Distribution of Protactinium-233 Between Magnesium–38% Thorium and Uranium-Rich Solutions

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URANIUM can be separated from a thorium-uranium alloy by dissolution of the thorium in magnesium (*1*, *2*). The uranium separates as a finely divided solid or liquid phase (99+% uranium) depending on the temperature. If enough chromium is added to form uranium-5.2% chromium eutectic the uranium can be separated as a liquid uranium-5.2% chromium phase on heating to above the uranium-chromium eutectic temperature, 860° C. In the case of neutron irradiated thorium the course taken by the 27.4 day half-life protactinium-233, precursor to uranium-233, in such a separation is of considerable importance in reactor technology. The purpose of this investigation was to determine the distribution of the protactinium between a magnesium-38% thorium liquid and a uranium or uranium-5.2% chromium liquid. The data showed that over 99% of the protactinium present will follow the uranium-rich phase in the separation of uranium from irradiated thorium by extraction with magnesium.

EXPERIMENTAL

Production grade uranium, thorium, and high purity magnesium were made available by the Ames Laboratory for these experiments. Magnesium-38% thorium alloy was irradiated at the Argonne National Laboratory under a thermal flux to give a total irradiation of 8 to 9 × 10^{15} neutrons per sq. cm. (*nvt*). Weighed amounts of the irradiated alloy and uranium (or uranium-5.2% chromium) were charged into tantalum crucibles which were then sealed by welding a preformed cap into the open end. These operations were carried out under an argon atmosphere. A graphite crucible fitted with a screw-cap top enclosed this assembly, which in turn was enclosed in a welded steel jacket 4 inches long by 2 inches in inside diameter. The purpose of the graphite crucible was to prevent contact between the charge and the steel liner in case the tantalum crucible failed. Both uranium and thorium form relatively low melting eutectics with iron (*3*). The final assembly was heated in an oscillating furnace. Some details on the type of furnace used have been published (*1*). In one experiment, the fourth charge listed in Table II, the furnace was rotated back and forth through an arc of approximately 180° once a minute; in all the other experiments for which data are presented, the furnace was rotated at approximately 50 oscillations per minute. Vigorous agitation was needed to break up interphase films and assure attainment of equilibrium in a reasonable period of time.

A typical processing schedule for changes containing uranium-5.2% chromium alloy was to mix at 980° C. for one hour, settle for one hour at approximetely the same temperature, cool to, and hold at 660° C. for an hour, and finally to furnace cool to room temperature. The uranium-chromium eutectic freezes at 860° C. whereas the magnesium-38% thorium phase freezes at 585° C. The latter settling period was to permit any uranium and accompanying protactinium precipitate to settle from the magnesium-rich liquid. The solubility of uranium in the magnesium-rich phase in weight per cent is approximately 0.14 at 1132° C., 0.034 at 850° C., and 0.007 at 650° C. (*2*). Consequently the amount of uranium in this solution relative to the total amount of uranium present is negligible. The small amount that precipitates on cooling from the equilibration temperature would not be expected to have a measurable effect on the activity in the bulk of the uranium-rich phase but may have a measurable effect on the small residual activity in the magnesium-rich phase. Charges containing pure uranium (melting point 1132° C.) were mixed at 1175 ± 10° C. for 20 to 30 minutes, permitted to settle at temperature for 10 to 15 minutes, cooled and held at 660° C. for one hour, and finally furnace cooled to room temperature.

The tantalum was mechanically stripped from the cylindrical ingots obtained. A thin layer was machined from the outer surfaces of the ingot, and the ingot was cut into horizontal sections and analysed for protactinium-233 activity. Analyses were made by dissolving the sections, taking aliquots, and counting the 90 k.e.v. (some cases 300 k.e.v.) gamma-ray transitions of protactinium-233 with a scintillation detector and spectrometer. A 1.5- or 2-inch diameter sodium iodide scintillation detector was fed into a Nuclear-Chicago Model 1820 single channel spectrometer. The 90- and 300-k.e.v. peaks of the complex decay scheme of protactinium-233 were considered the most useful for analytical counting. Early work, done with the 90-k.e.v. peak, is somewhat more sensitive to the protactinium-233 content of a sample than the 300-k.e.v. peak.

RESULTS

Detailed analyses of one ingot are presented in Table I to show the distribution of the protactinium in the charge. The sample numbers indicate successive horizontal sections taken from top to bottom of the ingot. These data show that there is a tendency for the protactinium activity to concentrate at interfaces—the magnesium-thorium-uranium-chromium interface, samples 12 and 13, as well as at the crucible-ingot interface as indicated by the analyses of the turnings from the ingot surface. This tendency is probably due to segregation or concentrations of impurities such as oxides or carbides at these interfaces; it implies that protactinium is more reactive toward these impurities than are the other components of the system.

The residual activity in the bulk of the magnesium-thorium phase is very low and the possibility was considered that much of this 90-k.e.v. activity may have been due to the presence of thorium-234, a daughter product of natural uranium which has a gamma transition of similar energy. To check this possibility unirradiated magnesium–38% thorium alloy was equilibrated with uranium or uranium–5.2% chromium using the same source materials and procedures. As expected, the major part of a 90-k.e.v. activity which was attributed to thorium-234 moved into the magnesium-rich phase. The distribution coefficients, counts per minute per gram in the uranium phase divided by counts per minute per gram in the magnesium phase, were 0.10 and 0.045, respectively, for the uranium and the uranium–5.2% chromium equilibrations. The equilibrium thorium content for the uranium phase at 1132° C. in contact with magnesium–38% thorium is approximately 1.0%, and, for the uranium–5.2 chromium phase at 860° C. it is 0.5%. On this basis, the calculated distribution coefficients expected are 0.085 and 0.035, respectively, which are in reasonably good agreement with the measured values.

Table I. Distribution of Protactinium Between Magnesium-Thorium and Uranium-Chromium Phases

Sample		Weight, G.	90-K.E.V. Activity 10^4 Counts/Min./G.
Original Mg-Th		66.6	1000
Mg-Th Phase	1	4.4	5.24
	2	2.5	3.02
	3	2.7	3.16
	4	2.2	3.31
	5	7.6	3.03
	6	4.3	3.10
	7	2.5	3.82
	8	3.3	3.58
	9	3.6	4.15
	10	3.2	5.40
	11	1.9	5.33
			Av. 3.92
Interface	12	3.2	542.0
Interface	13	2.7	1070.0
Original U-Cr		96.5	...
U-Cr Phase	14	21.8	598
	15	12.4	575
	16	10.0	589
	17	10.5	583
			Av. 586
Mg-Th Phase Turnings		3.9	49.8
U-Cr Phase Turnings		9.6	642

These data made it possible to correct the 90-k.e.v. measurements on the magensium-rich phase in Table I, and other equilibrations. The correction term was of the order of 5 to 15% of the residual activity in the magnesium-thorium phase. In some equilibrations the 300-k.e.v. gamma-ray transition for protactinium-233 was counted and no correction was necessary.

The final results on the distribution of protactinium are summarized in Table II. The per cent of the total initial protactinium activity ranges from 89 to 95%. The tantalum crucible walls showed a rather high activity after removal of the ingot, and, presumably, the activity not recovered remained with the crucible. The values for the distribution coefficient and decontamination factor show considerable scatter. However, since over 99% of the protactinium was extracted from the magnesium-thorium phase, small errors in measuring the final activity for this phase would be expected to produce a large variation in these values.

Table II. Distribution of Protactinium-233 Between Magnesium–38 Without Thorium, and Uranium or Uranium–5.2 Without Chromium Phases

Charge		Count Level,	Activity 10^4 Counts/	Distr.[a]		%Pa^{233} Extd. from Mg
G.	Phase	K.E.V.	Min./G.	Coeff.	D.F.[b]	Phase
26.5	Mg-38Th	90	0.280[c]	91	357	99.7
95.4	U	90	25.4			
33.1	Mg-38Th	90	0.485	74	206	99.5
90.8	U	90	35.8			
33.1	Mg-38Th	300	0.42	46	238	99.6
90.8	U	300	19.3			
62.0	Mg-38Th	90	3.57	72	132	99.2
101.5	U-5.2Cr	90	256			
66.6	Mg-38Th	90	3.68	159	271	99.6
96.5	U-5.2Cr	90	586			
33.2	Mg-38Th	300	0.241	193	415	99.8
86.7	U-5.2Cr	300	46.5			

[a] Distribution coefficient; Uranium phase divided by magnesium-rich phase in counts/min./g.

[b] Decontamination factor; initial divided by final counts/min./g. in magnesium-rich phase.

[c] Uncorrected value.

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