E	= subscript to a parameter, indicating that this parameter stands for a property of a mixed multicomponent filter as a whole
H	= shadow effect
l	= length of a pore
$\bar{l}$	= mean fiber length
L	= thickness of a filter
Δp	= pressure drop across a filter
Δp^*	= pressure drop across a filter of uniform pores
P	= aerosol penetration through a filter
v_s	= superficial velocity of air flow
$\bar{v}$	= mean flow velocity in a filter
v^*	= mean flow velocity in a filter of uniform pores
v_o	= maximum flow velocity in a filter
x	= weight fraction
x^*	= weight fraction corrected for shadow effect
z	= radial distance from center of a pore
β	= $-\log P_{exptl}/-\log P_{calcd}$
γ	= experimental parameter
ϵ	= porosity
η	= viscosity of air
λ	= $(a/a_o)^2$
λ_g	= geometrical mean of λ
$\Lambda(\lambda)$	= distribution function of λ
ρ_p	= density of aerosol fluid
σ, σ_g	= standard deviation and geometrical standard deviation
φ_v	= volume flow through a pore
$\phi(\ln d)$	= distribution function of fiber diameters
ψ	= inertial parameter

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SEPARATION OF CESIUM FROM FISSION PRODUCT WASTES BY ION EXCHANGE ON AMMONIUM MOLYBDOPHOSPHATE

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THERE is a large potential market for cesium-137 as a commercial source of gamma radiation, provided a cheap method is found for its large scale recovery from fission product waste solutions. Apart from its usefulness, the removal of this long-lived radioisotope from fission product waste solutions would reduce storage problems and simplify ultimate disposal of these wastes.

Several methods for cesium recovery have been proposed and a number of these, based mainly on precipitation and, lately, solvent extraction and ion exchange, are under active development. Earlier research effort concentrated on precipitation methods (*1, 3, 17*) but it is to be doubted if precipitation methods, with their inherent disadvantages of bulkiness, and hence excessive requirements of shielding, and the complexity of filtration and centrifugation operations, etc., in high radiation fluxes, will ever be competitive with continuous or semicontinuous processes such as ion exchange and solvent extraction.

Ion exchange on phenolic methylenesulfonic acid resins (*5, 6*) received a great deal of attention some years ago, but the emphasis has now shifted to mineral exchangers and inorganic ion exchange materials. These have the advantage of radiation stability and, in some cases, greater selectivity for

cesium than even the most selective organic ion exchange resins. Gel exchangers, such as zirconium phosphate, have a great affinity for the heavy alkali ions, but they are unsuitable if the loading solution is strongly acidic (*4*).

Of the mineral exchangers investigated, notably at the Hanford Laboratories, the natural zeolite clinoptilolite is claimed to be the most promising, and a recent report (*8*) describes the use of this mineral for recovering cesium from partially deacidified Purex waste. This exchanger is sufficiently stable only in alkaline, neutral, or moderately acidic solutions and its breakthrough capacity, which depends on the waste dilution factor, the concentration of added ions such as sodium, and temperature, is still modest.

A number of solvent extraction procedures have also been developed for cesium, the extractant to which preference is given (*2*) being 4-*sec*-butyl-2(α-methylbenzyl)phenol (BAMP). In the recent conceptual design of an envisaged plant for the annual production of megacurie quantities of cesium-137 and other fission product nuclides at Hanford (*7*), the process suggested for cesium-137 consists of two stages. The first comprises solvent extraction with a mixture of BAMP and di-2-ethylhexylphosphoric acid in hydrocarbon diluent at pH 4.5, and back-extraction into dilute acid. After separation of

A process is described for the large scale recovery of cesium-137 from acid fission product solutions by selective adsorption on columns of the crystalline inorganic ion exchanger ammonium 12-molybdophosphate (AMP). Specially prepared coarse AMP is used which allows suitably high flow rates. At a linear flow rate of 2.5 cm. per minute with Butex 150-fold waste concentrate, relatively shallow beds of AMP show a saturation capacity of about 0.65 equivalent of cesium per liter. Cesium is recovered from the column, after washing out impurities with dilute nitric acid, by stripping with hot concentrated ammonium nitrate solution, followed by chloride-catalyzed destruction of ammonium nitrate in nitric acid solution. Principal advantages of the process are simplicity, small size of equipment, the small quantities of active waste produced, and applicability to virtually any nonalkaline waste, including those of very high acid or salt content.

strontium by bicarbonate precipitation, the cesium is purified by extraction with BAMP in hydrocarbon at pH 13, and final stripping by oxalic acid solution. Disadvantages of this scheme include the need for prior neutralization, the rather large volumes of active waste produced, and the two-stage nature of the process, which necessitates an extra step for separating strontium and cesium.

This paper describes a process for separating cesium from fission product waste solutions which is based on selective ion exchange adsorption on the inorganic ion exchange material ammonium 12-molybdophosphate (AMP). The process does not require prior neutralization of the feed solution and is directly applicable to waste solutions of virtually any composition, provided they are of pH < 5. A particularly notable feature of the AMP is that its selectivity and capacity for cesium are almost unaffected by the presence in solution of large quantities of acid, sodium, calcium, or corrosion product cations.

Development of the process has been reported in a series of Harwell reports (11, 12, 14, 15). In the present paper a number of modifications to an earlier suggested flowsheet (14) are incorporated which bring about considerable further simplification.

Experimental

Preparation of AMP Column. The AMP exchanger was prepared (10) by bringing crystals of 12-molybdophosphoric acid in contact with a concentrated ammonium nitrate solution for a few minutes and wet-screening on nylon mesh sieves to obtain the 40 to 60 B.S. mesh fraction. Since particles of coarse AMP break up when dried, the desired size of the bed was obtained by first packing the AMP with $1M$ NH_4NO_3 into a glass column, of 2.1-cm. inside diameter, to give a wet column weight (including the liquid in the interstitial space) of 39 ± 0.1 grams. The AMP was then removed, fines were separated out by decanting with $1M$ NH_4NO_3, and the AMP was finally slurried into a similar but jacketed glass column to give a settled bed of dimensions 3.5 sq. cm. × 6.3 cm. (22 ml., of approximately 22-gram dry weight). The geometrical proportions of the column bed were deliberately chosen to give a depth-diameter ratio of approximately 3, to simulate the shallow columns of industry.

The bed was supported on a sintered glass disk of porosity 0, and water at 40° C. was circulated through the jacket from a thermostat bath during loading and washing. This temperature was chosen as likely to be similar in magnitude to that of fission product concentrate, because of the heat generated by

its radioactivity. For more efficient stripping of cesium, the temperature of the circulating water was raised to 90° C. during elution with ammonium nitrate solution.

In determining suitable conditions for cesium elution by ammonium nitrate–nitric acid solutions, a jacketed glass column of 0.9-sq. cm. inside diameter was used. Columns were either 1.0 ml. of 100- to 200-mesh AMP, prepared as above, or a physical mixture of 0.5 gram each of asbestos fiber and fine AMP precipitate, prepared according to the directions of Smit, Robb, and Jacobs (16). Each column was loaded with 10 mg. of cesium.

Fission Product Solution. Simulated Butex 150-fold fission product waste concentrate (Table I) was prepared from the various metal nitrates, and spiked by adding 0.3 mc. of 11-month-old gross fission product activity per liter. Before use, it was filtered and degassed by boiling under reflux.

Analytical Methods. Fission product effluent samples from the AMP column were weighed to determine their volume, and analyzed for cesium-137 by measuring its 0.661-m.e.v. gamma peak with a 256-channel gamma spectrometer, after precipitating interfering activities with sodium carbonate solution in the presence of cesium carrier. Effluent samples from other column experiments, where interfering activities were absent, were counted direct in a well-type scintillation counter.

Rubidium was determined by flame photometry after separation from cesium on a column of AMP-asbestos (16), and destruction of ammonium nitrate in the eluate by aqua regia.

Method and Results

Adsorption of Cesium on AMP. Several successful column runs with spiked fission product solutions have been made under the conditions described, while maintaining a linear flow rate of 2.5 ± 0.1 cm. per minute by means of a screw clip on PVC tubing attached to the bottom of the column. A liquid head of a few centimeters was maintained by siphoning from a container kept in the water bath.

Adsorption of cesium on the AMP column is illustrated by a typical breakthrough curve shown in Figure 1. The cesium concentration in the effluent first exceeded 1% of that of the feed solution at about 1000 ml., and the inflection point was reached at about 2000 ml. Washing of the column with 4 to 5 column volumes of $1M$ HNO_3, to displace other activities, also removed some cesium, but this constituted only a small fraction of the adsorbed cesium. The useful capacity of the AMP column for cesium under these experimental conditions, it may be calculated from the figure, is about 1.85 grams per 22-ml. bed, or 2100 curies of cesium-137 per liter.

Table I. Composition of Mock Fission Product Solution to Simulate Typical Butex Waste Concentrate

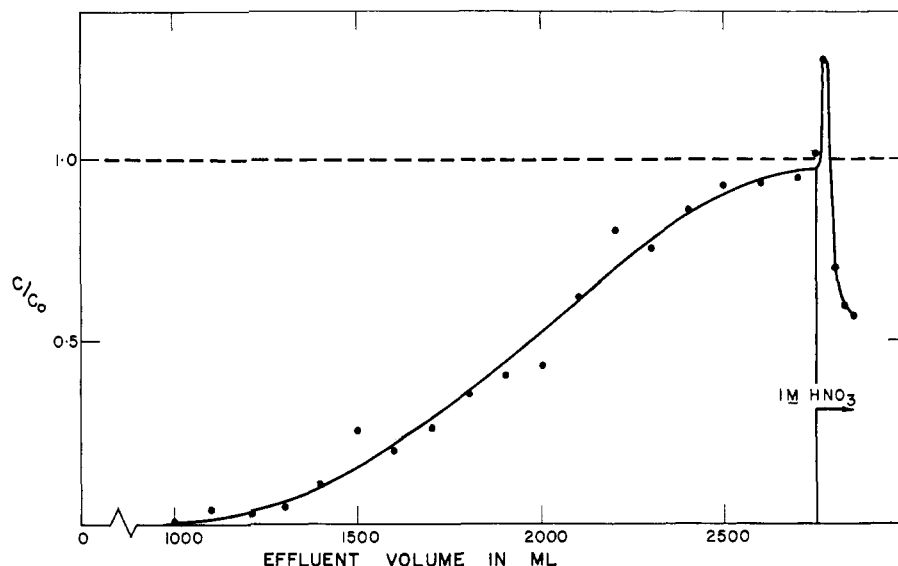| F.P. Elements	Cs	Rb	Sr	Ba	Y	La	Nd	Ce	Zr
Concn., mg./ml.	1.000	0.13	0.35	0.36	0.20	0.35	0.84	0.75	1.03
Nonfission elements			U	Fe	Al	Cr	Ni		
Concn., mg./ml.			60	30	25	2	3		
HNO_3 concentration, $3M$									

Figure 1. Adsorption of cesium on AMP column from simulated fission product waste concentrate

Elution of Cesium with Ammonium Nitrate Solution. The elution of cesium from AMP-asbestos columns at 60° C. by eluents containing varying concentrations of ammonium nitrate and nitric acid is shown in Figure 2. Efficiency of elution is greatly improved by the presence of nitric acid.

Cesium is held considerably more strongly on columns of coarse AMP than on AMP-asbestos columns. For reasonable efficiency at 60° C., say, the eluent must now be at least $3M$ ammonium nitrate in concentrated nitric acid. Elution efficiency with coarse AMP is highly dependent upon operating temperature, even more so than for AMP-asbestos columns (*11*)—for instance, the amount of eluent ($5M$ NH$_4$NO$_3$ in concentrated HNO$_3$) required for recovering 90% of the cesium from a column saturated with this ion was reduced by a factor greater than 3 when the operating temperature with this eluent was raised from 60° to 90° C.
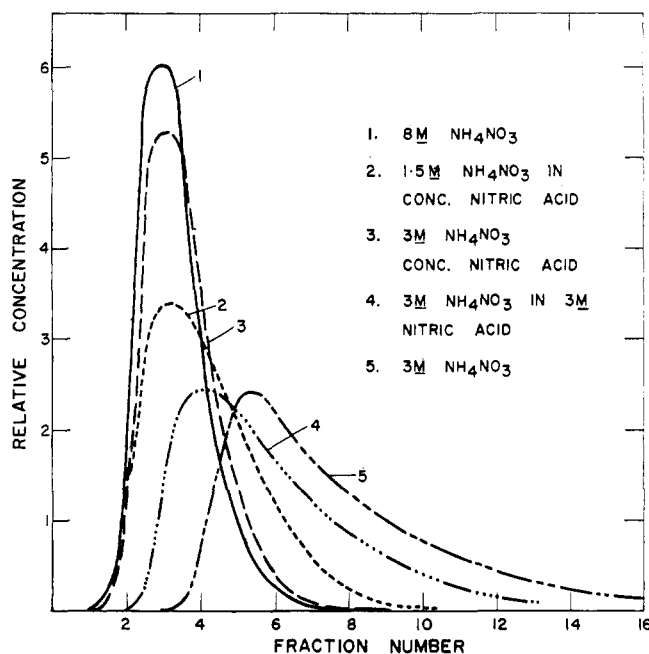

Figure 2. Elution of cesium from AMP-asbestos columns at 60° C. with various eluents

Although addition of acid to the ammonium nitrate eluent greatly improves the efficiency of cesium recovery, the presence of strong acid introduces certain difficulties. Above about $0.5M$ HNO$_3$ the equilibrium solubility of AMP rises appreciably with nitric acid concentration. Thus although concentrated nitric acid as solvent allows greater economy in ammonium nitrate, the cementing material responsible for holding together the microcrystals is more rapidly dissolved away by such eluents than by weakly acidic solutions, resulting in accelerated physical breakdown of the AMP particles. Preference has therefore been given to an eluent consisting of $10M$ ammonium nitrate in $0.2N$ nitric acid. This is approximately the optimum acidity for greatest stability of the 12-molybdo-phosphate anion, both in solution and in the solid, in contact with the aqueous phase. In the presence of large concentrations of metallic cations, the tolerance of AMP for acid is apparently very much higher.

Figure 3 shows an example of the elution of cesium from a 22-ml. column of 40- to 60-mesh AMP, onto which it had previously been adsorbed from spiked fission product solution (see Figure 1), using a flow rate of 2.5 cm. per minute and an operating temperature of 90° C. Approximately 4.8% of the cesium remained behind on the column, and it was calculated that more than 92% was recovered in the first 10 column volumes, and just less than 95% in 12 column volumes. In the first four fractions the cesium was contaminated by 5.15, 1.9, 0.3, and 0.15% rubidium, respectively, while for the combined eluate fractions the figure was less than 0.6%.

Cesium chloride was recovered from the eluate by pooling the fractions (after 2 ml. had been removed from each for analysis) and eliminating ammonium nitrate by chloride-catalyzed decomposition in nitric acid medium (*9*). This was accomplished by evaporating down to 210 ml., adding 100 ml. of 11.75M nitric acid and 10 ml. of 10.5M hydrochloric acid, and heating for 40 minutes under reflux, followed by evaporation almost to dryness. Any residual ammonium nitrate was finally eliminated by adding 12 ml. of aqua regia, and evaporating to dryness. The sample was now taken up in water, and the small amount of fine yellow precipitate (primarily cesium molybdophosphate) filtered off and weighed. The filtrate was evaporated to dryness, and two evaporations were made with 5 ml. of concentrated hydrochloric acid to ensure complete conversion to the chloride.

The dried chloride weighed 1.908 grams and had a specific activity which was 11.6% lower than that of cesium in the starting solution. The precipitate weighed 28.9 mg., of which 11.7 mg. (the yellow cesium molybdophosphate part) dissolved readily in aqueous ammonia.

Discussion

Of the various stages in the proposed process, the loading of cesium on the AMP column has proved to be the least troublesome. The coarse AMP particles performed very satisfactorily and, after one cycle, showed no sign of breaking up, provided the column bed, once packed, was not disturbed. A drop in flow rate was observed in a few of the earlier runs, but this was found to be due to clogging of the pores of the sintered glass support (porosity 1 or 2) by suspended material in the feed solution or by fine AMP particles incompletely removed during column preparation. After substituting a coarser supporting disk, the maximum flow rate that could be achieved was always well above 2.5 cm. per minute used in operation.

Washing the column free of impurities after the loading step is also fairly simple (11). Rubidium, because of its similar chemical properties, is partly coadsorbed with cesium (11), but is largely eliminated during subsequent washing. Rubidium contamination constitutes only a small percentage concentrated in the early eluate fractions; if it is desired to reduce this contamination still further, the rubidium may first be removed by elution with a more dilute ammonium nitrate solution.

Zirconium and niobium are partly retained by the AMP bed, even after the dilute acid wash (14), but are apparently not significantly displaced by the ammonium nitrate eluent. The eluate also contains small amounts of molybdate and phosphate which mainly precipitate as cesium molybdophosphate, zirconium phosphate, etc., during further processing, and these may be removed by decantation or filtration, if deemed necessary.

Recovery of Cesium from Loaded AMP. Undoubtedly the most difficult part of this study has been the search for the most suitable method of recovering cesium from the AMP column. Elution with concentrated ammonium nitrate solution, although recognized early in the project (11) as feasible, was later abandoned in view of the difficulty of subsequently separating cesium from the large amounts of ammonium nitrate.
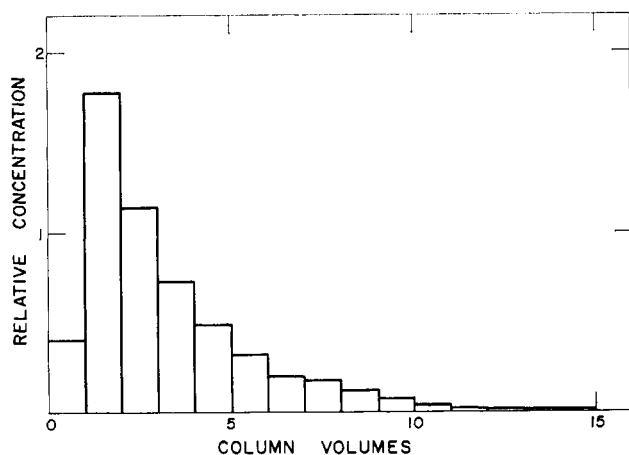
A number of alternative methods have therefore been considered (14). Each of these follows dissolution of the loaded AMP in caustic soda, thus limiting the use of the AMP bed to one cycle only. Zirconium and niobium retained on the bed form a small precipitate, whose separation should, however, not prove unduly difficult or expensive; ammonia (deriving from incompletely exchanged ammonium) may be eliminated by boiling, or destroyed with formaldehyde.

The methods considered are solvent extraction with dipicrylamine in nitrobenzene (15); precipitation with sodium dipicrylaminate, and recovery of cesium by leaching the precipitate with hydrochloric acid, or dissolving the precipitate in a suitable organic solvent—e.g., cyclohexanone—and extracting cesium with dilute sulfuric acid, preferred to hydrochloric acid recommended earlier (14), since the latter is partly miscible with cyclohexanone; and isolating cesium by ion exchange on zirconium phosphate cation exchanger, selectively eluting sodium with dilute acid, and recovering cesium by elution with stronger acid. Methods proposed for separating cesium from neutralized fission waste, such as precipitation or continuous ion exchange with phenolic methylene sulfonic acid resin in a Higgins contactor (6), would be equally applicable to the separation of cesium from the molybdate-phosphate solution, but in a much simplified form (14).

Most attention has been given to the method employing ion exchange of zirconium phosphate, and several published (14) and unpublished experiments have demonstrated the feasibility of this approach. The work has been hampered, however, by the unsatisfactory state of the art regarding these exchangers. Nevertheless, the method has been found suitable enough to allow working out of a proposed flowsheet (14).

With the discovery of a simple and cheap method of safely destroying large quantities of ammonium nitrate (9), it has become possible to do away with the zirconium phosphate column and to use each AMP column for several cycles. With our limited experience of the operation of AMP columns it is not possible at this stage to state the number of cycles for which
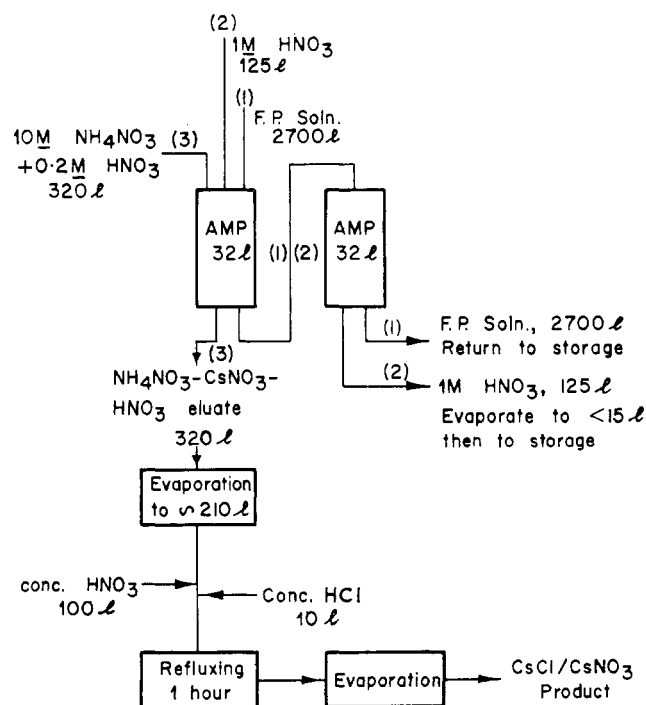
Figure 3. Elution of cesium from AMP column by 10M NH$_4$NO$_3$ + 0.2M HNO$_3$

Figure 4. Flowsheet for production of 67,000 curies of cesium-137 per two-day cycle

a column will hold good. Experience with 30-ml. columns of 100- to 200-mesh AMP, however, in which about one third of the column dissolved away while passing through 100 liters of sea water of pH $\approx$ 1 over a period of 7 days without any sign of serious disintegration of particles (13), suggests that the AMP columns should last for more than five cycles. The coarse AMP shows a slight tendency to peptize when changing over from one contacting solution to another. Peptization can be avoided by effecting the change-over gradually.

The results reported above show that a few per cent of the cesium is not eluted by ammonium nitrate solution. Smit (12) has ascribed this "fixation" of some of the cesium to irregularities in the AMP crystal lattice, brought about, for example, by partial breakdown of the 12-molybdophosphate anion to lower molybdophosphates, yielding patches of lower porosity (on an atomic scale) in the crystal lattice. Experience with repeated use of columns indicates that these few per cent of fixed cesium constitute a more or less constant proportion of the exchange sites, and that only very slight further buildup of cesium on the column occurs.

Proposed Flowsheet. A flowsheet for a two-day cycle operation based on a cesium-137 production rate of 10 megacuries per annum (300 round-the-clock working days assumed) is given in Figure 4. The necessary throughput cannot be achieved in a one-day cycle with columns of the same geometrical proportions and the same flow rate. (For constant flow rate and geometrical proportions of the column the throughput increases by a factor $\sqrt[3]{4} = 1.592$ faster than the capacity if the column volume and time for the cycle are both doubled.) Two AMP columns are used in series, reversing the sequence after each cycle.

Butex 150-fold concentrate containing 1.00 gram of cesium per liter (equivalent to 25 curies of cesium-137) has been assumed as feed solution. For column dimensions of 445 sq. cm. $\times$ 71.5 cm. (depth-diameter ratio approximately 3) and a flow rate of 2.5 cm. per minute the throughput capacity would be about 3200 liters per 48 hours, compared with about 3150 liters required.

The nitric acid wash liquor is evaporated to a small volume and returned to waste together with the barren fission product solution, which, therefore, undergoes no significant change in composition.

Feed solutions other than Butex concentrate are, of course, equally suitable. The useful capacity of AMP for cesium, which is approximately 0.7 meq. per gram for a pure, dilute solution of cesium (11), is only slightly reduced to about 0.63 meq. per gram with the introduction of acid and metal ions to the concentrations listed in Table I. Further increases in acid concentration, or addition of large concentrations of sodium ions, have little effect.

Cost. No attempt has been made so far to prepare a cost estimate, but some indication of costs may be derived from the following considerations.

The major items determining the cost of a process involving high-level radioactive materials are biological shielding and maintenance of equipment in the "hot" areas. To keep the cost of shielding to a minimum it is imperative that all process equipment for a given throughput should be as small as possible. In comparison with batch processes based on precipitation, the size of a plant using the semicontinuous AMP process should be very small indeed. This is a consequence of the fact that there is no appreciable holdup of the highly active fission product solution in any stage of the process, and of the large useful capacity of AMP for cesium under the process conditions. Consideration of the proposed flowsheet (Figure 4) reveals that that part of the equipment needed for the actual separation of cesium from the fission product solution—comprising the AMP columns—is small, even when compared with the evaporation stage for crystallizing cesium from the product solution.

It should therefore be feasible to house an entire plant for producing annually 1 to 10 megacuries, say, in two or three hot cells—one for the AMP columns and one for the encapsulation facility, and perhaps a separate cell for the refluxing and evaporation stages. Capital costs for such a plant should therefore be only a fraction of those for a plant of the same production capacity based on precipitation. On the same basis the AMP process would be expected to compare very favorably with solvent extraction processes, and those using mineral exchangers.

In the AMP process, standard ion exchange equipment would be used. By virtue of the simplicity and small scale of the process and of the small number of stages, a limited number of valves and other moving parts requiring maintenance would be incorporated. Running costs should therefore be considerably lower than for precipitation processes. All reagents used, moreover, are cheap, standard, commercially available chemicals. The cost of AMP is also modest and should contribute less than one cent per curie of cesium-137.

Conclusions

AMP is uniquely selective for cesium and capable of adsorbing it almost equally efficiently from dilute and concentrated solutions, as well as solutions containing large amounts of mineral acids. Because of the relatively large capacity for cesium realized in the treatment of fission product waste concentrates, the scale of operations is small compared with other methods, leading to great reductions in the cost of shielding requirements. All steps in the process are simple, incorporating only a small number of moving parts requiring maintenance.

Prior neutralization of acid wastes is not necessary.

The process is readily adaptable to any waste composition or concentration, if it is not strongly alkaline and does not contain substantial quantities of fluoride, which attacks AMP.

It satisfies the requirement for an ideal waste treatment process that no nonvolatile materials should be added to the waste. Actually, the only significant change undergone by the waste is substitution of ammonium for the cesium it contains.

The process can be adapted to remove cesium to any degree of decontamination desired, and could thus be incorporated in a waste disposal scheme.

All reagents used are cheap, commercially available chemicals.

Only a very small volume of low-level radioactive waste is produced.

Disadvantages of the process include relatively poor elution, and the need of introducing corrosive chloride ions during destruction of the ammonium nitrate. However, since the volume of eluate to be handled is small in relation to the amount (in curies) and value of the radioactive cesium chloride product, the use of special corrosion-resistant equipment should not raise over-all production costs much.

It should be possible, for the next few years, to satisfy the current world demand for cesium-137, estimated at 200 to 500 kilocuries per annum, with a production facility of pilot-plant size, as about 200 cycles with 1-liter AMP beds would yield the desired quantity. By virtue of the size and nature of the process operations, it should be possible to scale up production continually as demand grows.

Acknowledgment

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CRITICAL EVALUATION OF MATHEMATICAL MODELS USED FOR DYNAMIC ADSORPTION OF HYDROCARBONS

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In the process of analyzing a large amount of dynamic adsorption data for hydrocarbons a number of existing mathematical models have been used. Even though many of these can be used to "fit" the data to varying degrees, they involve assumptions that are incompatible with the proved physical mechanisms involved and/or are incapable of describing the concurrent adsorption of several adsorbates. Therefore, the ability of a model to fit the data has only empirical significance. Data are presented which illustrate the effect of temperature as well as other variables on dynamic performance.

IN RECENT years over 8000 basic data points have been obtained for natural gas containing as adsorbates the normal paraffins butane through heptane. Runs have been made with from one to three of these compounds present in the gas pressure range from 400 to 1200 p.s.i.g. The inlet temperature was held substantially constant at about 90° F. The desiccant bed diameter was varied from 2 to 4 inches. The pseudo-velocity of the gas (based on the empty tower cross section) has been from 9 to 45 feet per minute.

The lean gas effluent from a natural gasoline plant serving the city of Norman, Okla., was scrubbed, compressed to the desired pressure, cooled, and scrubbed again through carbon towers, and the desired quantity and mixture of adsorbate were injected. This passed into a mixing section before entering the desired tower. Both the inlet and effluent gas were monitored with a high speed chromatograph that would sample and analyze in less than 3 minutes, even when backflushing for the heavier components. Temperatures were measured at 5 to 10 points, depending on the tower length and diameter. Although most of the data are on 03 grade Davison silica gel, a wide range of desiccants was tested.

This program has led to a mass of data that have served many qualitative and quantitative purposes, including insight into the possible mechanisms involved.

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Basic Mass Balance Models

For isothermal adsorption of hydrocarbons on silica gel the over-all mechanisms which probably dominate the rate of mass transfer are (30):

The diffusion through the gas film which surrounds each desiccant particle (G mechanism).

The diffusion inside the desiccant particle (P mechanism). Diffusion inside the particle can include a variety of transport processes.

A combination of gas film diffusion and particle diffusion (PG mechanism). This mechanism is important only when the P and G resistances are about equal. A more complete discussion of the adsorption zone can be found in recent publications of Vermeulen (30) and Carter (4–7).

There have been several mathematical attempts to describe quantitatively single-component adsorption which utilizes the types of behavior previously described and various assumptions about the controlling mechanism.

Each mathematical development is based upon a particular set of assumptions, which in turn determines the ability of the resulting equations to describe dynamic hydrocarbon adsorption realistically.

All developments have several common assumptions:

1. The adsorption process is isothermal.
2. The pressure gradient along the length of the tower can be neglected.