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THE REPROCESSING OF HOMOGENEOUS BERYLLIUM–BASED REACTOR FUEL. A SUGGESTED SCHEME FOR THE SELECTIVE AQUEOUS DISSOLUTION OF THE MATRIX

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ABSTRACT

The matrix of a dilute homogeneous H.T.G.C. reactor fuel employing metallic beryllium as a moderator can be selectively dissolved by a caustic soda solution containing salicylate ion. At least 99 per cent. of the uranium and thorium can be recovered as insoluble solids, but in the case of irradiated material the uranium loss might be higher. Some decontamination of the resulting beryllium solution from fission products and Pa 233 can also be obtained. A tentative chemical flowsheet is proposed on the basis of the results obtained.

CONTENTS

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CONTENTS (continued)

1. INTRODUCTION

Homogeneous beryllium–based fuel in which the atomic ratio of U : Th : Be is of the order of 1 : 30 : 3000 may be processed by either completely dissolving the whole fuel element or by selectively dissolving the beryllium moderator, leaving the fertile and fissile material as solids.

If complete dissolution is used the resulting solution contains uranium at a very low concentration (c. 10^{-4} M) which has to be separated from a large excess of an inactive beryllium salt, and if the beryllium also has to be recovered, large volumes of the highly active solution have to be reprocessed. Alternatively, if the beryllium is not recovered, the waste solutions have a high salt content, which makes concentration difficult.

A selective dissolution of the beryllium matrix on the other hand would produce a concentrated uranium solution, containing most of the fission products. Subsequent recovery and decontamination of the beryllium would then allow the waste solutions to be concentrated for storage. Purification of the beryllium could be achieved by using simple processes, such as ion–exchange, which would otherwise be impossible because of the radiation levels.

Although there are various ways in which beryllium might be selectively removed from a metal system, the most obvious is to take advantage of its amphoteric nature by dissolving it in alkali. Goldowski (1945) reported that beryllium will not dissolve in boiling 3M caustic alkali solutions. Our preliminary experiments have not only confirmed this but have shown that the metal readily becomes passive in caustic alkali solutions less concentrated than 8M. Also there appears to be a critical temperature region in which the passive layer breaks down to allow the metal to dissolve vigorously and exothermically. This occurs from about 80 – 90 °C, depending on the alkali concentration and the initial condition of the metal surface. However, the beryllate solution formed is unstable to heat and deposits an insoluble form of beryllium hydroxide. Unless this can be prevented, alkali less concentrated than about 8M cannot be used as selective solvent for the metal.

2. PRELIMINARY EXPERIMENTS

It is well known that beryllium forms anionic chelate compounds with suitable ligands, for example oxalate ion (Sidgwick and Lewis 1926) and salicylate ion (Jones et al. 1930). In preliminary experiments using alkali concentrations below 8M, at temperatures near 100 °C, we found that addition of sufficient salicylate produced a clear solution, stable for several months at least; α – hydroxy β – naphthoate also produced a clear stable solution. Oxalate stabilized the solution temporarily, but precipitation occurred after a short time. Malonate had no effect.

Although the complexing agents were added in an attempt to stabilize the solution we found that under certain conditions they could increase the dissolving rate, presumably by preventing the formation of a passive layer on the metal. Their effectiveness in preventing passivity parallelled their effectiveness in stabilizing the beryllium solution, that is salicylate and α– hydroxy β– naphthoate were permanently effective, oxalate temporarily so, and malonate without effect.

This behaviour was reflected in the variations in the potential of a beryllium electrode immersed in alkali, which were produced when chelating agent was added to the solution. While potassium oxalate and salicylate both raised the electrode potential of the beryllium, the effect was greater and more permanent in the case of the salicylate. Oxalate increased the potential of the beryllium from its steady passive state of 0.56V to 0.75V in 2 to 3 minutes, the potential then slowly decreasing towards its original value. Further additions of oxalate gave a repetitive effect. Addition of salicylate increased the electrode potential to about 1.0V in about 5 minutes, but the potential continued to increase slowly to 1.45V after 24 hours. There was no collapse of the time–potential curve in the case of the salicylate.

Both sets of observations can be explained by assuming that a soluble beryllium complex is formed which removes or prevents the formation of the passive layer on the metal. The addition of salicylate produces a permanent change because the complex is stable in concentrated alkali. The effects produced by oxalate or malonate are transitory, probably because these ions are broken down more or less rapidly by alkali according to the reactions

(1) $(COONa)_2 \rightarrow Na_2CO_3 + CO$

(2) $CH_2(COONa)_2 + NaOH \rightarrow Na_2CO_3 + CH_3COONa$

A solution of caustic soda containing salicylate ion therefore appeared to be a promising reagent for the selective dissolution of Be from the metal fuel. This was tested in further experiments described in the remainder of this report.

3. DISSOLUTION OF BERYLLIUM IN SOLUTIONS OF SODIUM HYDROXIDE/SALICYLATE

3.1 Experimental

Dissolutions were made in standard Quickfit apparatus (Figure 1). Discs of beryllium, 1.85 cm in dia. x 0.32 cm thick, with a central hole, were fitted with Teflon washers and securing nut to a stainless shaft rotated in the boiling alkali at 200 r.p.m. The dissolution was followed by analysing samples withdrawn at suitable intervals. (Figure 1). After centrifuging, they were analysed colorimetrically by the method of Mustafin and Matveev (1958). Initial dissolving rates per unit area were calculated from the curves of weight loss versus time, (see Figures 2, 3, 4, and 5) and the geometric surface of the samp exposed. As a check, average dissolving rates were also calculated from the weight of the sample remai ing at the end of the experiment.

Analytical grade reagents were used except in the third series of dissolutions to test the effect of beryllium concentration on dissolving rate. There the required amount of moist Murex beryllium hydroxide was added to the solution of salicylic acid in caustic soda and the volume adjusted with demineralized water. Because of possible inhomogeneity in the beryllium hydroxide powder the solutions were standardized in each case.

3.2 Results and Discussion

3.2.1 Effect of alkali and salicylate on dissolving rate

In Tables 1, 2, and 3, alkali concentrations are expressed as "nominal", "total", and "free" respectively, these terms referring to initial concentrations in all cases. "Total alkali" is equal to the total concentration of Na^+ present, initially added as NaOH. "Nominal alkali" is the total alkali less the amount of salicylic acid added, assuming that only the $-COOH$ group is neutralized. "Free alkali" is the total alkali less the amount of salicylic acid added, assuming that both the phenol and the carbonyl groups are neutralized. In all runs except 14 and 15, the "free" alkali is a positive quantity. In 14 and 15 the values are negative.

Positive values of "free" alkali may be taken as a measure of the initial concentrations of OH^-

Figure 7 shows that the initial dissolution rates are directly proportional to free alkali above a threshold concentration of about 1M. The relation between total alkali and initial rate (Figure 8) shows a similar trend but the rate is lowered by increasing the salicylate concentration at the expense of the free alkali. When the initial rate is expressed as a function of initial salicylate for a given nominal alkali concentration, a maximum is found (Figure 6). The fall in rate at the higher salicylate concentration is at least partly caused by the buffering action of salicylate produced by the reaction

$$\text{NaOH} + \text{NaH Sal} \underset{\text{low pH}}{\overset{\text{high pH}}{\rightleftharpoons}} \text{Na}_2\ \text{Sal} + H_2O$$

The dissolving rate appears to be erratic in the absence of salicylate. Thus for practical purposes some uncomplexed salicylate ion must always be present, although the minimum concentration required is not known.

The few electrode potential measurements made suggest that the chelating agent acts on the surface layer on the metal. If this is so, probably only a small excess is required. In the present work the free salicylate concentration decreased during the experiment. Figure 6 shows that in the range of free alkali concentrations from 2 – 5 M an initial salicylate concentration of at least 0.4M is required to increase the initial dissolving rate but if the initial salicylate concentration is greater than 2M the initial rate is decreased even after allowance is made for the decrease in free alkali. The reason for this is not known.

3.2.2 Effect of beryllium concentration on dissolving rate

The rate diminishes as the reaction proceeds, even when free salicylate is present. This fall is not wholly caused by the drop in free alkali concentration. By adding beryllium salicylate at the start of the experiment, it can be shown that the rate is an inverse function of the concentration of beryllium present in solution. (See Figure 9).

3.2.3 Nature of the precipitate formed

Table 1 shows that precipitation occurs when insufficient salicylate is present. The results obtained by de Bruin, Kairaitis, and Temple (1961) imply that if sufficient ligand is present the beryllium should exist in strongly alkaline solutions almost entirely as the bis(salicylato) beryllium anion, and any uncomplexed beryllium in solution would almost certainly be in the form of the beryllate. The precipitate that forms in the presence of some salicylate could therefore be either beryllium hydroxide, formed by hydrolysis of the beryllate, or a mono-(salicylato) beryllium complex, which is known to be fairly insoluble (Jones et al. 1930). The chemical analysis of the precipitate was as follows:

	Be	Salicylate
Actual Analysis of Precipitate *	13.4%	0.4%
Calculated for Be Sal $2H_2O$	5.5%	72.9%
" " $Be(OH)_2\ 2H_2O$	14%	-

These results show that the precipitate was beryllium hydroxide, and this conclusion was confirmed by X-ray diffraction. Its pattern was very similar to that recorded by Seitz et al. (1950) for "β" -beryllium hydroxide.

3.2.4 Variations experienced with metal of different origin

The results of Table 1 were obtained with Péchiney metal extruded at A.E.R.E., Harwell, while those in Tables 2 and 3 were for Péchiney metal extruded at Lucas Heights. Samples from both sources appear to have similar, but not identical, chemical properties. For example, although the A.E.R.E. - extruded metal would dissolve readily in boiling 5M caustic soda, the Australian - extruded material would not. The addition of sufficient salicylate overcame the passivity in both cases, but to dissolve the Australian-made samples, higher concentrations of alkali and salicylate had to be used.

4. THE DISSOLUTION OF UBe_{13} AND $ThBe_{13}$ AND THEIR DISPERSIONS IN METALLIC BERYLLIUM

4.1 Experimental

The alloys, either as powder or compacted in a beryllium matrix, were boiled under reflux for a known time with caustic soda/salicylate solutions prepared as described in Section 3.1. After cooling, the solutions were centrifuged and the supernatant liquid removed with a Pasteur pipette.

The sludge was washed three times, the washings being separated in the same way. The combined liquid phases were then analysed for beryllium, and uranium or thorium. Beryllium analyses were made as before; thorium was determined colorimetrically using APANS (Fletcher 1957), uranium colorimetrically as isocyanate (Neitzel and Desesa 1957). The sludge was dissolved in 13M HNO_3 containing 0.05M fluoride. The resultant solution was also analysed for beryllium, uranium, and thorium as necessary.

4.2 Results and Discussion

Results of preliminary experiments are given in Table 4. The effects of alkali concentration and digestion-time on the dissolution of UBe_{13} and $ThBe_{13}$ powders are given in Tables 5 and 6 respectively. Figure 10 shows a dissolving rate curve for a compact, containing UBe_{13} and $ThBe_{13}$ in beryllium.

4.2.1 Dissolution of UBe_{13}

Beryllium was selectively dissolved from the UBe_{13} powder and from the compacted dispersion of UBe_{13} in beryllium using a solution containing salicylate in a free alkali concentration of 3-4M. The amount of uranium dissolved was found to increase with digestion-time; doubling the digestion-time trebled the uranium in solution. With the UBe_{13} powder, 99 per cent. of the beryllium was dissolved in 4 hours, together with 1 per cent. of the uranium. Figure 10 shows that less than 2 hours digestion will remove greater than 98 per cent. of the beryllium with a uranium loss of less than 1 per cent. The average dissolving rates observed for the compacts were between 6 and 10 mg $cm^{-2}\ min^{-1}$.

* From dissolution of Be in 5M NaOH containing salicylate to a final Be/Sal ratio of 1 : 0.3 .

4.2.2 Dissolution of $ThBe_{13}$

$ThBe_{13}$ powder, and the dispersion of $ThBe_{13}$ in Be both became passive in free-alkali concentrations of 3 and 4M, but not in 5M. The presence of the thorium appeared to diminish the rate of solution of the beryllium. Thorium losses appeared to be independent of digestion time and were low even after 7 hours. 98 per cent. of the beryllium was dissolved in 1 hour.

5. SELECTIVE REMOVAL OF BERYLLIUM FROM IRRADIATED SPECIMENS

During this part of the work the partitioning of the Pa and gross fission products between the alkaline solution and the metallic sludge was examined.

5.1 Experimental

Specimens of mixed UBe_{13} and $ThBe_{13}$ in beryllium in one case, and of $ThBe_{13}$ only in beryllium in the other, were prepared in the usual manner and irradiated in an average flux of 2×10^{12} n cm^{-2} sec^{-} for 25 days. They were then allowed to decay for periods from four to seven months. Each was treated as described in Section 4.1, but the equipment was located in a remote handling cell shielded with 4 inch lead walls. The apparatus is shown in Figures 11 and 12.

The alkaline solution from the selective dissolution step, and the acid solution obtained from the metallic sludge were both analysed for Be, U, and Th as described in the preceding sections. Pa was measured radiometrically using a method developed by Morgan (1961). Total γ counts and total β counts were registered by γ-scintillation and 2 π proportional counting respectively.

5.2 Results and Discussion

Details of the experiments are given in Table 7. The analytical results obtained are in Table 8, and the γ-spectrum analyses in Table 9.

5.2.1 Dissolution of irradiated $ThBe_{13}$/Be specimens

From the digestion of specimens B1, and B2 in a 5M NaOH/salicylate mixture it is evident that:

1. the matrix broke down rapidly,
2. little thorium entered the alkaline solution, (the loss of 3 per cent. for B 1 was probably in error because of an inefficient separation of the solid),
3. the beryllium recovery was good; for B2 it was probably nearer 99 per cent. than the 95 per cent. found for B1, and
4. the decontamination factor for Pa233 was about 500. Nearly all the activity in B1 and B2 arises from Pa233, very little being produced by the fission of U233.

5.2.2 Dissolution of irradiated UBe_{13}, $ThBe_{13}$/Be specimens

Some inferences can be made from Table 8, but the results of the uranium analyses are inconclusive. The matrix broke down readily, and the thorium lost to solution was about the same as for the $ThBe_{13}$/Be compacts. Beryllium removal appeared to be greater than 99 per cent.; the quantity of uranium lost to the alkaline solution appeared to be larger but uncertain. The apparent loss of 25 per cent. to solution would not have been expected from the previous work and may have been caused by poor solid/liquid separation. It was not caused by the formation of a soluble uranium carbonate complex by the carbonate present in the alkali. This is shown in the following table which gives the results of dissolutions of UBe_{13} powder in caustic soda/salicylate solutions containing known quantities of carbonate:

Na_2CO_3 Molarity (in the caustic soda-salicylate solution)	U Dissolved (after 1 hr digestion of UBe_{13} powder) $\mu g/ml$
0.54	42
0.29	33
0.04	29

The decontamination factor for Pa233 was at least an order of magnitude lower than in the case of the irradiated $ThBe_{13}$/Be specimens. The decontamination factor for gross γ and β emitters between the alkaline stream and the original sample was about 50. Because the quantities of protactinium and fission products present were small the accuracy obtainable with reasonable counting times was low.

6. GENERAL CONCLUSIONS

1. Beryllium will readily dissolve in caustic soda solutions containing salicylate ion.

2. Sufficient salicylate must be present at all times to complex the beryllium as the bis(salicylato) anion; this prevents precipitation of the insoluble hydroxide.

3. Neither thorium nor uranium readily dissolves in this reagent, which therefore offers a means of removing beryllium selectively from mixtures of these three metals.

4. Preliminary experiments on irradiated compacts of UBe_{13} and $ThBe_{13}$ in beryllium show that a good decontamination of the beryllium stream from Pa233 can be expected, and that some decontamination from fission products is also possible.

5. There is sufficient chemical evidence to warrant further work to discover

   (i) the effect of irradiation on the dissolution of the uranium and thorium,

   (ii) the precise decontamination factors that can be obtained, and

   (iii) the identity of the fission products entering the alkaline solution.

7. A TENTATIVE FLOWSHEET

If some assumptions are made about the type of fuel to be processed, a tentative chemical flowsheet can be drawn up from the results presented. (See Figure 12).

Further work on alternative methods of separating the beryllium from the alkaline solution seems desirable, if development of metal-based fuels continues. Experiments with more highly irradiated samples would also lead to more accurate figures for the decontamination factors obtainable.

8. ACKNOWLEDGMENTS

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TABLE 1

DISSOLUTION OF BRITISH-EXTRUDED PECHINEY BERYLLIUM METAL IN CAUSTIC SODA AND CAUSTIC SODA-SALICYLATE SOLUTIONS

Run No.	Total Alkali Na^+	Initial Salicylate Sal''	Nominal Alkali	Initial Free Alkali OH'	Initial Dissolving rate $mg\ cm^{-2}\ min^{-1}$	Final Mole Ratio Salicylate:Be	Appearance of Final Solution
17	1.0 M	nil	1.0 M	1.0 M	0.01	0 : 1	milky white precipitate forme
18	1.4	0.4 M	1.0	0.6	1.3	2.0 : 1	slight turbidity
16	1.8	0.8	1.0	0.2	0.9	2.4 : 1	v. slight turbidity
39	1.8	0.8	1.0	0.2	2.6	1.7 : 1	slight turbidity
15	2.2	1.2	1.0	−0.2	1.7	2.5 : 1	clear solution
14	2.6	1.6	1.0	−0.6	2.2	4.5 : 1	clear solution
23	3.0	nil	3.0	3.0	0.16	0 : 1	milky white precipitate
22	3.4	0.4	3.0	2.6	3.1	0.6 : 1	cloudy
21	3.8	0.8	3.0	2.2	4.8	1.1 : 1	cloudy
20	4.2	1.2	3.0	1.8	2.6	1.6 : 1	very cloudy
19	4.6	1.6	3.0	1.4	2.7	2.1 : 1	slightly cloudy
31	4.0	nil	4.0	4.0	4.6	0 : 1	precipitate
32	4.4	0.4	4.0	3.6	7.7	0.7 : 1	precipitate
33	4.8	0.8	4.0	3.2	9.0	1.4 : 1	less precipitate
34	5.2	1.2	4.0	2.8	7.6	1.7 : 1	very slight precipitate
40	5.2	1.2	4.0	2.8	14.6	2.2 : 1	clear
35	5.6	1.6	4.0	2.4	11.0	1.9 : 1	very slight precipitate
41	5.6	1.6	4.0	2.4	11.0	2.9 : 1	clear solution
42	6.0	2.0	4.0	2.0	9.3	3.0 : 1	clear solution straw-coloure
43	6.0	2.0	4.0	2.0	6.1	5.0 : 1	clear solution
26	5.0	nil	5.0	5.0	1.4	0 : 1	heavy white precipitate
27	5.4	0.4	5.0	4.6	11.4	0.5 : 1	large precipitate white
28	5.8	0.8	5.0	4.2	14.3	0.9 : 1	some precipitate
29	6.2	1.2	5.0	3.8	15.7	1.3 : 1	small precipitate
30	6.6	1.6	5.0	3.4	9.4	1.8 : 1	slight precipitate
36	6.6	1.6	5.0	3.4	14.3	1.8 : 1	very slight precipitate
37	7.0	2.0	5.0	3.0	5.3	3.0 : 1	clear solution
38	7.4	2.4	5.0	2.6	3.0	4.4 : 1	clear solution

TABLE 2

DISSOLUTION OF AUSTRALIAN-EXTRUDED PECHINEY
BERYLLIUM IN CAUSTIC SODA AND CAUSTIC SODA – SALICYLATE SOLUTIONS

Part	Run No	Total Na^+	Initial Sal''	Initial free Alkali OH'	Final Be	Final Mole Ratio Sal'' : Be^{++}	Total Dissolution Time, Minutes	Remarks
A	44	8.0M	1.5M	5.0M	0.22M	1.23 : 1	65	Straw-coloured solution. No precipitate
	45	5.8	6.4	5.0	0.58	0.70 : 1	12	Greyish solution: No white precipitate Grey metallic sludge on standing
	46	9.0	0.5	8.0	0.71	0.70 : 1	15	Breakaway reaction at 90°C Final solution clear, no turbidity
	47	8.5	0.025	8.0	0.67	0.50 : 1	15	
B	48	8.0	NIL	8.0	0.70	–	10	Breakaway reaction at 90°C leaving greyish solution which gave a grey metallic sludge on standing
	49	3.0	NIL	3.0	negligible	–		Passivated immediately
	50	5.0	NIL	5.0	v. small	–		Initial rapid reaction at 91°C followed by passivation after 10 minutes. No white precipitate Grey sludge
	51	7.0	NIL	7.0	1.4	–	8	Rapid reaction at 99°C. No passivation No white precipitate
C	52	5.0	(i)NIL at zero time	5.0	0.90	0.42 : 1 (final)	480	(i) Be passivated
			(ii)0.125 at 10 min.					(ii) Depassivation occurring – some reaction
			(iii)0.250 at 40 min.					(iii) Rapid breakaway reaction on exposure of Be to air and replacement in dissolver
			(iv) 0.375 at 60 min.					(iv) White precipitate formed (0.15g of Be) on breakaway. This precipitate would not dissolve in NaOH – salicylate. This precipitate was removed for examination and analyses.

TABLE 3

EFFECT OF BERYLLIUM CONCENTRATION ON DISSOLVING RATE OF BERYLLIUM METAL IN CAUSTIC SODA – SALICYLATE SOLUTIONS

Run No.	Total Alkali Na^+	Free Alkali OH^-	Total Salicylate Sal	Free Salicylate Sal''	Initial Beryllium Be^+	Final Beryllium Be^{++}	Total Initial Volume ml	Final Volume ml	Dissolving rate mg cm^{-2} min^{-1}	Final Ratio Sal'' : Be^{++}	Observations
53 Control	6.4M	4.0M	1.2M	1.2M	NIL	1.70M	200	185	15.00	0.76 : 1	Turbid, greyish solution
54	6.4	4.0	2.8	1.2	0.8M	1.80	200	186	5.40	1.56 : 1	Clear solution
56	8.0	4.0	3.0	1.0	1.0	2.10	200	165	0.98	1.72 : 1	Solution clear but grey
57	9.0	4.0	4.0	1.0	1.5	1.90	200	170	1.00	2.5 : 1	Turbid, grey solution
58	7.0	4.0	2.0	1.0	0.5	1.85	200	180	5.14	1.2 : 1	Clear solution
59 Control	6.0	4.0	1.0	1.0	NIL	1.50	200	180	13.10	0.74 : 1	Turbid with dark precipitate of metal
60	8.0	4.0	3.0	1.0	1.0	1.66	200	165	1.27	2.19 : 1	Solution clear but grey
61	9.0	4.0	4.0	1.0	1.5	1.60	200	170	0.30	2.94 : 1	Solution clear but yellow

TABLE 4

PRELIMINARY TESTS: DISSOLUTION OF A UBe_{13} AND A $U,ThBe_{13}$ DISPERSION IN A BERYLLIUM MATRIX IN CAUSTIC SODA – SALICYLATE SOLUTION

Specimen Description	Initial Alkali Molarity		Initial Salicylate Molarity	Beryllium Dissolved		Uranium Dissolved		Thorium Dissolved		Total Digestion Time Minutes	Remarks and Approximate Rate mg cm^{-2} min^{-1}
	Nominal	Free		mg	%	mg	%	mg	%		
Cylinder. Hot Pressed UBe_{13} dispersion in Be matrix 0.4" dia. x 0.5" length	5	3.65	1.35	1200	83	1.4	0.23	not present		70	No passivation 6.0
Disc. Hot Pressed $U,ThBe_{13}$ dispersion in a Be metal matrix ½" dia. x ⅛" thick	5	3.0	2.0	356	15	1.5	4.0	1.5	0.2	320	Specimen passivated slowly towards end of digestion time 0.5

TABLE 5

THE DISSOLUTION OF UBe_{13} IN CAUSTIC SODA – SALICYLATE SOLUTION

Run No.	Initial Free Alkali	Initial Salicylate	Initial Mass of UBe_{13} mg	Analyses (Total Present) Alkaline Dissolution/Acid Dissolution				U Loss to Alkaline Solution %	Be Recovery %	Digestion Time Minutes
				U mg	Be mg	U mg	Be mg			
1	3.0M	1.3M	355	0.5	91.4	220	14.6	0.25	85	60
2	3.0	1.3	355	4.5	80	238	15.0	2.0	84	120
3	5.0	1.8	353	3.0	92	250	17.5	1.0	85	120
4	5.0	1.5	457	2.25	147	301	1.7	0.7	99	240
5	5.0	1.5	472	7.75	149	305	1.7	2.4	99	420

TABLE 6

THE DISSOLUTION OF $ThBe_{13}$ IN A CAUSTIC SODA – SALICYLATE SOLUTION

Run No.	Initial Free Alkali	Initial Salicylate	Initial Mass of $ThBe_{13}$ mg	Analyses (Total Present) Alkaline Dissolution/Acid Dissolution				Th Loss to Alkaline Solution %	Be Recovery %	Digestion Time Minutes
				Th mg	Be mg	Th mg	Be mg			
6	3.0M	1.3M	349	trace	50	135*	54	v. low	50	120 passivation occurred
7	4.4	2.0	349	9	23	N.D.	78	3	23	120 passivation occurred after 60 minutes
8	4.6	1.8	351	3	102	235	1.3	1.0	98	65
9	5.0	1.5	474	0.5	171	290	3.5	0.2	98	240
10	5.0	1.5	333	0.5	110	210	2.6	0.3	98	420

* Th lost in acid dissolution due to precipitation of Th F_4 insoluble in acid

TABLE 7

THE DISSOLUTION OF IRRADIATED FUEL SPECIMENS IN CAUSTIC SODA – SALICYLATE SOLUTION: EXPERIMENTAL CONDITIONS

Specimen No.	Initial Composition			Cooling Time Weeks	Initial Free Alkali conc.	Initial Salicylate conc.	Digestion Times		Initial Acid Concentration	Initial Fluoride ion Concentration
	U mg	Th mg	Be mg				Alkali (hr)	Acid (hr)		
B1	NIL	431	2149	16	5.0 M	1.5 M	4.0	3	13.0 M	0.05 M
B2	NIL	427	2133	20	5.0	1.5	4.0	6	13.0	0.05
A1	224	224	2232	25	5.0	1.5	4.5	1.5	13.0	0.05
A2	222	222	2216	29	5.0	1.5	4.0	1.5	13.0	0.05

Each specimen was irradiated for 25 days in a 2×10^{12} n cm^{-2} sec^{-1} thermal flux.

TABLE 8

ANALYTICAL RESULTS: DISTRIBUTION OF U, Th, AND ACTIVITY AFTER DISSOLVING IRRADIATED FUEL SPECIMENS IN CAUSTIC SODA – SALICYLATE SOLUTION

Specimen No.	Sample		Constitution of Total Volume from Analyses						Decontamination Factor for Be with Respect to			U Loss %	Th Loss %	Be Recovery %
	No.	Type	Total γ counts/min	Total β counts/min	Pa233 counts/min	U mg	Th mg	Be mg	Total γ	Total β	Pa233			
B1 $ThBe_{13}/Be$	1	A	4.4×10^{6}	5.5×10^{6}	7.2×10^{6}	Not present	12	Not done	340	350	320	Not present	3	95
	2	B	1.5×10^{9}	1.9×10^{9}	2.3×10^{9}	,,	N.D.	117						
B2 $ThBe_{13}/Be$	1	A	4.4×10^{6}	1.8×10^{6}	5.4×10^{5}	,,	1	Not done	250	800	2000	,,	1/4	99
	2	B	1.1×10^{9}	1.4×10^{9}	1.1×10^{9}	,,	N.D.	22						
A1 $UThBe_{13}/Be$	1	A	1.1×10^{7}	9.9×10^{6}	4.5×10^{5}	Not detected insufficient sample	1.5	Not done	12	65	6	probably low	1/4	99
	2	B	1.3×10^{8}	6.5×10^{8}	2.7×10^{6}			22						
A2 $UThBe_{13}/Be$	1	A	1.0×10^{7}	1.4×10^{7}	6.1×10^{6}	53	84	Not done	47	70	40	* 25	* 40	99
	2	B	4.7×10^{8}	9.7×10^{8}	2.2×10^{8}			18						

A Alkali/salicylate solution

B Nitric acid solution

* the reason for these large "losses" is not known but they possibly arise from a poor solid/liquid separation

TABLE 9

γ – SPECTRUM ANALYSIS OF ALKALINE AND ACID

SOLUTIONS FROM THE DISSOLUTION OF SPECIMEN A 1

Peak Energy MeV	Count 14/3/61	Count 24/4/61	Half Life	Suggested Identification
0.05	106 [7900]	94 [2862]	long [28d]	[Pa 233]
0.12	306	179	60d	
0.21	131	132	long	
0.33	[2956]	[1006]	[28d]	[Pa 233]
0.34	200	200	long	
0.43	67	40	65d	
0.50	[276]	[193]	[110d]	[Ru 106]
0.54	225	136	70d	Ru
0.69	110	104	long	
0.76	[1105]	[705]	[70 d]	[Zr95]

The figures in square brackets are from analyses of the nitric acid dissolution. Cs 137 could be expected in the alkaline solution but was not detected.

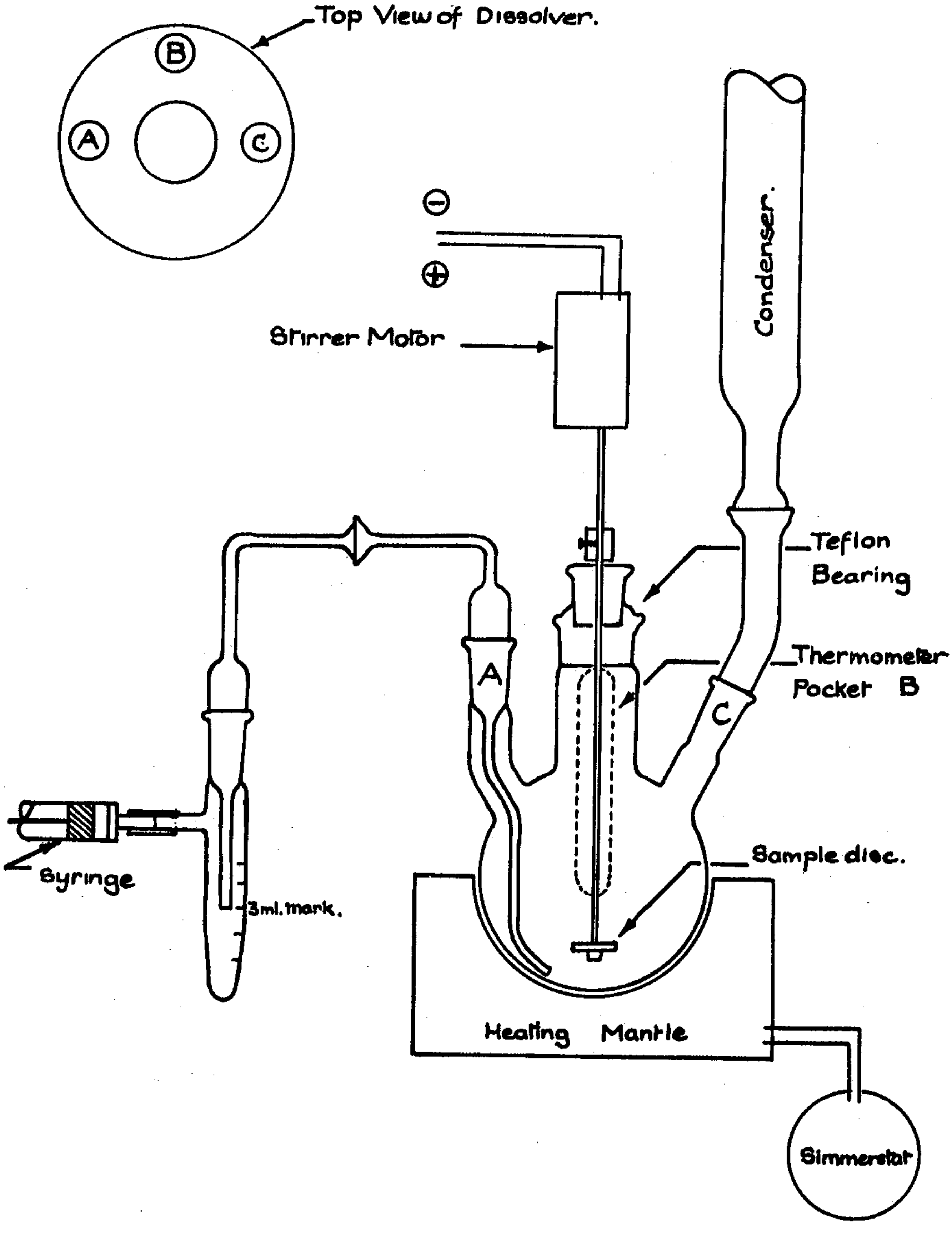


Fig 1. ~ GLASS DISSOLVER. ~ Scale :- Half-size.

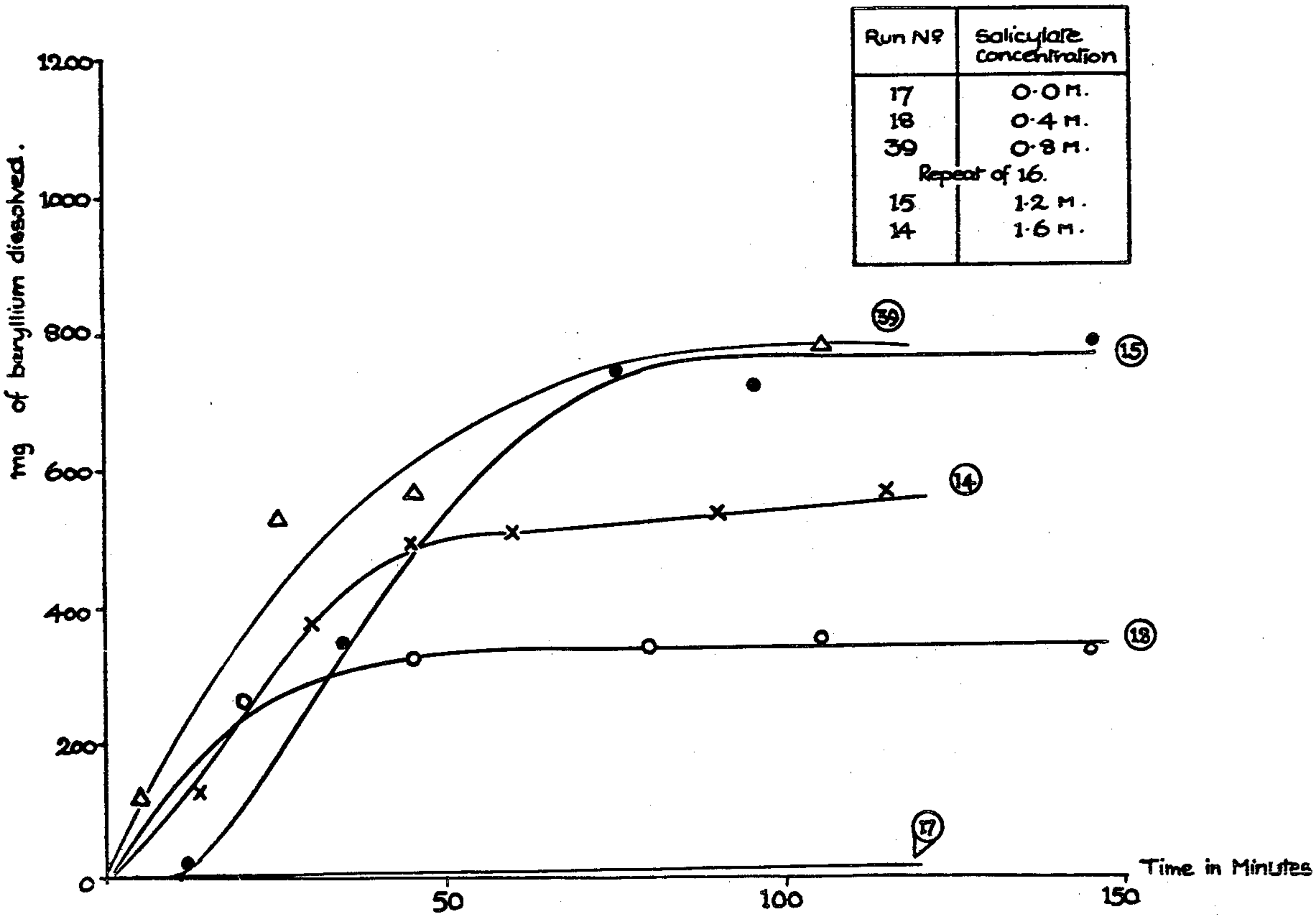


Fig 2 DISSOLUTION CURVES FOR BERYLLIUM METAL IN 1·0 M. (NOMINAL) NaOH SOLUTION.

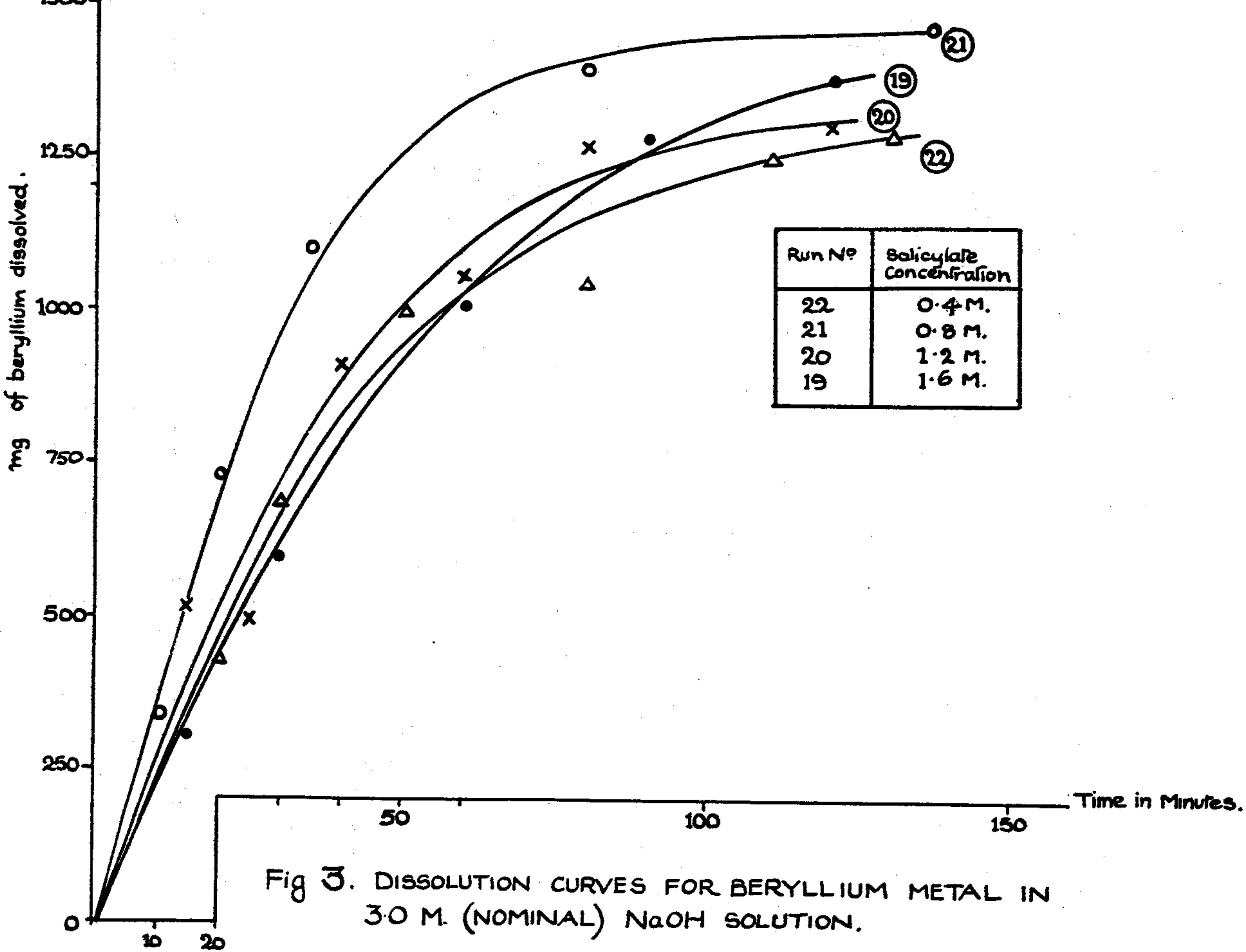


Fig 3. DISSOLUTION CURVES FOR BERYLLIUM METAL IN 3·0 M. (NOMINAL) NaOH SOLUTION.

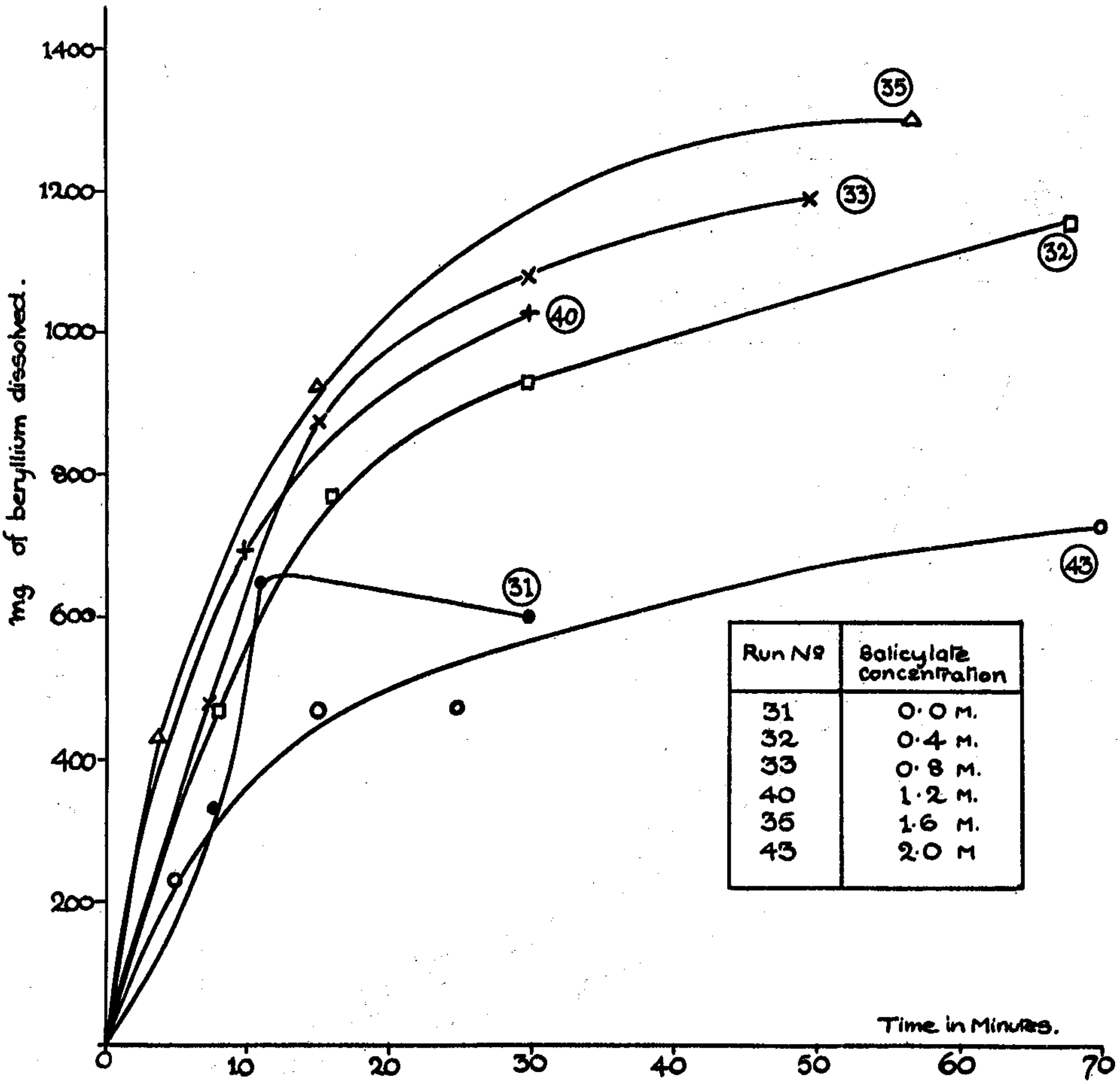


Fig 4. DISSOLUTION CURVES FOR BERYLLIUM METAL IN 4·0 M. (NOMINAL) NaOH SOLUTION.

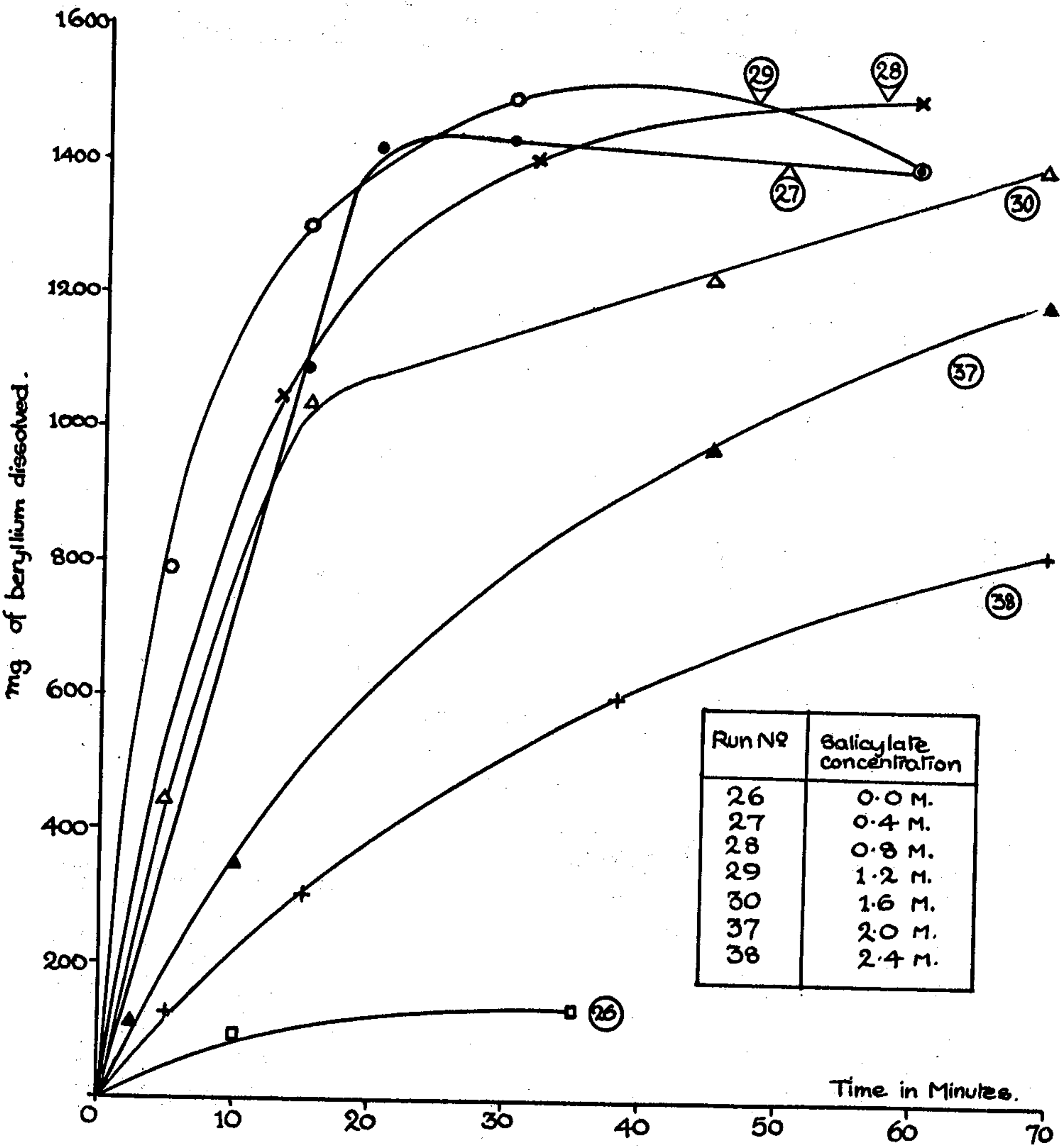


Fig 5 DISSOLUTION CURVES FOR BERYLLIUM METAL IN 5·0 M. (NOMINAL) NaOH SOLUTION.

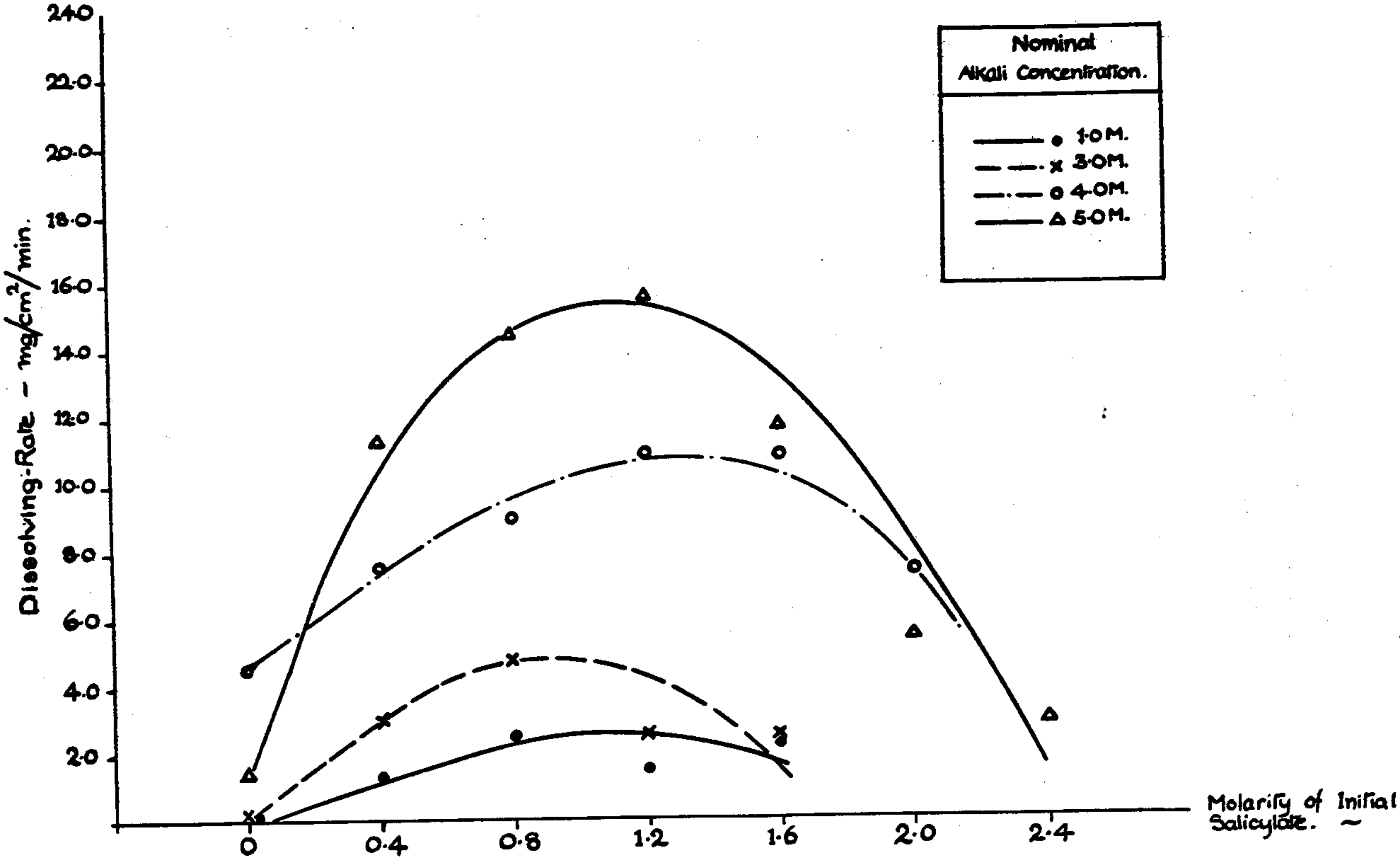


Fig 6. EFFECT OF INITIAL SALICYLATE CONCENTRATION ON THE DISSOLUTION OF BERYLLIUM METAL IN ALKALI-SALICYLATE SOLUTION.

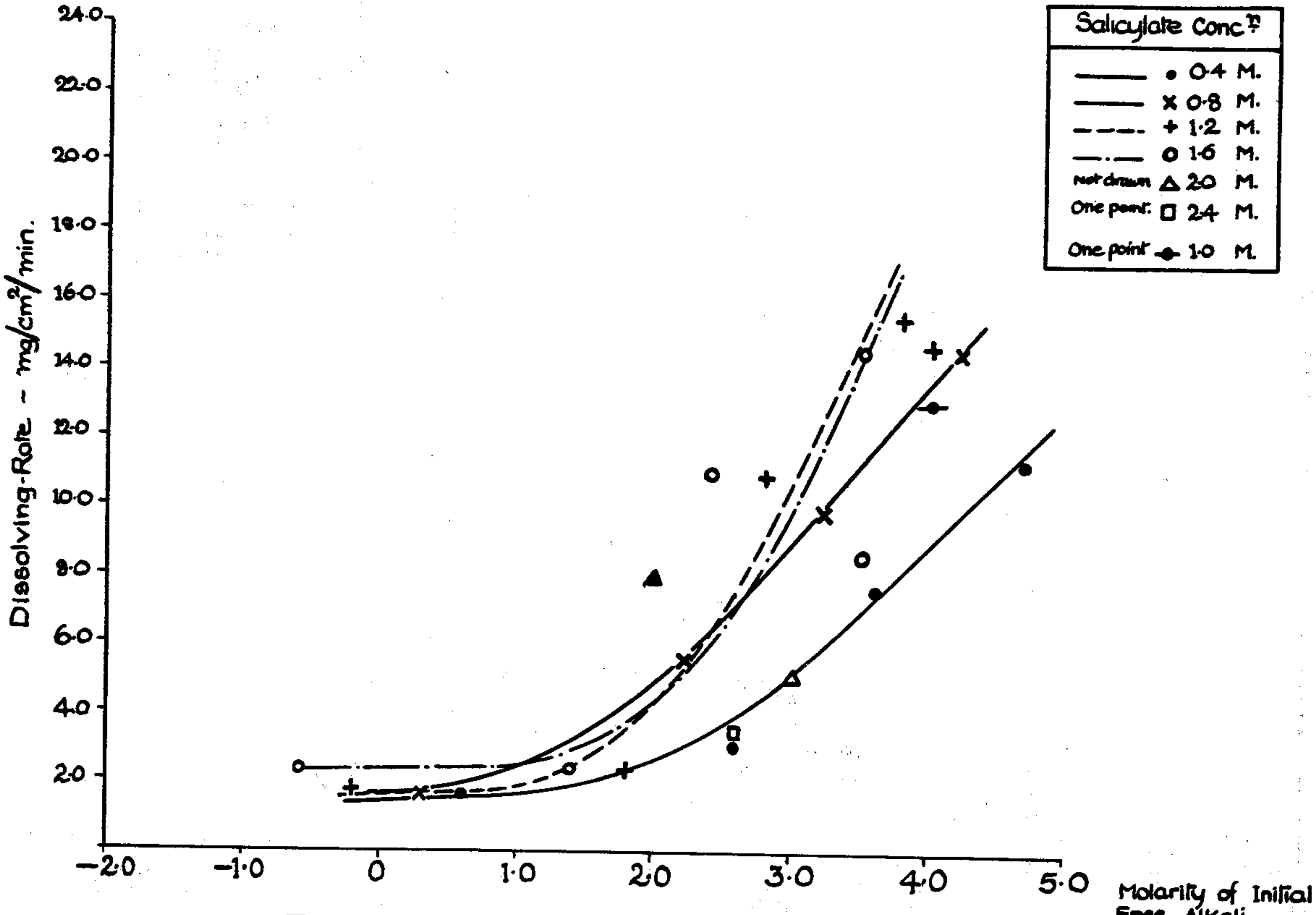


Fig 7. EFFECT OF FREE ALKALI ON THE DISSOLUTION OF BERYLLIUM METAL IN ALKALI-SALICYLATE SOLUTION.

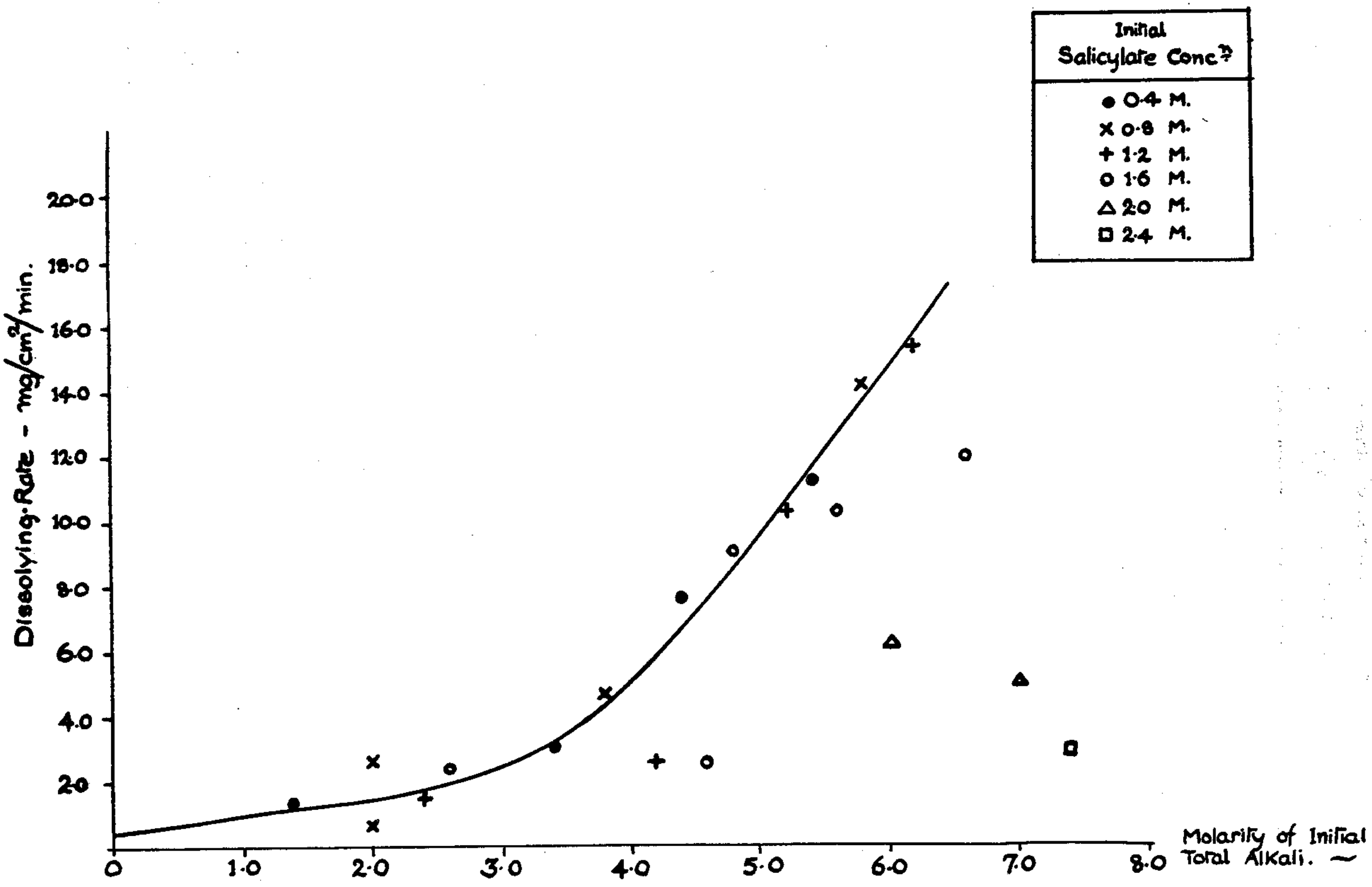


Fig 8. EFFECT OF TOTAL ALKALI ON THE DISSOLUTION OF BERYLLIUM METAL IN ALKALI-SALICYLATE SOLUTION.

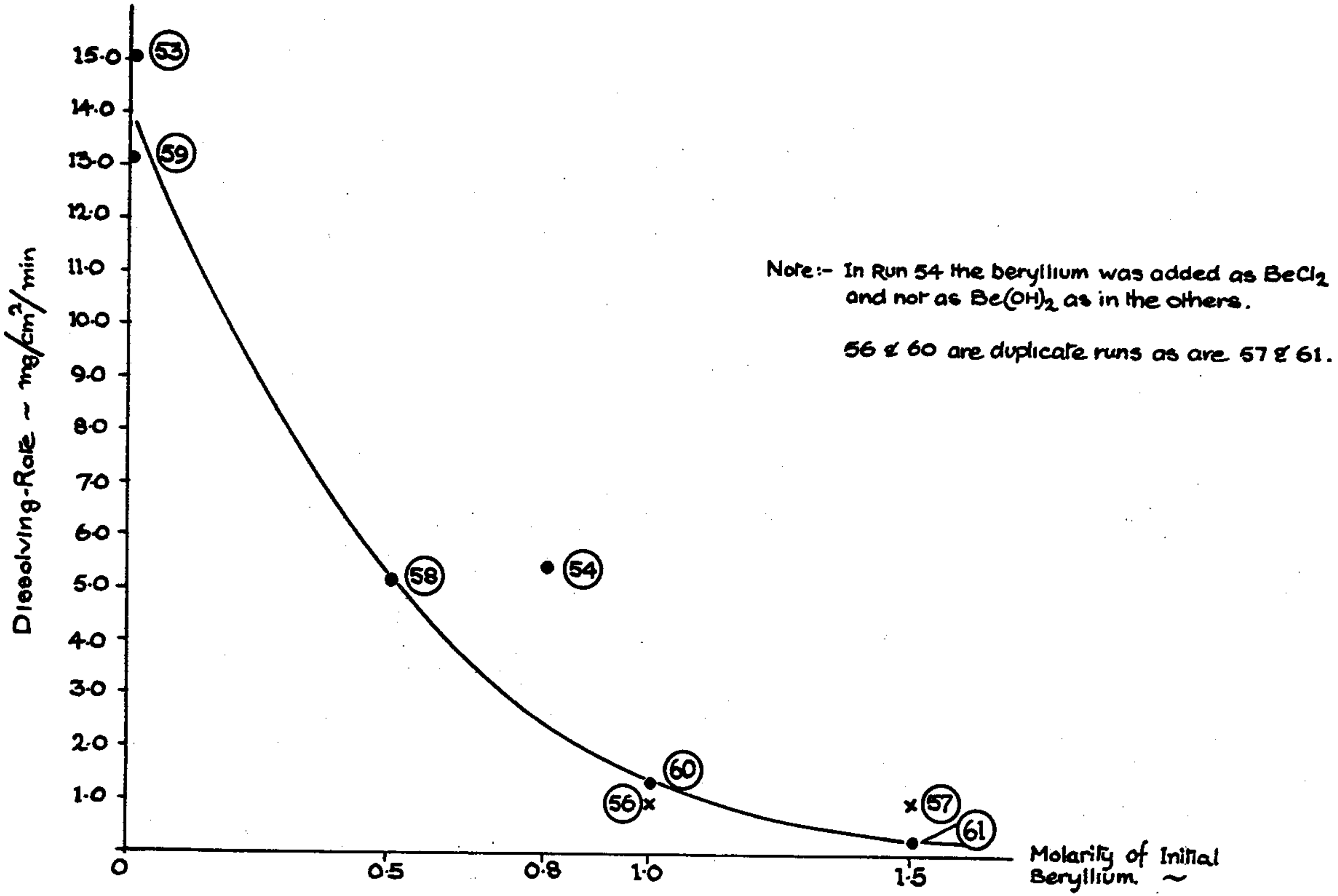
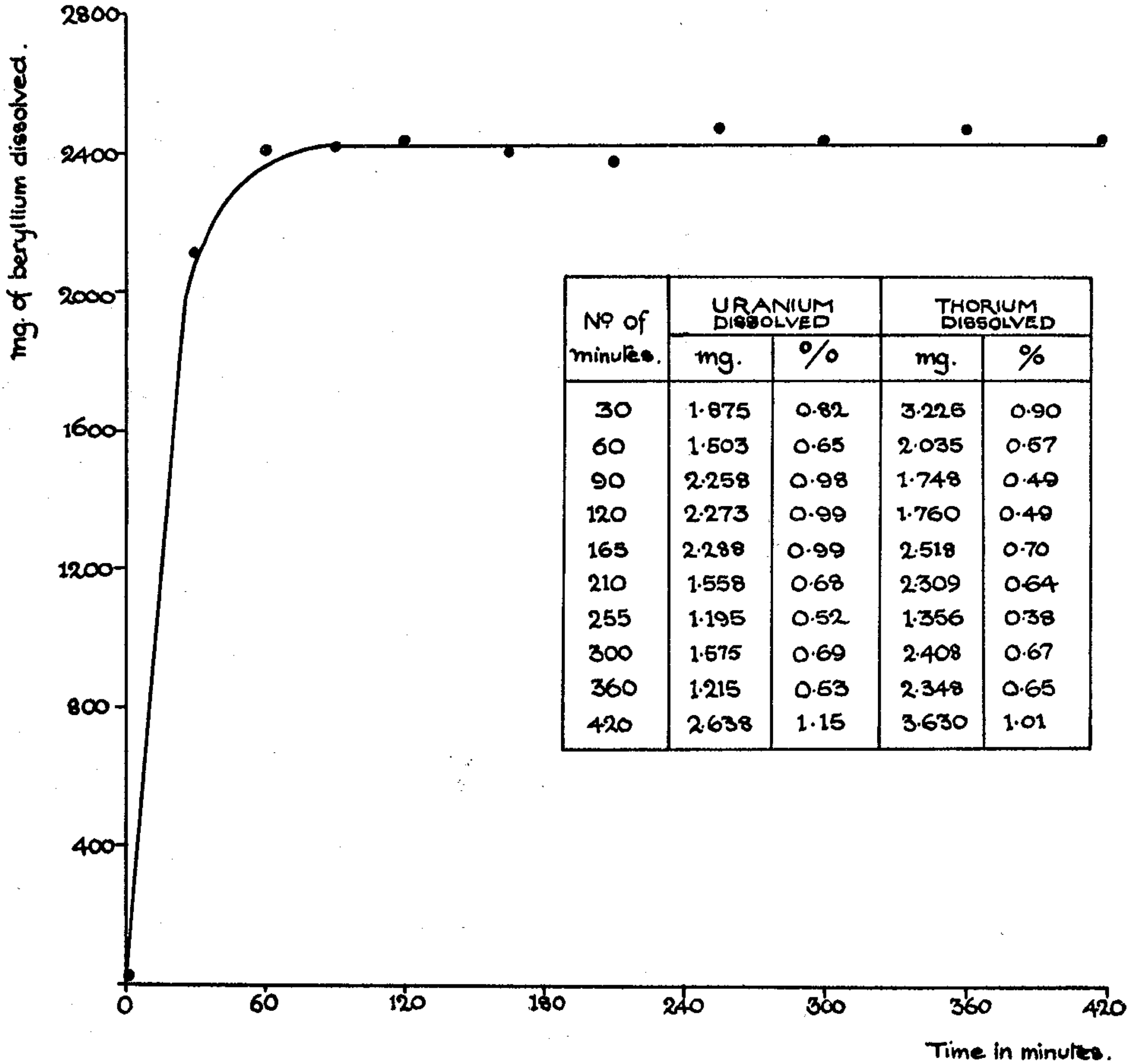
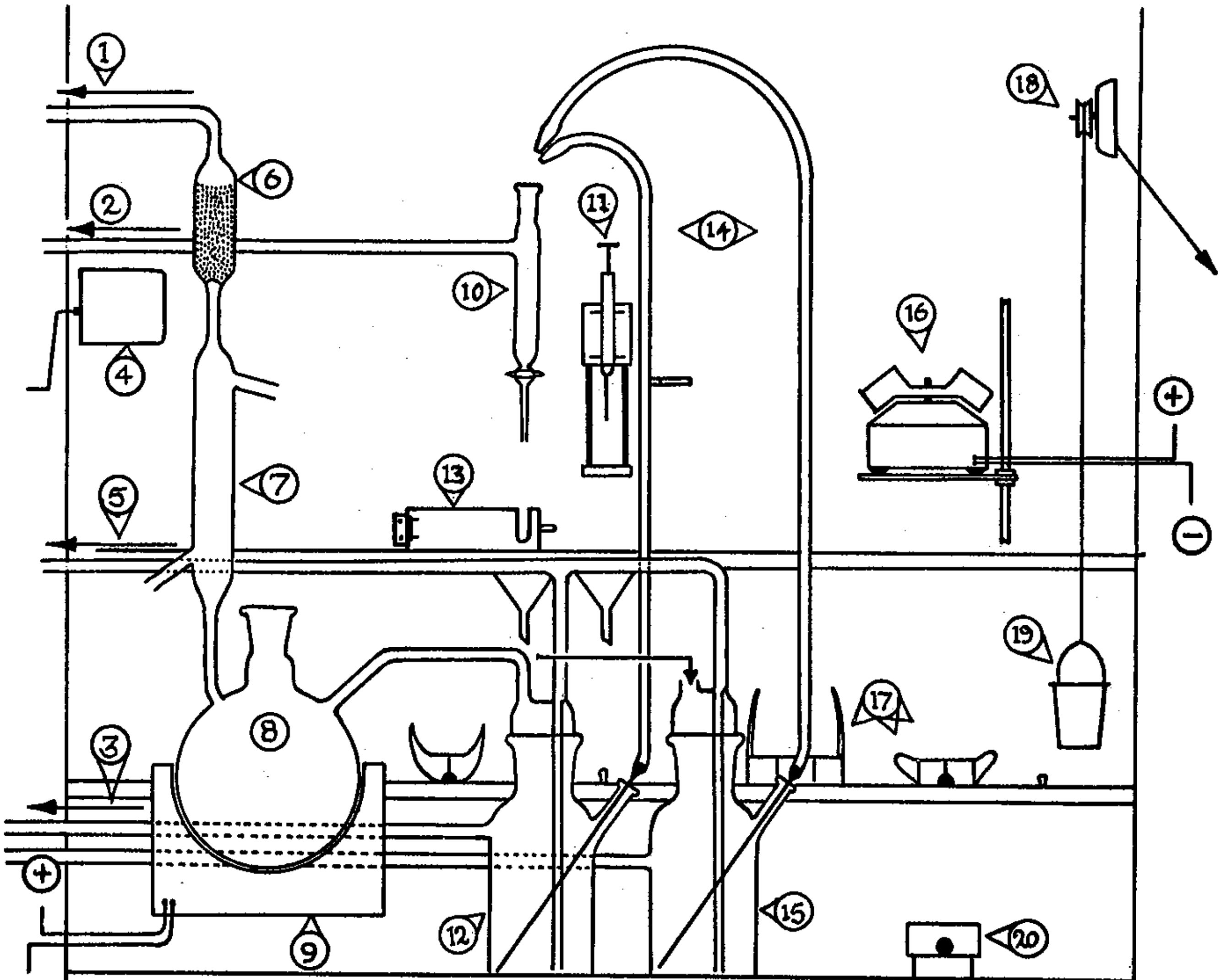


Fig 9. EFFECT OF BERYLLIUM CONCENTRATION ON THE DISSOLUTION OF BERYLLIUM METAL IN ALKALI-SALICYLATE SOLUTION.



Nº of minutes.	URANIUM DISSOLVED mg.	URANIUM DISSOLVED %	THORIUM DISSOLVED mg.	THORIUM DISSOLVED %
30	1·875	0·82	3·226	0·90
60	1·503	0·65	2·035	0·57
90	2·258	0·98	1·748	0·49
120	2·273	0·99	1·760	0·49
165	2·288	0·99	2·518	0·70
210	1·558	0·68	2·309	0·64
255	1·195	0·52	1·356	0·38
300	1·575	0·69	2·408	0·67
360	1·215	0·53	2·348	0·65
420	2·638	1·15	3·630	1·01

Fig 10 DISSOLUTION CURVE FOR AN INDIVIDUAL SPECIMEN OF UBe_{13}/$ThBe_{13}$/Be. IN CAUSTIC SODA - SALICYLATE SOLUTION.



KEY —

1. Outlet to stack.
2. & 3. Vacuum lines.
4. Radiation monitor head.
5. Active waste lines.
6. Packed Si gel tube.
7. Water condenser.
8. Dissolver
9. Heating mantle
10. Sample dispenser
11. Sampling syringe
12. Precipitator
13. Hinged centrifuge-cone holder.
14. Sampling lines
15. Conditioner
16. Centrifuge on swinging bracket.
17. Tong-head change stations.
18. Pulley
19. Specimen hoist.
20. Vice

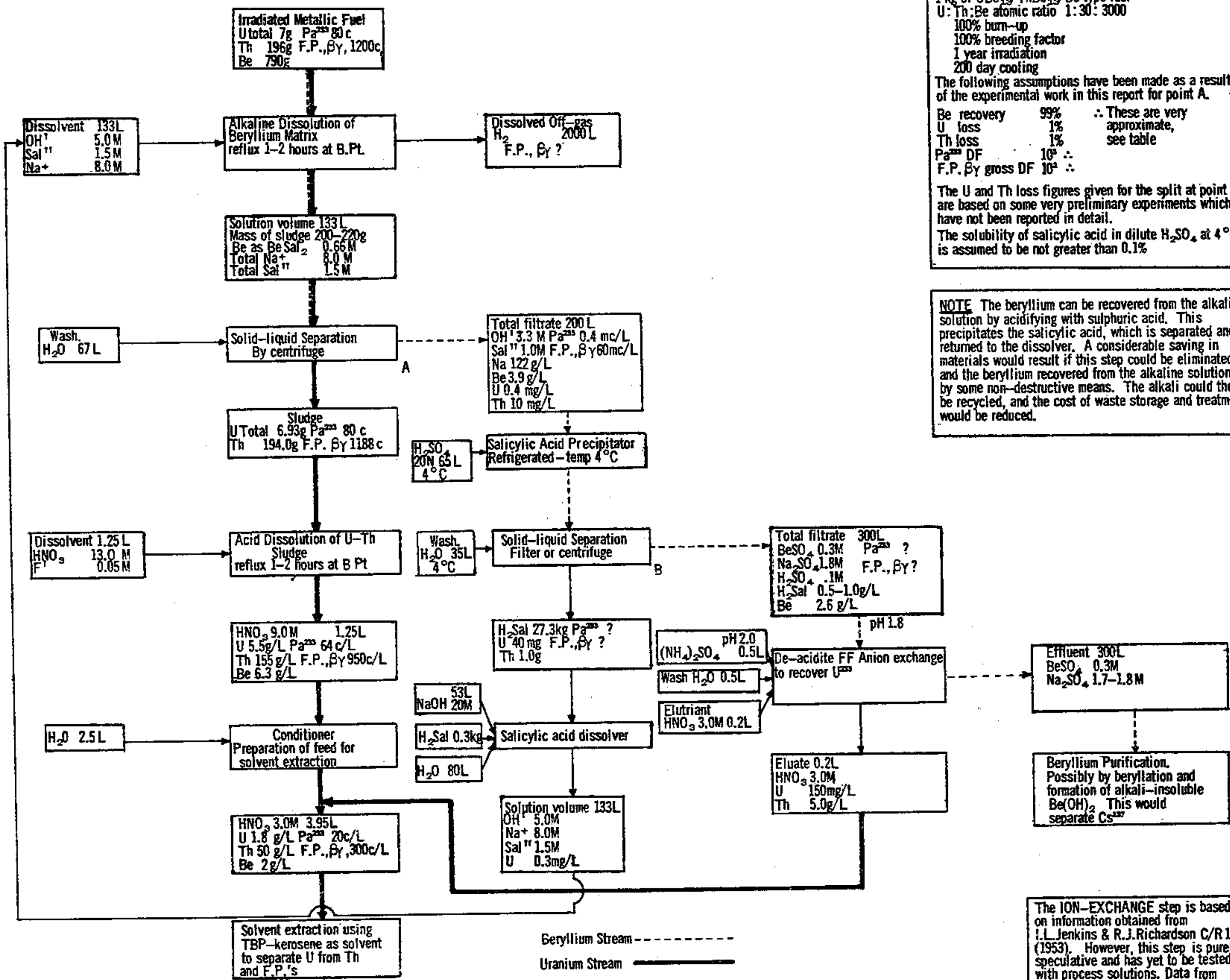
Fig 11. LAYOUT OF UPPER PART OF CELL.

The following assumptions have been made in order to construct this flowsheet and are not necessarily the final basis for flowsheet design
1 kg of UBe_{13}/$ThBe_{13}$/Be type fuel
U:Th:Be atomic ratio 1:30:3000
100% burn-up
100% breeding factor
1 year irradiation
200 day cooling
The following assumptions have been made as a result of the experimental work in this report for point A.

Be recovery	99%	∴ These are very approximate, see table
U loss	1%	
Th loss	1%	
Pa^{233} DF	10^3 ∴	
F.P. βγ gross DF	10^3 ∴	

The U and Th loss figures given for the split at point B are based on some very preliminary experiments which have not been reported in detail.
The solubility of salicylic acid in dilute H_2SO_4 at 4°C is assumed to be not greater than 0.1%

NOTE The beryllium can be recovered from the alkaline solution by acidifying with sulphuric acid. This precipitates the salicylic acid, which is separated and returned to the dissolver. A considerable saving in materials would result if this step could be eliminated and the beryllium recovered from the alkaline solution by some non-destructive means. The alkali could then be recycled, and the cost of waste storage and treatment would be reduced.



The ION–EXCHANGE step is based on information obtained from I.L.Jenkins & R.J.Richardson C/R 1217 (1953). However, this step is purely speculative and has yet to be tested with process solutions. Data from J.Fardy(A.A.E.C.–Unpublished work) were also used.

FIGURE 12 TENTATIVE CHEMICAL FLOWSHEET FOR THE SEPARATION OF BERYLLIUM FROM IRRADIATED H.T.G.C. METALLIC FUEL USING A SELECTIVE DISSOLVENT. – CAUSTIC SODA/SALICYLATE.