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**SOLVENT EXTRACTION OF CESIUM
FROM HANFORD ALKALINE SUPERNATE
BY 4-SEC-BUTYL-2(α -METHYLBENZYL)PHENOL
LABORATORY STUDIES**

L. A. BRAY

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By

L. A. Bray

Chemical Research Section

Chemistry Department

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INTRODUCTION

Fission product wastes from the separations facilities at Hanford are concentrated, treated with excess sodium hydroxide, and stored in underground mild steel tanks. Most of the fission products precipitate and slowly drop to the bottom of the tank leaving the cesium and sodium in the supernate (known as Alkaline Supernate). Since Cs^{137} is a gamma emitter (0.66 MeV), with a half-life of 30 yr, it is now partially recovered from this waste solution for use in radiotherapy, radiography, thermoelectric, and sterilization applications.

Previous Hanford research has demonstrated that cesium can be recovered from Hanford waste by precipitates such as the metal ferrocyanides, by absorption on natural clinoptilolite or artificial (DECALSO)[®] aluminum silicate ion exchange resins, or by solvent extraction with dipicrylamine-nitrobenzene⁽¹⁾ solutions. As of January, 1964, approximately 1,600,000 Ci of Cs^{137} had been shipped by the ion exchange isolation technique to the Oak Ridge National Laboratory. In the near future, the Hanford Waste Management program will require that all of the cesium-containing Alkaline Supernate waste tanks be processed to remove the heat generating isotopes. Therefore, a solvent extraction process may prove a more flexible and economical choice for cesium recovery. For this reason, and because of recent promising results (ORNL)^(2, 3, 4) on the extraction of cesium with high molecular weight phenols, an investigation was started to evaluate a promising phenol, 4-sec-butyl-2 (α -methylbenzyl)phenol (BAMBP) to waste compositions peculiar to the Hanford Waste Management program.

SUMMARY

A cesium solvent extractant, 4-sec-butyl-2(α -methylbenzyl)phenol, has been investigated for possible use at Hanford. The substituted phenol, diluted with a kerosene, was found to be a very selective extractant for cesium, both in the laboratory and, subsequently, by G. L. Richardson in pilot-plant-scale pulse column demonstrations.⁽⁵⁾ The extractant provides an efficient method for cesium recovery from the very large volumes of Alkaline Supernate now being stored at the separations facilities.

The extraction of cesium depends upon the concentration of phenol, the pH of the aqueous waste solution, the temperature of the equilibration, and the aqueous Na^+ concentration. Approximately 0.3 of a mole of additional OH^- was required per liter of synthetic Alkaline Supernate (9M Na^+ , pH 10.3) for maximum cesium extraction. Cesium distribution values are enhanced by an equilibration temperature decrease. The heat of extraction, $-\Delta H$, was found to be approximately 19 kcal. The cesium distribution ratio was also inversely dependent on the sodium concentration with a slope of slightly less than -2 over the range of 1 to 8M sodium.

Several phases of the phenol process are not included in this report:

- The mechanism of extraction,
- The extent of destruction of phenols by radiation and/or nitrite,
- The measurement of the mutual solubility of both the organic and aqueous phases.

EXPERIMENTAL

Experiments with synthetic Purex plant wastes (Table I) determined the effects of various physical and chemical variables.

The distribution ratios were determined by shaking the two phases in a constant temperature bath for a prescribed time, separating the two phases by centrifugation, and analyzing the tracer isotopes by their gamma energies.

The BAMBP was provided by the Dow Chemical Company, Midland, Michigan and the kerosene (SOLTROL-170) by the Phillips Petroleum Company, Bartlesville, Oklahoma.

TABLE I
COMPOSITION OF SYNTHETIC WASTES

	Salt Waste at pH 8.5	Alkaline Supernate at pH 10.3		Salt Waste at pH 8.5	Alkaline Supernate at pH 10.3
Na ⁺	0.122	9	NO ₂ ⁻	-	4.2
Sr ⁺⁺	-	-	NO ₃ ⁻	-	2.6
Cs ⁺	0.001	0.0004	PO ₄ ⁼	0.003	0.02
Ce ⁺⁺⁺	-	-	CO ₃ ⁼	-	1
Fe ⁺⁺⁺	0.067	-	Acetate	0.35	-
Ca ⁺⁺	-	-	Citrate	0.032	-
Cr ⁺⁺⁺	0.013	-	Tartrate	0.134	-
Al ⁺⁺⁺	0.034	-	HEDTA	0.186	-
Ni ⁺⁺	0.007	-			
SO ₄ ⁼	0.067	0.07			

RESULTS AND DISCUSSION

Solvent extraction processes for the recovery of radioactive cesium have been developed at ORNL, Brookhaven, and Hanford. A review ⁽¹⁾ of these potential cesium extractants had indicated that dipicrylamine in a nitrobenzene solvent would be a practical, sensitive, and selective extractant for cesium. Laboratory and hot-cell studies were completed, and the process was successfully demonstrated ⁽⁶⁾ in 9 ft high, 3 in. diameter, "cold" semiworks pulse columns.

K. B. Brown, et al ^(2,3,4) have similarly developed a phenol solvent extraction process and have applied it not only to the recovery of fission products, but to the recovery of cesium from ores. Experiments have been performed to verify the ORNL results and to extend the evaluation of one of the more promising phenols, BAMBP, to waste compositions peculiar to the Hanford Waste Management program.

BAMP was found to be very comparable to dipicrylamine in cesium extractability, selectivity and stripability. The major potential advantage of the phenol-kerosene extractant is that the density of kerosene (≈ 0.9) as compared with nitrobenzene (1.198) would always be less than that of the aqueous feed, scrub and strip streams, thus eliminating any inversion of phases. Also, kerosene (SOLTROL-170) solvent is presently in use in other parts of the Hanford separations recovery program.

Distribution of Cesium and Sodium as a Function of pH

The phenolic type extractants, such as BAMBP, extract cesium most effectively at high pH (Figure 1). It is desirable to add caustic to

FIGURE 1

Cesium and Sodium Distribution as a Function of pH

the Alkaline Supernate (pH 10.3) to increase the pH above 12. Using a 1M solution of BAMBP in the ORNL recommended diluent, diisopropyl benzene (flash point, 170 °F), a cesium distribution ratio (E_a^0) of 18 was obtained from the extraction of Alkaline Supernate (9M Na⁺) to which 0.2M per liter of additional NaOH had been added. Without the additional caustic, the ratio was only 0.05. High cesium distribution ratios (80) were also obtained with caustic-adjusted, tartrate-complexed, synthetic Salt Waste (effluent from the proposed di-2(ethylhexyl)phosphoric acid, D2EHPA) recovery of strontium and rare earths), as shown in Table II. However, cesium recovery is difficult from this type of waste because the iron drops out of solution at these high pH values.

TABLE II
CESIUM DISTRIBUTION AS A FUNCTION OF OH⁻ AND ORGANIC DILUENT

Organic: 1M BAMBP

o/a: 1

Temperature: 25 °C

Contact Time: 15 min

<u>Alkaline Supernate</u>		<u>Cesium Distribution Ratio, E_a^0</u>	
<u>Moles of OH⁻ per liter of</u>		<u>Diisopropyl Benzene</u>	<u>Soltrol-170</u>
<u>Adjusted Feed</u>			
0	(pH 10.3)	0.05	0.6
0.08		-	19
0.09		8	-
0.2		18	37
0.4		17	36
0.7		-	25
1.4		-	10
1.7		14	-
<u>Salt Waste</u>			
0	(pH 8.5)	0.002	0.05
0.08		-	0.09
0.09		0.8	1
0.2		10	34
0.4		-	104 *
0.7		36*	-
1.4		80*	60 *
1.7		69*	

* Precipitate noted

Effect of the Solvent on the Extraction of Cesium

SOLTROL-170, a branched chain kerosene, is a more effective diluent for the BAMBP extractant as compared to diisopropyl benzene. Using 1M BAMBP in SOLTROL-170, the cesium distribution ratios were again determined for the synthetic Salt Waste and the Alkaline Supernate (Table II), yielding results 2 to 3 times higher than with diisopropyl benzene. Table III shows a comparison of cesium distribution ratios for several other diluents. The high dielectric solvents that were most extractive for ion-pair cesium extractants such as dipicrylamine or tetraphenyl boron are inferior to kerosene when used as diluents for the phenolic extractants such as BAMBP.

TABLE III

CESIUM DISTRIBUTION AS A FUNCTION OF DILUENT

o/a: 1

Temperature: 25 °C

Aqueous: 1M NaOH, 0.001M CsCl

Contact Time: 15 min

<u>1 M BAMBP Diluted with:</u>	<u>Cesium Distribution Ratio, E_a^0</u>
Shell-2342	260
Soltrol-170	245
Diisopropylbenzene	100
Carbon Tetrachloride	94
AMSCO-D95	25
Nitrobenzene	19
Hexone	0.05

Mechanism of Extraction

The mechanism of cesium extraction with 4-sec-butyl-2(α -methylbenzyl)phenol,

is under investigation. From cesium loading studies (Figure 2), the maximum cesium loading was determined to be 1 mole of cesium per 5 moles of BAMBP. It is therefore postulated that 4 moles of BAMBP are required to solvate 1 mole of $\text{Cs} \cdot \text{BAMBP}$ salt.

FIGURE 2
Cesium Extraction Isotherm

Distribution of Cesium as a Function of Temperature

Cesium extraction into BAMBP is enhanced by a temperature decrease. The associated heat effect, $-\Delta H$, is equal to ≈ 18.6 kcal (Figure 3) and is more than twice that for dipicrylamine ($-\Delta H_{DPA}$, ~ 7.4 kcal).

FIGURE 3

Cesium Distribution as a Function of Temperature

The distribution of cesium as a function of temperature (Figure 3) indicates the need for temperature control for process and analytical cesium solvent extraction applications. It may be more desirable (if higher cesium distributions are required) to lower the temperature rather than to increase the phenol concentration. Where a batch contact is desirable and large cesium distributions are required, a lowering of the aqueous temperature seems more favorable than an equivalent increase in phenol concentration.

Distribution of Cesium and Sodium as a Function of Aqueous Sodium Concentration

Cesium and sodium distribution ratios were determined as a function of the aqueous sodium concentration (Figure 4).

FIGURE 4

Cesium and Sodium Distribution as a Function of Aqueous Sodium Concentration

All of the aqueous samples contained 1M of OH^- ; the sodium concentration was adjusted with NaNO_3 , and the cesium concentration was 0.001M CsCl . The sodium distribution ratio results were nearly constant ($E_{\text{aNa}}^{\text{O}} = 0.025$) while the cesium distribution ratios were inversely dependent on the sodium concentrations with a constant slope of slightly less than -2 over the range of 1 to 8M sodium. The sodium distribution ratio does not have the same dependence on the aqueous sodium concentrations with a similar negative slope. Karl Fisher titrations of the equilibrated organic phase have indicated that approximately 6 moles of H_2O are associated with the organic per mole of $\text{Na} \cdot \text{BAMBPate}$. Preliminary results indicate that the sodium in the organic phase may not be completely associated with the BAMBPate but rather with the dissolved H_2O as a nitrate.

Distribution of Cesium and Sodium as a Function of OH^- and BAMBP Concentration

A family of cesium and sodium distribution ratios were determined as a function of additional OH^- with varying BAMBP concentration. The Alkaline Supernate was adjusted by varying the OH^- concentration with 19M NaOH . Figure 5 shows that the cesium distribution passes through a maximum, and that the location of the maximum shifts (from ≈ 0.25 to 1M of additional OH^-) as the BAMBP concentration is varied from 1M to 0.1M . The sodium distribution ratios increase with increasing OH^- and do not reach a maximum within this experiment. Figure 6 contains the same data, but the cesium and sodium distribution ratios are plotted as a function of the BAMBP concentration.

Distribution of Cesium, Rubidium, Potassium, and Sodium as a Function of OH^-

Figure 7 shows the various distribution ratios for cesium, rubidium, potassium, and sodium from the Alkaline Supernate as a function of an increase in the OH^- concentration. The organic concentration was constant at 0.5M BAMBP. With these results, the separation factors (ratio of the distribution ratios) of cesium from rubidium, potassium, and sodium are 18, 113, and 3400, respectively, (distributions at 0.3M of added NaOH). Similar separation factors for 0.01M dipicrylamine were 6, 28, and 2500.⁽¹⁾

FIGURE 5

Cesium and Sodium Distribution as a Function of OH⁻
and BAMBP Concentration

FIGURE 6

Cesium and Sodium Distribution
as a Function of BAMBP Concentration and OH⁻

FIGURE 7
Cesium, Rubidium, Potassium and Sodium Distribution
as a Function of OH⁻

Distribution of Cesium as a Function of D2EHPA

The Alkaline Supernate (9M Na^+ , pH 10.3) has a very low cesium distribution value of 0.24 when extracted with 0.5M BAMBP. If the aqueous pH is increased by the addition of NaOH, the distribution is enhanced. A second method is the addition of D2EHPA to the BAMBP organic extraction system. Figure 8 shows that a BAMBP to D2EHPA ratio of 10 increases the cesium distribution from 0.24 to 2.4. The enhancement of the phenol extraction with the addition of D2EHPA will be discussed in a subsequent paper. (7)

FIGURE 8

Cesium Distribution as a Function of D2EHPA

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