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The Mound Laboratory Progress Report, issued monthly, is intended to be a means of reporting items of current technical interest in research and development programs. To issue this report as soon as possible after the end of the month, editorial work is limited; and since this is an informal progress report, the results and data presented are preliminary and subject to change.

These reports are not intended to constitute publication in any sense of the word. Final results either will be submitted for publication in regular professional journals or will be published in the form of MLM topical reports.

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Plastics Plastic strands have been extruded using the experimental rheometer. The swelling of these plastic strands gives an indication of the molecular weight of the polymer unit between the cross links. Because of polymerization during the extrusion from the rheometer, the molecular weight between the cross links can not be determined. These experiments will be continued to determine the average molecular weight of the polymer unit and the flow characteristics of clear diallyl phthalate.

Ranger X-Ray Sensor The relationship of deposition rates to the texture and the surface density of the beryllium coats is being studied. Preliminary results indicate that the surface density and the optical density of the beryllium are proportional only if the beryllium is deposited at a uniform evaporation rate on a film maintained at constant temperature. If the beryllium is deposited too rapidly, the beryllium coating contains a large number of minute pinholes.

Radioelements Four rare earth polonium compounds were made by reacting polonium-210 with rare earth metals at 1000°C. The melting points of these compounds were determined: gadolinium polonide melts at 1635 ± 50°C; praseodymium polonide melts at 1442 ± 50°C; samarium polonide melts at 1495 ± 50°C; and lanthanum polonide melts at approximately 1650 ± 50°C.

The separation of uranium-234 from aged plutonium-238 has been demonstrated. Previous work has indicated that an anion exchange process is advantageous over a solvent extraction system for the initial separation of uranium-234. This anion exchange behavior of plutonium and uranium is being investigated further using a small Dowex-1 ion exchange column.

Isotope Separation Prior to enrichment by thermal diffusion, the tritium content of helium-3 was reduced to 6.3×10^{-10} per cent by passing the product through a refrigerated chamber containing activated silica. Approximately 160 liters of helium-3 of this tritium concentration were made available using this system.

Commercial methane is being evaluated as a feed gas to separate carbon-13 by thermal diffusion. Commercial methane contains nitrogen, carbon monoxide and carbon dioxide as impurities. These impurities, which are heavier than methane, flow with the desired product during the thermal diffusion separation. These impurities may be separated by rapidly passing the gas through a thermal diffusion column; these heavy contaminants are drawn off at the bottom and almost pure methane is drawn off at the top.

A thermal diffusion column system is using carbon monoxide to concentrate carbon-13. The product from this system contains four per cent carbon-13. The methane prepared from the enriched carbon monoxide is being used as a feed gas in another thermal diffusion column system. The product of this separation contains about 45 per cent carbon-13.

Studies on the conversion of carbon monoxide to methane are being continued. A catalytic chamber, containing reduced nickel in a highly activated state, has been prepared to react the carbon monoxide with hydrogen to form methane. The water from the reaction is expected to be enriched in oxygen-17 and oxygen-18.

A literature search indicated that the infrared absorption spectrum of uranium hexafluoride may be used to establish possible wave lengths of light to assist in the photochemical separation of uranium isotopes. The photochemical separation of uranium isotopes involves the excitation of a particular isotope by a specific wave length of light, and the subsequent reaction of this excited isotope to form a compound for separation.

Alternate methods of isotope separation are also being studied. Niobium is being considered as the hot wire for gaseous thermal diffusion columns to separate uranium isotopes. These studies will be continued.

Reactor Fuels and Materials Development The latent heat of transformation of each of the five solid state phase changes in plutonium metal are being measured in the high-temperature calorimeter. The completion of the first series of measurements gave the following values: 813 calories/g-atom for the alpha to beta transition; 123 calories/g-atom for the beta to gamma; 140 calories/g-atom for the gamma to delta; 17 calories/g-atom for the delta to delta-prime; and 309 calories/g-atom for the delta-prime to epsilon. All of these values except for the delta-prime to epsilon value, which is 30 per cent low, are in good agreement with the values recently reported by R. G. Loasby, AWRE, Aldermaston.

The viscosity of the filtered liquid Pu-Ce-Co eutectic alloy which is being examined by LASL, K-Division, as a possible reactor fuel, was measured at ten different temperature from 444° to 931°C. Excellent agreement was obtained with an unfiltered sample of the same composition previously measured and reported.

Compatibility studies are underway to find a suitable container material for liquid uranium-plutonium alloys so that the viscosities of these alloys can be determined. Two identical yttrium crucibles were fabricated. One was filled with uranium and the other with plutonium. The yttrium showed no signs of attack by liquid uranium after 2.5 hours at 1200°C. Preliminary results indicate that yttrium metal is a suitable container for liquid uranium to 1200°C.

Development work on the maximum bubble pressure method for the measurement of the interfacial tension of immiscible liquids has continued. A modification of the method has been tested and proved satisfactory using organic-aqueous mixtures at room temperature.

The plutonium-cerium binary diagram based on differential thermal analysis results has been developed which does not agree in the cerium-rich portion with the diagram proposed by investigators at the Los Alamos Scientific Laboratory. The investigation has been continued using metallographic and electron probe analysis of specimens selected to define the limits of solid solubility of beta-cerium and delta-plutonium. Beta-cerium contains a maximum of approximately 34 atom per cent plutonium at 625°C. Preliminary results indicate a maximum solubility of cerium in delta-plutonium of 22 to 23 atom per cent at approximately 615°C.

The plutonium-cerium-copper ternary system is being investigated as a potential fuel system for the molten plutonium fast breeder reactor concept. The preliminary results of differential thermal analysis and metallographic studies indicate the presence of a ternary eutectic, (m.p., 419°C) in the cerium-rich portion of the ternary system, and a slender primary phase field for plutonium extends across the diagram to the 419°C ternary eutectic.

A program of high temperature oxide studies in in progress for the development and characterization of high temperature plutonium-bearing ceramic fuel materials. A pycnometric method for measuring the average density of PuO_2 microspheres gave an average value of 11.0 g/cc at 25°C. This value agrees with earlier measurements made on the high density PuO_2 microspheres by two different methods. PuO_2-UO_2 microspheres were produced in a pure argon and an oxygen enriched atmosphere (75% AR-25% O_2) in the induction-coupled plasma torch.

Leach tests, in water and dilute mineral acids designed to evaluate the chemical durability of the plutonium-bearing glasses, have been concluded after 19 months. As expected, mineral acids attacked the glass fibers more than the water. The least leaching was obtained for a glass of the following composition: SiO_2-60 w/o, Al_2O_3-5 w/o, CaO-5 w/o, Na_2O-15 w/o, K_2O-5 w/o and PuO_2-10 w/o. After 19 months of leaching in water, this glass formed into ten micron fibers lost only 0.533 per cent of its plutonium content. The attack on this glass in a massive form would be insignificant.

Work is being directed at the development of methods of producing plastics and adhesives having characteristics superior to those currently being used at Mound Laboratory and elsewhere. Variations in plastic formulations and molding procedures are being studied in an effort to produce plastic which consistently meet specifications.

Plastics To show the change in molecular weight along the strands extruded from the experimental rheometer, viscosity and swelling indices of segments of the strands are being determined. Because of further polymerization of the polymer during isolation, no accurate viscosity measurements have been obtained; however, inhibitors to prevent this unwanted polymerization will be used in future experiments. Swelling indices, which give an indication of the molecular weight of a polymer between cross links, have been obtained for ten strand segments and are listed in Table 1, The higher the numerical designation of the sample in the table, the greater the length of time before the sample from a given strand was extruded. Thus, Sample 1 would have been extruded before Sample 2. Samples 1 and 2 from the strand extruded at 120°C dissolved almost completely, and therefore, no swelling index for these samples are given. The first sample was taken from the beginning of each strand. Except for the 145°C strand, the last sample was taken from the end. The swelling index should decrease with increasing cross link density, and the cross link density should increase with numerical designation; however, this is not always the case. No conclusions have as yet been drawn from this apparent anomaly.

Table 1

SWELLING INDICES OF POLYMER STRANDS FROM THE RHEOMETER

Sample Number	Swelling Index		
	120°C	135°C	145°C
1	-	23.73	12.95
2	-	20.09	11.82
3	12.09	23.08	15.32
4	9.40	12.54	10.96

ADHESIVES RESEARCH Adhesive systems are being studied to obtain a formulation which has good handling and curing characteristics, has a fairly high flexibility at low temperature, and adequate tensile strength at elevated temperatures.

Five additional Oxiron-Polyol-anhydride adhesive formulations were prepared and tested. The pot-life and curing characteristics were determined from 40 gram batches which were manually spread into a few square inches of film. The composition of these adhesives is shown in Table 2. All of the formulations have desirable curing and handling characteristics.

Four of the formulations were selected for film casting with the Gardner film caster. Three were cured both at 80°F and at 100°F. The results of environmental testing are shown in Table 3 together with the results obtained with formulation EO-33, which is considered to be the best formulation of this type previously reported. After two weeks standing, test specimens from EO-43 and EO-46 show a slightly lower per cent elongation at -65°F, but slightly higher per cent elongations at room temperature. Of the three samples, EO-43 appears to have the highest tensile strength at 160°F.

Table 2

COMPOSITION AND CURING CHARACTERISTICS OF LOW TEMPERATURE CURED OXIRON ADHESIVES

Component	Weight % Components in Formulation				
	EO-42	EO-43	EO-44	EO-45	EO-46
Oxiron 2000 resin	47.5	47.5	47.5	47.5	47.5
Epoxol 9-5	15.0	14.0	16.0	17.0	17.0
1,4-Butanediol	-	-	2.0	1.0	-
1,4-Cyclohexanedimethanol	3.0	-	-	-	1.0
Polyglycol 11-80	-	4.0	-	-	-
HET-Mehtyl Nadic anhydride mixture (64-36 pbw)[a]	34.5	34.5	34.5	34.5	34.5
	100	100	100	100	100
Pot Life in Hours	1-¼	2	1	1	1-¾

NOTE: a - Added in molten state at 65°C

Table 3

EFFECT OF TEST TEMPERATURE ON TENSILE STRENGTH AND PER CENT ELONGATION OF ADHESIVE FILMS

Formulation and Cure Temperature[a]		-65°F[b]			Room Temperature[c]			160°F[d]		
		At Break		At 500 psi	At Break		At 500 psi	At Break		At 500 psi
Specimens aged 2 wks		psi	% Elong.	% Elong.	psi	% Elong.	% Elong.	psi	% Elong.	% Elong.
EO-42	80°F	6313	1.8	0.14	6569	5.8	0.44	196	53	-
EO-42	100°F	7997	2.9	0.18	7603	5.8	0.34	431	55	-
EO-43	80°F	6698	2.5	0.19	6219	8.8	0.53	344	48	-
EO-43	100°F	6676	2.2	0.17	7539	6.0	0.40	419	49	-
EO-45	80°F	6027	2.1	0.17	7480	6.2	0.41	272	44	-
EO-46	80°F	6115	2.0	0.16	7760	5.5	0.35	312	45	-
EO-46	100°F	8036	3.7	0.23	8049	5.0	0.31	615	53	40
EO-33	80°F	6536	3.3	0.25	7625	5.4	0.35	280	44	-
Specimens aged 5 wks										
EO-42	80°F	6707	2.4	0.18	6711	4.0	0.30	340	54	-
EO-42	100°F	7957	2.7	0.17	8130	4.4	0.27	555	60	54
EO-43	80°F	6480	2.0	0.15	7850	4.8	0.31	419	72	-
EO-43	100°F	7080	2.8	0.20	8259	5.3	0.32	515	49	44
EO-45	80°F	7376	2.6	0.18	8318	4.9	0.29	435	59	-
EO-46	80°F	6334	2.4	0.19	7377	4.3	0.29	419	63	-
EO-46	100°F	6895	2.5	0.18	8437	4.8	0.28	716	51	33

a - Films which were cured at 100° were held at this temperature for 3 days before aging at 80°F.

b - Test Speed 0.02 inches per minute.

c - Test Speed 0.2 inches per minute.

d - Test Speed 2.0 inches per minute.

RANGER X-RAY SENSOR

Mound Laboratory is developing techniques to vapor-deposit a thin beryllium coat on Formvar plastic films for use in detecting radiation in outer space.

The optical density and weight of a number of beryllium coated plastic films were measured. Optical density was determined by comparing apparent filament intensity from a 300-watt projection bulb in a conventional slide projector through the coated film with a Kodak Wratten gelatin filter. After the coated film was weighed on an analytical balance, the beryllium was removed from the plastic film, and the film weighed. The density was calculated from the weight of the deposited beryllium and the internal distance of each of the square-shaped film holders, as measured by Vernier calipers. The ratio of beryllium density to optical density differed considerably.

The texture differences of coatings deposited at different temperatures were studied using a steriomicroscope at 47 magnification. With proper vaporization techniques a bright reflective beryllium coat is obtained; however, excessive heat and rapid metal deposition produce a dark purple or a grayish white finish.

The color differences are due to grain size, amount of disorientation, and microscopic holes. When an acceptable film is viewed under the steriomicroscope, the metal is fine-grained and smooth with a porosity of 0.006 millimeter holes. The grayish deposit is large-grained, rough and disoriented, and has higher porosity and larger hole size than is acceptable. An excessive number of large holes (0.0125 millimeter average) is caused by the release of residual solvents or water in the plastic, or by partial decomposition of the Formvar plastic at elevated temperatures. The strength of the coated film is reduced if the plastic is subjected to very high heats during deposition.

Basic and applied research on a number of radioelements is being conducted to determine the physical properties, develop analytical techniques, and study the basic radiochemistry involved. Of particular interest are alpha emitters, their decay chains, their isotopes, and their chemical homologues.

POLONIUM-210 RARE-EARTH COMPOUNDS Five rare earth polonium compounds were synthesized and the melting points of three of these compounds were determined. All of these reactions contained slightly more polonium than the stoichiometric amount. The reactions were carried out in tubes constructed from six-inch lengths of nine millimeter id quartz tubing. One end of the tube was sealed and two constrictions were drawn to form two chambers of approximately equal size. The rare earth metals were cleaned, cut and loaded into the reaction tubes while in an inert atmosphere. The polonium was distilled into the reaction tube containing the rare earth, by heating the platinum gauze to 1000°C. The tube was evacuated to less than one micron pressure and sealed at the constriction nearest its open end. The reaction was completed by distilling the polonium to the end of the tube containing the rare earth and heating the entire tube in a furnace to initiate the reaction. After the reaction was complete, the excess polonium was distilled back into the chamber with the depleted platinum gauzes and the reaction product was separated from the excess polonium by sealing at the constriction. The chambers with the depleted gauzes and excess polonium were saved for calorimetric determination of polonium content. Data from these reactions of rare earth metals with polonium-210 metal are presented in Table 5.

Table 5

RARE EARTH POLONIUM-210 REACTIONS

Reaction Number	Rare Earth	Weight Reactants		% Excess	Reaction	Reaction	Est. %[a]
		R.E. (mgs)	Po^{210} (curies)	Po^{210} (RE_2Po_3)	Temp. °C	Time (min)	Completion
1	Pr[b]	2.0	22.06	104.7	1000	60	15
2	Gd	4.6	43.09	103.9	1000	90	95+
3	Pr	4.8	50.24	104.3	900	60	90
4	Sm	5.4	52.75	103.6	1000	90	90
5	Dy[c]	3.6	34.28	109.1	-	-	-
6	Ho	6.1	55.25	105.3	1000	330	20
7	Dy	4.3	39.36	104.8	1000	180	20
8	La	2.6	28.34	106.7	1000	180	90

a - The values in this column estimated from the fluorescence of the reacted and unreacted Po^{210}. Quantitative data will be obtained by calorimeter determinations.

b - Reaction tube developed a leak causing oxidation of metal.

c - Reaction tube broke before completion of the reaction.

General Procedure for Melting-Point Determinations A procedure for determining the melting points of the reaction products has been standardized after several runs. Unless stipulated otherwise, the following procedure will be used: after the reaction product has been isolated in the reaction chamber, the tube is opened and the contents of the tube are placed on a one-mil thick tungsten ribbon. The ribbon containing the rare earth-polonide is placed in a high temperature furnace. After the furnace has been evacuated, the temperature is increased at approximately 100°C per minute to 1000°C, and 50°C per minute above 1000°C. The temperatures were read with a Leeds and Northrup optical pyrometer. Insipient melting is detectable by the differences in emissivities of tungsten, the solid compound, and reaction product and the molten reaction product. The pyrometer readings were corrected by using a curve calibrated by using the melting points of gold, platinum, and alumina as standards. The tungsten ribbons from the melting point determinations were saved for metallographic studies of the corrosive properties of the rare earth polonides toward tungsten.

The gadolinium-polonium system appeared to have the fastest reaction and to have gone the nearest to completion. The gadolinium and lanthanum-polonium reaction products retained the approximate shape and size of the original rare earth metal. The praseodymium, samarium, dysprosium, and holmium polonides were powders having approximately twice the volume of the original rare earth sample. The gadolinium and lanthanum compounds glowed with red heat, but the only evidence of polonium in the other products was the fluorescence of the quartz at the point of contact. The melting point data from the reaction products of the rare earth-polonides are presented in Table 6.

Table 6

MELTING POINTS OF RARE EARTH-POLONIUM-210 REACTION PRODUCTS

Reaction Number	Rare Earth	M. P. °C
2	Gd	1635 ± 50
3	Pr	1442 ± 50
4	Sm	1495 ± 50
8	La	$\geq$ 1620 ± 50

From visual observations, there was a marked difference in the reaction rate of the polonides with air. The activities of the products were in the order: Pr > Sm > Gd > La. Praseodymium-polonide was slightly pyrophoric, but lanthanum-polonide showed no sign of attack during a five minute exposure to the atmosphere.

The remaining rare earth sesquipolonides will be prepared and characterized. Since most of these polonides react with air, the materials will be stored in either a vacuum or inert atmosphere throughout the entire preparation and property measurement procedures.

URANIUM-234 RECOVERY Previous work indicated that an anion exchange process is more advantageous than solvent extraction for the initial separation of uranium-234 from aged plutonium-238. The anion exchange behavior of plutonium and uranium is being investigated with a small Dowex-1X4 column. Poor adsorption of plutonium from the feed solution reported last month has been attributed to the presence of hexavalent plutonium. Of the reducing agents tested, ferrous sulfamate or hydroxylamine can be used to reduce the plutonium to the quadrivalent oxidation state.

For the evaluation of reducing agents the column was operated as described last month except that a much smaller number of samples, usually two or three, were collected for each type of feed solution. While little reliability can be assigned to the resulting values, they are indicative of relative efficiencies. Small changes in the age of the resin, amount of gas on the column, anf flow rates change the adsorption efficiency.

Previously reported data on the adsorption of plutonium from the untreated feed solution, and the adsorption of plutonium from samples treated with peroxide are given in Table 7 along with the new data. One point of interest is that solution IA previously had been run through the column and presumably all the quadrivalent plutonium had been removed. The data indicate that less than 20 per cent of the hexavalent plutonium was reduced. As reported last month the column effluents from the two runs with peroxide had nearly the same plutonium concentration, again indicating that less than 20 per cent of the hexavalent plutonium had been reduced. Concentrations have been calculated and are reported as total plutonium.

Table 7

SUMMARY OF ION EXCHANGE EXPERIMENTS

Feed Solution	Total Pu mg/ml	Reducing Agent	% Adsorption
B-63 Feed	2.72	None	72
B-63 Feed	2.72	H_2O_2	76
Soln. IA	0.836	H_2O_2	17
0604-1	0.655	[a] 2 ml $Fe(NH_2SO_3)_2$	98-99
0604-2	0.655	[a] 5 ml $Fe(NH_2SO_3)_2$	96-97
0618-1	0.655	[b] 5 ml $Fe(NH_2SO_3)_2$	98-99
0618-2	0.655	NH_2OH-HCl	92-94
0619-1	2.72	[b] 5 ml $Fe(NH_2SO_3)_2$	97

[a] Self oxidation of +3 to +4 upon standing overnight.
[b] $NaNO_3$ added to oxidize to +4 and destroy sulfamate.

Solutions of ferrous sulfamate have been used in previous work to reduce plutonium to the trivalent state. Different amounts of ferrous sulfamate solution (approximately 1.5 Molar) were added to 100 milliliter portions of solutions which had been passed through the column once (0604-1 and -2). The solution turned a deep blue color almost immediately, indicating reduction of the plutonium to the trivalent state. The solutions set overnight to air-oxidize to the quadrivalent state. Plutonium adsorption was improved; however, a great deal of gas formed on the column. When 10 milliliters of two molar sodium nitrate was added to similarly reduced solutions (0618-1, 0619-1) gas did not form on the column and the plutonium adsorption was better.

Hydroxylamine was found to be almost as effective as ferrous sulfamate as a reducing agent (0618-2). Four milliliters of two molar hydroxylamine hydrochloride was added to 100 milliliters of plutonium solution and set overnight. Although the literature reports that hydroxylamine will reduce plutonium to plutonium (111), the solution did not immediately turn blue. After the solution had been passed through the Dowex-1X4 resin, the effluent was treated with additional hydroxylamine hydrochloride at 80°C. The reducing agent decomposed instantaneously. Little or no adsorption was obtained when the solution was passed through the column again.

RESIDUE ADSORPTION The adsorption of trace radioelements evaporated to dryness on metal, glass, and and plastic surfaces is being studied as a function of the drying temperature, nature of the surface, and nature of the solvent from which they are deposited.

Spectrographic analysis showed that the yttrium nitrate used for carrier experiments (MLM-1138) was contaminated with dysprosium, gadolinium, and terbium. The experiments were therefore repeated with spectrographically pure yttrium.

The results (Figure 1) showed that there was no significant difference in the shape of the resulting adsorption isotherm. However, the brightly polished platinum used in the second series of experiments retained a maximum of only 12 micrograms of yttrium, whereas the dull-finished platinum used in the previous work retained up to 32 micrograms of yttrium. These results indicate that the rugosity and real area of the surface, rather than the apparent area, are the governing factors in the adsorptive capacity of the surface.

A series of carrier experiments was performed with 100 micrograms of yttrium on glass, Teflon, and stainless steel surfaces. Table 7 shows the retention of yttrium as a function of surface area.

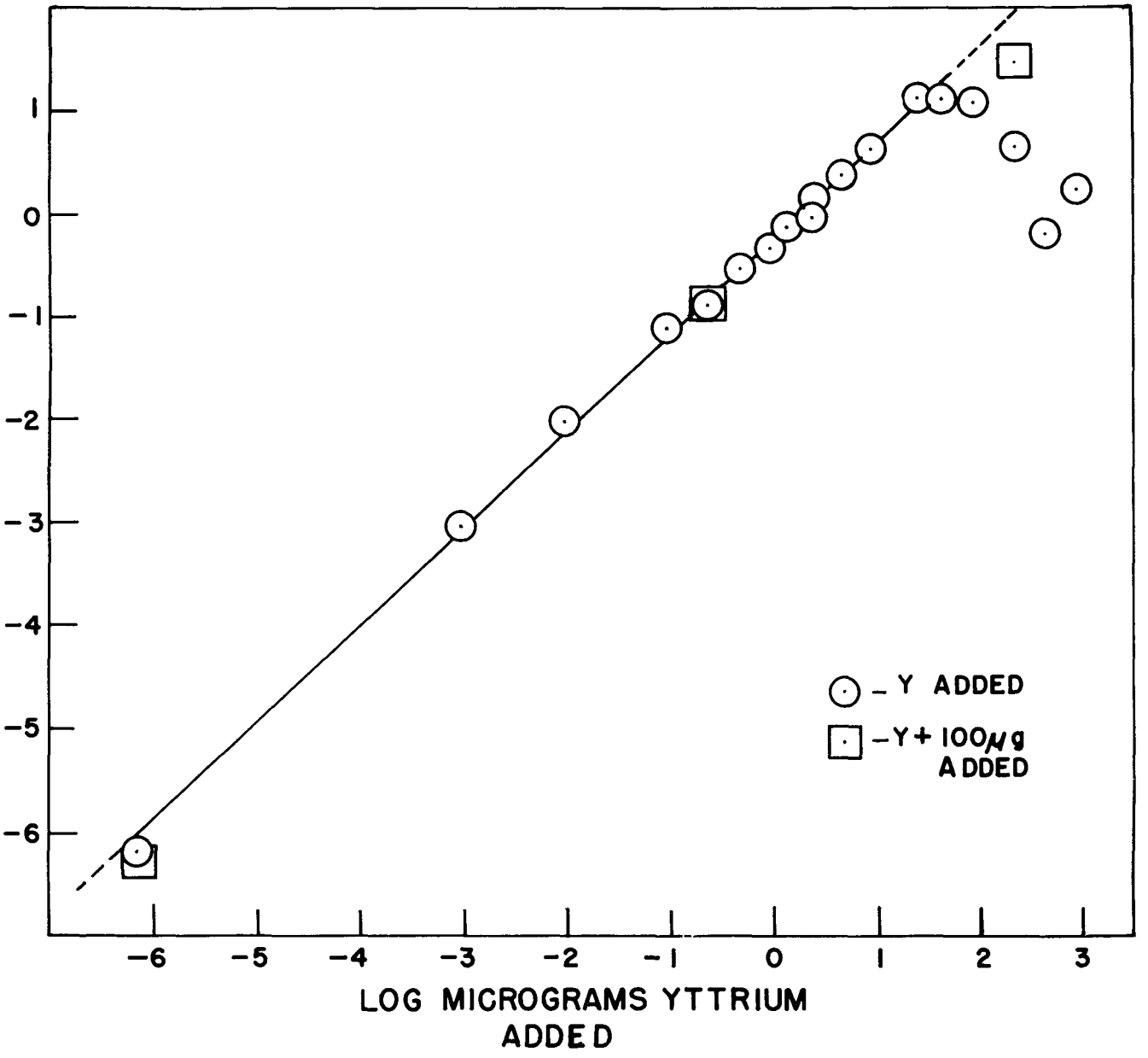

Figure 1

ADSORPTION OF YTTRIUM HYDROXIDE ON PLATINUM

Table 7

YTTRIUM RETAINED BY VARIOUS SURFACES
(100 Micrograms Yttrium Added)

Number	Surface	Apparent Area (cm^2)	Y Retained (micro-g/cm^2)	Rugosity Factor
288-8[a]	Dull Pt (hand polished)	1.8	17.9	2.8
299-4	Bright Pt (machine-buffed)	1.8	6.5	1.0
300-A	Soda-lime glass	1.8	6.4	1.0[b]
300-B	Teflon film	0.4	9.3	1.5
300-C	Bright Stainless Steel (mill-finished)	1.8	11.6	1.8
300-D	Bright Stainless Steel (mill-finished)	4.9	11.4	1.8

[a] Yttrium added was contaminated with Dy, Gd, Tb.
[b] Arbitrary

It is apparent that, if an appropriate standard surface can be found, residue adsorption can provide a rapid and simple method for the determination of the rugosity of metal, ceramic and plastic surfaces. Further work is planned to develop such a method.

The effect of pH on the adsorption of carrier-free yttrium-90 was studied with several mixtures of ammonium acetate, ammonium hydroxide, and acetic acid (Figure 2). In general, an increase in the initial pH resulted in higher retention of yttrium-90, but an increase in salt concentration inhibited the adsorption, probably because of the slow decomposition of ammonium acetate to acetic acid and ammonium hydroxide. Volatilization of the ammonia and the consequent increase in acetic acid concentration would tend to decrease the pH during the evaporation.

Work on the strontium-90/yttrium-90 system is now essentially cpmplete. Future work on residue adsorption will be devoted to a study of the adsorptive behavior of other radioelements and, particularly, the relative adsorption of the rare earths as a function of their basicities.

POLONIUM-208 AND 209 IN IRRADIATED BISMUTH After replating the polonium in a third 12-year-old sample to remove impurities, the ratio of polonium-210 to polonium-209 was determined by alpha pulse height analysis (MLM-1138). The activity ratio (R_{A_0}) and atom ratio (R_{N_0}) of polonium-210 to polonium-209, when first prepared, were 4.78×10^9 and 1.76×10^7, respectively. There is some indication that polonium-208 is also present in all three samples which have been examined. This can be determined with certainty when the polonium-210 has been decayed to a level where its alpha activity will not obscure the alpha particles from polonium-208.

The polonium in a six-year-old sample was radiochemically separated from the bismuth in which it was produced. An aliquot of the purified polonium solution was electrodeposited on a silver foil, and counted in a Frisch grid chamber. The relative amounts of polonium-208 and polonium-210 found by alpha pulse height analysis agreed well with those determined by calorimetry. In addition, it was possible to estimate the polonium-209 content. Several such foils have been prepared, having various levels of activity; they will be useful energy standards in further work.

A gamma ray pulse height analysis of the purified polonium solution showed the characteristic gamma rays of polonium-208 and polonium-209. Since no unexpected gamma rays were observed, the solution of the three polonium isotopes can be used as a gamma ray standard for positive identification of polonium-208 and polonium-209.

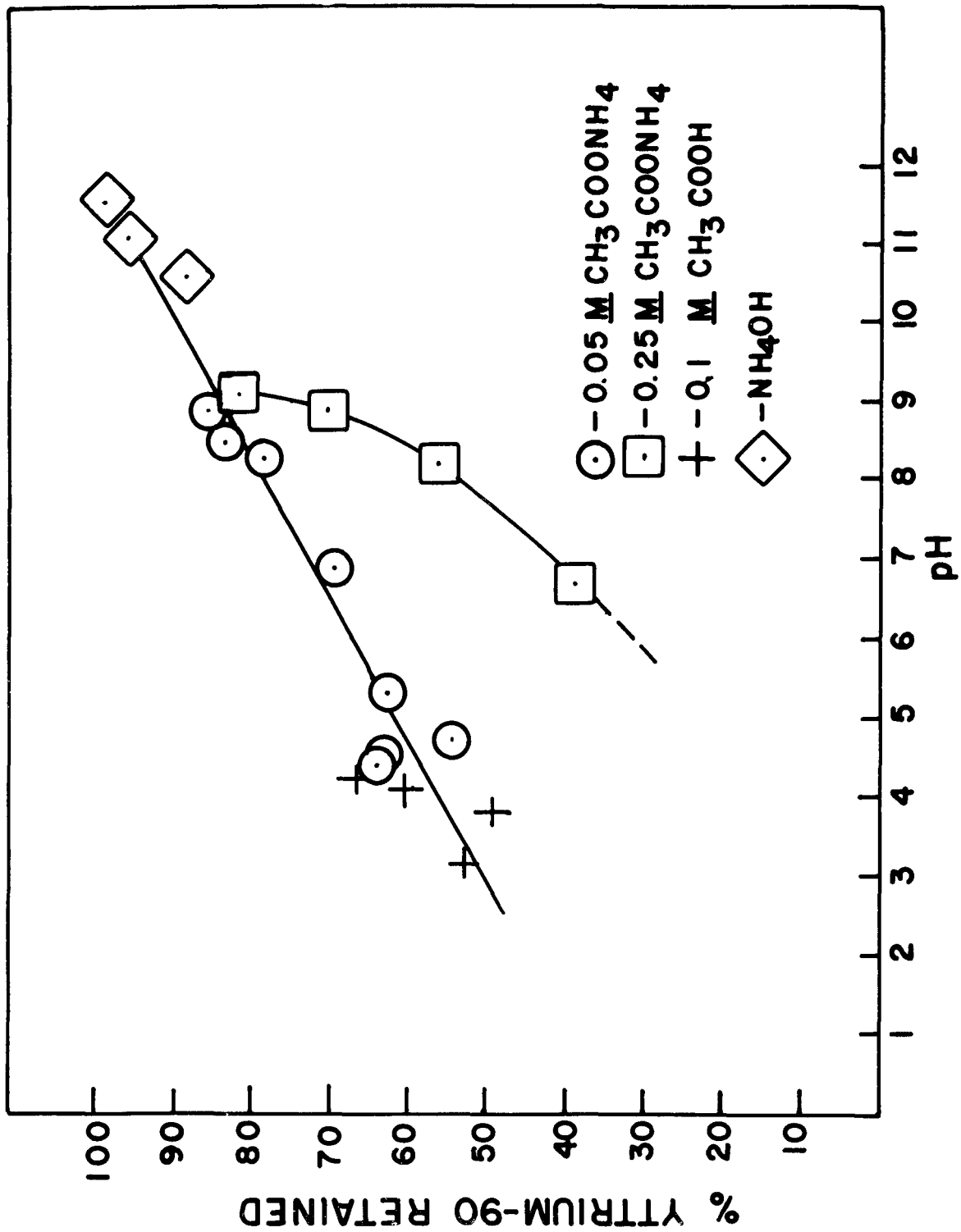

Figure 2

ADSORPTION OF YTTRIUM-90: EFFECT OF pH

ISOTOPE SEPARATION AND PURIFICATION

The development and improvement of processes for the recovery and purification of stable isotopes is a continued activity. The basic theory of isotope separation by thermal diffusion and other applicable techniques is being studied.

HELIUM ISOTOPE SEPARATION AND PURIFICATION Approximately 160 liters of helium-3, which had been processed through thermal diffusion columns, were processed through a freezeout chamber to reduce the tritium content. The gas was pumped at one liter per minute by a refrigeration compressor through a chamber containing activated silica at 4.2°K. The gas leaving the chamber was pumped by a second refrigeration compressor to a product storage tank and sampled. A direct beta counting indicated a tritium content of 6.3×10^{-10} per cent.

CARBON ISOTOPE SEPARATION

Thermal Diffusion Commercial methane is being evaluated as a feed to the thermal diffusion columns to separate carbon isotopes. Impurities such as nitrogen, carbon monoxide and carbon dioxide that are heavier than methane flow with the enriched carbon-13 fraction.

Two methods are presently being explored to solve this problem. The first method uses the 1-¼ inch diameter cascaded thermal diffusion columns as an initial purifier. Commercial methane is fed into the cascade. The heavier impurities are drawn off the bottom and purified methane is recovered from the top. The second method uses a clean-up column after the isotopic enrichment. Commercial methane is introduced in the first stage of a three-stage unit and the carbon-13 is enriched to 10 to 11 per cent. The impurities is the methane, which amount to about 50 per cent of the total volume, are drawn off the bottom of the clean-up thermal diffusion column and the methane is drawn off the top.

Since these methods do not adequately purify the methane, a small versatile fractional distillation unit is being designed. Such a unit with flexible condensing and heating capabilities should prove useful for a variety of separations in addition to the removal of oxygen, nitrogen, carbon monoxide and ethane from methane.

A catalyst chamber has been activated to react carbon monoxide with hydrogen to form methane for further enrichment by thermal diffusion. The nickel catalyst was prepared by treating 30 to 60 mesh chromatographic fire brick with a saturated aqueous nickel nitrate solution. The fire brick was then dried at 100°C, and the nickel nitrate was oxidized to nickel oxide at 250°C in oxygen. The nickel oxide was then reduced in hydrogen for three hours at 250°C and two hours at 300°C. The reduced nickel on the fire brick was cooled and stored in hydrogen.

URANIUM ISOTOPE SEPARATION A literature search has been continued to determine the most suitable approach to the photochemical separation of uranium isotopes. Recent investigations of the uranium hexafluoride molecule indicate that the visible and near ultra-violet electronic band spectra are more complicated than was originally believed. In common with most heavy polyatomic molecules, interaction of electronic, vibrational, and rotational energy states along with departures from transition rules result in very complex diffuse band spectrum. Because of this complexity it does not seem likely that one could take advantage of an isotopic shift for photochemical purposes.

A study of the infrared spectrum of uranium hexafluoride revealed that there are two fundamental molecular adsorption bands which are reasonably narrow in width. Nothing has been found in the literature concerning the magnitude of isotopic shifts for the uranium hexafluoride molecule in this region of the spectrum, but if these adsorption bands arise from uranium-to-fluoride bands, such a shift should be relatively large.

The problem would then reduce to location of a suitable low energy reaction involving uranium hexafluoride. The literature also indicates that crystals are now being developed for solid state optical masers which provide monochromatic radiation in this region of the spectrum so that low temperature reactions are a possibility.

Thermodynamic studies and calculations have been made in an effort to find a suitable material to withstand uranium hexafluoride at higher temperatures. Preliminary results indicate niobium might be sufficiently inert to avoid attack at elevated temperatures. Therefore, the possibility of using a niobium center wire for a thermal diffusion column to separate uranium isotopes becomes a possibility although nothing is known of the degree of departure of uranium hexafluoride from a Maxwellian gas at higher temperatures.

THEORETICAL RESEARCH The derivation of the differential equation for x_1, as a function of z and T, for the plane case was presented previously (MLM-1138). The differential equation for x_1 for the cylindrical case has been derived and is given below. The derivation is basically the same as the one given for the plane case. The partial differential equation for x_1 is:

$$\frac{Q^2}{r^2\lambda} m_2 \frac{n}{\rho} \frac{\delta}{\delta T} \frac{n D_{12}}{\lambda} \left[\frac{\delta x_1}{\delta T} + \frac{\alpha x_1 x_2}{T} \right] = nv \frac{\delta x_1}{\delta z} - nm_2 D_{12} \frac{\delta}{\delta z} \frac{n}{\rho} \frac{\delta x_1}{\delta z} \tag{1}$$

where v is given by the differential equation

$$\frac{Q^2}{\lambda r^2} \frac{d}{dT} \frac{\eta}{\lambda} \frac{dv}{dT} = \frac{dp}{dz} + \rho q \tag{2}$$

where Q is given by the equation for the temperature distribution

$$2\pi Q = -2\pi\lambda r \frac{dt}{dr} \tag{3}$$

where $2\pi Q$, the heat flow per unit length is given by

$$Q \ln \frac{r_1}{r_2} \int_{T_1}^{T_2} \lambda dT \tag{4}$$

where r_1 and r_2 are the radii of the outer and inner cylinders respectively, and T_1 and T_2 are the temperatures of the water and inner cylinders respectively.

These equations are essentially the same as those given by Jones and Furry. *(Furry, W. H. and Jones, R. Clark, Phys. Rev., 69 459 (1946).)*. Equation 1 differs from their equation (112) because they have assumed that $\frac{m_1 - m_2}{m_1} x_1 \ll 1$. The solution of equation (1) by the method used by Jones and Furry is currently being studied. Since their method contains several assumptions, the feasibility of solving equation (1) numerically is also being investigated.

A considerable amount of experimental data is available at Mound Laboratory on the separation of helium-3 from helium-4 by thermal diffusion. A paper given at the Gordon Conference in 1960 compared the experimental results with the results predicted by the Jones and Furry theory. Experimental data were given for concentrations ranging from 0.1 per cent to 97 per cent. Since $\frac{m_2 - m_1}{m_1} = 0.33$, one might expect to see significant deviations between the experimental results and Jones and Furry theory, especially at the higher concentrations. The data given in this paper are being analyzed to determine if there are any significant deviations.

Jones and Furry give the following equation for the transport of species 1 in the column:

$$t_1 = Hx_1 x_2 - K \frac{dx_1}{dz}$$

where H and K are constants for a given gas and a given column. They are functions of temperature, pressure, column dimensions and the transport properties of the gas. Since accurate values of the transport properties are not available, H and K cannot be accurately calculated. However, the ratio H/K can be calculated from experimental data of x_1 and a function of z. If both ends of the column are closed $t_1 = 0$, and

$$\frac{dx_1}{dz} = \gamma x_1 (1 - x_1)$$

where $\gamma = H/K$

Integrating, it is found that

$$\gamma z = \ln A \frac{x_1}{1-x}$$

The constant of integration, A, is evaluated from the condition that

$$\int_0^L x_1 \, dz = x_{10} L$$

where x_{10} is the initial concentration of species 1 so that

$$A = \frac{e^{\gamma L} - e^{x_{10} \gamma L}}{e^{x_{10}\gamma L} - 1}$$

Thus, if the initial concentration is known, γ can be calculated for each experimental value of x_1 and z. Values of γ evaluated in this manner were plotted as a function of x_1 (z). It was seen that the points were widely scattered and that the scattering increased as x_1 increased. It appears that equation (5) will not fit the experimental data, and that gamma may be a function of z. This point is being investigated both theoretically and through a further analysis of the experimental data.

REACTOR FUELS AND MATERIALS DEVELOPMENT

Reactor Fuels and Materials Development Program at Mound Laboratory is directed to the determination of fundamental information relative to plutonium-bearing materials which are of interest as potential reactor fuels. Plutonium is being considered as a fuel for power reactors of the fast breeder concept because of its high neutron efficiency. The program has been divided into three major research areas, which are: the measurement of physical and thermal properties of fuel systems; the determination of plutonium alloy phase equilibria and structures; and the formulation and evaluation of plutonium-bearing glass and oxide systems.

PHYSICAL PROPERTIES MEASUREMENTS A high temperature calorimeter has been constructed to measure the specific heat and the latent heat of transformation of plutonium and plutonium alloys in both the liquid and solid states. The thermal conductivity of liquid metals can be determined by suitable modifications of the calorimeter. The calorimeter as presently designed operates from 60° to 600°C.

The latent heats of transformation for each of the five solid state phase transformations in plutonium metal are being measured in the high-temperature calorimeter. A satisfactory procedure has recently been implemented which permits accurate measurements of the heats of transformation. The completion of the first series of determinations gave the following results: 813 calories/g-atom for the alpha to beta transformation; 123 calories/g-atom for the beta to gamma; 140 calories/g-atom for the gamma to delta; 17 calories/g-atom for the delta to delta-prime; and 309 calories/g-atom for the delta-prime to epsilon phase change. All of these values, except for the delta-prime to epsilon value which is 30 per cent low, are in good agreement with the values recently reported by R. G. Loasby, A. W. R. E., Aldermaston.

A second series of determinations for these same phase changes is planned so that the precision of the determinations can be measured. The heat of fusion at the melting point will be determined during the next series of measurements.

Viscosity Mound Laboratory is equipped to measure the viscosity of liquid metals from their melting points to 1000°C. The measurements are made in an oscillating cup viscosimeter. Measurements have been made on several plutonium alloys of interest to the molten plutonium fast reactor program as well as on several rare earth metals. A second viscosimeter of the same type is being constructed that will extend the temperature range of operations to 1300°C.

A rod of filtered eutectic Pu-Ce-Co alloy (19.6 a/o Pu, 56.2 a/o Ce, and 24.2 a/o Co) weighing 70.4558 grams was sealed in a tantalum viscosity capsule at the Los Alamos Scientific Laboratory and shipped to Mound Laboratory. The viscosity of this alloy was measured at ten different temperatures from 444° to 931°C. An unfiltered alloy of this same composition had been investigated earlier at Mound Laboratory between 446° and 801°C.

The change in viscosity of the ternary eutectic alloy as a function of reciprocal absolute temperature is shown in Figure 3. The values for the filtered alloy measured this month are represented as squares and show excellent agreement with the unfiltered sample previously measured (shown as circles). No significant change in the viscosity can be attributed to the use of a filtered metal sample.

The straight line drawn in Figure 3 represents a least squares solution for all 19 measurements of the viscosity of this alloy. The equation of the line is:

$$\log_{10} \eta = 1.086\,(1/T) - 0.330$$

where η = viscosity in centipoise, and

$T = {}^{\circ}K \times 10^{-3}$,

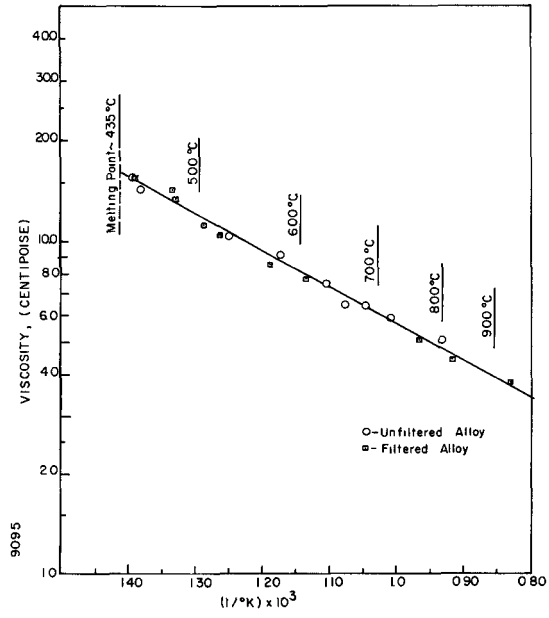

Figure 3

VISCOSITY OF A Pu-Ce-Co EUTECTIC ALLOY AS A FUNCTION OF ABSOLUTE TEMPERATURE

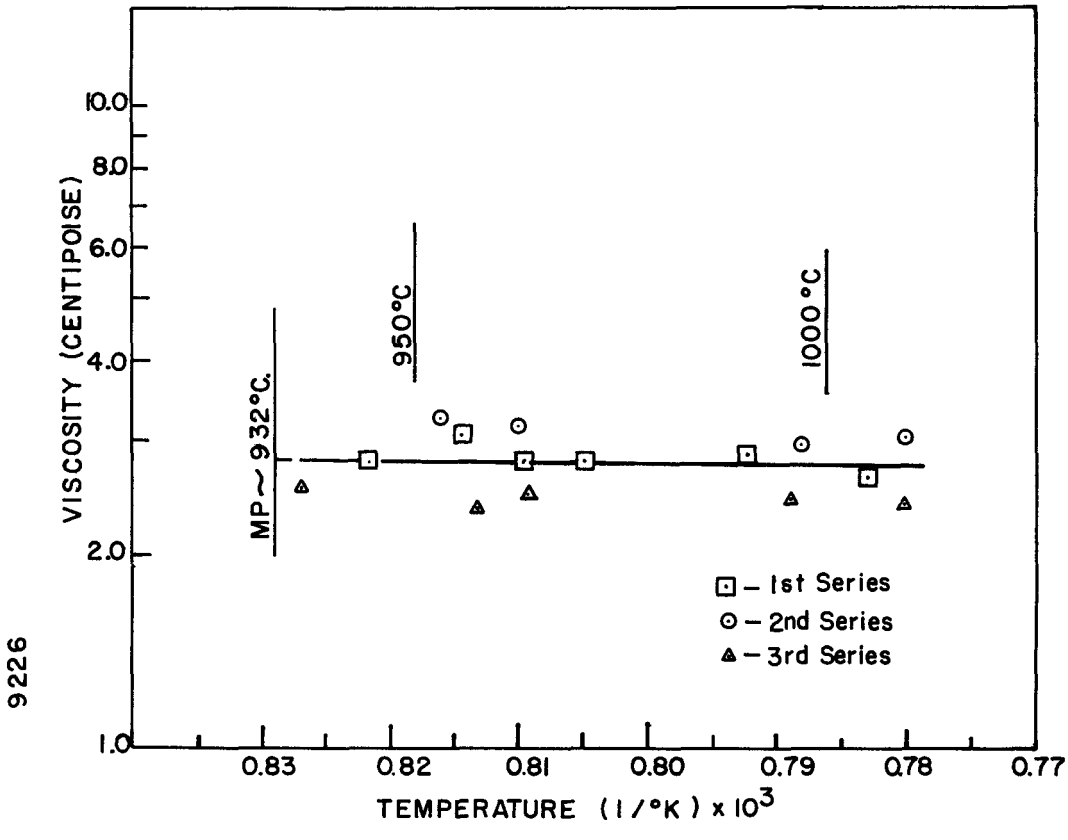

Figure 4

VISCOSITY OF PRASEODYMIUM AS A FUNCTION OF ABSOLUTE TEMPERATURE

The activation energy for viscous flow was calculated from the slope of this line to be 4975 calories/g-atom. This value compares with 5500 calories/g-atom for the Pu-Fe eutectic alloy and 3100 calories/g-atom for plutonium metal.

A rod of high purity praseodymium metal weighing 80.2467 grams was sealed in a tantalum viscosity capsule and the viscosity of the liquid praseodymium was measured at six temperatures between 944° and 1004°C. Figure 4 shows the viscosity of praseodymium as a function of reciprocal absolute temperature, and the straight line drawn represents a least squares solution for all six determinations. The equation of the line for the viscosity of liquid praseodymium is defined by:

$$\log_{10} \eta = 0.621\,(1/T) - 0.050$$

where η = viscosity in centipoise, and

$T = {}^{\circ}K \times 10^{-3}$

The activation energy for viscous flow of praseodymium is 2800 calories/g-atom, which compares with 1900 calories/gram-atom for lanthanum and 3100 calories/g-atom for liquid cerium.

Table 8

VISCOSITY DATA

Metal	Temperature °C	Density g/cc	Viscosity Centipoise
Pu-Ce-Co	444	8.980	15.40
	500	8.968	11.90
	600	8.943	8.22
	700	8.920	6.12
	800	8.893	4.83
	900	8.868	3.95
	931	8.860	3.75
Pr	944	6.610	2.88
	950	6.609	2.86
	975	6.604	2.80
	1004	6.599	2.73

Table 8 is a compilation of the viscosity data of both the liquid Pu-Ce-Co eutectic alloy and the liquid praseodymium. The viscosity values at each temperature were taken from the least squares lines drawn in Figures 3 and 4.

Studies are being made with uranium and plutonium with yttrium as a possible container material for the liquid metals. Liquid uranium will be investigated in the viscometer when the temperature range is extended to 1300°C. Yttrium crucibles were found to contain molten uranium at 1200°C for 2.5 hours (see Figure 5). When plutonium metal was placed in an identical crucible and heated to 1200°C, the plutonium severly attacked the yttrium crucible after 15 minutes as shown in Figure 6. Preliminary results indicate that yttrium will be a suitable container material for uranium to 1200°C, but the use of yttrium as a container for plutonium metal or a olutonium alloy is not feasible.

Interfacial Tension The use of sodium as a direct contact coolant for molten plutonium alloys in a power reactor experiment requires a knowledge of the interfacial energy (or tension) between the plutonium fuel and the sodium coolant. The interfacial energy between the fuel and coolant is being measured at Mound Laboratory.

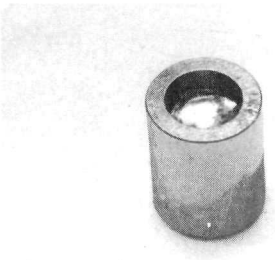

Figure 5

URANIUM METAL IN YTTRIUM CRUCIBLE AFTER 2-½ HOURS AT 1200°C

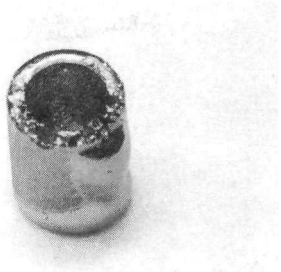

Figure 6

PLUTONIUM METAL IN YTTRIUM METAL CRUCIBLE AFTER 15 MINUTES AT 1200°C (note overflow)

Although numerous methods exist to measure the surface tension of liquids, only a few methods are adaptable to measure the interfacial tension between two immiscible liquid metals at high temperatures. The drop weight and maximum bubble pressure (m.b.p.) methods appeared to be most convenitntly adapted to the measurement of the interfacial tensions of liquid metals.

Attempts to measure interfacial tensions using the drop weight method were unsuccessful since serious difficulties were encountered in the development of a counting method for the number of drops of one liquid passing through a second liquid. Work since has centered about the m.b.p. technique.

With the m.b.p. technique the maximum pressure within a drop of one liquid immersed in a second liquid is measured immediately prior to the detachment of that drop into the second liquid. The method requires the less dense liquid be drawn up through a small tube protruding from a larger tube. The tube containing the lighter liquid is inserted into the dense liquid and the pressure required to detach a drop of the dense liquid at the tip of the small tube is measured.

Considerable success has been obtained using this technique to measure the interfacial tension of organic-aqueous mixtures. Several attempted measurements of the interfacial tension of mercury and gallium during the past month were unsuccessful because of excessive wetting of the glass capillaries by gallium. This difficulty will be avoided by substituting a thin walled stainless steel tube for the glass capillary tube.

The apparatus to measure interfacial tensions of liquid metals at high temperaturesis being designed. A probe has been designed and tested to measure the height of a liquid metal inside a narrow metal tube.

Previous measurements with the m.b.p. method forced a heavier liquid through a lighter liquid. Some question exists as to the appropriate radius (inner or outer) of the tube to be used in calculating the interfacial tension. Experience with the drop weight method has shown that when a lighter liquid is passed through a heavier liquid, the drop always detaches from the inner tube radius. Experiments conducted by passing a lighter liquid up through the heavier liquid have shown that a maximum pressure existed just prior to the detachment of the drop. Interfacial tension measurements on several organic-aqueous mixtures by this technique were in excellent agreement with the literature values. This modification of the technique will not require any major changes in the equipment which has already been designed. In addition, it requires a smaller amount of plutonium for the high temperature work.

Experiments will be continued with the metal tube for tests of the m.b.p. method on liquid metals. The possible use of a pressure transducer in place of a manometer to read the maximum pressure more accurately is being considered and will be tested as one becomes available.

PHASE STUDIES

The Plutonium-Cerium Binary System The plutonium-cerium binary system has been investigated by differential thermal analysis (DTA) and metallographic techniques as a prerequesitite to the investigation of the plutonium-cerium-copper ternary system. A binary diagram based on DTA results was presented previously (MLM-1137). This diagram differs in some respects from the diagram proposed by investigators at the Los Alamos Scientific Laboratory. Metallographic techniques are currently being used for verification of the proposed Mound DTA diagram, and to establish the solid solubility limits of beta cerium, delta plutonium and epsilon plutonium.

Alloy compositions which have been annealed at preselected temperatures are examined metallographically for a determination of the number and identity of the phases present. Samples which have been annealed in a two phase area are then examined with an electron probe x-ray analyzer which determines the compositions of each of the phases and locates the solid solubility limit lines of the system.

No major changes from the diagram proposed by DTA have been found from the electron probe x-ray analyses. These analyses indicate that the solubility of plutonium in beta cerium is about 34 atom per cent plutonium at 625°C and decreases to 22 atom per cent plutonium at 625°C. Samples are being annealed to extend this line to 400°C. The delta plutonium solid solubility lines are not accurately determined as yet, but preliminary results indicate a shift in the line of two to three atom per cent cerium lower than that proposed by Los Alamos (25 per cent cerium maximum at 592°C). The temperature of maximum solid solubility remains to be established, but it is above 595°C and apparently is 615°C. Only minor changes in the epsilon plutonium solid solubility line are proposed. A complete summary of the metallographic results will be included in a final report at a later date.

The microstructure of alloys containing 25 to 65 atom per cent cerium indicated that a eutectoid reaction might have occurred upon cooling. A fine lamellar structure was present in the high plutonium-bearing phase which resembled a eutectoid structure and precipitation from solid solution. Since a eutectoid reaction must originate from a single phase, and a quench from this single phase region should give a martensitic type structure, a search for a single phase area was initiated. No single phase area could be found. Electron probe analysis did not indicate any single phase areas and no martensitic type structure could be detected. The fine lamellar structure observed in these alloys is apparently the result of precipitation from solid solution.

The Plutonium-Cerium-Copper Ternary System The plutonium-cerium-copper ternary system is being investigated as a potential fuel system for the molten plutonium fast breeder reactor concept. The liquidus surface of the system is being defined by the coordinated efforts of differential thermal analysis (DTA) and metallographic examinations.

The data obtained in the early stages of the investigation were summarized previously (MLM-1138). The interpretation of data is difficult and speculative when the data are limited. Therefore, no graphical representation of the ternary system will be presented until sufficient results have been obtained to define portions of the system with reasonable accuracy.

Thirteen additional alloy compositions were prepared and analyzed by DTA. The results from these samples are presented in Table 9. The transitions have been assigned as liquidus, eutectic or other, but these identifications are only tentative. These results and earlier studies support the presence of a ternary eutectic at 419°C in the cerium-rich portion of the system. Another ternary eutectic at 792°C probably exists in the copper-rich portion of the system.

The phase identification by metallography, together with the DTA information, determine the primary phase fields and the phase boundaries of the ternary system. The complete crystallization path of an alloy composition can be determined by metallographic examination of the slowly-cooled specimen. When equilibrium is not established by slow-cooling, a quenching technique employing the vacuum quenching furnace is particularly useful in isolating the phases for identification as well as for establishing the order in which they appear. Small samples are heated in a vacuum to a temperature just below the liquidus temperature and slow cooled to a temperature just above the first transformation temperature as detected by DTA. Through this temperature region the primary phase is the only solid phase present. The sample is then quenched and examined metallographically. The isolated primary phase is identified by metallographic techniques and with the aid of the microhardness tester. The same technique is then employed to isolate the primary and secondary phases or the solid phases in equilibrium at any temperature in the crystallization path.

The first identification of primary phases from quenching studies is summarized in Table 10. These results indicate that the primary phase field of the binary compound, $PuCu_2$, occupies a large portion of the ternary system. A preliminary interpretation of the DTA data indicates that the compound, $CeCu_2$, also has a large primary phase field and that a slender primary phase field for plutonium extends across the diagram to the 419°C ternary eutectic.

Table 9

TRANSFORMATION DATA FROM THE Pu-Ce-Cu TERNARY BY DIFFERENTIAL THERMAL ANALYSIS

Composition Atom %			Temperature °C			
Pu	Ce	Cu	Liquidus	Eutectic	Peritectic	Other
90	5	5	623	-	-	609, 499, 128
75	5	20	695	-	-	635, 468, 343, 216, 128
45	10	45	730	-	-	623, 473, 128
35	55	10	605	419	-	579
35	5	60	837	-	-	626, 462, 128
30	45	25	544	419	-	466
20	55	25	555	419	-	431
20	50	30	537	419	-	473
20	15	65	834	-	-	673
15	15	70	820	792	-	-
10	65	25	452	419	-	-
10	25	65	827	-	-	-
5	60	35	488	421	-	-

Table 10

SUMMARY OF METALLOGRAPHIC ANALYSIS IN THE Ce-Cu-Pu TERNARY SYSTEM

Composition			Quenching	
Ce	Cu	Pu	Temperature °C	Primary Phase
5	15	80	640	$PuCu_2$
15	25	60	635	$PuCu_2$
20	40	40	641	$PuCu_2$
25	50	25	650	$PuCu_2$

CERAMIC FUELS

Plutonium-Bearing Glass Silicate glass systems containing plutonium oxide are being investigated as possible reactor fuel materials. The investigations have demonstrated that plutonium oxide can be incorporated into silicate glasses without causing devitrification, and most of these glasses can be shaped into fibers, rods, tubes, ribbons and microspheres. These glass formulations effectively retain the structurally bound plutonium, thus making a contamination-free surface.

Leach tests were started over one year ago to evaluate the chemical durability of plutonium bearing silicate glasses. The glasses were drawn into fibers approximately ten microns in diameter by the monofilament technique. The coiled fibers were placed in several different liquids at room temperature in closed containers. The liquids were analyzed periodically to determine the amount of plutonium leached out of the glass fibers. The final results are listed in Table 11 and the parent glass compositions are listed in Table 12.

Table 11

PLUTONIUM LEACHED FROM PLUTONIUM-BEARING GLASSES

Glass	Leaching Media	Time Months	% Pu Leached
X-1211 +10% PuO_2	Water	19	0.533
X-1211 +10% PuO_2	0.1 N HCl	19	2.048
X-1211 +10% PuO_2	0.5 N HNO_3	18	10.109
X-1227 +10% PuO_2	Water	12	0.801
X-1231 +10% PuO_2	Water	12	0.568
X-1211 +15% PuO_2	Water	15	0.464

Table 12

PARENT GLASS COMPOSITIONS
(Weight Per Cent)

Components	X-1211	X-1227	X-1231
SiO_2	66.58	59.42	66.58
Al_2O_3	5.55	2.56	5.55
CaO	5.55	5.55	4.00
MgO	-	-	1.55
Na_2O	16.65	16.73	20.20
K_2O	5.55	5.58	2.00
Fe_2O_3	0.12	0.12	0.12

After 19 months of leaching in water, glass X-1211 containing 10 weight per cent plutonium oxide has lost only 0.533 per cent of the plutonium. This composition has better chemical durability than either X-1227 or X-1231 containing 10 weight per cent plutonium oxide. In glass X-1227, the increase of silicon dioxide at the expense of aluminum oxide lowers the durability of the glass. The high sodium content of glass X-1231 probably explains the increased attack by water in comparison to X-1211. As the sodium oxide dissolves in the water, the alkaline solution attacks the silicate structure and accelerates the dissolution of the plutonium.

The results in dilute mineral acids show an increase in the amount of plutonium that was leached from the fibers as these leach solutions were more effective in attacking the sodium oxide and potassium oxide in the glass network. Glass X-1211 containing 15 weight per cent plutonium oxide was leached alternately in hot 50 per cent hydrochloric acid and hot water. This treatment removed most of the sodium oxide and potassium oxide along with 2.95 per cent of the plutonium. The fibers were then placed in water at room temperature. After 15 months only 0.464 per cent of the remaining plutonium was dissolved. The durability of this treated glass is very good in water because of the small amount of sodium oxide.

The good durability of the plutonium-bearing glasses from X-1211 after leaching in water for 19 months, represents excellent resistance to attack, particularly in view of the large surface area of the glass fibers which were exposed to the leach solution. Attack of this glass in massive form should be insignificant.

High Temperature Oxide Studies Ceramic systems are desirable as high temperature and high burn-up fuel systems. Plutonium dioxide appears particularly attractive since its simple crystal structure is expected to sustain a minimum amount of radiation damage. Mound Laboratory has the capability of sintering ceramics in vacuo or partial pressures of various gases to 2000°C. The induction-coupled argon plasma torch, which produces temperatures as high as 20,000°K has been a valuable tool for the study of

the ceramic materials. Contamination-free microspheres of the ceramic materials produced in the induction coupled plasma torch have been the unique aspect of the ceramic program at Mound Laboratory.

The high temperature oxide studies have continued during the past month in three areas: (1) the spheroidization of several sieve sizes of a sintered and ground 90 weight per cent PuO_2 - 10 weight per cent UO_2 mixture; (2) a new method for measuring the density of PuO_2 microspheres; and (3) the initiation of a study of the sintering and melting characteristics of stabilized and unstabilized zirconium dioxide.

A 90 weight per cent PuO_2 - 10 weight per cent UO_2 mixed powder sample was sintered in wet hydrogen for 30 minutes at 1550°C, and for 50 minutes at 1650°C. After the sintered pellet was ground,the resulting powder was sieved into five sieve fractions between -400 and -120, mesh. Each sieve fraction was divided into two parts; one part to be introduced into an oxygen-enriched plasma (75% Ar - 25% O_2) and the other into a pure argon plasma. Microspheres were produced from all sieve fractions in both atmospheres. All of the microspheres produced had the same general appearance.

A technique for filling x-ray capillary tubes in an alpha box enclosure and emerging with a contamination-free capillary was developed. Samples of the above materials before and after spheroidization were prepared and submitted for x-ray analysis. Preliminary photographs show the particle size to be in excess of that required for accurate lattice calculations. The results are being evaluated.

A pycnometric method for determining the density of microspheres was evaluated with high density PuO_2 microspheres. These microspheres as previously measured by two other methods had a density of 11.0 g/cc at 25°C (96% of theoretical crystalline density).

Two one-gram samples of the PuO_2 microspheres were placed in two calibrated one-mil volumetric flasks. Triple distilled mercury was "vacuum cast" into the flasks and a weight difference method was used to calculate the density. The apparent densities were 11.0 and 10.2 g/cc at 25°C. The two flasks were inverted after the determinations. In the 11.0 g/cc sample, the microspheres and the mercury were suspended in what looked like a solid matrix. The lower apparent density of the second sample was attributed to a bubble observed in the center of the sample when it was inverted. Instead of the solid "casting" that the first sample exhibited, a central region of loose microspheres was observed which fell away from those held fast by the mercury. The 11.0 g/cc value was accordingly determined to be the correct value. The method was accepted because of its convenience with the qualification that precautions must be taken which avoid the formation of central bubbles.

An investigation of the sintering and spheriodization characteristics of zirconia both stabilized and unstabilized with yttria was undertaken. This study is pertinent since zirconia may be useful as a diluent for plutonia.

Pellets were die-pressed from -325 mesh powder using beeswax dissolved in carbon tetrachloride as a die lubricant. The "green" pellets were measured with a micrometer and weighed on an analytical balance. The pellets were then sintered, remeasured and reweighed. Average densities in the "green" and fired conditions were calculated. Table 13 summarizes the sintering temperatures and densities observed in these determinations. All sintering was done in air.

The high temperature oxide studies will continue with the x-ray analysis of the PuO_2-UO_2 microspheres, spheroidization studies of the stabilized and unstabilized zirconia, and characterization of PuO_2 powders obtained from several calcination treatments of plutonium oxalate.

Table 13

SINTERING CHARACTERISTICS OF ZrO_2

Material	Green Density g/cc 25°C	Sintering Temperature °Centigrade	Sintering Time Hours	Fired Density g/cc 25°C
ZrO_2	3.08	1200	1-¾	4.17
ZrO_2-8% Y_2O_3	3.60	1450	1	4.07

PUBLICATIONS

1. "A High Temperature Calorimeter for Thermal Property Measurements of Plutonium Metal" by T. K. Engel, K. C. Jordan and D. M. Scott, has been accepted for presentation at the Third Conference on Nuclear Reactor Chemistry at Gatlinberg, Tennessee in October, 1962.

2. "High Density Plutonium Dioxide Microspheres for a Reactor Fuel" by L. V. Jones, Donald Ofte, P. A. Tucker and L. J. Wittenberg was accepted for presentation at the Third Conference on Nuclear Reactor Chemistry in October, 1962.

3. "Metallographic and Differential Thermal Analysis of the Purity of Cerium" by J. E. Selle, D. E. Etter, T. B. Rhinehammer and L. J. Wittenberg, was submitted to the Metallographic Society of the AIME for presentation at the 1962 Fall Meeting.

4. "Phase Equilibria for the Ternary Fused Salt System $NaF-BeF_2-UF_4$" by J. F. Eichelberger, C. R. Hudgens, L. V. Jones, G. Pish, T. B. Rhinehammer, P. A. Tucker and L. J. Wittenberg, was submitted to the Journal of The American Ceramic Society for publication.

5. "The Viscosity and Density of Molten Plutonium Metal and a Plutonium-Cerium-Cobalt Eutectic Alloy" by L. V. Jones, Donald Ofte, W. G. Rohr and L. J. Wittenberg, was accepted for presentation at the Technical Program of the 44th National Metal Congress and World Meeting Show in New York in October, 1962.

6. "Neutron Spectrum of a Plutonium-Beryllium Source" by M. E. Anderson and W. H. Bond, was submitted to Physical Review.

7. "The Viscosity of Bismuth Lead and Zinc to 1000°C" by Donald Ofte and L. J. Wittenberg was submitted to the Transactions of the Metallographic Society for publication.