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AEC RESEARCH AND DEVELOPMENT REPORT

SEPARATION OF ^{210}Po FROM BISMUTH BY LIQUID METAL DISTILLATION

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by

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ABSTRACT

This report summarizes the research and development
tests of laboratory and plant-scale semiworks equipment
that has established the engineering feasibility of using
liquid metal vacuum distillation to separate up to
10 kg ^{210}Po/year from irradiated bismuth.

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INTRODUCTION

Polonium-210 is a potentially useful alpha-emitting heat source (144 watts/g; half-life of 138 days) produced by the neutron irradiation of ^{209}Bi.[1] An investigation of the separation of ^{210}Po from bismuth by vacuum distillation was initiated at Mound Laboratory in 1949[1] and physicochemical data for the system were developed during these studies.[1,2] A prospective large-scale vacuum distillation process to concentrate up to 10 kg ^{210}Po/year to greater than 90 wt % from a bismuth feed containing 25 to 75 ppm ^{210}Po was first described in 1966.[3] This vacuum distillation process permits a high throughput in modest size equipment, is readily adaptable to the purification of bismuth for re-irradiation, requires no chemical reduction steps since both bismuth and polonium are retained in metallic form throughout the process, and is operable within the shielding and containment necessary to protect against penetrating radiation.

This report summarizes the research and development work carried out in laboratory and plant-scale semiworks equipment at the Savannah River Laboratory to establish the engineering feasibility of using liquid metal distillation to separate up to 10 kg ^{210}Po/year.

SUMMARY

The separation of ^{210}Po from bismuth by liquid metal distillation consists of two stages of simple vacuum distillation, a fractionation stage, and an additional vacuum distillation operation to purify the residual bismuth prior to its re-irradiation. This process yields ^{210}Po with a purity of >90%.

Laboratory distillations (in 2-inch-diameter stainless steel stills with tantalum liners) on both ^{210}Po and nonradioactive stand-ins (Te, Cd, Mg, and Zn) determined the separation efficiency and product purity. Design equations were developed for large-scale distillation equipment.[4] Stand-ins for use in large-scale semiworks distillation studies were evaluated.

Individual semiworks tests were made with full-scale prototypes of the melter, freeze valves, a pulse agitator, the vacuum bell jar, and the mockup of the final-stage still. Liquid metal distillations in a 2-ft-diameter stainless steel still and in an 8-inch-diameter tantalum prototype still used cadmium as a nonradioactive stand-in for ^{210}Po. These distillations demonstrated large-scale separation efficiencies, bismuth vaporization rates, the effect of agitation, the effect of oxide layers, high temperature liquid metal handling, and temperature and condensation patterns in the still.

Because several tantalum liners were embrittled and cracked, laboratory embrittlement tests determined the rate of embrittlement of tantalum by oxygen and bismuth oxide, and the rate of reduction of bismuth oxide by carbon monoxide. A tantalum packed getter bed was designed to remove the dissolved oxygen in the bismuth feed to the first-stage still.

PROCESS DESIGN

The separations process (Figure 1) consists of dejacketing and melting irradiated bismuth targets, two stages of a simple vacuum distillation (at 750 and 675°C) to increase the ^{210}Po concentration to about 1%, a stage of fractionation at 650°C to yield >90% ^{210}Po vapor, and another vacuum distillation to purify the residual bismuth before its re-irradiation. Molten bismuth is transferred by gravity from the melter to the first stage still, first through an underflow weir to trap any slag and then through a valve that can be closed by freezing the molten metal. Gravity flow and freeze valves are used throughout the process for liquid metal transfers. Molten bismuth containing polonium is held for several hours in a tantalum getter bed at 750°C before charging the first stage still; this bed removes any dissolved oxygen or entrained bismuth oxide that could cause embrittle-ment of the tantalum still (p 34). The concentrated ^{210}Po from the final stage still is condensed on extended surface condensers and transferred as a vapor to an extended surface storage vessel.
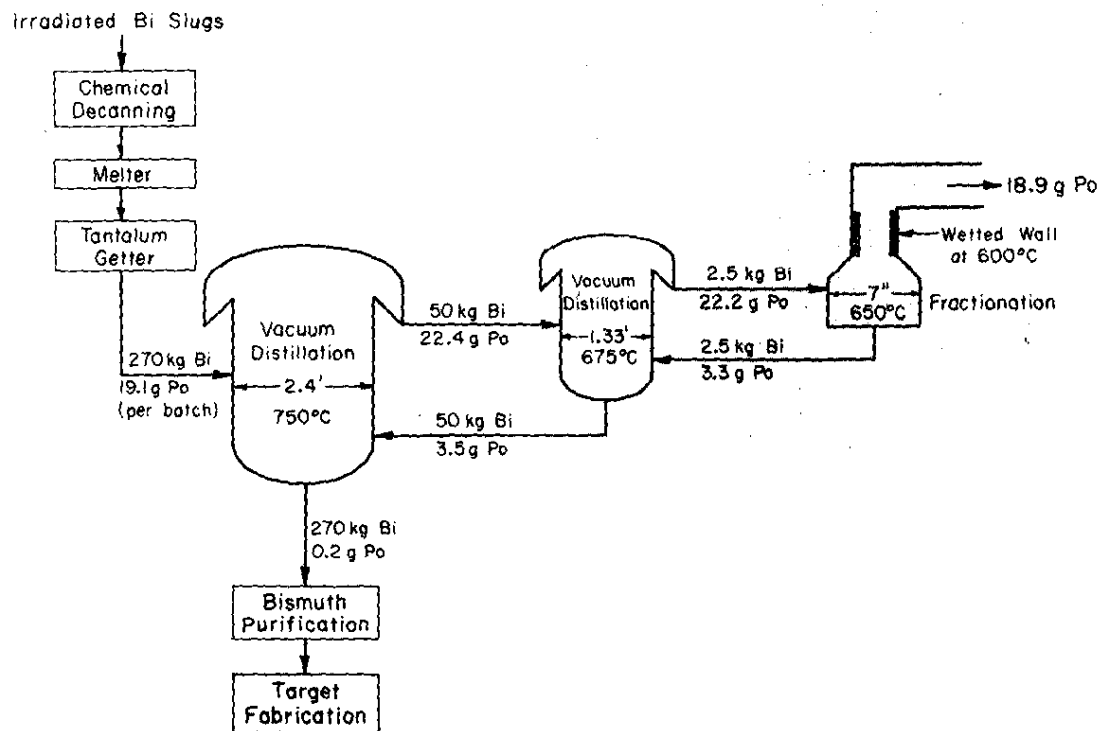

FIG. 1 MATERIAL BALANCE FLOWSHEET

The number of stages of distillation necessary to produce a high-purity ^{210}Po product is determined by the separation factor obtained in each stage. Although the separation factor is reduced by depletion, the effective relative volatility of the more volatile species at the liquid metal-vapor interface surface can still be quite large.

The size of the stills is determined by the amount of polonium to be removed in a single distillation. The relative volatility decreases with increasing temperature, so that at lower temperatures it is necessary to distill less bismuth.[2] However, the distillation rate is a function of temperature[2] so that practical operation of the first two stages for high ^{210}Po production rates is at approximately 650 to 750°C. One of the consequences of surface depletion, in addition to requiring further fractionation, is the increase in the amount of bismuth that must be vaporized to remove the ^{210}Po, and this requires a larger diameter still. If additional separation is required in the first two stages it can be obtained by operating one or both of these stages as wetted wall stills, or by operating the pots at a lower temperature to give a higher value of α_{eff}.

The size of the stills for a plant process is also determined by the recovery of ^{210}Po in the first stage. A flowsheet is given in Figure 1 for a 10 kg ^{210}Po/year separations process with 99% recovery of ^{210}Po in the first stage, assuming 50% utilization of each still for distillation and continuous operation. The distillation rate in the first two stages is assumed to be 1/3 of the maximum rate expected for molecular distillation (the rate attained in the two stills tested at the semiworks). The initial ^{210}Po concentration is assumed to be 70 ppm. The first two stages are a scale-up of the 8-inch-diameter prototype tantalum still (p 30) the main difference being the diameter and height (Figure 1) and provisions for more cooling air in the second stage condenser where ^{210}Po concentrations are 1%. Fractionation, as opposed to simple distillation, applies only to the third stage in this flowsheet.

The vacuum stills would be built of tantalum because it is easily fabricated, and it is corrosion resistant to liquid bismuth (only 0.02 mils/year at 750°C). The melter for the irradiated bismuth targets would be stainless steel because it is operated below 400°C.

The stills would be surrounded by a single vacuum bell jar with a lid that can be raised or lowered from above. The vacuum not only protects the tantalum from air oxidation at operating temperature, but also reduces heat losses from the stills, minimizes in-leakage to the stills, and provides secondary containment for alpha activity. The vacuum bell jar would be located in a shielded, controlled ventilation containment cell. Shielding would consist

of at least 24 inches of concrete for gamma radiation resulting from neutron activation of impurities in aluminum target jackets and in bismuth targets; 24 inches of concrete for gamma shielding would also be provided in all locations containing concentrated polonium. Some neutron shielding would also be provided for concentrated polonium deposited on tantalum because of the α,n reaction on oxygen impurities in the tantalum.

SEPARATION EFFICIENCY

Separation of ^{210}Po From Bismuth

To confirm that high-purity ^{210}Po could be obtained by vacuum distillation, a milligram-scale ^{210}Po vacuum distillation of irradiated bismuth was performed using the laboratory still (Figure 2) as a fractionator. Regulated temperatures ranging from 650°C at the bottom to 300°C at the top were imposed on the still. A tantalum screen above the bismuth-polonium melt provided condensation and re-evaporation for additional separation, and the stainless steel tube above the screen provided final enrichment. The purest product was deposited in the "Pyrex"* tube.

In addition to confirming that high-purity (>90%) ^{210}Po could be obtained, the test determined the amount of ^{210}Po that could be separated from the melt under conditions closely similar to those of simple distillation. A charge of 678 g of bismuth and 25 mg of polonium was distilled for 5 hours at 650°C. 26 g of bismuth and 10 mg of ^{210}Po were then removed from the screen and the walls above the pot. The 1 mg of product in the "Pyrex" condenser contained >90% ^{210}Po; these observations confirmed that the product purity to be obtained by vacuum distillation is not limited by the formation of an intermetallic compound of polonium and bismuth.

The amount of polonium vaporized from the melt was less than expected. According to the vaporization data from Mound Laboratory, a simple distillation at the test conditions should have removed 31 g of bismuth and about 24 mg of polonium from the melt (vs the 10 mg observed). The 26 g of bismuth recovered agrees fairly well with the predicted 31 g, indicating that little interference was imposed by any film of oxide that might otherwise be postulated to account for the low vaporization rate of polonium. Even if the 5 g difference between the expected and measured rates of vaporization of bismuth is attributed to reflux on the screen, the proportionate effect would only decrease the removal of polonium from 24 to 22 mg, not to the observed 10 mg.
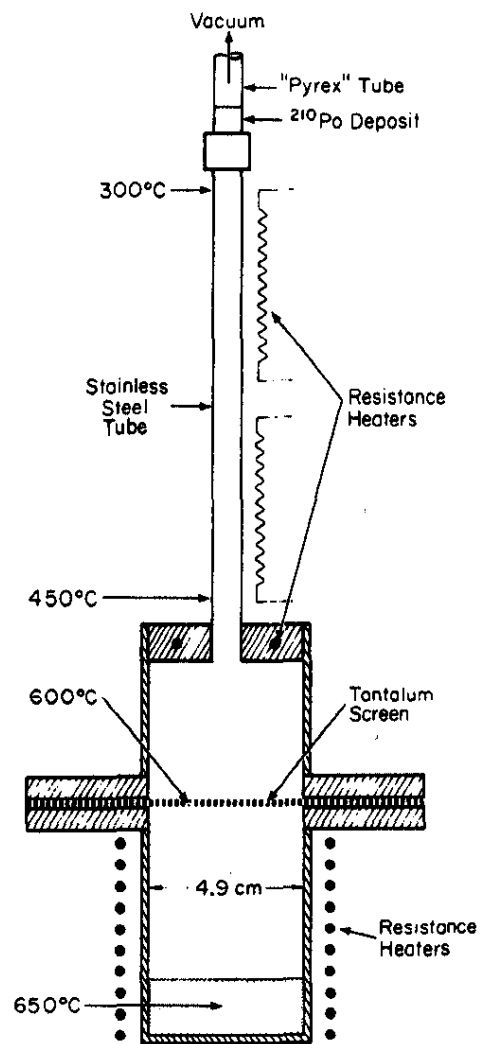
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* Registered trademark of Corning Glass Works.

Vacuum

"Pyrex" Tube

^{210}Po Deposit

300°C

Resistance Heaters

Stainless Steel Tube

450°C

600°C

Tantalum Screen

4.9 cm

Resistance Heaters

650°C

FIG. 2 LABORATORY ^{210}Po STILL

The slower removal of [210]Po was found instead to be due to surface depletion. A key step in the distillation of the relatively volatile [210]Po is the transport of the [210]Po to the liquid-metal surface.[4] Under the conditions of this distillation process, the rate of mass transfer of [210]Po to the surface by thermal convection is not sufficiently high to prevent a depletion of [210]Po at the surface relative to its bulk concentration. This surface depletion reduces the separation efficiency below that which could be attained theoretically if there were no concentration gradients in the liquid. Surface depletion can be reduced by mechanical agitation; however, the separation factors are still sufficiently large, even with no agitation, that an effective separation can be made by distillation. Surface depletion reduces efficiency, and it must be taken into account when sizing and staging a series of stills for a given throughput. Surface depletion is also the most important consideration in the choice of a stand-in to demonstrate the nonradioactive operation of the process.

The degree of separation in a simple distillation can be calculated by the equation:

$$\ln (Po_2/Po_1) = \alpha_{eff} \ln (Bi_2/Bi_1)$$

where

Po_1, Bi_1 = initial weights of [210]Po and bismuth in the pot

Po_2, Bi_2 = final weights in the pot

Because of surface depletion the value of α_{eff} is less than the maximum relative volatility for unrestricted vaporization, α. Methods were developed to calculate α_{eff} for [210]Po (or Zn, Cd, Te or Mg) in bismuth as a function of temperature, still pot dimensions, and degree of agitation. These studies also provided the basis for choosing cadmium as a stand-in for [210]Po in large-scale distillations. The design equations which were developed in this study are given in detail in Reference 4.

Fractionation

In the final stage of vacuum distillation, separation can be increased significantly by operating either with a partial condensing screen above the melt or with the sidewalls of the still at a slightly lower temperature than the pot so the wall of the still is a wetted wall partial condenser. Theoretical relationships among concentrations in the still, still vapor, condensate on screen or sidewall, and overhead vapor were confirmed experimentally with Mg-Bi and ^{210}Po-Bi solutions in laboratory distillations. The wetted wall gives superior performance and also has the advantage of simple construction.

In wetted wall or screen operation, a liquid phase with ^{210}Po depleted below the concentration in equilibrium with total condensation is returned to the still pot, and a vapor highly enriched in ^{210}Po is produced as overhead product (Figure 3). To be effective and feasible, distillation of ^{210}Po from the sidewall (or screen) must be rapid enough that its concentration in the sidewall (or screen) condensate is small compared to its concentration in the still pot vapor.
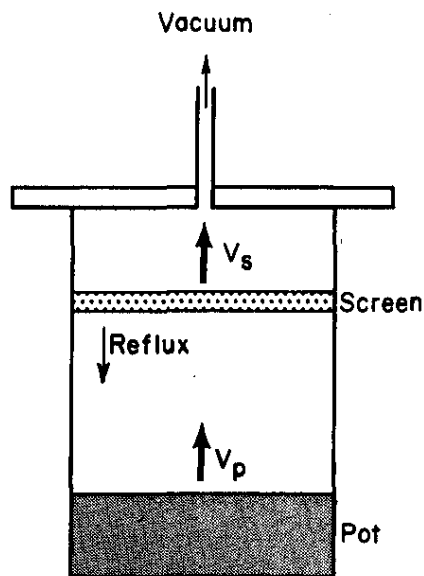

FIG. 3 APPARATUS FOR SCREEN STUDIES

The relationship between the concentration of the volatile species on the sidewall and in the vapor from the still is obtained from the sidewall (or screen) material balance:

Input - Output = Accumulation

$$V_p A_p \alpha_p X_p - [V_s A_s \alpha_s X_s - (V_p A_p - V_s A_s) X_s] = M \frac{dX_s}{dt} \qquad (1)$$

where V_p, V_s = vaporization rates from pot and sidewall (or screen)

$\quad\quad A_p$, A_s = vaporization surfaces

$\quad\quad \alpha_p$, α_s = relative volatilities

$\quad\quad X_p$, X_s = liquid concentrations

$\quad\quad\quad M$ = weight of metal on sidewall (or screen)

For the experiments, M is small, <3% of the total charge; therefore, at steady state:

$$\frac{X_s}{\alpha_p X_p} = \frac{X_s}{Y_p} = \frac{V_p A_p}{A_s V_s \alpha_s + V_p A_p - V_s A_s} \qquad (2)$$

Equation 2, which assumes no surface depletion on the sidewall or screen (and also assumes that A_s for a screen = A_p) correlates adequately test data obtained with a screen for the Mg-Bi system (Figure 4), and fixes the lower limit of sidewall (or screen) operating temperature as the temperature at which $X_s/Y_p = 1$ (total reflux); the upper limit is the pot temperature.

Confirmatory tests were made with ^{210}Po-Bi at the expected pot temperature of 650°C, with the screen and the sidewall alternating as the partial condenser. The sidewall was much more effective than the screen; this is attributed to the larger distillation area of the sidewall. Recovery at 472-480°C with the sidewall was as rapid as that with the screen at 525°C (Figure 5). The sidewall should, however, be operated above 550°C (for a pot temperature of 650°C) so that the pot will be depleted at satisfactory rate.

A summary of tests with the ^{210}Po-Bi system in the 2-inch-diameter still is shown in Table I. The results of these tests are correlated reasonably well using equation 2.

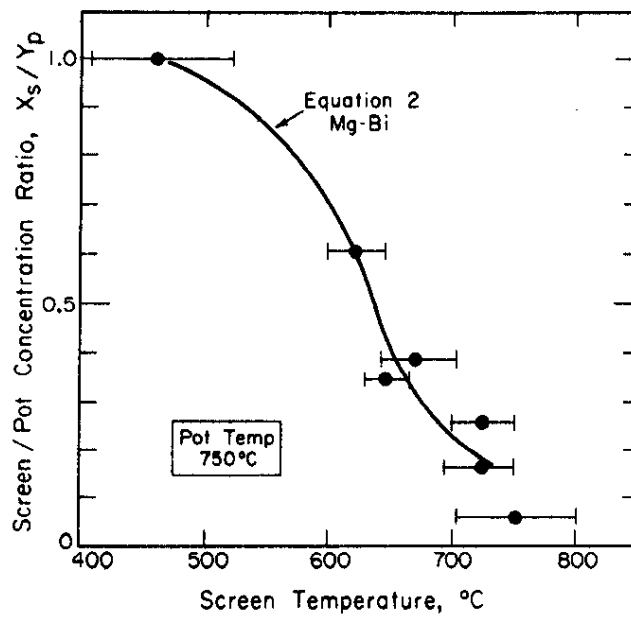FIG. 4   FRACTIONATION WITH SCREEN
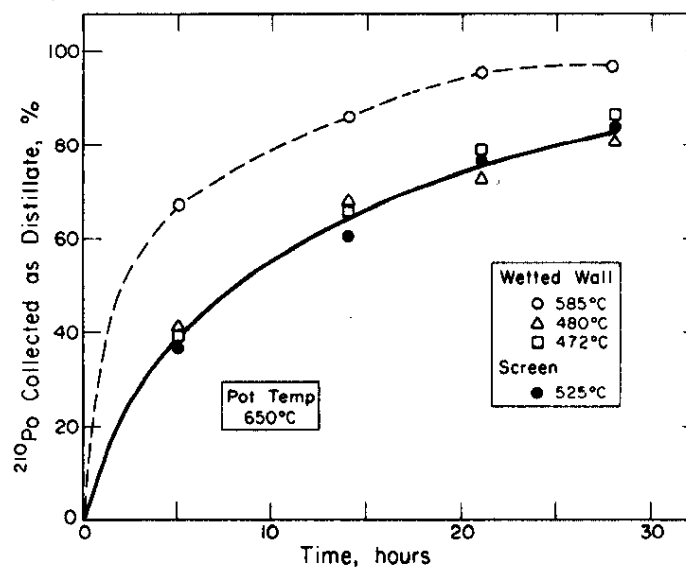
FIG. 5 ^{210}Po-Bi FRACTIONATION WITH WETTED SIDEWALL OR SCREEN

TABLE I

^{210}Po-Bi Fractionation

| Type | Temperature, °C | | X_s/Y_p | |
	Pot	Screen	Calculated by eq. 2	Measured
Screen	750	525	0.78	0.6
Screen	750	615	0.23	0.02
Screen	650	690	0.08	0.1
Sidewall	650	490	0.42	0.25
Sidewall	650	495	0.37	0.35
Sidewall	650	575	0.04	0.09

Removal of Gamma-Emitting Impurities

^{210}Po and the recycled bismuth must be separated from any long-lived (>60-day half-life) gamma-emitting impurities which, although negligible on a weight basis, might cause unacceptable gamma radiation levels. A high-purity conventional grade of bismuth was irradiated and then cooled for ∿15 months. The irradiated bismuth contained the gamma emitters ^{60}Co, ^{124}Sb, and ^{65}Zn, in addition to ^{210}Po, ^{207}Bi, and ^{210}Bi. Analysis of distillates and residues from two series of laboratory distillations showed that these gamma emitters have the following order of volatility and vapor pressure:

$$^{60}\text{Co} < {}^{207,210}\text{Bi} < {}^{124}\text{Sb} < {}^{65}\text{Zn} < {}^{210}\text{Po}$$
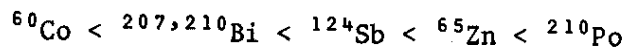
From the results of these distillations and the vapor pressure data shown in Table II, ^{60}Co is expected to remain in the residue of the bismuth purification still, ^{124}Sb to be recycled with the bismuth, and ^{65}Zn to be distilled with the ^{210}Po.

TABLE II

Vapor Pressures at 600°C

Element	Vapor Pressure, mm Hg
Po	12
Zn	10
Sb	2×10^{-3}
Bi	8×10^{-4}
Co	6×10^{-5}

From the measured ^{65}Zn, ^{210}Bi, and ^{210}Po in the irradiated targets, zinc in the bismuth raw material was calculated to be 10 ppb. This concentration is near the upper limit for a desirable ^{210}Po product (the number of ^{65}Zn gamma disintegrations is 2% of the ^{210}Po gamma disintegrations in the distillate).

In a similar manner, antimony in the bismuth raw material was calculated to be ∿0.1 and <0.02 ppb, respectively, from the two distillation experiments. At these concentrations, ^{124}Sb will contribute less than 1% to the shielding requirements for the recycled bismuth; these requirements will still be controlled by the ^{210}Po, ^{207}Bi, and ^{210}Bi.

EQUIPMENT TESTS

Bismuth Melter

The bismuth melter must supply oxide-free bismuth to the first-stage vacuum still in batches of up to 600 kg. The melter and associated apparatus used for these tests are shown in Figure 6.

The molten bismuth flows by gravity from the crucible of the melter through an underflow weir and a freeze valve to the test receiver that is substituted for the first vacuum still. The receiver has a capacity of 113 kg of bismuth and is subsequently inserted in the melter to recycle the bismuth.

The underflow weir was designed to prevent entry of surface oxides or corrosion products into the first vacuum still. The freeze valve holds the bismuth in the crucible during melting by means of a plug of bismuth that is kept frozen by air-cooled coils.

The tests with the bismuth melter:

● Developed experience in melting and transferring bismuth in vacuum.

● Evaluated the capability of the melter to supply oxide-free bismuth to the stills.

● Demonstrated the effectiveness of the freeze valve for stopping and starting the flow of bismuth and maintaining the vacuum.

● Developed suitable means of sampling the liquid bismuth during transfer.
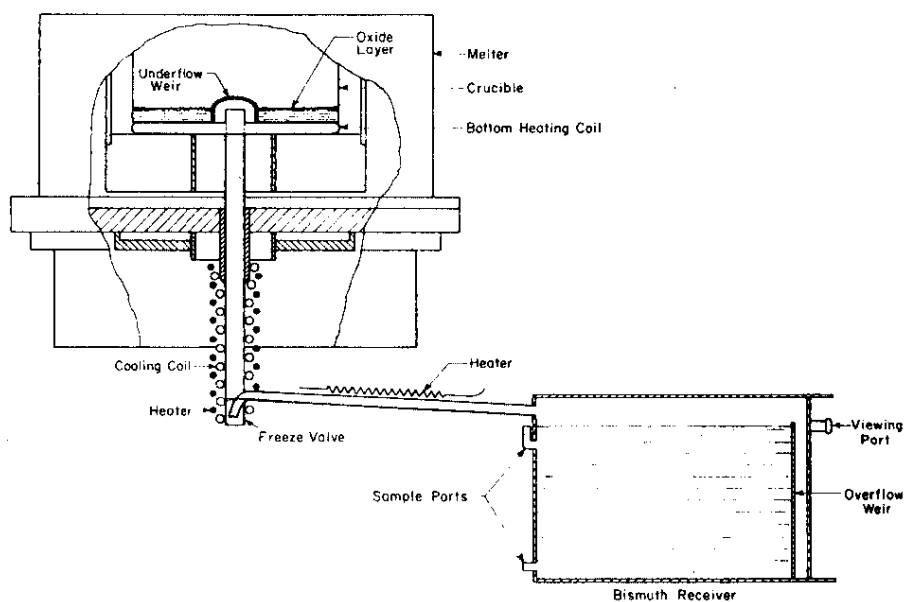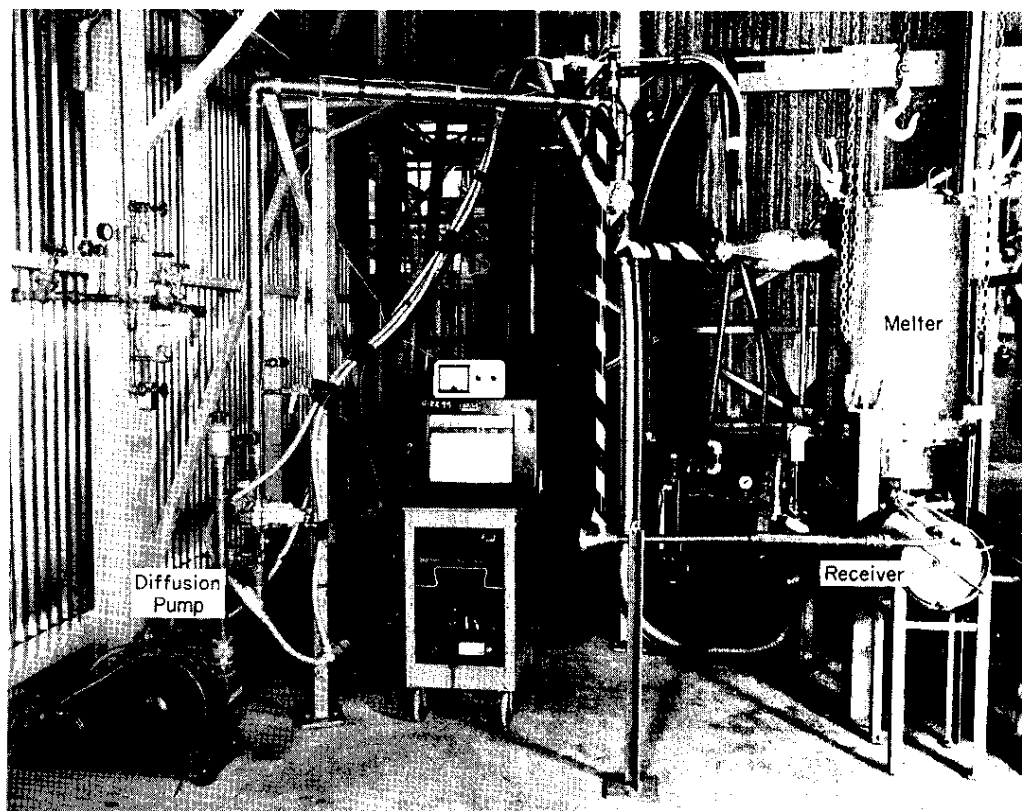
FIG. 6   BISMUTH MELTING TEST EQUIPMENT

Four charges of unirradiated bismuth elements were melted and transferred in vacuum. The first charge (25 kg) was intended to provide a "heel" in the crucible and a plug in the freeze valve, and to allow observation of a small transfer. The second and third charges were melted with the freeze valve sealed; bismuth was then transferred by raising the temperature of the freeze valve to 350°C. An orifice was installed in the transfer line to slow the discharge from the melter and a fourth 113 kg charge of bismuth was melted and transferred under vacuum. The data are summarized in Table III.

TABLE III

Summary of Bismuth Melter Tests

	Test 1	2	3	4
Bismuth charge, lb	55	189	245	245
Initial system pressure, microns Hg	<0.1	<0.1	<0.1	<0.1
Max heater temp, °C	450	540	540	540
Max system pressure, microns Hg	6	13	29	31
Max outgassing rate, microns Hg/min	16	34	120	180
Duration of melting, hr	2	4.5	4.5	4.3
Bismuth transferred, kg	9.5^a	86	111	110
Duration of transfer, min	<1	~1.0	~1.5	~6.0
System pressure after test, microns Hg	<1	<1	30^b	<1.0

a. 34 lb retained in system as crucible heel and freeze valve plug.
b. Due to loose fitting transfer line.

After each test, the melter was filled with argon, and the crucible was inspected and photographed. The surface of the heel of bismuth was dark gray (due to the bismuth oxide) except where unoxidized bismuth erupted during solidification. Bismuth oxide accumulated on the crucible wall and on the surface of the melt from test to test. The solidified bismuth remaining in the freeze valve and around the underflow weir formed an adequate seal after each test.

Samples were obtained of the bismuth transferred during each test. The surface of each sample was bright, which indicates that the underflow weir prevents the transfer of bismuth oxide and that the vacuum is adequate.

To determine whether the 304L stainless steel crucible corroded and whether corrosion products are retained in the melter, iron and nickel analyses were made of the bismuth charged to the melter, the melted bismuth transferred to the simulated vacuum still pot, and the heel of surface dross remaining in the melter after each test. The dross heel in the melter contained 100 ppm Fe and 40 ppm Ni; the feed bismuth and the melted bismuth in the still pot contained <2 ppm, the sensitivity of the method. Although the melter crucible is corroding, as shown by the iron and nickel in the dross, the corrosion products exceed their solubility limit in the molten bismuth and are retained in the crucible by the underflow weir.

Bismuth Freeze Valves

In addition to the freeze valve on the bismuth melter, a similar device is used on the outlet of each vacuum still in the ^{210}Po separations process. This valve, which must be kept closed by solid bismuth, is separated from the 750°C melt in the bottom of the still by only a 2-inch length of 1-inch pipe that is filled with molten bismuth. The valve must also provide a seal tight enough to permit distillation even if the upstream side of the valve is at atmospheric pressure.

A stainless steel test valve (Figure 7) was operated to show that sufficient heat is removed by an air-cooled coil to keep a plug of bismuth frozen while in contact with liquid bismuth at 700°C. The diameter of the vertical pipe is twice that of the proposed tantalum valve, to assure equal or greater flow of heat to the valve (tantalum has three times the thermal conductivity of stainless steel). Cooling coils are press-fitted to the valve, and Sauereisen* No. 78 cement is used as a heat transfer medium. Because the valves will normally be in a vacuum and hence partially insulated, the assembly was wrapped with a 1-inch thickness of asbestos tape to reduce the heat loss to the air.

After the bismuth was solified in the bottom of the valve, the chamber above the valve was filled with molten bismuth and heated to 700°C. The test showed that with 15 cfm of air at 40 psig passing through the coils, the equilibrium temperature of the bismuth plug was 70°C. (The melting temperature is 271°C.) The corresponding overall heat transfer coefficient between the air and bismuth, based on the surface area of the vertical tube, was calculated to be 4.1×10^{-3} cal/(sec)(cm^2)(°C).

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* Product of Sauereisen Cements Co., Pittsburgh, Pa.

FIG. 7 FREEZE VALVE TEST ASSEMBLY

Figure labels:
Heater Welded to Tube
I" Insulation
SS Tube I" OD, 35-mil wall
Vacuum
Solid Bismuth Max Temp 71°C
Molten Bismuth 700 °C
Thermowell
SS Tube 2" OD, 65-mil wall
Asbestos Tape
Cooling Air 15 cfm, 40 psig
$\frac{3}{8}$" SS Cooling Coils Bonded to Valve with "Sauereisen" 78 Cement
Thermowell
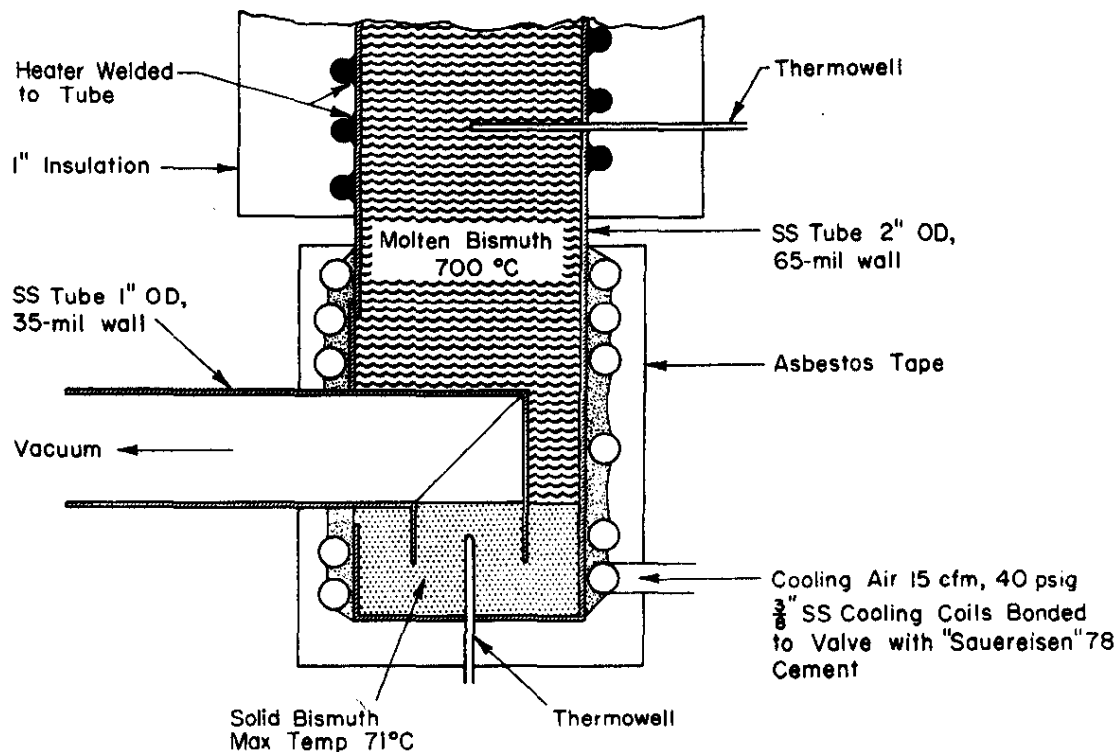
Tests were made with a prototype tantalum valve for the vacuum distillation units (1-inch-OD vertical pipe with 0.5-inch discharge tube, 35-mil wall, and dip leg length of 0.75 inch). In each test, a new bismuth plug was formed in an inert atmosphere, and, after cooling, the leak rate was measured across the seal. The rates ranged from (1.4 to 23) x 10^{-6} atm-cc/sec, and show that the valves provide an adequate seal.

Pulse Tube Agitator

A study was made to develop a practical method for agitating the surface of the liquid metal during distillation to reduce surface depletion and to disperse any solids floating on the surface.

Because conventional means of stirring or pumping are not feasible in the high-temperature, high-vacuum environment, several unconventional methods were investigated. Of these, a pulse tube appears to be the most dependable and practical. The glass equipment (Figure 8) was used in several tests with mercury substituted for liquid bismuth and with a film of 300-mesh bismuth oxide powder floating on the mercury. The helium measuring tube

between the two solenoid valves discharges sufficient helium to displace 7 inches of mercury in the pulse tube; the displaced mercury is jetted from the nozzles at the top of the pulse tube to agitate the pool of mercury in the vessel. The pulse tube is then evacuated and the mercury in the pulse tube returns to its original level, entering the tube through two 1/16-inch orifices. The supply of helium in the measuring tube is then replenished in preparation for the next pulse.

Tests were made with up to 30 pulses per minute. At 15 or more pulses per minute, the surface of the mercury pool was agitated continuously and the oxide powder was dispersed in the bulk of the mercury. When the pulsing was stopped, ∿5 seconds were required for the oxide to rise and re-form a film on the surface. The pulser transfers 2 kg of mercury per minute from the bottom of the reservoir to the surface when operated at 30 pulses per minute.
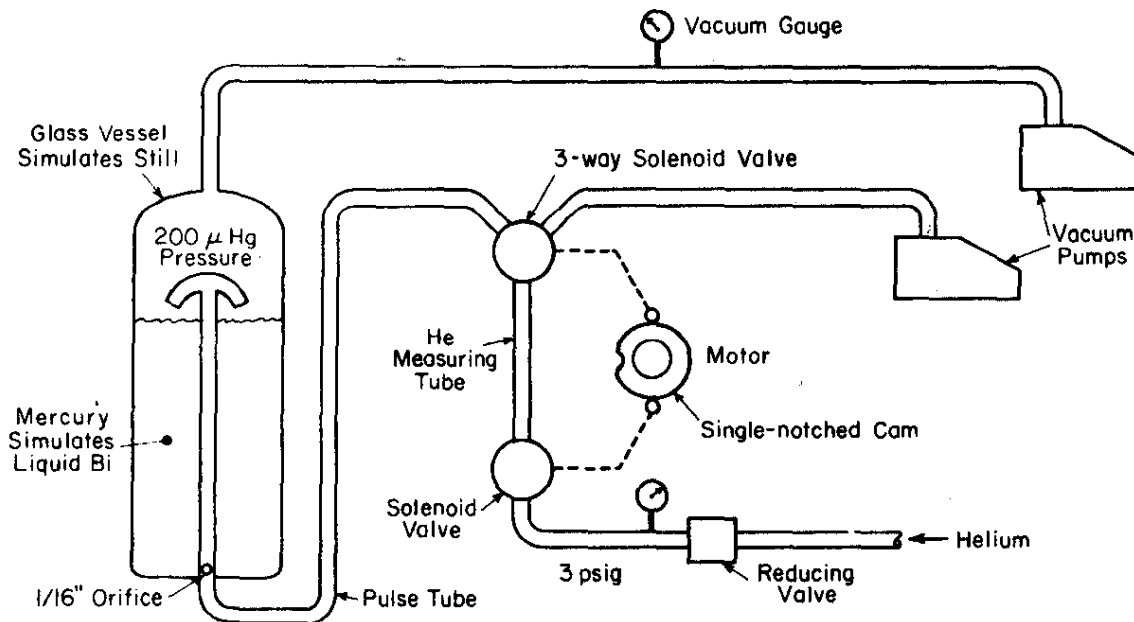

FIG. 8   PULSE TUBE AGITATOR FOR MERCURY

Two-Ft-Diameter Stainless Steel Still

Tests with a 2-ft-diameter stainless steel still, simulating the operation of the first-stage tantalum unit, measured rates of bismuth vaporization at 750°C and the enrichment of a Cd stand-in for polonium, with and without surface agitation. The still assembly (Figure 9) used a 24-inch pipe cap as the distillation pot, with a 24-inch-diameter duct to the condenser funnel. The pulser was used to determine the effect of surface agitation on the separation. A 6-inch-diameter flanged pipe cap at the base of the condenser funnel provided ready access to the distillate. The still was heated with bare resistance rods (0.289-inch "Nichrome"* wire), supported 1/2 inch from the still with ceramic insulators, and enclosed with 3 inches of high temperature insulation. Based on the sidewall surface area of the stainless steel still, the heaters could provide up to 20 watts/in^2. To maintain the still at an operating temperature of 750°C a heat flux of 9.8 watts/in^2 of still surface was necessary (under these conditions the heat flux at the outer surface of the "Nichrome" wire was 7.5 watts/in^2).
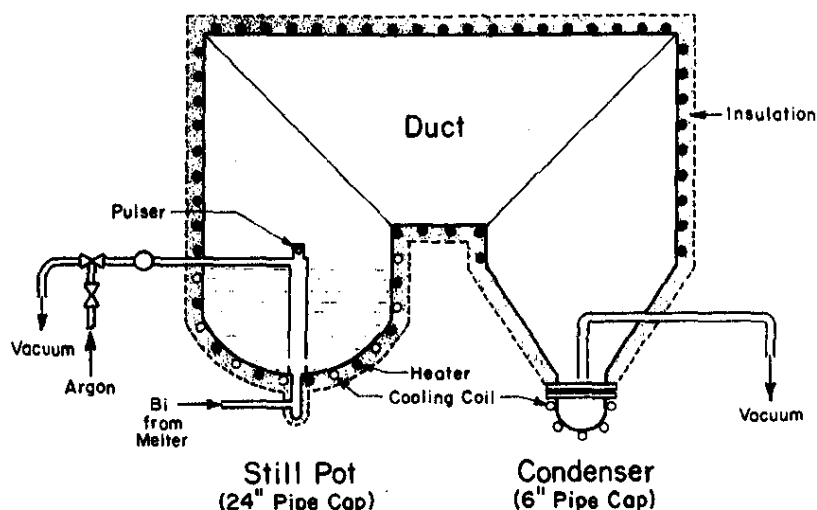
FIG. 9 STAINLESS STEEL STILL

The still was charged with 545 kg of bismuth from the melter with the objective of obtaining a surface free of bismuth oxide. However, an air leak during a transfer to the still and a leak through a thermowell in the still pot resulted in a thick black surface layer ($\sim$100 mg/cm^2) of oxide, mostly Bi_2O_3. The distillations are summarized in Table IV. In two distillations, Tests 1 and 2, with this thick oxide on the surface almost all of the vapor condensed on the 1-ft^2 area provided by the cooled pipe cap at the base of the funnel. The condenser area was then increased to 6 ft^2 by cooling the entire funnel, and Test 3 was made with the oxide present.

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* Registered trademark of Driver-Harris Co.

TABLE IV

Bismuth Distillation in Large Stainless Steel Still

Tests	Oxide, mg/cm^2	A_{cond}, ft^2	Distillate, kg Bi	Measured Ratio f	Calculated Ratio f		
					All R's[a]	R_{oxide} Omitted	R_{oxide} and R_{duct} Omitted
1	~100	~1	1.5	0.14	0.15	0.22	0.25
2	~100	~1	0.95	0.14			
3	~100	6	2.1	0.23	0.23	0.50	0.67
4	~2	6	2.6	0.39	0.39	0.50	0.67
5	~2	6	5.3	0.44			
6	~2	6	3.0	0.36			

a. Derived in Table V.

Before Tests 4, 5, and 6, the still was cooled and all of the bismuth oxide was scraped from the surface and removed by vacuum. The distillation times were from 20 to 45 minutes. The distillation rates were increased by both the increase in condenser area and the removal of the surface oxide, as detailed later.

Interior inspection of the still after the tests with the large condenser surface (Tests 3, 4, 5, 6) showed no condensation of bismuth in the connecting duct; the temperatures within the still during Test 5 are shown in Figure 10. However, in Tests 1 and 2, during which most of the funnel was intended to be at 750°C, bismuth condensed at each point on the funnel where a support member (acting as a heat sink) was attached. Structural members should not be attached to future stills between the bismuth surface and the condenser. Samples of the bismuth surfaces were obtained to a depth of ~1 cm after Test 5. The gray surface film was removed from the sample and consisted of ~2 mg of oxide/cm².

After each test, the bismuth was scraped from the condenser and weighed, and a relative distillation rate f was determined by dividing this weight of distillate by the weight that would evaporate into space during the same time and at the same temperature (by unrestricted or Langmuir evaporation). These relative rates f are shown in Table IV for the three groups of tests, and show that even under the best conditions (Tests 4, 5, 6) the observed rate averaged only ~39% of the rate for unrestricted evaporation.
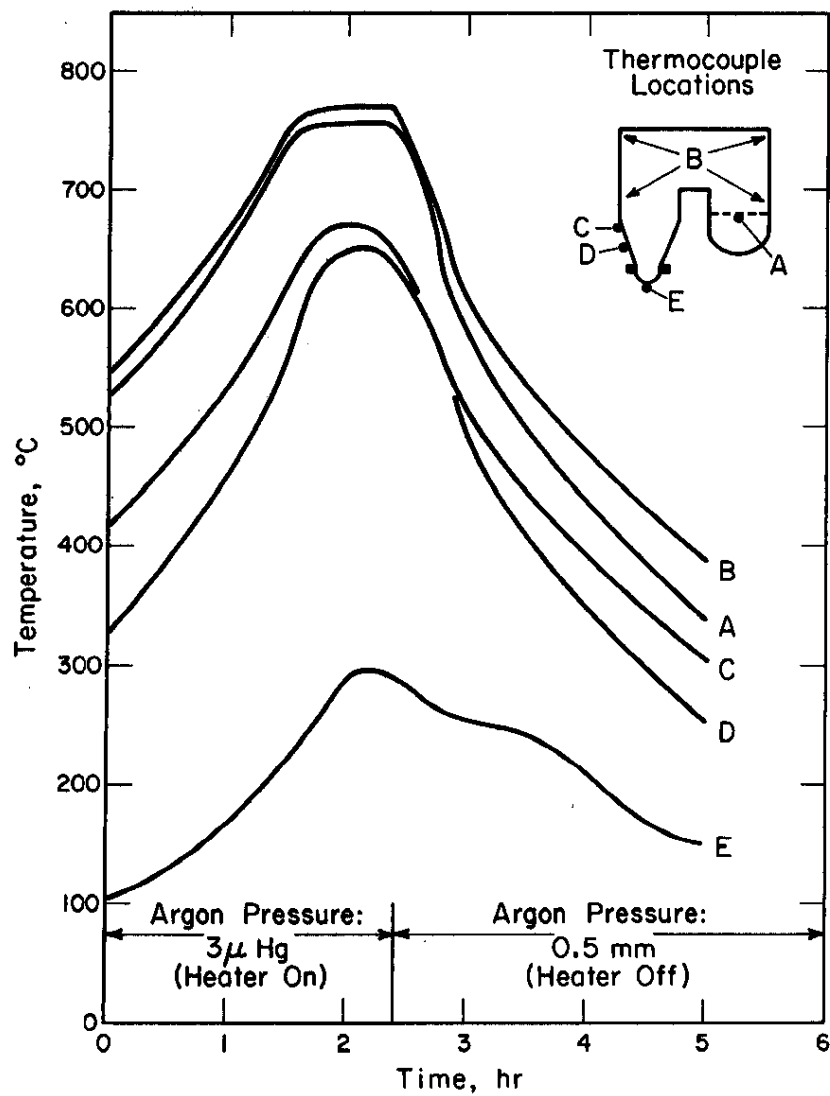
FIG. 10 BISMUTH DISTILLATION

However, unrestricted evaporation is not expected. In addition to this ideal, single, rate-limiting step, the vapor must also permeate through the oxide layer, move through the duct by viscous flow, and condense on the collector. Because the rate of transport for each of these steps is proportional to the pressure drop, the rate for each is a ratio of a pressure drop to a resistance, and the rate for the system is the ratio of the total pressure drop to the sum of the individual resistances (the total pressure drop is the vapor pressure, p_V, at the surface of the bismuth). Thus, as outlined in Table V, the value of f that can be expected for this system is the ratio of evaporative resistance to total resistance. The evaporative resistance was calculated from Mound data,[2] the duct flow resistance from viscous flow equations (with vapor density calculated at $\frac{1}{2} p_V$), and the condensative resistance from the product of evaporative resistance and the (still-pot)/condenser ratio of areas. The permeative resistance of the oxide layer was then determined by difference.

TABLE V

Derivation of Distillation Resistances

$$R_{meas} = \frac{p_V}{M_{meas}}; \quad R_{evap} = \frac{p_V}{M_{evap}}; \quad R_{duct} = \frac{16\mu L}{\pi r^4 \rho};$$

$$R_{cond} = R_{evap} \frac{A_{evap}}{A_{cond}}; \quad R_{oxide} = R_{meas} - (R_{evap} + R_{duct} + R_{cond});$$

$$R_{calc} = R_{evap} + R_{oxide} + R_{duct} + R_{cond}; \quad f_{calc} = \frac{R_{evap}}{R_{calc}}$$

Tests	R_{meas}	R_{evap}	R_{duct}	R_{cond}	R_{oxide}
1,2	158	22.1	13.7	66.3	50.5
3	96	22.1	11.0	11.0	50.5
4,5,6	58	22.1	11.0	11.0	12.9

where R = resistance, $\frac{dynes/cm^2}{g/sec}$

p_V = bismuth vapor pressure, dynes/cm^2

M_{meas} = measured rate of distillation, g/sec

M_{evap} = unrestricted evaporation rate[a] for still area, g/sec

μ = viscosity of bismuth vapor, poises

L = effective length of duct, cm

r = radius of duct, cm

ρ = bismuth vapor density at $\frac{1}{2} p_V$, g/cm^3

a. Mound data (Ref 2).

The calculated ratio of expected distillation rate to unrestricted evaporation rate for each of the three groups of tests is also tabulated. Agreement with the observed ratio f is good when all resistances are included in the calculation, and deteriorates increasingly when the oxide resistance and then the duct resistance are omitted. A single value for oxide resistance was used in calculating f for the thick layer in the first two groups of tests, and allows close agreement with the observed f despite the change in condenser area. The last group of tests, with the thin layer of oxide, required a value of oxide resistance that was ¼ of the resistance of the thick oxide, rather than the factor of only 1/50 indicated by relative thicknesses. The stainless steel oxide may really be less permeable than the Bi_2O_3, or the data may not be sufficiently precise. In any event, for Tests 4, 5, and 6 with the thin oxide layer, the observed rate is 0.39/0.50 = 78% of the rate that would be expected in the absence of an oxide layer.

After measuring the rate of bismuth vaporization, 25 g of cadmium was added to the bismuth melt as a stand-in for ^{210}Po (which could not be used in semiworks equipment). Two simple distillations were carried out at 750°C with no mechanical surface agitation. The effective relative volatility was calculated from the previously developed models for simple distillation with mixing by natural convection[4] and was found to correlate the measured values of α_{eff} well for the two runs with no mechanical agitation, as shown in Table VI.

TABLE VI

Cd-Bi Distillations in 2-ft-Diameter Still at 750°C

f	α	α_{eff} Calculated	α_{eff} Measured
0.35	21,000	152	120-160
0.41	21,000	127	101-140
0.45[a]	21,000	118	76-90

a. With pulser.

The natural convection model predicts that for a value of f = 1/3 the value of α_{eff} for the ^{210}Po-Bi system with natural convection in a 2-ft-diameter still at 750°C is 25. The maximum relative volatility with no surface depletion, α, for the ^{210}Po-Bi system at 750°C is 42.

Several different pulsers were built and tested in order to find the optimum design to increase surface agitation. Details of the pulser for liquid bismuth used in the 2-ft-diameter still are shown in Figure 11. The pulser was designed to give several jets which would reach all portions of the still surface at a high velocity. Although turbulence levels on the bismuth surface were high in the immediate vicinity of the jets, calculations showed that the turbulent energy was dissipated rapidly with respect to both time and distance. Using the model for simple distillation with mechanical surface agitation,[4] it was determined
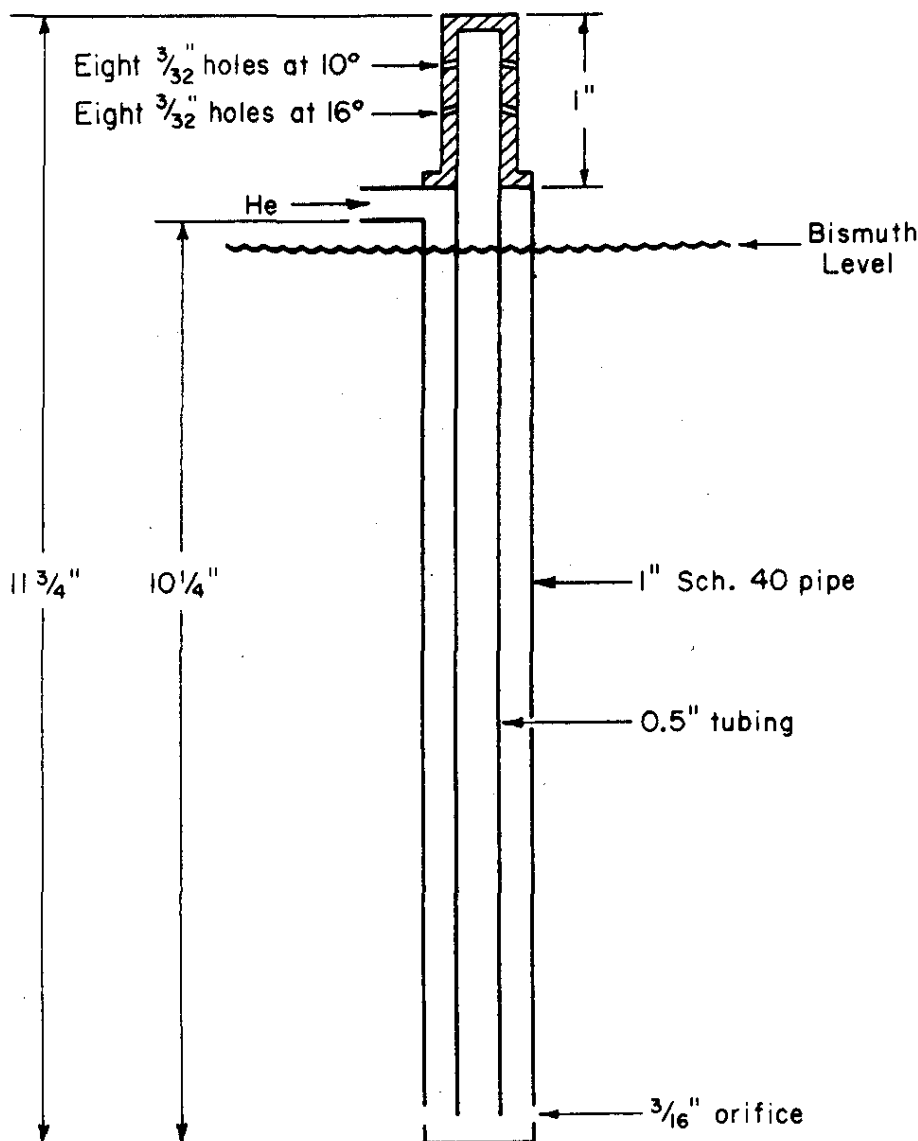
FIG. 11 PULSE TUBE AGITATOR FOR LIQUID BISMUTH

that less than 10% of the liquid metal surface was agitated sufficiently to significantly reduce surface depletion. Also, when the pulser was employed to increase the degree of turbulence on the bismuth surface it was observed that the liquid bismuth splattered. Many of the small drops produced by this splattering remained on the sides of the still wall. These drops were only a few millimeters in diameter, and were completely vaporized in 15 minutes or less. Since the distillation period is several hours, these drops were, in effect, transported from the pot to the condensate and reduced the overall separation factor. The lower value of α_{eff} which was measured during distillation with the pulser in operation is believed due to this splattering (Table VI).

The low volume, high velocity pulser used in these tests did not efficiently reduce surface depletion, nor did it increase the vaporization rate because the jets did not break up surface oxide layers to any significant extent. However, the size of the orifices in the pulser head could be increased to give a high volume, low velocity jet of bismuth which would provide a large area of fresh bismuth surface in order to maintain high vaporization rates in the presence of surface layers of oxides or corrosion products.

Vacuum Bell Jar

The tantalum stills are contained in a large vacuum bell jar to prevent air oxidation of the heated tantalum surfaces. The bell jar is 6.5-ft. diameter and 6-ft. high. A seal is provided around the circumference to permit removal of the top half of the bell jar. This seal consists of two coaxial seals with an intermediate vacuum (Figure 12). A bismuth and tin alloy would provide an effective and practical means of remotely sealing the bell jar to its base. Small-scale (one ft diameter) stainless steel bell jars were sealed with "Cerrotru",* a bismuth-42% tin eutectic, as the sealant. Leak rates of $\leq 10^{-5}$ atm-cm^3/sec were attained in these tests even after several heating cycles.

A prototype bell jar (6.5-ft. diameter and 6-ft. high) constructed of stainless steel was used at the Semiworks to house the 8-in-diameter tantalum still during distillation studies. Latex rubber was used as a gasket material sealing against a thin strip of Neoprene bonded to the lid. There were no leaks across the seal during operation. A vacuum of 10 to 15 microns was reached in the bell jar during distillation runs of over four hours with the still at 750°C. The bell jar was reopened after most runs. The 10 to 15 micron pressure was due to outgassing; lower pressures would be expected after extended operation without reopening of the bell jar.

* Registered trademark of Cerro De Pasco Corp.

The rubber seal was used instead of the bismuth-tin system because it was more convenient and economical for Semiworks tests. The bismuth-tin system would be used in a production facility since it is more easily operated remotely and is impervious to radiation.
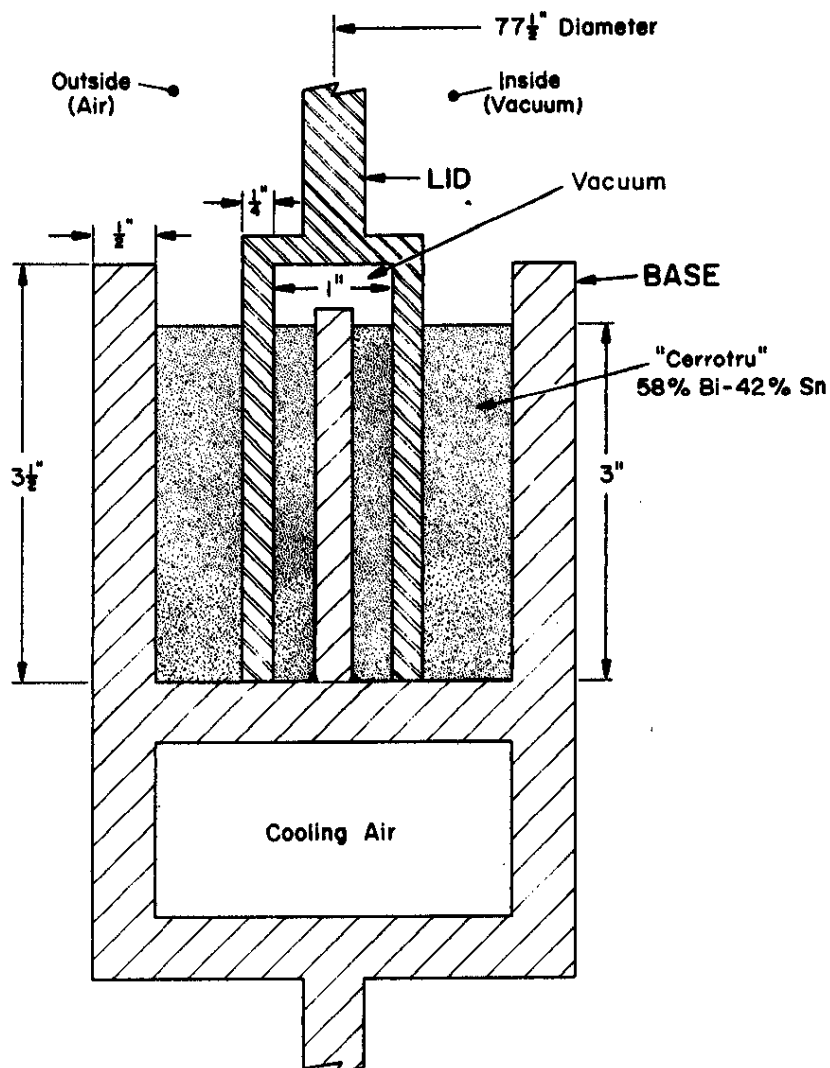

FIG. 12 BELL JAR SEAL

Eight-Inch-Diameter Tantalum Still

An 8-inch-diameter prototype tantalum still was operated in the vacuum bell jar (Figure 13). The still was heated with two bare resistance rods (1/2-inch-OD "Nichrome" tubing with 0.015-inch wall thickness) which were enclosed with high temperature insulation. The heaters could provide up to 44.5 watts/in^2 based on the side-wall surface area of the tantalum still. With the still operating at 750°C, 6.55 watts/in^2 was necessary, and under these conditions the heat flux through the outer surface of the "Nichrome" tubing was only 5.15 watts/in^2.
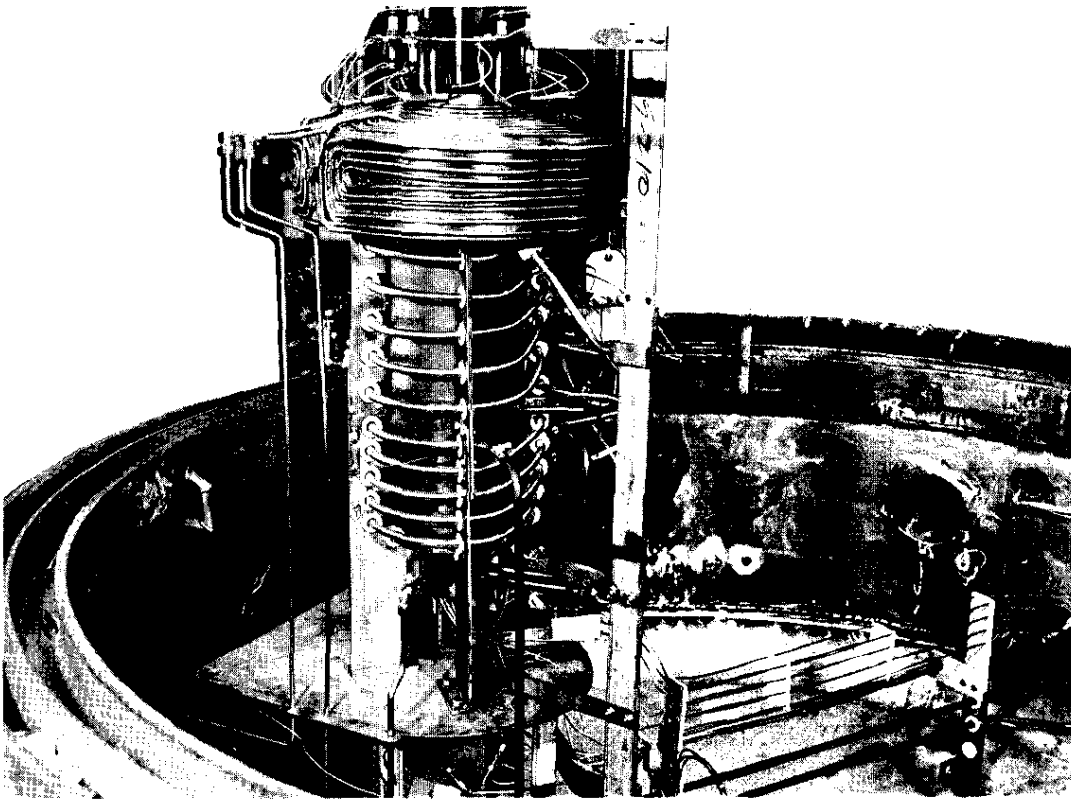

FIG. 13   8-INCH STILL IN BASE OF BELL JAR

The distillate was collected in the rim under the outer portions of the "top hat" (Figure 14). In two tests at 730°C the bismuth vaporization rate was satisfactory (30 to 40 percent of the theoretical maximum rate for molecular distillation). The attainable rate of distillation is limited by conductive losses. The still was operated so that bismuth condensed only in the outer

rim and there was no reflux to the pot. The heaters at the top
of the still effectively prevented local condensation in the "top
hat" region (Figure 14) from which condensate could have refluxed
to the melt and thus limited the effective collection of condensate
Holdup in the condenser of the 8-inch still was only 12% of the
total expected distillate; this could be reduced further by
inclining the still toward the condenser outlet.

Top Hat
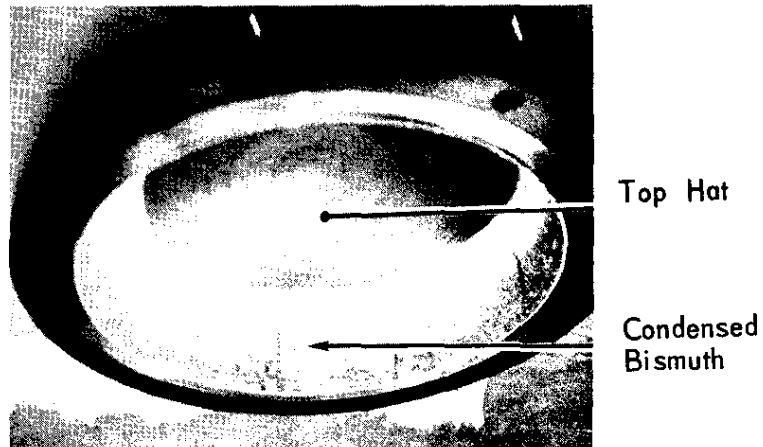
Condensed
Bismuth

Interior of Cover with "Top Hat" Dome
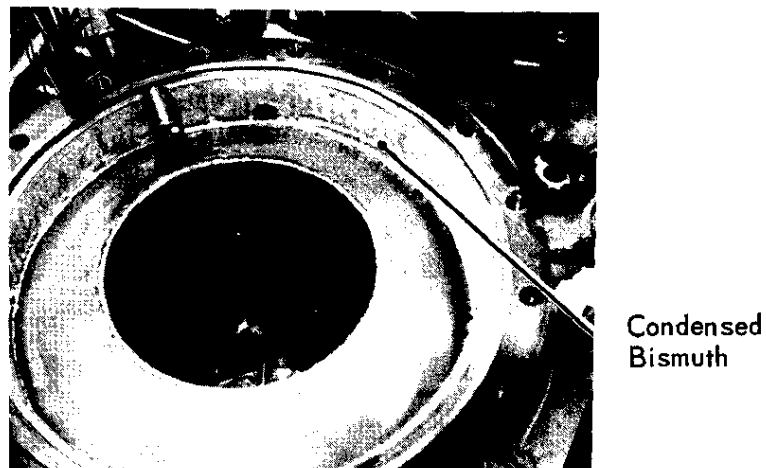
Condensed
Bismuth

Interior of Condenser

FIG. 14   CONDENSER OF 8-INCH STILL

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After measuring bismuth vaporization rates in the 8-inch-diameter still, cadmium was added as a stand-in to test separation efficiency. Repeated openings of the still (to observe condensation patterns from previous tests and to charge Cd for these tests) resulted in a visible oxide layer that reduced the rate of vaporization at 750°C to ~15% of the expected rate for a clean surface. (In a plant still the apparatus would not usually be exposed to the atmosphere after the initial charge.)

Distillations with a cadmium stand-in were carried out with a pot temperature of 750°C. The first test was a simple distillation in which no vapor was permitted to condense on the sidewall or "top hat," thus precluding reflux; the measured α_{eff} was 236. This value exceeds the α_{eff} of 70 which would be obtained with no oxide to inhibit bismuth vaporization. This behavior is expected for a volatile component such as cadmium (and to a lesser extent ^{210}Po).[4]

In the second test, the sidewall was operated at 700°C to provide a wetted wall condenser. Otherwise all conditions were identical to the first test. The measured α_{eff} for the wetted wall was 450. The increase in separation efficiency in the wetted wall test confirmed predictions from small-scale tests. The cadmium concentration of the bismuth that condensed on the wall was measured after the test and was found to be ~3% of that in the vapor from the pot; therefore, the amount of cadmium refluxed to the pot was negligible.

Bismuth was charged to the 8-inch still twice during the distillation studies. Since bismuth expands as it solidifies, all transfer lines had to be thick-walled so that they would not rupture when the bismuth cooled. The surface area of the bottom freeze valve on the still was not sufficient to solidify the flowing stream of bismuth from the melter. A solid bismuth plug in the freeze valves was necessary before startup to provide the initial seal.

The still was evacuated with a 4-inch-diameter diffusion pump. During distillation the pressure in the still was 1 to 7 microns.

Heat Transfer in Mockup of Final Stage

In the final fractionation stage, ^{210}Po-Bi solutions in the still could generate as much as 3 kw of nuclear heat. Tests established that the design for this still will remove this heat and also control the temperature over the required range from ~270 to 650°C.

A stainless steel mockup of the still (Figure 15) was tested
to demonstrate effective control of temperature with external gas
cooling. The still base is encased in a cooling jacket with three
coolant lines. The base contains four fins from the bottom of the
pot, which direct the flow of coolant gas and increase the heat
transfer area; total transfer surface is $\sim$500 cm^2. Because the
process still will probably be made of tantalum and will use
helium as coolant, the cooling jacket and piping are designed
for minimum pressure drop, both to avoid need for a high pressure
compressor and to minimize the thickness of tantalum wall of the
still required to contain the helium. In the mockup tests, air
was used as coolant, electric heaters simulated ^{210}Po, the pot
was charged with unirradiated bismuth, and the still was insulated
to prevent heat loss from areas other than the cooling jacket.

In the mockup tests, the pressure drop across the still was
<1 psi at total air flow of 100 scfm. Typical steady-state tem-
peratures for 2 kw heat input and 66 scfm air flow (22 per coolant
line) are: inside pot 270°C, inlet air 25°C, exit air from outer
lines 72°C, exit air from the central line 61°C. Calculated
overall heat transfer coefficient for the cooling jacket was
3.9 x 10^{-3} cal/(sec)(cm^2)(°C); calculated temperature drop across
the 1/8-inch wall of the pot was $\sim$3°C. The flowing air removed
1.8 kw; 0.2 kw was transferred through insulation to the atmosphere.

For the ^{210}Po heat load of 3 kw, bismuth is calculated from
these tests to be kept frozen on the inside surface of the pot with
helium flow of $\sim$240 scfm. The normal operating temperature of
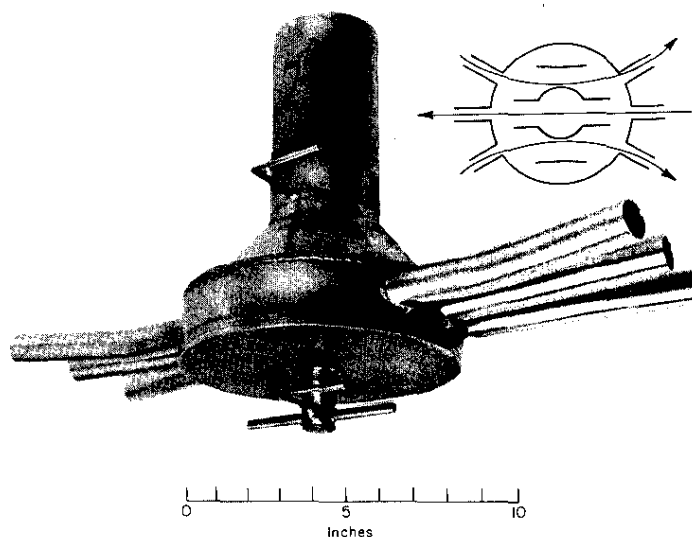650°C is calculated to be maintained with helium flow of $\sim$60 scfm.

FIG. 15 MOCKUP OF STILL BASE AND GAS COOLER

TANTALUM EMBRITTLEMENT

Embrittlement of Unprotected Distillation Equipment

During the course of the laboratory distillations, several tantalum liners became embrittled and cracked, a behavior attributable to absorption of oxygen from the liquid melt. In addition to causing embrittlement, oxygen also promoted intergranular corrosion of tantalum.

Tantalum becomes brittle at room temperature when its oxygen content reaches $\sim$700 ppm.[5] If Bi_2O_3 is present in the melter and oxygen reaches the equilibrium solubility in bismuth ($\sim$3 ppm at 400°C),[6] there would be sufficient oxygen in only 10 charges of bismuth to cause embrittlement of a first-stage tantalum still having a 0.3-cm wall thickness. Calculations have shown that tantalum will absorb oxygen from any bismuth solution containing $>10^{-9}$ ppm oxygen, and that a first stage still could become brittle after $\sim$225 hours operation ($\sim$40 charges) if the bismuth feed contained greater than 1 ppm oxygen.

Laboratory embrittlement tests were carried out with 1/16 x 1/8 x 3/4 inch specimens of tantalum exposed to molten bismuth at 750°C containing from 2 to 150 ppm oxygen. Identical specimens were exposed to solid Bi_2O_3 at 750°C. Embrittlement was determined by the number of times the specimens could withstand a 180° bend without fracture. The oxygen concentration of the specimens was also analyzed by an inert gas fusion technique.

These tests indicated that once the oxygen content of the tantalum reached 700 to 800 ppm, the tantalum was completely embrittled and fractured at the first bend (Figure 16). The tests also showed that tantalum absorbed oxygen from bismuth solution containing as little as 2 ppm dissolved oxygen, and that embrittlement increased as the oxygen diffused into the tantalum.

The oxygen content increased from 90 to 340 ppm in a tantalum specimen exposed to $\sim$2 ppm oxygen in molten bismuth for 200 hours at 750°C (Figure 17). The exposed specimen fractured at the second bend; unexposed specimens bend 5 to 8 times before fracture. In further tests with higher concentrations of dissolved oxygen, prepared by dissolving Bi_2O_3 in bismuth, the rate of embrittlement was independent of the concentration of oxygen in bismuth, which confirms that the rate of embrittlement is limited by solid phase diffusion.

The rate of the solid phase reaction of tantalum metal with Bi_2O_3 at 750°C was measured to be 3 mg of Ta_2O_5 per cm^2 per hour (Figure 18). The exposed tantalum specimens were completely brittle in <3 hours (fractured at first bend), as summarized in Table VII.
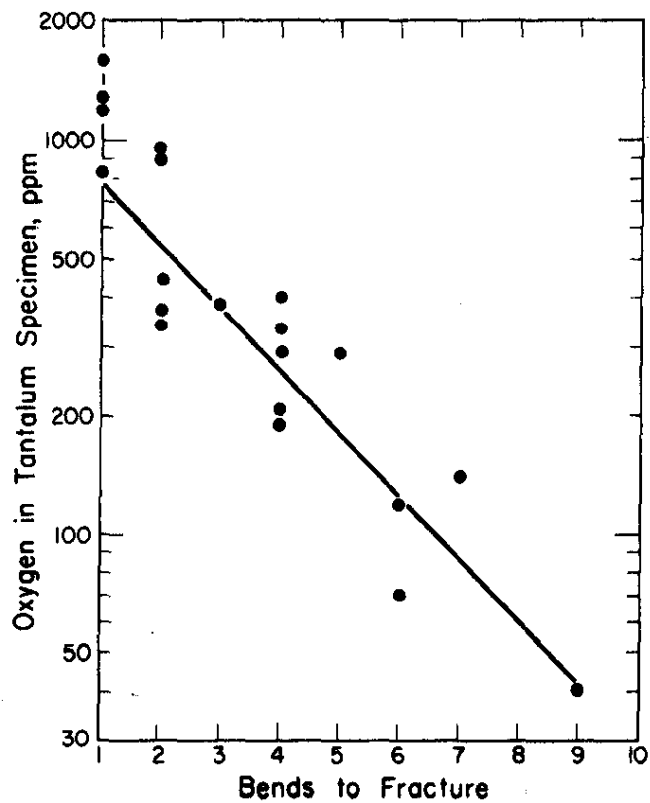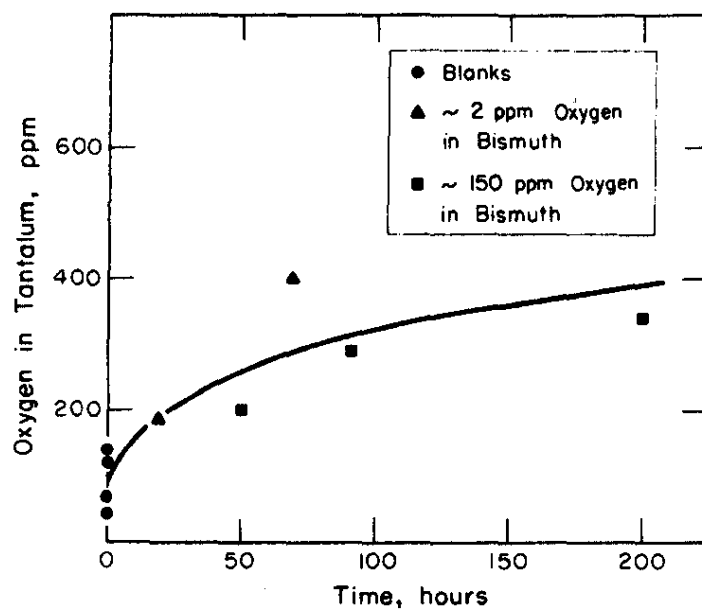
FIG. 16   EMBRITTLEMENT OF TANTALUM BY OXYGEN

FIG. 17   ABSORPTION OF DISSOLVED OXYGEN FROM
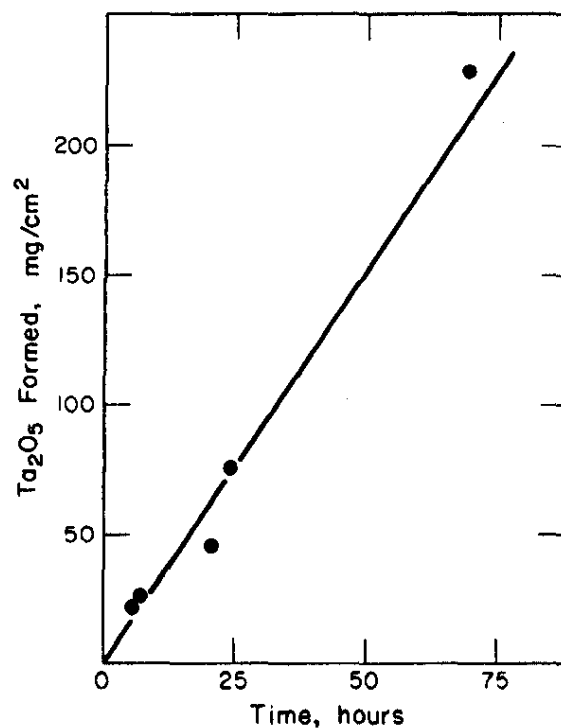BISMUTH BY TANTALUM AT 750°C

FIG. 18 SOLID PHASE REACTION BETWEEN Ta AND Bi$_2$O$_3$ at 750°C

TABLE VII

Tantalum Embrittlement at 750°C

Exposure	Time, hr	180° Bends to Fracture	Oxygen in Tantalum, ppm
Unexposed	0	6	120
controls	0	6	70
	144a	6	-
	7a	7	-
	0a	7	140
	0	9	-
	0	9	40
Solid Bi$_2$O$_3$	1	3	
	3	1	
	6	1	
	7	1	
	21	1	
	24	1	
	45	1	
	68	1	
Molten bismuth	5	5	
2 ppm oxygen	19	4	190
	69	4	400
	200	2	340
Molten bismuth	7	5	
150 ppm oxygen	50	4	200
	91	4	290

a. Heated in vacuum.

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Tantalum Getter

To protect the tantalum stills from dissolved oxygen or any other harmful impurity, a bed packed with tantalum can be added between the melter and the first-stage tantalum still. While a distillation is being carried out in the first stage, the next charge can reside in the packed bed for the same length of time and at the same temperature as the still. Under these conditions the amount of impurity which is taken up by the tantalum in the packed bed or the still is determined by the surface area of tantalum to which the bismuth is exposed. If the ratio of the surface area of tantalum to the volume of bismuth in the getter is approximately 50 times that of the first stage, then impurities which could have been taken up by the still can be completely removed by the packed bed. Impurities which are not removed by the packed bed presumably will not affect the still. The fraction of any impurity in the initial charge that attacks the first still was calculated to be greatest when the rates of absorption by tantalum in the bed and still are limited by solid phase diffusion. Under the most unfavorable conditions, this fraction does not exceed $\sim$2%.

On the basis of the measured rates of absorption of oxygen, calculations indicate that oxygen dissolved in the bismuth will be absorbed by the tantalum in the sacrificial bed within the first few minutes of operation, after which the oxygen would require $\sim$1 hour to diffuse to a uniform concentration throughout the sacrificial tantalum.

Packing for the bed was investigated, and the most convenient form is thin corrugated tantalum strips separated by thin flat pieces of tantalum, as shown in Figure 19.
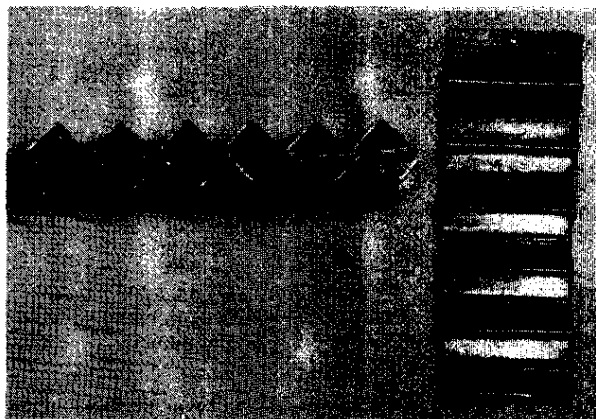

FIG. 19 PACKING FOR TANTALUM GETTER

Reduction of Bi_2O_3 by CO

The underflow weir of the melter is designed to remove solid Bi_2O_3 from the process feed, and the packed bed of sacrificial tantalum strip will remove dissolved oxygen. Bismuth oxide in the melter can also be reduced by carbon monoxide. The CO reactant and CO_2 product can readily be added and removed from the melter through vacuum lines. Experiments demonstrated that the oxide can be reduced with CO, in the melter, in about 6 hours at 400°C. Reduction with CO will remove severe contamination with oxide, such as might result from a vacuum failure (Figure 20).

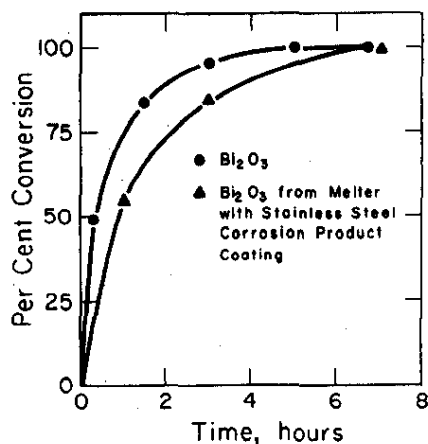FIG. 20   REDUCTION OF Bi_2O_3 BY CO AT 400°C

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