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EVALUATION OF PROCESS VARIABLES IN THE CATION EXCHANGE
RECOVERY OF PLUTONIUM FROM 234-5 BUILDING SUMP WATER

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PACIFIC NORTHWEST LABORATORY

RICHLAND, WASHINGTON

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INTRODUCTION

A flow sheet has been developed for the recovery of Pu from 234-5 Building sump water.⁽¹⁾ This sump water contains various steam condensates, cooling waters, dilute HF from the fluorinator off-gas, and neutralized caustic from dissolver scrubbers. Occasionally the plutonium content exceeds 8×10^{-4} g/l. above which level the recovery of the Pu is desired. The present flowsheet⁽¹⁾ calls for adjustment to 0.03M HNO_3 , the addition of NH_4HSO_3 for Pu reduction, and the addition of Al^{+3} to complex F^- followed by passage of the solution through a column of Dowex 50W-X8 (20-50 mesh). It is anticipated that only occasional sump batches will be processed (intermittent operation), and it is desired that the process be capable of processing at least 10 (and preferably more) sump batches before elution of the resin. This amounts to loading at least 600 column volumes of feed before significant breakthrough occurs.

In one laboratory column run, using the proposed flowsheet, R. S. Kingsley reported unsatisfactory performance due to high plutonium breakthrough (> 30 per cent at 600 column volumes) with simulated sump water⁽²⁾. The purpose of the present work is to determine if a satisfactory cation exchange recovery process is possible and to determine the optimum resin loading conditions.

SUMMARY AND CONCLUSIONS

Distribution coefficients were measured between Dowex 50W, X-8 resin and synthetic sump solutions under a variety of possible simulated flowsheet conditions. By far the highest distribution coefficients were obtained with Pu(III) without the addition of aluminum. The distribution coefficients with aluminum present were in good agreement with the results obtained by Kingsley in his

column run. The results with Pu(IV) varied from borderline to unsatisfactory depending on conditions. Results with Pu spiked plant sump water confirmed the good results with Pu(III) in the absence of Al. It appears, then, that the present process will be quite satisfactory if the Al addition is eliminated. It should be emphasized, however, that these distribution coefficients were measured using added Pu-238 tracer and that distribution coefficients could not be measured for the Pu actually present in the sump water due to inability to analyze for such low levels of Pu. Any irreversible complexing of this Pu might effect the result.

RESULTS AND EXPERIMENTAL

If a small volume of solution containing an ion in tracer concentration is placed on the top of an ion exchange column and solution is passed through the column at such a rate that equilibrium is maintained, the number of column volumes required to produce a peak in the concentration of the tracer ion in the effluent is equal to the volume distribution coefficient, D_v , of the ion from the solution used to elute it. In the recovery of Pu from sump water, it is planned to load the resin to only about 1 g/l which is a small fraction of its total exchange capacity. Because of this, it can be expected that to a first approximation, the number of column volumes that can be processed before high breakthrough occurs will be equal to D_v . In order to process greater than 10 sump batches without appreciable breakthrough, a D_v of about 10^3 or greater is required. Since batch distribution experiments are much more easily done than column experiments, a series of batch experiments were performed to test the effect of various variables on resin loading from sump solutions.

Plant sump solution is normally too low in plutonium to measure distribution coefficients directly and must be spiked with more Pu. In order to measure the very high distribution coefficients involved in this system without high resin loading, Pu²³⁸ was used as a tracer. The Pu²³⁸ was freshly purified by anion exchange. The anion exchange product was used directly in experiments where NaHSO₃

was present. For measurement of Pu(IV) distribution coefficients, the Pu²³⁸ stock solution was reduced by NaNO₂ at low acidity and was then converted completely to Pu(IV) by adjusting to 8M HNO₃ and thermally evaporating to insure an initial Pu(IV) valence.

Distribution coefficients for both Pu(III) and Pu(IV) were measured from 0.03M HNO₃, from 0.03M HNO₃ at two levels of fluoride with and without Al present, and from 0.03M HNO₃ with 0.015M Al but without fluoride. The resin was Dowex 50W, X-8 (20-50 mesh) in the hydrogen form. In all the cases where Al was present in the solution, the resin had been completely equilibrated (by column technique) with a solution which contained 0.015M Al⁺³, 0.015M F⁻, and 0.03M HNO₃ and rinsed with water to remove any physically entrained fluoride and aluminum. This treatment resulted in a loading (by analysis) of 25 g Al/l of resin corresponding roughly to a divalent ion (possibly AlF⁺⁺). All equilibrations were done in duplicate and an equilibration time of three days was used. Table I gives the results.

TABLE I

Solution*	D _v , Pu(III)	D _v , Pu(IV)
Clean	4.0 x 10 ⁵	5.9 x 10 ⁴
0.015M F ⁻	1.5 x 10 ⁵	1.6 x 10 ³
0.06M F ⁻	1.3 x 10 ⁵	6.2 x 10 ²
0.015M Al	3.0 x 10 ²	7.2 x 10 ²
0.015M Al, 0.015M F ⁻	5.7 x 10 ²	8.1 x 10 ²
0.015M Al, 0.06M F ⁻	6.8 x 10 ²	2.7 x 10 ²

*All solutions were 0.03M HNO₃ and the Pu(III) solutions were 0.05M NaHSO₃.

The data of Table I indicates that the Pu(IV) system is generally unsatisfactory although in the absence of aluminum it is borderline. The use of Al is quite unacceptable in the case of either Pu(III) or Pu(IV). In the Pu(III) system, the presence of Al is much more detrimental than the presence of F⁻ because of a

greater effect of Al competition for resin sites than of fluoride complexing of Pu(III). In the Pu(III) system, if appreciable Al is present, the presence of F^- is actually beneficial because it complexes the Al more strongly than it does Pu(III). Since the Pu(III) distribution coefficients at fluoride levels of 0 to 0.06M without Al are very much higher than the minimum required, it appears that adjustment of the sump water to about the pH of 0.03M HNO_3 , pH = 1.6, (if it is significantly higher than this initially) and to about 0.05 $NaHSO_3$ is all that is required in the way of feed adjustment.

This feed flowsheet was tested with actual plant samples collected on June 7, 8, 10, 14, 16, and 17, 1966. The samples were found to all be initially in the pH range 1.3 to 2.2. Those with pH above 1.6 were adjusted to 1.6 with HNO_3 and the solutions were made 0.05M $NaHSO_3$. Pu^{238} (initially Pu(IV)) was added as a tracer and the solutions were equilibrated with Dowex 50W, X-8 (20-50 mesh) for 20 hours. Fluoride analyses were also obtained. Table II gives the results.

TABLE II

<u>Date Sample Taken</u>	<u>D_v</u>	<u>F^- Molarity*</u>
6--7	4.9×10^4	0.063
6--8	1.4×10^4	0.058
6-10	8.5×10^3	0.053
6-14	7.3×10^4	0.0095
6-16	2.7×10^5	0.0016
6-17	2.1×10^5	< 0.0005

*The analytical method used determines free fluoride and not that strongly bound in complexes.

The results again indicate that simple adjustment of the feed to pH of about 1.6, if it is initially higher than this (no adjustment should be done if the pH is initially lower than 1.6), and to 0.05M $NaHSO_3$ should give very satisfactory

loading performance. It should be noted that since distribution coefficients could not actually be measured for the very small amounts of Pu^{239} already present in the sump solutions, any effects due to slow kinetics resulting from the past history of the solution (such as presence of Pu polymer) could not be evaluated. Pu polymer formation at these low Pu concentrations probably is not serious in the presence of the fluoride levels involved.

In order to settle with certainty the other possible questions remaining concerning the process (such as loading characteristics of the Pu initially present in the sump water, effect of intermittent loading, and elution performance) it would be necessary to carry out a column loading under actual anticipated plant conditions. This would entail use of actual batches of high Pu, plant sump water without spiking with additional Pu and intermittent loading over a period of weeks or months as the high Pu sump batches occurred.

References

1. G. L. Stiffler, The Removal of Plutonium from 234-5 Building Sump Water, HW-70406, July 20, 1961. (Declassified).
2. R. S. Kingsley, private communication.