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EXTRACTION OF URANIUM, MAGNESIUM, ZIRCONIUM, AND CERIUM FROM BISMUTH WITH A FUSED FLUORIDE SALT MIXTURE

by

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ABSTRACT

The extraction of uranium, magnesium, cerium, zirconium, and niobium from bismuth with a molten mixture of sodium fluoride and zirconium fluoride has been demonstrated. Comparative rates of extraction have been obtained. The effects of high concentrations of magnesium and of hydrogen fluoride sparging on the extraction process have been investigated. Tracer studies have demonstrated that exchange occurs between zirconium dissolved in the bismuth and zirconium in the fused salt.

The applicability of the fused fluoride extraction step to the processing of the "Liquid Metal Fuel Reactor" solution fuel is discussed.

INTRODUCTION

Development work on fused salt volatility processes for enriched reactor fuels has been in progress for several years at Oak Ridge National Laboratory[1] and at Argonne National Laboratory.[2] Consideration has been given to applying the Fluoride Volatility Process to the solution fuel, uranium dissolved in liquid bismuth, for the Liquid Metal Fuel Reactor.[3] The Fused Fluoride-Volatility Process for the LMFR fuel[4] is one in which uranium and some of the fission products are extracted from bismuth with a

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[1] Cathers, G. I., Carr, W. H., Lindauer, R. B., Milford, R. P., Whatley, M. E., The Recovery of Uranium from Highly Irradiated Reactor Fuel by a Fused Salt Volatility Process, Proceedings of 1958 International Conference on Peaceful Uses of Atomic Energy, Geneva, A/Conf. 15/P/535.

[2] Steunenberg, R., Fischer, J., Vogler, S., Steindler, M. J., Goring, G., Adams, M., Vogel, R. C., Rodger, W. A., Mecham, W. J., and Seefeldt, W. B., Recent Developments in Fluoride Volatility Processing of Reactor Fuels, Proceedings of 1958 International Conference on Peaceful Uses of Atomic Energy, Geneva, A/Conf. 15/P/539.

[3] Liquid Metal Fuel Reactor Technical Feasibility Report, BAW-2, June, 1955.

[4] Chemical Engineering Division Summary Report, ANL-5820, p. 35, February, 1958.

fused mixture of sodium fluoride and zirconium fluoride saturated with hydrogen fluoride. The salt is then sparged with fluorine and uranium is separated from the fission products and recovered by distillation as uranium hexafluoride. The pure uranium hexafluoride can than be reduced to uranium and returned to solution in the bismuth for further use in the reactor. An outline of this process is shown in Figure 1.

The primary purpose of the laboratory work covered in this report was to determine to what extent magnesium, cerium, uranium, and zirconium could be extracted from bismuth using a molten mixture of sodium fluoride and zirconium fluoride. Comparative rates of extraction, as well as the effects of hydrogen fluoride as an oxidant and magnesium as a reductant were studied.

EXPERIMENTAL

Materials - Bismuth was obtained from the Cerro de Pasco Company. Spectrographic analysis revealed only traces of materials other than bismuth. Before it was used this material was treated to remove surface oxides, inclusions and dissolved gases as follows: Bismuth, 250 grams, was broken from the ingots and melted in vacuum with about 0.25 grams of magnesium in a 28-mm OD Pyrex tube. The molten metal was held at 470 C, with periodic shaking, until evolution of gas had ceased. This required three to four hours. When the ingot was cool the surface film was removed by grinding.

A fused and ground mixture of sodium fluoride and zirconium fluoride was obtained from the Kawecki Chemical Company. A sufficient amount was obtained to allow all the work to be done using the same lot. The mixture was analyzed for sodium, zirconium, fluorine, and oxygen. Results of these analyses are given in Table 1.

Table 1

ANALYSIS OF SODIUM FLUORIDE-ZIRCONIUM FLUORIDE

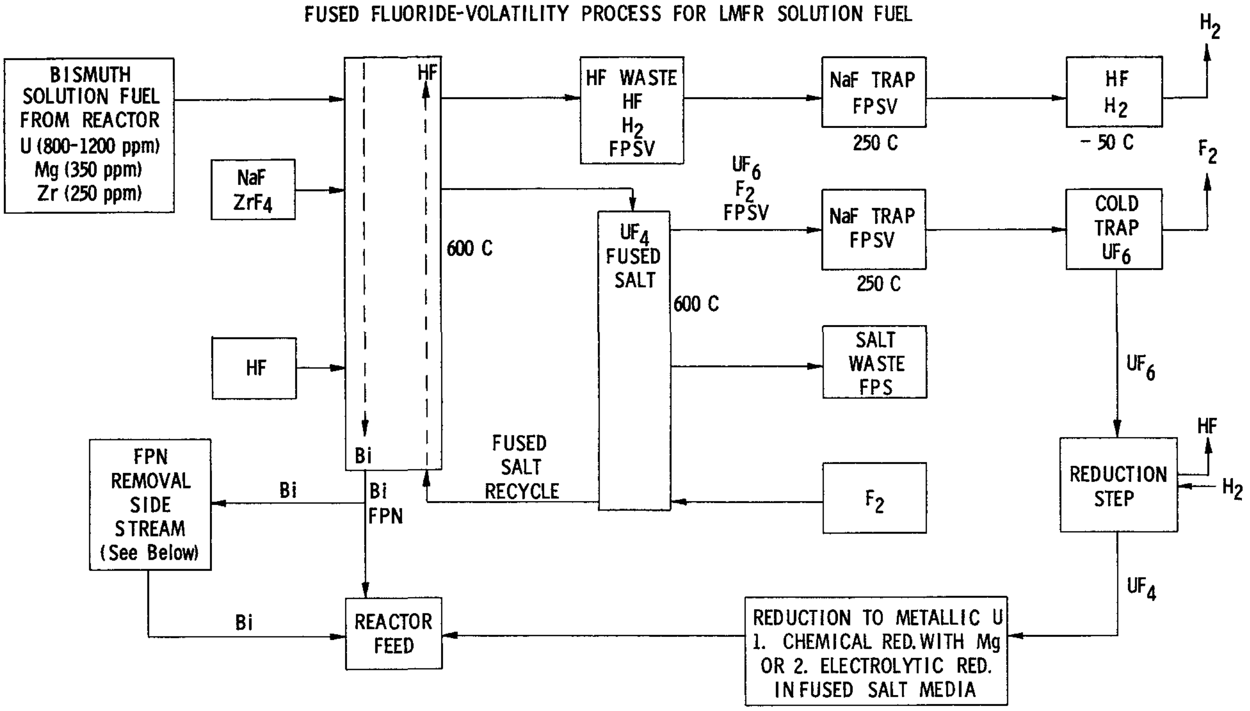
Constituent	Weight Per Cent
Sodium	13.2
Zirconium	41.3
Fluorine	45.3
Oxygen	0.02
	Weight Per Cent Calculated
Sodium Fluoride	24.0
Zirconium Fluoride	75.7
Total Salts	99.7
	Mole Per Cent Calculated
Sodium Fluoride	55.6
Zirconium Fluoride	44.4

Zirconium and cerium were irradiated in CP-5 for use in tracer experiments. Zirconium was free of hafnium, and the cerium was 99 per cent pure containing traces of other rare earths.

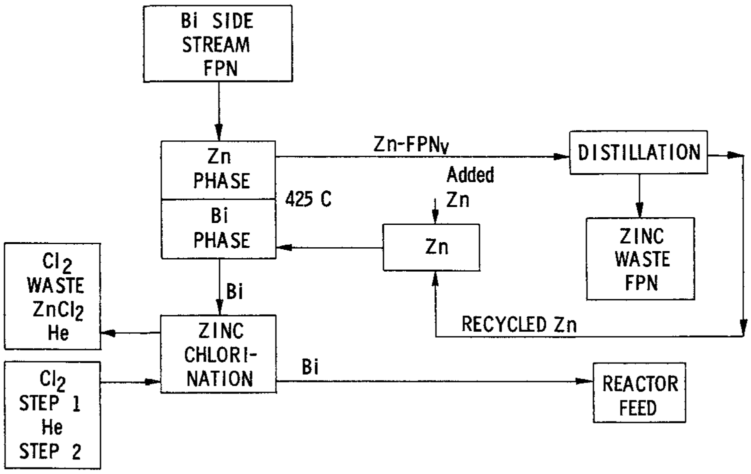
Argon and helium were used where inert atmospheres were required. Trace amounts of water were removed from the gases by passing them over Linde Molecular Sieves. By this method the water content was held to 10 ppm or less.

FIGURE 1

FUSED FLUORIDE-VOLATILITY PROCESS FOR LMFR SOLUTION FUEL



FPN REMOVAL SIDE STREAM



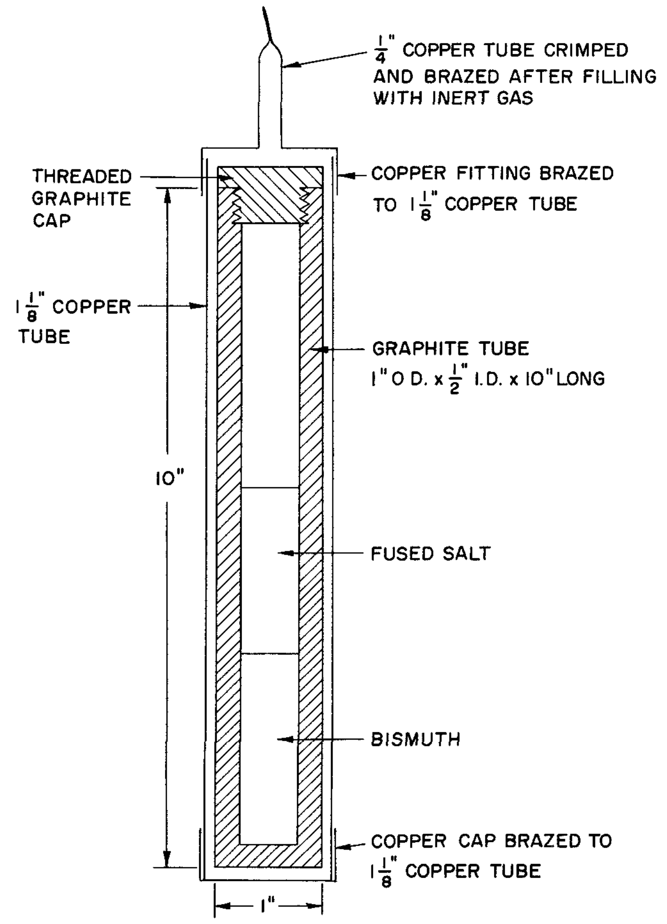
FPS = Non-Volatile Fission Product Fluorides Extracted by the Fused Salt.
FPSV = Volatile Fission Product Fluorides
FPN = Noble Fission Products - Not Extracted by the Fused Salt[a]

[a] FPN removal under investigation at American Smelting and Refining, under B.N.L. Subcontract

Equipment and Procedures - Several experiments were carried out in a rocking furnace assembly designed for small scale extraction studies. Six ceramic furnace tubes were set horizontally in a firebrick matrix. The tubes were wound with asbestos insulated nichrome wire. By spacing the windings closer together at the end of the tubes than at the middle a fairly uniform temperature over the length of the tube was obtained. Three thermocouples were attached to each furnace tube for control and recording purposes.

The firebricks surrounding the ceramic furnace tubes were covered with glass wool and aluminum foil. The assembly was placed in a transite box and mounted on a long axle. By means of a long lever arm, attached to a motor through a gear reduction system, the unit was rocked through an arc of about 40 degrees at one cycle per minute.

FIGURE 2
GRAPHITE CAPSULE FOR EXTRACTION EXPERIMENTS IN ROCKING FURNACE



Graphite tubes, 0.5 inch ID x one inch OD x ten inches long provided with a threaded plug on one end, were used as sample containers. Each tube was degassed at about 1400 C with continuous evacuation. Fifty grams of bismuth and 15 grams of salt were used in each experiment. These proportions provided approximately five liquid cc each of bismuth and salt since the density of bismuth is ten and that of the salt is about three. After loading, the graphite capsules were placed in $1\frac{1}{8}$ inch copper pipe. A copper cap was brazed over one end and a 1/4-inch copper tube was brazed on the other end. By means of this tube the vessel was first evacuated and then filled with argon. The 1/4-inch tube was then crimped, cut off and brazed over the crimp. A diagram of the unit is shown in Figure 2.

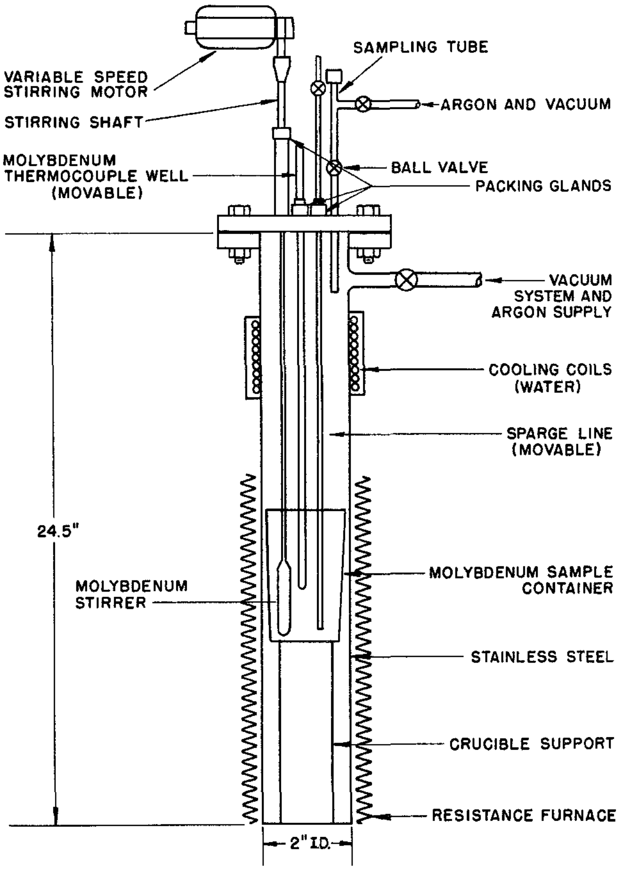


FIGURE 3
APPARATUS FOR STIRRING, SPARGING AND SAMPLING DURING EXTRACTION EXPERIMENTS

The apparatus used for the stirring-sparge tests is shown schematically in Figure 3. It consisted of a cylindrical vessel two inches in diameter and 24.5 inches long. It was heated by external resistance furnaces. The molybdenum crucible was supported by a graphite block to provide proper positioning within the hot zone. The vessel could be evacuated to less than one micron or pressurized with inert gas. A stirrer powered by a variable speed motor, a thermocouple well and a 1/4-inch tube for hydrogen fluoride gas sparging were all made of molybdenum. The sparge tube, stirrer, and thermocouple tube could be moved up or down through "Chemlon" packing glands for proper positioning and to permit their removal from the melt before the melt was frozen on completion of the experiment.

Corrosion experiments showed that molybdenum was compatible with both liquid bismuth and the fused fluoride salt in the presence of hydrogen fluoride at the operating temperatures. No visible corrosion of the molybdenum parts occurred during any of the extraction experiments.

Samples of the liquid bismuth were obtained with four mm quartz tubes. A tube was inserted through a rubber serum cap and through the ball valve into the melt. Proper manipulation of the vacuum and argon valves prevented the admission of air to the vessel. Samples of 10 to 20 grams of bismuth were drawn into the tube by means of a syringe connected with rubber tubing. The tube was then quickly raised to the cooled portion of the vessel to freeze the sample before it was removed through the valve and serum cap. The bismuth pin was then freed from the quartz tube and submitted for analysis.

In a typical experiment, after an alloy was prepared, sampled and cooled, the top flange of the apparatus was removed and the fluoride salt mixture was added to the crucible. The system was then alternately evacuated and filled with argon three times. The unit was heated during the final evacuation to a pressure of one micron. When the temperature reached about 450 C, argon was admitted to a pressure of 800 mm. At 550 C a sample of the bismuth was taken.

Immediately after this sample was taken, stirring (at 220 rpm) and sparging with hydrogen fluoride were started. Samples of the bismuth were taken at intervals during the experiment. At the end of the experiment a sample of the cold salt was taken. Liquid samples of the salt could be taken, but samples were too small for accurate analyses.

Preparation of Synthetic Fuel Solutions or Alloys - Bismuth solutions were prepared by one of two techniques depending on the type of experiment being carried out.

Samples used in the rocking furnace experiments were obtained from alloy ingots weighing about 250 grams which were prepared in Vycor tubes, in the following manner. About 0.5 grams of magnesium were placed in a small magnesium oxide crucible in a Vycor tube 30 mm OD and about 15 inches long. A vacuum connection was made to the open end of the tube with a large rubber tubing and a valve attached to a vacuum manifold. When evacuated, the tube was slowly lowered into a vertically mounted tube furnace at about 600 C. The magnesium evaporated and was condensed on the cooler walls of the tube above the furnace. As the tube was lowered some of the magnesium reacted with the Vycor to form a brown coating on the walls.

The cooled Vycor tube with the valve attached and still under vacuum, was transferred to a helium-filled dry box. In the dry box the rubber tubing was removed from the Vycor tube. The magnesium oxide crucible was removed and replaced in the previously prepared bismuth ingot, another small piece of magnesium and a weighed amount of uranium, zirconium, cerium, or a combination of these.

The vacuum connection was then replaced. The unit was removed from the dry box, attached to the vacuum system and again evacuated. It was placed in the tube furnace while the temperature was maintained at 600 C for several hours. About eighteen hours were required to dissolve the zirconium, which had the lowest dissolution rate.

After heating, the tube was removed from the furnace, it was shaken vigorously for about 30 seconds and quenched in water. The Vycor tube could then be broken away from the metal quite easily. The brown coating on the walls of the tube was apparently not attacked by the liquid metal.

The ingot was cut in half along the long axis and examined for homogeneity by autoradiography.

Alloys used in the stirring apparatus were prepared in the extraction equipment as they were required. Four hundred grams of the pre-melted bismuth and about 0.8 grams of clean magnesium were melted in a molybdenum cup under vacuum. The system was pressurized with argon to 800 mm at 450 C after which it was stirred continuously while the temperature was raised to 550 C. Uranium and other alloying materials were added by dropping the weighed pieces through a section of four mm quartz tubing which was passed through the ball valve and held just above the surface of the melt. Stirring of the bismuth was continued for about three hours before sampling, after which the furnace was cooled. Longer times were required to dissolve zirconium. The bismuth was then allowed to solidify in the argon atmosphere.

The mixture of sodium fluoride and zirconium fluoride was added to the bismuth and the extraction experiment was then run in the same molybdenum crucible and apparatus.

Autoradiography - Once the alloys to be used in the rocking furnace test had been prepared, an analytical technique was needed which would reveal their homogeneity. The samples taken for routine analyses from several locations in the alloy ingot did not give a complete answer. Counting at various locations with a partially shielded geiger tube was not much better. Autoradiography of the ingots provided a simple and effective method for a non-destructuve examination of each ingot.

Each ingot, prepared by the quartz tube method described previously, was cut in half through the long axis of the cylinder. One half was ground flat by filing and polishing by hand on emery paper. The ingot was placed in contact with a 5 x 7 inch sheet of Eastman Kodak Type KK X-ray film in a light-tight cardboard or wooden box. A photographic changing bag was used for all manipulations of the film.

Adequate autoradiographs could be obtained of most samples with exposures of 30 minutes to four hours. Natural uranium was the exception, requiring four to ten days when the concentration of uranium in bismuth was about 1000 ppm.

Processing of the film was carried out in a "daylight" developing tank. Kodak Liquid X-ray film developer and fixer were used. It was found especially important to keep the temperature near 20 C to avoid fogging the film.

When the elements added to the bismuth were present in low concentrations and when sufficient magnesium had been used, the alloys were generally homogeneous except for spots of higher activity on the outer surface. When the additives were present in higher concentrations, particularly in the case of cerium, the activity was found in the form of small discrete particles spread uniformaly throughout the bismuth. The alignment of these particles in the bismuth indicated that various zones were produced as the bismuth expanded on cooling. If the bismuth were not agitated before quenching the activity tended to rise to the top portion of the ingot.

The analytical procedures are described in the appendix.

RESULTS AND DISCUSSION

Magnesium Extraction - Magnesium may be added to the LMFR bismuth solutions in higher concentrations than any other constituent except uranium. The proposed concentration has varied from 350 ppm to 2000 ppm. Its function is to act as an antioxidant to prevent depletion of uranium in the LMFR fuel through reaction with accidental contaminants such as oxygen.

Since magnesium is the most active material present it would be expected that it would be oxidized and extracted first. Therefore, magnesium will have to be removed before some of the less active metals can be oxidized. Any magnesium remaining as the metal would tend to react with fluorides of less active metals, reducing them and keeping them in the bismuth solution.

Extraction of magnesium was demonstrated to be fast. In the time required to melt the salt and take the first sample the concentration had decreased by almost a factor of ten in one experiment. In another fifteen minutes extraction was complete. The data are shown in Table 2.

Two experiments were carried out to determine whether magnesium could reduce uranium tetrafluoride under the conditions of these experiments. Bismuth containing over 2000 ppm of magnesium was contacted with fused salt containing small amounts of uranium tetrafluoride in the rocking furnace. There was no reduction of the uranium tetrafluoride.

Uranium Extraction - The proposed uranium concentration in an LMFR solution fuel was in the range of 800 to 1300 ppm in bismuth. The bismuth solutions prepared for these experiments have contained 900 to 1500 ppm uranium.

For preliminary experiments a bismuth-uranium alloy was prepared which contained no magnesium or other additive or fission product metals. This alloy was heated with a fluoride salt mixture in a static system. The fluoride salt had been premelted and degassed. Uranium concentration in the bismuth was reduced from 1000 ppm to 3 ppm in one hour.

When relatively high concentrations of magnesium are present an oxidizing agent is required for complete extraction. Uranium can be extracted using sodium fluoride-zirconium fluoride mixtures in 15 to 30 minutes

Table 2

STIRRING EXTRACTION EXPERIMENTS WITH FUSED FLUORIDE SALT

Temperature: 550 C

Weight Bismuth g	Weight Salt g	Sample Stirring and Sparging Time, (minutes)	U ppm[a]	Mg ppm
500	45	Original	1425	2400
		Contact	950	
		15	235	
500	45	Original	1325	2820
		Contact	365	
		30	129	
		170	119	
		230	122	
400	72	Original	1310	2600
		Contact	1300	
		15	175	
		75	71	
		135	73	
		195	75	
400	90	Original	1340	2390
		Contact	16	
	HF sparge[f]	15	8	
		30	-[b]	
	in	45	-	
		105	-	
	metal	salt	3700	
400	90	Original	1400	1960
		Contact	1480	265
	HF sparge	15	-	15[c]
	in	30	-	15
	metal	90	-	15
400	90	Original	1530	ca 2500
		Contact	1045	
		5	176	
	HF sparge	15	47	
	in	30	38	
		90	-	
	salt	salt	4900	
400	90	Original	1520	2300[d]
	HF sparge	Contact	925	570
		5	85	25[e]
	in	10	57	25
	salt	15	17	25
		30	14	25
400	90	Original	1345	ca 2500
	HF sparge	Contact	685	
		5	57	
	in	10	104	
	metal	15	26	
		30	-	

Notes: [a] Corrected for 15 ppm blank uranium value
[b] Below blank value
[c] Below limit of detection
[d] Analyses done at Alliance Research Center of the Babcock and Wilcox Company
[e] Limit of detection for spectrographic standards in use
[f] HF sparge rate for all tests ~0.5 grams per minute

if the system is sparged with hydrogen fluoride. If hydrogen fluoride is not used the uranium concentration can be decreased to a final value of about 100 ppm in approximately thirty minutes.

Hydrogen fluoride is not the only oxidizing agent that can be used. In a series of experiments done in the rocking furnace, bismuth trifluoride was shown to enhance the extraction of uranium in the presence of magnesium. The addition of a stoichiometric amount of bismuth trifluoride to the salt mixture resulted in complete extraction of the uranium in two hours at 600 C. The data from these experiments are shown in Table 3.

Table 3

EXTRACTION OF URANIUM FROM BISMUTH USING BISMUTH TRIFLUORIDE AS AN OXIDANT

50 gram portions of the same master alloy were rocked with 15 grams NaF-ZrF_4 at 600 C. The quantity of BiF_3 added was just sufficient to react with all the magnesium, uranium, and zirconium present.

Initial Uranium Concentration (ppm)	935
Initial Magnesium Concentration (ppm)	2700
Bismuth trifluoride used (grams)	0.869

Time of Extraction (minutes)	U Remaining in Bismuth after Extraction (ppm)
15	41
30	34
60	21
120	None detected

The stirring and sparging equipment provided a better method for obtaining information on extraction behavior. A summary of the experiments is given in Table 2.

The method by which hydrogen fluoride was introduced was shown to affect the rate of removal. When the gas was passed through the metal and salt phases, extraction was more rapid than when it was passed through the salt phase alone.

In this particular equipment, which was not designed for highly efficient use of the hydrogen fluoride, less than eight times the stoichiometric weight of hydrogen fluoride was sufficient to remove all of the oxidizable metals.

Zirconium Extraction - Zirconium, like magnesium is a constituent of the fuel. While magnesium acts as an antioxidant for the uranium, zirconium is required as a corrosion inhibitor. At present a concentration of zirconium of about 200 ppm seems to be sufficient. In addition to that added, zirconium is produced in the reaction in significant amounts due to its relatively high fission yield.

Alloys were made up containing 300 to 800 ppm of irradiated zirconium in bismuth and extracted with salt either in the rocking furnace or the stirring equipment. It was possible to get some information about extraction of niobium from these experiments also due to the decay of 65-day Zr-95 to 35-day Nb-95; however, the niobium was present in very low unknown concentrations.

A separation of zirconium and niobium could be done on bismuth samples and each could be determined by radiochemical methods. Niobium came to an equilibrium distribution after a short time. An extraction factor* of 2.2 was attained in five minutes and did not change through the rest of a 30-minute extraction in which hydrogen fluoride was used continuously. This may not be significant in view of the extremely small quantity of niobium which was present.

The removal of fission product zirconium and additive zirconium is essentially a multiple reaction involving isotopic exchange, reduction of zirconium tetrafluoride and oxidation of zirconium. Table 4 shows the summation of data for zirconium extraction.

Rapid isotopic exchange of zirconium occurs between the zirconium in the bismuth and the large reservoir of zirconium in the fused salt as shown by the decrease in the zirconium activity of the metal. The ratio of zirconium γ activity to zirconium concentration in the metal phase remains constant after five minutes of sparging with hydrogen fluoride.

An initial redox reaction occurs between zirconium tetrafluoride in the fused salt and uranium and magnesium. Approximately 60% of the stoichiometric quantity of zirconium is transferred to the bismuth as uranium

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$$\text{*Extraction factor} = \frac{\text{total gamma counts in metal phase minus zirconium gamma counts in metal phase (before extraction)}}{\text{total gamma counts in metal phase minus zirconium gamma counts in metal phase (after extraction)}}$$

Table 4

RADIOCHEMICAL EXCHANGE OF ZIRCONIUM AND THE EXTRACTION OF ZIRCONIUM AND NIOBIUM WITH FUSED SODIUM FLUORIDE-ZIRCONIUM FLUORIDE AND HYDROGEN FLUORIDE

Temperature: 550 C
Bismuth: 400 g
Salt: 90 g

	Uranium ppm	Magnesium ppm[b]	A Zirconium ppm[b]	B Zirconium γ cpm/g of metal	B/A	Niobium γ cpm/g of metal
Original Alloy	1520	2300	245	5.8×10^4	2.4×10^2	4.2×10^4
Alloy after contact with salt	925	570	2300	4.0×10^4	1.7×10	2.2×10^4
Alloy after 5 min stirring and sparging with HF[a]	85	25[c]	2500	6.5×10^3	2.6	1.9×10^4
Alloy after 10 min stirring and sparging with HF	57	25	1800	4.2×10^3	2.3	1.9×10^4
Alloy after 15 min stirring and sparging with HF	17	25	1400	3.4×10^3	2.4	1.9×10^4
Alloy after 30 min stirring and sparging with HF	14	25	480	2.15×10^3	4.5[d]	1.9×10^4

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[a] HF sparge rate ~ 0.5 grams per minute

[b] Analyses done at Alliance Research Center of the Babcock and Wilcox Company.

[c] Limit of detection.

[d] High value probably due to counting error.

and magnesium are oxidized and extracted by the salt before hydrogen fluoride sparging. The zirconium is then oxidized by hydrogen fluoride at a much slower rate than the uranium or magnesium. Relative rates of extraction of the three constituents are shown in Figure 4.

During the 30-minute experiment the zirconium was not completely removed from the bismuth, but since it is an original constituent of the LMFR fuel it would be advantageous to leave about 250 ppm in the bismuth to facilitates fuel reconstitution.

Cerium - Cerium was used as a representative of the rare earth fission products. These represent the most important group of fission products with respect to LMFR processing, though the actual concentrations should be low (less than 100 ppm total).

Removal of these elements should present no problem. Data for extractions carried out in the rocking furnace are presented in Table 5.

FIGURE 4
EXCHANGE OF ZIRCONIUM AND EXTRACTION OF URANIUM AND MAGNESIUM IN BISMUTH AND SODIUM-ZIRCONIUM FLUORIDE SALT

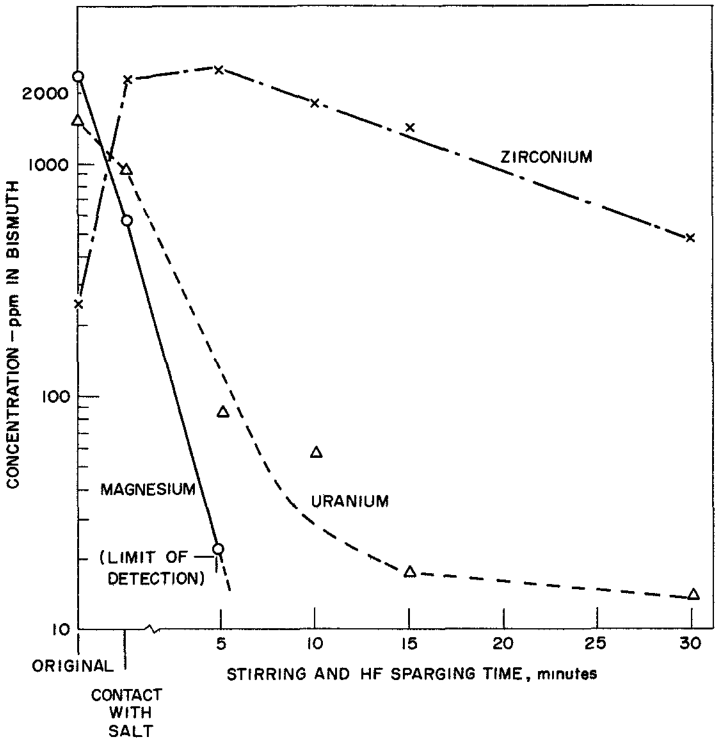

Table 5

EXTRACTION OF CERIUM WITH SODIUM FLUORIDE-ZIRCONIUM FLUORIDE

50 g bismuth alloy rocked at 600 C with 15 g salt mixture. No hydrogen fluoride was used.

Time of Contact Between Metal and Salt (minutes)	Activity of Original Alloy cpm/g of Metal	Activity of Bismuth After Extraction cpm/g of Metal	Extraction[a] Factor
5	2.5×10^3	84	30
5	5.1×10^3	102	31.5
30	2.5×10^3	3	840

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[a] Extraction Factor $= \dfrac{\text{Activity before extraction}}{\text{Activity after extraction}}$

The extraction is apparently complete in less than 30 minutes under these circumstances. Cerium can be extracted by the fused salt alone; however, with the use of hydrogen fluoride the extraction should be extremely rapid.

Economics of the Fluoride Volatility Process for the LMFR Solution Fuel - The fluoride process as originally conceived was shown in Figure 1. Fission products, uranium, magnesium, and zirconium were to be transferred from the bismuth into a fused fluoride-zirconium fluoride mixture by oxidation with hydrogen fluoride. The uranium could then be volatilized from the salt by further oxidation to the hexafluoride with fluorine. After purification of the uranium hexafluoride by distillation, it could be reduced to the metal and used to reconstitute the fuel solution.

Early qualitative economic considerations indicated that the highest cost factor in the operation of the fuel process might be the cost of the fused salt, which would be discarded. If the concentration of fission products in the discarded salt is high enough, the cost per kilowatt can be decreased accordingly. At a fission product concentration of 1.5 per cent in the salt, it can probably be discarded at reasonable cost. However, the practical reuse of the fused salt is hampered by the formation of magnesium fluoride.

Magnesium is a constituent of the fuel solution which will be transferred to the fused salt during processing. It will be present in the fuel in concentrations possibly as high as 2000 ppm. The magnesium concentration was increased in the fuel during the period this investigation was being carried out. Uranium will be the only material present in concentrations approaching this, but it can be removed periodically from the salt by intermittent conversion to uranium hexafluoride with fluorine. Magnesium fluoride, however, will continue to increase in concentration in the fused salt throughout the processing. If the salt were discharged to waste when it contained 1.5 per cent fission products, it would have the approximate molar composition: 86 per cent magnesium fluoride; 5.3 per cent sodium fluoride; and 8.2 per cent zirconium tetrafluoride, for the case in which the fuel contains 2000 ppm magnesium. If the fuel contained 350 ppm magnesium the final constitution of the salt would be: magnesium fluoride - 53.8 mole per cent; sodium fluoride - 18.2 mole per cent; zirconium tetrafluoride - 27.8 mole per cent.

As the fuel is processed, the salt would go from a binary sodium - zirconium tetrafluoride system to a quaternary system with magnesium fluoride increasing to become the major constituent. Uranium tetrafluoride would be the fourth constituent in that it might increase in concentration to five mole per cent just before fluorination, depending on the particular flowsheet used. The liquidus temperature could increase above that of 500 C for the starting system. The process could be made more attractive by removing magnesium from the fuel solution before the fused salt extraction or by removing magnesium fluoride from the salt phase.

APPENDIX A

ANALYTICAL PROCEDURES

All bismuth metal samples were dissolved by a procedure known as the Amalgam-Leach Dissolution. In this procedure, the metal sample is contacted with mercury and a dilute hydrochloric-hydrofluoric acid solution. The more active elements are leached out of the amalgam while more than 99 per cent of the bismuth remains in the mercury. Additional bismuth removal is achieved by the addition of metallic zinc. The resulting solution is sufficiently free of bismuth to permit the direct determination of all of the elements of interest except magnesium. To determine magnesium an additional separation is necessary to remove zirconium and uranium as well as the residual bismuth. When magnesium was the constituent being determined, fluoride was omitted from the leach solution.

The uranium content of the bismuth samples was determined polarographically by the standard addition technique[5] in sodium acetate-EDTA* solution. The accuracy of this method is ± 5 per cent and the lower limit of detection is approximately 20 ppm.

The magnesium was determined by an EDTA titration using Eriochrome Black T as an indicator. The bismuth, zirconium, and part of the uranium interferences were removed by extraction of their diethyl dithiocarbamate complexes into carbon tetrachloride. The accuracy of this determination is ± 1 per cent. The lower limit of detection is 15 ppm magnesium.

In metal samples containing activated zirconium the zirconium was determined by precipitating barium fluozirconate and gamma counting the precipitate in a well-type scintillation counter. The niobium activity of these samples was determined by taking a total gamma count and subtracting the counts due to zirconium. No radiochemical separations were made on samples of the fused salt containing activated zirconium.

The various procedures used in this work were checked in two ways. Uranium and magnesium procedures were tested on a standard alloy of bismuth and uranium, zirconium, and magnesium obtained from Brookhaven National Laboratory. The zirconium, niobium, and cerium techniques were checked by dissolving a portion of the samples by the amalgam-leach dissolution and another portion in nitric acid and comparing the counts. These results are summarized in Table 6.

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[5] I. J. Kolthoff and J. J. Lingane, Polarography, Vol. 1, Interscience, New York, 1952, p. 377.

*Ethylene Diamine Tetracetic Acid.

Table 6

RELIABILITY OF ANALYTICAL DETERMINATIONS

Element	Concentration, ppm		Activity, cpm/g	
	Known*	Found	Nitric	Amalgam-Leach
Uranium	828	815		
Magnesium	263	282		
Zirconium-Niobium			1.35×10^4	1.44×10^4
Cerium			5.25×10^4	5.42×10^4

*Brookhaven National Laboratory values - Uranium determined colorimetrically. Magnesium determined spectrographically.

The sodium-zirconium fluoride used was analyzed to determine the mole ratio of sodium fluoride to zirconium fluoride. The fluoride content was determined by pyrohydrolysis of the solid salt at 900 C. The evolved hydrogen fluoride was dissolved in water and titrated with standard base to a phenolphthalein end-point.

Sodium was determined on an aliquot of the dissolved sample by precipitation of sodium zinc uranyl acetate. The precipitate was ignited at 600 C and weighed as $Na_2U_2O_7 \cdot 2\ ZnU_2O_7$.

Zirconium was determined by precipitation of the cupferrate from sulfuric acid solution. The precipitate was ignited at 900 C and weighed as ZrO_2.

Oxygen was determined by the bromine trifluoride method.[6,7]

Amalgam-Leach Dissolution Procedure - To a one gram sample of bismuth alloy in a 50 ml beaker add about 10 ml of mercury and exactly 10.0 ml of the appropriate leach solution.* Stir with a magnetic stirrer for at least 20 minutes. The leach mixture should be stirred until all evidence of a solid metal phase has disappeared. This time will vary with the particle size of the sample. Add approximately 0.5 grams of metallic zinc and stir for five more minutes. Take an appropriate size aliquot of the leach solution for the determination of the element of interest.

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[6] Hoekstra, H. R., and Katz, J. J., Anal. Chem. 25, 1608 (1953).

[7] Sheft, I., Martin, A. F., and Katz, J. J., J. Am. Chem. Soc., 78, 1557 (1956).

*Use a leach solution of 4 M HCl for magnesium determinations, and 4 M HCl - 0.5 M HF leach solution for all others.

Sodium Fluoride-Zirconium Fluoride Salt Dissolution Procedure - Weigh accurately into a platinum dish approximately one gram of salt. Add 25 ml of concentrated hydrofluoric acid and digest on a sand bath for approximately 30 minutes. Add 20 ml 10 M sulfuric acid and evaporate until dense fumes appear. Cool, add 25 to 50 ml of water and heat on the sand bath until dissolution is complete.

Uranium Determination - Dissolve the sample according to the amalgam-leach procedure. Introduce an aliquot containing approximately 50 μg of uranium into a 50 ml beaker and evaporate to dryness. Dissolve the residue in 2 ml of 4 M sodium acetate and 2 ml of 0.2 M EDTA. Transfer to a 5 ml volumetric flask and dilute to the desired volume with water. After transferring the sample to the polarographic cell, deaerate with nitrogen. Record the height of the wave at -0.4 volts vs. the mercury pool. Add sufficient uranium standard solution to approximately double the wave height. Deaerate and record the height of the wave at -0.4 volts. Calculate the uranium concentration using the standard addition formula.[5]

Magnesium Determination - Dissolve the sample by the amalgam-leach dissolution procedure with 4 M hydrochloric acid. Do not add metallic zinc. Introduce an aliquot of the leach solution into a 25 ml separatory funnel. Neutralize with ammonium hydroxide until a faint cloudiness persists. Add concentrated hydrochloric acid until the cloudiness disappears. Add 100 mg solid sodium diethyl dithiocarbamate and extract with 10 ml of carbon tetrachloride. Repeat the addition of diethyl dithiocarbamate and extract until the addition of diethyl dithiocarbamate produces no more precipitate. Transfer the aqueous phase to a titration vessel, add approximately 50 mg of solid ammonium carbonate and 10 ml of buffer. Add two or three drops of Eriochrome Black T solution and titrate with standard EDTA.