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INVESTIGATION OF FUSED-SALT PROCESSES FOR THE PREPARATION OF URANIUM SULFIDES

by

D. R. Messier

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ABSTRACT

Attempts were made to prepare uranium monosulfide by two fused-salt processes. The first consisted of bubbling a H_2 - H_2S stream through molten alkali halides containing dissolved UF_4 . In the second, UF_4 or UCl_4 with various sulfides was electrolyzed in fused chloride media. Mixtures of UOS and UO_2 were obtained by the bubbling method under uncontrolled drying conditions. No product was obtained when careful drying was done. Under the driest electrolysis conditions, UOS was obtained. It was concluded that the monosulfide cannot be produced by the gas reaction method, and that improved experimental conditions would be necessary for success with the electrolytic method.

INTRODUCTION

The potential of uranium monosulfide as a reactor fuel material has created interest in its preparation and properties.⁽¹⁾ The most successful preparation process that has been developed consists of the reaction of finely divided uranium metal with a stoichiometric amount of H_2S gas in a closed vessel followed by high-temperature ($1800^\circ C$) homogenization to yield the monosulfide.⁽¹⁻³⁾ Some disadvantages of this method are: (1) several hydriding-dehydriding cycles are necessary to get the uranium metal finely divided enough to react, (2) high-temperature homogenization is required, (3) the gas-reaction process is slow, and (4) the method is unsuitable for large-scale production. Since it appeared that a fused-salt preparation process would have none of these disadvantages, this investigation was initiated.

Two sets of experiments were carried out. The first involved the reaction of UF_4 dissolved in molten alkali chlorides with an H_2 - H_2S gas mixture which was bubbled through the melt. The second was concerned with an electrolytic method similar to that used for the preparation of ThS.⁽⁴⁾ UCl_4 and UF_4 were electrolytically reacted with various sulfides in fused chloride media.

EXPERIMENTAL CONDITIONS

Materials

It was desired to establish operating conditions approximating those which would exist in large-scale production and to determine what impurity levels were tolerable. Therefore, no effort was spent in obtaining high-purity starting materials. The various halides and sulfides used were "off-the-shelf" reagent-grade materials. The UF_4 and UCl_4 were obtained from commercial suppliers (National Lead Co., and K and K Laboratories, respectively).

Apparatus

Preliminary attempts to obtain gas reactions were done in a mullite reaction vessel using a graphite crucible and graphite-tipped stainless steel bubbler tube. Figure 1 shows the final version of the apparatus as modified for electrolysis.

Figure 1
Fused-salt Reaction Apparatus

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The apparatus was installed in a hood. The reaction chamber itself was made from Type 446 stainless steel. The rest of the apparatus, including gas lines, etc., was constructed mainly from Type 304 stainless steel. The gas-flow system was of conventional design. A mechanical vacuum pump was used to evacuate the system for purging. When the apparatus was used for the gas reaction, the top flange was replaced by a simpler one containing a centered bubbler tube.

The crucibles, 57 mm OD x 95 mm tall x 5 mm wall, were fabricated from ATJ graphite (National Carbon Co.). For the electrolysis

experiments, the crucible itself served as the anode. A good anode connection could be made by forcing the platinum wire anode lead into a hole drilled in the crucible wall. The cathodes were either molybdenum paddles or threaded graphite stirrers attached to shafts of 6-mm stainless steel tubing. A laboratory stirring motor was used to rotate the stirrers at about 200 rpm. The electrode compartments were separated by porous alumina extraction thimbles (Norton RA98).

Most of the materials resisted attack quite well. The portion of the molybdenum paddle above the melt was somewhat corroded, but a single paddle was usable for a large number of runs. Attack of the graphite crucible under certain conditions is discussed later. Although the stainless steel parts underwent some attack, they held up satisfactorily.

Procedure

Gas Reaction

Except for variations in experimental conditions, the general procedure was the same for all gas-reaction runs. After drying and weighing, the salts were mechanically mixed and loaded into a graphite crucible. The charge was then melted under either vacuum or flowing, dry argon. Drying with HCl was done in some runs by bubbling HCl gas through the melt, followed by scavenging with argon to remove the dissolved HCl. The reaction was started by bubbling a gas stream composed of H_2 at approximately 80 cc/min and H_2S at 60 cc/min through the melt.

Electrolysis

The uranium, sodium, and potassium chlorides used for electrolysis were stored in a vacuum drier at 100°C. The sodium sulfide, with the nominal formula $Na_2S \cdot 9H_2O$, was in the form of wet lumps, which blew apart when attempts were made to dry them in a vacuum drier. Better results were obtained by storing the material in a vacuum desiccator for several weeks. The calcium sulfide was less hygroscopic and was vacuum dried at 100°C in the early experiments. For the final runs, it was dried by vacuum calcination at 1200°C.

As much of the batch preparation as possible was done in an argon-atmosphere glovebox. The vacuum drier was located in the box, but weighing had to be done outside the box. All transfer operations were done in a manner such as to reduce exposure of the batch to the room atmosphere.

The melting and drying procedure for electrolysis was the same as that described for the gas reaction. An atmosphere of flowing, dry argon was used. In addition to HCl drying, electrolytic drying was employed. This was done by applying and holding an emf of 2.0 V until the current reached a low value (0.1-0.2 Amp).⁽⁴⁾ The current decrease was

accompanied by a rise in the back emf, which approached 2.0 V. Back-emf measurement was done by momentarily switching off the power supply and recording the voltmeter reading. After the completion of drying, reaction was initiated by increasing the applied emf to 5.0 V.

RESULTS AND DISCUSSIONS

Gas-reaction Method

Preliminary experiments were done with batches composed of 100 g of NaCl-KCl eutectic and 10 g of UF_4 reacted at about 850°C . No drying of the melt was done. When the H_2 - H_2S gas mixture was introduced into the melt, a temperature rise was observed, indicating that an exothermic reaction was occurring. The run time was 2 hr.

The reacted batch was in the form of a solid ingot and was easily separated from the graphite crucible. Examination of a section of the ingot showed a black deposit at the bottom. This lower portion containing the precipitated product was mechanically separated from the remaining salts and leached with distilled water to remove the adhering chlorides.

X-ray patterns of the product material were initially interpreted as indicating that a mixture of UOS and US had been obtained.⁽⁵⁾ However, the patterns for UO_2 and US are very similar and easily confused. A careful re-examination of the X-ray results showed the second major phase to be UO_2 rather than US.

The presence of US seemed to be confirmed by gravimetric data indicating partial solubility of the product in hot 10% H_2SO_4 , in which US is soluble.⁽¹⁾ However, the interpretation of such an analysis is complicated by the possibilities of the presence of water-insoluble fluorides, of incomplete leaching, and of the presence of undetected, acid-soluble US_2 .

Subsequent gas-reaction runs were done in the apparatus shown in Figure 1. Reaction conditions differed from those in earlier runs. The fused-salt medium consisted of either LiCl-KCl eutectic at about 500°C or NaF-LiF at 700°C . Table I summarizes the experimental results for this phase of the study.

It is evident from Table I that under "dry" conditions, i.e., those in which HCl drying or a fluoride melt is used, no product was obtained. Under "wet" conditions a UO_2 -UOS product resulted. The final run, done under wet conditions with H_2S alone as the gaseous reactant, indicated that hydrogen was unnecessary for reaction to occur.

Table I
RESULTS OF ATTEMPTS TO PREPARE US BY GAS REACTION

Run No.	Salt Charge (g)	Reaction Temp (°C)	Reaction Time (hr)	Drying Conditions	Results
US-2	41.4 LiCl 48.6 KCl 10 UF ₄	450	2	No Drying	Very small yield, chiefly UO ₂ .
US-3	41.4 LiCl 48.6 KCl 10 UF ₄	500	3	No Drying	Substantial yield - UO ₂ + UOS.
US-4	41.4 LiCl 48.6 KCl 10 UF ₄	530	4	65-hr vacuum dry at 400°C. Ice-CaCl ₂ cold trap.	Good yield - UO ₂ + UOS.
US-5	25 LiF 25 NaF 50 UF ₄	700	2.2	16-hr vacuum dry at 300°C. Dry ice-acetone cold trap.	No visible product.
US-7	25 LiF 25 NaF 50 UF ₄	750	2.5	18-hr vacuum dry at 300°C.	No visible product.
US-8-9	41.4 LiCl 48.6 KCl 10 UF ₄	570	3	22-hr vacuum dry at 200°C. 1 hr HCl bubble at 570°C.	No visible product.
US-10	41.4 LiCl 48.6 KCl 10 UF ₄	570	3	No Drying	Good yield of black product.
US-12	41.4 LiCl 48.6 KCl 10 UF ₄	570	3	No Drying	H ₂ S alone used. Good yield - UO ₂ + UOS.

During the final stages of the gas-reaction work, the results of attempts by Allbutt and Junkison to use this method became available.⁽⁶⁾ They were also unable to produce the monosulfide. Under drying conditions more stringent than ours, they obtained a product composed of UOS and US₂. The absence of detectable amounts of US₂ in our product may be due to the difference in drying conditions and the higher temperature (800°C) used by Allbutt and Junkison.

In the present experiments, the presence of water appeared to be essential for any reaction at all to occur. It is possible that water catalyzes some reaction leading to the simultaneous formation of UO₂ and UOS. However, the lack of thermodynamic data and complex nature of the system make it impossible to write specific equations for the probable reactions involved.

Although it has been demonstrated that the gas-reaction method is incapable of producing monosulfide, it is possible that, under the proper conditions, the method might be useful for preparing UOS.

Electrolytic Method

Table II summarizes the results of attempts to prepare US electrolytically. In a typical run, the application of the 5-V emf resulted in a rapid rise in back emf to a characteristic value for given experimental conditions. The back emf remained at this value for the reaction time listed in Table II. The emf application was usually accompanied by a temperature rise, indicating that an exothermic reaction was occurring. The apparent end of reaction was indicated by a simultaneous drop of back emf and current rise. The currents listed in Table II are given rather than current

Table II
RESULTS OF ATTEMPTS TO PREPARE US ELECTROLYTICALLY

Run No.	Salt Charge (g)	Temp (°C)	Applied emf (V)	Back emf (V)	Current (Amp)	Time (min)	Products	Remarks
E-4	41.4 LiCl 48.6 KCl 30 $\text{Na}_2\text{S} \cdot \text{XH}_2\text{O}$ 4 UF_4	500	5.0	3.5	4	125	UO_2 UOS U Alkali Metal	All of the UF_4 appeared to react.
E-9	39.6 NaCl 50.4 KCl 30 $\text{Na}_2\text{S} \cdot \text{XH}_2\text{O}$ 4 UCl_4	700	5.0	3.2	4.5	52	UOS UO_2	Salts vacuum dried 4 hr at 800°C. 1/2-hr HCl dry.
E-13	39.6 NaCl 50.4 KCl 19 PbS 4 UCl_4	700	5.0	-	-	10	-	Mo cathode dissolved.
E-14	39.6 NaCl 50.4 KCl 2.5 PbS 4 UCl_4	700	5.0	2.9	4	140	Pb S	Graphite cathode.
E-15	39.6 NaCl 50.4 KCl 1 CaS 4 UCl_4	700	5.0	2.2	3.5	35	-	Mo cathode dissolved.
E-16	39.6 NaCl 50.4 KCl 1 CaS 4 UCl_4	700	5.0	2.6	3.5	100	UO_2 some UOS	Graphite cathode.
E-19	39.6 NaCl 50.4 KCl 10 CaS 5 UCl_4	680	5.0	3.0	1.9-3.5	210	UOS	HCl and electrolytic drying. Graphite contamination in product. UC_2 produced during heat treatment.
E-20	39.6 NaCl 50.4 KCl 5 CaS	670	5.0	2.5	1.9-3.8	95	-	Crucible badly attacked.
E-21	39.6 NaCl 50.4 KCl 2 CaS 10 UCl_4	700	5.0	2.6	3.2-4.0	170	UOS UO_2 S	CaS pre-dried at 1200°C. Graphite contamination in product. UC produced during heat treatment.

densities because the depth of immersion of the paddle was not accurately known, owing to difficulties in positioning it, and melt loss through evaporation and spillage.

The product was usually located in the cathode compartment, although in some runs material was found between the electrode compartments. The salt mass stuck tightly to the crucible, making product removal difficult. The graphite crucible had to be broken after each run for product removal. The product was mechanically separated from the rest of the salt mass. Excess salts were removed by vacuum heat treatment at 1200°C.

The first electrolyses were done with LiCl-KCl as the solvent and UF_4 and $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ as additives. The result of run number E-4 (see Table II) is typical of these early attempts. Although the melt was vacuum dried, the resulting product contained large oxygen contamination.

These first attempts indicated that drier conditions were necessary to avoid oxygen contamination. The presence of alkali metal suggested that stirring was needed to prevent concentration polarization.⁽⁷⁾ In addition, it appeared that the use of NaCl-KCl eutectic rather than LiCl-KCl would reduce the hygroscopicity problem associated with the latter and allow operation at higher temperature to increase the reaction rate. These changes were made for subsequent runs.

The result of run E-9, listed in Table II, is typical of those in which sodium sulfide was used. The probable cause of the oxygen contamination was believed to be the sodium sulfide, which is extremely difficult to dry. Attempts to dry it by vacuum calcination at 800°C resulted in large evaporation losses and apparent decomposition. It was therefore decided to try other sulfides as additives.

In runs E-13 through E-21 either calcium or lead sulfide was used. The molybdenum cathodes quickly dissolved in these sulfides, evidently because of the formation of low-melting calcium and lead alloys. A change was made to graphite cathodes, which appeared to be resistant to attack. The result of run E-14 indicated that lead sulfide was unsatisfactory. Evidently, lead was preferentially reduced over uranium at the cathode. If one assumes that the uranium reaction at the cathode is the reduction of U^{+4} , the above result is consistent with single-electrode-potential data, which predict the order of deposition to be, Pb, U, Na, Ca, Li, and K.⁽⁷⁾

The best product obtained with CaS was that of run E-19. Even in this run, under the driest conditions attainable, the product was mainly oxysulfide. Furthermore, the product was heavily contaminated with carbon, which reacted during heat treatment to form uranium dicarbide. The carbon contamination may have resulted from alkali attack of the cathode, similar to that reported by Didchenko and Litz.⁽⁴⁾ The crucibles were also attacked and cracked near the melt line in almost every run.

The overall electrolysis results indicate that at least partial success was obtained. The oxidation of S^{--} to sulfur was evident from the lead sulfide result and from the observation of free sulfur in the reaction chamber after several of the runs. It also appeared that a uranium-bearing species was being reduced at the cathode. In addition, in runs in which UF_4 was used, the characteristic green color of UF_4 disappeared from the melt during reaction. The destruction of the molybdenum cathode by calcium indicates that calcium may also have been deposited at the cathode. However, since little free calcium was found, perhaps a secondary cathode process could have occurred in which calcium reduced the uranium ions. A similar secondary process was proposed by Chene in the electrolytic synthesis of metallic phosphides.⁽⁸⁾ At any rate, the reaction process is probably complex, and the available experimental data are insufficient for detailed speculation concerning the reaction mechanism.

SUMMARY AND CONCLUSIONS

Gas-reaction Method

The results of this study and a concurrent one⁽⁶⁾ indicate that uranium monosulfide cannot be synthesized by bubbling an H_2 - H_2S gas mixture through a fused-salt melt containing a dissolved uranium halide.

Electrolytic Method

Under the experimental conditions employed the electrolytic method was unsuitable for the production of uranium monosulfide. With further development, the method may still be successful. The major problem appears to be the attainment of sufficiently dry operating conditions. The problem may be analogous to that encountered in the electrolytic production of high-purity uranium for which it has been reported that even slight amounts of water completely disrupt the process.⁽⁹⁾ It therefore seems that a number of steps would be necessary to successfully produce high-purity US. These include:

1. the synthesis of high-purity UCl_4 and CaS for starting materials;
2. careful salt purification;⁽¹⁰⁾
3. a search for attack-resistant cathode and crucible materials;
4. carrying out the entire preparation and reaction process under inert-atmosphere glovebox conditions.

The requirements outlined above appear to make the electrolytic process compare unfavorably with the uranium metal- H_2S gas reaction

process currently in use.⁽¹⁾ In addition, further work would require the setup of an elaborate glovebox facility. For these reasons, the electrolysis experiments have been terminated.

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