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CONSOLIDATION OF LANTHANON FISSION PRODUCTS IN ALLOYS

by

J. B. Knighton, R. A. Mancini,
and R. K. Steunenberg

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CONSOLIDATION OF LANTHANON FISSION PRODUCTS IN ALLOYS

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SUMMARY

In certain pyrochemical processes for the reclamation of irradiated nuclear fuels, the lanthanon (rare earth) fission products are collected in a molten chloride salt. The feasibility of extracting the lanthanon elements from the salt into binary magnesium alloys which could serve as a medium for both interim and permanent disposal, and possibly as a useful source of heat and activity, was investigated. The salt composition selected was the ternary system 50 m/o MgCl_2 -30 m/o NaCl -20 m/o KCl (m.p. 396°C). Distribution coefficients of praseodymium, a representative lanthanon fission product, were determined between the molten salt and liquid binary alloys of magnesium with aluminum, copper, lead, antimony, and nickel. The results were compared with earlier praseodymium distribution data for magnesium-cadmium and magnesium-zinc alloys and the same salt. Since the most favorable distribution coefficients were obtained with the magnesium-aluminum system, it was selected for further study.

Distribution coefficients of yttrium, lanthanum, cerium, and praseodymium between the salt and magnesium-aluminum alloys were determined, and their solubilities in the liquid-metal phase were measured at various temperatures and magnesium concentrations. The results indicated that an aluminum-20 w/o magnesium alloy provides excellent removal of lanthanons from the salt in a single-stage extraction. The technique also appears to be applicable to fission product oxide and fluoride wastes, and to the consolidation of noble and refractory metal fission products, as well as lanthanons, in metallic alloys.

I. INTRODUCTION

Pyrochemical processes that utilize liquid-metal-molten salt extraction techniques for the basic separations are being developed for the reclamation of irradiated reactor fuels. Such processes involve the separation of uranium and plutonium or of uranium and thorium from each other and from fission products. Among those fission products to be removed are yttrium and lanthanon (rare earth) elements, which are extracted into a molten salt, such as the 50 m/o MgCl_2 -30 m/o NaCl -20 m/o KCl used in this study.

Earlier studies had indicated the possibility of extracting the lanthanon fission products from the salt into a magnesium alloy, thereby consolidating much of the activity in a compact metallic ingot that should be suitable for interim and permanent disposal, and possibly for interim use as a convenient source of fission product heat and activity. The purified salt could then be recycled to the process.

The objective of this investigation was to determine the effectiveness of various binary magnesium alloys that have a liquid region at 600°C for the extraction of yttrium and lanthanons from the above-mentioned salt. The efficacy of the separation was determined by measuring distribution coefficients of several lanthanons in the salt-metal systems. The distribution coefficient was defined* as

$$K_d = \frac{w/o \text{ lanthanon in salt}}{w/o \text{ lanthanon in metal}} \quad (1)$$

It is also desirable that the magnesium alloy have a high thermal conductivity for heat dissipation, be reasonably noncorrosive and corrosion-resistant, and be inexpensive in order to serve as a satisfactory medium for waste disposal.

In the initial studies, praseodymium was selected as a representative lanthanon fission product element for measurements of distribution coefficients between the molten chloride salt and various binary magnesium alloys. Since the initial results indicated the aluminum-magnesium system to be the most promising, distribution coefficients for yttrium, lanthanum, cerium, and praseodymium were measured between this alloy and the molten chloride salt. Yttrium, although not a lanthanon, was included because it is a relatively high-yield fission product and its chemical properties resemble those of the lanthanons. For analytical convenience, the materials were neutron irradiated to form Y^{90} , La^{140} , Ce^{141} , and Pr^{142} , which were determined by gamma-ray spectrometry.

II. THEORY

The equilibrium that determines the distribution of a lanthanon fission product between a liquid-metal phase containing magnesium and a magnesium chloride-bearing molten salt can be described by the following reaction:

*It is also possible to define the distribution coefficient on a mole fraction basis for theoretical purposes, where $K_d = \frac{\text{mole fraction lanthanon in salt}}{\text{atom fraction lanthanon in metal}}$. Unless indicated otherwise, the weight basis has been used in this report because of its greater convenience in process calculations.

where M represents the lanthanon metal. The equilibrium constant is then

$$K_{eq} = a_{Mg}^{3/2} a_{MCl_3} / a_{MgCl_2}^{3/2} a_M, \quad (3)$$

where a is the activity of the substance in its respective salt or metal phase. In terms of activity coefficients γ and mole fractions x the expression becomes

$$K_{eq} = \frac{x_{Mg}^{3/2} x_{MCl_3} \gamma_{Mg}^{3/2} \gamma_{MCl_3}}{x_{MgCl_2}^{3/2} x_M \gamma_{MgCl_2}^{3/2} \gamma_M}. \quad (4)$$

For a fixed temperature and solvent salt composition, and at low concentrations of MCl_3 in the salt phase, x_{MgCl_2} , γ_{MgCl_2} , and γ_{MCl_3} may be assumed to be approximately constant. Therefore, let

$$A = \gamma_{MCl_3} / x_{MgCl_2}^{3/2} \gamma_{MgCl_2}^{3/2}. \quad (5)$$

Then

$$K_{eq} = A \left[\frac{x_{Mg}^{3/2} x_{MCl_3} \gamma_{Mg}^{3/2}}{x_M \gamma_M} \right]. \quad (6)$$

When the distribution coefficient K_d is defined on a mole fraction basis as

$$K_d' = x_{MCl_3} / x_M, \quad (7)$$

we have

$$K_{eq} = A K_d' [x_{Mg}^{3/2} \gamma_{Mg}^{3/2} / \gamma_M] \quad (8)$$

and

$$K_d' = \frac{K_{eq}}{A} \left[\frac{\gamma_M}{x_{Mg}^{3/2} \gamma_{Mg}^{3/2}} \right]. \quad (9)$$

For a given lanthanon and a specified temperature, K_{eq} has a constant value determined by the free energy change of reaction (2):

$$\Delta F^\circ = -RT \ln K_{eq}. \quad (10)$$

Since A is also essentially constant, it is evident from Eq. (9) that the distribution coefficient of a lanthanon between the magnesium alloy and 50 m/o $MgCl_2$ -30 m/o $NaCl$ -20 m/o KCl will depend primarily upon the magnesium concentration in the alloy and the activity coefficients of magnesium and the lanthanon metal in the alloy.

Previous work¹ had shown that the activity coefficients of lanthanons and actinide elements in binary alloys of magnesium with zinc and cadmium deviate widely from ideality. Furthermore, the activity coefficients of these elements, as well as that of magnesium, are strongly influenced both by the magnesium concentration and the particular metal used as a diluent for the magnesium. Therefore, in order to find a system in which lanthanon fission products would be extracted efficiently from the salt, the experimental work was directed toward various binary alloys of magnesium.

III. EXPERIMENTAL PROCEDURE

The experiments were conducted in a tantalum crucible which was placed within a secondary container of graphite and located inside a resistance-heated stainless steel furnace tube. The temperature was measured by means of a thermocouple inserted into a thermowell which extended into the melt. Stirring was provided by a motor-driven tantalum paddle, and the tantalum crucible was equipped with internal baffles to enhance mixing of the liquid-metal and molten salt phases. Samples of the two liquid phases were withdrawn by pressurizing the interior of the furnace sufficiently with argon to force the liquid up into a sample tube whose end was immersed in the melt. The samples were taken in 1/4-in. tantalum tubes fitted with sintered tantalum filters. All components of the equipment exposed to the liquid metal and molten salt were constructed of tantalum, and an argon atmosphere was maintained over the melt at all times.

The distribution coefficients were determined by radiochemical analyses of the filtered salt and metal samples. The lanthanon under investigation was activated by neutron irradiation and added to a charge consisting of the binary magnesium alloy and 50 m/o MgCl_2 -30 m/o NaCl -20 m/o KCl . The charge was then heated to the desired temperature and allowed to equilibrate with mixing. The distribution coefficient, on a weight basis, was then obtained as

$$K_d = \frac{\text{cpm/g salt}}{\text{cpm/g metal}}$$

To determine the corresponding lanthanon concentrations involved, specific-activity determinations were made with control samples of the radioactive materials.

IV. EXPLORATORY STUDIES

Several exploratory experiments were performed to determine the distribution of praseodymium between various binary alloys of magnesium and 50 m/o MgCl_2 -30 m/o NaCl -20 m/o KCl . In order to conduct the experiments at the desired temperature of 600°C , it was necessary to restrict the choice of binary alloys to those having a liquid region at that temperature. On the other hand, it is desirable for the alloy to have a sufficiently high melting point to remain solid in the presence of considerable decay heat of the fission products. Five systems were selected for study: the binary alloys of magnesium with aluminum, copper, lead, antimony, and nickel. The experimental results, together with distribution data from previous studies² with cadmium and zinc alloys of magnesium, are listed in Table 1. The data are also presented in graphical form in Fig. 1.

TABLE 1. Distribution of Praseodymium between 50 m/o MgCl_2 -30 m/o NaCl -20 m/o KCl and Selected Binary Magnesium Alloys at 600°C

Metal Phase		Salt Phase	Distribution Coefficient ^a (K _d)
Mg Conc (w/o)	Pr Conc (w/o)	Pr Conc (w/o)	
<u>Aluminum-Magnesium</u>			
13.0	1.77	8.72 x 10 ⁻⁴	4.93 x 10 ⁻⁴
16.3	1.57	6.42 x 10 ⁻⁴	4.09 x 10 ⁻⁴
27.9	1.41	7.24 x 10 ⁻⁴	5.13 x 10 ⁻⁴
35.4	1.26	1.06 x 10 ⁻³	8.41 x 10 ⁻⁴
45.2	1.11	1.81 x 10 ⁻³	1.63 x 10 ⁻³
53.6	0.967	2.89 x 10 ⁻³	2.99 x 10 ⁻³
65.3	0.523	6.18 x 10 ⁻³	1.18 x 10 ⁻²
<u>Cadmium-Magnesium</u>			
0.029	0.0014	0.464	334
0.80	0.0259	0.374	14.4
3.60	0.0983	0.253	2.57
7.14	0.131	0.197	1.50
11.4	0.142	0.188	1.32
17.1	0.134	0.198	1.48
23.8	0.112	0.217	1.94
64.7	0.0876	0.372	4.25
49.4	0.0969	0.311	3.21
32.9	0.106	0.248	2.34
24.9	0.109	0.206	1.89

TABLE 1 (Contd.)

Metal Phase		Salt Phase	Distribution Coefficient ^a (K _d)
Mg Conc (w/o)	Pr Conc (w/o)	Pr Conc (w/o)	
<u>Copper-Magnesium</u>			
33.5	0.0120	1.31	109.2
39.9	0.0193	1.28	66.3
49.7	0.0335	1.24	37.0
59.5	0.0428	1.19	27.8
69.8	0.0500	1.10	22.0
<u>Nickel-Magnesium</u>			
72.3	0.0352	0.501	14.2
85.0	0.0343	0.467	13.6
<u>Lead-Magnesium</u>			
5.00	0.204	0.0513	0.251
9.60	0.455	0.0605	0.133
19.6	0.583	0.0653	0.112
30.1	0.465	0.184	0.396
39.2	0.372	0.289	0.777
49.4	0.292	0.375	1.28
<u>Antimony-Magnesium</u>			
2.96	0.363	8.88 × 10 ⁻⁴	2.45 × 10 ⁻³
2.94	0.383	9.94 × 10 ⁻⁴	2.60 × 10 ⁻³
<u>Zinc-Magnesium</u>			
0.02	0.0007	0.959	~1400
2.77	0.0386	0.0030	0.0788
8.72	0.0405	0.0024	0.0602
15.0	0.0756	0.0055	0.0726
21.6	0.246	0.0369	0.150
24.8	0.400	0.0738	0.185
36.6	0.292	0.162	0.555
84.4	0.198	0.730	3.69
76.9	0.203	0.662	3.26
59.7	0.295	0.520	1.76
46.7	0.358	0.336	0.940
35.1	0.380	0.163	0.429
26.0	0.321	0.0960	0.299
20.2	0.236	0.0528	0.224

^a Distribution Coefficient, $K_d = \frac{\text{w/o Pr in salt}}{\text{w/o Pr in metal}}$

Fig. 1. Distribution of Praseodymium between 50 m/o MgCl_2 -30 m/o NaCl -20 m/o KCl and Binary Magnesium Alloys at 600°C

nesium, with a minimum melting point of 579°C at approximately 3.2 w/o magnesium. Duplicate determinations of the distribution coefficient for praseodymium were made at a magnesium concentration of 3.2 w/o and a temperature of 600°C . The results (see Fig. 1) showed praseodymium distributing strongly to the metal phase, with a distribution coefficient of 2.45×10^{-3} . This low value suggests that the antimony-magnesium system might also be considered as a medium for the extraction of lanthanon fission products from process salt.

C. Lead-Magnesium

The liquid region in the lead-magnesium system at 600°C extends from 0 to about 60 w/o magnesium. The distribution coefficient curve for praseodymium over this range is also presented in Fig. 1. This curve lies close to one obtained earlier with the zinc-magnesium system.² Its potential usefulness for the purification of recycled salt appears to be minimal.

A. Aluminum-Magnesium

At 600°C the aluminum-magnesium system has a liquid region over the range from about 12 to 90 w/o magnesium. The distribution coefficient measured for praseodymium in this range of composition are shown in Fig. 1. The praseodymium distributed very strongly to the metal phase, with a minimum value of 4.5×10^{-4} at about 20 w/o magnesium. The aluminum concentration in the salt averaged 3.4×10^{-3} w/o, corresponding to a distribution coefficient of about 4×10^{-5} between the salt and the aluminum-20 w/o magnesium alloy. These results indicate that an aluminum-20 w/o magnesium alloy would provide excellent removal of lanthanon fission products from recycled salt in a single-stage extraction without significant contamination of the salt by aluminum.

B. Antimony-Magnesium.

The liquid region in the antimony-magnesium system at 600°C is limited to a narrow range between about 1.7 and 3.7 w/o mag-

D. Copper-Magnesium

The copper-magnesium system possesses good to excellent properties as a medium for waste disposal from the standpoint of melting point, thermal conductivity, corrosion resistance, and a wide liquid range

from 32 to 86 w/o magnesium at 600°C. However, as the curve in Fig. 1 indicates, praseodymium in this system distributed strongly to the salt phase. This behavior precludes its direct use for the extraction of lanthanon fission products from recycled salt.

Fig. 2. Distribution of Praseodymium and Plutonium between 50 m/o MgCl_2 -30 m/o NaCl -20 m/o KCl and Copper-Magnesium Alloys

The copper-magnesium system does appear attractive, however, as a potential means of separating lanthanon fission products from plutonium. Distribution coefficient curves for plutonium² and praseodymium at 600°C are compared in Fig. 2. Separation factors $[K_d(\text{Pr})/K_d(\text{Pu})]$ as high as 240 are available in this system, which may provide an adequate separation of lanthanon fission products from plutonium in a single-stage extraction. This possibility is being investigated further, but these studies are outside the scope of this report.

E. Nickel-Magnesium

This system has a liquid region between about 72 and 88 w/o

magnesium at 600°C. As in the copper-magnesium system, praseodymium distributed to the salt phase (see Fig. 1). The distribution coefficient was also determined at a higher temperature (800°C) with 80 w/o magnesium in the metal phase. At this magnesium concentration the distribution coefficient for praseodymium decreased from 13.8 at 600°C to 8.23 at 800°C.

The marked effect of composition of the metal phase on the distribution of praseodymium between the salt and metal was evident from the results of this study. As illustrated in Fig. 1, the distribution coefficient varied by 10^4 to 10^5 with changes in the magnesium concentration in the liquid-metal phase and with the different binary magnesium alloy systems. The praseodymium distribution coefficient curves should of necessity

converge at a common point at a magnesium concentration of 100%. However, the point of convergence has only a theoretical meaning under these conditions, since the experiments were conducted at 600°C and the melting point of pure magnesium is 650°C. The point was therefore estimated, as indicated by the dotted portions of the curves in Fig. 1.

As suggested by Eq. (4), it is also possible to alter distribution coefficients through variations in the composition of the molten salt phase (primarily in the MgCl_2 concentration). In general, the distribution coefficients become larger with increasing MgCl_2 concentration.

Of the binary alloys of magnesium investigated, the aluminum-magnesium system showed the greatest promise for the removal of lanthanon fission products from recycled salt. The antimony-magnesium system appeared to be a possible alternative. On the basis of these results, the aluminum-magnesium system was selected for further study.

V. STUDIES OF THE ALUMINUM-MAGNESIUM SYSTEM

A series of experiments was undertaken to determine the distribution behavior of several major lanthanon fission product elements: yttrium, lanthanum, cerium, and praseodymium at various temperatures and magnesium concentrations in the aluminum-magnesium system. Sufficient amounts of the elements were added to the system to saturate the liquid-metal phase, so that their solubilities could be determined at the same time from the filtered samples of the metal. The magnesium concentrations were limited to the region of about 13 to 30 w/o in the metal phase. In all experiments the salt was 50 m/o MgCl_2 -30 m/o NaCl -20 m/o KCl . The analytical results from this investigation are listed in Table 2.

TABLE 2. Solubilities of Selected Group III Elements in Aluminum-Magnesium Alloys and Their Distribution between 50 m/o MgCl_2 -30 m/o NaCl -20 m/o KCl and Aluminum-Magnesium Alloys

Temperature		Metal Phase			Salt Phase	Distribution Coefficient ^c (K _D)
(°C)	(10 ⁴ /T°K)	Al Conc ^a (w/o)	Mg Conc (w/o)	Ln Solubility ^b (w/o)	Ln Conc ^b (w/o)	
Yttrium						
875	8.71	78.8	11.1	10.1	0.538	5.33 × 10 ⁻²
800	9.32	78.1	11.4	10.5	0.315	3.00 × 10 ⁻²
600	11.45	83.9	12.7	3.45	0.0151	4.38 × 10 ⁻³
800	9.32	72.1	18.7	9.20	0.233	2.53 × 10 ⁻²
700	10.28	75.0	19.4	5.62	0.0565	1.01 × 10 ⁻²
600	11.45	77.5	21.0	1.50	0.00850	5.67 × 10 ⁻³
550	12.15	78.0	21.1	0.91	0.00211	2.32 × 10 ⁻³
650	10.83	76.6	20.5	2.87	0.434	1.51 × 10 ^{-2d}
750	9.77	73.3	20.4	6.29	0.125	1.99 × 10 ⁻²
600	11.45	64.9	34.5	0.65	0.00671	1.03 × 10 ⁻²

TABLE 2 (Contd.)

Temperature		Metal Phase			Salt Phase	Distribution
(°C)	($10^4/T^{\circ}\text{K}$)	Al Conc ^a (w/o)	Mg Conc (w/o)	Ln Solubility ^b (w/o)	Ln Conc ^b (w/o)	Coefficient ^c (K_d)
<u>Lanthanum</u>						
800	9.32	78.2	10.9	10.9	0.403	3.70×10^{-2}
900	8.52	78.9	11.3	9.78	0.732	7.48×10^{-2}
600	11.45	84.1	11.2	4.65	0.0327	7.03×10^{-3}
600	11.45	74.9	21.7	3.43	0.0189	5.51×10^{-3}
700	10.28	72.9	19.9	7.18	0.109	1.52×10^{-2}
800	9.32	73.7	20.7	5.62	0.201	3.58×10^{-2}
750	9.77	74.2	20.0	5.76	0.102	1.77×10^{-2}
650	10.83	77.1	18.3	4.55	0.0525	1.15×10^{-2}
550	12.15	76.1	21.7	2.23	0.00630	2.83×10^{-3}
600	11.45	61.7	36.0	2.32	0.0215	9.27×10^{-3}
<u>Cerium</u>						
900	8.52	82.0	9.20	8.80	0.150	1.70×10^{-2}
800	9.32	79.7	11.4	8.89	0.0653	7.35×10^{-3}
600	11.45	82.1	12.7	5.18	0.00337	6.51×10^{-4}
600	11.45	76.2	20.5	3.27	0.00232	7.09×10^{-4}
700	10.28	72.8	18.9	8.26	0.0171	2.07×10^{-3}
800	9.32	73.6	18.4	8.02	0.0546	6.81×10^{-3}
750	9.77	71.3	19.9	8.81	0.0357	4.05×10^{-3}
650	10.83	75.1	20.1	4.82	0.00670	1.39×10^{-3}
550	12.15	76.8	21.0	2.24	0.000944	4.21×10^{-4}
600	11.45	65.4	32.4	2.24	0.00263	1.17×10^{-3}
<u>Praseodymium</u>						
887	8.62	79.6	11.8	8.64		
800	9.32	79.9	11.2	8.88		
600	11.45	82.7	12.4	4.93		
600	11.45	76.7	19.4	3.91		
700	10.28	74.7	18.0	7.34		
800	9.32	76.9	17.3	5.83		
750	9.77	74.2	18.0	7.77		
650	10.83	75.1	19.1	5.81		
550	12.15	77.3	20.2	2.53		
600	11.45	68.1	29.7	2.19		

^aBy difference.^bThe symbol Ln represents the lanthanon element under investigation, i.e., Y, La, Ce, and Pr.^cDistribution coefficient, $K_d = \frac{\text{cpm/g salt}}{\text{cpm/g metal}}$ or $\frac{\text{w/o in salt}}{\text{w/o in metal}}$.^dQuestionable value.A. Yttrium

The data for the distribution of yttrium are shown in Fig. 3, where the logarithm of the distribution coefficient is plotted against $10^4/T(^{\circ}\text{K})$. The distribution coefficient increased with rising temperature. Thus, low temperatures favor the extraction of yttrium from the process salt. Although the distribution coefficient of yttrium was approximately the same in 12 and 20 w/o magnesium, it increased about twofold when the magnesium concentration was raised to 34 w/o.

Fig. 3. Distribution of Yttrium between 50 m/o MgCl_2 -30 m/o NaCl -20 m/o KCl and Aluminum-Magnesium Alloys

In addition to the temperature dependence of yttrium solubility in aluminum-magnesium alloy, Fig. 4 also indicates that the solubility increased with decreasing magnesium concentration.

B. Lanthanum

The distribution coefficients and solubilities for lanthanum are shown in Figs. 5 and 6. The variations with temperature and magnesium concentration in the metal phase proved to be similar to those found for yttrium. The solubility in aluminum-20 w/o magnesium alloy reached a maximum of 7 w/o at about 700°C and exhibited retrograde behavior at higher temperatures.

C. Cerium

As indicated in Figs. 7 and 8, the distribution coefficients and solubilities of cerium showed the same general pattern observed for yttrium and lanthanum. The distribution coefficients, however, were about an order of magnitude lower (7.1×10^{-4} at 600°C and 20 w/o magnesium, as compared to 4.3×10^{-3} for yttrium and 6.0×10^{-3} for lanthanum under

The solubility of yttrium, presented in Fig. 4 as a function of temperature and magnesium concentration, increased with rising temperature to a maximum (in the 20 w/o magnesium system) of about 10 w/o in the vicinity of 750°C. At higher temperatures, the solubility showed retrograde behavior, decreasing with rising temperature. This phenomenon had been observed in other systems (e.g., uranium in cadmium solutions³) in which different solid phases were in equilibrium with the saturated solution at different temperatures.

Fig. 4. Solubility of Yttrium in Aluminum-Magnesium Alloys

the same conditions). The maximum solubility of cerium was about the same as that for yttrium (10 w/o in aluminum-20 w/o magnesium at approximately 725°C).

Fig. 5. Distribution of Lanthanum between 50 m/o MgCl_2 -30 m/o NaCl -20 m/o KCl and Aluminum-Magnesium Alloys

Fig. 6. Solubility of Lanthanum in Aluminum-Magnesium Alloys

Fig. 7. Distribution of Cerium between 50 m/o MgCl_2 -30 m/o NaCl -20 m/o KCl and Aluminum-Magnesium Alloys

Fig. 8. Solubility of Cerium in Aluminum-Magnesium Alloys

D. Praseodymium

A similar experiment was performed with praseodymium. The preliminary results showed the distribution coefficients to be about an order of magnitude higher than those that had been determined previously (see Fig. 1). It was discovered, however, that the source of praseodymium used had been slightly contaminated with lanthanum, which has a higher distribution coefficient.

Fig. 9. Solubility of Praseodymium in Aluminum-Magnesium Alloys

between 50 m/o MgCl_2 -30 m/o NaCl -20 m/o KCl and aluminum-magnesium alloy as a function of temperature. The distribution coefficients for yttrium, lanthanum, and cerium were obtained under conditions in which the liquid metal was saturated with the element throughout the temperature range of the measurements. Although the praseodymium data were not obtained at saturation, other work⁴ has shown that the distribution coefficient is not affected by this condition.

The effects of magnesium concentration and temperature on the solubilities of these four elements in aluminum-magnesium alloys are summarized in Figs. 11 and 12, respectively. Lanthanum, cerium, and praseodymium showed much the same dependence of solubility on magnesium concentration, the solubility decreasing with rising magnesium concentration. This effect was somewhat more pronounced with yttrium. In aluminum-20 w/o magnesium, all four elements exhibited retrograde solubility at temperatures

The gamma energies are similar, making it difficult to discriminate during counting. Furthermore, the fact that La^{140} has a half-life of 40.2 hr, compared to 19.2 hr for Pr^{142} , accentuated the problem, as the samples were not counted until 3 to 5 days after irradiation. Because of this, the distribution coefficients of praseodymium are not reported. The solubilities of praseodymium, which would not be affected significantly by the La^{140} contamination, are presented in Fig. 9.

Figure 10 summarizes the distribution coefficient data for yttrium, lanthanum, cerium, and praseodymium

Fig. 10. Distribution of Yttrium, Lanthanum, Cerium, and Praseodymium between 50 m/o MgCl_2 -30 m/o NaCl -m/o KCl and Aluminum-20 w/o Magnesium Alloy

above about 700 to 750°C. The solubilities of lanthanum, cerium, and praseodymium were similar for temperatures below the retrograde region. The solubility of yttrium decreased more rapidly with decreasing temperature.

Fig. 11. Solubilities of Yttrium, Lanthanum, Cerium, and Praseodymium in Aluminum-Magnesium Alloys at 600°C

Fig. 12. Solubilities of Yttrium, Lanthanum, Cerium, and Praseodymium in Aluminum-20 w/o Magnesium Alloy

Low solubilities of yttrium and the lanthanon elements can lead to improved separations, since the solubility of the element in the liquid-metal solution can be exceeded without affecting the distribution coefficient. On the other hand, there is a question as to how much inhomogeneity of the final ingot can be tolerated in view of the localized fission product decay heat. Although the lanthanon element is precipitated as an intermetallic compound when the ingot is frozen, greater dispersion of the intermetallic compound throughout the solid ingot is likely to occur with higher solubility of the lanthanon in the liquid alloy.

VI. PREPARATION OF CERIUM-ALUMINUM-MAGNESIUM INGOT

In order to examine the nature of alloys produced by the lanthanon extraction procedure, an ingot composed of 10 w/o cerium, 20 w/o magnesium, and 70 w/o aluminum was prepared for metallographic and autoradiographic examination. A slice of the ingot was polished and etched. Figure 13 shows different portions of the specimen at 54X magnification. The large, columnar, needle-like crystals are presumably the cerium intermetallic compound, CeAl_4 .⁵

A section of the cerium-magnesium-aluminum alloy was then neutron irradiated in the Juggernaut reactor to produce radioactive Ce^{141} ($t_{1/2} = 32.5$ days). An autoradiograph of this section is shown at about 2X magnification in Fig. 14. The cerium is readily visible as needle-like deposits believed to be CeAl_4 . This intermetallic compound is reasonably

well dispersed in the magnesium-aluminum matrix, although some segregation is evident at the sides and bottom of the ingot.

Fig. 13. Sections of 10 w/o Cerium-20 w/o Magnesium-70 w/o Aluminum Alloy at 54X Magnification

Fig. 14. Autoradiograph of 10 w/o Cerium (Activated)-20 w/o Magnesium-70 w/o Aluminum Alloy at Approximately 2X Magnification

Other lanthanon elements would be expected to deposit in a similar manner in magnesium-aluminum alloy. The pattern of segregation may be different, however, for fission product lanthanons which would be generating significant amounts of fission product decay heat. Because of the high thermal conductivity of the matrix alloy, excessive localized heating would be reduced.

VII. DISCUSSION

The incorporation of fission product wastes in metals for storage and disposal is a natural outgrowth of the development of pyrochemical processes for irradiated fuels. Incorporation of fission products in a metallic matrix has several attractive features: (1) high fission product loadings should be feasible because of the high thermal conductivity and stability of the matrix, (2) the alloy is readily handled and can be cast as desired, (3) it may be possible to add other alloying agents to impart desirable properties, such as corrosion resistance toward ground water,

(4) the fission product wastes from a pyrochemical process, except the rare gases, the alkali and alkaline earths, the halogens, and samarium, can be incorporated into the metal,

(5) these alloys are suitable for both interim and permanent storage of fission product wastes, (6) utilization of fission product heat and radioactivity during interim cooling may be feasible.

Fig. 15. Calculated Power Densities of Lanthanum Fission Products in 20 w/o Magnesium-Aluminum Alloy

The loadings of lanthanum fission products that appear to be possible in magnesium-aluminum alloy are high enough to provide significant amounts of heat. Calculated power densities, in kilowatts per liter of alloy, for lanthanum fission products in an aluminum-20 w/o magnesium alloy are shown in Fig. 15 as a function of cooling time and lanthanum concentration. The calculations were based upon 2% burnup of the heavy atoms in a fuel (uranium

and plutonium) in a period of 135 days. The upper curve represents a lanthanum concentration of 100% and merely establishes the upper theoretical limit of power density. For a 10 w/o concentration of lanthanum in the alloy, the specific power ranges from about 0.1 to 1 kW/liter for cooling times of 1 to 2 yr. Higher power densities could be achieved by incorporating other fission products into the alloy and by using shorter cooling times. Heat and radiation sources of this type may be suitable for various special applications.

Alloys containing fission products could be cast directly into metal containers of suitable materials, size, and shape for heat removal and corrosion resistance during interim and ultimate storage.

This technique for the fixation of certain fission products in metallic alloys might be extended to calcined aqueous wastes and fluoride volatility wastes, since oxide and fluorides of most fission products are presumably reduced by aluminum-magnesium alloy in the presence of a suitable molten halide salt.

VIII. CONCLUSIONS

Aluminum-20 w/o magnesium alloy appears to be a very satisfactory medium for the extraction of yttrium and lanthanum fission products from 50 m/o MgCl_2 -30 m/o NaCl -20 m/o KCl used as a process salt. Large amounts of the salt can be purified for recycle by a single-stage contact

with the alloy because of the low distribution coefficients yttrium and the lanthanons exhibit in this system. The resulting aluminum contamination of the salt is less than 10^{-2} w/o.

The alloy is capable of containing relatively high concentrations of these fission product elements, and it has attractive properties for the fixation of wastes in a medium that is suitable for both interim and ultimate storage. It might also serve as a useful source of heat and radiation during the interim period before its permanent disposal.

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