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**REDUCTION OF URANIUM DIOXIDE
IN MOLTEN SALT-METAL SYSTEMS**

by

**D. A. Wenz, R. D. Wolson,
and I. Johnson**

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Chemical Engineering Division

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ABSTRACT

A study has been made of the reducibility of sintered UO_2 powder and pellets in agitated, immiscible molten salt-metal alloy systems. Systems consisting of a salt mixture having less than about 25 mol % MgCl_2 and the alloy Mg-44 at. % Cu proved to be unsatisfactory media for UO_2 reductions. The use of salts containing about 50 mol % MgCl_2 with the above alloy allowed good reductions of UO_2 powder, but reductions of larger particles of UO_2 were too slow for process purposes. These results suggest an inhibition of reduction by the insoluble MgO reduction product. Utilization of a CaCl_2 salt/Cu-Mg-Ca alloy reduction system, where the CaO reduction product dissolves in the salt phase, gave rapid, complete reduction of even UO_2 pellets. The experimental data suggest that UO_2 reduction proceeds through reaction of UO_2 at the solid-particle surface with magnesium or calcium metal dissolved in the salt phase (as the species Mg_2^{2+} or Ca_2^{2+}).

I. INTRODUCTION

New methods of separating and recovering uranium and plutonium from spent nuclear-reactor fuels are being developed in this laboratory. One of these, pyrochemical processing, uses the differences in the distribution of the various elements of the fuel between selected immiscible molten halide salt and metal alloy phases to effect the desired separations. The fuel components are either dissolved in the salt phase as their halides or in the metal phase as the elements when they are partitioned between the two phases.

Most of the existing and proposed reactors use oxide fuels. Other types of fuel such as carbides can be readily oxidized. Since it is easier to reduce the oxides to metals than to convert them to chlorides, the first step in the proposed pyrochemical processes is the reduction of the fuel oxides into a molten metal phase. This is done by placing the powdered

oxides in a molten salt-reducing metal alloy system that is being stirred vigorously. The reductant metal oxide by-product is collected in the salt, which can be separated from the metal phase to remove oxygen from the system.

Knighton *et al.*, have studied the reduction of U_3O_8 (Ref. 1), ThO_2 (Ref. 2), and PuO_2 (Ref. 3) in molten halide salt/Zn-Mg alloy systems. They found that the rate of reduction increased as the stirring rate increased and as the oxide particle size decreased. With U_3O_8 and ThO_2 , it was necessary to have approximately 50 mol % $MgCl_2$, or more, and at least several mole percent metal fluoride in the salt to obtain rapid reductions. No systematic study of the reduction of UO_2 was made, however.

The UO_2 reactor fuels are in the form of high-density, sintered pellets, which may become partially fused and cracked during irradiation. It is desirable to be able to introduce such pellets directly into the reduction step of a pyrochemical reprocessing scheme; therefore, an experimental program was needed to determine the reducibility of sintered UO_2 .

One of the important and difficult steps in fuel reprocessing is the separation of rare-earth element fission products from the uranium and plutonium fuel. It had been suggested⁴ that in pyrochemical processing this separation be combined with the reduction step by use of a Mg-44 at. % Cu reducing alloy and a molten salt containing about 15-20 mol % $MgCl_2$. In this system, rare earths distribute to the salt phase, whereas uranium and plutonium remain largely in the metal phase.

The purpose of the research described here was to specify conditions under which UO_2 powder and pellets can readily be reduced. This required a systematic study of the factors affecting UO_2 reduction. Emphasis was initially placed on the preferred Mg-44 at. % Cu/15-20 mol % $MgCl_2$ system. The effects on UO_2 reduction rate of changing the physical and chemical conditions, including the use of a calcium reduction system, were studied.

II. EXPERIMENTAL PROCEDURE

A. Apparatus

The UO_2 reductions were performed in a 2.5-in.-ID x 6.5-in.-high baffled tantalum crucibles in a furnace well attached to the bottom of a helium-atmosphere glovebox. A flange covering the furnace well contained openings through which a stirrer, a thermocouple protection tube, and a sampling device could be inserted and lowered into the reduction crucible. The stirrer was rotated by a dc motor by means of an O-ring belt drive.

The furnace well and crucible were heated with a Marshall furnace, and the desired experimental temperature was maintained to within $\pm 2^\circ\text{C}$ with a West controller. The moisture level in the glovebox was kept below 5 ppm by circulating the atmosphere through a charcoal trap cooled to -194°C .⁵

B. Procedure

The initial step of each experiment was to prepare the reduction alloy. Two hundred grams of copper and 100 g of magnesium were loaded into a tantalum crucible. In the calcium reduction studies, about 10 g of calcium metal was added. The crucible was placed in the glovebox furnace well and heated while the metal was stirred. Agitation was provided by tantalum stirrers having a 1.5-in.-wide x 0.75-in.-high flat-blade paddle, except where otherwise indicated.

Approximately 150 g of the appropriate salt mixture was added to the crucible, the crucible was brought to the desired reduction temperature, and then the system was agitated gently. The stirrer was located in the alloy, with the top near the quiescent salt-metal interface. When temperature equilibrium was attained, and while the metal was stirred slowly, about 25 g of UO_2 powder or pellets was added to the system. The stirring rate was immediately increased to 800 rpm, except for the studies on the effect of agitation on reduction. At the end of a reduction run, the crucible was rapidly cooled by lowering the furnace away from the furnace tube.

C. Analytical Procedure

To measure the extent of UO_2 reduction, the salt and metal phases were physically separated, dissolved in nitric acid, and analyzed for uranium. The calculated fraction of UO_2 reduced was the ratio of the amount of uranium found in the metal to the total uranium in both the salt and metal phases. The uranium material balance for these experiments was generally 98% or better.

Uranium has low solubility in the Mg-44 at. % Cu alloy used in these reductions,⁶ and UO_2 is virtually insoluble in any of the salts.⁷ Therefore, homogeneous samples of neither phase can be taken during a reduction to determine the fraction of UO_2 reduced at any time. It has been found⁸ that uranium daughters (thorium and protactinium) reduce at the same rate as UO_2 and are dissolved in the Mg-44 at. % Cu alloy. Thus, to estimate the amount of uranium reduction during a run, samples of the metal phase were taken using tantalum tubes with porous sintered-tantalum filters. The filtered samples were counted for the gamma emissions of the soluble uranium daughters. The amount of uranium reduced into the metal phase was assumed to be proportional to the gamma count rate per gram of sample multiplied by the total weight of the metal phase.⁸ The proportionality constant

was calculated for each run from the gamma count rate of the last metal sample, the alloy weight, and the overall extent of UO_2 reduction, which was determined as discussed in the paragraph above.

D. Materials

The copper metal used in these experiments was reagent-grade shot. The calcium and magnesium metals were of greater than 99.5 and 99.99% purity, respectively. Calcium chloride, CaF_2 , NaCl , LiF , and MgF_2 were reagent-grade anhydrous chemicals that were further dried in an oven at 200°C . Water was removed from commercial anhydrous MgCl_2 by contacting the molten salt with magnesium metal. The solid MgO produced by this treatment was allowed to settle, and the supernatant salt was separated for use in the experiments. Lithium chloride was purified by sparging the molten salt with HCl gas. The -100 mesh UO_2 powder for this study was produced by ball-milling sintered UO_2 pellets under a helium atmosphere. All materials were stored and handled in the helium-atmosphere glovebox.

III. RESULTS AND DISCUSSION

A. Reduction of UO_2 in Magnesium Systems

1. Effect of Temperature

The experimental results in Table I show that the extent of UO_2 reduction at 2-4 hr in the indicated 15 mol % MgCl_2 salt is affected relatively little by increasing the temperature from 700 to 800°C . The rates of reduction in the early stages, however, appear to be greater at the higher temperatures. The reasons for the slower reductions at 600°C are not

TABLE I. Effect of Temperature on UO_2 Reduction

Salt: 150 g of 42.5 mol % NaCl -37.5 mol % CaCl_2 -
15 mol % MgCl_2 -5 mol % CaF_2
Metal: 300 g of Mg-44 at. % Cu
Oxide: ~25 g of -100 mesh UO_2 powder
Stirring: 800 rpm by 0.75- x 1.5-in. blade paddle

Temperature, $^\circ\text{C}$	Percent Reduction		
	1 hr	2 hr	4 hr
600	43	52	66
700	74	85	87
750	76	-	83
800	85	86	89

known, but one reason may be the higher viscosity of salt near its melting point. It can be inferred from the negligible effect of temperature between 700 and 800°C on the rate of reduction that after about 1 hr in salts of low $MgCl_2$ concentration the rate is controlled by diffusion, rather than by the chemical reaction.

2. Effect of Stirring

Table II gives the results of the studies on the effect of stirring upon UO_2 reduction rates in the Mg-44 at. % Cu/15 mol % $MgCl_2$ salt system. The data show that increasing the size of the paddle and/or the rate of stirring causes an increase in the rate of UO_2 powder reduction up to some limit, but further increases in the amount of agitation have little effect on reduction rate. Probably when the UO_2 particles are completely suspended in the liquid, and the metal and salt phases are well dispersed in each other, no greater agitation is necessary or useful.

TABLE II. Effect of Stirring on UO_2 Reduction

Salt:	150 g of 42.5 mol % $NaCl$ -37.5 mol % $CaCl_2$ - 15 mol % $MgCl_2$ -5 mol % CaF_2
Metal:	300 g of Mg-44 at. % Cu
Oxide:	~25 g of -100 mesh UO_2 powder
Temperature:	700°C
Time:	4 hr

Type of Agitator	Stirrer Speed, rpm	Percent Reduction
1.5-in.-wide x 0.75-in.-high flat blade	500-1000	87
1.25-in.-wide x 0.5-in.-high two-blade turbine	800	82
1-in.-wide x 0.5-in.-high four-blade turbine	800	60
1-in.-wide x 0.5-in.-high flat blade	1000	90 ^a
1-in.-wide x 0.5-in.-high flat blade	800	70

^a800°C.

3. Effect of Salt Composition

Table III shows the effect of salt composition on the rate of UO_2 reduction. Salt 1 is the mixture originally suggested for use in UO_2 reductions.

TABLE III. Effect of Salt Composition on UO_2 Reduction in Magnesium Systems

Metal:	300 g of Mg-44 at. % Cu
Oxide:	~25 g of -100 mesh UO_2 powder
Stirring:	800 rpm by 0.75- x 1.5-in. blade paddle
Temperature:	800°C

Salt No.	Salt Composition, mol %						Percent Reduction				
	$MgCl_2$	$CaCl_2$	$NaCl$	$LiCl$	CaF_2	MgF_2	30 min	60 min	120 min	180 min	240 min
1	15	37.5	42.5		5		80	85	86	88	89
2	15	42.5	42.5								70
3	15	50		30	5						85
4	15	40	35		10						90
5	25	35	30		10						90
6	20		75			5	80	87	90	92	93
7	50	45			5						96

The reduction is rapid for the first 80%, but becomes very slow beyond that point. Even with fine powders, an impractically long time would be required to attain complete reduction with this salt. Past experience¹ with oxide reductions suggested that increases in the magnesium ion and fluoride ion concentrations of the salts would increase the rate of UO_2 reduction. This was the basis for the composition changes in salts 2-7.

Elimination of CaF_2 from salt 1 to give salt 2 produced a marked decrease in the fraction of UO_2 reduced after 240 min. A similar effect was observed in engineering demonstration reductions,⁸ where nearly complete UO_2 reduction was achieved in 120 min with the salt 45 mol % MgCl_2 -45 mol % CaCl_2 -10 mol % CaF_2 , but only about 60% of the UO_2 was reduced in the same time when no CaF_2 was present in equimolar MgCl_2 - CaCl_2 .

The extent of UO_2 reduction after 240 min increased gradually as the concentration of magnesium cation increased in salts 1 and 3-7. Essentially complete reduction of UO_2 was attained only with the salt containing 50 mol % MgCl_2 .

The low rate of UO_2 reduction after about 80% had been reduced in salts of low MgCl_2 concentration suggested that these reductions were being inhibited by insoluble MgO . Microscopic examination of salts from incomplete UO_2 reductions revealed evidence of a protective coating of MgO on UO_2 particles. A similar observation had been made previously on CaCl_2 - MgCl_2 salts from uranium oxide reductions by Zn-Mg alloys.¹⁴ Salts with low MgCl_2 concentrations do not appear to be acceptable as a UO_2 reduction medium. Engineering demonstration reductions⁸ have shown that even with salts containing about 50 mol % MgCl_2 , only about 40% of granular -12, +45 mesh UO_2 particles could be reduced in 4 hr. Thus, to be able to reduce large pieces of UO_2 , such as pellets requires some other reduction medium.

B. Reduction of UO_2 in Calcium Systems

1. Effect of Salt Composition

Data in the literature indicate that CaO has an appreciable solubility in alkali chlorides,^{9,10} and in CaCl_2 .¹¹ If CaO , which would be soluble in a CaCl_2 salt, were the product of reduction, no protective coating should form on partially reduced UO_2 particles and good reductions might result. For this reason, the salts shown in Table IV were used in UO_2 reductions where calcium metal as the reductant was added to the Mg-44 at. % Cu alloy. The rapid and complete reductions obtained in these systems suggest that the above hypothesis of a reduction-inhibiting MgO coating was correct.

2. Effect of Particle Size

Table V shows the effect of UO_2 particle size on the rate of reduction. The reduction rate decreased appreciably when the UO_2 particle size was increased considerably, but complete reduction was attained in a

reasonable time. Engineering studies⁸ have shown that, although the rate of reduction was slower than that for powders, 0.375-in.-diam UO_2 pellets could be completely reduced in about 4 hr in the CaCl_2 - CaF_2 /Ca-alloy reduction system. This is a great improvement over the 50 mol % MgCl_2 /Mg-alloy system, where only 40% of -12, +45 mesh UO_2 powder was reduced in the same period of time.

TABLE IV. Effect of Salt Composition on UO_2 Reduction in Calcium Systems

Metal: 300 g of Mg-44 at. % Cu + 10 g of Ca
 Oxide: ~25 g of -100 mesh UO_2 powder
 Stirring: 800 rpm by 0.75- x 1.5-in. blade paddle
 Temperature: 800°C

Salt No.	Salt Composition, mol %				Percent Reduction				
	CaCl_2	NaCl	LiCl	CaF_2	30 min	60 min	120 min	180 min	240 min
8	20	75		5	72	88	98	98	98
9	20		75	5	95	97	98	98	98
10	80			20	97	99	99	99	99

TABLE V. Example of the Effect of Particle Size on UO_2 Reduction Rates

Salt: 150 g of CaCl_2 -20 mol % CaF
 Metal: 300 g of Mg-44 at. % Cu + 15 g Ca
 Oxide: ~25 g as indicated
 Stirring: 800 rpm by 0.75- x 1.5-in. blade paddle
 Temperature: 800°C

UO_2 Particle Size	Percent Reduction				
	30 min	60 min	120 min	180 min	240 min
-100 mesh powder	97	99	99	99	99
~0.25-in.-diam pellet pieces	63	87	96	98	99

C. Reduction Mechanism Implications

The above reduction experiments, and solubility information available (Table VI) for alkaline earth oxides and metals and UO_2 in molten chloride salts, can be used to evaluate possible UO_2 reduction mechanisms. Uranium dioxide has a very low solubility in all the salts, but is slightly lower in CaCl_2 than in MgCl_2 . The data in Table VI show that calcium and CaO are much more soluble in CaCl_2 than are magnesium and MgO in MgCl_2 . Little is known about the solubilities of magnesium metal and MgO in alkali or alkaline chloride mixtures with MgCl_2 , but qualitatively these would be expected to increase as the MgCl_2 concentration increases.

TABLE VI. Solubility of Several Solutes in Selected Solvents at 800°C

Solute	Solubility in Solvent, mol %				
	MgCl ₂	CaCl ₂ -50 mol % MgCl ₂	LiCl	NaCl	CaCl ₂
Mg	0.019 ^a				
Ca					2.7 ^b
UO ₂ ^c	1 x 10 ⁻⁴	1 x 10 ⁻⁴	~1 x 10 ⁻⁵		4 x 10 ⁻⁵
CaO			0.004 ^d	0.001 ^e	13 ^{c,f}
MgO		< 0.005 ^{c,g}	2 x 10 ⁻⁵		

^aRef. 13. ^cRef. 7. ^eRef. 10. ^gAt -500°C.
^bRef. 12. ^dRef. 9. ^fRef. 11.

The fact that UO₂ is slightly less soluble in CaCl₂ than in MgCl₂, but reduces much faster in a CaCl₂ salt than in a MgCl₂ salt, indicates that reduction of a uranium oxide species dissolved in the salt is not an important step in these reductions. Since oxide particles are not wet by the alloy, direct reaction of solid UO₂ with the liquid metal probably does not make a significant contribution to the overall reduction. The only remaining alternative is reaction of solid UO₂ particles with magnesium or calcium metals dissolved in the salt (as Mg²⁺ or Ca²⁺ ions presumably¹²). This reaction will produce MgO or CaO and metallic uranium; the latter would then transfer to the alloy phase. Insoluble MgO might inhibit these steps. The high solubility of both calcium and CaO, as compared with magnesium and MgO, in their respective chloride salts would lead one to predict higher UO₂ reduction rates in the calcium system. The reductions made with calcium metal-CaCl₂ salt media confirmed these predictions. The relative effect of calcium or CaO solubility on the reductions cannot be determined from these experiments.

Although the effects of particle size and stirring on reduction could be explained by other reaction mechanisms, they are not in disagreement with reduction at the UO₂ particle surface by calcium or magnesium metal dissolved in the salt. A mathematical, diminishing-sphere model of this reduction reaction could not be correlated with the observed data, probably because the model is based on uniformly sized spheres, whereas irregularly shaped particles of various sizes were present in the experiments.

IV. CONCLUSIONS

This study shows that acceptable reductions of UO₂ powder by Mg-44 at. % Cu alloys are not possible in the presence of salts containing less than about 50 mol % MgCl₂. Larger particles of UO₂ are only slowly reduced in salts of high MgCl₂ concentration. Even UO₂ pellets, however, can be readily reduced in the presence of a CaCl₂-20 mol % CaF₂ salt with a Cu-Mg-Ca alloy.

Consideration of available UO_2 reduction data suggests that reduction occurs at the UO_2 particle surface by reaction with magnesium or calcium dissolved in the salt phase as a lower-valent species such as Mg_2^{2+} or Ca_2^{2+} . An inhibiting layer of MgO might form in magnesium reductions, and this layer might drastically reduce reduction rates. Since CaO is quite soluble in CaCl_2 salts, no such reduction-inhibiting layer forms in calcium reductions.

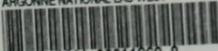
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