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MOUND LABORATORY MONTHLY PROGRESS REPORT FOR MARCH, 1962

J. F. Eichelberger

AEC Research and Development REPORT

MONSANTO RESEARCH CORPORATION

A SUBSIDIARY OF MONSANTO CHEMICAL COMPANY

M O U N D L A B O R A T O R Y

MIAMISBURG, OHIO

OPERATED FOR

UNITED STATES ATOMIC ENERGY COMMISSION

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J. F. Eichelberger

Date: March 30, 1962

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.

MONSANTO RESEARCH CORPORATION

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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 Flow curves were run on production lots PW-70, PW-71, PW-72, PW-73 and PW-74 asbestos-filled diallyl phthalate formulations. All of these lots had acceptable flow properties. Tables 1 presents the complete tabular data.

Table 1
FLOW CURVE DATA, MOUND PRODUCED ASBESTOS-FILLED
DAP MOLDING COMPOUND

Force Applied (tons)	Average Flow Times (sec)				
	PW-70	PW-71	PW-72	PW-73	PW-74
15	3.13	3.93	2.93	2.94	3.93
12.5	4.30	5.06	4.06	3.66	4.99
10	5.53	6.96	5.47	5.35	6.57
7.5	8.12	9.98	7.57	7.13	9.52
5	11.72	14.47	11.24	10.00	14.37
2.5	20.22	nc	nc	17.97	nc
Cup Wt (g)	39.92	40.52	39.94	39.97	40.42
% Residual Volatiles †	0.82	1.07	1.42	1.26	0.72

nc - no close at pressure applied

Physical Testing Evaluation tests on Batch DB141 - DB156 which was a Dacron^{*}-filled diallyl phthalate molding compound produced in the Plastics Formulation Shop, were conducted. This is a composite of 16 mill lots which were blended together during a grinding operation. The average test values are tabulated below:

Flow Time (sec)	Cup Wt. (g)	Residual Volatiles (%)	Izod Impact (Ft. Lbs./ In. Notch)	Tensile (psi)
28.53	30.72	1.89	5.25	5824

This formulation molded well and the average physical properties were good. The Izod Impact strength of this blend was unusually good. Test values exceeded the minimum tentative specifications for ML-DAP-D-1.

ADHESIVES RESEARCH During the third week of February, films were cast to prepare test specimens of the initial 13 adhesive formulations for evaluation after 26 weeks cure time. The tensile strength and per cent elongation is being determined with 12 week old specimens.

^{*}Trademark of E. I. duPont deNemours

Five additional formulations (B1, B2, MOA1, EO22 and AD216) will be included in the evaluation project. Film casting and preparation of test specimens of this group of adhesives were completed during the last two days of February. Their composition and curing characteristics are shown below:

Component	Per Cent by Weight of Components in Formulation				
	B-1	B-2	MOA-1	EO-22	AD-216
Bakelite ERL-2774 Resin	80	75	-	-	-
FMC Oxiron-2001 Resin	-	-	-	37.5	-
Adiprene L-100	-	-	90.1	-	-
Adiprene L-167	-	-	-	-	33.2
Adiprene L-213	-	-	-	-	33.2
Bakelite ERL-2793 Hardener	20	-	-	-	-
Versamid 140	-	25	-	-	-
HET-Nadic Methyl Anhyd. Mix (55-45% by weight, added at 55°C)	-	-	-	43.8	-
MOCA	-	-	9.9 ^a	-	15.0
Epoxide 269	-	-	-	-	18.6
Epon 812	-	-	-	13.1	-
Polyglycol P-400	-	-	-	5.6	-
	<u>100</u>	<u>100</u>	<u>100</u>	<u>100</u>	<u>100</u>
Pot Life in Hrs.	¼	2	1	2½	1

a) Added in molten state at 95°C

Considerable difficulties were encountered in the preparation of test specimens of B1. Test specimens had to be cut from the films within three hours after casting before the exterior became too brittle, while the interior was still too soft. Approximately 30 test specimens were obtained from four separate batches.

RADIOELEMENTS

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

KINETICS OF REDUCTION OF Po(IV) BY FERROUS ION A study of the kinetics of the reduction of polonium(IV) to polonium(II) by ferrous ion in hydrochloric acid has been started. The potential of the polonium(II) - polonium(IV) electrode is close to the iron(II) - iron(III) (Pt) electrode potential in approximately two normal hydrochloric acid. Thus, polonium(IV) may be partially reduced to polonium(II) by adjusting the activity ratio of iron(III) to iron(II). The polonium(IV) can be coprecipitated with the insoluble salt cesium chlorostannate while the polonium(II) remains in solution.

Because cesium chlorostannate is only partially soluble, a solid residue remains on evaporating an aliquot of the supernatant solution, thus making conventional gas-flow proportional alpha-counting unreliable. Liquid scintillation counting offers a very convenient method for alpha-counting in such solutions, since there is no self-absorption in the sample.

The major problem encountered is that of dissolving the sample in the liquid scintillation solution without causing the scintillation flashes to be quenched. The usual scintillation solvent is toluene, but even small amounts of water cause considerable quenching in this solvent. Since aqueous solutions are to be counted, a dioxane-base scintillation solution is used. The composition of the liquid scintillator is as follows:

750	ml 1,4-dioxane
125	ml 1,3-dimethoxyethane
125	methyl phenyl ether
12.0	g 2,5-diphenyl oxazole (PPO)
0.5	g 1,4-di-[2-(5-phenyloxazolyl)] - benzene (POPOP)

PPO functions as the scintillator, and POPOP acts as a wave-length shifter in the system. Small aliquots (10 to 200 microliters) of aqueous solutions may be dissolved in 20 milliliters of this liquid scintillator, with no appreciable quenching.

A Tri-Carb liquid scintillation counter has been used for counting polonium-210 alpha particles. The instrument was designed chiefly for beta-counting, but is easily adapted for alpha-counting. A series of counting experiments was made to determine the optimum instrument settings and the overall counting efficiency. The high voltage and gain attenuation settings of 850 volts and 2, respectively, place the 5.4 Mev alpha peak well within the discriminator windows. Background counting rates are of the order of 20 counts per minute.

The overall counting efficiency was determined by counting a 50 microliter aliquot of a polonium-210 stock solution in two normal hydrochloric acid in a windowless proportional counter after evaporation on a platinum plate, and also a 50 microliter aliquot of the same solution dissolved in the liquid scintillator. Using 51.7 per cent geometry for the platinum-backed sample, a counting efficiency of 95 per cent for liquid scintillation counting was obtained. Lack of optical coupling between the sample vial and phototubes probably accounts for the departure from 100 per cent efficiency obtained by other workers.

SELECTIVE ADSORPTION OF TRACE ELEMENTS The adsorption of trace radioelements evaporated to dryness on metal and glass 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.

In a previous report (MLM-CF-62-1-268, PP. 105-6), the qualitative separation of strontium-90 and yttrium-90 was demonstrated. Quantitative separation has now been achieved, and the method can be used to prepare carrier-free strontium-90 and/or yttrium-90 of any desired degree of radiochemical purity.

The following procedure was used in a series of experiments testing the effect of the leaching agent and the nature of the substrate:

The backing material (lime glass, Type 430 stainless steel, and gold-plated stainless steel) was cleaned by agitation in alcohol potassium hydroxide, distilled water, and acid (6 N HCl for glass, 1 N HNO₃ for the metals). The surfaces were thoroughly rinsed with distilled water and dried with absorbent paper.

The surface was masked with an inverted glass vial (15 ml in diameter) and sprayed with Krylon*, a clear plastic spray coating. The coating was allowed to dry thoroughly at room temperature, and the masking vial was removed. The surface was rinsed with distilled water and dried at 90 (±3)°C on a temperature-controlled hot plate.

The hot plate temperature was determined with the aid of Tempilstiks**, and was held within the range 87° - 93°C.

Counting was carried out in a Nuclear Measurements Corp. PHA-1CA spectrometer equipped with a sodium iodide (thallium-activated) crystal, two inches in diameter and one-half inch thick, covered with 0.001 inch aluminum. The lower discriminator of the spectrometer was set on the 609 Kev gamma peak of bismuth-214 (radium C), and the upper discriminator was disabled.

Since the maximum beta energy of strontium-90 is 0.61 Mev, all of the beta-bremsstrahlung counting rate was due to yttrium-90, and it was not necessary to make a counting yield determination so long as a standard strontium-90 equilibrium sample on the same backing material was available. The yttrium-90 distribution could thus be determined directly; the strontium-90 distribution was determined by differential decay from two counts two or three days apart. The yttrium-90 half-life was taken to be 64.029 hours.

An equilibrium mixture of strontium-90 and yttrium-90 in 0.25 milliliter of one normal nitric acid was deposited in the uncoated area of the backing plate and evaporated to dryness at 90°C. The residue was covered with 0.25 milliliter of distilled water and again evaporated to dryness.

The dried residue was covered with 0.25 milliliter of distilled water and one drop of concentrated ammonium hydroxide and evaporated to dryness at 90°C. Heating was continued for five minutes after the residue was dry.

The residue was covered with 0.5 milliliter of the leaching agent (boiled and cooled distilled water, various concentrations of nitric acid) and heated for five minutes at 90°C. The solution was transferred, by means of a transfer pipet, to a second masked and coated plate of the same material. The first residue was again covered with 0.5 milliliter of leaching agent and heated five minutes. The solution was transferred to the second plate, and both plates were dried at 90°C.

The fractions were counted at precisely determined times, and the counting rates above 610 Kev were compared with that of a standard sample. The results are shown in Table 2.

Additional purification of the yttrium-90 residues on the stainless steel and gold plates was begun by redissolving and re-evaporating each of the residues in 0.25 milliliter of 0.1 normal nitric acid. The ammonium hydroxide treatment was repeated, and the residues were again washed twice with 0.5-milliliter portions of distilled water.

*Trademark of Pitt-Photo Litho. Co., Pittsburgh, Pa.

**Trademark of Tempil Corp., N. Y., N.Y.

Table 2

**SEPARATION OF STRONTIUM-90 AND YTTRIUM-90 BY
SELECTIVE ADSORPTION ON VARIOUS MATERIALS**

Substrate	Leaching Agent	% Sr ⁹⁰ Retained	% Y ⁹⁰ Retained
Au	H ₂ O	1.7	98.5
S.S. ^a	H ₂ O	27.5	98.2
Lime Glass ^b	H ₂ O	44.0	98.3
Lime Glass	H ₂ O	21.1	98.7
Lime Glass	0.0001 N HNO ₃	3.4	82.1
Lime Glass	0.01 N HNO ₃	6.6	7.9

^aType 430 bright-annealed No. 2 mill finish stainless steel. A slight brown discoloration of the residue from the original evaporation (1 N HNO₃) indicated possible attack on the metal.

^bPoor adherence of the coating permitted some liquid to flow under the plastic.

The stainless steel plate retained 1.8 per cent of the original strontium-90 and 98.8 per cent of the original yttrium-90 (the slight increase in yttrium-90 retention is attributable to counting variations and growth from the retained strontium-90).

The gold plate retained 0.3 per cent of the original strontium-90 and 96.3 per cent of the original yttrium-90.

It is apparent that further decontamination of the yttrium-90 could be achieved with relatively little sacrifice of yield by repetition of the dissolution and leaching procedures.

Because of mechanical difficulties in masking the glass surface with an adherent plastic spray coating, it is not certain that the marked differences, shown in Table 2, between glass and metal surfaces are real. If they are reproducible, they may provide a useful clue to the mechanism of the separation.

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.

XENON Five runs were made on the low temperature distillation apparatus. The reflux rate was improved and it was possible for the first time to operate the condenser at liquid xenon temperatures. The slope of the decreasing krypton-85 count versus time curve was flattened considerably after the initial drop due to the removal of krypton-85 enriched gas. These runs point out the importance of having very pure xenon-krypton mixtures for use in the static runs.

Gas Chromatography After calibration of the flow meters used in the experiments, the separation time plotted against the reciprocal of the flow rate gave straight lines defined by the following equations:

$$t_{\text{Xe}} = \frac{13.12}{F} + 5.47 \quad t_{\text{Kr}} = \frac{6.91}{F} - 1.88 \quad \Delta t = \frac{6.21}{F} + 7.36$$

where

t_{Xe} and t_{Kr} = The retention time, the time from elution start to the peak of output in minutes.

Δt = The time separation between xenon and krypton peaks in minutes.

F = The flow rate of elutant gas in liters per minute.

HYDROGEN Equipment is being set up for a rough evaluation of the heats of adsorption of the gases of interest on various adsorbents as a function of surface area. A brief literature survey was made for data on the heat of adsorption versus surface area. Although the amount of data was limited, the difference of the heat of adsorption of deuterium and hydrogen on chrome-alumina at 66°K is being used to correlate the available data in the literature on the separation of the hydrogen isotopes by gas chromatography.

CARBON ISOTOPE SEPARATION

Decomposition Experiments were conducted with a clean unoxidized Nichrome-V wire to supplant the data reported last month using a preoxidized wire. The data from last month is repeated in Figure 1 along with the data obtained using the unoxidized wire. Again, the data permit two choices for the curve at the higher temperatures.

The unoxidized wire used in this last series of experiments was sent to the instrumental analysis section. X-ray analysis showed the green coating to be oxides of both nickel and chromium with a small amount of nickel carbide.

Experiments have begun using a carbon rod for these decomposition experiments. The decomposition data are not complete; however, a preliminary check of isotopic exchange showed agreement with the calculations of Urey and Grief. This preliminary result is indicated in Figure 2.

Thermal Diffusion Methane is still being processed in the three-stage system and over a gram of eleven per cent carbon-13 has been produced. This product is being collected for recycle through the three-stage system.

Figure 1 - CO DECOMPOSITION FROM PRESSURE MEASUREMENTS

Figure 2 - ISOTOPE EXCHANGE

RANGER X-RAY SENSOR

FILM CASTING TECHNIQUES A technique for producing a large number of thin Formvar* films has been developed. The procedure consists of spreading a thin film of Formvar solution (approximately 0.6% Formvar in CHCl_3), uniformly over a polished, unmarred glass plate using a film casting machine. The thickness of the film can be varied by changing either the concentration of the solution or the thickness of the layer on the glass plate. The desired weight of the film should be between 40 and 50 micrograms per square centimeter. The chloroform evaporates, leaving the film of Formvar on the glass plate. The plate is then immersed in distilled water and the film floats free on the water surface.

With the present apparatus and facilities, six films can be made from each cast Formvar sheet. The frames are placed on the glass plate, which is then raised until the film rests over the frames. The plate is removed from the water and the Formvar sheet cut into six pieces. The mounted films are then removed, washed with distilled water and placed in an oven to dry (oven temperature approximately 40°C).

Experiments are now being conducted on the preparation of films from other plastics. To date, a polycarbonate polymer and a styrene-acrylonitrile copolymer have been cast into films and are being evaluated. Several other polymer systems are being investigated for casting into films. The limiting factor in making a thin film from any selected polymer is finding a suitable solvent for the plastic.

BERYLLIUM METALLOGRAPHY A small sample from the very high purity beryllium obtained from Nuclear Metals Inc. was studied metallographically. This beryllium, made by vacuum distillation of Pechiney Flake starting material, has an approximate analysis in ppm as follows: iron - 4.0; nickel - 1; chromium - 3; manganese - 5; carbon - 35. No other analytical data are available for the sample. There was no evidence of any intermetallic phase in the microstructure, but small gray inclusions, just visible at 50 magnification, can be assumed to be carbides associated with some oxide. The metal was quite porous, and the grain size large, as would be expected for this method of formation. The beryllium had been deposited on a tantalum collector, and the sample received no other treatment prior to study.

BERYLLIUM VAPOR DEPOSITION UPON PLASTIC FILMS Stainless steel, square frames covered with a uniform microfilm of Formvar of 30 to 50 micrograms per square centimeter have been used almost exclusively for recent deposition tests. The films unsupported by any form of substrate were rotated above or positioned upon stationary racks at varied distances from the filament cup containing the high-purity Pechiney Flake beryllium. A number of short 15 to 25-minute depositions were made at 5×10^{-5} mm Hg or less and filament temperatures of 1050° to 1200°C . Coatings of optical density 1.0 or 2.0 was the expected maximum for any single run, but in actual practice two or three runs per side proved to be a minimum for completing the films.

Since Formvar is rated with a distortion temperature of 100°F and is softened by continuous heat, filament heatshields with filament designs were used to expose the maximum surface of heated beryllium and to reduce film-exposure to heat either by rotation of the films, increasing the distance between film and heat source, or by applying the beryllium in many fast depositions.

Three different film support systems have been used with excellent results. These supports are: a five-film stationary unit, a six-film rotating, "Merry-Go-Round" unit and a six-film rotating, squirrel-cage unit. A stationary filament is located below the films in each system. The only completed films of acceptable quality were made on the stationary support. The number of usable films obtained from this system has been approximately three from every five films. The film support on the stationary unit can be varied in its distance from the heat source, but with the exception of minimizing "skyrocket" damage, the 10 to 11 inches used seemed to have little advantage over the shorter distance of five inches.

*Shawinigan Resins Corp., Springfield, Mass.

A squirrel-cage rotor holding six films exposes each film surface at a filament distance of five inches, reduced by only 0.25 inch at any point on the flat surface rotating through the rotor arc. Preliminary results are promising. The coatings obtained with the six-film rotating pinholes. The greatest disadvantage is that this method may require, on the average, about four hours or more deposition time to obtain a coat equivalent to those obtained on the stationary support.

Many methods for vaporizing beryllium, ranging from direct resistance heating of the metal to electron-beam methods, have been examined. Numerous types of filaments were designed and tested. One of the most promising methods utilizes a single $\frac{3}{4}$ -inch wide strip of tantalum one to 1.5 inches in length, shielded on the top by a tantalum shield having a 0.5 by one-inch hole to permit escape of the vapor. A flat, trough-type tantalum crucible varying from $\frac{3}{16}$ to $\frac{3}{4}$ -inch in width was used, but the beryllium was often heated unevenly. Furthermore, if a reasonable amount of beryllium was moved in a short time, the coated films often broke during the fourth or fifth run. Slow order deposition, requiring much longer exposure to heat, may ruin the texture of the plastic, but can yield higher quality films.

The beryllium wire method has not been examined extensively. During heating and vaporization, one wire sample broke after a short time, although its heat was kept as low as practical. The electron beam method is useable only if an effective shield for the filament can be formed. The high temperatures of the filament damage the films quite readily.

Resistance heating of a solid chunk of beryllium clamped between two terminals was attempted but the 17.5 amperes necessary to bring the metal to the sublimation point also heated the electrical leads to red heat. A circular ceramic cup, drilled so that electrodes could be introduced from opposite sides, was partially filled with flake beryllium, a small diameter tungsten wire, acting as a current limiting device, was used to connect the various types of electrodes that were tested. Heavy copper wire fused the beryllium into a current conducting state, but the copper became so hot it melted before much beryllium could be deposited.

Heat shields for the filament, which apparently will be required to protect the plastic film from excessive heat, severely retard the deposition rates. This, in turn, would demand an increase in temperature for the same rate of sublimation obtained without a shield. There should be a satisfactory medium between the desirable heat reduction and the resulting higher temperature demands for equal sublimation rates. A large aluminum block fitted with a chimney, with and without a wire screen shield, was used to surround the filament and while it kept film damage to a minimum due to heat, it also collected an estimated 75 to 80 per cent of the beryllium vaporized from the filament. Small tantalum shields fastened to one end of the crucible gave the best results but these, if too close or too small, often heat to a temperature only slightly less than that of the crucible. Depending upon the size and shape of the shield orifice, the shield can restrict "sky-rockets" and excessive thermal radiation.

FILM DENSITY MEASUREMENTS BY ALPHA COUNTING Calibration of the end-window proportional counter has been undertaken with several films "standardized" on the zinc sulfide scintillation counter. It was observed that fluctuations of the order of five per cent existed in the height of the plateau curves. It was also observed that count rate fluctuations existed when repeated measurements were made on the standard films. These fluctuations were significantly greater than that due to normal radioactive decay or statistical error in the count. Since they appeared to vary from day to day rather than during a given 24 hour period, an investigation was made to determine the cause of the fluctuations.

As a part of this investigation a study was carried out to determine whether the counting rate fluctuations were related to changes in the counting geometry. The counting technique requires that the source-shelf be moved from, and then replaced beneath the end-window detector so that the thin films can be located between the alpha-source and the detector. The source-shelf was moved in the normal manner and one minute counts were made following each moving of the source-shelf. These measurements considered only the air path as an attenuator. For comparison, one minute counts were taken without moving the source-shelf.

Then one minute measurements were made when a thin film was removed and then replaced on the source shelf. The results of these measurements, presented in Table 3, indicate that the various geometric conditions yield a count rate distribution which is reasonably Poissonian except for the results in the second and fifth lines. These latter, however, fall within the tabular χ^2 limits shown, if a single extreme observation is rejected in each case.

Table 3
COUNTING RATE REPRODUCIBILITY AS A FUNCTION OF GEOMETRY

Conditions	Pressure (mm/Hg)	No. of Observations	Ave (cpm)	$\chi^2_{0.95}$	$\chi^2_{0.95}$	χ^2
Source Shelf not moved	734.3 736.1	20	101,540	10.1	30.1	18.5
Source Shelf moved	736.3 736.6	10	99,799	3.3	16.9	20.1
Source Shelf moved	741.1 741.1	10	91,222	3.3	16.9	13.5
Source Shelf and film moved	741.1 741.4	10	72,484	3.3	16.9	13.9
Source Shelf and film moved	741.1	10	72,847	3.3	16.9	20.0

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

Differential Thermal Analysis The development of a new differential thermal analysis apparatus for temperatures up to 1400°C has been undertaken. The apparatus presently in use has a maximum reliable operating temperature of 950°C. The temperature controls used in the new equipment consist of a program controller in conjunction with a magnetic amplifier and saturable core reactor. This method is expected to yield more precise furnace control than the full power on-off type now in use. The apparatus also includes the standard X-Y recorder and timer mechanisms which will automatically control a selected heating and cooling rate as well as desired soak periods.

The development of several types of high temperature furnaces is also under investigation. One unit is a tubular platinum-rhodium wound furnace equipped with shunt taps to allow adjustment of the element current at a selected location within the furnace. This allows better control of the isothermal region. A vacuum tight mullite ceramic tube, containing the DTA block assembly, is placed inside the furnace. The second type of furnace is a tantalum-wound element which is located inside a mullite ceramic tube with the DTA block assembly, and is operated under vacuum or inert atmosphere. Studies are being made to establish the best possible isothermal region and thermocouple balance throughout the temperature ranges of these furnaces.

Interfacial Tension A study is being made of the bubble pressure method for the determination of interfacial tensions. This method involves the measurement of the maximum pressure required immediately prior to the detachment of the drop of one liquid into a second liquid.

Two sets of apparatus have been designed which will measure the difference of the pressures for two capillaries of different diameters. The measurement of these differences is expected to be the basis of the calculation of the interfacial tension between the two liquids. Preliminary experiments indicate that the maximum pressure at drop detachment can be satisfactorily measured with the small capillary system. Some uncertainty, however, exists in the measurement of the maximum pressure in the larger, comparison capillary.

A modification of the pressurization technique in progress is expected to make the measurement of the maximum pressure in the larger capillary acceptable.

Viscosity The viscosity of cerium has been measured from 812° to 1011°C with the Mound Laboratory oscillating cup viscometer. Four series of determinations were made at a total of 16 different temperatures.

A 111.3618 gram rod of cerium was sealed in a 3/4-inch diameter tantalum viscosity capsule and suspended on a 0.005-inch diameter platinum-tungsten fiber. The viscosity was measured at three different temperatures between 853° and 1001°C. Next, a 69.2415 gram rod of cerium was sealed in a 5/8-inch diameter tantalum viscosity capsule and suspended on a 0.010-inch diameter molybdenum fiber. The viscosity was measured at five different temperatures from 812° to 966°C. Finally, a 53.6881 gram rod of cerium was sealed in a 5/8-inch diameter capsule on a 0.010-inch diameter molybdenum fiber. The viscosity was measured at three different temperatures (853° to 1004°C) on the 0.005-inch fiber and at five different temperatures (858° to 1011°C) on

the 0.010-inch fiber. The results are tabulated in Table 4 and represented graphically in Figure 3. The equation of the line in Figure 3 is:

$$\text{Log}_{10} \eta = 0.6728 \times \frac{1000}{T} - 0.1323$$

where η is viscosity in centipoise and T is temperature in °K.

The standard deviation in the experimentally determined values from this line is ± 0.32 centipoise.

The activation energy for viscous flow for this metal was calculated to be 3075 calories per gram atom.

The first two determinations were made with a high purity cerium metal obtained from St. Eloi Chemical Company. The remaining two determinations were made with cerium which had been filtered through a sintered tantalum filter to remove suspended cerium oxide. Slightly higher values were obtained with the filtered cerium.

Viscosity measurements are also being made on a binary eutectic alloy of 70 atom per cent cerium and 30 atom per cent cobalt. A 64.58 gram rod was sealed in a $\frac{5}{8}$ -inch diameter tantalum capsule and suspended on a 0.010-inch diameter molybdenum fiber. The data are currently being evaluated.

Table 4
VISCOSITY DETERMINATION OF CERIUM

Series No.	Temp. (°C)	Density (g/cc)	Period of Oscillations (sec)	Viscosity (centipoise)
1	1001	6.630	13.467	2.48
	903	6.658	13.629	2.39
	853	6.670	13.517	2.62
2	966	6.640	2.73	2.66
	965	6.641	2.73	2.20
	909	6.657	2.73	2.18
	822	6.679	2.73	3.52
	812	6.680	2.73	2.71
3	1004	6.632	13.016	2.54
	900	6.658	13.011	2.76
	853	6.670	13.012	2.94
4	1011	6.640	2.643	2.83
	954	6.650	2.642	2.75
	902	6.660	2.643	3.03
	858	6.670	2.642	3.28
	858	6.670	2.643	3.34

Latent Heat Measurements The recent measurements in the Mound Laboratory high-temperature calorimeter of the latent heat of transformation of the alpha to beta transition in plutonium yielded a value which was approximately 100 cal/gram-atom less than the value reported by R. G. Loasby, AEWE, Aldermaston.

After the plutonium had been removed from calorimeter the cause of this discrepancy was examined through a series of calibration measurements with the "empty" calorimeter. The unit is considered to be "empty"

Figure 3 - VISCOSITY OF CERIUM AS A FUNCTION OF TEMPERATURE

if the sample is removed but the "dummy" is retained in place in the calorimeter. The recalibration indicated that the original calibration had shifted, and that the calibration changes each time the calorimeter is heated above 400°C. Above 400°C the tantalum in the dummy side acts as a "getter" which causes the change in the basecurve of the calorimeter.

PHASE STRUCTURE DEVELOPMENT A microphotographic record has been made of the alpha-beta transformation of plutonium, using a 16 mm camera with the vacuum hot stage. Approximately seven to eight minutes were required for complete transformation of the alpha to beta phase at temperatures which increased continuously throughout the transformation between 160° and 200°C. These temperatures are measured at the pedestal inside the stage upon which the sample rests and are, therefore, not accurate measurements of the sample surface temperature.

The indicated temperature was increased to about 300°C in an attempt to photograph the beta-gamma transformation. Due to the distortion of the sample as a result of the alpha-beta transformation, the beta-gamma transformation was very difficult to detect. No change was observed through the microscope; however, a detailed examination of the film may show a record of the transformation.

PLUTONIUM-BEARING GLASS Twenty-six grams of ten weight per cent plutonium oxide glass, rough ground to less than $\frac{1}{8}$ -inch but larger than forty mesh, was prepared as part of a 40-gram lot which was shipped to Argonne National Laboratory for reactor fuel studies.

Five grams of minus 75 mesh 10 weight per cent plutonium oxide-glass microspheres were prepared for shipment to Argonne National Laboratory for irradiation studies. These microspheres were prepared by passing minus 200-mesh crushed glass through an argon coupled induction plasma torch. The crushed glass was introduced into the argon stream and carried upward in a glass tube so that the gas stream would separate the small particles. After passing through the torch, the small microspheres were collected in water in an open beaker. However, many of the smaller microspheres were swept away by gas currents in the box before they reached the water.

Twenty weight per cent plutonium oxide glass was prepared by melting a mixture of plutonium oxide and high temperature glass to 2000°C in an iridium crucible in an argon atmosphere. This 20 weight per cent glass is less elastic than 10 weight per cent plutonium oxide glass. During the heating of the glass at 2000°C, condensed vapors appeared on the inside of the quartz reactor. These vapors, dark gray, were removed easily, but contained an appreciable amount of radioactivity. Apparently some of the plutonium oxide vaporizes with the silicon dioxide near 2000°C. The appreciable vaporization of plutonium oxide had not been observed at lower temperatures.

WELDING AND CAPSULE DESIGN EVALUATION Welding studies on Haynes alloy-25 mock capsules have continued. Using a 0.065-inch wall lip, 0.035-inch shoulder and a flush cap with raised center plateau, attempts were made to attain maximum penetration on a circumferential weld to join the cap-capsule interface without involving the edge of the tube. When the capsule edges are involved in the weld, the total strength of the weld decreases because the distance from the root of the weld to the top corner of the tube is shortened. The weld failed at this point from the resultant vector forces during impact tests. The impact tests also showed that a shoulder on which the cap may seat is necessary to transmit the forces directly from the cap to the wall, thereby reducing shearing forces on the weld. By lowering the Haynes capsule deeper into the aluminum cooling block, a deeper and more uniform weld is obtained. Under optimum conditions with the top of the capsule flush or 0.005 to 0.010 inch below the cooling block surface, penetration of 0.080 to 0.090-inch is attained. Strength at least equal to or better than the 0.065-inch base metal wall is assured. With a wall of 0.100 inch, penetration in excess of 0.100 inch can be obtained.

Four mock capsules fabricated by the Martin Marietta Corporation were sent to Mound to be welded for impact testing. Welds were made to Martin specifications. The 0.100-inch wall capsules contained a 0.035-inch shoulder machined inside the top of the capsule leaving a 0.065-inch lip for welding to the cap. The tube received a cap having a 0.100-inch deep by 0.060-inch wide groove milled into the top to provide a 0.065-inch cap lip to match the capsule lip. A 0.140-inch plateau 0.608 inches in diameter in the center of the cap permitted an overlay of Haynes alloy-25 to be added over the first fusion-filler weld. Metallographic examination of a test sample demonstrated that the fusion and fillet welds were satisfactory. The first two capsules subjected to impact testing failed at the welds. Consequently, one of the remaining capsules were cut in half to reduce the mass, rewelded in the same manner and will be subjected to impact testing.

The caps of all future capsules will not include the "U" shaped groove milled in the surface to provide a thin welding lip. A wide, flush cap surface allows greater weld penetration and eliminates the possibility of voids. Impact failures apparently are caused both by mushrooming of the area at the top of the capsule and by deformation in the wall just below the top. It appears that impact failure could be eliminated by deeper weld penetration at the cap-wall interface. The only feasible method is a double weld involving a weld through the side of the 0.065-inch wall of the capsule into the cap just below the fusion weld of the cap-wall interface. By lengthening the weld zone in this manner the cap would be more nearly an integral part of the tube and strength would be increased. Capsules containing a shoulder and caps with and without the center plateau are being fabricated and will receive the two-step fusion welds before impact testing. Inlays or fillet welds over the initial deep fusion weld will also be included in the tests.

Microhardness traverses were made on Haynes alloy-25 welds. Base metal, heat affected zone, and weld metal areas were studied. In the as welded condition the weld metal showed hardness of 100 to 150 Vickers higher than adjacent base metal.

Hardness of the Haynes alloy outside the weld ranged between 297 and 357 Vickers, while hardness of the weld itself averaged 450 (11 measurements). There did not seem to be a characterized hardness gradient from the edge of the weld into the matrix or parent material since the change in hardness was quite abrupt at the edge of the weld zone.

METALLOGRAPHIC EXAMINATION OF "SNAP" SOURCES The metallographic examination of two mock SNAP sources previously loaded with plutonium-239 metal was completed. One of these sources had been heated to 2000°F while the other had been heated to 2375°F during the burn tests.

In the mock source heated to 2375°F the tantalum inner container ruptured and released the liquid plutonium. The seam weld along the length of the tantalum can failed. The molten plutonium then apparently flowed through the crack at high velocity, dissolved the Haynes alloy-25 outer container and filled the cavity

between the tantalum can and the outer container of tantalum used to hold the source during the test heat cycle. The plutonium then alloyed with the Haynes 25 container until the plutonium reached the outside of the container. The solution of Haynes 25 in the plutonium then began to alloy with the tantalum. This alloy formation was revealed by a layer of grains of alloy which were seen on the outer edge of the tantalum. Also, it was observed during sectioning that some reaction had taken place between the tantalum and the Haynes 25. This reaction was not found in the source which did not fail.

When the tantalum was seam welded, extremely large grains were formed, and these grains extended completely through the structure. Single large grains result in a weaker structure and probably explains why the weld failed. No evidence of impurities or cracks were found in the seam weld area examined. The source heated to 2000°F was examined to determine if there were any deleterious effects of the plutonium on the tantalum. While no reaction occurred between the tantalum and the plutonium, there was a reaction between the tantalum and impurities in the plutonium. The plutonium contained a large amount of impurities probably plutonium carbide or plutonium nitride. The high impurity level of the plutonium was indicated by the large masses of iron-plutonium eutectic observed in the plutonium. At various points along the plutonium-tantalum interface, particles could be seen adhering to the tantalum and alloying with the tantalum. Two different compounds were formed. The layer next to the tantalum averaged 2.8 to 5.4 microns in thickness, while the layer next to the plutonium averaged 1.1 to 2.5 microns in thickness.

Large masses of the impurity phase were observed in the plutonium. Accordingly, large masses of tantalum compound could be observed at the interface, indicating that when these large masses came in contact with the tantalum, reaction took place and left these large masses of tantalum compound.

Microhardness measurements on the tantalum revealed an average of 416 VHN on the Mound weld, 179 VHN on the seam weld, and 186 VHN on the base metal. The closure weld of the cap of tantalum inner container welded by Mound Laboratory research personnel remained intact throughout the heat cycle and the destruction of the container.

RECOVERY OF URANIUM-234 The feasibility of recovering nearly pure uranium-234 from aged plutonium-238 materials has been demonstrated, and a separation and purification scheme proposed. Further improvements in the process are being evaluated.

One additional batch of styrene-divinylbenzene copolymer (designated as Batch III) has been sulfonated by the procedure reported last month. A temperature of 96°C and a 2:1 weight ratio of sulfuric acid to dry copolymer was used. Potentiometric titration indicated 0.0055 milliequivalent of acid per gram of dry sulfonated copolymer.

A sample of Batch III (designated as Batch IIIA) was swelled with a mixture of hexone and carbon tetrachloride (51% hexone by weight). The weight increase indicated 36 per cent organic in the swelled copolymer. A qualitative evaluation of uranium absorption was made with a column. The problem of resin floating, previously encountered, was satisfactorily solved by placing a plug of glass wool on the top of the column to hold it in place. However, the yellow color of the uranium solution appeared shortly in the effluent, indicating little or no uranium absorption. No color was visible when the column was stripped with water.

A portion of Batch IIA copolymer was swelled with a 44 per cent by weight solution of tributyl phosphate (TBP) in trichloroethylene. When this material was used in a column, the effluent from a uranium sample was colorless, and no visible color developed when peroxide and caustic were added to a small sample of the effluent. The uranium appeared to be completely removed from the column with about two column volumes of water. Since the plutonium(III) ion is weakly extracted by TBP, plutonium-uranium separations using TBP swelled copolymers appear possible.

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.

CALORIMETRY

Radium-223 Half-Life Half-life measurements have been concluded on the second radium-223 sample. The sample was sealed in a tantalum container by welding techniques. Chemical effects in the first sample (MLM-1119) had prevented a definitive half-life measurement. The present sample had no spurious effects in excess of the expected deviations of the two microcalorimeters 67 and 60.

The half-life value calculated from the results obtained with thermoelectric calorimeter 67 is 11.4344 ($\pm$ probable error 0.0011) days for equal weighting in microwatts of 37 measurements, starting at 557.54 microwatts and extending to 1.64 microwatts at 96 days. The probable error of a single measurement was 0.055 microwatts.

The half-life value calculated from the results with resistance bridge calorimeter 60 is 11.4432 ($\pm$ probable error 0.0057) days for equal weighting in microwatts of 15 measurements starting one day earlier than with calorimeter 67 and covering 36 days. The probable error (PE) of a single measurement was 0.25 microwatts.

The probable errors were determined by the usual method and express only the degree to which the results could be repeated with the same calorimeter, sample, operator, measuring equipment, etc. It is an untrustworthy base from which to judge the absolute probable errors. The fallacy in judgement usually originates in the following statement: "There are no spurious heating effects since measurement is equal to the known probable error of the calorimeter and there are no noticeable trends to the deviation of each measurement with time; therefore, the precision probable error in the half-life is a reasonable absolute value also."

The latter part of the statement is false, since the absolute probable error must contain the proof of the first part of the statement. To do this, one must include additional unknowns into the solution. A reasonable assumption would be to assume a spurious heating effect that could be represented by an exponential term (which would be entirely correct if the spurious effect was caused by an unsuspected radioactive isotope). If in the solution the second exponential turns out to have a small contribution of unknown origin, the half-life with a single exponential should be reported along with the probable error from the solution with two exponentials. This probable error can be considered absolute and might be 10 or more times greater than the one obtained by assuming a single exponential.

An attempt will be made to put absolute limits on the present results.

"Stretching" Effect The "stretching" effect has been eliminated from an integrator by the use of helium. The integrator was evacuated for one day with 1.6 watts of heat in the heater. The integrator was filled with helium and evacuated under the same conditions for two days. After the integrator was filled with air, the "stretching" effect was less than two in 45,000 microvolts.

Previously, the stretching effect had been eliminated by the use of a combination treatment with argon and helium (MLM-CF-61-12-281, page 117; MLM-CF-62-2-188, page 5). An attempt will be made to eliminate the "stretching" effect without heat in the heater during the evacuation.

COMPUTER A new program was written for the reduction of mass spectrometer data. This new program is general enough to permit any method of calculation presently being used to be run by using the proper "header" tape (a "header" tape specifies the direction a branch in the general program should take). It includes two types of sensitivity factor adjustments and several methods of sample composition calculation.

The program will correct the sample spectrum for instrument background, inlet system pressure decrease during analysis, variation in sensitivity of the gases, and contributions to peaks by ions from fractionation and multiple ionization. A peak may be mathematically resolved into two or more components by assuming either the total calculated pressure must equal the observed inlet system pressure or a condition of equilibrium exists between a component of the peak being resolved and other peaks in the spectrum. Finally, the determination of the sensitivity factor of a gas may be calculated either by the standard (almost pure sample) technique or by the nearly applied equilibrium technique.

A test program for thermal diffusion work has been written to calculate the coefficient of viscosity of a pure gas at any temperature to a third approximation from the equation¹.

$$[\eta]_3 = 0.26693 \times 10^{-4} \frac{\sqrt{MT}}{\sigma^2 \Omega^{(2,2)} T^*} f_{\eta}^{(3)}$$

where η = viscosity in g/cm sec.
 T = temperature in °K
 M = molecular weight
 σ = collision diameter in Å
 $\Omega^{(2,2)}$ = Omega integral at the reduced temperature T^*
 $f_{\eta}^{(3)}$ = function for the third approximation

It is hoped that further study of the results of this program as compared to the viscosity calculations using the multicomponent system will indicate the better method of calculating the viscosity of a pure gas having an isotopic mixture. If this program replaces the multicomponent program, considerable computer time would be saved.

A program to evaluate the omega integrals used in calculating transport coefficients has been written for the IBM 704. After several programming problems were encountered, it was revised on the IBM 1620 to facilitate the running at Argonne.

Since the trial and error method is used to design a cascade consisting of a small number of large columns, a program was written to prepare data tapes for this purpose. These data tapes contain several cascade designs varying slightly from a given basic design. By calculating the performance of each design, the best one can then be chosen.

A new SPS system will be issued shortly by IBM and in it, floating point numbers will be of the form $\overline{XXXXXX}X$ where the first five numbers are the mantissa and the last two numbers are the characteristic. The mantissa may contain as many as 45 digits. The data tape preparation program reported last month has been changed to accommodate this system.

A new Fortran system has been received from IBM. This system consists of a processor and a subroutine tape and has the added feature of FORMAT control for input/output data fields. A subroutine to calculate the absolute value of an argument has been added to this system.

The IBM Fortran pre-compiler which detects and permits the correction of language errors in a Fortran source program before compilation has been received.

¹Hirschfelder, Curtiss and Bird Molecular Theory of Gases and Liquids John Wiley and Sons, Inc , p 528

X-RAY DIFFRACTION An x-ray diffraction analysis of 17 powdered boron samples revealed that they were predominantly crystalline. However, the prominent interplanar spacing at 7.99 Å showed a large degree of line broadening, indicative of preferred orientation or short range ordering.

Lattice parameter computations of plutonium oxide microspheres subjected to different annealing procedures indicated the predominant species to be PuO₂ in all cases. However, faint lines corresponding to Pu₂O₃ were present leading to the conclusion that a small percentage of Pu₂O₃ was present. This problem is presently being pursued and it is hoped that more definite results can be drawn.

The plutonium-bearing glass x-ray structure study is being pursued. The experimental intensity versus diffraction angle of the solvent glass, X-1211, has been recorded. The coherent and incoherent scattering functions based on a unit of composition on an atom fraction basis have been calculated. The absolute intensity in electron units will be obtained by fitting the experimental intensity to the total independent scattering at large $\sin \theta/\lambda$ values.

Ultimately, the radial distribution curve as a function of the interatomic distance will be determined from these data.

X-RAY FLUORESCENCE An investigation was made to see if uranium, iron and nickel could be rapidly and accurately determined by an x-ray fluorescence technique. A representative sample was prepared and analyzed for uranium, iron and nickel. Although the sensitivity of detection for iron and nickel seem adequate, the limit of detection for uranium is much higher than anticipated. The cause of the poor sensitivity has not been determined.