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MASTER

PROCESS TECHNOLOGY FOR THE MOLTEN-SALT
REACTOR ^{233}U -Th CYCLE*

J. R. Hightower, Jr.

Oak Ridge National Laboratory
P. O. Box X
Oak Ridge, Tennessee 37830

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1. INTRODUCTION

Molten-salt reactor technology, under development at Oak Ridge National Laboratory since 1947, has led to a concept of a high-temperature, thermal-neutron breeder reactor that operates on the ²³³U-Th fuel cycle. An on-site processing plant that continuously removes protactinium and fission products from the fuel salt is required for the reactor to perform as a breeder. In this paper the following questions will be considered briefly: What are the design features of the molten-salt breeder reactor? What processes are currently proposed for removal of protactinium and fission products? How effectively will fuel and thorium resources be utilized with this reactor concept? What is the status of fuel processing technology? And what are the problems facing the future of fuel processing development?

In this paper the author is summarizing the work of many others at Oak Ridge National Laboratory. In particular, the synthesis and optimization of the present processing flowsheet ^{was} done under the direction of L. E. McNeese, the present director of the Molten-Salt Reactor Program at ORNL. Others who have contributed to the fuel processing technology described in this paper are M. R. Bennett, C. H. Brown, Jr., W. L. Carter, R. M. Counce, L. M. Ferris, B. A. Hannaford, A. D. Kelmers, J. A. Klein, R. B. Lindauer, H. C. Savage, J. S. Watson, H. O. Weeren, and E. L. Youngblood.

2. DESIGN FEATURES OF THE MOLTEN-SALT BREEDER REACTOR

The basic concept of the single-fluid molten-salt breeder reactor¹ is shown in Fig. 1. The fuel salt is a mixture of the fluorides of lithium-7, beryllium, thorium, and uranium having the composition 71.7 mole % ⁷LiF, 16 mole % BeF₂, 12 mole % ThF₄, and 0.3 mole % UF₄. This salt mixture melts at about 500°C, and at the reactor operating temperature it has a viscosity of about 10 cP and a vapor pressure less than 0.1 torr. As shown in the figure the salt flows upward through the core where it is heated to 700°C, and then it is pumped through a heat exchanger where the heat is transferred to a eutectic mixture of sodium fluoroborate and sodium fluoride (92-8 mole %). The intermediate coolant transports the heat to a steam system where supercritical steam at 540°C is generated. The core is formed from an array of bare graphite bars having open channels that provide for the passage of salt. The volume fraction left for salt is different in different regions of the core, and in an annular space it has been made high enough that this volume is undermoderated and acts like a blanket where most of the escaping neutrons are absorbed in the thorium. All metal surfaces in the reactor that contact molten salt are made from Hastelloy N, a nickel-based alloy especially developed for use in molten-salt reactors.

3. FUEL PROCESSING FOR MSB. s

3.1 Processing Requirements

Operation of a molten-salt breeder reactor requires the isolation of ²³³Pa from the region of high neutron flux during its decay to ²³³U and the removal of fission products in order to minimize neutron absorptions in these materials. The rare earths and zirconium are the principal fission products

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Fig. 1. Single-fluid, two-region molten salt breeder reactor. For 1000 MW(e), the fuel salt flow rate through the core is 55,000 gpm, but less than 1 gpm passes through the processing plant. Electricity is produced from supercritical steam with an overall efficiency of 44%.

removed in the fuel processing plant. It is also necessary to remove the excess uranium which is produced, to maintain the proper redox potential of the fuel salt, and to maintain oxide and corrosion product concentrations at acceptable levels.

Processes involving the selective chemical reduction of materials from the fuel salt into liquid bismuth appear to be the most promising processing methods currently available, and the development of these processes has been the subject of the recent work on fuel processing. We have known for some time² that the isolation of protactinium is straightforward since its extraction behavior is significantly different from that of uranium, thorium, and lithium. More recently, McNeese³ utilized the selective distribution of rare earths into molten lithium chloride from bismuth solutions to synthesize an improved rare-earth removal step known as the metal transfer process.

3.2 Reference Flowsheet Description

The reference processing flowsheet⁴ is shown in Fig. 2. Fuel salt containing 0.3 mole % UF_4 and approximately 0.0035 mole % PaF_4 is withdrawn from the reactor on a 10-day cycle; * for a 1000-MW(e) MSBR this represents a flow rate of 0.88 gpm. Salt passes first to a continuous fluorinator where 99% of the uranium is removed as volatile UF_6 . The fluorinator will be an open bubble column⁵ having an active inside diameter of about 8 in. and a height of about 18 ft. The U-free salt is then sent to the protactinium removal step where the fuel salt is contacted with 0.13 gpm of bismuth containing about 0.23 at. % Th (90% of Th solubility at 640°C) and about 0.2 at. % lithium as reductants. The contactor is equivalent to about 5 equilibrium

* Processing cycle time is the time required for processing a volume of fuel salt equal to that contained in the reactor.

Figure 2.

stages. Protactinium and fission product zirconium are extracted into the bismuth according to the following reactions:

Thorium is also extracted according to the reaction

but operating conditions are fixed to minimize extraction of thorium. Thorium is also a reductant for protactinium and uranium and it is partially returned to the salt stream by the reactions

The protactinium and zirconium (as well as Li and Th) are removed from the bismuth by hydrofluorinating the bismuth in the presence of a captive secondary salt stream circulating through a 160-ft³ decay tank where Pa decays to ²³³U and through a fluorinator where about 90% of the uranium is removed.

The uranium inventory in the decay tank is less than 0.2% of that in the primary circuit. Fluorides of lithium, thorium, zirconium, and nickel accumulate in the tank at a total rate of about 0.1 ft³/day. These materials are removed to a final Pa decay and fluorination operation.

The U- and Pa-free fuel salt passes from the Pa removal step to the metal transfer process where the rare-earth fission products are removed. The salt is contacted in the first contactor with 12.5 gpm of bismuth. This bismuth stream is contacted in the second contactor with a 33-gpm lithium chloride stream. These two contactors are each equivalent to three equilibrium stages. The trivalent and divalent rare earths are removed in separate

contactors in order to minimize the amount of lithium required. Only 2% of the LiCl or 0.66 gpm is fed to the two-stage divalent rare-earth removal contactor where it is contacted with a 2.2-liters/day bismuth stream containing 50 at. % lithium. The trivalent stripper where the LiCl is contacted with bismuth containing 5 at. % lithium is equivalent to one equilibrium stage.

The bismuth stream containing the reductant necessary for the isolation of protactinium is actually fed to the recirculating bismuth stream in the rare-earth removal system. An equivalent amount of bismuth is withdrawn from the stream after it passes through the fuel salt contactor and is fed to the protactinium isolation contactor. This results in more complete extraction of protactinium and provides a means for removing materials which might otherwise accumulate in the recirculating stream.

Uranium is returned to the fuel salt in the fuel reconstitution step before the salt is sent back to the reactor. The uranium addition is accomplished by absorbing the UF_6 stream from the fluorinators into a recycle salt stream containing dissolved UF_4 . The UF_6 reacts rapidly with the UF_4 to form dissolved, nonvolatile UF_5 according to the reaction

The dissolved UF_5 is reduced to UF_4 via the reaction

A purification step is included to remove traces of bismuth before the salt is returned to the reactor.

The removal time^{*} of protactinium obtained with the flowsheet is 10 days and the rare-earth removal times range from 17 to 51 days with the rare earths of most importance being removed on 27- to 30-day cycles. Bell and McNecese^{4,6} have made calculations which indicate that the flowsheet is relatively insensitive to minor variations in operating conditions such as changes in temperature, flow rates, reductant concentrations, etc.

3.3 Resource Utilization in MSBR's

The rapid removal of fission products and protactinium from a molten-salt breeder reactor, coupled with the absence of strongly neutron absorbing materials in the core structure, makes it feasible to achieve a significant breeding gain^{**} in a thermal reactor. Physics analyses⁷ of the reactor described in the ORNL conceptual design report¹ and having the protactinium and fission products removed by the processing plant just described show that the major characteristics of the reactor to be the following:

Average core power density - 22 kW/liter

Fissile uranium inventory of reactor and processing plant - 1500 kg

Breeding ratio - 1.07

Fuel doubling time (exponential) at 80% plant factor - 19 years.

Although the breeding gain is low, when it is combined with the low specific inventory[†] found in MSBR's, good utilization of uranium ore resources⁸ is achieved. In Fig. 3 is shown the relative ore requirements for a U.S. nuclear power industry based on various postulated combinations of converters and possible future breeders, having different breeding ratios

^{*} The removal time for a given material is equal to the processing cycle time (defined previously) divided by the fraction of material that is removed in a pass through the processing system.

^{**} Breeding gain is the breeding ratio minus 1.0.

[†] Fissile inventory divided by electrical power output.

and specific fuel inventories [kg fissile/MW(e)]. This figure is based also on a particular set of assumptions about the growth of electrical power generation. The absolute values of ore requirements depend upon what assumptions are made, but relative requirements are reasonably insensitive to these assumptions. These curves show that a breeder reactor with a (compound) doubling time of 20 years, and a specific inventory of 1.5 kg/MW(e), would be expected to require very little more ore than a breeder with a doubling time of 10 years and a specific inventory of 4 kg/MW(e). (These might be, respectively, a thermal breeder with a breeding ratio of 1.07 and a fast breeder with a breeding ratio of 1.35.)

Thus, a thermal breeder reactor with a low specific fuel inventory may have breeding performance comparable to a fast breeder with a larger fuel inventory, even if the doubling time of the fast breeder is much shorter than that of the thermal breeder.

In the processing plant various waste streams are combined and require that salt be discarded at the rate of 60 ft³ every 220 days.⁵ In this salt, thorium is discarded at the rate of about 50 moles/day. Although the cost of replacing thorium is low⁹ (0.0184 mill/kWh at ThF₄ prices of \$6.50/lb), the resulting thorium utilization is only about 13%. At the time the flowsheet analyses were made thorium was relatively cheap and it was felt that it was more economic not to recover the thorium. Flowsheet modifications are being developed, however, that will not require discard of thorium and will result in almost complete utilization, if desired.

Fig. 3. The effect of the fuel utilization characteristics of breeders on the cumulative uranium ore requirements for a growing U.S. nuclear power economy.

4. RECENT DEVELOPMENTS IN PROCESSING TECHNOLOGY

Recent reviews¹⁰⁻¹¹ have discussed the status of molten-salt reactor processing technology as it existed in late 1972. In the remainder of this report are summarized the technical developments which have occurred since these last reviews.

4.1 Continuous Fluorinator Development

Continuous fluorinators are used at two points in the reference flow-sheet. The first of these is the primary fluorinator, where 99% of the uranium is removed from the fuel salt prior to the removal of ^{233}Pa by reductive extraction. The second point is where uranium, produced by decay of ^{233}Pa , is removed from the secondary fluoride salt in the protactinium decay tank circuit. These fluorinators will be protected from fluorine corrosion by forming frozen salt layers on the internal surfaces of the fluorinator which are exposed to both fluorine and molten salt. The fluorinators will be made of nickel alloys which exhibit satisfactory resistance to fluorine corrosion when molten salts are absent. This resistance results from a passivating film of NiF_2 corrosion product. However, when molten salts are present, the NiF_2 is dissolved, leaving the metal substrate unprotected. It is proposed that the NiF_2 film be maintained intact by covering the walls with frozen salt.

In order to maintain the salt frozen near the wall while the inner core is molten, an internal heat source is necessary to support the temperature gradient. Heat from decay of the fission products in the salt will be used in the processing plant where heat generation rates in the molten salt will be about 13 kW/ft^3 . In order to test frozen wall fluorinators in nonradioactive systems, another internal heat source is necessary. Ideally, this heat source should not be attacked by fluorine.

Autoresistance heating of the molten salt by passing an alternating current through the molten salt has been pursued as a means for providing the requisite heat. Using this method, an electrode contacts the molten salt through an electrically-insulating flange in a side arm near the top of the fluorinating section (see Fig. 4). The lower part of the vessel serves as the other electrode, and an electrically-insulating frozen salt film must be present on the vessel walls to cause the heating current to pass along the section in which the fluorination reaction will be carried out.

Preliminary experiments were carried out in a vessel which had no side arm,^{13,14} using binary salt mixtures of Li-BeF₂ whose compositions fell on either side of the eutectic composition 67.2 mole % LiF-32.8 mole % BeF₂. Frozen salt films ranging from 1.0-1.4 in. thick were successfully formed and held on the walls of the test section under steady-state conditions. Specific heat generation rates ranged from 9 to 16 kW/ft³ of molten salt. Measured thickness of the frozen salt layer agreed well with values predicted by heat transfer calculations and with values based upon measured total resistance of the conducting salt path. It was found that an electrically insulating salt film could be formed reliably if the temperature of the wall was held below the salt solidus temperature.

Lindauer¹⁵ has installed equipment in which autoresistance heating of MSBR fuel carrier salt (LiF-BeF₂-ThF₄--72-16-12 mole %) can be studied in a vessel having a side arm and having a design similar to a fluorinator to be installed in a new experimental facility. In this experiment salt is circulated through the test vessel in order to help equalize freezing rates in the side arm and in the vertical test section. A flow diagram of the

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Fig. 4. Internal heat generation by autoresistance heating for demonstration of frozen wall corrosion protection in a continuous fluorinator.

experiment is shown in Fig. 5. Salt is pumped from a dual-diameter surge tank (composed of sections 6 in. in diameter by 4 ft long and 24 in. in diameter by 11 in. long) by means of a gas-lift pump to a gas-liquid separator. Salt flows by gravity to the test vessel, entering the vessel through the electrode in the side arm and leaving from the bottom of the vertical test section. The salt returns to the surge tank through a heat flow meter where flow rate can be determined from the temperature rise resulting from transfer of a known amount of heat to the flowing salt stream. The test section and side arm of the test vessel are made from 6-in. sched 40 nickel pipe. Above the vertical test section is an 8-in.-diam x 15-in.-long gas-salt disengagement space. Overall height of the test vessel is 69 in. About six runs have been made with salt flow rates up to 500 cc/min. The desired mode of operation is to generate heat internally and remove it at the test vessel walls using an air-water mixture in cooling coils attached to the vessel walls. The walls are cooled below the salt solidus temperature of 350°C (liquidus temperature is about 500°C). In our runs to date, complete success has not been achieved in forming electrically insulating frozen salt films in this equipment. Salt freezing in the electrode as it enters the vessel side arm interrupts experiments before correct operating conditions can be achieved. Although not entirely successful, the results which have been seen are encouraging.

Studies of hydrodynamics and mass transfer in open bubble columns have been completed. These studies provide much of the information which will be used to design fluorinators for the processing plant.

Mixing effects in open bubble columns have been measured and expressed¹⁶ as a dispersion coefficient defined by the one-dimension diffusion equation:

Fig.5. Flow diagram for experiment to study autoresistance heating of molten salts.

$$E(1 - \epsilon) \frac{d^2 c}{dz^2} - v_1 \frac{dc}{dz} = 0 \quad (1)$$

where

E = axial dispersion coefficient, cm^2/sec ,

ϵ = gas holdup fraction in the liquid,

c = concentration of solute in liquid, moles/cm^3 ,

v_1 = superficial liquid velocity, cm/sec ,

z = position measured from top of column, cm .

It has been observed that the hydrodynamic performance of open bubble columns is characterized by two flow regimes with an intermediate transition region. At low superficial gas velocities, the gas rises in the form of discrete single bubbles. This flow regime is called the "bubbly regime." At high superficial gas velocities the gas surges through the column in large cylindrical slugs occupying nearly the entire cross section of the column. This flow regime is called the "slugging regime."

In the bubbly flow regime the axial dispersion coefficient has been correlated¹⁶ using dimensionless groups as follows:

$$N_{Pe} = 11.12 N_{Re}^{0.82} N_{Ar}^{-0.45} \quad (2)$$

where

N_{Pe} = Peclet number = Dv_g/E ,

N_{Re} = Reynolds number = Dv_g/ν ,

N_{Ar} = Archimedes number = $D^3 g/\nu^2$,

D = column diameter,

v_g = superficial gas velocity,

E = axial dispersion coefficient,

ν = liquid kinematic viscosity,

g = acceleration of gravity.

(The expression in Ref. 16 has the wrong sign for the exponent on N_{Ar} .) In the slugging regime the axial dispersion coefficient has been correlated using dimensionless groups as follows:

$$N_{Pe} = 0.387 N_{Re}^{0.25} N_{Su}^{-0.13} \quad (3)$$

where

$$N_{Su} = \text{Suratman number} = D\rho\sigma/\mu^2,$$

ρ = liquid density,

σ = interfacial tension,

μ = liquid viscosity.

The transition between bubbly flow and slugging flow may be reliably predicted from the intersection of Eqs. (2) and (3). The observed Peclet number tends to follow the lower value (greater axial mixing) of the Peclet number across the transition.

Using this method for predicting the transition in flow regime, it has been possible to correlate data for gas phase holdup in each regime as follows:

in the bubbly regime,

$$\epsilon = 0.322 \left(\frac{\rho v_g^4}{g\sigma} \right)^{0.219}; \quad (4)$$

in the slugging regime,

$$\epsilon = 0.848 \left(\frac{v_g^2}{gD} \right)^{0.362}; \quad (5)$$

where ϵ = gas holdup fraction.

The correlations for axial mixing and gas holdup comprise a thorough description of the hydrodynamic performance of open bubble columns. Details of the experimental procedure and data analysis have been presented elsewhere.^{17,18}

Begovich and Watson measured the liquid-phase-controlled mass transfer of CO_2 between air and aqueous solutions in open bubble columns.¹⁹ Correlations were developed for estimating the effects of gas velocity, liquid viscosity, and column diameter on liquid-film mass transfer coefficients. The best correlation of dimensionless groups is as follows:

$$N_{\text{Sh}} = (1.11 \times 10^{-11}) N_{\text{Re}}^{0.849} N_{\text{Sc}}^{1.80} N_{\text{Su}}^{1.15} \quad (6)$$

where

$$N_{\text{Sh}} = \text{Sherwood number} = (k_1 a) D^2 / D_{12} ,$$

$$N_{\text{Sc}} = \text{Schmidt number} = \mu / \rho D_{12} ,$$

$$(k_1 a) = \text{volumetric mass transfer coefficient, sec}^{-1}, \text{ and}$$

$$D_{12} = \text{molecular diffusivity of diffusing species 1 in liquid 2, cm}^2/\text{sec}.$$

These correlations provide the information for designing the continuous fluorinators in the MSBR processing plant.

4.2 Fuel Reconstitution Development

In the fuel reconstitution step uranium is returned to the processed salt before the salt returns to the reactor. Figure 6 shows one way that this might be accomplished. Salt containing no UF_4 is mixed with a recycle stream which contains dissolved UF_4 , and the combined stream is fed to a column where UF_6 is bubbled through the salt. The UF_6 reacts with the UF_4 to form soluble UF_5 . Salt containing UF_5 is fed to another column where hydrogen is also fed to reduce the UF_5 to UF_4 . Part of the stream leaving this column is recycled to the first column. In this manner uranium is reduced in the molten salt and there is no need to handle UF_4 powder.

Bennett and Ferris studied the reaction of UF_6 and dissolved UF_4 in small gold equipment.²⁰ These studies showed that the reaction went essentially to

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Fig. 6. Fuel reconstitution process.

completion and that the UF_6 was quantitatively absorbed in a salt depth of 2-4 cm. Bennett and Kelmers have also studied the reduction of UF_5 by hydrogen.²¹ In these experiments the reaction between H_2 and dissolved UF_5 followed zero-order kinetics at 550°C, where the rate of reaction was independent of UF_5 concentration in the salt and hydrogen flow rate. At 675°C the reaction followed first-order kinetics. At both temperatures the hydrogen utilization was less than 1%. When platinum-black catalyst was added to the salt, the reaction rate increased dramatically and the hydrogen utilization was 90-100%. Small amounts of platinum catalyst adhering to the gold reaction vessel offered sufficient catalytic activity to provide rapid UF_5 reduction and near-stoichiometric hydrogen utilization.

Counce has installed equipment to carry out engineering studies of fuel reconstitution.²²⁻²⁴ A flow diagram of the experimental equipment is shown in Fig. 7. In this experiment salt containing dissolved UF_4 can be fed to a UF_6 absorption vessel for reaction of UF_6 with the UF_4 . Salt containing UF_5 from this vessel overflows to a hydrogen reduction column where H_2 reduces the UF_5 to UF_4 . Sample ports are provided for taking liquid samples from the reaction vessel effluent streams and instrumentation is provided for measuring UF_6 and $HF-H_2$ concentration in the vessel off-gas streams. Traps filled with NaF are provided for disposing of UF_6 and HF in the off-gas streams. The reaction vessels and the interconnecting piping will be gold-lined in order to provide corrosion protection against the UF_6 , UF_5 , and HF which are corrosive. This experiment will demonstrate fuel reconstitution using salt flow rates which will be about 5% of those required in a plant processing fuel salt from a 1000 MW(e) reactor. Data will be obtained for designing a larger scale engineering experiment in which the fluorination operation will be

Fig. 7. Flow diagram for equipment used in Fuel Reconstitution Engineering Experiment.

combined with the reconstitution step. Methods of introducing catalysts into the hydrogen reduction column will also be tested. In the initial experiment the interior of the hydrogen reduction column will be plated with an active platinum coating.

4.3 Salt-Bismuth Contactor Development

Removal of ^{233}Pa and the rare-earth fission products from the fuel salt of an MSBR is accomplished by extracting these materials from the salt into molten bismuth containing reductant. Design of contactors for this extraction requires extrapolation of technology developed for aqueous-organic extraction systems. Two types of contactors have been considered for the salt-bismuth reductive extractions: packed columns and mechanically agitated nondispersing contactors. At present the latter are favored because entrainment of bismuth into fuel salt returning to the reactor is minimized and because fabrication from molybdenum and graphite components is facilitated. For both types of contactors, however, extrapolation of existing correlations for hydrodynamic performance and mass transfer performance fails because the properties of salt-bismuth systems are so far removed from those of aqueous-organic systems for which correlations were developed. The main difference is thought to be due to the difference in densities of the two immiscible phases. It is rare to find the density difference in aqueous-organic systems to be greater than about 1.0, whereas the density differences between the salt and bismuth phases found in the MSBR processing plant are about 5.5 and 7.5.

A new correlation has been proposed and tested by Watson et al. which predicts flooding rates for Raschig-ring-packed columns with significantly greater accuracy than previous correlations over a wide range of fluid properties.²⁵ Recent measurements have provided information on variations in

physical properties for systems of high density difference,²⁶ as well as for data of high-density halocarbons (CCl_4 and CH_2Br_2).²⁷ The column packing in these studies was restricted to Raschig rings. Although considerable data are available for other packing materials, especially Berl saddles, there is not sufficient information on any other single packing to permit a correlation as comprehensive as that presented here.

Examination of both the literature and new ORNL results indicated that flooding data can be approximated reasonably well as a straight line when the square root of the superficial velocity of one phase is plotted vs the square root of the superficial velocity of the other phase. Thus, flooding points were fitted to a straight line with the form

$$v_{c,f}^{1/2} + k_1 v_{d,f}^{1/2} = k_2, \quad (7)$$

where

$v_{c,f}$ = superficial continuous-phase velocity at flooding, cm/sec,

$v_{d,f}$ = superficial dispersed-phase velocity at flooding, cm/sec.

The parameters k_1 and k_2 were correlated with fluid and packing properties.

The resulting correlations were:

$$k_1 = 0.844 \Delta\rho^{0.145} d_p^{0.298} \mu_c^{-0.084} \epsilon^{-0.078}, \quad (8)$$

$$k_2 = 23.8 \Delta\rho^{0.269} d_p^{0.494} \mu_c^{-0.084} \epsilon^{0.5}, \quad (9)$$

where

$\Delta\rho$ = difference in density of the two phases, g/cm^3 ,

d_p = packing diameter, cm,

μ_c = viscosity of continuous phase, poise,

ϵ = void fraction of packing, dimensionless.

This equation, which is based on more extensive data and a wider range of physical properties than any previous correlation, should be more reliable in predicting flooding rates for new systems where no data exist. Its advantages will be most evident for systems with high density differences; however, since it is not a dimensionless correlation, care must be taken to choose correct units.

Mechanically agitated nondispersing salt-bismuth contactors are being considered because with them entrainment of bismuth into the fuel salt would be minimized, and fabrication from molybdenum and graphite could be done less expensively than with packed column contactors. These contactors are simply baffled vessels containing approximately equal volumes of salt and bismuth with stirrers in each phase mounted on a common shaft. Weeren²⁸ and Klein²⁹ have surveyed the literature on mass transfer in this type of contactor. Of the correlations which have been presented for mass transfer coefficients in nondispersing contactors, that of J. B. Lewis^{30,31} is simplest and reproduces data about as well as other proposed correlations. No correlation has been tested over wide ranges of physical properties or dimensions of contacting devices. Although its inadequacies are recognized, measured mass transfer coefficients were compared with the Lewis correlation, which is given as follows:

$$\frac{60 k_1}{v_1} = (6.76 \times 10^{-6}) \left(N_{Re_1} + N_{Re_2} \frac{\mu_2}{\mu_1} \right)^{1.65} + 1, \quad (10)$$

where

k_1 = mass transfer coefficient across interfacial film in phase 1, cm/sec,

v_1 = kinematic viscosity of phase 1, cm²/sec,

$N_{Re} = nD_A^2/v$, dimensionless,

D_A = agitator diameter, cm,

n = agitator speed, rps,

μ = viscosity, poise.

The subscripts refer to phase 1 and 2. Note that the left-hand side of Eq. (10) is not dimensionless.

Brown has measured the rates of mass transfer of ^{237}U and ^{97}Zr between MSBR fuel carrier salt and bismuth containing thorium reductant in a 6-in.-diam baffled carbon-steel contactor.³² The agitator in each phase was a 2-7/8-in.-diam flat-bladed paddle with four vanes made from molybdenum. The distribution coefficient was adjusted to such a high value that all of the mass transfer resistance was in the salt phase. Figure 8 shows these results compared with the Lewis correlation. The mass transfer coefficient measured in the salt-bismuth contactor fell in the range of 30-60% of the Lewis correlation at values of the Reynolds number group less than about 18,000 (which corresponds to an agitator speed of ~ 170 rpm). At values of the Reynolds number group above 18,000 the values fall above the Lewis correlation. We believe that at about 170 rpm in this experiment, phase dispersal begins to occur and the increase in apparent mass transfer coefficient is a manifestation of an increase in surface area available for mass transfer. The effect of the variables other than agitator speed which are implicit in the dimensionless groups has not been adequately tested. A program is in progress to study these effects and to determine the scaling laws for this type of contactor using mercury and water to simulate bismuth and molten salt.

EXPERIMENTAL RESULTS FROM THE SALT-METAL CONTACTOR

4.4 Metal Transfer Process Development

The metal transfer process for removal of rare earths and separating them from thorium is based upon the selective extraction of rare earths from bismuth into LiCl.^{33,34} In this process³ rare earths and thorium are extracted into bismuth containing lithium reductant (0.2 at. %), and the rare earths are selectively removed from the bismuth by contact with LiCl. Divalent and trivalent rare earths are removed separately from the LiCl by extraction into Bi-Li streams containing 50 at. % Li and 5 at. % Li, respectively.

Four engineering-scale experiments (MTE-1, -2, -2B, and -3) have been carried out to study the steps in the metal transfer process and to obtain information, such as mass transfer rates of rare earths between the salt and bismuth phases, which is necessary to determine the size and type of equipment needed for the process. Results from these experiments have been reported.³⁵⁻³⁹ Experiments MTE-1, -2, and -2B demonstrated the selective removal of rare earths (lanthanum and ¹⁴⁷Nd) from MSBR fuel carrier salt and the transfer to a Li-Bi acceptor alloy. Experiment MTE-3 was a larger experiment that included features such as mechanical agitation of the salt and metal phases to improve mass transfer rates of the rare earths across the three salt-metal interfaces. This equipment was designed to measure mass transfer rates across the three interfaces as a function of agitator speed for comparison with calculated values using the Lewis correlation. Metal Transfer Experiment MTE-3 (Fig. 9) consisted of three interconnected vessels: a 14-in.-diam fuel salt reservoir, a 10-in.-diam partitioned salt-metal contactor, and a 6-in.-diam mechanically agitated rare-earth stripper. The salt-metal contactor was divided into two compartments that were interconnected through an opening in the bottom of the divider by a pool of bismuth containing thorium and lithium. The stripper contained a lithium-bismuth solution (5-95 at. %).

Fig. 9. Flow diagram for Metal Transfer Experiment MTE-3.

Mechanical agitators were used in both compartments of the contactor and in the lithium-bismuth stripper to promote mass transfer across the three salt-metal interfaces.

The purpose of MTE-3 was to evaluate this type of contactor and stripper for use in removing rare earths from molten-salt reactor fuel. Fluoride salt and LiCl flow rates in the MTE-3 system were about 1% of those required for removing rare earths from a 1000-MW(e) MSBR. The operating temperature was 650°C; phases were $\text{LiF-BiF}_2\text{-ThF}_4$ (72-16-12 mole %) fuel carrier salt, bismuth-lithium-thorium (99.7-0.17-0.13 at. %) solution, and lithium-bismuth (5-95 at. %) stripper alloy. In this experiment the rare earths were extracted from the fuel carrier salt into the Bi-Li-Th solution. Next, the rare earths were extracted from the Bi-Li-Th with molten LiCl; and, finally, they were stripped from the LiCl into the Li-Bi alloy.

Mass transfer coefficients for radium, europium, lanthanum, and neodymium were measured during 13 runs at agitator speeds ranging from 100 to 400 rpm. A comparison of the experimentally obtained results with values predicted by the Lewis correlation is shown in Table 1. With the exception of radium, which was studied during the first four runs only and for which the distribution coefficient between fluoride salt and bismuth-lithium-thorium have not been measured, the experimentally determined values are substantially lower (from 0.5 to 30% of the predicted values). However, the results show the same general dependence on agitator speed as predicted.⁴⁰ The lower mass transfer rates were thought to be due to the presence of films (composed of solids) at the interfaces (particularly the LiCl--Bi-Li-Th interface) formed by the entry of impurities such as oxides into the system.

Table 1. Overall mass transfer coefficients^a measured during metal transfer experiment MTE-3

Material	Agitator speed (rpm)	K1 (mm/sec) ^b		K2 (mm/sec) ^b		K3 (mm/sec) ^b	
		Measured value	% of predicted value	Measured value	% of predicted value	Measured value	% of predicted value
Radium ^c	100	0.00052	100	0.61×10^{-4}	100	0.032	100
	150	0.00083	100	1.0×10^{-4}	100	0.062	100
	200	0.0016	100	1.9×10^{-4}	100	0.1	100
Europium	100	0.001	30	0.15×10^{-4}	10	0.011	10
	200	0.003	30	0.48×10^{-4}	10	0.033	10
Lanthanum	100	0.0006	15	0.39×10^{-3}	0.5	0.062	7
	150	0.0014	15	1.1×10^{-3}	0.5	0.12	7
	200	0.002	15	1.3×10^{-3}	0.5	0.2	7
	200 ^d	0.002	15	2.0×10^{-2}	10	0.2	7
	300 ^d	0.0026	15	3.2×10^{-2}	10	0.2	4
	300	0.0026	15	3.2×10^{-2}	10	0.2	4
Neodymium	200	0.002	15	6.5×10^{-2}	10	0.2	7
	300	0.0032	15	1.1×10^{-1}	10	0.2	4

^a The mass transfer coefficients are based on the rare-earth concentration in the salt phase.

^b $\frac{1}{K_1} = \frac{1}{k_1} + \frac{1}{k_2 D_A}$, at fluoride salt--Bi-Li-Th interface,

$\frac{1}{K_2} = \frac{1}{k_3} + \frac{D_B}{k_4}$, at lithium chloride--Bi-Li-Th interface,

$\frac{1}{K_3} = \frac{1}{k_4} + \frac{1}{k_3 D_C}$, at lithium chloride--Li-Bi interface,

k_1 = individual mass transfer coefficient, fluoride salt to bismuth,

k_2 = individual mass transfer coefficient, bismuth to fluoride salt,

k_3 = individual mass transfer coefficient, bismuth to lithium chloride,

k_4 = individual mass transfer coefficient, lithium chloride to bismuth,

where

D_A = distribution coefficient between fluoride salt and Bi-Li-Th,

D_B = distribution coefficient between LiCl and Bi-Li-Th,

D_C = distribution coefficient between LiCl and Li-Bi.

^c Extrapolated values for the distribution coefficient of radium were used in calculating the mass transfer coefficients.

^d With spargers in operation in the LiCl compartment of the contactor and the Li-Bi vessel.

Savage has installed equipment^{41,42} which duplicates the equipment for experiment MTE-3 in order to determine if solid films were causing the low rates of mass transfer seen in experiment MTE-3. Two runs have been completed in the new experiment (experiment MTE-3B) in which the rate of transfer of Nd from the fluoride fuel salt to the lithium-bismuth stripper alloy has been measured. The agitator speed in both of these runs was 300 rpm. Results from only the first run are complete⁴³ and these indicate the following values for the overall mass transfer coefficients:

$$K_1 = 0.0035 \text{ mm/s (39\% of predicted),}$$

$$K_2 = 0.25 \text{ mm/s (20\% of predicted), and}$$

$$K_3 = 0.13 \text{ mm/s (2.5\% of predicted).}$$

These mass transfer coefficients are not greatly different from values obtained previously. The agreement with the previous results causes the theory of low mass transfer due to oxide films to be questionable. Since low mass transfer rates were seen in the first run of experiment MTE-3B, any oxide formation must have occurred much more rapidly than in experiment MTE-3. This is very unlikely since the same stringent precautions were taken during installation and operation of experiment MTE-3B as were taken during experiment MTE-3. What is more likely is that the Lewis correlation does not predict closely mass transfer coefficients in systems where physical properties are far removed from those of the aqueous-organic systems for which it was derived. We are examining this possibility further.

5. PROBLEMS AND PLANS FOR FUEL PROCESSING DEVELOPMENT

The successful operation of a processing plant based on the reference flowsheet is contingent on the development program meeting several objectives. These include the following:

1. developing continuous fluorinators having an acceptably low corrosion rate and an adequate efficiency for uranium removal,
2. identifying materials of construction that are compatible with molten salts and bismuth containing dissolved reductant,
3. maintaining the concentration of bismuth in the fuel salt returning to the reactor at acceptably low levels, and
4. developing on-line instrumentation necessary for plant operation.

Experimental work carried out to date on processing has demonstrated the chemical feasibility of the various process steps. Most of the further work that is required to demonstrate processing technology is related to the operation of equipment items of a sufficient size that evaluation and design can be carried out for the processing system for a 1000-MW(e) MSBR.

Hydrofluorination of bismuth in the presence of molten salt is required at several points in the reference processing flowsheet. Thus far, there has been no effort directed toward the development of this operation, but some experience has been obtained from operation of a batch hydrofluorinator in a facility for studying salt-bismuth contactors. The main problems associated with development of hydrofluorinators are concerned with achieving acceptable mass transfer rates in a three-phase contacting device and finding acceptable materials of construction. A continuous hydrofluorinator will be required in a planned continuous reductive extraction process facility (to be described later). Initial hydrofluorinator tests will be carried out in conjunction with the installation of this facility.

The work required on fluorination and fuel reconstitution consists of studies of the chemistry involved with these steps, the operation of a fluorination facility that will be about 25%-50% of the size required for removing uranium from a 1000-MW(e) MSBR, and the operation of a combined fluorination-reconstitution facility that will be about 25%-50% of the size required for a 1000-MW(e) MSBR. At the end of this time, sufficient information should be available to allow the evaluation and design of continuous fluorinators and fuel reconstitution systems for full-scale processing plants. It is estimated that this work will require about three years for completion.

The work remaining on the reductive extraction of uranium and protactinium consists of mass transfer studies and hydrodynamic studies in salt--bismuth contactors, operation of a continuous reductive extraction process facility [25% of 1000-MW(e) MSBR scale], and an engineering demonstration of the steps involved in isolation of protactinium using representative protactinium concentrations. This work will require about 3.5 years for completion.

Work on rare-earth removal by the metal transfer process consists of completion of engineering experiment MTE-3B [1% of 1000-MW(e) MSBR scale] and operation of engineering experiment MTE-4 [5 to 10% of 1000-MW(e) MSBR scale]. This work will require about three years for completion.

The final area of work required for demonstrating the processing technology consists of operation of an integrated processing experiment. The system will be between 25% and 100% of 1000-MW(e) MSBR scale and will contain all steps required in the processing plant. With a reasonable funding level, this work could be completed in about six years.

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