SOLUBILITY RELATIONS AMONG RARE-EARTH FLUORIDES
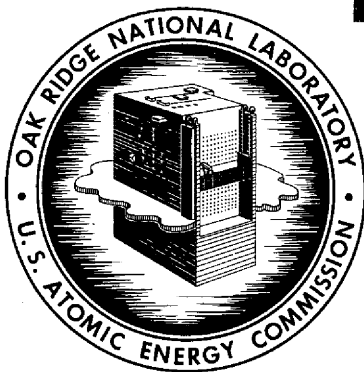
IN SELECTED MOLTEN FLUORIDE SOLVENTS

W. T. Ward
R. A. Strehlow
W. R. Grimes
G. M. Watson

OAK RIDGE NATIONAL LABORATORY

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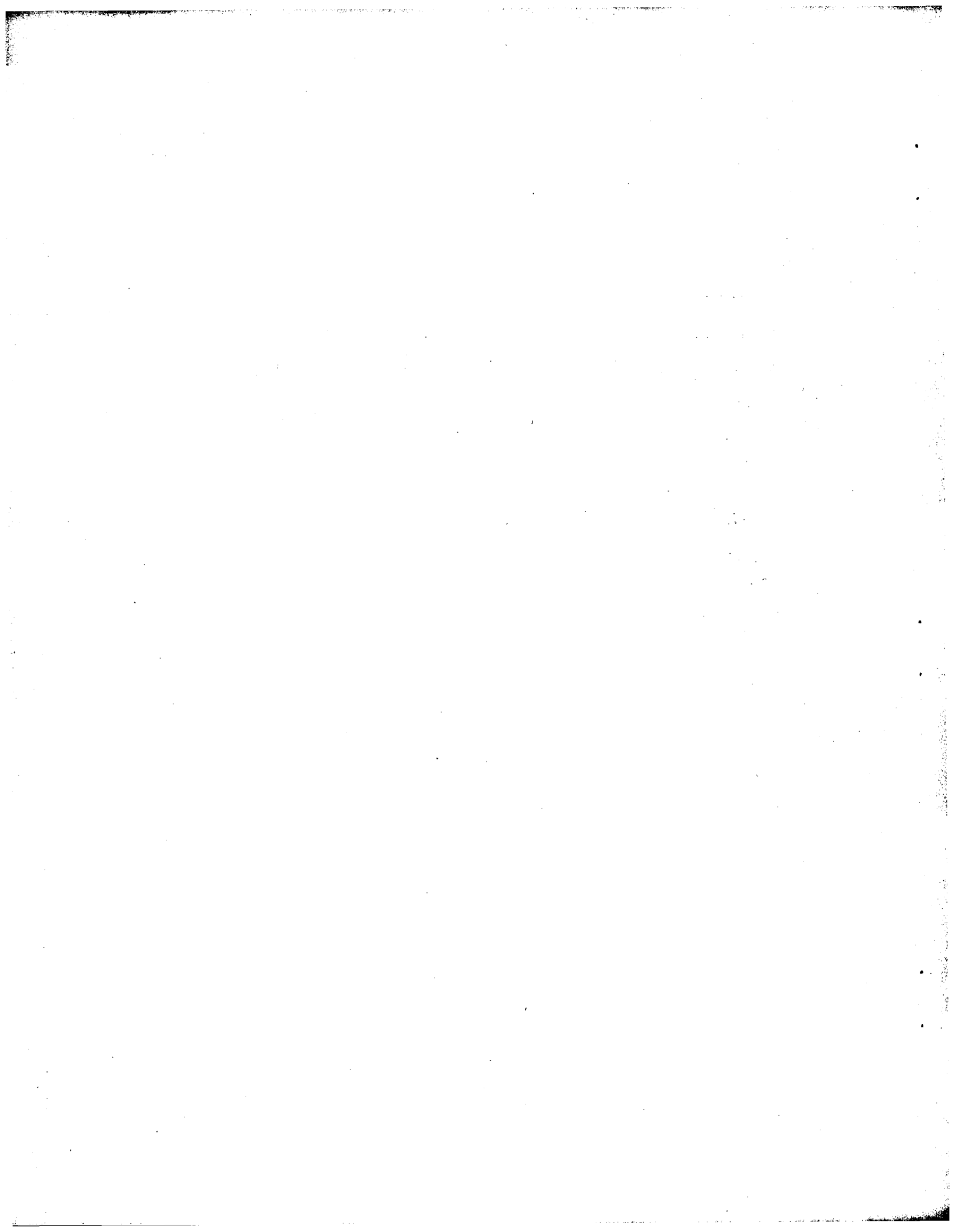W. T. Ward   R. A. Strehlow   W. R. Grimes   G. M. Watson

ABSTRACT

Solubility measurements of rare-earth and yttrium fluorides have been made in various solvents containing zirconium or beryllium fluoride with certain alkali-metal fluorides, and in some cases uranium fluoride, present. Tests have been performed which pertain to the development of a method of removal of rare earth fluoride nuclear poisons from certain mixtures of interest to the Molten Salt Power Reactor Program. The method is shown to be effective in several concentration ranges.

INTRODUCTION

Rare-earth fission products formed in a reactor fueled with a circulating molten fluoride solution may be expected to account for significant neutron loss. Appreciation of this fact has motivated studies of solubilities which would be pertinent to the design and operation of such a reactor. The feasibility of several processes in which rare earths could be extracted from molten fluoride solutions depends substantially on the solubility relations among the rare-earth fluorides. This same information also is of interest with regard to the maintenance of homogeneity of the fuel, since precipitation of a rare-earth fluoride in the fuel circuit of the reactor might interfere with its satisfactory operation.

This report presents some of the data obtained on the solubilities of LaF_3, CeF_3, SmF_3, and YF_3 in solvents containing sodium fluoride and zirconium fluoride and in others containing beryllium fluoride with lithium or sodium fluoride.

Two specific uranium-containing compositions which are potentially useful in a molten-fluoride-fueled reactor have been selected. In addition, a sufficient variety of non-uranium-containing solvents have been chosen to assure that the solubility relations among this selection of rare-earth fluorides would be adequately known. This is a continuation of work reported earlier[1] concerning a solvent of composition NaF-ZrF_4-UF_4

(50-46-4 mole %). The same radiotracer technique was used for the present work.

RESULTS

Solubility of Single Rare-Earth Fluorides

The solubilities of CeF_3, LaF_3, and SmF_3 measured in the solvent, LiF-BeF_2-UF_4 (62.8-36.4-0.8 mole %), are shown in Fig. 1 along with the corresponding results from the earlier work. Although the solubility levels of these solutes in the LiF-BeF_2-UF_4 solvent mixture are considerably lower than in the NaF-ZrF_4-UF_4 composition, they are still adequate to assure that precipitation of the rare-earth fluorides would not be inimical to reactor operation at probable burnup rates for about four or five years.[2] A second feature of the data is the closer approximation of the data for the beryllium-containing solvents to a straight line on the plot of log solubility vs T^{-1}, which may be interpreted as implying a lower degree of interaction in the solution between solute and solvent cations. This approach to ideality of the solute in the beryllium system would not be expected to affect the feasibility of a solid solvent extraction process, since both the substituting ion [presumably Ce(III)] and the extracted ions [e.g., Sm(III)] would behave similarly.

For comparison, the solubility of YF_3, along with that of CeF_3, is shown in Fig. 2 for a single NaF-BeF_2 composition (61-39 mole %). From these results it may be inferred that the same qualitative

[1]W. T. Ward et al., *Solubility Relations Among Some Fission Product Fluorides in NaF-ZrF₄-UF₄ (50-46-4 mole %)*, ORNL-2421 (Jan. 15, 1958).

[2]*Molten Salt Reactor Program Status Report*, ORNL-2634, p 234 (Nov. 12, 1958).
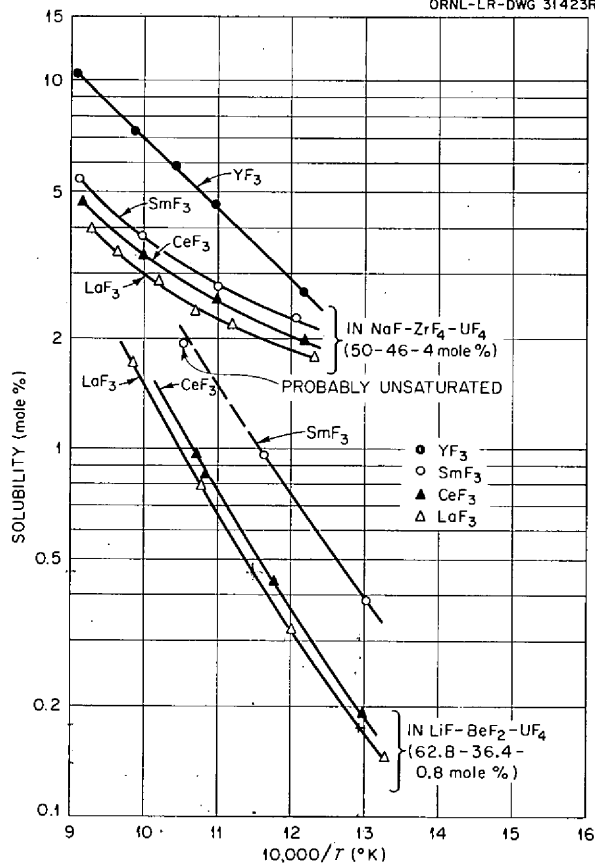
Fig. 1. Solubility of Some Fission-Product Trifluorides in Molten Fluoride Fuels.

Fig. 2. Solubility (mole %) of YF$_3$ and of CeF$_3$ in NaF-BeF$_2$ (61-39 mole %).

order of solubilities exists for the rare-earth fluorides in these solvents as was observed in the NaF-ZrF$_4$-UF$_4$ (50-46-4 mole %) and LiF-BeF$_2$-UF$_4$ (62.8-36.4-0.8 mole %) solvents. This decrease in solubility with increase in the size of the trivalent solute cation is probably related to an as yet unmeasured trend of the heats of fusion of the trifluorides.

Solubility of Rare-Earth Fluorides as Functions of Composition

Figure 3 shows that the presence of UF$_4$ in small amounts does not affect the rare-earth solubility greatly. The proportion of alkali-metal fluoride to BeF$_2$ or ZrF$_4$, however, has a considerable effect.

Several experiments were performed to determine the solubility of a typical rare-earth fluoride, CeF$_3$, in various solvents in each of the systems

NaF-ZrF$_4$, LiF-BeF$_2$, NaF-BeF$_2$, and LiF-NaF-BeF$_2$. Figures 4 to 6 show the graphically interpolated solubilities in the selected compositions in the four systems for several temperatures. Data from which these curves were obtained are listed in the Appendix. Figure 7 displays the 600°C isotherm for the solubility of CeF$_3$ in the three solvent systems containing beryllium. These curves indicate the magnitude of the solvent interaction, which is apparently less in the LiF-BeF$_2$ system than in those containing NaF. The solubilities exhibit minima in each case at compositions near 37 mole % BeF$_2$. These minima appear to occur at slightly higher BeF$_2$ concentrations at higher temperatures (Figs. 5 and 6).

Solubilities of Mixed Rare-Earth Fluorides in LiF-BeF$_2$-UF$_4$ (62.8-36.4-0.8 Mole %)

Rare-earth fluorides form solid solutions with each other. However, they apparently do not form solid solutions with the fuel solvent components. These facts, coupled with the strong temperature dependence of their solubilities, suggest that a solid-solvent extraction might be a feasible method
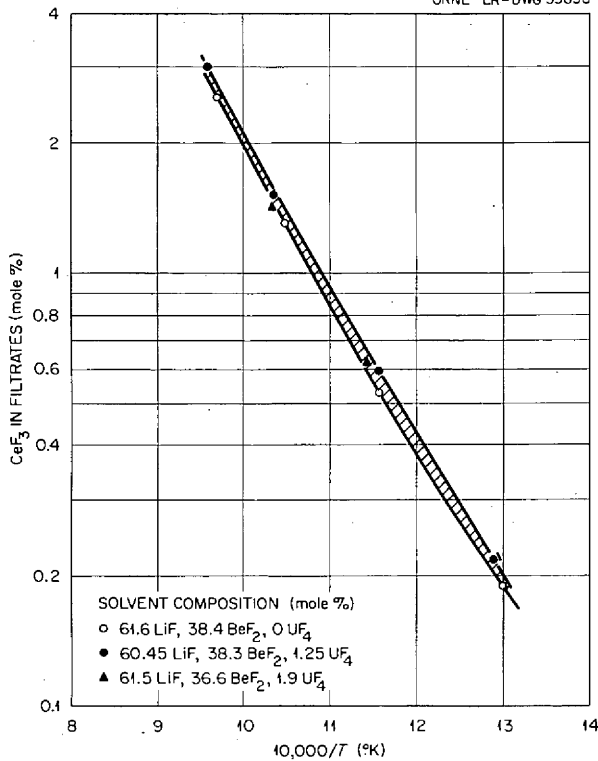
Fig. 3. Effect of UF$_4$ on Solubility of CeF$_3$ in LiF-BeF$_2$ (62-38 mole %). Solvent composition calculated from filtrate analyses (average values).

Fig. 4. Solubility of CeF$_3$ in NaF-ZrF$_4$ Solvents.

for substituting a low-cross-section rare earth (e.g., Ce) for the high-cross-section ones (e.g., Sm). For a thermal reactor the differences in poisoning between Ce and, say, Sm are large. The advantages from the standpoint of neutron economy of such a scheme are, consequently, great. The advantage of this type of extraction for an intermediate- or fast-neutron reactor is considerably less. In the consideration of any of the extraction schemes which are based on the substitution of an innocuous rare-earth fluoride for a high-cross-section one, the required data include the solubility behavior of mixed rare-earth fluorides. Such information will allow the single-stage equilibrium distribution to be calculated.

The solubilities of selected pairs of rare-earth fluorides in LiF-BeF$_2$-UF$_4$ (62.8-36.4-0.8 mole %) have been determined, with substantially the same techniques as those reported earlier.[1] In the earlier work it was shown that the pairs LaF$_3$-

CeF$_3$ and CeF$_3$-SmF$_3$ form solid solutions and behave in fairly predictable ways.

The equation representing a single equilibrium stage for the extraction of a poison (e.g., SmF$_3$) from the solvent by a solid (e.g., CeF$_3$) is

$$CeF_3(ss) + SmF_3(d) = CeF_3(d) + SmF_3(ss) \ ,$$
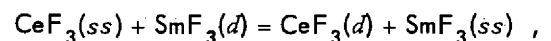
where (d) indicates that the rare-earth fluoride is dissolved in the solvent, and (ss) that it is in solid solution. With suitable restrictive conditions the equilibrium constant for this reaction can be shown to be approximately equal to a

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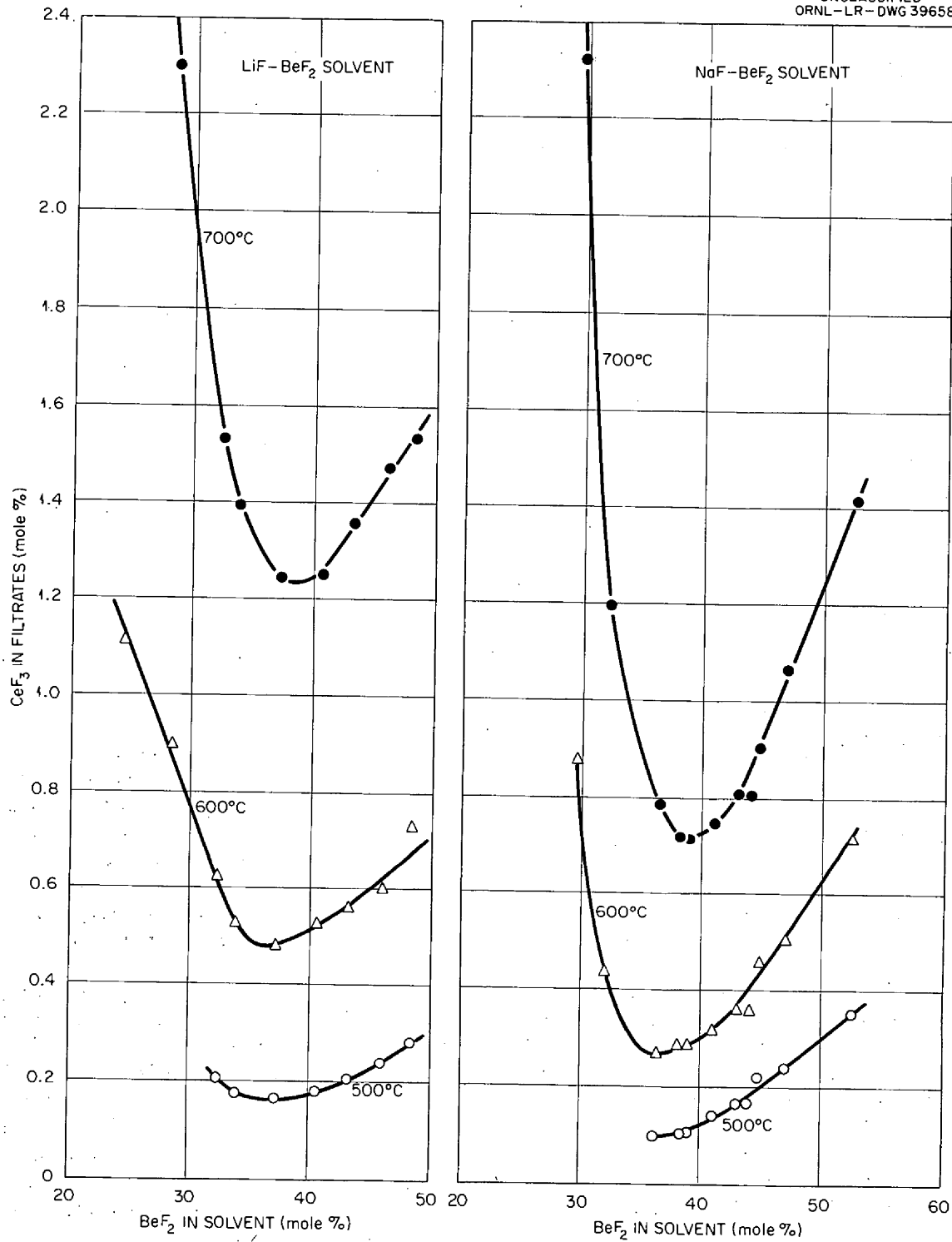
Fig. 5. Comparison of CeF$_3$ Solubility (mole %) in LiF-BeF$_2$ and in NaF-BeF$_2$.
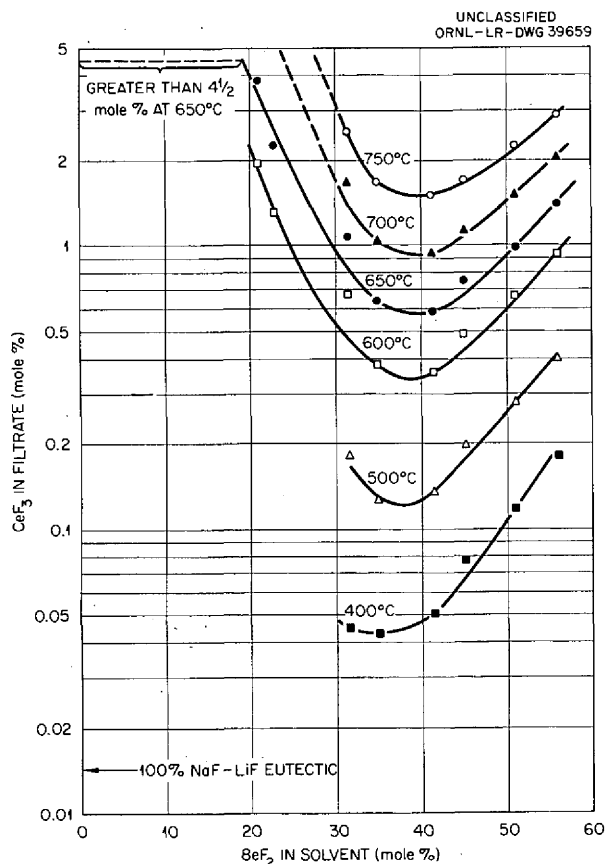
Fig. 6. Solubility (mole %) of CeF_3 in NaF-LiF-BeF$_2$ Solvents.

Fig. 7. Comparison of CeF_3 Solubility (mole %) in LiF-BeF$_2$, in LiF-NaF-BeF$_2$, and in NaF-BeF$_2$ at 600°C.

simple solubility ratio:[1]

$$K = \frac{N_{CeF_3}(d)\; N_{SmF_3}(ss)}{N_{SmF_3}(d)\; N_{CeF_3}(ss)} = \frac{S^0_{CeF_3}}{S^0_{SmF_3}} \;,$$

where N is the mole fraction of the given species in the specified phase and S^0 is the mole fraction of the given species in a saturated solution in the absence of the other rare-earth fluoride, all at the same temperature.

The results of equilibrating CeF_3-LaF_3-solvent mixtures of several different compositions are shown in Fig. 8. For the three relative compositions of CeF_3-LaF_3 used as solutes, the total rare-earth solubility in virtually every case fell between the solubilities of the pure rare-earth fluorides. Figure 9 shows the corresponding results with one mixed composition in the CeF_3-

SmF_3-solvent system. These results are consistent with those observed for the NaF-ZrF$_4$-UF$_4$ (50-46-4 mole %) solvent.[1] Table 1 shows the calculated extraction coefficients along with those based on the experimental results for the CeF_3-LaF_3 system. Although the estimated values are somewhat poorer than in the earlier work, the present data appear to be entirely adequate for practical purposes.

A possibility existed that AlF_3 might offer some advantage as the solid extractant in view of its lower cost and neutron cross section. Solubility measurements of AlF_3 in the same LiF-BeF$_2$-UF$_4$ solvent indicated that the solubility increases with the amount of AlF_3 added. The data presented in Fig. 10 show also that the addition of CeF_3 decreases the AlF_3 solubility somewhat. The precipitating phase is probably $3LiF$-AlF_3 (ref 3). Figure 11 shows that the solubility of CeF_3 is somewhat higher in the presence of AlF_3 than in

[3]P. P. Fedotieff and K. Timofeeff, Z. anorg. u. allgem. Chem. 206, 266 (1932).

CALCULATED TOTAL COMPOSITION (mole %)
○ 1.80 CeF$_3$, NO LaF$_3$
● 1.82 CeF$_3$, 0.78 LaF$_3$
△ 1.85 CeF$_3$, 2.27 LaF$_3$
▲ 1.83 CeF$_3$, 3.30 LaF$_3$
■ NO CeF$_3$, 2.20 LaF$_3$

TOTAL RARE-EARTH FLUORIDE IN FILTRATE (mole %)

10,000 / T (°K)

TOTAL RARE-EARTH FLUORIDE IN FILTRATE (mole %)

○ SmF$_3$ ONLY (NO CeF$_3$ PRESENT)
□ CeF$_3$ ONLY (NO SmF$_3$ PRESENT)
● SUM OF SOLUBILITIES WHEN BOTH ARE PRESENT
(TOTAL COMPOSITION: 2.83 mole % CeF$_3$,
2.22 mole % SmF$_3$)

10,000 / T (°K)
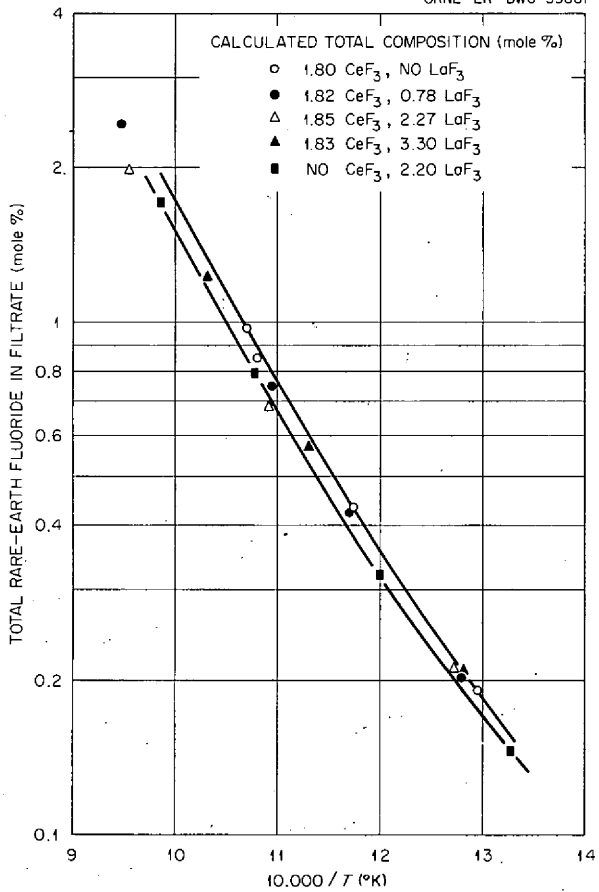
Fig. 8. Solubility of CeF$_3$ and of LaF$_3$ (Separately and Mixed) in LiF-BeF$_2$-UF$_4$ (62.8-36.4-0.8 mole %).
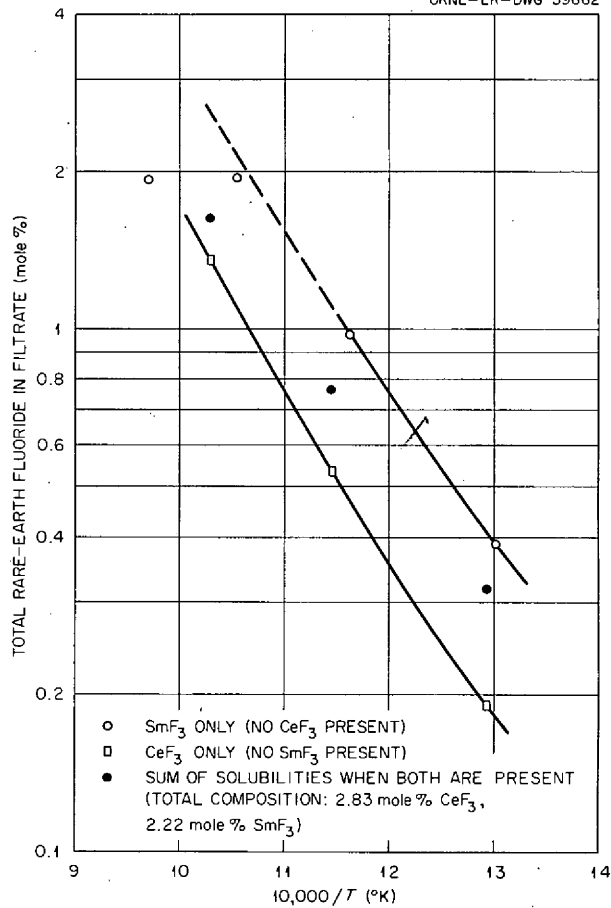
Fig. 9. Solubility of CeF$_3$ and of SmF$_3$ (Separately and Mixed) in LiF-BeF$_2$-UF$_4$ (62.8-36.4-0.8 mole %).

Table 1. Extraction Coefficients for the Process CeF$_3$(ss) + LaF$_3$(d) = CeF$_3$(d) + LaF$_3$(ss)
in LiF-BeF$_2$-UF$_4$ (62.8-36.4-0.8 Mole %)

Temperature (°C)	$S^0_{CeF_3}/S^0_{LaF_3}$	$K*$		
		1.82 Mole % CeF$_3$, 0.78 Mole % LaF$_3$**	1.85 Mole % CeF$_3$, 2.27 Mole % LaF$_3$**	1.83 Mole % CeF$_3$, 3.30 Mole % LaF$_3$**
700	1.14	0.97	1.55	1.18
600	1.15	1.18	1.82	1.38
500	1.09	1.52	2.28	1.68

$$*K = \frac{N_{CeF_3(d)} \; N_{LaF_3(ss)}}{N_{LaF_3(d)} \; N_{CeF_3(ss)}} \; .$$

**Total composition in container.

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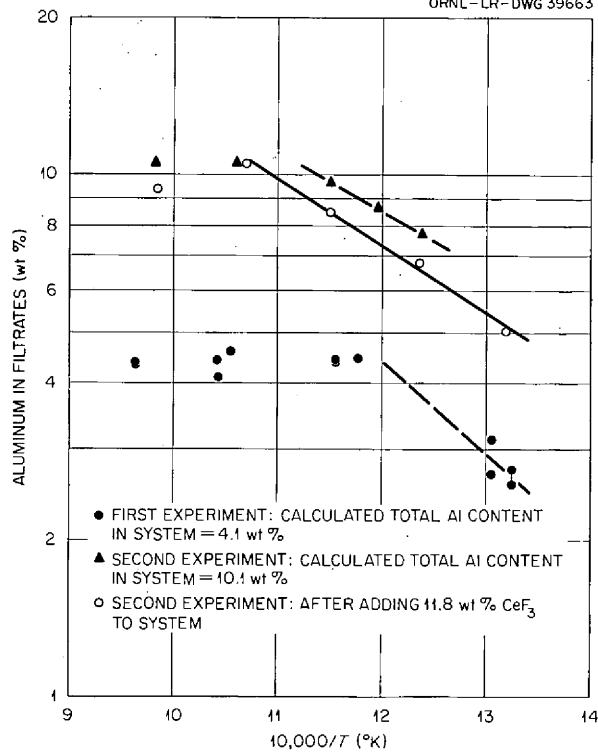
Fig. 10. Solubility of AlF_3 in $LiF\text{-}BeF_2\text{-}UF_4$ (62.8-36.4-0.8 mole %).

Fig. 11. Effect of AlF_3 on Solubility of CeF_3.

its absence, probably due to a change in solvent similar to that seen above upon addition of BeF_2. As a consequence of this behavior, it is clear that AlF_3 cannot be used as a solid extractant for rare earths.

Additional Data Pertinent to a Solid-Solvent Extraction of Rare-Earth Poisons

In addition to determining the single-stage equilibrium extraction coefficients, it is necessary to know something of the rate of reaction of dissolved rare earth with solid extractant and to know whether trace amounts of rare earth would be extracted as predicted. A simple isothermal experiment was performed at 500°C which used unlabeled LaF_3 as solid extractant for 0.15 wt % CeF_3 (tracer labeled) dissolved in $LiF\text{-}BeF_2$ (63-37 mole %). An amount of LaF_3 equal to about four times the amount necessary to saturate the solution was added. One minute after the addition, the CeF_3 content in the liquid phase had dropped to 0.04 wt % and 5 min later (when the second filtrate

was taken) it had dropped to the equilibrium value of 0.03 wt %.

To determine whether trace amounts of rare-earth fluorides would behave as predicted, a polythermal experiment was carried out in which solid CeF_3 (unlabeled) was added in two increments to $LiF\text{-}BeF_2\text{-}UF_4$ (62.8-36.4-0.8 mole %) in which was dissolved 0.0795 wt % SmF_3 (tracer labeled). The results of this experiment are shown in Table 2. The really excellent agreement with the calculated amounts of SmF_3 indicates that trace amounts of rare-earth poisons act in an essentially predictable manner.

An initial attempt at performing a solid-solvent extraction was made in which LaF_3 was packed in a horizontal column as the solid extractant for dissolved CeF_3 in $LiF\text{-}BeF_2$ (63-37 mole %). The solution was saturated with LaF_3 and then forced

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Table 2. Removal of Traces of SmF_3 by Addition of CeF_3 to LiF-BeF_2-UF_4 (62.8-36.4-0.8 Mole %)

| | Total Rare-Earth Fluoride (wt %) in System (calc.) | | Filtrate Temperature (°C) | Rare-Earth Fluoride (wt %) in Filtrates | | |
| | | | | CeF_3[a] | SmF_3 | |
	CeF_3	SmF_3			Observed	Predicted[b]
Before CeF_3 addition	0	0.0795	749		0.0795	
First CeF_3 addition	2.12	0.0778	695	2.1[c]	0.0750	
	2.12	0.0780	580	2.1[c]	0.0757	
	2.12	0.0781	487	0.90	0.0542	0.0471
Second CeF_3 addition	10.1	0.0731	736	8.34	0.0662	0.0662
	10.2	0.0735	587	2.57	0.0397	0.0300
	10.7	0.0757	492	0.96	0.0262	0.0131

[a]Determined in a separate experiment; disregards effect of small amount of SmF_3 in system.

[b]Calculated from relationship $N_{SmF_3(d)} = \left[\dfrac{S^0_{SmF_3} N_{SmF_3(ss)}}{S^0_{CeF_3} N_{CeF_3(ss)}} \right] N_{CeF_3(d)}$.

[c]Unsaturated.

by gas pressure through the column. The CeF_3 concentrations of four successive effluent liquid samples are shown below:

	Concentration (ppm)
Starting material	1000
Effluent sample	
No. 1	80
No. 2	50
No. 3	30
No. 4	30

The drop in CeF_3 content of successive samples is probably related to a change in flow rate as the column filled with liquid. The thirtyfold reduction in CeF_3 concentration obtained for this experiment indicates that quite large decontamination factors may be ultimately achieved.

Appendix

SOLUBILITY DATA FOR CeF$_3$ IN VARIOUS SOLVENTS

Table A. 1. Solubilities of CeF$_3$ in NaF-ZrF$_4$ Solvents of Various Compositions at Three Temperatures

Average Analyzed Solvent Composition (mole %)*		Molecular Weight (g/mole) of Solvent Mixture	Solubility (mole %) of CeF$_3$**		
NaF	ZrF$_4$		At 550°C	At 675°C	At 800°C
42	58	114.6	3.0	8.2	10.3
50	50	104.5	2.12	3.0	4.4
53	47	100.9	1.64	2.37	3.9
59	41	93.3	0.56	0.62	1.61
63	37	88.4	0.26	0.44	1.07
80.5	19.5	66.4			4.71

*±0.5.
**Graphically interpolated.

Table A. 2. Solubility of CeF$_3$ in LiF-BeF$_2$ Solvents

BeF$_2$ in Solvent (mole %)*	Temperature (°C)	CeF$_3$ in Filtrate (mole %)	BeF$_2$ in Solvent (mole %)*	Temperature (°C)	CeF$_3$ in Filtrate (mole %)
24.4	766	>1.8**	37.3	720	1.50
	722	>1.8**		643	0.73
	681	>1.8**		556	0.31
	623	1.35		467	0.108
	600	1.10	40.7	704	1.29
28.5	733	2.04		627	0.68
	648	1.44		544	0.286
	573	0.67		476	0.128
	510	0.207	43.3	723	1.64
32.5	740	1.57		612	0.62
	666	1.15		508	0.219
	586	0.55		425	0.082
	513	0.232	46.2	717	1.76
34.5	734	2.13		~655	1.00
	729	1.79		632	0.79
	662	1.00		511	0.27
	656	0.92		412	0.094
	566	0.34	48.4	726	1.80
	556	0.32		615	0.83
	476	0.127		501	0.284
	474	0.123		407	0.105

*From chemical analyses of filtrates.
**Not saturated.

Table A.3. Solubility of CeF_3 in $NaF-BeF_2$ Solvents

BeF in Solvent (mole %)*	Temperature (°C)	CeF in Filtrate (mole %)	BeF in Solvent (mole %)*	Temperature (°C)	CeF in Filtrate (mole %)
23.9	794	>3.3*	38.6	676	0.55
	768	>3.3*		596	0.256
	744	>3.3*		516	0.155
	714	>3.3*		425	0.060
29.7	742	2.71	41.1	749	1.14
	684	1.99		668	0.56
	613	0.98		584	0.258
32.2	748	1.96		503	0.133
	684	1.03		423	0.062
	617	0.51	46.0	738	1.39
35.5	763	1.41		668	0.72
	677	0.60		592	0.46
	616	0.312		513	0.232
	537	0.134		429	0.134
	463	0.065	52.5	733	1.73
37.5	752	1.24		678	1.21
	673	0.62		589	0.64
	605	0.272		509	0.366
	527	0.116		405	0.175
	440	0.054			

*From chemical analyses of filtrates.
**Not saturated.

Table A. 4. Solubility of CeF_3 in LiF-NaF-BeF_2 Solvents (LiF-NaF Eutectic, 60-40 Mole %, + BeF_2 Shown)

BeF_2 in Solvent (mole %)*	Temperature (°C)	CeF_3 in Filtrate (mole %)	BeF_2 in Solvent (mole %)*	Temperature (°C)	CeF_3 in Filtrate (mole %)
None	778	>4.5**	31.5	743	2.41
	732	>4.5**		648	1.04
	712	>4.5**		544	0.380
	671	>4.5**		449	0.085
4.0	806	>4.5**		366	0.029
	750	>4.5**	34.9	738	1.47
	707	>4.5**		653	0.65
	654	>4.5**		546	0.207
10.4	790	>4.5**		453	0.075
	748	>4.5**		357	0.027
	692	>4.5**	41.4	751	1.50
	669	>4.5**		640	0.52
12.2	803	>4.5**		537	0.192
	754	>4.5**		453	0.085
	702	>4.5**		364	0.035
	664	>4.5**	45.2	716	1.29
	642	>4.5**		623	0.57
21.2	796	>4.5**		522	0.241
	762	>4.5**		440	0.112
	716	>4.5**		359	0.054
	687	>4.5**	51.2	736	1.99
	652	3.86		641	0.91
	613	2.30		542	0.398
22.9	728	>2.40**		446	0.176
	692	>2.40**		358	0.085
	666	>2.40**	56.2	727	2.45
	658	>2.40**		638	1.26
	634	2.04		529	0.50
	614	1.73		443	0.249
	599	1.28		363	0.142
	580	0.88			

*From chemical analyses of filtrates.

**Not saturated.

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