

# Cleaning and passivation of copper surfaces to remove surface radioactivity and prevent oxide formation

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## Abstract

High-purity copper is an attractive material for constructing ultra-low-background radiation measurement devices. Many low-background experiments using high-purity copper have indicated surface contamination emerges as the dominant background. Radon daughters plate out on exposed surfaces, leaving a residual <sup>210</sup>Pb background that is difficult to avoid. Dust is also a problem; even under cleanroom conditions, the amount of U and Th deposited on surfaces can represent the largest remaining background. To control these backgrounds, a copper cleaning chemistry has been developed. Designed to replace an effective, but overly aggressive concentrated nitric acid etch, this peroxide-based solution allows for a more controlled cleaning of surfaces. The acidified hydrogen peroxide solution will generally target the Cu<sup>+</sup>/Cu<sup>2+</sup> species which are the predominant surface participants, leaving the bulk of copper metal intact. This preserves the critical tolerances of parts and eliminates significant waste disposal issues. Accompanying passivation chemistry has also been developed that protects copper surfaces from oxidation. Using a high-activity polonium surface spike, the most difficult-to-remove daughter isotope of radon, the performance of these methods are quantified. © 2001 Elsevier Science. All rights reserved

*Keywords:* ultra-low background; surface contamination; surface preparation; surface passivation; high-purity copper; double-beta decay

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## 1. Introduction

High-purity copper is an attractive material for constructing ultra-low-background radiation detectors. Copper has favorable mechanical, electrical, and thermal properties, and is easily purified. Intrinsically low in primordial radioisotopes (U, Th) and having no long-lived radioisotopes itself, copper benefits from the “electrowinning” process used during refinement. This processing step electroplates the material from a sulfate solution onto cathodes. Many contaminants of radiopurity significance do not follow copper in this step by virtue of their negative electrochemical values, and the resulting material, known as “electrolytic tough pitch” copper, is rather pure. Further processing, including smelting to improve purity and hot rolling to improve density and mechanical properties, is usually performed on commercial high-purity copper.

When even higher purity is required, additional electrolytic and chemical purification can be combined with a final fabrication step, resulting in “electroformed” copper parts of extreme purity. This electroforming process can even be done underground, providing a potential way to eliminate cosmogenic activation products seen in copper with above-ground exposure, e.g. <sup>60</sup>Co.

The low-background spectrometer history leading to the development of electroformed copper for this application has shown backgrounds evolving downward over fifteen years of radioassay and double-beta decay research at PNNL[1]. By the end of this period, cosmogenic backgrounds were recognized as being important factors. Electroformed copper had emerged as a material-of-choice for purity, as it allowed copper cosmogenic isotopes to be removed and its production technique allowed components of reduced mass.

Many low-background experiments which employ high-purity copper, e.g. Cuoricino[2], have indicated surface contamination emerges as the dominant background. Radon

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daughters plate out on exposed surfaces, leaving a residual  $^{210}\text{Pb}$  background that is difficult to avoid. Dust is also a problem; even under cleanroom conditions, the amount of U and Th deposited on surfaces can represent the largest remaining background.

Radiopurity is not the only motivation for surface cleaning; final machining processes also leave unwanted residues and copper fragments that make assembly difficult. Additionally, copper oxides can remain, creating unwanted absorptive surface area. Surface cleaning and preparation is thus critical to ensuring high purity copper parts and desired performance.

To address all these factors, an improved copper cleaning chemistry has been developed, the details of which are described below. Designed to replace an effective, but overly aggressive concentrated nitric acid etch, this peroxide-based method allows for a more controlled cleaning of surfaces.

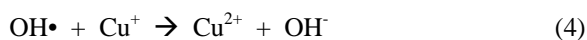
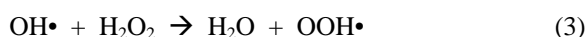
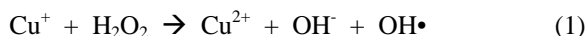
Additionally, a passivation technique was developed to inhibit the reformation of oxides on the surface in an effort to minimize recontamination.

## 2. Methods

Previously a strong nitric acid etch was employed for surface cleaning of high-purity copper; two examples of such baths are discussed in Reference [3]. It was not immediately clear that this aggressive cleaning process was necessary since nitric acid dissolves the bulk copper and could alter critical mechanical tolerances. To alleviate this problem, a refined technique was developed that removes loose fragments and surface contaminants with less impact on the base copper metal.

The new process developed (PNNL method) relies upon ultrasonic cleaning for gross fragment removal and an acidified peroxide chemistry for fine fragment, surface contamination, and oxide removal. The acidified hydrogen peroxide solution will generally target the  $\text{Cu}^+/\text{Cu}^{2+}$  species which are the predominant surface participants, leaving the copper metal intact. This preserves the critical tolerances of parts and eliminates significant waste disposal issues.

The following are the participant species of an acid-catalyzed peroxide-copper solution based on the Fenton's mechanisms,



Fenton oxidation is capable of self-generating oxidants (chiefly the OH radical, OOH radical, and oxygen species) when catalyzed by cupric or cuprous ion. The role of

hydrogen peroxide is complex; acting as both an oxidant in the first reaction and as a reductant in the second. The hydroxyl radical produced is one of the most potent oxidative species known with an  $E^\circ = \text{ca. } +3.0$  volts, rendering this a very effective cleaning method even at dilute concentrations.

A surface passivation step was required to prevent the reformation of oxides and control the IR emissivity of the copper. After testing ~30 passivation procedures[4], the preferred method for passivation was found to be room-temperature immersion in a 1% aqueous solution of citric acid. Cleaned copper parts are immediately immersed in the citric acid solution for up to several minutes. Excellent results have been achieved with this passivation step which was found to be made more resilient by baking 24 hours at 100°C.

In order to demonstrate the effectiveness of the cleaning and passivation processes, several small, identical copper disks cut from the same source material have been tested. Disks were subjected to differing combinations of the cleaning and passivation processes. Scanning electron microscopy was used to document the physical changes to the surfaces.

To evaluate the removal of radon daughters, polonium was chosen as a worst case scenario by virtue of its  $E^\circ = \text{ca. } +0.76$  volts, much greater than that of others formed.  $^{209}\text{Po}$  was used since its high specific activity and lack of environmental background eases measurement. One side only of the disk was subjected to a Po solution, allowing the Po to deposit onto the copper surface. After drying, alpha spectroscopy was used to quantify the Po deposited onto the surface. After cleaning, the side of initial Po deposit was counted for Po removal and the remaining side counted to evaluate redeposition of Po from the cleaning solution.

## 3. Results

### 3.1. SEM interrogation

Several copper coupons were scored on the surface to create fine copper fragments and to create a topographical reference. Scanning electron micrographs were obtained of each coupon before treatment as shown in Figure 1. Each was then subjected to a variety of processes. The passivated surface appeared the least affected by the cleaning process, as shown in Fig. 1-b. As expected, as the time and/or concentration of the treatment increased, the impact on the surface increased as well. The most aggressive cleaning treatment was concentrated nitric, which completely removed the scored surface and revealed a crystalline substructure. The acid/peroxide used for 2 and 5 minutes also revealed this substructure.

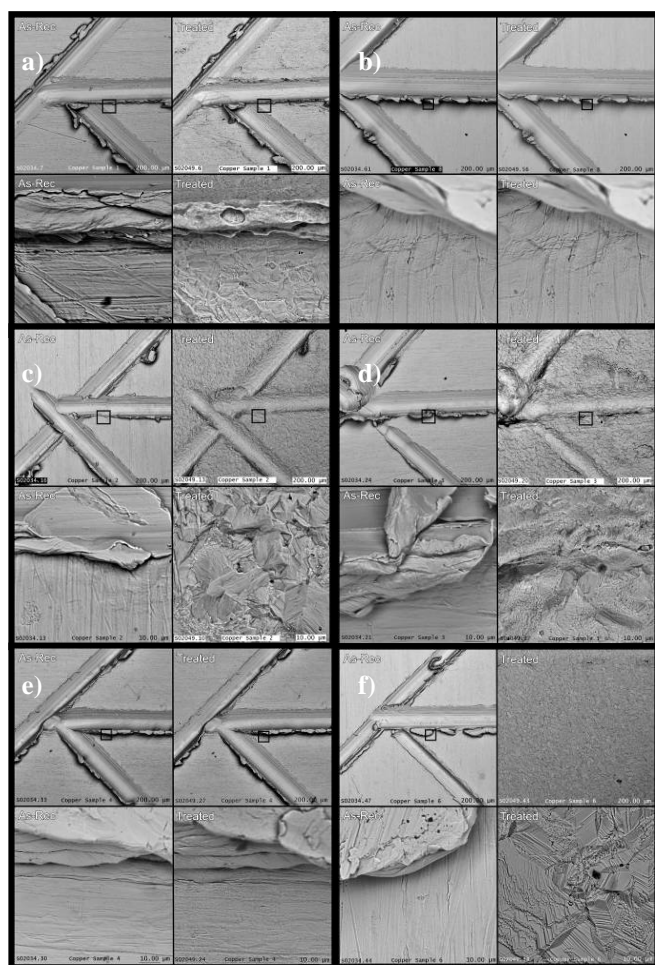


Fig 1: SEM images of copper coupons, left are before (top 200x and bottom 2000x magnification) and right, after treatment with various cleaning methods: a) PNNL method for 1 minute, b) passivated, baked, and then cleaned with the PNNL method for 1 minute, c) PNNL method for 2 minutes, d) PNNL method for 5 minutes, e) 4 M nitric acid for 1 minute, and f) concentrated (16 M) nitric acid for 1 minute.

### 3.2. Alpha spectroscopy of Po spiked Cu disks

#### 3.2.1. Experimental Procedure

A  $^{209}\text{Po}$  solution was prepared by drying down an existing solution in an HCl matrix and reconstituting in 1.3 M  $\text{H}_2\text{SO}_4$ . The activity of the reconstituted stock  $^{209}\text{Po}$  solution was calculated as 6.3 ( $\pm 0.4$ ) nCi/mL based on the certified value of the original  $^{209}\text{Po}$  solution. The  $^{209}\text{Po}$  was electrodeposited onto 24 copper disks (22-mm diameter) by placing 100  $\mu\text{L}$  of the stock  $^{209}\text{Po}$  tracer onto the surface and allowing the reaction to take place for 15 minutes. Three copper disks were spiked with a 1:100 dilution of the stock  $^{209}\text{Po}$  solution in the same manner. The disks were then rinsed with a stream of de-ionized (DI) water for approximately 10 seconds and allowed to air dry before counting via alpha spectroscopy.

Alpha spectroscopy measurements were performed with 25.4-mm diameter silicon diode charged-particle spectrometers calibrated at distances of 3 mm and 11 mm from the detector face. Upon completion of initial counts for the spiked disks, the disks were cleaned to remove the  $^{209}\text{Po}$  from the copper surface. The cleaning procedures used included submersion into 40 ml of 4 M, 6 M, and a concentrated nitric acid, and a 3% hydrogen peroxide/1% sulfuric acid mixture for variable lengths of time. The cleaned disks were rinsed with a stream of DI water to remove any residual acid and allowed to air dry.

The cleaned disks were then counted via alpha spectroscopy, using the same detector on which the initial spiked count was performed for each disk. The reverse sides of the cleaned disks were also counted to determine if redeposition of polonium was significant in the cleaning processes. Background counts, blank disks, and cleaned disks (front and back) were counted for 20 hours at 3 mm from the detector. Spiked counts were counted for 1 hour at 11 mm from the detector, with the exception of the disks spiked with the diluted tracer, which were counted for 16 hours at 3 mm from the detector.

#### 3.2.2. Cu Cleaning Results

With the polonium tracer used representing one of the most difficult-to-remove radon daughter isotopes, the cleaning results summarized below represent a worst-case test of each cleaning methodology. Figure 2 compares the cleaning techniques by presenting moles of copper removed versus the moles of polonium removed.

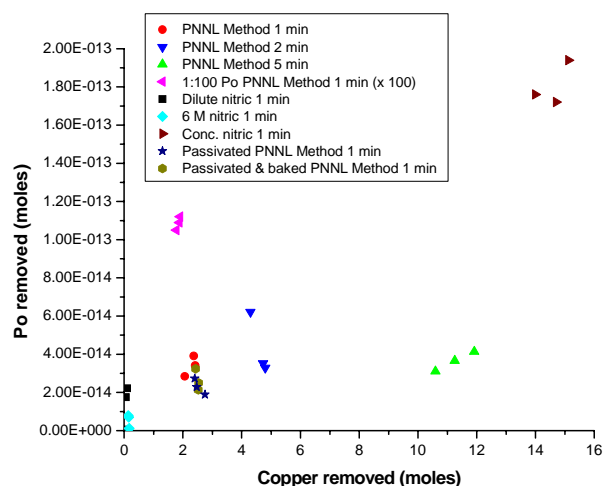


Fig 2: Comparison of molar quantities of material removed

Examination of the 4 M (dilute), 6 M, and concentrated nitric acid results show a roughly constant proportionality between the amount of  $^{209}\text{Po}$  removed and the amount of copper removed. Concentrated nitric acid was the most successful at removing the  $^{209}\text{Po}$  contamination and the greatest quantity of copper was removed as well. Dilute nitric removed less  $^{209}\text{Po}$  and less copper in similar

proportions. This suggests that for the nitric acid treatments a given quantity of  $^{209}\text{Po}$  removal is always accompanied by the loss of a proportional amount of copper. In the case of the acidified peroxide treatment, the data in Table 1 indicate the mass of copper removed was nearly linear in proportion to the treatment time. Although the amount of  $^{209}\text{Po}$  removed also increased with the treatment time, this increase was not proportional and was only an additional few percent, falling off sharply in the five-minute treatment. This was likely due to the copper ion concentration approaching that of the sulfate ion in solution. Redeeposited activity was also observed for this case further supporting that the capacity of the solution may have been reached.

A much greater proportion of the  $^{209}\text{Po}$  was removed from the surface when the concentration of the surface contamination spike was reduced by a factor of 100.

#### 4. Conclusions

These data demonstrate that an acidified peroxide cleaning method offers a more controlled removal of base copper metal than a classical concentrated nitric acid etch. This method may be preferable, particularly in more-realistic cases where surface contamination from polonium is much less. The quantity of polonium used in this study would represent gross contamination. In instances of significant contamination, concentrated nitric acid cleaning may still be indicated.

Although subjective, the SEM results demonstrated that surface details are best retained using acid peroxide cleaning, particularly when the surface is passivated and baked. However, passivation does seem to render the surface more subject to copper removal and may be the only mechanism at work. Typically the passivation is only used after the initial cleaning so it is difficult to assess if it would help to prevent radon daughter deposition on the surface or ease subsequent cleaning. It was observed to be slightly hydrophobic during the deposition of polonium.

#### References:

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Cleaning Process	% Mass Removed	% Activity Removed	% Activity Redeeposited
Clean w/ PNNL method 1 min	3.80%	16.01%	N/A
Clean w/ PNNL method 1 min	4.34%	18.62%	0.05%
Clean w/ PNNL method 1 min	4.18%	21.35%	0.03%
Clean w/ PNNL 1 min + 1 min	7.68%	19.65%	0.07%
Clean w/ PNNL 1 min + 1 min	8.25%	19.69%	0.08%
Clean w/ PNNL 1 min + 1 min	8.34%	28.57%	0.08%
Clean w/ PNNL method 2 min	8.43%	18.77%	0.12%
Clean w/ PNNL method 2 min	8.65%	17.33%	0.13%
Clean w/ PNNL method 2 min	7.78%	34.86%	0.12%
Clean w/ PNNL method 5 min	19.31%	21.21%	0.39%
Clean w/ PNNL method 5 min	19.28%	16.87%	0.48%
Clean w/ PNNL method 5 min	20.68%	24.18%	0.48%
1:100 dilution of Po, Clean w/ PNNL 1 min	3.40%	66.11%	< 0.47%
1:100 dilution of Po, Clean w/ PNNL 1 min	3.36%	54.71%	0.37%
1:100 dilution of Po, Clean w/ PNNL 1 min	3.22%	62.33%	< 0.51%
Clean w/ 4 M nitric acid 1 min	0.19%	12.58%	0.01%
Clean w/ 4 M nitric acid 1 min	0.15%	0.31%	0.01%
Clean w/ 4 M nitric acid 1 min	0.10%	10.49%	0.02%
Clean w/ 6M nitric acid 1 min	0.27%	3.68%	0.02%
Clean w/ 6M nitric acid 1 min	0.25%	4.15%	0.02%
Clean w/ 6M nitric acid 1 min	0.31%	0.63%	0.03%
Clean w/ conc. nitric acid 1 min	26.57%	96.35%	0.09%
Clean w/ conc. nitric acid 1 min	26.98%	99.56%	0.05%
Clean w/ conc. nitric acid 1 min	24.68%	98.26%	0.05%
Pass., Clean w/ PNNL 1 min	4.41%	13.89%	0.13%
Pass., Clean w/ PNNL 1 min	5.11%	10.62%	0.06%
Pass., Clean w/ PNNL 1 min	4.29%	16.09%	0.07%
Pass., Clean w/ PNNL method 1 min + 1 min	7.60%	19.38%	0.14%
Pass., Clean w/ PNNL method 1 min + 1 min	9.46%	10.14%	0.11%
Pass., Clean w/ PNNL method 1 min + 1 min	8.4%	28.86%	0.12%
Pass./Bake, clean w/ PNNL method 1 min	4.53%	18.52%	0.05%
Pass./Bake, clean w/ PNNL method 1 min	4.44%	12.06%	0.04%
Pass./Bake, clean w/ PNNL method 1 min	4.53%	15.03%	0.04%

Table 1: Quantity of copper dissolved, surface contamination removed, and contamination redeeposited for a given surface treatment.