AAEC/E189

AUSTRALIAN ATOMIC ENERGY COMMISSION

RESEARCH ESTABLISHMENT
LUCAS HEIGHTS

DEVELOPMENT OF SOLVENT EXTRACTION PROCESSES FOR THE H.T.G.C.R. FUEL CYCLE

PART 3. CHEMICAL DATA FOR THE EXTRACTION OF ACTINIDES AND FISSION PRODUCTS FROM AQUEOUS BERYLLIUM SULPHATE SOLUTIONS USING AMINES

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ABSTRACT

Chemical data are presented for the actinides (uranium, plutonium and thorium), the fission products (cerium, zirconium, niobium and ruthenium) and beryllium in the extraction of these from beryllium sulphate solutions by amines, in particular Primene-JMT and Alamine-336. The data so obtained define the major chemical parameters requiring control in a solvent extraction process to decontaminate beryllium sulphate, and indicate that the use of the solvent Primene-JMT/Solvesso-100 will adequately remove the uranium, thorium, plutonium, cerium, zirconium and niobium without extracting significant quantities of beryllium. Ruthenium is not highly extractable and strontium and caesium are extractable only in trace quantity. Although this process will be adequate for primary decontamination of the beryllium sulphate, a further step to remove residual ruthenium, strontium and caesium may be required.

The actinides with the extracted fission products are readily stripped from the amine phase with nitric acid, thus permitting recovery of the actinides by a conventional tributyl phosphate process. The amine phase is readily converted back to the free-base form using sodium carbonate. This is necessary to prevent recycling of the nitrate which would inhibit the extraction of thorium, plutonium and the fission products.

PREFACE

The following list details a series of reports dealing with the fuel cycle of the High Temperature Gas-Cooled Reactor. This report (AAEC/E189) is the third of the second group of reports dealing with the Development of Solvent Extraction Processes for the H.T.G.C.R. Fuel Cycle.

Laboratory Development of the Grind-Leach Process for the H.T.G.C.R. Fuel Cycle

Part 1. Dissolution of Urania-Thoria Fuel Particles in Nitric Acid Solutions, by M.S. Farrell and S.R. Isaacs. AAEC/E143.

Part 2. Dissolution of Beryllia in Nitric Acid Solutions, by M.S. Farrell, S.R. Isaacs and M.E. Shying. AAEC/E154.

Part 3. Comminution of Beryllia Matrix Fuels, by M.G. Baillie and R.W. Hubery. AAEC/E162.

Part 4. Leaching and Dissolution of Beryllia-Based Fuels, by M.E. Shying, E.J. Lee and M.S. Farrell. AAEC/E180.

Development of Solvent Extraction Processes for the H.T.G.C.R. Fuel Cycle

Part 1. Design of a Flowsheet for the Recovery of Actinides, by M.G. Baillie and R.K. Ryan. AAEC/E139.

Part 2. Solvent Extraction of Thorium and Uranium from Beryllium Nitrate Feeds by Tri-n-Butyl Phosphate, by R.C. Cairns, M.G. Baillie, B.J. Fox, and R.K. Ryan. Industrial and Engineering Chemistry, Process Design and Development Quarterly. In Press.

Part 3. Chemical Data for the Extraction of Actinides and Fission Products from Aqueous Beryllium Sulphate Solutions using Amines, by J.J. Fardy, M.S. Farrell and D.G. Pinchbeck. AAEC/E189.

Economics of the H.T.G.C.R. Fuel Cycle

Part 1. Pre-design Cost Study of Fuel Cycle Facility, by J.R. May and J.M. Devine. AAEC/E175.

Part 2. Fuel Cycle Cost Studies, by R.W. Hubery and M.G. Baillie. AAEC/E179.

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1. INTRODUCTION

A dispersion-type fuel with a beryllia matrix as moderator, described by Smith (1964), was chosen for the Australian study of a high temperature gas-cooled reactor (H.T.G.C.R.). For such a reactor to operate economically as a breeder, not only must the fissile component (U233) be recovered and recycled, but also the bulk of the beryllia moderator should be recovered and recycled.

Cairns (1964) proposed a grind-leach head-end process to bring the actinide components of the fuel into solution by leaching the comminuted fuel elements in nitric acid solution and leaving the bulk of the beryllia as residue insoluble in nitric acid. Following this proposal a three-step head-end process was developed (Farrell and Isaacs 1965, Farrell, Isaacs and Shying 1966, Baillie and Hubery 1966, and Shying, Lee and Farrell 1967). The steps in this process are:

(i) Comminution of the fuelled beryllia pebble elements.

(ii) Nitric acid leaching of the actinides from the comminuted material.

(iii) Dissolution of the beryllia residue in sulphuric acid.

About 10 to 20 wt per cent of the beryllia is dissolved in the nitric acid.

The bulk of the actinides is readily extracted from the beryllium nitrate/nitric acid stream by using a solvent extraction process with tributyl phosphate as the solvent (Baillie and Ryan 1965). However, a small quantity of the actinides and an equivalent or perhaps greater quantity of fission products remain with the beryllia residue and enter the sulphuric acid stream. The quantity and composition of the actinides and fission products entering this stream depend on the behaviour of these components in the head-end process.

Both residual actinides and fission products have to be removed from the beryllium sulphate stream to permit its recycle to the reactor as beryllia. This report presents data and experimental conditions for removing both actinides and fission products from beryllium sulphate solution before the beryllium sulphate tetrahydrate is crystallised out and calcined to beryllia. The beryllia is transformed to sulphate and back to oxide in the fuel cycle. By keeping to a minimum the number of chemical transformations of beryllium, the major component in the fuel, an economic process for beryllia recycle may be possible.

After consideration of the possible aqueous separation methods available for removing some or all of the contaminants in the beryllium sulphate solution, a solvent extraction using amine was chosen. This decision was based chiefly on the results of research with amines at the Oak Ridge National Laboratory (Coleman 1964).

2. EXPERIMENTAL

2.1 Equilibration Technique

Equilibrations of the chosen aqueous and organic phases were made at 25 °C in a machine previously described by Bishop et al.(1960). Aliquots of the phases were shaken in glass bottles of 30 ml volume and sealed with screw caps fitted with neoprene inserts. After shaking for 15 minutes and allowing the phases to separate, extraction coefficients were determined by analysis using the relationship:

$$E_a^o = \frac{\text{concentration in organic}}{\text{concentration in aqueous.}}$$

The beryllium and the individual fission products in both phases were analysed by radiometric methods. The γ-emitting tracers Be7, Sr85, Cs137, Zr95, Nb95, Ru106 and Ce144 were used in conjunction with a γ scintillation counter (A.A.E.C. Scaler Type 2A unit in tandem with a Scaler unit Type 1009E). For mixed fission product samples the individual distributions were determined by γ scintillation counting and γ spectrometry with a 256-channel analyser.

For each phase the uranium concentration was determined by fluorimetry (Rodden and Wharf 1950), the thorium by colorimetry using Thoronol (Thomason et al. 1949) and the plutonium by radiometry using a gas-flow proportional α-counter. For plutonium a correction to the α count was required as Am^{241} was present and this concentrated in the aqueous phase. The Am^{241} was determined by α spectroscopy using a solid-state detector and the 256-channel analyser.

2.2 Materials and Reagents

Aqueous phases. The composition of the beryllium sulphate stream from the grind-leach process depended on the head-end process selected. The chief compositions studied were:

(a) 2.0M [Be] + 2.5M [SO_4], generally produced by the simple dissolution of beryllia residue in excess 10M H_2SO_4, or

(b) 2.0M [Be] + 2.0M [SO_4], a solution of lower acidity produced by crystallising $BeSO_4.4H_2O$ from the solution, removing the mother liquor and redissolving the crystals in water (Shying et al. 1967).

The necessary quantities of uranium, thorium, plutonium, or fission product sulphate solutions were added to beryllium sulphate solution. Generally the initial aqueous phase concentrations used were 300 μg/ml for thorium and 30 μg/ml for uranium, while plutonium and fission products were in trace-level quantities. Throughout the studies the pH was adjusted when necessary using H_2SO_4 or NH_4OH.

The beryllium sulphate was prepared by dissolving Brush UOX-grade beryllia in slightly less than the stoichiometric quantity of 10M H_2SO_4 acid; the uranium sulphate was prepared by dissolving UO_2 (Mallinckrodt ceramic grade) in strong sulphuric acid (under the conditions of this dissolution U(VI) resulted and not U(IV)); the thorium sulphate was prepared by dissolving finely divided thorium metal in (10M H_2SO_4 + 0.01M F^-) solution, precipitating the hydroxide with NH_4OH and redissolving it in the stoichiometric quantity of sulphuric acid. The plutonium sulphate was prepared from plutonium metal by first dissolving the metal in hydrochloric acid, then precipitating the hydroxide from the solution, washing the precipitate, and redissolving it in strong sulphuric acid.

The radioactive tracers used were obtained from the Radiochemical Centre, Amersham, England, as aqueous solutions; if necessary they were converted to the sulphate form before use. The fourteen-month-old mixed fission product sulphate solution used in the higher level activity (mCi) experiments had been obtained by the dissolution of irradiated $^{235}UO_2$–ThO_2 pellets in sulphuric acid after comminution in a hot cell. The thorium sulphate which forms and crystallises in the strong sulphuric acid redissolves on dilution with water. The irradiation of the pellets had been such that a sufficiently high specific activity per unit volume of solution was retained after dilution.

The stock solutions of uranium, thorium and plutonium were analysed by the methods described in Section 2.1, and beryllium was determined by colorimetry with Chrome Azurol S (Pakalns 1963). Total sulphate in the solutions was determined by the method of Archer (1957) using lead nitrate titration with dithizone as the indicator. Acidity (pH) was measured using a glass electrode and a standard calomel half-cell.

For the investigation of the effect of anions on the extraction of beryllium, Be^7 was added to 0.1M aqueous solutions of the ammonium salt of the chosen anion. All reagents were of analytical reagent grade quality unless otherwise specified.

Organic Phases. The organic phase consisted of a selected amine dissolved in a selected diluent. To decrease the emulsification and formation of a third phase a polar modifier, capryl alcohol (C.A.) was added to the organic phase when required. The capryl alcohol was laboratory grade (L.R.) reagent from Light and Co. Non-aqueous titration methods based on those of Fritz (1952), Pifer and Worfish (1952), and Pifer et al. (1953) were used to determine equivalent weights and primary, secondary, and tertiary amine contents. These amines were of commercial grade, from various sources, and not treated further before use. They are listed in the Appendix.

The diluents were commercially available hydrocarbons and also were used without further purification. They were either essentially aliphatic, such as odourless mineral spirits R-100 (O.M.S.) (from Vacuum Oil Co. Pty. Ltd.), or essentially aromatic, such as Solvesso-100 and -150 (from Esso Standard Oil (Aust.) Ltd.). The Solvesso -100 and -150 are mixtures of the trimethyl benzenes, the -150 having a higher proportion of C10 aromatics and consequently a higher flash-point. Boralene-1120 (from Boral Ltd.) contains a high proportion of n-dodecane but is more aromatic than O.M.S.

3. RESULTS AND DISCUSSION

3.1 Choice of an Amine and a Diluent for the Solvent

Using the 2.0M Be + 2.5M SO_4 aqueous phase, adjusted to pH 1.0 with ammonium hydroxide and organic phase combinations of 0.05M amine and various diluents, the extraction coefficients for uranium, thorium and beryllium (Table 1) were determined. Thorium was highly extractable with Primene-JMT, U less so (uranium at low concentrations in sulphate solution, exists in the hexavalent state) and Be was very low with an extraction coefficient (E_a^o) less than 0.01. Whereas the use of the aliphatic O.M.S. diluent or the aromatic Solvesso-100 diluent had little effect on the extraction coefficients, the separation of the phases with the O.M.S. diluent was slower. The addition of capryl alcohol increased the rate of phase disengagement but decreased the uranium extraction coefficient by half. However, the diluent type had a more marked effect on the uranium extraction when either a secondary or tertiary amine was used, the aromatic-type diluents being superior. Phase separation with the cyclo- and benzyl-amines was poor, stable emulsions forming as third phases. The use of capryl alcohol did not overcome this problem and these particular amine-types were considered unsatisfactory.

For the extraction of U, the amine and diluent types may be ranked in the following decreasing order of general effectiveness for extraction thus: tertiary > secondary > primary, and Solvesso-100 > Benzene > Boralene 1120 > (Odourless Mineral Spirits + 5 v/o capryl alcohol). For Th extraction primary amines were much more effective than tertiary and this occurred for tetravalent Pu as well. With Primene-JMT/Solvesso-100, Pu had an extraction coefficient greater than 520.

Using conditions identical to those above for the actinides and beryllium, the extraction coefficients for the fission product elements Ce, Zr, Nb, Ru, Sr and Cs were determined (Table 2). There was negligible extraction of Sr and Cs but appreciable extraction of the others. The Ce was extracted most effectively by primary amines. On the other hand Zr and Nb, in spite of having the highest distribution coefficients with Primene-JMT, gave significant extraction with both secondary and tertiary amines. Ru extraction was poor, extraction coefficients being less than unity with all three classes of amine, the best being the tertiary.

Thus tertiary amines, such as Alamine-336 are best for extraction of U, but primary amines, such as Primene-JMT are best for extracting Th, Pu, Ce and Zr. Solvesso-100 is the most effective diluent for use with Primene-JMT.

Some further extractions were made with mixtures of Alamine-336 and Primene-JMT with the expectation of obtaining at least the equivalent extraction for both U and the other elements. However, the data in Table 3 and the Figures 1 and 2 show that the benefits of the mixed amine system for an increased U extraction were obtained only when the primary to tertiary amine ratio was about 1.0. However, the expected Th:U atomic ratio of 20:1 in the feed solution favours the use of an extractant containing mainly primary amine.

The mixed-amine systems were characterised by slow-breaking emulsions and this makes practical application doubtful. The addition of capryl alcohol improved phase separation but reduced the uranium extraction.

The use of Primene-JMT in Solvesso-100 was the most favoured solvent for a primary scavenging of the contaminants from the beryllium sulphate solution.

3.2 Effect of Amine Concentration

From the results in Section 3.1, Figures 1 and 2, the extractions of U, Th and Be are generally

directly proportional to the amine concentration in the organic phase, $[A]_o$. Uranium extraction studies were extended to include distribution data obtained from both aqueous phase compositions used, (2.0M Be + 2.0M SO_4) and (2.0M Be + 2.5M SO_4). Both were at pH 1.0 with organic phases of 0.01M to 1.0M Primene-JMT in Solvesso-100 and in (O.M.S. + 5 v/o C.A.), and 0.01M to 0.5M Alamine-336 in Solvesso-100, and results demonstrated that the extraction of U was directly proportional to $[A]_o$ in all cases. The log-log plots of the extraction coefficient for uranium, $E_a^o(U)$ against $[A]_o$ (Figure 3) are linear with slopes of near unity (1.0 to 1.1). There was also confirmation from these results that the solvent Alamine-336/Solvesso-100 was superior to Primene-JMT/Solvesso-100 for U extraction. Primene-JMT/ (O.M.S. + 5 v/o C.A.) had a lower extracting power than when Solvesso-100 was the diluent.

For both Th and Pu there was a greater than 99.9 per cent extraction by the Primene-JMT/ Solvesso-100 solvent for $[A]_o > 0.01M$. In contrast the extraction coefficient for thorium E_a^o (Th) was low, but directly proportional to $[A]_o$ when Alamine-336 was used (Figure 4).

Although the extraction coefficient for beryllium, $E_a^o(Be)$, was low in all systems used (less than 0.2) the extraction was directly proportional to $[A]_o$. A log-log plot (Figure 5) for $E_a^o(Be)$ against $[A]_o$ gave a relationship with a slope of unity for the two solvents Primene-JMT/Solvesso-100 and Alamine-336/Solvesso-100, but a slope of 1.4 for the Primene-JMT/(O.M.S. + 5 v/o C.A.) solvent. Primene-JMT was a stronger extractant for Be than Alamine-336.

Similarly, the extraction of the individual fission product elements as a function of $[A]_o$ was measured using only the Primene-JMT/Solvesso-100 solvent. The results (Figures 6 and 7) confirm that in this solvent these elements are extracted in the order Zr> Nb>> Ce>>> Ru and that this order is not changed by an increase in the total initial sulphate concentration of the aqueous phase from 2.0 to 2.5M with the pH constant at 1.0. The power dependence of the amine concentrations was less than unity for all the fission product elements examined. The relationships obtained from the linear log-log plots of the extraction coefficient E_a^o against $[A]_o$ are summarised in Table 4.

3.3 Effect of Sulphate Concentration and pH

The extraction of uranium from beryllium sulphate with Primene-JMT/Solvesso-100 sensitively depended on both pH and initial sulphate concentration in the aqueous phase. The decrease in U extraction with increasing sulphate concentration (Figure 8) is similar to the results obtained by Bunney et al. (1959) with anion exchange resin, and implies qualitatively that an ion-exchange mechanism is operating. There is also a decrease in the extraction of U with decreasing pH (below a pH value of 1.5) at a fixed sulphate concentration (Figure 9). This decrease is attributed to successful competition for the amine by bisulphate formation. The results also indicate that improved extraction can be obtained for U at low pH values (<1.0) if the sulphate concentration is kept as low as possible.

Whereas the extraction of U with 0.1M Primene-JMT/Solvesso-100 from beryllium sulphate solutions was sensitive to both sulphate concentration and pH of the aqueous phase, the extraction of Th remained high ($E_a^o(Th) > 10^3$) over the range investigated. The extraction of Be was not sensitive to either changes in total sulphate concentration (1.0M – 2.0M) or in aqueous phase pH (0.5–2.0). A comparison of the extraction coefficients for Th, and Be by Primene-JMT/Solvesso-100 and Alamine-336/Solvesso-100 is given in Table 5 for the investigated ranges of aqueous phase sulphate concentration $[SO_4]_a$ and pH.

It may be noted that with 0.1M Alamine-336/Solvesso-100, the beryllium and Th extraction was not very sensitive to changes in either total sulphate concentration (2.0M – 2.5M) or pH of the aqueous phase (1.0 – 2.0) with a 2M concentration of beryllium. However there appears to be an optimum pH of 1.0 – 1.5 for the U extraction. The extraction of U with 0.05M Primene-JMT (O.M.S. + 5 v/o C.A.) was not very sensitive to total sulphate concentration (2.25M – 3.0M) or pH of the aqueous phase (1.5 – 2.0) with a 2M beryllium solution.

Similarly, Table 6 presents the coefficients for the extraction of the fission product elements Ce, Nb, Zr, Ru, Sr and Cs by 0.1M Primene-JMT/Solvesso-100 as a function of beryllium together with total sulphate concentrations and pH of the aqueous phase. Neither Ce nor Ru extraction was sensitive to total sulphate concentration, though a small decrease occurred with increase in sulphate. This decrease was more marked for the Zr and Nb. Neither Sr nor Cs were significantly extracted

over the range of conditions used. The extraction of both Zr and Nb was significantly reduced as the pH was increased, owing to the hydrolysis of the hydrated metal ions and possible subsequent polymerisation. However, the extraction of Ru and Ce did not change significantly with increasing pH. The extraction of Ce144, Zr95–Nb95 and Ru106 was not significantly affected by beryllium concentration in the range 1.0 – 2.0M.

To summarise: The optimum extraction of uranium (also Th and Pu) together with the extractable fission product elements Zr, Nb, Ce and Ru can be obtained by using an aqueous feed solution containing less than 2.0M beryllium with a total sulphate such that the pH is not greater than 1.0 but not less than 0.5. A low free-acid feed solution from the grind-leach step is essential for this solvent-extraction process.

3.4 Effect of Other Anions

The most likely foreign anion to enter the sulphate system is nitrate, particularly if the amine in the nitrate form after stripping is not returned to the free-base form (see Section 3.7 below). There is evidence (Brown et al. 1954) that the presence of nitrate markedly reduces the uranium extraction by secondary and tertiary amines from 1M H_2SO_4 acid. Results in Table 7 demonstrate that for uranium extraction from beryllium sulphate with Primene-JMT there was an unexpected increase in extraction on the addition of nitrate (approximately 10 times for an increase in nitrate concentrations from 0 to 0.2M) followed by a decrease after 0.2M, to almost zero extraction at 0.5M HNO_3. With 1.0M SO_4 (H_2SO_4 and $(NH_4)_2SO_4$) as a mixture of solutions but no beryllium, Primene-JMT extraction of U also increased with small additions of nitrate (approximately 20 times for an addition of nitrate to give a concentration of 0.05M). However it decreased as the nitrate concentration was increased. Thus the effect of nitrate addition was independent of the beryllium. With a tertiary amine, tri-iso-octylamine, there was an immediate decrease in U extraction, with no initial increase.

The Primene-JMT extraction of thorium, plutonium and the fission product elements Ce, Zr-Nb and Ru is seriously decreased by the addition of nitrate even at low concentration.

It appears from the results of these experiments (Table 7) that before re-use as an extractant, the stripped Primene-JMT in the nitrate form should be reconverted to the free-base form in order to prevent poor extraction of the uranium, and to a lesser extent the fission products.

Very little (less than 1 per cent) of the beryllium is extracted by the Primene-JMT from the sulphate solutions. This quantity of beryllium is neither a significant loss nor a significant impurity in the organic phase and therefore a scrubbing section is not required to prevent the beryllium concentration becoming excessive in the organic phase.

There is, however, a remote possibility that fluoride and phosphate ions in low concentration entering the amine solvent extraction process from other parts or processes of the overall fuel cycle, (see Section 1 above) could increase beryllium extraction.

To test the sensitivity of the Primene-JMT extraction of Be to the presence of other anions, a small separate study was made of the effects of various anions in Primene-JMT beryllium extraction.

This study used Be7 tracer, the aqueous phases being various ammonium salt solutions. The anion effect on the amount of beryllium extracted, obtained from the extraction coefficients shown (Table 8), was that beryllium extraction was greatest with phosphate $\geq$ fluoride > thiocyanate > sulphate >> nitrate or chloride.

With fluoride, however, the presence of sulphate, as in the process under development, inhibits extraction of beryllium fluoro-complexes but does not inhibit extraction of beryllium phosphate complexes. For example a large extraction (E_a^o(Be) = 59) was obtained for beryllium from (0.05M $BeSO_4$ + 0.1M $NH_4H_2PO_4$) solution (Table 8). Phosphate must be kept out of the amine process.

3.5 The Effect of Amine Loading

The atomic ratios of Pu, U and Th in the spent fuel arising from operation of the H.T.G.C. Reactor are 1 : 22: 480 (Cairns et al. 1966). It is not certain whether these atomic ratios had changed by the time the residual actinides from the leaching step entered the beryllium sulphate stream. Assuming they were approximately the same, the effect of the major component thorium, with its high extraction coefficient, would be to saturate the organic phase only, decreasing at least the uranium extraction and possibly the extraction of plutonium and the fission product elements.

For this reason a study was made to determine the degree of thorium loading of the organic phase which would affect the extraction of the uranium, which as the U233 isotope is the most important constituent to be recovered from the beryllium sulphate stream.

The thorium loading characteristics of the Primene-JMT/Solvesso-100 solvent and its effect upon uranium extraction were studied by contacting a particular sample of organic phase with successive volumes of fresh aqueous phase

(a) with the phase ratio constant (a:o = 1:1)

(b) with the phase ratio varied.

From the results Table 9 and Figure 10 it was established that:

(i) The maximum thorium concentration that could be obtained in the organic phase was 2,900 μg Th/ml (0.0125M Th), at which concentration negligible U was extracted. This maximum thorium loading in 0.1M Primene-JMT/Solvesso 100 gives a thorium to amine mole ratio of 1 : 8. Crouse and Denis (1955) obtained a similar value when extracting thorium from sulphuric acid solution.

(ii) The extraction of U was found to be dependent on the thorium loading of the organic phase, the extraction remaining constant until the thorium concentration in the organic phase reached 1250 μg Th/ml. Neither a change in the U:Th ratio in the aqueous phase nor an increase in the total sulphate concentration (2.0 to 2.5M) greatly affected this result.

Thus for optimum co-extraction of uranium and thorium the thorium concentration in the organic phase must not exceed 1250 μg Th/ml.

The required phase ratio using 0.1M Primene-JMT/Solvesso-100 to obtain this optimum co-extraction is equal to the maximum permissible thorium concentration in the organic phase, viz. 1250 μg Th/ml, divided by the thorium concentration in the initial aqueous phase in μg/ml.

Using the above data (see Figure 11) an empirical equation was obtained for the extraction of thorium by Primene-JMT/Solvesso-100 from beryllium sulphate solution:

$$E_a^o(\mathrm{Th}) = 20{,}000 \{[A]_o - 8[\mathrm{Th}]_o\}^4/0.10,$$

where $[A]_o$ is the total amine concentration in the organic phase both complexed and uncomplexed.

The dependence of the E_a^o (Th) value on the concentration of the uncomplexed amine was derived (Figure 12) but because of the high thorium extraction obtained, some uncertainty surrounds this value.

Pu was not seriously affected by thorium loading though a small decrease in E_a^o(Pu) values was detected as $[\mathrm{Th}]_o$ was increased.

The effect of thorium loading of the organic phase on the extraction of the fission product elements is summarised in Figure 13. Initially there was an increase in the extraction of mixed fission products as measured by the gross γ distribution coefficient $E_a^o(\gamma)$ but after a $[\mathrm{Th}]_o$ of

0.9 g/l had been reached, a decrease occurred. This maximum in the $E_a^o(\gamma)$ was caused by E_a^o(Nb) and E_a^o(Zr) values increasing with increasing $[Th]_o$, while E_a^o (Ce) decreased. E_a^o(Ru) increased initially with increase in $[Th]_o$, and then decreased, but the overall effect was small.

In this particular process, extraction of all elements present except beryllium is required. Under these circumstances, excessive loading of the amine phase with thorium should be avoided so that extraction of all possible metals is achieved. However, too much excess amine in the organic phase, although permitting a higher extraction of bisulphate will result in an increase in the sulphate content of the nitrate strip solution which is to be recycled to the tributyl phosphate (refer to Introduction above). Sulphate inhibits separation of the actinides from fission products in the tributyl phosphate process and its concentration in the nitrate feed solution to this process must be kept as low as possible.

3.6 Stripping of Actinides and Fission Products

The excellent extraction of the actinides from beryllium sulphate by Primene-JMT/Solvesso-100 indicates the possible use of a less selective grind-leach process, a higher quantity of the actinides being recoverable in the beryllium sulphate purification step. As stated in the introduction, the actinides (U, Pu and Th) are separated from the fission products in the beryllium nitrate nitric acid stream by solvent extraction using tributyl phosphate (Baillie and Ryan 1965). To permit easy recycle of fission-product-contaminated actinides from the amine-sulphate process, it is necessary to strip them from the organic amine phase with nitric acid, and send the resulting nitrate-sulphate solution to the tributyl phosphate process. For this reason, stripping studies were restricted to the use of nitric acid.

Each 0.1M Primene-JMT/Solvesso-100 phase was loaded with actinides by contacting it with a fresh aqueous phase (a/o = 1/1) of 2.0M $BeSO_4$ solution (pH 1.0) which contained the actinides. The loaded organic phases were then contacted with the nitric acid stripping solutions. The results (Table 10) show that, with an o/a ratio of 1/1, at least 1.0M HNO_3 was required to strip the Pu and Th, the former being the most difficult to strip. With the 1.0M HNO_3 strip, as the o/a ratio was increased from 1/1 through 3/1 to 5/1, the S_o^a (Th) and S_o^a (Pu) values, where S_o^a is defined as the ratio of the concentrations of the metal ion in the aqueous to that in the organic phase, both decreased. With a 5/1 o/a ratio the nitric acid concentration of the strip solution was required to be 1.5M to increase S_o^a(Pu) from 9 to 1400. U was most easily stripped.

In a similar fashion, the S_o^a values for the fission product elements (Ce, Zr, Nb and Ru) were obtained using 1.0M HNO_3 acid (Table 11). Ce was readily stripped and S_o^a (Ce) was independent of phase ratio under these conditions. Ru was not so readily stripped but S_o^a (Ru) was also independent of phase ratio. The stripping of Zr and Nb depended largely on phase ratio, but with an o/a value of 3/1, S_o^a values for both elements were greater than 100.

A strip solution of 1.0M HNO_3 with an o/a ratio of 3/1 appears to be adequate for stripping both actinides and fission products from an 0.1M Primene-JMT/Solvesso-100 organic phase.

3.7 Reconversion of the Amine to Free-Base Form

Recycling of the amine in the nitrate form ($RNH_2.HNO_3$) will introduce nitrate ion into the sulphate extraction system. As previously shown under Section 3.4, this nitrate will depress the extraction of all elements involved except perhaps the U. To ensure that the introduction of nitrate with the recycled amine will not decrease the extraction coefficients, it is necessary to treat the amine with a stronger base, such as sodium hydroxide, sodium carbonate or ammonium hydroxide. The amine in the free-base form can then be safely recycled to the sulphate extraction step without introducing nitrate.

In spite of changes in the a/o ratio from 1/1 to 1/8, sodium hydroxide solution gave rise to slow-breaking emulsions and its use proved impractical.

Amine in the nitrate form was prepared by contacting 0.1M Primene-JMT/Solvesso-100 with equal volumes of 1.0M nitric acid to give $[NO_3^-]_o$ = 0.11M. Both Na_2CO_3 and NH_4OH solutions proved to be effective in stripping the nitrate from the amine (Table 12), but with lower phase

ratios (a/o) of 1/8 the ammonium hydroxide gave longer phase-disengagement times. For these reasons, 1.0M Na_2CO_3 solution was selected as the regenerating base with a phase ratio (a/o) of 1/5.

3.8 Optimisation – Calculation of the Number of Stages

The quantity of uranium and thorium entering the beryllium sulphate stream from the grind-leach process had not been established prior to the laboratory development of this process for the decontamination of the beryllium sulphate solution. U233 is the most valuable component occurring as a contaminant in the beryllium sulphate solution but of the actinides in the process, as U(VI) it is the least extractable.

Using the extraction data obtained above, and selecting a range of uranium and thorium concentrations in the beryllium sulphate, the number of theoretical stages required to extract the uranium was calculated for several systems using the following equations from Haas (1961):

$$\frac{x_1}{x_0} = \frac{1}{1 + E_f}, \quad \frac{x_n}{x_0} = \frac{1}{(1 + E_f)^n}, \text{ and } \frac{x_n}{x_0} = \frac{E_f - 1}{E_f^{n+1} - 1} .$$

These are for single stage, multi-stage cocurrent, and multi-stage counter current extractions respectively, where the fraction of solute remaining in the aqueous phase, x_n/x_0, is expressed as a function of distribution ratio (E_f) and number of stages or contacts (n). Also the distribution ratio:

$$E_f = E_a^o \cdot \frac{o}{a} .$$

It was assumed that equilibrium was reached at each contact, the phase ratio being limited to $1250/[Th]_a$, where $[Th]_a$ is expressed in μg/ml, (see Section 3.5 above) and the E_a^o (U) value remained constant for the particular initial feed composition selected.

The results of these calculations are summarised in Table 13, the number of stages for the extraction of the uranium ranging from 1 to 5 depending upon the system chosen. In a similar fashion, the number of stages required for stripping thorium from the organic phase using 1.0M nitric acid was calculated. With a phase ratio (o/a) of 5/1 it was calculated that two stages were required to strip the thorium although a phase ratio of 3/1 gave optimum stripping in a single contact.

The optimum extraction and strip parameters were confirmed experimentally in a multi-stage cocurrent system for uranium and thorium. However, for both extraction and stripping of the fission products, measured as gross γ, at least three stages in extraction appear necessary and three for stripping (Table 14). Even so, only 92 per cent of the γ-emitting fission products were extracted, the residual 8 per cent of γ-emitting fission products being Cs137 and Ru106. The pure β-emitter Sr90 was not extractable.

Although a more intensive study of ruthenium chemistry in sulphate media might produce conditions for improving Ru extraction, it is unlikely that Cs or Sr can be removed by this amine-scavenging process, and a further process, or second cycle, is required to obtain a greater decontamination of the beryllium sulphate and thus achieve the required decontamination factor (D.F.) of 10^3 (Cairns et al. 1966). Using an ion-exchange method developed for decontaminating beryllium nitrate solutions from fission products (Fardy 1966), it has been demonstrated (Fardy 1967) that it is possible to attain a D.F. of 10^3 with 0.5M beryllium sulphate at the millicurie level of radioactivity, and this process may therefore be a suitable second cycle.

The use of amine solvent extraction as a first-cycle beryllium sulphate decontamination process has the advantage that the actinides, particularly the U233, can be recovered and recycled. This permits greater flexibility in the operation of the head-end, grind-leach process, and ensures sufficient recovery of the U233 for the breeder cycle.

In discussing the attainment of the overall D.F. of 10^3 for the beryllium in the H.T.G.C.R. fuel cycle (Figure 14), the D.F.'s obtained, both in the head-end process and in the crystallisation

of $BeSO_4.4H_2O$ prior to calcination to BeO, have to be considered. If these each prove to have D.F. values of 10 or greater for gross fission products, then a single amine solvent extraction cycle for the decontamination of the beryllium sulphate may be adequate.

3.9 Chemical Flowsheet

Using the above data and the fuel cycle data published by Cairns et al. (1966), a preliminary chemical flowsheet has been constructed and is shown in Figure 15. This flowsheet requires testing with high levels of radioactivity and the correct or nearly correct feed stream composition.

4. GENERAL CONCLUSIONS

A primary amine dissolved in an aromatic diluent, such as the commercial Primene-JMT in Solvesso-100, can quantitatively extract Th, U and Pu from acidic beryllium sulphate solutions. The same extractant can also be used for the fission product elements Zr, Nb and Ce.

However, Ru is not sufficiently extracted and Cs and Sr are relatively non-extractable and thus the procedure does not give a high overall decontamination for gross fission products.

The method appears to be primarily useful for the separation of actinides from beryllium sulphate solution, and would lend itself to the primary decontamination of beryllium-based fuel solutions if this was required, particularly as the extracted species can be readily stripped with nitric acid, thus permitting a conventional tributyl phosphate second-cycle process.

Further development of this process requires its integration with the head-end grind-leach process for H.T.G.C.R. fuel, in a series of high-activity experiments using irradiated fuel of the required composition.

5. ACKNOWLEDGEMENTS

The authors wish to acknowledge in particular the assistance of Mr. P.G. Alfredson, Fuel Cycle Development Section, for his technical advice and Mr. P. Pakalns, Analytical Chemistry Section, for the many uranium and thorium analyses performed. They also wish to thank Dr. R.C.P.Cairns, Head of Fuel Cycle Development Section, for his encouragement and advice.

6. REFERENCES

Archer, E.E. (1957). – The Analyst, 82, 208.

Baillie, M.G. and Hubery, R.W. (1966). – AAEC/E162.

Baillie, M.G. and Ryan, R.K. (1965). – AAEC/E139.

Bishop, L., de Bruin, H.J. and Temple, R.B. (1960). – J. Sci. Inst., 37, 220.

Brown, K.B., Coleman, C.F., Crouse, D.J., Denis, J.O. and Moore, J.G. (1954). – AECD-4142.

Bunney, L.R., Ballou, N.E., Pascual, J. and Foti, S. (1959). – Anal Chem., 31 (3), 324.

Cairns, R.C. (1964). – J. Nuclear Materials, 14, 55–68.

Cairns, R.C., Baillie, M.G., Farrell, M.S. and May, J.R. (1966). – Fuel Cycle Studies for a Beryllium Oxide Moderated High Temperature Gas-Cooled Reactor. Second International Thorium Fuel Cycle Symposium, Gatlinburg, Tennessee.

Coleman, C.F. (1964). – Atomic Energy Review, July 1964.

Crouse, D.J. and Denis, J.O. (1955). – ORNL-1859.

Fardy, J.J.M. (1966). – AAEC/E152.

Fardy, J.J.M. (1967). – AAEC report (in the press).

Farrell, M.S. and Isaacs, S.R. (1965). – AAEC/E143.

Farrell, M.S., Isaacs, S.R. and Shying, M.E. (1966). – AAEC/E154.

Fritz, J.S. (1952). – Acid-base titration in non-aqueous solvents, Columbus, O.: G. Frederick Smith Chem. Co. 47 pp.

Haas, W.O. (1961). – Chemical Processing of Reactor Fuels. Ch.IV. Solvent Extraction, ed. J. Flagg, Acad. Press, New York.

Pakalns, P. (1963). – AAEC/TM175.

Pifer, C.E. and Worfish, E.C. (1952). – Anal. Chem., 24, 300.

Pifer, C.E., Worfish, E.C. and Schmall, M. (1953). – Anal. Chem., 25, 310.

Rodden, C.J. and Wharf, J.C. (1950). – Fluorometric Analysis, Anal. Chem of Manhattan Project, Nat. Nucl. Energy Series Div. XIII, Vol. 1, McGraw Hill Publishing Co.

Shying, M.E., Lee, E.J. and Farrell, M.S. (1967). – AAEC/E180.

Smith, R. (1964). – Third Int. Conf. on the Peaceful Uses of Atomic Energy, Geneva 1964, Paper 543.

Thomason, P.F., Perry, M.A. and Byerly, W.M. (1949). – Anal. Chem., 21, 1239.

APPENDIX

A LIST OF AMINES USED

Amine Class	Common Name	Source	Chemical Nomenclature	Formula
Primary	Primene-JMT	Rohm and Haas Co. U.S.A.	Trialkylmethylamine	$H_2N-C(R)(R^{I})(R^{III})$ where $R + R^{I} + R^{II}$ = 16 to 23 carbon atoms
Secondary	Amberlite -LA-1	Rohm and Haas Co. U.S.A.	N-dodecenyl(trialkylmethyl)-amine	$HN\langle^{C(R)(R^{I})(R^{II})}_{CH_2.CH:CH.CH_2.C(CH_3)_2.CH_2.C(CH_3)_3}$
Secondary	Amberlite-LA-2	Rohm and Haas Co. U.S.A.	N-lauryl(trialkylmethyl)amine	$HN\langle^{C(R)(R^{I})(R^{II})}_{CH_2(CH_2)_{10}CH_3}$
Secondary	–	Kao Soap Co. Ltd. Japan	N-cyclohexyloctylamine	$HN\langle^{C_6H_{11}}_{CH_2(CH_2)_7CH_3}$
Secondary	–	Kao Soap Co. Ltd. Japan	N-cyclohexylstearylamine	$HN\langle^{C_6H_{11}}_{CH_2(CH_2)_{15}CH_3}$
Secondary	–	Kao Soap Co. Ltd. Japan	N-benzyl-laurylamine	$HN\langle^{CH_2.C_6H_5}_{CH_2(CH_2)_{10}CH_3}$
Tertiary	Alamine-336	General Mills Inc. U.S.A.	Trialkylamines (from trihexylamine to tridecyl-amine)	$N - [(CH_2)_{7 \text{ to } 11}CH_3]_3$
Tertiary	TIOA	Union Carbide Chemical Co. U.S.A.	Triisooctylamine (a mixture of 3,5–,4,5–, and 3, + dimethyl hexyl amines)	$N - [(CH_2)_2.CH(CH_3).CH_2.CH(CH_3).CH_3]_3$
Tertiary	–	Kao Soap Co. Ltd. Japan	N-benzyldilaurylamine	$N\langle^{CH_2.C_6H_5}_{[CH_2.(CH_2)_{10}CH_3]_2}$

TABLE 1

THE EXTRACTION OF U, Th, Pu AND Be BY AMINES

Amine	Diluent	Extraction Coefficients			
		E_a^o U(VI)	E_a^o Pu(IV)	E_a^o Th(IV)	E_a^o Be(II)
Primene-JMT	O.M.S.* + 5 v/o C.A.**	6.2		$>10^3$	4.5×10^{-3}
Primene-JMT	O.M.S.	11.4		$>10^3$	6.0×10^{-3}
Primene-JMT	Boralene 1124	7.3		$>10^3$	
Primene-JMT	Benzene	10.4		$>10^3$	
Primene-JMT	Solvesso-100	12.0	>520	$>10^3$	6.2×10^{-3}
Primene-JMT	Solvesso-150	13.5		$>10^3$	6.6×10^{-3}
Alamine-336	O.M.S. + 5 v/o C.A.	12.8		0.10	
Amberlite LA-1	O.M.S. + 5 v/o C.A.	3.7			
Amberlite LA-2	O.M.S. + 5 v/o C.A.	5.0	519		
Tri-iso-octylamine	O.M.S. + 5 v/o C.A.	4.7			
Alamine-336	Solvesso-100	214	6	0.13	1.1×10^{-3}
Amberlite LA-1	Solvesso-100	204			
Amberlite LA-2	Solvesso-100	75			
Tri-iso-octylamine	Solvesso-100	96	4.5	>1.0	
Cyclohexyloctylamine	Solvesso-100	3.8			
Cyclohexylstearylamine	Solvesso-100	emulsified			
Benzylamylamine	Solvesso-100	emulsified			
Benzyldilaurylamine	Solvesso-100	emulsified			

* O.M.S. = Odourless mineral spirits

** C.A. = Capryl alcohol

v/o = Volume per cent

Initial Phase Compositions:

Aqueous Phase : 2.0M $BeSO_4$, 2.5M Total SO_4, pH = 1.0

30 μg U/ml, 300 μg Th/ml, Pu-tracer level

Organic Phase : 0.05M amine in the chosen diluent

Phase ratio (a/o) 1:1

TABLE 2

THE EXTRACTION OF INDIVIDUAL FISSION PRODUCT ELEMENTS BY AMINES

Amine	Extraction Coefficients E_a^o					
	Ce144	Zr95–Nb95	Nb95	Ru106	Sr85	Cs137
Primene-JMT	9.9	52	3.5	2.5×10^{-1}	1.2×10^{-3}	2.1×10^{-3}
Cyclohexyloctylamine	6×10^{-3}	3×10^{-1}	10	4.5×10^{-3}	negligible	1.9×10^{-3}
Cyclohexylstearylamine	emulsified					
Amberlite LA-1	2.6×10^{-3}	5.2	3.6	7.4×10^{-1}	negligible	8×10^{-4}
Amberlite LA-2	negligible	3.2	3.8	7.1×10^{-1}	9×10^{-4}	9.5×10^{-4}
N-Benzyldilaurylamine	emulsified					
N-Benzylaurylamine	emulsified					
Tri-iso-octylamine	negligible	1.1	1.7	6.4×10^{-1}	negligible	negligible
Alamine-336	negligible	1.4	3.6	7×10^{-1}	negligible	4.4×10^{-4}

Initial Phase Compositions:

Aqueous Phase : 2.0M $BeSO_4$, 2.5M total sulphate, pH = 1.0

Tracer level fission product elements

Organic Phase : 0.05M amine in Solvesso-100

Phase ratio (a/o) 1:1

TABLE 3

THE EXTRACTION OF U, Th, Pu AND Be BY AMINES

Amine and Concentration	Phase Separation Time Minutes	Extraction Coefficients E_a^o		
		U(VI)	Th(IV)	Be(II)
0.05M Primene-JMT	2	10.3	$>10^3$	5.7×10^{-3}
0.0375M Primene-JMT 0.0125M Alamine-336	2	12.3	$>10^3$	4.3×10^{-3}
0.025M Primene-JMT 0.025M Alamine-336	2	49.2	$>10^3$	2.5×10^{-3}
0.0125M Primene-JMT 0.0375M Alamine-336	1½	86.5	49.6	2.3×10^{-3}
0.05M Alamine-336	1¼	269	0.11	1.2×10^{-3}
0.1M Primene-JMT	2	22	$>10^3$	1.1×10^{-2}
0.075M Primene-JMT 0.025M Alamine-336	3	33	$>10^3$	7.5×10^{-3}
0.05M Primene-JMT 0.05M Alamine-336	>4	91	$>10^3$	5.5×10^{-3}
0.025M Primene-JMT 0.075M Alamine-336	>4	219	$>10^3$	1.9×10^{-3}
0.1M Alamine-336	3½	264	0.3	1.6×10^{-3}
0.05M Primene-JMT 0.05M Alamine-336 + 5 v/o C.A. *	1¼	40.3	1243	4.9×10^{-3}
0.05M Primene-JMT 0.05M Alamine-336 + 10 v/o C.A.	1	16.5	533	4.2×10^{-3}

* C.A. = Capryl alcohol

Initial Phase Compositions:

Aqueous Phase : 2.0M $BeSO_4$, 2.5M total sulphate, pH = 1.0

30 μg U/ml, 300 μg Th/ml

Organic Phase : Selected amine or amines in concentrations given in table in Solvesso-100

Phase ratio (a/o) 1:1

TABLE 4

EMPIRICAL RELATIONSHIPS FOR FISSION PRODUCT ELEMENTS

EXTRACTION AS A FUNCTION OF PRIMENE-JMT CONCENTRATION

Fission Product Element	Empirical Extraction Relationship	
	2.0M Total Sulphate	2.5M Total Sulphate
Ce144	E_a^o (Ce144) = 108 [JMT]$^{0.76}$	E_a^o (Ce144) = 92 [JMT]$^{0.75}$
Zr95-Nb95	E_a^o (Zr95-Nb95) = 292 [JMT]$^{0.47}$	E_a^o (Zr95-Nb95) = 220 [JMT]$^{0.48}$
Nb95	E_a^o (Nb95) = 193 [JMT]$^{0.4}$	E_a^o (Nb95) = 114 [JMT]$^{0.44}$
Ru106	E_a^o (Ru106) = 1.65 [JMT]$^{0.7}$	E_a^o (Ru106)= 1.15 [JMT]$^{0.68}$
Mixed Fission Products (Gross γ)	E_a^o (γ) = 5.1 [JMT]$^{0.23}$	–

Initial Phase Compositions:

Aqueous Phase : 2.0M $BeSO_4$, total sulphate as above, pH = 1.0

Fission product elements used at tracer level

Organic Phase : Primene-JMT/Solvesso-100

Phase ratio (a/o) 1:1

TABLE 5

THE EXTRACTION OF U, Th, Be BY AMINES AS A FUNCTION OF

BERYLLIUM CONCENTRATION, SULPHATE CONCENTRATION AND pH

Initial Aqueous Phase Concentrations			Extraction Coefficients E_a^o							
			0.05M Primene-JMT / O.M.S. + 5 v/o C.A.	0.1M Primene-JMT/ Solvesso-100			0.05M Alamine-336/ O.M.S. + 5 v/o C.A.	0.1M Alamine-336/ Solvesso-100		
Be (M)	SO_4 (M)	pH	U(VI)	U(VI)	Th(IV)	Be(II)	U(VI)	U(VI)	Th(IV)	Be(II)
2.0	2.0	1.0		66	$>10^3$	1.3×10^{-2}		2,080	0.83	$<5\times10^{-4}$
2.0	2.0	1.5		65	$>10^3$	1.3×10^{-2}		2,880	0.84	$<5\times10^{-4}$
2.0	2.0	2.0		68	$>10^3$	1.35×10^{-2}		370	0.59	$<5\times10^{-4}$
2.0	2.25	0.5	7.3	33	$>10^3$	1.1×10^{-2}	27	190	0.12	$<5\times10^{-4}$
2.0	2.25	1.0	7.9	43	$>10^3$	1.2×10^{-2}	29	930	0.49	$<5\times10^{-4}$
2.0	2.25	1.5	8.1	49	$>10^3$	1.2×10^{-2}	28	1,200	0.73	$<5\times10^{-4}$
2.0	2.25	2.0	9.3	51	$>10^3$	1.2×10^{-2}	17	900	0.62	$<5\times10^{-4}$
2.0	2.50	0.5	4.0	18	$>10^3$	1.2×10^{-2}	18	470	0.07	$<5\times10^{-4}$
2.0	2.50	1.0	5.0	29	$>10^3$	1.2×10^{-2}	26	2,110	0.43	$<5\times10^{-4}$
2.0	2.50	1.5	6.3	37	$>10^3$	1.4×10^{-2}	20	2,030	0.62	$<5\times10^{-4}$
2.0	2.50	2.0	7.3	38	$>10^3$	1.2×10^{-2}	15	630	0.51	$<5\times10^{-4}$
2.0	2.75	0.5	2.2				12			
2.0	2.75	1.0	3.5				19			
2.0	2.75	1.5	4.4				20			
2.0	2.75	2.0	4.7				11			
2.0	3.0	0.5	1.7				9			
2.0	3.0	1.0	2.8				13			
2.0	3.0	1.5	3.2				15			
2.0	3.0	2.0								
2.0	2.0	1.0		47	$>10^3$	0.95×10^{-2}				
1.75	1.75	1.0		51	$>10^3$	1.2×10^{-2}				
1.50	1.50	1.0		71	$>10^3$	1.4×10^{-2}				
1.25	1.25	1.0		81	$>10^3$	1.6×10^{-2}				
1.00	1.00	1.0		104	$>10^3$	1.8×10^{-2}				

Initial aqueous phase concentrations: Th, 300 μg/ml; U, 30 μg/ml; Be7, tracer level.

Phase ratio (a/o) 1:1

TABLE 6

THE EXTRACTION OF FISSION PRODUCTS BY 0.1M PRIMENE-JMT/SOLVESSO-100 AS A FUNCTION OF BERYLLIUM CONCENTRATION, SULPHATE CONCENTRATION AND pH

Initial Aqueous Phase Concentration			Extraction Coefficients E_a^o					
Be (M)	SO_4 (M)	pH	Ce144	Zr95–Nb95	Nb95	Ru106	Sr85	Cs137
2.0	2.0	1.0	19	123	75	0.47	6.4×10^{-3}	4.0×10^{-3}
2.0	2.0	1.5		95	14	0.47		
2.0	2.0	2.0		63	9.5	0.41		
2.0	2.25	0.5	11 *	190	89	0.41		
2.0	2.25	1.0	11 *	94	56	0.48	4.6×10^{-3}	2.8×10^{-3}
2.0	2.25	1.5	10 *	68	25	0.41		
2.0	2.25	2.0	10 *	54	14	0.39		
2.0	2.5	0.5	8.9 *	140	75	0.33		
2.0	2.5	1.0	9.5 *	74	42	0.38	1.2×10^{-3}	2.1×10^{-3}
2.0	2.5	1.5	8.5 *	45	23	0.38		
2.0	2.5	2.0	8.4 *	36	14	0.37		
2.0	2.75	0.5	8.4 *					
2.0	2.75	1.0	8.6 *					
2.0	2.75	1.5	7.9 *					
2.0	2.75	2.0	7.6 *					
2.0	3.0	0.5	4.9 *					
2.0	3.0	1.0	7.7 *					
2.0	3.0	1.5	7.0 *					
2.0	3.0	2.0	6.4 *					
2.0	2.0	1.5	11.1 *	140		0.29		
1.75	1.75	1.5	12.2 *	150		0.31		
1.50	1.50	1.5	15.2 *	93		0.34		
1.25	1.25	1.5	18.5 *	120		0.37		
1.0	1.0	1.5	24.0 *	115		0.42		

* 0.05M Primene-JMT/Solvesso-100 used.

TABLE 7

THE EFFECT OF NITRATE ION ON THE AMINE EXTRACTION OF ACTINIDE AND FISSION PRODUCT ELEMENTS FROM AQUEOUS SULPHATE SOLUTION

Aqueous Phase Concentrations				Organic Phase		Extraction Coefficients						
Be (M)	SO_4 (M)	NO_3 (M)	pH	Amine	Conc. Amine (M)	U(VI)	Th(IV)	Pu(IV)	Ce144	Zr95–Nb95	Ru106	Fission Products Gross γ
2.0	2.0	0	1.0	Primene-JMT/ Solvesso-100	0.1	67	$>10^3$	>500	14	104	0.26	3.2
2.0	2.0	0.02	1.0		0.1	–	$>10^3$	>500	–	86	0.23	3.0
2.0	2.0	0.05	1.0		0.1	117	–	–	8	66	0.19	2.8
2.0	2.0	0.10	1.0		0.1	279	$>10^3$	>500	1	35	0.08	1.6
2.0	2.0	0.20	1.0		0.1	603	$>10^3$	>500	–	–	–	–
2.0	2.0	0.50	1.0		0.1	0.04	–	–	–	–	–	–
Nil	1.0	0	1.0	Primene-JMT/ Solvesso-100	0.1	91	$>10^3$					
"	1.0	0.02	1.0		0.1	1,790	$>10^3$					
"	1.0	0.05	1.0		0.1	2,400	$>10^3$					
"	1.0	0.10	1.0		0.1	1,320	$>10^3$					
Nil	1.0	0	1.0	Tri-octylamine/ Solvesso-100	0.1	39						
"	1.0	0.02	1.0		0.1	15						
"	1.0	0.05	1.0		0.1	2						

Initial aqueous phase concentrations:

U 30 μg/ml
Th 300 μg/ml
Pu tracer level

Phase ratio (a/o) 1:1

TABLE 8

THE EXTRACTION OF BERYLLIUM BY PRIMENE-JMT

THE EFFECT OF ANION TYPE ON EXTRACTION

Anion Used	E_a^o (Be)	Diluent Used	Remarks
Nitrate	Negligible	O.M.S. + 5 v/o C.A.	Carrier Free Be^7 used
Chloride	Negligible	O.M.S. + 5 v/o C.A.	
Sulphate	0.001	O.M.S. + 5 v/o C.A.	
Thiocyanate	0.08	O.M.S. + 5 v/o C.A.	
Fluoride	0.18	O.M.S. + 5 v/o C.A.	
Phosphate	7.6	O.M.S. + 5 v/o C.A.	
Phosphate	60	Benzene	Carrier Free Be^7 only
Phosphate	59	Benzene	Aqueous Phase also contained 0.05M $BeSO_4$
Fluoride	15	Chloroform	Carrier Free Be^7 only
Fluoride	5.4	Chloroform	Aqueous Phase contained 0.01M $BeSO_4$
Fluoride	0.03	Chloroform	Aqueous Phase contained 0.05M $BeSO_4$

Initial Phase Compositions:

Aqueous Phase : 0.1M Ammonium salt of chosen anion

Organic Phase : 0.1M Primene-JMT in diluent listed

Phase ratio (a/o) 1:1

TABLE 9

THE EFFECT OF THORIUM LOADING OF THE AMINE PHASE ON THE EXTRACTION OF URANIUM

Initial Aqueous Phase Conditions				Phase Ratio a:o	U and Th Concentrations After Equilibration (μg/ml)				Extraction Coefficients E_a^o		
					Aqueous		Organic				
Be (M)	SO_4 (M)	pH	U:Th atomic ratio		U	Th	U	Th	U(VI)	Th(IV)	Pu(IV)
2.0	2.0	1.0	20 A	1	0.77	<1	23	630	30	$>10^3$	
			20	1	2.10	<1	52	1,370	25	$>10^3$	
			20	1	3.15	<1	60	1,840	20	$>10^3$	
			20	1	4.75	<1	84	2,060	18	$>10^3$	
			20	1	140	50	1.5	2,210	0.6	44	
			20	1	30	564	0.08	2,530	0.002	4.5	
			10 B	1	0.85	<1	28	320	33	$>10^3$	>800
			10	1.5	1.10	<1	37	490	34	$>10^3$	>800
			10	2.0	1.60	<1	53	660	33	$>10^3$	>800
			10	2.5	2.5	<1	83	810	33	$>10^3$	>800
			10	3.0	3.5	<1	107	1,030	31	$>10^3$	>800
			10	3.5	3.8	<1	125	1,230	33	$>10^3$	>800
			10	4.0	5.4	<1	138	1,380	26	$>10^3$	824
			10	4.5	6.3	<1	144	1,470	23	$>10^3$	774
			10	5.0	85	<1	152	1,670	18	$>10^3$	730
			10	10.0	310	100	0.4	2,900	0.001	29	192
2.0	2.5	1.0	10	1	1.3	<1	30	350	24	10^3	
			10	3	3.8	<1	90	1,020	24	10^3	
			10	5	13	<1	120	1,580	9.7	10^3	
			10	10	302	73	0.2	2,910	<0.001	40	

Initial Phase Compositions:

Aqueous Phase : As shown

Organic Phase : 0.1M Primene-JMT in Solvesso-100

A produced by contacting the organic phase with successive aliquots of fresh aqueous phase.

B Produced by varying the phase ratio in a single contact between the phases.

TABLE 10

THE STRIPPING OF ACTINIDES FROM PRIMENE-JMT/SOLVESSO-100

WITH NITRIC ACID

Nitric Acid Concentration in Stripping Solution (M)	Phase Ratio o/a	Stripping Coefficients S_o^a		
		U(VI)	Th(IV)	Pu(IV)
0.1	1	55	0.10	
0.2	1	97	1.0	
0.5	1	1,890	51	11
1.0	1	3,930	6,610	4,310
1.0	3	4,510	1,470	430
1.0	5	1,440	480	9.4
1.5	5	–	–	1,400
2.0	5	–	–	>4,000
1.0	8	1,200	68	0.49

Initial Phase Compositions:

Aqueous Phase : Nitric acid at concentrations shown

Organic Phase : 0.1M Primene-JMT/Solvesso-100 loaded with chosen actinides in sulphate form by contacting with aqueous phase containing Th (300 μg/ml); U (30 μg/ml); Pu (tracer level).

TABLE 11

THE STRIPPING OF FISSION PRODUCT ELEMENTS FROM PRIMENE-JMT/SOLVESSO-100 WITH NITRIC ACID THE EFFECT OF PHASE RATIO

Fission Product Element	Phase Ratio o/a	Stripping Coefficient S_o^a
Ce144	3	$>10^4$
	5	$>10^4$
	8	$>10^4$
Zr95–Nb95	3	124
	5	13
	8	11
Nb95	3	228
	5	41
	8	40
Ru106	3	54
	5	56
	8	56

Initial Phase Composition:

Aqueous Phase : 1.0M HNO_3

Organic Phase : 0.1M Primene-JMT/Solvesso-100 loaded with fission product, tracer in sulphate form

TABLE 12

RECONVERSION OF THE AMINE NITRATE TO THE FREE-BASE FORM

Reacting Base (Aqueous Phase)		Phase Ratio o/a	Phase Separation Time (min)	Final Aqueous Phase Nitrate Concentration (M)
Type	Concentration			
Na_2CO_3	0.2	1	2.5	0.105
	0.5	1	1	0.103
	1.0	1	1	0.105
	2.0	1	2.0	0.110
	2.5	1	1.25	0.102
	1.0	1	1	0.105
		1/3	2	0.317
		1/5	1	0.548
		1/8	1	0.820
NH_4OH	0.2	1	1.5	0.108
	0.5	1	3.0	0.109
	1.0	1	1.5	0.108
	1.5	1	1.5	0.115
	2.0	1	2.0	0.108
	1.0	1	1.5	0.104
		1/3	3.0	0.324
		1/5	5.0	0.516
		1/8	5.0	0.834

Initial Phase Compositions:

Aqueous Phase : Na_2CO_3 or NH_4OH at concentrations shown in table

Organic Phase : 0.1M Primene-JMT/Solvesso-100 equilibrated with nitric acid and containing 0.11M HNO_3

TABLE 13

MULTI-STAGE EXTRACTION OF URANIUM BY PRIMENE-JMT

CALCULATION OF NUMBER OF EQUILIBRIUM STAGES

% of the initial U in the fuel entering the $BeSO_4$ solution		1		5		10	
% recovery of U required from $BeSO_4$ solution to ensure an overall recovery of 99.9% in the fuel cycle		90		98		99	
Thorium concentration in $BeSO_4$ solution – $\mu g/ml$		58		290		580	
Maximum phase ratio – a/o		20/1		4/1		2/1	
Aqueous phase composition		A	B	A	B	A	B
Single Contact	a/o	6/1	3/1	1/1	0.5/1	0.6/1	0.25/1
	n	1	1	1	1	1	1
Multi-stage cocurrent	a/o	20/1	20/1	4/1	4/1	2/1	2/1
	n	2	3	2	2	2	2
Multi-stage countercurrent	a/o	20/1	20/1	4/1	4/1	2/1	2/1
	n	2	5	2	3	2	2

n = number of calculated stages

a/o = aqueous to organic volume ratio

Initial Phase Compositions:

Aqueous Phase : A ; 2.0M Be, 2.0M SO_4, pH = 1.0, U(VI) = 66

B : 2.0M Be, 2.5M SO_4, pH = 1.0, U(VI) = 29

Organic Phase : 0.1M Primene-JMT in Solvesso-100

TABLE 14

MULTI-STAGE COCURRENT BATCH EXTRACTION AND

STRIPPING OF ACTINIDES AND FISSION PRODUCTS

Cycle	Stage	Extraction and Stripping Coefficients E_a^o and S_o^a			Gross γ(F.P.) % Extracted or Stripped	Gross γ(F.P.) % Remaining	Gross γ Decontamination Factor
		U(VI)	Th(IV)	Gross γ(F.P.)			
Extraction	1	146	>1000	7.6	79	21	4.6
	2	65		2.65	51	49	2.0
	1+2				89	11	9.4
	3			0.66	6	84	1.2
	1+2+3				92	8	11.2
Strip	1	323	129	32	87	13	7.8
	2	173	20	93	40	60	16.6
	1+2				>93	<7	130
	3			9	Nil	<7	<1
	1+2+3				>93	<7	117

Initial Phase Compositions:

Extraction

Aqueous Phase : 2.0M $BeSO_4$, 2.0M total SO_4, pH = 1.0,
30 μg U(VI)/ml, 380 μg Th(IV)/ml
+ gross fission products

Organic Phase : 0.1M Primene-JMT in Solvesso-100,
a/o ratio, 2/1, No. of stages = 3

Strip

Aqueous Phase : 1.0M HNO_3, a/o ratio 1/5, No. of stages = 3

Organic Phase : Loaded organic phase from extraction

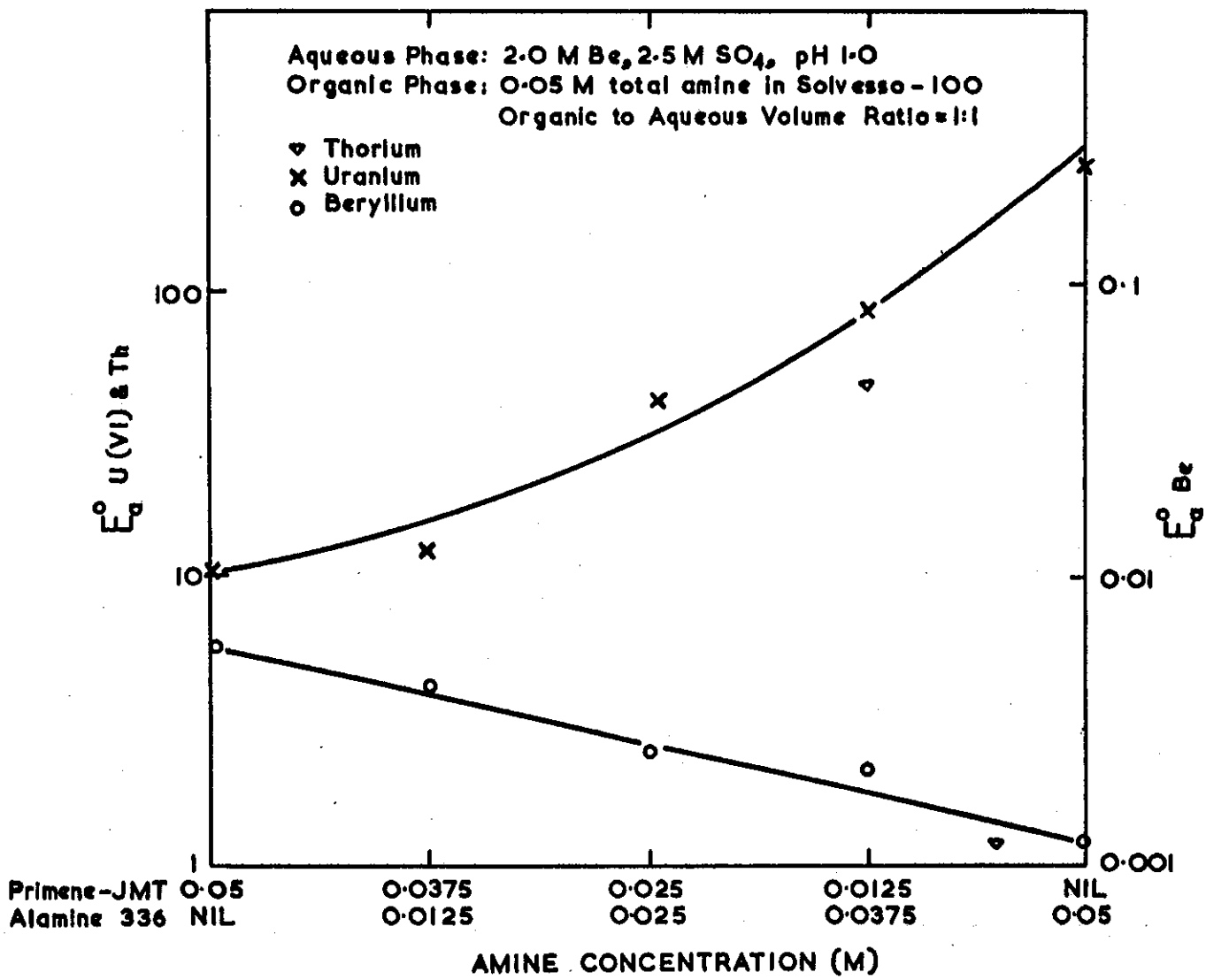

FIGURE 1. EXTRACTION OF U, Th, Be BY 0.05M MIXED AMINES FROM BERYLLIUM SULPHATE SOLUTION

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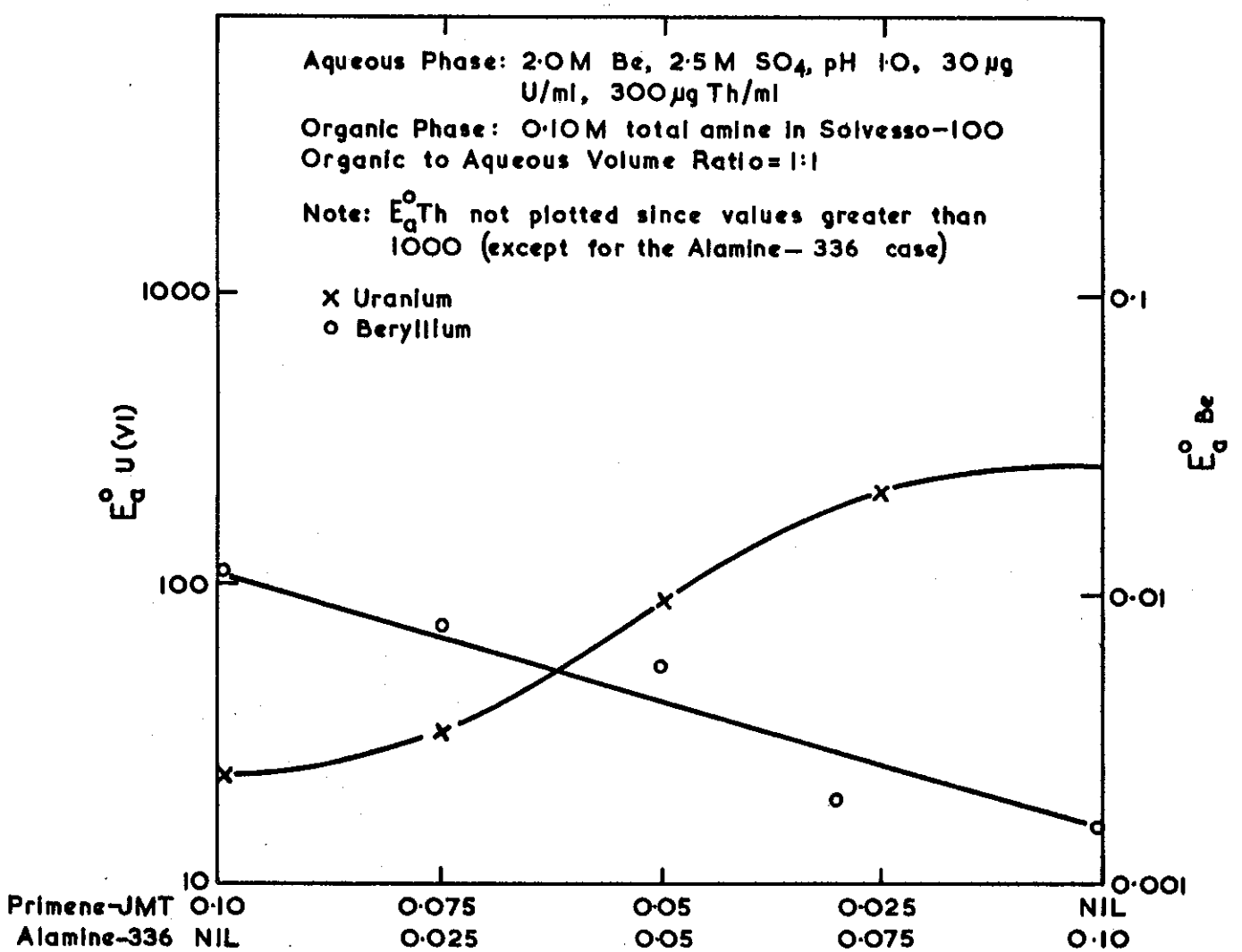

FIGURE 2. EXTRACTION OF U, AND Be BY 0.1M MIXED AMINES FROM BERYLLIUM SULPHATE SOLUTION

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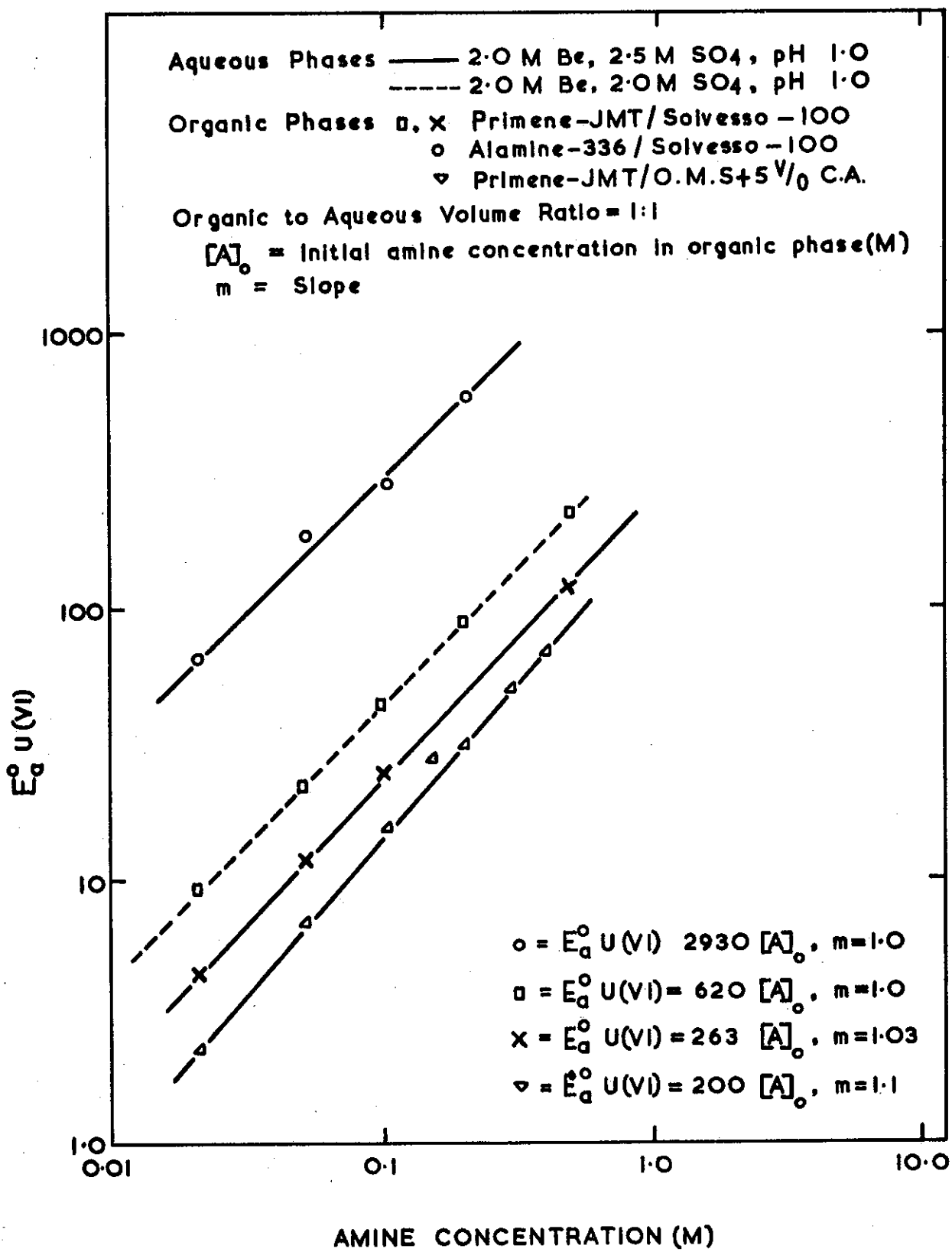

FIGURE 3. EXTRACTION OF U BY PRIMENE-JMT AND BY ALAMINE-336 FROM BERYLLIUM SULPHATE SOLUTIONS: THE EFFECT OF AMINE CONCENTRATION

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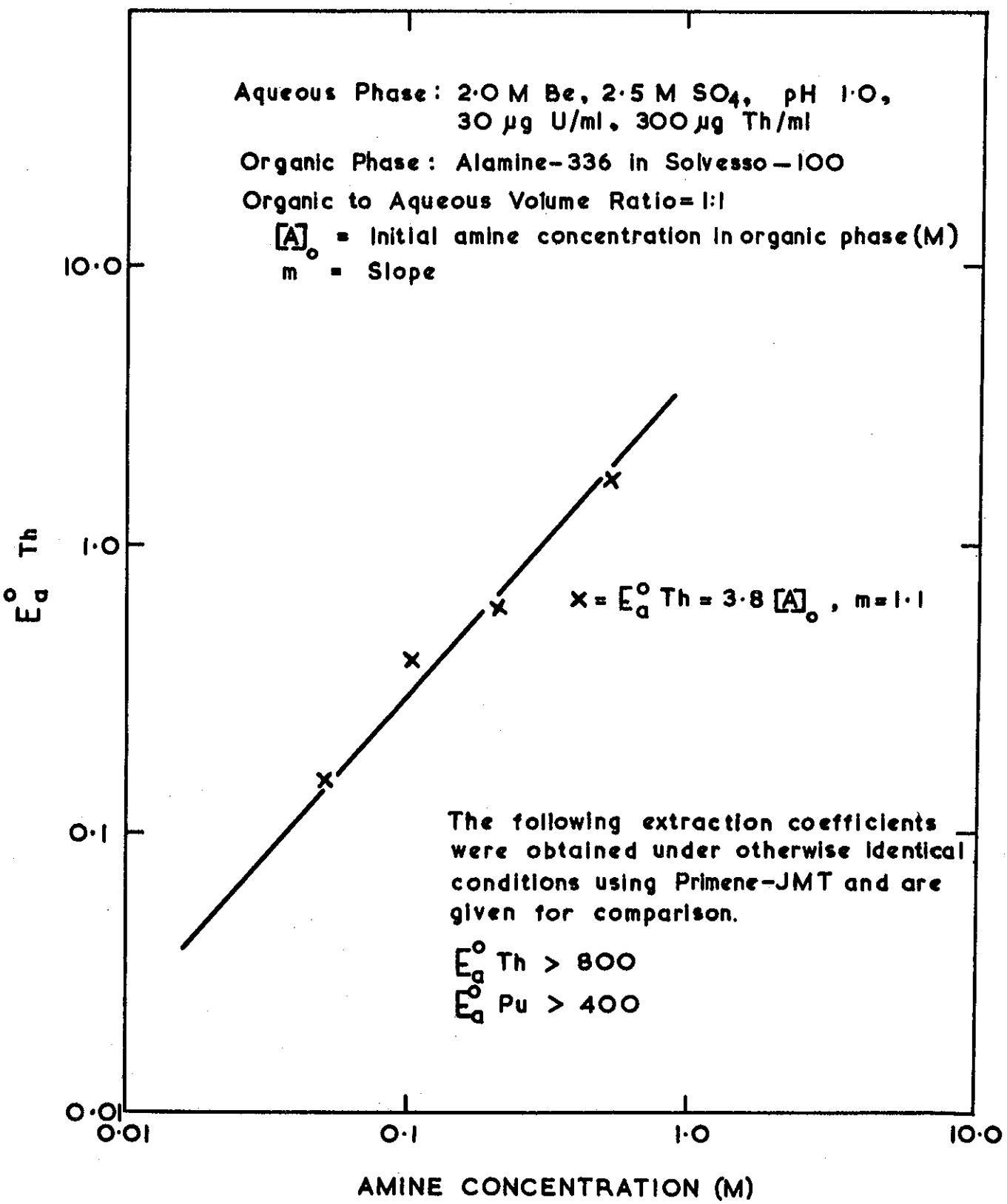

FIGURE 4. EXTRACTION OF Th BY ALAMINE 336 FROM BERYLLIUM SULPHATE SOLUTION: THE EFFECT OF AMINE CONCENTRATION

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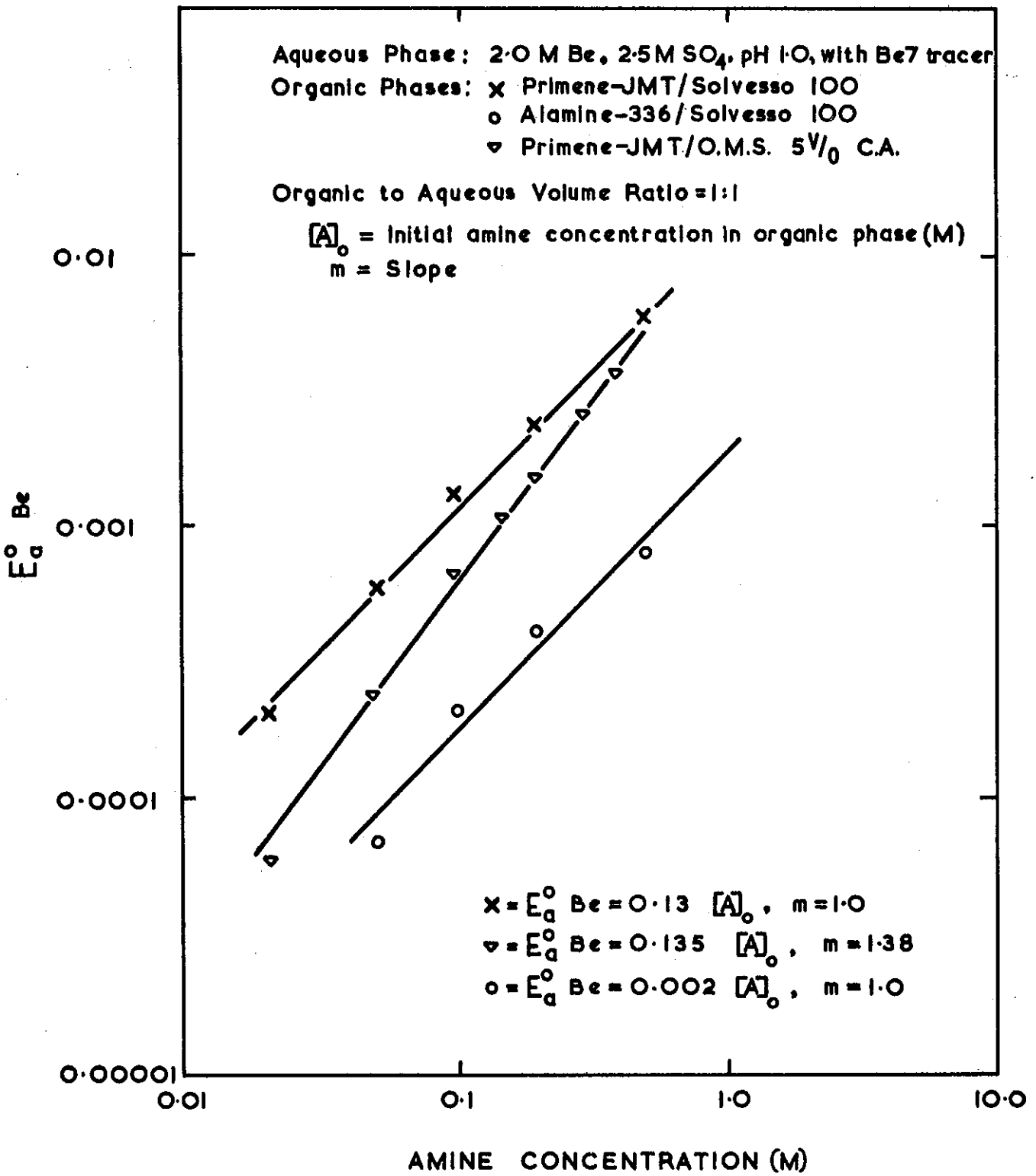

FIGURE 5. EXTRACTION OF Be BY ALAMINE-336 AND PRIMENE-JMT FROM BERYLLIUM SULPHATE SOLUTION: THE EFFECT OF AMINE CONCENTRATION

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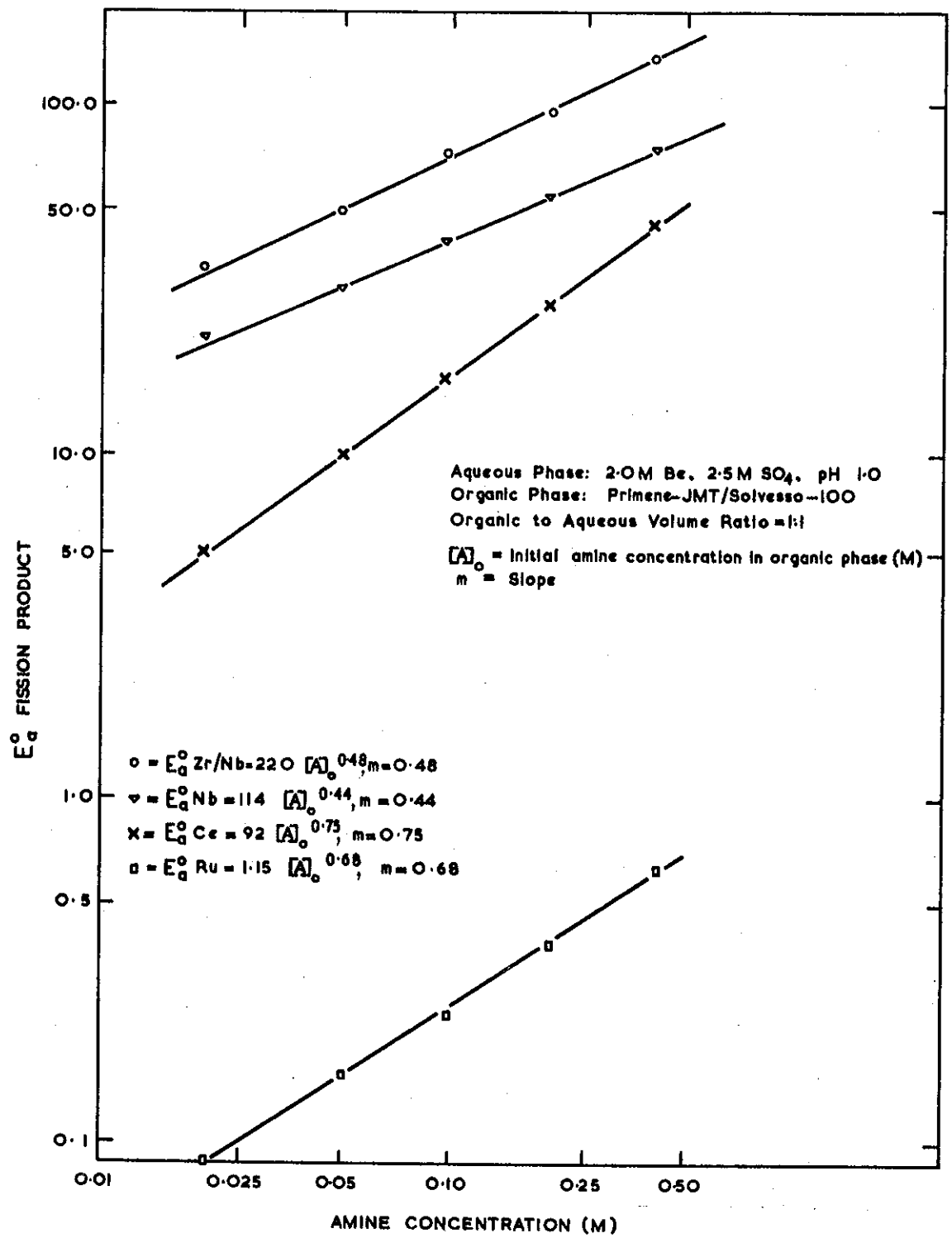

FIGURE 6. EXTRACTION OF FISSION PRODUCT ELEMENTS BY PRIMENE-JMT FROM BERYLLIUM SULPHATE SOLUTION: EFFECT OF AMINE CONCENTRATION

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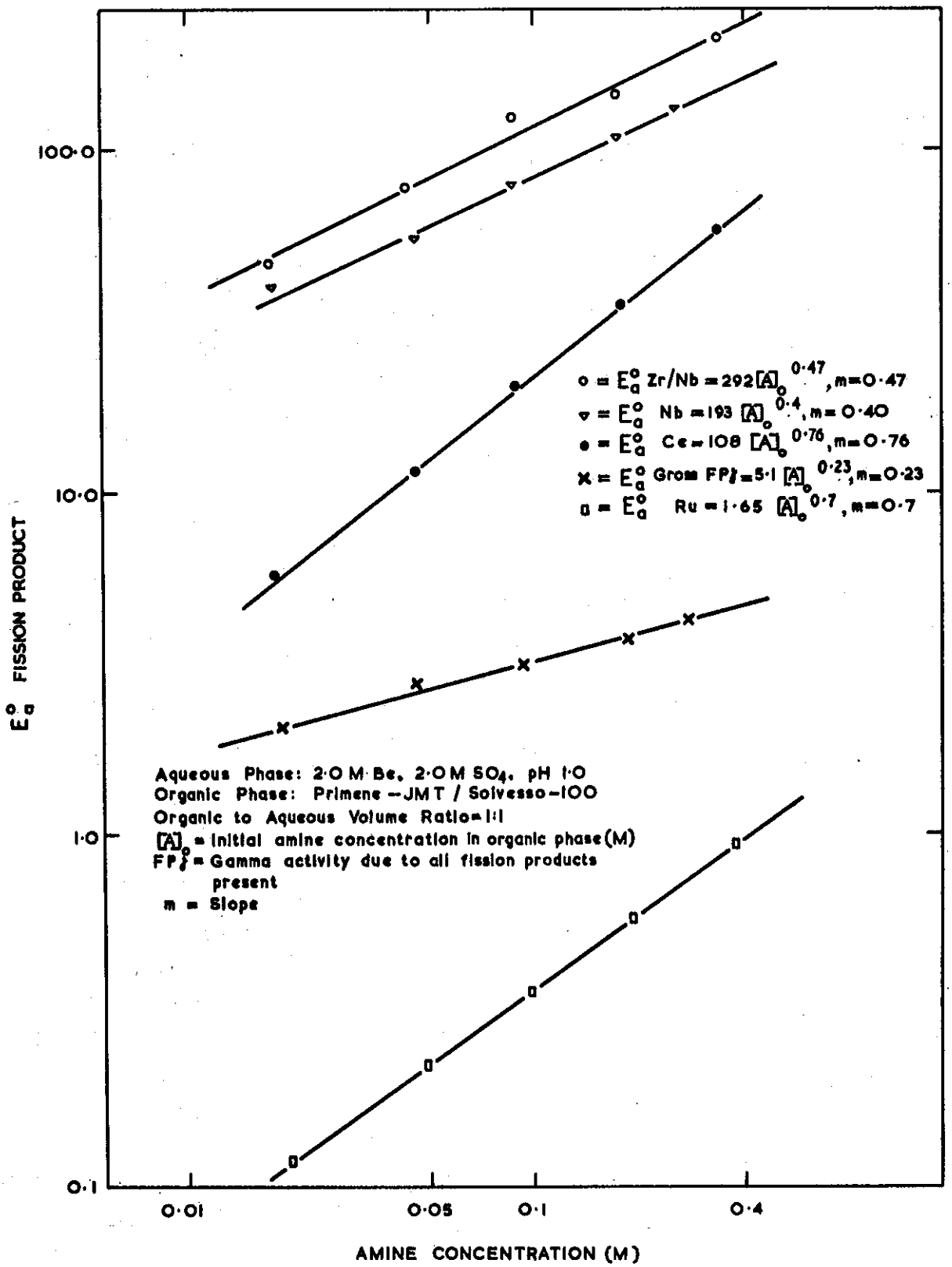

FIGURE 7. EXTRACTION OF FISSION PRODUCT ELEMENTS BY PRIMENE-JMT FROM BERYLLIUM SULPHATE SOLUTION: EFFECT OF AMINE CONCENTRATION (2.0M TOTAL SULPHATE)

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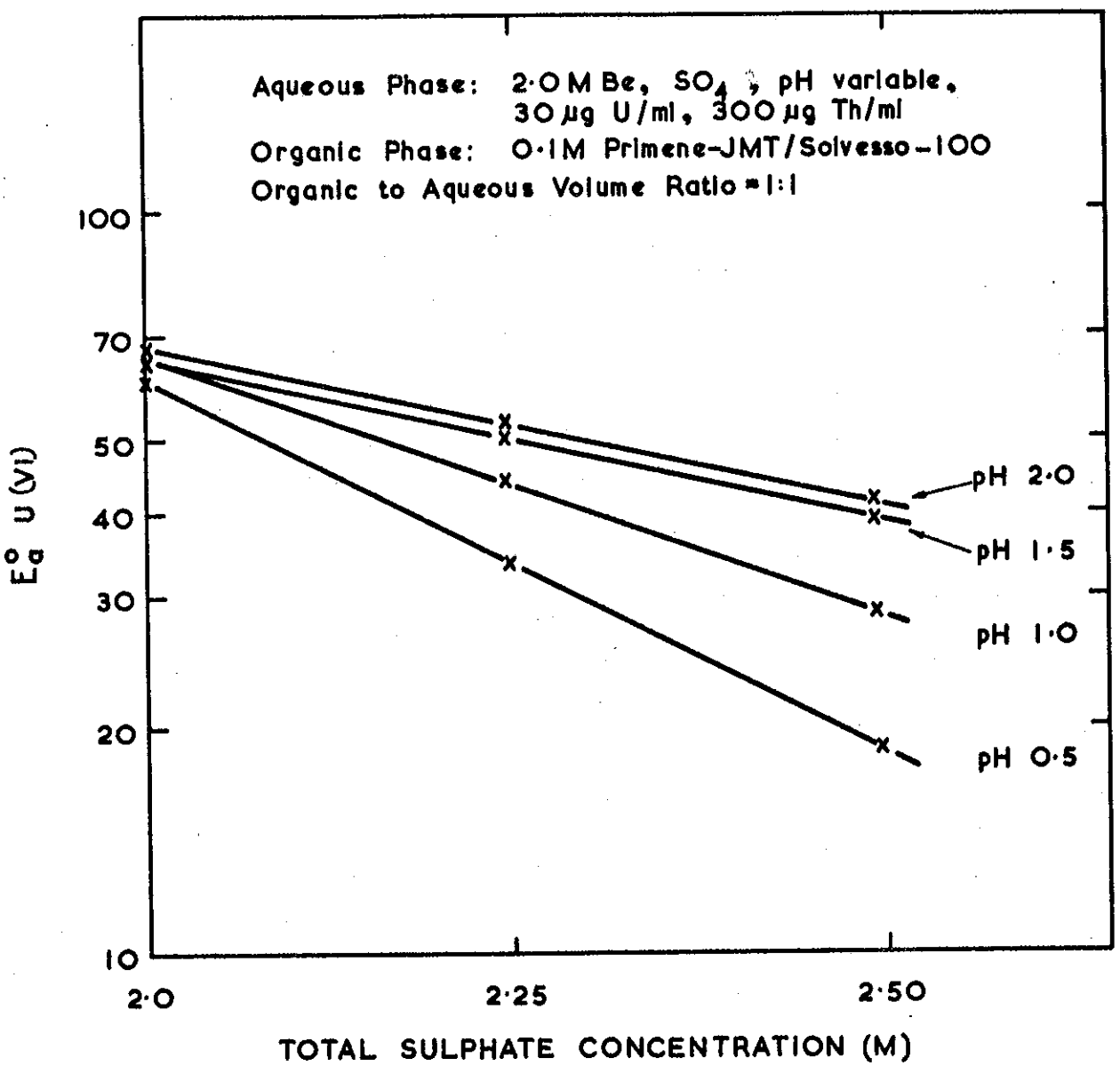

FIGURE 8. EXTRACTION OF URANIUM BY PRIMENE-JMT FROM BERYLLIUM SULPHATE SOLUTION: THE EFFECT OF TOTAL SULPHATE CONCENTRATION

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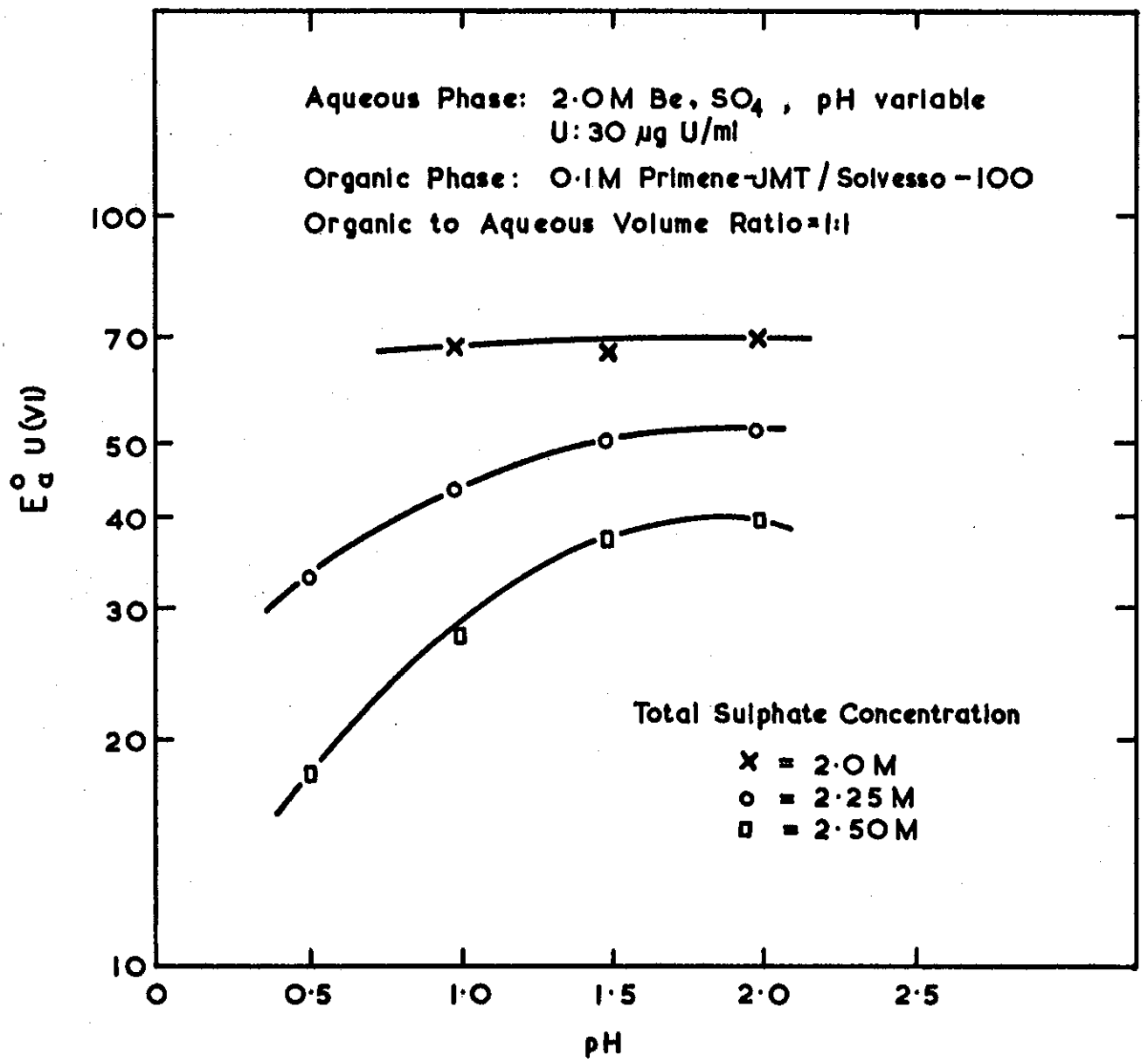

FIGURE 9. EXTRACTION OF URANIUM BY PRIMENE-JMT FROM BERYLLIUM SULPHATE SOLUTIONS: THE EFFECT OF pH

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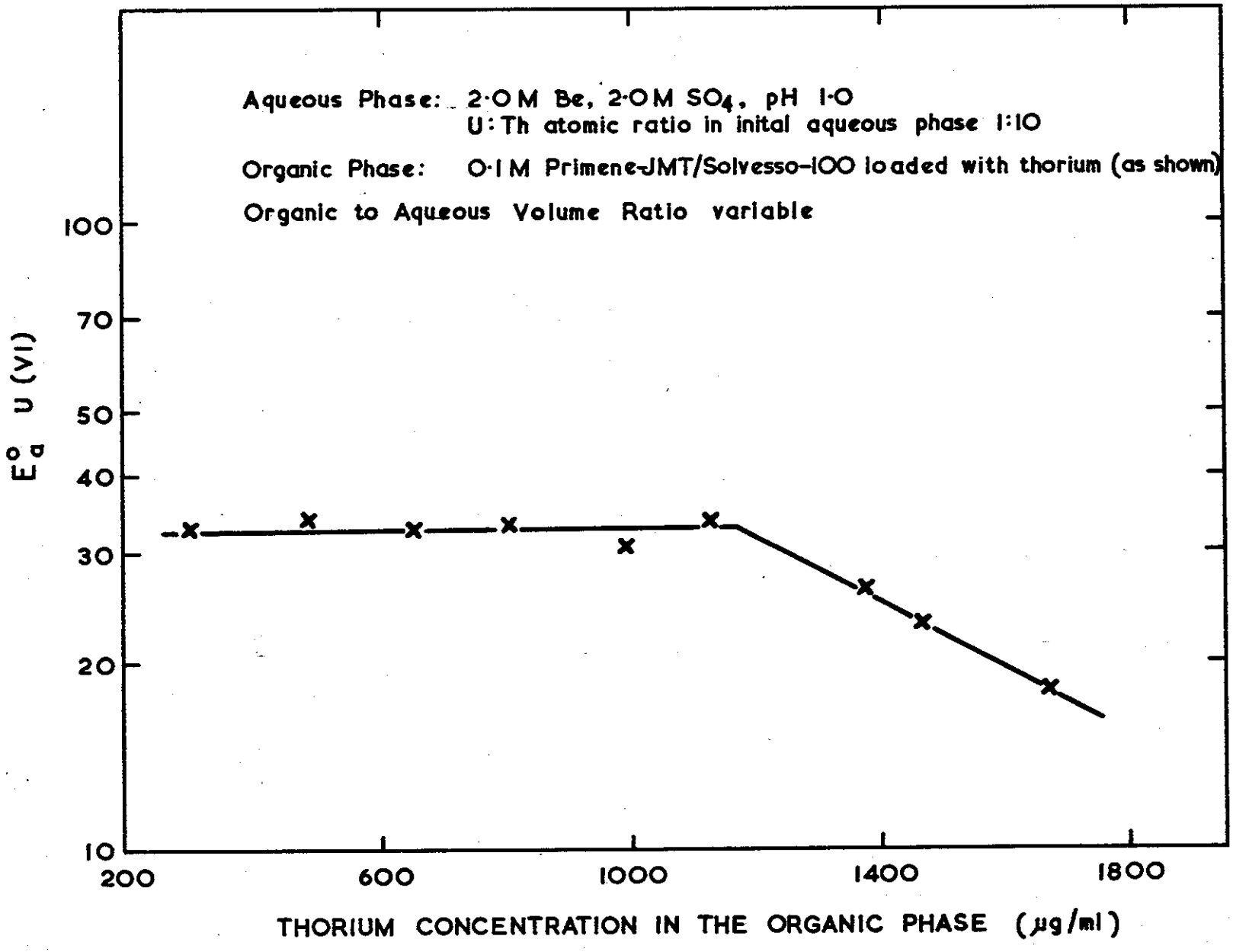

FIGURE 10. EXTRACTION OF URANIUM BY PRIMENE-JMT: THE EFFECT OF THORIUM LOADING OF THE ORGANIC PHASE

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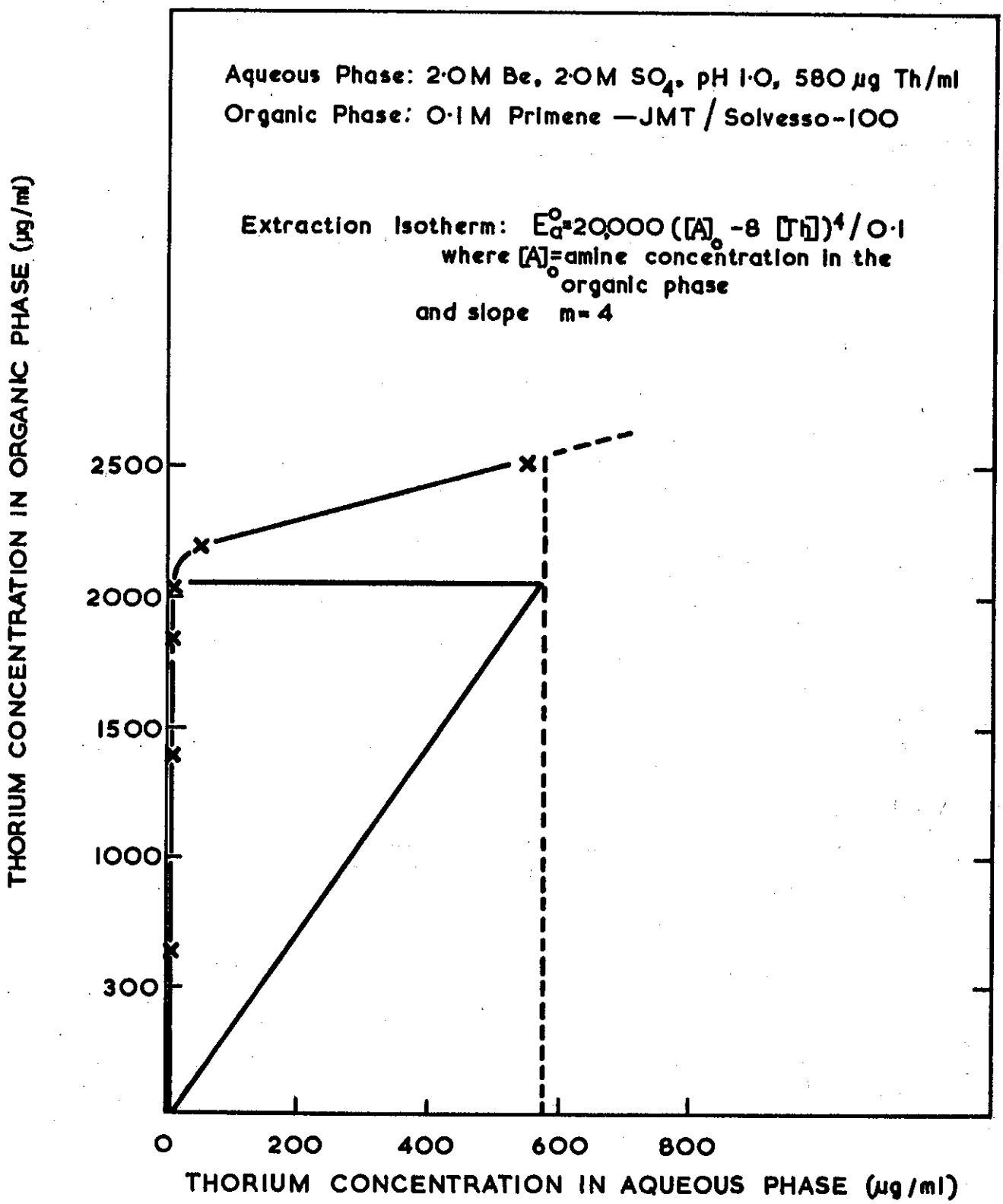

FIGURE 11. EXTRACTION ISOTHERM FOR THORIUM

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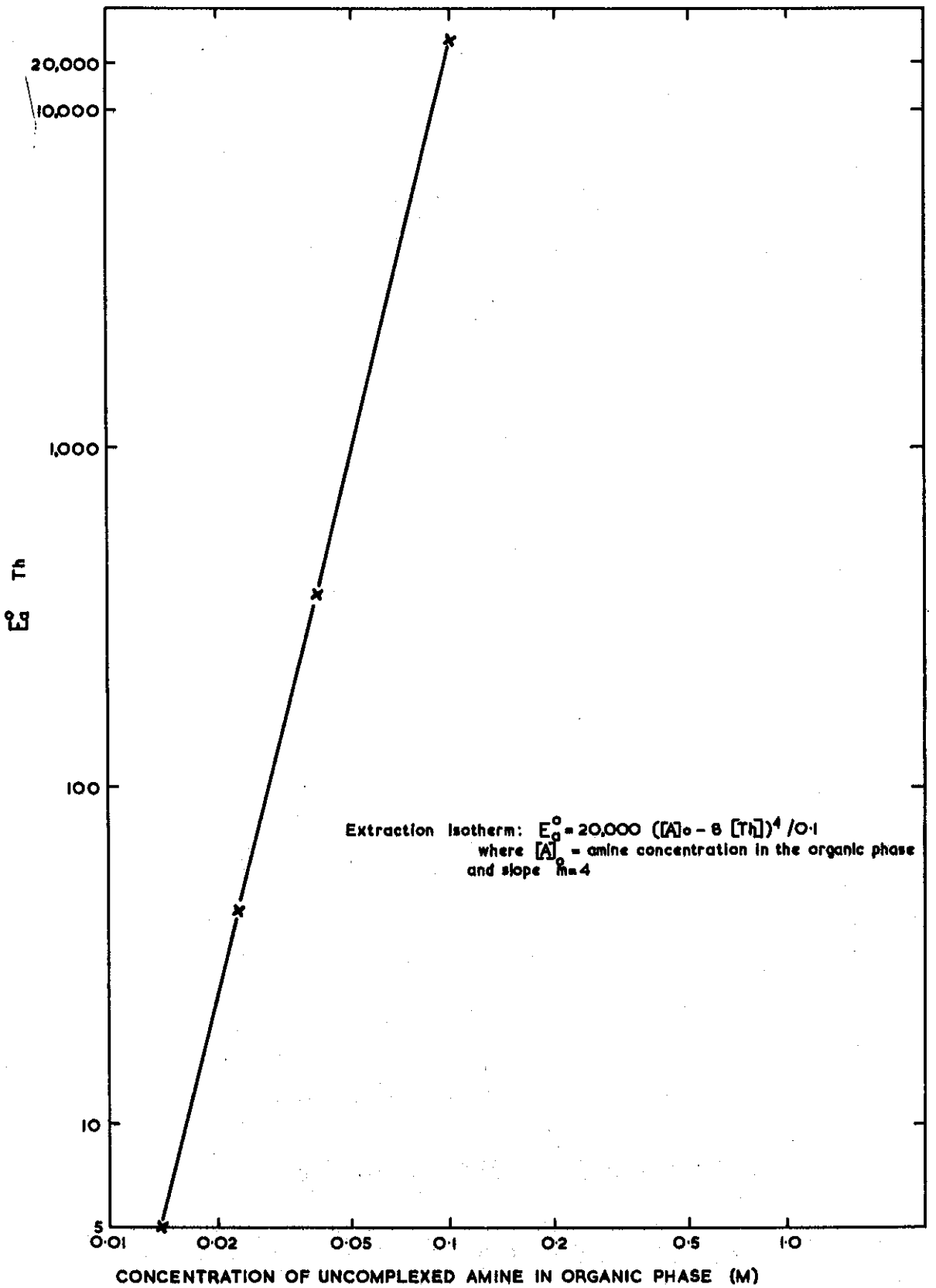

FIGURE 12. EXTRACTION OF THORIUM BY PRIMENE-JMT FROM SULPHATE SOLUTION: EFFECT OF UNCOMPLEXED AMINE CONCENTRATION

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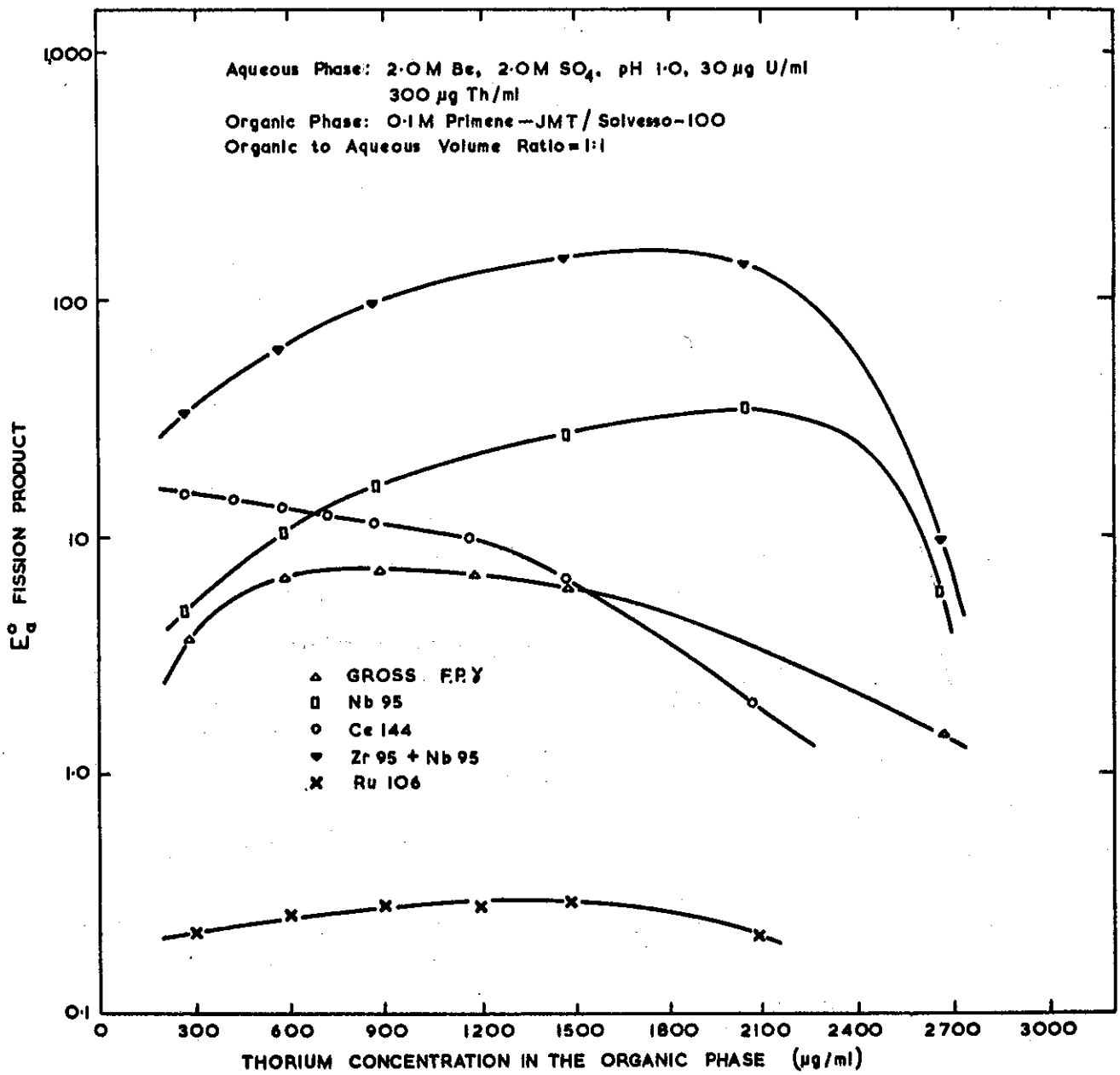

FIGURE 13. EXTRACTION OF FISSION PRODUCTS BY PRIMENE-JMT FROM BERYLLIUM SULPHATE SOLUTION: THE EFFECT OF THORIUM LOADING OF THE ORGANIC PHASE

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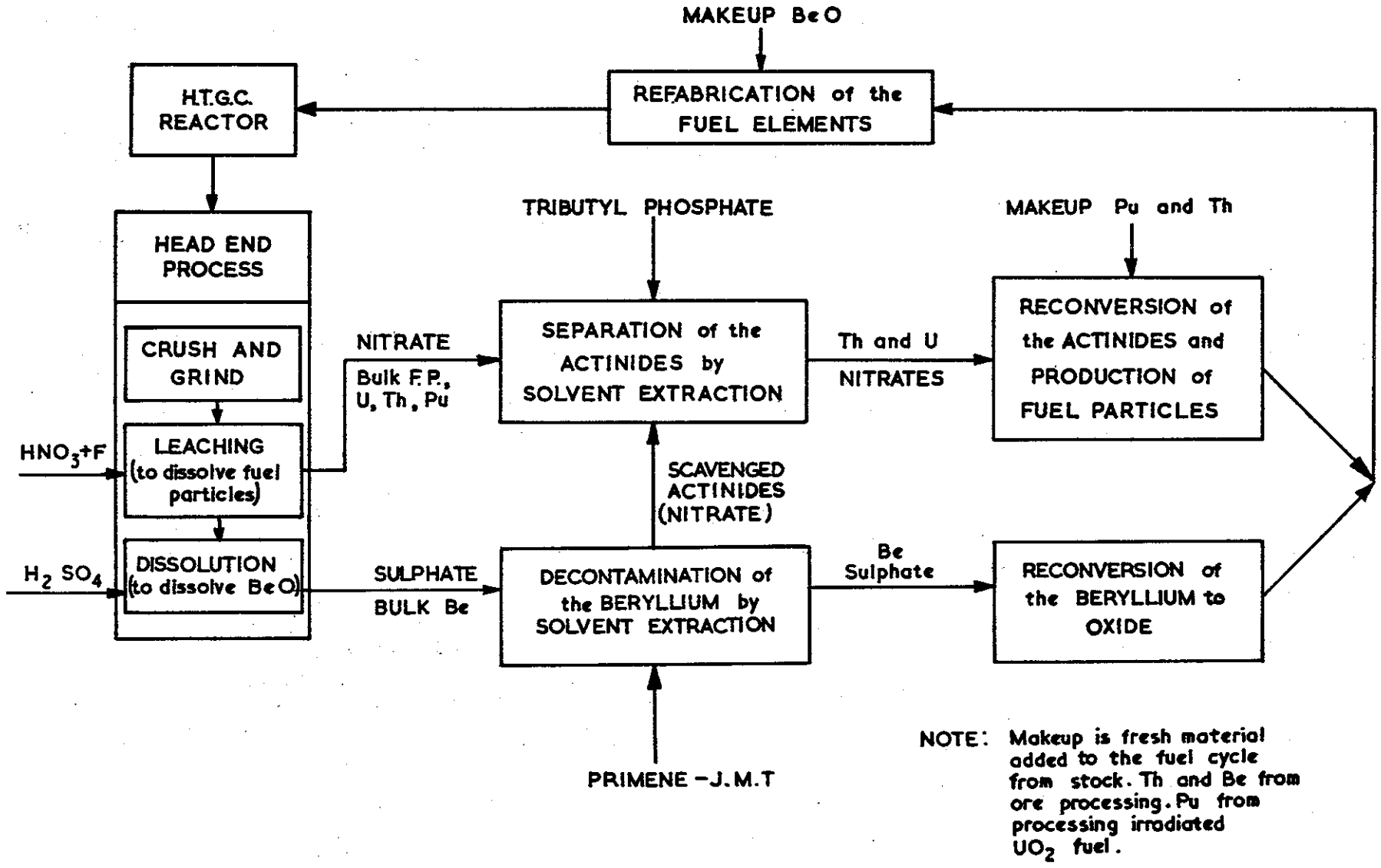

FIGURE 14. H.T.G.C.R. FUEL CYCLE

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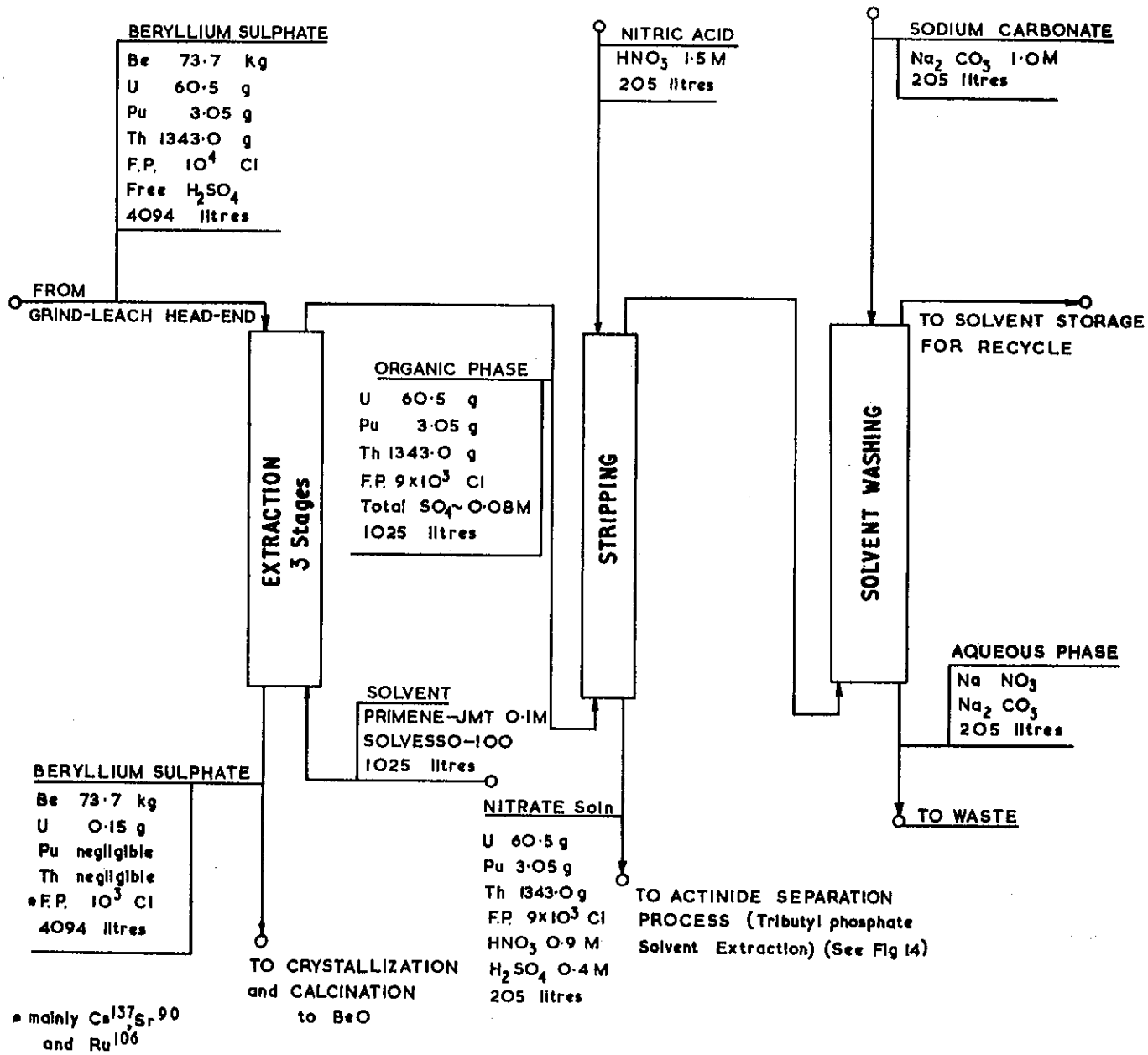

FIGURE 15. CHEMICAL FLOWSHEET FOR RECOVERY OF THE ACTINIDES AND PARTIAL DECONTAMINATION OF THE BERYLLIUM SULPHATE

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