JAN 28 1966

IS-T-71

MASTER

AMES LABORATORY

Iowa State University

Ames, Iowa

AEC Contract No. W-7405-eng-82

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SEPARATION OF CADMIUM FROM THE LEAD-BISMUTH EUTECTIC BY HIGH VACUUM SINGLE STAGE DISTILLATION: CHAMBER DESIGN AND DISTILLATE PURITY

by

Lawrence Bryson Murdoch

M. S. Thesis, November, 1965

RELEASED FOR ANNOUNCEMENT
IN NUCLEAR SCIENCE ABSTRACTS

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BY HIGH VACUUM SINGLE STAGE DISTILLATION:
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Lawrence Bryson Murdoch

A Thesis Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
MASTER OF SCIENCE

Major Subject: Chemical Engineering

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November, 1965

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Lawrence Bryson Murdoch

ABSTRACT

A distillation chamber was evaluated to determine its effectiveness for separating liquid metals by a continuous high vacuum distillation process. This previously constructed chamber had an integral condenser which was cooled by a sodium-potassium eutectic. The metal to be separated flowed down an inclined distribution plate, opposite the condenser. The chamber was installed in a loop in which circulation of the liquid metal was effected by a remote diaphragm pump.

Partial separation of cadmium from the lead-bismuth eutectic was achieved, verifying the method of operation. Distillate purity was found to be low, the cadmium concentration varying from 0.12 to 0.47 mass fraction.

The cause of the low purity was investigated and determined to be the result of some design features of the distillation chamber. The distilland was short-circuiting from the distribution plate to the condensate receiver due to a combination of the steep slant of the distribution plate and the type of baffles on the plate. Contamination rates were determined to be related to the distilland flow rate through the chamber. Contamination rates varied from 0.69 to 1.0 gm/sec for the comparable theoretical distillation range of 0.423 to 1.80 gm/sec.

Despite the effect of the contamination, distillation temperature and distilland concentration were found to have a strong effect upon the distillate purity.

Redesign of the distillation chamber with particular attention to the distribution plate was recommended as a next step of this investigation. Additional supporting work for this study such as control simplification, condensation studies, and basic distillation studies using additional metal systems, would be of considerable value.

*USAEC Report IS-T-71. This work was performed under Contract W-7405-eng-82 with the Atomic Energy Commission.

INTRODUCTION

In the design of economically feasible nuclear power reactor systems, fuel supply and fuel reprocessing are important factors in the over-all cost system. For example, the two main processing problems of a breeder type reactor system are: 1. the recovery of generated fuel from a dilute mixture in a form suitable for use as a nuclear fuel and 2. the removal of fission products from the spent reactor fuel and recovery of the unburned nuclear fuel. A compact process which would not alter the chemical form of the fuel material would be a significant development.

Due to the large differences in the vapor pressures of metals at high temperatures, vacuum distillation has been of interest as a method of reprocessing reactor fuels. Use of this method may be possible since most fission products are of higher volatility than the unburned fuel.

Suitable construction materials and ultra-high vacua have in the past limited such liquid metal separations. Due to improvements in these requirements during the past decade, separation of metals by high temperature vacuum distillation has become more feasible as an industrial process.

In addition to applications in the nuclear power field, such separations of metals are currently being utilized in the metallurgical industry. Conventional distillation has

been used for many years for the separation of lead, cadmium and zinc. Mercury, lead and several other metals are purified by vacuum distillation. Metals are used in coating other objects under the name of vapor plating. In this case, the object acts as a condenser while the metal is vaporized under vacuum.

The advantages of using high vacuum are: 1. to approach "molecular distillation," that is, to remove residual molecules so that the probability of the vaporizing metal molecules reaching the condenser unhindered is increased, 2. to reduce the problem of oxidation on the distilling surface of the metal and 3. to achieve separation at lower temperatures. This investigation was performed at the upper limit of pressures commonly referred to as "molecular distillation" or more appropriately in this study as high vacuum distillation. In molecular distillation the rate of evaporation is controlled by the rate at which molecules can escape from the free surface of the liquid. The maximum rate of distillation occurs when these molecules can reach the condenser unhindered by molecules of gas or of returning vapor. Therefore, a low residual gas pressure should be maintained in the space between the evaporating surface and the condenser.

Although considerable work has been done in the separation of metals by batch processes, few attempts have been

made to apply this work to a more practical, continuous process. Several theoretical approaches to a continuous process have been made. The economical advantages of a continuous process are readily apparent.

This study utilized a system previously designed for the continuous separation of liquid metals. Only minor modifications were made in the system. The purpose of this investigation was to more thoroughly evaluate the forced circulation loop and distillation chamber as to the variables involved in the separation of liquid metals. In addition to obtaining performance characteristics, suggestions were made for the redesign of the distillation chamber.

LITERATURE REVIEW

The following paragraphs represent some of the basic theoretical concepts and experimental results which are found in the literature. Considerable work has been done in vacuum distillation of organics. However the applications to liquid metal distillation have been fairly recent and few applications to continuous processes exist, most processes being of the batch type.

The literature reviewed here will be that which is pertinent to the present investigation. Considerable work has been done in the general area of vacuum metallurgy and the reader is referred to the work of Westerheide and Burnet (32), which includes an excellent and very comprehensive bibliography of molecular distillation and vacuum technology.

Molecular Distillation Theory

By means of the kinetic theory of gases, Langmuir (19) arrived at a relationship between the pressure exerted on a surface by a perfect gas and the rate at which molecules strike the surface during vaporization. This expression is given as

$$m = \alpha KP \sqrt{M/T} \text{ gm/sec-cm}^2 \quad (1)$$

where: P = equilibrium pressure

T = absolute temperature

M = molecular weight

$K = \sqrt{1/2\pi R}$, R = gas constant

α = (1 - coefficient of reflection) = ratio between the rate at which molecules actually condense on the surface and the rate at which they strike the surface.

Langmuir further states that if the vapor pressure of a substance is sufficiently low, the actual rate of evaporation of a substance is independent of the presence of vapor around it. Thus Equation 1, which is for an equilibrium process, can be applied to non-equilibrium processes and becomes

$$m = \alpha\beta KP \sqrt{M/T} \text{ gm/sec-cm}^2 \quad (2)$$

where: β = condensation coefficient which is related to condenser temperature and material of construction.

A good understanding of high vacuum distillation may be obtained from the review of high vacuum distillation of organics. Two of the foremost investigators of this field are Hickman and Burrows. Hickman and Trevoy (15) discuss the coefficient of reflection and conclude that perfectly clean liquid surfaces will evaporate at the calculated rate, at least if the rate is low. Knudsen's (18) experiments with pure mercury affirm the conclusions of Hickman. Burrows (5,6)

explains the mechanism of molecular collisions between the vaporizing molecules and relates the effect of angle of approach before collision upon the velocity after impact.

Littlewood and Rideal (20) observed that materials with high thermal conductivities, such as metals, have evaporation coefficients, α , near unity when evaporation takes place in vacua. Thus they suggested that thermal conditions at the interface affect the evaporation coefficient. Paul (25) also made a survey of evaporation coefficients and indicated that for metals, the value of the evaporation coefficient is approximately unity.

Condensation coefficients measured for metal vapors condensing and crystallizing on solid surfaces, were reviewed by Wexler (34). The survey for various metals indicates that condensation coefficients increase with decreasing surface temperature and with increasing thickness of the deposited layer. However these coefficients were determined under conditions different than those encountered in typical engineering studies.

Other factors to be considered when making distillation studies are surface oxide effects, temperature gradients, surface depletion, and geometrical considerations. These must be considered when designing distillation equipment. Spendlove (28) has discussed the temperature gradient effect and Argonne Laboratory (7) has studied temperature gradient

effects for stills heated from the bottom. Walsh (31) investigated the problem of surface depletion of the volatile component as applied to distillation of metals. He concluded that depletion is negligible if some turbulence of the melt exists.

Metallurgical Applications

One of the first cases of molecular distillation being used for the separation of metals was the application to the separation of the isotopes of mercury by Bronsted and Hevesy (2). But it was some years later until any serious thought was given to the use of high vacuum distillation of other metals on a practical scale.

Martin (21) theoretically investigated the use of high vacuum in the separation of metals and the differences existing between the distillation of organics and metals. He gave particular emphasis to the volatility ratios and changes in condensate and melt composition during distillation. In a later article (22) Martin sought to apply his theoretical analysis to the purification of beryllium. He devised an experimental batch apparatus with which to remove from the beryllium, the impurities calcium, sodium, magnesium, manganese, aluminum, silicon, and iron. Theoretical calculations were made, but no experimental work was performed.

The most significant recent work in the metal distillation

field has been conducted by T. R. A. Davey. Davey has conducted studies on a continuous method of removing zinc from lead by vacuum distillation under moderately high vacuum. The first article (12) dealt with the outline of the problem and the mathematical treatment of the distillation. This study was patterned after a process existing since 1947 at the Broken Hill Associated Smelters Ltd., Australia. Davey interrelated the rate of distillation with the area available, zinc concentration, and amount of lead to be treated. In the mathematical analysis a correction was made to allow for high velocities of diffusion which somewhat change the common concept of pressure. In a later article (13), Davey compared his theoretical calculations with some actual data gained from the existing process, but indicated that a more practical account of the vacuum distillation would be reported after his proposed equipment was operative. At the present, this report has not been made.

Pazukhin and Loukaschenko (26) gave several interesting comments on this work of Davey, which were in turn answered by Davey. Among these was the modification of Langmuir's equation for use of the basis for calculated distillation rates.

Applications to Reprocessing Nuclear Fuels

During the early 1950's interest developed in processing spent reactor fuels by vacuum distillation of metal mixtures. One of the first studies was a completely theoretical one by Vivian (30). Using the Raleigh equation for batch distillation and Raoult's law, several equations were developed which could possibly be applied to separation of plutonium from uranium by vacuum distillation. A possible design for such a process was also made.

At about the same time, Rosser (27) developed an equation similar to that of Vivian's for the volatilization of plutonium from a dilute solution of plutonium in uranium metal. Raoult's law was also assumed to hold in this case. Rosser defined an enrichment factor as

$$\frac{\left(\frac{\text{wt. Pu in distillate}}{\text{wt. U in distillate}}\right)}{\left(\frac{\text{wt. Pu in original melt}}{\text{wt. U in original melt}}\right)} \quad (3)$$

This enrichment factor was seen to decrease with an increase in vaporization temperature and with an increase in fraction of plutonium removed from the melt.

Cubieciotti (10) verified the accuracy of Rosser's analysis with experimental studies. He studied the rate of volatilization of plutonium from molten uranium in vacuum. At the higher temperatures the fraction of plutonium volatilized

agreed reasonably well with the calculated values of Rosser, while at the lower temperatures considerable deviation existed with the calculated values based on Raoult's law. Cubicciotti also mentioned the feasibility of a large scale process for the recovery of plutonium from uranium by distillation. He continued his investigation with an experimental study of rates of evaporation and degree of completeness of removal (11). These experiments were of greater accuracy and verified his previous work. All of Cubicciotti's studies were laboratory scale.

Milne and Young (24) in 1956 expanded previous experimental work to investigate the removal of volatile fission products such as cerium, other rare earths, strontium, and cesium from thorium metal fuels. Varying amounts of these fission products were removed by distillation at high temperatures while contained in tantalum crucibles. Because of small differences in their vapor pressures the removal of uranium from thorium by distillation was found to be impractical.

Equipment Design

Few designs of practical liquid metal distillation systems have been made. Most experimental work has been performed in laboratory, batch type apparatus. However, there is considerable literature in the fields of vacuum technology,

high temperature processing and corrosion that can be adapted to the design of equipment.

Some of the most significant work in the application of techniques to the design of a distillation apparatus has been conducted at Ames Laboratory. Design of a circulating loop and corrosion studies were made by Clifford (8) while Clifford and Burnet (9) developed vacuum tight, corrosion resistant steel flanges for use in these liquid metal studies. Buchanan (3) investigated condenser design and concluded that a sodium-potassium eutectic performed well as a condenser coolant. Temperature of the coolant was controlled by varying the pressure in the coolant section. Kenefick (17) and Kappraff (16) made studies of the distillation of metal mixtures.

The major design problems are those associated with a continuous process. Martin and Brown (23) indicated the need for a continuous distillation process to be used with liquid fueled reactors. One of the major problems is the design of a condenser which is continuous in operation and still assures short path molecular distillation. The continuous nature of the process requires that the condensate be collected and removed from the system. Martin and Brown (23) indicated that their condenser design may have been the cause of the low distillation rates experienced in their work. Westerheide and Burnet (32) designed a continuous type

condenser which was an integral part of the distillation chamber.

In his book, Bockris (1) deals with methods of obtaining high temperatures which are useful in designing heating apparatus, while Dushman (14) is an accepted authority in the field of vacuum technology. Burdi (4) compiled a useful handbook on the general properties, engineering properties and hazardous properties of the alkali metals and sodium-potassium mixtures.

APPARATUS

The apparatus used in this study was essentially that designed and operated previously by Westerheide and Burnet (32). Some repair and modification of the apparatus was needed.

The main components of the apparatus consisted of a circulation loop of 3/4 inch nominal, schedule 40, 430 stainless steel piping, a charge tank, an expansion tank, a bulk tank, a cold trap and a distillation chamber. Circulation was effected by a special remote diaphragm pump designed by Westerheide, Clifford and Burnet (33). The apparatus is shown in Figures 1, 2 and 3.

Distillation Chamber

The distillation unit was constructed of 430 stainless steel and is shown in Figure 4. Two concentric, half cylinders of 3 and 4 1/2 inch radii were welded to a flat 1/2 inch thick plate. This formed an integral distillation chamber and condenser. Distillation occurred in the inner chamber and the condenser coolant was contained in the outer annulus. The coolant section extended 5 inches above the distillation plate and this portion was cooled by water coils. The condenser coolant used was a sodium-potassium alloy containing 78 percent potassium. The boiling temperature of

Figure 1. Experimental distillation apparatus

Figure 2. Forced circulation distillation loop

Figure 3. Modified pulsafeeder pump, remote head inside firebrick insulation

Figure 4. Pictorial view of the distillation unit

the coolant was controlled by varying the pressure in the annulus.

The distribution plate was placed in the circulation loop at an angle of $30 \pm 0.25^\circ$ from the vertical plane. It was 30 inches in length and welded on the inside were guide vanes so that the metal would have increased area and increased turbulence as it moved down the plate.

At the termination of the previous study (32), the chamber had been removed from the loop and cut open. This necessitated the reconstruction of the unit and replacement into the loop. Replacement thermocouples on the chamber were chromel-alumel. Three electrical resistance heaters made of nichrome heating wire were attached to the back of the distribution plate. The resistance of these from top to bottom were 18, 19 and 20 ohms. To preheat the sodium-potassium coolant, a 500 watt "Calrod" heater was placed on the condenser side of the chamber.

Distillate was removed from the chamber by means of a vacuum tight ball valve, through which a graphite cup could be passed into the bottom of the chamber. Because of previous difficulty of operation, the temperature of this valve was carefully controlled by heating tapes. This sampling valve was operated with a separate vacuum system.

Circulation Loop

A forced circulation loop was needed to furnish a continuous type distillation operation. This loop also served as a means of providing heat to the metal system. The piping was wound with preheat coils of nichrome heating wire, the purpose of which was to preheat the loop for charging. The heating was performed by and the desired temperature profile was maintained by six clamshell type resistance furnaces spaced on the loop.

Impurities were removed by a cold trap located beneath the distillation chamber. It was constructed of 430 stainless steel and filled with 430 stainless steel turnings. This trap was kept at the lowest temperature in the loop and was air cooled.

A bulk tank in the loop provided a means of making flow rate tests and eased the charging procedure. This tank, also made of 430 stainless steel, contained a level probe and a vacuum line in its top.

The charge tank, located at the lowest point in the system, enabled the loop to be charged with metal and to be drained easily. It was equipped with heating elements to melt the charge and a stirrer to mix the melt. Vacuum connections, inert cover gas connections, and flange cooling coils were installed on the tank.

The expansion tank was located at the highest point in

the circulation loop and served as a metal reservoir during the distillation runs and as a metal makeup pot between the distillation runs. It contained a removable flanged cover, which had a level indicator, sampling valve and vacuum-inert gas lines.

Flow of metal in the loop could be stopped or diverted by freezeplugs formed by using copper water cooling coils wrapped around the pipe in strategic places. These are indicated in Figure 1. A 110 volt heating tape was located at each of these cooling coils so that the freezeplugs could be melted.

Approximately 34 chromel-alumel thermocouples were located on the apparatus. These temperatures were continuously recorded on three multipoint recorders during runs and were important to the charging procedure. By observing the fluctuation of the temperatures the progress of the metal in the loop could be followed during charging.

Metal System

The lead-bismuth eutectic with cadmium as the volatile component was retained for use in these studies. Previous and present experience with the lead-bismuth eutectic at Ames Laboratory (8, 29) could thus be applied to the present studies. The vapor pressure of cadmium is quite high as compared with that of lead and bismuth. In the temperature

range used in this study, the lead and bismuth were essentially non-volatile.

Vacuum System

The main vacuum system was headed by a Duo-Seal model No. 1397 forepump, having an ultimate vacuum of 10^{-4} mm Hg and a pumping speed of 425 liters per minute. Two Duo-Seal model No. 1404 forepumps assisted the main forepump. Two oil diffusion pumps were used in series in this system, one being a three stage Consolidated Vacuum Corporation (CVC) model No. 1384F pump, and the other being a three stage CVC model No. 1384E. A manifold allowed all parts of the loop except the sampling valve and the NaK annulus of the chamber to be evacuated by this system.

A smaller vacuum system controlled the pressure over the condenser coolant. A Duo-Seal model No. 1405 forepump was used with a two stage CVC model No. 1385E oil diffusion pump.

A Duo-Seal model No. 1405 forepump was used to evacuate the sampling valve.

EXPERIMENTAL PROCEDURE

To study the separation of cadmium from the lead-bismuth eutectic by high vacuum distillation, the following procedure was used. All letters refer to Figure 1. Before beginning the procedure all controls on power to the heaters and water to the cooling coils were in the off position.

Charging the Loop

Preheating the apparatus

The top of the charge tank OO was removed and enough solid metal of the desired composition was added to the charge tank to fill the loop. The top was replaced and the water was turned on to the coils NN and PP and the power to the heating coils on the charge tank was turned on. The metal was heated to 300°C.

Cooling water was turned on at R, BB, and DD to isolate the distillation chamber during charging. Power to furnaces K, RR, QQ, KK, and FF was turned on, as well as to the upper and lower preheat coils, the cold trap preheat, the expansion tank preheat and the bulk tank preheat. Cooling coils GG were turned on to cool the expansion tank flange. Power was adjusted until the thermocouples indicated that all parts of the loop were approximately 300°C, except for the isolated part.

Charging of the metal

The loop was evacuated and the charge tank was pressurized to 10 lbs. of argon pressure. The water to coil PP was turned off and the heating tape at PP was turned on to melt the plug of metal. This took approximately one hour. Prior to the melting of the plug, the metal in the charge tank was well mixed with plunger LL. The melting of the plug was accompanied by a release of steam from the cooling coils and considerable noise.

The progress of the molten metal through the loop was followed by the fluctuation of the temperature in various parts of the loop. Additional inert gas pressure was bled into the charge tank to bring gauge MM to 15 lbs.

Stopping the charging

The metal filled the lower loop first, eventually reaching the top of the loop and the top of the bulk tank I. A volt-ohm meter had been connected to the probe J and the wall of the bulk tank. The probe was electrically insulated from the tank and when the probe was contacted by the metal, the indicator on the meter deflected to zero resistance and the water to coil H was quickly turned on to freeze a plug. The tip of the probe was one inch from the top of the bulk tank and a plug could be frozen before the metal reached the top of the tank.

The freezing of the plug at H forced the metal back up through the slant leg and into the expansion tank JJ. The level in the expansion tank could be located by the movable probe HH. A volt-ohm meter was connected between the probe and the tank, and upon contacting the metal the deflection was noticed on the meter as with the operation of the bulk tank. When a level of 1 1/2 inches of metal in the expansion tank was reached, the heating tape at PP was turned off and the water to the cooling coil was quickly turned on to freeze a plug in the line to the charge tank.

Pumping the metal

After the loop was charged, the motor A to the pump B was turned on. Circulation of the metal could be verified by a periodic deflection of the meter needle at probe HH indicating a slight change in the metal level in the expansion tank. Circulation could also be verified by pressurizing the loop to 2 lbs. argon at gauge II. Satisfactory pumping was indicated by a periodic deflection of the needle of gauge II.

Distillation

Preheat of chamber

In preparation for diverting the metal through the distillation chamber W, the three resistance heaters T on the distribution plate were energized. Current was also

turned on to the NaK preheat coil X. Water was then turned on to cooling coils Z, AA, and U. The heating tape on the sampling valve M was energized with one ampere of current. The chamber heaters were brought up to the desired operating temperature (450-600°C) in steps of about 100°C per hour to avoid stresses to the heaters and to the chamber.

Diversion of metal

To divert the metal through the chamber, the pump was stopped on a displacement stroke. Cooling coils Q, S, and EE were turned on to freeze plugs in the slant legs and cooling coils BB, DD, and R were turned off. Heating tapes at R, BB, DD and the furnace CC were energized.

After approximately one hour, the freezeplug at R melted and the power to the pump was turned on. Shortly thereafter the plugs at BB and DD melted and circulation began.

Distillation run

Until time to perform a distillation run, the loop contained an inert cover to prevent distillation. The desired pumping rate was obtained by adjusting the pump stroke length. To begin the run, a vacuum was quickly drawn on the system. It required approximately one minute to obtain the desired operating pressure. Distillate was

removed from the sampling valve M at known intervals of time.

Operation of sampling valve

In removing distillate from the bottom of the chamber, the ball valve was initially closed. The flange and withdrawal rod were removed from the assembly (see Figure 5) by removing the stud bolts. A graphite sampling cup was screwed onto the end of the rod and then the rod and flange were replaced. Vacuum was then drawn on the sampling device. The ball was rotated and the sample cup was pushed up into the pipe from the product receiver. It was pulled back and the ball was rotated to close the assembly from the chamber. The vacuum system was isolated and the flange was removed along with the rod and the cup with the distillate. Occasionally a torch was needed to maintain a high enough temperature to remove the cup from the pipe, as it was difficult to prevent the metal from solidifying. The cup was then removed and a new one placed on the rod for the next run.

Single pass runs

A number of single pass runs were made. For these runs, the pump was not used. Freezeplugs were formed in the vertical leg by turning off the power to furnace KK. Metal was drained from the cold trap P, through the valve N. A solid sample of metal was placed in the expansion tank and a

Figure 5. Ball valve sampling device for use with the distillation chamber

vacuum was drawn on the system. The melting of the solid sample was controlled by varying the heat input to the expansion tank. Thus rough control of the flow rate was obtained. Distilland was removed from valve N after each run and distillate was removed from the sampling valve. These runs were short and maintenance of a constant flow rate was doubtful.

Charging of the Sodium-Potassium Coolant

Charging and discharging of the NaK to and from the system was done under inert gas and strict adherence to instructions was followed. After draining the chamber, the residual NaK was neutralized with methanol. This was done outside the building and with caution, as hydrogen was liberated by the reaction and despite precautions, two explosions occurred as the result of ignition of the hydrogen.

Contamination Studies

In-loop studies

After it was realized that product contamination from material flowing down the distribution plate was occurring, several runs were made similar to the continuous distillation runs; however the loop contained inert gas and no distillation occurred. All metal removed from the product side was considered as being contaminant.

Other studies

Further contamination studies were made with the distillation chamber removed from the loop. The chamber was mounted on a stand so that the slope of the distribution plate could be varied. Mercury was used in these studies to simulate the lead-bismuth eutectic because of similarity of physical properties. Mercury, from a constant head tank, was allowed to flow through the chamber at various flow rates and at different angles of the distribution plate. The effects of flow rate and plate angle were correlated with the amount of metal collected from the product receiver.

RESULTS AND DISCUSSION

Results of this study reaffirmed this method of separating metals by high vacuum distillation, and at the same time led to some important design problems which must be overcome before any further work is performed with this equipment. The major design problems are concerned with the distillation chamber and became readily apparent during operation of the system.

The chamber was installed in the loop with the distribution plate at an angle of three degrees from the vertical. This angle proved to be too steep and was the major cause of the serious contamination problems encountered during this study. Results of the distillation runs are given in Table 1. As can be seen, the actual data obtained were not in close agreement with values given by theoretical calculations. Theoretical calculations, assuming lead and bismuth to be essentially non-volatile at the operating temperatures, gave cadmium concentrations greater than 99 percent, whereas the highest actual cadmium concentration realized was 47 percent.

After the first few distillation runs were performed, it was realized that short-circuiting of the distilland into the product side of the chamber was occurring. Consequently, studies were undertaken to determine the cause of this contamination. It was decided that the contamination could

be caused by one or more of several design features of the system. Possible causes of contamination identified were the angle of inclination of the distribution plate, back up from the distilland outlet pipe, and entrainment of lead and bismuth during cadmium vaporization.

As the first step, runs were made identical to the distillation runs except that distillation was not allowed to occur by maintaining a high inert gas pressure in the distillation chamber. Results from these runs are given in Figure 6 and Table 2. As can be seen, the amount of contaminant removed from the product side of the chamber was directly related to the flow rate of distilland through the chamber. To determine if there were any effects from the pulsating nature of the pump, several runs were made without the use of the pump. These were similar to the single pass distillation runs. No noticeable difference in contamination was observed and it was concluded that pulsating of the pump had little or no effect on the amount of contamination.

These tests did not rule out the possibility of the metal backing up into the bottom of the chamber and flowing over the weir into the product side of the chamber. To investigate this possible source of contamination, the chamber was removed from the loop and mounted on a stand. This stand was constructed so that the angle of the distribution plate could be easily adjusted. Results of these runs are shown in

Figure 6. Percent of distilland short-circuiting into the product receiver as a function of distilland flow rate with lead-bismuth as the fluid at a plate angle of 3 degrees from the vertical

Figure 7 and Table 3. Although the data were somewhat scattered, the curve fitted to the data was similar in shape to that in Figure 6, suggesting the same type of contamination. The data of wide deviation are from runs made at the extreme high and low distribution plate angles. Between these extremes, the amount of contamination seemed to be little affected by the distribution plate angle. The individual scatter of the data was probably due to the short lengths of the runs and to the fact that between three degrees and six degrees, plate angle does have some effect upon the amount of contamination. This study ruled out the possibility of contamination by the distilland backing up into the product weir.

Figures 6 and 7 illustrate similarities in that they indicate that the percentage of the distilland short-circuiting into the product receiver decreases with an increase in flow rate. Moreover this short-circuiting seems to approach a constant value of approximately one percent at high flow rates. This can be explained by the behavior of the liquid metal at various flow rates. Figure 8A is a photograph of mercury at a flow rate of 1000 gm/min on a plastic model of the distribution plate. The metal tends to break apart into many separate globules which are somewhat unstable in movement. These globules find it easy to fall off the edges of the guide vanes. Figure 8B shows a higher flow rate of

Figure 7. Percent of mercury short-circuiting as a function of mercury flow rate with a plate angle of 2 to 8 degrees from the vertical

A

B

Figure 8. Mercury flowing on a plastic model of the distribution plate at flow rates of A: 1000 gm/min and B: 25,000 gm/min at a plate angle of 3 degrees

25,000 gm/min. The metal forms a steady stream which is not as subject to random movements as with the low flow rates. Thus a smaller percentage of the total flow falls off the guide vanes.

The flow rates in Figure 7 constitute only a small range of the flow rates of those of Figure 6. Larger flow rates were not attempted because of the cost of the mercury involved and because the chief interest centered in the range of flow rates used in the distillation runs.

The contamination can be seen occurring in Figure 8. If one looks closely at these photographs, metal can be seen falling off the edges of the guide vanes. This metal would then strike the lower guide vanes, bouncing off into the product side of the chamber, in turn contaminating the metal which was accumulating in the receiver from distillation.

The first impression was that the spilling was avoidable by slanting the distribution plate at a larger angle with the vertical. This was done in the contamination studies with mercury and only at the angle of eight degrees was a decrease in the amount of contamination noticed. However at this angle the splashing was still an appreciable amount and on the basis of the study made on the plastic model, the angle of inclination would have to be in excess of 15 degrees to safely avoid this short-circuiting.

It is felt that a design can be made to eliminate this

short-circuiting but merely increasing the slant of the distribution plate complicates two other features of the chamber. The metal molecules of distilland must be able to "see" the condenser, that is to have a straight line path to the condenser, because mobile molecules cannot travel around corners. If the plate angle were increased, the metal would be in a trough formed by the guide vanes and very little distilling metal would reach the condenser wall. Thus a redesign of the guide vanes would be necessary. The original purposes of these guide vanes were for agitation and distribution of the metal and these purposes would have to be retained in redesign.

Another design criterion which must be met is compatibility of the condenser portion of the chamber with the distillation portion. Because the distillate is collected as a liquid, the condenser surface must be oriented so as to drain the condensate without it dripping back into the distilland. Therefore there is a maximum angle at which the condenser can be oriented.

Given in Table 1 are the contamination rates for each distillation run obtained from the contamination studies. These contamination rates are of similar magnitude to the distillation rates and this readily explains why the product had low cadmium concentrations.

Despite the overshadowing influence of contamination on

the product composition, a distinct relationship between product composition and distillation temperature was noticed. In the first six runs the distilland flow rate was constant and the inlet cadmium concentration varied from 0.041 to 0.052 mass fraction. Distillate concentration was plotted versus distillation temperature with initial concentration as the parameter in Figure 9. An increase in distillation temperature resulted in a distillate of higher cadmium concentration, indicating an increase in distillation rate. This is due to the large influence of temperature on the vapor pressure of metals. This strong temperature dependency is in agreement with previous studies (32). The relationship between initial concentration and product composition is also to be expected. Because of the uncertainty due to contamination, no quantitative conclusions should be made from these runs.

The areas used in the calculations of the theoretical distillation rates were taken from the correlation of flow rate with area as given by Westerheide and Burnet (32). Redesign of the chamber should be based upon data from an improved method for determining the area available for distillation. The area is dependent upon the flow rate and accurate determination of this dependency is difficult. The present distribution plate is inefficient in that the maximum area of the plate covered by metal at any flow rate is approximately

Figure 9. Effect of distillation temperature and initial distilland composition, W_0 , on the product composition

ten percent. A distribution plate completely covered by a film of metal would give an exact knowledge of the area and at the same time result in the most efficient distillation.

No mention has been made of entrainment during distillation, but it is possible that some of the contamination of the distillate was a result of entrainment of lead and bismuth by the vaporizing cadmium. This entrainment has been reported by others when dealing with high distillation rates (7). However in these studies it is believed that this entrainment was slight in comparison with the major source of contamination.

CONCLUSIONS

1. Some degree of separation of cadmium from the lead-bismuth eutectic was achieved. However the distillation was accompanied by contamination which considerably reduced the overall separation. Cadmium concentration in the distillate was from 12 to 47 mass percent at distillation temperatures of 450°C to 550°C.
2. Contamination of the distillate was the result of the design of the distillation chamber. Distilland was found to be short-circuiting from the distribution plate into the condensate receiver.
3. The percent of distilland short-circuiting was directly related to the distilland flow rate. Actual contamination rates were from 0.69 gm/sec to 1.0 gm/sec. Percent of total flow short-circuiting was from 2.0% to 2.75% for the flow rates used in the distillation studies.
4. The redesign problem is more complicated than merely increasing the slant of the distribution plate.
5. Distillation temperature and distilland composition have a strong effect upon the distillation rate.
6. Pulsed flow from the pump does not influence the contamination problem.

RECOMMENDATIONS

1. Redesign of the chamber should be undertaken to eliminate contamination problems. This redesign should retain the basic design if possible, while eliminating or modifying the baffles and increasing the slant of the distribution plate. The ideal design would have a completely horizontal distribution plate, in order to eliminate the uncertainty in the area determination. This would require redesign of the condenser.
2. Redesign of the auxiliary loop is needed with emphasis on simplicity of operation to ensure continuous operation.
3. In order to better design condensers which collect the condensate as a liquid, wetting studies of condensate on condenser surfaces would be useful.
4. Valves should be used to stop and start the flow of metal, instead of the freeze plug method.
5. Additional automatic temperature control is needed to simplify operation and ensure closer temperature control.
6. Future vacuum systems should utilize larger diameter piping and simpler design. The level of vacuum was limited in this study by small diameter pipe and excessive right angle bends.
7. Additional metal systems should be investigated, in particular those having more than a single volatile

component. Associated with this a study should be made to determine if higher temperature operation is feasible.

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ACKNOWLEDGEMENTS

The author wishes to express his gratitude to Dr. George Burnet for his guidance and encouragement during this investigation. Appreciation is also expressed to Mr. Edward Clark and Mr. Glen Accola for their excellent service in the repair of the equipment used in this investigation.

APPENDIX

Table 1. Results and data for the distillation runs at a condenser temperature of $340^{\circ}\pm 10^{\circ}\text{C}$, and operating pressure of 10^{-3} mm Hg

Run no.	Cadmium conc. in product W_d (mass frac.)	Distil-land flow rate F (gm/sec)	Distil-lation tempera-ture T_d ($^{\circ}\text{C}\pm 10^{\circ}\text{C}$)	Initial cadmium conc. W_o (mass frac.)	Theoretical exit cadmium conc. W_p (mass frac.) ^a	Theoretical distillation rate D (gm/sec) ^b	Contamination rate (from Figure 7) C (gm/sec)
1	0.1216	34	450	0.042	0.0300	0.423	0.800
2	0.1760	34	450	0.050	0.0357	0.507	0.800
3	0.2110	34	500	0.043	0.0183	0.853	0.800
4	0.2750	34	500	0.048	0.0204	0.967	0.800
5	0.3311	34	550	0.041	0.0044	1.25	0.800
6	0.4060	34	550	0.052	0.0056	1.59	0.800
7	0.4725	34	550	0.059	0.0064	1.80	0.800
8	0.2702	23	500	0.048	0.0200	0.658	0.685
9	0.4385	51	500	0.051	0.0236	1.43	1.03

^aUsing the derivation of Westerheide and Burnet (32).

^bCalculated from material balance $W_p(F - D) = W_o(F) - D$.

Table 2. Contamination runs with the chamber in the loop at a distribution plate angle of three degrees from the vertical using lead-bismuth as the fluid

Flow rate (cc/min)	Flow rate (gm/min)	Contamination rate (gm/min)	Contamination rate (% of total flow)
100	1016	37	3.64
200	2035	48	2.36
270	2740	60	2.19
350	3560	65	1.83
440	4470	66	1.48
530	5380	78	1.45
700	7120	81	1.14
880	8950	89	1.00
1130	11500	104	0.90
1930	19600	109	0.55
2280	23200	163	0.70
2630	26700	237	0.88
3000	30500	282	0.90

Table 3. Contamination runs with the chamber removed from the loop at various distribution plate angles using mercury as the fluid

Plate angle (degrees from vertical)	Flow rate (cc/min)	Flow rate (gm/min)	Contamina- tion rate (gm/min)	Contamina- tion rate (% of total flow)
2	310	4215	294	7.0
2	340	4625	219	4.8
3	106	1440	47	3.2
3	185	2510	61	2.4
3	360	4890	74	1.5
4	104	1415	52	3.7
4	193	2620	40	1.5
4	224	3045	54	1.8
4	277	3760	50	1.3
4	321	4370	48	1.1
6	103	1400	45	3.2
6	119	1620	54	3.4
6	121	1645	44	2.7
6	184	2500	41	1.6
6	202	2745	70	2.5
6	294	4000	54	1.3
8	64	870	16	1.8
8	98	1330	10	0.8

Cd-Pb-Bi Analysis

In a 400 ml beaker, dissolve a 0.5 to 1.0 gm alloy sample in a minimum amount of concentrated nitric acid. Evaporate to a small volume. Dilute to 150 ml with water and boil briefly. Transfer into a 250 ml volumetric flask and dilute to mark with water. Into a 250 ml beaker, pipette a known volume of 50 ml of this solution and add 100 ml water. Adjust the pH to 1.2 with HNO_3 or NH_4OH . Add ten drops of indicator (a 0.05% water solution of xylenol orange) and titrate with 0.05 M EDTA from a purple to a lemon-yellow end point. Record the amount of EDTA used, as this corresponds to the bismuth present. To the solution now add small amounts of hexamethylenamine until an intensely red-violet color persists (pH of approximately 5.0). Again titrate with EDTA in the same manner. Small amounts of hexamethylenamine may be added to insure a sharp end point. The further consumption of EDTA corresponds to the lead and cadmium content. Now add 5 to 10 ml of 0.05 M o-phenanthroline solution and note if the indicator changes. If so, continue the titration with $\text{Pb}(\text{NO}_3)_2$. The consumption of $\text{Pb}(\text{NO}_3)_2$ corresponds to the cadmium content.

An alternate approach is sometimes advantageous when an adequate amount of sample is available as a sharper end point is obtained. In a second aliquot again titrate the bismuth with EDTA, then add some o-phenanthroline and adjust the pH

with hexamethylenamine as above. Now titrate with EDTA; the volume used in the second titration corresponds to the amount of lead present.

Figure 10. Variation of vapor pressure with temperature for cadmium, bismuth and lead

Figure 11. Variation of vapor pressure with temperature for NaK 78