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CHLORINATION OF URANIUM AND FISSION PRODUCT OXIDES IN MOLTEN HALIDE MEDIA

by

J. P. LaPlante, D. A. Wenz,
and
R. K. Steunenberg

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TABLE OF CONTENTS

	<u>Page</u>
ABSTRACT	3
I. INTRODUCTION	3
II. EXPERIMENTAL PROCEDURE	4
III. RESULTS	5
IV. DISCUSSION	8
V. CONCLUSIONS	9
ACKNOWLEDGEMENTS	10
BIBLIOGRAPHY	10

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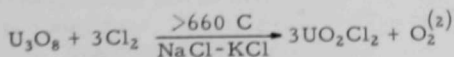
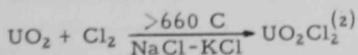
ABSTRACT

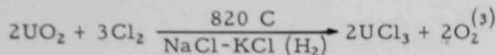
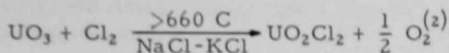
The chlorination of mixtures of uranium and fission product oxides in various molten halide systems by sparging with a chlorine-carbon monoxide mixture was investigated. The chlorination reaction causes the suspended oxide to form species that are soluble in the molten salt and removes some of the fission product elements by volatilization of the chlorides. The rate of oxide dissolution and the fission product behavior both proved to be dependent upon the composition of the molten halide medium used.

I. INTRODUCTION

The chlorination of uranium-fission product oxide mixtures to form species soluble in molten salts is a potentially useful operation in the pyrochemical reprocessing of reactor fuels. This investigation was undertaken in connection with development work on methods for the recovery of uranium from skulls produced in the melt refining process for EBR-II (Experimental Breeder Reactor No. 2) fuel.⁽¹⁾ In order to remove the skulls from the crucibles for further processing, they are oxidized to form a mixture of U_3O_8 and fission product oxides. Dissolution of the oxides through chlorination permits the material to be handled as a single liquid phase in subsequent process steps. Although current plans do not call for the use of this procedure in the process of skull recovery, the results of this investigation are believed to be of some general interest.

The chlorination of uranium oxides in molten sodium chloride-potassium chloride eutectic and in various other alkali and alkaline earth metal chloride systems has been reported in the literature.^(2,3) The following reactions have been proposed:





Phosgene and aluminum chloride are also effective chlorinating agents.⁽²⁾ Gibson *et al.*⁽³⁾ have chlorinated thorium and beryllium oxides with chlorine and carbon monoxide or carbon in the presence of a ferric chloride catalyst.

Since the uranium oxide is suspended in the molten salt as a solid, the chlorination is a heterogeneous situation involving at least 2, and possibly 3, phases. The rate of chlorination tends to decrease with increasing particle size of the solid.

During the chlorination of uranium-fissium* oxide mixtures, some of the fission product elements are removed from the salt medium in varying degrees through the formation of volatile chlorides. Zirconium, niobium, ruthenium, and molybdenum represent the major fission products capable of volatile chloride formation.⁽⁴⁾ It is possible that certain other fission product elements may not undergo chlorination, but remain in suspension as insoluble oxide. This behavior has not been observed experimentally, however.

Some of the chemical aspects of reactions of this type have been discussed in a general review article on recent molten salt research by Blomgren and Van Artsdalen.⁽⁵⁾

II. EXPERIMENTAL PROCEDURE

The chlorination experiments were performed in an alumina crucible located in a Hoskins Type FD104 furnace and fitted with a Transite cover. Provisions were made for a quartz stirrer, a Vycor sample tube, a porcelain thermocouple well, and quartz sparging and venting tubes. A two-to-threefold excess of the carbon monoxide-chlorine mixture (2:1) was passed through 200 g of a selected molten halide salt containing 20 g of uranium-fissium oxide (primarily U_3O_8) in suspension. The system was maintained at a temperature of 800 to 850 C and agitated during the chlorination. Filtered samples of the salt were taken periodically

*The term "fissium" refers to a synthetic mixture of inactive elements corresponding in composition to the fission products present in an irradiated fuel. The composition of the corresponding oxide was (w/o): uranium, 64.6; cerium, 4.3; zirconium, 3.86; molybdenum, 2.34; ruthenium, 1.29; palladium, 0.85.

in Vycor tubes fitted with graphite filters. The salt samples were analyzed by standard techniques.

III. RESULTS

It was assumed that the elements which did not appear as soluble species in the salt samples had not been chlorinated or had been removed from the system as volatile chlorides. The percentages of several elements in the salt are listed in Table 1 for various chlorination times and flux compositions. The data for uranium, molybdenum, and palladium are also plotted in Figures 1, 2, and 3, respectively.

Table 1

CHLORINATION OF URANIUM-FISSIUM OXIDE IN MOLTEN HALIDE MEDIA

Oxide: 20 g uranium-fissium oxide (see text for composition)
 Molten Salt: 200 g, composition as indicated
 Chlorinating Agent: CO-Cl_2 2:1 ratio; 2 to 3 times the stoichiometric requirement
 Temperature: 800 to 850 C
 Stirring: 640 rpm, propeller-type agitator
 Materials: Vycor sample tubes, graphite filters, porcelain thermocouple well, alumina crucible, quartz stirrer^a

Expt	Molten Salt System	Percentage of element found in solution in molten salt										
		Time (min)										
		10	20	30	40	50	60	70	90	120	150	180
Uranium												
1	50 ml ₀ NaCl-50 ml ₀ KCl	-	-	72	-	-	102	-	99	100	102	-
2	50 ml ₀ NaCl-50 ml ₀ KCl ^a	29	74	75	77	78	73	66	62	57	-	-
3	50 ml ₀ NaCl-50 ml ₀ KCl + 10 g Fe	-	100	96	-	-	-	-	94	-	-	-
4	47.5 ml ₀ NaCl-47.5 ml ₀ KCl-5.0 ml ₀ ZnCl ₂	-	-	100	-	-	100	-	-	-	-	100
5	47.5 ml ₀ LiCl-47.5 ml ₀ MgCl ₂ -5.0 ml ₀ MgF ₂	11	8	7	6	6	7	-	7	6	-	-
6	47.5 ml ₀ LiCl-47.5 ml ₀ BaCl ₂ -5.0 ml ₀ MgF ₂	-	4	4	-	-	-	-	-	-	-	100
Molybdenum												
1	50 ml ₀ NaCl-50 ml ₀ KCl	-	-	68	-	-	<1	-	<0.5	<0.5	<0.5	-
2	50 ml ₀ NaCl-50 ml ₀ KCl ^a	50	48	31	14	0.5	1.4	1.5	0.2	0.1	-	-
3	50 ml ₀ NaCl-50 ml ₀ KCl + 10 g Fe	-	63	61	-	-	-	-	52	-	-	-
4	47.5 ml ₀ NaCl-47.5 ml ₀ KCl-5.0 ml ₀ ZnCl ₂	-	-	16	-	-	0.1	-	-	-	-	<0.5
5	47.5 ml ₀ LiCl-47.5 ml ₀ MgCl ₂ -5.0 ml ₀ MgF ₂	95	100	100	100	95	93	-	72	77	-	-
6	47.5 ml ₀ LiCl-47.5 ml ₀ BaCl ₂ -5.0 ml ₀ MgF ₂	-	73	74	-	-	-	-	-	-	-	1.3
Palladium												
1	50 ml ₀ NaCl-50 ml ₀ KCl	-	-	-	-	-	-	-	-	-	-	-
2	50 ml ₀ NaCl-50 ml ₀ KCl ^a	47	43	48	43	43	43	41	39	38	-	-
3	50 ml ₀ NaCl-50 ml ₀ KCl + 10 g Fe	-	67	59	-	-	-	-	59	-	-	-
4	47.5 ml ₀ NaCl-47.5 ml ₀ KCl-5.0 ml ₀ ZnCl ₂	-	-	67	-	-	69	-	-	-	-	67
5	47.5 ml ₀ LiCl-47.5 ml ₀ MgCl ₂ -5.0 ml ₀ MgF ₂	100	96	89	79	77	71	-	51	35	-	-
6	47.5 ml ₀ LiCl-47.5 ml ₀ BaCl ₂ -5.0 ml ₀ MgF ₂	-	67	73	-	-	-	-	-	-	-	59
Cerium												
1	50 ml ₀ NaCl-50 ml ₀ KCl	-	-	22	-	-	43	-	43	47	57	-
2	50 ml ₀ NaCl-50 ml ₀ KCl ^a	-	-	100	96	81	-	-	61	89	-	-
3	50 ml ₀ NaCl-50 ml ₀ KCl + 10 g Fe	-	35	29	-	-	-	-	34	-	-	-
4	47.5 ml ₀ NaCl-47.5 ml ₀ KCl-5.0 ml ₀ ZnCl ₂	-	-	30	-	-	25	-	-	-	-	26
5	47.5 ml ₀ LiCl-47.5 ml ₀ MgCl ₂ -5.0 ml ₀ MgF ₂	32	27	36	31	33	33	-	34	28	-	-
6	47.5 ml ₀ LiCl-47.5 ml ₀ BaCl ₂ -5.0 ml ₀ MgF ₂	-	33	-	-	-	-	-	-	-	-	51
Zirconium												
1	50 ml ₀ NaCl-50 ml ₀ KCl	-	-	-	-	-	6	-	-	7	9	-
2	50 ml ₀ NaCl-50 ml ₀ KCl ^a	<0.6	<0.6	2	2	6	6	4	3	4	-	-
3	50 ml ₀ NaCl-50 ml ₀ KCl + 10 g Fe	-	<0.4	<0.6	-	-	-	-	<3	-	-	-
4	47.5 ml ₀ NaCl-47.5 ml ₀ KCl-5.0 ml ₀ ZnCl ₂	-	-	6	-	-	21	-	-	-	-	19
5	47.5 ml ₀ LiCl-47.5 ml ₀ MgCl ₂ -5.0 ml ₀ MgF ₂	<0.8	<0.3	<1.0	<0.8	<0.6	<0.6	-	<0.6	<0.6	-	-
6	47.5 ml ₀ LiCl-47.5 ml ₀ BaCl ₂ -5.0 ml ₀ MgF ₂	-	<0.8	<1.1	-	-	-	-	-	-	-	5
Ruthenium												
1	50 ml ₀ NaCl-50 ml ₀ KCl	-	-	-	-	-	75	-	56	38	-	-
2	50 ml ₀ NaCl-50 ml ₀ KCl ^a	-	-	<0.5	<0.5	<0.6	<9	<5	<4	<0.3	-	-
3	50 ml ₀ NaCl-50 ml ₀ KCl + 10 g Fe	-	<0.9	<0.6	-	-	-	-	3	-	-	-
4	47.5 ml ₀ NaCl-47.5 ml ₀ KCl-5.0 ml ₀ ZnCl ₂	-	-	<0.2	-	-	100	-	-	-	-	96
5	47.5 ml ₀ LiCl-47.5 ml ₀ MgCl ₂ -5.0 ml ₀ MgF ₂	<0.5	<0.4	<0.6	<0.4	<0.4	<0.3	-	<0.4	-	-	-
6	47.5 ml ₀ LiCl-47.5 ml ₀ BaCl ₂ -5.0 ml ₀ MgF ₂	-	-	-	-	-	-	-	-	-	-	79

^aTantalum stirrer in Experiment 2; quartz in all others.

Figure 1
CHLORINATION OF FISSIUM OXIDE

Oxide: 20 g reconstituted fissium oxide
 Temperature: 800-850 C
 Chlorinating Agent: CO-Cl₂
 Stirring rate: 640 rpm
 Flux: 200 g

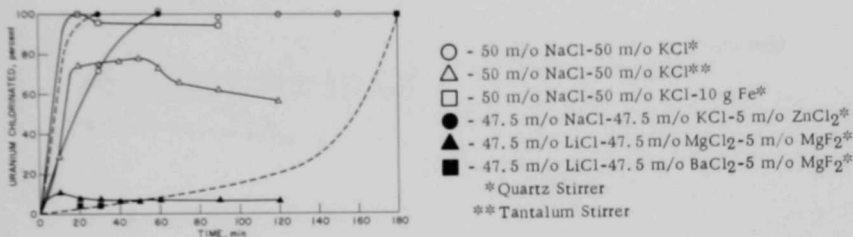
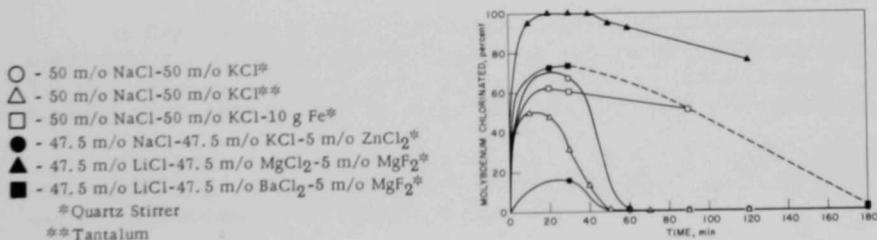


Figure 2
CHLORINATION OF FISSIUM OXIDE

Oxide: 20 g reconstituted fissium oxide
 Temperature: 800-850 C
 Chlorinating Agent: CO-Cl₂
 Stirring rate: 640 rpm
 Flux: 200 g

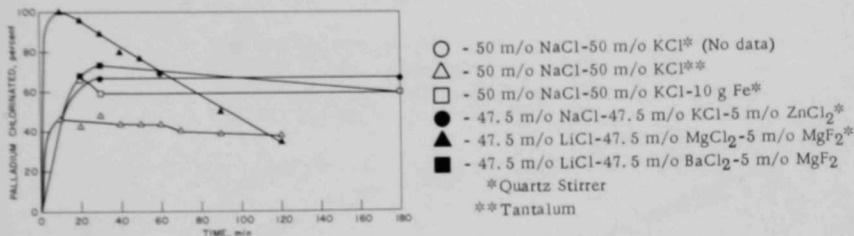


The first two experiments with a 50 m/o sodium chloride-50 m/o potassium chloride melt were identical, except for a quartz stirrer used in Experiment 1 and a tantalum stirrer in Experiment 2. The quartz was only slightly etched by the melt, whereas the tantalum suffered severe attack. It appears that the tantalum causes a decrease in the amount of uranium in solution. The maximum in uranium concentration as a function of time suggests an extraneous reaction that removes it from solution when tantalum is present. The percentage of cerium in solution, on the other hand, was greater in Experiment 2 than in Experiment 1.

Figure 3

CHLORINATION OF FISSION OXIDE

Oxide: 20 g reconstituted fission oxide
 Temperature: 800-850 C
 Chlorinating Agent: CO-Cl_2
 Stirring rate: 640 rpm
 Flux: 200 g



In Experiment 3, the presence of ferric chloride (formed by adding iron to the sodium chloride-potassium chloride melt) resulted in a significant increase in the chlorination rate of uranium oxide.

The addition of 5 mole percent zinc chloride to the sodium chloride-potassium chloride melt in Experiment 4 also increased the chlorination rates of uranium, molybdenum, palladium, zirconium, and ruthenium, but the volatilization of ruthenium chloride appeared to have been inhibited.

In Experiment 5, the chlorination of uranium oxide was relatively ineffectual in a 47.5 m/o lithium chloride-47.5 m/o magnesium chloride-5.0 m/o magnesium fluoride melt. The chlorination of cerium oxide, however, proceeded at about the same rate as in the other salt systems.

The chlorination of uranium oxide was slow in the 47.5 m/o lithium chloride-47.5 m/o barium chloride-5.0 m/o magnesium fluoride system used in Experiment 6, but it was complete after 3 hr.

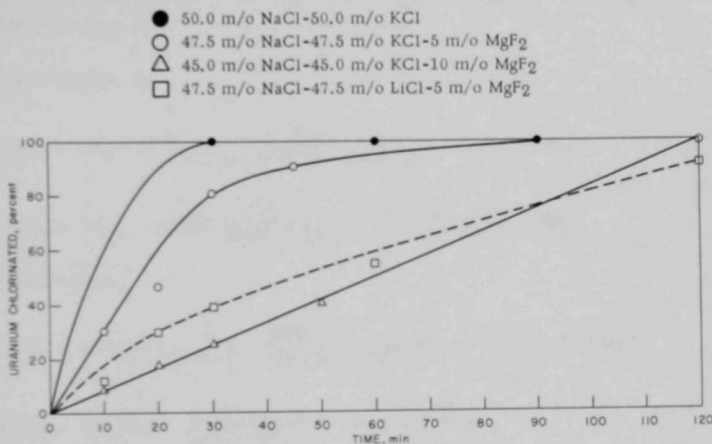
In all 6 experiments, varying amounts of zirconium, molybdenum, and ruthenium were removed from the salt, presumably through the formation of volatile chlorides.⁽⁴⁾

The effects of magnesium fluoride concentration and the substitution of lithium chloride for potassium chloride were examined briefly in a separate set of experiments. The results are shown in Figure 4. An increase in magnesium fluoride concentration and the substitution of lithium chloride for potassium chloride in a sodium chloride-potassium chloride-magnesium fluoride melt both decreased the rate of uranium oxide chlorination.

Figure 4

CHLORINATION OF URANIUM OXIDE

Oxide: 20 g reconstituted uranium oxide
 Temperature: 800-850 C
 Chlorinating Agent: CO-Cl₂
 Stirrer: Quartz
 Stirring rate: 640 rpm
 Flux: 200 g



IV. DISCUSSION

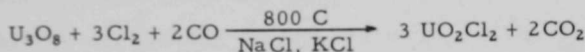
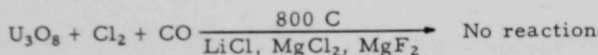
Chlorination of a suspension of uranium and fission oxides in molten halide media to form soluble species appears to be a practical procedure with several potential process applications. Noble metal fission products, for example, can be extracted from such a solution by selective reduction into molten zinc. This procedure can be used directly for the solid oxides suspended in the salt,⁽⁶⁾ but it is more effective with the chlorinated system where the oxide lattice has been destroyed. The uranyl ion formed in the chlorination reaction can be reduced to uranium dioxide electrolytically or by any of several metals.⁽²⁾ Under more strenuous conditions, a zinc-magnesium alloy will produce reduction to uranium metal.⁽⁶⁾ Since certain uranium-fission product separations are possible in these reactions, they are potentially useful in pyrochemical processes for the recovery of uranium from irradiated reactor fuels.

The effect of salt composition on the chlorination of uranium oxides indicates that the salt not only serves as a medium for the reaction, but that it also enters actively into the mechanism. The chlorination rates of

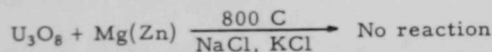
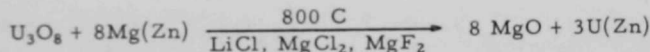
uranium-fissium oxides as a function of salt composition show the same type of periodic variation as that observed in the reduction of uranium oxides suspended in salt media,⁽⁶⁾ but in reverse order. Thus, the rate of oxide reduction decreases and the rate of oxide chlorination increases as the atomic radii of the Group I and II cations in the flux are increased. Similarly, increasing the fluoride concentration in the flux enhances the reduction rate, but decreases the chlorination rate.

The equations for the chlorination and reduction of uranium oxide in 47.5 m/o LiCl-47.5 m/o MgCl₂-5.0 m/o MgF₂ and 50 m/o NaCl-50 m/o KCl fluxes are:

(Chlorination)



(Reduction)



It is reasonable to expect that the stability of the uranyl species formed in the chlorination reaction would depend on the atomic radii of the ions in the salt medium and the coordination number of the cations.^(5,7) Although this effect may account to some extent for the effect of salt composition on the stability of the uranyl ion in solution toward various reactants, a number of other factors are probably involved, e.g., degree of ionization of the salt, activity coefficients, diffusion, and solubility.

V. CONCLUSIONS

Chlorination of uranium-fissium oxide mixtures by sparging with chlorine and carbon monoxide in molten halide media is an effective method of achieving a homogeneous system. The rate of oxide dissolution varies with the salt composition, increasing with the size of alkali and alkaline earth metal cations in the salt. The rate is also increased by the addition of iron or zinc chlorides. Significant removals of molybdenum, zirconium, and ruthenium from the system were attributed to the formation of volatile chlorides. The technique is believed to have potential applications in pyrochemical processes for irradiated reactor fuels.

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