Acc# 732136
DP-MS-68-52

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R. F. Bradley and D. S. Webster

Savannah River Laboratory
E. I. du Pont de Nemours and Co.
Aiken, South Carolina 29801

Proposed for publication in Nuclear Science and Engineering.

6/24/68

This document was prepared in conjunction with work accomplished under Contract No. AT(07-2)-1 with the U.S. Department of Energy.

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Surface depletion was investigated in laboratory- and plant-scale distillation units with mixing by natural convection or by mechanical surface agitation. During the distillation of ^{210}Po, Zn, Cd, Te, and Mg from bismuth at 650-750°C, surface depletion was significant for the more volatile components: ^{210}Po, Zn, and Cd. The extent of surface depletion was decreased by relatively intense agitation of the entire liquid metal surface. A model was developed for predicting the degree of surface depletion during the distillation of metals from bismuth as a function of temperature, still pot dimensions, and degree of agitation.

INTRODUCTION

The Savannah River Laboratory is developing a multistage vacuum distillation process to separate 10-100 ppm of polonium-210, a potentially useful heat source, from irradiated bismuth metal. Vacuum distillation is attractive because large quantities of metal can be processed with no chemical changes. The principal disadvantages are the high temperatures (600-800°C) and high vacuum required.

A key step in the distillation process is the transport of the more volatile component to the surface; inadequate mixing can lead to surface depletion of the more volatile component, thus reducing separation efficiency. This paper reports our investigation of the surface depletion effect in laboratory- and plant-scale distillations.

Laboratory distillations with and without mechanical agitation were made with five metal pairs: ^{210}Po-Bi, Zn-Bi, Cd-Bi, Te-Bi, and Mg-Bi. A model was developed to calculate the extent of surface depletion in simple liquid metal distillations at low concentrations in bismuth. The model includes the effects of temperature and of mixing (natural convection or surface agitation). The laboratory distillations also provided a basis for selecting cadmium as a suitable stand-in for ^{210}Po. The degree of separation of cadmium from bismuth was then measured in plant-scale distillations.

EXPERIMENTAL

For the laboratory experiments, a 2-inch-diameter stainless steel still with a tantalum liner was used (Fig. 1). A small, measured amount of metal (^{210}Po, Te, Cd, Mg, or Zn) was added to a 3.5-cm-deep charge of bismuth in the still. The return of condensate was made negligibly small by distilling for a short enough time that the drops of condensate on the wall could not coalesce sufficiently to drain to the pot: ~1 hour at 650°C, and ~5 minutes at 750°C (tests were terminated by admission of argon). The experimental conditions were set so that the bismuth vaporization rate was near the maximum or "unrestricted" rate. At the conclusion of a test, the still was cooled, and all material on the walls above the melt was removed, weighed, and analyzed; the pot contents were also analyzed.

The pulsed experiments were identical, except that the mechanical agitator--a perforated tantalum plate--oscillated vertically at ~2 cycles/sec in the top 0.5 cm of liquid.

Enrichment was measured in a 2-foot-diameter stainless steel still at 750°C using a cadmium stand-in for polonium. The still assembly (Fig. 2) consisted of a 24-inch pipe cap as the distillation pot, with a 24-inch-diameter duct to the condenser funnel. A 6-inch-diameter flanged pipe cap provided ready access to the distillate. The still was heated with bare resistance rods, supported 1/2 inch from the still with ceramic insulators and enclosed with 3 inches of high temperature insulation. Cadmium was added to the 1200-lb bismuth charge (50 ppm) and then distilled; the residual gas pressure was less than 3 microns of mercury. After each run, the condensate and samples from the pot were analyzed.

Data from each test were used to calculate α_{eff}, the effective relative volatility defined by

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

where

Po_1, Bi_1 = initial weights of ^{210}Po and bismuth in the pot

Po_2, Bi_2 = final weights in the pot

The maximum relative volatility for unrestricted vaporization with no surface depletion, α, has been measured for the ^{210}Po-Bi system.(1) Values of α for the stand-ins were calculated from data in standard references assuming Raoult's Law for Bi and Henry's Law for the volatile component:

$$\alpha_{i\text{-}Bi} = \frac{\gamma_i p_i}{p_{Bi}} \sqrt{\frac{M_{Bi}}{M_i}}$$

where

γ_i = activity coefficient

p = vapor pressure

M = molecular weight in vapor phase

The relation between α_{eff} and α is:

$$\frac{\alpha_{eff}}{\alpha} = \frac{x_i(\text{surface})}{x_i(\text{bulk})}$$

RESULTS

Results from the 2-inch-diameter still are listed in Table I. For ^{210}Po, Cd, and Zn, α_{eff} is less than α due to surface depletion, and the difference increases as the temperature increases. Agitation raises α_{eff} for the more volatile metals such as cadmium.

Results of the Cd-Bi distillations in the 2-foot-diameter still are shown in Table II. Since the vaporization rates for these tests were less than the maximum, it is necessary to introduce a new variable f defined as the ratio of the weight of condensate obtained to the rate that would evaporate into space during the same time at the same temperature (by "unrestricted" or Langmuir vaporization(2)). The reduction of the vaporization rate was due to a surface layer of corrosion and oxidation products (~2 mg/cm^2) and to flow resistance in the duct.

SURFACE DEPLETION MODEL

Surface depletion in nonboiling liquids is due to relatively slow mass transfer of the volatile component through the surface of the liquid. Previous investigations have considered the case of molecular diffusion through a stagnant melt(3), and forced convection mass transfer(4). The following derivations pertain to natural convection and surface agitation in dilute solutions.

From a mass balance on the more volatile component:

$$N_1 = k_\ell \rho_\ell \left[x_{1(\text{bulk})} - x_{1(\text{surface})} \right] = k_v \rho_\ell x_{1(\text{surface})} \qquad (1)$$

The following equation can then be derived:

$$\frac{\alpha_{\text{eff}}}{\alpha} = \frac{\text{Surface conc of component 1}}{\text{Bulk conc of component 1}} = \frac{k_\ell}{k_\ell + k_v} \qquad (2)$$

where k's are the mass transfer coefficients defined by Eq. (1). Equation (2) shows that when k_v is small relative to k_ℓ, α_{eff} is essentially equal to α; and when k_v is relatively large, $\frac{\alpha_{\text{eff}}}{\alpha} \approx \frac{k_\ell}{k_v}$. From the equation for the relative volatility in a dilute solution ($\alpha_{1\text{-Bi}} = \frac{y_1}{x_1}$), the relationship for k_v is:

$$k_v = \frac{\alpha \, N_{\text{Bi}} f}{\rho_\ell} \qquad (3)$$

where

N_{Bi} = "unrestricted" vaporization rate of bismuth, g/(cm^2)(sec)

ρ_ℓ = liquid density, g/cm^3

Values of k_v can be calculated from data reported by Mound Laboratory(1) for N_{Bi} and α (for dilute ^{210}Po-Bi mixtures). For other metal systems, α can be calculated. The value of ρ_ℓ is essentially the density of mismuth for dilute solutions. Normally the still would be designed so that f approaches one. Values of f less than one can be estimated by taking into account all resistance to vapor flow (in this case surface layers, duct, and condenser). For all of the systems used, this vapor phase mass transfer coefficient increases rapidly with temperature, reflecting the change in N_{Bi}.

The liquid phase mass transfer coefficient can be estimated by penetration theory(5):

$$k_\ell = 2\sqrt{\frac{D}{\pi \bar{t}}} \tag{4}$$

where D is the diffusivity of the minor component in the liquid in cm^2/sec, and $\bar{t}$ is the mean residence time of a fluid element at the surface (Eq. (4) is applicable only for relatively short mean residence times).

Natural Convection

Thermal convection brings liquid up the heated walls and across the surface, where it cools by radiation and partially vaporizes; the mean residence time is essentially the time required to move inward nearly a radius and sink downward, at a velocity set by thermal convection. The following equations will be derived assuming:

1) The melt is heated through the side walls.

2) The heat flux in through the side walls is equal to the radiant heat loss from the melt surface plus the heat required to vaporize the liquid metal.

3) There is a single convection cell in the still.

The mean velocity of the liquid u_m, can be determined from standard relationships (6) for the conditions encountered in this study:

$$u_m = \left(g\beta\ X\ \Delta T\right)^{\frac{1}{2}} \qquad (5)$$

where

X = depth of liquid

$\Delta T = T_{wall} - T_{bulk}$

The value of ΔT can also be expressed in terms of fluid properties, fluid depth, X, and heat flux at the wall, q, (7):

$$\Delta T = q^{\frac{4}{5}}(0.59\ k)^{-\frac{4}{5}}\ X^{\frac{1}{5}}\left[\frac{\rho^2 g\ \beta}{\mu^2}\left(\frac{C_p\mu}{k}\right)\right]^{-\frac{1}{5}} \qquad (6)$$

From Assumption 2), above,

$$q = (q_{Rad} + q_{Vap})\ \frac{R}{2X} \qquad (7)$$

where

R = still radius

When Eqs. (6) and (7) are substituted into Eq. (5), the mean velocity can be expressed in terms of fluid properties and still dimensions. This mean velocity can then be used to estimate the mean residence time $\bar{t}$ for substitution into Eq. (4) ($\bar{t} = \frac{R}{u_M}$):

$$k_\ell = 6.4 \times 10^{-3}\ D^{0.5}\ \mu^{0.1}\ X^{0.1}\ R^{-0.3}(q_{Rad} + q_{Vap})^{0.2} \qquad (8)$$

The numerical constant includes a group (density, heat capacity, thermal expansion coefficient, thermal conductivity) that is taken to the $-\frac{1}{5}$ power, hence changes little with conditions. The depth of melt X and the radius of the still pot R are in centimeters, diffusivity is in cm^2/sec, and viscosity in poises.

Because no published diffusivities were available for use in Eq. (8), the diffusivity of ^{210}Po in bismuth was estimated from the Stokes-Einstein equation for atoms of the same size:

$$D = 1.85 \times 10^{-9} \frac{T}{\mu \bar{V}^{\frac{1}{3}}} \tag{9}$$

(Bismuth viscosities were obtained from the literature; $\bar{V}$ = molar volume of ^{210}Po, cm^3/g mole.) Equation (8) was then used to calculate k_ℓ and Eq. (3) to calculate k_v for ^{210}Po in bismuth. These numbers were substituted into Eq. (2) to obtain a calculated value for α_{eff}; the agreement with observed values of α_{eff} is good, as illustrated in Fig. 3.

Data from the distillation of cadmium and zinc in bismuth were treated in a somewhat similar manner, although the Stokes-Einstein diffusivity had to be adjusted to align the data for each of the two elements (because the atomic sizes are smaller than that of bismuth). When diffusing molecules are smaller than solvent molecules, the Stokes-Einstein diffusivity represents a minimum value(8). The adjusted diffusivity for the Zn-Bi system was 1.3 times the Stokes-Einstein value; the Cd-Bi system was 2.1 times the value. The calculated lines appear in Fig. 4, and again correlate the data well.

Surface Agitation

The derivation of equations for the experiments with surface agitation were the same as those for thermal convection down to Eq. (4); here, a new definition of the mean residence time at the surface $\bar{t}$ is required. Because turbulence is involved, $\bar{t}$ is taken as the time for a turbulence eddy of mean diameter L to roll through 1/2 turn at its mean peripheral velocity $\bar{u}$: $\bar{t} = \frac{\pi L}{2\bar{u}}$. The value of L can be estimated from the rate of turbulent energy dissipation per unit mass ϵ (9):

$$L = \frac{\bar{u}^3}{2.8\ \epsilon} \tag{10}$$

A value for ϵ in these experiments was estimated by assuming that an element of fluid is accelerated to the average velocity of the agitator plate and that the resulting energy is dissipated between strokes. The mean peripheral velocity, $\bar{u}$, during this period is taken as half of this average plate velocity. The value of L calculated in this manner is 0.18 cm, approximately the distance between holes in the tantalum plate. This result is in agreement with mixing studies (10) that indicate that fluctuating velocity components are of the same magnitude as the mean flow and that the scale of turbulence is of the same order as the dimensions of the impeller.

The extent of surface depletions during the agitated distillations were calculated by the preceding method. The case of the highly volatile cadmium, in which the liquid phase coefficient is clearly controlling the rate, shows best the agreement between the calculated line and the observed data. Because surface depletion at a specified temperature, degree of agitation, and still dimensions is a function of $\alpha/\sqrt{D}$ only, depletion at 750°C is plotted against $\alpha/\sqrt{D}$ in Fig. 5 both for convection and mechanical agitation. Again, calculated and observed depletion values agree well.

Inspection of Fig. 5 indicates that α_{eff} for tellurium and magnesium is approximately equal to α (very little surface depletion). The distillation rate for these metals is limited essentially by the ideal, single step of unrestricted vaporization. In contrast, the distillation rates of cadmium and zinc are completely controlled by the liquid phase mass transfer rate. The distillation rates of these metals can be greatly increased by intense surface agitation. The ^{210}Po-Bi system is in a transition region between these two extremes.

Distillation with Natural Convection in Large Still

The values of α_{eff} for the two Cd-Bi distillations in the 2-foot-ID still were calculated with the natural convection model, using Eq. (3) for k_v and Eq. (8) for k_ℓ; the value of diffusivity used in Eq. (8) was that found to correlate results for the small still. To adjust for the different geometry, the depth, X, in Eq. (8) was taken as the total heated path length along the bottom and sides of the large still. Relative volatilities are given in Table III.

The values of α_{eff} calculated by the natural convection model agree well with the measured values.

Under these conditions, the distillation rate for Cd is completely controlled by the liquid phase mass transfer rate and $\frac{\alpha_{eff}}{\alpha} \approx \frac{k_\ell}{k_v}$. When the relationships for k_ℓ and k_v are substituted, the model predicts $\alpha_{eff} \approx \frac{\text{constant}}{f}$, i.e., decreasing the distillation rate (f) at fixed temperature and still dimensions increases α_{eff} by an inversely proportional amount. The experimental results tend to support this prediction. Thus, under certain conditions, it might be advantageous to purposely reduce the distillation rate by restricting the flow of vapor.

CONCLUSIONS

In simple liquid-metal vacuum distillation of metals from bismuth:

1. Surface depletion can be estimated from liquid and "vapor" phase mass transfer coefficients. These coefficients can be determined from the thermodynamic and transport properties of the system, standard relations for natural convection and turbulence, and penetration theory.
2. The degree of surface depletion is determined by the ratio $\alpha/\sqrt{D}$ at a fixed temperature, degree of agitation, and still dimensions. This ratio is the main criterion for choosing a stand-in for surface depletion studies.
3. Surface agitation could provide a dual benefit in breaking up surface layers of corrosion products and in reducing surface depletion. However, the agitation would have to be relatively intense and cover the major portion of the surface area.

ACKNOWLEDGMENT

The information contained in this article was developed during the course of work under Contract AT(07-2)-1 with the U. S. Atomic Energy Commission.

NOMENCLATURE

C_ρ = specific heat at constant temperature, $\frac{\text{cal}}{\text{g}\ {}^\circ\text{C}}$

D = diffusivity, cm^2/sec

f = ratio of condensate to amount attainable by "unrestricted" or Langmuir vaporization

g = acceleration of gravity, cm/sec^2

k_ℓ, k_v = mass transfer coefficients, $\frac{\text{cm}}{\text{sec}}$

k = thermal conductivity, $\frac{\text{cal}}{\text{sec cm}\ {}^\circ\text{C}}$

L = mean diameter of turbulence eddy, cm

M = molecular weight, g/g mole

N_i = mass flux of component i, g/cm^2 sec

N_{Bi} = maximum or "unrestricted" vaporization rate of bismuth, g/cm^2 sec

p = vapor pressure, dynes/cm^2

q = heat flux, cal/cm^2 sec

$\bar{R}$ = ideal gas constant

R = radius of still pot, cm

T = temperature, ${}^\circ$K

$\bar{t}$ = mean residence time of a fluid element at the surface, sec

$\bar{u}$ = mean velocity of a turbulence eddy, $\frac{\text{cm}}{\text{sec}}$

u_M = mean velocity of surface fluid element in still heated by natural convection, $\frac{\text{cm}}{\text{sec}}$

$\bar{V}$ = molar volume, cm^3/g mole

X = liquid metal depth, cm

x_i = mole fraction of component i in liquid

y_i = mole fraction of component i in vapor

α = relative volatility for vacuum distillation

$\alpha_{i\text{-}Bi}$ = relative volatility for metal i in bismuth

β = coefficient of thermal expansion, $^{o}C^{-1}$

γ = activity coefficient

ϵ = turbulent energy dissipation per unit mass, ergs/sec g

μ = viscosity, poises

ρ = density, g/cm^3

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TABLE I

Relative Volatilities in the 2-Inch-Diameter Still

Components	Temp, °C	α	α_{eff}
Po-Bi	650	77	69
Po-Bi	700	58	41
Po-Bi	750	42	23
Po-Bi	765	39	18
Po-Bi[a]	750	42	24-40
Cd-Bi	650	60,000	547-600
Cd-Bi	700	32,000	175-192
Cd-Bi	705	31,000	184-188
Cd-Bi	760	19,000	57-98
Cd-Bi[a]	750	21,000	387-840
Zn-Bi	700	25,000	131-141
Zn-Bi	750	19,000	54-60
Te-Bi	750	5	5
Te-Bi[a]	750	5	5
Mg-Bi	750	9	7-9

[a] Agitated mechanically

TABLE II

Cd-Bi Relative Volatilities in 2-foot-diameter Still

Temp (°C)	Measured Ratio, f	α_{eff}
750	0.35	120-160
750	0.41	101-140

TABLE III

Cd-Bi Relative Volatilities in 2-ft-ID Still at 750°C

f	α	α_{eff} (calc.)	α_{eff} (meas.)
0.35	21,000	152	120-160
0.41	21,000	127	101-140

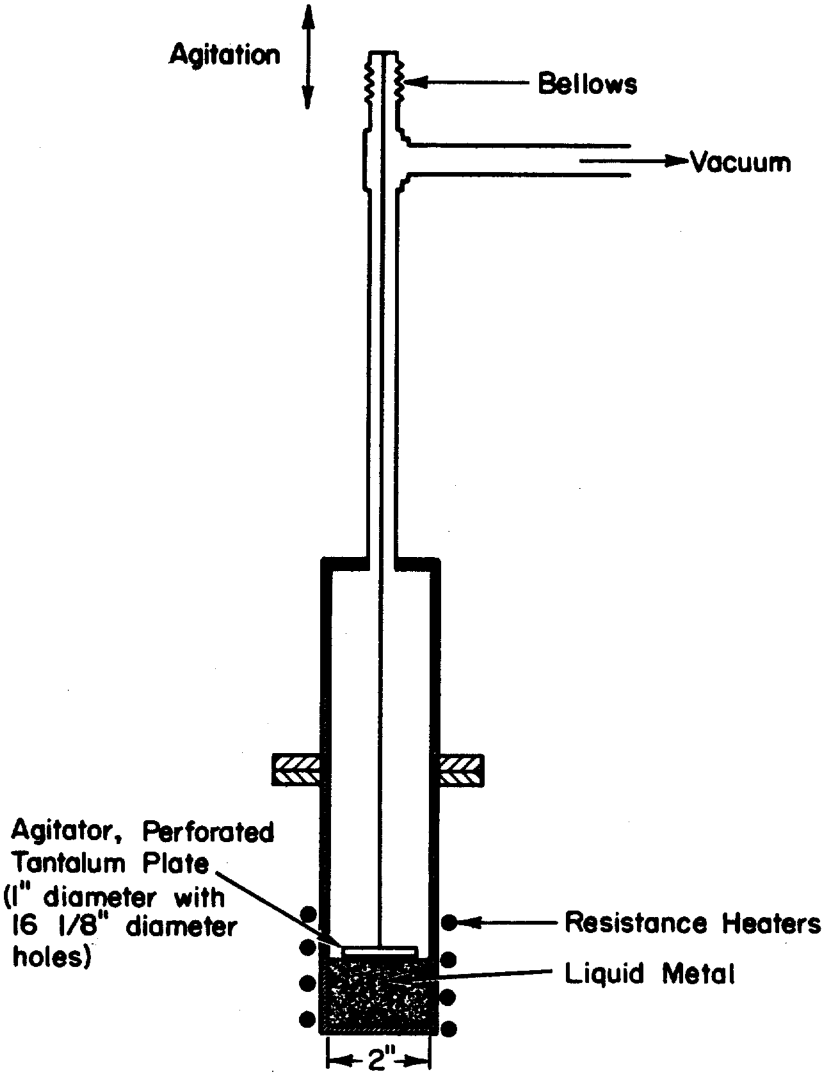

FIG. 1 TWO-INCH-ID LABORATORY STILL WITH MECHANICAL AGITATOR

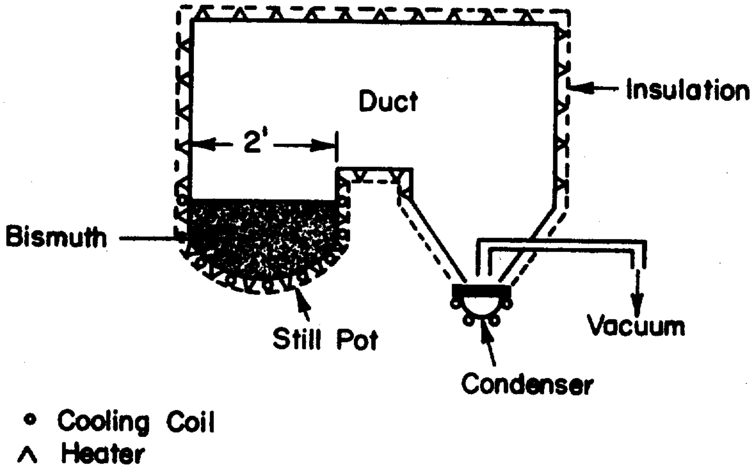

FIG. 2 PLANT-SCALE STAINLESS STEEL STILL

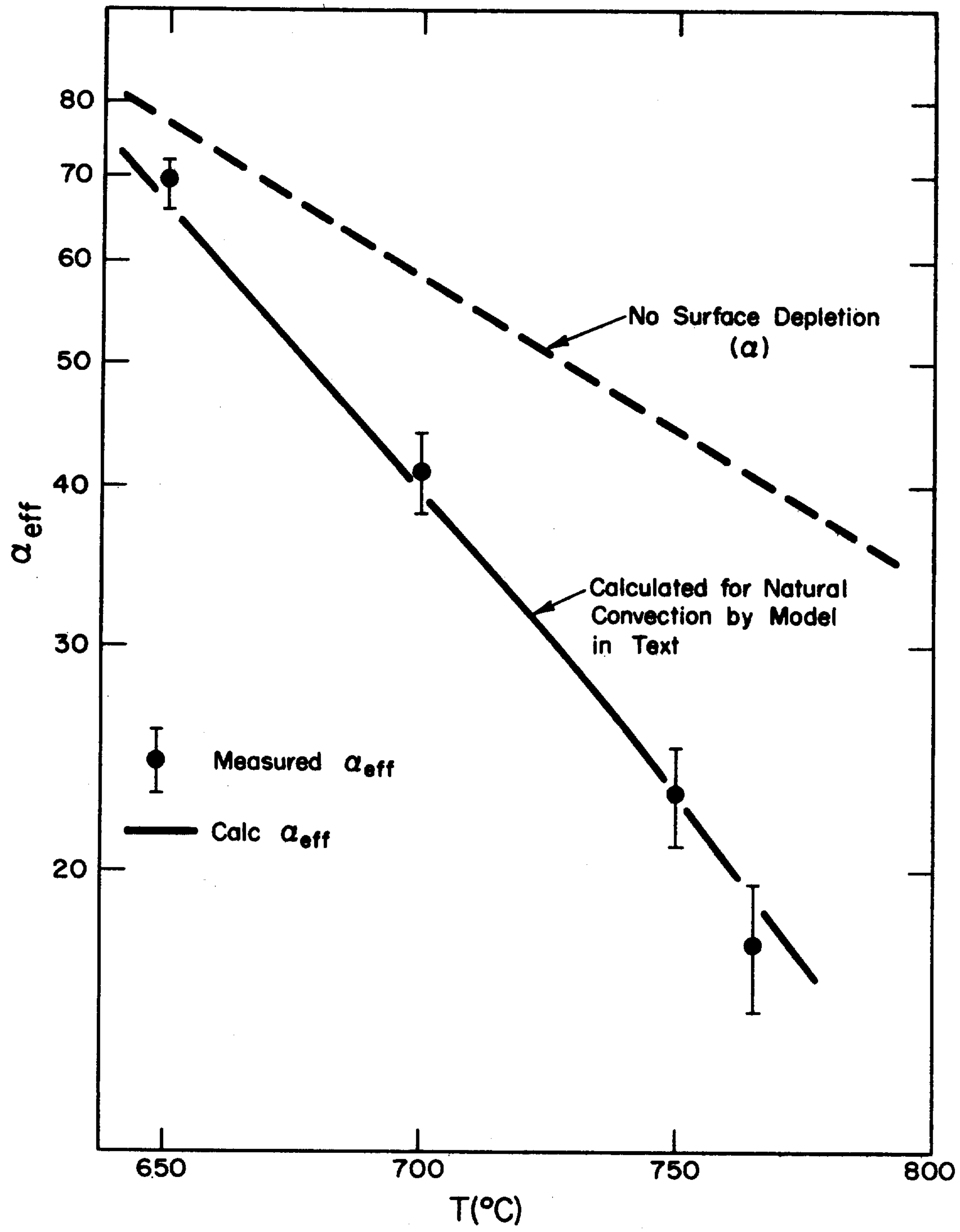

FIG. 3 RELATIVE VOLATILITY OF ^{210}Po-Bi WITH NATURAL CONVECTION IN 2-INCH-ID STILL

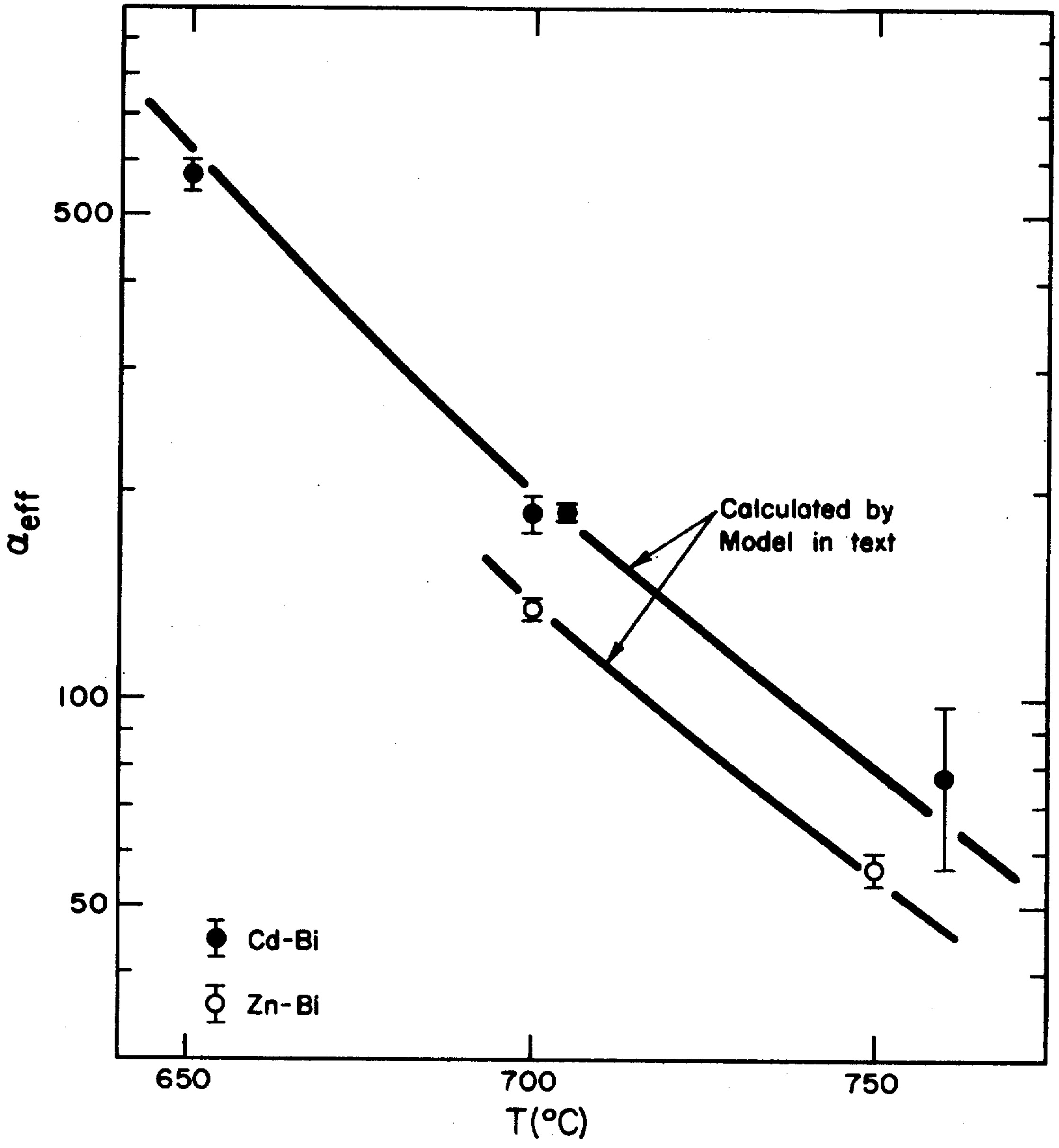

FIG. 4 RELATIVE VOLATILITY OF Cd-Bi AND Zn-Bi WITH NATURAL CONVECTION IN 2-INCH-ID STILL

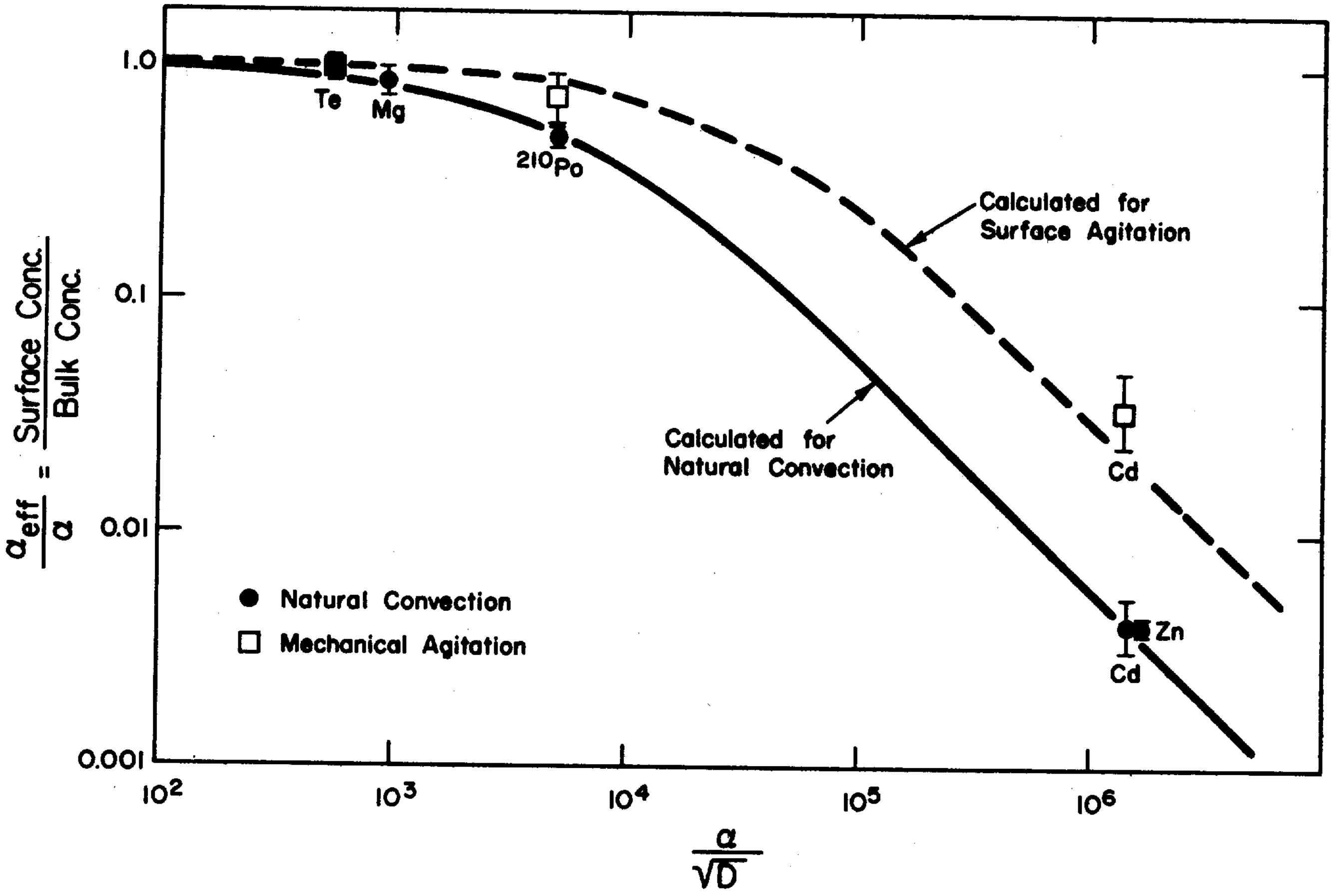

FIG. 5 SURFACE DEPLETION AT 750°C IN 2-INCH-ID STILL