Process for Fission-product Removal from Uranium-bismuth Reactor Fuels by Use of Fused-salt Extraction

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The liquid-metal–fuel reactor under development at the Brookhaven National Laboratory uses a fuel which is a solution of U^{233}, Mg, and Zr in liquid bismuth. For a power-breeder thermal reactor, high neutron economy is essential, and this calls for low concentrations of those fission products in the fuel which are high neutron capturers. Roughly 45% by weight of the fission products can be continuously removed from the fuel by salt extraction with alkali and alkaline-earth fused-salt mixtures. These fission products contain the highly "poisonous" rare earths. This paper will present a discussion of process-design considerations and proposed flow sheets.

The L.M.F.R. (liquid-metal–fuel reactor) being developed for power purposes at the Brookhaven National Laboratory is a thermal breeder reactor and uses as a fuel a dilute solution of uranium-233, magnesium, and zirconium in liquid bismuth. The breeding is done in a blanket surrounding the core of the reactor, the most promising blanket material being a thorium-bismuthide slurry in bismuth. Since the η value for U^{233} at thermal energies is only 2.31, it is necessary to maintain low concentrations of fission products in the fuel in order to breed with g values significantly greater than unity. The L.M.F.R. can also operate as a converter, "burning" U^{235} and producing U^{233}. The η for U^{235}, 2.08, is even lower than that for U^{233}, indicating that if the L.M.F.R. were to operate as a converter, neutron economy would possibly be even more critical.

For the low fission-product concentrations desired in the L.M.F.R. the rate of fuel processing is necessarily high when one thinks in terms of the pounds of fuel which must be handled per day; but for a high-density liquid fuel such as uranium bismuth, where continuous operation can be used, actual flow rates are estimated to be less than 1 gal./min. for reactors having heat rates as high as 1,000 Mw. In other words, L.M.F.R. economics are apparently such that the concentration of fission products in the fuel will be low.

In the L.M.F.R. the fission products can be divided arbitrarily into three groups: (*a*) those elements, or compounds formed from fission-product elements, which are appreciably volatile at operating temperatures; (*b*) nonvolatile elements which form chlorides more stable thermodynamically than UCl_3 and elements which, as anions, form salts; and (*c*) nonvolatile elements which form chlorides less stable than UCl_3. For convenience, the names of these three groups have been abbreviated to F.P.V., F.P.S., and F.P.N., respectively. As reactor poisons, the first two groups are by far the worst, the first because of Xe^{135} with its 2.7×10^6—barn cross section, and the second because of the rare earths, particularly Sm^{149}, with its 47,000-barn cross section. The fission products in the third group, owing to their low poisoning effect, can be allowed to build up to considerably higher concentrations in the fuel with less frequent processing of the fuel for their removal. It is proposed to remove the F.P.V.'s by a volatilization process, either gas sparging or simple desorption, the latter carried out under low pressure conditions if necessary. It is the F.P.S.'s with which the present paper is concerned—their poisoning capacity and their continuous removal from the fuel.

In a commercial L.M.F.R. the individual concentrations of the three groups of fission products would, of course, be determined by economic considerations; however, it is felt that their combined poisoning effect would probably be less than 5%; i.e., they would absorb less than one-twentieth as many neutrons as the uranium.

POISONING EFFECT OF F.P.S.'S

The method of determining the poisoning effect of this group of fission products will be described. The fission products extractable as chlorides by fused salts are rubidium, strontium, ythrium, cesium, barium, lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, and gadolinium. In addition, iodine and bromine, as salts, would presumably transfer to the salt with very high partition coefficients. Table 1 gives the yields (for U^{235}) of the fission products for the pertinent chains and the estimated atom fraction of each chain which is removed from the fuel with the F.P.S. group.

Although the L.M.F.R. is nominally a thermal breeder, such reactors would have to operate for some years as converters. For this reason, the treatment given below is based on the use of U^{235}, and not U^{233}, as the fissile material.

With reference to Table 1 again, in estimating the fraction of certain chains leaving the fuel stream as F.P.S.'s, it was assumed arbitrarily that 10% of the iodine and bromine left the fuel with the F.P.V. group. From the figures in Table 1, the average mass number of the F.P.S.'s is calculated to be 128.0, and their weight percentage of the total fission products turns out to be 43.2.

There are eight nuclides which are particularly bad poisons—Sr^{89}, I^{131}, Nd^{143}, Nd^{145}, Sm^{149}, Sm^{151}, Eu^{155}, and Gd^{157}, and they must be given special consideration. As a result, there will be three subgroups of the F.P.S.'s—group A, consisting of the chains listed in Table 1 minus chains 89, 131, 143, 145, 149, 151, 155, and 157; group B, consisting of chains 89, 131, 143, 145, 149, 151, 155, and 157 minus the eight high-cross-section nuclides listed above; and group C, consisting of the eight nuclides. Group A is shown in Table 2. Many of the cross-section values used in this paper were taken from a recent Brookhaven Laboratory report (*3*).

From the figures given in Table 2, the average cross section for group A is calculated to be 7.9 barns. The poisoning effect of this group is relatively

TABLE 1. FISSION CHAINS FROM U^{235} RELATIVE TO F.P.S.'S

Mass	% Yield	Estimated fraction in F.P.S.'s	Mass	% Yield	Fraction in F.P.S.'s
81	0.18	0.90	142	5.68	1.00
83	0.62	0.05	143	5.35	1.00
85	1.55	0.05	144	4.75	1.00
87	2.80	0.25	145	4.00	1.00
88	3.64	0.20	146	3.15	1.00
89	4.40	1.00	147	2.45	1.00
90	5.13	1.00	148	1.85	1.00
91	5.60	0.95	149	1.28	1.00
92	5.73	0.05	150	0.82	1.00
127	0.21	0.90	151	0.49	1.00
129	1.08	0.90	152	0.26	1.00
131	3.0	0.50	153	0.11	1.00
133	6.74	0.05	154	0.05	1.00
137	6.15	0.90	155	0.03	1.00
138	6.36	0.80	156	0.02	1.00
139	6.34	1.00	157	0.01	1.00
140	6.23	1.00	158	0.002	1.00
141	6.00	1.00			

TABLE 2. F.P.S.'S IN GROUP A

Mass	(% Yield) × (fraction in F.P.S.'s)	Cross section, barns
81	0.16	2.6
83	0.03	10.0*
85	0.08	0.9
87	0.70	0.14
88	0.73	0.005
90	5.13	1.0
91	5.32	1.52
92	0.29	1*
127	0.19	6.1
129	0.97	11.0
133	0.34	29.0
137	5.53	2.0
138	5.08	0.6
139	6.34	8.4
140	6.23	1.0*
141	6.00	10.0*
142	5.68	1.8
144	4.75	5.0
146	3.15	9.8
147	2.45	60.0
148	1.85	3.3
150	0.82	2.9
152	0.26	150
153	0.11	420
154	0.05	5.5
156	0.02	750
158	0.002	4.0

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*Assumed.

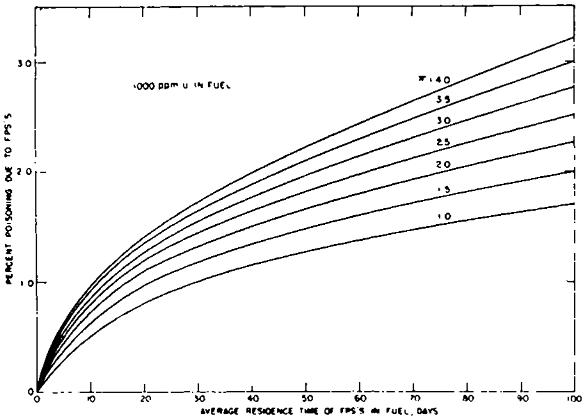

Fig. 1. Poisoning effect of F.P.S.'s in L.M.F.R.

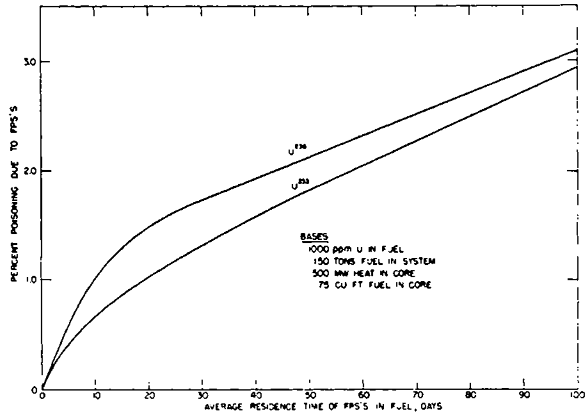

Fig. 2. Comparison of U^{233} and U^{235} with respect to F.P.S. poisoning effect.

small and assumed to be the same for all conditions of reactor operation. The poisoning effects of the other two groups varies appreciably with operating conditions, and the methods used in estimating them will be explained. The following treatment is based on the continuous removal of the F.P.S.'s, the existence of steady state conditions, and the assumption that all the F.P.S.'s transfer from the metal to the salt phase to the same degree.

The concentration of a given nuclide in the fuel stream depends upon a number of processes which govern its rate of formation and its rate of disappearance from the system. The following rates are involved, expressed in atoms/sec.:

1. Rate of formation from fission

$$= N^{235}V_c\sigma_{5f}\phi f \qquad (1)$$

2. Rate of formation resulting from neutron capture

$$= N_t V_c\sigma_t\phi \qquad (2)$$

3. Rate of formation resulting from decay of parent

$$= \lambda_p N_p V_t \qquad (3)$$

4. Rate of disappearance by decay

$$= \lambda N V_t \qquad (4)$$

5. Rate of disappearance by neutron capture

$$= N V_c\sigma\phi \qquad (5)$$

6. Rate of disappearance by extraction in fused salt

$$= \frac{W_s k N}{\rho_s} = \frac{V_t N}{t_r} \qquad (6)$$

Of course, not all the foregoing processes apply in a particular case. In fact, for practical purposes process 2 can be neglected entirely, because it so happens that none of the really serious poisons have significant rates of formation as a result of neutron capture, owing to the low cross sections of the neutron-capturing species.

From the foregoing equations, the steady state concentration of a chain-initiating nuclide or a nuclide whose precursors have negligibly short halflives is found to be expressed by the equation

$$N = \frac{N^{235} V_c \sigma_{5f} \phi f}{\lambda V_t + V_c \sigma \phi + \dfrac{W_s k}{\rho_s}} \qquad (7)$$

which can be converted to the more convenient form

$$N = \frac{f}{\dfrac{\left(\lambda + \dfrac{1}{t_r}\right) V_t}{3.15 \times 10^{16} P} + \dfrac{\sigma}{\sigma_{5f} N^{235}}} \qquad (7a)$$

For a nuclide inside the chain ends, the corresponding equations are

$$N = \frac{\lambda_p N_p V_t}{\lambda V_t + V_c \sigma \phi + \dfrac{W_s k}{\rho_s}} \qquad (8)$$

and

$$N = \frac{\lambda_p N_p}{\lambda + \dfrac{1}{t_r} + \dfrac{3.15 \times 10^{16} \sigma P}{V_t \sigma_{5f} N^{235}}} \qquad (8a)$$

and for a chain-terminating nuclide, the two equations are

$$N = \frac{\lambda_p N_p V_t}{V_c \sigma \phi + \dfrac{W_s k}{\rho_s}} \qquad (9)$$

and

$$N = \frac{\lambda_p N_p}{\dfrac{1}{t_r} + \dfrac{3.15 \times 10^{16} \sigma P}{V_t \sigma_{5f} N^{235}}} \qquad (9a)$$

In the foregoing equations the factor 3.15×10^{16} represents the number of fissions per second per megawatt of heat release.

By use of the preceding equations, say (7*a*), (8*a*), and (9*a*), the concentration of each of the nuclides in the eight chains containing the high–cross-section species can be determined. From this point on, in illustrations of the method of determining the poisoning effect, the calculations will be based on the following set of typical operating conditions:

1,000 p.p.m. U^{235} in fuel
300 tons fuel in system
500-Mw. (heat) reactor
20-day residence time for F.P.S.'s in fuel

Table 3. F.P.S.'s in Group *B* for U^{235}

Nuclides	Calculated fraction of total chain	Chain yield, %	Cross section, barns
89 chain minus Sr	0.208	4.40	1.4
131 chain minus I	0.000	3.00	
143 chain minus Nd	0.548	5.35	50*
145 chain minus Nd	0.018	4.00	10*
149 chain minus Sm	0.380	1.28	50*
151 chain minus Sm	0.000	0.49	
155 chain minus Eu	0.000	0.03	
157 chain minus Gd	0.351	0.01	1,000*

*Assumed.

For these conditions, Tables 3, 4, and 5 summarize the calculated results. Tables 3 and 4 present the results for groups *B* and *C*, respectively, and Table 5 shows a comparison of all three groups. The average cross section of 40 barns for group *B* is very much of a guess, as it is based primarily on the assumed cross sections shown in Table 3; but since this group contributes less than 1% of the total F.P.S. poisoning effect, the uncertainty of its average cross section does not have a significant effect on the results. It will be noticed that, for the conditions considered, the eight nuclides of group *C* account for 96.3% of the F.P.S. poisoning effect, and it is interesting to note that one of these (Sm^{149}) alone accounts for 70.5%. The rare earths, as a group, account for 93.5%. The reactor poisoning due to the F.P.S.'s, expressed on a percentage basis, will be

$$p = \left(\frac{\sum (N\sigma)}{N^{235} \sigma_{5a}}\right) 100 \qquad (10)$$

In the present case N^{235} and σ_{5a} are 2.51×10^{19} atoms/cc. and 687 barns, respectively, which makes *p* equal to 1.02. Thus for every 100 neutrons absorbed by the U^{235}, 1.02 will be captured by the F.P.S.'s. It is felt that this would be a typical figure for an eventual commercial L.M.F.R. power breeder with fully integrated fuel processing. For the conditions of the foregoing example, the concentration of the F.P.S.'s would be 16.85 p.p.m. This would seem a very low concentration upon which to base a continuous-extraction process, but for a high-temperature liquid-metal–fused-salt system such as the one under consideration here, it is more than adequate.

Figure 1 shows a family of curves presenting the poisoning effect of the F.P.S.'s as a function of their average residence time in, and the power density of, the reactor system. Offhand, one might expect the poisoning effect to be proportional to the power density π because of the direct effect of concentration; i.e., for a fixed residence time and total heat rate, when π is doubled and V_T is halved, then the concentration must be doubled. But the average cross section of the F.P.S.'s does not remain the same, owing to the fact that the more concentrated the F.P.S.'s, the less the relative concentrations of the high–cross-section nuclides. The concentrations of such nuclides, owing to the fact that their disappearance is due primarily to neutron capture, tend to remain constant.

Figure 2 shows a comparison of U^{235} and U^{233} with respect to the poisoning effects of their respective F.P.S.'s. It is seen that, other things being equal, the poisoning effect with U^{235} is appreciably greater than that with U^{233}; for example, for 1% poisoning, under the conditions of the plot, the average residence times for the F.P.S.'s from U^{235} and U^{233} are 10 and 19 days respectively. Or, in other words, the concentrations would be 18 and 34 p.p.m., respectively. The considerably greater poisoning effect of the F.P.S.'s from U^{235} is due to the much higher fission yields of the rare earths from this isotope.

The power figures in the foregoing discussion are on a *total* basis; i.e., they include all the heat obtainable from the radioactive decay of the fission products.

Table 4. F.P.S.'s in Group *C* for U^{235}

Nuclide	*N*, atoms/cc.	σ, barns
Sr^{89}	3.39×10^{16}	110
I^{131}	1.07×10^{16}	600
Nd^{143}	2.33×10^{16}	290
Nd^{145}	3.81×10^{16}	52
Sm^{149}	2.65×10^{15}	47,000
Sm^{151}	3.22×10^{15}	7,200
Eu^{155}	1.56×10^{14}	13,000
Gd^{157}	7.93×10^{12}	160,000

CHEMISTRY

The use of fused chlorides for extracting fission products from a uranium-bismuth reactor fuel was first proposed by Winsche and studied experimentally by Bareis at Brookhaven. Equilibrium results on some of the rare earths in the U–Bi/LiCl–KCl system were shown by Wiswall to be consistent with the postulation that the transfer of the rare earths from metal to salt was due to their selective oxidation, the degree of transfer being determined by the limitations of chemical equilibrium. An article by these three workers recently appeared in the unclassified literature (*4*).

Table 5. Poisoning Effects of F.P.S. Subgroups for U^{235}

Group	ΣN, (atoms/cc.)10^{-17}	$\bar{\sigma}$, barns	$[(\Sigma N)\bar{\sigma}] \times 10^{-20}$	% of F.P.S. poisoning
A	6.27	7.88	0.0494	2.8
B	0.394	40	0.0158	0.9
C	1.120	1,518	1.700	96.3
Total F.P.S.'s	7.78	225	1.765	100.0

TABLE 6. FREE ENERGIES OF FORMATION OF CERTAIN CHLORIDES AT 500°C.

Compound	$-\Delta F$, kcal./g. atom Cl	Compound	$-\Delta F$, kcal./g. atom Cl
$EuCl_2$	90.5	$CeCl_3$	70
$BaCl_2$	87.5	$PmCl_3$	69
KCl	87	$NdCl_3$	67
$SmCl_2$	85	$GdCl_3$	65.5
RbCl	85	YCl_3	65
CsCl	85	$MgCl_2$	61.5
$SrCl_2$	84	$ZrCl_2$	59
LiCl	83.5	UCl_3	58
$CaCl_2$	82	$CrCl_2$	35.5
NaCl	81	$FeCl_2$	29
$LaCl_3$	70	$NiCl_2$	24
$PrCl_3$	70	$BiCl_3$	18.5

Table 6 presents free-energy-of-formation values for the rare earths, alkali metals, and certain other metals of particular interest in the present discussion. These figures are for 500°C., on the basis of an atom of chlorine, and were obtained principally from two sources (*1*, *2*). They give a direct measure of chemical stability or tendency to chloride formation. It is seen that the free energy of formation of UCl_3 is well below that for any of the rare earths and the fission products in groups *IA*, *IIA*, and *IIIA* of the Periodic Table, indicating that it should be possible to oxidize these elements out of a uranium-bismuth solution without materially affecting the uranium. There are two approaches to accomplishing this. One involves the use of a buffer system, and the other is based on the use of the so-called "stoichiometric" method.

The only buffer system which has thus far shown promise of success is the Mg^{++}-Mg system. From the free-energy values in Table 6, one would predict that if a salt mixture of KCl-NaCl-$MgCl_2$ were contacted with a metal phase consisting of U-Bi-Sm, the Sm would reduce the $MgCl_2$ and transfer from the metal to the salt phase, according to the equation

$$MgCl_2 + Sm \rightarrow Mg + SmCl_2$$

It is assumed, of course, that the solubilities would be such that the reduced Mg would transfer quantitatively to the metal phase and the $SmCl_2$ to the salt phase. Moreover, the degree of separation achieved would depend on the "activities" of the reacting components in the two phases, besides the question of the extent of approach to equilibrium. The Mg in the metal phase would buffer the uranium, tending to prevent it from being oxidized. The oxidation-reduction potential of this type of system is not affected by small changes in concentration of the $MgCl_2$ in the salt or Mg in the metal and therefore can be easily controlled. The concentrations of the Mg and $MgCl_2$ will always be greatly in excess of those of the F.P.S.'s in the two phases. With the system KCl-NaCl-$MgCl_2$/-Bi-U-R.E.*, separation factors in the order of 100 have been obtained. The separation factor is defined by the relation

$$\frac{(\text{p.p.m. F.P.S. in salt})/(\text{p.p.m. U in salt})}{(\text{p.p.m. F.P.S. in metal})/(\text{p.p.m. U in metal})}$$

Appreciably increasing or decreasing the concentration of Mg in the metal will make the system more or less reductive, respectively, even though the separation factor remains substantially constant. With the eutectic mixture KCl-NaCl-$MgCl_2$ (m.p. 396°C.) the Mg concentration in the metal should be no more than about 100 p.p.m.

The stoichiometric method involves the use of a relatively strong oxidant in the salt mixture, like UCl_3 or $BiCl_3$, in concentrations just great enough to remove the greater portion of the F.P.S.'s from the fuel stream without oxidizing an appreciable amount of the uranium.

With UCl_3 as the oxident, uranium is added to the metal, which means that in actual practice this method of F.P.S. removal has the advantage of adding uranium make-up to the fuel. The stoichiometric relationships are such, however, that the F.P.S.'s will not transfer sufficient uranium to replace that which is consumed. The additional uranium can be transformed with magnesium.

Bismuth chloride is a very strong oxidizing agent, and one which does not add a solute to the fuel. It must, of course, be added to the carrier salt in just the right amount to extract the F.P.S.'s and not the uranium. It should give separation factors at least as great as those obtainable with $MgCl_2$. The F.P.S.'s are, as it were, titrated out. It is evident that this method has the disadvantage of requiring very careful control of the oxidant in the salt stream. On the other hand, the buffer system described above may work only when the Mg concentration is below that desired in the fuel for inhibiting corrosion and mass transfer. For this reason, the stoichiometric method appears more promising. In such a system the salt mixture carrying the oxidant could be any satisfactorily low-melting mixture of chlorides with individual salts at least as stable as magnesium chloride.

PROCESS DESIGNS FOR F.P.S. REMOVAL

The flow sheets described below are not based on the results of continuous pilot plant operation but are proposed for such on the basis of small batch-type experiments.

Use of Buffer System

A flow sheet, with typical numerical values, explaining the removal of F.P.S.'s from the L.M.F.R. fuel and based on the "buffer" chemical system described above, is shown in Figure 3. The flow rates, concentrations, and equilibrium stages indicated on this diagram are based on a total heat rate of 570 Mw. and a F.P.S. concentration in the fuel of 15 p.p.m. For a U^{235} concentration of 600 p.p.m. and a representative fuel inventory of 300 tons, or a π of about 2, this would amount to about 1.0% reactor poisoning. The numerical values in the flow sheet are based on the following four assumptions: (*a*) there is no entrainment; (*b*) partition coefficients for F.P.S.'s and U between salt and metal phases are constant over concentration ranges involved; (*c*) all F.P.S.'s have the same partition coefficients; (*d*) the separation factor, as defined above is the same for all extraction columns and equals 100. The individual values for the F.P.S. and U partition coefficients between salt and metal phases depends on the buffering action, and therefore the concentration, of the magnesium in the metal. The process outlined in Figure 3 does not represent a careful optimization of the several operating variables but is nevertheless believed to be typical as far as indicated sizes, concentrations, and flow rates are concerned.

Columns 1, 2, and 3 are countercurrent extraction columns of 3.9, 4.1, and 4.5 equilibrium stages, respectively. They could all be spray columns in which the liquid-metal fuel fell in the form of fine droplets through the slowly rising salt. The columns should preferably contain some baffling to prevent vertical mixing of the salt. Viscosity, interfacial tension, and density conditions are such as to make the bismuth-salt system a good one for this type of operation. Carryover, or entrainment, as judged on the basis of small-scale laboratory experiments, should be negligible. The relative velocity of the falling metal with respect to the rising salt should be about 2 ft./sec. This, together with the fact that the flowing streams are very small, means that the diameters of the columns are also very small. For example, column 1, the largest, would need to be no more than 3 or 4 in. in diameter. The heights of the columns will depend on their efficiencies and the separations required, but in any case it is expected that they would not need to be much taller than 3 ft. The height of column equivalent to a theoretical stage has not been experimentally determined but has been estimated on the basis of mercury-water heat transfer in spray columns, use being made of the analogy between heat and mass transfer. Rates of approach to equilibrium in bismuth-salt systems at 500°C. are found to be extremely rapid in small-scale batch experiments. Generally speaking, diffusivities in liquid-metal and fused-salt

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*R. E. = Rare earth.

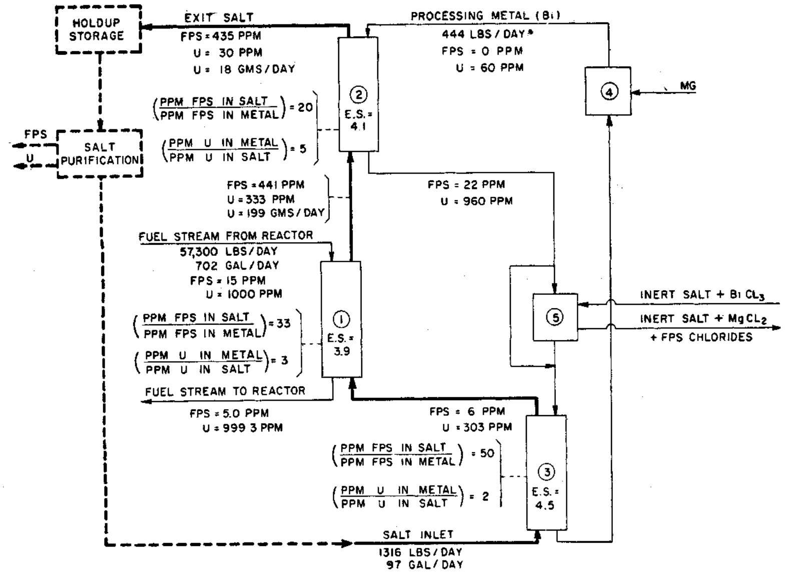

Fig. 3. Proposed flow sheet for F.P.S. removal from L.M.F.R. fuel by use of buffer method.

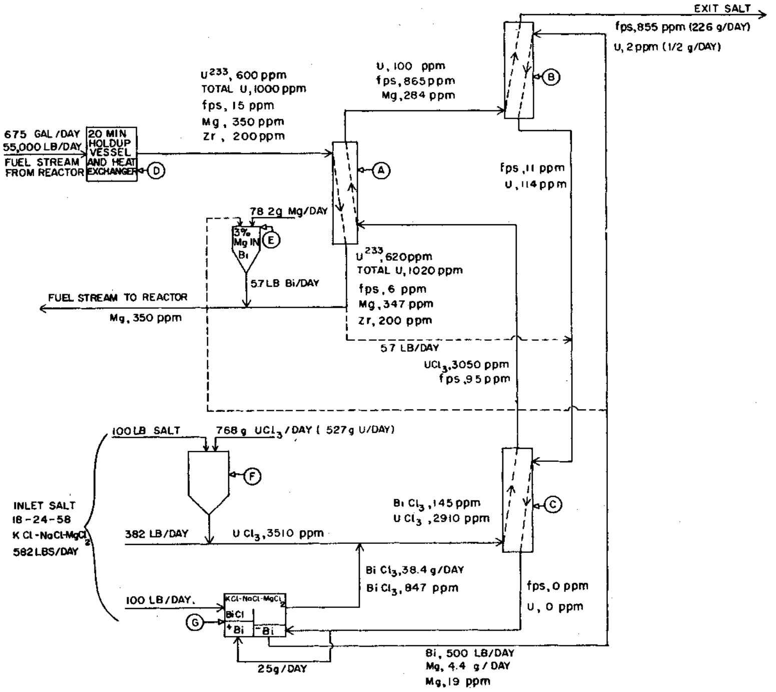

Fig. 4. Proposed flow sheet for F.P.S. removal from L.M.F.R. fuel by use of stoichiometric method.

systems at this temperature are high in comparison with those in ordinary liquids.

In column 1 the fission products are extracted from the fuel; in column 2 the uranium is recovered from the salt leaving column 1; and in column 3 the uranium is recovered from the processing metal stream by the incoming salt. The same salt stream passes through all three columns. The partition coefficients, indicated on the flow sheet, are varied among all three columns by changing of the oxidation-reduction potential in each by variation of the Mg concentration in the metal phase. It is estimated that the Mg concentrations in columns 1, 2, and 3 should be about 50, 65, and 35 p.p.m., respectively. Column 2 is more reductive than 1 to promote transfer of uranium to the metal phase, and column 3 is more oxidative than 1 to promote transfer of uranium to the salt. Units 4 and 5 on the flow sheet are for adding Mg to, and removing Mg from, the processing metal stream, respectively, to give the desired partition coefficients in columns 2 and 3. The Mg could be added by means of an electrochemical cell in which Mg and Bi are the anode and cathode, respectively, and in which the salt bridge could consist of the ternary KCl–NaCl–$MgCl_2$. Or the Mg could be added mechanically in the form of a bismuth solution. Item 5 is a salt-metal contactor in which sufficient $BiCl_3$ is added to the carrier salt to oxidize the desired fraction of the magnesium without oxidizing a significant amount of uranium. This operation would probably be done on a batch basis, owing to the very small flow rate of the processing metal stream.

After leaving column 1, the salt must be cooled to remove decay heat; but heat exchangers have not been included in the figure for the sake of simplicity. Heat release from the F.P.S.'s will be discussed briefly in a later section. The dashed portion of the flow sheet in Figure 3 is simply a schematic representation of the salt-decontamination step as it relates to the main processing plant.

Use of the Stoichiometric System

A second flow sheet for a proposed L.M.F.R. fuel-processing plant, based on the stoichiometric chemical system, is shown in Figure 4. From an engineering standpoint, the two flow sheets are similar. The second flow sheet is based upon a 500-Mw. heat rate with U^{233} as the fissile material.

With reference to the figure, the fuel from the reactor is first held up in a heat exchanger *D* to allow the fission products to "cool off" before flowing through extraction column *A*. In this column approximately two thirds of the F.P.S.'s are removed from the fuel; but before it is returned to the reactor, its Mg concentration is brought up to its original value by the addition about once daily of a 3% solution of Mg in bismuth. The UCl_3 carried in the salt from column *A* is nearly all recovered in column *B* by contacting the salt with a Mg–Bi solution. The uranium, accompanied by a small amount of F.P.S.'s, is recovered from the metal stream leaving column *B* by contacting it with the incoming salt in column *C*. The electrochemical cell *G* introduces $BiCl_3$ into the inlet salt stream and magnesium into the processing metal stream in the proper stoichiometric quantities to accomplish the two-step transfer of the uranium from the out-going salt to the in-going salt. Uranium chloride is added to the salt stream from mixing tank *F* at the required rate to supply the necessary U make-up to the fuel stream. In other words, UCl_3 as the oxidant in the salt simultaneously removes the fission products from, and adds U to, the fuel. The stoichiometric quantities are such that a small amount of Mg must be oxidized along with the F.P.S.'s in order to add the required amount of uranium. The UCl_3 addition of 768 g./day does not include the U make-up required for neutron capture by the U. If it is not desired to add the uranium to the fuel by this method, then the oxidant would be $BiCl_3$.

In the stoichiometric system a typical carrier salt would be the NaCl–KCl–$MgCl_2$ eutectic. The salt stream, of course, becomes very radioactive and must be cooled. As in

Figure 3, the heat exchangers for this have been omitted. It is pointed out again that the numerical values shown in Figure 4 are not the result of careful economic optimization but are nevertheless believed to be fairly representative of commercial operation.

It will be noticed that the flow rates shown in Figures 3 and 4 are very small, an indication that the equipment is correspondingly small. The largest conduit lines need to be no greater than ¼ in. in diameter and the largest contactor column 3 in. in diameter. The small equipment, which is mainly a consequence of the facts that the operation is continuous and that the chemistry is nonaqueous, means that the shielding required, though thick, is not expensive. From the standpoint of investment costs, instrumentation and control equipment will be major items. It is expected that electrochemical cells can be used for adding small amounts of solutes to both salt and metal streams and that electromotiveforce cells can be used for control of concentrations of critical materials. At Brookhaven both the austenitic type-347 and the ferritic 400-series stainless steels have been used with good success, as long as the systems are quite oxygen free. As Table 6 shows, the chlorides of iron, chromium, and nickel are at the bottom of the list, an indication of their relatively low tendency of formation. Pretreatment and conditioning of equipment before use includes such operations as electropolishing, degassing under high vacuum at temperatures in the neighborhood of 800°C., and contacting with magnesium-bismuth solutions. It is essential that the equipment and piping be absolutely gas tight. This calls for either canned-rotor or canned-motor pumps and bellows-sealed valves and pressure transmitters.

Since the average residence time of the F.P.S.'s in the reactor would probably be only a few days, they are very radioactive at the time of their removal and provide an excellent source of high-intensity ionizing radiation. For an average residence time of 20 days, it is estimated that the specific activity of the F.P.S.'s may be as high as 50,000 to 100,000 curies/g., depending upon their holdup time after removal. The radiation capacity associated with the F.P.S.'s dissolved in the fused salt in a large L.M.F.R. plant, say one of 500 to 1,000 Mw. heat rate, could be as great as several million curies. Moreover, since the F.P.S.'s are dissolved in the molten salt, they are in an easily handlable form. Thus, it is assumed that high-intensity gamma-radiation facilities would be an integral part of a commercial L.M.F.R. power plant.

After a suitable storage period, the salt can be purified for reuse. Complete decontamination, however, is unnecessary. The F.P.S.'s can be removed from the salt by contacting it with liquid lead containing a strong reductant like magnesium or calcium and they can then be removed from the lead by direct oxidation with an air stream. Alternatively, they may be left in the lead for indefinite storage.

Presumably, in the stoichiometric scheme the salt could be used over and over again with just "cooling" between cycles. What limits the concentration of F.P.S.'s in the salt during each pass through the plant is simply the resulting heat-generation rate per unit volume of salt.

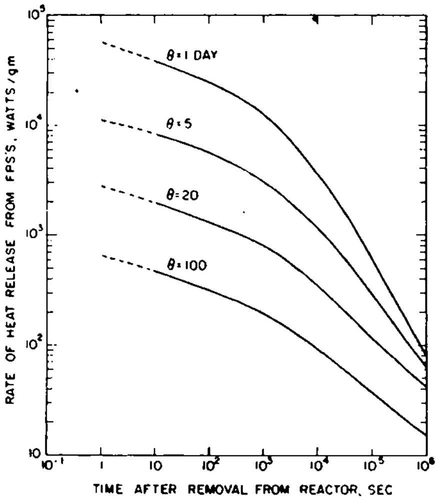

Fig. 5. Energy release from F.P.S.'s.

HEAT RELEASE FROM FISSION PRODUCTS

An important consideration in the design of processes and equipment for handling radioactive fission products is the problem of heat removal. This is particularly true in the present case, because of the relatively short age of the fission products at the time of their extraction from the fuel. However, heat removal from fused salts does not present a difficult problem.

Figure 5 shows a family of curves giving the specific heat rates for the F.P.S.'s as a function of average residence time in the reactor and time after removal therefrom. The curves were calculated from fission-product heat-release data obtained from the Argonne National Laboratory (*5*). Extrapolations to short decay times were made with the aid of the Way-Wigner (*6*) expression for fission-product–decay heat.

In Figure 4 the exit salt from Column *A* contains 865 p.p.m. of F.P.S.'s which have been held up 20 min. after removal from the reactor. Assuming a typical fuel inventory of 300 tons, the average residence time of the F.P.S.'s in the fuel will be about 18 days. From Figure 5 it is seen that the specific heat release for the F.P.S. under these conditions will be about 850 watts/g. This amounts to a total energy release of about 130,000 B.t.u./(hr.)(cu. ft. of salt). Had the F.P.S. concentration in the fuel been 5 p.p.m., the corresponding figure would be about 400,000 B.t.u./(hr.)(cu. ft. of salt). The energy will be divided about equally between beta and gamma radiation. The former energy will be liberated as heat at essentially the point of liberation, but the fraction of the gamma energy converted to heat in the heat exchanger will depend upon design of the exchanger and density of the coolant.

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NOTATION

f = fraction of uranium atoms fissioning to a particular mass chain
g = breeding ratio, atoms of fissile material produced per atom of fissile material burned
k = (atoms F.P.S./cc in exit salt)/(atoms F.P.S./cc. in fuel)
N = concentration of a given nuclide in fuel, atoms/cc.
N_p = concentration of parent nuclide in radioactive decay, atoms/cc.
N_t = concentration of target nuclide in neutron capture, atoms/cc.
N^{235} = concentration of U^{235}, atoms/cc.
p = percentage of poisoning, defined by Equation (10)
P = thermal power of reactor, Mw.
t = time, sec.
t_r = average residence time of N in fuel, sec.
V_c = fuel volume in core, cc.
V_t = fuel volume in reactor system, cc.
W_s = salt flow rate, g./sec.
η = number of neutrons produced per thermal neutron absorbed in uranium
θ = average residence time in fuel, days
λ = radioactive decay constant for N, $sec.^{-1}$
λ_p = radioactive decay constant for parent nuclide, $sec.^{-1}$
π = power density, Mw. of heat per ton of fuel
ρ_s = salt density, g./cc.
σ = thermal-neutron cross section for N, barns
σ_t = thermal-neutron cross section for target nucleus, barns
σ_{5a} = thermal-absorption cross section for U^{235}, barns
σ_{5f} = thermal-fission cross section for U^{235}, barns
ϕ = thermal-neutron flux, neutrons/(sq. cm.)(sec.)

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