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Reduction of Iron Dissolved in Molten $LiF-ThF_4$

C. J. Barton and H. H. Stone

ABSTRACT

Additions of ^{59}Fe tracer to $LiF-ThF_4$ (73-27 mole %) permitted rapid and sensitive measurements of the iron content of filtered samples of molten material. More than 40 hours were required for nearly complete removal of iron from the melt by hydrogen reduction at about 600°C while reduction of iron by metallic thorium at the same temperature was virtually complete after three hours. Disappearance of a relatively large quantity of solid thorium on long exposure to the molten salt will require further investigation. Comparison of the data obtained by use of ^{59}Fe tracer counts with the results of colorimetric iron determinations by two different laboratories seems to indicate that the colorimetric iron method employed when these tests were performed did not give reliable iron results at low iron concentrations. Colorimetric nickel determinations by the two laboratories give divergent data for more than half of the samples.

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INTRODUCTION

Many samples of $LiF-ThF_4$ (73-27 mole %) from protactinium recovery experiments[1,2,3] have been analyzed for iron and some for nickel. In some cases it has been possible to correlate the iron and protactinium results but the low iron and nickel concentrations expected in filtered salt samples reduced with metallic thorium have seldom been confirmed by the analytical data. We decided, therefore, to conduct an experiment in which ^{59}Fe tracer would be used to follow the reduction of iron dissolved in molten $LiF-ThF_4$ and to compare the ^{59}Fe results obtained with analytical values obtained by two laboratories that routinely perform iron and nickel determinations using colorimetric methods. It appears that similar studies have been performed at least twice before during the history of the molten salt project at ORNL. The results were not documented in any detail on either occasion, but the data obtained are in general agreement with the findings of the present investigation.

EXPERIMENTAL PROCEDURE

The $LiF-ThF_4$ (73-27 mole %) used as the solvent material in this experiment was supplied by J. H. Shaffer (Reactor Chemistry Division, ORNL) as part of a large (3.5 kg) batch that had received the usual purification treatment including hydrofluorination with a $HF-H_2$ mixture followed by prolonged hydrogen reduction to remove iron, nickel, and other reducible impurities.

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We obtained approximately one millicurie of ^{59}Fe tracer by purchasing 10 mg of iron in the form of Fe_2O_3 that had been enriched in ^{58}Fe isotope and irradiating it in the LITR. The irradiated material was mixed with enough inactive Fe_2O_3 to give approximately 600 ppm of Fe when completely dissolved in 320 g of salt. The salt and iron oxide were placed in a nickel container, heated to approximately 600°C in flowing helium, treated with mixed helium and anhydrous HF followed by a brief hydrogen treatment and then with mixed hydrogen and HF in an effort to remove oxygen and to dissolve the added iron. We believe, on the basis of thermodynamic data,[4] that this treatment also reduced Fe^{3+} to Fe^{2+}. Subsequent analyses of filtered samples indicated that part of the added iron was not dissolved by this treatment. Hydrogen reduction was then started. This gas was purified by passing it through a Deoxo unit to convert any oxygen present to water and then through a column of Drierite and a liquid-nitrogen-cooled trap to remove water. Hydrogen treatment continued until the ^{59}Fe count on filtered samples indicated that only a slight trace of iron remained in the melt. The melt temperature varied during this period from about 590 to 625°C due to daily variations in the line voltage that supplied the furnace.

The melt was treated with mixed hydrogen-HF and with helium-HF to redissolve the hydrogen-reduced iron. When the ^{59}Fe counts indicated that no further increase in the iron content of filtered samples was occurring, we gave the melt a brief hydrogen treatment (1-1/2 hours) to effect at least partial reduction of dissolved Ni^{2+} and removal of dissolved HF. Thorium rods approximately 1/4 inch in diameter were exposed to the melt for three, 1-hr periods and one, 16-hr period, taking a filtered sample each time after the rod was removed. The rods were cleaned by filing before they were reused. This experiment was performed

in a hood located in the High Alpha Molten Salt Laboratory since no protactinium was added to the melt. The samples were handled in the hood as far as possible because of the hazard of airborne thorium.

Most samples were removed by filtering through sintered copper filters following the procedure previously described[5]. The frozen salt samples were removed from the fiter sticks and crushed in porcelain mortars. One-gram portions of the samples were placed in small plastic vials, sealed in plastic bags, and given the following analytical treatment. The gamma activity of the solid samples was first measured by use of a multichannel analyzer. The samples were then dissolved in the High Level Alpha Radiation Laboratory (Building 3508) and analyzed for iron and nickel content by colorimetric methods. Portions of the solutions were transferred to the General Hot Analysis Laboratory (Building 2026) for similar determinations and the the Radioisotopes Radiochemistry Laboratory (Building 3019) for ^{59}Fe counting. Selected samples were also submitted for spectrographic analysis as indicated in Table I.

ANALYTICAL DATA

Most of the analytical data obtained from the experiment are displayed in Table 1. It was necessary to calculate a factor for converting the ^{59}Fe counts into iron concentrations. This was accomplished by choosing one or two samples for which the 2026 and 3508 colorimetric analyses agreed reasonably well, and dividing the average of their results by the ^{59}Fe count (per minute). The values calculated from the ^{59}Fe counts obtained with solutions were slightly more consistent than the values calculated from the ^{59}Fe counts on solid samples using less refined counting techniques. The iron concentration values shown in parentheses in the ^{59}Fe column of Table 1 are the values assumed to be correct for the calculation of the conversion factor. The factor used for the

hydrogen reduction phase of the experiment was not applicable in the last part of the experiment. Although the ^{59}Fe counts were approximately the same for samples 14 and 15 as for samples 2-5, the colorimetric iron values were much higher. We believe that some iron was introduced into the salt by use of stainless steel samplers at a time when no copper samplers were available or that the second hydrofluorination treatment was more effective in dissolving the added iron oxide than the initial treatment.

Good agreement among the results of iron determination of the three laboratories is noted for about 1/3 of the samples analyzed. The largest discrepancies between colorimetric determinations and ^{59}Fe count values were obtained with samples that were almost certainly contaminated. (Samples 12, 13, 19, and 21). Exclusing these samples, reasonable agreement was obtained with almost half of the samples analyzed by the three laboratories. In general, agreement was poorest where the iron concentration calculated from tracer counts was less than 0.10 Fe/g.

An effort was made to ascertain whether the discrepancy observed at low iron concentrations was due to some deficiency in the colorimetric iron method or to sample contamination. Several samples, including the as received salt, were submitted for spectrographic analysis. The value reported for the as received salt, 0.011 mg/g, was lower than any of the colorimetric values obtained. These ranged from 0.03 mg/g (General Analysis Laboratory) to 0.13 mg/g (2026 lab.). Of course, no tracer result was obtained with this sample. The spectrographic concentrations determined for the other three samples analyzed by this method were all higher than the values calculated from ^{59}Fe counts. In each case, the spectrographic result was in good agreement with at least one colorimetric value but it was lower than most of the data obtained by this method. If the spectrographic data are correct, then we must assume that the samples were slightly

contaminated with iron either in our laboratory or in the analytical laboratory. Any solid iron or nickel or compounds of either metal, that was introduced into a sample after it was removed from the melt would have been dissolved and thus would contaminate the sample solution. It appears, however, that the colorimetric iron method tends to give high results with samples having a low iron concentration.

Much less attention has been given to the colorimetric nickel data because we had no tracer for this element. The results obtained by the 2026 laboratory were lower than those reported by the 3508 laboratory for a majority of the samples but the cause of the observed discrepancies has not been determined. Since Ni^{2+} is thermodynamically incompatible with Fe^{0} at 600°C, high nickel values in filtered, reduced samples of salt are unlikely to be correct unless the samples were contaminated or metallic nickel particles were small enough to pass through the sampler filters.

IRON REDUCTION

The plot of iron concentration as a function of time is shown in Fig. 1. The hydrogen reduction process is obviously quite slow and the reduction rate seems to diminish with decreasing iron concentration. It is not clear whether any significance can be attached to the apparently linear rates during the initial and middle fractions of the reduction period as indicated in Fig. 1 but the data indicate that the first 10% of the iron was reduced in less than three hours while approximately 12 hours were required to remove the last 10%.

The thorium reduction process was quite rapid in comparison to hydrogen reduction and there was no indication of a change in reduction rate during the initial three-hour period when 97.5% of the iron activity was removed from solution.

THORIUM LOSS

A puzzling aspect of this experiment was that during the 16-hr period between samples 22 and 23, the thorium rod (estimated to weigh about 12 g) used to reduce the iron completely disappeared. Samples 25-28 were obtained during the post-mortem phase of the experiment when the nickel pot was cut through and its contents were removed for examination and analysis. Black lumps of varying size were removed from the frozen salt, ground to pass a 40-mesh sieve and submitted for analysis. The complete analysis of samples 25-27 is given in Table 2. In addition to the chemical analysis, which is not entirely satisfactory because none of the totals came close to 100%, sample 25 (the largest black lumps) was submitted for X-ray diffraction examination. The only definitely identified component of the material was Li_3ThF_7 but LiF and $LiThF_5$ were reported to be possibly present and a number of unidentified lines were also found.

If we assume that all the fluoride ions were combined either with lithium or thorium, calculations show that 170 mg/g of thorium was present as metal in sample 25 and 290 mg/g in sample 26. Since metallic nickel and thorium were not found in sample 25 by X-ray diffraction, it is possible that these metals were present as an intermetallic compound of unknown composition.

The fact that the black material composing samples 25 and 26 could be ground to small particles seems to indicate that the metals present were deposited from the melt.

The disappearance of a significant quantity of solid thorium on long exposure to molten LiF-ThF_4 served as a reminder of similar behavior in an experiment, Run 2-22 (66), reported earlier.[5] There, a 6-hr exposure resulted in removal of 28 g of thorium from a larger rod than that used here. In that

instance, it was speculated that the thorium rod came in contact with the bottom of the nickel pot causing a current to flow that eroded the thorium rod. In both experiments the thorium rod was supported by a 1/8-in nickel rod that was electrically insulated from the container by a Teflon plug. Black magnetic material removed from the nickel pot after cooling to room temperature in the earlier experiment analyzed 45% nickel and 30% thorium, while non-magnetic material contained 22% nickel and 49.5% thorium. The chunks of black material found in the pot were quite brittle, as in the present experiment, which was interpreted to mean that they were aggregates of finely divided thorium and nickel particles.

While the same explanation of thorium loss given earlier could be offered here, an alternative explanation can be given although it is purely speculative at present. This assumes that the reaction

$$3ThF_4 + Th^0 \rightarrow 4ThF_3$$

can occur in the molten mixture and that the ThF_3, when it diffuses to the nickel wall, disproportionates because of formation of Th-Ni intermetallic compounds. Failure to find X-ray evidence of such compounds in sample 25 weakens the argument for this explanation, but since the form of the nickel present has not been determined, the question remains open. Since ThF_3 is not observed in our frozen salt samples, and it has not been reported in the literature, we must assume that if the above reaction occurs at 600° it must be reversed on cooling.

Since ThF_3, if it exists, may be strongly colored, we plan to expose molten $LiF-ThF_4$ to solid thorium in a furnace that allows visual observation of the melted material.

Conclusions

1. Use of ^{59}Fe tracer gives a sensitive measure of the iron content of fluoride salt samples.

2. The colorimetric iron method presently employed by the 2026 and 3508 laboratories does not appear to give reliable results at low iron concentrations.

3. There is a large and presently unexplained discrepancy in the nickel analyses by the 2026 and 3509 laboratories for a large fraction of the samples.

4. Disappearance of a comparatively large amount of thorium metal on long exposure to molten $LiF-ThF_4$ raises the possibility that a lower-than-normal valence state of thorium may occur in melts exposed to solid thorium. In addition to its scientific interest, this reaction could affect the use of solid thorium as the reductant for protactinium and we are planning further examination of this phenomenon.

Table 1. Analysis of Samples from Iron Reduction Experiment

Sample No.	Iron Concentration (mg/g)				Nickel Conc. (mg/g)		Sample Description
	2026 Lab.	3508 Lab.	^{59}Fe Count	Spec. Anal.	2026 Lab.	3508 Lab.	
0	0.13	0.07	-	0.011	< 0.01	0.04	Salt as received
1	0.52	< 0.01	0.21		0.06	0.02	Filtered salt - $1\frac{1}{2}$ hr He-HF
2	0.27	0.02	0.31		< 0.01	0.26	Filtered salt - $2\frac{1}{4}$ hr He-HF
3	0.18	0.04	0.33		< 0.01	0.12	Filtered salt - $1\frac{1}{2}$ hr H_2
4	0.29	0.34	(0.315)		< 0.01	0.35	Filtered salt - 1 hr H_2-HF
5	0.29	0.30	(0.295)		< 0.01	0.32	Filtered salt - 2 hr H_2
6	0.25	0.22	0.22		< 0.01	0.08	Filtered salt - $7\frac{1}{2}$ hr H_2
7	0.20	0.01	0.13		0.06	0.17	Filtered salt - 18 hr H_2
8	0.21	0.09	0.07		< 0.01	0.17	Filtered salt - 26 hr H_2
9	0.18	0.10 - 0.27 - < 0.01	0.030	0.15	0.07	0.14	Filtered salt - $31\frac{1}{2}$ hr H_2
10	0.12	0.05 - 0.17 - 0.10	0.002	0.04	< 0.01	0.29	Filtered salt - $41\frac{1}{2}$ hr H_2
11	0.14	0.02 - 0.16 - 0.07	0.003	0.03	0.09	0.12	Filtered salt - $49\frac{1}{4}$ hr H_2
12	0.67[a]	0.10 - 0.61[a]	0.021		0.21	0.24	Filtered salt - 1 hr H_2-HF
13	1.85[a]	2.10[a]	0.07		0.29	0.27	Filtered salt - 3 hr H_2-HF
14	0.13	0.17	0.55[c]		< 0.01	0.04	Filtered salt - $5\frac{1}{2}$ hr H_2-HF
15	0.53	0.58	(0.55)		< 0.01	0.17	Filtered salt - 16 hr He-HF
16	0.43	0.47	0.50		0.33	0.27	Filtered salt - 2 hr H_2-HF
17	0.48	0.54	0.52		< 0.01	0.03	Filtered salt - $1\frac{1}{2}$ hr H_2
18	0.38	0.47	0.43		< 0.01	0.11	Filtered salt - 1 hr Th exp.
19	14.3 [b]	14.9 [b]	0.11		0.18	0.22	Filings from Th rod
20	0.17	0.20	0.13		< 0.01	0.11	Filtered salt - 2 hr Th exp.
21	2.89[b]	2.99[b]	0.07		0.16	0.14	Filings from 2nd Th rod
22	0.14	0.05	0.01		0.33	0.50	Filtered salt - 3 hr Th exp.
23	< 0.01	< 0.01	0.04		< 0.01	2.23	Filtered salt - 19 hr Th exp.
24	< 0.01	0.27	1.05		240	205	Crust from Ni support rod
25	-	1.03	1.32		-	140-218	Large black lumps from salt
26	-	1.84	1.36		-	131-137	Small black lumps from salt
27	-	0.53	0.37		-	3.7-5.5	Ground unfiltered salt
28	Total	34.5	25.7		-	-	Material leached from vessel wall by acid

[a]Contaminated by stainless steel sampler.

[b]Probably contaminated by iron from file used to remove surface of Th rod.

[c]The higher iron concentration in this and subsequent samples, as compared to earlier uncontaminated samples, is possibly due to use of stainless steel samplers for samples 12 and 13, or to solution of some of the added iron that did not dissolve in the initial hydrofluorination treatment.

Table 2. Analysis of Material

Removed from Nickel Pot

Sample No.	Concentration (mg/g)					
	Th	Li	F	Fe	Ni	Total
25	524	21.2	174	1.03	218	936
26	646	24.1	150	1.84	134	956
27	561	44.1	310	0.53	4.6	920
Theoretical (pure salt)	615	49.5	335	-	-	1000

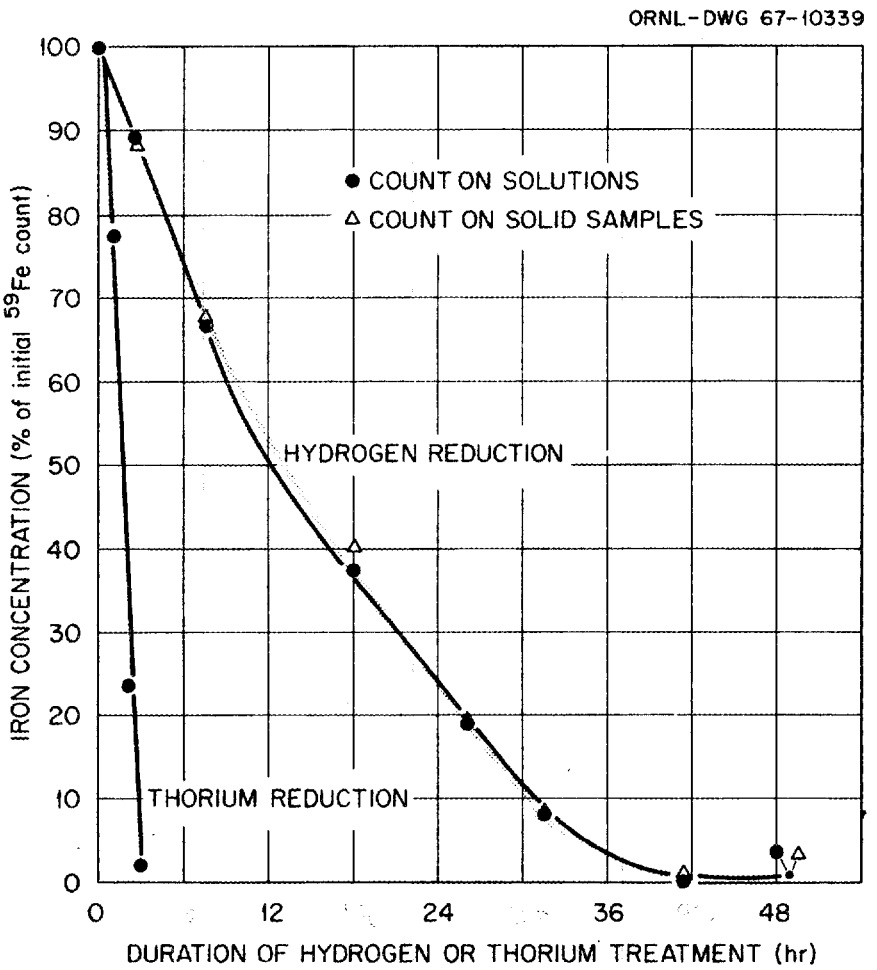

Fig. 1. Reduction of Fe^{2+} in $LiF-ThF_4$ (73-27 mole %) as Indicated by ^{59}Fe Counts on Filtered Samples.

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