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DECONTAMINATION OF URANIUM RECOVERY PROCESS STORED WASTES INTERIM REPORT

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J.H. Wells 8-2-94

PM Eck 8-2-94

by

W. W. Schulz

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Plant Processes Sub-Section
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ENGINEERING DEPARTMENT

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BY *W. Jordan* DATE *6-30-81*

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DECONTAMINATION OF URANIUM RECOVERY PROCESS
STORED WASTES - INTERIM REPORT

I. INTRODUCTION

Nickel ferrocyanide scavenging of Uranium Recovery Plant aqueous wastes to reduce the radioactive cesium content to cribbing levels was incorporated in the plant operating procedure in late 1954. Prior to this date, the aqueous wastes were neutralized, concentrated, and stored in underground tanks. More than eight million gallons of these wastes are now stored. Nickel ferrocyanide scavenging of the stored wastes and subsequent cribbing of the supernatant liquids has been proposed as a means of providing storage capacity for other process wastes. A program to determine pertinent physical characteristics and suitable scavenging procedures is now in progress. Although the study is not complete, data so far obtained are presented at this time to assist in the design of plant facilities needed for scavenging and cribbing the wastes.

II. SUMMARY

Physical and chemical properties and scavenging behavior of stored Uranium Recovery Plant wastes from six underground tanks (representing about 3×10^6 gallons) have been studied. In all cases, scavenging of the wastes with nickel ferrocyanide (0.0025 moles per liter of waste) at pH 9 reduced the radioactive cesium content to less than 0.2 uc/ml. Residual radioactive strontium content ranged from 0.007 to 1.5 uc/ml. Scavenging with a combination of nickel ferrocyanide and calcium nitrate, 0.0025 and 0.01 moles per liter respectively, produced supernatant liquids containing, in all cases, less than 0.1 uc/ml of either cesium or strontium.

In most cases, the nickel ferrocyanide precipitate settled (unhindered) from one to four feet per day. One sample studied contained an appreciable amount of aluminum which precipitated when the pH was adjusted for scavenging. The solid produced settled much slower than when aluminum was absent.

Clear point temperatures of the wastes after adjustment to pH 9 ranged from 14 to 19°C. Dilution of the wastes (at pH 9) with water reduced the clear point temperatures, although 300 per cent dilution was necessary to obtain clear point temperatures of about 10°C. Reproducible freezing point data were difficult to obtain. Values of 4-5°C. were observed for clarified waste solutions at pH 9. Although the clear points of these wastes, even with dilution, are relatively high, wintertime transfer through overland piping of wastes of similar composition has been done without line plugging in connection with current waste scavenging at the Uranium Recovery Plant.

Phosphate concentrations of the stored waste solutions varied from 0.14 to 0.27 molar. Investigations made by the Soil Sciences Unit show that a phosphate concentration of about 0.1 is necessary to assure good retention of strontium by the soil. Greater than 100 per cent dilution of the stored wastes would reduce phosphate to concentrations lower than desirable for cribbing.

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III. EXPERIMENTAL AND DISCUSSION

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A. Composition of Stored Wastes

It should be emphasized that data with respect to the properties and composition of stored wastes have been obtained so far for samples from only six of the tanks considered for scavenging. Also, each of these samples represents only 500 milliliters from a tank containing about 500,000 gallons. In view of the probability that solutions in these large tanks are stratified, it must be admitted that the samples tested may not represent an adequate cross-section of the total volume of waste to be processed. It is encouraging, therefore, to find that solutions from tanks selected at random are all low in strontium activity and have acceptable phosphate concentrations. Scavenging results also indicate that each solution can be adequately decontaminated by one set of scavenging conditions. These facts tend to minimize the danger involved in extrapolating from results obtained with only six samples of stored waste.

Table I shows the composition of samples (supernatant liquid) from six tanks of Uranium Recovery Plant stored waste. The tanks from which these samples were taken were so chosen as to reflect differences in plant neutralization procedure and include solutions ranging in pH from 9.2 to 12.0.

Samples of stored waste examined to date are characterized by high cesium and low strontium activity levels. The low strontium activity levels are the result of the scavenging action of hydroxide and phosphate precipitates formed during neutralization of the wastes prior to storage. With the exception of solutions from tanks 112 C and 109 BX, strontium levels are above the provisional 0.1 uc/ml specification for cribbing at 6,000 gal./ft.² by factors of only one to five.⁽¹⁾ Solutions 112 C and 109 BX are in the pH range 10.4 - 10.6. The poor strontium scavenging by hydroxide and phosphate carriers in this pH range has been observed previously in connection with current in-line scavenging in the Uranium Recovery plant. The reason for it is not known.

Phosphate concentrations for these samples range from 0.14 to 0.27 molar. Recent work by the Earth Sciences Unit indicates that a phosphate concentration of at least 0.1 molar is needed for effective soil retention of strontium.

B. Crystallization and Clear Point Temperatures

Crystallization and clear point temperatures were measured for waste samples from four storage tanks. This information is of interest since it is planned to pump scavenged solutions about two miles across country through a contour pipe line which will have minimum provision for removal of obstacles. It is desirable, therefore, to insure against plugging the line through deposition of solids which might be frozen out of the scavenged waste. Prior to measuring crystallization and clear point temperatures, each solution was adjusted to pH 9.0 since it is probable that scavenging will be performed at or near this pH and since it is known that the clear point of these solutions is pH dependent. The solution was then stirred

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TABLE I

COMPOSITION OF STORED URANIUM RECOVERY PLANT WASTE SOLUTIONS

Solution, Tank Number	pH**	Composition*				
		Cesium uc/ml	Strontium uc/ml	Phosphate M	Sulfate M	Sodium M
106 C	9.2	54.2	0.44	0.19	—	—
108 BX	9.3	132.4	0.26	0.22	0.18	7.8
109 BX***	10.4	56.3	1.08	0.14	—	6.7
112 C	10.6	25.8	1.2	0.17	—	5.1
109 C	11.2	40.7	0.46	0.19	0.02	6.3
111 C	12.0	34.5	0.10	0.27	0.11	4.9

* Supernatant liquid only.

** Measured with Beckman Type 1190-80 Glass Electrode and not corrected for sodium error.

*** Solution as received contained about 50 volume percent black solids. Values reported here are for clear supernatant liquid above solids.

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and cooled slowly in a dry ice bath until crystals first appeared. The mixture of crystals and solution was then warmed slowly until a clear solution was obtained. Temperatures were noted at both the point of appearance (crystallization temperature) and disappearance (clear point temperature) of crystals. This same procedure was repeated after diluting the waste solution at pH 9 with water to 125, 150, 200, and 300 per cent, respectively, of the original volume. Data obtained for the four solutions are shown in Table II.

Small amounts of a yellow precipitate formed when solutions 109 and 112 C were neutralized to pH 9.0. This precipitate has not been identified but is thought to be an iron phosphate.

Neutralization of solution 111 C to pH 9.0 produced a white precipitate. Qualitative analyses of a solution of this material in nitric acid showed the presence of large amounts of aluminum and phosphate and traces of iron. This suggests that the precipitate is aluminum phosphate, aluminum hydroxide, or a mixture of these two compounds. The presence of aluminum in this solution may be accounted for in the following manner. Several of the tanks of stored TBP wastes, including tank 111 C, originally contained Bismuth Phosphate Plant coating removal and First Cycle wastes. Neutralization of these wastes produced a sludge containing aluminum hydroxide. When tank 111 C was filled with Uranium Recovery Plant waste at pH 12.0, evidently some of this aluminum hydroxide was dissolved.

Crystallization and clear point temperatures could not be accurately determined in the presence of these precipitates. Since only solid-free supernatant liquid will be pumped through the pipe line, most of the measurements made involved filtered solutions. The phosphate concentration of solution 111 C was 0.12 molar after removal of the aluminum precipitate.

For the undiluted solutions clear point temperatures ranged from 14 to 19°C. Clear point temperatures for these solutions may be correlated with phosphate concentrations. Thus, solutions 106, 109, and 112 C, with phosphate concentrations of 0.17 - 0.19 molar, had essentially identical clear points. Solution 111 C had a lower phosphate concentration, 0.12 molar, and correspondingly a lower clear point. This behavior is consistent with the hypothesis that the crystallizing substance is a sodium phosphate.

Crystallization temperatures for these solutions were found to be 5-15 degrees lower than corresponding clear point temperatures. However, these solutions exhibit supersaturation and crystallization temperatures observed depended on such factors as the degree of agitation during cooling and the presence or absence of foreign particles. The effect of the latter variable is illustrated by the difference in crystallization temperatures for solution 112 C before and after clarification.

Crystallization and clear point temperatures are both lowered by dilution. The dilution effect is not large, however. For these solutions approximately 0.2 molar in phosphate 200 to 300 per cent dilution is required to lower

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TABLE II

CRYSTALLIZATION AND CLEAR POINT TEMPERATURES OF STORED WASTE SOLUTIONS

Procedure: Solution pH was adjusted to 9.0. Solution was cooled with dry ice until crystals formed and then slowly warmed until solution cleared. The temperature was noted for both appearance and disappearance of crystals.

<u>Solution, Tank Number</u>	<u>Dilution, Per Cent*</u>	<u>Crystallization Temperature, °C.</u>	<u>Clear Point Temperature, °C.</u>
106 C	0.00	5.	19.
	125.	7.	17.
	150.	8.	16.
	200.	3.	13.
	300.	1.	10.
112 C	0.00	13.**	17.**
	0.00	3.	17.
	125.	5.	16.
	150.	4.	14.
	200.	3.	12.
300.	1.	8.	
109 C	0.00	7.**	16.**
	0.00	4.	16.
	125.	4.	15.
	150.	4.	14.
	200.	1.	11.
300.	-2.	11.	
111 C	0.00	5.	14.
	125.	0.	14.
	150.	2.	12.
	200.	---	9.
	300.	---	5.

* Represents the ratio of final volume to initial volume.

** Measured in the presence of a precipitate which formed when the solution was adjusted to pH 9.0.

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clear point temperature to 10°C. A dilution of this order has the disadvantage of decreasing phosphate concentrations below the value ($> 0.1 \text{ M}$) desired for soil retention of strontium.

Because of the uncertainty of crystallization temperatures, prediction of the behavior of scavenged stored waste solutions at low temperatures is difficult. In this connection, however, recent Metal Recovery Plant experience in wintertime piping of current scavenged wastes is of interest. During the period December 1954 to April 1955 the Metal Recovery Plant pumped several million gallons of scavenged wastes through an overland pipe line approximately one-fifth mile long without any plugging difficulties. The chemical similarity of current scavenged waste to the solutions which will be produced when stored wastes are scavenged indicates that the latter can be transferred through a buried line without plugging difficulties.

C. Nickel Ferrocyanide Scavenging of Stored Wastes

In the Uranium Recovery Plant, nickel ferrocyanide scavenging of waste solutions is carried out at pH 9 \pm 1. Scavenging agent concentrations of 0.005 M $\text{K}_4\text{Fe}(\text{CN})_6$ and 0.005 M NiSO_4 are used. These same conditions were used to test nickel ferrocyanide scavenging of stored waste solutions. Data obtained for each of the six samples of stored waste are presented in Table III. They show that cesium is removed effectively under these scavenging conditions. Cesium activity levels after scavenging were 0.1 uc/ml or less for five of the solutions and 0.2 uc/ml for the sixth.

Strontium activity levels for the scavenged solutions were generally higher than corresponding cesium levels. However, with the exception of solutions 109 BX and 112 C, the highest strontium activity level was a factor of only three above 0.1 uc/ml . Solutions 112 C and 109 BX, as already pointed out, are initially in the pH range 10.4 - 10.5 and have higher initial strontium levels than wastes stored at either higher or lower pH. Nickel ferrocyanide scavenging of these two solutions at pH 9 did not lower appreciably the strontium levels.

Strontium was most effectively removed from solution 111 C. The improved strontium decontamination is attributed to the presence of the aluminum precipitate during scavenging. Neutralization to pH 9.0 and removal of the aluminum precipitate reduced the strontium level of solution 111 C by a factor of three. Conversely, the yellow precipitate formed when solutions 109 and 112 C were neutralized to pH 9 carried little or no strontium.

D. Combined Nickel Ferrocyanide - Calcium Phosphate Scavenging of Stored Wastes

Recent experiments with current Uranium Recovery Plant wastes show that the addition of calcium nitrate during nickel ferrocyanide scavenging improves strontium decontamination appreciably. Calcium phosphate is precipitated and the improved strontium decontamination is attributed to the scavenging action of this compound. Combined nickel ferrocyanide and calcium phosphate scavenging was tried on five samples of stored waste. Experimental

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TABLE III

NICKEL FERROCYANIDE SCAVENGING OF STORED WASTES

Experimental Conditions: Solution pH was adjusted to 9.0 - 9.3. While stirring the solution, 0.005 moles per liter of $K_4Fe(CN)_6$ and $NiSO_4$ were added. Slurry was stirred one hour at 23 - 25°C. and then centrifuged.

Solution, Tank Number	Activity Level After Scavenging			
	Cesium		Strontium	
	uc/ml	DF	uc/ml	DF
106 C	0.10	540	0.21	2.0
106 C	0.045	1200	0.17	2.6
108 BX	0.037	3600	0.17	1.5
108 BX	0.022	6000	0.15	1.8
109 BX	0.14	400	---	---
109 BX	0.19	300	0.76	1.4
112 C	0.053	490	0.96	1.2
112 C	0.060	430	1.5	1.0
112 C*	0.038	700	0.77	1.6
109 C	0.005	8000	0.11	4.2
109 C	0.001	41000	0.12	3.8
109 C*	0.014	2900	0.049	9.4
111 C	0.009	3800	0.003	33.
111 C	0.003	11000	0.007	14.

* Precipitate which formed when the solution was adjusted to pH was removed before scavenging with nickel ferrocyanide.

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conditions and results are given in Table IV. For comparison, results obtained without calcium are also listed.

Addition of calcium improved strontium decontamination in every case. The results for solution 109 BX and 112 C were particularly encouraging. Although scavenging was slightly more effective at 0.03 M $\text{Ca}(\text{NO}_3)_2$, the addition of 0.01 M $\text{Ca}(\text{NO}_3)_2$ was sufficient to reduce strontium levels for these two solutions to 0.1 uc/ml. Strontium levels for the other solutions were well below 0.1 uc/ml for both 0.01 and 0.03 M $\text{Ca}(\text{NO}_3)_2$. The lower calcium concentration has the advantage of decreasing the volume of precipitate to be stored.

Cesium levels for all solutions were below 0.1 uc/ml at both 0.01 and 0.03 M $\text{Ca}(\text{NO}_3)_2$ addition. The addition of calcium apparently improved cesium decontamination for solution 109 BX. The validity of this improvement is questionable, however, since cesium decontamination for the other solutions was not affected appreciably by the addition of calcium.

A point of interest in these experiments is that addition of calcium nitrate reduced the pH. For solutions initially at pH 9.0, addition of calcium nitrate to a concentration 0.03 molar caused a change in pH from 9.0 to ca. 8.2. At 0.01 M $\text{Ca}(\text{NO}_3)_2$ the change was from pH 9.0 to pH 8.8. The decrease in pH is accounted for by the fact that the concentrations of HPO_4^{2-} and H_2PO_4^- at pH 9 are large in comparison to the concentration of PO_4^{3-4} . When calcium nitrate is added, $\text{Ca}_3(\text{PO}_4)_2$ is precipitated and hydrogen ions are released.

In the present experiments no pH adjustment was made after addition of calcium. Scavenging was thus carried out at pH 8.2 and pH 8.8 for 0.03 and 0.01 M $\text{Ca}(\text{NO}_3)_2$, respectively. The fact that strontium removal was improved at both pH's suggests that combined nickel ferrocyanide - calcium phosphate scavenging is effective over a range of pH values. Experiments to define this range are now in progress.

E. Settling Rate Studies

Experiments were performed with three stored waste solutions to determine settling rates of nickel ferrocyanide precipitates. In each experiment 0.0025 moles/liter of nickel ferrocyanide were precipitated from 20 milliliters of stored waste at pH 9.0. The slurry was stirred one hour and transferred to a 25 milliliter graduated cylinder in a water bath maintained at the desired temperature. Settling was observed as a function of time.

Settling rates were determined by plotting the height of settled precipitate as a function of settling time. These plots were essentially straight lines for the period of unhindered settling. The slopes of the straight-line regions were taken to represent settling rates for unhindered settling. Rates determined by this procedure are shown in Table V.

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TABLE IV
COMBINED NICKEL FERROCYANIDE - CALCIUM PHOSPHATE SCAVENGING
OF STORED WASTES

Experimental Conditions: Solution pH was adjusted to 9.0. While solution was stirred, 0.005 moles/liter of $K_4Fe(CN)_6$ and $NiSO_4$ were added. $Ca(NO_3)_2$ was added to the indicated concentration. Slurry was stirred one hour at 23 - 25°C. and then centrifuged.

Solution, Tank Number	Ca(NO ₃) ₂ , M	Activity Level After Scavenging			
		Cesium		Strontium	
		uc/LI	DF	uc/ml	DF
106 C*	0.0	0.073	740	0.19	2.3
106 C	0.01	0.054	1000	0.018	25.
106 C	0.03	0.031	1800	0.020	22.
108 BX*	0.0	0.030	4800	0.16	1.7
108 BX	0.01	0.061	2200	0.007	43.
108 BX	0.03	0.029	5000	0.004	65.
109 BX*	0.0	0.17	350	0.76	1.4
109 BX	0.01	0.050	1100	0.11	16.
109 BX	0.03	0.047	1200	0.069	10.
112 C*	0.0	0.050	500	1.1	1.0
112 C	0.01	0.092	300	0.11	10.
112 C	0.03	0.063	400	0.055	20.
109 C*	0.0	0.010	4100	0.091	5.0
109 C	0.01	0.014	2900	0.011	42.
109 C	0.03	0.014	2900	0.009	51.

* Average of duplicate results.

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TABLE V

SETTLING OF NICKEL FERROCYANIDE PRECIPITATES

<u>Solution, Tank No.</u>	<u>Settling Temp. C.</u>	<u>Settling Rate During Unhindered Settling, in./hr.</u>	<u>Settled Volume of Precipitate,* Per Cent</u>
111 C**	25.	0.19	32.
106 C	25.	0.57	9.
112 C***	25.	1.8	15.
106 C	30.	1.2	15.
112 C***	30.	3.2	11.
106 C	40.	1.5	14.
112 C***	40.	4.5	11.

* Represents per cent of total volume occupied by precipitate after settling for 24 to 72 hours.

** White aluminum precipitate which formed when solution was adjusted to pH 9.0 also present.

*** Yellow precipitate which formed when solution was adjusted to pH 9.0 also present.

Settling rates of nickel ferrocyanide precipitates will vary from tank to tank of stored wastes. Settling rates and settled precipitate volumes for those slurries which also contain aluminum or iron precipitates depend on the settling properties of these foreign precipitates. Particularly slow settling may be expected for those slurries which contain aluminum precipitates. Rates observed at 25°C. and in the absence of aluminum correspond to one - four feet per day. At these rates two to three weeks would be sufficient for settling in 750,000 gallon tanks. Settling rates at 30°C. and 40°C. were about two and 2.5 times, respectively, as high as those at 25°C. Experiments to determine settling rates of combined nickel ferrocyanide - calcium phosphate precipitates have not yet been performed. The settled volumes of the precipitates indicate qualitatively the differences among the various solutions. They should not be taken to represent ultimate precipitate volumes in the waste settling tanks.

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