LA-UR-24-28607

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Title:	Application of an Empirical Density Law for Aqueous Plutonium Chloride Systems and its Potential Reactivity Effects
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Intended for:	2024 MCNP User Sympsium, 2024-08-19/2024-08-22 (Los Alamos, New Mexico, United States)
Issued:	2024-08-09

Application of an Empirical Density Law for Aqueous Plutonium Chloride Systems and its Potential Reactivity Effects

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2024 MCNP User Symposium
August 19th-22nd, 2024

Presentation Agenda

- Background
- Methodology
- Calculations
- Results
- Conclusions and Future Work

Background – Work Motivation

- Limited data exists for solution modeling in neutron transport codes such as MCNP
- Currently, $PuCl_3$-HCl-H_2O is modeled as a fictitious metal-water mixture- while this is widely accepted as conservative, this introduces significant bias in material modeling
  - Current modeling strictly considers full-density Pu Metal and pure water; no acid or salt components are accounted for
  - Thus, no credit is taken for the neutron capture of chlorine in the system
  - More accurate modeling would benefit operations by improving NCS limits
- Tools have been developed using various density modeling methods for aqueous plutonium nitrate ($Pu(NO_3)_4$-HNO_3-H_2O) systems for use with both SCALE and MCNP

Background – Preceding work

- Density measurements of $PuCl_x$-HCl-H_2O at varying Pu and acid contents, as well as various temperatures, have been taken by the actinide analytical chemistry group at LANL
  - Previously, no density data for such a solution system was available
  - Note that while density measurements contained Pu in multiple valence states, study showed the valence state had a negligible effect on density. Thus, the tool assumes all Pu in the Pu(III) state to conservatively model the chlorine present
- These density measurements have enabled the development of a density law, implemented via Python herein

- Benchmarks with sensitivity to the same nuclear data range for the application scenario also were not represented in the ICSBEP Handbook, which resulted in the design, performance, and newly accepted ICSBEP benchmark entitled the “Chlorine Worth Study”
  - This work enables the validation of chlorine for relevant NCS applications

Methodology – Considered Density Methods

- Multiple density prediction methods were considered to develop the density law

1) the Isopiestic method, and
   - Predicts solution density of a number of solutions using binary solution data for constituent solutions of equal pressure/water activity
   - Binary data may be regressed for a ternary solution for which a) binary data is not readily available, as in this case due to the nature of $PuCl_x$ in H2O, and b) solutions systems with different water activities
2) the Pitzer method,
   - Predicts solution density and solution interaction via ion interaction parameters; semi-empirical
   - Requires Pitzer parameters/ion interaction parameters to be determined for a system, typically through binary data
3) Empirical methods.
   - Fit data over a specified range for which experimental data is available. Note that errors/biases in data collection would be propagated here, although prediction will highly accurate to experimental data

Methodology – Method selection

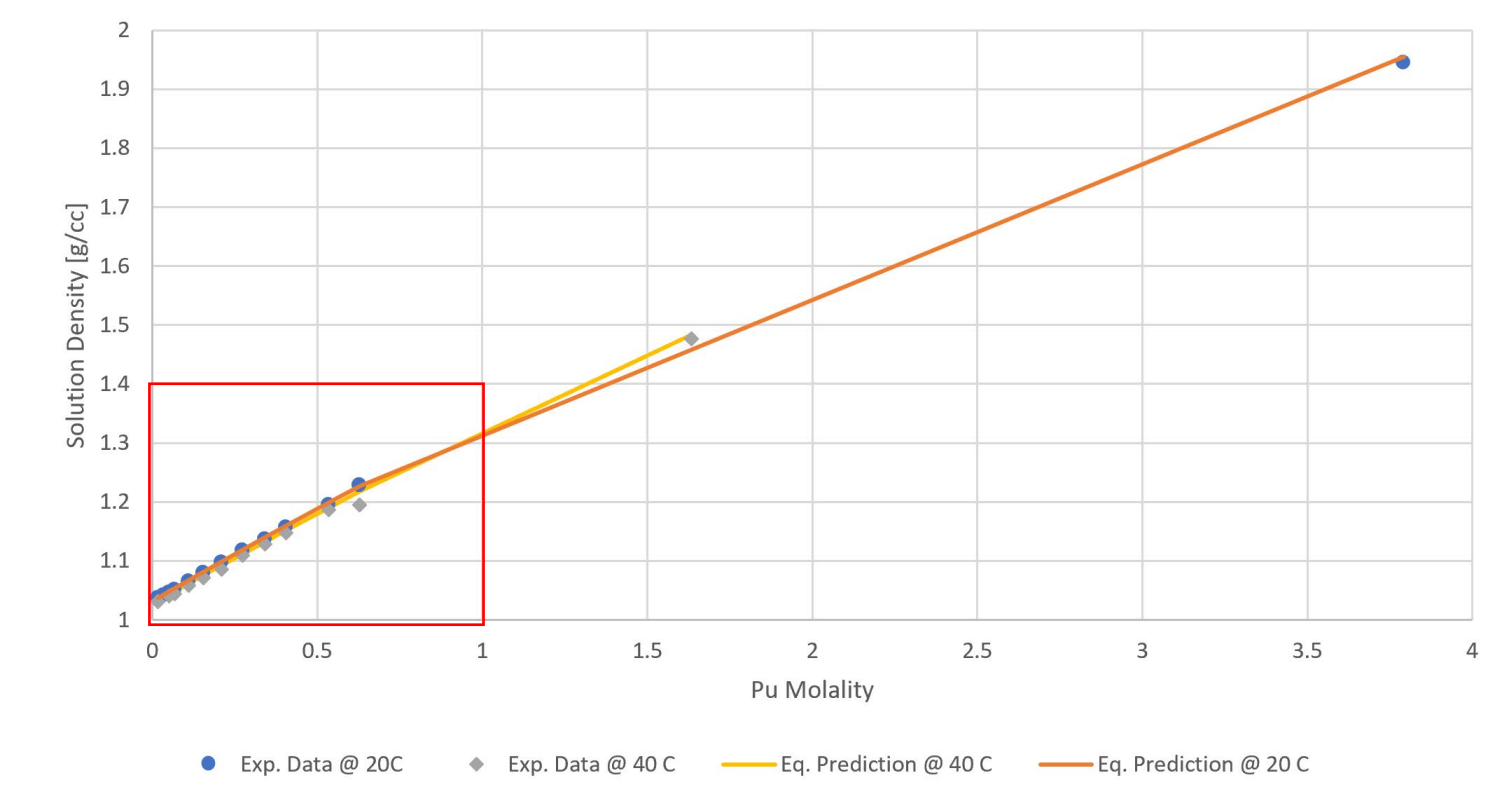
- Pitzer method has been used for similar tools for aqueous plutonium nitrate solutions for use with SCALE and MCNP
  - MCNP tool also has an empirical law
  - Isopiestic and “isotemp” law have also been proven successful in modeling these solutions
  - Pitzer parameter and binary data derivation entail significant time and effort
- Ultimately, an empirical density law approach was chosen for this system
  - Available data covers a large range with a low error, and covers most all NCS areas if interest
  - Possibility to expand tool to also incorporate Pitzer Method in the future
- Empirical method is a best fit of the equation from Weber and Hopper:

$$d_{soln} = d_0 + Am_{Pu} + Bm_H + CT + Dm_{Pu}m_H + Em_{Pu}T + Fm_{Pu}^2 + Gm_H^2$$

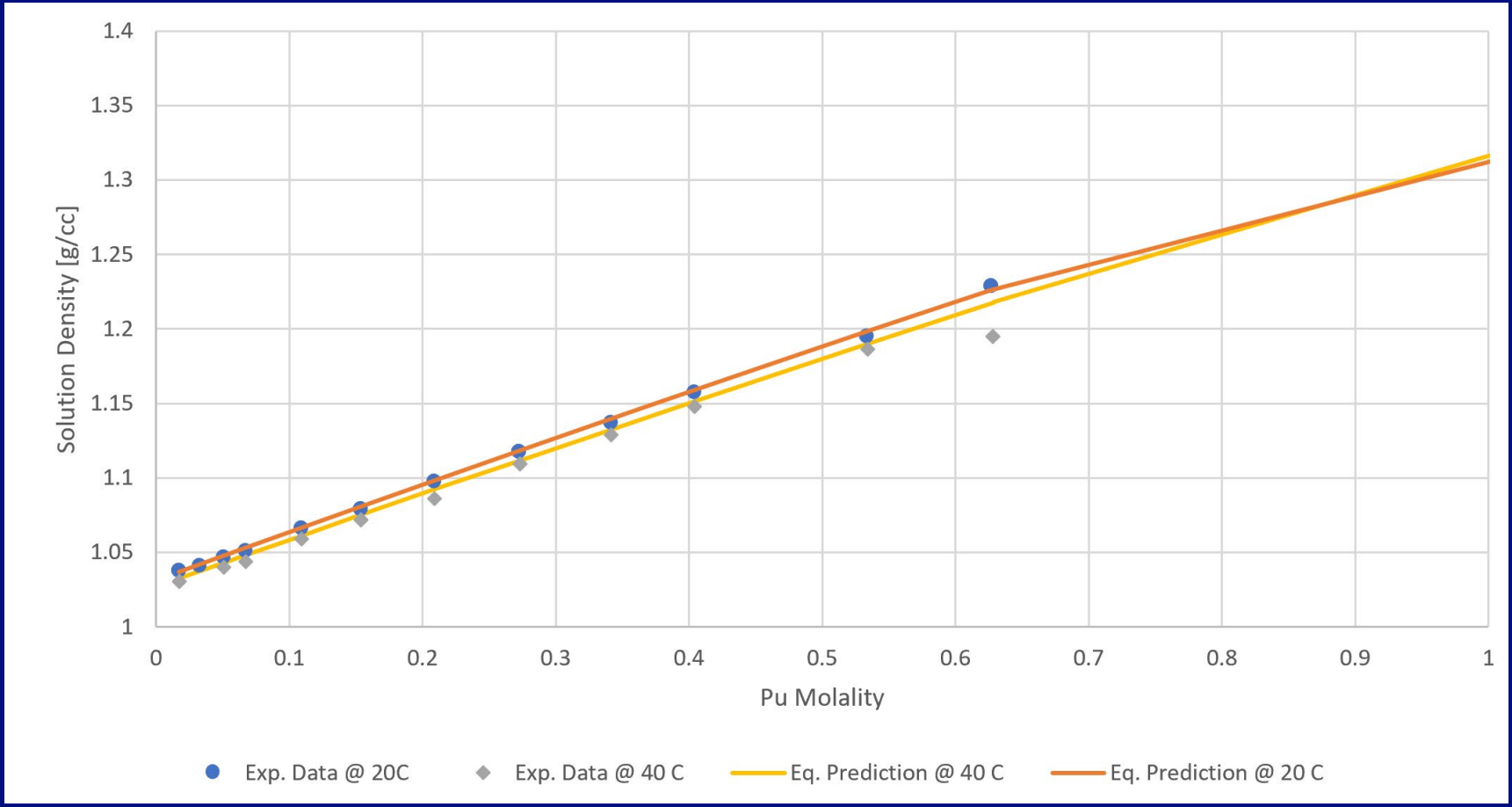
Wherein *m* is molality, d_0 is the density of pure water, *T* is in degrees Celsius, and the optimal coefficients (A-G) are determined by a best curve fit of the experimental data to the equation

Calculations – Density

- Based upon experimental data, the coefficients were solved, yielding the equation seen below plotted alongside some sample experimental data points.
  - Data is all at ~2 mol HCl/ kg H_2O in below figure



Calculations – Density



Calculations – Density

- Equation input in in molality, which Pu and acid content of a system are typically known in molarity and/or concentration. Therefore, conversion between these values must be made to improve usability of tool
  - Calculating molality from molarity/concentration requires knowledge of the density
  - The tool must iteratively solve for density in order to make this conversion- assuming 1kg of H_2O

$$m_i = \frac{1000 * M_i}{(1000 * d_{soln,bulk)} + (M_i * gmm_i) + (M_j * gmm_j) + \cdots . + (M_n * gmm_n)}$$

$$\frac{M_{Pu}}{M_H} = \frac{m_{Pu}}{m_H}$$

Where m=molality [mol/kg water], M=molarity [mol/L], dsoln,bulk=final density of solution [g/cc], and gmm is the gram molar mass [g/mol]

Calculations – Material Card

- The tool also has an option to read in an MCNP input file, and edit the file for density and a material definition card
- This material card is solved by determining the weight fraction of each isotope within the solution as follows:

$$WF_i = wf_i \frac{M_i gmm_i}{1000 * d_{soln,bulk}}$$

Where *i* is the isotope of interest, WF_i= the weight fraction of the isotope in the total solution, wf_i= the isotopic weight fraction in the total element, M_i=molarity of the element [mol/L], gmm_i= the gram molar mass of i [g/mol], *and* $d_{soln,bulk}$=the bulk density of the solution [g/cc]

- In generating a material card, the user may also enter a weight percent content of Pu-240 to account for solution impurities

Python Tool

- Currently, 2 codes with differing user interfaces and 18 functions exist in the Python tool named “PuCS”, for Plutonium (**Pu**) **C**hloride **S**olution Tool
- For both codes and all functions, the user must enter the Pu content, acid content, and temperature of the solution
  - Pu and Acid content may be entered in and combination of molality, molarity, and concentration
  - Temperature is entered in Celsius
- If the user wishes to edit an MCNP file, then Pu-240 content, input file name, and desired name for the edited input file must be entered as well

Python Tool – Code using Density Functions

```
import density_functions_chloride as PuCS
import numpy as np

conc_Pu=[10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 125, 150, 175, 200, 250,

molar_HCl=[1, 1, 1, 1, 1, 1.5, 1.5, 1.5, 1.5, 1.5, 2, 2, 2, 2, 2, 2.5, 2.5,

T=25

ind=0
Results=np.zeros([len(conc_Pu),4])

for i in range(0,len(conc_Pu)):

            Results[(ind),0]=T
            Results[(ind),1]=conc_Pu[i]
            Results[(ind),2]=molar_HCl[i]
            Results[(ind),3]=PuCS.density7(conc_Pu[i], molar_HCl[i], T)

            ind=ind+1
```

Python Tool – Code using Solution Editor Functions

```
import density_functions_chlorine as PuCS
import numpy as np

conc_Pu=[10, 20, 30, 40, 50, 60, 70, 80, 90, 100]

molar_HCl=2

T=25

inputfile="input.txt"
for i in range(0, len(conc_Pu)):
    newfile="newfile_"+str(conc_Pu[i])+".txt"
    PuCS.SolnEditor7(conc_Pu[i], molar_HCl, T, 0, inputfile, newfile)
```

Python Tool – Interactive Code

```
Plutonium Content: Enter 1 to input molality [mol/kg H2O], 2 to input molarity [mol/L], or 3 to input
concentration [g/L]:
3

HCl Content: Enter 1 to input molality [mol/kg H2O], 2 to input molarity [mol/L], or 3 to input
concentration [g HCl/L]:
2

Enter Pu Concentration:
30

Enter HCl Molarity:
2

Enter Temperature in Celcius:
25

 Your solution density is 1.07273 g/cc.
```

```
Edit MCNP File for density value and Material Card? Y/N
Y

Enter desired wt% of Pu-240 (0-100):
0

Enter MCNP File Name:
input.txt

Enter desired name of new MCNP file:
new.txt
New input file made successfully.  Thank you for using PuCS
```

Interface in MCNP6 input file

- User Input:

```
c        CELL CARDS
10       1  @   -3     u=1                imp:n=1
```

```
c Material cards
c
m1
mt1 lwtr.20t
```

After PuCS Editor:

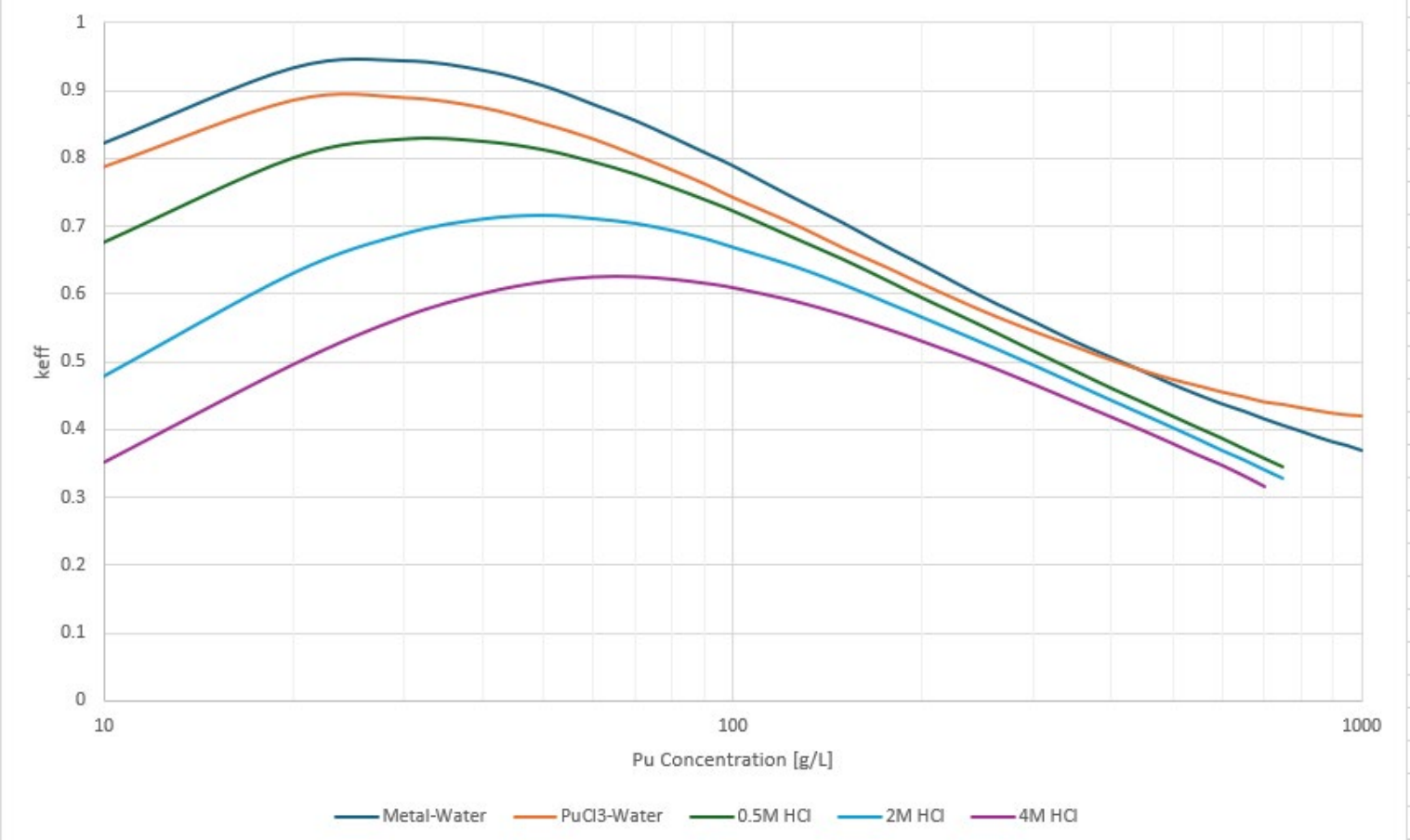
```
c        CELL CARDS
10 1 -1.07273 -3 u=1 imp:n=1
```

```
c Material cards
c
m1     1001   -0.10165861731083167
       8016   -0.7917799946339521
      17035   -0.05872017797702245
      17037   -0.01986094665305611 4
      94239   -0.027980263425137628
mt1 lwtr.20t
```

- Note that the any S(α, β) libraries and the nuclear data library must be specified by the user

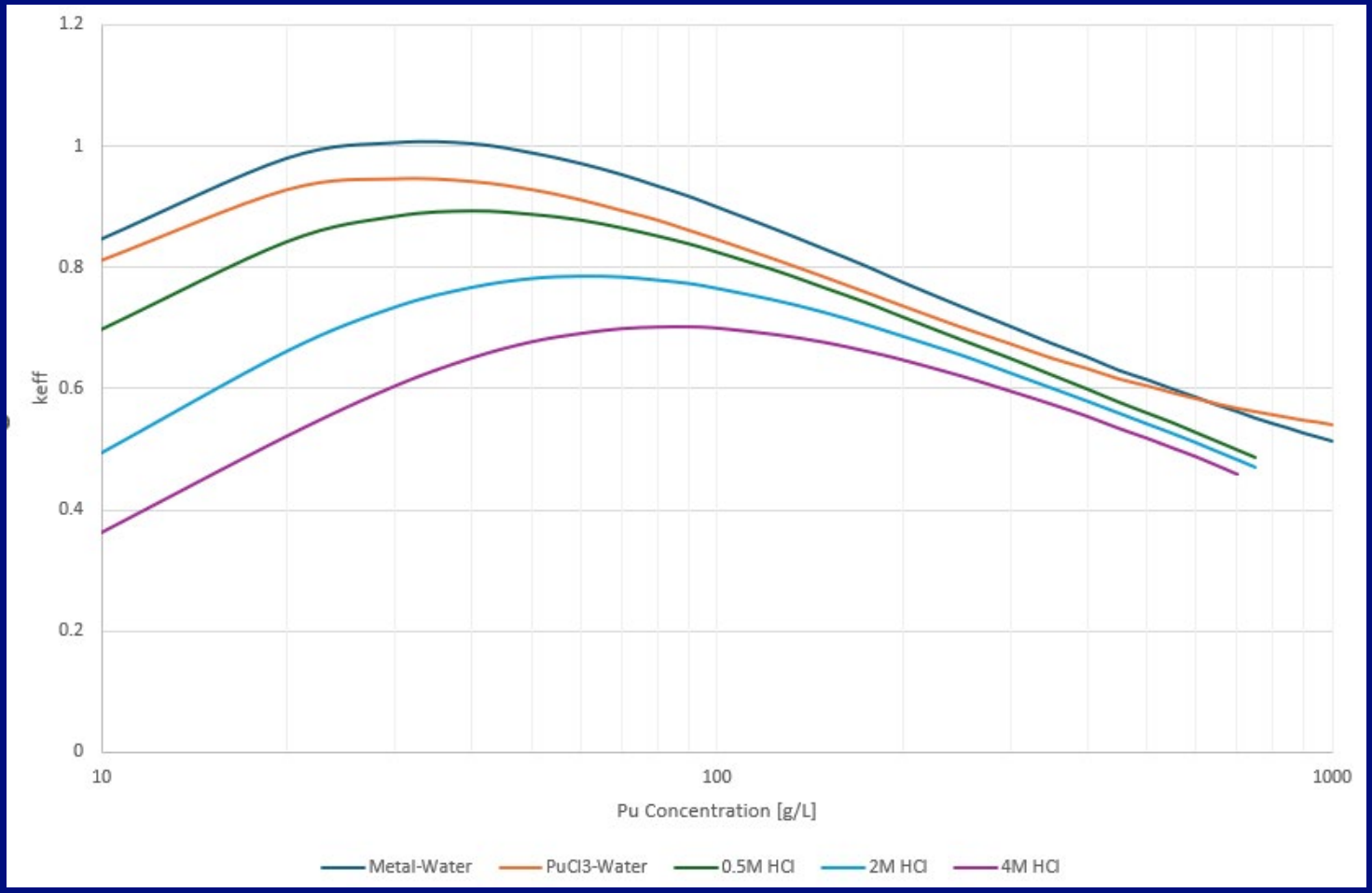
Effects on Reactivity – MCNP Comparison Study Results

- Comparison of composition modeling [520g Pu in a sphere, varying concentrations, with 1-in 4π water reflection]



Effects on Reactivity – MCNP Comparison Study Results

- Same model as previous slide, but with full (12-in) water reflection



Effects on Reactivity

1-in Reflection:

Data Set	Maximum Reactivity	Difference from Current Modeling
Metal-Water	0.944	0
PuCl3-Water	0.889	-5.8%
Density Law at 0.5M HCl	0.829	-12.1%
Density Law at 2M HCl	0.716	-24.1%
Density Law at 4M HCl	0.626	-33.7%

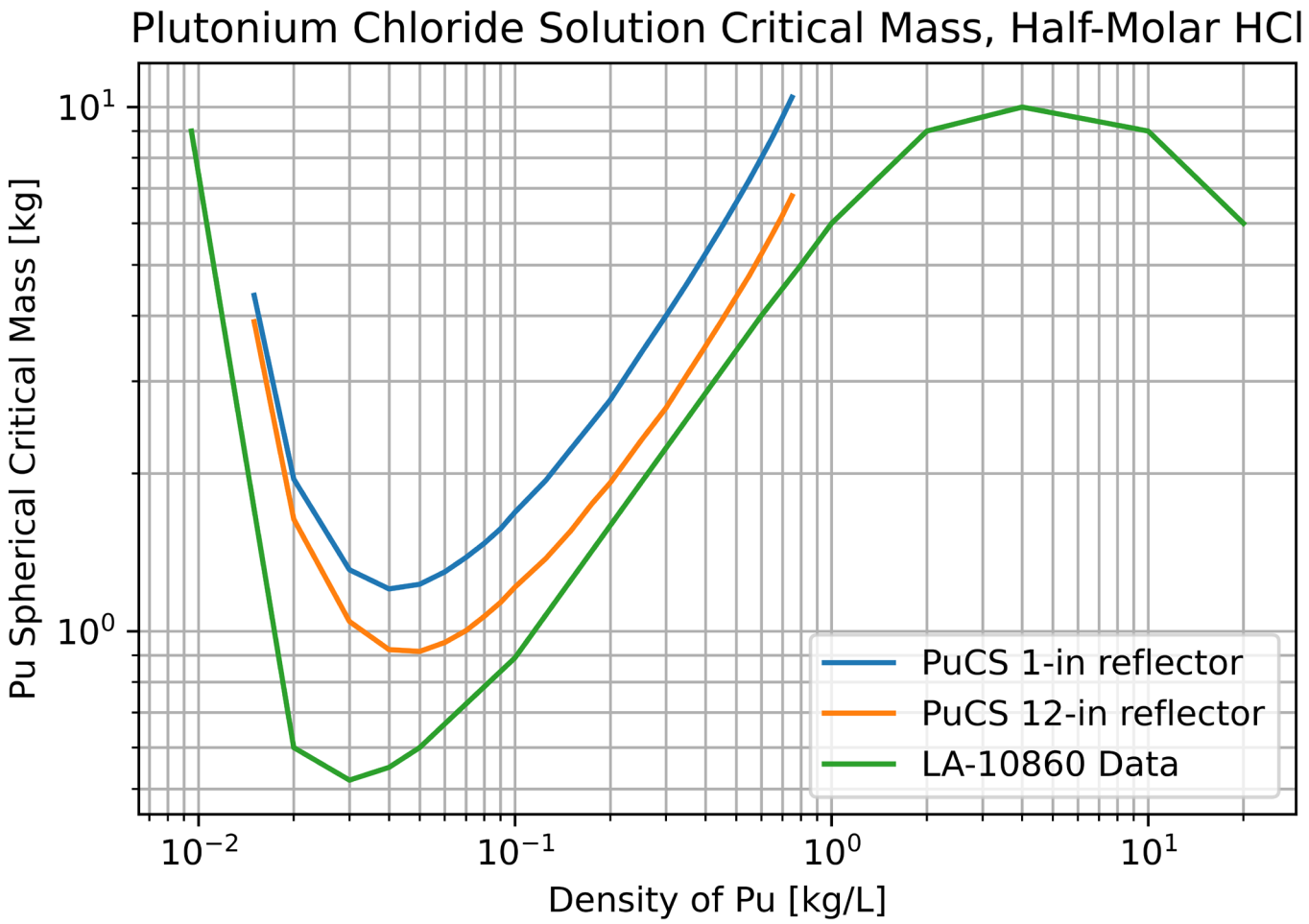
12-in Reflection:

Data Set	Maximum Reactivity	Difference from Current Modeling
Metal-Water	1.005	0
PuCl3-Water	0.945	-5.9%
Density Law at 0.5M HCl	0.892	-11.2%
Density Law at 2M HCl	0.785	-21.9%
Density Law at 4M HCl	0.702	-30.2%

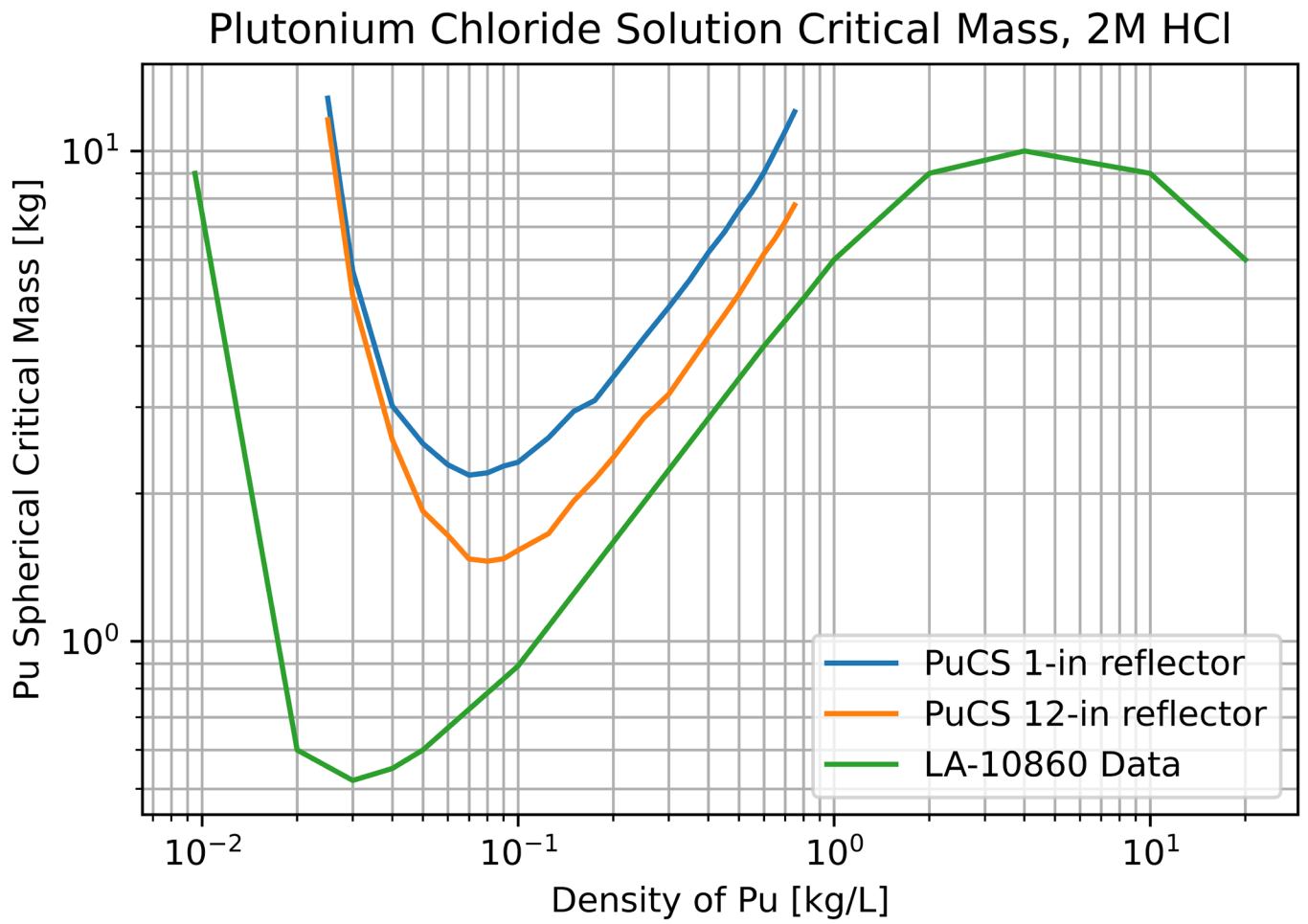
Effects on Critical Mass

- Critical mass was found using WORM_SOLVE
  - Perl script that works with WORM (write once, read many) to find MCNP input file variables that result in a specified keff value
  - Iterates a given input based on a specified variable to find what value of that variable yields a specified keff value
    - The user specifies a range for the variable to be searched
    - In this case, the variable was plutonium mass, and the target keff was 1.0.
- Cases were run over the applicable plutonium concentration (up to 750 g/L), an HCL concentration of 0.5M, at room temperature (25 C) with both 1-in and full water reflection.
- Results were then compared to the Pu Bathtub Curve (Figure 31 of LA-10860)

Effects on Critical Mass



Effects on Critical Mass



Effects on Critical Mass

Data Set	Minimum Critical Mass [kg]	Increase from handbook data
LA-10860	0.520	0
0.5M HCl, 12-in water reflector	0.9152	+76%
0.5M HCl, 1-in water reflector	1.205	+132%
2M HCl, 12-in water reflector	1.456	+180%
2M HCl, 1-in water reflector	2.181	+319%

Conclusions and Future Work

- An empirical density law for aqueous plutonium chloride has been implemented via a Python tool that may be used for MCNP6
- The empirical method predicts density within 2-3% of experimental data points
- This tool allows for more accurate modeling of these solutions and improve criticality safety evaluations to allow for operational flexibility

- Future work:
  - Potentially derive Pitzer parameters for $PuCl_3$-HCl-H_2O solution systems
  - Expand to include other actinide solutions if data is available
  - Improve Interface with MCNP
  - Validate for use with NCS calculations and quantify effect on reactivity and USL calculations

Acknowledgements

- This work was supported by the U.S. Department of Energy through the Los Alamos National Laboratory. Los Alamos National Laboratory is operated by Triad National Security, LLC, for the National Nuclear Security Administration of U.S. Department of Energy (Contract No. 89233218CNA000001).
- This work and the supporting critical experiment was funded under the Material Recycle and Recovery Program, NNSA Plutonium Program Office (NA-191), under Office of Production Modernization (NA-19), funded and managed by the National Nuclear Security Administration for the Department of Energy. Research on critical experiment design was supported by the U.S. Department of Energy LDRD program at Los Alamos National Laboratory.

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