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CHEMICAL APPLICATIONS OF NUCLEAR EXPLOSIONS (CANE):

PROGRESS REPORT FOR OCTOBER 1 TO DECEMBER 31, 1966

Compiled by:

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ABSTRACT

The amount of ^{106}Ru contamination in cement copper products increased by a factor of about 2.5 when the initial ruthenium concentration in the copper leach liquor was doubled. The ^{106}Ru in the cement copper also increased with increase in pH and temperature.

Green River oil shale has been retorted successfully in the laboratory unit. The oil distilled at shale temperatures between 300° and 350°C and the yield was about the same as obtained by the Fisher assay. In runs where the shale was moistened with tritiated water, less than 0.5% of the tritium was found in the water-scrubbed oil product.

Tritium and hydrogen exchange between tritiated water and methane is linear with respect to time and occurs at the rate of 0.7×10^{-6} mc/liter-day in a liter flask containing methane at approximately 1 atmosphere and ~ 20 mc tritium in tritiated water.

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1. INTRODUCTION

The purpose of this program is to conduct research, development, and evaluation studies as needed in selected areas of the Plowshare Program, especially those areas concerned principally with chemistry and chemical or metallurgical engineering. The emphasis placed on the various aspects of study at ORNL is related directly to the planning and scheduling of the overall Plowshare Program.

Projects which are receiving attention at this time, and which are described in this report include (1) studies of the distribution and possible fate of radionuclides formed during the use of nuclear devices to aid in the recovery of copper from ore deposits, (2) studies of the distribution and possible fate of radionuclides formed during the use of nuclear devices to aid in the recovery of oil from oil shales, and (3) the measurement of rates of exchange of tritium and hydrogen in water and natural gas under conditions which will aid the feasibility studies of the stimulation of gas production from wells by nuclear explosives (Project Gasbuggy).

Other projects that are receiving attention at ORNL are as follows:

- (1) Studies of hypervelocity jet sampling as a means of removing a specimen after irradiation in the neutron flux of a detonation, but ahead of the shock wave. The wood used to catch the jetted targets in the 5 final tests at the Vincentown, N. J., test range has been shipped to ORNL. The 100 pounds of plywood splinters could contain several grams of gold. No suitable method has been found to leach gold from "salted" plywood cubes so preparations are being made to burn the plywood and leach the ashes.
- (2) Thermal analysis of actinide compounds. The differential thermal analysis and thermalbalance apparatus designed and assembled for this program have performed satisfactorily in the shake-down tests at 1600°C with plutonium oxides.

2. NUCLEAR EXPLOSIVES IN COPPER ORE PROCESSING

D. J. Crouse F. J. Hurst
W. D. Arnold

Fracturing of copper ore deposits with nuclear explosives, followed

by in-situ leaching is being studied for the AEC by Lawrence Radiation Laboratory (LRL) and by the U.S. Bureau of Mines at Tucson, Arizona. The Oak Ridge National Laboratory is cooperating in this program by studying potential problems that might arise from the introduction of radioactive contaminants into the processing cycle. The proposed flow-sheet for recovering copper involves percolating dilute sulfuric acid down through the nuclear-broken ore to dissolve the copper, collecting the leach liquor at the bottom of the ore body and pumping it to the surface, recovering a copper concentrate from the solution by cementation on iron, and recycling the barren solution to leaching after fortifying it with acid.

2.1 Ruthenium Contamination of Cement Copper

Studies were continued of variables affecting the amount of ruthenium that cements with the copper. In earlier tests,¹⁻³ ruthenium was the only radionuclide that appeared important with respect to contamination of the cement copper products. Although ruthenium is separated effectively from copper during final purification by electrolysis, it is still desirable to reduce contamination of the cement copper in order to minimize contamination of the electrolytic processing facility.

The cementation tests were made with a ^{106}Ru -traced synthetic leach liquor (pH 2.0) containing about 0.15 M SO_4^{2-} and, in grams per liter, 2 Cu^{2+} , 1 Fe^{3+} , 3 Fe^{2+} and 0.5 NaCl. Copper was cemented by stirring 200 ml of the liquor in a beaker with 0.7 g of sheet iron (detinned cans), which had an initial surface area of about 1.5 in.² Samples of the supernatant solution were withdrawn at 15-min intervals and analyzed for ^{106}Ru and copper. The ruthenium content of the cement copper was calculated on the basis of the head liquor and supernate analyses.

2.1.1 Effect of Initial Ruthenium Concentration

Ruthenium contamination of the cement copper increased with increasing ruthenium concentration in the leach liquor. In the range of ^{106}Ru concentration studied (1000 to 40,000 counts $\text{min}^{-1} \text{ml}^{-1}$, equivalent to about 0.001 to 0.05 $\mu\text{C/ml}$), doubling the initial ruthenium concentration increased the ruthenium concentration in the copper by a factor of about

2.5 (Fig. 1). About 95% of the copper was cemented in all tests, whereas the amount of ruthenium cemented increased from 7.5% for the liquor containing the lowest concentration of ^{106}Ru to 33% for the highest. It was estimated previously¹ that the ^{106}Ru concentration* in the circulating leach liquor would probably not exceed 0.001 $\mu\text{c}/\text{ml}$ which is about the lowest of the concentrations examined in these tests.

For some unknown reason, the recoveries of copper obtained in this test series (95%) were much higher than are ordinarily obtained by cementing with the same amount and kind of iron for 45 min. The usual recoveries under similar conditions are about 60-65% (see results of tests described in subsequent sections of this report).

2.1.2 Effect of pH

Ruthenium contamination of the cement copper increased with decreasing acidity of the leach liquor (Fig. 2). This was due to an increase in the amount of ruthenium cemented at lower acidities since the amount of copper cemented was about constant at 65% in all tests. The ruthenium concentration in the cement copper was about 80% higher for the test at the lowest acidity (initial pH 2.1, final pH 4.1) than for the test at the highest acidity (initial pH 1.5, final pH 1.6).

2.1.3 Effect of Temperature

Increasing the temperature in the range of 16°C to 43°C increased ruthenium contamination of the copper (Fig. 3). However, the test results were somewhat erratic and it is likely that the effect of temperature change was masked by changes in other variables. For example, the final cementation pH increased with increasing temperature. The results shown in Fig. 3 are for 30-min contacts rather than 45-min because precipitation occurred within 45 min at the higher temperatures owing to pH rise.

* In making this estimate, it was assumed that the energy of the device would be derived predominantly from fusion. For an all-fission device, the ^{106}Ru concentration in the system would be much higher.

ORNL DWG 67-1501

Fig. 1. Effect of Initial Ruthenium Concentration on ^{106}Ru Contamination of Cement Copper. Solutions: Synthetic leach liquor (pH 2.0) containing 0.15 M SO_4^{2-} and 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 min⁻¹ ml⁻¹ of ^{106}Ru . Procedure: 200 ml of solution stirred at ~25°C with 0.7 g detinned cans for 45 min.

Fig. 2. Effect of pH on Ruthenium Contamination of Cement Copper. Solution: synthetic copper leach liquor (analysis in Fig. 1) adjusted to various pH levels and spiked with about 2000 counts min⁻¹ ml⁻¹ of ^{106}Ru . Procedure: 200 ml of solution stirred at ~25°C with 0.7 g detinned cans for 45 min.

Fig. 3. Effect of Temperature on Ruthenium Contamination of Cement Copper. Solution: synthetic copper leach liquor (analysis in Fig. 1) spiked with about 2000 counts min⁻¹ ml⁻¹ of ^{106}Ru . Procedure: 200 ml of solution stirred with 0.7 g of detinned cans for 30 min.

2.1.4 Effect of Excess Iron

Increasing the amount of iron supplied to the system had no significant effect on ruthenium contamination of the cement copper (Table 1). As expected, the amounts of both copper and ruthenium cemented in 45 min increased with increase in the amount of iron supplied.

2.1.5 Cementation of Ruthenium with Copper Absent

A cementation test was made with a synthetic leach liquor of the same composition as used in the tests described above except that copper was not present. The initial pH of the solution was 2.0 and the pH after 45-min contact with the sheet iron was 2.1. About 9% of the ruthenium cemented on the iron, which is about the same amount that cements under the same conditions when copper is present. When copper is present, essentially all of the cemented ruthenium is found with the cement copper, with only a negligible amount being associated with the residual sheet iron. On the other hand, no removal of ruthenium from solution is obtained using cement copper (or other forms of copper metal) in the absence of iron.

3. DISTRIBUTION AND POSSIBLE FATE OF RADIONUCLIDES DURING RECOVERY OF OIL FROM SHALES

J. W. Landry C. A. Blake, Jr.
J. M. Schmitt

Samples (100 gm each) of Green River oil shale have been retorted successfully in the laboratory unit. The design of the retort was described previously.⁴ A mixture of nitrogen (46 ml/min) and carbon dioxide (63 ml/min) was heated and passed through the crushed shale. The shale temperature was increased from 15 to 500°C in 4 hr. The exit gasses were passed successively through (1) a condenser held at 38°C (approximating the temperature in a nuclear chimney 1 year after detonation) which catches essentially all of the oil, (2) a condenser held at a few degrees below 0°C, (3) a column of Raschig rings coated with a light mineral oil, and finally, (4) a water scrubber.

The yield of oil in each of the runs was 12-13 gm which is in close agreement with the analysis given for this shale sample by the Bureau of Mines at Laramie.² Distillation of the oil began when the shale temperature

was about 300°C and was essentially complete when the shale temperature was about 350°C.

In 2 runs the shale was moistened with water (0.5 ml per 100 g) containing 0.5 mc tritium as tritiated water. In each test, less than 0.5% of the tritium was found in the oil product after washing with water.

4. TRITIUM EXCHANGE IN NATURAL GAS-WATER SYSTEMS

C. A. Blake, Jr. J. M. Schmitt

The rate of exchange of tritium and hydrogen between tritiated water and methane has been measured over a period of 111 days in a 1-liter flask containing (initially) 0.715 g methane and 19 mc tritium in ~0.01 g tritiated water at 1 atm total pressure and 25°C. Periodic analysis for tritiated methane in the gas phase indicates a linear tritium-hydrogen exchange rate of 7×10^{-6} mc/liter-day:

<u>Days of Exchange at 25°C</u>	<u>Millicuries ³H Exchanged in 1 liter</u>	<u>Rate of Exchange mc/liter-day</u>
12	9.7	0.8×10^{-5}
50	28	0.6×10^{-5}
111	75	0.7×10^{-5}

5. REPORTS ISSUED

1. C. A. Blake, Jr., K. B. Brown, and D. J. Crouse, Chemical Applications of Nuclear Explosions (CANE): Progress Report for July 1 to September 30, 1966, ORNL-TM-1688 (Nov. 9, 1966).
2. Other progress reports in this series:
 - ORNL-TM-1582 April 1 - June 30, 1966
 - ORNL-TM-1496 January 1 - March 31, 1966
 - ORNL-TM-1394 October 1 - December 31, 1965
 - ORNL-TM-1275 July 1 - September 30, 1965
 - ORNL-TM-1191 January 1 - June 30, 1965
 - ORNL-TM-1040 October 1 - December 31, 1964
 - ORNL-TM-963 July 1 - September 30, 1964

Table 1. Effect of the Amount of Sheet Iron on
Ruthenium Contamination of Cement Copper

Solution: Synthetic copper leach liquor (pH 2.0, analysis in Fig. 1) containing about 2000 counts min^{-1} ml^{-1} of ^{106}Ru .

Procedure: 200 ml of solution stirred at about 25°C with sheet iron (detinned cans) for 45 min.

Amount of Sheet Iron ^a (g)	Final pH	Amount Cemented (%)		^{106}Ru in Cement Copper (Counts $\text{min}^{-1} \text{g}^{-1}$)
		Cu	Ru	
0.72	2.90	57	20.6	3.96×10^5
0.97	2.60	75	26.5	4.05×10^5
1.21	2.75	80	29.9	3.64×10^5
1.63	2.90	87	36.9	3.59×10^5

^aStoichiometric iron requirement for reducing all of the ferric iron and copper in the liquor (but neglecting side reaction formation of H_2) is about 0.45 g.

6. TALKS PRESENTED

J. W. Landry, "The Reformed Sword: Peaceful Nuclear Explosives," presented at the Armistice Day dinner of the Athens, Tennessee, Kiwanis Club, Athens, Tennessee, November 11, 1966.

J. W. Landry, "Geographic Engineering with Peaceful Nuclear Explosives," presented at the Quarterly Dinner Meeting of the Atlanta Chapter of the Military Order of the World Wars, Fort McPherson, Atlanta, Georgia, November 16, 1966.

J. W. Landry, "The Converted Sword," presented to the Catholic Youth Organization, Oak Ridge, Tennessee, November 27, 1966.

J. W. Landry, "Nuclear Digging for Canals and Harbors," presented to the Annual United States Navy Nuclear Science Seminar, Oak Ridge, Tennessee, December 2, 1966.

J. W. Landry, "The Engineering Explosion is Coming!" presented to the Nashville subsection of the American Society of Mechanical Engineers, Nashville, Tennessee, December 14, 1966.

7. REFERENCES

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2. Chemical Applications of Nuclear Explosions (CANE): Progress Report for January 1 to March 31, 1966, ORNL-TM-1496 (April 20, 1966).
3. Chemical Applications of Nuclear Explosions (CANE): Progress Report for July 1 to September 30, 1966, ORNL-TM-1688 (November 9, 1966).
4. C. A. Blake, J. M. Landry, Report of Visit to the Laramie, Wyoming Petroleum Research Center of the U.S. Bureau of Mines and the Experimental Oil-Shale Plant near Rifle, Colorado, ORNL-CF-65-10-4, October 7, 1965.

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