Title: Mystery of PuO2 Dissolutions: What really happens in that solution?

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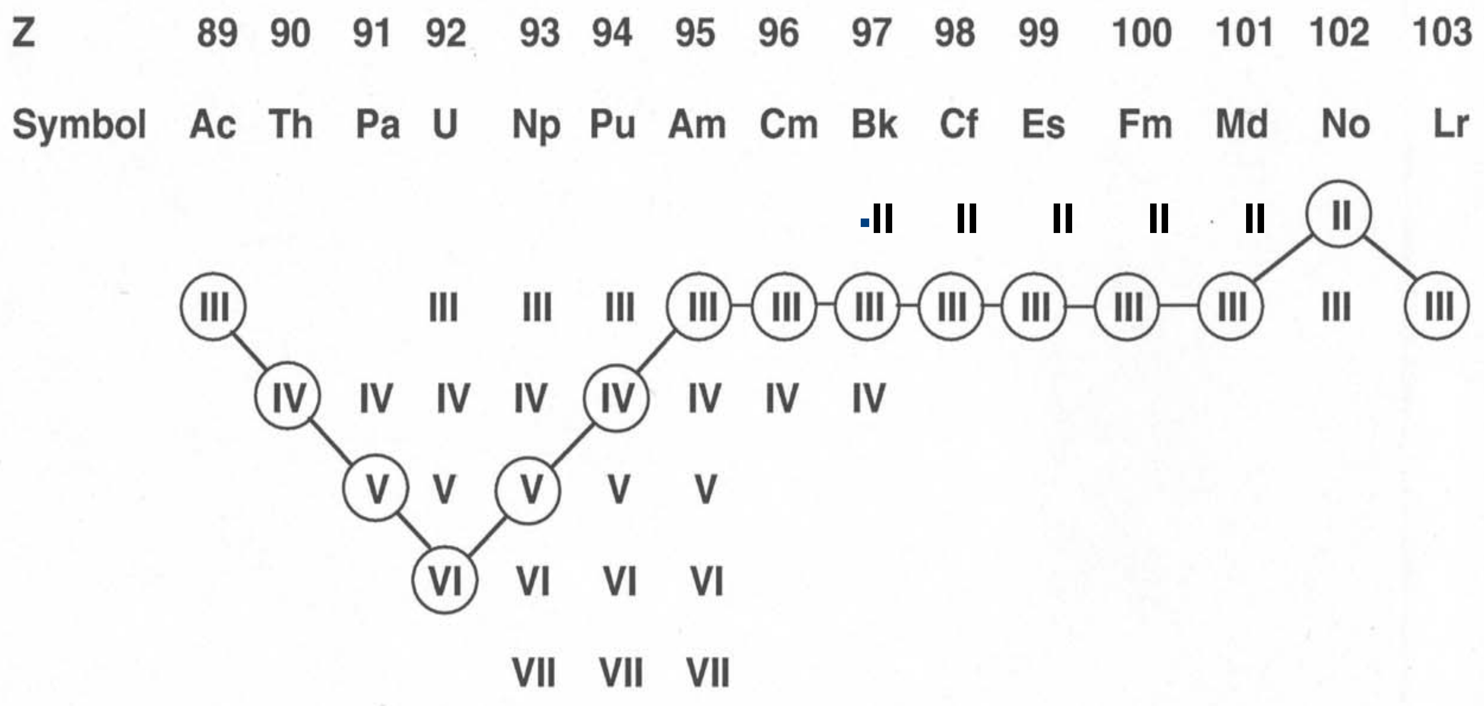
Mystery of PuO_2 Dissolutions:

What really happens in that solution?

Lisa Colletti

Why is Pu chemistry so complicated?



Z	89	90	91	92	93	94	95	96	97	98	99	100	101	102	103
Symbol	Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr
									II	II	II	II	II	II	
	III			III	III	III	III	III	III	III	III	III	III	III	III
		IV	IV	IV	IV	IV	IV	IV	IV						
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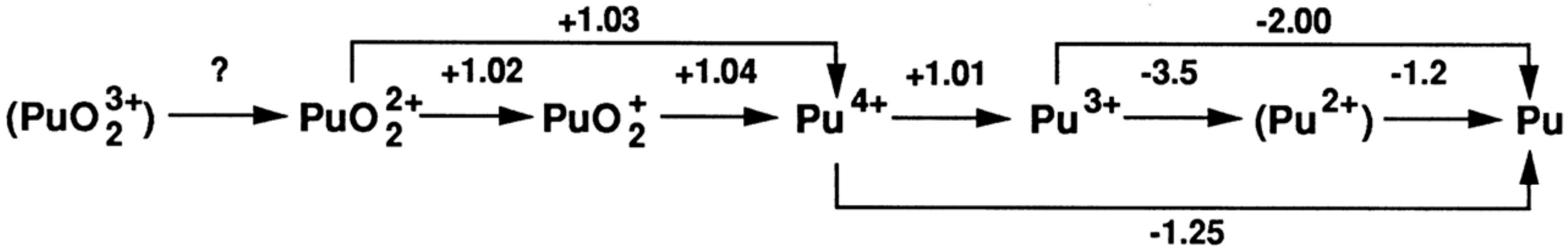
				VI	VI	VI	VI								
					VII	VII	VII								

Complications continued…



- $Pu^{3+} = Pu^{4+} + e^-$ $E^0 = 1.01$ Volts/NHE
- $PuO_2^{+} = PuO_2^{2+} + e^-$ $E^0 = 1.02$ Volts/NHE
- Thus all four oxidation states can co-exist simultaneously in solution!

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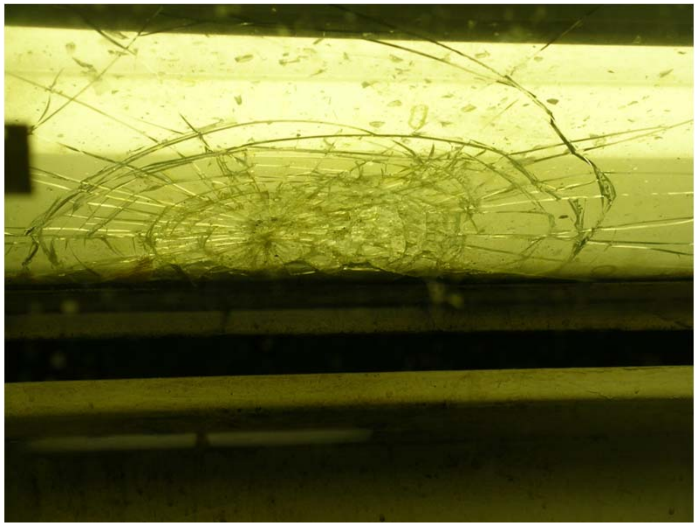
Why do we care, didn't we figure this all out in the 60s and early 70's? Yes and No…….

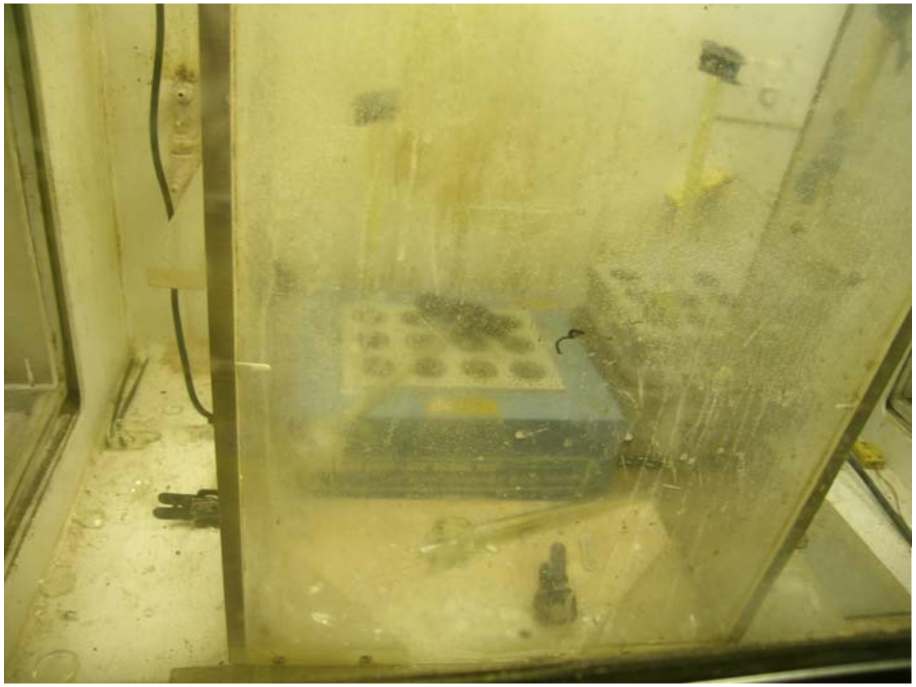
- ***Sealed-Tube Dissolution Method with Applications to Plutonium Containing Materials.*** **1966, Metz and Waterbury**
  - Used for high fired and refractory materials.
  - High temperatures (350°C and pressures 3500-4000 psi)
  - Perchloric acid used as an oxidant in an 36% HCl matrix typically.
  - Based on Wichers ,et all of the National Bureau of Standards, 1944 article on dissolution of refractory materials. (data still referred to by PAR and Berkoff application materials).
  - Even under these extreme temperature and pressures dissolution for 0.25 grams of high fired PuO_2 (fired at 2200°C) took 50 hours to dissolve.
- **This method discontinued in Mid 1990's due to increasing safety regulations in nuclear facilities. Use of $HClO_4$ also discontinued due a fire at Rocky Flats. Could take out whole lab…..**
- **This left a gap in our ability to analyze high fired materials that still remains.**

For PuO_2 not high fired (i.e., up to about 1000°C)

- ***Sealed Reflux Dissolution System.* 1975 Dahlby, Geoffrios, Waterbury**
- **This became part of the ASTM C1168-08 standard methods.**
  - Good for lower fired materials. Will partially dissolve some higher fired materials/refractory materials, but never completely.
  - 5 mL of 12 *M* HCl, 3 drops 16 *M* HNO3, 3 drops 1.3 *M* HF
  - Heat at 150°C for up to overnight, temp could be raised if sample not completely dissolved.
  - Generates ~86 psi at this temperature.
  - This has been our standard method for most oxides going through Assay, MS, or RC for last 40 years.

Then last September……Boom!





Problems identified….

- If using 160^{o}C with HCl then pressure can continue to increase!…Was a side note in paper for small samples (.1g in 10 mL dissolution tubes) but never captured in working documents or mentioned with the larger 30 mL tube used for 0.25g-1g of samples.
- In the 1980s a technician had an issue with pressure not holding in these dissolution vessels and decided to put on an additional clamp. He did not test at what pressure the double clamp released. He trained all remaining technicians to do it his way and the double clamp became part of the method.
- Tests showed that double clamping will not release pressure building…it's rate of building slows down, but continues to increase indefinitely. Single clamping release pressure at about 120 psi.
- **But what else don't we know about this system? None of these papers/procedures talk about the chemistry that is actually occurring or the mechanisms involved…..**

Myths and Lore handed down and associated with PuO_2 dissolutions

- **HCl won’t dissolve PuO_2**
- **High fired materials are difficult to dissolve because they have perfect crystal structures**
- **High fired materials are difficult to dissolve because they are denser**
- **We only use HF to stabilize other elements, Pu doesn’t care about it.**
- **HF is catalytic….**
  - Catalysis is the change in rate of a chemical reaction due to the participation of a substance called a catalyst. Unlike other reagents that participate in the chemical reaction, a catalyst is not consumed by the reaction itself.

What is really going on?

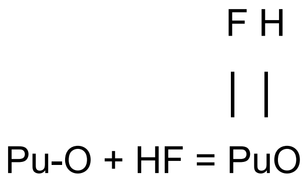
- **1969, Miner showed that HF was critical to dissolution, but did not identify the mechanism. He did note that the rate was also related to surface area and not crystal size.**
- **1970, Shying, Florence, and Carswell proposed the roll of fluoride in the dissolution of Thoria in a HF/HNO_3 acid system.**
- **1973, Barney set out a generic mechanism for the HF/HNO_3 system.**
  - Formation of a protective surface layer
  - Diffusion of un-dissociated HF through surface layer
  - Reaction of HF to form soluble Pu species
  - Diffusion of soluble Pu species to solution

  Noted 2nd bullet as the rate determining step.

  Barney did not make the connection with the 1970 Thoria paper.

More history

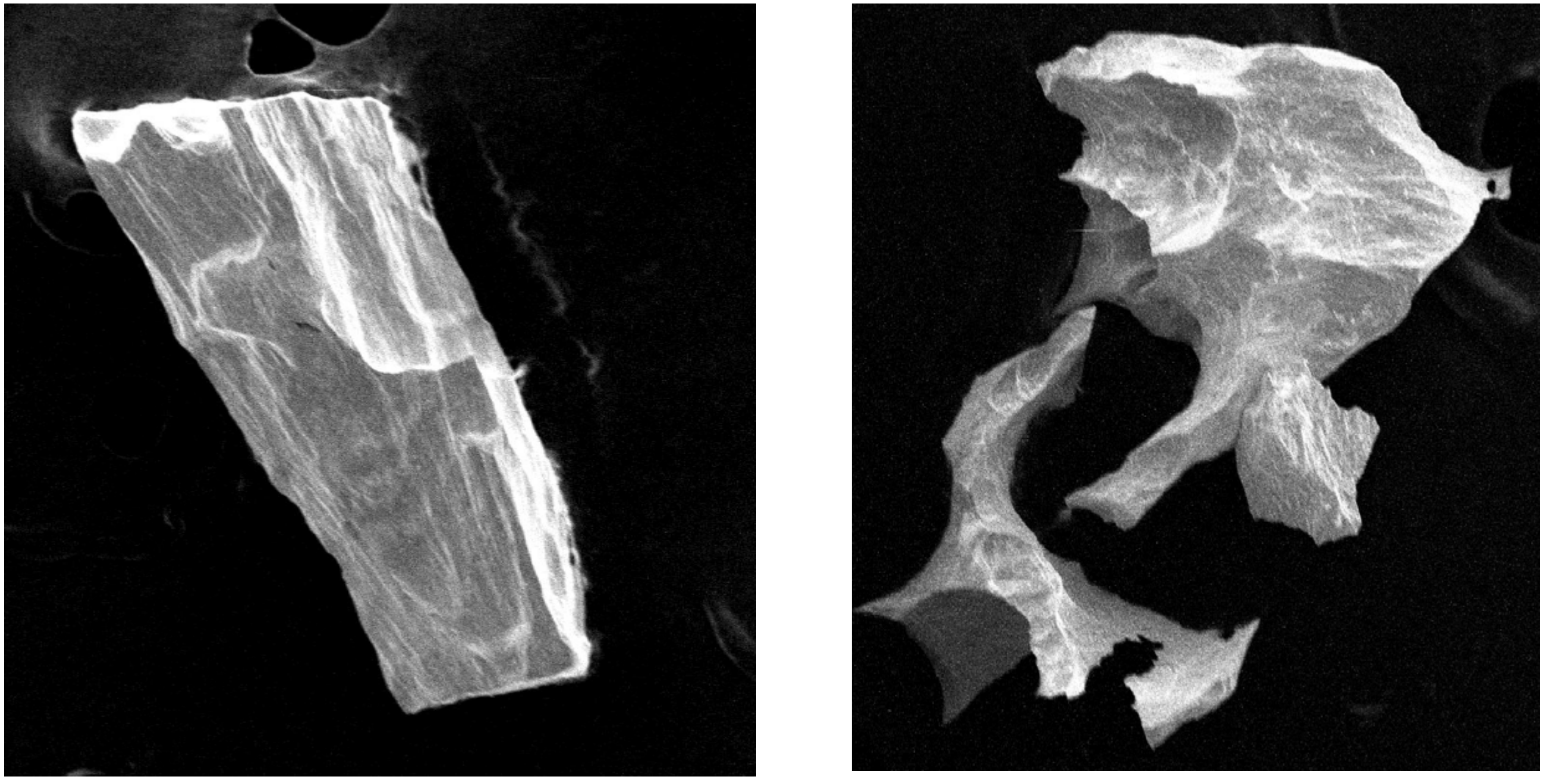
- **1975, Fogler, Lund, and McCune found that the dissolution of feldspar in HF/HCl mixtures is limited by the rate the HF attacks the feldspar surface.**
- **1977, Definitive paper on PuO_2 mechanism and kinetics by Barney. Suggests that the mechanism is similar to the Thoria dissolution proposed in 1970 and proceeds to prove it.**
  - The results of this kinetic study indicate that the rate-controlling step in the dissolution is attack of the oxide surface by **undissociated** HF. This can occur by several different mechanisms:



$$\text{Pu-O} + \text{HF} = \overset{\overset{\text{F}}{|}}{\text{Pu}}\overset{\overset{\text{H}}{|}}{\text{O}}$$

- **Each *step* results in breaking a Pu-O bond and substitution of F for O or OH (hydrated surface) . This process is repeated until all the Pu-O bonds are broken.**

Dissolution of High Fired Material



- Dissolution of plutonium dioxide particles in Teflon pressure vessel using
  - HNO_3 /HF mixture (starting material left; partially dissolved right)

- SEM photos courtesy of Dan Schwartz

Why not just dissolve in high concentrations of HF?

- The amount of HF which can be used in the dissolution is limited by the solubility of $PuF_4*2.5H_2O$.
- This fluoride is precipitated when: $0.1\ M > [HF] << 0.2M$ (in HNO_3)
- There is some evidence that the precipitate begins to redissolve as more Pu goes into solution, probably by reactions similar to

$$PuF_4*2.5H_2O + 3Pu^{4+} = 4\ PuF^{3+} + 2.5H_2O$$

Very slow though….

Ok, so what does the HNO_3 do? Why do I need a high concentration?

- **Forces HF to stay associated (critical reagent at surface)**
  - $HF = H^+ + F^-$
- **Prevents higher order fluorides from forming and**
  - Complexes such as PuF_2^{2+} and PuF_3^+ are present in significant quantities when $HNO_3 < 10$ M.
  - These will be more stable at low HNO_3 concentration because of the equilibrium reaction

$$PuF_x^{(4-x)+} + HF = PuF_{x+1}^{(3-x)+} + H^+$$

- **Concentrations lower than 10 M HNO_3 should not be used.**

What else might be at play?

- Temperatures affect reaction rates and to which side the equilibrium of the reactions proceed towards.
- Solution to solid ratios….can affect molar balance and thus dissolution and formation of PuF_4.
- Pressure does not affect the rate as it is surface limited.
- Surface area: hard to control for when it is inherent in customer's sample.
- Time: Analytical labs would like high through-put but often will require overnight or longer.
- Open or closed systems. Open systems allow volatiles to be lost and may require replenishing during the dissolution process.
- Presence of impurities (and dissolution vessel material). Some materials will have a greater affinity for fluoride than Pu. This will reduce the available HF for dissolution of the Pu oxide.
- Agitation: Keeps a steady flow of HF to surface when used.
- Acid Matrix: What is best matrix?

Has anyone other than LANL tried HCl and HF before?

- Yes
- 1986, Bray, Ryan and Wheelwright looked at dissolution using 6M HCl and various HF to Pu ratios.
- Found that F:Pu ratios of 2:1 most effective.
- Proposed same mechanism as for HF/HNO_3 system.
- Used a reflux system.
- Noted surface area of PuO_2 at different firing temperatures

PuO_2, fired to (°C)	Surface Area, m^2/g
350	48.74
500	39.4
950	1.5
1700	0.54

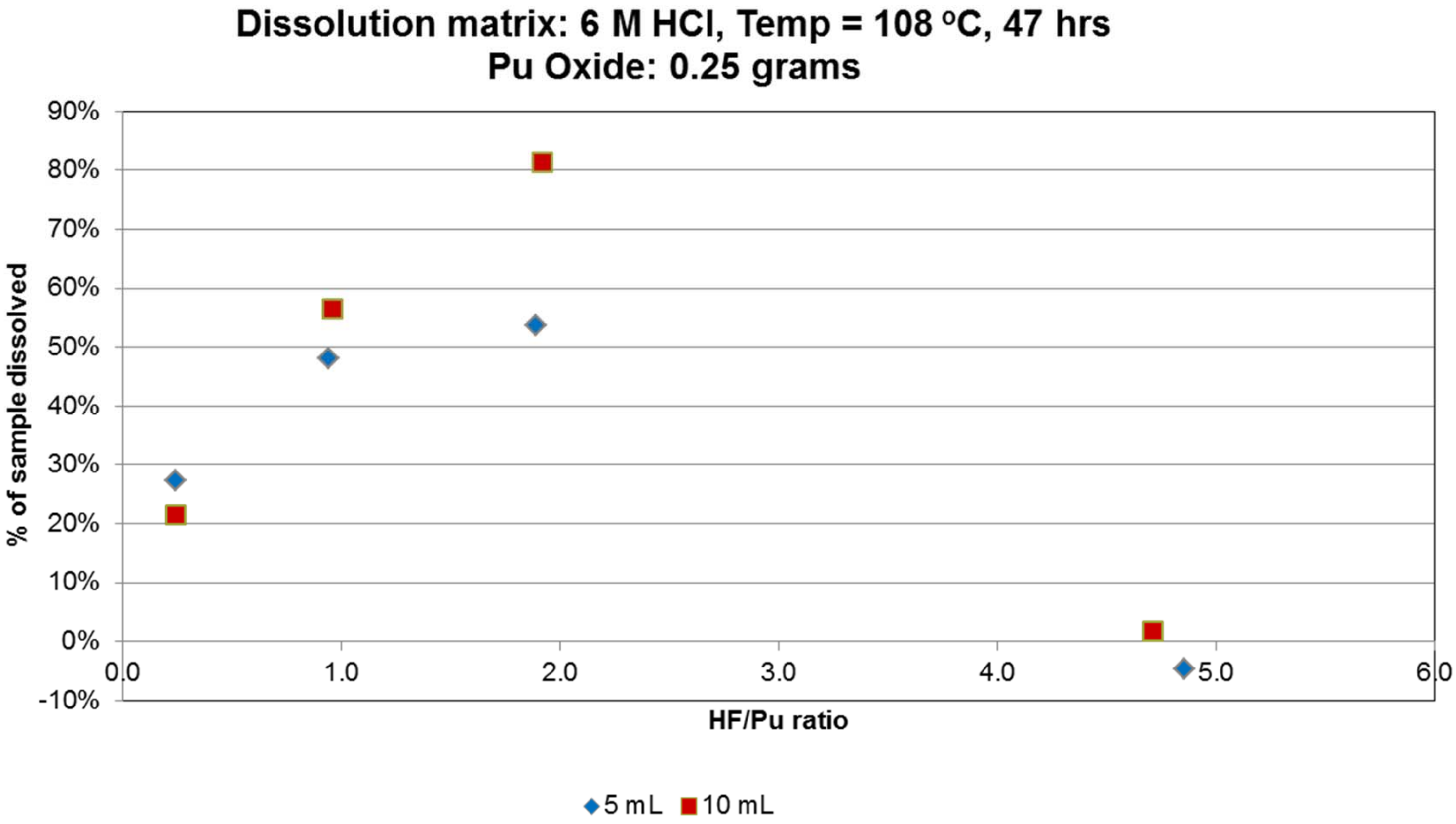
Ok, so now how do we apply this? AKA, we don't do reflux systems a liter at a time.

Using a hot block and 60 or 120 mL Seville dissolution vessels

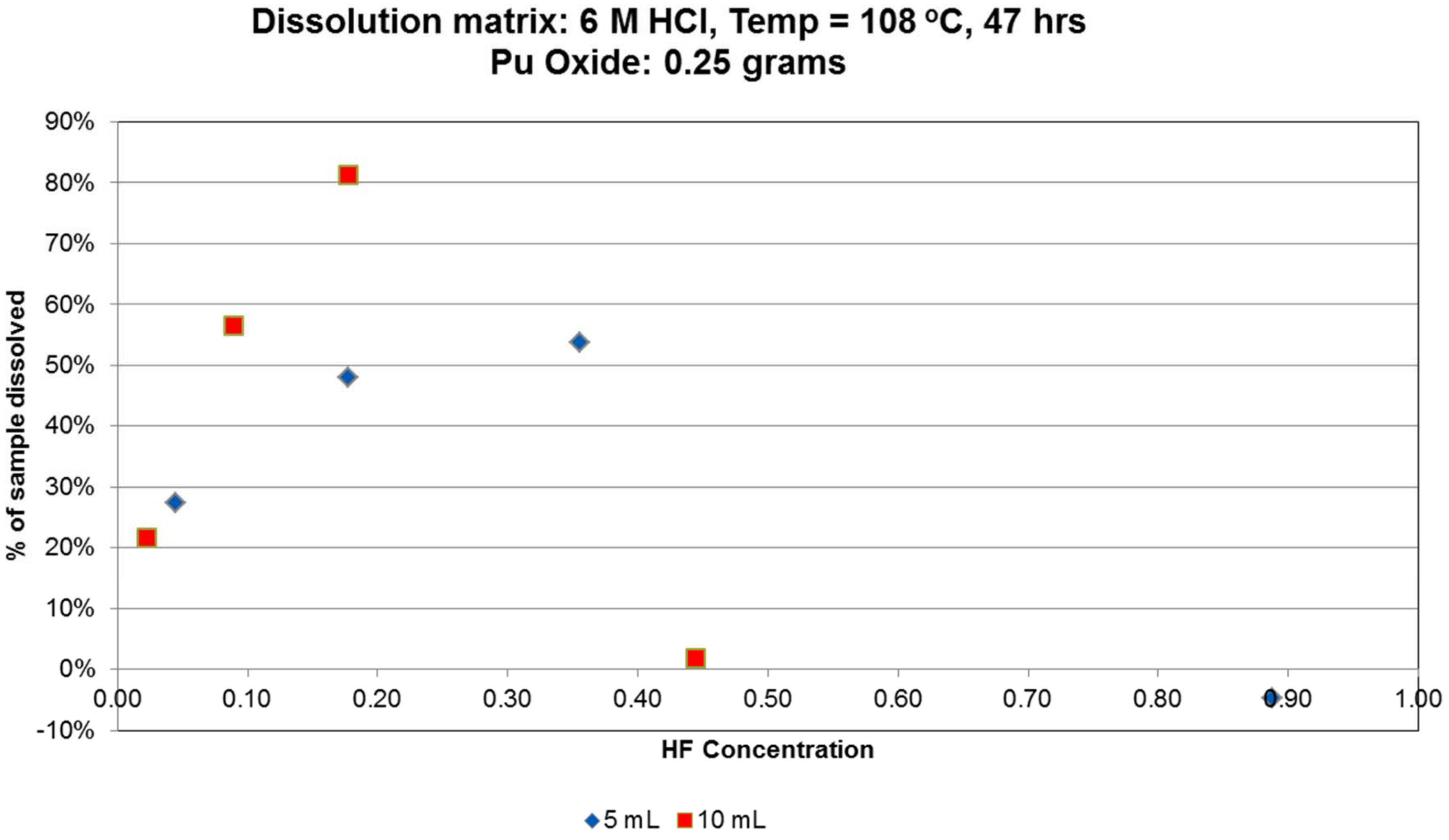
- **Look at various matrix acids**
- **Look at various HF ratios/concentrations**
- **Look at other supporting acids**
- **Look at sample size**
- **Look at temperature**
- **Look at solution volume**

Can I reproduce the HCl work in a closed system?

Original 1986 work used 28 g PuO_2/L (Initial concentration).



HF concentration plays a part too…..

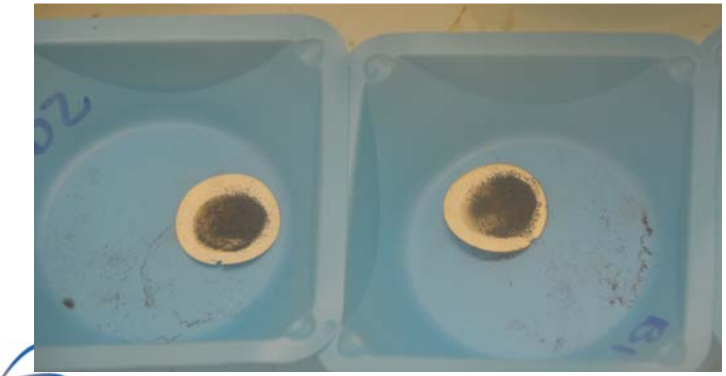


What was left on the filter, does that help tell us what is going on?

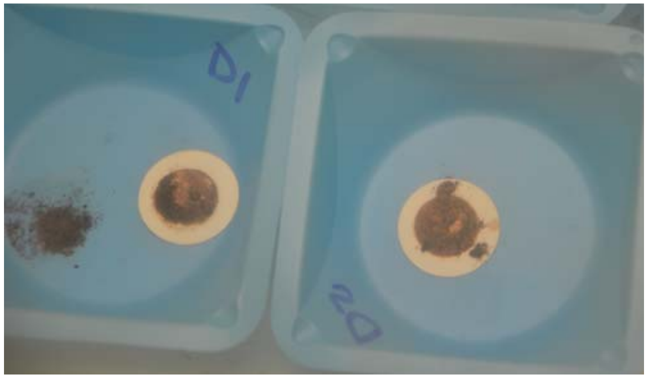
- F/Pu = 0.2

- F/Pu = 1.9

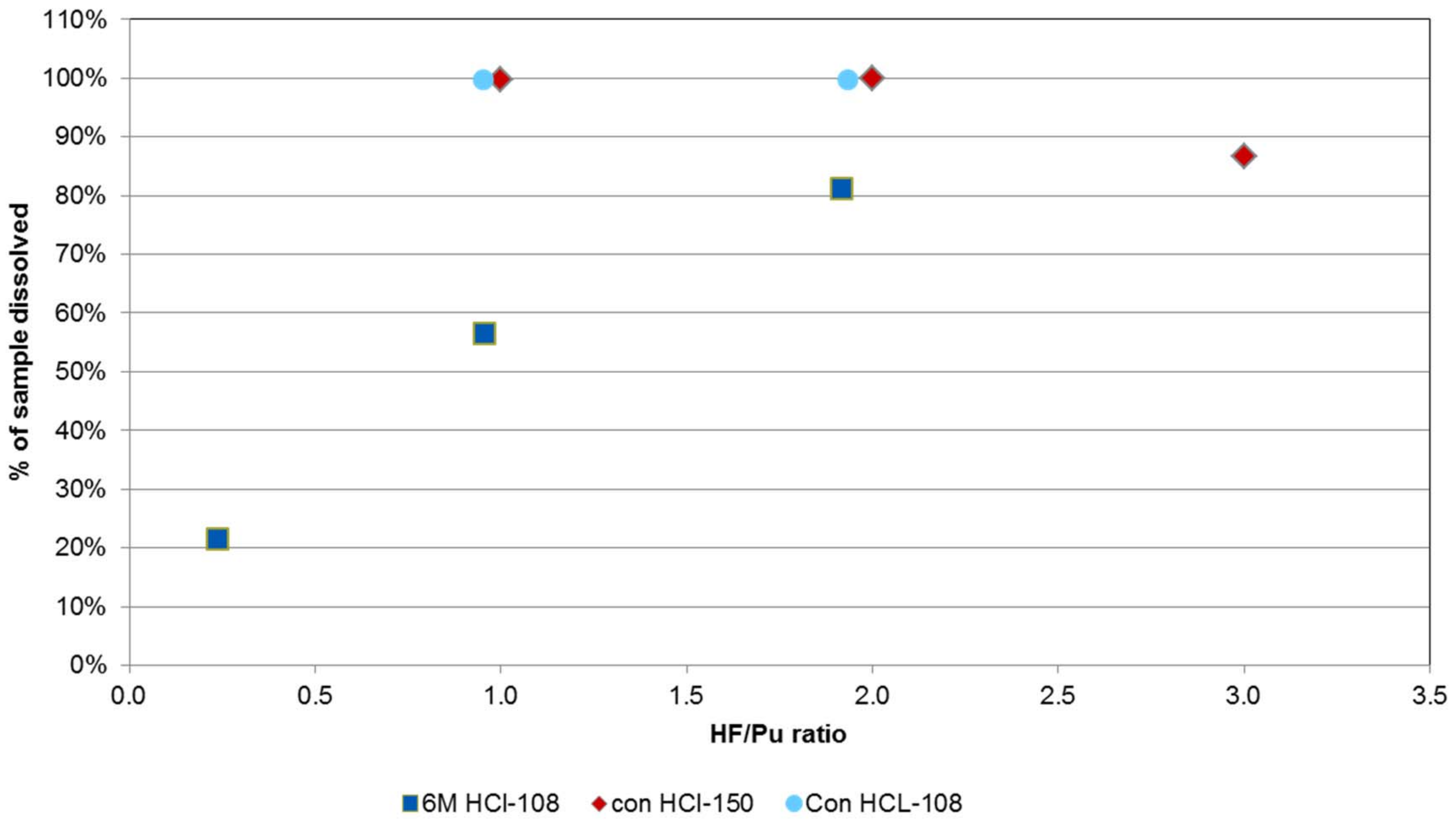
- F/Pu = 0.9



- F/Pu = 4.9



Comparison of different conditions
10 mL volumes, HCl is matrix acid



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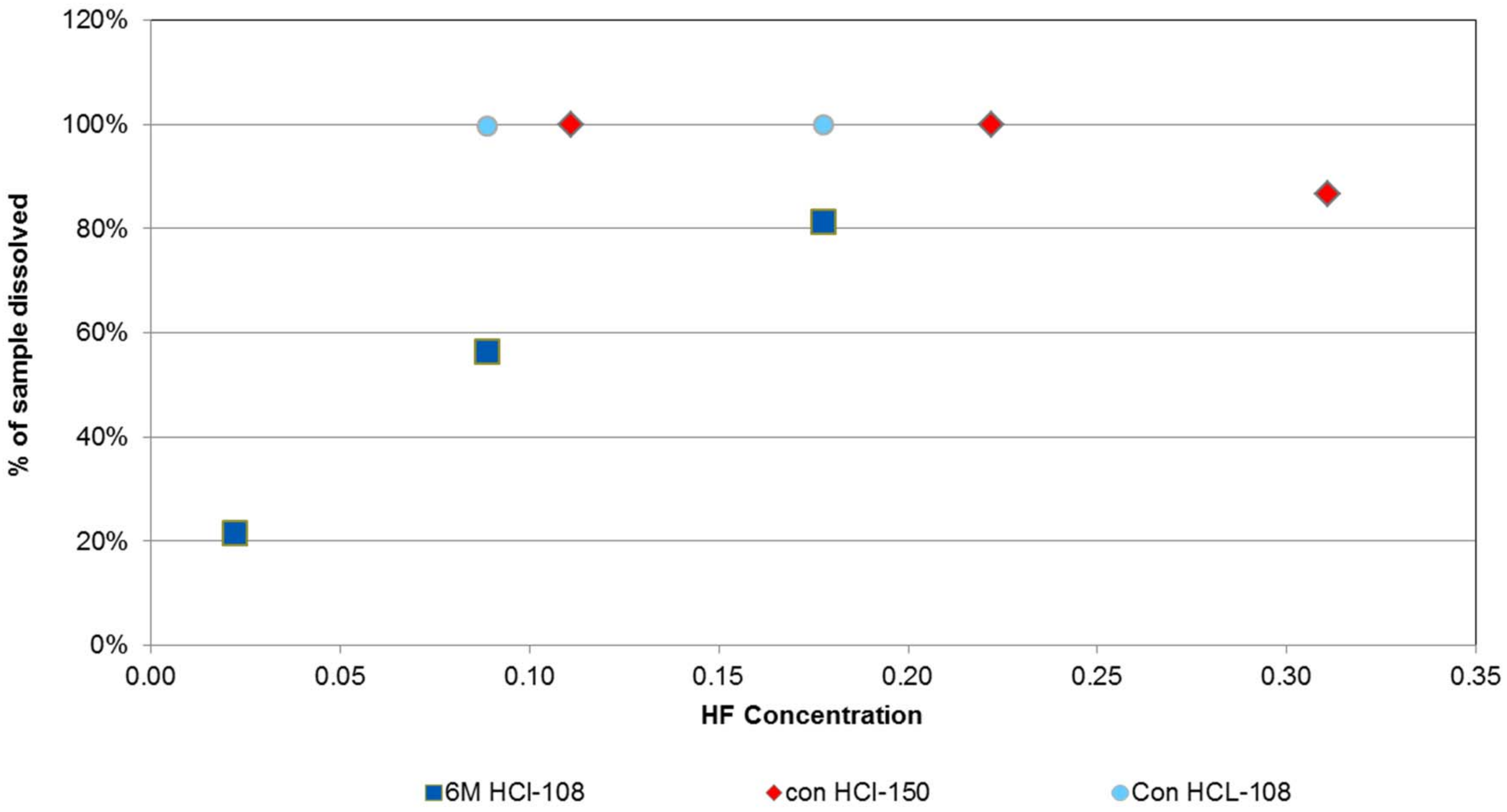
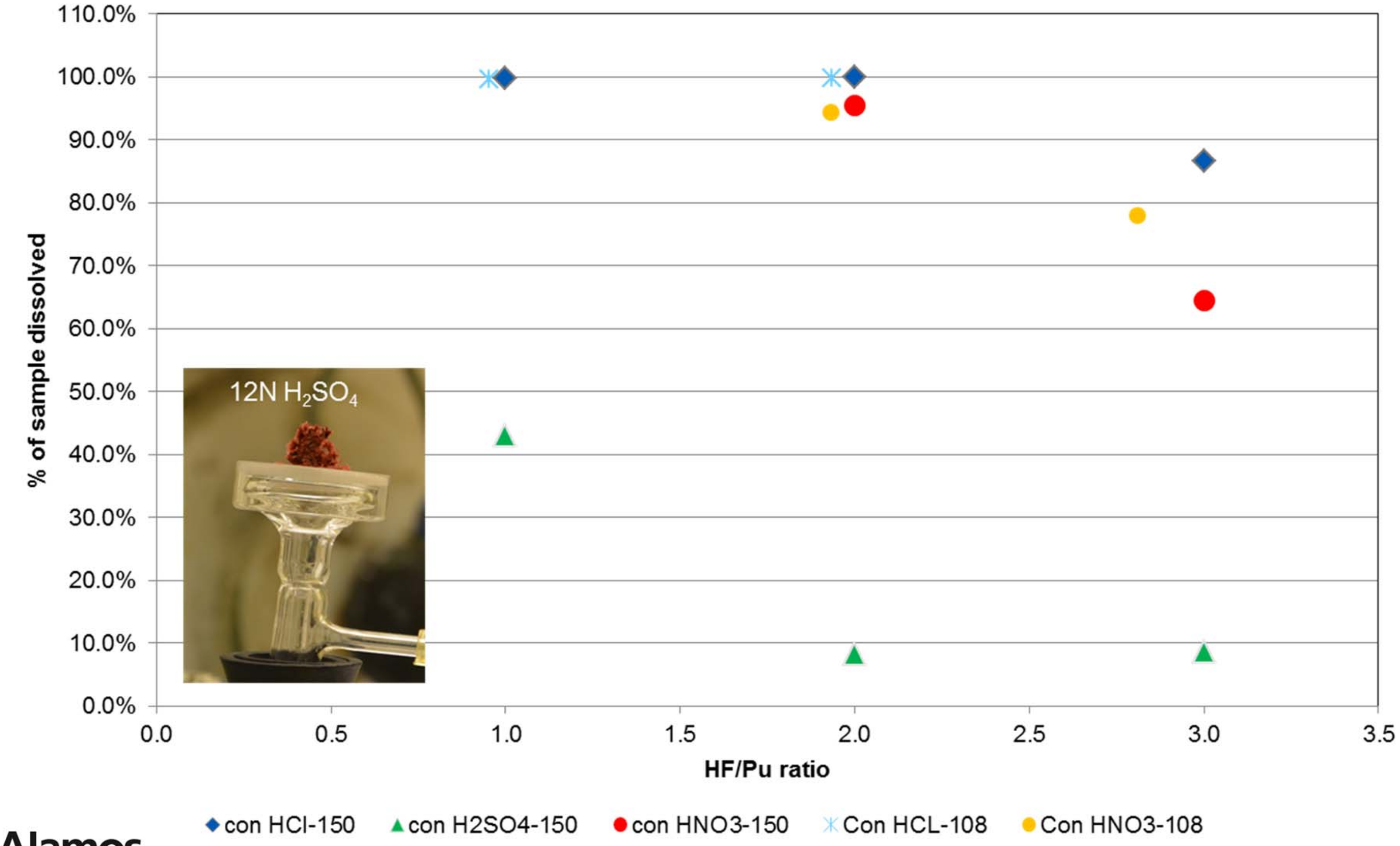
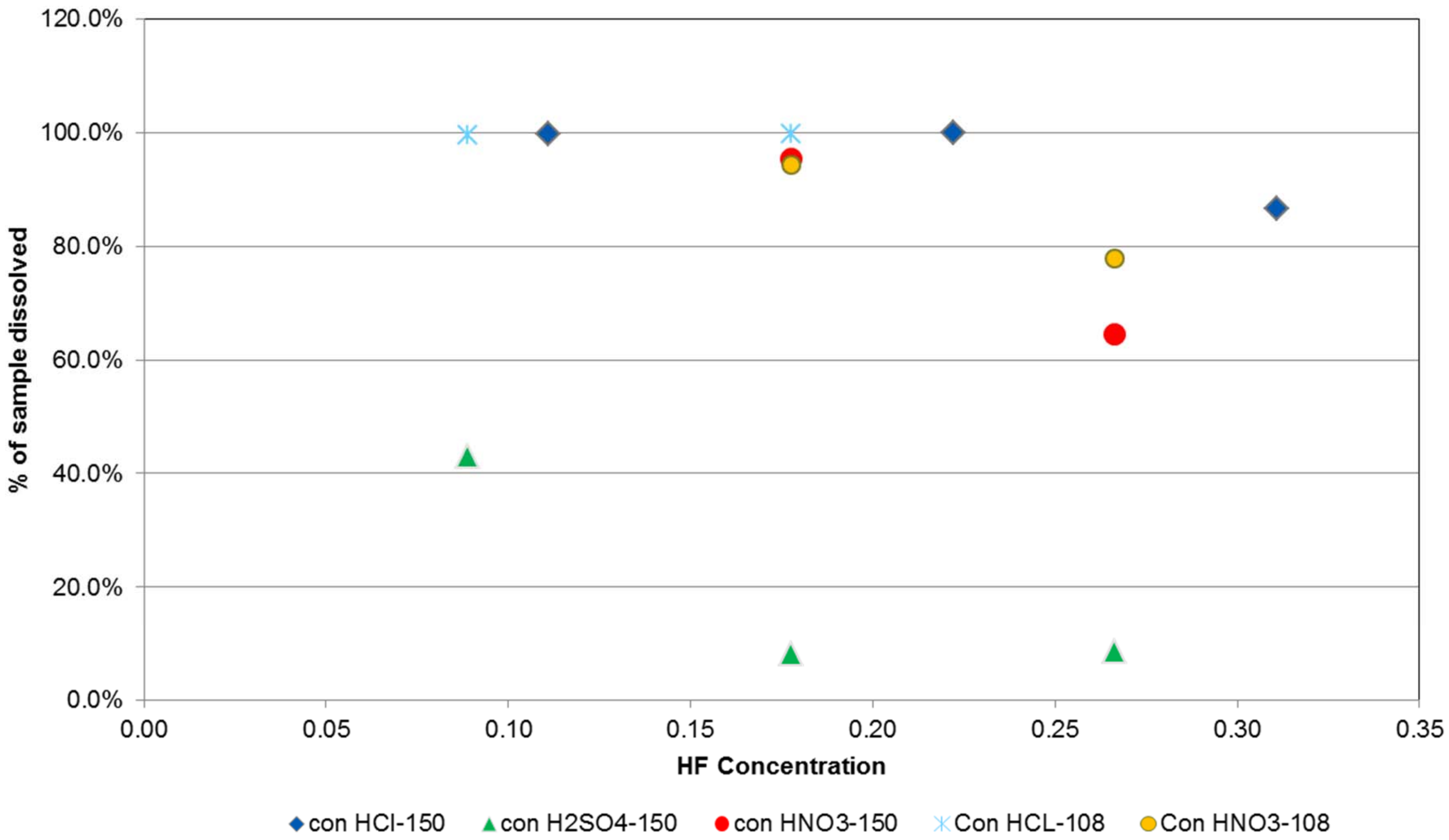


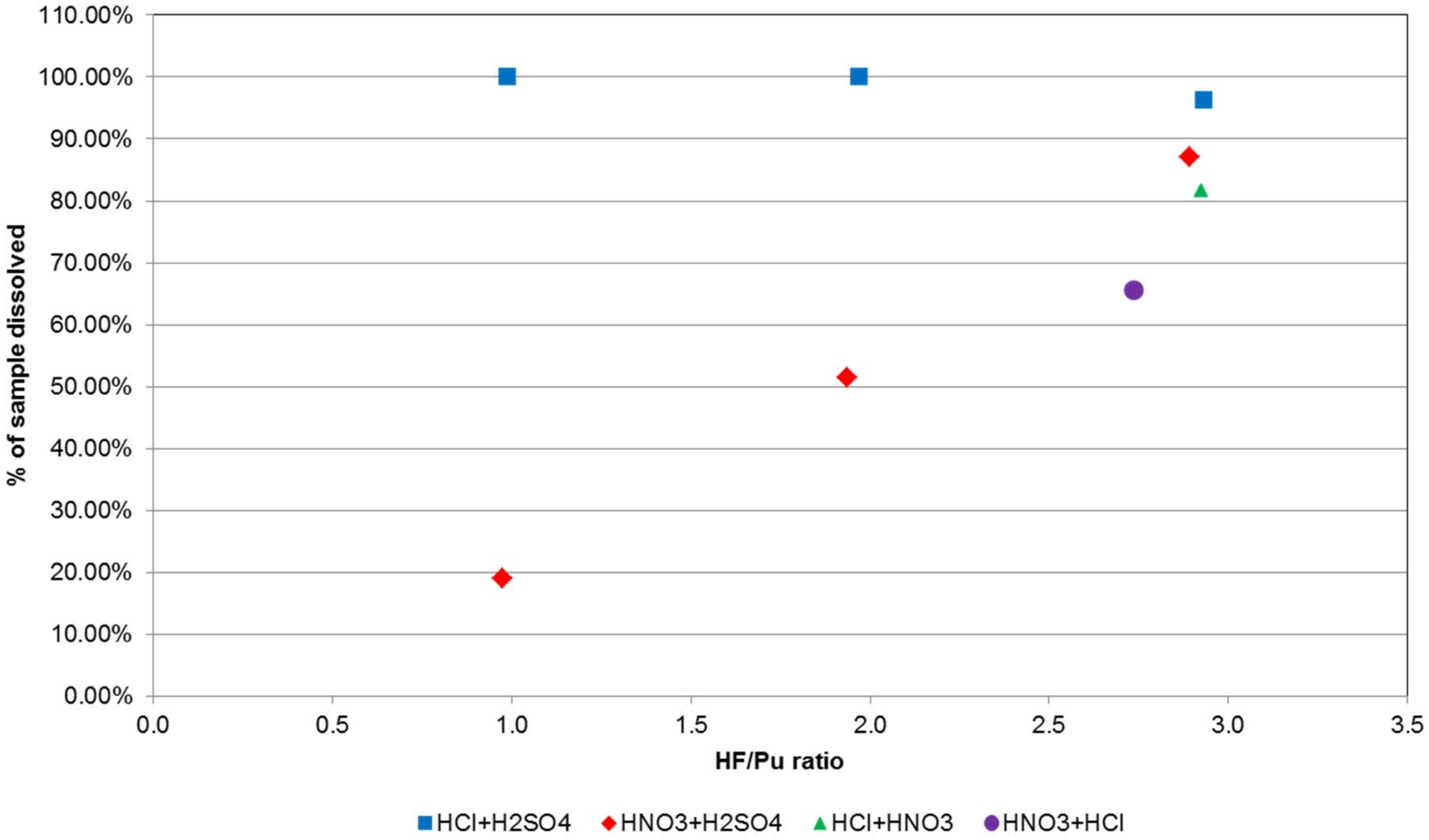
Comparison of Different Matrix Acids, 10 mL volumes



Viewed vs. HF concentration



Is a mix of matrix acids beneficial?



Why can you use more HF with HCl matrices?

- **Theory that it is related to the binding strength of the anion.**
  - Cl^- only binds Pu^{+4} very weakly. So once PuF^{+3} or higher fluorides are formed Cl^- cannot displace it so F^- cannot go back into the solution to form higher fluorides.
  - NO_3^- will bind Pu^{+4} fairly well and so will compete with F^- to bind the Pu. If PuF^{+3} or higher is formed, some NO_3^- will replace F^-, allowing it to go back into solution. At a high enough F^- concentration the F will make the PuF_4 and precipitate out.
  - SO_4^{-2} seems to have a similar binding energy as F^- so if there is a large excess of SO_4^{-2} , then $Pu(SO_4)_2$ crystals are formed. Only when a large enough F- is present will you start to get PuF_4 formation.

  - Will take other suggestions…

Investigation continuing….

- **Determine the max limit of HF for the HCL system before PuF_4 is formed. Somewhere between 2-2.9 F/Pu ratio (0.22-0.27 M HF).**
- **Determine the max limit of HF for the HNO_3 system. Somewhere between 1 and 1.5 F/Pu ratio (0.1 and 0.15M HF)**
- **Will mix of HCl and HNO_3 closer to aqua regia ratios be more effective than just a trace of either for extremely high fired materials (over 1000°C). Pressure safety a concern with this mix.**
- **Determine optimal temperature required for dissolution for HCl and HNO_3 matrices. Lower is better from a safety point of view.**
- **Maximum sample size (or best solution/solid ratio)**

Conclusions

- Dissolution methods should be reviewed against original publications where possible to identify and document any changes that have occurred over past decades.
- Dissolutions for analytical methods should be re-evaluated against literature more frequently than has occurred in the past to identify new information that can be utilized.
- Dissolution testing is absolutely required for different equipment sets ups. A large number of factors play into dissolution of PuO_2 that are inter-related and inter-dependent. A small change in one factor can cause large changes in results.
- HCl and HNO_3 are both good matrices for dissolution of PuO_2 but H_2SO_4 is not.
- PuO_2 dissolutions are highly dependent on HF concentrations and F/Pu ratios and maximums are different depending on matrices chosen.
- Lower temperatures than we have been using can achieve 100% dissolution.