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SALT PHASE CHLORINATION OF REACTOR FUELS
IV - NIOBIUM BEHAVIOR IN THE
LEAD CHLORIDE AND CHLORINE-LEAD CHLORIDE SYSTEMS

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NATIONAL REACTOR TESTING STATION
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A B S T R A C T

Investigation of the behavior of niobium in lead chloride has shown that the rate of dissolution of niobium is quite low. Since stirring increases the rate appreciably, it is likely that the initial reaction is diffusion controlled. A subsequent reaction is linear in rate with an activation energy of 23.4 Kcal per mole. Incomplete volatilization of dissolved niobium from lead chloride is due to the presence of lower oxidation states of niobium.

The addition of chlorine to lead chloride increases the rate of dissolution of niobium. The rate is high enough at reasonable temperatures to be practical for fuel dissolution, e.g. $12 \text{ mg min}^{-1} \text{ cm}^{-2}$ at 550°C and 120 mg min^{-1} chlorine. Volatilization of niobium pentachloride is 99.9% complete at 550°C .

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I - SUMMARY

Fused chloride systems have been shown to hold considerable promise in the processing of nuclear fuels. In particular, lead chloride melts provide an excellent solvent for many types of fuel elements. The present study was initiated to determine the behavior of niobium, a fission product and potential alloy component, in lead chloride and chlorine-lead chloride systems.

The results indicate that:

- (1) the rate of dissolution of niobium in lead chloride is quite low. Since stirring increases the rate appreciably, it is likely that the initial reaction is diffusion controlled. A subsequent reaction is linear in rate with an activation energy of 23.4 Kcal per mole.
- (2) incomplete volatilization of dissolved niobium from lead chloride is due to the presence of lower oxidation states of niobium.
- (3) the rate of dissolution in chlorine-lead chloride melts is high enough at reasonable temperatures to be practical for fuel dissolution, e.g. $12 \text{ mg min}^{-1} \text{ cm}^{-2}$ at 550°C and 120 mg min^{-1} chlorine. Volatilization of niobium pentachloride is 99.9% complete at 550°C .

II - INTRODUCTION

Fused chloride systems have been shown to hold considerable promise in the processing of nuclear fuels.⁽¹⁾ In particular, lead chloride melts provide an excellent solvent for many types of fuel elements. Little is

known of the behavior of niobium in fused lead chloride and, since niobium may be present as either an alloy component or a fission product, both kinetic and phase studies are needed.

Past experience with niobium as a fission product in lead chloride was lacking, since relatively long-cooled fuel coupons were tested previously.⁽¹⁾ On a larger scale, dissolution experiments with gram amounts of niobium indicated that its rate of dissolution in lead chloride was very slow, but that addition of chlorine to the melt produced quite satisfactory rates at 550°C. In the work reported here dissolution rates were measured and some insight obtained as to reaction mechanism and species in both the niobium-lead chloride and niobium-chlorine-lead chloride systems.

III - EXPERIMENTAL

A. Materials

The lead chloride used was Baker's Analyzed Reagent. Commercial niobium pentachloride was obtained from Stauffer Chemical Company, New York, N. Y., with a spectrographic lot analysis of

Ta	< 600 ppm	Zr	N.D.
Si	1.5 ppm	P	< 15 ppm
Ti	N.D.	Mn	N.D.
Fe	1.5 ppm	W	< 200 ppm (wet analysis)

This niobium pentachloride was used in the described preparation of niobium trichloride.

The niobium coupons were all cut from the same 1/16 inch sheet, from a lot obtained from Westinghouse Electric Corporation, Bettis Plant, Large, Pennsylvania. The analysis of this sample showed the following impurities (wt %):

Al	0.04	Si	0.07
Fe	0.02	Ta	< 0.3
Mg	0.005	V	0.1

Chlorine was obtained from a five-pound cylinder supplied by the Matheson Company, Incorporated, East Rutherford, New Jersey.

B. Apparatus

1. Lead Chloride Experiments

The apparatus consisted of a three-inch diameter crucible furnace in which the temperature was controlled to $\pm 5^\circ\text{C}$ by first a Tipp-tronic controller and later by a Wheelco controller. Runs at 700°C and 800°C , and experiments which required more than 24 hours at 650°C , were carried out in Vycor test tubes. The dissolutions at lower temperatures were carried out in Pyrex test tubes.

2. Chlorine-Lead Chloride Experiments

All dissolutions were carried out in Pyrex tubes containing a 20 mm diameter, medium porosity glass frit through which the chlorine could be introduced⁽¹⁾ (Figure 1). The chlorine delivery system consisted of the storage cylinder, a No. 15-660 Matheson regulator with Monel check valve, a sulfuric acid bubbler, and an Ace Glass Model #7485 flowmeter gauge. All connecting tubing was polyethylene, and connections were sealed with Glyptal.

Excess chlorine was collected in a potassium iodide scrubber, in which the potassium iodide solution was circulated by means of a Sigma-motor finger pump.

C. Procedure

1. Lead Chloride Experiments

The test tubes were loaded with the desired amount of lead chloride (normally 7.5 g) and inserted into the preheated furnace. When

Figure 1
Chlorination Tube

CPP-S-2130

thermal equilibrium was attained, a measured and weighed niobium coupon was inserted into the test tube and the timing of the experiment started. At the end of the experiment the tube was removed from the furnace and the contents poured into a crucible. The niobium coupon was placed in boiling concentrated hydrochloric acid to remove any adhering lead chloride reaction products. If necessary, a final cleaning was effected in a potassium carbonate-30% hydrogen peroxide solution. This treatment has no effect on metallic niobium.⁽²⁾ The coupon was then rinsed in water and acetone, and reweighed.

A static blanket of argon in the reaction tubes was used in all except about one half of the 600°C experiments. However, independent experiments established that the presence or absence of the argon blanket had no appreciable effect on the dissolution rates obtained.

Certain of the reaction tubes, at the completion of an experiment, were broken at appropriate points along their lengths (determined by fractionation of product) and the separate sections analyzed for niobium, lead and chloride in order to determine product distribution.

2. Chlorine-Lead Chloride Experiments

Reaction tubes were loaded as previously described, the chlorine flow started, and the system brought up to the reaction temperature ($550^{\circ}\text{C} \pm 5^{\circ}\text{C}$). At thermal equilibrium the weighed and measured niobium coupon is inserted into the reaction tube and the chlorine flow rate adjusted to a predetermined level. Excess chlorine passing through the melt was collected in the potassium iodide scrubber and the resulting iodide titrated with sodium thiosulfate. The amount of chlorine reacted was determined from the niobium dissolved, assuming the sole reaction product to be niobium pentachloride. (This assumption will be justified in the section on Results.) The average chlorine flow rate was then determined from the excess chlorine collected and the amount of chlorine reacted. A series of sublimate collection trays above the reaction zone was used to fractionate the volatile product.

IV - RESULTS

A. Niobium-Lead Chloride System

Experimental niobium dissolutions in lead chloride were conducted at 550°C, 600°C, 650°C, 700°C, and 800°C with contact times up to four hours. The data for weight loss as a function of contact time at each temperature appeared to fit a straight line after an initial period (up to 40 minutes) of faster reaction. No attempt was made to define the initial rate by the experimental technique used; it is entirely possible that this portion is parabolic. The data for each temperature were given a least squares treatment⁽³⁾ to fit the general linear equation $y = a + bx$ (where $y = \text{mg cm}^{-2}$ niobium loss, $x = \text{minutes}$, a and b are constants to be determined). These rates are given in Table I as a function of temperature.

Table I
Linear Niobium Dissolution Rates in PbCl_2 vs Temperature

<u>Rate ($\text{mg min}^{-1} \text{ cm}^{-2}$)</u>	<u>Standard Deviation</u>	<u>Temperature ($^{\circ}\text{C}$)</u>
0.0200	0.0014	550°
0.0459	0.005	600°
0.115	0.008	650°
0.180	0.008	700°
0.569	0.023	800°

The slope of the Arrhenius plot of $\log \text{rate}$ vs $1/T$ then enables one to calculate the activation energy of the linear reaction. Least squares analysis of the data in Table I yields an activation energy of 23.4 Kcal mole⁻¹ for the reaction of niobium with lead chloride over the range of 550-800°C.

Niobium dissolutions, during which the lead chloride melt was stirred, were conducted at 650°C and at varying speeds. It was found that stirring considerably increased the dissolution rate, as shown in Figure 2. The latter observation implies that the reaction mechanism is diffusion controlled. The apparent anomaly of a diffusion controlled

reaction with an activation energy as high as 23 kilocalories per mole may be explained on the basis of two concurrent reactions.

In the first reaction the niobium reacts with the solvent to form a barrier film, possibly niobium trichloride. The rate of metal consumption is determined by diffusion across this layer. The rate of growth of the film controls the early stages of reaction, and it is this film which is partially swept away by convection. The film reacts in turn to form the final product, niobium pentachloride, and in so doing it reaches a steady-state thickness. In this latter stage of reaction the relatively constant area of the film gives rise to the linear kinetics observed. This type of behavior is observed in gas-solid reactions and it is not unreasonable to expect it in a liquid-solid system such as we have here.

The identity of the film has not been established. However, of the two known lower chlorides, niobium(III) and niobium(IV) chlorides, the tetrachloride boils at 275°C and disproportionates to the (III)

and (V) states⁽⁴⁾. Hence the trichloride is the most likely candidate.

While it might be anticipated that the production of lead at the metal-film interface would disrupt the film, in this case it apparently does not. This suggests that the reaction may not occur at the metal-film interface, but instead occurs at the film-solution interface after the migration of niobium ions through

Figure 2

Niobium Weight Loss in $PbCl_2$ at 650°C
as a Function of Stirring Rate

the film. An analogy would be the reaction of silver with liquid sulfur at the silver sulfide-sulfur boundary. An alternative explanation, that the barrier layer is lead itself, seems rather improbable since no wetting tendency of lead on niobium was noted, nor would this give rise to a subsequent linear reaction rate.

The distribution of reaction products has been rather intensively studied, although some factors are not yet understood. The stoichiometry does not follow completely the expected overall reaction:

Approximately 60% of the niobium dissolved is retained in the melt phase. After dissolution of the melt in distilled water, about 54% of this niobium is found in the form of insoluble niobium(IV) oxide. Although niobium dioxide is not detectable by X-ray analysis in the solid salt product, this may be due to the low concentration involved, or to masking of its lines by the lead chloride. The presence of niobium dioxide in the aqueous extract is taken to indicate the presence in the melt of niobium(IV) or a lower oxidation state.

The remaining 40% of the niobium dissolved can be detected in the sublimate, about nine-tenths present as niobium pentachloride (niobium and chloride analysis) with some niobium oxychloride. The latter evidently results from reaction with oxygen or water present as an impurity in the lead chloride (although dried at 100°C) or the argon (passed through U-tubes loaded with magnesium perchlorate).

Approximately one-tenth of the sublimate is a species thought to be niobium trichloride from its appearance, and lack of reaction with water, hydrofluoric acid, and dilute nitric acid.⁽⁵⁾ This material is deposited in the reaction tube in a zone of higher temperature than niobium pentachloride, indicating lower volatility. X-ray analysis of this material gives a definite crystalline pattern, but a niobium trichloride pattern is not available in the ASTM file for comparison.

To establish the identity of this unknown, a small amount of niobium pentachloride was reduced at 350°C with hydrogen⁽⁶⁾ in a system static except for periodic removal of the product hydrogen chloride. The black deposit in the region farthest removed from the pentachloride source was collected. Analysis revealed 482.2 mg niobium and 486.8 mg of chlorine per gram of sample, corresponding to a chlorine-to-niobium ratio of 2.65. However, only 96.9% of the sample is accounted for. If it is assumed that the missing material is chlorine, the ratio is raised to 2.81.

The X-ray pattern of this niobium trichloride is presented in Table IV and comparison is made with the unknown sublimate species.

Table II
X-ray Patterns of Black Unknown Sublimate,
Niobium Trichloride and Lead Chloride

Unknown		PbCl ₂		NbCl ₃	
<u>D, Å</u>	<u>I/I₁</u>	<u>D, Å</u>	<u>I/I₁</u>	<u>D, Å</u>	<u>I/I₁</u>
6.85	< 5				
6.20	100			6.1	v.s.
5.90	< 5				
4.55		4.52	18		
4.25	< 5				
4.06		4.06	34		
3.90	16	3.89	73		
3.82		3.81	43		
3.75	< 5			3.76	v.w.
3.59	20	3.58	100		
2.96		2.95	7		
2.92		2.92	23	2.90	w.
2.78		2.78	56		
2.64	6			2.62	m.s.
2.51		2.51	48		
2.27		2.27	23		
2.22		2.22	28		

2.17	< 5	2.17	10		
2.16		2.15	32		
2.12	< 5				
2.10		2.10	38	2.10	s.
2.06	6			2.04	s.
1.97		1.96	18		
1.95		1.95	13	1.92	v.w.
1.69		1.69	4		
1.68	< 5			1.68	s.
1.64		1.64	11	1.62	w.
1.60		1.60	7		
1.58		1.59	15		
1.54	6	1.57	3	1.53	w.
1.40				1.41	w.

It would appear that all lines of the unknown are accounted for except the weak lines at 4.25 and 6.85 Å.

B. Niobium-Chlorine-Lead Chloride System

The reaction rate of niobium at 550°C for 30-minute contact times was found to increase with the chlorine flow rate according to the relationship $y = 5.28x - 0.018x^2$, where $y = \text{Nb wt. loss (mg cm}^{-2}\text{)}$ and $x = \text{Cl}_2 \text{ flow rate (mg min}^{-1}\text{)}$. This is shown in Figure 3. Limited experiments at

Figure 3

Niobium Weight Loss in PbCl_2 at 550°C as a Function of Rate of Chlorine Flow

other contact times showed no significant time dependence of the reaction rate. Since the rate is more rapid in the absence of lead chloride, it is possible that the above relationship is specific for the system used.

Chloride and niobium analysis of the volatile reaction product indicated niobium pentachloride to be the only significant species present. (Theoretical for niobium pentachloride, Nb = 34.39%, Cl = 65.61%, Cl/Nb = 5.00; Analytical results, Nb = 33.26%, Cl = 63.64%, Cl/Nb = 5.01). Some difficulty is involved in the analysis of niobium pentachloride due to the extreme sensitivity of the product toward hydrolysis from traces of moisture in the reaction tube, the chlorine, etc. All samples to be analyzed were transferred in a dry box from a previously sealed reaction tube into weighing bottles.

Analysis of the melt phase showed that volatilization of the niobium pentachloride at 550°C was essentially complete (in agreement with its boiling point of 240.5°C), with only 0.1 weight per cent niobium (7.5 mg Nb/7.5 g PbCl₂) being detected in the melt. This would indicate very little interaction between the lead and niobium chloride involved, which may be contrasted to the results obtained in the simple lead chloride system.

Additional experiments at 550°C using varying amounts of lead chloride showed no effect of the melt volume upon the dissolution rate, again at variance with results obtained in the PbCl₂ system. Experiments in which the coupon size was varied showed no change in the rate of niobium loss as a function of chlorine flow rate. Varying the size of the glass frit used to support the niobium coupons and to admit chlorine to the system also showed no effect upon the rate of niobium dissolution.

Chlorination experiments in which the niobium coupons were suspended in the lead chloride melt instead of lying on the frit were somewhat inconclusive, but appear to indicate a rate difference that can be accounted for by the actual difference in area that is in direct contact with the stream of chlorine bubbles. This in turn is somewhat dependent upon the geometry of the system and was especially noted during experiments with suspended coupons. Some of the hooks broke and allowed the coupons to lie at an angle to the chlorine streams, instead of vertically. A

noticeably larger reaction rate was obtained, and visible etching on the lower side of the coupon was observed to decrease with distance from the end of the coupon in contact with the glass frit.

V - CONCLUSIONS AND DISCUSSION

The addition of chlorine to lead chloride is required to obtain satisfactory dissolution rates of niobium. The dissolution rate of niobium in lead chloride melts is too low even at 800°C ($0.569 \text{ mg min}^{-1} \text{ cm}^{-2}$) to prove feasible as a reactor fuel dissolution process, and too high to serve as a process containment vessel.

The dissolution rate of niobium in the advanced ARCO (chlorine-lead chloride) system is several orders of magnitude higher. For example, at a temperature of 550°C and a chlorine flow rate of 120 mg min^{-1} a dissolution rate of $12 \text{ mg min}^{-1} \text{ cm}^{-2}$ can be obtained. This is quite satisfactory for use as a fuel dissolution step. The dissolution rate can be smoothly controlled and further increased with higher chlorine rates if desired.

The volatility of niobium pentachloride would make a separation between uranium and niobium a simple one-step operation. About 99.9% of the niobium pentachloride volatilizes from the lead chloride melt, giving a niobium decontamination factor of 10^3 or better.

When gaseous chlorine is added to niobium in lead chloride, the only species detected is pentavalent niobium. However, the dissolution product of niobium in lead chloride contains a mixture of niobium(IV) and possibly lower oxidation states in both the melt and sublimate phases. Although these lower oxidation states have not been positively identified, evidence for their existence is found in

- a. the presence of niobium(IV) in aqueous extracts of the melt,
- b. the essentially complete volatilization of niobium(V) from the melt only after chlorine is added, and
- c. the presence of a small amount of an unreactive, less volatile compound (tentatively identified as niobium trichloride) in the niobium pentachloride sublimate.

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