A review and outlook for the removal of radon-generated ^{210}Po surface contamination

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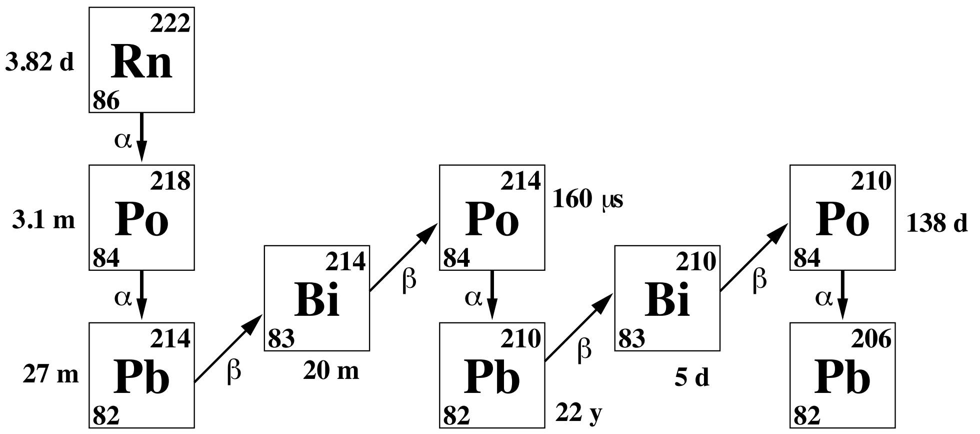
Motivation

Exposure to radon gas leaves behind progeny on surfaces.

- ^{210}Pb is long lived
- ^{210}Po is an alpha emitter



A problem for all low background, rare event searches

- Degraded alpha can fall into $0\nu\beta\beta$ region of interest
- Nuclear recoils and (α,n) a problem for dark matter detectors
- All low background experiments study this background

Exposure to radon gas leaves behind Rn progeny

- The short-lived portion of the radon decay chain deposit on a surface
  - ^{218}Po and ^{214}Po alpha decays can recoil the daughter nuclei deeper into a material surface
  - An implanted distribution of ^{210}Pb down to 0.05 - 0.1 μm
- Radon gas can diffuse into the material during exposure
  - Contribution depends on the material (plastics vs metals)
  - Progeny are then deposited deeper into the subsurface

Motivation

The deposition of Rn progeny continues to be modeled and studied

Evaluation of cleaning and surface removal of Rn progeny is on going

Some of the past LRT proceedings articles that focus solely on deposition or removal of Rn progeny

LRT 2015

- M. Bruemmer et al AIP Conf. Proc 1672 , 140005 (2015)
- K. Kobayashi AIP Conf. Proc 1672, 050003 (2015)
- G. Zuzel et al AIP Conf. Proc 1672, 150002 (2015)

LRT 2013

- L. Pattavina AIP Conf. Proc 1549, 82 (2013)
- G. Perumpilly et al. AIP Conf. Proc 1549, 239 (2013)
- R. W. Schnee et al. AIP Conf. Proc 1549, 128 (2013)
- C. Jillings AIP Conf. Proc 1549, 86 (2013)

LRT 2010

- V. E. Guiseppe et al. AIP Conf. Proc 1338, 95 (2011)
- M. Wójcik et al. AIP Conf. Proc 1338, 224 (2011)

LRT 2006

- M. Wójcik et al AIP Conf. Proc 897, 53 (2007)

LRT 2004

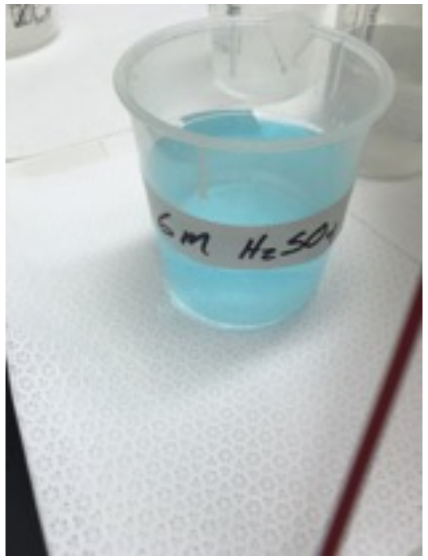
- M. Leung AIP Conf. Proc 785, 184 (2005)

… and more studies published elsewhere or in experiment overview papers

Po Cleaning

Findings from studies evaluating cleaning and surface removal techniques:

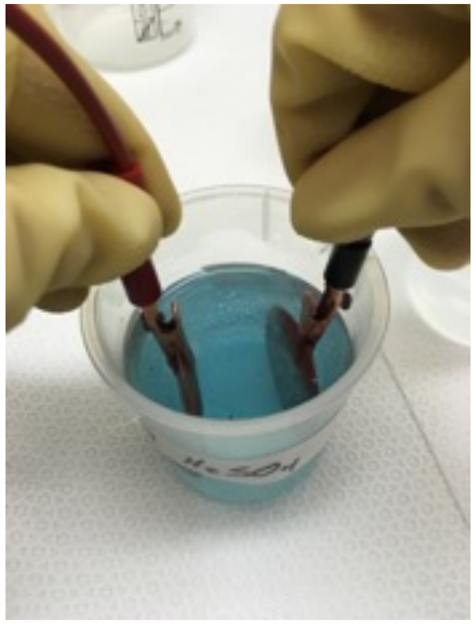
- Pb and Bi generally removed easily using a variety of standard methods
- Po has been more difficult to remove - more aggressive techniques recommended



Next generation experiments will have more parts with greater surface contamination control requirements.

Cleaning requirements and considerations:

- Efficient in removing Rn progeny, specifically ^{210}Po
- Quantities and purity of chemicals needed
- Chemical waste
- Generation of chemical fumes
- Underground operation limitations
- Number of parts and process automation
- Maintain dimensional and mechanical tolerances



Po Surface Location

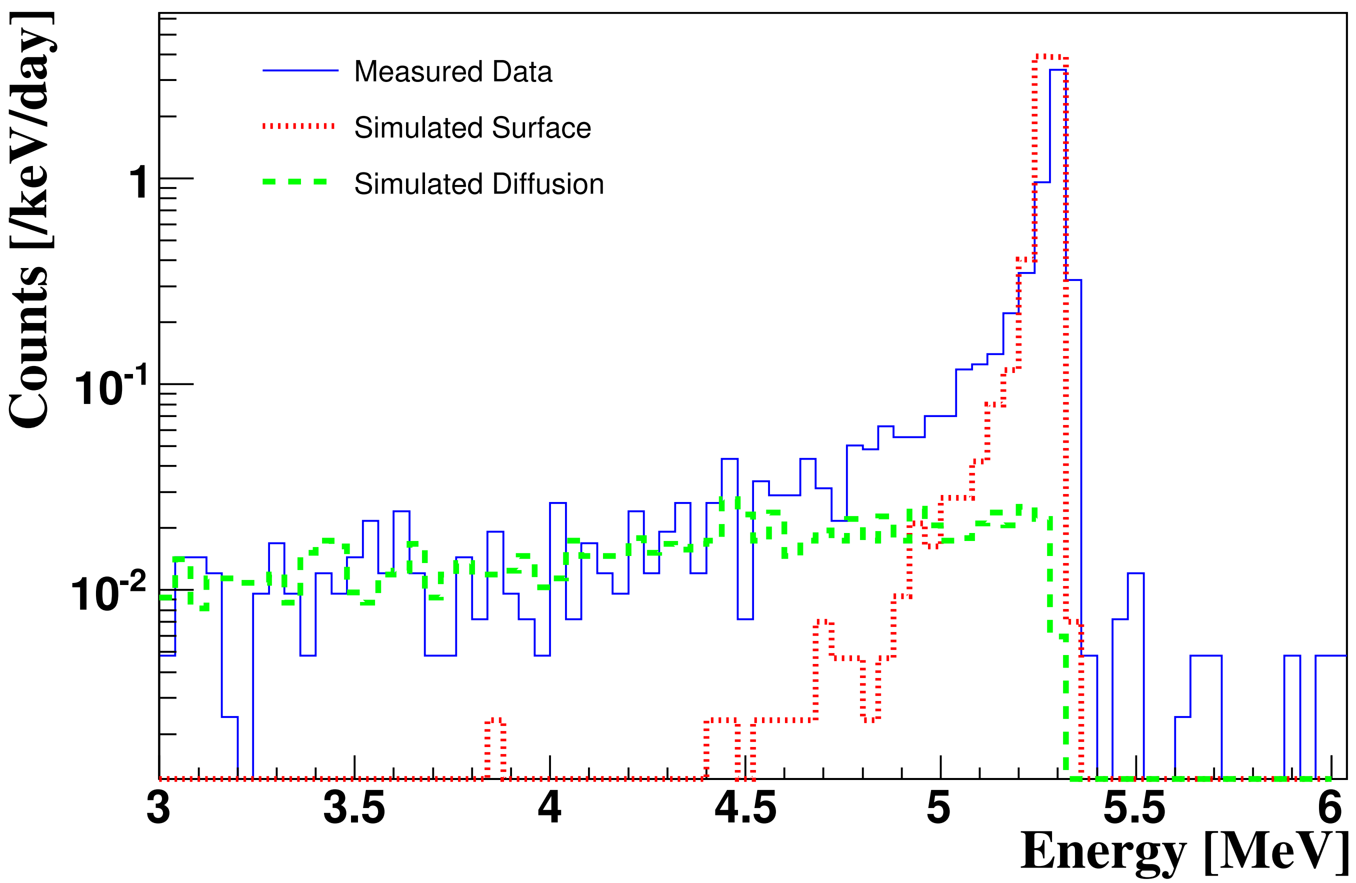
If ^{210}Po resides directly on a surface, the emitted alpha would be detected at its full energy

For Rn-exposed surfaces, the alpha energy is degraded due to:

- Surface roughness affects the amount of degradation due to the extra material an alpha must penetrate
- Bulk or diffused contamination

Stainless steel example

Simulation includes an effective roughness parameter (red) and deeper (green) contributions



G. Perumpilly et al. AIP Conf. Proc 1549, 239 (2013)

The range of a 5 MeV alpha is ~20 μm in metals

You would expect that cleaning of surfaces would easily remove the majority of Po atoms implanted within 0.05 - 0.1 μm

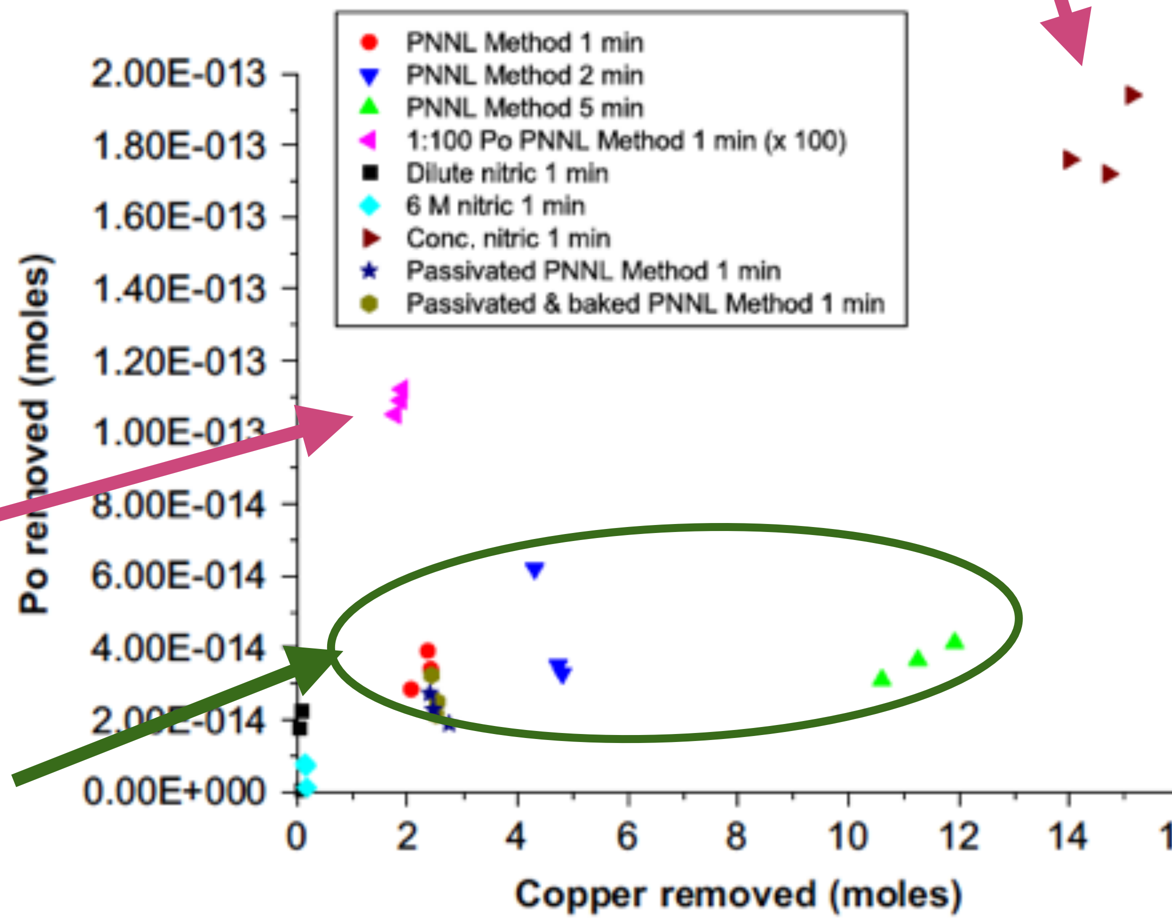
Po Removal Techniques

Surface cleaning techniques have been evaluated with varying results

E.W. Hoppe et. al [NIM **A579** (2007) 486]

- Nitric Etch of Cu
  - Very effective at removing all surface contaminants
  - Not the most practical for a controlled process
- PNNL method: H_2SO_4 and H_2O_2
  - Shows promise for ^{210}Po removal
  - Some concern with Po solubility
  - Method works for removing surface U/Th
    - (see previous talk by C. Christofferson for MAJORANA experience)

Nitric most effective



Improved Po removal with lower Po concentration

Limited Po removal

Po Removal Techniques

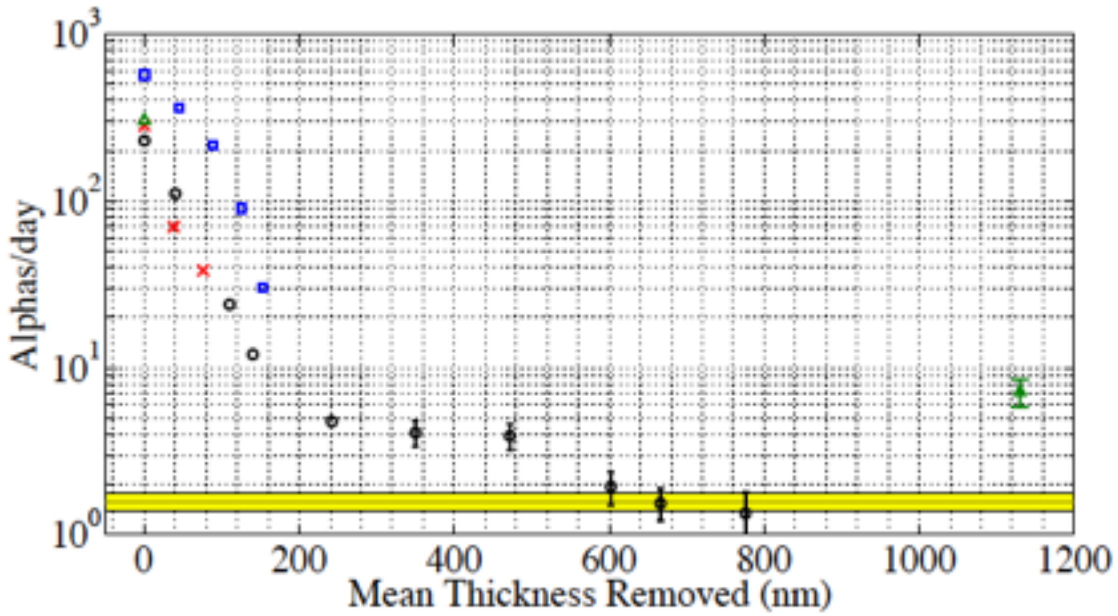
G. Zuzel *et al.* [AIP Conf. Proc. **1672** (2015) 150002] + several other papers

- Etching: Cu by PNNL method; Steel by HNO_3+HF; Ge by CP4
  - Greater reduction of Po in Steel and Ge than in Cu
- Electropolishing: Cu: H_3PO_4 + 1-butanol + ΔV; Steel H_3PO_4 + H_2SO_4 + CrO_3 +ΔV
  - More efficient reduction, especially for Po

Isotope	Activity reduction factors after etching / electro-polishing			
	Copper	Stainless steel	Germanium	
			NPGe	HPGe
^{210}Pb	50 / 300	100 / 400	100	700
^{210}Bi	50 / 300	100 / 800	400	800
^{210}Po	1 / 400	20 / 700	1000	100

R. Schnee et al [AIP Conf. Proc. **1549** (2013) 128]

- Electropolishing steel: H_3PO_4 + H_2SO_4 @ 2.4 V



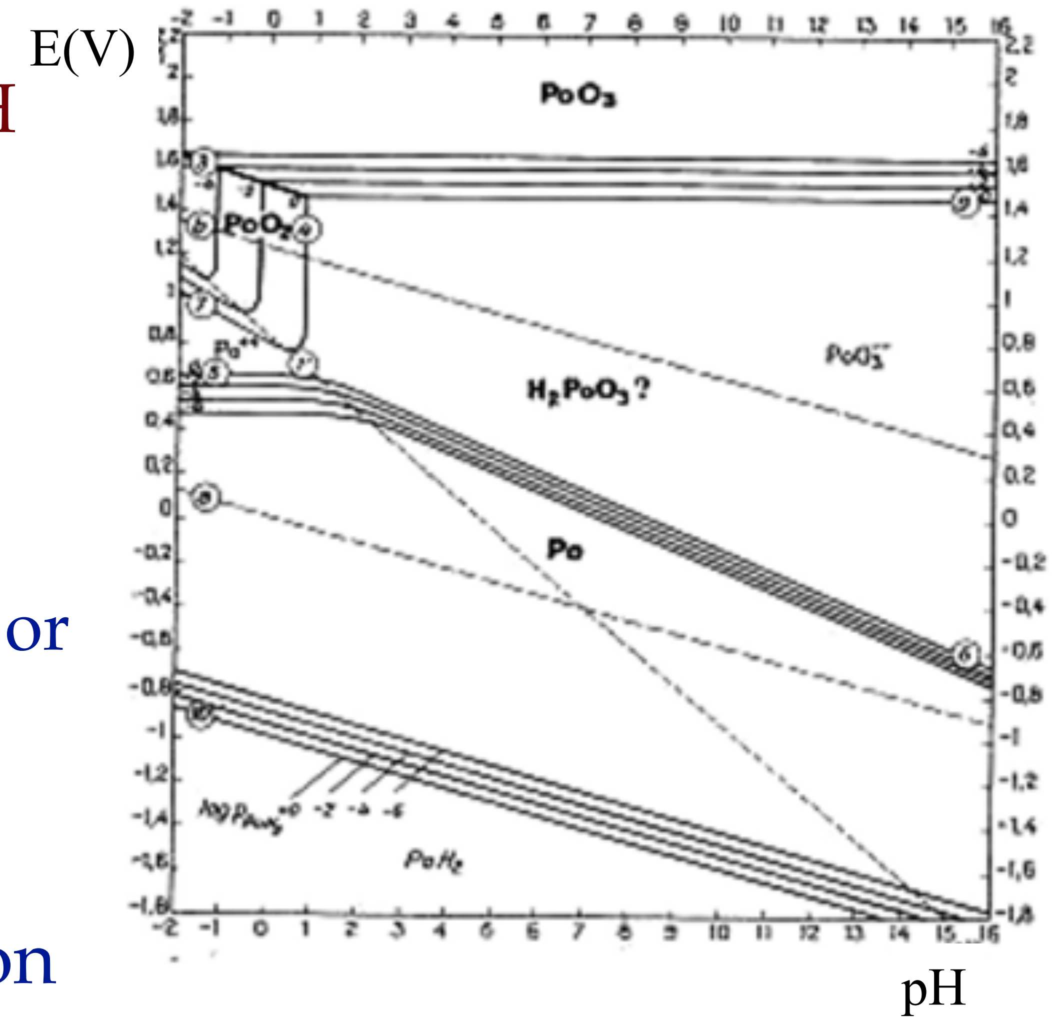
Po Chemical Behavior

Why the mixed results for surface ^{210}Po removal?

All methods use an acidic solution

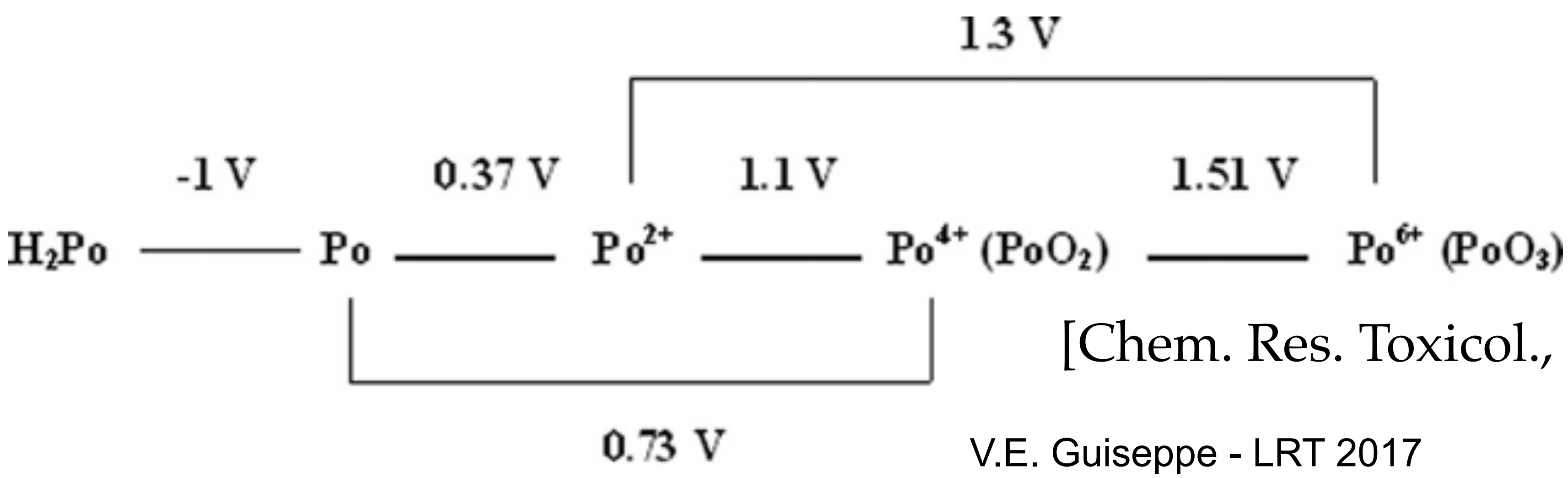
- Po (neutral) can exist in solution over the entire pH range
    - But, Po can redeposit or plate-out on the sample
- At low pH, Po can exist in a stable ion state
    - Favors staying in solution
    - Forced through applying an oxidation potential or an oxidizing agent

Po Pourbaix Diagram



The Po^{4+} state is expected to be the most stable in solution

Standard electrode potential of Po in acid solution



[Chem. Res. Toxicol., 2012, 25 (8), pp 1551–1564]

Po Behavior

The presence of an acidic solution is only the start.

Requirements to keep Po off the sample surface:

- Force Po into an ion state through oxidation, favorably Po^{4+}
- Sufficient solubility for the Po ions
- Stability of ion state hinders redeposition

The substrate atoms (e.g. Cu) is being oxidized as well

- Now there could be competition for the oxidizer (by applied potential or solution chemistry)

The kinetics of oxidation may be different between Po and the substrate atoms

- **Sufficient exposure to the oxidizer may be the determining factor of effective Po removal**
- Greater exposure can be accomplished several ways:
  - Agitation to make use of the full volume of solution, greater concentrations of the oxidizing agent, longer time, larger volumes of solution, etc.

Po Behavior

Why the mixed results for surface ^{210}Po removal?

Concentrated Nitric acid works well

- Aggressive on all metals
- Large amount of material removal

Electropolishing works well

- Aggressive acids
- Applied oxidizing potential
- Large amount of material removal

PNNL method: acidified H_2O_2 solution

- The H_2O_2 is the oxidizing agent
- Modest material removal - important for tight dimensional tolerances on small parts

Range of starting Po surface concentration by over a factor of 10 (0.2 - 3 cpm)

Activity generated by:

- electrodeposition of ^{209}Po
- Exposure to Rn gas to deposit progeny and build-up ^{210}Po

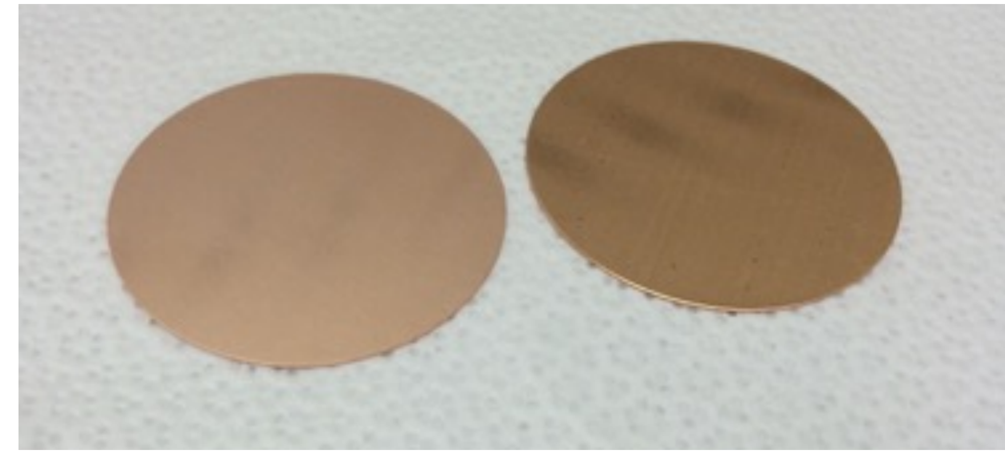
General conclusion is that higher Po surface activity requires more aggressive cleaning

Mixed results reinforce the role played by kinetics and competing ion concentration or solubility

Po Removal Stud

Focus on removal of ^{210}Po from Cu

- ^{210}Pb and ^{210}Bi removal well demonstrated



Cu samples

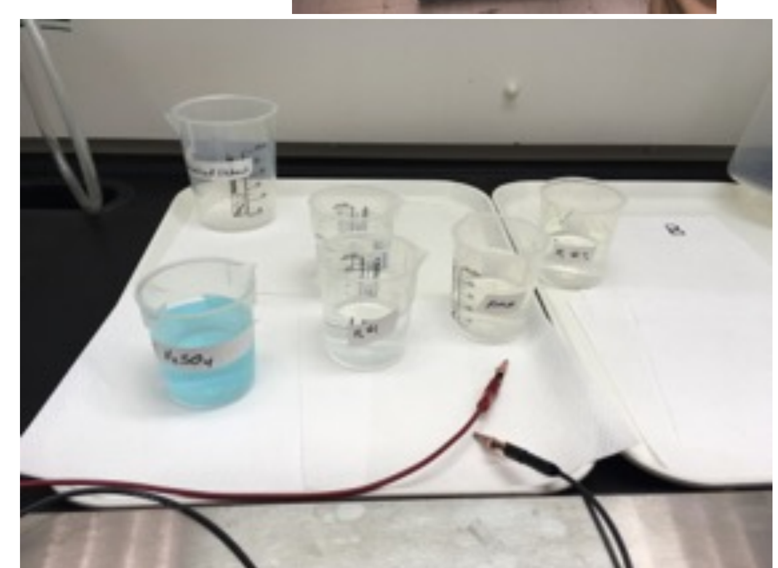
- 50-mm diameter, 0.5 mm-thick Cu foil disks
- Exposed to a 100 kBq radon source for ~ 1 month
- Achieved an alpha count rate of 300 counts/day

Alpha Detector

- Alpha spectrometer with an ion-implanted silicon detector.
- Samples counted before and after treatment
- Background of 6 counts/day

Goals:

- Study a combination of oxidizing methods
  - Increased hydrogen peroxide concentration
  - Apply a cell potential in solutions
  - Vary the pH



Po Removal Results

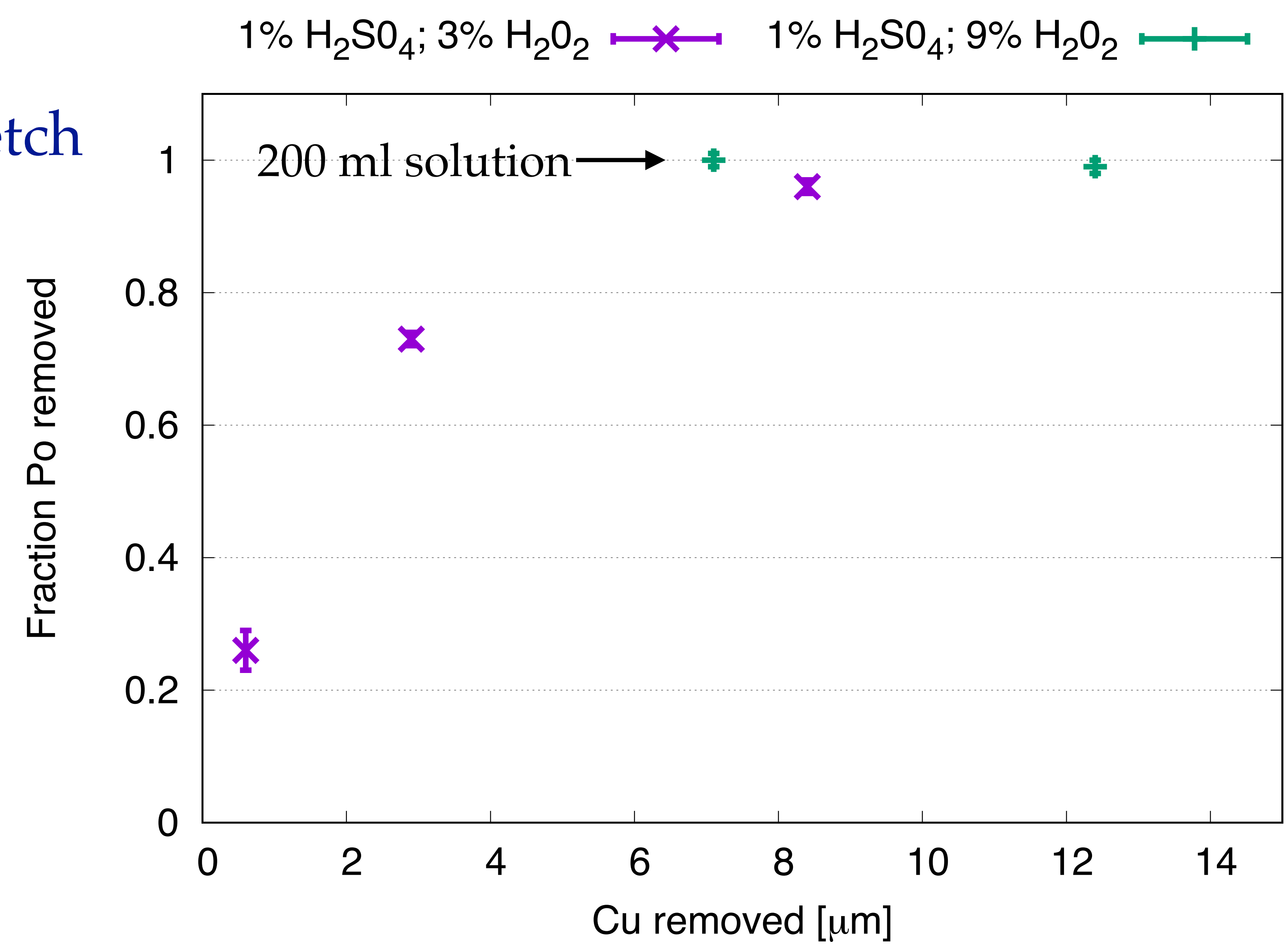
PNNL chemical solution

Samples agitated during the etch

100 ml solutions (one exception)

Adjusted the etching time and H_2O_2 concentration (the exposure to the oxidizing agent)

General trend in surface Po removal independant of H_2O_2 concentration



Should not generalize that the removal of Po achieved after sufficient depth of Cu removed

The implanted Po should exist <0.05 μm of depth

It's *not* the etch depth that alone determines the efficiency to remove Po

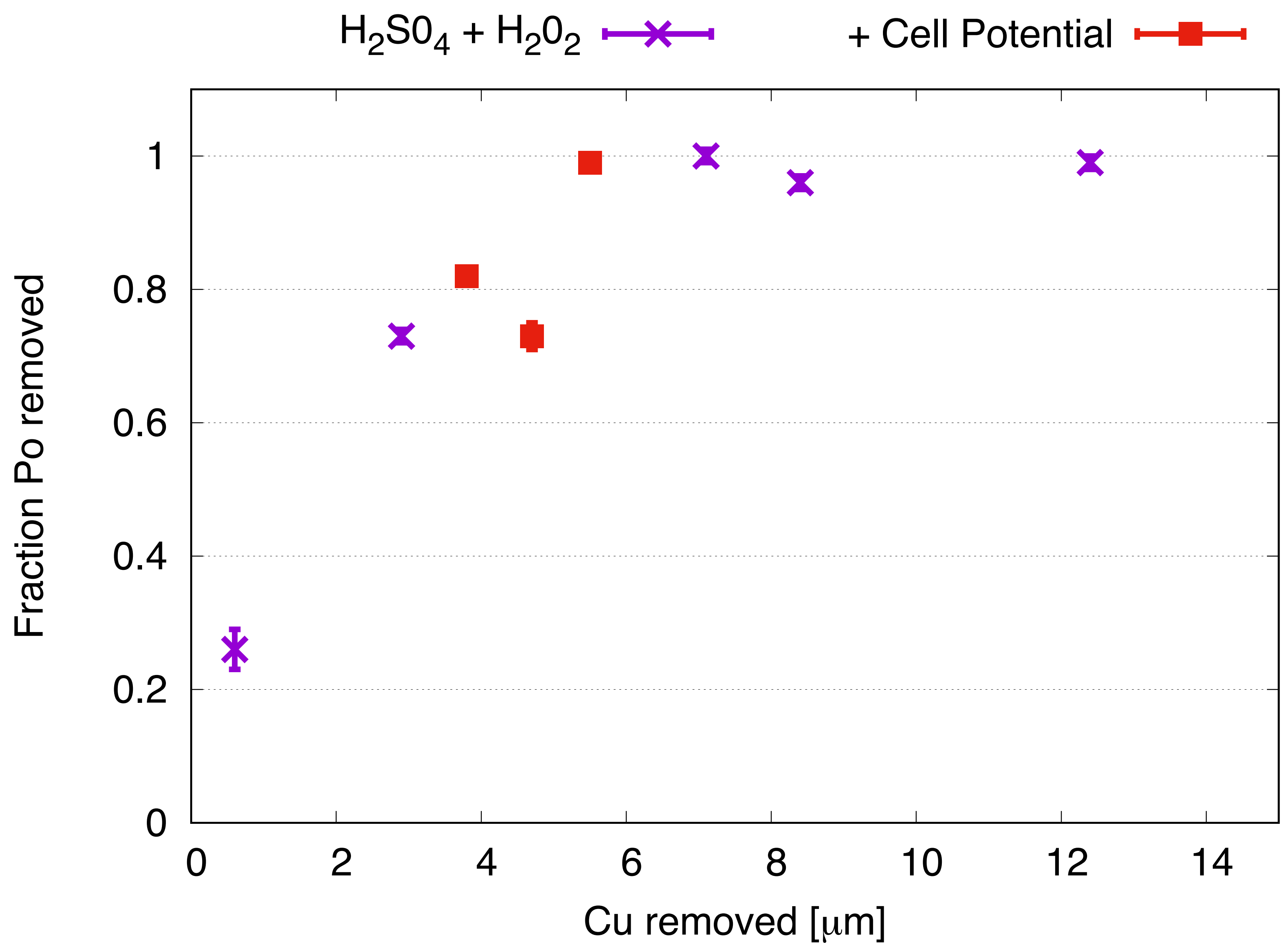
Po Removal Results

PNNL chemical solution

with a cell potential

Goal was to see if the cell potential increased the oxidation of Po

Can see that is not the case, no added benefit observed



Though the general trend is to improve Po removal, there exists some variability when only plotting against exposure

Next, look at initial Po surface concentration for effective treatments

(where > 2 um Cu removed)

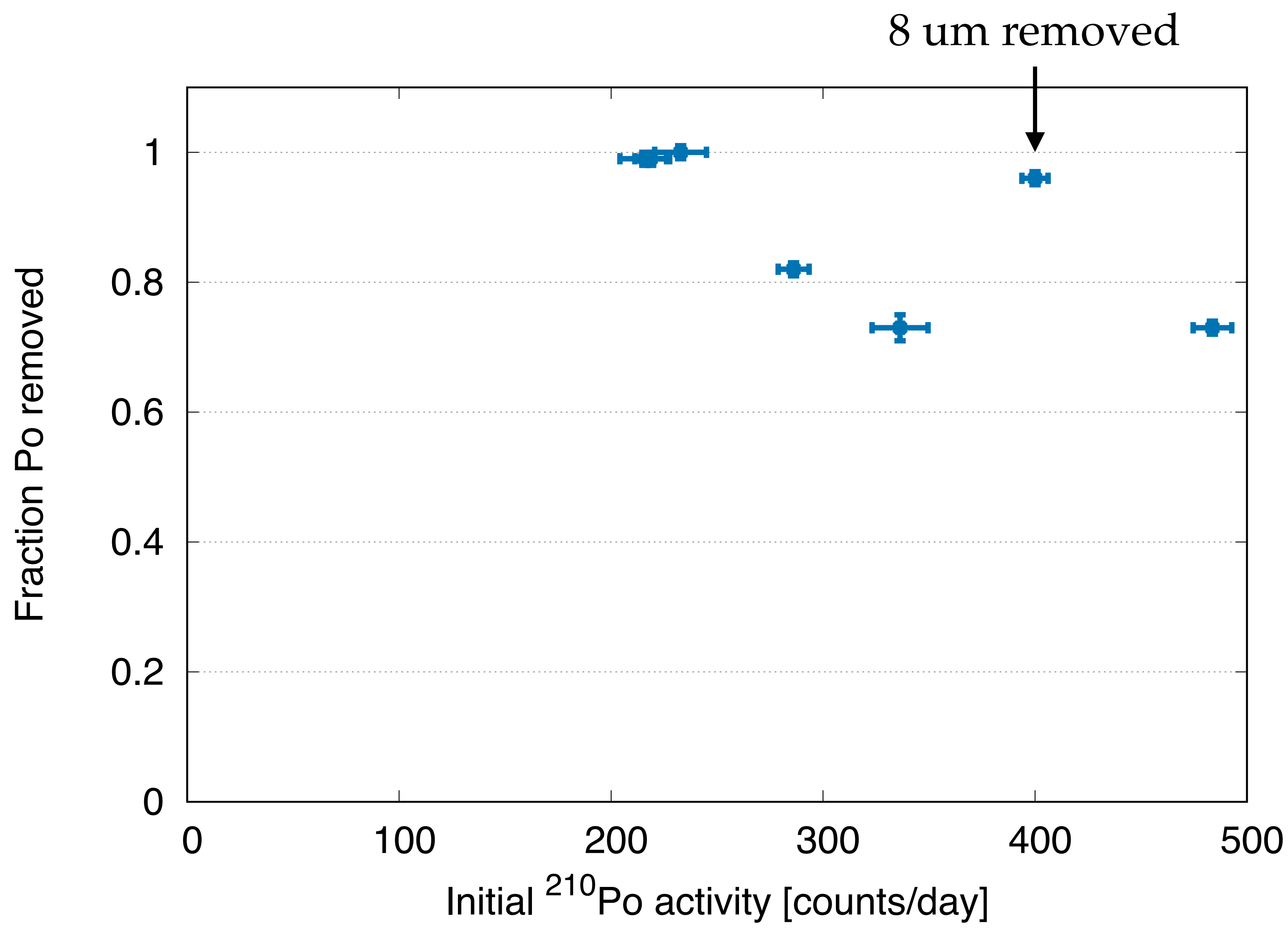
Po Removal Results

PNNL chemical solution

Reduction as a function of initial Po activity

Lower Po concentration generally improves Po removal

Noted sample did have deep Cu etch suggesting greater solution exposure



Suggests the concentration of Po on the surface relates to exposure required in solution

When the exposure to the oxidizing agent was increased, the Po removal was optimized

Po Removal Results

Alternate cleaning methods

Separate the peroxide oxidizing agent from cell potential

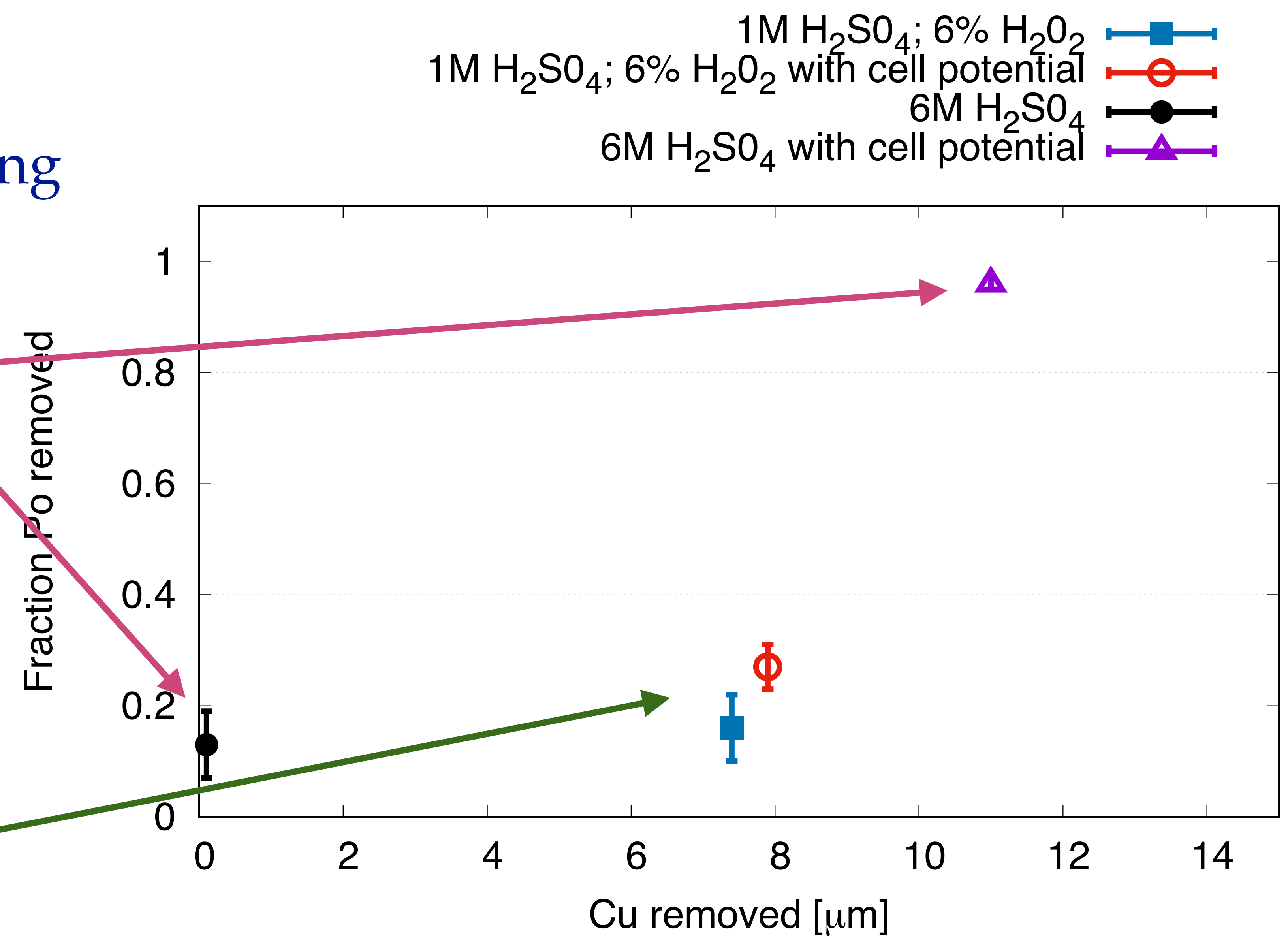
No peroxide

Cell potential required to remove Po and (and Cu)

Higher acidity in combination with peroxide

Not effective at removing Po, marginal improvement with an applied potential

Have a competition between Po and Cu, advantage to Cu with a lower oxidation potential



A cell potential alone can oxidize Po in an acidic environment - similar to standard electropolishing

No obvious advantage of applying a potential when an oxidizing agent is present

Outlook

- Rich history of studying radon progeny deposition and plate out
  - Likewise, successful studies that demonstrate methods to remove radon progeny from surfaces, including problematic ^{210}Po
- Next generation experiments will have even stronger demands for cleaning Rn progeny surface contamination
  - Desirable to use methods that provide efficient removal and ease of implementation
- Several factors that determine if the problematic ^{210}Po will stay in solution during cleaning and be removed from a surface
  - Oxidizing the Po should keep it in solution and prevent redeposition
  - Oxidation can be achieved by a oxidizing agent or an applied potential in the right environment
- The PNNL method is capable of efficiently removing Po from Cu
  - Need sufficient exposure to the oxidizing agent, especially when higher Po surface concentration is present: agitation of samples: greater solution volume
- Need further studies to better explore the effects of solubility and Po concentration on various substrates (i.e anode, witness plate, electrolyte)