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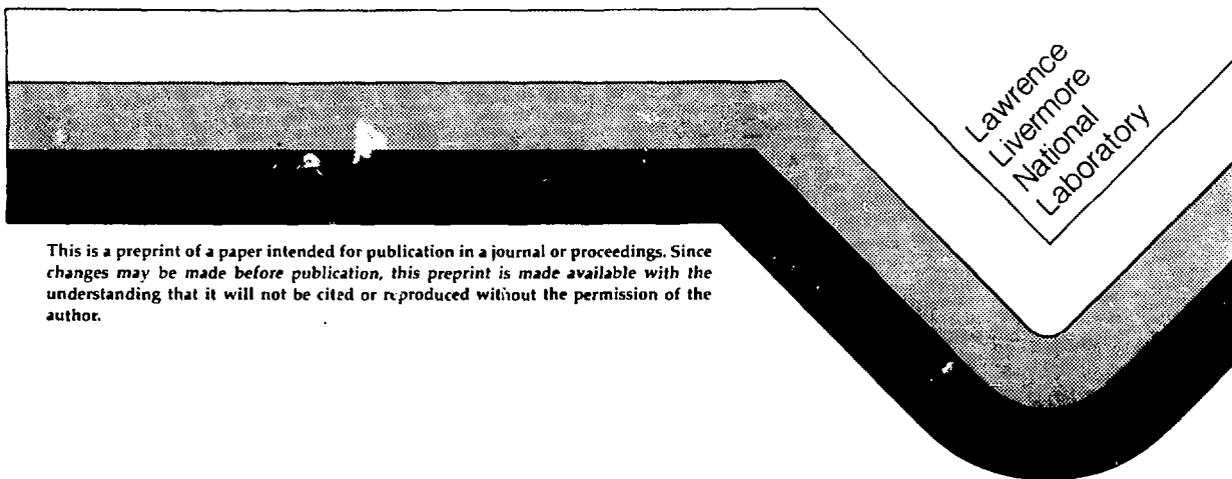
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STEELS AND COPPER-BASED MATERIALS IN
GAMMA-IRRADIATED AQUEOUS ENVIRONMENTS

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CORROSION PROCESSES OF AUSTENITIC STAINLESS STEELS AND COPPER-BASED MATERIALS IN GAMMA-IRRADIATED AQUEOUS ENVIRONMENTS⁽¹⁾

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ABSTRACT

The U. S. Department of Energy is evaluating a site located at Yucca Mountain in Nye County, Nevada, as a potential high-level nuclear waste repository. The rock at the proposed repository horizon (above the water table) is densely welded, devitrified tuff, and the fluid environment in the repository is expected to be primarily air-steam. A more severe environment would be present in the unlikely case of intrusion of vadose groundwater into the repository site. For this repository location, austenitic stainless steels and copper-based materials are under consideration for waste container fabrication. This study focuses on the effects of gamma irradiation on the electrochemical mechanisms of corrosion for the prospective waste container materials. The radiolytic production of such species as hydrogen per-

oxide and nitric acid are shown to exert an influence on corrosion mechanisms and kinetics.

INTRODUCTION

The permanent disposal of high level nuclear waste materials is a current technological challenge. For geologic disposal, the U. S. Nuclear Regulatory Commission regulations require packages that provide "substantially complete" waste containment for time periods of 300 to 1000 years.

Currently, the U. S. Department of Energy is evaluating a site located at Yucca Mountain in Nye County, Nevada, as a potential high-level nuclear waste repository. The rock at the repository horizon is densely welded, devitrified tuff. For this repository location, austenitic stainless steels (e.g., AISI 304L and 316L) are the primary materials under evaluation for use as potential waste containers. Also under consideration as waste canister materials are copper and some of its alloys, namely the

(1) Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-ENG-48.

cupronickels and aluminum bronzes. Copper is thermodynamically stable in certain aqueous geological environments. However, the oxidizing nature of the environment in a tuff repository in the unsaturated zone, in combination with the effects of gamma irradiation, may present more corrosive conditions for these materials than for austenitic stainless steels.

For the proposed repository, the fluid environment is expected to be primarily air-steam. A more severe-case environment for the waste packages would be present if vadose groundwater intruded into the repository site. This is thought to be unlikely, but still needs to be considered. The low annual precipitation at the site and low rate of percolation of water downward would minimize the actual amount of water entering the waste package environment. In addition, the heat generated from the nuclear waste would vaporize incoming water at temperatures above 95°C (boiling point of water at the repository elevation). For the large majority of waste packages, container surface temperatures would be expected to remain above 95°C for several hundreds of years.¹

In addition to groundwater that contains naturally occurring concentrations of dissolved species, it is also of interest to consider solutions in which these species are more concentrated. Evaporative processes at the repository site could lead to concentration of the electrolyte, by a mechanism such as the following: Groundwater might intrude into the repository site prior to the time that the container surface had cooled to below boiling temperature. It would then evaporate and leave behind salt deposits. Subsequent repetition of these events at the same locations could conceivably result in local salt build-up. When the container surface temperature later cooled to below the boiling point, further wetting at locations of salt build-up could lead to a concentrated electrolyte.

In designing metallic engineered barriers for waste disposal, one must evaluate the susceptibility to failure modes normally encountered in corrosion studies (e.g., uniform corrosion, pitting, crevice attack, and stress cor-

rosion cracking). In so doing, it is necessary to understand the interaction of gamma radiation from the nuclear waste with the surrounding chemical environment in light of possible effects on corrosion mechanisms. These latter effects are just beginning to be explored for potential repository sites.

Previous investigations have found an increased susceptibility of sensitized AISI 304 stainless steel towards intergranular stress corrosion cracking in high temperature water under gamma irradiation.^{2,3} Other reports have claimed an increased resistance to crevice corrosion for austenitic stainless steels in aqueous solutions under gamma irradiation.⁴ For carbon steel and AISI 304 stainless steel, gamma irradiation in high temperature (250°C) water containing low oxygen levels has been shown to increase the release rates of insoluble corrosion products but not to increase the release rates of soluble products.⁵

Several reports have demonstrated effects of gamma irradiation on the corrosion potentials of austenitic stainless steels in aqueous media.^{4,6-10} However, in general, a fundamental understanding of the effects of gamma irradiation on the mechanisms of corrosion of austenitic stainless steels and copper alloys is lacking. In particular, in aqueous environments having near-neutral pH, the introduction of new electrochemical reactions by the radiolytically-generated oxidants has received little mechanistic investigation. However, species such as $\cdot\text{OH}$, H_2O_2 , O_2 , HO_2 , and O_2^- , which are generated radiolytically, are generally assumed to increase the oxidizing nature of the environment.

In this study, in-situ electrochemical measurements have been made of corrosion potential shifts produced by gamma irradiation. These potential shifts are in the positive direction and reflect the production of such oxidizing species as $\cdot\text{OH}$ and H_2O_2 . The detailed nature of the interfacial electrochemical mechanisms responsible for these potential shifts is being explored for austenitic stainless steels and copper alloys. In addition, the alterations in the susceptibility to localized corrosion (e.g., pitting and crevice corrosion) are being

evaluated by in-situ anodic polarization curves and occluded cell experiments, which will be described elsewhere.

EXPERIMENTAL

In this section the experimental details are briefly summarized. A more detailed description is provided elsewhere.¹⁰

Rods of both AISI 316L stainless steel (0.02C; 1.71 Mn; 0.033 P; 0.014 S; 0.56 Si; 10.29 Ni; 16.51 Cr; 2.07 Mo; 0.10 Co; 0.28 Cu; 0.054 N, bal. Fe) and Type CDA102 copper (>99.95% Cu) were used as the working electrodes. Thermo-mechanical treatment was as-received. All samples were polished to at least 1 μ finish with Al_2O_3 slurries prior to use.

The groundwater used in these experiments was obtained from Well J-13, which is located near the repository site. The J-13 well penetrates the same tuff formation below the water table, at a lower elevation than that of the proposed repository site. The composition of the groundwater is shown in Table I. Analyses of the constituents were made by ion chromatography, inductively-coupled plasma emission spectroscopy, and Technicon AutoAnalyzer. In some experiments, concentrated forms of this groundwater (10x and 100x) were used. Boil-down under atmospheric pressure was used to obtain the more concentrated electrolytes.

The electrochemical apparatus used in this work consisted of two chambers. The reference electrode (SCE) was placed in a reservoir containing saturated KCl in the upper chamber. The upper and lower chambers were connected by a Luggin probe, approximately 1.4 m long, and terminating with a porous vycor tip, filled with saturated KCl. The lower chamber, which was the only part of the system surrounded by the gamma ray sources, contained the Pyrex electrochemical cell. The cell itself had ports for the reference electrode Luggin probe, the working electrode, a counter electrode and an inlet for deaeration. In this arrangement the reference electrode was isolated from the gamma ray sources.

The gamma ray sources consisted of

stainless-steel-encapsulated ^{60}Co pencils in a cylindrical (napkin ring) arrangement. The lower chamber of the electrochemical apparatus was inserted into the inside of the cylinder, at the center of which the dose rate was 3.3 Mrad/hr ($\pm 20\%$). All experiments were performed at 30°C ($\pm 5^\circ C$).

Open-circuit potential vs time and anodic polarization curves were obtained with the aid of a Princeton Applied Research Model 173 potentiostat and a Model 176 current-to-voltage converter.

RESULTS AND DISCUSSION

Aqueous Environment and Radiation Chemistry

Before proceeding to interpret the electrochemical experiments, it is helpful to consider present knowledge of the bulk radiation chemistry of aqueous solutions from past work in this field. Because the groundwater contains only low concentrations of solutes, most of which do not undergo high-rate reactions with radiolytic radicals, its initial radiation chemistry should be similar to that of pure water. The interaction of gamma radiation with aqueous environments produces a host of transient radicals, ions, and stable molecular species including H^\bullet , $^{\bullet}OH$, e_{aq}^- , H_3O^+ , OH^- , H_2 , H_2O_2 , O_2 , $O_2^{\bullet -}$, and HO_2^{\bullet} .¹¹⁻¹³ Species such as e_{aq}^- , H^\bullet , and H_2 can act as reducing agents, while others, such as H_2O_2 , $^{\bullet}OH$, O_2 , $O_2^{\bullet -}$ and HO_2^{\bullet} , can act as oxidizing agents. As a result of the production of such active species under gamma irradiation, one can expect alterations in the rates or mechanisms of corrosion attack modes.

Under radiolysis of air-saturated J-13 well water or its concentrated forms (e.g., up to 100x concentration), we expect an oxidizing environment with O_2 and H_2O_2 as the dominant oxidizing species, a much smaller concentration of $O_2^{\bullet -}$ and still much smaller steady-state concentrations of HO_2^{\bullet} , $^{\bullet}OH$, H_2 , e_{aq}^- , and H^\bullet .¹⁰ In addition to these species, various oxides of nitrogen and nitric acid are capable of being formed in a moist air phase, if one is present, and subsequently entering the solution. Irradiation of water containing either CO_2 or HCO_3^- with O_2 gives rise to pro-

duction of carboxylic acids (formic and/or oxalic).

Potential Measurements and Electrochemical Mechanisms

This section will be divided into the results obtained for AISI 316L stainless steel and those for Type CDAl02 copper. A more comprehensive discussion of the electrochemistry of austenitic stainless steels in irradiated environments can be found elsewhere.¹⁰

Austenitic Stainless Steels

As a result of the production of a more oxidizing environment under gamma irradiation, the corrosion potentials of austenitic stainless steels are shifted in the positive direction. Such a result for AISI 316L in 10x concentrated J-13 is shown in Fig. 1. In this figure, "on" refers to lowering of the cell into the center of the gamma ray sources and "off" refers to raising the cell 1.3 to 1.5 m above the sources, where the cell was shielded by intervening water. Several "on/off" cycles are shown. Similar positive potential shifts upon imposition of the gamma field were observed for AISI 316L in more highly concentrated ground-water (e.g., 100x), and in non-concentrated J-13 well water, and with AISI 304L stainless steel as the electrode material. The corrosion potential shifts under all these conditions and for both materials were typically 150-200 mV.

Following exposure of AISI 316L to gamma-irradiated environments, the electrochemical cell was removed from the gamma sources and the corrosion potential was continuously monitored for several hours (generally more than 14 hours). The potential in each case was found to remain in the range of the high (relative) positive values that were observed immediately after termination of the irradiation.

In order to test whether the observed effects resulted from stable oxidizing species in the solution or from permanent changes in the oxide film on the electrode, the following experiment was performed: Following several "on/off" cycles for Type 316L stainless

steel in J-13 water, the cell was removed from the gamma facility and the irradiated solution was replaced by "fresh" non-irradiated J-13 water. When this was done, the corrosion potential immediately shifted in the negative direction (see Fig. 2). This indicates that the initial positive potential shifts observed were due principally to radiolytically generated stable oxidizing species rather than to oxide film changes. If the latter had been the case, the oxide layer would not have been expected to change back to its original state when the solution was replaced, particularly not as rapidly as the observed change in potential occurred.

As discussed above, H_2O_2 is the dominant stable oxidizing species produced under radiolysis. In J-13, following 3.5 hours of exposure at the dose rate employed in this study, we measured the concentration of H_2O_2 produced to be 0.14 mM using the titanium oxalate method.¹⁴ To see whether H_2O_2 alone could produce the potential shifts of the magnitude observed under irradiation, one drop of 30% H_2O_2 solution was added to the fresh J-13 water in the cell from the experiment above, producing a concentration of about 4.4 mM. The potential was observed to shift in the positive direction immediately (see Fig. 2). The observed change when H_2O_2 was added to the solution, coupled with the knowledge that H_2O_2 is the most concentrated radiolytic species present in an irradiated, aerated solution, provides strong evidence that it is responsible for the potential shift observed upon irradiation in these solutions.

In a similar experiment, successive additions of 30% H_2O_2 solution were made to an unirradiated J-13 solution in which a freshly prepared AISI 316L electrode was immersed. The results of this experiment are shown in Fig. 3. In this figure, a one-drop addition to the solution represents a concentration increase of approximately 0.5 mM, which is near the 0.14 mM concentration which was experimentally measured under the conditions above. It can be seen that the potential shift observed following the addition of the first drop is near the bottom end of the range of potential shifts observed under radiolysis (150-200 mV). These results add further support to the

interpretation that the production of H_2O_2 under radiolysis leads to the long-term potential shifts observed. However, the production of other oxidizing species (e.g., $\cdot OH$) under radiolysis will also assist in producing positive potential shifts.

CDA102 Copper

Although some of the general features (e.g., positive corrosion potential shifts) are similar, the behavior of copper in gamma-irradiated environments differs from that of stainless steel. Figure 4 shows the corrosion potential vs. time behavior of CDA102 in J-13 water when subjected to gamma irradiation. Upon initiation of irradiation the corrosion potential jumped approximately 100 mV positive, then rapidly decayed to more negative values. If achievement of steady-state had been allowed, the final potential probably would have reached nearly the same value as that attained prior to irradiation (or at most 10-20 mV higher). This is in contrast to the much larger and longer term potential shifts observed for stainless steels in this medium. Upon termination of irradiation, the corrosion potential dropped (in the negative direction), which is analogous to the behavior with stainless steels. Results similar to those for CDA102 were obtained for the copper alloy CDA715 (70 Cu-30 Ni).

A similar corrosion potential vs time relationship was observed when H_2O_2 was added to unirradiated J-13 water in which a CDA102 electrode was immersed. Results of this experiment are shown in Fig. 5. In this figure, one drop of a 30% H_2O_2 solution again represents a resulting concentration in J-13 water of approximately 0.5 mM. The solution was stirred during the addition of H_2O_2 .

The similarity of the potential rise and decay observed in Figs. 4 and 5 for copper indicates that the radiolytic product H_2O_2 is a major determinant of the electrochemical behavior of copper in irradiated environments, as it is for AISI 316L stainless steel. It is noted that the initial potential rise and the apparent steady-state potential after the decay are more positive in the ex-situ case (Fig. 5) than in the irradiation

experiment (Fig. 4). This is probably because the concentration of H_2O_2 added in the ex situ experiment was a factor of 3 to 4 times higher than was reached in the irradiation experiment. Also, continuous stirring of the solution in the ex-situ experiment increased the mass transfer of the oxidant (H_2O_2) to the electrode surface. When the magnetic stirrer was turned off (see Fig. 5) the corrosion potential immediately fell to more negative values, apparently because the H_2O_2 in the diffusion layer next to the copper electrode was consumed by decomposition into H_2O and O_2 , and the reaction became diffusion limited.

In closed systems consisting of J-13 well water and moist air, CDA102 was found to be much more susceptible than AISI 316L stainless steel to vapor phase attack in irradiated environments. This is likely a result of the known formation of ozone and various oxides of nitrogen as well as nitric acid in systems containing O_2 , N_2 and H_2O vapor.^{15,16} The products are corrosive to copper but much less so to stainless steel. A photograph of a sample of the vapor phase corrosion of CDA102 is shown in Fig. 6. In this case, the left half of the length of the rod was immersed in J-13 well water and the right half to the atmosphere above it in a sealed glass tube. The total duration of the irradiation was 15 days. Although oxidation of both the vapor and solution phase surfaces is apparent, much more severe oxidation has occurred in the vapor phase. The oxide that formed was identified as Cu_2O by x-ray diffraction. Previous studies of the irradiation of copper in moist air without a liquid phase have revealed formation of what appeared to be copper hydroxide nitrate, $Cu_2(OH)_3 NO_3$ (also known as basic copper nitrate), instead of Cu_2O .^{4,17} The absence of detectable nitrate in the present case may have resulted either from the relatively small dose or from dissolution of some of the nitrogenous gases in the liquid phase, preventing their reaction with the surface of the sample in the vapor phase region. It is known that reaction of pure NO_2 with copper produces Cu_2O .¹⁸

Electrochemical Mechanisms

The electrochemistry of potential

waste container materials relevant to corrosion processes in irradiated environments is obviously very complex. In what follows, some of the major points are discussed. Space does not allow an elaborate discussion here. The interested reader can find a more detailed discussion elsewhere.¹⁰

It seems likely from the above that the radiolytically generated H_2O_2 and probably also the oxidizing transient radical $\cdot OH$ play important roles in the electrochemistry of metals in irradiated environments. The initial rapid rise of potential for AISI 316L stainless steel and CDA102 copper upon initiation of irradiation is most likely due to the production of these species in the solution layers next to the electrode surface.

It has been recognized for a long time that copper is catalytic towards the decomposition of hydrogen peroxide, while stainless steels are only mildly so.¹⁹ In acidic media, H_2O_2 has been shown to increase the rate of the auto-dissolution process of copper by a catalytic mechanism.²⁰ In this mechanism, cupric ions are formed from the solution phase oxidation of cuprous ions. The cupric ions can then act as cathodic depolarizers to accelerate the corrosion process.

The behavior of the copper corrosion potential upon initiation of irradiation is interesting. The initial large positive jump in potential indicates a rapid response to the presence of H_2O_2 and $\cdot OH$ radicals. Then, the almost immediate negative decline in potential may indicate a decreased catalytic efficiency for reduction of H_2O_2 , and may correspond to the oxidation of the surface or alteration of the oxide film on copper (e.g., by adsorption of intermediates). Visually, the surface of copper is observed to be oxidized under irradiation. The appearance of the surface of AISI 316L stainless steel is not nearly as affected by irradiation as is that of copper.

Of course, the corrosion potential under irradiation will be determined by a superposition of all the anodic (e.g., metal dissolution) and cathodic processes occurring on the surface. Possible

sets of anodic and cathodic reactions for stainless steels under the conditions employed in these experiments are given in Table II. These reactions will probably dominate under gamma irradiation of aerated aqueous systems similar to J-13 well water and its concentrated (10x, 100x) forms, when the pH is neutral to mildly alkaline. Analogous reaction sets can be written for copper.

In the first cathodic redox reaction given in Table II (that involving an equilibrium between adsorbed hydroxyl radicals and hydroxide ion in solution), the adsorbed hydroxyl radicals can come from the surface-catalyzed decomposition of H_2O_2 , i.e.,

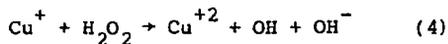


or by direct adsorption of transient radiolytic $\cdot OH$ radicals. This redox reaction has previously been proposed to account for the open-circuit potentials observed for Pt in high-purity aqueous solutions of H_2O_2 .²¹ A mechanism for the cyclical catalytic decomposition of H_2O_2 on Pt that involves adsorbed species ($\cdot OH$ and HO_2) resulting from the electrochemical discharge of H_2O_2 has also been advanced to account for the observed open-circuit behavior of Pt in aqueous H_2O_2 solutions, particularly at higher pH.²² In the cyclical mechanism, H_2O and the additional cathodic depolarizer O_2 are liberated. This cyclical mechanism is probably the more likely pathway.

In analogy to these studies on Pt, similar mechanisms may explain the observed results for stainless steel and for Cu and its alloys in irradiated aqueous solutions. However, the situation will surely be more complex for these materials in our environments than for Pt in high-purity aqueous solutions of H_2O_2 . This will result from the additional anodic reactions of metal dissolution and the presence of other species capable of participating in redox reactions (e.g., HCO_3^- and NO_3^-). In addition, for copper and its alloys, the presence of H_2O_2 may catalytically accelerate the autodissolution process via the following reaction series:



with Cu^{+2} , acting as an oxidant, being generated from the solution reaction:



As mentioned above, the open circuit behavior as a function of time during irradiation is somewhat different for copper than for stainless steels. Upon initiation of irradiation the potential immediately shifts by about 100 mV. The potential then declines to less positive values. This may indicate a decreased catalytic efficiency for H_2O_2 decomposition, either because of the oxidation of the copper surface or perhaps because of the adsorption of species such as $\cdot\text{OH}$ which block surface sites.²⁰

SUMMARY

Gamma irradiation increases the oxidizing nature of the aqueous solutions used in this study through production of $\cdot\text{OH}$ and H_2O_2 . These species probably account for the observed positive corrosion potential shifts for stainless steels, copper, and copper alloys. The observed corrosion potentials are mixed potentials, resulting from a complex superposition of all the cathodic processes (e.g., reduction of $\cdot\text{OH}$, O_2 , and H_2O_2) and anodic processes (e.g., metal dissolution) occurring at the metal surface.

Copper and its alloys are known to be very catalytic towards the decomposition of H_2O_2 , a radiolytic product. In solution, the surfaces of copper and its alloys appear to be more affected (oxidized) in irradiated environments than those of stainless steels. With regard to corrosion potential shifts under irradiation, the same general behavior as for stainless steels (positive corrosion potential shifts) is observed initially. However, the corrosion potentials then decline to relatively less positive values. This may be related to a decreased efficiency for catalytic decomposition of H_2O_2 , resulting from surface oxidation or adsorption of intermediate species.

In addition to the work reported above, preliminary results from other experiments involving stainless steels,

copper, and copper alloys in J-13 well water and its concentrated forms (to 100x), show that the positive corrosion potential shifts observed under irradiation are not sufficient to shift the metal into the pitting corrosion regime. Detailed studies are currently underway to evaluate the effect of irradiation on localized corrosion susceptibility (e.g., to pitting and crevice corrosion) of prospective nuclear waste container materials.

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TABLE I - Average Composition of J-13
Well Water (based upon measurements
using ICP-OES, IC, and Technicon
AutoAnalyzer)

Species	(mg/L)
HCO ₃ ⁻	125
SO ₄ ²⁻	19
NO ₃ ⁻	9.6
Cl ⁻	6.9
F ⁻	2.2
Na ⁺	44
Ca ²⁺	12.5
K ⁺	5.1
Mg ²⁺	1.9
Si	27

TABLE II - Possible Redox Reactions in Gamma-Irradiated J-13 Water

Cathodic reactions:	Anodic reactions:
$(\cdot\text{OH})_{\text{ads}} + e^- \rightarrow \text{OH}^-$	$\text{Fe} \rightarrow \text{Fe}^{+2} + 2e^-$
$\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4\text{OH}^-$	$\text{Cr} \rightarrow \text{Cr}^{+3} + 3e^-$
$\text{O}_2^- + \text{H}_2\text{O} + e^- \rightarrow \text{HO}_2^- + \text{OH}^-$ (small contribution)	$\text{Ni} \rightarrow \text{Ni}^{+2} + 2e^-$
$\text{HO}_2^- + \text{H}_2\text{O} + 2e^- \rightarrow 3\text{OH}^-$ (very small contribution)	

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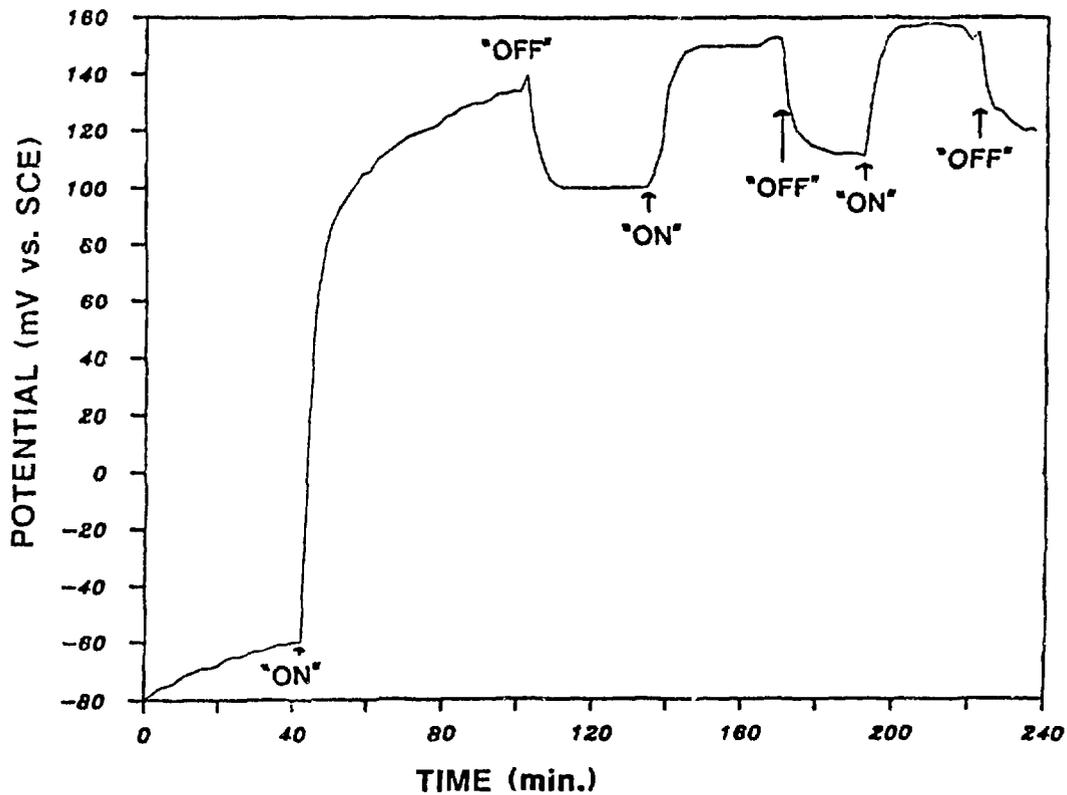


FIG. 1. Corrosion potential behavior for AISI 316L stainless steel in 10X concentrated J-13 well water under gamma irradiation. The solution was not exposed to irradiation prior to initiation of the first "on/off" irradiation cycle.

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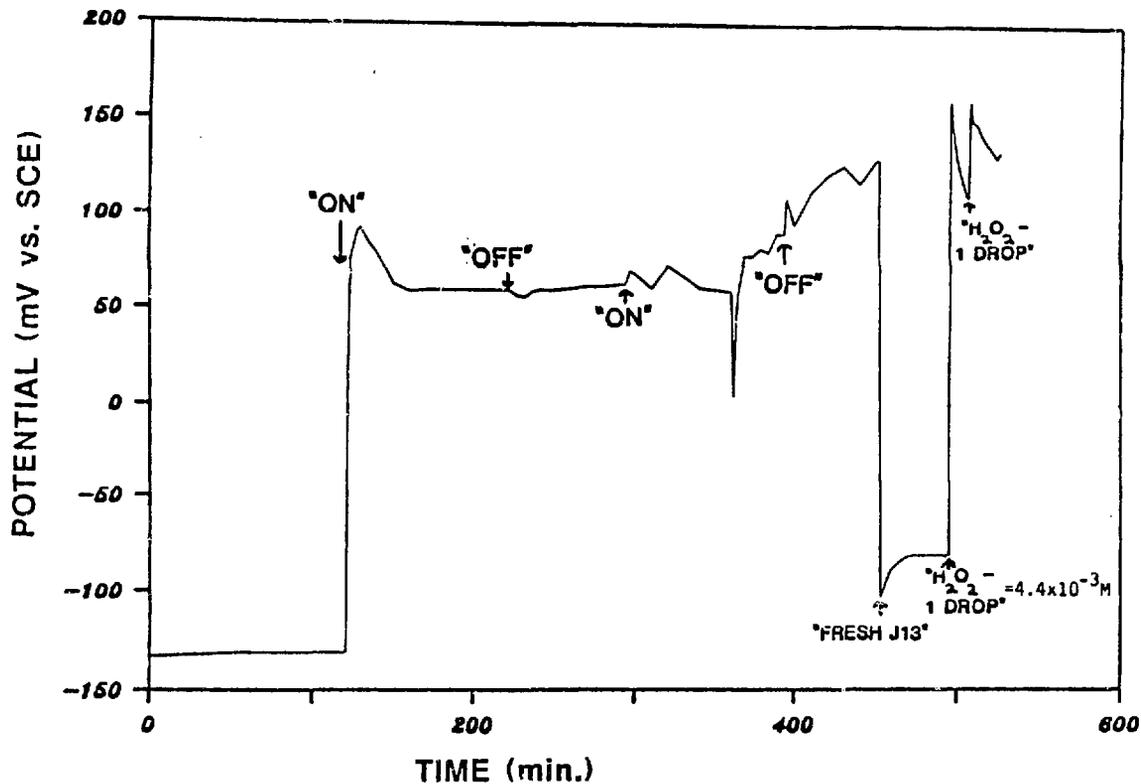


FIG. 2. Corrosion potential behavior for AISI 316L stainless steel in gamma-irradiated J-13 well water. Following the last "off" half-cycle the irradiated solution was decanted and replaced by a fresh, unirradiated solution. Following this, two drops of H₂O₂ (from a 30% solution) were added successively. One drop of H₂O₂ represents a resulting solution concentration of 4.4 mM.

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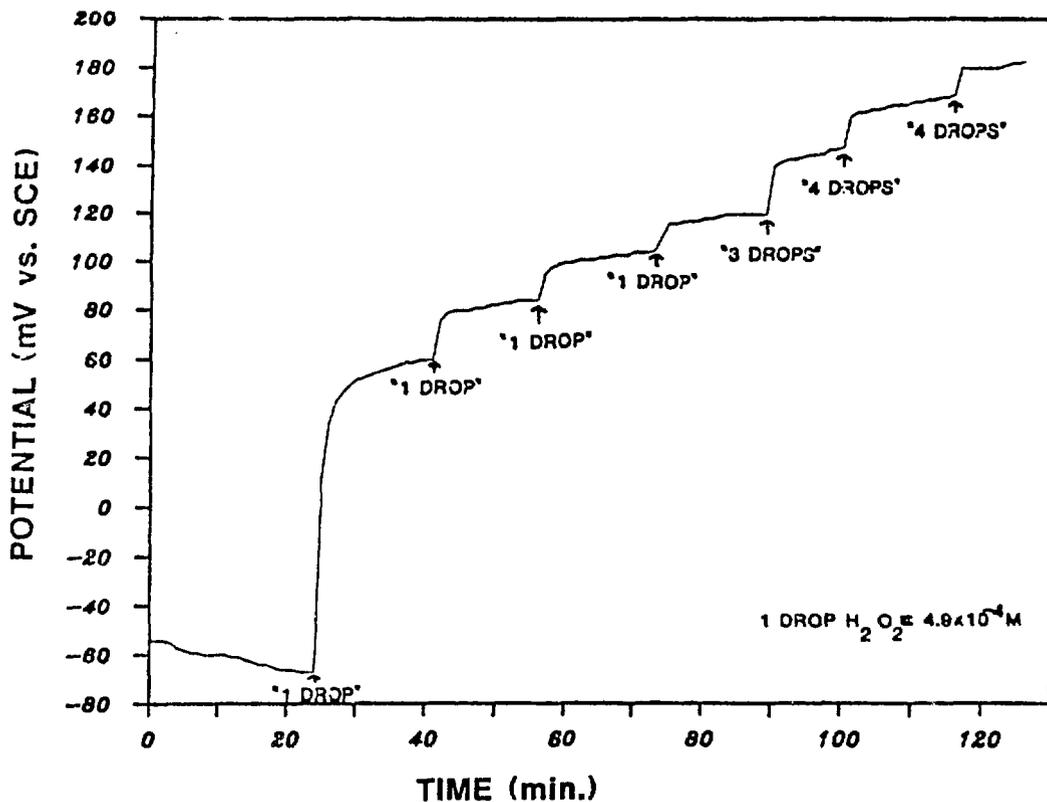


FIG. 3. Response of the corrosion potential for AISI 316L stainless steel in unirradiated J-13 well water to which successive additions of H₂O₂ were made. In this figure, one drop of H₂O₂ (from a 30% solution) represents a resulting solution concentration of 0.5 mM. The solution was continuously stirred by a magnetic stirrer throughout the experiment.

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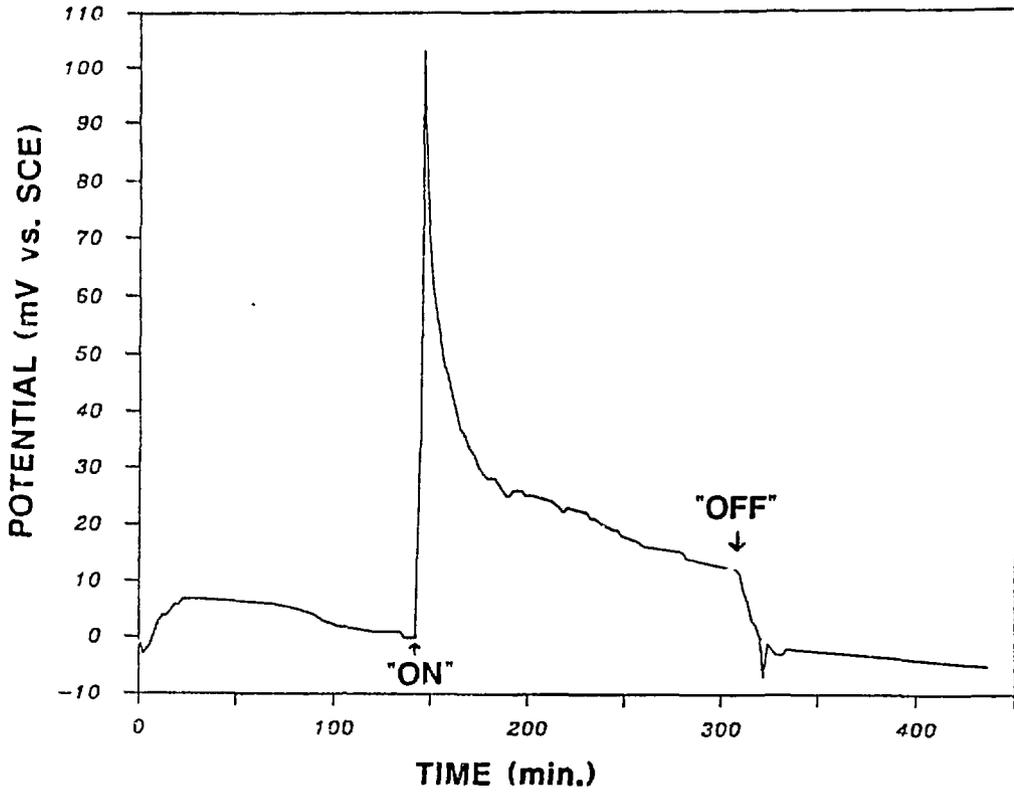


FIG. 4. Corrosion potential behavior for CDA102 copper irradiated in J-13 well water at 3.3 Mrad/h.

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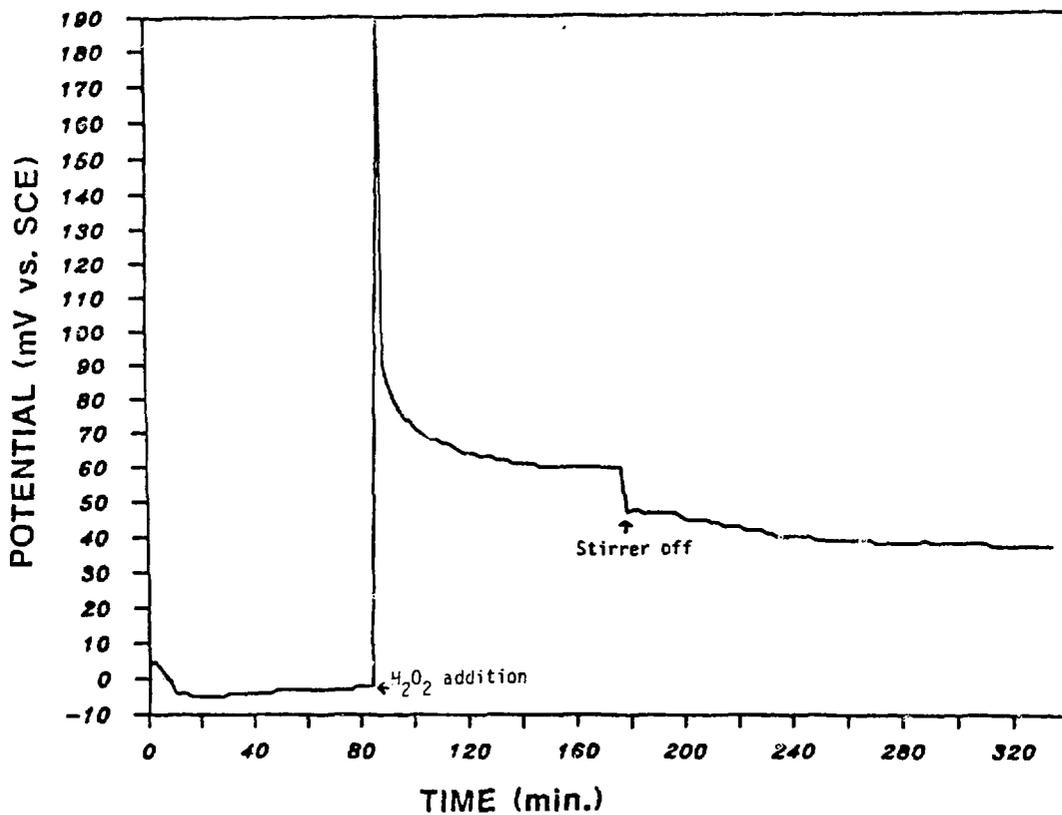


FIG. 5. Response of the corrosion potential for CDA102 copper in unirradiated J-13 well water to which one drop of 30% H₂O₂ solution was added, corresponding to a solution concentration of 0.5 mM. The solution was stirred until indicated on the Figure.

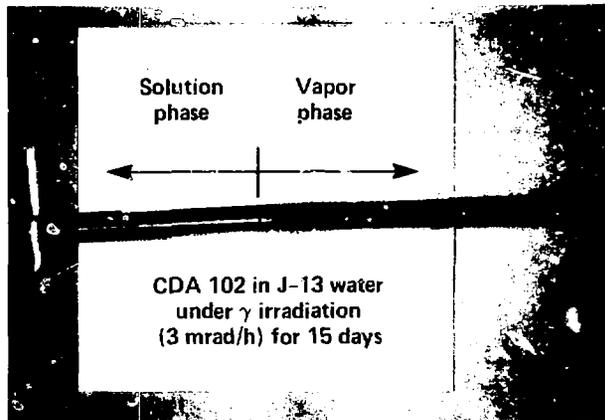


FIG. 6 Photograph of CDA102 copper rod that was gamma-irradiated at 3 Mrad/h for 15 days. Left half was submerged in J-13 well water, and right half was in contact with moist air during irradiation.