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SOME CHEMICAL ASPECTS OF MOLTEN-SALT REACTOR SAFETY: (1) DISSOLUTION OF COOLANT AND FUEL MIXTURES IN H_2O , (2) A PORTION OF THE SYSTEM $LiF-BeF_2-H_2O$ AT 25, 60 AND NEAR $100^\circ C$

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Abstract

In connection with safety aspects of the ORNL Molten-Salt Reactor Program, the solubilities of MSRE fuel and coolant were determined in H_2O solution at $25^\circ C$ and at higher temperatures. In a separate study, portions of the system $LiF-BeF_2-H_2O$ were investigated at temperatures of 25, 60 and near $100^\circ C$. Under conditions of the experiments, the results showed that (1) from the MSRE fuel, uranium dissolved to the extent of at least 0.010 molal--probably due to oxidation of U(IV) to U(VI)--and (2) LiF and an unidentified salt or salts of LiF and BeF_2 were found to exist in the system $LiF-BeF_2-H_2O$.

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1. INTRODUCTION

Safety aspects of the ORNL Molten-Salt Reactor Program make it important to know the short- and long-term effects of a spill of molten reactor fuel or of reactor coolant into the water-sand mixture at the bottom of the containment shell. Since this shell is designed to withstand a maximum pressure of 5 atmospheres (approximately equivalent to the vapor pressure of H₂O at 150°C), the maximum temperature of interest, when considering long-term effects, would be 150°C. In this study, solubilities of reactor coolant (Li₂BeF₄) and fuel mixture (LiF-BeF₂-ZrF₄-ThF₄-UF₄, 70-23-5-1-1 mole %) in water have been explored at 25°C and at higher temperatures. In addition, investigations on the solubility of LiF, and of a compound of LiF and BeF₂ of unspecified composition, in aqueous solutions varying from 0 to 50 wt % BeF₂ were carried out at 25, 60 and near 100°C. These latter studies are of further use in evaluating the behavior of molten-salt coolant in contact with water.

2. EXPERIMENTAL PROCEDURES

Solid Li₂BeF₄ and MSRE (Molten-Salt Reactor Experiment) fuel mixture were obtained from the fluoride production facility of the Reactor Chemistry Division, ORNL.¹ The Li₂BeF₄ contained approximately 2 wt % excess LiF. Chemically pure LiF was obtained from Foote Mineral Company. A stock solution of concentrated BeF₂ was prepared by dissolving a weighed amount of BeF₂ solid, obtained from the Beryllium Corporation, in water solution. The mixture was refluxed at a little above 100°C for 24 hr in order to

¹F. A. Doss, J. E. Eorgan and J. H. Shaffer, Reactor Chemistry Division Annual Report for Per. End. Jan. 31, 1962, ORNL-3262, p 27-30.



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dissolve the BeF_2 . At lower temperatures the rate of dissolution was very slow. A radioactive tracer, Be-7, was added to the stock solution, and portions of this solution were diluted with water to give a series of aqueous solutions of decreasing concentrations of BeF_2 .

All solids were ground to fine powders (in a glove box for the beryllium-containing solids) and were added separately to flasks containing water. In some experiments, LiF solid was added to flasks containing solutions of BeF_2 in H_2O .

The mixtures of MSRE fuel and of coolant were stirred at room temperature and at controlled temperatures up to 90°C . Separate mixtures of LiF and of Li_2BeF_4 in contact with BeF_2 solutions were rocked at controlled temperatures of $25^\circ \pm 0.2^\circ$ and $60^\circ \pm 0.3^\circ\text{C}$ and were refluxed at temperatures a little over 100°C . The latter temperatures were those at which the solutions boiled at atmospheric pressure.

Samples of the solution phases were obtained after periods of time varying from 4 hours to 28 days. The concentrations of lithium were determined by flame photometry, and fluoride by pyrohydrolysis and subsequent acid-base titration of the distillate.² Zirconium, uranium, thorium, and beryllium were analyzed spectrophotometrically by the pyrocatechol violet method, thiocyanate method, thoron procedure, and the differential p-nitrobenzeneazo-orcinol method, respectively. Beryllium was determined also by counting of radioactive Be-7 and comparison of the number of counts with those from an aliquot portion of a standard solution containing Be-7. Selected solid phases were separated from the

²All chemical analyses were performed by the Analytical Chemistry Division, ORNL.

solution phases and dried between sheets of filter paper. These solids were examined by means of a petrographic microscope; LiF was identified through its x-ray diffraction pattern.³

3. DISSOLUTION OF Li_2BeF_4 in H_2O

The concentrations of Li, Be, and F found in solution, when excess Li_2BeF_4 solid was mixed with H_2O at 25°C , are given in Fig. 1 as a function of time. Based on the data for lithium and beryllium, it appeared that equilibrium was attained at least within six days and perhaps sooner. The changes in the compositions of the solutions (revealing a higher ratio of beryllium to lithium than that in the original solid) require the appearance of some solid which is richer in lithium than the starting material and which is presumably LiF. The data suggest that an invariant point may have been established. Nevertheless, these results are in contradiction to the solubilities of LiF and of Li_2BeF_2 in $\text{BeF}_2\text{-H}_2\text{O}$ solutions given in the table and in Fig. 5. It is possible that, although equilibrium appeared to have been attained, a relatively inert coating of a new solid on the surface of the Li_2BeF_4 solid may have formed and prevented further dissolution of Li_2BeF_4 .

The concentrations of Li, Be, and F found in solution are given in Fig. 2 as a function of temperature. Included in Fig. 2 are some experimental values by F. H. Perfect⁴ which were obtained by analyses of liquid phases after approximately 24 hours of mixing with solid. Perfect

³C. F. Weaver of the Reactor Chemistry Division, ORNL, contributed to this part of the study.

⁴F. H. Perfect, Proc. Penn. Acad. Sci. 26, 54 (1952).

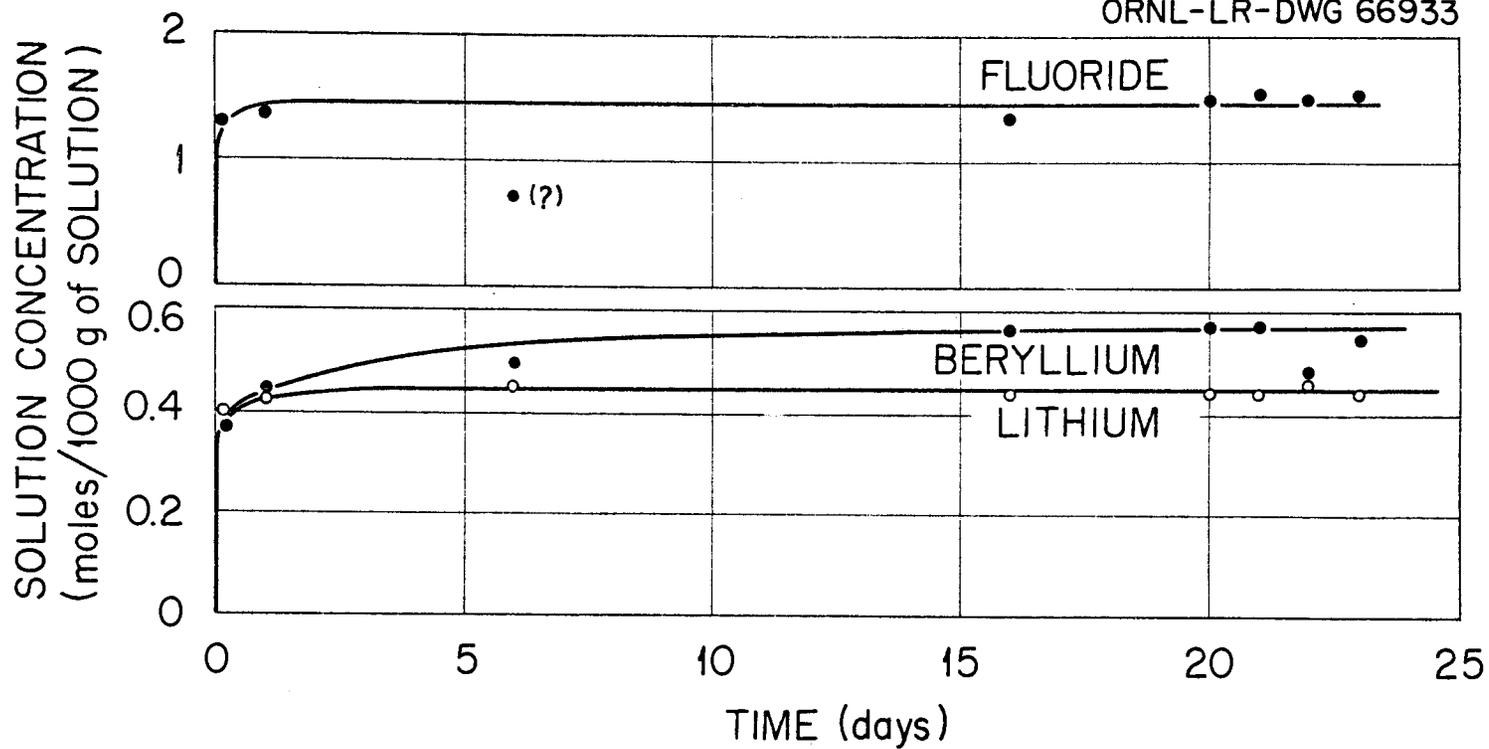


Fig. 1. Effect of Time on Dissolution of Li_2BeF_4 in H_2O at 25°C .

Portions of System LiF-BeF₂-H₂O at 25°, 60° C
and Temperatures of Boiling (at 1 atmosphere)

Mixing Time** (hr)	BeF ₂ (wt %)	LiF (wt %)	Identified Solid Phases	Mixing Time** (hr)	BeF ₂ (wt %)	LiF (wt %)	Identified Solid Phases
Temperature: 25°C, Starting Materials: BeF ₂ -H ₂ O Solutions + LiF Solid				600	5.05	1.13	
				600	9.50	2.07	
				600	14.38	3.01	
				600	18.81	4.22	
				600	23.27	5.63	
264	5.05	0.722	a, c*	600	26.88	6.03	
264	9.67	1.41		600	25.62	4.23	
264	14.55	2.08		600	29.93	4.31	
264	19.10	2.80		600	35.26	4.48	
264	23.56	3.58					
264	28.23	4.77	a, c	672	4.94	1.10	a
264	32.42	5.73	a, c	672	9.49	2.05	a
264	36.93	6.91	a, c	672	14.32	2.93	a
264	40.93	6.61	a, b, c	672	18.75	4.03	a
				672	23.26	5.28	a, c
360	4.92	0.799		672	26.20	4.63	a, c
360	9.70	1.49		672	24.87	3.65	a, c
360	14.75	2.23		672	28.97	3.71	c
360	18.95	2.94		672	34.73	4.10	c
360	23.71	3.86					
360	27.76	5.24		Temperature: 60°C, Starting Materials: BeF ₂ -H ₂ O Solutions + LiF Solid			
360	32.29	6.41					
360	36.22	6.65					
360	39.70	6.26					
504	4.96	0.811		4	5.03	1.13	
504	9.71	1.47		4	9.69	1.97	
504	14.35	2.28		4	14.49	2.96	
504	19.01	3.04		4	18.94	3.85	
504	24.00	3.86		4	28.14	6.38	
504	27.92	5.34		4	31.03	5.99	
504	32.18	6.34		4	33.28	5.49	
504	34.43	5.45		4	37.50	4.90	
504	37.82	5.10					

* Key: a = LiF, Identified by petrography
b = LiF, Identified by x-ray pattern
c = birefringent solid, Identified by petrography

** Cumulative time.

Mixing Time* (hr)	BeF ₂ (wt %)	LiF (wt %)	Identified Solid Phases	Mixing Time* (hr)	BeF ₂ (wt %)	LiF (wt %)	Identified Solid Phases
(continued)				Temperature: Boiling, Starting Materials: BeF ₂ -H ₂ O Solutions + Li ₂ BeF ₄ Solid			
27	4.98	1.04		2	38.96	6.67	
27	9.64	2.01		60	42.07	6.79	
27	14.25	2.92		84	42.15	7.02	
27	18.62	4.10		108	43.61	7.48	
27	23.27	5.59		132	43.43	7.07	
27	27.83	6.36					
27	25.90	4.63					
27	30.31	4.75					
27	36.16	4.84					
Temperature: 60°C, Starting Materials: BeF ₂ -H ₂ O Solutions + Li ₂ BeF ₄ Solid				Temperature: Boiling, Starting Materials: BeF ₂ -H ₂ O Solutions + LiF Solid			
24	23.17	3.97		24	22.56	4.81	
24	28.39	4.22		24	32.69	5.83	
24	31.68	4.54		24	37.65	6.44	
24	37.40	4.70		24	45.75	7.42	
24	42.24	5.02		48	22.69	4.88	
48	22.68	3.86		48	33.36	6.06	
48	27.81	4.08		48	37.98	6.85	
48	33.09	4.34		48	49.74	7.89	
48	38.29	4.60					
48	42.98	4.83					
Temperature: Boiling, Starting Materials: H ₂ O + Li ₂ BeF ₄ Solid							
24	2.01	1.15					
48	2.18	1.18					

* Cumulative time.

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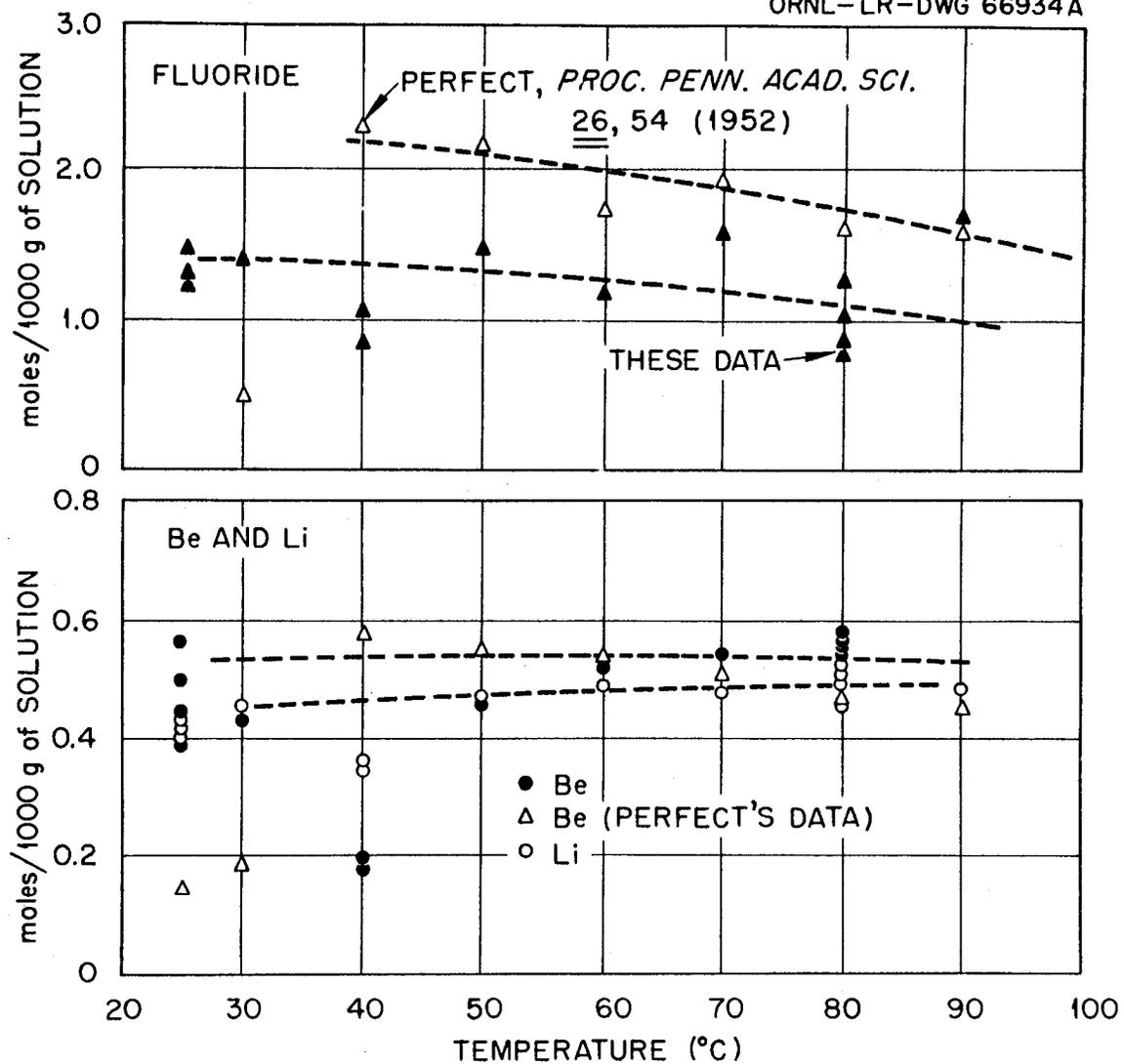


Fig. 2. Effect of Temperature on Dissolution of Li_2BeF_4 in H_2O .

commented that the results were not entirely satisfactory and may have been complicated by the appearance of two separate solubility curves-- one for a hydrated salt $\text{Li}_2\text{BeF}_4 \cdot x\text{H}_2\text{O}$ and one for an anhydrous salt. In a further comment, with reference to a patent,⁵ it was felt that the anhydrous salt either dissolved very slowly in cold water, had a low solubility, or had both a low rate of dissolution and low solubility. In our own experiments, mixtures of solution and Li_2BeF_4 solid were equilibrated 4 hours to 3 days before taking samples of the solution phases for analyses. Also included are the data obtained at 25°C (from Fig. 1).

4. DISSOLUTION OF MSRE FUEL MIXTURE

The analytical results from the run with fuel mixture at 25°C as a function of time are shown in Fig. 3. As with the reactor coolant, equilibrium appeared to be attained within six days. Nevertheless, a consistent increase in concentration of lithium and uranium was noted. In this experiment it was presumed that tetravalent uranium from the solid phases had been converted to the hexavalent state in the solution phase⁶ by the action of oxygen from the air, and also that an inert coating may have hindered further dissolution of the solid phase.

In Fig. 4 are shown analytical results for solution concentrations of U, Li, Th, Zr, and Be as a function of temperature. The time of equilibration at each temperature before sampling was one day. Also included is one value for uranium and one for lithium obtained previously.⁷ The

⁵H. C. Kawecki, U.S. Patent No. 2,490,633 (to the Beryllium Corporation), Dec. 6, 1949.

⁶H. C. Nikolaef and Yu. A. Luk'yanchef, Atomnaya Energ. 11 67 (1961).

⁷R. F. Apple, Analytical Chemistry Division, ORNL (1961).

Li, Be, Zr, Th, U 1, 1, 1, 1, 1 mole %

*Net solubility $\approx 17g/l$
 $\rightarrow 70,000 gal to dissolve 5 MT of fuel salt$*

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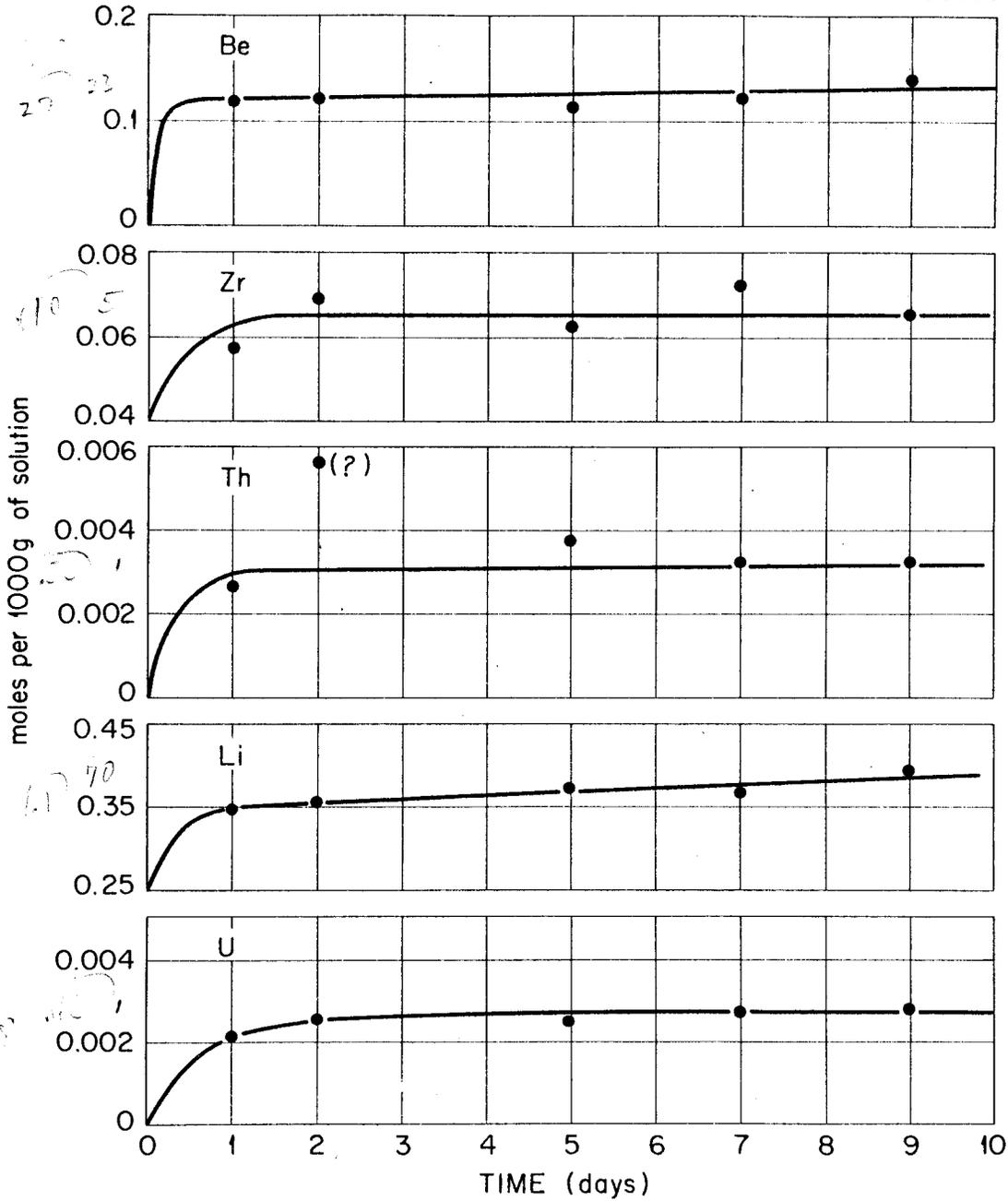


Fig. 3. Effect of Time on Dissolution of MSRE Solid Fuel in H₂O at 25°C.

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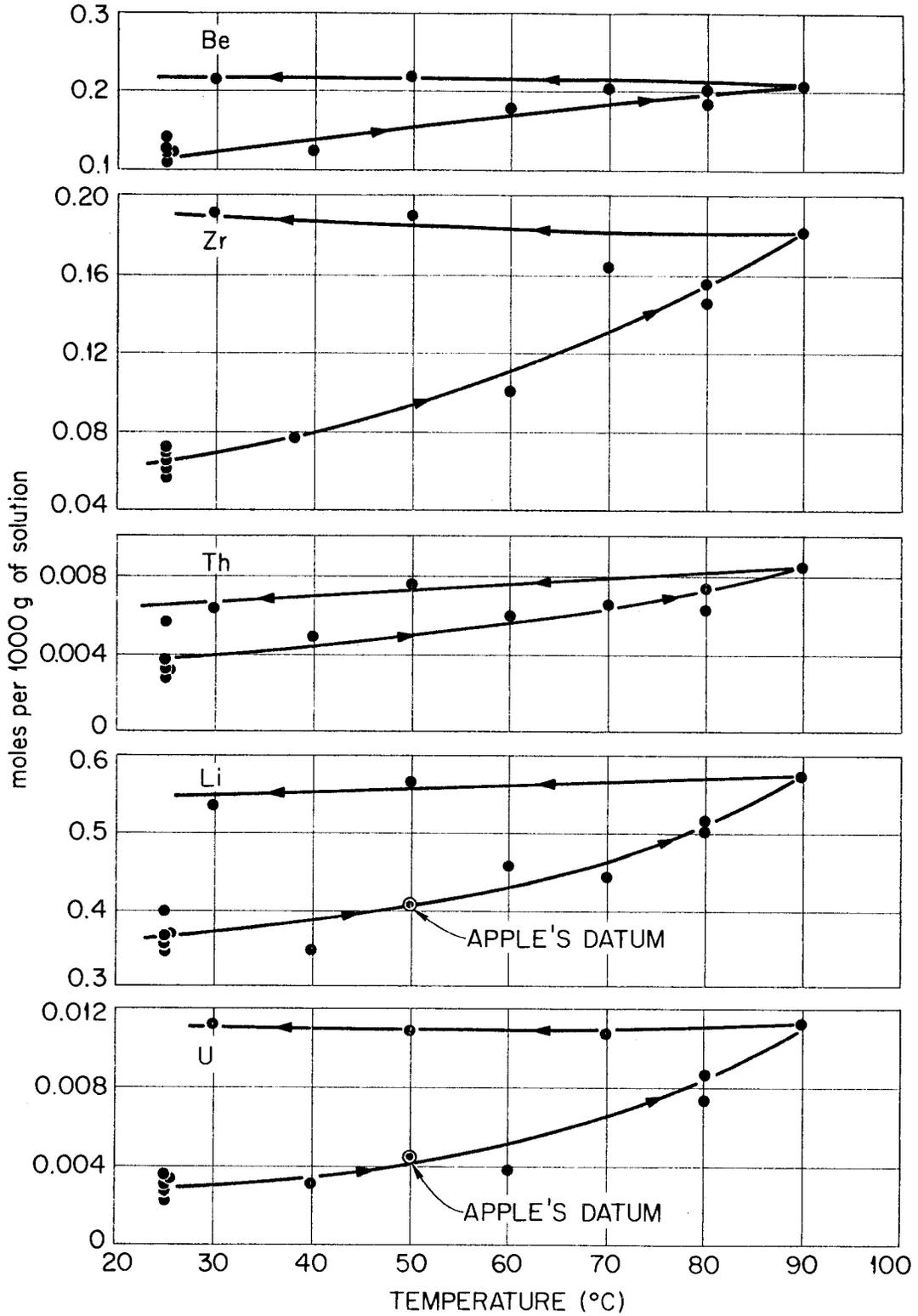


Fig. 4. Effect of Temperature on Dissolution of MSRE Solid Fuel in H₂O.

analytical results from samples taken upon stepwise lowering of the temperature of the solution-solid mixture consistently gave higher values for the solution concentrations of the various components. It is believed that equilibrium either was not reached on cooling or had never been reached.

In view of the appreciable uranium concentration found in solution under these conditions, it has been recommended that neutron poisons be present in any water which could mix with the fuel in the event of a reactor accident.

5. A PORTION OF THE SYSTEM $\text{LiF}-\text{BeF}_2-\text{H}_2\text{O}$
AT 25, 60 AND NEAR 100°C

Compositions of liquid phases of BeF_2 and H_2O which were rocked or refluxed at several temperatures in contact separately with LiF and with Li_2BeF_4 are given in the table. The initial reagents and times of rocking or refluxing are specified; also, some designations of solid phases are given. In all cases a solid or solids were present. When these data are plotted as the composition of LiF vs that of BeF_2 (Fig. 5) and consideration is given to the times of mixing and temperature cycling, then there appears to be metastability of LiF solid phase in equilibrium with solutions containing high concentrations of BeF_2 . We believe that the continuous curves which are drawn on Fig. 5 represent stable equilibria and the dashed curves show the solubility of a metastable solid. Data which fall between these two curves represent in-progress changes between metastable and stable conditions. The only salt definitely identified by the x-ray diffraction method was LiF . Another salt, proposed to be some compound of LiF and BeF_2 , was not identified by optical

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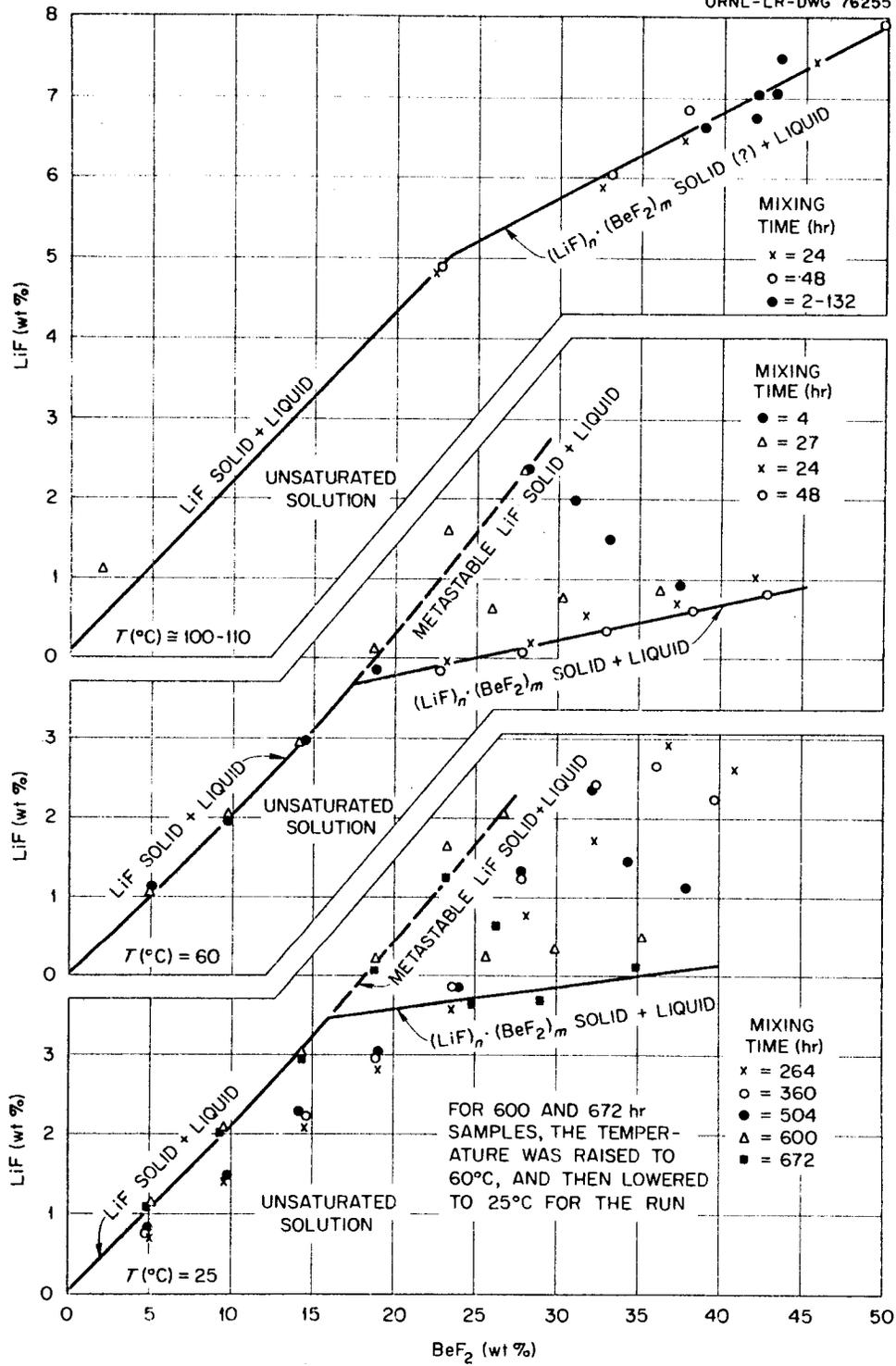


Fig. 5. Some Solubility Behavior in the System LiF-BeF₂-H₂O, 25,100°C.

petrography or x-ray diffraction. Since a solid which may have been present, other than LiF, could be formed only from LiF and $\text{BeF}_2\text{-H}_2\text{O}$ solution, it is possible that Li_2BeF_4 , in an amorphous, unidentifiable form, was present. By means of optical petrography, birefringent refraction lines were observed for the unknown solid.³ Similar lines are observed for Li_2BeF_4 solid.

A conventional, three-component phase diagram of a portion of the condensed system at 25, 60 and 100°C^+ is shown in Fig. 6. The data are omitted; the curves are drawn to represent the solubilities for the stable solids to the continuous curves shown in Fig. 5.

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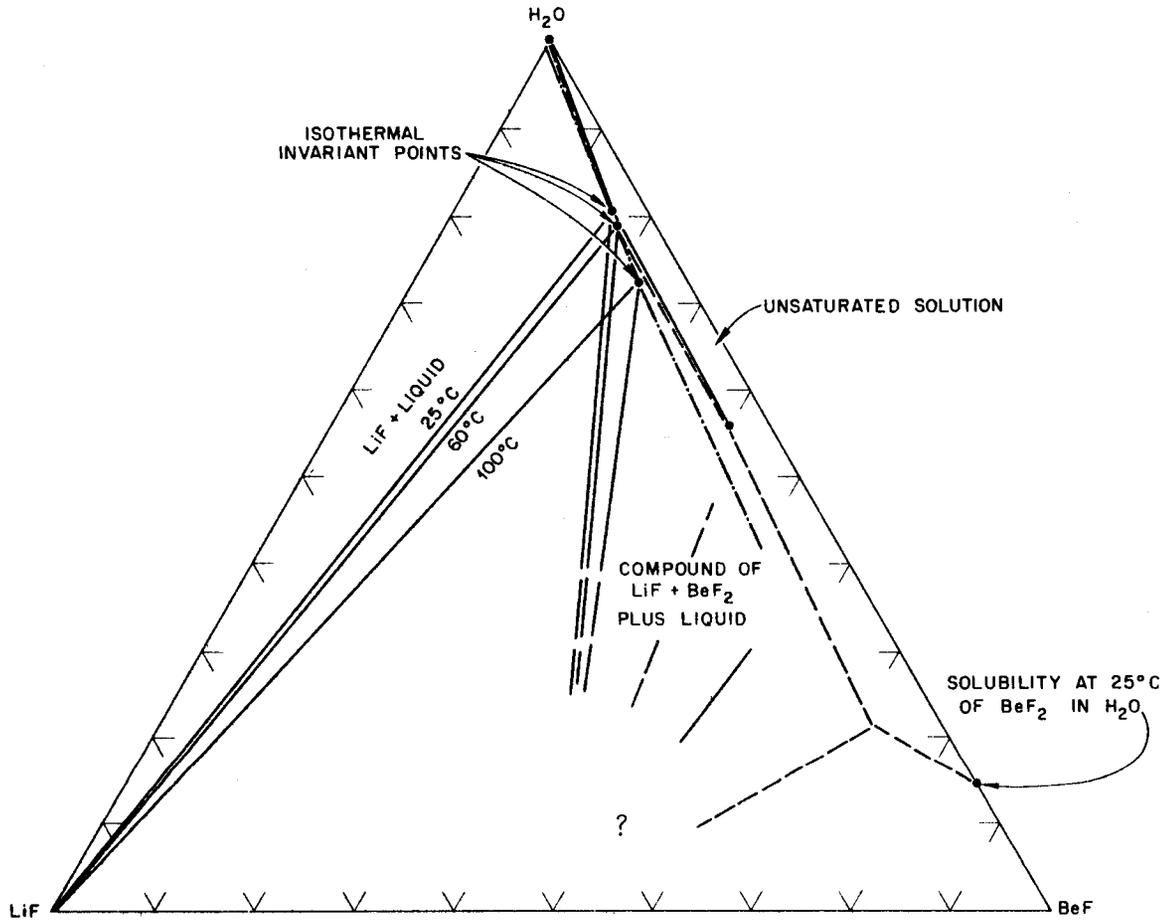


Fig. 6. Representation of a Portion of the System LiF-BeF₂-H₂O at 25, 60, and Near 100°C.

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