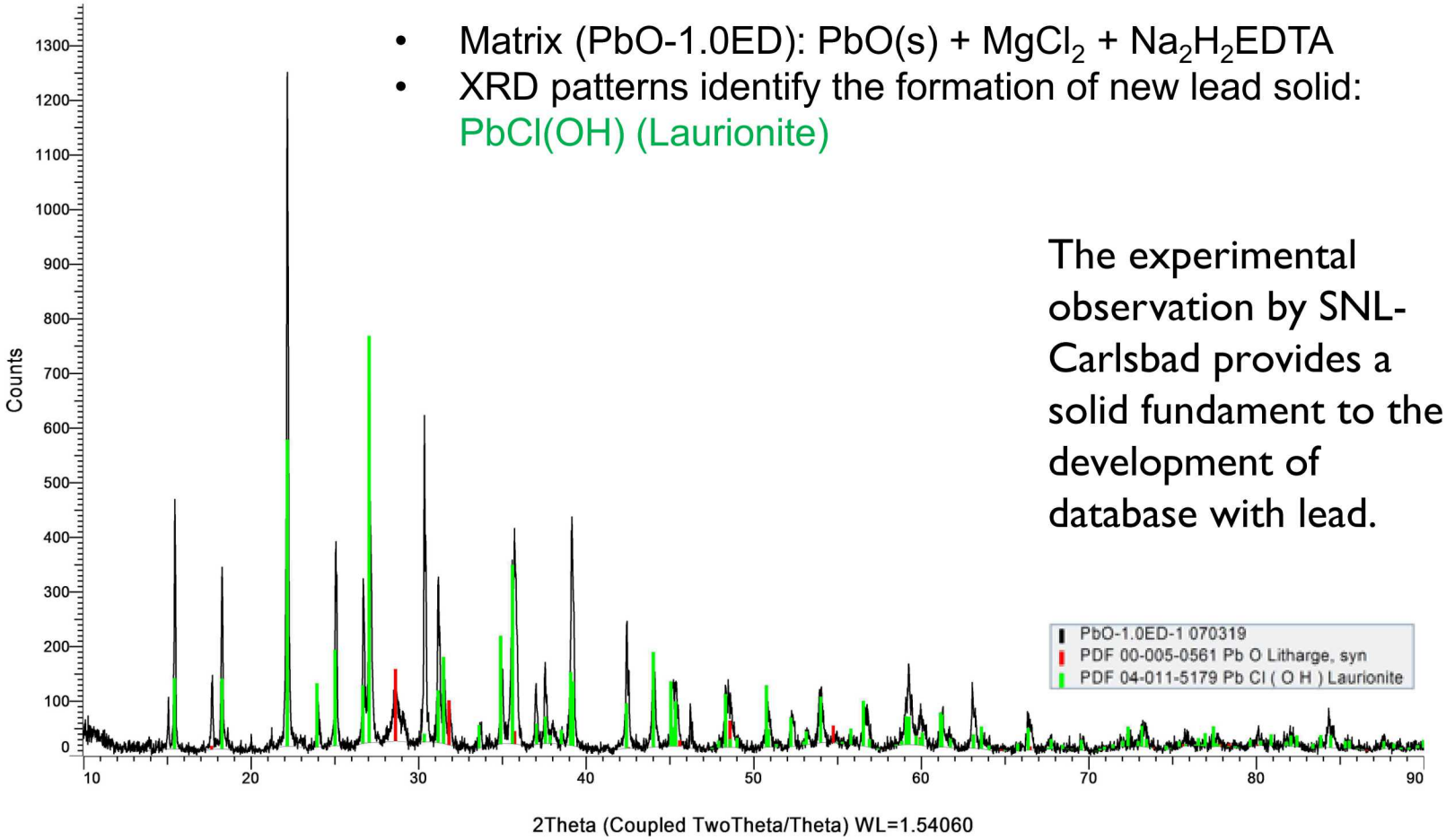
https://wipp.energy.gov/wipp-site.asp

Motivation

- Introduction of lead to the WIPP primarily through waste packaging via shielding containers and other packaging materials.
- An increasing lead volume projected in a recent WIPP inventory report.
- Complexity of lead chemistry at the WIPP conditions
- Development of an appropriate WIPP QA database with an inclusion of lead for the 2024 Compliance Recertification Application (CRA-2024).
- SNL-Carlsbad experimental program: measure lead solubility and address solid phase transformation at the WIPP conditions. All experimental data provides a solid fundament to the database.

Lead Solids from Exp. - XRD

- Matrix (PbO-1.0ED): PbO(s) + $MgCl_2$ + Na_2H_2EDTA
- XRD patterns identify the formation of new lead solid: PbCl(OH) (Laurionite)

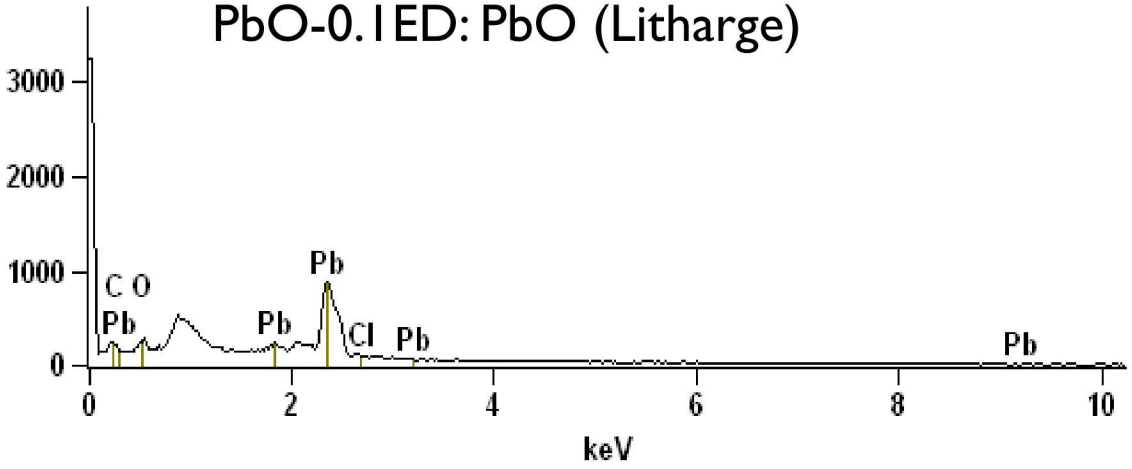


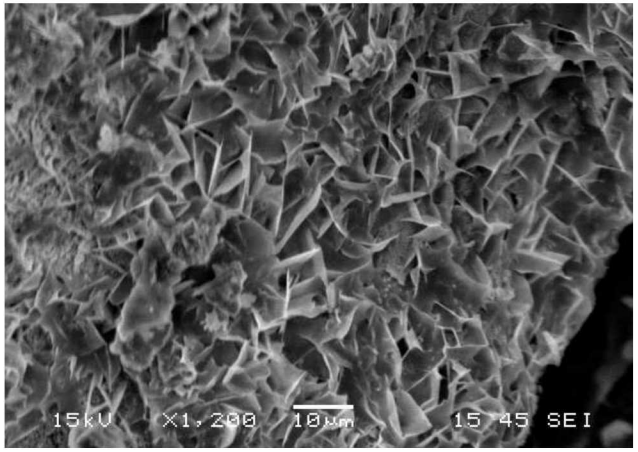
The experimental observation by SNL-Carlsbad provides a solid fundament to the development of database with lead.

Kirkes et al. "Solid transformation of litharge into laurionite and blixite", Goldschmidt 2020.

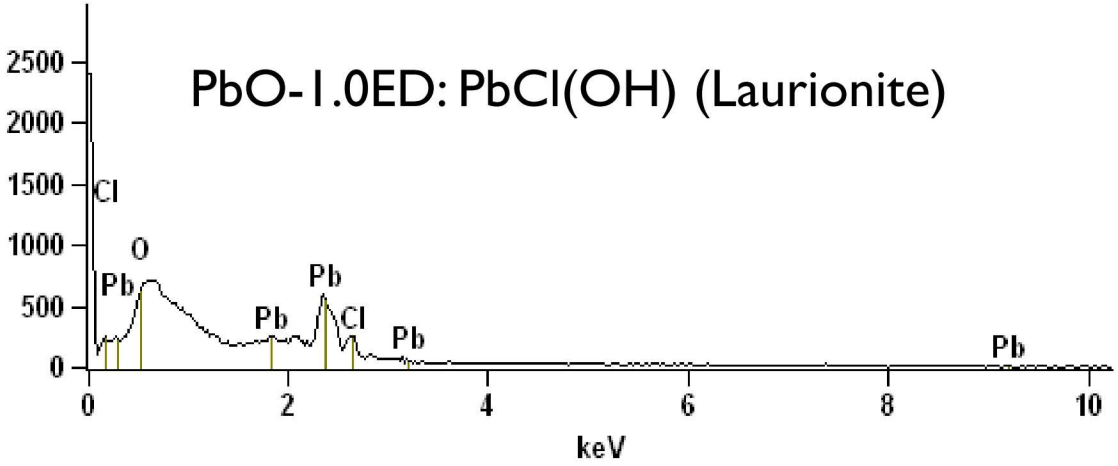
Lead Solids from Exp. - SEM/EDS

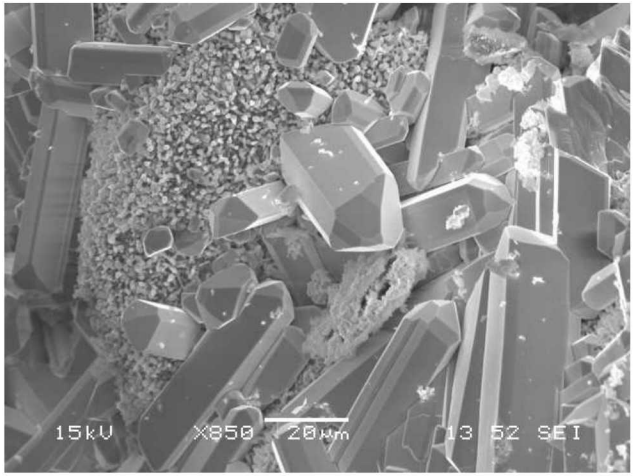
PbO-0.1ED: PbO (Litharge)





PbO-1.0ED: PbCl(OH) (Laurionite)



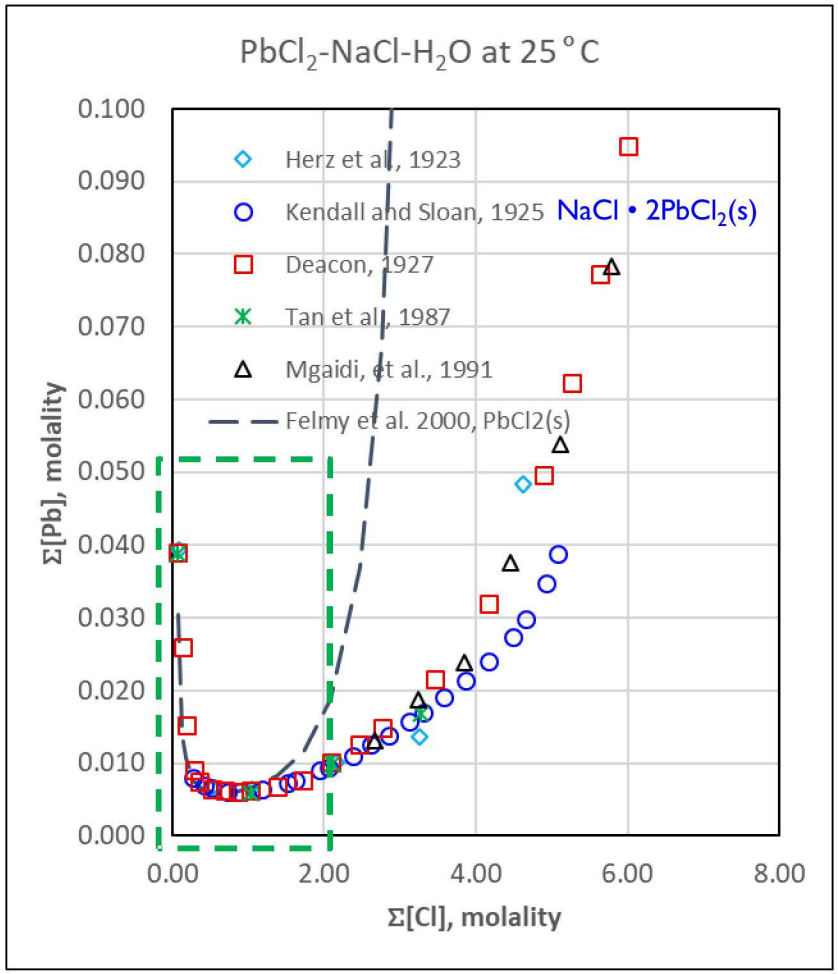


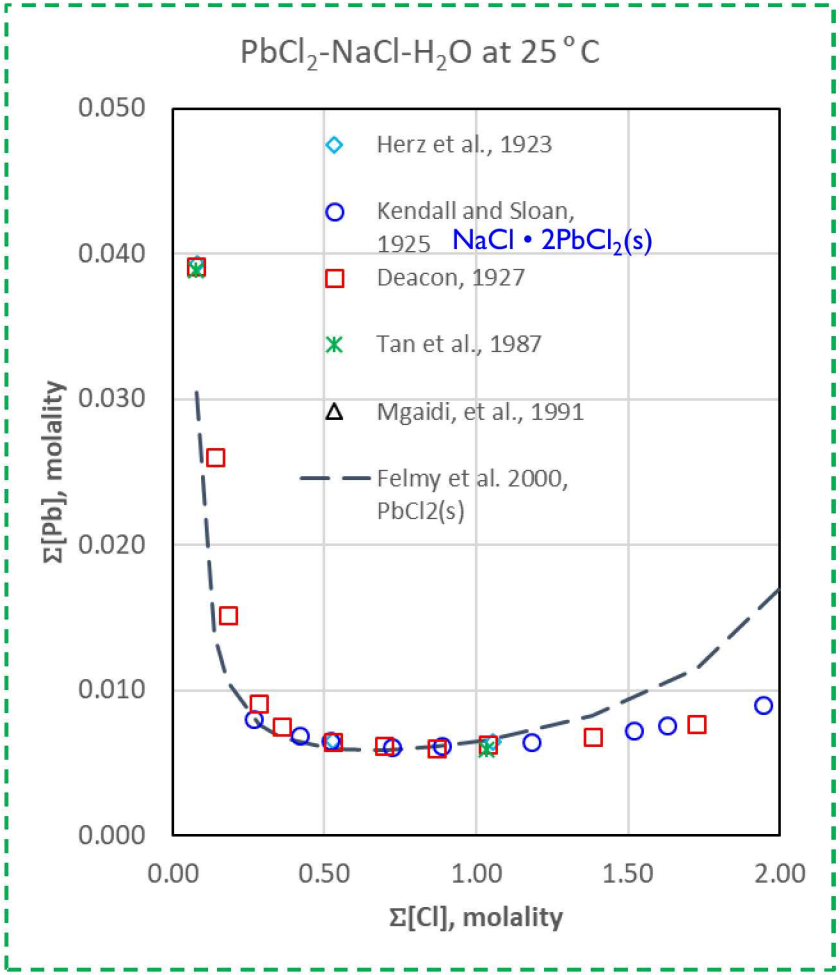
Kirkes et al. "Solid transformation of litharge into laurionite and blixite", Goldschmidt 2020.

Road to a Database with the Pitzer Model

- Examination of modeling results by preliminary Pb database
- Evaluation of available experimental measurements (solubility data, lead solids identification)
- Fitting Pitzer Interaction Parameters (PIPs) to
  - the solubility of cotunnite $PbCl_2(s)$ in simple subsystems (literature)
  - the solubility of litharge PbO(s) in EDTA systems at the WIPP relevant conditions (SNL-Carlsbad)
- Update and qualify database
- Prediction and comparison

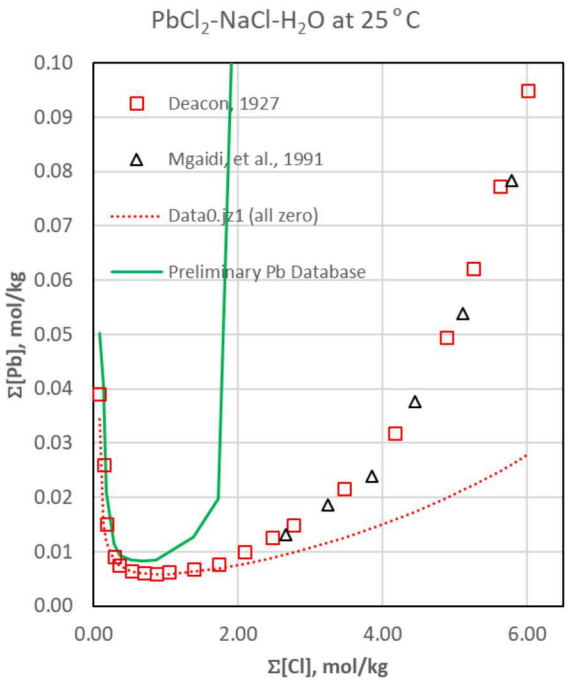
Modeling by Felmy et al. (2000)

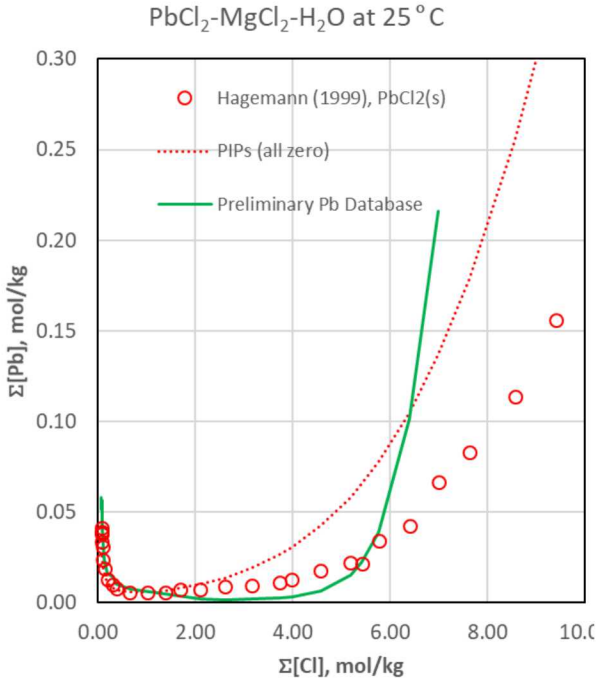


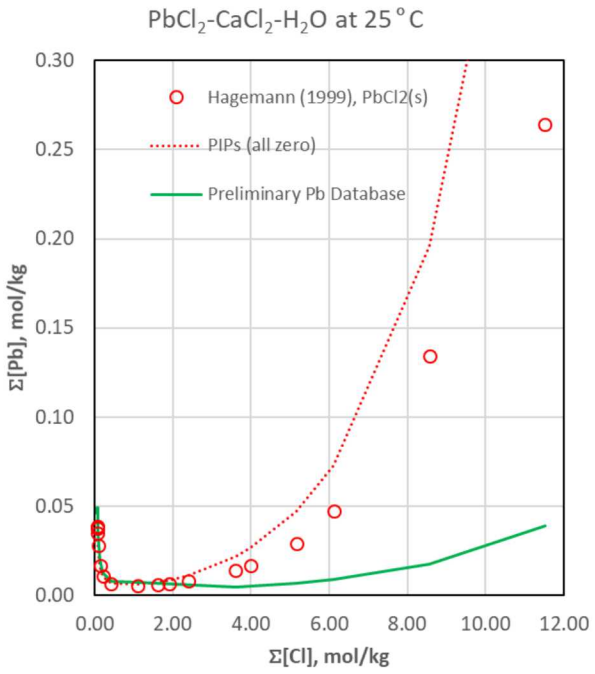


- Solid NaCl• $2PbCl_2$(s): Kendall and Sloan (1925) when [Cl-] >0.8 mol/kg
- Cotunnite $PbCl_2$(s): Others cover all [Cl-] concentrations.

Prediction by the Pitzer Model







- Modeling of Cotunnite solubility ($PbCl_2(s)$) doesn't agree with experimental measurements when [Cl^-]> 2.0 mol/kg.

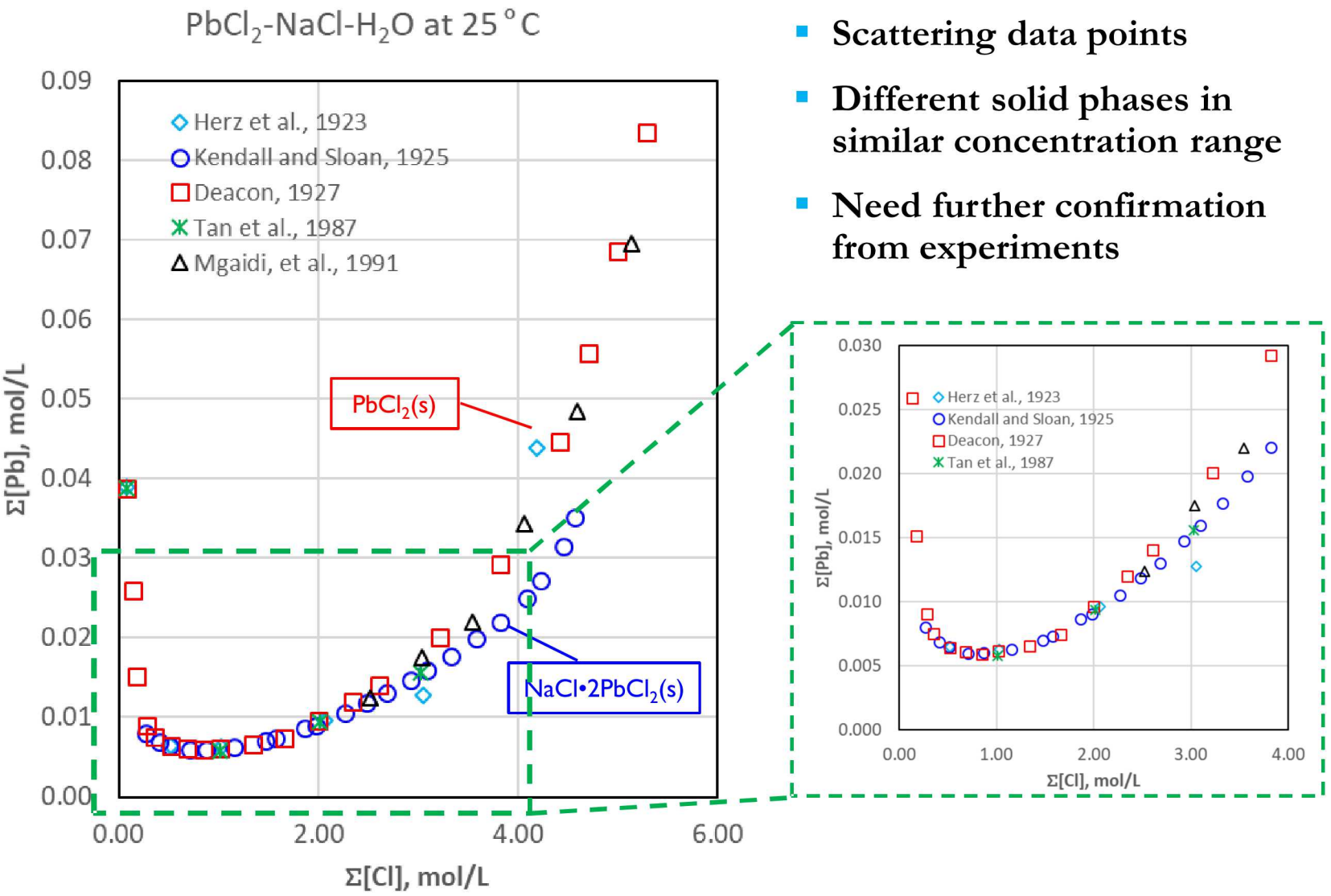
Fitting PIPs to the Solubility Data

- Chemical Model (e.g., $PbCl_2$-NaCl-H_2O)

Reaction	LogK	Source
Aqueous Dissociation		
$PbCl^+ = Pb^{2+} + Cl^-$	-1.48	Millero and Byrne (1984)
$PbCl_2(aq) = Pb^{2+} + 2Cl^-$	-2.03	
$PbCl_3^- = Pb^{2+} + 3Cl^-$	-1.86	
Solid Dissolution		
$PbCl_2(s) = Pb^{2+} + 2Cl^-$	-4.83	Edwards et al. (1992)

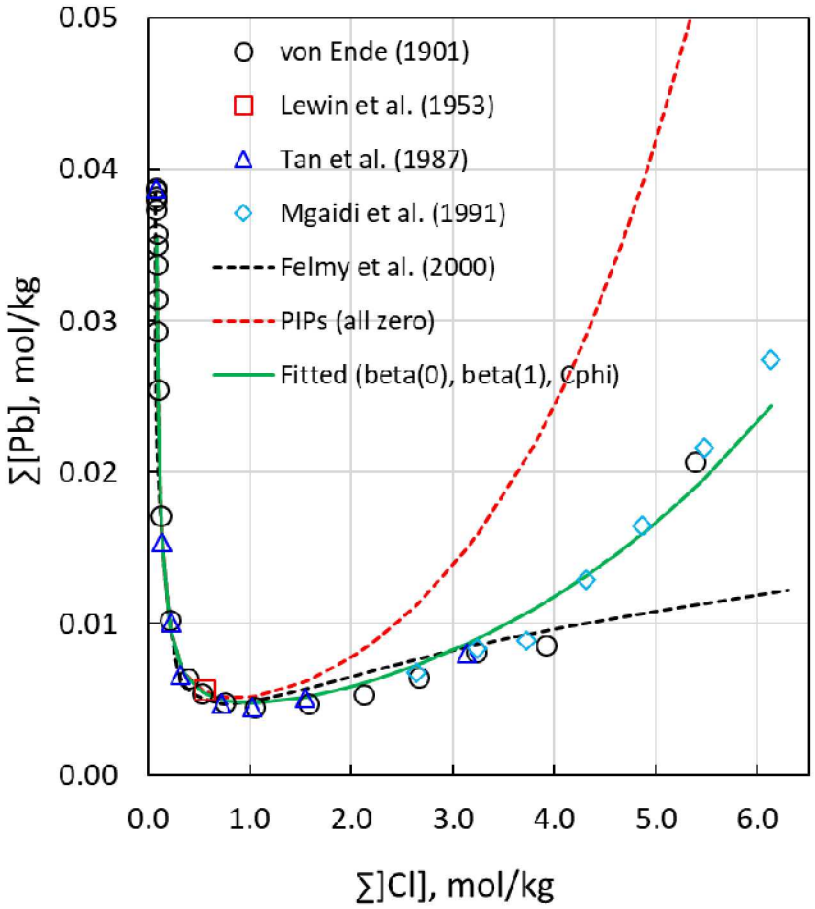
- Evaluation/selection of available solubility data and solid phase identification
- Fitting PIPs ($\beta^{(0)}$, $\beta^{(1)}$, $\beta^{(2)}$, C^{ϕ}) for pair ($Na^+ - PbCl_3^-$) within a certain total residual (TR):
  - First fitting $\beta^{(0)}$
  - Fitting $\beta^{(1)}$ and/or other PIPs ($\beta^{(2)}$, C^{ϕ}) by fixing the fitted $\beta^{(0)}$

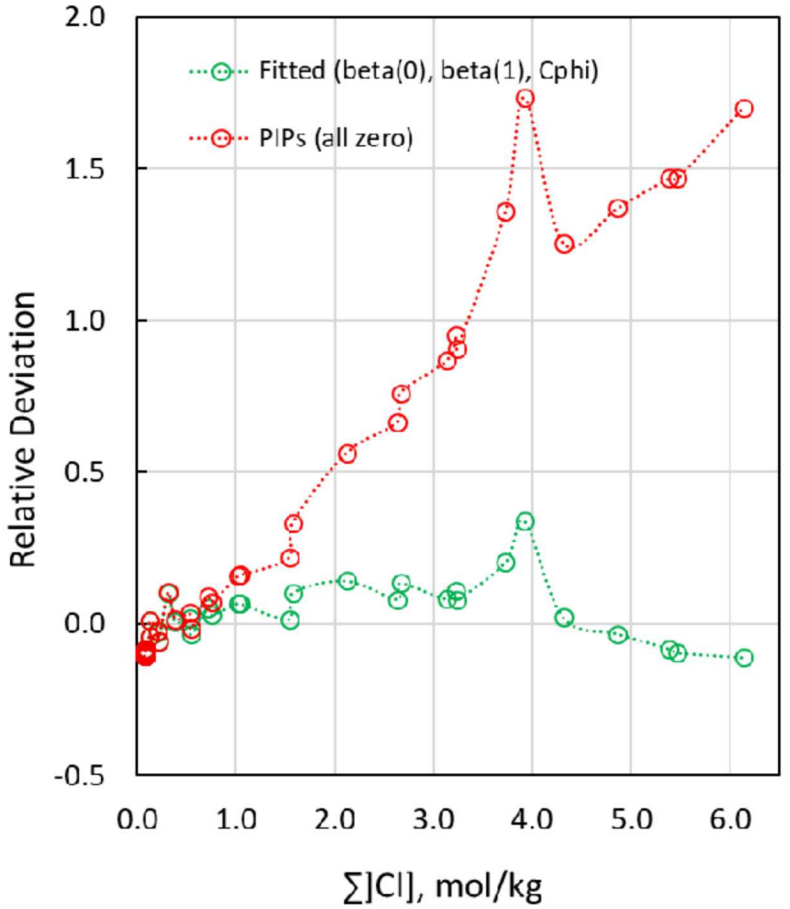
Experimental Data in Literature



- Scattering data points
- Different solid phases in similar concentration range
- Need further confirmation from experiments

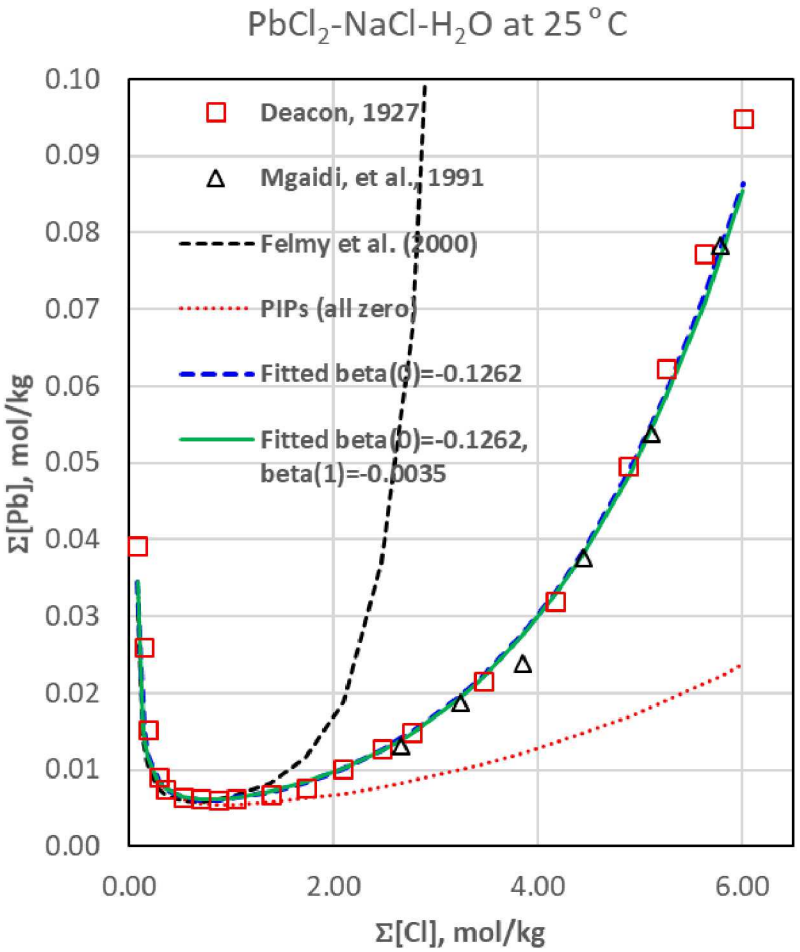
Fitting to Solubility of $PbCl_2$-HCl-H_2O

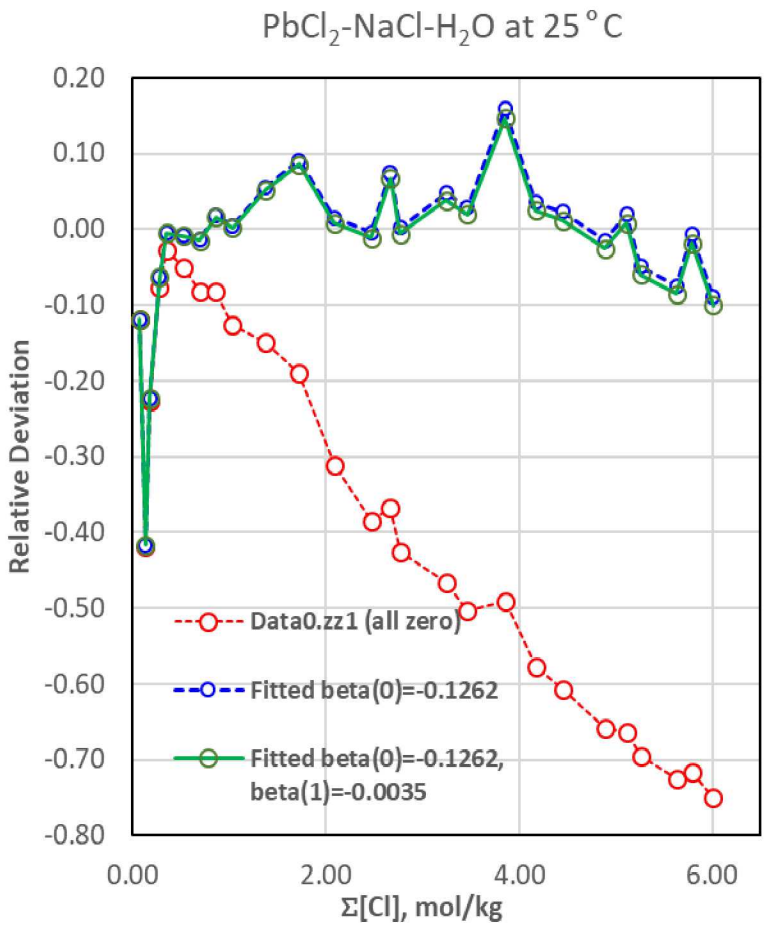




- Fitting to solubility data of cotunnite $PbCl_2$(s) only.
- Fitted PIPs ($\beta^{(0)}$=0.0108, $\beta^{(1)}$=0.0403, C^{Φ} =-0.0035) represent well all solubility measurements in a range of [Cl] concentrations up to 6.5 mol/kg.

Fitting to Solubility of $PbCl_2$-NaCl-H_2O



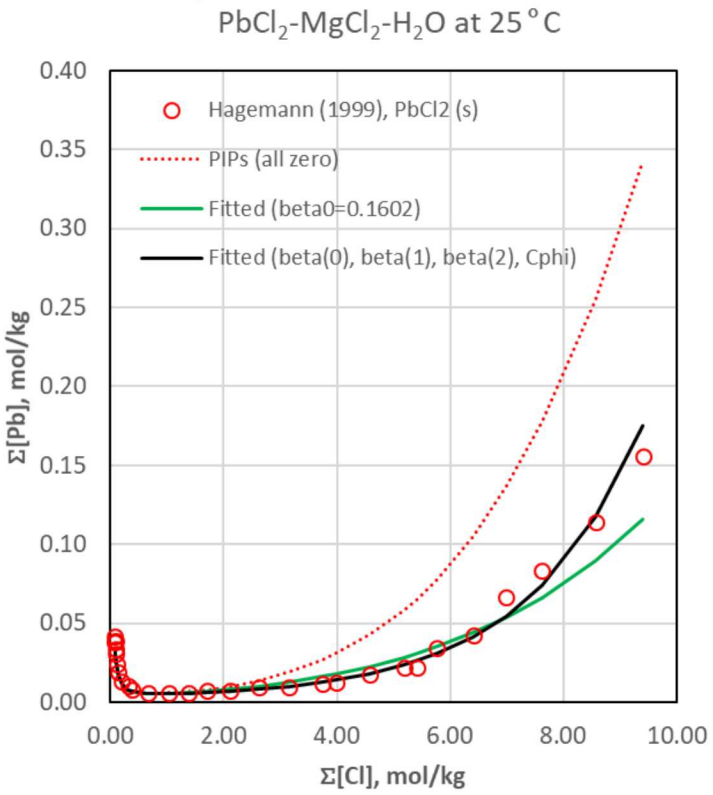


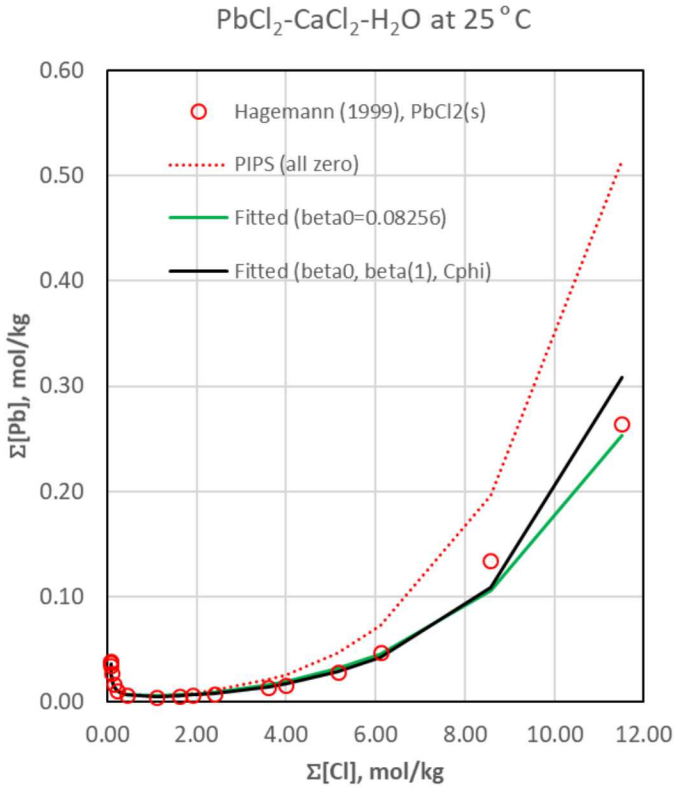
- Fitting to solubility data of cotunnite $PbCl_2$(s) only ([Cl]<6.0 mol/kg).
- Fitted to $\beta^{(0)}$ only or to both $\beta^{(0)}$ and $\beta^{(1)}$ does not show significant improvement of modeling results.

Fitted PIPs

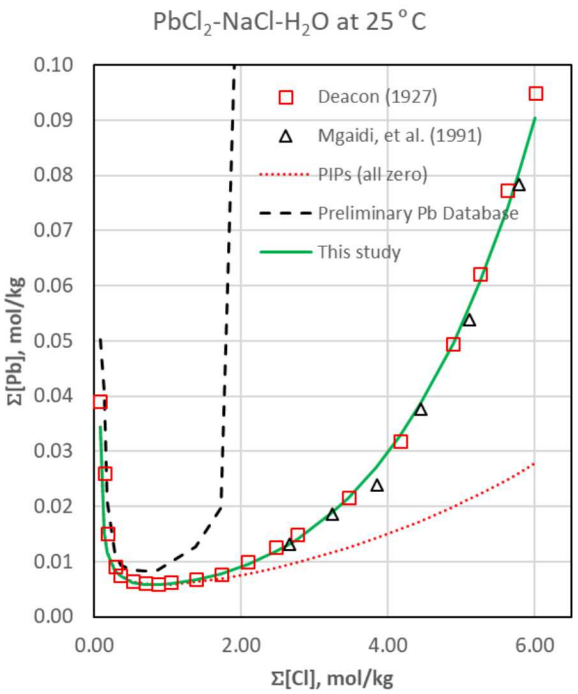
Binary Parameters

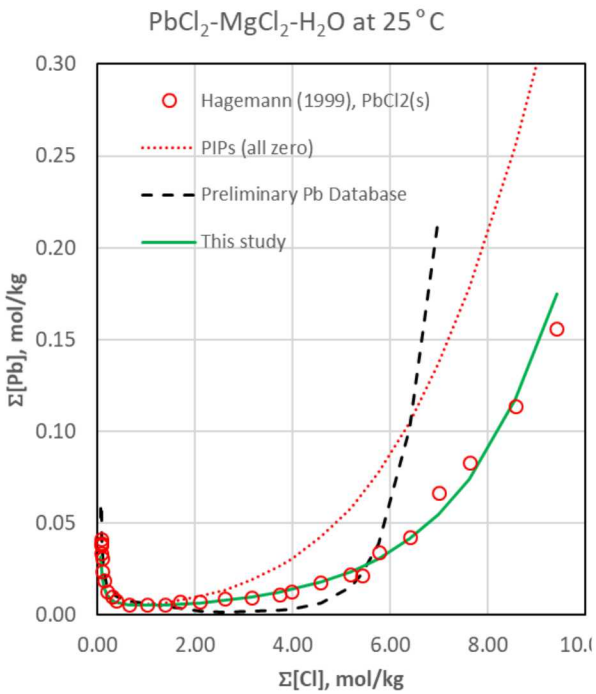
Species	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^{ϕ}
$H^+ - PbCl_3^-$	0.0108	0.0403	0.0	-0.0035
$Na^+ - PbCl_3^-$	-0.1262	-0.0035	0.0	0.0
$Mg^{2+} - PbCl_3^-$	0.2883	0.2570	-0.2699	-0.05870
$Ca^{2+} - PbCl_3^-$	0.1199	0.2468	0.0	-0.01707

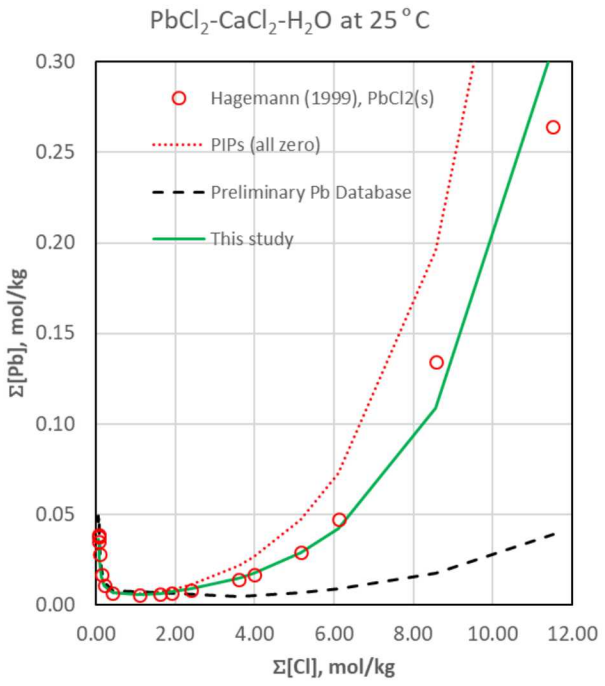




Comparison of Modeling to Experiment

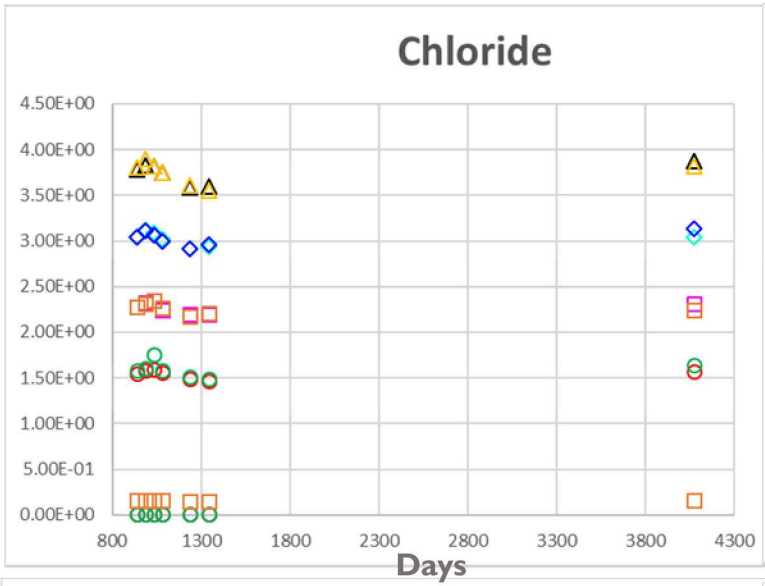


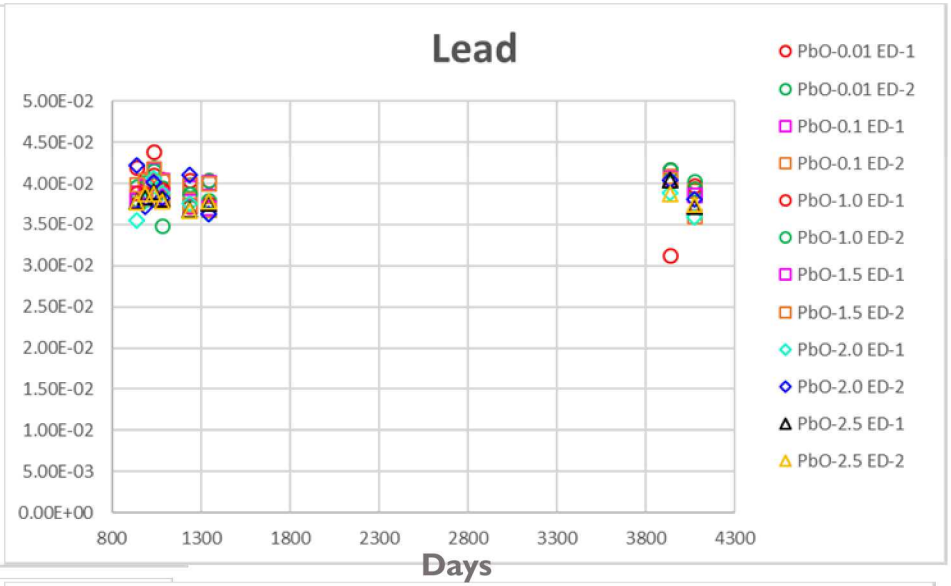


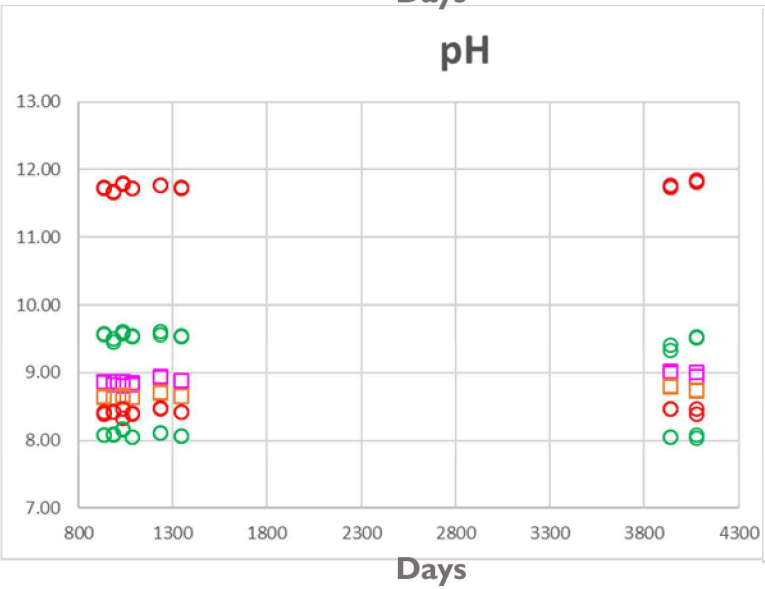


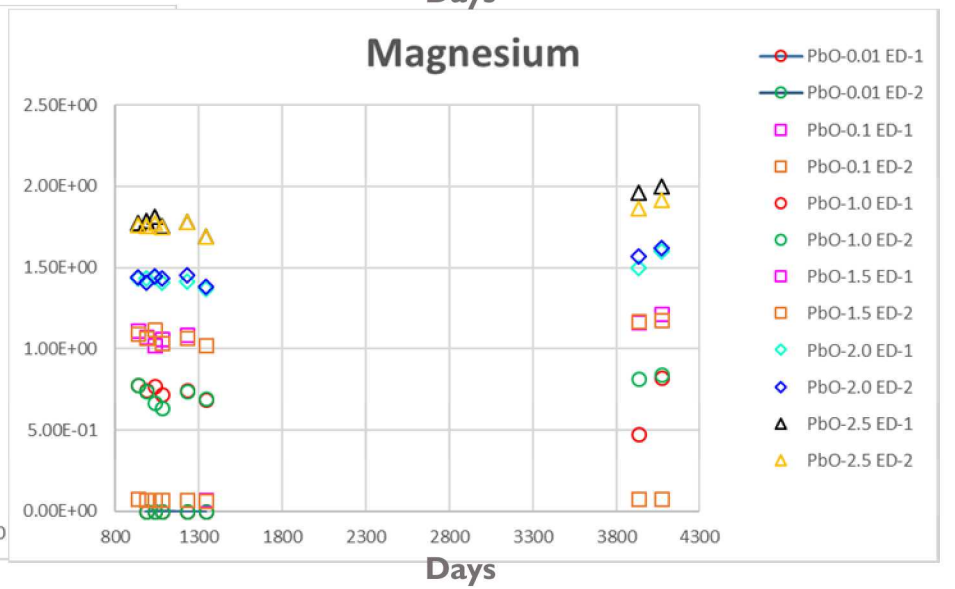
- Excellent fitting to solubility of cotunnite solubility ($PbCl_2$(s)) when [Cl^-] < 6.0 mol/kg.
- The fitted PIPs are added to the database with lead.

Lead Solubility Exp. in EDTA (4,000+ days)









* Concentrations are in mol/L

Fitted/Updated PIPs for Lead Systems

(Preliminary Data, Do Not Cite)

Reaction	LogK	Source
Aqueous Dissociation		
$PbCl^+ = Pb^{2+} + Cl^-$	-1.48	Millero and Byrne (1984)
$PbCl_2(aq) = Pb^{2+} + 2Cl^-$	-2.03	
$PbCl_3^- = Pb^{2+} + 3Cl^-$	-1.86	
$PbEDTA^{2-} = Pb^{2+} + EDTA^{4-}$	-20.0	Uhler and Helz (1984)
Solid Dissolution		
Cotunnite: $PbCl_2(s) = Pb^{2+} + 2Cl^-$	-4.83	Edwards et al. (1992)
Laurionite: $PbCl(OH)(s) + H^+ = Pb^{2+} + Cl^- + H2O$	0.62	
Litharge: $PbO(s) + 2H^+ = Pb^{2+} + H_2O$	12.6	
Blixite: $Pb_2Cl(OH)_3(s) + 3H^+ = 2Pb^{2+} + Cl^- + 3H_2O$	10.2	

Pitzer Interaction Parameters (PIPs)

Binary Parameters

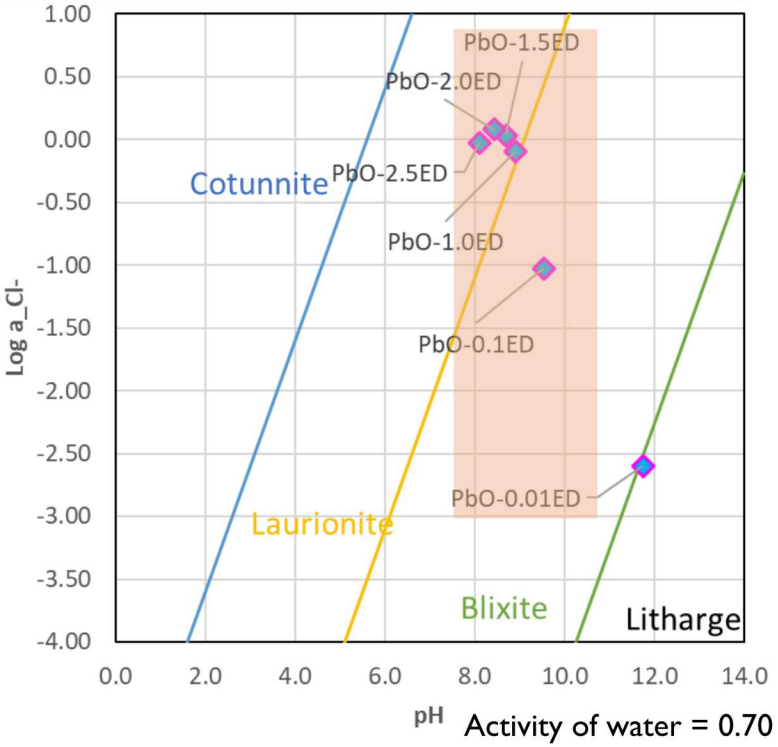
Species	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^ϕ
$H^+ - PbCl_3^-$	0.0108	0.0403	0.0	-0.0035
$Na^+ - PbCl_3^-$	-0.1262	-0.0035	0.0	0.0
$Mg^{2+} - PbCl_3^-$	0.2883	0.2570	-0.2699	-0.05870
$Ca^{2+} - PbCl_3^-$	0.1199	0.2468	0.0	-0.01707
$Na^+ - PbEDTA^{2-}$	0.6585	0.0	0.0	0.03311
$Mg^{2+} - PbEDTA^{2-}$	2.3286	0.0	0.0	-0.19848

Lead Solid Phases by Modeling and Experiment

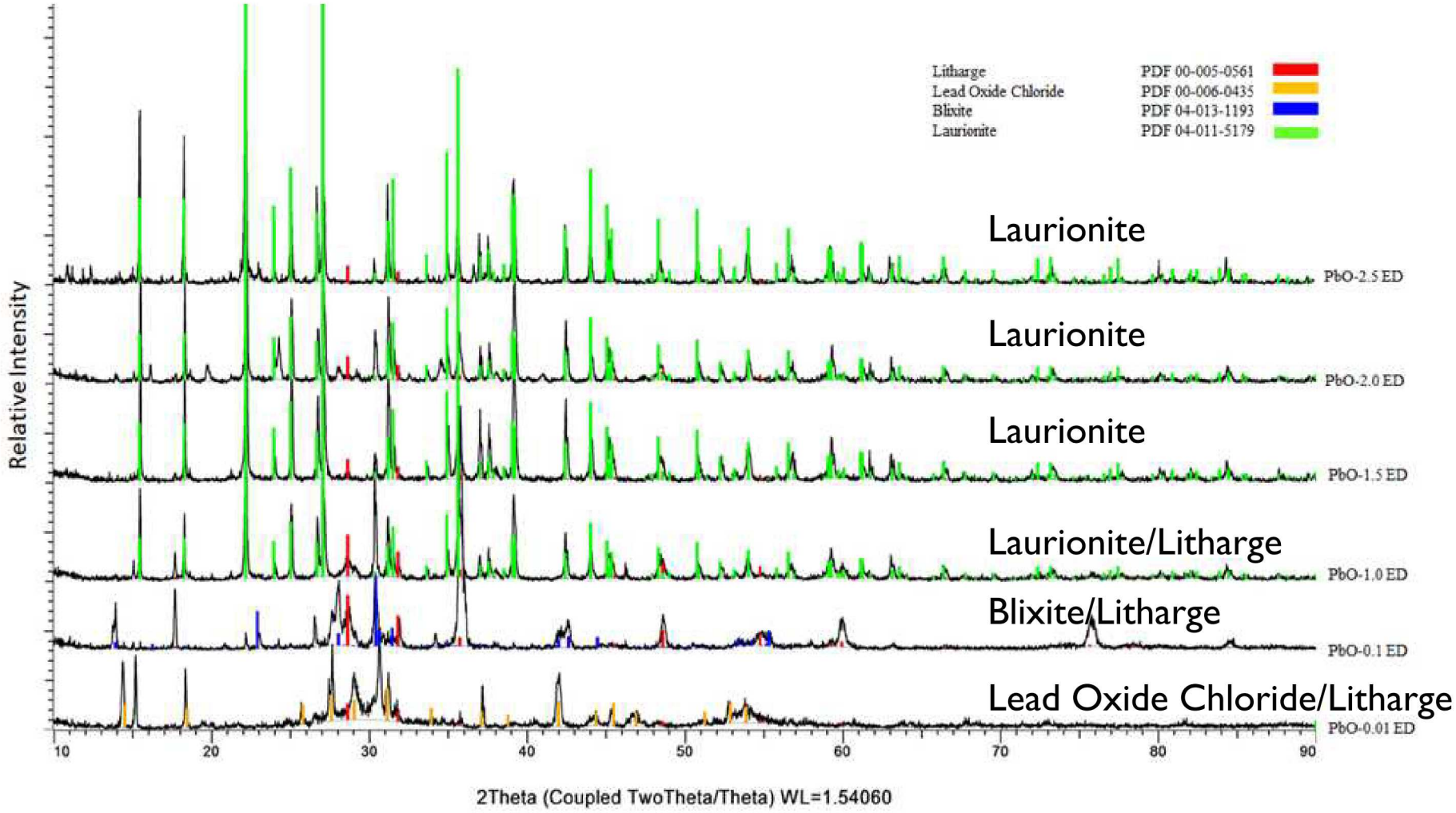
Matrix ID	pH	Pb^{2+}	Mg^{2+}	Cl^-	Log[a_{Cl-}] Modeling	Lead Solid Phase, Exp.
PbO-0.01ED	11.75	4.06E-02	4.36E-06	3.76E-03	-2.5987	Litharge
PbO-0.1 ED	9.54	4.02E-02	7.14E-02	1.54E-01	-1.0246	Blixite
PbO-1.0 ED	8.91	3.85E-02	7.18E-02	1.56E+00	-0.0987	Laurionite
PbO-1.5 ED	8.69	3.87E-02	1.10E+00	2.24E+00	0.0342	Laurionite
PbO-2.0 ED	8.43	3.85E-02	1.47E+00	2.98E+00	0.0776	Laurionite
PbO-2.5 ED	8.10	3.80E-02	1.81E+00	3.68E+00	-0.0273	Laurionite

* Concentrations are in mol/L

- Laurionite is formed in PbO-$MgCl_2$-Na_2H_2EDTA-H_2O at higher [Cl^-] concentrations.
- Shadow area covers the WIPP conditions



Lead Solids from Experiments



Laurionite (green), Blixite (blue), Litharge (red), Lead Oxide Chloride (orange)

Kirkes et al. "Solid transformation of litharge into laurionite and blixite", Goldschmidt 2020.

Summary

- Complexes of lead and chloride were added to the database with lead.
- New lead solid phases are added to the database.
- Pitzer Interaction Parameters (PIPs) were obtained by fitting experimental solubility measurements (solubility data and lead phase identifications for inorganic systems)
- The Pitzer model with the updated preliminary Pb database can predict the lead solid phase formation (laurionite) observed in experiments.
- More experimental measurements are needed for refining PIPs and log Ks for a database which addresses chemical conditions for the WIPP.

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Q&A

Thank you

E-mail: lnzhan@sandia.gov