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**EVALUATION OF NICKEL FERROCYANIDE SCAVENGING
OF URANIUM RECOVERY PLANT
SOLVENT EXTRACTION WASTE**

BY

M. J. STEDWELL

**TECHNICAL SECTION
ENGINEERING DEPARTMENT**

MARCH 22, 1954

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Plant Processes Unit
Separations Technology Sub-Section

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EVALUATION OF NICKEL FERROCYANIDE SCAVENGING OF
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INTRODUCTION

The Uranium Recovery Plant, over the life of the operation, will be required to attain maximum recovery of stored uranium and to produce aqueous waste in a volume equivalent to the volume of stored uranium waste which, after acidification, constitutes the feed stream for the process. Due to variations in the composition of the feed stream, the waste stream does not consistently have a volume equivalent to the volume of the stored metal waste. This variation in volume equivalence impedes tank farm scheduling because of the necessity for return of the process waste to underground tanks made available by the recovery operations.

More important to the long range Hanford Atomic Products Operation economics is the use of underground storage, with initial costs of approximately 35 to 45 cents per gallon and current replacement costs of 22 cents per gallon, for these comparatively moderate radioactive Uranium Recovery Plant wastes. A means of removing the long-lived fission products has been the objective of investigations conducted by the Applied Research Sub-Section, since studies conducted by the Radiological Sciences Department indicate that long-lived Cs-137 and Sr-90 are the isotopes which could migrate and enter the biological cycle via underground water movement.

A plant test, using nickel ferrocyanide to remove Cs-137 and Sr-90 from the Uranium Recovery Plant wastes, as proposed in HW-29383, ⁽¹⁾ has been completed and this memorandum has been prepared to summarize and report the results obtained from this test.

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SUMMARY AND CONCLUSIONS

Removal of Cs-137 and Sr-90 from the Uranium Recovery Plant solvent extraction wastes (combined RAW-ROW) by scavenging on a precipitate of nickel ferrocyanide $[\text{Ni}_2\text{Fe}(\text{CN})_6 \cdot x \text{H}_2\text{O}]$ was demonstrated by the plant test to attain a 420 to 10,000 and 40 to 200 fold decontamination for cesium and strontium, respectively, provided the pH of the neutralized waste was controlled within the range of 8 to 10. It is expected that scavenging of the plant solvent extraction wastes could routinely attain at least a 400 fold and probably greater decontamination of cesium and about a 40 fold decontamination of strontium.

Evaluation of the soil conditions, following the cribbing of about 250,000 gallons of scavenged waste and other parallel soil column studies allowed the Earth Sciences group of the Biophysics Section to conclude that up to 6,000 gallons of neutralized, scavenged, unconcentrated, settled solvent extraction waste supernate per square foot of crib bottom surface area, could be routinely cribbed.⁽³⁾

During the test, approximately 8,500 gallons of solvent extraction waste per ton of uranium processed was scavenged with about 93 pounds of $\text{Ni}_2\text{SO}_4 \cdot 6\text{H}_2\text{O}$ and 149 pounds of $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$. The volume of precipitate obtained in Tank 101-T was about 600 gallons per ton of uranium processed or about seven volume per cent of the waste.

A net saving of about \$500 per ton of uranium processed can be attained through reduction of underground storage volume (\$530), and elimination of steam required for two-stage evaporation (\$40), by the expenditure of approximately \$70 for scavenging chemicals.

DISCUSSION OF THE TEST

In October, 1953, approximately 500,000 gallons of Uranium Recovery Plant solvent extraction waste, produced during the processing of approximately 60 tons of uranium, were scavenged with nickel ferrocyanide by the procedure presented in HW-29383.⁽¹⁾ The scavenged waste

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was shipped to underground storage Tank 101-T for settling. During the production of the waste, pH values for the first one-half (approximately 240,000 gal.) of the waste averaged 12.0 with Cs-137 decontamination factors of 1 to 1.3, but reduction of the amount of NaOH added during neutralization reduced pH values for the second one-half (approximately 265,000 gal.) of the waste to an average of 9.8 with Cs-137 decontamination factors 420 to 10,000. Sample analytical data obtained from samples taken at one foot levels through two separate risers from Tank 101-T indicated that the waste was stratified so that the lower pH material was contained in the upper eight feet of liquid. (Analytical data are summarized in Tables I, II, and III).

On the basis of soil column studies (data are summarized in Table IV), Earth Sciences group, Radiological Sciences Department, recommended that the supernate in the upper eight feet of tank 101-T could be pumped to a 10 foot by 10 foot square crib located near test well 241-T-17.⁽²⁾ Cribbing of the upper eight feet of tank 101-T started on December 8 and was completed on December 21, 1953. Evaluation of the soil conditions, after the cribbing of the scavenged Uranium Recovery Plant wastes and other parallel laboratory studies, permitted the Earth Sciences group, Radiological Sciences Department, to recommend that up to 6,000 gallons per square foot of crib area of future scavenged, unconcentrated, settled Uranium Recovery Plant solvent extraction supernate wastes containing either Fe^{++} or $\text{C}_2\text{O}_4^{--}$ ion could be routinely transferred to cribs located near an East Area tank farm.⁽³⁾

After the completion of the transfer of the upper 8 feet of liquid from tank 101-T to the crib, the remaining supernate was transferred to tank 107-T. Measurement of the remaining volume indicated that approximately 36,000 gallons of sludge remained in tank 101-T or about 600 gallons of sludge per ton of uranium processed. In an attempt to clean the tank so that it could be reused for another purpose, the tank was flushed with water. Inspection of the tank indicated that the sludge was removed

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from a wide path leading from the risers where the water was added to the heel jet, but large quantities of sludge remain over the surface where the water did not reach it.

pH CONTROL

In the Uranium Recovery Plant, the pH of the neutralizer is measured and recorded on a continuous basis by a pH electrode inserted in a continuous sampler cell. Since the plant startup in November, 1952, the pH sampler has frequently plugged and then given erroneous pH values until the sampler is flushed and returned to a normal service. During the first portion of this test, the above conditions existed and resulted in the inadvertent over-neutralization of about 240,000 gallons of the scavenged waste. During the last one-half of the test, samples were frequently tested with pH paper and the caustic addition rate was adjusted to control the pH in the range of 8 to 10.

After the completion of the scavenging test, the Instrument Development group, Chemistry Unit, modified the pH sampler unit by the addition of a periodic (every 10 min.) dilute phosphoric acid flush. This modification has essentially eliminated the difficulties encountered with the pH monitor. Samples analyzed by the laboratory agree fairly well with the recorded pH values. It is expected that this modification will be sufficient to insure that the pH during routine scavenging can be controlled within the range of 8 to 10.

COST CONSIDERATIONS

During the test, approximately 506,000 gallons of unconcentrated scavenged waste was produced during the processing of about 60 tons of uranium or 8,500 gallons of waste per ton of uranium. From this waste approximately 36,000 gallons of settled sludge was obtained or approximately 600 gallons of sludge per ton of uranium.

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For comparison, costs for the current and scavenging processes are summarized below:

	<u>Present Process</u>	<u>Scavenging Process</u>
Volume of stored waste/Ton U	3,000 gal. (a)	600 gal.
Cost of storage space/Ton U	\$660.00	\$132.00
Cost of Chemicals/Ton U	<u>42.75 (steam)</u>	<u>71.43</u>
Total Cost/Ton U	\$702.75	\$203.43

(a) The waste is routinely evaporated from 8,500 to 3,000 gallons per ton of uranium by two stages, 1) the UR Plant primary waste evaporators and 2) the BiPO_4 first cycle evaporators.

From the above summary, it may be noted that storage space valued at about \$530 may be saved by the expenditure of only \$29 additional for chemicals in place of steam (Note: Cost of labor for the two processes is assumed to be equal).

FUTURE WORK

Studies for the possible future scavenging and cribbing of currently stored concentrated Uranium Recovery and reevaporated Uranium Recovery and Bismuth Phosphate first-cycle wastes are in progress.

ACKNOWLEDGEMENT

The cooperation of R. E. Brown and D. W. Rhodes, Radiological Sciences Department, W. G. Browne, J. J. Courtney, E. F. Curren, and L. W. Finch, Manufacturing Department, R. E. Burns and C. E. Michelson, Chemistry Unit, and members of their groups, in the completion and evaluation of this test, is appreciated.

MJS:ag

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REFERENCES

- (1) HW-29383, "Test Procedure to Evaluate Scavenging of TBP Plant Solvent Extraction Waste with Nickel Ferrocyanide," J. G. Bradley.
- (2) Letter to L. W. Finch, "Cribbing of Scavenged RAW", J. M. Smith, November 16, 1953.
- (3) HW-30652, "TBP Waste Disposal Criteria for Cribbing of Scavenged RAW," H. V. Clukey.
- (4) Analytical data obtained from R. E. Burns, Applied Research Sub-Section, Chemistry Unit.

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SUMMARY OF ANALYTICAL DATA OBTAINED ON SAMPLES
FROM THE TEST OPERATION⁽⁴⁾

TABLE I

Samples during Test

No. *	pH	Decontamination Factor	
		Cs-137	Sr-90
1	12.5	1.3	42
2	12.5	1	160
3	12.5	1	200
4	10.2	3,600	47
5	8.75	4,500	35
6	9.75	10,000	37

*Samples Obtained Daily during the Test.

TABLE II

Samples Obtained from Tank 101-T

No.	pH	Decontamination Factor	
		Cs-137	Sr-90
1 (a)	11.7	12	270
3 ft. (b)	9.8	660	287
8 ft. (b)	9.8	-	254
13 ft. (b)	13.6 (c)	12	2,000

(a) Taken from 101-T at 50 Per Cent Full.

(b) Taken from 101-T Three Days after Filling and before Complete Sludge Settling.

(c) Corrected for Sodium.

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TABLE III

Samples from Tank 101-T

Fifteen samples were obtained through the 12-inch pump pit riser and 16 samples were obtained through the 12-inch sluice pit riser. Samples were obtained through each riser at one foot intervals from the surface of the liquid to the lower level.

Sample Level*	pH	Pu D/m/ml	U G/L	Decontamination Factor			
				Cs-137	Sr-90	Gross Gamma	Gross Beta
Surface to 8 ft.	9.8	270	0.15	420	220	83	41
9 ft.	11.0	76	0.15	155	275	51	29
10 to 15 ft.	12.0	14	0.05	6.0**	1460**	2.8	3.1

* Sample level expressed in feet below liquid surface.

** Sr-90 decontaminates better at higher pH values while the Cs-137 DF decreases.

pH values for satisfactory decontamination of both are 8 to 10.

TABLE IV

Effluent samples from the Soil Column run of a sample obtained three feet below 101-T liquid surface.

No. *	Cs-137 Beta c/m/ml	Cs-137 DF
1	40	*Average additional DF from Analysis at 3 ft. level is 490.
2	9	
3	39	
4	10	
5	16	
6	18	
7	30	

* Represents samples from three column volumes of effluent.

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