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DISSOLUTION OF METALS IN FUSED FLUORIDES

R. E. Leuze
G. I. Cathers
C. E. Schilling

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Chemical Development Section

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1.0 ABSTRACT

In scouting tests, a number of metals used in nuclear reactor fuel elements were dissolved by 44.5-48.5-7.0 mole % ZrF_4-KF-NaF fused salt at 675°C through which HF was being passed. These included type 304 stainless steel at 4 mils/hr; type 347Nb stainless steel at 7 mils/hr; thorium at 14 mils/hr; nonirradiated uranium at 17 mils/hr; zirconium at 22-35 mils/hr; titanium at 31 mils/hr; and Zircaloy-2 at 22-46 mils/hr. Only small amounts of volatile fission products formed when irradiated uranium was dissolved. Variables that appear to affect the dissolution rate are the composition of the fused fluoride, the fused fluoride temperature, the HF flow rate, the metallurgical characteristics of the material being dissolved, and the presence of other metals. The low dissolution rate of 0.001 mil/hr observed for nickel suggests that it may be suitable as a material of construction for reaction vessels.

2.0 INTRODUCTION

It has been known for some time that many metals react with anhydrous HF to form protective films which prevent further attack. A possible method of carrying the dissolution reaction to completion is to contact the metal with HF in the presence of a suitable molten fluoride bath to dissolve the protective film. The dissolution of enriched reactor fuel elements in this way followed by bubbling F_2 gas through the molten bath[1,2] to distill out UF_6 is an attractive basis for an economical chemical processing scheme. This report gives the results of a number of scouting experiments performed to determine whether practical dissolving rates could be obtained, to determine which variables affect the dissolution rate, and to obtain preliminary information on the behavior of fission products during such a dissolution.

3.0 DISSOLUTION RATES

In a series of scouting tests made to determine the feasibility of converting metals to the fluorides and dissolving the resulting fluorides in a fused fluoride bath, dissolution rates ranged from 0.001 mil/hr for nickel to complete, instantaneous dissolution of tin and zinc. In these studies, coupons, 2-6 sq cm total surface, of the materials studied were placed in a molten bath of 44.5-48.5-7.0 mole % ZrF_4-KF-NaF at 675°C through which HF was being bubbled. After 0.5-1 hr, the coupons were removed, washed, dried, and weighed.

The results (see Table 1) cannot be used to calculate the total dissolution time for a given sample without further investigation of the actual material to be processed, since the character of the metal has a considerable effect on the dissolution rate. However, the data indicate which metals can be readily dissolved under these conditions and suggest the use of nickel or Monel for materials of construction because of their relatively slow dissolution rates. It is encouraging to note that a number of nuclear reactor materials (stainless steel, thorium, uranium, zirconium, and Zircaloy-2) dissolved at reasonably fast rates.

The behavior of several finely divided materials in the same fused fluoride is shown in Table 2. Perhaps the material of most interest is UO_2 since it is being used as a nuclear fuel. UO_2 prepared by calcination at 2000°C dissolved readily. However, U_3O_8 was only partly converted to the fluoride and did not dissolve completely in the fused fluoride. The fused fluoride decomposed both powdered B_4C and UC_2, converting the boron and uranium to the fluoride while the carbon floated on the salt without reacting.

3.1 Variables Governing Dissolution Rate

Preliminary tests were made to determine which variables are important in the dissolution process. The dissolution rate appeared

Table 1. Dissolution Rates of Metals in Fused Fluorides

Fused fluoride: 44.5-48.5-7.0 mole % ZrF_4-KF-NaF

Temperature: 675°C

HF flow rate: 50 ml/min

Nitrogen or argon blanket over fused salt

Material	Penetration Rate (mils/hr)
Nickel	0.001
Monel	0.02
Molybdenum	0.03
Tungsten	0.06
Silicon carbide[a]	2
Type 304 stainless steel	4
Type 347Nb stainless steel	7
Niobium	7
Tantalum	8
Manganese	10
Mild steel (Unistrut)	13
Thorium, 1/8-in. plate	14
Uranium	17
Zirconium[b]	22-35
Chromium	31
Titanium	31
Zircaloy-2[b]	22-46
98 wt % uranium—5 wt % zirconium alloy	50
Tin	Sample melted and dissolved instantly
Zinc	Sample melted and dissolved instantly

(a) Disintegrated, leaving suspended material.

(b) Range due to metallurgical differences in metal.

Table 2. Behavior of Finely Divided Materials in Fused Fluorides

Fused fluoride: 44.5-48.5-7.0 mole % ZrF_4-KF-NaF

Temperature: 675°C

HF flow rate: 50 ml/min

Nitrogen blanket over fused salt

Monel container

Material	Observation
Vanadium shot	Negligible reaction; settled to bottom
Silicon powder	Negligible reaction; settled to bottom
Ruthenium powder	Negligible reaction; settled to bottom
Tellurium powder	Negligible reaction; settled to bottom
Molybdenum powder	Negligible reaction; settled to bottom
U_3O_8 powder	Partly converted to UF_4; some settled to bottom
B_4C powder	3 g dissolved in 1 hr; carbon floated and did not dissolve; much gas evolved
UC_2 powder	Rapid dissolution; carbon floated and did not dissolve
UO_2 powder	Material had been fired at 2000°C; reacted rapidly

to be affected by (1) the composition of the fused fluoride, (2) the temperature of the fused fluoride, (3) the HF flow rate, (4) the metallurgical characteristics of the material being dissolved, and (5) the presence of other metals.

Composition of the Fused Fluoride. The composition of the fused fluoride has a great effect on the metal dissolution rate. Rates of zirconium dissolution varied by more than a factor of 10 for different fused fluoride baths (see Table 3). The fused fluoride composition giving the highest zirconium dissolution rate also gave the lowest uranium dissolution rate. However, a direct comparison between zirconium, zirconium-uranium alloy, and uranium dissolution rates cannot be made since the metallurgical characteristics of the metals were different. It should also be noted that the data for fused fluorides containing large amounts of HF are for initial conditions. Penetration rates decreased rapidly as the reaction progressed owing to loss of HF or to the presence of the metal fluorides which formed and did not dissolve in HF-rich mixtures.

Temperature of Fused Fluoride. Increasing the fused fluoride temperature increased the zirconium dissolution rate (see Fig. 1). For the 44.5-48.5-7.0 mole % ZrF_4-KF-NaF fused salt, at a constant HF flow rate, the penetration rate increased about 0.05 mil/hr/°C over the temperature range from 475 to 675°C.

Hydrogen Fluoride Flow Rate. At constant temperature, greater HF flow rates resulted in a faster rate of zirconium dissolution (see Fig. 1). This increase may be the result of better agitation caused by the increased flow of gas or the result of continually resaturating the fused salt with HF as it is consumed. In other experiments an initial reaction rate of 6 mils/hr was obtained in this bath at 675°C with no HF added; however, the rate decreased rapidly with time.

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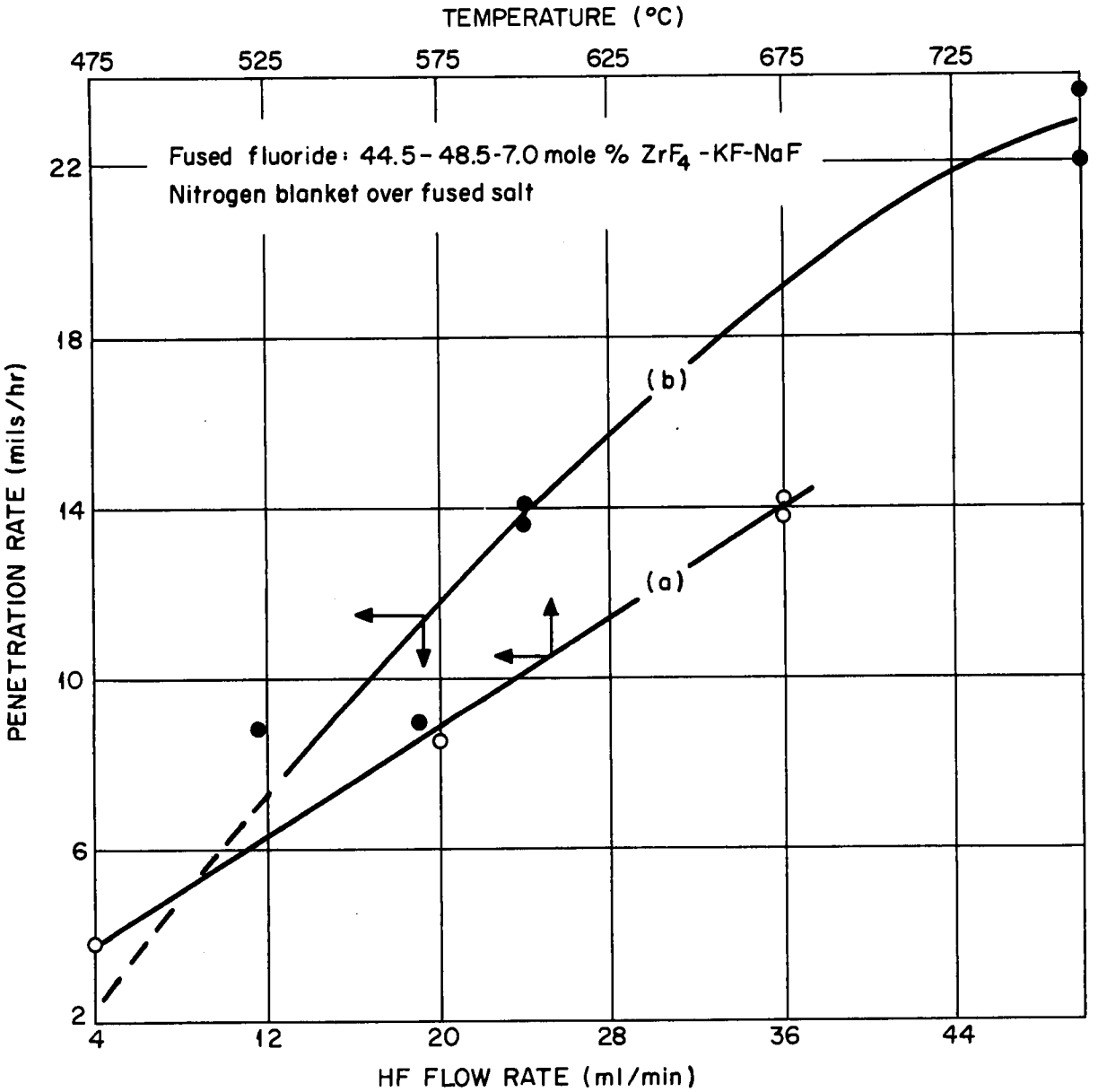

Fig. 1. Effect on Zirconium Dissolution Rate of (a) temperature of fused fluoride at HF flow rate of 24 ml/min and (b) HF flow rate at temperature of 675°C.

Table 3. Metal Dissolution Rates in Various Fused Fluorides

Bath Composition	Temp. (°C)	Dissolution Rate (mils/hr)		
		Zirconium	95 wt % Uranium 5 wt % Zirconium	Uranium
20-80 mole % KF-HF	75	290[c]	13[c]	0.14[c]
90-10 mole % KF-NaF[a]	275	160[c]		5[c]
KHF_2	300	130[c]		28[c]
44.5-55.5 mole % ZrF_4-NaF[b]	640			21
38-13-49 mole % ZrF_4-KF-NaF[b]	675	27		
44.5-48.5-7.0 mole % ZrF_4-KF-NaF[b]	675	22	50	17

(a) Saturated with HF at 250°C.

(b) HF bubbled through fused salt at a rate of about 50 ml/min.

(c) These are approximate initial rates. Rates decreased rapidly owing to either loss of HF or presence of metal fluoride formed.

Metallurgical Characteristics of Material Being Dissolved. The metallurgical history of the material being dissolved has a considerable effect on the dissolution rate (see Table 4). Dissolution rates varied by a factor of 2 for various samples of zirconium and of Zircaloy-2. Data are too preliminary for an exact correlation to be made. However, it can be generally stated that metals that had received the most mechanical working, such as rolling, drawing, or swaging, dissolved most rapidly. The presence of impurities in the metal may also result in unusually rapid dissolution rates.

Presence of Other Metals. The dissolution rate of a metal apparently is affected by the presence of other metals. This was noted in a single experiment in which copper and nickel were both suspended in fused fluoride. The nickel dissolved slowly and the copper was nickel-plated. This arrangement or a similar one may be useful in retarding corrosion of construction materials.

3.2 Volatilization of Fission Products in Dissolution of Irradiated Uranium

When short-decayed irradiated uranium was dissolved in HF-fused fluoride, very little of the short-half-life fission product contamination was volatilized (see Table 5). Either HF does not form the more volatile fluorides (IF_7, MoF_6, TeF_6, RuF_5) under these conditions, or does not significantly sparge out any that are formed. When long-decayed material was sparged with a large amount of HF, niobium was preferentially volatilized (see Table 6).

Two runs were made with short-decayed material. In each a 6-g uranium metal slug (0.2 in. dia, 0.6 in. long), irradiated to 40 Mwd/ton and decayed 21 days, was dissolved in 67 g of 55.5-44.5 mole % $NaF-ZrF_4$ at 650°C. The slug was supported in a 1-in.-dia nickel reactor on a sieve plate, which provided better

Table 4. Effect of Metallurgical Characteristics on Dissolution Rate

Fused fluoride: 44.5-48.5-7.0 mole % ZrF_4-KF-NaF
Temperature: 675°C
HF flow rate: 50 ml/min
Nitrogen or argon blanket over fused salt

Metal	Description	Dissolution Rate (mils/hr)
Zirconium	Arc-melted crystal bar	18
	Ingot with some rolling	22
		22
		24
	Impure crystal bar	35
Zircaloy-2	Weld metal	23
	1/4-in. soft sheet	26
	1/4-in. hydrogen-embrittled sheet	40
	1/8-in. hard sheet	46

Table 5. Volatility of Radioactivity in Dissolution of Uranium Metal in $NaF-ZrF_4$ with HF

6-g uranium metal slug completely dissolved in 67 g of $NaF-ZrF_4$ (55.5-44.5 mole %) over a period of 12 hr

HF rate: 20 ml/min

Uranium irradiation: 40 Mwd/ton; decayed 21 days

	Activity in HF (% of total)	
	Run 1	Run 2
Gross $\beta^{(a)}$	1.3×10^{-4}	0.012
I $\beta^{(b)}$	0.030	0.4
Te $\beta^{(b)}$	2.0	---
Mo $\beta^{(b)}$	0.2	---
Ru $\beta^{(a)}$	0.0051	0.026
Nb $\beta^{(a)}$	0.0015	0.74

(a) Calculated on the basis of activity found in similar uranium slugs after aqueous dissolution.

(b) Calculated on the basis of activity found in UF_6 trap after fluorinating the $UF_4-NaF-ZrF_4$ salt at 650°C.

Table 6. Sparging of Activity from UF_4-NaF-ZrF_4 Salt with HF

30 g of UF_4-NaF-ZrF_4 (4-52-44 mole %) at 650°C sparged with HF at a flow rate of 600-1500 ml/min; effluent collected in acetone—dry ice cold trap

Fraction	HF Trapped (moles)	Nb β (c/min/mole HF)	Nb β (% of gross β in HF)
1	1.24	6.81×10^5	89
2	1.26	1.71×10^5	83
3	0.96	1.74×10^4	100
4	1.43	1.79×10^5	100
5	3.80	4.69×10^4	94
6	3.64	1.15×10^4	80

dispersion of the HF gas. The HF was passed in at a rate of 20 ml/min for 12 hr to achieve complete dissolution. The effluent HF was condensed in an acetone--dry ice cold trap, diluted with water, and analyzed for its fission product content.

Only one test was made on sparging of long-decayed material. Thirty grams of UF_4-NaF-ZrF_4 (4-52-44 mole %) was sparged at 650°C with HF at a high rate, 500-1500 ml/min (total HF, 250 g). In six different HF fractions collected in an acetone--dry ice trap, only about 1% of the gross β, Ru β, and Zr β activities in the original fluoride was found in the cold trap along with only 0.005% of the initial total rare earth activity. About 6% of the original niobium β activity was volatilized, forming nearly all the activity in the condensed HF. Ruthenium and zirconium β activities were negligible in every fraction.

3.3 Efficiency of HF Utilization

In a 4-hr partial dissolution run, HF flowing at a rate of 230 ml/min was utilized with an efficiency of 4.6%. In the two 12-hr complete dissolution runs described in Sec. 3.2, with HF flow rates of 15 and 21 ml/min, the efficiencies were 21 and 15%, respectively. In a third 12-hr run the over-all efficiency was 28%.

4.0 APPLICATION OF FUSED SALT DISSOLUTION

Dissolution of various enriched reactor fuels in fused fluoride followed by volatilization[1,2] of UF_6 with F_2 appears feasible. The feasibility of processing normal uranium containing plutonium by this method is questionable, since the volatility of plutonium hexafluoride under these conditions is apparently small in comparison to that of uranium hexafluoride.[2]

It seems highly probable that U^{235} can be recovered from zirconium-clad fuel elements by fused fluoride processing. Both zirconium and uranium can be readily dissolved by hydrofluorination in a fused salt such as $NaF \cdot ZrF_4$. By maintaining a recycle, only NaF need be added to keep the proper bath composition. Fluorine costs for volatilizing $U^{235}F_6$ would be low because of the small quantities of uranium involved.

Processing of U^{235} in stainless steel claddings by fused salt—volatility techniques should also be economical. The demonstrated penetration rates of 4-7 mils/hr for stainless steel would give reasonable dissolution times for small tube or plate structures. It would probably be necessary to filter the fused salt after dissolution since a test dissolving of a mock-up stainless steel fuel element gave considerable quantities of a black precipitate.

Many other uses of fused salt dissolving can be made, but these two appear to be the most promising at the present time.

5.0 REFERENCES

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2. G. I. Cathers, M. R. Bennett, "A Fused Salt—Fluoride Volatility Process for Recovery and Decontamination of Uranium," ORNL-1885 (in preparation).