

ORNL-3241

Contract No. W-7405-eng-26
CHEMICAL TECHNOLOGY DIVISION
Chemical Development Section B

THE CHEMISTRY OF NIOBIUM IN PROCESSING OF NUCLEAR FUELS

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DATE ISSUED

FEB - 5 1962

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Oak Ridge, Tennessee
Operated by
UNION CARBIDE CORPORATION
for the
U. S. ATOMIC ENERGY COMMISSION

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ABSTRACT

The chemical and industrial literature and early laboratory work of interest to those concerned with processing of niobium-containing nuclear fuels are reviewed.

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1.0 INTRODUCTION

The use of niobium in future nuclear reactors seems assured because of its high melting point (2470°C), moderately low thermal neutron cross section (1.15 barns), high tensile strength at elevated temperatures, and various other desirable properties such as compatibility with uranium-alloy fuels. One of the more desirable properties, chemical inertness to coolant gases, molten metals, and pressurized water, will pose a problem to the chemists and chemical engineers concerned with processing of niobium-containing fuels to recover valuable fissionable or fertile material. The goal of early laboratory work was generally to develop head-end processes for the conventional aqueous solvent extraction systems. Nonaqueous pretreatment, such as reaction with gases at high temperature or dissolution in fused salts, may be necessary because of the chemical inertness of niobium. Interest in processing of niobium-containing fuels has been stimulated by the need for processing one such fuel already discharged from the Experimental Boiling Water Reactor, a small power reactor (1). The purpose of this report is to review much of the literature on niobium of importance to fuel processing and outline results of early laboratory work. Several recent publications reflect the rapidly mounting interest in the metallurgy of niobium (2-8), and much of the new chemical work concerns production of new compounds for high-temperature use. However, the industrial and analytical chemical literature also contains much of interest to those involved in fuel processing (9-16).

2.0 STATUS OF DISSOLUTION PROCEDURES

Much of the chemical behavior of niobium can be inferred from its position in the periodic table in family IVb and in the second short transition series. The filling up of the next to outer 4d orbital brings about variable oxidation states and permits formation of many complex compounds. The general decrease in electropositive behavior through the series is evident in the slight amphoteric behavior of zirconium, zirconates being stable only in strong caustic; the slightly greater amphoteric behavior of niobium, which forms a stable and water-soluble potassium oxyfluoride but precipitates as oxide in basic sodium fluoride solutions; and the stronger amphoteric behavior of molybdenum, which forms soluble molybdates in only moderately strong caustic. The tendency to form bonds of increasingly covalent nature is evident in the series from the generally increasing vapor pressures of the halides and oxyhalides of zirconium, niobium, and molybdenum in their highest valence states. The chemistry of niobium is very similar to that of tantalum because tantalum is only the second element past the lanthanide contraction.

The chemical property of niobium of most importance is probably the stability of the crystalline pentoxide (ΔH_f at 298°K = -227.6 kcal/mole of niobium vs -190.5 and -431 kcal/mole for the pentachloride and pentafluoride, respectively (17-20)) and the low solubility of the pentoxide in acid (21). Since the pentafluoride is more stable and the pentachloride is less stable than the pentoxide, moderate amounts of fluoride and much

larger amounts of chloride can be used to form soluble complexes in acidic solutions. A chemical property of more importance in nonaqueous processing is the moderate stability and low volatility of trivalent niobium compounds.

2.1 Industrial Separations

The major problem in industrial processes is the separation of niobium from its chemical twin, tantalum. The older method, the Marignac process (11,22), involved preparation of complex potassium fluoride compounds and precipitation of the less soluble tantalum complex. More recently, a methyl isobutyl ketone solvent extraction process developed by the U. S. Bureau of Mines has been used to separate the fluorides of niobium and tantalum (9, 11). Fractional distillation of the chlorides is thought to be used in processes developed only recently (2).

In the Marignac process, the niobium-tantalum ore is broken by fusion in excess sodium carbonate to yield the orthoniobate, Na_3NbO_4 and orthotitanate, Na_3TaO_4 . Treatment with water yields insoluble sodium metaniobate, $\text{NaNbO}_3 \cdot 3\text{H}_2\text{O}$, still contaminated with tantalum. After dissolution of these niobium and tantalum compounds in hydrochloric acid, potassium fluoride is added to precipitate K_2TaF_7 . Niobium stays in solution as K_2NbOF_5 .

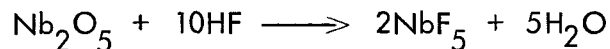
Several chlorination processes have been proposed for the recovery and purification of niobium or tantalum chlorides (23-26). The relative volatility ($\text{TaCl}_5:\text{NbCl}_5$) at atmospheric pressure was found to be 1.36 over the whole range of mixture compositions (27). Since the melting and normal boiling points of tantalum pentachloride are 220.0 and 232.9°C, respectively, and of niobium pentachloride are 209.5 and 247.4°C, respectively (27,28), separation by vapor-liquid distillation should be possible. The presence of any oxygen-containing impurities would probably cause formation of some niobium oxychloride, NbOCl_3 . This oxychloride, which has a vapor pressure of 20.8 mm of Hg at 250°C (29), would be expected to have some effect if present during the vapor-liquid distillation. The trichloride of niobium is also quite stable while that of tantalum is less stable (30,31).

2.2 Important Compounds

The niobium compounds of particular interest in fuel processing are those soluble in water since aqueous dissolution of the niobium-containing fuel will not proceed rapidly unless the product is soluble, present technology requires solvent extraction of uranium from aqueous solutions, and it is highly desirable to avoid solid-liquid separations in radiochemical operations.

Acidic Solutions. In acidic solutions, niobium forms an insoluble oxide unless a large amount of strongly complexing anion is present. Fluoride is the most efficient of the common niobium-complexing anions. Between about 30 and 5 (1,32) moles of fluoride is required to dissolve 1 mole of niobium. The lowest figure was obtained in a detailed phase study of the $\text{HF-NbF}_5\text{-H}_2\text{O}$ system at 20°C and was further verified by potentiometric titration (32).

The presence of an oxidant that promotes hydrolysis of the soluble niobium pentafluoride to insoluble oxide probably accounts for observations where more than 5 moles of fluoride is required to solubilize 1 mole of niobium. Thus, these solubility measurements actually include equilibrium values for the reaction



in addition to the solubility of niobium pentoxide in hydrofluoric acid. The most important acid-soluble compound appears to be the completely fluorinated complex rather than the pentoxide or the oxyfluoride complexes, which are stable and soluble in basic potassium solutions. Although niobium is soluble in hydrofluoric acid, metallic niobium will not dissolve in this acid unless an oxidant such as nitric acid or hydrogen peroxide is present. The oxidant apparently is needed because hydrogen gas cannot evolve from the niobium surface and must be removed by reaction with the oxidant if dissolution is to continue. The inability of hydrogen to evolve from the metal surface is probably caused by a high hydrogen overvoltage, not of the niobium itself but of the protective films which form consistently and rapidly on niobium in aqueous solutions (33,34). This need for an oxidant greatly complicates aqueous dissolution of metallic niobium, since hydrofluoric acid mixed with an oxidant is a good dissolvent for all the common construction metals.

Niobium chloride is soluble to less than 0.5 M in very concentrated hydrochloric acid, probably as a niobium pentachloride complex (35). At lower concentrations of hydrochloric acid, as the pentachloride hydrolyzed to the oxychloride, the solubility was decreased greatly. In 12 M HCl, the solubility of niobium pentoxide is only 0.02 M (21). This hydrolysis to less soluble compounds, the very slow rate of attack on niobium metal, and the corrosiveness of hydrochloric acid makes the use of this acid unattractive in processing of niobium-containing fuels. Sulfate ion reportedly (21) will complex and solubilize niobium ions approximately as well as chloride ions. The high concentrations required to dissolve niobium metal (Sect. 3) make the use of sulfuric acid unattractive, since the concentrated acid is very corrosive.

Neutral Solutions. Niobium forms many other anionic complex compounds that are soluble in neutral or weakly acidic or basic solutions. The solubility of potassium niobium oxyfluoride, $\text{K}_2\text{NbOF}_5 \cdot \text{H}_2\text{O}$, used in industrial separations is about 0.3 M in 1 M HF at 20°C and increases rapidly with increasing temperature (12). Many hydroxy-acid complex compounds, particularly the α -hydroxy, are water soluble. An example is oxaloniobic acid, which resembles the oxyfluoride in that one oxygen atom is directly bonded to the niobium in the complex (16). Fairbrother and Taylor (36,37) have shown experimentally that the soluble hydroxy-organic acid compounds are 5-membered cyclic anionic complexes. They report that niobic acid is also appreciably soluble in chromic and ortho- and polyphosphoric acids and forms five-membered chelate rings with hydroxyl amines (36-38). None of these soluble complex niobium compounds has been investigated in detail for use in fuel processing. Their use in processes in which uranium is recovered by solvent extraction

as uranyl nitrate is unlikely since the organic complexes are probably not sufficiently stable in nitrate solution and the inorganic complexes would introduce corrosion problems. The soluble perniobic acid, which can be made by dissolving bisulfate melts containing niobium in mixed hydrogen peroxide-dilute sulfuric acid (39), appears to be of little use in processing since great excesses of hydrogen peroxide are needed and the equilibrium constant greatly favors formation of the insoluble pentoxide (40).

Oxidation of niobium cladding could probably be used as a method for opening niobium-clad fuel to expose the core to conventional acid dissolution. At 760 mm Hg oxygen pressure, a linear oxidation-penetration rate of about 4 mils/hr has been observed at 800°C (8,41).

Table 1 is a preliminary list of some of the more important compounds of niobium with some properties of these compounds. The data were drawn from many sources, without attempting to reference the sources or to be comprehensive.

3.0 LABORATORY DISSOLUTION STUDIES

Laboratory work has consisted generally of a preliminary search for dissolution methods for niobium metal. No method has been found which is compatible with present radiochemical plant technology, since all acidic aqueous reagents which attack niobium rapidly are too corrosive for containment in any readily available construction metals. The method of attack that appears most promising is gas-phase chlorination at about 300°C.

3.1 Aqueous Solutions

Niobium does not dissolve in pure hydrofluoric acid but dissolves rapidly in mixed HF-HNO₃ (Fig. 1). For example, laboratory measurements predict initial reaction rates of 5 mg cm⁻² min⁻¹ in 3, 6, and 9 M HF containing about 2, 1, and 2 M HNO₃, respectively. Rate studies were not made in HF-H₂O₂, but dissolution rates are probably comparable to those in HF-HNO₃. The latter reagent produces no off-gas during dissolution. Corrosion rate studies made in the HF-H₂O₂ system (42) indicate that none of the common or newer construction materials would make a satisfactory container.

Niobium can be dissolved in refluxing sulfuric acid more concentrated than 14 M (Fig. 2). The dissolution rate increased rapidly with sulfuric acid concentration to 6 mg cm⁻² min⁻¹ at 18.3 M H₂SO₄, the point at which the reflux temperature is maximum. The dissolution rate increased less rapidly as the sulfuric acid (or sulfur trioxide) concentration increased above 18.3 M, probably because the reflux temperature decreased.

Table 1. Niobium Compounds

Abbreviations are those used in Lange's Handbook of Chemistry

Formula	Formula Weight	Appearance	SG	MP, °C	BP, °C	Solubility in 100 Parts		
						Cold Water	Hot Water	Other
Nb	92.91		8.57	2470	5140	i	i	S. HF+HNO ₃ , KOH
<u>Oxides</u>								
Nb ₂ O ₅	265.82	wh. cr.	4.6	1520	-	i	i	S. HF, H ₂ SO ₄ , HCl
3Nb ₂ O ₅ · 7H ₂ O	923.6	wh. amor.	4.3	d.	-	i	i	"
NbO	108.91	bl. cb.	6.3-6.7	-	-	i	i	"
NbO ₂	124.91	bk.	-	-	-	i	i	S. hot KOH
<u>Halides and Oxyhalides</u>								
NbF ₃	149.91	dk. blue	-	-	-	-	-	-
NbF ₅	187.91	col. mn.	3.29	75.5	229	d	-	S. HNO ₃
NbCl ₃	199.29	bl.	-	-	-	i	i	d, HNO ₃
NbCl ₅	270.20	yel, delq. red	2.75	194	240.5	d	-	S. HD, CCl ₄ , d. al.
NbBr ₅	492.49	purple-red	-	150	270	d	-	d. al.
NbOF ₃	165.91	-	-	-	-	d	-	-
NbO ₂ F	143.91	wh.	-	-	-	i	i	S. HF+HNO ₃
NbOCl ₃	215.28	wh. rd.	-	subl. 300	-	d	-	S, H ₂ SO ₄ , al.
NbO ₂ Cl	160.37	-	-	d.	-	-	-	-
NbOBr ₃	348.66	yel. cr.	-	subl.	-	d	-	-
<u>Other Simple Salts</u>								
NbH	93.92	gray pd.	6.0-6.6	d	-	-	-	S. HF
NbN	106.92	bk.	-	-	-	-	-	S. HF, +HNO ₃
Nb ₂ OS ₃	298.0	bk.	-	d.	-	i	i	S. H ₂ SO ₄ , HF
NbC	104.91	-	-	3500	-	-	-	S. HF+HNO ₃
<u>Complex Compounds</u>								
Nb(HC ₂ O ₄) ₅	538.06	mn.	-	-	-	d	-	S. H ₂ C ₂ O ₄ ; d. al.
KNbOF ₅ · H ₂ O	300.1	-	-	-	-	8	S	d. a.
K ₂ NbF ₅	266.11	-	-	-	-	-	-	S. HF; d. a.
K ₃ NbOF ₆	340.21	-	-	-	-	-	S	d. a.

Aqueous ammonium fluoride solution (Zirflex reagent) has been used satisfactorily to dissolve U-Zr-1.5% Nb alloy (1). However, this reagent does not appear attractive for niobium metal or alloys containing large percentages of niobium. The dissolution rate of pure niobium in ammonium fluoride, $\text{NH}_4\text{F-NH}_4\text{NO}_3$, or $\text{NH}_4\text{F-H}_2\text{O}_2$ was very slow. The solubility of the dissolution product, $(\text{NH}_4)_2\text{NbF}_7$, was about 0.01 M. Addition of 3 M HNO_3 to the product caused part of the niobium to precipitate as oxide and about 1 mole of niobium per 30 moles of fluoride stayed in solution.

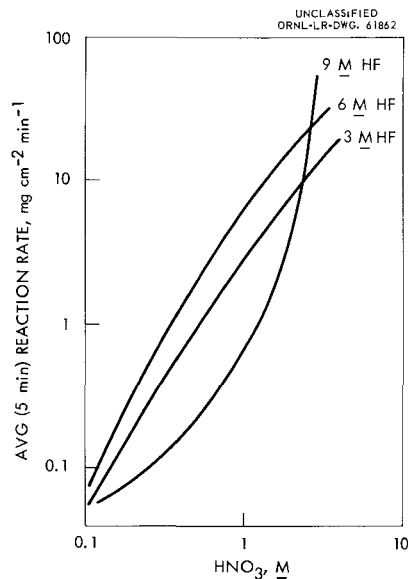


Fig. 1. Dissolution of niobium in refluxing nitric-hydrofluoric acid.

3.2 Organic Solutions (43)

In preliminary studies alcoholic hydrogen chloride or alcohol-mercuric chloride appeared promising as niobium dissolvents because of high dissolution rates and low corrosion rates. The more rapid dissolution in the anhydrous reagent is probably due to the absence of surface films, which always form on niobium in aqueous solutions (33,34). In alcoholic hydrogen chloride, hydrogen ion is reduced and hydrogen gas is evolved; in alcohol-mercuric chloride, mercuric ion is reduced to mercurous ion or mercury as niobium dissolves. Transfer of the uranium to an aqueous solution in preparation for solvent extraction was demonstrated in both cases. However, serious problems make eventual use of either of these reagents improbable. Alcoholic hydrogen chloride reacts rapidly, as the temperature is increased, to produce ethyl chloride and water. Water causes hydrolysis of the soluble dissolution products to undesirable insoluble compounds. The dissolution reaction is exothermic, and it would be difficult to keep the reagent cool while maintaining rapid dissolution. The process using mercuric chloride would require several mercury-recycle operations, all of which have been demonstrated on a laboratory scale but have not been evaluated on engineering scale.

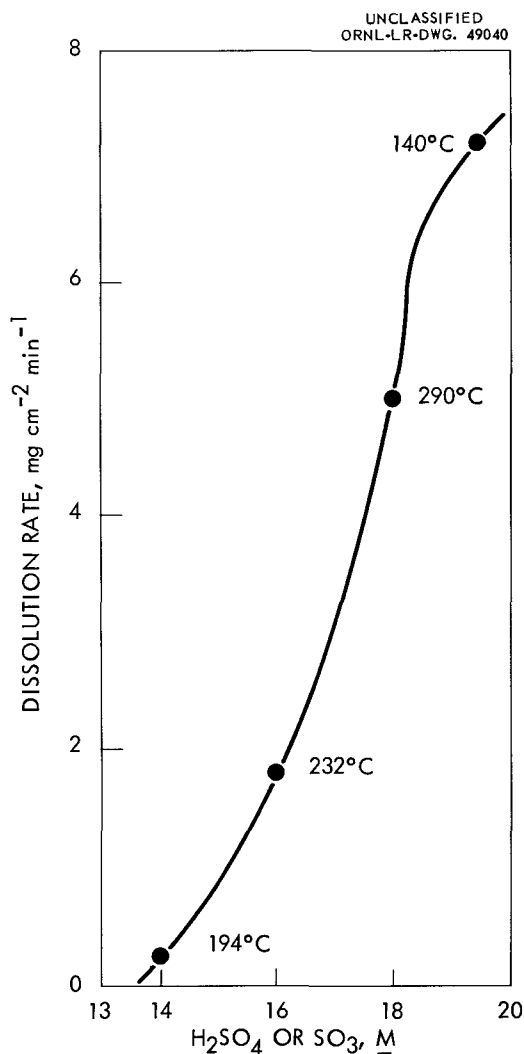


Fig. 2. Dissolution of niobium in refluxing sulfuric acid.

3.3 High-temperature Gas-Solid Reactions

Niobium reacted readily with halide gases at high temperatures, particularly with chlorine, where the reaction rate exceeded $10 \text{ mg cm}^{-2} \text{ min}^{-1}$ at furnace temperatures above 300°C (Fig. 3). Other workers have also reported rapid reaction rates above 300°C with chlorine (28) and have examined the nonvolatile lower valence products which are formed by reaction with hydrogen chloride (30,44-47) and hydrogen fluoride (47). Much volatile pentachloride and pentafluoride are also produced in reactions with hydrogen chloride or hydrogen fluoride. The nonvolatile products probably decrease the reaction rates. Excess chlorine reportedly is needed to convert niobium trichloride to the pentachloride (30). The x-ray pattern of niobium trifluoride was identified in the nonvolatile blue compound that formed during hydrofluorination of niobium. Niobium reportedly reacts readily with fluorine or hydrogen fluoride at 300°C (48). Alloys of niobium with uranium and zirconium have been hydrochlorinated at satisfactory rates (49,50).

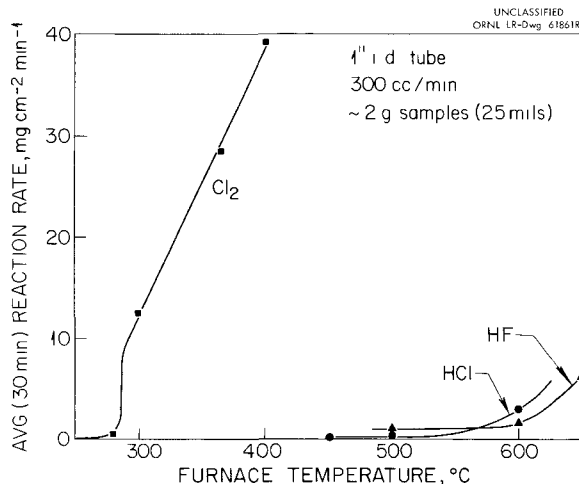


Fig. 3. Reaction rates of niobium in halogen gases.

A disadvantage in hydrochlorination is that the more stable and nonvolatile niobium pentoxide, rather than the pentachloride, can form from oxygen-containing impurities introduced into the system. Under practical operating conditions, some oxygen-containing impurities will always be present. However, the pentoxide can be converted rapidly to pentachloride by treatment with carbon tetrachloride vapor at temperatures above 250°C (50,51), or by mixing with carbon and treatment with chlorine gas (24-26).

Niobium pentachloride may be separated from zirconium tetrachloride by absorption of the latter on sodium or potassium chloride beds at elevated temperatures (26,49,52). The decomposition temperatures of the niobium chloride-sodium and potassium chloride complexes are 287 and 562°C, respectively (26). The decomposition pressures of the zirconium chloride-sodium and potassium chloride complexes are 2.8 and 1.97 mm Hg at 432 and 650°C, respectively (26).

The volatile niobium pentachloride can be condensed as a liquid which melts at 209.5°C and boils at 247.4°C at 1 atm pressure.

3.4 Fused Salts

The dissolution rate of niobium in potassium hydroxide solution increased from 0.1 to 5.5 mg cm⁻² min⁻¹ as the potassium hydroxide concentration increased from 10 M (refluxing) to 30 M (325°C) (Fig. 4). Addition of 5 M or 10 M KF only decreased the dissolution rate. Niobium dissolved in fused sodium hydroxide at 400°C at 0.035 mg cm⁻² min⁻¹. The rate in 10 M LiOH was too slow to measure and in 10 M KOH-1 M RbF was 0.04 mg cm⁻² min⁻¹, about half that in 10 M KOH alone.

Processing of niobium-containing fuels in the ORNL Fluoride Volatility Process (53) is being investigated. The dissolution rate at 600°C was measured as 1.8-2.4 mg cm⁻² min⁻¹ (54). Niobium also dissolved in fused ammonium bifluoride at a rate of 1.6 mg cm⁻² min⁻¹ at 220°C (1).

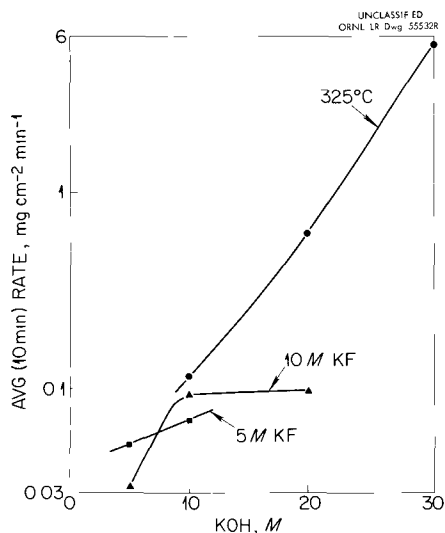


Fig. 4. Dissolution of niobium in potassium hydroxide solutions. All solutions except 30 M KOH were refluxing.

Fused chlorides do not attack niobium as rapidly as does chlorine gas. Uranium-zirconium alloys containing 10% Nb dissolved in refluxing $3\text{ZrCl}_4 \cdot 2\text{POCl}_3$ (360°C) at $9\text{--}12 \text{ mg cm}^{-2} \text{ min}^{-1}$ (55). The niobium product is thought to be $\text{NbCl}_5 \cdot \text{POCl}_3$, which has a normal boiling point of 263°C (56). In a fused lead chloride process being developed at the Idaho Chemical Processing Plant, the dissolution of many materials, among which is niobium, is being investigated (57).

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