

ION EXCHANGE ABSORPTION OF CESIUM BY
POTASSIUM HEXACYANOCOBALT(II)FERRATE(II)*

by

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ABSTRACT

A description is given of the preparation and properties of a granular form of potassium hexacyanocobalt(II)ferrate(II) that is a highly selective absorbent for cesium ion. The material is suitable for use in a large-scale ion exchange column, and offers the possibility of isolating and concentrating Cs¹³⁷ from the fission product waste solutions which arise from the processing of nuclear fuels.

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INTRODUCTION

Barton, et al.⁽¹⁾, demonstrated that ferrocyanides and ferricyanides of the transition metals, such as zinc ferrocyanide, precipitated cesium from acidic or slightly alkaline solutions. Tananaev and coworkers⁽²⁾ measured the solubilities of complex ferrocyanides of the general type illustrated by $K_2[CoFe(CN)_6]$, where the composition can be varied to include alkali metals other than potassium and transition metals other than cobalt. They reported that the solubilities could be arranged in the following sequence, when only the alkali metal was varied:



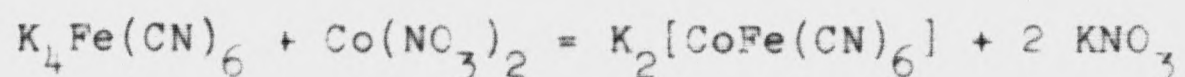
Sodium and lithium were not placed in this series because it is doubtful that they form true compounds of this type.

From these earlier studies we concluded that the potassium ion in such compounds might exchange with other alkali metal ions, and that the equilibria might favor the replacement of potassium ion by the heavier alkali metal ions. If a complex cyanide compound could be prepared in a form suitable for use in a column, this material would provide a potential means of removing radioactive cesium-137 from large volumes of aqueous solutions, such as those encountered in the processing of nuclear fuels.

This paper describes the successful preparation of a granular form of potassium hexacyanocobalt(II)ferrate(II) (abbreviated KCFC) and presents some preliminary observations on the ion exchange absorption of cesium by the compound.

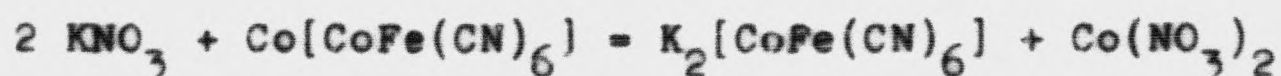
EXPERIMENTAL

Granular KCFC was prepared by adding one volume of 0.5M $K_4Fe(CN)_6$ solution to 2.4 volumes of 0.3M $Co(NO_3)_2$ over a period of 30 minutes at room temperature. The reaction was:



The order of addition of the reagents and the presence of an approximate 40% excess of $Co(NO_3)_2$ were important in preventing the formation of colloidal products or slimes that were difficult to centrifuge and dried to fine powders. The slurry of KCFC was centrifuged, washed several times with water, and dried at 115°C. The resulting granules were crushed and dry screened to 20-60 mesh size. The graded particles were hydraulically classified with water to remove fines and then redried.

X-ray diffraction analysis of the product showed that the complex cyanide has the same crystal structure as Prussian blue⁽³⁾. By inference, it consists of an iron-cyanide-cobalt framework having either cobalt or iron atoms at the corners of cubic units, and potassium ions at the centers of the cubes. Analyses of the product for potassium, cobalt, and iron by atomic absorption spectroscopy showed the atom ratio of K:Co:Fe to be 1.6:1.4:1.0. These data indicate that the product is not pure $K_2[CoFe(CN)_6]$, but is probably a mixture of $K_2[CoFe(CN)_6]$, $Co[CoFe(CN)_6]$, and some included $K_4Fe(CN)_6$. The presence of $K_4Fe(CN)_6$ is not surprising when one considers that the cage structure of this type of compound leads to clathrate inclusion. Formation of $K_2[CoFe(CN)_6]$ in the following steps may account for the presence of $Co[CoFe(CN)_6]$ in the crystal.



In the designation of these compounds, the brackets are intended to indicate the atoms that are included in the cubic lattice, while the atoms outside the brackets are assumed to be body-centered ions.

Attempts were made to prepare other granular salts of this type by reacting sodium and potassium ferro- and ferricyanides with metal salts of zinc, manganese, cadmium, uranium, iron, nickel, and chromium. The products of these reactions produced slimes that readily formed colloids when washed with water, and that dried to fine powders. Although these compounds absorbed cesium from solution they were not suitable for large-scale column operation.

Two types of experiments were performed to demonstrate the ion exchange absorption of cesium. In batch equilibrations known masses of KCFC were mixed with measured volumes of solutions containing cesium traced with Cs^{137} . During the mixing period, the distribution of cesium between the solution and solid was determined by analyzing the solution phase for Cs^{137} . The results were expressed in terms of a distribution coefficient, K_d , defined as the ratio of cesium absorbed per gram of KCFC to the cesium remaining in solution, per ml of solution. The solutions contained, in addition to cesium ions, relatively high concentrations of potassium and sodium ions to demonstrate the selectivity of the absorption of cesium by KCFC.

In other experiments, the solution containing cesium was passed through a fixed bed of KCFC. The performance of the column was determined by measuring the Cs^{137} content of the effluent.

RESULTS AND DISCUSSION

Chemical and Physical Properties

Chemical tests showed that KCFC is stable in nitric and hydrochloric acids and in highly salted alkaline solutions. In one series of tests, KCFC was stable in boiling concentrated nitric and

hydrochloric acids, but dissolved readily in boiling concentrated sulfuric acid. Solutions of sodium hydroxide greater than 0.01M caused KCFC to peptize and form stable colloids. The addition of sodium nitrate to the alkaline solutions greatly reduced the tendency to form colloids. KCFC was stable in 1M NaOH if the solution contained 4M NaNO₃.

Tests were also made of the stability of KCFC containing absorbed cesium. Samples containing absorbed cesium were immersed in 0.3M NaOH-4M NaNO₃ solution and allowed to stand for 40 days at 25 and 60°C. The amount of cesium in the solution phase remained constant during the test period, indicating good stability under these conditions. In another test KCFC was added to an alkaline waste solution from the processing of nuclear fuels, and the cesium was absorbed. This mixture was then exposed in a cobalt-60 gamma source to a total dose of 6×10^8 rad. The absorbed cesium decreased from 95% of the total in the original solution to 72%, indicating that KCFC is decomposed to a small extent at very high radiation doses.

Pressure drop characteristics of columns of granular KCFC are similar to those of organic ion exchange resin beads of similar mesh size. Thus, very little attrition of the KCFC occurred during typical operation of columns. Typical pressure drop data for wet-screened, granular KCFC are shown in Figure 1.

Absorption Properties

Cesium is absorbed from solution by the replacement of potassium ions in the KCFC crystals. To demonstrate this ion exchange mechanism, a column containing KCFC was saturated with cesium. Analyses of the column effluent for cesium and potassium ions showed that the KCFC absorbed 0.36 milliequivalents of cesium (0.3 meq/g KCFC) and that 0.25 milliequivalents of potassium were released. The results demonstrated the Cs-K exchange qualitatively.

More quantitative agreement is not expected because of the heterogeneous nature of the absorbent, as previously described.

The batch equilibration tests, Table I, show that the absorption of cesium by KCFC is rapid; equilibrium was reached in about one hour. The data in Table II show the increased absorption by material of smaller particle size. The larger distribution coefficients for the smaller particles indicate that a large fraction of the cesium is absorbed near the surface. The selectivity of KCFC for the absorption of cesium in the presence of large concentrations of Na and K is also demonstrated by the results of these tests.

Columns of granular KCFC demonstrated excellent absorption of cesium from large volumes of typical high activity waste solutions. The results of column tests (Figure 2) show that a column of KCFC removed greater than 99.9% of the cesium from 500 bed volumes* of waste solution containing 0.3 curie of Cs¹³⁷ per liter. With a waste solution containing 1.0 curie of Cs¹³⁷ per liter, a column removed 99% of the cesium from 300 bed volumes of waste. In these tests, 250 and 460 millicuries of Cs¹³⁷ were absorbed per gram of KCFC.

Additional data were obtained on the selectivity for cesium and on the volumetric capacity of KCFC for waste solutions containing tracer concentrations of Cs¹³⁷. In these tests two feed solutions traced with Cs¹³⁷ were fed through columns containing 10 ml of 30-60 mesh KCFC. One solution contained a high salt concentration, the other was a dilute solution of NH₄OH. The results in Table III show that the KCFC removed greater than 99.9% of the cesium from at least 25,000 bed volumes of solution.

Cesium Exchange Capacity

The cesium exchange capacity of KCFC was determined in acidic, neutral, and alkaline solutions by saturating KCFC with cesium. The amount of cesium absorbed by the KCFC was determined, and the results were expressed as milliequivalents of cesium per gram

* A bed volume is defined as the volume of settled absorbent in the column.

of dry KCFC. The results in Table IV show that the capacity is the same for both acidic and alkaline solutions, but is less for neutral solutions.

The theoretical capacity is about 6 meq/gram, based on the exchange reaction:



Although the operating capacity of 30-60 mesh KCFC was only about 0.5 meq/gram, the capacity is undoubtedly related to the particle size and the available surface area of the particles. To demonstrate the formation of $Cs_2[CoFe(CN)_6]$, a solution containing 10 millimoles of cobalt and 25 millimoles of cesium was titrated with a standard solution of $H_4Fe(CN)_6$ until all the cobalt was precipitated. Analyses of the solution phase after titration showed that the precipitate contained 2 moles of cesium per mole of cobalt or ferrocyanide.

Elution of Absorbed Cesium

Attempts to elute the cesium absorbed by KCFC were only partially successful. No satisfactory procedure for elution and regeneration is presently available. Solutions of 1M KNO_3 , 4M HNO_3 and 1M NH_4Cl removed very little Cs^{137} , but efficiently removed the daughter activity, Ba^{137} . About 95% of the absorbed cesium was removed with 20 bed volumes of 0.1M $Hg(NO_3)_2$, but the mechanism was not one of simple ion exchange in that the KCFC was partially decomposed by this reagent.

Thallium nitrate was effective in eluting cesium. In one test, 7 bed volumes of 0.02M $TlNO_3$ eluted greater than 99% of the absorbed cesium. Although KCFC eluted with Tl^{1+} could not be simply regenerated with potassium ions, replacement of thallium with potassium may be possible, if thallium can be oxidized to the (III) valence state.

SUMMARY

The work described in this paper was designed to provide a granular alkali metal ferrocyanide suitable for the absorption of cesium from acidic and alkaline solutions by column techniques.

Procedures are given for the preparation of granular potassium hexacyanocobalt(II)ferrate(II) suitable for large-scale column operation. By using a column of the granular material, it was possible to remove Cs¹³⁷ from highly radioactive waste solutions produced in the processing of nuclear fuels. The absorbed cesium could be eluted with a solution containing thallos salts; however, the KCFC could not be regenerated.

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TABLE I

Rate of Absorption of Cesium

Solution: 50 ml of simulated radioactive waste:
1.5M NaOH; 4.7M NaNO₃; 1.2M NaAlO₂;
0.05M Na₂SO₄; 0.005M KNO₃; 0.0002M CsNO₃;
traced with Cs¹³⁷, 5 x 10⁴ d/(min)(ml).

Absorbent: 100 mg of 30-60 mesh KCFC

<u>Equilibration Time,</u> <u>minutes</u>	<u>Distribution Coefficient,</u> <u>K_d (a)</u>
0.1	600
1.0	1,170
7	1,300
15	1,800
31	6,100
60	10,100
120	10,500

$$(a) K_d = \frac{\text{Cs per g of solid}}{\text{Cs per ml solution}}$$

TABLE II

Effect of KCFC Particle Size on Absorption of Cesium

Solution: Actual radioactive waste: 0.3M NaOH;
4.5M NaNO₃; 0.03M KNO₃; 9 x 10⁻⁵M CsNO₃;
6.24 x 10⁸ gamma d/(min)(ml);
6.22 x 10⁸ Cs¹³⁷ d/(min)(ml).

Absorbent: Granular KCFC

Equilibration Time: One hour

<u>Particle Size,</u> <u>U.S. Std. Mesh Size</u>	<u>Distribution Coefficient,</u> <u>K_d</u>
30-60	8,300
60-80	11,400
-100	15,100

TABLE III

Removal of Cesium from Low-Level Radioactive Waste

Absorbent: 10 ml column of 30-60 mesh KCFC

Flow: 1.5 ml/min

<u>Composition of Feed^(a)</u>	<u>Bed Volumes of Feed^(b)</u>
4.25M NaCl	24,000
200 mg NH ₄ OH, 84 mg NaNO ₃ , 3 mg KNO ₃ per liter	23,000

(a) Each feed solution contained 5×10^4 d/(min)(ml) of Cs¹³⁷.

(b) When this paper was written, these columns were still in operation and were removing greater than 99.9% of the cesium present in the feed.

TABLE IV

Cesium Exchange Capacity of KCFC

Absorbent: 5 ml (3 grams) of 30-60 mesh KCFC

Flow: 0.7 ml/min

<u>Composition of Feed Solution, M</u>				<u>Capacity,</u>
<u>CsNO₃</u>	<u>HNO₃</u>	<u>NaOH</u>	<u>NaNO₃</u>	<u>meq Cs/gram KCFC</u>
0.001	-	-	-	0.3
0.001	-	0.5	4.0	0.5
0.008	0.5	-	4.0	0.5

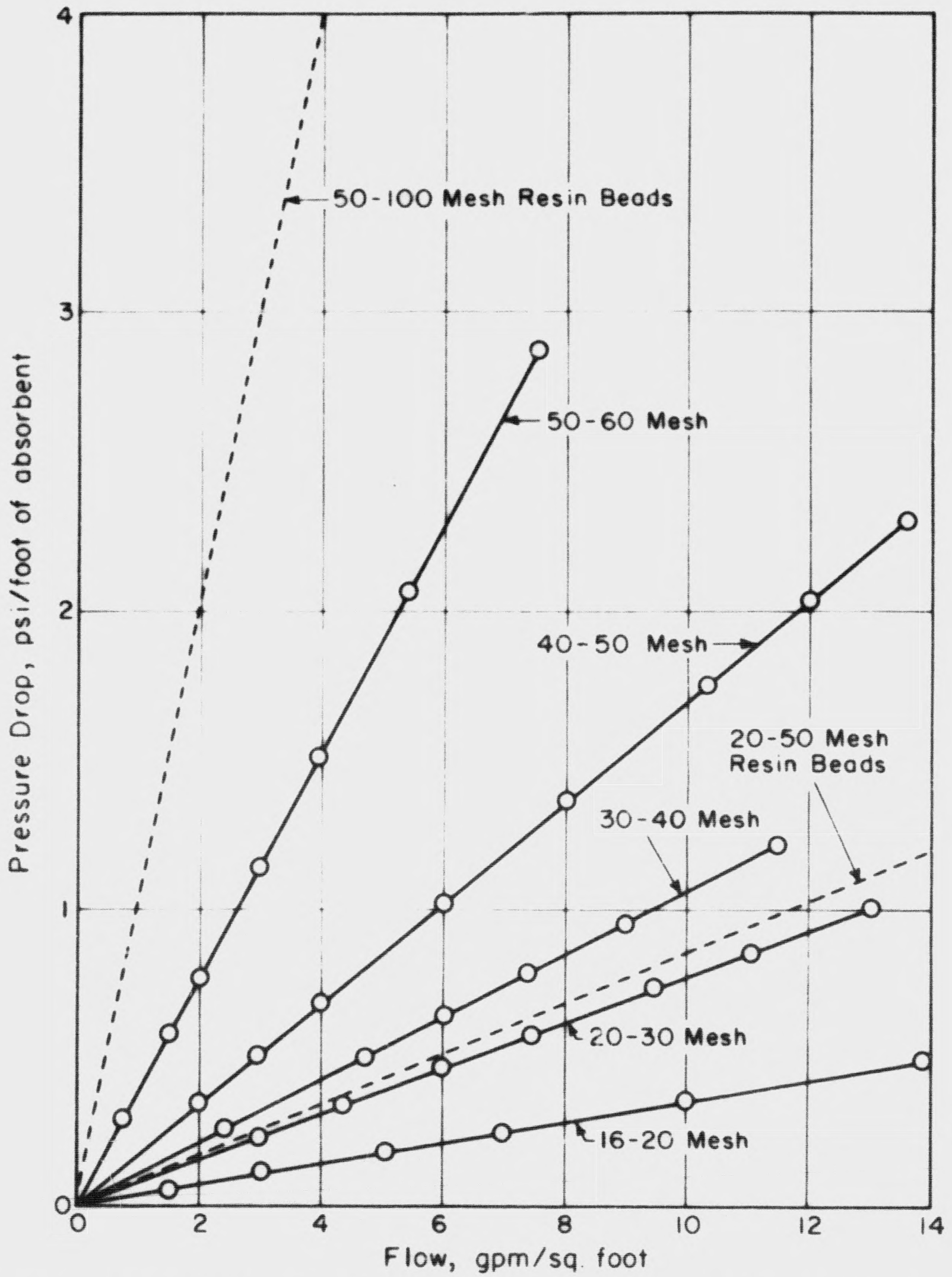


FIG. 1 PRESSURE DROP CHARACTERISTICS OF GRANULAR KCFC AT VARIOUS MESH SIZES AND FLOWS, 25°C

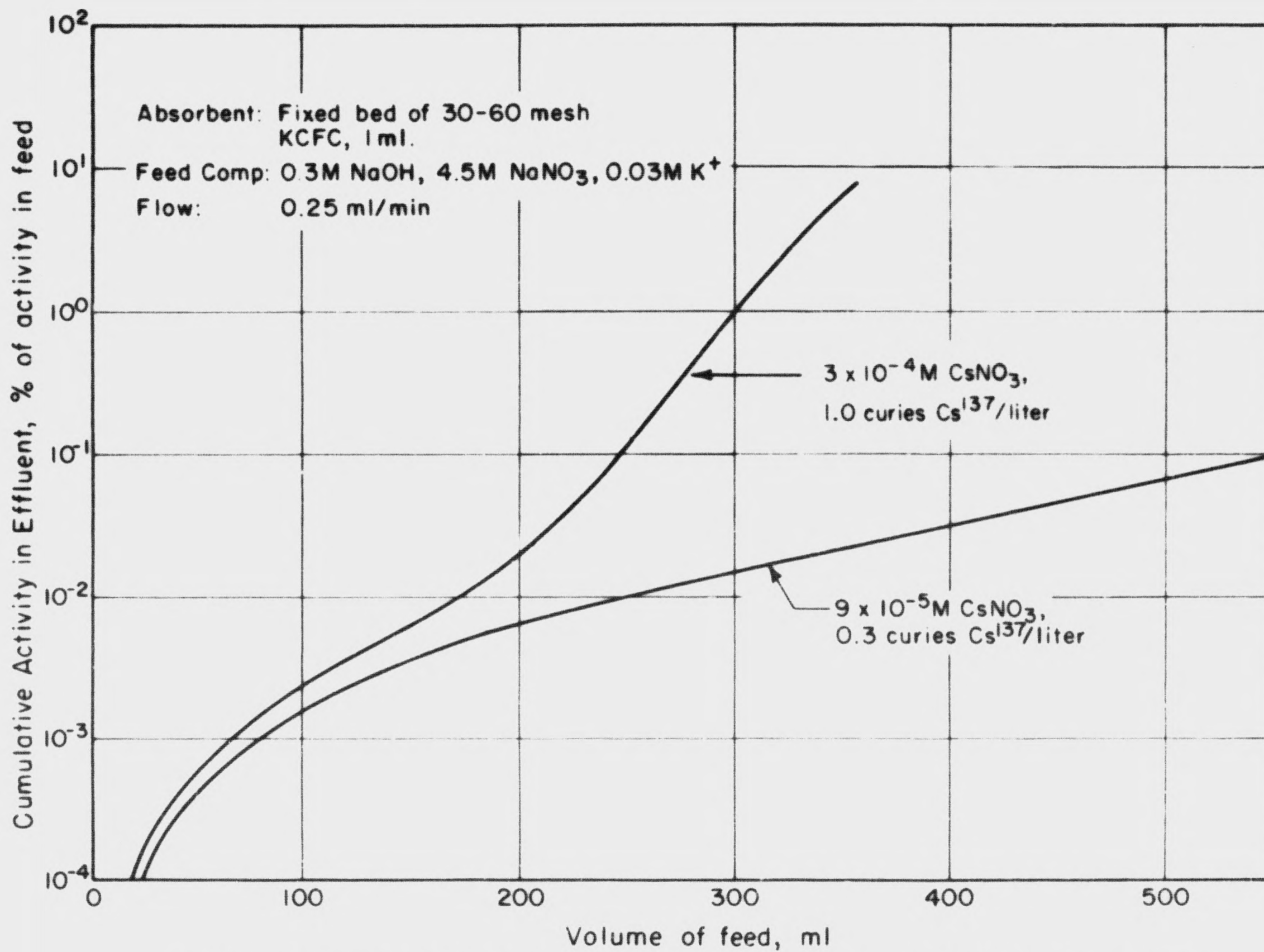


FIG. 2 ABSORPTION OF CESIUM FROM ACTUAL RADIOACTIVE WASTE

END