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Peaceful Applications

**RADIOACTIVE CONTAMINATION OF
COPPER RECOVERED FROM ORE FRACTURED
WITH NUCLEAR EXPLOSIONS**

W. D. Arnold
D. J. Crouse

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FROM ORE FRACTURED WITH NUCLEAR EXPLOSIVES

W. D. Arnold
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SEPTEMBER 1971

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Oak Ridge, Tennessee
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ABSTRACT

Results of laboratory tests simulating the processing of copper ore after fracturing with nuclear explosives indicate that only very small fractions of the radioactive fission products and neutron activation products will be dissolved on leaching with sulfuric acid. Tritium (as tritiated water) will be, by far, the dominant radionuclide in the circulating leach liquor, assuming use of a fusion device.

Copper that was recovered from the leach solution by cementation was significantly contaminated with ^{106}Ru . The ^{106}Ru was rejected effectively in electrolytic purification; therefore, the final copper product should be very weakly radioactive and not hazardous to the customer. However, the radioactivity level may be high enough to make the copper unsuitable for some specific uses. The tritiated water in the leach liquor and the ^{106}Ru in the cement copper are potential problems at the plant site and should be carefully considered in the design and in the operation of the facility. However, since the radioactivity levels would be low, adequate protection for the operating personnel should be neither difficult nor costly to provide.

Results of our tests showed that the use of solvent extraction as an alternative to cementation for recovering copper from the leach liquor would have important advantages. Since copper is efficiently separated from radionuclides in the extraction step, radioactivity in the processing operations beyond the extraction contactors should be negligible. The radioactivity level of the final copper product recovered from the solvent extraction strip solution by electrowinning should be almost undetectable; therefore, marketing of the copper should not present any difficulties. Because of the superior marketability of the product and the much simpler radiation control problems at the processing site, use of the solvent extraction--electrowinning flowsheet is recommended.

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1. INTRODUCTION

The fracturing of copper-bearing ore bodies with nuclear explosives, with subsequent leaching of the copper from the ore in place, has been proposed as a potential low-cost method for recovering copper from deep deposits that cannot be mined economically in the usual manner. The technical and economical feasibility of this proposal has been examined over a period of years by the Division of Peaceful Nuclear Explosives of the U.S. Atomic Energy Commission in cooperation with associated contractors and with the Kennecott Copper Corporation. An experiment (Project Sloop) was designed to field test the application in a deep low-grade copper ore deposit owned by Kennecott near Safford, Arizona.^{1,2} The Chemical Technology Division of the Oak Ridge National Laboratory has cooperated in this program by evaluating potential problems that might arise from the presence of radioactive contaminants in the processing cycle.

The nuclear detonation would create a chimney, several hundred feet high and approximately cylindrical in shape, containing several million tons of ore rubble. The recovery flowsheet involves percolating dilute sulfuric acid down through the broken ore to dissolve the copper, collecting the leach liquor at the bottom of the chimney and pumping it to the surface, recovering a copper concentrate from the solution by precipitation (cementation) or solvent extraction, upgrading the concentrate to pure copper metal, and recycling the copper-barren solution to the leaching step after fortifying it with acid (Fig. 1).

We have grouped the potential problems arising from the presence of radionuclides in the system under three main categories: (1) evaluation of radiation hazards to operating personnel in the processing complex; (2) possible radiocontamination of the copper product, which, of course, could affect its marketability; and (3) potential radiation hazards to the general public, which would arise from disposal of process wastes or from underground migration of radionuclides to the off-site environment. The last is outside the scope of the present studies but has been considered by Stead and others.^{3,4}

This report is the final summary of studies made at ORNL in relation to this program. It includes information that was reported previously at

ORNL DWG 71-140

Fig. 1. Copper Recovery by In-Situ Leaching of Copper Ore Broken by Use of a Nuclear Device.

a Plowshare Symposium⁶ and, in more detail, in our quarterly progress reports.⁶ In this report, an estimate is made of the amounts of the different radionuclides that would be present in the broken rock, their leachability under expected flowsheet conditions, and their behavior in processing steps such as copper cementation, solvent extraction, and electrolytic purification of copper. Finally, an assessment is made of potential hazards from radionuclides at the processing site and of the suitability of the copper products.

2. RADIONUCLIDES PRESENT

The quantities of tritium and each of the fission products produced by a detonation of a given yield depend, of course, on the type of device used. Figure 2 gives a rough estimate of the amounts of tritium and the more important fission products as a function of time following an arbitrarily assumed 50-kiloton shot in which 90% of the energy is derived from fusion and 10% from plutonium fission. The estimated production of 25,000 Ci of tritium per kiloton of fusion is the approximate midpoint of the range specified by Miskel⁷ (i.e., 7000 to 50,000 Ci/kiloton). Isotopes such as ¹⁴⁰Ba and ¹⁴³Pr, with half-lives in the range of 11 to 14 days, would be present in large amounts shortly after the detonation but would essentially disappear before the start of leaching at about 300 days. Other isotopes such as ¹⁰³Ru, ⁹¹Y, and ⁹⁵Zr-⁹⁵Nb, with half-lives of intermediate range, would be present in significant amounts at the start of leaching but would rapidly diminish in importance over the 1- to 2-year period of leaching. This would leave ¹⁰⁶Ru, ¹⁴⁷Pm, ¹⁴⁴Ce, ¹³⁷Cs, ⁹⁰Sr, and ¹²⁶Sb as the most significant fission products in the chimney during the time of processing. At 300 days, the activity of the tritium would be more than an order of magnitude greater than the total fission product activities. Choice of an all-fission device would, of course, greatly increase the relative importance of the fission products as compared with tritium.

Previous Plowshare experience with contained underground nuclear explosions has shown that most of the fission products are trapped fairly efficiently in the melted rock that accumulates at the bottom of the ore

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Fig. 2. Estimated Amounts of Radioactive Fission Products and Tritium Resulting from a 50-kiloton Shot (90% Fusion--10% Plutonium Fission).

chimney. This fused material is not very leachable. However, appreciable amounts of certain fission products, for example, ^{137}Cs and ^{90}Sr (which have gaseous precursors) and ^{106}Ru and ^{125}Sb (which form volatile compounds), move up into the chimney and deposit on the ore rubble in a more leachable form. The tritium should be present as tritiated water and, therefore, in a completely soluble form.

In addition to the fission products and tritium, radionuclides that are formed by neutron activation of the device components and of the surrounding ore will be present. The quantities of the radionuclides that are produced depend on the composition of the ore and on certain conditions of the experiment. The principal induced radionuclides present in an ore sample from the Safford deposit after irradiation in the Oak Ridge Research Reactor and a cooling period of 300 days were ^{48}Sc , ^{60}Co , ^{54}Mn , and ^{65}Zn (see Sect. 6.3). Since most of the released neutrons would be captured in the immediate vicinity of the detonation, the bulk of the activation products would be contained in the glassy melt and should be in a relatively unleachable form.⁸

3. PROCESS FLOWSHEET

The original process flowsheet (i.e., the flowsheet considered for Project Sloop) involves recovery of a copper concentrate from the leach liquor by cementation on scrap iron (Fig. 3). The cement copper from this operation would be melted into consumable anodes and purified by electrolysis before being marketed as copper metal. Most of our studies of the behavior of radionuclides were made assuming use of this flowsheet. Over the period of the studies, a new solvent extraction process^{9,10} was developed in industry as an alternative to cementation, and this process is obtaining rapid acceptance in copper ore processing. Our studies have indicated that the solvent extraction route (Fig. 3) provides a much more efficient separation of copper from the radionuclides than does the cementation route, and entails fewer personnel radiation protection problems at the processing site. For these reasons, solvent extraction appears to be the best process for use when nuclear explosives are employed in copper recovery.

Fig. 3. Cementation-Electrolysis and Solvent Extraction--
Electrowinning Flowsheets for Copper Recovery.

4. LEACHING OF RADIOACTIVE DEBRIS

Because copper ore that had been broken by nuclear explosives was not available for leaching tests, we studied the leaching of radionuclides from debris samples that were recovered from two underground test shots at the Nevada Test Site. Radiochemical analyses of these samples are given in Table 1. The samples were leached for several days at room temperature in the pH range of 1 to 3.5. Sulfuric acid was added during the leaching step to maintain the pH at the desired level.

The debris from test shot 1 was in the form of puddle glass (fused rock) and rubble from the bottom of the chimney. Under the expected flow-sheet leaching conditions (pH 2 to 3), less than 2% of any of the long-lived radionuclides were dissolved from the puddle glass (Fig. 4). However,

Table 1. Radiochemical Analysis of Test Shot Debris

Test shot 1: puddle glass and rubble from the bottom of the chimney; about 3-1/2 years old.
Test shot 2: sampled about 200 ft above the shot point; about 2 years old.

Radionuclide	Concentration (dis min ⁻¹ g ⁻¹ x 10 ⁴)		
	Test Shot 1		Test Shot 2
	Puddle Glass	Rubble	Rubble
¹³⁷ Cs	1.4	2.2	2.1
¹⁴⁴ Ce	2.2	0.04	<0.03
⁹⁰ Sr	4.1	0.09	0.2
¹⁰⁶ Ru	2.0	0.12	1.4
⁶⁰ Co	3.7	0.01	a
¹²⁵ Sb	a	a	0.4
Gross Gamma	2.6 ^b	0.23 ^b	1.0 ^b

^aNot detected.

^bGross gamma activity in counts min⁻¹ g⁻¹.

Fig. 4. Leaching of Test Shot Debris with Sulfuric Acid.

Procedure: 10-g samples of minus 4-mesh debris (test shot 1, analyses in Table 1) leached for two days at room temperature with 20 ml of dilute H_2SO_4 ; acid added during leaching to maintain the pH approximately constant at 1.0, 2.5, or 4. The supernate was analyzed for the various radionuclides.

about 50% of the ^{90}Sr , about 20% of the ^{144}Ce , and 5 to 10% of the ^{106}Ru were dissolved in this pH range from the ore rubble, which was sampled in the vicinity of the melted rock. These debris samples were about 3-1/2 years old at the time of leaching and thus did not contain detectable amounts of some radioisotopes, for example, ^{95}Zr - ^{95}Nb , that would be present at the time of copper recovery.

The second debris sample, which was taken about 200 ft above the shot point, was approximately 2 years old. The principal radionuclides in this sample were ^{106}Ru and ^{137}Cs ; smaller concentrations of ^{125}Sb and ^{90}Sr were also present. About 50% of the ^{90}Sr and 30 to 35% of the ^{106}Ru were dissolved in the pH range of 1 to 2 (Fig. 5). The amounts of ^{125}Sb and ^{137}Cs that were leached decreased from about 12% at pH 1 to 4% and 2%, respectively, at pH 2. In the test at pH 3.6, the gross gamma activity of the leach solution was only 1% of that obtained at pH 1 and was too low to permit analyses for the individual radionuclides.

4.1 Adsorption of Radionuclides by Copper Ore

The ion exchange properties of the copper ore would be highly important in regulating the quantities of certain radionuclides that would be dissolved and carried to the surface processing operation. Batch distribution tests with soluble radionuclides showed that some are adsorbed very strongly by the ore from acid leach solutions (Fig. 6). In these tests, soluble radioisotopes were added to a copper ore leach liquor that was adjusted to various pH levels and the solutions were then contacted with Safford ore leach tailings. Certain of the fission products such as ^{137}Cs , ^{95}Zr - ^{95}Nb , and ^{125}Sb and certain potential activation products such as tungsten and silver were adsorbed strongly, with distribution coefficient (K_D = counts per gram of ore, divided by counts per milliliter of solution) values of 10 or higher. Strontium was adsorbed much less readily, although still to a significant degree. The K_D values were less than 0.25 (<4% adsorption) for a number of elements including Ru, Fe, Eu, Sc, Y, Cr, Co, Zn, and Cd.

In other adsorption tests (results not shown) with Safford ore tailings and with solutions prepared by leaching radioactive debris, cesium adsorption coefficients were high and ruthenium and strontium adsorption

Fig. 5. Leaching of Debris from Test Shot 2. Procedure: 100-g samples of test shot debris (test shot 2) leached 6 days with 200 ml of synthetic copper ore leach liquor (2 g of Cu^{2+} , 1 g of Fe^{3+} , and 3 g of Fe^{2+} per liter as sulfates). Sulfuric acid was added during leaching to maintain the pH approximately constant at 1.0, 2.0, or 3.6. Amounts dissolved are based on analyses of the original debris and the supernate.

Fig. 6. Adsorption of Radionuclides by Safford Copper Ore.

Procedure: 5 ml of Safford copper ore leach liquor (adjusted to different pH levels and spiked with the appropriate radioisotope) was contacted 16 hr with 1 g of minus 20-mesh ore tailings; amount adsorbed was calculated on the basis of analyses of the head solution and the supernate. Less than 4% ($K_D < 0.25$) of Ru, Fe, Eu, Sc, Y, Cr, Co, Zn, and Cd were adsorbed in the pH range of 1.5 to 2.8.

coefficients were similar to those obtained by adding soluble radioisotopes to the liquor. Antimony, however, was not strongly adsorbed as before, suggesting that the chemical form of antimony in solution was different for the two experiments.

In an actual leaching operation, the chimney of broken ore would function as an ion exchange column several hundred feet high. Radionuclides dissolved from the ore in the bottom of the chimney in the early phases of the leaching cycle would adsorb on the ore as the leach solution was recycled through the ore column. Even distribution coefficients considerably less than 1 would result in appreciable ion exchange retention of the radionuclides by the ore because of the relatively large ore/solution weight ratio (possibly 10/1) that would prevail in the system. This would be expected to limit the buildup of radionuclides in the leach liquor to concentration levels far below those that would be predicted on the basis of simple batch leach test results such as those shown in Figs. 4 and 5. Small-scale column leaching tests, in which soluble radionuclides were added to a column of ore, confirmed this behavior (see Sects. 6.2 and 8.2).

5. CEMENTATION TESTS

Cementation tests were run with a simulated copper ore leach liquor to which various radioisotopes had been added. The purpose of these tests was to determine which of these radioisotopes might contaminate the cement copper. As expected, the more noble metals, such as silver, cemented almost quantitatively with the copper (Fig. 7). Also, about 25 to 40% of the tin, antimony, and ^{95}Zr - ^{95}Nb , and 15% of the ^{106}Ru were removed with 95% of the copper from the solution over the 90-min cementation period. No cementation (<2%) of ^{134}Cs , ^{51}Cr , ^{46}Sc , ^{59}Fe , ^{144}Ce , 152 - ^{154}Eu , ^{86}Sr , ^{65}Zn , or ^{60}Co was detected.

Because ^{125}Sb exhibited anomalous behavior in some tests, additional cementation tests were made with this isotope under a variety of conditions. The fraction of ^{125}Sb that cemented with the copper in 60-min tracer tests decreased from about 40% to 15% when the initial activity of ^{125}Sb in the liquor was decreased from 10^5 dis min^{-1} ml^{-1} to 10^3 dis min^{-1} ml^{-1} . In tests made with a liquor that was derived from leaching radioactive debris

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Fig. 7. Contamination of Copper Cementation Product. Procedure: 200 ml of copper ore leach liquor (2 g of copper per liter, pH 2.5) contacted with 0.7 g of detinned cans for 90 min. Amount of radioisotope removed from solution was calculated on basis of analyses of the head solution and the supernate. Less than 2% of the ¹³⁴Cs, ⁵¹Cr, ⁴⁶Sc, ⁵⁹Fe, ¹⁴⁴Ce, ¹⁵²⁻¹⁵⁴Eu, ⁸⁵Sr, ⁶⁵Zn, and ⁶⁰Co were removed with the copper.

and had an ^{125}Sb activity level of only $70 \text{ dis min}^{-1} \text{ ml}^{-1}$, no cementation of ^{125}Sb ($<2\%$) was detected (Table 2). As in the tracer tests, there was no significant cementation of ^{90}Sr or ^{137}Cs . The amounts of ^{106}Ru cemented were 14% at pH 1 and 8% at pH 2; these results fall within the range of 5 to 25% usually obtained with ^{106}Ru .

In studies of the variables affecting ^{106}Ru contamination of cement copper, only a slight change was found to occur in the amount of contamination as the pH or iron concentration of the liquor, or the rate of agitation during cementation, was changed. Although some of these variables affected the rate of copper cementation, there was usually a corresponding change in the rate of ^{106}Ru cementation so that the ^{106}Ru concentration in the copper product was relatively constant. As expected, the ruthenium contamination of the cement copper increased when the initial concentration of ruthenium in the leach liquor was increased while maintaining the copper concentration

Table 2. Results of Cementation Tests

Leach Liquor: Synthetic copper ore leach liquor after leaching of rubble from test shot 2.

Procedure: 100-ml samples of liquor (initial pH 1.0 or 2.0) contacted with 0.35 g of sheet iron (detinned cans) for 1 hr.^a

Radionuclide	Liquor from pH 1.0 Leach Test		Liquor from pH 2.0 Leach Test	
	Conc. in Liquor ($\text{dis min}^{-1} \text{ ml}^{-1}$)	Amount Cemented (%)	Conc. in Liquor ($\text{dis min}^{-1} \text{ ml}^{-1}$)	Amount Cemented (%)
^{90}Sr	460	<2	420	<2
^{106}Ru	2130	14	2040	8
^{125}Sb	215	<2	70	<2
^{137}Cs	1160	<2	210	<2
Gross gamma	890 ^b	7.5	490 ^b	7.5

^a60 to 70% of the copper cemented in these tests.

^bGross gamma activity measured in counts $\text{min}^{-1} \text{ ml}^{-1}$.

constant, but the effect was not linear. In the range of ^{106}Ru concentrations studied (1000 to 40,000 counts $\text{min}^{-1} \text{ml}^{-1}$, equivalent to about 0.001 to 0.05 $\mu\text{Ci/ml}$), increasing the initial ^{106}Ru concentration by a factor of 10 increased the ^{106}Ru concentration in the cement copper by a factor of about 20 (Fig. 3). About 95% of the copper was cemented in all tests, whereas the amount of ^{106}Ru cemented increased from 7.5% for the liquor containing the lowest concentration of ^{106}Ru to 33% for the highest. We have estimated that the ^{106}Ru in the circulating leach liquor would probably not exceed 0.001 $\mu\text{Ci/ml}$, which is about the lowest of the concentrations examined in this experiment.

Although certain potential radioactive activation products such as the silver and mercury isotopes cement quantitatively with copper (see Fig. 7), they should be present in extremely small amounts and the amounts present, even if in leachable form, would be held tenaciously by the ore through ion exchange mechanisms. Fission products such as ^{95}Zr - ^{95}Nb and tin cement appreciably with the copper; however, they also are adsorbed efficiently by the ore and, therefore, should not be present in significant amounts in the circulating leach liquor.

After considering the quantities of each of the various radionuclides that we would expect to be present in the leach liquor and the behavior of these radionuclides in the cementation process, we conclude that ^{106}Ru is the only radioisotope of importance with respect to radiocontamination of the cement copper. Attempts were made to remove ^{106}Ru from the leach liquor with various types of ion exchangers and other adsorbents, but none of these was very effective. Most of the ^{106}Ru can be removed from the recycle liquor by partial neutralization with lime to a pH of about 4.5. This method could be used to reduce, but not eliminate, the ^{106}Ru contamination. Fortunately, as described later (see Fig. 10 in Sect. 6.2), the ^{106}Ru is efficiently separated from the copper during electrolytic purification.

6. COLUMN LEACHING TESTS

To delineate the paths followed by some of the more important radionuclides in the copper recovery system, several column leaching--cementation

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Fig. 8. Effect of Initial ^{106}Ru Concentration on ^{106}Ru Contamination of Cement Copper. Solutions: synthetic leach liquor (pH 2.0) that was 0.15 M in SO_4^{2-} and contained, in grams per liter: 2.0 Cu^{2+} , 1.0 Fe^{3+} , 3.0 Fe^{2+} , and 0.5 NaCl; "spiked" with 1000 to 40,000 counts ^{106}Ru min⁻¹ ml⁻¹. Procedure: 200 ml of solution stirred at about 25°C with 0.7 g of detinned cans for 45 min.

tests were made. In these tests, samples of Safford ore (see Table 3) were "spiked" with the appropriate radionuclides and percolation-leached with dilute sulfuric acid by the open drainage--trickle leach method. The dissolved copper was recovered from the column effluent by cementation on detinned cans, and the depleted solution was acidified and recycled to the column. The behavior of the radionuclides was followed by measuring the contamination of the leach solutions and the cement copper products.

6.1 Tritium

If it is assumed that most of the energy of the device used to break the ore will be derived from fusion, tritium will be the dominant radionuclide in the chimney. The tritium will be present as tritiated water and should eventually all be taken into the leaching solution. To determine the manner in which tritiated water might be washed from the ore column, a 300-g ore sample was wetted with 3 ml of water containing about 180 μCi of tritiated water and heated at 85°C for 1 week in a closed 1-in.-ID column to allow equilibration of the tritiated water with any bound water in the ore. The tritiated water was added about 3 in. from the bottom of the 16-in. ore bed. About 80% of the tritium was removed in the first 0.4 bed volume of effluent when the column was leached with dilute sulfuric acid

Table 3. Composition of Safford Ore Sample

Element	Concentration (%)	Element	Concentration (%)
Cu	1.27	Ti	0.66
Al	7.31	K	4.03
Ca	0.006	Na	1.98
Mg	0.73	F	0.10
Fe	3.71	CO ₂	0.28
Mn	0.002	Σ S	0.62
Ni	0.011	SiO ₂	58.5

(pH 1.8) at the rate of 0.12 ml/min (Fig. 9). Less than 0.5% of the copper was dissolved in this volume of effluent. These test results suggest that the tritium concentration in the circulating leach liquor, and correspondingly the tritium hazard to the plant workers, could be appreciably decreased by discarding (rather than recycling) some of the initial effluent that contains most of the tritium but little or no copper.

6.2 Fission Products

Fission product behavior was studied by leaching 4-in.-diam columns of Safford ore (containing added radionuclides) with dilute sulfuric acid. In the first test, a 1500-g sample of minus 1/2-in. ore was mixed with 2000 g of rubble from test shot 1 (Table 1) and added to the column between 500-g layers of minus 1/2-in. ore. The ore was leached until about 80% of the copper was recovered. The pH of the dilute sulfuric acid fed to the column was adjusted in the range of 1.2 to 1.8 during the run so that the pH of the effluent was always above 2.0. The rubble contained a considerable amount of acid-consuming material since more than 5 liters of solution was passed through the column before the pH of the effluent fell below 7. Throughout the run, the gamma activity of the leach solution was less than 20% higher than the background activity. The ^{106}Ru content of the column effluent ranged from 25 to 45 dis $\text{min}^{-1} \text{ ml}^{-1}$, very close to the limit of detection. Only traces of ^{90}Sr and ^{137}Cs , and no ^{60}Co or ^{144}Ce , were detected in the effluents.

Fifteen batch cementations were made during the test. Of the radio-nuclides present in the column, only ^{106}Ru contaminated the products. The combined products contained about 8% of the total ^{106}Ru added to the column, and another 1% was in solution at the end of the test. The ^{106}Ru concentration of the cement copper products increased steadily with each cementation through the first eight (Fig. 10). About 10 to 20% of the ^{106}Ru in solution cemented with the copper in each cementation. Following cementations 8 through 11, the barren effluent was adjusted with lime to a pH of 4-5 to remove ruthenium before the solution was acidified and recycled to the column. The effect of this treatment is evident in the decreased ^{106}Ru concentration of subsequent products. When the lime treatment was discontinued, the ^{106}Ru contamination of the cement copper again increased

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Fig. 9. Elution of Tritium from a Column of Ore. Procedure: . 300 g of Safford ore and 3 ml of H_2O containing 180 μCi of tritiated water were heated at $85^\circ C$ in a stoppered 1-in.-diam column for one week. The ore was then leached with dilute H_2SO_4 (pH 1.8) at a flow rate of 0.12 ml/min.

Fig. 10. Ruthenium Contamination of Cement Copper Products.

Procedure: 2500 g of minus 0.5-in. Safford copper ore and 2000 g of test shot rubble mixed and placed in 4-in.-diam column; leached at 0.5 ml/min with recycle liquor; copper recovered from column effluent by cementation on detinned cans; barren cementation solution acidified with H_2SO_4 to pH 1.2-1.8 and recycled to column.

steadily. About 3 g of Ca(OH)_2 per liter of solution was required for adjustment to pH 4, and 9 g/liter was required for adjustment to pH 5.

A second run was made in which the fission products were added to the column in soluble form. A small volume of solution containing ^{86}Sr , ^{95}Zr - ^{95}Nb , ^{106}Ru , ^{134}Cs , and ^{144}Ce , each at a radioactivity level of 2×10^7 counts/min, was mixed with 1500 g of ore and added to the column as a layer about 2 to 8 in. above the bottom of the 16-in. bed. About 65% of the copper was leached from the ore with dilute sulfuric acid and recovered as cement copper in daily cementations on sheet iron. Appreciable fractions (10 to 30%) of the ^{86}Sr , ^{106}Ru , and ^{144}Ce were leached from the ore column. Almost none of the ^{95}Zr - ^{95}Nb or ^{134}Cs was found in the column effluent because they were strongly adsorbed by the ore. The initial portions of the effluent contained principally ^{86}Sr , but the concentration of this nuclide slowly decreased as the solution was recycled through the column. The concentrations of ^{106}Ru and ^{144}Ce , however, increased slowly as the pH of the effluent decreased to about 2 and did not change greatly thereafter. Near the end of the run, about 54% of the total activity of the effluent was due to ^{144}Ce , 42% was due to ^{106}Ru , and 3% was due to ^{86}Sr . Only ^{106}Ru was found in the cement copper in appreciable amounts. The ^{106}Ru contamination of the copper increased with each successive cementation; near the end of the run, the products contained about 0.1 μCi of ^{106}Ru per gram of copper.

6.3 Activation Products

In studying the behavior of the neutron activation products in the copper recovery system, a 2.4-g sample of reactor-irradiated Safford ore that had been cooled for 52 days (analysis in Table 4) was mixed with the layer of ore about 4 to 8 in. above the bottom of the 16-in. bed. The 4-in.-ID ore column was leached with dilute sulfuric acid, and copper was cemented from the effluent until about 55% was recovered. Only small fractions (1 to 10%) of the radioisotopes were dissolved during leaching, and less than 3% of the amounts dissolved reported to the cement copper products (Table 5). Considering these results and those obtained in the distribution and cementation tests described in Sect. 3, the neutron

Table 4. Neutron Activation Product Content of
Irradiated Safford Copper Ore

(Cooled 52 days)

Isotope	Half-Life	Concentration ($\mu\text{Ci/g}$)	Calc. Concentration After 300 Days of Cooling ($\mu\text{Ci/g}$)
^{46}Sc	84 d	109 ± 3.2	14.1
^{54}Mn	314 d	11.9 ± 1.4	6.9
^{59}Fe	45 d	77.8 ± 6.4	1.7
^{60}Co	5.3 y	13.5 ± 1.3	12.3
^{65}Zn	245 d	11.0 ± 6.3	5.5
^{75}Se	120 d	6.9 ± 0.5	1.6
^{95}Zr	65 d	1.4 ± 0.6	0.1

activation products appear to be a much less important consideration than the fission products in recovering copper from nuclear-broken ore.

7. PURIFICATION OF CEMENT COPPER

The cement copper will probably first be melted to produce impure copper metal in the form of a consumable anode and then converted to pure copper metal by electrolysis. Alternatively, the cement copper could be purified by dissolution in sulfuric acid and subsequent recovery of copper metal from the solution by electrowinning. Small-scale tests demonstrated that both procedures give efficient separation of copper from ^{106}Ru .

7.1 Melting and Electrolysis

In measuring the separation achieved by the melting-electrolysis route, cement copper that was contaminated with about 8.2×10^5 counts of ^{106}Ru per minute per gram was melted in a graphite crucible at 1300 to 1350°C in the presence of CaO , SiO_2 , and carbon. This level of ^{106}Ru contamination, equivalent to about $0.7 \mu\text{Ci/g}$, is probably at least one or

Table 5. Behavior of Neutron Activation Products in Copper Recovery System

Test procedure: 4500 g of Arizona copper ore, spiked with irradiated ore, was leached in a 4-in.-diam column at a flow rate of 0.5 ml/min with synthetic well water (0.4 g of Na_2SO_4 , 0.5 g of NaCl per liter) adjusted to pH 1.2 with H_2SO_4 . The first 400 ml of column effluent was discarded. For the remainder of the test, copper was cemented from the effluent once daily, and the cementation barrens were adjusted to pH 1.2-2.0 and recycled to the column.

Isotope	Amount Added to Column (μCi)	Isotope Distribution (% of total initially present)					In Column at End of Test ^a
		Decayed During Test	In Discarded Effluent	In Copper Products	In Final Leach Solution	In Analytical Samples	
⁴⁶ Sc	260	22.6	<0.1	0.07	1.1	0.7	75.5
⁵⁴ Mn	28.5	6.7	4.3	0.06	5.3	2.8	80.8
⁵⁹ Fe	186	38.0	<0.1	0.02	1.9	1.1	58.9
⁶⁰ Co	32.5	1.1	2.9	0.08	5.7	1.6	88.6
⁶⁵ Zn	26.3	8.4	3.1	0.17	9.7	4.7	73.9
⁷⁵ Se	16.6	16.4	<0.1	0.20	1.2	0.4	81.7
⁹⁵ Zr	3.3	32.8	<0.1	0.21	3.0	<1.0	63.0

^aBy difference.

two orders of magnitude higher than would be expected in routine processing. The molten copper was cooled, separated from the slag, and cast into two anodes. Each anode measured $3/4 \times 3/4 \times 1/16$ in. and weighed about 4.8 g. No separation of ^{106}Ru from the copper occurred in the melting process; the anodes had essentially the same ^{106}Ru concentration as the cement copper.

The two anodes were electrolyzed in consecutive runs in the same electrolyte (45 g of copper and 200 g of H_2SO_4 per liter) at a current density of about 13 A/ft² and a cell potential of 0.2 V. Separate copper sheets were used for cathodes in the two runs. About 75% of each of the anodes was electrolyzed, yielding a total of about 7 g of cathode copper product. The ^{106}Ru concentration in the electrolyte increased at a constant rate throughout the tests (Fig. 11), indicating that the ^{106}Ru was uniformly distributed (alloyed with the copper) in the anodes. About two-thirds of the ^{106}Ru released from the anodes was found in the electrolyte, and one-third of it was found in the "anode mud" that settled to the bottom of the electrolytic cell. Only 1 to 2% was found in the cathodes; the first cathode product contained 6800 counts of ^{106}Ru per minute per gram, and the second contained 14,000 counts min⁻¹ g⁻¹. These concentrations are lower by factors of 120 and 60, respectively, than the concentration in the cement copper.

7.2 Dissolution and Electrowinning

When ^{106}Ru -contaminated cement copper was dissolved in dilute aerated sulfuric acid at 80°C, about two-thirds of the ruthenium dissolved in the acid solution. About 0.5% of the cement copper was insoluble in the acid and settled out as a finely divided black sludge that resembled the "anode mud" formed during electrolytic purification of anodes that were cast from cement copper. This sludge contained the other one-third of the ruthenium.

The ^{106}Ru contamination of copper products prepared by electrowinning copper from the contaminated electrolyte solutions increased from 0.0014 to 0.20 μCi of ^{106}Ru per gram of copper as the ^{106}Ru concentration in the electrolyte was increased from 0.0027 to 0.43 $\mu\text{Ci/ml}$ (Fig. 12). In these tests, the electrolyte solutions initially contained 25 g of copper and

Fig. 11. Accumulation of ^{106}Ru in the Cell Electrolyte. Anodes containing 8.2×10^5 counts of ^{106}Ru per minute per gram were electrolyzed in a solution containing 45 g of copper and 200 g of H_2SO_4 per liter.

Fig. 12. Effect of ^{106}Ru Concentration in the Cell Electrolyte on the Contamination of Cathode Copper Products from Electrowinning Cell. Conditions: cell temperature of 55°C and current density of 10 A/ft^2 .

50 g of H_2SO_4 per liter. Copper was recovered from samples of the electrolyte solutions by treatment in a small cell for 6 hr at a current density of about 10 A/ft² and a cell potential of about 2 V. Both of the electrodes were platinum, and the cell temperature was 55°C. The cathode deposits contained about 14% of the copper and about 0.2% of the ^{106}Ru initially present in the electrolytes. The cathode copper products contained less ^{106}Ru by factors of 100 to 300, than the cement copper; this is about the same degree of separation that was obtained by melting and electrolysis.

7.3 Control of ^{106}Ru

As described in Sects. 7.1 and 7.2, ^{106}Ru accumulates rapidly in the cell electrolyte and eventually would become a significant radiation problem. Also, contamination of the cathode copper product increases as the ^{106}Ru concentration in the solution is increased. Consequently, some means of preventing excessive buildup of ^{106}Ru in the solution would be required. Attempts to scavenge ^{106}Ru from the electrolyte by sorption and solvent extraction techniques were not successful. Oxidation of the ruthenium, followed by sparging of the solution to remove volatile ruthenium tetroxide, gave good results, and this procedure appears to provide a satisfactory solution to the problem.

In the initial tests, the ruthenium was oxidized with sodium persulfate and the resulting oxidation product was removed by sparging the heated (or boiling) solution with air. Although as much as 80% of the ruthenium was removed from solution, most of it plated out on the walls of the equipment. Better results were obtained by using ozone as an oxidant. In this case, the volatilized ruthenium was carried efficiently from the system in the gas stream.

In batch tests, up to 90% of the ^{106}Ru was volatilized in 15 min at 90°C from simulated electrolyte solutions by sparging with air containing about 30 mg of ozone per liter. The removal of ruthenium was more efficient at 90°C than at 80°C. Use of ozonized oxygen instead of ozonized air had little effect on the ^{106}Ru removal efficiency.

Continuous Tests. - In a series of tests at 90°C, preheated electrolyte was fed continuously to an agitated vessel that had a capacity of about 45 ml of solution. Ozonized air was preheated and dispersed into the

solution through a fine glass frit. From 80 to 90% of the ^{106}Ru was volatilized using a solution residence time of 15 min, provided that the amount of ozone supplied was more than 0.5 mole per mole of Fe^{2+} in the electrolyte; none of it was removed when the mole ratio was less than 0.5 (Table 6). These results are in accord with the stoichiometric requirements for ozone, based on the reaction

They show that ozone equivalent to the Fe^{2+} must be supplied before any ruthenium can be oxidized and volatilized. A relatively small excess of ozone over that needed to oxidize the Fe^{2+} is necessary for efficient ruthenium removal.

Table 6. Oxidation and Volatilization of ^{106}Ru from Electrolyte Solutions with Ozonized Air

Procedure: About 300 cc of air per minute, containing about 30 mg of ozone per liter, was dispersed through a fine glass frit into simulated electrolyte solution (2 M H_2SO_4 containing 50 g of copper per liter and Fe^{2+} as shown; traced with $\sim 5 \times 10^4$ counts min^{-1} ml^{-1} of ^{106}Ru) at about 90°C .

Run No.	Fe^{2+} Concentration in Electrolyte (M)	Calculated Mole Ratio, $\text{O}_3/\text{Fe}^{2+}$	Solution Residence Time ^a (min)	Amount ^b of ^{106}Ru Volatilized (%)
1	0	-	15	80
2	0.05	1.2	15	90
3	0.10	0.66	15	81
4	0.20	0.37	15	0
5	0.20	0.18	7.5	0
6	0.20	0.74	30	92

^a Solution residence time in the reactor, which had a 45-ml holdup volume, was varied by varying the solution feed rate in the range of 1.5 to 6 ml per minute.

^b Average of four samples of effluent electrolyte solution taken during last half of each experimental run.

These results suggest that the ^{106}Ru concentration in the cell electrolyte could be controlled at a tolerable level by continuously withdrawing cell electrolyte at a low rate (possibly 10% of the electrolyte inventory per day) for a ruthenium removal treatment and then returning the partially decontaminated solution to the cell. Available data from production plants indicate that the Fe^{2+} concentration in the electrolyte is usually in the range of 0.02 to 0.05 M. Assuming that the maximum Fe^{2+} concentration is in this range, the estimated cost for ozone to treat 10% of the electrolyte volume per day would be less than 0.01¢ per pound of recovered copper.

Ruthenium Trapping. - In the ^{106}Ru volatilization experiments, the ^{106}Ru was quantitatively removed from the off-gas stream by passing it through a bed of activated carbon; scrubbing the off-gas with 1 M NaOH solution was only about 95% efficient. A 1-g sample of carbon (Type OL, 20-50 mesh, Pittsburgh Chemical Company) sorbed 5 μCi of ^{106}Ru without any measurable breakthrough. A saturation loading test (with breakthrough) showed the carbon to have a capacity of 2 mCi of ^{106}Ru per gram under the prevailing test conditions.

Sludge Removal. - Since about one-third of the ^{106}Ru was found in the "anode mud" that accumulated in the electrolytic cell (see Sect. 7.1), some provision would be needed for removing this radioactive sludge from the cell and disposing of it.

8. SOLVENT EXTRACTION OF COPPER

As an alternative to the cementation process, copper can be recovered from dilute acid liquors by solvent extraction (Fig. 3). The extracted copper is stripped from the solvent with sulfuric acid and purified directly by electrowinning. As mentioned previously, this process is now used commercially and is claimed⁹ to be a more economical route to the recovery of copper metal than the cementation-electrolysis process. The behavior of radionuclides during solvent extraction was first examined in batch tests and then in a small-scale column leaching--solvent extraction--electrowinning circuit. Results of the tests indicate that the copper product should be essentially free of radioactive contaminants.

8.1 Batch Extraction Tests

Two commercially available copper extraction reagents, LIX-64 (General Mills Company) and Kelex 100 (Ashland Chemical Company), were tested. Both are cation exchange reagents and efficient copper extractants. The Kelex 100 is supplied as Kelex 100-25, a 25% solution of Kelex 100 in tridecanol.

Isotherms for the extraction of copper from a simulated leach liquor that contained 2 g of copper per liter showed ~~maximum~~ copper loadings of about 2.3 g/liter for 15 vol % Kelex 100-25 in kerosene and about 2.9 g per liter for 10 w/v % LIX-64 in Varsol (Fig. 13). The pH of the aqueous phase decreased from an initial value of 2.0 during extraction owing to the exchange of copper for hydrogen ions; after extraction of essentially all of the copper, it was 1.5 in the test with LIX-64 and 1.35 in the test with Kelex 100. Kelex 100 is a stronger copper extractant (as evidenced by the steeper isotherm at low copper loadings) and capable of more efficient copper extraction at higher acidities than LIX-64*. Conversely, copper is more readily stripped from LIX-64 with sulfuric acid. Stripping tests with 2 M H₂SO₄ indicated that the maximum copper loading of the strip solution obtainable at room temperature when extracts containing about 2.5 g of copper per liter are stripped would be about 50 g/liter for 10 w/v % LIX-64 in Varsol and 30 g/liter for 15 vol % Kelex 100-25 in kerosene.

Of 11 radionuclides tested, only ⁹⁵Zr-⁹⁵Nb, ⁵⁹Fe, and ¹¹⁰Ag had extraction coefficients higher than 0.01 in the pH range of 1.5 to 2.5 when 10 w/v % LIX-64 in Varsol was used as the extractant (Fig. 14). These tests were made with simulated copper ore leach liquors that contained 0.2 g of copper per liter and tracer amounts of radionuclides. Ruthenium-106, the most troublesome contaminant in the cementation process, had extraction coefficients of less than 0.005 over this pH range, as did ¹³⁴Cs, ⁸⁵Sr, ⁶⁰Co, ⁴⁸Sc, ⁶⁵Zn, and ¹⁴⁴Ce. Copper coefficients were 10 or higher in all tests. Further study of the extraction of ⁹⁵Zr-⁹⁵Nb, ⁵⁹Fe, and ¹¹⁰Ag showed the extractions of the first two to be time dependent. The extraction

*Very recently, the General Mills Company announced the availability of LIX-64N, a modification of LIX-64, which extracts copper at higher acidities than does LIX-64. We have not tested the LIX-64N material.

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Fig. 13. Copper Extraction Isotherms. Aqueous phase: simulated copper ore leach liquor (initial pH 2.0) that was 0.1 M in SO_4^{2-} and contained, in g/liter, 2.0 Cu^{2+} , 1.0 Fe^{3+} , 3.0 Fe^{2+} , and 0.5 NaCl.

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Fig. 14. Effect of pH on the Extraction of Radioactive Contaminants with LIX-64. Organic phase: 10 w/v % LIX-64 in Varsol. Aqueous phase: simulated copper ore leach liquor that was 0.1 M in SO_4^{2-} and contained, in g/liter, 0.2 Cu^{2+} , 1.0 Fe^{3+} , 3.0 Fe^{2+} , and 0.5 NaCl; traced with the radioactive contaminants. Contact: 5 min at phase ratio of 1/1. Radionuclides that had extraction coefficients less than 0.005 were ^{106}Ru , ^{134}Cs , ^{88}Sr , ^{144}Ce , ^{60}Co , ^{66}Zn , and ^{46}Sc . The coefficient for distribution of tritiated water between the phases also was very low (<0.005).

coefficient for ^{59}Fe leveled off at about 0.15 after a 30-min contact period. After 60 min, the coefficient for ^{95}Zr - ^{95}Nb was 50 and still increasing. Essentially all of the ^{59}Fe but only about 30% of the ^{110}Ag and 20% of the ^{95}Zr - ^{95}Nb were stripped from the extracts with 2 M H_2SO_4 in a 10-min contact at a phase ratio of 1/1.

Extraction coefficients for the radionuclides were slightly higher with 15 vol % Kelex 100-25 in kerosene (Fig. 15). In 10-min extractions, coefficients were less than 0.01 for ^{106}Ru , ^{134}Cs , and ^{144}Ce , and between 0.01 and 0.05 for ^{60}Co , ^{85}Sr , and ^{125}Sb . As in the tests with LIX-64, extractions of ^{95}Zr - ^{95}Nb , ^{110}Ag , and ^{59}Fe were significant. Extraction coefficients for ^{95}Zr - ^{95}Nb were about 30. Iron extraction was time dependent; the extraction coefficient increased from 0.05 to 0.25 when the contact time was increased from 5 to 60 min. Material balances for ^{110}Ag were poor, and data for extraction of this radionuclide are not shown; some ^{110}Ag extraction did occur, however. The extraction coefficient for copper was 8 at a pH of 0.9 and more than 200 at a pH of 2.3 and higher.

Fortunately, it is anticipated that the concentrations of ^{95}Zr - ^{95}Nb , ^{59}Fe , and ^{110}Ag in the leach liquors obtained by in situ leaching of nuclear-broken ore should be extremely low; therefore, these radionuclides should not present any problem in copper recovery by solvent extraction.

8.2 Demonstration of Column Leaching-- Solvent Extraction--Electrowinning Flowsheet

A small-scale cyclic column leaching--solvent extraction--electrowinning circuit was operated to measure the separation of copper from radioactive contaminants by this process. Although relatively large amounts of several radionuclides in soluble form were added to the column of ore, the radioactivity of the copper metal products was so low that it was detectable only in a special low-level counting facility. A detailed description of the demonstration run follows.

A flow diagram for the test circuit is shown in Fig. 16. The 4-in.-ID column was loaded with 4500 g of minus 0.5-in. Safford ore. About 25 ml of solution containing ^{85}Sr , ^{95}Zr - ^{95}Nb , ^{106}Ru , ^{125}Sb , and ^{134}Cs , each at the radioactivity level of 2×10^7 counts/min, was added to the ore layer about 3 to 7 in. from the bottom of the 15-in. bed. Due to different gamma

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Fig. 15. Extraction of Radioactive Contaminants with Kelex 100.

Organic phase: 15 vol % Kelex 100-25 in kerosene. Aqueous phase: simulated copper ore leach liquor that was 0.1 M in SO_4^{2-} and contained, in g/liter, 0.2 Cu^{2+} , 1.0 Fe^{3+} , 3.0 Fe^{2+} , and 0.5 NaCl; traced with the radioactive contaminants. Contact: 10 min at phase ratio of 1/1. Radionuclides that had extraction coefficients less than 0.01 were ^{106}Ru , ^{134}Cs , and ^{144}Ce .

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Fig. 16. Flowsheet for Column Leaching--Solvent Extraction--Electrowinning Circuit.

counting efficiencies for the radionuclides, the amounts of each ranged from 12.5 μCi (for ^{134}Cs) to 52 μCi (for ^{106}Ru). These amounts are higher by factors of 4 to 40 than those we estimate would be in the nuclear-broken chimney (in this case, strontium would be present as ^{90}Sr rather than ^{88}Sr , and cesium would be present as ^{137}Cs rather than ^{134}Cs) in leachable form 300 days after use of a 90% fusion--10% plutonium fission device.

The leach solution flow rate was about 0.5 ml/min. Leaching was started with simulated well water (0.5 g of NaCl and 0.4 g of Na_2SO_4 per liter) that had been adjusted to pH 2.0 with sulfuric acid; the inventory of circulating leach solution in the system was about 1200 ml. In the initial part of the test, the column effluent had a pH above 4 and a low copper concentration; the effluent, which was collected in daily batches, was not treated by solvent extraction but, instead, was acidified to a pH of 2.0 with sulfuric acid and recycled to the column. The solvent extraction circuit was activated when the copper concentration in the effluent reached about 2 g per liter. Copper was recovered from the effluent by batch countercurrent extraction with 10 w/v % LIX-64 in Varsol, and the copper-barren liquor was recycled to leaching. The solvent extract was scrubbed with water to remove entrained liquor and stripped by batch countercurrent contact with about 4 N H_2SO_4 ; then the stripped solvent was recycled to extraction. The strip solution was treated in a small electrolytic cell to deposit part of the copper and subsequently recycled to the stripping system.

The concentration of copper in solutions in each of the process circuits during the run is shown in Fig. 17.

Leaching Circuit. - Based on analyses of the head ore and analyses of the column feed and effluent, about 65% of the copper was leached from the ore in 24.6 liters of effluent (about nine column volumes). About 6.6 liters of solution passed through the column before the copper concentration reached 2 g per liter (Fig. 18). The pH of the solution fed to the column decreased to about 1.4 after startup of the solvent extraction system. The copper concentration in the column effluent reached a maximum at an effluent pH of about 3.5, where most of the copper was leached. The test was discontinued when the copper concentration in the effluent fell to 1.2 g per liter.

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Fig. 17. Profile of Copper Concentrations in the Copper Recovery System.

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Fig. 18. Copper Concentration and pH of the Column Effluent.

Because of ion exchange retention on the ore, only minor fractions of the radionuclides reported to the column effluent. Strontium-85 was the dominant radionuclide in the initial effluent, and ^{106}Ru was dominant in the final effluent (Fig. 19). About 20% of the ^{86}Sr was in solution during the first half of the test; about 4% of it was in solution at the end. The amount of ^{106}Ru in solution increased from less than 1% in the early part of the test, when the pH of the effluent was high, to about 16% at the end. Less than 1% of the ^{125}Sb or ^{134}Cs was in solution at a given time, and ^{95}Zr - ^{95}Nb was not detected in any of the effluent samples.

Solvent Extraction Circuit. - Copper was recovered from the effluent by batch countercurrent extraction in three stages with 10 w/v % LIX-64 in Varsol. The organic-to-aqueous phase ratio in the extraction system was adjusted to provide a solvent copper loading of about 2 g per liter. Based on analyses of the leach liquor and raffinate samples, more than 98% of the copper was extracted (Fig. 17). The extracts contained from 1.8 to 2.0 g of copper per liter, and the raffinates contained 0.01 to 0.04 g/liter. The copper was separated efficiently from the radioactive contaminants in the extraction step. Most of the samples of solvent extract had gross gamma count rates less than 5% higher than background; the highest count rate for any sample was only about 8% above background.

The solvent extract was scrubbed with water at an organic/aqueous phase ratio of 10/1, primarily to prevent carry-over of any entrained leach liquor to the strip section. The scrub solutions contained 0.01 g of copper per liter at a pH of about 2.4 and essentially no radionuclides; the gross gamma activity of the individual solutions was less than 10% above background. In this test, the scrub solution was discarded; in process operation, it could be used in the makeup of leach solution.

The two-stage batch countercurrent stripping system was started with about 4.6 N H_2SO_4 . The residual acid concentration decreased to about 4 N after contact with the extract at an organic/aqueous phase ratio of 14/1 to yield copper concentrations of about 26 g/liter and 0.05 g/liter in the aqueous and the stripped organic, respectively. After a strip solution inventory sufficient to operate the electrowinning system was generated, the stripping phase ratio was adjusted to 2.8/1. Under these conditions, the concentration of copper in the stripped organic was usually in the

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Fig. 19. Concentration of Radionuclides in the Column Effluent.
The ⁹⁵Zr-⁹⁵Nb concentration was less than 20 dis min⁻¹ ml⁻¹ in all samples.

range of 0.1 to 0.2 g/liter; the concentration in the strip product solution averaged about 22.6 g/liter (Fig. 17). All of the samples of strip solution collected during the test had a gross gamma count that was less than 5% above background.

Electrowinning Circuit. - A total of 21.9 g of copper was recovered from the strip solutions in the small electrolytic cell. The copper was deposited on three 1.5 x 1.9 x 0.01 in. copper starting sheets spaced between four lead anodes of the same size. Two sets of cathodes were used during the run. The cell was operated at a current density of about 7.5 A/ft², a cell potential of about 2 V, and a cell temperature of 55°C. The average copper concentration of the electrolyte decreased from 22.6 to 17.6 g/liter as the electrolyte passed through the cell (Fig. 17). At the same time, the average sulfuric acid concentration increased from 4.01 N to 4.17 N, equal to 1.0 equivalent of acid for each equivalent of copper deposited. The acid generated during electrowinning, after exchange to the organic phase during stripping and to the leach liquor during extraction, was ultimately used to leach copper from the ore. After startup of the solvent extraction and electrowinning systems, no acid was added to the leaching system except for a small amount included in the acidified simulated well water that was added during the run to maintain the leach solution inventory.

We were not able to detect radioactivity in the cathode copper products using our counting instrument. Two of the cathodes were submitted to the ORNL Analytical Chemistry Division for direct analysis in a new low-level counting facility. Trace concentrations of ¹⁰⁶Ru, but no other radio-nuclides, were detected. The activities of copper products obtained early and late in the run, respectively, were measured to be 9×10^{-6} and 2×10^{-5} μ Ci/g. Analysis of the final electrolyte solution showed it to contain 0.005 μ Ci of ⁹⁵Zr-⁹⁵Nb and 0.01 μ Ci of ¹⁰⁶Ru per liter.

Kelex 100 Extractant. - Batch extractions were made with a 15 vol % solution of Kelex 100-25 in Varsol from a sample of the leach liquor that was in the system at the end of the test. Results of these extractions indicated that the separation of copper from radiocontaminants obtained with this reagent was approximately equivalent to that obtained with LIX-64.

The gross gamma count rate of the Kelex 100 copper extracts was only 2 to 6% higher than background.

Cementation Products. - For comparison, copper cementation products were prepared from three samples of leach liquor taken during the run. As expected, the cement copper was appreciably contaminated with ^{106}Ru . The amount of contamination increased from 0.02 to 1.0 μCi of ^{106}Ru per gram of copper as the $^{106}\text{Ru}/\text{Cu}$ ratio in the solution increased during the run (Fig. 20). Much lower, although significant, amounts of ^{125}Sb also contaminated the cement copper products. Assuming a decontamination factor of 100 from ^{106}Ru during electrorefining of the cement copper, the activity of the final copper products would be one to three orders of magnitude higher than the activity of products that were obtained by the solvent extraction--electrowinning process.

9. PROCESS EVALUATION

In this section, both the cementation--copper casting--electrolytic purification flowsheet and the solvent extraction--electrowinning flowsheet are assessed from the standpoint of radionuclide control problems. Considerations of potential hazards to operating personnel, suitability of the final copper product, and waste disposal are included. Based on our test results, the presence of radionuclides in the processing plant should be a manageable problem. The radioactive contamination of the copper product produced by either process should be extremely low and not hazardous to the customer. The solvent extraction--electrowinning flowsheet appears to have important advantages over the cementation process flowsheet in each of the above categories and is the recommended process route.

9.1 Leaching Circuit

Assuming the amounts of radionuclides present in the system to be those shown in Fig. 2, a rough estimate was made of the concentration of each that might be present in the circulating leach liquor (Table 7). The estimates of the fraction of each radionuclide that would be dissolved are based on our leaching results and also general Plowshare experience that

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Fig. 20. Radioactive Contamination of Cement Copper Products.

Procedure: 100-ml samples of column effluent were stirred for 1 hr with 0.35 g of sheet iron. The cement copper contained less than 0.002 μCi of ⁸⁵Sr, ⁹⁵Zr-⁹⁵Nb, or ¹³⁴Cs per gram.

Table 7. Estimated Concentrations of Radionuclides
in Circulating Leach Liquor

- Assumption: (1) No migration of radionuclides from the chimney.
(2) Leaching at 300 days after the shot.
(3) Uniform distribution of the dissolved radionuclides
in 45 million gallons of circulating leach liquor.

Isotope	Percent of Dissolution Assumed	Concentration in Leach Liquor ($\mu\text{Ci/ml}$)
$^{95}\text{Zr}-^{95}\text{Nb}$	0.01 - 1	$6 \times 10^{-6} - 6 \times 10^{-4}$
^{144}Ce	0.01 - 1	$5 \times 10^{-6} - 5 \times 10^{-4}$
^{141}Ce	0.1 - 2	$2 \times 10^{-6} - 5 \times 10^{-5}$
^{106}Ru	0.1 - 2	$6 \times 10^{-6} - 9 \times 10^{-4}$
^{103}Ru	0.1 - 2	$4 \times 10^{-6} - 7 \times 10^{-5}$
^{137}Cs	0.1 - 2	$7 \times 10^{-6} - 1 \times 10^{-4}$
^{126}Sb	0.1 - 2	$3 \times 10^{-6} - 5 \times 10^{-5}$
^{90}Sr	0.5 - 5	$1 \times 10^{-5} - 1 \times 10^{-4}$
^{89}Sr	0.5 - 5	$3 \times 10^{-5} - 3 \times 10^{-4}$
^{91}Y	0.5 - 5	$5 \times 10^{-5} - 5 \times 10^{-4}$
^{147}Pm	0.001 - 0.1	$1 \times 10^{-7} - 1 \times 10^{-5}$
^3H	100	6

only the fission product elements having gaseous precursors and those forming volatile compounds escape the pre-collapse cavity and contaminate the ore rubble; most of the fission products are trapped efficiently in the melted rock in unleachable form. Consideration was also given to the fact that a large portion of the soluble fraction of some isotopes (e.g., ^{137}Cs) would be held firmly by the ore through ion exchange mechanisms (see Sect. 4.1). The calculations indicate that the expected activity levels should be sufficiently low to make shielding of the process equipment (to prevent excessive exposure of personnel to radiation) unnecessary. With the exception of tritium, the potential hazards due to radioactivity appear to be of the same order as those in the uranium ore processing industry.

Tritium requires special consideration since it would be completely leached and in volatile form; the principal tritium hazard would be from tritiated water vapor. Since exposure to process vapors could be minimized by covering the processing tanks, the greatest potential for exposure to tritiated water vapor would be in underground operations* such as the servicing of pumps that force leach liquor to the surface. Table 8 shows estimated tritiated water concentrations in saturated air at 60 to 100°F, assuming that all of the water vapor in the air is derived from a leach liquor containing 6 μCi of tritiated water per cubic centimeter. These concentrations exceed the maximum allowed¹¹ for occupational workers (40-hr week) by factors of 16 to 55. This, of course, represents an extreme case since part of the water vapor in the air would come from sources other than the leach liquor and the presence of operating personnel underground would be required intermittently rather than continuously; also, protective clothing and respirators could be worn if necessary. Our leaching results (see Fig. 9) indicate that the tritiated water would be removed from the ore chimney at relatively high concentration in the initial portions of effluent and, therefore, uniform distribution of tritiated water in the liquor would occur only after the solution was recycled many times through

* Assuming that leach liquor collects in a tunnel under the formation as proposed for Project Sloop.¹ Retrieval of the leach liquor from the chimney by techniques other than tunneling has been considered but may not be feasible.

Table 8. Estimated Concentration of Tritium in Saturated Air

Temperature (°F)	Grams H ₂ O per m ³ of Saturated Air	Tritium Concentration in Air	
		μCi/cc ^a	Times the MPC ^b
60	13.3	8.0 x 10 ⁻⁵	16
70	18.4	11.0 x 10 ⁻⁵	22
90	34.2	20.5 x 10 ⁻⁵	34
100	45.7	27.4 x 10 ⁻⁵	55

^a Assuming saturation of air from a solution containing 6 μCi of tritiated water per cc.

^b MPC for tritiated water in air for occupational workers (40-hr week) is 0.5 x 10⁻⁵ μCi/cc.

the column. The tritium concentration in the circulating liquor could be significantly decreased by discarding the initial effluent. Whether this would be worthwhile, however, is questionable since it would complicate waste disposal problems by increasing the waste solution volume. Also, process water is scarce in the vicinity of the Safford ore deposits.

9.2 Cementation--Anode Casting--Electrolysis Flowsheet

Our tests have shown conclusively that significant contamination of the cement copper with ¹⁰⁶Ru can be expected. The expected level of contamination, however, is uncertain primarily because the fraction of the ¹⁰⁶Ru that would be present in the chimney in a leachable form is not known. The column leaching tests indicate that the copper/¹⁰⁶Ru ratio in the leach liquor would be considerably higher in the initial stages of the leaching cycle (high-pH effluent) than in the later stages; thus the ¹⁰⁶Ru contamination of the cement copper should increase as the leaching proceeds. This would be counteracted to some extent by the loss of some leach solution from the system and by decay of the ¹⁰⁶Ru. Considering all of these factors and assuming that the total amounts of ¹⁰⁶Ru in the system correspond to the use of the particular device considered in Fig. 2,* we

* Concerning effects of different devices, see refs. 12 and 13.

estimate that the ^{106}Ru content of the cement copper would probably not exceed 0.05 μCi per gram at any time over the period of processing and, for most of the copper recovered, would be considerably less than this value. Although not high, this level of contamination dictates that care be taken in the design and operation of the facility in order to minimize contact of the operating personnel with the cement copper.

Areas for potential exposure to large amounts of radiocontaminated cement copper include the cementation cones, maintenance tunnels underneath the thickeners that are used to reduce the moisture content of the cement copper concentrates, and the filters. For an operation of this type, use of continuous self-discharging filters rather than, for example, filter presses would appear desirable in order to minimize exposure of personnel. Good housekeeping should be practiced to avoid contamination of the processing area, and particular care should be taken to prevent the cement copper from spreading by drying and dusting.

Anode Casting. - The melting of the cement copper and the casting into consumable anodes do not result in any separation of ^{106}Ru from the copper (see Sect. 7.1). Although large amounts of slightly radioactive copper would be handled in these operations, this could be done remotely and the potential for significant radiation exposure would be small. The slag formed during the melting of the cement copper would be radioactive to the extent that it contains copper, and provision for its safe disposal would be required.

Handling and Storage of Anodes. - To obtain a rough idea of the maximum gamma-radiation dose that operating personnel conceivably could receive in handling the contaminated copper, calculations were made of the dose that would be received in a room in which copper anodes were stored prior to electrolytic purification. It was assumed that a worker would be situated in a corridor between copper anodes stacked to a height of 10 ft. The estimated gamma-radiation dose rates under these conditions are 0.2 and 10 mR/hr, respectively, for concentrations of ^{106}Ru in the copper of 0.001 and 0.05 $\mu\text{Ci/g}$. The higher dose rate would require that the worker's time in this area be limited to about 10 hr/week in order not to exceed acceptable dose limits. As mentioned above, a ^{106}Ru concentration of 0.05 $\mu\text{Ci/g}$ is the highest level of contamination that we estimate will occur; the

concentration should usually be much lower than this value. Estimates of the beta-radiation dose to the hands that would occur on contact of bare hands with the copper anodes are 4 and 200 mR/hr, respectively, for assumed ^{106}Ru concentrations in the copper of 0.001 and 0.05 $\mu\text{Ci/g}$. Use of gloves, which would undoubtedly be required if hand contact with the anodes was necessary, would greatly reduce the dose rates. Based on these estimates, control of the gamma or beta exposures within acceptable limits should not be difficult, provided proper monitoring techniques and protective equipment are used.

Electrolytic Purification. - As described in Sect. 7.1, efficient separation of ^{106}Ru from the copper (decontamination factor of 50 to 100) is obtained during electrolytic purification. Most of the ^{106}Ru accumulates in the cell electrolyte; the balance is found in the "anode mud" that accumulates at the bottom of the cell. Some provision for limiting ^{106}Ru accumulation in the cell electrolyte by, for example, volatilizing it with ozonized air (Sect. 7.3) would be required. The ^{106}Ru is easily trapped from the air with activated carbon. Suitable methods for handling and disposing of this carbon and of the radioactive anode sludge on its removal from the cell would be needed. However, it appears that providing for the protection of personnel in the electrolytic purification facility should not be difficult.

Because of the expected efficient separation of copper from ^{106}Ru during electrolytic purification, the radioactivity of the final copper product should be very low ($<0.001 \mu\text{Ci}$ of ^{106}Ru per gram of copper) and not hazardous to the customer. This activity level, however, could possibly be high enough to make the copper unsuitable for certain specialized uses, for example, in radiometric counting instruments, in the photographic industry, and for copper cooking vessels.

9.3 Solvent Extraction--Electrowinning Flowsheet

Solvent extraction provides a highly efficient separation of the copper from the radioactive contaminants in the leach liquor (see Sect. 8). Our tests indicate that the processing operations beyond the extraction contactors should be almost free of radioactivity. The radioactivity of

the leach liquor (Table 7) would be too low to constitute a significant radiation hazard to operators of the solvent extraction circuit. Provided the contactors were covered to minimize the release of tritium (as tritiated water vapor), tritium exposures to the operators also should be far below the allowable limit.

Our test results indicate that the radioactivity of the final copper product recovered by solvent extraction and electrowinning would be negligible (essentially undetectable); therefore, marketing of the copper should not present a problem. The superior marketability of the product and the much simpler radiation control problems (at the processing site) that result from the use of solvent extraction as compared with the cementation process are very important advantages. Thus solvent extraction is recommended.

9.4 Waste Disposal

If the solvent extraction--electrowinning flowsheet is used, the only apparent waste disposal problem would be final disposal of the leach solution. The volume of solution in the aboveground operations would not be large (a few million gallons at most) since almost all of the leach solution is absorbed and thus held by the ore. The solution in the processing tanks could be drained into the chimney at the conclusion of processing. The Safford ore body is dry and far above any known water table.¹ Any solution that drained from the chimney would be absorbed by the ore surrounding the chimney before it traveled a significant distance.

Use of the cementation--electrolytic purification flowsheet would yield additional wastes. These include slag from the anode forming operation (Sect. 7.1), anode sludge from the electrolytic cells (Sect. 7.1), and activated carbon used to trap ^{106}Ru that is volatilized from the cell electrolyte (Sect. 7.3). Since the only significant radionuclide in these wastes would be ^{106}Ru , which has a relatively short half-life (1 year), safe disposal of these wastes should not be difficult. Presumably, ground burial would be a suitable method of disposal. Alternatively, the material could be slurried in solution and pumped to the ore chimney.

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