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REMOVAL OF CESIUM FROM URANIUM RECOVERY PROCESS WASTES

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REMOVAL OF CESIUM FROM URANIUM RECOVERY PROCESS WASTE

I. INTRODUCTION

The Uranium Recovery Process (TBP Process) at Hanford extracts and decontaminates uranium from the Metal Waste produced in the Bismuth Phosphate Process. Aqueous waste, approximately equal in volume to that of the Metal Waste itself, results from the process. Although of several years' age, these wastes are still sufficiently radioactive that they must be returned to underground tanks for storage. Since the total volume of these wastes which will be produced amounts to millions of gallons, and since the cost per gallon of underground storage space is currently about 22 cents, storage of the wastes in underground tanks will represent a very considerable expense.

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For several years aqueous wastes of low radioactive content have been discharged to ground at Hanford. In connection with these cribbing activities, extensive studies of the adsorption of fission products by the sandy soils underlying the discharge areas and of the migration of the ground waters under the areas have been made by the Radiological Sciences Department at Hanford. Polyvalent cations are strongly adsorbed by the soil. Monovalent cations are poorly adsorbed if present in solutions of high salt content. Ground waters migrate toward the Columbia River very slowly; as much as 1500 years may be required for them to reach the river if they continue their present direction of flow. Under the most pessimistic conditions, involving a change in direction of flow, they may reach the river in 50 years. These observations point out the desirability of removing, from wastes to be cribbed, those long-lived radioactive constituents which are poorly adsorbed by soil. Cesium (Cs-137) and strontium (Sr-90) are the principal constituents of Hanford wastes which possess these characteristics. Strontium, while more hazardous biologically, is of somewhat less concern than cesium because it is better adsorbed from high-salt solutions by soils. This report describes research done to develop on inexpensive process for the removal of fission products, especially cesium, from Uranium Recovery Process Wastes.

II. SUMMARY

Of a number of scavenging agents tried, various metal ferro-and ferricyanides were found to be the most effective for the removal of cesium from high-salt-content wastes such as the Uranium Recovery Process RAW stream. Nickel ferro-and ferricyanides and copper, cobalt, and iron ferrocyanides all gave cesium decontamination factors of from several hundred to more than a thousand when precipitated in the waste at acidities ranging from 2.5 M to pH 4. Above pH 4, ferric ferrocyanide loses its effectiveness for cesium carrying as does copper ferrocyanide at pH greater than eight. Cobalt and nickel ferrocyanide are effective at pH up to ten.

In a plant production test in which 500,000 gallons of RAW were scavenged with nickel ferrocyanide, cesium decontamination factors of about four hundred were obtained during that part of the test in which satisfactory pH control during neutralization of the waste was maintained.

Laboratory studies showed that these metal ferrocyanides can be used to remove cesium effectively not only from currently produced RAW, but also from the supernatants above already stored Uranium Recovery Process wastes and from the RAW stream which will result if oxalic acid is used in the RA column scrub instead of the ferrous sulfamate now used. This latter modification to the Uranium Recovery Process was scheduled for a plant production test at the time these studies were made.

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III. EXPERIMENTAL

A. General

The Uranium Recovery Process produces an aqueous waste (RAW) which approximates the composition shown in Table I, Column 2. In ordinary practice, the waste is neutralized to pH about 9.5, concentrated by evaporation of uranium and stored in mild steel underground tanks of either 530,000 or 750,000 gallon capacity. The waste then has a composition approximating that shown in Table I, Column 3. Iron compounds, ferric phosphate and/or ferric hydroxide, are precipitated when the waste is neutralized and concentrated. At low pH, 6 to 8, the phosphate predominates

TABLE I

COMPOSITION OF URANIUM RECOVERY PROCESS AQUEOUS WASTE (RAW)[1]

	Moles per Liter	
Constituent	Acidic, Not Concentrated	Basic, Concentrated
UNH	0.00093	---
$SO_4^{=}$	0.214	0.35
$PO_4^{\equiv}$	0.179	0.25
NO_3^-	4.45	6.2
Cl^-	0.016	0.022
$H_2NSO_3^-$	0.034	---
H^+	2.60	---
Na^+	2.80	7.6
Fe^{++}	0.017	
NH_4^+	0.034	
$Na_2U_2O_7$	---	0.0013
$Fe(OH)_3$ - $FePO_4$	---	0.0024

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(1) HW#4 flowsheet, HW-19140, Uranium Recovery Technical Manual, Nov. 10, 1951, Figure 1-2

while at high pH, > 11, the iron is present mainly as the hydroxide. Although these iron compounds are very good carriers for some radioactive constituents of the waste such as strontium, rare earths, plutonium, etc., they carry little, if any, cesium. The removal of cesium from the RAW stream by precipitation of metal ferrocyanides to supplement the scavenging action of the alkaline insoluble materials already present has been studied in considerable detail.

At the time these studies were made, an appreciable part of the Metal Waste at Hanford had been processed through the Uranium Recovery plant and the aqueous waste (RAW) had been neutralized, concentrated, and returned to the underground storage tanks. Alkaline insoluble materials previously mentioned settle out of these wastes leaving a supernatant whose radioactivity, in wastes several years old, is due almost entirely to Cs^{137}. Further decontamination of these supernatants by scavenging them with metal ferrocyanides has been studied.

Iron present in the RAW results from the use of ferrous sulfamate in the extraction column scrub (RAS) to assure that plutonium will be in the tervalent oxidation state and, consequently, not extracted by tributyl phosphate. Consideration is being given to the substitution of oxalic acid for ferrous sulfamate in the RAS. Extraction of plutonium would then be prevented by the formation of aqueous-favoring oxalate complexes. The effect of this modification on the decontamination of the resulting aqueous wastes by various metal ferrocyanides was studied.

B. Preliminary Investigations of Proposed Cesium Carriers

Several suggested cesium precipitants or carriers were investigated for possible application to TBP process wastes. Dipicryl amine (an analytical reagent for potassium), $KClO_4$, $Ca_3(PO_4)_2$, and NH_4CaPO_4 were tried under conditions considered optimum for cesium carrying. Negligible-to-poor cesium removal was obtained. NH_4IO_3 precipitated from 0.6 $\underline{M}$ HIO_3 - 0.4 $\underline{M}$ NH_4NO_3 solution carried 87 per cent of the cesium present.

This carrier was not investigated in an RAW system because of its inherent expense. $(NH_4)_3\,Co(NO_2)_6$ and $K_3Co(NO_2)_6$ were both found to be good cesium carriers under specialized conditions but neither was effective in removing cesium from neutralized RAW presumably because of the high sodium ion concentration.

C. Scavenging of RAW with Metal Ferrocyanides

Some work done at Mound Laboratory on the decontamination of Uranium Recovery Process wastes indicated that ferrous ferrocyanide is an effective cesium carrier.(2) Further work at HAPO has shown that several metal ferro - and ferricyanides are excellent cesium carriers. Nickelous, cobaltous, cupric, and ferrous ferrocyanides and nickel ferricyanide have all been shown to be very effective in removing cesium from RAW provided the precipitation is made in an acceptable pH range. Tables II and III show cesium decontamination factors obtained when synthetic RAW solution, spiked with inert and radioactive cesium, was scavenged with various ferrocyanides. The data in Table II show that ferrous ferrocyanide, formed when $K_4Fe(CN)_6$ is added to RAW, effectively removes cesium at pH values as high as 10 especially if the $K_4Fe(CN)_6$ is added before the waste is brought to high pH.

It was desired to find a carrier for cesium which would be effective at a sufficiently high pH to permit allowing the slurries to settle in mild steel tanks without corroding the tanks. Presumably, any pH above 7.5 would be satisfactory from this standpoint. However, exact control of the pH of neutralized RAW is difficult plantwise because of the manner of addition of NaOH and because the solution is not buffered in the pH range from 7 to 10. Although the plant aims for a pH of 8.5, variations of ± two pH units from this value are not uncommon. In view of these facts it was considered desirable to find a cesium carrier effective to a pH of at least 10.

TABLE II

SCAVENGING OF CESIUM FROM SYNTHETIC RAW BY IRON FERROCYANIDES

Solution: Synthetic RAW (See Table I) spiked with inert Cs and Cs^{137}

Procedure: Reagents added. Slurry agitated short time by shaking. Slurry allowed to settle.

$\underline{M}$ $K_4Fe(CN)_6$	pH	Settling Time	Cs D.F.
0.01	$7^{(1)}$	3 hr	49
		3 d	550
0.005		3 hr	110
		5 d	4000
0.001		3 hr	52
		3 d	2000
0.01	$10^{(1)}$	3 hr	5.5
		3 d	58
0.005		3 hr	1.8
		3 d	35
0.001		3 hr	1.1
		3 d	7.
0.0025	$2.5\underline{M}\,H^{+(2)}$	2 hr	6.3
		1 d	2.5
0.0025	$7.7^{(2)}$	2 hr	275
		1 d	1170
0.0025	$9.9^{(2)}$	2 hr	84
		1 d	110
0.0025	$10.8^{(2)}$	2 hr	38
		1 d	55

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(1) Solution brought to pH before addition of $K_4Fe(CN)_6$.

(2) $K_4Fe(CN)_6$ added before pH adjustment made.

Studies of the removal of cesium from stored waste supernatant by ferric ferrocyanide (See Part D, Section III) showed this carrier to be uneffective at pH above six. Doubt as to the amount of ferrous iron which would be present in plant RAW and as to the stability of ferrous ferrocyanide toward oxidation to ferric ferrocyanide on long contact with an alkaline solution made the use of ferrous ferrocyanide unattractive for a plant test.

Table III shows cesium removal from synthetic RAW by cupric, cobaltous, nickelous, and manganous ferrocyanides at pH 10. Although copper ferrocyanide is reasonably effective initially, cesium is gradually desorbed from it. Manganous ferrocyanide is considerably less effective than the nickelous and cobaltous salts. These latter gave very good cesium decontaminations even at low concentrations and they showed no tendency to desorb cesium on long standing. Heating the slurry either before or after precipitating nickel ferrocyanide appeared to have no effect on cesium carrying. However, it is necessary to add $K_4Fe(CN)_6$ first if the precipitation is made in an alkaline solution. When nickel is added first, cesium carrying is initially very poor although it improves on long contact with the solution. This behavior was interpreted on the basis of an initial precipitation of nickel hydroxide or phosphate which converts slowly to the ferrocyanide .

Table IV shows cesium and other fission product decontamination obtained by precipitation of copper ferrocyanide in plant RAW. Cesium removal was good at pH values less than 10. While actual cesium analysis were not obtained at pH 10, the low gamma decontamination obtained was taken as evidence that cesium was not carried. Time did not permit a similar laboratory study on the decontamination of plant RAW by nickel ferrocyanide even though it was recommended for the plant production test for RAW scavenging. However, reference to Table XIII in Section IV will show that decontamination by nickel ferrocyanide at pH 10 is similar to that by copper ferrocyanide at pH 8.

D. Decontamination of Stored Waste Supernatant

A large volume of aqueous waste (RAW) has already been produced in operation of the Uranium Recovery plant. This waste has been neutralized concentrated and stored in underground tanks. Alkaline insoluble materials have settled leaving supernatants approximating in ionic content that shown in Column 3, Table I. A sample of the supernatant, taken from the 109T

TABLE III

REMOVAL OF CESIUM FROM SYNTHETIC RAW AT pH 10 BY VARIOUS METAL FERROCYANIDES

Solution: Synthetic RAW (see Table I) spiked with inert Cs and Cs^{137}.

Procedure: Reagent additions, agitation and settling as indicated.

M^{++}	$\underline{M}\ M^{++}$	$\underline{M}\ K_4Fe(CN)_6$	Agitation	Settling Time	Cs DF
Cu^{++}(1)	0.005	0.02	Short(2)	1 hr	90
				3 d	48
				12 d	23
	0.005	0.005	Short	3 hr	4
				1 d	4
				20 d	10
	0.0025		Short	18 hr	1.1
				7 d	6
Mn^{++}(1)	0.005	0.02	Short	1 hr	11
				3 d	40
				19 d	44
Co^{++}(1)	0.005	0.02	Short	1 hr	530
				3 d	440
				12 d	6600
	0.005	0.005	Short	3 hr	180
				1 d	636
				9 d	4500
	0.0025	0.0025	Short	18 hr	90
				7 d	250
				33 d	750
Ni^{++}(1)	0.005	0.02	Short	1 hr	320
				3 d	580
				19 d	1100
	0.005	0.005	Short	3 hr	110
				1 d	1000
				20 d	> 2000
	0.0025	0.0025	Short	1.2 hr	120
				3 d	> 500
			1.2 hr(3)		114
			3 d(3)		160
Ni^{++}(4)	0.0025	0.0025	Short	1 d	> 500
				5 d	> 500

TABLE III (Cont.)

M^{++}	$\underline{M}$ M^{++}	$\underline{M}$ $K_4Fe(CN)_6$	Agitation	Settling Time	Cs DF
Ni^{++}(5)	0.0025	0.0025	Short	1 d	>500
				5 d	>500
Ni^{++}(6)	0.0025	0.0025	Short	30 m	1.0
				4 hr	1.3
				3 d	200
			2 hr(3)		1.1
			3 d(3)		>500

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(1) $K_4Fe(CN)_6$ and metal ion as nitrate added to acidic RAW. pH then adjusted with 50% NaOH.

(2) Slurries were shaken for a short time, ca. 1 min. and then allowed to settle.

(3) Slurries agitated by shaking for the time indicated and then centrifuged.

(4) Precipitation made at room temperature. Slurry held at 75°C. for 30 min. Allowed to settle at room temperature.

(5) Precipitation made at 75°C. Held at this temperature 30 min. Allowed to settle at room temperature.

(6) Nickel nitrate added to acidic RAW. pH adjusted to 10. $K_4Fe(CN)_6$ added.

TABLE IV

DECONTAMINATION OF PLANT RAW BY COPPER FERROCYANIDE

Solution: Plant RAW having the following radiochemical composition.

	C/m/ml
Gross β	1.2×10^7
Gross γ	5.9×10^6
Cs β	3.8×10^6
Sr β	2.3×10^6
Ce β	2.1×10^5
Ru β	1.7×10^5
RE + Y -Ce β	2.4×10^6

Procedure: Solution brought to pH with 50% NaOH, $K_4Fe(CN)_6$ and $Cu(NO_3)_2$ added. Slurry stirred and centrifuged.

pH	M $K_4Fe(CN)_6$	M $Cu(NO_3)_2$	Stirring Time, hrs	Decontamination Factors					
				Gross β	Gross γ	Cs	Sr	Ru	T.R.E.
5	0.00125	0.005	1	7.9	76				
8	0.00125	0.005	0.5	59	89				
			1.0	62	90				
			3.0	67	91	350	40	-	-
8	0.0025	0.01	0.5	77	114				
			1.0	78	118				
			3.0	82	118	1000	75		
8(1)	0.005	0.005	0.08	51	64	1200	180	3.3	39
			1.0	55	58	1000	170	3.6	41
9(1)	0.00125	0.005	0.08	68	85				
			0.5	68	92				
			1.0	71	90				
10	0.00125	0.005	0.5	2.1	1.1				
			1.0	2.2	1.1				

---

(1) $K_4Fe(CN)_6$ and $Cu(NO_3)_2$ added at pH 6. Slurry stirred 30 minutes before adjusting to final pH.

tank, contained the radiochemical constitutents shown in Table V. It is apparent that cesium accounts for about 99 per cent of the radioactivity, both beta and gamma, in this solution. Decontamination of the solution by the precipitation of various ferrocyanides at pH values from two to 12 is shown in Table VI. Ferric ferrocyanide is very effective for cesium removal at low pH but poor at pH 6 or above. Cupric ferrocyanide is a good cesium scavenger at pH values up to eight. It also removes strontium effectively at pH 8. Nickel ferrocyanide gives good cesium decontamination at pH values to 10 but its carrying efficiency drops off rapidly at higher pH. It carries strontium only moderately well when the precipitation is made at room temperature but strontium decontamination is markedly improved if the precipitation is made at high temperature. Studies of the variation of gross decontamination factors during long contact of the precipitate with supernatant are shown in Table VII. Although gross beta and gamma decontamination factors remain constant over a long settling period for copper ferrocyanide at pH 7, they decrease markedly at pH 8 indicating desorption of cesium. Similar desorption from nickel and cobalt ferrocyanides does not occur. Data obtained concerning the volume of settled solids shows that increased pH results in better packing of the solids and that nickel ferrocyanide settles to a considerably smaller volume than copper ferrocyanide at the same pH. Cobalt ferrocyanide is even better than nickel ferrocyanide from a settled volume standpoint but was not recommended for plant use because of expense.

The pH of the 109 T tank supernatant was 12. From a titration curve for the solution, quantities of HNO_3 required to bring the waste to various pH values were determined in order to obtain the approximate cost, reagentwise, to make necessary pH adjustments. These are shown in Table VIII. It should be noted that currently the concentrated waste leaves the TBP plant for storage at pH about 9.5 except in those cases when pH adjustment is out of control. Supernatants from these wastes would need little or no pH adjustment prior to scavenging.

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TABLE V

RADIOCHEMICAL COMPOSITION OF URANIUM RECOVERY PROCESS STORED WASTE SUPERNATANT (Tank 109 T)

	β c/m/ml(1)	β μc/ml(2)	γ c/m/ml(3)	γ μc/ml(4)
Gross β	3.7×10^6	23		
Gross γ			5.3×10^6	24
Cs	3.8×10^6	23	5.0×10^6	23
Ru	5.7×10^4	0.35	4.4×10^4	0.2
Y	1.6×10^3	0.009		
Rare Earths-Ce	1.6×10^3	0.009	< 100	< 0.0005
Sr	2.9×10^3	0.018		
Ce	36	0.0002	Neg.	Neg.

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(1) All β counts on 2nd shelf, no absorber.
(2) Assuming 7.5 % geometry.
(3) All γ counts on contact position gamma scintillation counter.
(4) Assuming 10 % geometry.

TABLE VI

DECONTAMINATION OF URANIUM RECOVERY PROCESS STORED WASTE SUPERNATANT BY VARIOUS FERROCYANIDES

Solution: Supernatant from the 109 T tank.

Procedure: Solution brought to pH indicated with 5 M HNO_3, made 0.01 M in $K_4Fe(CN)_6$ and metal ion as nitrate. Slurry stirred for the indicated time and centrifuged 35 minutes at ca. 700G.

Metal Ion	pH	Stirring Time, hrs.	Decontamination Factors				
			Gross β	Gross γ	Cs	Ru	Sr
Fe^{+++}	2	1	82	79			
		22	118	200	4100	7.6	3.3
Fe^{+++}	4	1	66	87			
Fe^{+++}	6	1	9	8.5			
		24	6	6			
Fe^{+++}	8	1	1.4	1.2			
Cu^{++}	2	1	75	117			
Cu^{++}	4	1	124	214			
		23	190	330	10000	11	6.4
Cu^{++}	6	1	131	230			
		23	108	145			
Cu^{++}	8	2	131	204			
		6	120	184			
		71	96	134	1700	2.2	280
Cu^{++}	10	1	5.5	5.9			
		6	6.0	6.2			
		71	9.2	10.5			
Cu^{++}	11.5	1	< 4	1.2			
		5	1.1	1.1			
Ni^{++}	8	1	220	875	5300	4.2	
Ni^{++}	10	1	112	244	7400	1.9	16
Ni^{++}	10(1)	1	81	124	1100	1.6	320
Ni^{++}	11	1	19	19	12	1.8	95
Ni^{++}	12	1	< 4	1.0			
Co^{++}	10	1	98	206	12000	2	9.4

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(1) Precipitation and stirring at 80°C.

TABLE VII

SETTLING STUDIES. URANIUM RECOVERY PROCESS STORED WASTE SUPERNATANT SCAVENGED WITH FERROCYANIDES

Procedure: 109 T supernatant brought to pH indicated with 5 M HNO_3 and made 0.01 M $K_4Fe(CN)_6$ and metal nitrate. Slurries stirred one hour at room temperature and allowed to settle.

Metal Ion	pH	Settling Time, hrs	Volume Reduction Factor(1)	Decontamination Factors				
				Gross β	Gross γ	Cs	Ru	Sr
Cu^{++}	7	17	2.1	270	450			
		65	2.4	290	520			
		185	3.1	310	610			
		380	3.4	310	500	7000	19	175
		470	3.6	290	640			
		900	3.7	320	700			
Cu^{++}	8	23	2.1	130	200			
		120	4.6	91	120			
		290	5.9	52	58	160	4.2	440
		550	6.2	45	48	160	2.7	240
Ni^{++}	8	18	2.3	190	640			
		90	3.8	280	610			
		165	4.5	280	500			
Ni^{++}	10	18	4.0	78	130			
		89	5.8	120	300			
		260	6.9	130	280			
		520	7.4	120	270			
		840	7.4	120	280			
Ni^{++}	11	1.2	4.3	-	-			
		68	7.2	33	35			
		144	8.2	42	47			
Co^{++}	10	4	3.9	-	-			
		72	7.4	100	220			
		240	9.2	105	240			
		500	9.5	103	240			
		820	11	100	200			

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(1) Volume of the 109 T supernatant used in the experiment divided by volume of the settled solid.

TABLE VIII

HNO_3 REQUIRED FOR 109 T SUPERNATANT pH ADJUSTMENT

pH	Moles HNO_3/l	Cost of HNO_3 (1) ¢/gal
12	0.	0.
11.9	0.05	0.092
11.7	0.15	0.27
10.8	0.25	0.46
10.1	0.3	0.55
9.5	0.35	0.64
6.5	0.4	0.73
5.6	0.45	0.83
3.0	0.5	0.92
2.0	0.53	0.98

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(1) Assuming 3.5 cents/lb. HNO_3 for technical grade 60% nitric acid.

To summarize these studies, it is apparent that nickel ferrocyanide can be used to scavenge most of the cesium and some of the remaining strontium from Uranium Recovery Process stored waste supernatant. The amount of carrier used in these studies is more than adequate to give the necessary cesium decontamination and it is recommended that 0.005 M instead of 0.01 M $K_4Fe(CN)_6$ and $NiSO_4$ be used in any plant test of the procedure. Settled volume of the solid under these conditions should be eight to ten per cent of the initial waste volume if the precipitation is made at pH 10.

E. Scavenging of RAW by Ferrocyanides when RAS Contains Oxalate Instead of Ferrous Sulfamate

Aqueous wastes which would be produced by the Uranium Recovery Process under a suggested flow sheet modification in which oxalic acid would be substituted for ferrous sulfamate in the extraction column scrub (RAS) would have a composition approximating that shown in Table IX. Removal of cesium from a solution having this composition by various metal ferrocyanides is shown in Table X. Nickel and cobalt ferrocyanides are the most promising cesium scavengers for this waste. Cupric and ferrous ferrocyanides, while producing moderately good cesium decontamination initially at pH 10, tend to desorb cesium on long contact. Manganous ferrocyanide is only moderately effective and zinc and ferric ferrocyanides carry very little cesium at pH 10.

Plant RAW containing oxalate is, of course, not available since use of oxalic acid in RAS has not yet been tried in the plant. To simulate the solution, one volume of plant feed solution (RAF) was combined with one-half volume of a solution 0.05 M in $H_2C_2O_4$ and 2.0 M in HNO_3. This solution (simulating RAFS) was then contacted four times in succession with one-volume portions of 20 per cent TBP in Amsco. The residual aqueous solution was very pale yellow in color. When portions of it were brought to pH values in the range of eight to nine a very small

TABLE IX

COMPOSITION OF URANIUM RECOVERY PROCESS AQUEOUS WASTE (RAW) WITH OXALIC ACID IN RAS

By calculation assuming $H_2C_2O_4$ in RAS is 0.05 M

Constituent	Molarity: Acidic, Not Concentrated	Molarity: Basic Concentrated
UNH	0.00093	-------
$SO_4^=$	0.179	0.25
$PO_4^{\equiv}$	0.179	0.25
NO_3^-	4.45	6.2
Cl^-	0.016	0.022
H^+	2.57	-------
Na^+	2.80	7.5
$H_2C_2O_4$	0.017	0.024
$Na_2U_2O_7$	-------	0.00047

TABLE X

REMOVAL OF CESIUM FROM RAW CONTAINING OXALATE BY VARIOUS FERROCYANIDES AT pH 10.2

Solution: Synthetic RAW having the composition shown in Table IX.

Procedure: Solution brought to pH 10.2 with 50% NaOH and made 0.0055 M in $K_4Fe(CN)_6$ and 0.02 M in metal nitrate. Slurry shaken for ca. one minute and allowed to settle.

Metal Ion	CS DF at Various Settling Times: 1 day	4 days	11 days
Co^{++}	400	400	460
Cu^{++}	270	52	55
Fe^{+++}(1)	1	1.1	1.2
Mn^{++}	33	31	70
Ni^{++}	900	370	390
Zn^{++}	1.4	2.1	2.5
Fe^{++}	94	48	45

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(1) Solution made 0.0133 M in $Fe(NO_3)_3$

amount of pale yellow precipitate was formed, indicating that practically all of the uranium had been removed and that very little iron was present. Portions of the solution were scavenged with nickel and copper ferrocyanides with the results shown in Table XI. As was expected, cesium removal by copper ferrocyanide was only moderately good at pH 9.1 while that by nickel ferrocyanide at pH 9.3 was very good. Neither carrier was very effective for strontium. Further studies on decontamination of oxalate - containing RAW will be made, particularly with reference to improving strontium decontamination, when plant solutions are available.

IV. PLANT PRODUCTION TEST OF RAW SCAVENGING

About 500,00 gallons of plant RAW was scavenged with nickel ferrocyanide to test the effectiveness of the procedure under plant conditions. Acidic RAW was made 0.005 M in $K_4Fe(CN)_6$, neutralized, made 0.005 M in $NiSO_4$, agitated thoroughly and discharged to an underground storage tank for settling. A sample of the untreated (acidic) RAW and grab samples of the slurry, before discharge to storage, were taken during the test. Decontamination factors for cesium and strontium are shown in Table XII. During the first half of the test (samples 1, 2 and 3) pH of the neutralized RAW was out of control and much too high for good cesium removal. Control of pH was satisfactory during the last half of the test and cesium removal was good. Strontium decontamination was somewhat better at high than at low pH. Gamma ray spectrometer scans of the supernatants from samples 4, 5 and 6 showed that gamma activity present was due almost entirely to ruthenium and antimony.

After the scavenged waste had settled for about a week in the underground storage tank, samples of the supernatant were taken at each one foot level at two widely separated points in the tank. Gross beta, gross gamma, cesium, strontium, plutonium and antimony plus cesium

TABLE XI

DECONTAMINATION OF RAW CONTAINING OXALATE WITH NICKEL AND COPPER FERROCYANIDES

Procedure: RAW solution was brought to pH with 50% NaOH and made 0.005 M in $K_4Fe(CN)_6$ and $Ni(NO_3)_2$ or $CuSO_4$. Slurry was stirred 30 minutes at room temperature and centrifuged.

		Decontamination Factors						
Metal Ion	pH	Gross β	Gross γ	Zr	R. E.	Cs	Sr	Nb
Ni^{++}	9.3	330	78	1	31	930	12	1
Cu^{++}	9.1	230	24	1	40	34	11	1

Radiochemical Composition of the RAW

Constituent	C/m/ml
Gross β(1)	8.6×10^6
Gross γ(2)	2.1×10^6
Zr γ	2.9×10^3
Rare Earth β	3.4×10^6
Cs β	3.5×10^6
Sr β	1.4×10^6
Nb γ	4.3×10^3

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(1) All β counting on 2nd shelf BGO. Geometry 7.5% RaDEF

(2) All γ counting on scintillation counter. Geometry 3.36% Cs^{137}

TABLE XII

CESIUM AND STRONTIUM DECONTAMINATION OF RAW DURING PLANT SCAVENGING TEST

Sample(4)	pH(1)	β c/m/ml(2)		Decontamination Factors(3)	
		Cs	Sr	Cs	Sr
RAW(Acidic)		4.7×10^6	1.26×10^6		
1	12.5	3.9×10^6	3.0×10^4	1.2	40
2	12.5	3.9×10^6	8.0×10^3	1.2	160
3	12.5	3.7×10^6	6.2×10^3	1.3	200
4	10.2	1.3×10^3	2.7×10^4	3600	46
5	8.75	700	2.4×10^4	6800	53
6	9.75	320	2.3×10^4	15000	55

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(1) Standard glass electrode. Not corrected for sodium ion concentration.

(2) Second shelf BGO. Geometry 7.5% RaDEF.

(3) Ratio of c/m/ml in RAW to c/m/ml in scavenged waste supernatant. Does not account for dilution during neutralization.

(4) Volume of waste treated at time the samples were taken is not accurately known. Tank was about half full when pH was brought under control (samples 4, 5 and 6).

content of the samples taken at one sampling point are shown in Table XIII. Data for samples at the same depth but from the other sampling point were almost identical to these. It was apparent that the tank was definitely layered, the bottom half being at high pH with consequent poor cesium removal while the top half was at a satisfactory pH for cesium removal. The cesium decontamination factor for the top half averaged about 450 based on the cesium content of the acidic RAW (See Table XII).

V. SOIL COLUMN STUDIES WITH SCAVENGED RAW SUPERNATANT

Members of the Earth Sciences Group, Biophysics Section, conducted studies to determine the retention, by soils typical of those underlying cribbing areas, of the radioactive constituents remaining in the supernatant from scavenged RAW(3). A composite supernatant sample was prepared by combining samples taken at different depths from the top half of the underground tank in which the scavenged RAW was settled. This solution was passed through soil columns and radioactive constituents, particularly cesium, were determined in the effluent. It was found that from three to four column volumes of the supernatant could be passed through the columns before cesium appeared in the effluent in amounts greater than permissible for drinking water. Since the effective depth (to ground water) of the soil column underlying cribbing areas is from 100 to 200 feet, two to four thousand gallons of the supernatant could be discharged safely per square foot of crib surface before cesium would appear in the ground water in hazardous amounts. A document giving details of these studies will be issued soon by members of the Earth Sciences Group.

TABLE XIII

RADIOACTIVE CONSTITUENTS PRESENT IN SUPERNATANT FROM SCAVENGED RAW

Depth from Surface, ft.	pH(1)	Pu, d/m/ml	Gross β(2) c/m/ml x 10^{-4}	Gross γ(3) c/m/ml x 10^{-4}	Cs β c/m/ml x 10^{-4}	Sr β c/m/ml x 10^{-4}	Sb + Cs γ(4) events/m/ml x 10^{-4}
0	9.8	260	8.6	2.6	1.2	0.64	22
1	9.7	220	9.2	2.5	1.1	0.64	22
2	9.7	230	9.0	2.5	1.25	0.65	23
3	9.6	240	9.1	2.7	1.1	0.59	23
4	9.6	260	9.5	2.5	0.99	0.53	22
5	9.6	440	8.5	2.6	0.99	0.55	20
6	9.7	250	9.5	2.4	1.1	0.56	33
7	9.6	280	8.6	2.5	1.0	0.58	32
8	9.7	280	9.3	2.7	1.0	0.56	25
9	11.1	76	15.	5.	3.5	0.40	82
10	11.9	10	48	21	19	0.06	390
11	11.9	30	46	21	19	0.06	390
12	11.8	16	46	20	14	0.04	300
13	11.9	8	89	44	33	0.04	700
14	11.9	6	130	71	49	0.06	1000
15	12.1	12	>230	240	190	0.26	3900

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(1) Standard glass electrode. Not corrected for sodium concentration

(2) All β counting 2nd shelf BGO. Geometry 7.5% RaDEF

(3) Gamma scintillation counter. Geometry 3.36% Cs^{137}

(4) Determined from gamma ray spectrometer scans. Cs^{137} and Sb^{125} gamma peaks too close for separation

VI. TEST CRIBBING OF SCAVENGED RAW SUPERNATANT

On the basis of the favorable results of soil column studies with scavenged RAW supernatant it was decided to conduct a test cribbing of the supernatant from the top half of the underground storage tank in which the scavenged RAW was settled. Two hundred and seventy thousand gallons of the supernatant was discharged to a ten feet square crib. The crib was located near a test well which permitted monitoring the migration of the radioactive constitutents through the soil underlying the crib. Monitoring studies were conducted by the Earth Sciences Group. Details of these studies will be presented in a report which will be issued soon by the group.

Preliminary results of the test cribbing program were sufficiently favorable that the Radiological Sciences Department has approved the large-scale cribbing of scavenged Metal Recovery Process RAW on the basis of 6000 gallons per square foot of crib area provided the concentration of neither cesium nor strontium exceeds 0.1 µc per milliliter. Details of the approval may be found in HW-30652, issued by H.V. Clukey(4).

VII. CONCLUSIONS

Concentrations of cesium or strontium of 0.1 µc per milliliter in scavenged RAW supernatants, as approved by the Radiological Sciences Department for large scale cribbing, represent decontamination factors of about 300 for cesium and 80 for strontium based on the RAW used for the plant production test described above. These decontamination factors were achieved in the last half of the plant production test even though pH was out of control during the first half and poorly scavenged waste produced during the first half had a chance to mix in the underground tank with that produced during the last half. Based on these studies it is proposed to include scavenging of RAW, with ultimate cribbing of the supernatant, as an integral part of the Uranium Recovery

Process. As a result of this plant modification it will be possible to recover a very considerable amount of tank space.

Samples of Uranium Recovery Process stored waste supernatant obtained so far have contained less than 0.1 μc of stontium per milliliter (see Table V). Further scavenging of strontium prior to cribbing is not necessary. These studies have shown that cesium may be reduced to less than 0.1 μc per milliliter by scavenging with various metal ferrocyanides. Total cost, reagentwise, for this operation would be less than two cents per gallon. A proposal to conduct a production test on scavenging and cribbing supernatants from stored Uranium Recovery Process wastes is being considered.

The ability to obtain satisfactory cesium decontamination of the RAW which will be produced if oxalic acid is substituted for ferrous sulfamate in the RAW was demonstrated by these studies. Satisfactory strontium decontamination was not achieved in the limited studies made. Further research effort needs to be and will be expended on this point when plant solutions are available and if the plant production test indicates that the use of oxalic acid is desirable.

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R. L. Brandt

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REB:RLB:jw

VIII. REFERENCES

A. Cited in this Report

1. HW-19140, Uranium Recovery Technical Manual, Nov. 10, 1951, Figure 1-2.

2. MLM-621, Decontamination of Process Waste Solutions Containing Fission Products by Adsorption and Coprecipitation Methods, Nov. 13, 1951.

3. Personal Communications with R. E. Brown and D. W. Rhodes. A Report of these studies will be issued soon.

4. HW-30652, H. V. Clukey, TBP Waste Disposal Project Criteria for Cribbing Scavenged RAW, Jan. 27, 1954.

B. Other Documents Pertaining to this Project

1. HW-28408, Burns, R. E., Decontamination of Metal Recovery Process Wastes: Interim Report, June 22, 1953.
2. HW-28715, Sloat, R. J., Copper Ferrocyanide Scavenging of TBP Wastes, July 15, 1953.
3. HW-29383, Bradley, J. G., Test Procedure to Evaluate Scavenging of TBP Plant Solvent Extraction Waste with Nickel Ferrocyanide, Sept. 18, 1953.

4. HW-29814, Stedwell, M. J., Scavenging and Cribbing of TBP Plant Wastes (Meeting 0830, Oct. 29, 1953), Oct. 30, 1953.

5. HW-30399, Sloat, R. J., TBP Plant Nickel Ferrocyanide Scavenging Flowsheet, Jan. 8, 1954.

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