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RECONSTITUTION OF MSR FUEL BY REDUCING UF_6 GAS TO UF_4 IN A MOLTEN SALT

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ABSTRACT

The direct reduction of UF_6 to UF_4 in a molten salt is proposed as a step in the purification of fuel salt from a molten salt reactor. This step would replace the conventional method of reduction in which UF_6 is reduced to UF_4 powder in a H_2 - F_2 flame. Reduction of the UF_6 in a molten salt will result in a shorter and more direct process for fuel salt purification. The reduction is to be effected in two steps which consist of absorption of UF_6 into a molten salt containing UF_4 and of reduction of the resulting intermediate fluorides to UF_4 with hydrogen. Experimental data on the absorption step are presented and information concerning the reduction of intermediate fluorides is considered.

INTRODUCTION

One proposed processing step for Molten Salt Reactor (MSR) fuel is the reduction of purified UF_6 to UF_4 so that the UF_4 can be returned to barren, purified fuel salt.[1] The usual method for reducing UF_6 to UF_4 is by use of H_2 in a H_2-F_2 flame:

$$UF_6 + H_2 \xrightarrow{(H_2 + F_2)} UF_4 + 2HF.$$

This reduction is carried out in a tall column where the UF_6 and H_2 are introduced into a H_2-F_2 flame and dry UF_4 powder (finely divided) is collected. It is a routine production operation and there is much available operating information.[2,3] Such a process would not be desirable for remote operation. It involves a solids handling problem which routinely requires equipment access and process control is sometimes difficult.

It would be desirable to reduce the UF_6 to UF_4 in a molten salt environment, and thus circumvent the problems of solids handling and fuel make-up. Past experience of other workers has indicated the feasibility of absorbing UF_6 into molten salt which contains UF_4 and reducing the absorbed UF_6 to UF_4 by sparging with H_2. Kirslis[4] found that corrosion was not severe in absorption of F_2 by molten salt containing U until the intermediate fluoride of uranium had a fluoride content greater than UF_5. Long[5] found that H_2 would reduce UF_4 to UF_3 in a molten salt and Blood[6] has reduced various metal fluorides in molten salts by use of H_2.

This report presents a proposed continuous processing method for the reduction of UF_6 to UF_4 in a molten salt environment by absorption of UF_6 in the salt and reduction with H_2. The results from a scouting test are analyzed to indicate process feasibility.

PROPOSED PROCESS AND APPLICATION TO MSR PROCESSING

The current scheme for processing Molten Salt Reactor (MSR) fuel consists of removal of uranium as UF_6 and volatile fission products (FP) from the salt by fluorination, separation of refractory FP from the salt by distillation, and recombination of the volatilized uranium and purified barren salt for return to the MSR (Fig. 1)[1]. During the fluorination step, both uranium and volatile fission products are removed from the salt by the reactions:

$$UF_{4(\text{in molten salt})} + F_2 \longrightarrow UF_6,$$

$$FP_{(\text{in molten salt})} + F_2 \longrightarrow \text{volatile FP fluorides.}$$

The UF_6 and volatile FP fluorides will be separated by sorption techniques and the uranium will then be reintroduced as UF_4 to the purified barren salt to form the MSR fuel. Thus, there must be a method for reducing UF_6 to UF_4.

Since the end result of the UF_6 reduction will be a solution of UF_4 in molten salt rather than UF_4 as a dry powder, it is attractive to carry on the reduction in a molten salt environment and preferably in the purified barren salt. To achieve this requirement, UF_6 can be contacted with a molten fluoride salt containing some uranium as UF_4 where it will be absorbed by reaction with the UF_4 to form an equivalent intermediate fluoride of uranium, such as UF_5, in the salt:

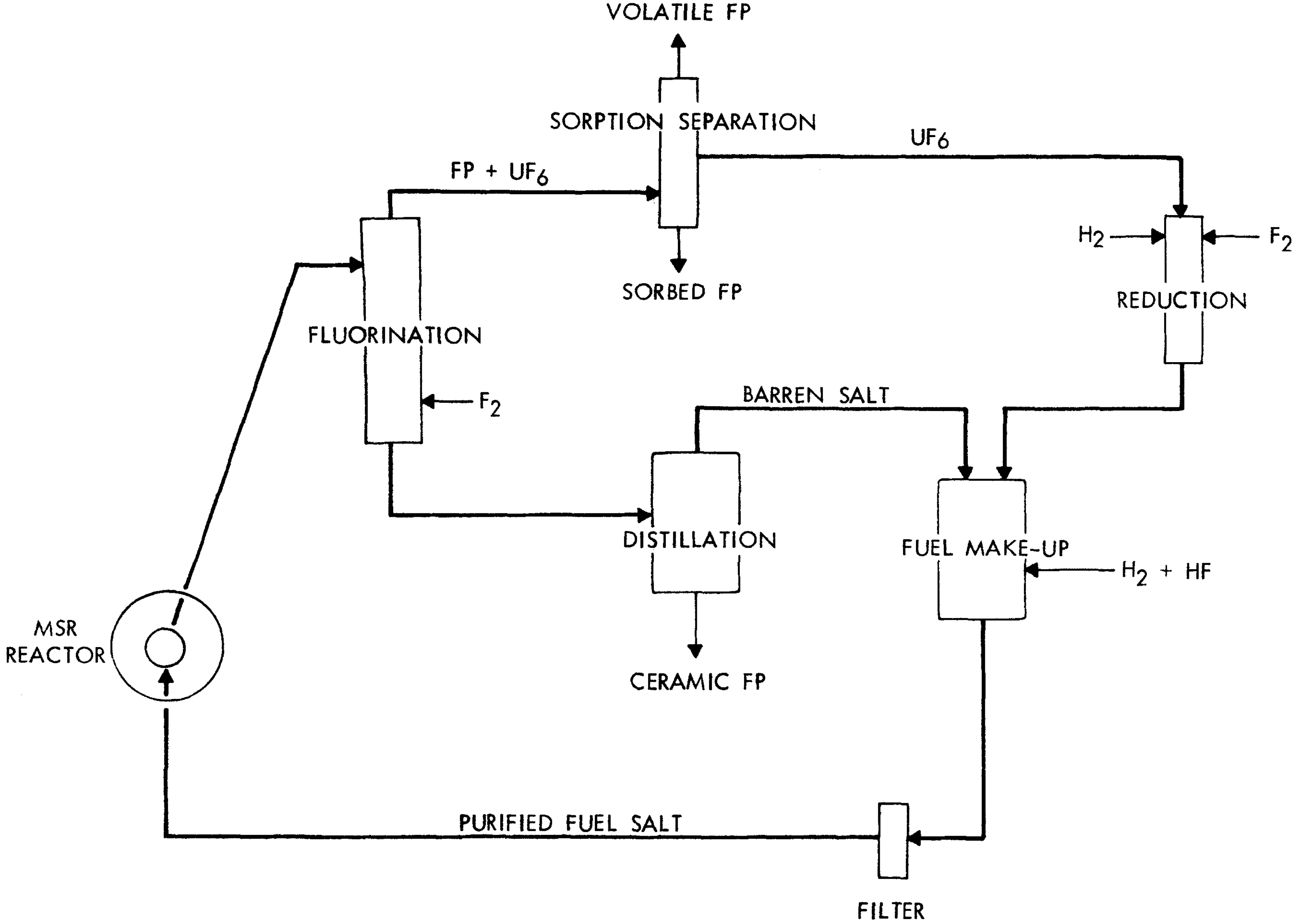

Fig. 1. MSR Fuel Processing with Conventional UF_6 Reduction.

$$UF_{4(salt)} + UF_6 \longrightarrow UF_{5(salt)}$$

This intermediate fluoride will then be reduced to UF_4 in the salt by means of H_2:

$$UF_{5(salt)} + 1/2H_2 \longrightarrow UF_{4(salt)} + HF \ .$$

Such a process could be carried out continuously in a column in which the barren salt and UF_6 are introduced at the bottom of the column along with salt containing UF_4 which is recycled from the top of the column (Fig. 2). As the salt and UF_6 progress up the column, the UF_6 will be absorbed in the salt and subsequently reduced to UF_4 as it passes into the H_2 reduction section. The column off-gas will be a mixture of H_2 and HF and a side stream of the overhead molten salt will be ready for return to the nuclear reactor core after filtration since the HF and H_2 sparge usually given make-up salt will have been achieved in the reduction column. When this reduction step is incorporated into the flowsheet, the resulting process is more direct and shorter (Fig. 3).

Initial tests (next sect.) indicate that the absorption step is very rapid, however, it will be desirable to keep the fluoride content of the intermediate fluoride below that equivalent to UF_5 in order to minimize corrosion. The rate of the hydrogen reduction reaction is not known, although the limited data available looks favorable. In studying the reduction of UF_4 to UF_3 in molten salt by H_2 by the reaction:

$$UF_{4(salt)} + 1/2H_2 \longrightarrow UF_{3(salt)} + HF \ ,$$

Long[5] observed that equilibrium was established between a H_2-HF stream and molten salt containing uranium fluorides after the gas bubbles had risen a few inches through the salt. His data also indicate only 1% reduction of UF_4 to UF_3 by a gas stream containing 1% HF in H_2 at a pressure of 1 atm at $600^\circ C$.

EXPERIMENTAL EQUIPMENT AND PROCEDURE

The experimental equipment was assembled from existing equipment available as a result of work in support of the Molten Salt Fluoride Volatility Process. Means were provided for contacting UF_4, dissolved in molten salt, with UF_6 in the first step of the reduction process and

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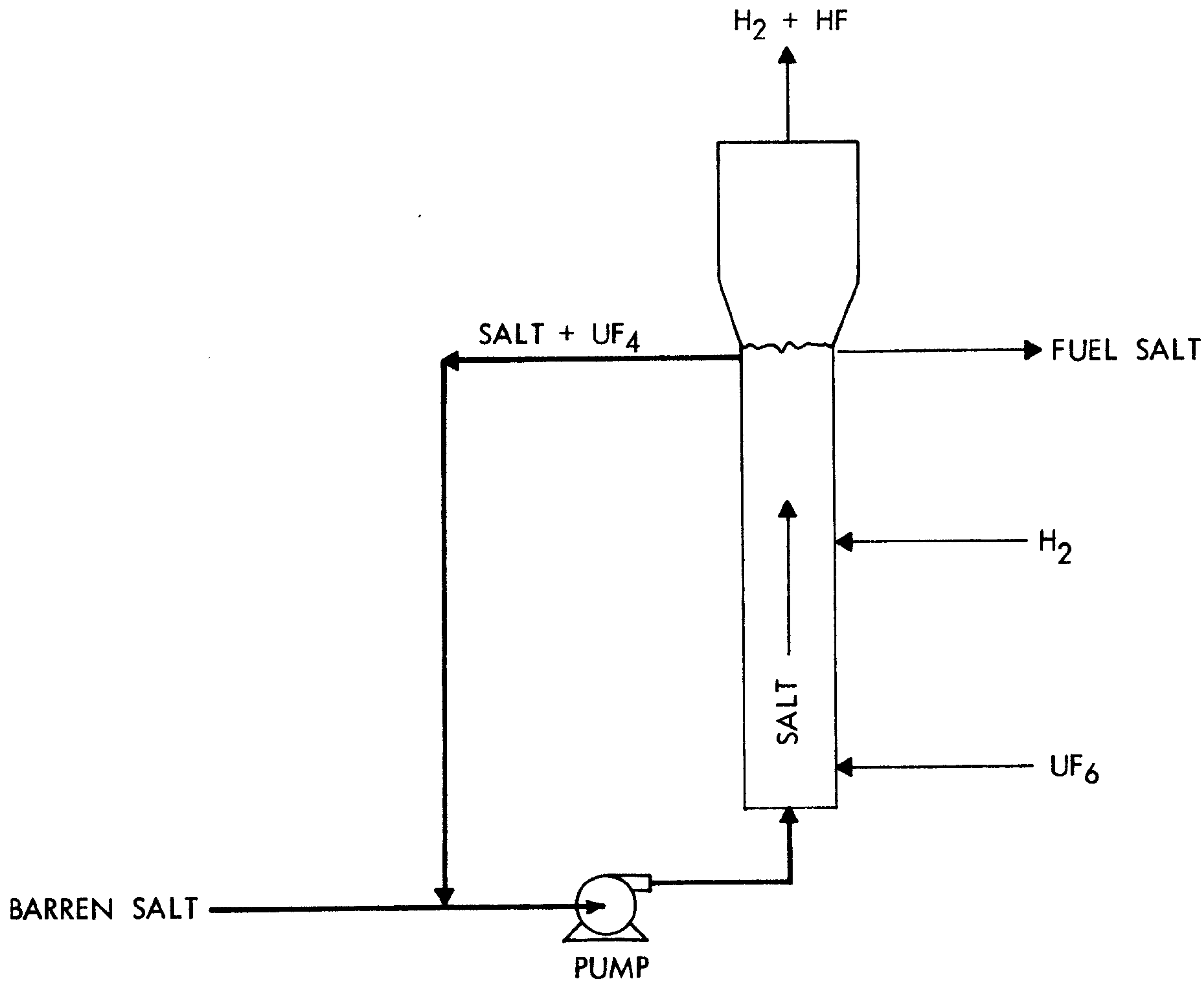

Fig. 2. Continuous Reduction of UF_6 by H_2 in a Molten Salt.

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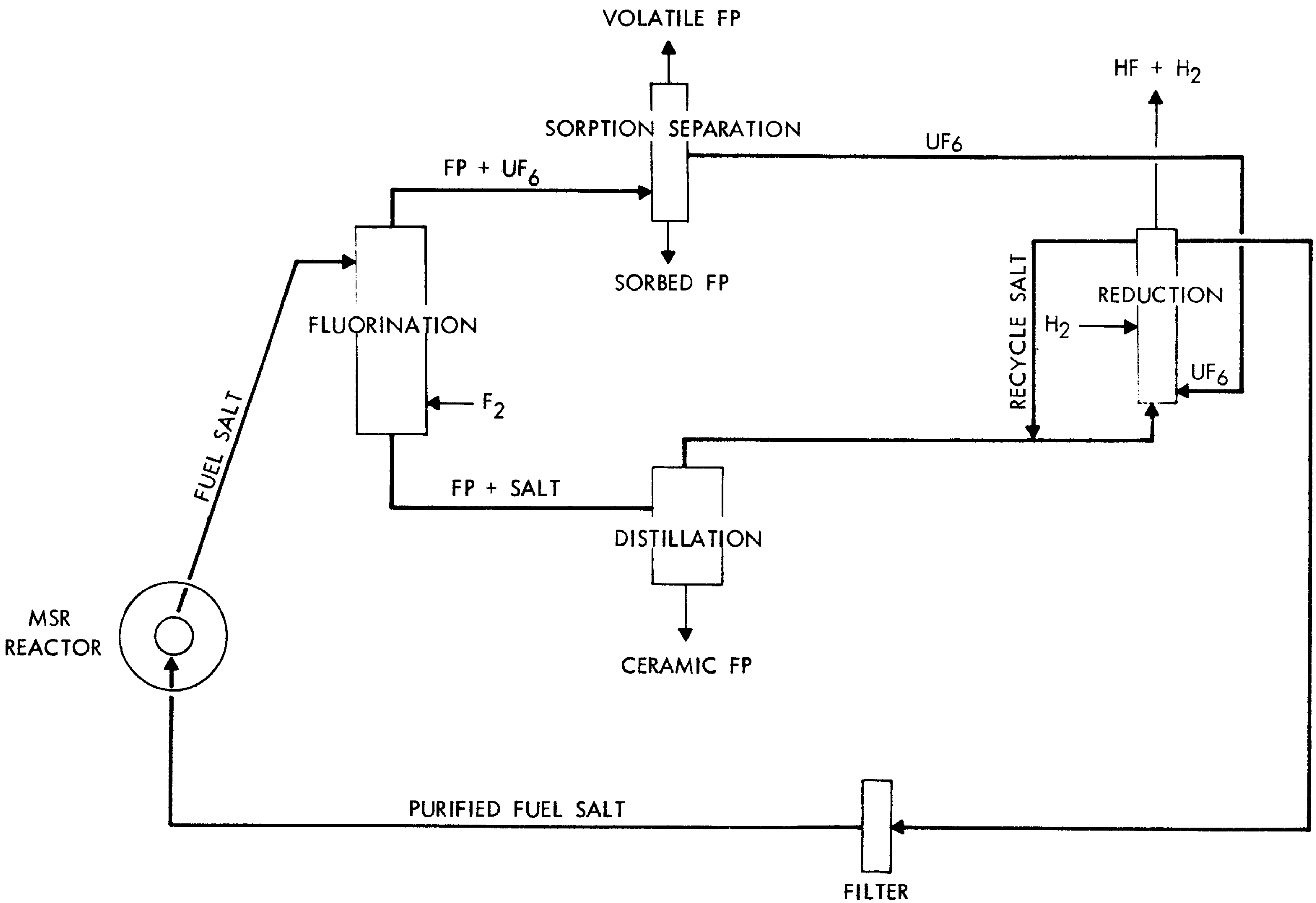

Fig. 3. MSR Fuel Processing with Continuous UF_6 Reduction in Molten Salt.

for contacting the resulting uranium fluoride with hydrogen in the second step. Details of the experimental equipment and of the procedure for testing the reduction process are discussed in the following sections.

EQUIPMENT AND MATERIALS

The reduction test was carried out in the vessel shown schematically in Fig. 4. The vessel was constructed from 4-in.-diam Sch 40 nickel pipe and was 26 inches in length. A 3/8-in. nickel inlet line was located in the center of the vessel and terminated 1/4-in. from the bottom of the vessel. A 3/4-in. fitting on the top flange allowed the insertion of a cold, 3/8-in. nickel rod which was used for sampling the salt. The vessel was heated by two nichrome wire resistance furnaces.

A flow diagram for the equipment used in the test is shown in Fig. 5. The equipment included a UF_6 metering system, a hydrogen metering system, means for purging both the UF_6 system and H_2 system with N_2, the reduction vessel, and a NaF trap downstream from the vessel for absorbing UF_6 or HF from the off-gas of the reduction vessel.

The salt charge was prepared by mixing LiF, ZrF_4 and UF_4. The LiF was reagent grade and contained < 0.23 wt % impurities (mostly NaF). The zirconium content of the ZrF_4 was found by analysis to be 54.78% which compares favorably with the stoichiometrical value of 54.6%; the uranium content of the UF_4 was found to be 76.9% which also compares favorably with the stoichiometrical value of 75.8%; and the uranium hexafluoride contained less than 200 ppm impurities. Hydrogen that was used contained less than 0.005 vol fraction impurities.

EXPERIMENTAL PROCEDURE

A salt charge consisting of 5320 g ZrF_4, 863 g LiF, and 61.8 g UF_4 (0.197 gmole UF_4) was placed in the reduction vessel and heated to 600°C. At this temperature the depth of molten salt was 12 inches. The salt mixture had a UF_4 concentration of 1 wt % and a melting point of approximately 510°C. A salt sample (UR-1) was taken by insertion of a cold 3/8-in.-diam nickel rod into the molten salt. A UF_6 flow of 1.5 g/min was then fed through the by-pass around the reduction vessel for 16

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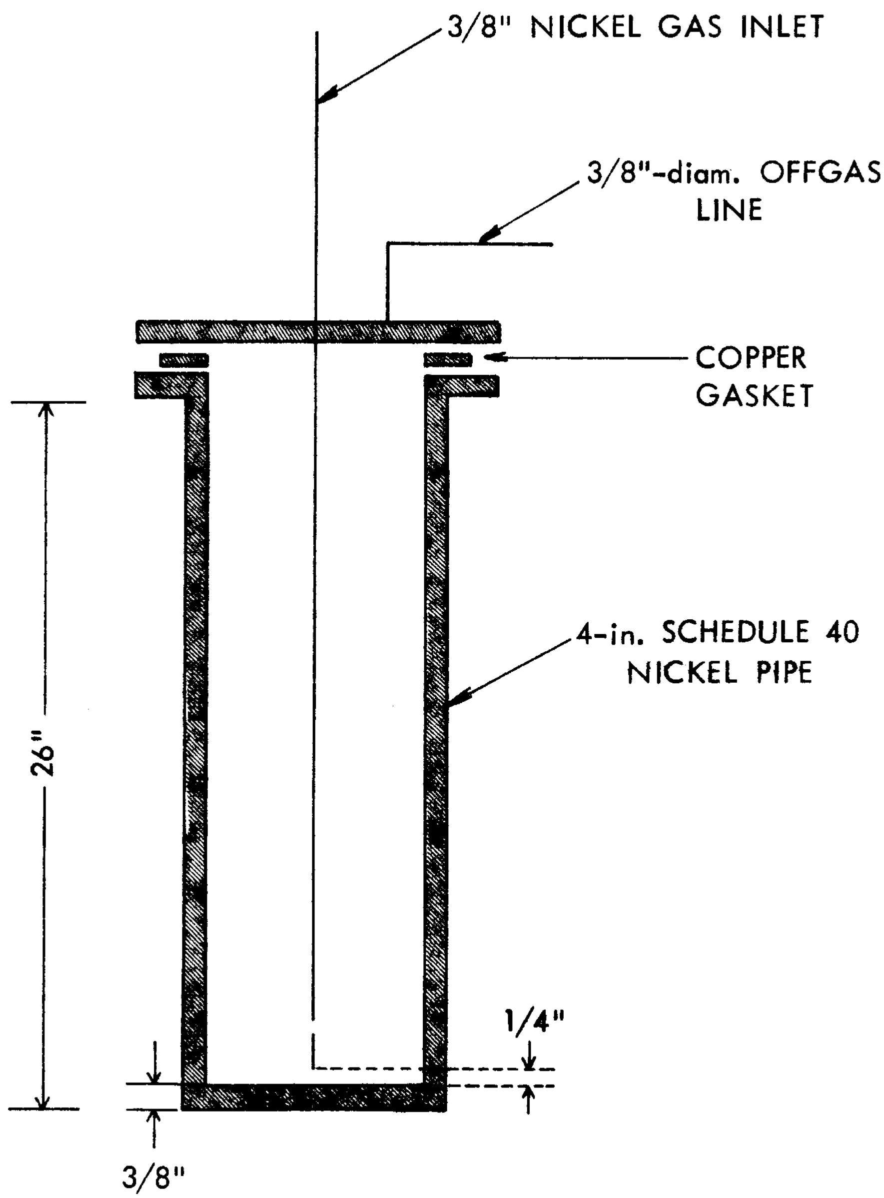

Fig. 4. Vessel Used for Reduction of UF_6 to UF_4 in a Molten Salt.

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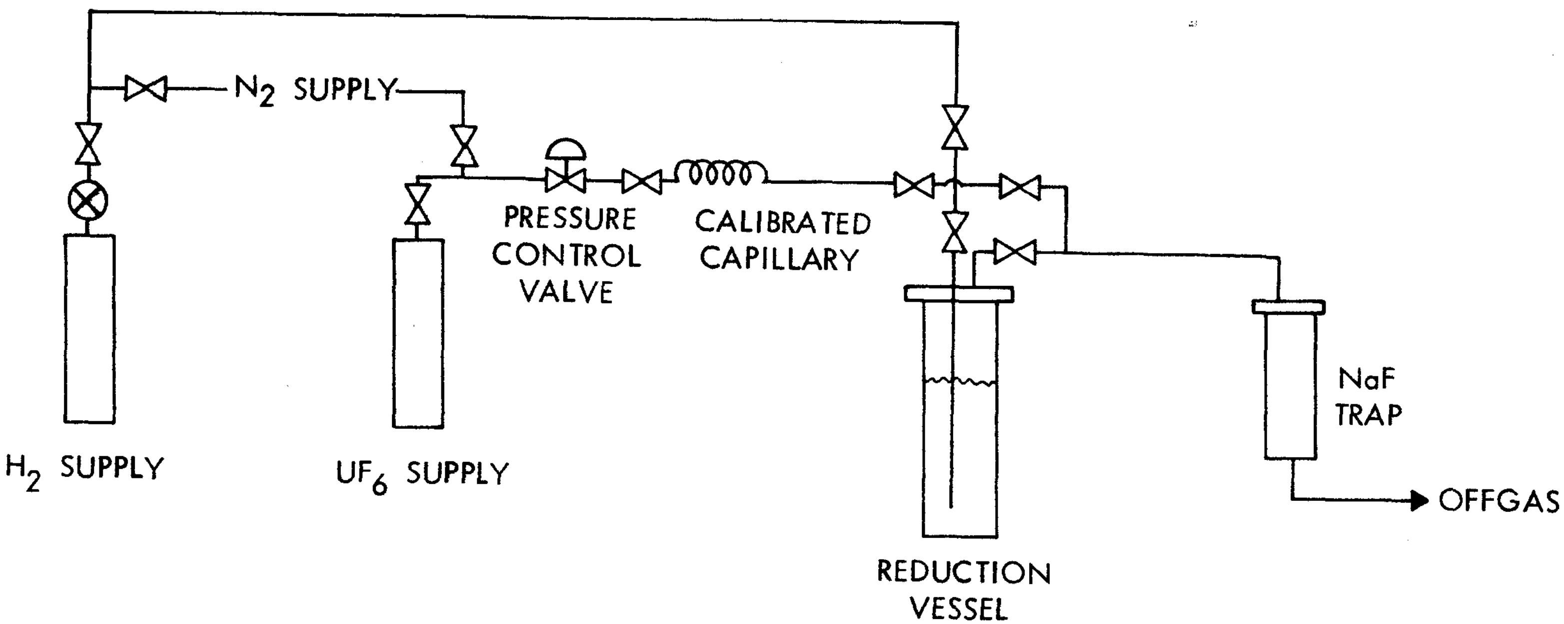

Fig. 5. Flow Diagram for Equipment Used in Reduction of UF_6 to UF_4 in a Molten Salt.

minutes in order to free the system of N_2. The UF_6 flow was then diverted into the dip line of the reduction vessel and was continued for 25 minutes. At this time, the UF_6 flow was stopped and the system was purged with N_2 for 5 minutes after which a salt sample (UR-2) was taken. The quantity of UF_6 fed to the system during this step was 38.2 g (0.108 gmoles). The salt was then purged with H_2 at the rate of 95 st. cm^3/min for 25 minutes. A total of 0.107 gmoles H_2 was added during this step. After the system was purged with N_2 for 10 min, a salt sample (UR-3) was taken. The system was then allowed to cool down overnight. The following day the system was heated to 600°C and a salt sample was taken (UR-4). The salt was then sparged with H_2 at a rate of 85 st. cm^3/min for 20 min during which a total of 0.076 gmoles H_2 was fed to the system. The system was then purged with N_2 for 10 min and a salt sample (UR-5) was taken. The system was then cooled and the test concluded.

DISCUSSION OF EXPERIMENTAL RESULTS

Two questions related to the experimental work are of primary interest. These are (1) the fraction of UF_6 which was absorbed by the molten salt and (2) the valence of the uranium in the resulting mixture. Also, of interest are the concentration level of trace impurities such as Ni and O_2.

The composition of the various salt samples is given in Table 1. The uranium concentration in the initial salt (UR-1) was found by analysis to be 0.666 wt % which is 11.2% lower than the calculated uranium concentration of 0.75 wt %. The calculated uranium concentration for complete absorption of the UF_6 bubbled through the salt during the 25 min addition period was 1.15 wt %. The average uranium concentration after the UF_6 addition was found by analysis to be 1.07 wt % which is 7% lower than the calculated value. It was concluded that, within the accuracy of the experimental data, complete absorption of the UF_6 had occurred.

It is believed that the addition of UF_6 to a salt containing UF_4 results in the formation of dissolved fluorides of uranium with a valence intermediate between +4 and +6. This behavior is indicated by

Table 1. Composition of Salt Samples Taken During Uranium Reduction Experiment

Sample	U wt %	U^{+4} wt %	U^{+6} wt %	Zr wt %	Li wt %	Ni ppm	O_2 ppm	Remarks
UR-1	0.666			46.65	3.64	874	4045	Initial salt melt
UR-2	1.05	.954	< .01			933	4695	After UF_6 addition
UR-3	1.01	1.074	< .01			1002	4940	After 1st H_2 addition
UR-4	1.07	0.990	< .01			1007	3060	After cooling overnight and remelting
UR-5	1.14	0.922	< .01			862	3245	After 2nd H_2 sparge

the fact that quantities of F_2 sufficient for the formation of UF_5 can be absorbed by molten salt containing UF_4 without the evolution of UF_6. A similar behavior is also noted in reactions between UF_4 and UF_6 in the absence of molten salt to yield intermediate fluorides such as U_4F_{17}. It is assumed that uranium present in a molten salt as an intermediate fluoride will appear as U^{+4} and U^{+6} after dissolution in phosphoric acid in preparation for analysis.[7]

The concentration of U^{+6} in the sample after UF_6 addition was below the limit of detection of 0.01 wt % and the U^{+4} concentration was 0.95 wt % (Table 1). After the first and second hydrogen sparges, the U^{+4} concentration was found to be 1.07 wt % and 0.922 wt %, respectively. Although differences in U^{+4} concentration were observed, it is felt that these are within the limits of analytical error and are not meaningful. Reduction of the U^{+6} to U^{+4} probably occurred during the addition of UF_6 by reaction of the intermediate fluoride with nickel from the vessel wall or with reduced fluorides of nickel, chromium, or iron initially present in the salt. The nickel concentration increased from 874 ppm initially to approximately 1000 ppm during the UF_6 addition and the initial hydrogen treatment. This increase in Ni concentration of approximately 130 ppm is sufficient for the reduction of approximately 15% of the UF_6 added. The concentration of oxide in the salt during the test was approximately 4000 ppm.

In the absence of conclusive information on the reduction of uranium fluorides intermediate between UF_4 and UF_6, reference can be made to data on materials having similar characteristics. The equilibrium between UF_4 and UF_3 in molten mixtures of LiF and BeF_2 has been studied by Long[5] by observing the concentration of HF in H_2 in equilibrium with the salt. Equilibrium was observed to have been established during the rise of H_2 bubbles through a few inches of molten salt. The data indicated that reduction of UF_4 to UF_3 could be achieved over a wide range of operating conditions.

The reduction of NiF_2, CrF_2, FeF_2 to the metals by hydrogen is utilized for removal of these contaminants from molten salt. It was also observed that molten salts containing uranium fluoride with a valence > 5 are quite corrosive toward nickel metal.[4] Since the reactions:

$$2UF_5 + Ni \longrightarrow 2UF_4 + NiF_2$$

$$NiF_2 + H_2 \longrightarrow Ni + 2HF$$

are known to occur in molten salts, it is felt that the reaction:

$$UF_5 + 1/2H_2 \longrightarrow UF_4 + HF$$

will also occur.

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions have been made on the basis of the material presented in the preceding sections.

1. Uranium hexafluoride is absorbed rapidly by molten fluoride salt containing approx. 1 wt % UF_4 at 600°C. It is believed that the absorption results in the formation of an intermediate fluoride of uranium.
2. It is likely that reduction of the intermediate fluoride to UF_4 can be accomplished by contact with hydrogen.
3. Incorporation of the proposed reduction step into the flowsheet for MSR processing results in a shorter and more direct process.

It is recommended that experimental work on the reduction of UF_6 to UF_4 in a molten salt environment be continued with emphasis in the following areas:

1. rate of reduction of intermediate uranium fluoride to UF_4 by hydrogen.
2. corrosivity of molten fluoride melts containing intermediate uranium fluorides.
3. adaptation of the reduction process to continuous operation.

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