

CORROSION PRODUCT IDENTIFICATION AND RELATIVE RATES OF CORROSION OF
CANDIDATE METALS IN AN
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ABSTRACT

Previously reported work by others indicates that dicopper trihydroxide nitrate, $\text{Cu}_2\text{NO}_3(\text{OH})_3$, forms on copper and copper alloys subjected to irradiated moist air near room temperature. We have performed experiments over a range of temperature and humidity, and have found that this species is formed at temperatures up to at least 150°C if low to intermediate relative humidities are present. At 150°C and 100% relative humidity, only Cu_2O and CuO were observed. The relative general corrosion rates of the copper materials tested in 1-month experiments at dose rates of 0.7 and 2.0 kGy/h were $\text{Cu} > 70/30 \text{ Cu-Ni} > \text{Al-bronze}$. High-nickel alloy 825 showed no observable corrosion.

INTRODUCTION

The U.S. Department of Energy, through its Office of Civilian Radioactive Waste Management, is conducting the Yucca Mountain Project. The purpose of this project is to determine the suitability of Yucca Mountain, in southern Nevada, as a location for a high level nuclear waste repository. Lawrence Livermore National Laboratory (LLNL) is concerned with evaluating waste package performance for the proposed repository, and Argonne National Laboratory is under subcontract to LLNL to perform experimental work.

In order to give "reasonable assurance" of "substantially complete" containment for 300 to 1000 years, as required in federal regulation 10CFR Part 60, we need to develop a rather complete understanding of the oxidation and corrosion behavior of the waste package material in the expected environment over long time periods. This understanding is needed both for selection of the container material and for assessment of waste package performance.

The expected environment in the unsaturated zone proposed for the repository is moist air. The temperatures of the packages are expected to rise initially because of nuclear decay heat and then to drop slowly over long times. The highest temperature expected at a container surface is about 200 to 250°C . For many packages the surface temperature will be maintained above the local boiling point (96°C) throughout the containment period, preventing the existence of

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more than a few molecular layers of liquid water on the container surface. After the temperature drops below the boiling point, the packages are still expected to remain dry, because the vadose water is expected to be confined to pores in the rock and to undergo matrix flow under the influence of capillary forces and gravity. In addition, since each package will always be at a higher surface-averaged temperature than the nearby rock wall, any liquid water on a package would tend to undergo net evaporation from the package and condensation on the rock.

A significant difference between the waste package environment and the usual moist air corrosion environments is the presence of ionizing radiation near the containers. The only significant form of ionizing radiation that will be present outside the containers is gamma radiation [1]. The highest dose rates are expected to be in the 10^2 Gy/h range and to decrease with time approximately in accordance with the 30-year half-life of Cs-137, the principal gamma emitter during the containment period.

Currently six primary candidate materials are being considered for the container: three austenitic alloys, namely types 304L and 316L stainless steels and high-nickel alloy 825, and three copper-based materials, namely CDA 102 (oxygen-free copper), CDA 613 (7% aluminum bronze), and CDA 715 (70/30 copper-nickel). There is considerable experience with the use of these materials in moist air environments, but, particularly in the case of the copper-based candidates, less is known about their performance when radiation is present.

This paper reviews previous research on the behavior of copper-based materials in irradiated moist air and gives an account of short-term experiments we have performed to identify the corrosion products formed on the copper-based candidates and on alloy 825 in this environment over a range of temperature and relative humidity.

PAST OBSERVATIONS OF THE OXIDATION/CORROSION OF COPPER-BASED MATERIALS IN IRRADIATED MOIST AIR

In 1954, Prinsak and Fuchs [2] reported that "certain metals and alloys which are subject to nitric acid corrosion (e.g., aluminum, cobalt, copper, inconel, lead, and nickel) were coated with nitrates or basic nitrates when irradiated in moist air, while others not subject to nitric acid corrosion remained uncoated (gold, stainless steel)." The connection with nitric acid is that it forms when moist air is irradiated, as discussed below. They found no corrosion in irradiated dry air. They also reported that "E.J. Hart (Argonne National Laboratory) brought to our attention a polonium sample which he had suspended in a jar with a copper battery clip some six months previous. The battery clip was coated with a rather heavy blue-green deposit which must have been hydrated cupric nitrate." Actual chemical analysis of this deposit was not reported, nor was an estimate of the dose reported. The supposition that it was hydrated cupric nitrate was apparently based on a knowledge of the reaction of nitric acid with copper. It now seems more likely to us, based on our results, that it was dicopper trihydroxide nitrate.

Shatalov and Nikitina [3] (1958) investigated the oxidation-corrosion behavior of copper, aluminum, stainless steel, and carbon steel in both dry and humid air with and without alpha irradiation. The temperatures were between 20 and 25°C. Relative humidities of 100%, 73%, 44%, and 9% were used, in addition to air dried with silica gel. The vessel was made of glass and had a volume of 375 cm³. The alpha radiation sources were made of Po-210, with activities of 5.6, 28, and 56 GBq. The experiments lasted up to 30 days. Weight gains of the samples were monitored by microgravimetry. The surface area of the samples was not given, but appears from the diagram, data, and specified uncertainty in the paper to have been of the order of 1 cm². If one assumes that all the alpha particles were absorbed in the air (an overestimate by perhaps a factor of 2) the dose rate using the 56 GBq source would have been 0.38 MGy/h, and the dose at 30 days would have been 0.27 Ggy.

Shatalov and Nikitina found that the rates of weight gain for irradiated dry air were similar to those for non-irradiated air in their room temperature experiments. However, the presence of both humidity and irradiation together gave significant increases in the weight gains of copper, aluminum, and carbon steel, with copper showing the largest weight gains. The relative weight gains of copper, aluminum, and carbon steel in this order were 1.8:1.1:0.8 for 73% relative humidity. The stainless steel did not show observable weight changes. The copper weight gains increased with increases of humidity and of dose rate. At 9% relative humidity, the weight increase of copper was logarithmic with time. At 44 and 73%, it was parabolic. At 100% relative humidity, it was linear with time. The copper samples tested at relative humidities of 100, 73, and 44% became coated with a thick layer of moist, blue-colored corrosion products which were reported to be Cu(NO₃)₂·3H₂O, but the method of chemical analysis was not given. (It now appears likely to us that this material was dicopper trihydroxide nitrate.) The highest rate of weight gain was observed for copper at 100% relative humidity and a source strength of 56 GBq. The rate amounted to 0.454 g/m².h.

Byalobzheskii [4] (1970) reported experiments in which a 99.99% pure copper sheet specimen was placed in a glass vessel of volume in the range 600 to 800 cm³ and was bombarded using a 4.1 microampere, 800 kV electron accelerator in the presence of air at 20°C and 98% relative humidity. The resulting dose rate in the air was 0.16 MGy/h. After 16 hours of irradiation, the sample had an "olive-green band on the periphery and brown-red corrosion products in the middle." [Presumably, the olive-green phase was dicopper trihydroxide nitrate (see below), and the brown-red phase was Cu₂O.] The increase in the weight of the sample was 7.50 g/m². The surface area of the sample was not given, but appears from the drawings to have been no more than a few cm².

In the absence of irradiation, Byalobzheskii observed no change, all other conditions being the same. Comparison experiments showed Armco iron to be twice as heavily corroded as copper, while zinc and aluminum were less corroded, and stainless steel showed no observable corrosion at all. Further experiments with iron samples showed that the corrosion was inhibited when the sample was directly bombarded

with electrons at a sufficient power level such that it heated up to "iridescent temperatures". Byalobzheskii stated that corrosion was most severe when the temperature was maintained low enough that a liquid film could exist on the sample. The rate of corrosion increased both with increases in dose rate and in humidity. Irradiated dry air was found not to produce observable corrosion. X-ray diffraction analysis of corrosion products on copper reportedly "failed to show evidence of any distinct phase." Chemical analysis revealed "nitrate salts whose composition could not be determined with accuracy. In addition the analytical data indicated the presence of a certain amount of copper hydroxide." It is not clear from this whether x-ray diffraction peaks were not observed, or whether they were observed but could not be identified with the data library then available to Byalobzheskii. If the latter was the case, as seems likely, it appears that these observations are consistent with the presence of dicopper trihydroxide nitrate on the samples.

Makepeace [5] (1974) performed corrosion tests on sixteen metals in 100% relative humidity air at room temperature for six months in a gamma radiation field ranging from 1 to 60 kGy/h. He used a sealed aluminum vessel with deionized liquid water in the bottom. Copper-containing samples included oxygen-free copper, 70/30 brass tubing and strip, and K-Monel. The brass specimens exhibited severe cracking. The oxygen-free copper exhibited general corrosion rates which were about an order of magnitude greater than those of the stainless steels, and also about an order of magnitude less than those of mild steel. The K-Monel corroded about twice as fast as the stainless steels. The corrosion rates of the stainless steels were less than 0.13 micrometers per year. Makepeace identified a mixture of $\text{Cu}_2\text{NO}_3(\text{OH})_3$ and zinc dihydroxide nitrate on the brass specimens by x-ray diffraction. Atacamite (dicopper chloride trihydroxide) was also found, the chloride coming from the water.

In 1984, it was noted by one of the present authors (R.V.K.) that a light blue-green deposit covered the outside surface of an internally water-cooled copper block exposed to the room air near the beam stop in the "zero degree cave" of the 100-MeV electron linear accelerator at Lawrence Livermore National Laboratory. This block was thought to have been in place for several years (the facility was about 15 years old), and the area was subject to very high but variable and unquantified levels of ionizing radiation during accelerator operation. The total dose is thought to be greater than 0.1 GGy. A powder sample was collected by scraping. X-ray diffraction analysis clearly revealed it to be composed of the monoclinic form of $\text{Cu}_2\text{NO}_3(\text{OH})_3$, as is shown in Table I. No other phases were found.

Recently, as part of the Yucca Mountain Project, Yunker [6-8] performed irradiated corrosion experiments on CDA 102 (oxygen-free copper), CDA 613 (7% Al-bronze), and CDA 715 (70/30 copper-nickel) in moist air at 95°C and 150°C using gamma ray dose rates in the range 0.02 to 5 kGy/h for periods up to 16 months. These experiments were part of a limited-time feasibility study directed toward identifying any major effects that might be produced by corrosion under irradiation. As such, a large number of specimens were placed in a small volume to improve the statistics of the results, and only

the middle portions of the corrosion layers were examined in detail. In the 95°C irradiation, the air was nearly saturated with water vapor, but care was taken to keep it slightly unsaturated. For the 150°C irradiation the air was humidified by bubbling it through water at 75 to 80°C before heating. General corrosion rates varied from 0.25 to 3.8 micrometers per year at 10,000 hours of exposure. Only CuO and Cu₂O were found on pure copper, as identified by X-ray diffraction. The compound (Cu_{0.2}Ni_{0.8})O was identified on one copper-nickel specimen. No nitrates were observed. Nitrogen was sought but not found in Auger analysis of corrosion layers. Subsequent XRD analysis at Argonne National Laboratory of greenish phases evident on some of the immersed coupons showed that these phases were associated with constituents of the Well J-13 water used, and were not nitrates.

Recently, Brehm [9] reported significant increases in the corrosion rates of copper and 90/10 cupronickel irradiated in an air-steam mixture at a temperature of 250°C and dose rates up to 100 Gy/h. No description of the corrosion products was given.

FORMATION OF DICOPPER TRIHYDROXIDE NITRATE IN IRRADIATED MOIST AIR

The detailed mechanism of formation of Cu₂NO₃(OH)₃ on copper in irradiated moist air is not known. However, it is clear that at least nitrogen and water vapor must be present. The presence of molecular oxygen is also necessary, since ammonia is found to be the primary product in water-nitrogen mixtures, and this would not lead to formation of Cu₂NO₃(OH)₃. The relationship between the initial oxygen content and nitrogen dioxide yield (which is the precursor to nitric acid formation), was determined by Jones [10] and goes through a maximum at 15.4 mole%, which is slightly less than the concentration of oxygen in air.

Molecular nitrogen in the air cannot participate in Cu₂NO₃(OH)₃ formation until it is decomposed by the irradiation. Although, as was pointed out by Lewis and Randall [11] in 1923, molecular nitrogen is thermodynamically unstable in the presence of atmospheric oxygen and water with respect to formation of nitric acid, the kinetics of this reaction are extremely slow, and nitrogen is in fact inert at moderate temperatures. In practice, significant fixation of atmospheric nitrogen occurs only as a result of electrical discharge (such as lightning or corona), high temperature processes (such as in automobile engines or fossil-fueled power plants), the action of certain bacteria, or bombardment by ionizing radiation (such as cosmic rays).

The processes involved in the irradiation of moist air have been reviewed by Reed and Van Konyenburg [12]. Briefly, irradiation produces a host of ionized, excited, and free radical species, which interact with each other and with the oxygen and water vapor in the air, producing ozone and nitrogenous species. The total rate of fixation of nitrogen as NO, NO₂, and HNO₃ is limited by the radiation-chemical yield of atomic nitrogen (N). This yield has been measured at values ranging between G = 3.9 and 7.3 N atoms per 100 eV of absorbed energy, depending on conditions.

BACKGROUND ON DICOPPER TRIHYDROXIDE NITRATE

The compound of composition $\text{Cu}_2\text{NO}_3(\text{OH})_3$ (also written as $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{Cu}(\text{OH})_2$) is now known as dicopper trihydroxide nitrate by the 1970 rules of I.U.P.A.C. nomenclature [13]. In the past it has also been referred to variously as copper hydroxynitrate, cupric trihydroxy-nitrate, basic cupric nitrate, basic copper nitrate, or copper hydroxide nitrate. Early data on this compound are summarized by Mellor [14] and Gmelin [15]. It can be synthesized from aqueous solutions in the laboratory in various ways, two of them being by the heating of copper (II) nitrate solution and by precipitation from copper (II) nitrate solution by addition of alkali hydroxide or ammonium hydroxide [16].

The compound assumes two crystalline forms: monoclinic and orthorhombic. Laboratory synthetic methods lead predominantly to the monoclinic form. The orthorhombic form, on the other hand, occurs as a rare natural green mineral (Gerhardtite) in Zaire and in Arizona [17,18]. In these occurrences it is found as a secondary mineral in the oxidation zone of massive cuprite (Cu_2O) deposits. The natural mineral was named Gerhardtite by Wells and Penfield [19] in honor of Charles F. Gerhardt, the chemist who was the first to determine the true composition of the synthesized form.

$\text{Cu}_2\text{NO}_3(\text{OH})_3$ is also occasionally observed as a product of atmospheric corrosion of copper [20]. One example is the patina on copper conductors for railways in the Japanese Alps. Aoyama [21] notes that the $\text{Cu}_2\text{NO}_3(\text{OH})_3$ forms near areas where electrical discharges occur on the conductor. In addition, there are frequent thunderstorms there, which lead to the fixation of nitrogen by lightning, and this is also thought by Aoyama to contribute to the formation of $\text{Cu}_2\text{NO}_3(\text{OH})_3$. Mattsson and Holm [22] have reported observation of this corrosion product on copper-based materials from a 7-year field test in Sweden, primarily on specimens exposed in a rural area.

Le Ny et al. [23] have produced $\text{Cu}_2\text{NO}_3(\text{OH})_3$ in the laboratory by corona discharge in air between copper electrodes. Raffalovich [24] has observed it in the bellows of copper waveguides as a result of arcing within the bellows.

Two chemical properties of $\text{Cu}_2\text{NO}_3(\text{OH})_3$ are of interest in the present context: solubility and thermal decomposition. The solubility in water at 18°C is less than 10^{-5} moles of Cu per liter [15]. No information is available on the temperature dependence of the solubility. In boiling water, $\text{Cu}_2\text{NO}_3(\text{OH})_3$ darkens in color but does not decompose. The temperature of the onset of thermal decomposition has been reported by various early researchers to be as low as 165°C and as high as 400°C [15]. Gmelin suggests that the lower values apply to decomposition of moist salt, whereas the higher values apply to the dry state. The most recent studies have been performed by Auffredic et al [25] and by Ilcheva et al [26]. The former observed the beginning of decomposition at about 170°C, using a heating rate of 3°C per hour. The latter reported the onset at

about 205°C, with heating rates in the range from 240 to 1200°C per hour.

Mattsson [27] has presented a diagram showing the domain of thermodynamic stability of $\text{Cu}_2\text{NO}_3(\text{OH})_3$ in terms of pH and nitrate concentration, for an aerated aqueous solution at 25°C and 0.1 M Cu concentration. His diagram shows that $\text{Cu}_2\text{NO}_3(\text{OH})_3$ is stable only for nitrate concentrations above about 3×10^{-2} M, and in a narrow pH range between about pH 4 and pH 6. This accounts for the success of laboratory synthetic methods involving relatively concentrated solutions of copper (II) nitrate, since the Cu (II) ion-copper (II) hydroxide equilibrium holds the pH in the proper range for $\text{Cu}_2\text{NO}_3(\text{OH})_3$ stability in such solutions. This is also compatible with the copious formation of $\text{Cu}_2\text{NO}_3(\text{OH})_3$ observed in the recent YMP-sponsored experiments of H.D. Smith [28], in which 0.1 M nitrate concentrations (as copper (II) nitrate) were maintained at 90°C in contact with copper metal.

DESCRIPTION OF EXPERIMENTS

A series of short-term experiments was performed in irradiated moist air to determine the relationship between corrosion product formation and the irradiation environment. These experiments were performed at several values of relative humidity and temperature, at pressures that were equal to the sum of 88 ± 3 kPa of air at the temperature of the experiment and the vapor pressure of the water content corresponding to the stated relative humidity at the temperature of the experiment. For example, the experiment at 150°C and 100% RH had a total pressure of 88 kPa plus 476 kPa, for a total of 564 kPa.

One coupon each of four of the six candidate materials was exposed in each experiment. The candidate materials selected were high-nickel alloy 825 and copper alloys CDA 102, CDA 613 and CDA 715. All coupons were cut using a water-cooled cut-off wheel. Typical dimensions of the coupons were 1-2 mm thick, 1 cm wide, and 2 cm long. The coupons typically weighed 2 to 3 grams. All coupons were polished to 600 grit, cleaned according to ASTM procedures and rinsed ultrasonically in high-purity water. After air drying, they were suspended in the irradiation vessel from a fused silica support.

The irradiation vessel was made of 304L stainless steel and fitted with an H-series stainless steel bellows valve. The vessel had a 6.0 cm ID with a height of 8.9 cm, corresponding to a volume of 256 cm³ and steel surface area of 224 cm². Dosimetry was performed in-situ using nitrous oxide as the dosimeter gas.

The initial set of experiments was performed at 120°C. The dose rate in this set was 2 kGy/h. Three relative humidities were investigated: 0(+ 0.1, -0)% , 1.5 \pm 0.3%, and 15 \pm 3%. To move toward more repository-relevant conditions, subsequent experiments were performed at a lower dose rate and with a wider range of relative humidities. Experiments at 90 and 120°C were performed at 0.7 kGy/h with relative humidities of 0(+ 0.1, -0.)%, 15 \pm 1%, and 100%. The purpose of the 100% relative humidity experiments was to

provide data to compare with two-phase and high-humidity experiments performed elsewhere.

The initial and final gas phases were analyzed via gas chromatography for nitrogen, oxygen, carbon monoxide, carbon dioxide and nitrous oxide content. Following gas chromatography analysis, the post-irradiation gas phase was trapped in a 1:500 sulfuric acid solution and subsequently analyzed for nitrate using a nitrate-specific ion-selective electrode. The irradiation vessel walls were also rinsed with the 1:500 sulfuric acid solution and analyzed for nitrate content. Corrosion products, when formed in sufficient quantities, were analyzed using a combination of XRD and SEM/EDS. Weight gain and weight loss measurements were also made.

RESULTS OF EXPERIMENTS

The temperatures, doses, initial gas composition, and final gas compositions for the experiments are given in Table II. The major and minor phases identified as corrosion products are given in Table III. The irradiated moist-air system was relatively aggressive towards copper-based materials, with the extent of corrosion strongly dependent on the moisture content of the gas phase.

In the experiments performed, at all three temperatures, no evidence of atmospheric corrosion was noted on the Alloy 825 coupons (based on weight change and visual evidence under a 50X microscope). These went in and came out "mirror" shiny. This material was less reactive than 304L stainless steel (composition of the irradiation vessel), as light tarnishing and dulling of the vessels were noted in high-moisture, irradiated experiments.

The copper coupons exhibited the most extensive uniform corrosion of the materials tested. The corrosion products were copper(I) oxide and $\text{Cu}_2\text{NO}_3(\text{OH})_3$ in the intermediate (15% RH) and low moisture experiments performed. Only copper(I) and copper(II) oxides were found in the high-moisture 90°C and 150°C experiments. At the higher temperatures the appearance of the coupons changed progressively as a function of the moisture content of the irradiation environment. In dry-air systems, only light tarnish was noted. At intermediate moisture levels, a brown/yellow scale began to develop, turning into a black/brown scale in the 100% RH 150°C experiment. Light pitting was noted in the 15% RH experiment performed at 150°C.

The copper/nickel coupons were also very reactive in the irradiated environments. In dry-air experiments, a light dulling was evident, turning the color of the coupon from silver to bronze. As the moisture content was increased, a darker (almost black) scale developed. This was primarily a nitrate phase at intermediate moisture levels, becoming predominately Cu_2O at 100% RH. Pitting was noted in the 15% RH experiments performed at 120°C. These pits were filled with a green phase that was identified as $\text{Cu}_2\text{NO}_3(\text{OH})_3$.

The aluminum bronze coupons were also reactive in the irradiated moist-air system, but appeared to react more uniformly. In dry-air experiments, only a light dulling was noted, with no significant change in color. A trace amount of a nitrate phase was noted. In intermediate moisture experiments (15% RH) a darkening of the coupon

was noted, but there was no scale formation. The major corrosion product was $\text{Cu}_2\text{NO}_3(\text{OH})_3$. At high moisture levels (100% RH at 90°C and 150°C), a patchy dark bronze/black scale was noted over the entire surface of the coupon. The corrosion product identified was copper (I) oxide with lesser but substantial amounts of copper (II) oxide. No nitrate phase was evident. No evidence of pitting was noticed on any of the aluminum bronze coupons.

COMPARISON WITH PREVIOUS EXPERIMENTS AND OBSERVATIONS

Table IV summarizes the previous research by others. With the exception of Yunker's work, all these experiments and observations were conducted under room temperature, low absolute humidity conditions, and all showed corrosion products which were consistent in appearance and gross composition with identification as dicopper trihydroxide nitrate, even though they were not all positively identified as such.

In the experiments of Yunker, higher temperatures and higher absolute humidities were used, as well as lower "normalized doses" (shown in Table IV as AxBxC , and representing the approximate relative amount of radiolytically fixed nitrogen per unit area of exposed metal). It was not clear until completion of the present experiments why only CuO and Cu_2O were observed as corrosion products by Yunker, whereas $\text{Cu}_2\text{NO}_3(\text{OH})_3$ was the primary product observed by the others.

On the basis of the present results, we can now conclude that a key factor is the humidity, since $\text{Cu}_2\text{NO}_3(\text{OH})_3$ was observed in our experiments over the entire temperature range up to 150°C, and the "normalized dose" was even smaller in the present experiments than in Yunker's experiments. Therefore, neither the elevated temperatures nor the lower normalized doses appear to be responsible for the differences between his results and those of others. The remaining significant difference appears to be his higher humidities. The fact that we did not observe the nitrate phase at 150°C and 100% relative humidity supports the conclusion that the high humidities in Yunker's experiments account for the absence of the nitrate corrosion product.

One significant issue for projecting the long-term corrosion rate of nuclear waste package materials is the rate law obeyed by the corrosion process. Shtalov and Nikitina have reported a linear growth rate under conditions of 100% relative humidity near room temperature. It appears that $\text{Cu}_2\text{NO}_3(\text{OH})_3$ was the corrosion product under these conditions. It therefore would appear that this species is nonprotective. We intend to perform long-term experiments to check this inference.

SUMMARY

1. Previous work by others indicates that dicopper trihydroxide nitrate, $\text{Cu}_2\text{NO}_3(\text{OH})_3$, forms on copper and copper alloys subjected to irradiated moist air near room temperature.

2. In the present work, the nature of the corrosion products formed on the coupons of the copper-based materials CDA 102, CDA 613, and CDA 715 was found to depend on the irradiation environment, primarily its moisture content. Nitrate phases, principally $\text{Cu}_2\text{NO}_3(\text{OH})_3$, as well as copper oxides, were observed in intermediate and low moisture experiments. No nitrates were observed, however, in the experiments at 150°C with 100% relative humidity.
3. The copper-based materials showed significant rates of general corrosion, which depended on the moisture content of the system. The relative rates in descending order were $\text{Cu} > 70/30 \text{ Cu-Ni} > \text{Al-bronze}$.
4. Localized corrosion, in the form of pitting, was noted on the Cu/Ni coupon irradiated in 15% RH air at 120°C and on the copper coupon irradiated in 15% RH air at 150°C . These results should be considered tentative, since only a single coupon of each material was present in each irradiation vessel.
5. High-nickel alloy 825 did not undergo significant corrosion in any of the experiments performed.

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Table I. X-ray Diffractometry of Corrosion Product on Copper from Target Cave of 100-MeV Electron Linac

<u>Observed</u>		<u>Known Spectrum [29] of Cu₂N₂O₃(OH)₃</u>		<u>Observed</u>		<u>Known Spectrum [29] of Cu₂N₂O₃(OH)₃</u>	
<u>d (nm)</u>	<u>Peak Area</u>	<u>d (nm)</u>	<u>Relative Intensity</u>	<u>d (nm)</u>	<u>Peak Area</u>	<u>d (nm)</u>	<u>Relative Intensity</u>
0.790	0.2			0.2656	27.4	0.2669	80
0.685	100.0	0.691	100	0.2511	5.4	0.2532	20
0.5606	0.3	0.5597	5	0.2450	37.7	0.2460	70
0.5510	0.2					0.2441	10
0.5398	0.2			0.2376	0.3	0.2331	10
0.4554	0.5	0.4550	13	0.2298	2.6	0.2303	20
		0.4188	10			0.2283	5
0.4096	4.0	0.4121	40	0.2254	13.3	0.2264	50
0.3610	2.5	0.3631	30	0.2218	0.8		
0.3440	58.9	0.3454	70	0.2187	0.3	0.2193	5
0.3184	0.3			0.2145	8.5	0.2155	40
0.3027	1.6	0.3047	10	0.2085	3.2	0.2093	20
0.3000	3.4	0.3006	20	0.2069	18.4	0.2077	60
0.2927	0.3			0.2014	0.3	0.2006	10
0.2842	0.2	0.2843	5	0.2001	0.4	0.1980	5
0.2781	9.6	0.2795	40	0.1937	0.1	0.1942	5
0.2712	0.3	0.2725	5				

Table II. Initial and Final Composition of the Gas Phase (Other Than Water) for the 90, 120 and 150 °C Corrosion Experiments

<u>Run</u>	<u>Absorbed Dose (MGy)</u>	<u>Description</u>	<u>Gas Composition (mole%)</u>					
			<u>O₂</u>	<u>N₂</u>	<u>CO</u>	<u>CO₂</u>	<u>N₂O</u>	<u>NO₂</u>
Initial Air			21.0±0.3	78.5±0.3	ND	tr	ND	NA
<u>90 °C Experiments: Final Gas</u>								
C7	0.48±0.04	dry air	20.9±0.3	79.0±0.3	0.007±0.001	0.039±0.002	0.063±0.001	NA
C8	0.48±0.04	15±1%RH	20.8±0.3	79.0±0.3	0.011±0.002	0.067±0.003	0.063±0.001	NA
C9	0.48±0.04	100%RH	20.0±0.3	79.6±0.3	ND	0.26±0.02	0.041±0.002	NA
<u>120 °C Experiments: Final Gas</u>								
C1	1.69±0.12	dry air	19.6±0.1	79.9±0.1	0.032±0.02	0.23±0.005	0.24±0.005	0.018±0.04
C3	1.64±0.12	0.006±0.001%RH	19.4±0.1	79.9±0.1	0.017±0.001	0.24±0.1	0.32±0.01	0.01±0.01
C2	1.64±0.12	15±1%RH	19.4±0.1	79.9±0.1	0.014±0.001	0.29±0.01	0.38±0.01	0.019±0.011
<u>150 °C Experiments: Final Gas</u>								
C6	0.51±0.04	dry air	20.1±0.3	79.6±0.3	ND	0.28±0.01	0.031±0.003	NA
C4	0.51±0.04	15±1%RH	20.0±0.3	79.2±0.3	ND	0.70±0.05	0.037±0.003	NA
C5	0.51±0.04	100%RH	18.9±0.3	80.4±0.3	ND	0.69±0.01	0.012±0.001	NA

NA = Not analyzed for; ND = Not detected; tr = trace

Table III. Corrosion Products Identified as a Function of Irradiation Conditions

<u>Metal</u>	<u>Environment</u>	<u>Color Observed</u>	<u>Major Component</u>	<u>Lesser Components</u>
Aluminum Bronze	90 °C, 100%RH 120 °C, 15%RH 150 °C, dry air 150 °C, 15%RH 150 °C, 100%RH		Cu ₂ O Cu ₂ NO ₃ (OH) ₃ Cu ₂ O Cu ₂ NO ₃ (OH) ₃ Cu ₂ O	CuO Cu (solid solution) Cu ₂ NO ₃ (OH) ₃ , CuO amorphous Cu ₂ NO ₃ (OH) ₃ CuO
Copper	90 °C, 100%RH 120 °C, 15%RH 120 °C, 15%RH 150 °C, dry air 150 °C, 15%RH 150 °C, 15%RH 150 °C, 100%RH	yellow red black yellow	Cu ₂ O Cu Cu ₂ O Cu Cu ₂ O Cu ₂ O Cu ₂ O	CuO Cu ₂ O, Cu ₂ NO ₃ (OH) ₃ Cu ₂ NO ₃ (OH) ₃ Cu ₂ O, Cu ₂ NO ₃ (OH) ₃ Cu ₂ NO ₃ (OH) ₃ Cu ₂ NO ₃ (OH) ₃ CuO
70/30 Copper Nickel	90 °C, 100%RH 120 °C, 15%RH 120 °C, 15%RH 150 °C, dry air	green specks black spots	Cu ₂ O Cu ₂ NO ₃ (OH) ₃ Cu ₂ NO ₃ (OH) ₃ Cu ₂ O	Cu ₂ NO ₃ (OH) ₃ and CuO Cu ₂ O, Cu solid solution CuO, Cu ₂ NO ₃ (OH) ₃

Table IV. Summary of Previous Research

<u>Reference</u>	Temp. (°C)	A <u>Partial Pressure (10⁵ Pa)</u>				B <u>Ratio*</u>	C <u>Max. Dose (Gy)</u>	<u>Product A×B×C</u>	<u>Reported Corrosion Product</u>
		<u>N₂</u>	<u>O₂</u>	<u>H₂</u>	<u>H₂O</u>				
Primak and Fuchs (1954)	not specified	0.8	0.2	0	"moist"	not specified	not specified	-	"nitrates or basic nitrates"
Shatalov and Nikitina (1958)	20-25	0.8	0.2	0	up to 0.03	>100	2.7×10 ⁸	>2×10 ¹⁰	Cu(NO ₃) ₂ ·3H ₂ O
Byalobzheskii (1970)	20	0.8	0.2	0	0.023	>100	2.6×10 ⁶	>2×10 ⁸	"nitrate salts" and "copper hydroxide"
Makepeace (1974)	room temp.	0.8	0.2	not specified	0.025	1.3	2.6×10 ⁸	2.7×10 ⁸	Cu ₂ NO ₃ (OH) ₃
LLNL Linac target room	room temp.	0.8	0.2	0	variable	~1000	>10 ⁸	>8×10 ¹⁰	Cu ₂ NO ₃ (OH) ₃
Yunker (1988)	95	0.8 (init.) 0.1-0.9 (range)	0.2 (init.) 0.1-0.9 (range)	0 (init.) Up to 1.7	0.8-0.9	0.87	4.6×10 ⁷	3×10 ⁷	CuO, Cu ₂ O
Yunker (1988)	150	0.47	0.11	0	0.42	0.78	2.9×10 ⁷	1×10 ⁷	CuO, Cu ₂ O

* Ratio of gas volume to total metal area (cm³/cm²)