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MOUND LABORATORY PROGRESS REPORT FOR JUNE, 1962

G. R. Grove, L. V. Jones and J. F. Eichelberger

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MIAMISBURG, OHIO

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MOUND LABORATORY PROGRESS REPORT FOR JUNE, 1962

G. R. Grove
L. V. Jones
J. F. Eichelberger

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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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TABLE OF CONTENTS

	Page
<u>PLASTICS RESEARCH</u>	4
Plastics	4
Adhesives	4
<u>ANALYTICAL</u>	8
Emission Spectroscopy	8
Calorimetry	8
Heavy Element Mass Spectrometry	9
Computer	10
Nuclear Magnetic Resonance	10
<u>RADIOELEMENTS</u>	12
Half-Life of Radium-223	12
High-Melting Compounds of Polonium	12
Polonium-208 and 209 in Irradiated Bismuth	14
<u>ISOTOPE SEPARATION and PURIFICATION</u>	15
Physical Properties of Gases	15
Krypton-85 in Xenon	15
<u>REACTOR FUELS and MATERIALS DEVELOPMENT</u>	16
Physical Properties Measurements	16
Phase Diagram Studies	17
Plutonium-Bearing Glass	18
<u>RANGER X-RAY SENSOR PROGRAM</u>	19
<u>SNAP IX</u>	20

PLASTICS RESEARCH

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 The rheometer testing and data evaluation on clear and filled diallyl phthalate has continued. Correlations have been obtained for the amount of filled material extruded through the orifice as a function of temperature and testing speed (see Figures 1 and 2).

Further investigations are indicated to extend the temperature and speed limits of these correlations. A further check of these correlations by actual molding of parts is also indicated.

ADHESIVES The main object of the current study of anhydride-cured Oxiron systems is to obtain epoxy adhesive formulations which have the following properties:

- 1 Are compatible with explosives
- 2 Can be easily handled by production workers
- 3 Have fairly high flexibility at low temperature (elongation of at least several per cent at -65°F)
- 4 Have adequate tensile strength at high temperature (at least 500 psi at 160°F)

As reported last month, exploratory work was done by first screening 19 formulations, the compositions of which are shown in the last report (MLM-1137). A few square inches of film from each 40-gram pot were cast manually on aluminum foil. Rough estimates of flexibility and strength properties were obtained from the feel of these crude films. Six formulations were then selected for film casting with the use of a Gardner film caster and tensile test specimens were cut from these films. In addition to the six films (one for each formulation) cured at room temperature (80°F), three were cured at 90°F .

The two-week old specimens were tested at -65°F , 160°F and at room temperature. In subsequent evaluation low temperature testing was omitted whenever it seemed advisable to save machine time. The results of the selected environmental testing so far are shown in Table 1. The results from the two-weeks old specimens seemed to indicate that all formulations in Table 1 are too brittle and testing at -65°F was omitted for the four weeks period. Since in most cases testing could be readily carried out at 160°F and at room temperature, this work was continued to obtain additional information for subsequent formulation work. From the results in Table 1 the following observations can be made:

- 1 EO-33, which is slightly more flexible and stronger at room temperature than EO-29, has greater tensile strength also at 160°F . Both are probably too brittle at -65°F .
- 2 EO-35, which is a composite of EO-29 and EO-33, has physical properties which are roughly averages of those of the two formulations.
- 3 Raising the cure temperature from 80°F to 90°F significantly increased high-temperature tensile strength of these anhydride-cured Oxiron adhesives. The effect was more pronounced in EO-33, which is based on Oxiron 2000 resin, than in EO-29, its Oxiron 2001 counterpart.
- 4 Although incorporation of Oxiron 2002 in the resin or addition of propylene glycol to the curing system could effectively flexibilize these types of Oxiron adhesives at room temperature, such modification did not give flexibility at -65°F and significantly lowered the tensile strength at 160°F .

Figure 1

Figure 2

Table 1

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

		-65°F					
Formulation and Cure Temp. ^a	Age of Specimen	XHead Speed in./min	At Break		At Yield Pt.		% Elon at 500 psi
			psi	% Elon	psi	% Elon	
EO-29, 80°F	2 Weeks	0.02	4204	0.8		No Y.P.	0.095
EO-29, 90°F	2 Weeks	0.02	4329	1.3		No Y.P.	0.15
EO-33, 80°F	2 Weeks	0.02	6536	3.3		No Y.P.	0.25
EO-33, 90°F	2 Weeks	0.02	6617	2.0		No Y.P.	0.15
EO-35, 80°F	2 Weeks	0.02	4962	1.3		No Y.P.	0.13
EO-35, 90°F	2 Weeks	0.02	5511	1.2		No Y.P.	0.11
EO-37, 80°F	2 Weeks	0.02	6512	1.4		No Y.P.	0.11
EO-39, 80°F	2 Weeks	0.02	5123	1.3		No Y.P.	0.2
EO-50, 80°F	2 Weeks	0.02	5866	1.7		No Y.P.	0.2
EO-29, 90°F	4 Weeks		Not	Yet	Determined		
EO-33, 80°F	4 Weeks		Not	Yet	Determined		
EO-33, 90°F	4 Weeks		Not	Yet	Determined		
EO-35, 80°F	4 Weeks		Not	Yet	Determined		
EO-35, 90°F	4 Weeks		Not	Yet	Determined		
Room Temperature							
EO-29, 80°F	2 Weeks	0.02	6623	4.1		No Y.P.	0.31
EO-29, 90°F	2 Weeks	0.2	6254	3.6		No Y.P.	0.29
EO-33, 80°F	2 Weeks	0.2	7625	5.4		No Y.P.	0.35
EO-33, 90°F	2 Weeks	0.2	7982	5.0		No Y.P.	0.31
EO-35, 80°F	2 Weeks	0.2	6466	4.3		No Y.P.	0.33
EO-35, 90°F	2 Weeks	0.2	6581	4.4		No Y.P.	0.33
EO-37, 80°F	2 Weeks	0.2	4019	10.3	5248	5.9	0.56
EO-39, 80°F	2 Weeks	0.2	7061	5.3		No Y.P.	0.38
EO-50, 80°F	2 Weeks	0.2	2130	38.9	2028	9.9	2.3
EO-29, 90°F	4 Weeks	0.2	6456	3.3		No Y.P.	0.26
EO-33, 80°F	4 Weeks	0.2	7890	4.3		No Y.P.	0.27
EO-33, 90°F	4 Weeks	0.2	9012	4.2		No Y.P.	0.23
EO-35, 80°F	4 Weeks	0.2	7107	3.7		No Y.P.	0.26
EO-35, 90°F	4 Weeks	0.2	6905	3.7		No Y.P.	0.27
160°F							
EO-29, 80°F	2 Weeks	2.0	270	65		No Y.P.	Break
EO-29, 90°F	2 Weeks	2.0	309	59		No Y.P.	Break
EO-33, 80°F	2 Weeks	2.0	280	44		No Y.P.	Break
EO-33, 90°F	2 Weeks	2.0	374	41		No Y.P.	Break
EO-35, 80°F	2 Weeks	2.0	311	54		No Y.P.	Break
EO-35, 90°F	2 Weeks	2.0	351	50		No Y.P.	Break
EO-37, 80°F	2 Weeks	2.0	169	43		No Y.P.	Break
EO-39, 80°F	2 Weeks	2.0	275	44		No Y.P.	Break
EO-50, 80°F	2 Weeks	2.0	181	30		No Y.P.	Break
EO-29, 90°F	4 Weeks	2.0	392	66		No Y.P.	Break
EO-33, 80°F	4 Weeks	2.0	330	53		No Y.P.	Break
EO-33, 90°F	4 Weeks	2.0	508	41		No Y.P.	40
EO-35, 80°F	4 Weeks	2.0	438	68		No Y.P.	Break
EO-35, 90°F	4 Weeks	2.0	477	55		No Y.P.	Break

^aFilms which were cured at 90°F, were left at this temperature for three days before aging at 80°F.

ANALYTICAL

Methods of analyzing elements and compounds are being developed to support other programs at Mound Laboratory. These methods include instrumental techniques and classical wet methods

EMISSION SPECTROSCOPY The carrier distillation method of analysis developed for refractory oxides is based on the use of 100-milligram samples, but the use of such large samples involves great health hazards when applied to plutonium oxide samples. Therefore, an investigation was undertaken to determine whether sample size could be profitably reduced and/or whether some other substance could be substituted for plutonium oxide as matrix material without affecting intensity values

A sample of UO_2 was divided into two portions. One portion was converted to U_3O_8 by heating for two hours at 900°C . One hundred-milligram samples of the converted U_3O_8 and of the UO_2 were burned and the spectra were compared.

One hundred-milligram and 10-milligram samples of U_3O_8 were prepared so that equal amounts of impurities were present in both samples. The samples were burned and the intensities of their spectra compared. The process was repeated using ThO_2 in place of U_3O_8 . Anode cups of varied dimension were used with the 10-milligram samples to determine the effect of electrode size on intensities.

A comparison of the spectra of converted U_3O_8 and of UO_2 showed the intensity of the impurities were higher in U_3O_8 than in UO_2 except for the intensities of boron and silicon. The comparison of the intensities of impurities in the 100- and 10-milligram samples showed the values were higher for the 10-milligram samples. This was true for both the U_3O_8 and ThO_2 samples. With the 10-milligram size samples, five millimeter depth cups produced higher intensities than the standard eight-millimeter depth cups. The background intensity was approximately the same in each case.

CALORIMETRY

Calorimeter 89 Calorimeter 89, a twin-bridge macrocalorimeter for research purposes, has been completed and is being tested. It incorporates some construction changes to reduce the "stretching" effect and other slow variations. It has two built-in heaters for automatic operation at a constant temperature with two temperature controllers - similar to the operation of any twin-bath calorimeter.

The first construction change was the elimination of the bottom Lucite sleeve which normally would support the heater leads. Instead, the heater leads were wound in grooves cut in the three-inch long Lucite thermel ends to eliminate two surfaces leading out of the calorimeter that could contribute to the migration of adsorbed gases. The movement of adsorbed gases along surfaces in the direction of temperature gradients is the cause of the "stretching" effect. Secondly, on the inside and outside surfaces of all four Lucite ends, radial grooves were cut $\frac{1}{8}$ -inch apart and 0.05-inch deep with an 0.006-inch circular mill saw to increase the effective surface length and to decrease the thermal conductance out the ends. The heaters were bifilar wound in grooves cut in the aluminum section of the thermel. To have a good surface over which to wind the bridge, masking tape in axial strips was used to cover the entire surface of the thermel. The bridge wire was No. 37 double-Nylon covered 99-alloy wire in a single layer of four departures. The surface of the bridge was not treated. The calorimeter was assembled in such a manner that the air gaps are hermetically sealed, but can be reached by a separate tube extending out of the base. This was done so that samples could be easily assayed with various gases in the air gaps.

Slow Variations in Calorimeter Outputs The cause of the slow variations in all calorimeter outputs is still being investigated. The data indicate that the period of the prime variation is approximately 14 days. Other variations occur daily, monthly and yearly. A plot of the zero bridge potential of Calorimeter 58 over a period

of nine years shows that every year the low values occur from June to September and high values from December through March. There has been no net change in the zero during this time and it is surprising to find that the predominant changes are on a yearly cycle. This result, however, is consistent with the reported observation that varnished resistance elements change resistance yearly. Calorimeter 58 was the last macro calorimeter to have a varnished bridge.

The chief cause of the variations originates in the process of removing and reinserting the sample container. The elapsed time that the sample container is out of the calorimeter is a factor. In order to study this effect systematically, an automatic loading device was constructed and is being used to lift a tritium half life sample out of Calorimeter 51 four times a day. It remains out for two hours and is automatically lowered into the calorimeter again. The sample is removed at 1 p.m., 7 p.m., 1 a.m., and 7 a.m. The bridge output is recorded by an L & N Speedomax recorder using an expanded scale of 1.3 per cent of the total output. Suppression is achieved by a 675,000 ohm shunt across one arm of the bridge. After 11 days of operation, the results are consistent with the less systematic observations of other calorimeters.

1. Each equilibrium does not drift
2. Each change can be attributed to a shift in the zero bridge potential
3. The behavior is independent of the time of day or day of the week
4. The bridge potential increased in an irregular but non random manner for nine days and appears to be going through a peak of 40 microvolts out of 7000 at 1 a.m. June 18
5. The most radical increases (3 microvolts) occurred on the 7 a.m. June 9th equilibrium and the 1 a.m. June 15th equilibrium. The most radical decrease (3 microvolts) was at the 7 p.m. equilibrium on June 18

The weekly trend in the assay of the standard tritium source in automated Calorimeter 77 was reduced to a bi-monthly trend by reducing the bath temperature from 28.9°C to 25°C. Previously the sample and heater sensitivities were both changing. After reducing the bath temperature to room temperature, only the sample sensitivity seemed to change.

HEAVY ELEMENT MASS SPECTROMETRY More analyses were made on the National Bureau of Standards uranium samples in an effort to definitely establish the magnitude of error in the analyses. The analyses included a second determination on a previously analyzed sample. A fresh uranium sample was mounted and analyzed. A new sample was made up from the two NBS uranium samples to contain a 50-50 mixture of U^{235} and U^{238} . This 50-50 mixture was analyzed and the results are tabulated below. The tabulation compares the isotopic abundances of the U-800 sample obtained by the mass spectrometer to the Bureau of Standards values.

Sample	% U^{234}	% U^{235}	% U^{236}	% U^{238}	Number of Scans
U-800 I (Used)	0.735	79.09	0.274	19.90	12
U-800 II	0.731	79.09	0.271	19.91	12
NBS Values	0.660	80.07	0.246	19.02	
% Error		1.2%		+4.7%	
50-50 Mixture	0.475	51.43	0.269	47.83	8
Calc. NBS Values	0.373	51.29	0.228	48.11	
% Error		+0.27%		0.6%	

The errors in the uranium-235 and uranium-238 values decreased in the 50-50 mixture. The uranium-234 and uranium-236 are expected to be in error because the slit adjustment is wide in the spectrometer to get maximum sensitivity. The resulting decrease in resolution causes some uranium-235 to be measured in the uranium-234 and uranium-236 region.

Since uranium-235 and uranium-238 are low when they are present at approximately 80 per cent and high when at approximately 20 per cent, it was suspected that there was nonlinearity in the instruments response. Both vibrating reed electrometers were checked against known current sources and were found to be linear. The electron multiplier was incompletely checked because of the difficulty of finding a current source in the range that it measures. Since the isotope that is 80 per cent in abundance is always measured in the 30 volt range on the vibrating reed electrometer, it is planned to measure this peak on a lower range.

COMPUTER A program for methane calculations has been written and the radial distribution function for x-ray diffraction has been programmed. The program is set up to reduce data from both the CEC Model 21-201 and CEC Model 21-620 mass spectrometers. All the necessary calculations for the analyses are performed using the data from the MS201. Data from the MS620 analyses must be run first on the general mass spectrometer analysis program and the output is then used as input for the methane program for the final percentage calculations.

A program has been written to evaluate the electronic radial distribution function from x-ray diffraction measurements using the expression:

$$4\pi r^2 \sum_m K_m g_m = 4\pi r^2 g_0 \sum_m K_m + \frac{2r}{\pi} \sum_m K_m^2 \int_0^\infty \text{si}(s) e^{-As^2} \sin(rs) ds$$

where

r = radial distance

K_m = effective atomic number

g_0 = average electron density

$s = 4\pi \sin\theta/\lambda$

$i(s) = \frac{K' I_{\text{obs}} - I_{\text{total theoretical}}}{I_{\text{coherent theoretical}}}$

e^{-As^2} = temperature correction factor

λ = wavelength of the radiation

A supplementary program has been written to calculate the normalization factor K' for $i(s)$ and to evaluate several integrals for intermediate results.

NUCLEAR MAGNETIC RESONANCE Carbon-13 has been detected in its natural abundance in a few chemical solvents, e.g., benzene, toluene, xylene, carbon tetrachloride and carbon disulfide. The spectra obtained were comparable to those published in the literature, indicating agreement with other workers in the field of NMR carbon-13 resonance. To observe the resonance of carbon-13 in a gaseous mixture, the carbon-13 nuclei must be concentrated in the region of the probe receiver coil by liquefaction of the gas sample.

The carbon-13 was detected at 8.8 megacycles per second (Mc/s) in a field of about 8220 gauss. To obtain the largest signal a 15 mm ID sample tube was used. The resonances of manganese-55 from an aqueous solution of potassium permanganate and of sodium-23 from an aqueous solution of sodium carbonate were

obtained to bracket the resonance of carbon 13. After calibration of the fine current control of the magnet power supply, carbon-13 resonance was obtained with only minor difficulty. The dispersion mode of carbon 13 resonance was employed with radiofrequency (r f) fields (H_1) of from five to 15 milligauss and rapid sweep rates of about 1000 cycles per second. The carbon-13 nucleus possesses a relatively long thermal relaxation time (T_1) therefore, 15 seconds separated successive sweeps through resonance.

The carbon 13 resonances occurring in natural abundance can now be routinely detected in a variety of carbon containing compounds. It is felt that this ability to detect carbon-13 will be greatly enhanced with enrichment and that a quantitative method will evolve.

RADIOELEMENTS

Processes are being developed for separating and purifying radioelements and potential sources of supply are being evaluated

HALF-LIFE OF RADIUM-223 The half life of radium-223 is being redetermined by alpha counting. The source of the radioisotope is the same as that used by the Calorimetry Group, which reported the half-life to be $11\,4344 \pm 0\,0011$ days in the thermoelectric calorimeter and $11\,4432 \pm 0\,0057$ days in the resistance bridge calorimeter (MLM 1135).

The alpha-counting determination is being made by the method of decaying pairs (MLM-1128). Table 2 shows the results of computer analysis for the first 172 days of counting. The weighted grand mean half life for 45 pairs is $11\,4089 \pm 0\,0404$ days.

HIGH-MELTING COMPOUNDS OF POLONIUM Several methods have been explored for the preparation of milligram amounts of oxide-free rare-earth metals with a large surface to volume ratio. Previous studies at Mound have shown that complete reaction of polonium and yttrium could not be obtained with massive chunks of rare-earth metal.

The molten potassium chloride lithium chloride eutectic bath (42 mole % KCl, 58 mole % LiCl, mp-350°C) removes the oxide from the rare-earth metal. Lanthanum with extensive surface oxidation was successfully cleaned by submerging the metal in the molten salt mixture at about 600°C. The molten metal can be drawn into a fine capillary with a plug of the eutectic salt at both ends of the capillary to prevent oxidation. From the density of the rare earth and the diameter of the wire, the weight of rare earth metal required for an experiment may be readily measured.

A second method of preparing finely divided rare earth metals has been attempted. The rare earth is introduced into a glove box with a helium atmosphere and the oxide film is removed by filing. When the metal surface appears bright and shiny, a new file is employed and the filings are collected in a weighing bottle. The rare earth is then weighed by difference into a reaction tube.

Table 2

PRELIMINARY CALCULATION OF THE HALF-LIFE OF RADIUM-223

Pair Number	Half-Life (Days)	Probable Error (Days)
1 2	10.9214	0.0475
1 3	10.2585	0.0812
1 4	11.2961	0.0227
1 5	11.3221	0.0082
1 6	11.1259	0.0420
1 7	11.4339	0.0092
1 8	11.4513	0.0140
1 9	11.3873	0.0100
1 10	11.4413	0.0147
2 3	10.8689	0.0503
2 4	10.7352	0.1008
2 5	11.1478	0.0244
2 6	11.2710	0.0155
2 7	11.4465	0.0085
2 8	11.4771	0.0125
2 9	11.3888	0.0108
2 10	11.4388	0.0126
3 4	11.3275	0.0198
3 5	11.3167	0.0079
3 6	11.1844	0.0252
3 7	11.4323	0.0079
3 8	11.4591	0.0128
3 9	11.3779	0.0104
3 10	11.4442	0.0127
4 5	11.1063	0.0156
4 6	11.2555	0.0089
4 7	11.4189	0.0060
4 8	11.4463	0.0088
4 9	11.4016	0.0083
4 10	11.4240	0.0073
5 6	11.3777	0.0098
5 7	11.4419	0.0057
5 8	11.4559	0.0086
5 9	11.4124	0.0090
5 10	11.4302	0.0054
6 7	11.4387	0.0054
6 8	11.4506	0.0076
6 9	11.4252	0.0088
6 10	11.4248	0.0054
7 8	11.4017	0.0071
7 9	11.4186	0.0058
7 10	11.3885	0.0079
8 9	11.3743	0.0169
9 10	11.4236	0.0061

Grand Mean (Weighted) 11.4089 ± 0.0404 days

Cerium monopolonide (CePo) has been prepared by reacting cerium metal filings (4.40 mg, weighed out by the second procedure given above) with polonium in a quartz reaction tube, designed to maintain physical separation of the rare earth and the polonium-plated platinum gauzes. Then, 30.33 curies of polonium-210 (102.5 % of stoichiometric for CePo) on two platinum gauzes were introduced to the reaction tube, which was then evacuated and flushed with helium three times. Finally, the tube was evacuated to 0.1 mm Hg, and sealed. The tube was placed in an electric tube furnace with the rare-earth end protruding to volatilize the polonium from the platinum into the rare-earth section. The temperature was raised to 800°C in 18 minutes. Although all the polonium volatilized to the cerium section, little or no reaction occurred between the two metals.

The reaction tube was fully inserted in the furnace and maintained at 800°C for 30 minutes. At the end of this heating period about 95 per cent of the polonium was associated with the cerium as determined by gamma-scanning. The reaction tube was heated for an additional 60 minutes at 800°C. Almost all of the polonium reacted with the cerium forming a material of much smaller particle size than the original cerium filings. The gamma-ray flux, the alpha-bombardment-induced fluorescence of the quartz, and the heating effect were all found to be a function of the location of the powder in the tube.

The reaction tube was returned to the furnace with a portion of the tube insulated from the heat by an asbestos flap. When heated at 800°C for 30 minutes, no polonium was volatilized from the cerium-polonium, indicating that a compound had been formed.

POLONIUM-208 AND -209 IN IRRADIATED BISMUTH The alpha activity of the polonium isotopes from three 12-year old polonium ampoules was examined by pulse-height analysis using a Frisch grid chamber. All three polonium samples contained polonium-209 and one sample may contain polonium-208. Energy resolution of the latter sample was very poor; the polonium has been redeposited on a silver foil and will be run again.

The polonium-209 content at the time of preparation of the ampoules has been calculated for the two samples having good resolution by means of the original polonium-210 content, the relative activity of polonium-209 and polonium-210 at the present time, and the radiochemical yield. Two values for each sample were calculated: R_{Ao} , defined as the ratio of activities of polonium-210 to polonium-209 when the ampoule was prepared, and R_{No} , the atom ratio at the same time. The results are tabulated below:

Sample Number	R_{Ao}	R_{No}
T-1916	2.61×10^9	9.61×10^6
T-2301	3.45×10^9	1.27×10^7

In these two samples there was some indication that polonium-208 might be present. However, low-energy tailing of the polonium-210 alpha group at 5.305 Mev would tend to obscure the polonium-208 alpha group at 5.108 Mev. As the polonium-210 decays, the presence or absence of polonium-208 can be established with certainty.

An investigation of the beta-decay systematics at mass numbers 208, 209 and 210 has shown that the polonium-208 and polonium-209 must arise from (n,xn) or (γ ,xn) reactions on polonium-210 since the two polonium nuclides of interest decay (to a very small extent) by electron capture to bismuth isotopes.

Q-values for the production of polonium-208 and polonium-209 by (n,xn) or (γ ,xn) reactions on polonium-210 are 14.23 Mev and 7.66 Mev, respectively. It would be of interest to explore the neutron cross-section of polonium-210 in the five to 20 Mev range.

ISOTOPE SEPARATION AND PURIFICATION

Processes are being developed for separating and purifying the isotopes of a number of elements including hydrogen, the noble gases, carbon and uranium. Potential sources of supply of these materials are being evaluated.

PHYSICAL PROPERTIES OF GASES In calculating the thermal conductivities of multicomponent isotopic mixtures, one obtains with very little extra effort, the coefficients of thermal diffusion, D_T^T , of the various components. Upon analysis it was found that the thermal conductivity computations performed last month yielded an anomalous result. Although the conductivities themselves were in good agreement with experiment, the thermal diffusion coefficients underwent a change of sign as the concentration was varied. This may be interpreted as an effect which would send the light isotope to the cold wall instead of the hot wire, and thereby form an azeotrope in the column. This has not been observed experimentally, and it is probable that an error exists in the computation.

The treatment of the axial temperature distribution in a hot wire was changed to that of a boundary value problem. The initial conditions assumed are apparently not exact and lead to physically unrealistic results when the differential equation is solved by the Acceleration Plane Method.

A rigorous mathematical derivation of the lower boundary of integration in the Omega Integrals Program has been obtained and the results are found to be compatible with Mason's previous work. The boundary in question is defined as:

- (a) $\psi(r_c)$ in the region $0 < r_c < \sigma$,
when σ is the root of $\psi(r_c)$
- (b) the locus of a point having a maximum in the region of the potential energy minimum, r_m , passing through the energy zero at σ and approaching zero asymptotically as the impact parameter approaches zero. The maximum of this curve is determined by the point of inflection in the singular iso-impact parameter curve having such a point. The locus of a point at larger interaction distances is defined by the positive minima of the remaining curves in the one-parameter family. The position of the boundary in the region from σ to the locus maximum is defined by the smaller of the two interaction distances defined at constant energy on the same iso-impact parameter curve. The integration is to be performed from this boundary to infinity in two dimensions. The necessary changes in the Omega Integrals Program are being made and will be tested in the near future.

The rederivation of the Jones and Furry thermal diffusion theory is being made without the assumption that it applies only to heavy isotopes or to very low concentrations of one of the isotopes. The plane case is being developed first.

MEASUREMENT OF LOW LEVEL KRYPTON-85 IN XENON The average background counting rate of the William H. Johnston one-liter proportional chamber, containing P-10 gas and located inside the low level lead shield, has been 47 ± 4 counts per minute. It is known from the literature that counting rates of approximately 25 per cent of this value have been obtained by other workers employing similar equipment. The relatively high background counting rate does not hinder work now in progress, but it has stimulated an investigation into possible methods of reducing this background.

The background counting rate was not reduced by using a greater thickness of lead. Although an extensive study of the origin of this background radiation has not been conducted, it may possibly be an internal rather than an external problem. If this is the case, the low level lead shield would have to be replaced by a contamination-free steel shield to make a significant reduction in the counting rate.

Ten parts of methane and 90 parts of xenon have been mixed in the gas handling system. This particular P-10 mixture has been introduced in a William H. Johnston one-liter proportional chamber at a pressure of 619 mm (0°C), and a plateau of approximately 300 volts in width has been obtained, which might indicate the presence of contaminants in the P-10 gas. Samples of this gas have been submitted for mass spectrometry and gas chromatography analysis.

REACTOR FUELS AND MATERIALS DEVELOPMENT

The 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 fuels systems, the determination of plutonium alloy phase equilibria and structures, and the formulation and evaluation of plutonium-bearing glass systems

PHYSICAL PROPERTIES MEASUREMENTS The thermal properties of plutonium are being determined in the high temperature calorimeter. The heats of the alpha to beta to gamma transformations have been determined by a method in which the sample chamber sensitivity is the only independent variable involved in the calculation. Neither the thermal capacity contribution from the nickel liner and tantalum container, nor the contribution from the calorimeter need to be considered. Since the sample chamber sensitivity can be determined quite accurately by an absolute method, the latent heat values are accurate to one per cent or less.

One value for each transformation has been calculated by this method. These will be supported by further values as future determinations are made, so that a mean value can be eventually given. The first value for each transformation was calculated to be 867 calories/gram-atom for the heat of transformation from the alpha to beta phase, and 123 calories/gram-atom for the heat of transformation from the beta to gamma phase. These values agree favorably with R. G. Loasby's reported values of 803 ± 10 calories/gram-atom, and 152 ± 15 calories/gram-atom, respectively.

VISCOSITY Six determinations of the viscosity of liquid praseodymium metal were made between 944 and 1004°C. These viscosity data are presently being calculated and interpreted.

A tantalum capsule containing a cerium-cobalt eutectic alloy was sectioned and examined metallographically for possible segregation of the alloy constituents or corrosive attack on the tantalum container. The alloy had been maintained in the liquid state for 10 days during which time the viscosity was measured at 13 temperatures between 450° and 1010°C. During the last five days, the three lowest temperatures (456°, 504° and 558°C) exhibited viscosities from 40 to 80 per cent higher than the values previously determined for the same sample. Examination of the sectioned capsule revealed a thin reaction layer between the tantalum container and the cerium-cobalt alloy. The layer had a bright, silvery appearance and was adherent to the tantalum. One compound, TaCo_2 , that decomposes incongruently at 1593°C is known to exist in the tantalum-cobalt binary system. Apparently, where the TaCo_2 compound was formed on the walls of the tantalum crucible, the cerium-cobalt eutectic alloy became deficient in cobalt. In the cerium-cobalt binary system the liquidus temperature rises rapidly from the eutectic temperature of 432°C to the melting point of cerium at 797°C. As the system cooled the liquidus of the hypoeutectic alloy was intercepted and primary cerium precipitated, causing the anomalous rise in viscosity. The viscosity of this alloy will have to be redetermined.

INTERFACIAL TENSION The maximum bubble pressure method for the measurement of interfacial tension has successfully measured several organic aqueous mixtures. Two measurements of the interfacial tension of mercury and gallium failed because of experimental difficulties. One measurement terminated prematurely when the column of gallium split while in the capillary tube. The second measurement gave results approximately twice the value reported in the literature. The gallium may have adhered to the glass wall of the larger tube as the gallium came out of the capillary tip so that a large air pocket was trapped at the base of the tube.

PHASE DIAGRAM STUDIES The investigation of the plutonium-cerium-copper ternary system by differential thermal analysis has been resumed. A thorough knowledge of the liquidus surface of the system is the immediate objective of this study.

To date, a total of 28 compositions have been analyzed. The transformation data are presented in Table 3 along with a preliminary interpretation of the data in terms of liquidus eutectic and peritectic phase reactions.

Table 3

TRANSFORMATION DATA FROM THE Pu-Ce-Cu TERNARY SYSTEM BY DTA

Tube No.	Composition at/o			Temperature °C			
	Pu	Ce	Cu	Liquidus	Eutectic	Peritectic	Other
125	85	10	5	626	-	-	516
113	85	5	10	664	-	483	626
119	80	15	5	626	420	-	548
101	80	10	10	630	-	520-485	593-506
118	80	5	15	678	-	-	626-473
126	75	20	5	626	420	-	567
124	75	15	10	624	419	516-485	501
122	75	10	15	633	410	518-485	626-497
120	70	20	10	624	419	-	537-478
123	70	15	15	626	420	520-485	588
112	70	10	20	662	-	514-483	624
121	65	20	15	626	422	520-488	-
107	60	30	10	616	416	-	567
117	60	15	25	640	-	576-485	626-466
111	55	15	30	654	-	513-480	624
110	50	40	10	615	419	-	584-508
109	50	25	25	630	422	520-490	581
106	40	20	40	654	-	513-483	616
103	30	50	20	614	419	-	504
108	30	30	40	623	419	518-485	-
110A	25	25	50	716	-	513-485	638-623
104	20	65	15	568	420	-	-
105	20	40	40	574	420	516-485	-
116	20	35	45	661	424	520-485	584
100	15	55	30	459	422	-	-
115	40	50	10	685	422	487	-
114	10	30	60	792	-	513-485	562
102	5	75	20	525	422	-	-

Metallographic studies on the cerium-plutonium binary system were continued. Samples were annealed and examined to identify phase fields. Additional annealed samples were prepared for analysis by the electron probe. Probe analysis samples are equilibrated in the two phase solid solubility region at a given temperature. Analysis of the compositions of the phases will then indicate the limits of solid solubility of the phases at that temperature. Some difficulty was encountered in preparing samples for probe analysis, and it has become apparent that the quality of the etch is extremely important in obtaining accurate analysis. Essentially, two sets of data were obtained for both the beta cerium and the delta plutonium solid solubility lines. One set of data was completely irrational, and had to be discarded. The difference was probably caused by a film on the surface of the sample formed by the etchant.

The data obtained thus far indicate two changes in the cerium-plutonium diagram as proposed by differential thermal analysis. The temperature of maximum solid solubility in beta cerium appears to be 626°C instead of 595°C. Also, metallographic examination has failed to identify a two-phase, liquid plus beta cerium, region between gamma cerium solid solution and beta cerium solid solution. This is the region presented as an inverse peritectic. Samples quenched from this region, which should have been two phase alloys, were identified as only a single phase alloy. Electron probe data confirm that at equilibrium this area is a single phase. A more complete summary of these results, along with the revised diagram, will be presented at a later date.

The long flat portion of the "S" shaped liquidus curve suggests the possibility of a miscibility gap in the binary system. This possibility was checked when a sample containing 35 atom per cent cerium was heated to 716°C for 30 minutes, quenched, and examined metallographically for the presence of two different characteristic forms of quenched liquid. A preliminary examination indicates that no miscibility gap exists at this composition.

PLUTONIUM-BEARING GLASS Ribbons of plutonium-bearing glass were pulled from a rectangular slot cut in the bottom of a platinum crucible. The ribbons approximately 3/8-inch wide are reasonably flat on both faces, although the edges are rounded. These flat ribbons are presently being studied for structural analysis of the glass by x-ray diffraction. The x-ray intensity curves for the five and 10 weight per cent plutonium oxide dissolved in the X-1211 glass have been determined. The theoretical incoherent scattering factor for plutonium as a function of $\sin \theta/\lambda$ is being calculated by the method of Bewilogua. [R. W. James, "The Optical Principles of the Diffraction of X-Rays", P 462, MacMillan and Co., Ltd, London, England, (1948)]. The necessary preliminary computations and intensity distributions are being determined.

The method of Krogh-Moe, [*Acta Crystallographica*, 9, 951 (1956)], for converting relative experimental x-ray intensities to an absolute scale has been employed. An exponential temperature factor correction has been introduced to suppress spurious interaction peaks.

The coefficient of thermal expansion was determined for two glass compositions by dilatometric techniques. The two compositions were glass X-638A containing 9.09 weight per cent U_3O_8 and glass X-1211 containing five weight per cent plutonium oxide. A heating rate of approximately 2° to 3°C per minute was used. The results are listed in Table 4.

The contraction during cooling from the second run on the plutonium-bearing glass was recorded. The rod was shorter after the run, probably from annealing the glass during the heating cycle.

Table 4
COEFFICIENT OF THERMAL EXPANSION (β)

Temperature (°C)	U-glass ($\beta \times 10^7$)	Pu-glass ($\beta \times 10^7$)	
		First Run	Second Run
Pu-50	98.37	99.26	105.2
50-100	92.10	101.6	98.40
100-150	93.68	101.2	100.4
150-200	96.84	112.1	110.0
200-250	102.1	113.1	114.4
250-300	103.7	111.6	114.8
300-350	105.5	99.20	122.4
350-400			
400-450	107.4	95.24	118.4
450-500	88.4	85.76	140.4
500-550	47.9	256.8	260.8
550-600	117.4	222.0	

RANGER X-RAY SENSOR PROGRAM

Mass production techniques to vapor-deposit beryllium onto Formvar plastic films are being developed. From 100 deposition runs, a total of 87 films were completed with optical densities of six or more. Usually eight or ten runs are required to make films of this optical density, and the films should be shifted every run or so to coat both sides and to eliminate shadowing effects. Because of this rotation system and because of an unpredictable film breakage rate, the daily output varied between zero and 18 films on the one vacuum system. An average of ten films per day seems to be a reasonable production rate.

The optical densities (including pinholes) were checked by a modification of the method described previously (MLM-1129). The holes in the one-foot square wooden viewing board were enlarged to accommodate the three-inch square films, cardboard masks were taped into position so that both openings were 2-1/2 inches by 2-1/8 inches to provide equal light areas and retard stray light rays at the point of contact between the film frame and the viewing board. With a standard 6.0 neutral optical density filter covering one port, the board was located at a fixed distance and angle in reference to the lenses of a 300-watt conventional slide projector, a cardboard box in which the photoelectric cell of a Weston Photographic Analyzer had been mounted was placed over the lighted area of the filter and light intensity was checked on the meter. Several readings were made and the highest light intensity point marked on the meter. The coated films were then clamped into position (film toward the projector) and light transmission intensity checked. If the light transmission was less than that through the 6.0 filter, the film was kept.

Several readings were made while turning the film to different positions but there seemed to be very little difference in the metered value; a neutral density filter of 3.0 and another of 3.7 were checked and a reasonably large difference existed. The photoelectric "head" had a sensitivity diameter of 1-3/4 inch and was fixed about 7/8 inch from the surface of the film. Hence, the area view was representative of the film's area. One or two bright holes will give an overall optical density of less than six, but five or six medium-sized or about 20 tiny holes would pass the film.

By employing a suitable jig, plastic films could be mounted on wire frames designed for the Ranger windows and enough beryllium could be deposited on both sides to create the desired optical density. No estimates of production rates or breakage for this type operation have been obtained.

A beryllia crucible heated by thermal radiation is now being used to evaporate the beryllium. Molten beryllium does not attack the crucible and none of the beryllia crucibles have cracked from thermal shock.

A simple monitor, consisting of a glass plate half of which is coated with diffusion pump oil, is now being used to control the amount of deposition. Beryllium does not deposit on the oil-coated part or the plate, and comparison of the source brightness through coated and uncoated parts of the plate gives a value of the optical density.

Several difficulties have been encountered in trying to rapidly deposit the beryllium. In addition to frequent breakage of the films upon cooling, the beryllium coating becomes gray and non-specular. Interference fringes shift with the incidence of reflected light and the transmitted light is partially diffused. Microscopic examination of the window shows a highly granular and sometimes, a web-like deposit. This type of film is extremely brittle and should be rejected. No real explanation for the brittleness has been found, but it is suspected that excessive temperature of the film causes deterioration of the Formvar substrate.

Previous work indicated that an anion exchange process has advantages for the initial separation of uranium-234 from aged plutonium-238. The anion exchange behavior of plutonium and uranium was investigated with a small Dowex-1X4 column.

The feed solution selected for the initial work was a supernate remaining from a peroxide precipitation of PuO_2 which had been evaporated to less than one liter. The solution was calorimetered and found to contain 2.49 grams of plutonium-238 (2.99 grams of total plutonium). Results from a mass spectrometer analysis indicated approximately 15 milligrams of uranium-234 (a precise determination was not possible due to lack of adequate standards). While the uranium concentration of this solution was lower than desirable, it was sufficiently high for the initial work. Titration of a 25-microliter sample of this solution with 0.05 normal base indicated an acidity of 11.3 normal. Therefore, 412 milliliters of 0.35 normal nitric acid was added to the solution (measured volume of 686 ml) to produce 1098 milliliters of solution 7.2 normal in nitric acid. This solution was used as the feed for the ion exchange runs. LOGAC counting of 10 microliters of this solution indicated a plutonium-238 concentration of 2.196 milligrams per milliliter, slightly lower than the value of 2.268 milligrams per milliliter calculated from the calorimeter value.

For the first ion exchange run a small column (cross sectional area 1.2 sq. cm., resin volume of 12 ml) containing Dowex-1X4 (50-100 mesh) was conditioned with about 20 milliliters of 7.2 normal nitric acid. A total of 262 milliliters of feed solution was run through the column. Periodically, a two-drop sample was collected in a clean numbered vial, and subsequently, ten-microliter mounts were prepared and counted. No difficulties were encountered in the early part of the feed cycle. The absorption front slowly advanced down the column, accompanied by some shrinkage of the resin bed. After 200 milliliters of feed solution had been added and the column was approximately half loaded, the flow rate became slow and gas bubbles formed in the column. The column was backwashed to expand the resin bed to remove the trapped gas. In the process, the loaded and fresh resin mixed, and the loaded resin tended to settle faster. It was necessary to backwash a second time before the feed was stopped. Although the resin was not completely loaded at this point, the feed cycle was terminated. The column was washed with 7.2 normal nitric acid and then eluted with dilute (0.35 normal) nitric acid. It was necessary to backwash twice more when the flow rate decreased and/or gassing occurred.

The raffinate, wash, and elutriant fractions were collected in separate bottles, and small samples taken for mounting and counting. The results are shown in Table 5. These results along with the counting of the samples taken during the run indicate that the absorption of plutonium was less than desired. The plutonium content of the effluent increased to about 37 per cent of the feed concentration during the first 100 milliliters of feed. For the remainder of the feed cycle the effluent averaged 37.6 per cent of the feed concentration. Washing dropped the plutonium concentration slowly to about 27 per cent. When dilute acid was added to elute the plutonium, about 30 milliliters were required to remove the excess acid held on the resin. The plutonium was then removed very quickly, with the major portion being removed in about 30 milliliters. Continued washing removed the last traces of plutonium so that after a total of 200 milliliters, the effluent contained only 0.3 per cent of the original feed concentration.

Table 5
ANALYSIS OF SOLUTIONS

Solution	Volume (ml)	Pu ²³⁸ (mg/ml)	Total Pu ²³⁸ (mg)
Feed	262	2.196	575
Raffinate(I-A)	277	0.675	187
Wash(I-B)	40	0.563	23
Elute(I-C)	200	1.951	<u>380</u>
TOTAL			590

From this first run two problems became apparent; the plutonium absorption was very poor, and a great deal of gas formed in the column. Elution of the column was quite satisfactory. Two possible explanations are advanced for the poor absorption of the plutonium. During the evaporation and storage of this solution, oxidation to the hexavalent state may have occurred. Hexavalent plutonium is held only weakly on the resin under these conditions. Another less likely possibility is that the plutonium is present in a polymerized form which is weakly held by the resin.

Since hydrogen peroxide is routinely used to adjust the oxidation state of plutonium, one to two milliliters of 30 per cent hydrogen peroxide was added to the feed solution and Bottle IA (Raffinate). After setting overnight the solutions were run through the ion exchange column in much the same way as the first run. Fewer samples were taken since the overall characteristics had been established on the earlier run. The effluents of the feed solution averaged 24.4 per cent of the original plutonium concentration. The effluents from IA showed approximately the same plutonium concentration as the raffinate from the original feed solution. Thus the absorption of plutonium was slightly better, but is still far from satisfactory.

Runs with other reducing agents are in progress, but no quantitative data are available at this time. Evaluation of these experiments will be deferred until this information is available.