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RESEARCH ESTABLISHMENT

LUCAS HEIGHTS

MASTER

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SEPARATION OF BERYLLIUM FROM FISSION PRODUCTS  
IN A NITRATE MEDIUM - PRELIMINARY EXPERIMENTS  
USING SOLVENT EXTRACTION

by

J. AGGETT

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SEPARATION OF BERYLLIUM FROM FISSION PRODUCTS

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ABSTRACT

Preliminary experiments using acetylacetone in the presence of ethylenediaminetetraacetic acid to separate major quantities of beryllium from fission products are reported.

Using 2M beryllium solutions, decontamination factors of the order of  $10^3$  were obtained with trace quantities of the more important fission products. This is sufficiently encouraging for the work to be repeated at higher activity levels.

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## 1. INTRODUCTION

The work presented in this report is a part of an attempt to assess the chemical possibility of recovering beryllium from the raffinate from an HTGCR fuel-recovery process. The processing scheme proposed by Cairns, Clayton, and Kernebone (1962) assumes a cooling period of 9 months to allow decay of Pa-233. At the end of this period the calculated percentage activities of the major fission products would be:

Ce <sup>144</sup> + La <sup>144</sup>	57.90%
Zr <sup>95</sup>	2.79%
Nb <sup>95</sup>	7.15%
Pm <sup>147</sup>	10.20%
Sr <sup>90</sup> + Y <sup>90</sup>	6.95%
Cs <sup>137</sup> + Ba <sup>137</sup>	6.73%
Ru <sup>106</sup> + Rh <sup>106</sup>	3.88%
Y <sup>91</sup>	2.25%
Sr <sup>89</sup>	1.17%
Ir <sup>85</sup>	0.48%
Bu <sup>103</sup>	0.22%
Ce <sup>141</sup>	0.17%

A method that seemed promising for separating beryllium from these fission products makes use of the fact that beryllium is almost alone in forming a strong complex with acetylacetonate, while at the same time having a very low tendency to form an EDTA complex. Hence it may be possible to achieve a separation from fission products in a single step. This procedure has been used to purify a kilogram quantity of BeO from non-radioactive impurities (Moore, Shaffer, and McDuffie 1962). It was also used by Tabushi (1959) to separate uranium from fission products and thorium. This method was therefore chosen for further study using trace quantities of the most important fission products.

Because of the high ionic strength of the raffinate, and the need to use a high concentration of acetylacetonate to extract the beryllium, the data available for the extraction of acetylacetonates cannot be used with much confidence when seeking optimum conditions for separations; however the data are useful qualitatively.

The extraction of trace quantities of Zr-95/Nb-95 by acetylacetone has been studied by Suzuki and Omori (1962). Zirconium is extracted even from 0.1N acid, but Krishen (1957) has found that EDTA greatly reduces the distribution ratio. At pH 4 a 15-fold excess reduces the extraction from 70 to 2 per cent.

Extraction of rare earths into acetylacetone commences at about pH 3.5, but in most cases less than 2 per cent is extracted below pH 4 (Brown 1959).  $pH_1$  for Ce(III) depends on the nature of the organic phase. Krishen (1957) found that  $pH_1 = 3.2$  when acetylacetone is both ligand and solvent, while Tabushi (1959) found values of 4.5 and 5.0 for acetylacetone dissolved in butylacetate and chloroform respectively. The differences may be related to variations in the metal distribution ratios for the three solvents. The extraction of Ce(III) is not greatly affected by the presence of a ten-fold excess of EDTA (Krishen 1957).

Tabushi (1959) also investigated the extraction of yttrium and strontium. Yttrium was found to be poorly extracted, and not at all below pH 5, while strontium was not extracted in the pH range from 4-10. No data are available for other fission products, but extraction of neither caesium nor barium would be expected. The known behaviour of ruthenium in other systems makes it seem unlikely that this element could be extracted as the acetylacetonate unless the contact time is prolonged or the temperature is raised.

Beryllium is extracted by acetylacetone at low pH ( $pH_1 = 0.67$  into pure acetylacetone,  $pH_1 = 3$  into 1 per cent acetylacetone/cyclohexane) (Green and Alexander 1962) and the extraction is not affected by EDTA (Tabushi 1959). It was therefore decided that the optimum pH for extraction into 10 per cent acetylacetone/chloroform would be  $< 4$ . At this pH, extraction of beryllium is high and interference by cerium and rare earth ions low.

## 2. EXPERIMENTAL

The beryllium concentration was constant at 2M in all experiments. The presence of such a large concentration of beryllium, and the subsequent release of hydrogen ions by complex formation with the acetylacetone made it necessary to devise a means of keeping the pH constant. A suitable buffer was provided by using an excess of a mixture of acetylacetone and its sodium or ammonium salt, and converting  $Be(NO_3)_2$  to the basic nitrate, which can be represented as  $Be(OH)NO_3$ , before the extraction. The complex formation and extraction could then be represented by the expression



Single-stage batch experiments were conducted on individual fission products using Ce-144, Zr-95/Nb-95, Sr-85, Cs-137, and Ru-106 as the nitrosyl nitrate, as tracers; the count rates of the solutions were adjusted to convenient levels. In all experiments other than those on ruthenium the fission product concentration was adjusted to  $10^{-4}$ M with carrier; no carrier was used for ruthenium.

The following procedure was used:

The pH of the solution containing beryllium plus fission product was adjusted to about 3.5 and the amount of the disodium salt of EDTA necessary to make a  $10^{-2}$ M solution was added to it; the solution was then shaken for ten minutes with the extracting agent, the phases separated, centrifuged, and counted.

The recovery of beryllium was determined gravimetrically by evaporating a known volume of the organic phase to obtain crystalline bisacetylacetonoberyllium(II).

From the information gained in the preliminary experiments a revised decontamination procedure was drawn up as follows and used to separate beryllium from mixed fission products obtained from irradiated uranium-thorium:

1. Adjust pH of the beryllium/fission product solution to 3.5 - 4.0.
2. Dissolve sufficient disodium salt of EDTA to make the concentration  $10^{-2}$ M.
3. Reflux for five hours. Allow to cool.
4. Extract beryllium with acetylacetonone/ammonium acetylacetonate using chloroform as diluent and a minimum phase ratio of 2:1 .

### 3. RESULTS AND DISCUSSION

The results of the preliminary decontamination experiments are given in Table 1.

The Decontamination Factor (D.F.) is defined by

$$\text{D.F.} = \frac{\text{Total Activity in System}}{\text{Activity in Organic Phase}} \times \frac{\text{Wt. of Be in Organic Phase}}{\text{Total Wt. of Be in System}}$$

TABLE 1

DECONTAMINATION FACTORS FOR FISSION PRODUCTS

Fission Product	Equilibrium pH	D.F.
Ce( $10^{-4}$ M)	3.93	$6 \times 10^3$
Sr( $10^{-4}$ M)	3.90	$>1 \times 10^4$
Cs( $10^{-4}$ M)	4.0	$>4 \times 10^4$
* Zr( $10^{-4}$ M)	4.0	70
Ru (tracer)	4.0	7.52

\* 44% total activity lost in slight crud and on glass vessel

It therefore appeared that neither zirconium nor ruthenium could be separated from beryllium by this simple technique.

The co-extraction of ruthenium could not be caused by the formation of the trisacetylacetonate, as the ruthenium(III) ion is too inert for significant complex formation to have occurred under the conditions of the experiment. Hence it seemed probable that the extracted species was a neutral nitrosyl-nitrate complex soluble in chloroform and that this could be destroyed by heating the solution at pH 4 in the presence of EDTA before the extraction took place. Decontamination factors for ruthenium were determined as a function of heating time, and are listed in Table 2. These results show that excellent decontamination factors can be obtained after suitable heat treatment.

TABLE 2DECONTAMINATION FACTORS FOR RUTHENIUM

Heating Time	Decontamination Factor
None	7.52
1 hr.	30.2
2 hr.	$4.25 \times 10^2$
4 hr.	$2.45 \times 10^3$
6 hr.	$3.1 \times 10^4$

The slight interfacial crud present in some experiments slowly disappeared on standing, which suggested that it was caused by local hydrolysis of beryllium, and that the hydroxide was only slowly attacked by acid at pH 3.5 - 4.0. The decontamination factor for zirconium was determined after the disappearance of the crud and a value of  $2.8 \times 10^2$  was then obtained; about 7 per cent of the total activity was lost from the solution. A further experiment was made in which the beryllium/zirconium solution was refluxed for four hours in the presence of  $10^{-2}$ M EDTA at pH 4, to bring about formation of the zirconium - EDTA complex before extraction of beryllium. In this experiment the decontamination factor was  $> 1.2 \times 10^3$ , and within the experimental error no loss of total activity was detected.

### 3.1 Beryllium Recovery

The results given in Table 3 show that recovery is excellent under the conditions used.



TABLE 3RECOVERY OF BERYLLIUM

pH	% Recovered
3.05	77
3.40	84
3.80	91
3.89	91
4.00	94

The results obtained with the revised decontamination procedure are as follows:

Equilibrium pH	3.5
Beryllium extracted	85%
Decontamination factor:	
γ activity	$\geq 1.02 \times 10^3$
β activity	$\geq 1.7 \times 10^3$

#### 4. FURTHER CONSIDERATIONS

The chemical evidence obtained so far indicates that recovery of beryllium from aqueous nitrate solutions and its subsequent decontamination might be achieved by a process based on the procedure outlined in this report. However further experiments at much higher levels of radioactivity are necessary before the chemical feasibility of the suggested process can be demonstrated. Another major consideration is that the radiation-stability of the process chemicals is not known under dynamic conditions. Also, chloroform may not be the best diluent for large scale work. A high-boiling-point aromatic diluent would not impair performance, and would probably have a higher radiation-stability. The solubility of

the beryllium complex in saturated hydrocarbons such as kerosene would be too low. It may also be possible to improve the radiation stability of the extracting agent by using a substituted  $\beta$ -diketone. This should not affect the basic concept of the process, but may necessitate the use of a different pH for optimum decontamination.

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