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DECONTAMINATION OF BISMUTH PHOSPHATE
PROCESS FIRST CYCLE AND COATING
REMOVAL WASTES

Interim Report

INTRODUCTION

Recent successes with the use of metal ferrocyanides, particularly nickel ferrocyanide, for the removal of cesium from Uranium Recovery Process wastes prompted an investigation into the use of this carrier for the removal of cesium from wastes produced in the coating-removal and first-decontamination-cycle steps of the Bismuth Phosphate Process. Both in-line treatment of the wastes currently produced and treatment of supernatant liquids from wastes already stored in underground tanks were considered.

SUMMARY

Supernatant liquid from combined first cycle and coating removal wastes stored in underground tanks is already sufficiently low in Sr content (<0.1 uc/ml) to permit cribbing.

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Scavenging this liquid with nickel ferrocyanide reduced the Cs content to well below the permissible content for cribbing (<0.1 uc/ml).

Overall decontamination of fresh first cycle waste obtained by nickel ferrocyanide scavenging combined with decontamination due to alkaline insoluble salts formed when the waste is neutralized produced a supernatant liquid containing <0.1 uc/ml of either Sr or Cs. Similar treatment of combined fresh first cycle and coating removal wastes also produced a supernatant liquid containing <0.1 uc/ml of either Sr or Cs. However, this procedure results in the precipitation of all of the aluminum in the coating removal waste as aluminum hydroxide during pH adjustment. Some of the aluminum hydroxide may not redissolve at the maximum pH and would, consequently, have to be permanently stored.

Neutralization and nickel ferrocyanide scavenging of first cycle waste followed by addition of coating removal waste also produced a supernatant liquid containing <0.1 uc/ml of Cs. For some as yet unknown reason, Sr content of the liquid was high. Further study of this procedure is in progress. It is meant to simulate a plant process wherein first cycle waste would be neutralized and scavenged before transfer to underground storage while coating removal waste would be sent to the same underground tanks without treatment. It should be emphasized that, in the laboratory experiments noted here, mixing of the two wastes was far more thorough than could be expected in underground storage tanks.

EXPERIMENTAL

A. Decontamination of Supernatant Liquid from Stored Wastes

A sample of supernatant liquid from the 109 TX tank was obtained about April 1, 1954. Fresh first cycle and coating removal waste from the T plant had been discharged into this tank until February, 1954. Fission product, plutonium and uranium content of the waste liquid is shown in Table I; pH of the waste was 10.5. To determine scavenging of the waste by nickel ferrocyanide, a portion was brought to pH 8.5 by addition of HNO_3 and 0.005 moles of $\text{K}_4\text{Fe}(\text{CN})_6$ and of $\text{Ni}(\text{NO}_3)_2$ were added per liter. The resulting slurry was stirred one-half hour and centrifuged 10 minutes. Fission product, plutonium and uranium content of the centrifugate are shown in Table I.

TABLE I
DECONTAMINATION OF BISMUTH PHOSPHATE
PROCESS FIRST CYCLE WASTE SUPERNATANT LIQUID

Constituent	Fission Product Content, uc/ml (1)	
	As Received	Scavenged
Gross β	5.7	3.1
Gross γ	12.	6.8
Cs, γ	0.88	0.00065
Sr, β	0.0085	0.0051
Rare Earths + Y, β	0.60	0.23
Ru, β	2.2	1.3
Zr, γ	5.0	3.0
Nb, γ	3.0	1.5
Pu, d/m/ml	900.	1200.
U, g/l	0.060	0.0079

(1) Calculated from c/m/ml assuming 7.5% geometry where beta was counted and 3.36% geometry where gamma was counted.

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Initial radioactive cesium content of the stored waste liquid was a factor of about 10 over the 0.1 uc/ml recommended by the Radiological Sciences Department for wastes to be cribbed on a large scale (600 gallons per square foot of crib).⁽¹⁾ Scavenging with nickel ferrocyanide reduced the cesium content to about 7×10^{-4} uc/ml which is well below the tolerance just stated. Initial radioactive strontium content of the waste was well below the stated 0.1 uc/ml tolerance for large scale cribbing.⁽¹⁾

B. In-line Treatment of Currently Produced Wastes

Ferrocyanide scavenging of first cycle waste as it is produced in the Bismuth Phosphate Process is complicated by the fact that coating removal waste is jetted through the same waste receiving tank (15-8) in the canyon and also stored in the same underground tanks. Although individual batches of first cycle waste are neutralized to a pH of about nine, which is satisfactory for cesium scavenging by nickel ferrocyanide, the subsequent addition of coating removal waste (a highly alkaline solution) produces an overall pH in the stored waste of about 10.5. This is somewhat higher than desirable (<10) for optimum nickel ferrocyanide scavenging of cesium. The effect of the addition of coating removal waste to nickel ferrocyanide-scavenged first cycle waste was studied as well as the decontamination obtained by nickel ferrocyanide treatment of first cycle waste both alone and when combined with coating removal waste prior to scavenging.

Samples of first cycle (acidic) and coating removal wastes were obtained from the T plant on June 17, 1954. Fission product and plutonium content of these wastes are shown in Table II. Both wastes contained some solid material which is to be expected since coating removal waste always contains some solid material from alkaline insoluble impurities in the aluminum cans and since the BiPO_4 by-product cake is generally not completely dissolved as it is slurried from the centrifuge. Analyses given are for the clear solution only.

TABLE II
DECONTAMINATION OF FIRST CYCLE AND COATING REMOVAL WASTES

Constituent	Activity Content uc/ml ⁽¹⁾					
	Soln. A	Soln. B	Soln. C	Soln. D	Soln. E	Soln. F
Gross β	250	9.1	2.4	0.85	1.4	1.0
Gross γ	430	27	1.1	19.	3.2	3.8
Cs, β	0.18	1.2	0.0007	0.006	0.004	0.0003
Sr, β	13	0.54	0.043	3.2	0.0053	0.0085
R.E. + γ , β	180	0.21	2.2	--(2)	--	--
Zr, γ	103	8.0	0.49	--	--	--
Nb, γ	340	6.2	0.12	--	--	--
Ru, β	0.79	0.0	0.29	--	--	--
Pu, α /m/ml	2400	1500.	--	--	--	--
Volume solid/total volume waste			0.12	0.30	0.45	0.27

Soln. A - Acidic first cycle waste liquid.

Soln. B - Coating removal waste liquid.

Soln. C - Supernatant liquid from nickel ferrocyanide scavenged first cycle waste.

Solns. D, E, and F - See Page 4.

(1) Calculated values based on beta counting at 7.5% geometry (Ru DEF) and gamma counting at 3.3% geometry (Cs 137).

(2) Not determined for these solutions.

- Soln. D - Supernatant liquid from mixture of coating removal waste and nickel ferrocyanide scavenged first cycle waste.
- Soln. E - Supernatant liquid from nickel ferrocyanide scavenged mixture of coating removal and first cycle wastes. Vol. CRW/1st CyW = 0.26.
- Soln. F - As Soln. E. Vol. CRW/1st CyW = 0.4.

A sample of the acidic first cycle waste was made 0.005 M in $K_4Fe(CN)_6$, brought to pH 9.1 with 50% NaOH and made ca. 0.005 M in $Ni(NO_3)_2$. The resulting slurry was stirred one-half hour and centrifuged. Fission product content of the supernatant liquid is shown in Table II (Soln. C). Centrifuged solid volume was about 19 per cent of the neutralized waste volume.

One volume of the acidic first cycle waste was treated as described in the previous paragraph except that, prior to centrifugation, 0.22 volumes of coating removal waste were added, and this mixture was stirred one hour. This procedure was intended to simulate combination of coating removal waste with scavenged first cycle waste in underground storage tanks. Mixing of the two wastes was much more complete in this experiment than would be expected in plant practice. On addition of the coating removal waste, the pH of the mixture increased to 10.7, and the solid present changed from pale blue to tan. The volume of centrifuged solid was about 30 per cent of the total waste volume. Fission product content of the supernatant liquid is shown in Table II (Soln. D).

Although not now done in the plant, the possibility was considered that first cycle and coating removal waste could be combined in the 15-8 tank, neutralized to a pH of about 10, scavenged, and discharged to storage. The high pH in the storage tanks due to excess caustic in the coating removal waste could thus be avoided. To simulate this procedure, one volume of acidic first cycle waste was combined with 0.26 volumes of coating removal waste. The pH of the mixture at this point was 0.4, and only a small amount of solid was present. The mixture was made 0.0045 M in $K_4Fe(CN)_6$, and 50% NaOH was added to bring the pH to 9.0. During caustic addition the slurry became quite thick with aluminum hydroxide and stirring was difficult with the equipment used. At the final pH, the slurry was reasonably fluid. The mixture was made ca. 0.0045 M in $Ni(NO_3)_2$, stirred one-half hour and centrifuged. Solid volume was about 45 per cent of the total waste volume. Fission product content of the supernatant liquid is shown in Table II (Soln. E).

The experiment described in the previous paragraph was repeated with equipment to provide more positive stirring during neutralization. Volume ratio of coating removal to first cycle waste was 0.4. This ratio approximates that to be expected under present T plant operating conditions, namely, 865 gallons of coating removal waste per dissolver load and 1965 gallons of acidic first cycle waste per run.⁽²⁾ Volume of centrifuged solid at pH 9 was 27 per cent of the total waste volume. Fission product content of the supernatant liquid is shown in Table II (Soln. F).

IV. Discussion

As previously noted, the Radiological Sciences Department has recommended maximum Cs^{137} and Sr^{90} contents of 0.1 uc/ml for Uranium Recovery Process wastes to be cribbed on a large scale (600 gallons per square foot of crib). Supernatant liquids from scavenged first cycle and coating removal wastes are chemically similar to the Uranium Recovery Process wastes although somewhat lower in total gross salt content. Recommended maximum Cs^{137} and Sr^{90} contents for cribbing of supernatant liquids may well be approximately the same as those for Uranium Recovery Process wastes.

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To the extent that the samples of first cycle and coating removal waste obtained are representative, an appreciable part of the cesium present in supernatant liquid from the combination of these wastes when stored is contributed by the coating waste. In fact the first cycle waste is only slightly above large scale cribbing tolerance without any scavenging. It is apparent that neutralization plus nickel ferrocyanide scavenging of the first cycle waste alone will produce a supernatant liquid well below the proposed cribbing tolerances for both cesium and strontium (Soln. C). Addition of coating removal waste to scavenged and neutralized first cycle waste does not interfere with cesium removal even though the final pH is above that previously recommended for cesium removal (Soln. D). This observation confirms experience previously noted with respect to cesium carrying on nickel ferrocyanide, namely, that although scavenging is poor when the precipitation is made at pH's in excess of 10, it is difficult to remove cesium from the solid after it has been scavenged during precipitation at a lower pH⁽³⁾. Indeed, in this particular experiment cesium was removed from the coating removal waste at relatively high pH and on preformed nickel ferrocyanide. This suggests the possibility that preformed metal ferrocyanides may be useful for removing cesium from highly alkaline solutions such as coating removal waste and stored Redox process waste. This point is under study. The high strontium content of Soln. D is difficult to explain. Reanalysis of sample confirmed the value shown. Further experiments concerning this point are underway. The increased solid volume noted in this experiment as compared to that when first cycle waste alone was neutralized and scavenged indicates that some aluminum hydroxide is precipitated at the pH of the combined wastes.

Combination of first cycle and coating removal wastes prior to neutralization and scavenging, in order that the final pH of the stored waste can be controlled, results in supernatant liquids satisfactory for large scale cribbing from the standpoint of either Sr⁹⁰ or Cs¹³⁷ content. However, this procedure has the disadvantage of resulting in more solid due to aluminum hydroxide precipitation at the lower pH.

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V. References

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