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LIQUID METAL EXTRACTION OF LANTHANUM AND BARIUM FROM THE URANIUM-CHROMIUM EUTECTIC BY MAGNESIUM

Part I. - Solute Distribution

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Alan D. Pasternak and Donald R. Olander

Inorganic Materials Research Division, Lawrence Radiation Laboratory,
Department of Nuclear Engineering, College of Engineering,
University of California, Berkeley, California

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ABSTRACT

The distribution of lanthanum and barium between the immiscible solvents magnesium and the uranium-chromium eutectic has been studied at temperatures from 900 to 1100°C. The partitioning of lanthanum was determined by direct measurement of the activity of La^{140}. Barium distribution was inferred from the time dependence of the La^{140} activity after equilibration. The measured distribution coefficients were compared to the values calculated from regular solution theory.

INTRODUCTION

Reprocessing of spent reactor fuel is conventionally accomplished by aqueous chemical techniques involving dissolution, extraction, and calcination of the fuel material. During the past fifteen years, a number of laboratories have investigated reprocessing techniques in which the fuel is treated as a liquid metal rather than in aqueous solution. These processes utilize the chemical and physical properties of fuel at elevated temperatures to achieve decontamination from fission products. Among these "pyrochemical processes" is liquid metal extraction, which is the subject of the work reported here.

THE IMMISCIBLE SOLVENT PHASES: U-Cr Eutectic and Mg

All pyrochemical processes applied to nuclear fuels involve treating uranium either as a pure liquid or as a solute in other liquid metals. Aside from the practical interest, the extraction kinetics may exhibit unusual features because of the high viscosity and surface tension of liquid uranium. However, pure uranium melts at 1132°C, and operation at these elevated temperatures is difficult because of the attack of most container materials by the liquid metals. In order to retain the features characteristic of a uranium-rich liquid yet reduce the experimental temperature, the eutectic alloy of uranium and chromium was employed. This binary contains 95 w/o uranium (80 a/o), yet melts at 859°C. (12)

Magnesium and silver are two solvents immiscible with uranium for which some equilibrium information is available. However, silver was not used because of the rather large amounts required for extraction kinetic studies. Magnesium is a satisfactory solvent except for its high vapor pressure. At 1000°C, the vapor pressure is 300 mm Hg. If

pure uranium at its melting point of 1132°C had been used, the magnesium vapor pressure would have been about 3 atm., and a pressurized system would have been required.

The phase diagram for the magnesium-uranium system at 3 atmospheres has been established by Chiotti, Tracy, and Wilhelm. (3) They found limited mutual solubility at temperatures up to 1255°C. At 1135°C, the magnesium-rich phase contains 0.14 ± 0.05 w-% uranium and the uranium-rich phase contains 0.004 w-% magnesium.

The magnesium ——U-Cr eutectic system has not been as thoroughly studied as has the Mg-U system. Some measurements have been reported by the Argonne National Laboratory. (16) When the uranium-chromium eutectic was equilibrated with magnesium at 940°C, the magnesium phase contained 0.05 w-% U and 0.06 w-% Cr.

Figure 1 is a section showing the interface between the U-Cr phase (bottom) and the magnesium phase (top) obtained in the present study. The sample illustrated was heated to 1000°C under argon in a graphite crucible. Magnesium has a silver color; the U-Cr surface has a slight yellow tint due to oxidation during sawing.

THE TRANSFERRING SOLUTES: La^{140} and Ba^{140}

The solute directly measured in the experiments was the rare earth, lanthanum - 140. This nuclide is not produced directly by uranium fission, but is the daughter of barium-140 which is produced with a direct fission yield of 6.4%. The decay scheme is:

$$Ba^{140} \xrightarrow[12.8\ d]{\beta^-} La^{140} \xrightarrow[40.2\ hr]{\beta^-} Ce^{140} \qquad (1)$$

The fission of uranium produces a wide range of radioactive fission products. Those nuclides which emit high energy gamma rays tend to have short half-lives. Because of the long half-life of its parent, however,

the 1.6 MeV photon from La^{140} decay dominates the gamma ray spectrum of uranium which has been cooled for several days. Figure 2 shows the gamma ray spectrum of a sample of the U-Cr eutectic which was irradiated for two days and allowed to cool for 24 days. Even though the uranium was depleted (0.2% U^{235}), the peak due to the 1.6 MeV photon from La^{140} is unmistakable.

Since the lanthanum activity depends upon the 12.8 day half-life of its precursor Ba^{140}, the amount of barium extracted can be determined by following the decay of the lanthanum after an experiment. This can be qualitatively illustrated by considering the two extreme cases. If only lanthanum were extracted, its activity would decay with a half-life of 40.2 hours. However, if only barium were extracted, the lanthanum activity would initially increase from zero to some maximum and then decrease, asymptotically approaching the 12.8 day half-life of the barium precursor. In general the decay of the lanthanum is governed by the well-known relation for batch decay of a two member chain (2):

$$\frac{a_{La}}{a^{o}_{La}} = \frac{e^{-\lambda_{Ba} t}}{F} + \left(1 - \frac{1}{F}\right) e^{-\lambda_{La} t} \qquad (2)$$

where the parameter F depends upon the initial ratio of the two nuclides:

$$F = \frac{N^{o}_{La}}{N^{o}_{Ba}} \; \frac{\lambda_{La} - \lambda_{Ba}}{\lambda_{Ba}} \qquad (3)$$

If the initial ratio is such that F is unity, the lanthanum activity decays with the half-life of the barium precursor. This situation is known as secular equilibrium and for the chain of Eq. (1) is attained after about 12 days in uranium irradiated for two days (11).

In the experiments reported here, the lanthanum activity of the U-Cr sample before extraction and the activity of the two phases (separately) as a function of time after extraction were measured. The activities before and immediately after the experiment are related to the amount of lanthanum extracted. According to Eq. (2), a plot of $(a_{La}/a^{0}_{La}) \exp \lambda_{Ba} t$ versus $\exp [-(\lambda_{La}-\lambda_{Ba})t]$ should yield a straight line with an intercept of 1/F. The parameter F is related to the amount of barium extracted in the process, and its interpretation will be considered in detail later. The unique feature of this approach is that the time dependence of the activity of one member of a two member decay chain yields information on the extraction behavior of both species.

The distribution experiments reported here were undertaken primarily to resolve a two order of magnitude discrepancy in the literature. The Ames laboratory has reported values of the distribution coefficients of cerium and barium between magnesium and the uranium-chromium eutectic of $m_{Ce} \simeq 500$ and $m_{Ba} \simeq 5$ (17). The temperature was not reported but was probably near the melting point of the eutectic (860°C).

Barney and Keneshea (1) have measured the distribution coefficients of various fission products between pure uranium and magnesium at 1150°C. Based upon two experiments, the values are:

$$K^{x}_{Ce} = 1.9 \pm 0.4, \; K^{x}_{RE} = 1.0 \pm 0.6, \text{ and } K^{x}_{Ba} = 0.031 \pm 0.008.$$

In terms of concentration distribution coefficients, these values are

$$m_{Ce} = 1.5, \; m_{RE} = 0.8, \text{ and } m_{Ba} = 0.025.$$

It is unlikely that these large differences could be a real effect due to the change from pure uranium to the uranium-chromium eutectic and to the difference in temperature. Haefling and Daane (7) found the

solubility of cerium in uranium to be 1.16% w/o at 1150°C, which is in good agreement with the measured solubility of 1.2 w/o reported by Voigt (14) for the same system. Voigt also measured the solubility of cerium in the uranium-chromium eutectic as 1.5% at 970°C, not very different from the value in pure uranium at 1150°C. Since the solubility of cerium is about the same in the uranium-chromium eutectic at 970°C, as in pure uranium at 1150°C, one would expect its distribution between magnesium and the U-Cr eutectic to be about the same as between magnesium and uranium.

EXPERIMENTAL PROCEDURE

The equilibrium experiments were performed with 5 gm samples of lightly irradiated (11 hours in a flux of 2×10^{13} n/cm^2-sec) uranium-chromium eutectic, which was contacted with an equal volume (0.6 gm) of magnesium.

The U-Cr eutectic alloy was purchased from the National Lead Company in the form of cylindrical pellets 1/4 in. in diameter and about 3/8 in. long. The alloy was made of depleted uranium containing about 0.2 w-% U^{235}. (Natural uranium contains 0.7 w-% U^{235}.) The supplier reported the melting point as 860°C. Analysis of alloy samples showed the chromium content to be 4.28 w-% (the eutectic alloy contains 5-w% Cr). Spectrographic analysis showed no constituents other than Cr and U present in the samples. Magnesium was obtained from the United Mineral and Chemical Corporation.

Small graphite crucibles 3/4 in. O.D. with a 1-1/2 in. deep 1/4 in. hole were used. Each crucible was baked out at 1000°C for 45 minutes under argon to remove traces of oxygen and water. The weighed irradiated U-Cr slug was placed in the crucible with an equal volume of magnesium

on top of it. The crucible was then closed with a tightly fitting graphite plug. The charging operation was done under an argon stream. The crucible was then placed in a tantalum basked and suspended inside a stainless steel sheath in a resistance furnace by means of a steel chain. By jerking the chain at intervals during the heating period, the molten metal phases were agitated. A stream of argon was kept flowing in the sheath. The duration of the experiments was 30 minutes. The temperature inside the crucible was calibrated against the reading of the furnace thermocouple at the position where the tantalum basked was suspended by a probe thermocouple. Agitation was stopped about 5 minutes before the end of the heating period to prevent inclusion of uranium in magnesium. At the end of the heating period, the tantalum basket was pulled up out of the furnace and into a stainless steel "cooling can". The purpose of the cooling device was to freeze the two metal phases as quickly as possible so that the measured equilibrium distribution would be characteristic of the elevated temperature of the heating period. A slow cooling period might have permitted the equilibrium distribution to shift to that existing at 860°C, the melting point of the eutectic. An argon stream was kept flowing vigorously through the cooling device to prevent oxidation of the tantalum or entry of oxygen into the crucible while the metals cooled.

After a 10-15 minute cooling period, the graphite crucible was smashed (inside a polyethylene bag to trap radioactive particles) and the metal ingot recovered and weighed. Magnesium loss during heating was about 4%. The ingot was placed inside a glove box where the two phases were sawed apart. The cut was made in the magnesium phase about 1/16 in. from the interface. The 1/16 in. of Mg remaining on the U-Cr

slug was dissolved in HCl. Some of the U-Cr nearest the interface was also dissolved. In order to remove any rare earth carbides which might be present on the surface, the recovered magnesium was placed in dilute HCl for a few seconds until the surface was bright. This procedure was designed to avoid measurements of radioactivity present at the metal-crucible and metal-metal interfaces. Chiotti and Voigt (4), in a study of cerium extraction from uranium by silver, reported accumulation of cerium radioactivity at the U-Ag interface and at the metal-tantalum crucible interface. Voigt (14), in his equilibrium studies, also avoided measurements of radioactivity at the interface. Therefore, in determining the distribution coefficients, only the radioactivity in the bulk metal phases was counted.

After washing in HCl, the U-Cr and Mg phases were weighed and the activity of La^{140} in each phase was then measured by gamma counting of the 1.6 MeV peak, as described in reference (11). The decay of La^{140} activity in each phase was followed in order to determine the La to Ba ratio immediately after extraction.

RESULTS

The distribution coefficient of lanthanum on a concentration basis is related to the measured activities in each phase by:

$$m_{La} = \frac{\left(a^{o}_{La}\right)_{Mg}}{\left(a^{o}_{La}\right)_{U-Cr}} \frac{W_{U-Cr}}{W_{mg}} \frac{\rho_{Mg}}{\rho_{U-Cr}} \qquad (4)$$

For dilue solutions, distribution coefficients on an atom fraction basis are:

$$K^{x}_{La} = \frac{\left(a^{o}_{La}\right)_{Mg}}{\left(a^{o}_{La}\right)_{U-Cr}} \frac{W_{U-Cr}}{W_{Mg}} \frac{M_{Mg}}{M_{U-Cr}} \qquad (5)$$

The barium distribution coefficient can also be represented by an expression similar to Eq. (4). For barium, however, the activities in the two phases have not been directly measured. The distribution coefficients of the two species are related by:

$$\frac{m_{La}}{m_{Ba}} = \frac{\left(a^{o}_{La}/a^{o}_{Ba}\right)_{Mg}}{\left(a^{o}_{La}/a^{o}_{Ba}\right)_{U-Cr}} = \frac{\left(N^{o}_{La}/N^{o}_{Ba}\right)_{Mg}}{\left(N^{o}_{La}/N^{o}_{Ba}\right)_{U-Cr}} \tag{6}$$

The second equality of Eq. (6) results from the proportionality of the activities and the number of atoms. The initial atom ratios are related to the F' parameters, which have been obtained from the time dependence of the La^{140} decay in each phase. Using Eq. (3) in Eq. (6):

$$m_{Ba} = \frac{F_{U-Cr}}{F_{Mg}} \, m_{La} \tag{7}$$

Figure 3 shows a plot of Eq. (2) after an experiment at 1000°C. The intercept of the line for the uranium phase indicates that the lanthanum to barium ratio was approximately 1/2 of that before extraction, when the species were in secular equilibrium (F = 1). The magnesium phase line of Fig. 3 is simply a plot of the pure exponential decay of 40.2 hr half-life La^{140} and indicates immeasurably small quantities of barium in the magnesium ($F_{Mg} \approx \infty$). The behavior shown in Fig. 3 was typical of all four equilibration experiments performed, except for the one at the highest temperature (1100°C) in which barium was found in the magnesium phase. The results are shown in Table 1.

Material balances on each phase were performed, counting only the activity in the recovered bulk phases. Between 25 and 60 percent of the initial activity was recovered, which suggests that lanthanum or barium pickup at the walls or accumulation at the interface was

Table 1

Lanthanum and Barium Distribution Between Magnesium and the Uranium-Chromium Eutectic

T, °C	m_{La}	m_{Ba}
900	0.08	0
1000	0.09	0
1000	0.19	0
1100	0.40	0.007

significant. Despite the loss of activity from the bulk phases, it was assumed that the rate of interphase transfer (aided by manual agitation) was sufficiently large to maintain equilibrium. After the container was removed from the furnace into the cooling can, the temperature rapidly dropped to the freezing point of the uranium phase (~900°C). However, the magnesium phase remained liquid during the time required to cool from 900°C to 650°C. In this interval, losses of barium or lanthanum from the magnesium could no longer be replenished by transfer from the uranium phase. However, the cool-down time was a small fraction (10-15%) of the equilibration time, and the major losses of activity to the wall and interface probably occurred while both phases were liquid.

Estimation of Lanthanum Partitioning from Regular Solution Theory*

If the pure liquid standard state is chosen for the solute in both phases, the thermodynamic activities in the two solvents must be

* In the previous discussion, the term "activity" was used to denote radioactivity. In the following discussion, activity is to be interpreted in the thermodynamic sense.

equal. Hence the measured ratio of the atom fractions is equal to the ratio of the activity coefficients:

$$K^x = \frac{x^{Mg}}{x^{U-Cr}} = \frac{\gamma^{U-Cr}}{\gamma^{Mg}} \tag{8}$$

Since the solutions are sufficiently dilute to be in the Henry's law region in each phase, the activity coefficients are concentration independent.

Pitzer and Brewer (9) have shown how regular solution theory can be applied to liquid metals to predict mutual solubilities. For the systems considered here, the solute concentration is quite small, and the regular solution theory for the activity coefficient takes the form:

$$\ln\gamma_2 = \frac{\left(\delta_1 - \delta_2\right)^2 b_2}{RT} \tag{9}$$

The molecular volume parameter b_2 is usually taken to be the solute molar volume, although for liquid metals, it should be adjusted to fit the available data for the particular system (9). The solubility parameter is:

$$\delta = \left(\frac{\Delta H^V - RT}{V}\right)^{1/2} \tag{10}$$

Both δ and b_2 are assumed to be independent of temperature.

For the rare earths in magnesium, there are no data from which the parameter b_2 can be estimated. In applying Eq. (9) to magnesium solvent, b_2 has been taken as the solute molar volume, obtained from the densities reported in Ref. 15. The solubility parameters at 1000°C have been calculated from Eq. (10) using the heat of vaporization data from Ref. 13. The computed solubility parameters are 42.0, 58.5, and

63.3 $(cals/cc)^{1/2}$ for magnesium, cerium, and lanthanum, respectively. The activity coefficients are shown in Table 2.

Table 2

Activity Coefficients of Cerium and Lanthanum in Magnesium

T, °C	Cerium	Lanthanum
900	11.8	94
1000	9.7	67
1100	8.2	50
1150	7.6	44

Activity coefficients in the uranium-chromium phase can also be estimated from regular solution theory, but in this case, there are data on closely related systems which permit an estimate of some of the parameters in Eq. (9). Haefling and Daane (7) have measured the solubility of cerium and lanthanum in pure uranium and Voight (14) has reported the solubility of cerium in the U-Cr eutectic. These solubility measurements can be converted into solute activity coefficients. If two essentially immiscible liquids are equilibrated, the activity of each component in its rich phase is close to unity. The activity coefficient in the lean phase is simply the reciprocal of the solubility.

With the additional information provided by these measurements, the parameter b_2 need not be approximated by the solute molar volume, as was necessary for magnesium solutions. Instead, Eq. (9) can be solved for the ratio of the solute molar volume to the parameter b_2 for pure uranium solvent:

$$\left(\frac{V_2}{b_2}\right)^{1/2} = (\delta_U - \delta_2)\left(\frac{RT\ \ell n\ \gamma_2^U}{V_2}\right)^{-1/2} \qquad (11)$$

From the data of Ref. 7, the group $(RT\ln\gamma_2^U/V_2)^{1/2}$ for solute cerium is 22.95 $(cal/cc)^{1/2}$ at 1150°C and 23.00 $(cal/cc)^{1/2}$ at 1250°C. The constancy of this group is in accord with regular solution theory. The solubility parameter for uranium has been estimated from heat of vaporization and liquid density data as 93 $(cal/cc)^{1/2}$. Using these figures in Eq. (11) yields $(V_{Ce}/b_{Ce})^{1/2} = 1.50$.

For lanthanum solute, the group $(RT\ln\gamma_2^U/V_2)^{1/2}$ is 22.80 at 1150°C and 23.20 at 1225°C. Using Eq. (11), $(V_{La}/b_{La})^{1/2} = 1.29$.

For the U-Cr eutectic, Eq. (9) can be solved for the solubility parameter of the mixed solvent:

$$\delta_{U\text{-}Cr} = \delta_2 + \left(\frac{RT\ \ln\gamma_2^{U\text{-}Cr}}{V_2}\right)^{1/2} \left(\frac{V_2}{b_2}\right)^{1/2} \qquad (12)$$

From Voight's (14) determination of the solubility of cerium in the U-Cr eutectic at 970°C, $(RT\ \ln\gamma_{Ce}^{U\text{-}Cr}/V_{Ce})^{1/2} = 21.20\ (cal/cc)^{1/2}$.

The solubility parameter of the mixed solvent can be calculated from the volume fraction average of the two pure solvent constituents. However, because of the cerium solubility measurement in U-Cr, this approximation is not necessary. The solubility parameter for the mixed solvent can be determined from Eq. (12) by using the solubility parameter for pure cerium, the measured activity coefficient of cerium in the eutectic, and the ratio $(V_{Ce}/b_{Ce})^{1/2}$ determined previously from the solubility of cerium in pure uranium. Equation (12) yields $\delta_{U\text{-}Cr} = 90.3\ (cal/cc)^{1/2}$. The value computed from the volume fraction average of $\delta_U = 93$ and $\delta_{Cr} = 106$ is 95.5.

Using the former value of $\delta_{U\text{-}Cr}$, and $(V_{La}/b_{La})^{1/2} = 1.29$, the activity coefficient of lanthanum in the uranium-chromium eutectic is:

$$\ln\gamma_{La}^{U\text{-}Cr} = \frac{10{,}200}{RT} \qquad (13)$$

Table 3. Activity Coefficients of Cerium and Lanthanum in Uranium and the Uranium-Chromium Eutectic

T, °C	cerium in uranium	lanthanum in uranium	lanthanum in the U-Cr Eutectic +ℓ (Eq.13)
900	117*	112*	80
1000	81*	94*	57
1100	59*	81*	43
1150	51	76	37
1225	--	70	--
1250	40	--	--

*Extrapolated from the data at higher temperatures.

The experimental results of this study and the data of Barney and Keneshea (1) are compared with the theoretical predictions in Fig. 4. Theory and experiment agree to within an order of magnitude, which is all that can be expected from the approximations involved in the theory and the precision of the experiments (the reproducibility of the experiments, shown by the two points at 1000°C, is about a factor of two). The agreement is quite acceptable at high temperatures, but becomes poorer at lower temperatures. A value of $\Delta H = 26$ kcal/mole is obtained for the experimental lanthanum distribution coefficient between magnesium and the U-Cr eutectic, while the values computed from regular solution theory are practically temperature independent. If the ratio $(V_{La}/b_{La})^{1/2}$ had been taken as ~1.3 in the magnesium solvent as it was found to be in the U-Cr phase, the agreement between the regular solution and experimental distribution coefficients would have been considerably improved, both in

magnitude and in temperature dependence. The only other liquid metal distribution study in which the effect of temperature was investigated is that of McKenzie (10). He found the ΔH for the distribution of plutonium between uranium and silver to be 12.5 kcal/mole.

Distribution of Barium between Magnesium and U-Cr

The single value of the distribution coefficient of barium between magnesium and U-Cr at 1100°C can be compared with the measurement of barium distribution between uranium and magnesium at 1150°C. To correct Barney and Keneshea's datum for the presence of chromium in the uranium phase, the factor 0.52 obtained earlier for solute cerium is employed. In addition the temperature coefficient for barium is assumed to be the same as that measured for lanthanum, so that the distribution coefficient at 1100°C should be smaller than that at 1150°C by a factor of 0.7. Applying these two corrections to the m_{Ba} value of 0.025 reported by Barney and Keneshea, the distribution coefficient at 1100°C between magnesium and the U-Cr eutectic should be 0.009. The measured value from Table 1 is 0.007.

The general agreement between the measurements of Barney and Keneshea and those reported here is good for both lanthanum and barium solutes. Both sets of experiments are well within an order of magnitude of the predictions based upon the solubility data and regular solution theory.

Reaction of Barium with the Graphite Crucible

One aspect of the data which deserves closer scrutiny is the absence of barium in the magnesium phase after equilibration at 900 and 1000°C. From the single measurement at 1100°C and assuming a temperature dependence equal to that of lanthanum, the barium concentration coefficient

at 1000°C should be ~0.004. In the 1000°C experiment for which the F plot is shown in Fig. 3, $F_{U-Cr} = 0.52$ and $m_{La} = 0.09$. Inserting these figures in Eq. (7) a value of F_{Mg} of 11 is obtained. This represents an intercept of ~0.09 for the lower line of Fig. 3, which should have been observed.

The loss of barium from the uranium phase is not catastrophic, since an F_{U-Cr} of 0.52 implies that the barium-to-lanthanum ratio is twice as large as in the original irradiated pellet. As mentioned earlier, the preferential loss of barium from the magnesium probably occurs during the cooling period from the freezing point of the eutectic to that of magnesium.

The removal of barium might be attributable to reaction with graphite, especially in view of Culpin's observation that pure liquid barium attacked graphite vigorously above the melting point (5). If barium is to react with graphite, the equilibrium thermodynamic activity determined by reaction (9) must be exceeded:

$$Ba(sol'n) + 2C(s) = BaC_2(s) \qquad (9)$$

Hoch (8) and Flowers and Rauh (6) have investigated the thermochemical properties of the reaction:

$$Ba(g) + 2C(s) = BaC_2(s) \qquad (10)$$

From the results of reference 6, $\Delta H = -54.7$ kcal/mole and $\Delta S = -13.7$ eu. Using the vapor pressure-temperature curve of liquid barium, the reaction:

$$Ba(\ell) + 2C(s) = BaC_2(s) \qquad (11)$$

is characterized by $\Delta H = -18.6$ kcal/mole and $\Delta S = 5.3$ eu. Neglecting solid solution of barium carbide in graphite, the equilibrium activity

of barium in reaction (9) increases from 2.3×10^{-5} at 900°C to 7.5×10^{-5} at 1100°C. The activity coefficient of barium in magnesium has been estimated by regular solution theory to decrease from 48 at 900°C to 27 at 1100°C. The equilibrium atom fraction of barium in magnesium solutions in contact with graphite and pure barium carbide is 0.5×10^{-6} at 900°C and 2.8×10^{-6} at 1100°C. If Hoch's (8) ΔH and ΔS for reaction (10) are used, the equilibrium atom fractions are larger by a factor of ~20.

Using the neutron reaction and radioactive decay equations appropriate to barium produced from U^{235} fission in a flux of 2×10^{13} (2), the atom fraction of barium in the irradiated U-Cr pellet is estimated to be 2.5×10^{-8}. Because the partitioning of barium between the two solvents favors the uranium phase, the atom fraction in the magnesium phase is $\sim 10^{-9}$. This is at least three orders of magnitude smaller than the barium concentrations required to form barium carbide by reaction with graphite. Unless the thermodynamic activity of barium in the graphite is decreased by an equivalent amount due to solid solution, graphite should not remove appreciable amounts of barium from magnesium solutions at temperatures around 1000°C. The decrease in barium activity due to solid solution does not appear to be significant, however. From the data of reference 6, the barium pressure over $BaC_{3.25}$ is approximately 30% less than the pressure over BaC_2.

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NOTATION

a	activity, counts/min
b_2	solute molar volume parameter in regular solution theory, $(cal/cc)^{1/2}$
F	factor defined by Eq. (3)
ΔH	enthalpy change, kcal/mole
K^x	atom fraction distribution coefficient (magnesium to uranium)
m	molar concentration distribution coefficient (magnesium to uranium)
M	atomic weight
N	number of atoms
R	gas constant, cal/mole-°K
ΔS	entropy change, eu
t	time after extraction, sec
V	atomic volume, cc/gm atom
W	sample weight, gms
λ	decay constant, sec^{-1}
ρ	density, gms/cc
γ_2^1	activity coefficient (pure liquid solute standard state) of solute 2 in solvent 1
δ	Hildebrand solubility parameter

Subscripts

1	solvent
2	solute
RE	rare earths

Superscripts

o	immediately after extraction
v	vaporization

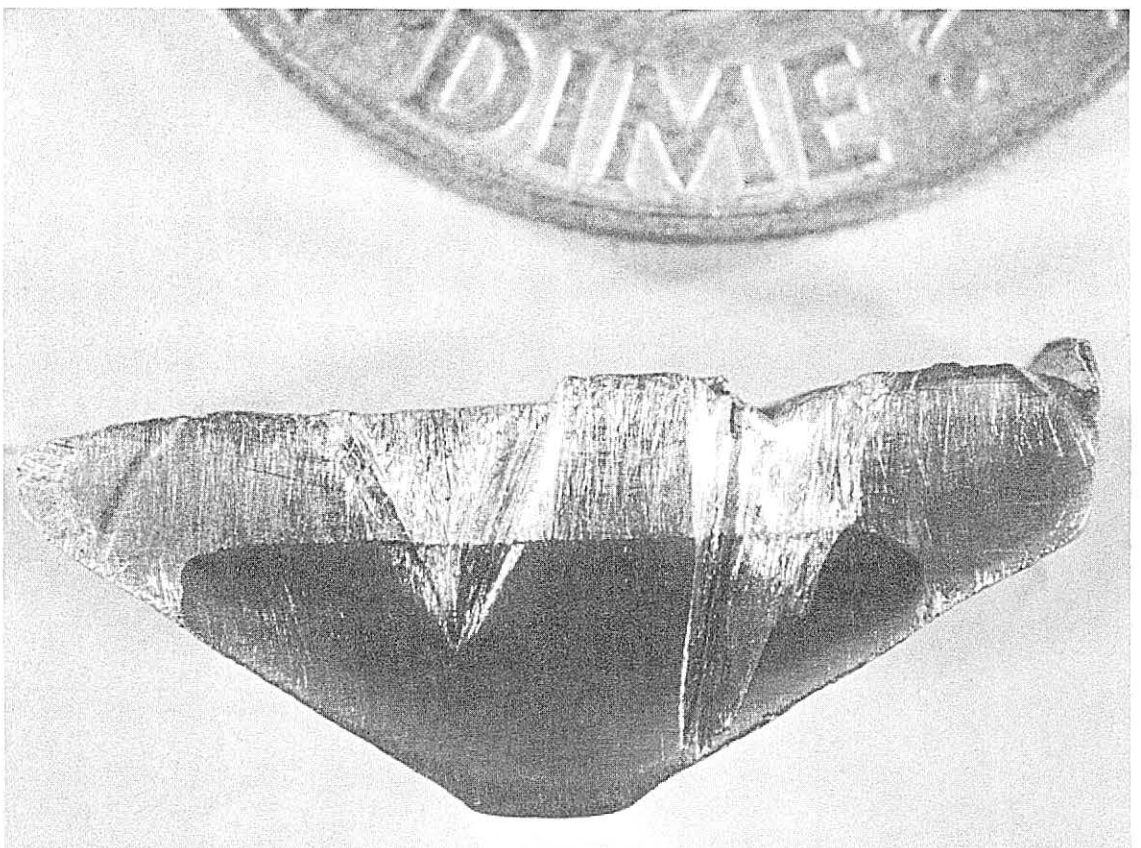
FIGURE CAPTIONS

Fig. 1 The immiscible magnesium-uranium-chromium system.

Fig. 2 Gamma ray spectrum of irradiated U-Cr.

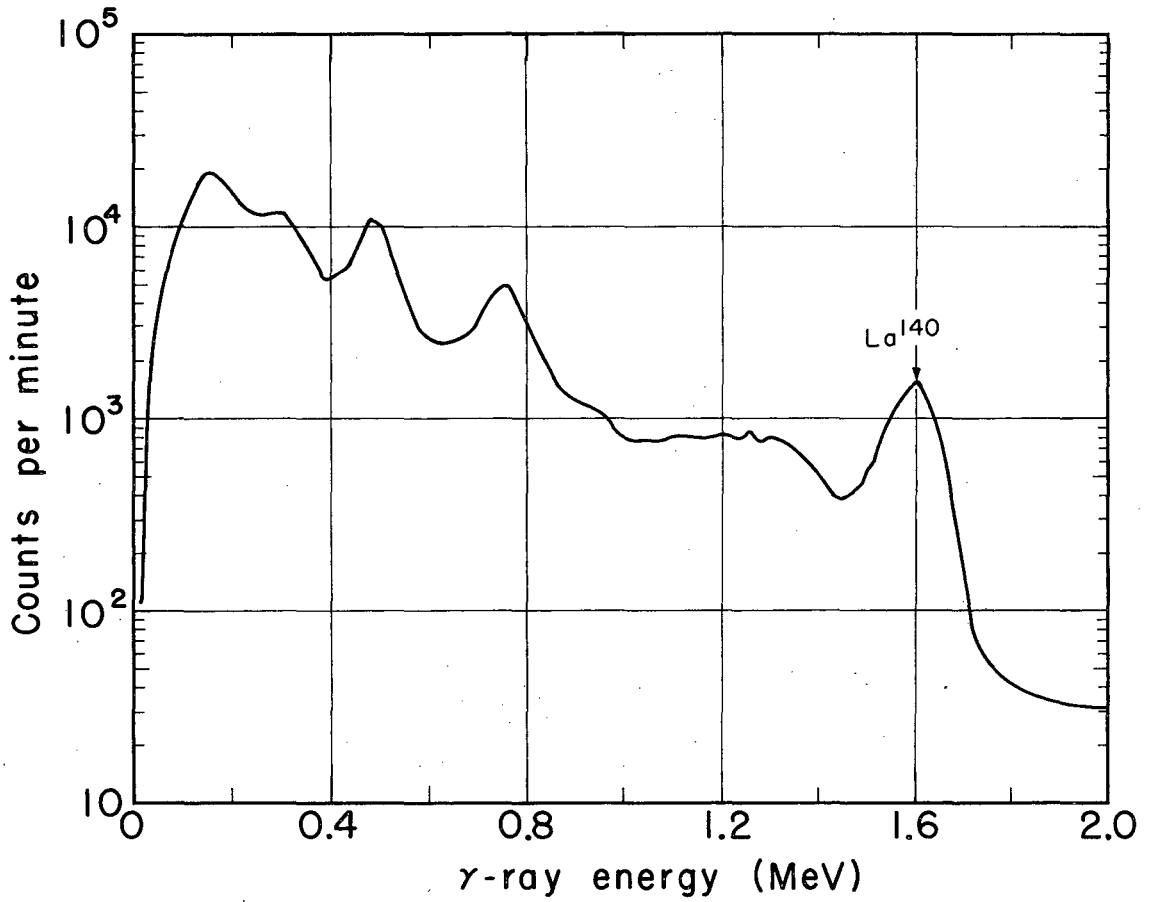
Fig. 3 Decay of the La^{140} activity in the magnesium and U-Cr phases after equilibration at 1000°C.

Fig. 4 Experimental and calculated distribution coefficients.



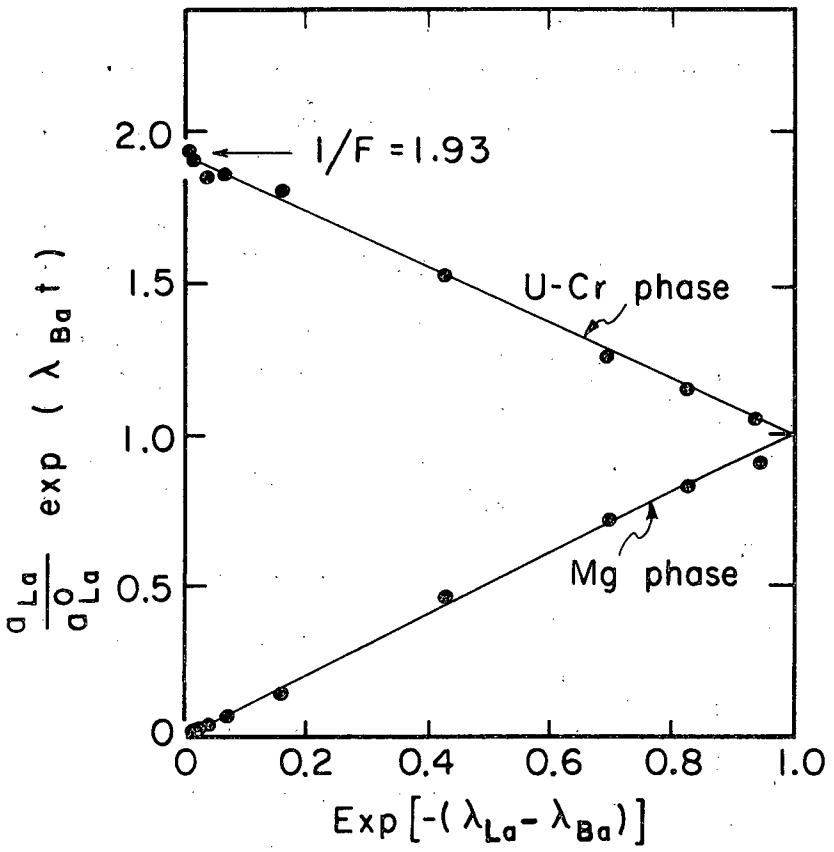
ZN-5472

Fig. 1



MUB-6388

Fig. 2



MU-37032

Fig. 3

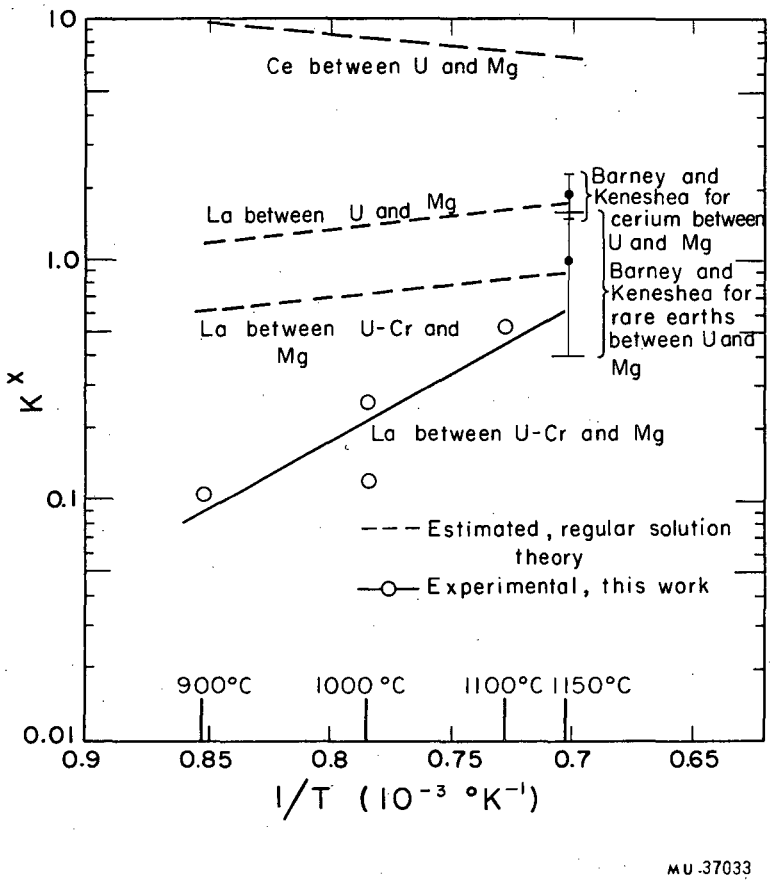

10
1.0
0.1
0.01
K
Ce between U and Mg
La between U and Mg
La between U-Cr and Mg
Barney and Keneshea for cerium between U and Mg
Barney and Keneshea for rare earths between U and Mg
La between U-Cr and Mg
Estimated, regular solution theory
Experimental, this work
900°C
1000°C
1100°C
1150°C
0.9
0.85
0.8
0.75
0.7
0.65
1/T (10⁻³ °K⁻¹)
MU-37033

Fig. 4

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