Subject Category: METALLURGY AND CERAMICS

UNITED STATES ATOMIC ENERGY COMMISSION

THE CHEMISTRY AND METALLURGY
OF MISCELLANEOUS MATERIALS

Edited by
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September 1955
TIS Issuance Date

Technical Information Service, Oak Ridge, Tennessee

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EDITOR'S PREFACE

In planning the written record for the Metallurgical Project,* it was recognized that considerable data on metallurgy, refractories, and general chemistry had been obtained which logically did not belong in any of the volumes dealing with major subject fields of the Project. Volume 19B of the Plutonium Project Record was designed as a Collected Papers volume to include reports and summary articles on these topics. The title of the volume became "Chemistry and Metallurgy of Miscellaneous Materials." Since many of the manuscripts collected for Volume 19B dealt with thermodynamics, they were grouped together under the subtitle "Thermodynamics." This volume was published in 1950 by the McGraw-Hill Book Company, Inc., as Volume 19B, Division IV, of the National Nuclear Energy Series.

The remaining papers on miscellaneous chemical, metallurgical, and structural subjects have been collected into this volume now designated as TID-5212, "Chemistry and Metallurgy of Miscellaneous Materials," originally planned for publication as Volume 19C, Division IV, of the National Nuclear Energy Series. Several of the papers originally intended for this volume have appeared in rewritten form in the scientific journals and were, therefore, omitted. These are listed in the Bibliography at the end of the volume.

The original volume editorial committee was composed of Frank H. Spedding, Ermon D. Eastman, Farrington Daniels, Harrison S. Brown, and John Chipman, with Laurence L. Quill as chairman. After the death of Dr. Eastman, Leo Brewer was named to the vacant position. The committee was assisted in the collection and preparation of manuscripts by Albert R. Kaufman at the Massachusetts Institute of Technology, George Boyd and Edward R. Tomkins at the Clinton Laboratories, and James C. Warf and Wayne H. Keller at Iowa State College.

To compile a list of titles for this volume, requests for contributions were made of all volume editors and of section chiefs and division leaders at the various sites of the Metallurgical Laboratory. From the titles thus obtained, a list was prepared and circulated for corrections and additions. Suggestions were also made by members of the Information Division of the Metallurgical Laboratory as a result of their scrutiny of the mass of filed reports. As the writing program progressed, several papers proposed for this volume were transferred to other volumes and vice versa.

After the organization of the Manhattan District Editorial Advisory Board late in 1945 and the start of declassification, additional titles for inclusion in this volume were proposed by representatives of the Publications Sections of the Manhattan District. When the Atomic Energy Commission entered the picture, additional papers were suggested by the Technical Information Division of the Commission. In its final form, this volume includes papers on the crystal chemistry of many materials, on geochemistry, and on the chemistry and metallurgy of beryllium and the rare earth elements as well as on some other topics.

The extensive and laborious task of preparing copies of the papers for declassification and for technical editing was supervised by Hoylande D. Young, first as technical editor of the Plutonium Project Record and later as General Editor of the volumes. Special credit is due her and her associates for their assistance and cooperation.

Laurence L. Quill

*The Project had its origin in work carried on in 1940-1941, mainly at Columbia and Princeton on the development of the chain-reacting pile and at the University of California at Berkeley on the production and chemistry of transuranic elements. In January 1942 this work was concentrated in the newly organized Metallurgical Laboratory at Chicago under the leadership of A. H. Compton. The Metallurgical Project grew out of the Metallurgical Laboratory. The Project was dissolved June 30, 1945.

The Plutonium Project Record covers most of the scientific and technical work of the Metallurgical Laboratory and the Metallurgical Project up to the date of the dissolution of the Project. This record forms Division IV of the National Nuclear Energy Series.

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Paper 1

The Rate of Sublimation of Solids*

GEORGE E. MacWOOD

ABSTRACT

A theory of the sublimation of solids is presented and compared with experimental data on UCl_4 .

1. INTRODUCTION

The development of a theory of the rate of sublimation of solids is given and is compared with the experimental results of Mueller¹ on uranium tetrachloride. The experimental approach to this problem is made difficult by the large number of possible variables involved. For this reason it was desirable to have a theoretical approach to the problem which takes account of first order effects.

2. THEORY OF SUBLIMATION

In most treatments of evaporation processes, the tacit assumption of an infinitesimal rate is made so that the steady state vapor pressure may be taken as equal to the equilibrium value. When the rate increases, the steady state surface temperature will fall and the corresponding vapor pressure will be lower. The only approach to this problem of a finite rate of evaporation which seems to have been published is that of Crout.^{2,3} The following is a condensed account of this theory with modifications to suit problems encountered in working with UCl_4 .

The assumption is made that, because of the finite drift velocity away from the surface, the vapor in the immediate neighborhood of the surface is anisotropic, gradually becoming isotropic in the course of a few mean free paths due to collision as the vapor moves away from the surface. It is assumed as well that the rate of sublimation does not involve secondary emission, so that the velocity distributions of the evaporating and condensing molecules do not interact with one another.

The velocity distribution of the evaporating molecules must be the same as that in the equilibrium vapor at the same temperature, that is, the Maxwell distribution:

*Contribution from the University of California, Radiation Laboratory. Based on Radiation Laboratory Report BC-15, a declassified version of which was issued as MDDC-605.

$$dN = \nu_0 \left(\frac{\beta_0 m}{\pi} \right)^{3/2} e^{-\beta_0 m(u^2 + v^2 + w^2)} du dv dw \quad u \geq 0 \quad (1)$$

where u , v , and w are the velocity components parallel to the x , y , and z axes, respectively, the origin of the axes being at the solid surface; dN is the number of molecules emitted per second per square centimeter of surface having the velocity spread du , dv , and dw ; ν_0 is the molecular density of the saturated vapor and m the molecular mass; $\beta_0 = 1/2 kT_0$; and T_0 is the surface temperature. In the case of polyatomic molecules, it is also necessary to allow for the distribution of internal energy.

$$dE_j = \frac{F - 3}{4\beta_0} dN \quad (2)$$

where dE_j is the internal energy of the dN emitted molecules and F is the total number of degrees of freedom. This involves the additional assumption of classical statistics. Equations 1 and 2 specify completely the mechanical behavior of the solid.

The relations for a gas in a steady state, whether or not it is isotropic, are now obtained. Consider a portion of a gas between fixed boundaries. For this system, the conservation conditions must hold for mass, momentum, and energy.

Before applying these conditions to the problem, it is necessary to introduce the following notation for the flow of gas across a unit area placed parallel to the solid surface at distance x from it:

Γ_1 = mass flux in the positive direction.

μ_1 = x -component of the momentum flux in the positive direction.

E_1 = energy flux in the positive direction.

For the solid surface, let

Γ_{10}^0 = mass flux away from the surface.

μ_{10}^0 = momentum flux away from the surface.

E_{10}^0 = energy flux away from the surface.

In the immediate neighborhood of the surface, the conservation conditions require that

$$\begin{aligned} \Gamma_{10}^0 &= \Gamma_{10} \\ \mu_{10}^0 &= \mu_{10} \\ E_{10}^0 &= E_{10} \end{aligned} \quad (3)$$

where the superscript 0 corresponds to the hypothetical plane at $x = 0$.

The velocity distribution in the anisotropic vapor near the solid surface is unknown. However, it must be symmetrical about the normal to the surface, hence it must be an even function of v and w . It is assumed that it has the form

$$f_a = A \exp\{-m[\beta_s(u - u_0)^2 + \beta_p(v^2 + w^2)]\} \quad (4)$$

where A , β_s , β_p , u_0 are constants, u_0 being the mass velocity. By the usual arguments,

$$A = \nu \left(\frac{\beta_s \beta_p^2 m^3}{\pi^3} \right)^{1/2} \quad (5)$$

and the two temperature coefficients are defined by

$$T_s = \frac{1}{2k\beta_s} = \text{longitudinal temperature} \quad (6)$$

$$T_p = \frac{1}{2k\beta_p} = \text{transverse temperature} \quad (7)$$

For the internal energy, it is assumed that the distribution function has the form

$$f_j = (F-3) \left[\frac{1}{4\beta_0} + \gamma \left(\frac{1}{4\beta_s} + \frac{1}{2\beta_p} \frac{3}{4\beta_0} \right) \right] \quad (8)$$

where γ is an undetermined number.

As the vapor moves away from the surface, the distribution is smoothed out as a result of collision, so that in the course of a few mean free paths, the gas is isotropic and is describable by the Maxwell distribution function

$$f = \nu_1 \left(\frac{\beta_1 m}{\pi} \right)^{3/2} \exp \{ -\beta_1 m [(u - u_0)^2 + v^2 + w^2] \} \quad (9)$$

To determine the parameters of the distribution functions given by Eqs. 4 and 9, it is necessary initially to calculate the transfer of mass, momentum, and external energy across a unit area normal to the direction of the mass velocity. Let

$$f_{a,u} = \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f_a dv dw = \nu \left(\frac{\beta_s m}{\pi} \right)^{1/2} e^{-\beta_s m (u - u_0)^2} \quad (10)$$

represent the distribution function for the u -component of velocity and

$$\rho = u_0 \sqrt{\beta_s m} \quad (11)$$

$$\sigma = \frac{\beta_s}{\beta_p} \quad (12)$$

$$\phi(\rho) = \frac{2}{\pi} \int_0^\rho e^{-x^2} dx \quad (13)$$

In terms of the above quantities, the various fluxes become

$$\Gamma_{i0} = m \int_0^{\infty} u f_{au} du = \frac{\nu}{2} \sqrt{\frac{m}{\beta_s}} \left[\frac{e^{-\rho^2}}{\sqrt{\pi}} + i\rho (1 + i\phi) \right] \quad i = 1, -1 \quad (14)$$

$$\mu_{i0} = m \int_0^{\infty} u^2 f_{au} du = \frac{\nu}{2\beta_s} \left[\rho \frac{e^{-\rho^2}}{\sqrt{\pi}} + i \left(\frac{1}{2} + \rho^2 \right) (1 + i\phi) \right] \quad (15)$$

$$\begin{aligned} E_{i0} &= \frac{m}{2} \int_0^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} u (u^2 + v^2 + w^2) f_a du dv dw \\ &= \frac{m\nu}{4(\beta_s m)^{3/2}} \left[1 + \rho^2 + \sigma^2 \right] \frac{e^{-\rho^2}}{\sqrt{\pi}} + i\rho \left(\frac{3}{2} + \rho^2 + \sigma \right) (1 + i\phi) \end{aligned} \quad (16)$$

$$E_{j0} = g_j \frac{\Gamma_0}{m} \quad (17)$$

g_j being the number of internal degrees of freedom.

The transfer equations for the solid are obtained by placing $\rho = 0$, $\sigma = 1$, $\beta_s = \beta_0$ and $\nu = \nu_0$, giving

$$\Gamma_{i0}^0 = \frac{\nu}{2} \sqrt{\frac{m}{\pi\beta_0}} \quad (18)$$

$$\mu_{i0}^0 = \frac{\nu}{4\beta_0} \quad (19)$$

$$E_{10}^0 = \frac{\nu_0}{2\sqrt{\pi m \beta_0^3}} \quad (20)$$

$$E_{j0}^0 = \frac{\nu_0(F-3)}{8\sqrt{\pi m \beta_0^3}} \quad (21)$$

For a small region in the vapor contiguous to the surface, application of the conditions for a steady state requires that

$$\frac{\nu_0}{\sqrt{\pi \beta_0^3}} = \frac{\nu}{\sqrt{\beta_s}} \left[\frac{e^{-\rho^2}}{\sqrt{\pi}} + \rho(1+\phi) \right] \quad (22)$$

$$\frac{\nu_0}{2\beta_0} = \frac{\nu}{\beta_s} \left[\rho \frac{e^{-\rho^2}}{\sqrt{\pi}} + \left(\frac{1}{2} + \rho^2 \right) (1+\phi) \right] \quad (23)$$

$$\frac{\nu_0}{\sqrt{\pi \beta_0^3}} \left[1 + \frac{\gamma(F-3)}{4} \right] = \frac{\nu}{2\sqrt{\beta_s^3}} \left\{ \left[(1+\rho^2+\sigma) \frac{e^{-\rho^2}}{\sqrt{\pi}} + \rho \left(\frac{3}{2} + \rho^2 + \sigma \right) (1+\phi) \right] + \frac{2\gamma\beta_s}{3} (F-3) \left(\frac{1}{4\beta_s} + \frac{1}{2\beta_t} \right) \left[\frac{e^{-\rho^2}}{\sqrt{\pi}} + \rho(1+\phi) \right] \right\} \quad (24)$$

Introduction of the following substitutions

$$\nu' = \frac{\nu}{\nu_0} \quad (25)$$

$$\beta_s^1 = \frac{\beta_s}{\beta_0} \quad \beta_p^1 = \frac{\beta_p}{\beta_0} \quad (26)$$

$$\psi_1(\rho) = \frac{e^{-\rho^2}}{\sqrt{\pi}} + \rho(1+\phi) \quad (27)$$

$$\psi_2(\rho) = \frac{\rho}{\sqrt{\pi}} e^{-\rho^2} + \left(\frac{1}{2} + \rho^2 \right) (1+\phi) \quad (28)$$

$$\psi_3(\rho) = (1+\rho^2+\sigma) \frac{e^{-\rho^2}}{\sqrt{\pi}} + \rho \left(\frac{3}{2} + \rho^2 + \sigma \right) (1+\phi) \quad (29)$$

into Eqs. 22, 23, and 24 gives

$$\frac{\nu' \sqrt{\pi}}{\sqrt{\beta_s^1}} \psi_1 = 1 \quad (30)$$

$$\frac{2\nu'}{\beta_s^1} \psi_2 = 1 \quad (31)$$

$$\frac{\nu' \sqrt{\pi}}{2\beta_s^{3/2}} \left[\psi_3 + \frac{1}{3} \gamma (F-3) \left(\frac{1}{2} + \sigma \right) \psi_1 \right] = 1 + \frac{1}{4} \gamma (F-3) \quad (32)$$

Solving these equations in terms of ρ , it is found that

$$\left[1 + \frac{1}{3} \gamma (F-3) \right] \psi_1 \sigma = \left\{ \frac{2\psi_2^2}{\pi \psi_1} \left[4 + \gamma (F-3) \right] - \frac{1}{6} \gamma (F-3) \psi_1 - (1+\rho^2) \frac{e^{-\rho^2}}{\sqrt{\pi}} - \rho \left(\frac{3}{2} + \rho^2 \right) (1+\phi) \right\} \quad (33)$$

$$\beta'_s = \frac{4}{\pi} \left(\frac{\psi_2}{\psi_1} \right)^2 \quad (34)$$

$$\nu' = \frac{2}{\pi} \left(\frac{\psi^2}{\psi_1^2} \right) \quad (35)$$

The rate of sublimation per unit area of solid surface is, by definition,

$$\Gamma = \Gamma_{10} - \Gamma_{-10} = m\nu u_0 = \nu \rho \sqrt{\frac{m}{\beta_s}} \quad (36)$$

whence, using Eqs. 18, 34, and 35, it is found that

$$\frac{\Gamma}{\Gamma_{10}^0} = \frac{2\rho}{\psi_1} \quad (37)$$

The pressure, p_s , exerted on the surface is obtained from a consideration of Eq. 3 giving:

$$p_s = \mu_{10}^0 - \mu_{-10} = \mu_{10} - \mu_{-10} = \frac{\nu}{\beta_s} \left(\frac{1}{2} + \rho^2 \right) \quad (38)$$

The saturated vapor pressure may be obtained from this equation by placing $\nu = \nu_0$, $\beta_s = \beta_0$, and $\rho = 0$; whence

$$p_0 = \frac{\nu_0}{2\beta_0} \quad (39)$$

and

$$\frac{p_s}{p_0} = \frac{1}{\psi_2} \left(\frac{1}{2} + \rho^2 \right) \quad (40)$$

It is seen that the various constants of the anisotropic vapor have been obtained in terms of those of the saturated vapor and the parameters ρ , γ , and F . The quantities β'_s , ν' , Γ/Γ_{10}^0 , and p_s/p_0 are independent of F and γ and are, therefore, the same for all gases.

Having considered the state of the vapor at the solid surface, the next step is to determine its state at a distance sufficiently far from the surface so that it may be considered isotropic. Let x_1 be this distance, the subscript 1, in general, applying to the isotropic vapor. Then, the steady state conditions may be written

$$\Gamma_{11} - \Gamma_{-11} = \Gamma_{10} - \Gamma_{-10} \quad (41)$$

$$\mu_{11} - \mu_{-11} = \mu_{10} - \mu_{-10} \quad (42)$$

$$E_{11} - E_{-11} = E_{10} - E_{-10} \quad (43)$$

The right-hand sides of these equations are given by Eqs. 14, 15, 16, and 17, respectively. The left-hand sides can be obtained from these by placing $x = x_1$, $\nu = \nu_1$, $\beta_s = \beta_1$, $\sigma = 1$, and $\rho_1 = u_1 \sqrt{\beta_1 m}$ in place of ρ . From Eqs. 41, 42, and 43, it is found that

$$\frac{\nu_1 \rho_1}{\sqrt{\beta_1}} = \rho \quad (44)$$

$$\frac{\nu_1}{\beta_1} \left(\frac{1}{2} + \rho_1^2 \right) = \frac{1}{2} + \rho^2 \quad (45)$$

where

$$\frac{\nu_1' \rho_1}{\beta_1'^{3/2}} \left(1 + \rho_1^2 + \frac{1}{2} F \right) = \rho \left\{ \rho^2 + \sigma \left[1 + \frac{\gamma}{3} (F - 3) \right] \right\} \quad (46)$$

$$\nu_1' = \frac{\nu_1}{\nu} \quad (47)$$

$$\beta_1' = \frac{\beta_1}{\beta_s} \quad (48)$$

Solving these equations, the following results are obtained

$$\rho_1^2 = \frac{\alpha - 1 - \frac{1}{2} F \pm \sqrt{\left(1 + \frac{1}{2} F \right)^2 - \alpha(1 + F)}}{2(1 - \alpha)} \quad (49)$$

$$\beta_1' = \left[\frac{\rho \left(\frac{1}{2} + \rho_1^2 \right)}{\rho_1 \left(\frac{1}{2} + \rho^2 \right)} \right]^2 \quad (50)$$

where

$$\alpha = \frac{\rho^2}{\left(\frac{1}{2} + \rho^2 \right)^2} \left[\frac{3}{2} + \rho^2 + \sigma_0 + \frac{1}{2} \beta_s' (F - 3) \right] \quad (51)$$

and

$$\sigma_0 = \frac{1}{\psi_1} \left[\frac{8\psi_2^2}{\pi\psi_1} - (1 + \rho^2) \frac{e^{-\rho^2}}{\sqrt{\pi}} - \rho \left(\frac{3}{2} + \rho^2 \right) (1 + \phi) \right] \quad (52)$$

It is to be noticed that σ_0 is the value of σ for a monatomic gas and that α is independent of γ .

The value of β_1 from Eq. 50 combined with Eq. 34 gives

$$\frac{\beta_1}{\beta_0} \beta_1' \beta_s' = \frac{T_0}{T_1} \quad (53)$$

The pressure ratio is given by

$$\frac{\rho_1}{\rho_0} = \frac{\nu_1 \beta_0}{\nu_0 \beta_1} = \frac{\nu_1' \nu_1'}{\beta_s' \beta_1'} = \frac{1}{2\psi_2} \left(\frac{1 + 2\rho^2}{1 + 2\rho_1^2} \right) \quad (54)$$

or

$$\frac{P_1}{P_0} = \left(\frac{1}{1 + 2\rho_1^2} \right) \frac{P_s}{P_0} \quad (55)$$

The density ratio is

$$\frac{\nu_1}{\nu_0} = \frac{\beta_1 P_1}{\beta_0 P_0} \quad (56)$$

The above development gives, therefore, the constants of the isotropic vapor in terms of ρ for a given value of F , independent of γ .

An investigation of the above equations for ρ_1 and α indicates that the range of possible variation of ρ is between zero and some critical value, which for $F = 3$ is less than 0.55. For $F = 3, 5$, and ∞ , the corresponding critical values of ρ are 0.508, 0.457, and 0.377, respectively. The mass velocity, therefore, has a maximum corresponding to the critical value of ρ and, in all cases, it is equal to the velocity of sound through the isotropic vapor. This result is independent of the assumed form of the distribution function.

The development, as pointed out previously, up to this point has been made on the basis of classical statistics. Removal of this restriction results in F losing its meaning, but this can be taken care of by redefining it by the equation;

$$\frac{1}{2} RT F(P, T) = U(P, T) \quad (57)$$

where U is the total energy of the gas. With this change, there is no change in the form of the resulting equations as compared with the classical results and all the previous conclusions still hold. However, for most practical applications of this theory, the particular F value chosen is not critical, so that quantum statistical modifications are an unnecessary refinement.

In the application of this theory to the problem of the sublimation of a solid, it is desired to know the amount of energy flowing away from the surface. The molecular energy flux may be obtained from Eq. 46 for $\gamma = 0$:

$$E_{11} - E_{-11} = \frac{\nu_1 \rho_1}{2 \sqrt{m} \beta_1^3} \left[1 + \rho_1^2 + \frac{2\beta_1}{A} U(T_1, P_1) \right] \quad (58)$$

If L_0 denotes the energy required to sublime one gram of solid at a rate so slow that the energy due to the mass velocity of the vapor is negligible compared with the thermal energy, and, if U_{00} is the energy of the solid at temperature T_0 , then

$$\frac{U_{00}}{M} + L_0 = \frac{1}{2\beta_0 m} + \frac{1}{A m} U(T_0, P_0) \quad (59)$$

It then follows that

$$E_{11} - E_{-11} - \frac{\nu_1 \rho_1 U_{00}}{A \sqrt{\beta_1} m} = \frac{\nu_1 \rho_1}{2 \sqrt{m} \beta_1^3} \left\{ 1 + \rho_1^2 + 2m\beta_1 L_0 - \frac{\beta_1}{\beta_0} - \frac{2\beta_1}{A} [U(T_0, P_0) - U(T_1, P_1)] \right\} \quad (60)$$

or, since the left hand-side of Eq. 60 is the rate at which energy must be supplied per unit area of the solid surface to maintain sublimation.

$$L = L_0 + \frac{1}{2} U_1^2 + \frac{R}{2M} (T_0 - T_1) (2 + F) \quad (61)$$

where L is the energy which must be supplied per gram to maintain sublimation.

Mueller¹ has made an extensive and very careful investigation of the sublimation characteristics of uranium tetrachloride. A complete description and discussion of these experiments are given in another paper.⁴ For the purposes of this paper, it is assumed that the heating of the charge is completely by radiation transfer and that the solid has a melted surface of area A_0 . The vapor passes through an orifice of area A_1 . With this idealized arrangement, the problem is to determine the sublimation rate with the aid of the above theory when the energy necessary for sublimation is supplied to the surface by radiation from a surface at temperature T_1 and the rate of escape of the vapor is controlled by an orifice, the vapor pressure of the solid being known. Since the sublimation rate is a function of the parameter ρ , the problem reduces to one of determining this quantity for various values of T_1 and A_1/A_0 . Since ρ enters the theory in a rather complicated fashion, it is necessary to make a series of graphical solutions.

The first of these graphical solutions is made using the sublimation energy and radiant energy which must be equal in a steady state. Eq. 61 can be cast in the form

$$L_s = \Gamma_{10}^0 \left[L_0 - \frac{4RT_0}{M} + \frac{RT_0}{M} (1 + \rho_1^2) \frac{T_1}{T_0} \right] \quad (62)$$

which is a function of T_1 for a given surface temperature, T_0 . The radiant energy is given by the modified Stefan-Boltzmann law,

$$L_R = F\sigma(T_1^4 - T_0^4) \quad (63)$$

where F is a factor to take care of the non-blackness of the surfaces involved in the transfer. The solution in this case gives L_R as a function of T_0 and T_1 .

The second graphical solution is made using the rate of sublimation as determined from the flow through an orifice and the rate of sublimation as determined from the theory. The solution gives Γ/Γ_{10}^0 as a function of ρ and A_1/A_0 .

With the aid of these two sets of values, Γ can be obtained quite easily as a function of T_1 and A_1/A_0 .

3. DISCUSSION

Two different types of comparison are made with the experimental results of Mueller.¹ In the first, the calculated values of Γ are compared with the experimental values for two temperatures. Figures 1.1 and 1.2 show this comparison. It is interesting to observe that the general behavior is reproduced by the theory by simply varying one parameter, F . It should be pointed out that at the higher pressures and for large values of A_1/A_0 the effusion law no longer holds; in this region there is an approach to the laws governing hydrodynamic flow through an orifice. The rates, in this case, will require larger values of ρ and, therefore, higher rates of sublimation than are given by the usual effusion formula.

The second comparison with experiment has to do with an experiment suggested by the theoretical development, namely measurement of the temperature gradient in the subliming solid. Figure 1.3 shows the manner in which the maximum temperature lowering of the surface compares with the theoretically predicted values.⁴ The agreement again is mainly qualitative. For the experimental data, it is impossible to define the emissivity factor, F , exactly or to estimate the area ratio, complicated as this is by the fact that vapor escapes from at least several layers of particles instead of the plane surface postulated. Furthermore, heat is delivered to the subliming particles to some extent from the side walls of the container and by vapor transport up through the solid. These factors would tend to diminish the thermal effect calculated on the basis of zero heat conductivity within the solid. The data, however, show that if the emissivity factor is given a reasonable value (between 1 and 0.5) the area ratio required is the range of 0.25 to 0.1. If an emissivity factor of 0.1 is used, such as would be indicated by the comparison between rate of sublimation data and the theory, then the area ratio would have to be taken of the order of 0.03 to 0.04. For the emissivity factor to be as low as 0.1 the only suggested explanation is that the temperature difference is divided between several interfaces, each acting as a baffle for radiation as well as vapor flow, thus giving a low over-all emissivity and low transport.

As indicated in the above discussion, there are a number of other factors that affect the rate of sublimation. However, it is believed that the theory as proposed takes adequate account of the main factors involved in sublimation.

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Fig. 1.1.

Fig. 1.2—Rate of Sublimation of UCl_4 as a Function of Area Ratio.

Fig. 1.3.

Paper 2

The Preparation of Cerium by Electrolysis of Molten Salts*

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ABSTRACT

Electrolysis of cerium chloride or fluoride in the potassium chloride-lithium chloride eutectic mixture, or of cerium chloride in the calcium fluoride-lithium fluoride eutectic at 850 to 1000°C produces cerium metal in clean ingots in up to 80 per cent yield. Losses are chiefly due to oxyhalide formation in the presence of oxygen. In the absence of oxygen, losses are due either to the failure of finely dispersed metal to coagulate into the ingot or to the appreciable concentration of cerium salt in equilibrium with the bath in reactions of the type

No direct evidence in proof of the latter concept is available. However, yields of over 90 per cent were obtained by electrolysis of cerium bromide in barium or strontium bromide. This is in agreement with a comparison of all the Periodic Group I and II halides based on the calculation of the extent of such equilibria from the available thermodynamic data.

1. INTRODUCTION

Various methods are described in the literature for the preparation of cerium by electrolysis from molten salts. The methods, in general, describe the preparation of 10 to 20 g. amounts of metal with up to 70 per cent yields. Kremers and Beuker¹ prepared about 300 g of metallic cerium free from iron by electrolysis of fused cerous chloride at well below 800°C, using graphite cells and carbon anodes. Trombe² electrolyzed cerium trichloride in a potassium chloride bath at 850°C, with at best a yield of 70 per cent. In somewhat similar experiments Weibke³ obtained lanthanum metal at 1000°C. It is not clear in the latter work just what the net yields were, but they apparently were at least 50 per cent at 1000°C and considerably poorer at lower temperatures. In industrial processes up to about 90 per cent yields have

*Work done at the Department of Chemistry, University of California, Berkeley. Based on Metallurgical Project Reports CC-2256, September 25, 1944; CT-2762, March 6, 1945; and later unpublished data. Originally prepared as ANL-HDY-64, a declassified version of which was issued as MDDC-603.

been obtained from cerium chloride-calcium chloride mixtures on a 12 to 14 kg scale, and 70 per cent or less from pure cerium trichloride according to Engelhardt.⁴ The metal produced in the latter processes contains from 7 to 8 per cent iron.

The aim of the work described here was to develop an electrolytic method which would yield pure cerium metal in amounts up to about 100 g with high net efficiency. Perhaps the major difficulty in this problem, as noted by both Trombe² and Weibke,³ is to effect the conglomeration of the reduced cerium into a single ingot.

The yields of metal referred to in this paper are, unless otherwise noted, yields of metal recovered in the form of solid ingots only. The yields are calculated on the basis of total rare earth recovery, since no appreciable electrolytical separation from cerium is to be expected. This is borne out by analysis of the metal ingots. For convenience, the dispersed metal has been referred to throughout as "metal fog." The amount of the dispersed metal is determined by measurement of the hydrogen gas evolved on treatment of the salt bath with dilute hydrochloric acid, after removal of the metal ingot.

The electrolysis of pure cerium trichloride was not considered in the present work because, obviously, complete reduction of a given sample could not be achieved and complete reduction was not considered desirable in this process. Furthermore, the electrolysis of pure cerium chloride can never be very efficient because of the extremely high solubility of cerium metal in cerium chloride. Approximately 40 mole % cerium in cerium chloride melts at 721°C according to Cubicciotti.⁵ The melting points of cerium and cerium trichloride are given as 775° and approximately 800°C, respectively.

2. EXPERIMENTAL PROCEDURE

The apparatus used was very similar in principle to that used by both Trombe² and Weibke.³ A graphite crucible of 1½ to 2 in. I.D., 6 to 7 in. tall, and ½ to ¾ in. wall thickness functioned as the anode. A tungsten rod ¾ in. in diameter served as cathode. The latter was lowered to within about 1 in. of the bottom of the graphite crucible and rotated at 90 to 180 rpm. Tungsten is the best cathode material; molybdenum is very badly attacked at 1000°C. The attack on the cathode occurs just above the melt during electrolysis; a close fitting mullite sleeve around the tungsten was therefore ordinarily used to protect this portion of the cathode.

A small crucible of some non-conducting refractory material was placed directly below the cathode inside the graphite crucible. The metal formed dropped off the cathode and collected in this small crucible. The electrolytically produced metal whether in the form of ingot or finely divided "fog" was actually always found in a relatively small lower layer inside the inner crucible. Initially, two forms of the inner crucible were employed: a "short" form in which at least an inch depth of molten bath always existed above the top edge of the inner crucible, and a "tall" form in which the crucible totally shielded the portion of the cathode in the melt from the anode walls except for a few narrow slits. A highly erratic behavior of the electrolysis was finally traced to the use of the "tall" inner crucibles. Unless otherwise noted, "short" inner crucibles about 1½ in. tall and 1½ in. diameter were used in all experiments reported. These crucibles were made of beryllia, BeO, which appeared to be the best refractory for this purpose. Although these crucibles darkened, no appreciable disintegration or attack appeared to occur. Zirconia, ZrO₂, crucibles appeared to be satisfactory, but zircon, ZrSiO₄, crucibles were very badly attacked.

In the initial experiments atmospheric oxygen was not excluded, or it was only inefficiently excluded with a stream of argon played over the top of the apparatus. Modifications of this procedure were employed in some of the later experiments. The scale of operations varied considerably on a weight basis. In general, 30 to 60 g of cerium halide with from 100 to 350 g of additional salt was used, depending on the particular system being studied. An effort was made to keep the volume of the melt and the concentration of the cerium salt roughly constant throughout the experiments. All salts were carefully dried, whether they were hydrated or not, and all handling in so far as possible was done in dry boxes.

Temperatures are those measured by a chromel-alumel thermocouple imbedded in the graphite crucible wall at a point just about at the top level of the melt. Temperature was controlled to within about $\pm 10^\circ\text{C}$. Electric furnaces supplied heat. In general, the electrolysis was carried out at a potential of 6 to 12 volts for currents from 20 to 80 amp. In the discussions to follow, the time of electrolysis is given in all cases as a multiple of the theoretical time, the time theoretically required to reduce the amount of cerium halide being used at the particular current employed. This varied from approximately 45 min to $1\frac{1}{2}$ hr, in general.

3. ELECTROLYSIS IN THE CeCl_3 -KCl-LiCl SYSTEM

3.1 Early Comparison with Other Systems

The first two electrolysis experiments employed a cerium chloride-potassium chloride mixture at 1000°C approximating that used by Weibke³ for lanthanum. No ingot of metal was obtained although considerable finely dispersed metal was formed. Although Weibke had noted a marked decrease in yield in going to lower temperatures, several lower melting eutectic baths were then tried in the hope that the effect Weibke noted was really due to a change in viscosity of the bath. It is not certain that the lower melting baths listed in Table 2.1 would differ appreciably in viscosity at 1000°C , but it is apparent that the composition of the bath has a marked effect on the yield of metal ingot.

The addition of small amounts, about 5 per cent, of fluorides to the chloride baths tended to be detrimental. The initial success in the potassium chloride-lithium chloride bath, combined with the fact that it is the lowest melting binary mixture of any of the alkali or alkaline earth metal chlorides, led to consideration of the system in some detail.

Table 2.1—Effect of Composition of Salt Bath
(Temperature, 1000°C ; Current, 40 amp; Time, $3X^*$)

Exp. No.	Salt bath	Melting point of pure bath, $^\circ\text{C}$	Ingot yield, %
2	KCl	776	0
24	NaCl-KCl	663	38
22	LiCl-KCl	350	76
32	NaF-NaCl	675	0

*X = theoretical time required to reduce the amount of cerium halide being used at the particular current employed.

3.2 Effect of Cerium Trichloride Concentration

The effect of the concentration of cerium trichloride in the potassium chloride-lithium chloride was not studied over a very extensive range. However, it is apparent from Experiments 7 and L-24 shown in Table 2.2, (and many other intermediate experiments not shown) that where all the ingredients are mixed together before electrolysis, no appreciable difference in yield is observed over the range of 5.5 to 15 mole % CeCl_3 . These concentrations correspond to 21 and 44 wt. %, respectively.

Table 2.2—Effect of Concentration of Cerium Trichloride
(Temperature, 1000°C; Current, 40 amp; Bath, KCl-LiCl; Time, 2X)

Exp. No.	Mole %, CeCl_3	Method of addition of CeCl_3	Ingot yield, %
L-24	5.5	All mixed before electrolysis	51
7	15.5	All mixed before electrolysis	51
L-19	(4.4)	Added continuously during 2X period	0 (fog)
L-20	(5.5)	Added continuously during first X period	0 (considerable amount small beads)

Although no experiments of the usual type were done below a concentration of about 5 mole % cerium chloride, it appears from Experiments L-19 and L-20 (see Table 2.2) that a low effective concentration of cerium chloride during the electrolysis results in a poor yield of metal ingot. Further evidence of this concentration effect was noted in a series of experiments in the sodium chloride-potassium chloride bath. When the concentration of cerium chloride was below approximately 4 to 5 mole % the yields of metal appeared to drop quite sharply.

3.3 The Effect of Cathode Current Density on Current Efficiency

The effective cathode surface on the 0.1-in. diameter tungsten rod was approximately 2.0 cm^2 , so that at 40 amp, for example, the cathode current density was about 20 amp/cm^2 . The results reported in Table 2.3 reveal that the current efficiencies, up to at least 75 per cent recovery were about 25 and 50 per cent, at 20 and 40 amp/cm^2 , respectively. A few experiments at 40 amp total current with $\frac{1}{2}$ - and $\frac{1}{4}$ -in. diameter cathodes, giving effectively about 4 and 8 amp/cm^2 , respectively, appeared to result in a current efficiency lower than 25 per cent. Similar results were reported by Weibke.³

Table 2.3—Effect of Cathode Current Density on Current Efficiency
(Cathode, 0.1 in. diam with $\sim 2 \text{ cm}^2$ effective area; Bath, KCl-LiCl; Temperature, 1000°C)

Exp. No.	Mole %, CeCl_3	Total current, ampere	Time, X	% yield	
				Ingot	Fog
7	15.0	40	1.7	51	
33	5.5	40	2	59	
22	5.3	40	3	76	
L-27	5.0	40	4	70	
L-31	7.8	40	4	78	6
41	5.5	80	4	78	
40	6.3	80	3	74	4
42	5.9	80	2	75	3
50	6.6	80	2	82	
43	14.2	80	2	78	3
54	15.1	80	2	69	
36	6.2	80	1	47	

In Experiment 33 the melt was allowed to stand at 1000°C for a period of time equivalent to twice the theoretical after the electrolytic current was shut off. No appreciable increase in yield resulted. Increased current efficiency (Experiments 40, 41, 42) did not appreciably change the yield of metal ingot and even of "total metal" from typical results observed at lower currents (Experiment L-31). Increasing the concentration of cerium chloride (Experiments 43 and 54) did not improve the yield of either the ingot or total metal as has been previously noted. These effects suggested that some irreversible loss of cerium was occurring. An incomplete analysis made on Run 54 revealed the presence of a large amount (~14 per cent) of a water-insoluble cerium compound, presumably cerium oxychloride, which appeared to be insoluble also in the molten salt bath. An electrolysis was attempted in a bath containing 7.2 mole % cerium chloride and 2.6 mole % cerium dioxide. This was run at 80 amp for twice the theoretical time required to reduce both the chloride and oxide. The yield of ingot was only 59 per cent on the basis of cerium chloride alone, or 43 per cent on the total cerium available. The oxide, or oxyhalide, was essentially insoluble in the molten bath judging from the appearance of the melt after freezing.

3.4 "Continuous-Batch" Operation

The unelectrolyzed cerium in the usual experiment could be due to true "hold-up," that is, caused by the low concentration of unchanged cerium chloride. In such a case, adding a new batch of cerium chloride, equal in amount, say, to the original amount added, should result in improved over-all yields. However, in the presence of atmospheric oxygen at least, where the loss appears as an irreversible one, no improvement in the over-all yield should be observed. The experiments shown in Table 2.4 were performed to obtain some information on this and in any case to determine the effect of reusing the electrolytic bath.

The results of these experiments revealed that the over-all yield in continuous-batch operation was actually no better than that in the individual experiments. A total of 78 and 270 g of cerium metal was obtained in Runs 46 and 53, respectively. The mole per cent cerium chloride noted was approximate for each addition, neglecting that remaining from the previous addition. The metal ingot was removed before each addition of cerium chloride.

Table 2.4—Continuous-Batch Operation

(Bath, LiCl-KCl; Current, 80 amp; Temperature, 1000°C; Time, 2X)

Exp. No.	Mole %, CeCl_3	No. of additions	Ingot yield, %	Over-all yield, %
			72	
46	6	2	89	81
53	18	3	73	
			84	77
			73	

3.5 The Effect of Temperature and of Purity of the Cerium Salt

In some very early experiments ingots of metal were not obtained in the potassium chloride-lithium chloride bath at temperatures below about 900°C although the fluoride systems, to be discussed later, operated equally well at 1000 or 850°C. A recheck of the chloride system revealed that it also operated satisfactorily at 850°C. Gravimetric and volumetric analyses of the cerium chloride stocks revealed that the ratio of total rare earths to cerium in the cerium chloride used in the later experiments differed from that of stocks used in the earlier work. The earlier cerium chloride stock was the least pure with respect to cerium. Therefore, this old

stock of cerium chloride was used in Experiment 72 (see Table 2.5). The yield of metal was markedly poorer in this experiment, and the ingot was considerably rougher and more uneven than in the experiments with purer cerium chloride, Runs L-37, 70, and 71. The latter runs also illustrate the essentially similar behavior at 850 and 1000°C with this purer stock of cerium chloride, for example, Run L-31, Table 2.3.

The result of Experiment 72 was considerably better than was to be expected from earlier experiences, although the only other difference is that the runs noted in Table 2.5 were done with a close fitting "head" into which argon was passed; the earlier runs were done with "tall" form zircon inner crucibles.

Table 2.5—Effect of Purity of Cerium

(Bath, KCl-LiCl; Current, 40 amp; Temperature, 850°C; Time, 4X)

Exp. No.	Mole %, CeCl ₃	Ratio total rare earths/Ce	% yield	
			Ingot	Fog
L-37*	8.0	1.071	72	
70	4.8	1.050	73.8	8.5
71	6.8	1.050	74	13
72	5.4	1.140	60	17.1

*Contained 5 wt. % CaF₂.

Run 70 was analyzed as follows. After removal of the ingot, the fused salt was divided into two fractions consisting of that salt inside the beryllia inner crucible and that above it ("beryllia" and "salt" fractions, respectively). The hydrogen evolution in acid ("fog" in Table 2.5) was all obtained from the beryllia fraction; the salt fraction evolved no appreciable gas in acid. The two fractions were then analyzed for total cerium. There was found, respectively, 21.8 per cent and 1.8 per cent cerium in the beryllia and salt fractions. A total of 97.4 per cent of the original cerium was thus accounted for. The fact that the bulk of the unreduced cerium, after allowing for the 8.5 per cent in this fraction that was due to metal fog, was found in the lower beryllia fraction indicates quite certainly that the approximately 15 per cent total of unelectrolyzed material was probably cerium oxychloride which is insoluble in the melt and sinks to the bottom. Experiments on the solubility of cerium trichloride in potassium chloride-lithium chloride mixtures revealed that up to 8 mole % cerium chloride was completely soluble at about 470°C; the melting point of the eutectic bath was 350°C.

4. ELECTROLYSIS IN THE CeCl₃-CaF₂-LiF SYSTEM

The 50-50 wt. % eutectic mixture of calcium fluoride and lithium fluoride melts at 630°C. Electrolysis of cerium chloride in this bath gives clean ingots in good yields at high current efficiency equally well at 1000 or 850°C and at 80 or 40 amp. However, it was found impossible to electrolyze this system for as long as twice the theoretical time because of the appearance of the so-called "anode effect."⁶ This accounts for the erratic time of electrolysis noted in Table 2.6.

Table 2.6—Electrolysis in $\text{CaF}_2\text{-LiF}$

Exp. No.	Mole %, CeCl_3	Temp., $^{\circ}\text{C}$	Current, ampere	Time, X	Ingot yield, %
55	10.9	1000	80	1.5	58
56	10.1	1000	80	2	74
57	10.6	850	80	1.8	75
59	5.4	850	80	1.7	64
60	6.4	850	40	1.7	78

It is of interest to note that an attempt to electrolyze cerium chloride from the sodium fluoride-calcium fluoride eutectic (m.p. 810°C) at 1000°C was unsuccessful; no metal was formed. An identical result obtained in the sodium fluoride-sodium chloride system is reported in Table 2.1. The values of the free energies of formation of the halides at high temperatures obtained from data collected by Brewer⁷ reveal that the relative electropositivities of cerium and sodium or potassium are reversed in going from the chloride to the fluoride, whereas, for example, lithium and calcium do not change relative to cerium. Apparently, systems of molten salts containing cerium, sodium, and fluoride ions may preferentially electrolyze out sodium rather than cerium. How this can occur in the presence of chloride ion, however, is not understood. The electrolytic apparatus used in the present work would very probably have a zero current efficiency for the production of a light metal like sodium; hence the complete absence of metal in the above-mentioned experiments.

5. THE ELECTROLYSIS OF CERIUM TRIFLUORIDE

The relative ease of handling of cerium fluoride over cerium chloride made it desirable to compare the behavior of cerium fluoride with that of the chloride in the electrolytic system thus far studied.

Table 2.7—Electrolysis of CeF_3 in KCl-LiCl

(Temperature, 850°C ; Current, 40 amp)

Exp. No.	Mole %, CeF_3	Time, X	Ingot yield, %
64	9.1	2	70
65	7.9	4	62
66	8.2	4	59
67	8.7	4	67
68	8.0	4	76
69	3.6	4	56

The electrolysis of cerium fluoride in the calcium fluoride-lithium fluoride bath yielded no ingot of metal, but finely dispersed metal was found throughout the bath, and the beryllia inner crucible was very considerably attacked. Fairly good yields were obtained in the potassium chloride-lithium chloride bath (Table 2.7).

Experiments 65 and 66 were done with cerium fluoride which gave by analysis a total-rare-earth to cerium ratio of 1.096; all the other experiments were done with a preparation which had a value of 1.000 for the same ratio. This might account for the slightly lower yields in

Runs 65 and 66. The lower yield in No. 69 may be due to typical concentration effect. Considerable metal fog was present in all experiments. Holding the melt for a longer period of time at 850°C, after electrolysis (Experiment 66 as compared with 65) had no apparent effect on the yield of metal ingot, although a similar heating period at 1000°C after electrolysis at 850°C appeared to have a beneficial effect (Experiment 68 as compared with 67). All of the above effects may be within the usual limits of erratic errors experienced in this type of experiment.

6. ELECTROLYSIS IN THE COMPLETE ABSENCE OF OXYGEN

In order to determine the efficiency of the electrolysis being studied the loss of cerium through formation of oxide or oxyhalide must be avoided. Accordingly, the apparatus was enclosed completely in a large refractory porcelain tube that could be evacuated while being heated in the furnace. The usual precautions of handling in dry boxes and predrying of the salts were observed. The apparatus was continuously evacuated at 10^{-2} to 10^{-3} mm while it was carefully heated up to 400 or 500°C; argon was then admitted and allowed to flow continuously through the apparatus while it was heated up to 850°C and throughout the electrolytic process and subsequent cooling period. The gas outlet was quite small and the argon flow fairly vigorous so that no air could get back into the apparatus. The results obtained are tabulated in Table 2.8.

It is apparent that of the four systems studied, cerium chloride or cerium fluoride in each of the two baths, potassium chloride-lithium chloride and calcium fluoride-lithium fluoride, the $\text{CeCl}_3\text{-KCl-LiCl}$ system gives the best results under comparable conditions. However, the yield of metal ingot is not appreciably affected in spite of the fact that the complete absence of oxygen results in higher "total" metal yield, about 92 to 97 per cent in the $\text{CeCl}_3\text{-KCl-LiCl}$ system, as compared to about 82 per cent in the earlier experiments in which oxygen was not excluded. In Runs L-42, L-43, L-44, and L-46, the cerium fluoride and cerium chloride used were both prepared from the same source of cerium. Further, this latter cerium had a total rare earth to cerium ratio of 1.000, whereas the ratio was 1.071 in Experiments L-38 and L-39; 1.042 in L-41, L-48, and L-49; and 1.096 in L-40. Thus, the cerium purity appears to have no appreciable effect within the above limits under these conditions.

In general, the results observed in the closed system are not appreciably different from those obtained by the previously employed technique, with respect to the yield of metal ingot. In the $\text{CeF}_3\text{-CaF}_2\text{-LiF}$ system all of the metal is found in a dispersed state, and the beryllia inner crucible is considerably attacked, as in earlier experiments. The "anode effect" still appears in the $\text{CeCl}_3\text{-CaF}_2\text{-LiF}$ system, when operated at lower currents (Experiment L-48), and effectively prevents electrolyzing for the desired length of time. However, by passing hydrogen gas up along the inside surfaces of the graphite crucible-anode it was found possible to prevent the anode effect from occurring in this system. Under these conditions (Experiment L-49 in Table 2.8) the fluoride bath appears to function as well as the chloride bath for the electrolysis of cerium chloride.

7. EFFECT OF THE COMPOSITION OF THE BATH

It is apparent, from the experiments described in the previous section, that the problem of obtaining better yields has resolved into the one of being able to effect the agglomeration of the dispersed metal or fog into the main ingot. In the molten state this metal is undoubtedly in actual solution in the liquid phase either as dissolved metal or through the formation of subhalides, for example

Table 2.8—Electrolysis in the Absence of Oxygen
(Temperature, 850°C; Current, 40 amp)

Exp. No.	Mole %, Ce Salt	Bath	Time, X	% yield	
				Ingot	Fog
L-38	8.0 CeCl ₃	LiCl-KCl*	4	83	
L-39	8.2 CeCl ₃	LiCl-KCl	4	81.5	12.3
L-41	8.1 CeCl ₃	LiCl-KCl	4	76.5	20.5
L-40	7.3 CeF ₃	LiCl-KCl	4	58.3	29.2
L-42	7.1 CeF ₃	LiCl-KCl	3	58.6	17.1
L-43	6.7 CeCl ₃	LiCl-KCl	3	78.5	13
L-44	7.0 CeF ₃	CaF ₂ -LiF	3	0	~100
L-46	6.8 CeCl ₃	CaF ₂ -LiF	1.5	59.0	
L-48	7.2 CeCl ₃	CaF ₂ -LiF	2†	59.5	20
L-49	7.0 CeCl ₃	CaF ₂ -LiF	3‡	81	13

*5 per cent CaF₂

†At 20 amp

‡H₂ anode

In any case, on freezing, metal in a finely dispersed state is obtained. It has been assumed up to this point that this finely dispersed metal is cerium.

Calculations were made of the actual concentration of cerium halide which would be in equilibrium with a mixture of excess cerium metal and alkali metal halide or alkaline earth metal halide in the reactions. The free energies of formation

or

were taken from the data collected by Brewer.⁷ The results of the calculations reveal that, in the systems employed here, the equilibrium concentration of cerium chloride could readily account for the inability, in general, to obtain more than approximately 80 per cent ingot yield. In this case, the finely dispersed metal is not cerium but alkali metal or alkaline earth metal.

Unfortunately, we cannot distinguish between cerium metal alone and a mixture of cerium chloride plus an equivalent amount of alkali metal or alkaline earth metal by a combined analysis of hydrogen evolution and specific chemical analysis for cerium. In fact, even after a considerable amount of work, Gwinn⁸ of this laboratory has not achieved satisfactory differentiation between, say, cerium and calcium metals in the finely dispersed state in solid calcium chloride.

In any case, it appeared advisable to compare the extent of reaction of all the Group I and II halides with cerium as calculated from the free energy data. The following order of increasing concentration of cerium halide at equilibrium with excess salt and cerium metal, according to Eqs. 1 and 2, was obtained:

1. BaI ₂	7. KI, RbBr	13. RbCl, CaCl ₂	19. CaF ₂
2. CsI	8. SrBr ₂	14. LiI, KCl, CaBr ₂	20. NaCl
3. BaBr ₂	9. KBr	15. NaI	21. BaF ₂
4. RbI	10. SrCl ₂	16. LiBr	22. LiF
5. SrI ₂	11. CaI ₂	17. LiCl	23. SrF ₂
6. BaCl ₂ , CsBr	12. CsCl	18. NaBr	

Typical values of the equilibrium mole fractions of cerium halide at 1000 and 1500°K, respectively, are potassium chloride, 0.0032 and 0.023, and barium bromide, 0.000042 and 0.0017.

Subhalide formation should be considered also; for example, in the reactions

In such a case the equilibrium concentration of cerium halide (which is the subhalide in this instance) is increased considerably, and the differences between Group I and II halides are very considerably decreased. On the basis of reactions 3 and 4 the equilibrium mole fractions of cerium subhalide at 1000 and 1500°K, respectively, are potassium chloride 0.0080 and 0.048, and barium bromide, 0.0030 and 0.022.

A few electrolysis experiments were done to test the above ideas. Although, in general, the iodides appear to be the best halides for the purpose of obtaining the maximum yield of cerium metal, the great difficulty of preparing pure anhydrous cerium triiodide made it advisable to pick the best bromide. The first experiment was done with barium bromide. This had to be done at 950°C because of the high melting point of barium bromide. Experiments with strontium bromide at both 950 and 850°C afforded a comparison with the large number of earlier experiments that were done at 850°C. Finally, as an example of a bath that would be expected to be very poor for the desired purpose, sodium bromide was tried. Bromides were used consistently in these comparisons so that the same stock of cerium bromide could be employed throughout, thus avoiding unnecessary variables. The experiments, tabulated in Table 2.9, were all done in the complete absence of oxygen, in exactly the same manner as those described in the previous section (Table 2.8).

The yields of cerium of over 90 per cent in barium bromide at 950°C and in strontium bromide at 850°C were considerably better than any previously obtained. The yield obtained in sodium bromide was unexpectedly high. The effect of subhalide formation on the differences between the various salts may account for this latter result; it is felt that subhalides certainly are concerned in the reactions being considered.

Table 2.9—Effect of the Composition of the Bath
(Time, 3X)

Exp. No.	Mole %, CeBr ₃	Bath	Temp., °C	% yield	
				Ingot	Fog
L-51	8.7	BaBr ₂	950	93	4.6
L-52	10.7	SrBr ₂	950	83	12.5
L-53	10.2	SrBr ₂	850	91	7.3
L-54	10.8	SrBr ₂	700	(63)	(31)
L-56	9.2	SrBr ₂	850	94	
L-55	8.1	NaBr	850	81	80

It must be realized that the cerium metal produced in an electrolysis has certainly not reached equilibrium with the entire bath, with respect to the equilibria considered in Eqs. 1 and 2, or 3 and 4. The rate of approaching equilibrium thus becomes an unknown complicating factor.

Experiment L-54 was done below the melting point of cerium to determine whether the cerium metal might plate out on the cathode. Only part of the cerium was obtained on the cathode, and this was in an unsuitable, porous condition. Lower current densities might yield better deposits. (See, for example, Piontelli.⁸) Cerium metal was obtained from NaCl-KCl baths at 650 to 750°C, but yields are not given.

In Experiment L-56 the electrolyzing current was left on throughout the cooling process after running three times the theoretical time at 850°C. No appreciable increase in yield was obtained, although considerable free strontium metal was found dispersed throughout the bath.

In conclusion it may be said that the few experiments noted in Table 2.9 neither prove nor disprove the ideas involved in the thermodynamic considerations made above. The comparison, on such a basis, of salts to be used for electrolytic baths is undoubtedly desirable. It is felt, however, that the various factors involved in the electrolytic process have been sufficiently surveyed to permit comparison with other methods of metal reduction.¹⁰

8. SUMMARY

Yields of cerium metal up to 80 per cent were obtained by electrolysis in the CeCl_3 -KCl-LiCl system. Clean ingots of metal were obtained equally well at 850 or 1000°C, provided the cerium used contained less than about 10 per cent of other rare earths. From 15 to 100 g of metal has been prepared in a single run, and the bath can be reused several times. When cerium chloride is electrolyzed in the presence of atmospheric oxygen, a considerable part of the loss of cerium is due to oxyhalide formation. The current efficiency increases with increased cathode current density and decrease in temperature. The current efficiency is greater than 50 per cent at temperatures of 1000 and 850°C with cathode current densities of 40 and 20 amp/cm², respectively. Essentially similar results are observed in the CeCl_3 - CaF_2 -LiF and CeF_2 -KCl-LiCl systems; whereas in CeF_2 - CaF_2 -LiF mixtures only finely dispersed metal is obtained.

No better yields of metal ingot are observed in the complete absence of oxygen, although practically complete reduction of the cerium salt apparently occurs. The loss in this case is due either to failure of the finely dispersed cerium metal to coagulate into the ingots, or to the appreciable concentration of cerium salt at equilibrium with the bath in reactions of the type

Thermodynamic calculations for all the Periodic Group I and II halides reveal that the equilibria of the above type are shifted to the left in the following increasing orders: sodium, lithium, potassium, rubidium, cesium and magnesium, calcium, strontium, and barium, and, for any one metal, fluoride, chloride, bromide, and iodide. As expected, then, an improved yield of over 90 per cent was observed in the electrolysis of cerium bromide in barium bromide at 950°C and in strontium bromide at 850°C. Direct evidence in proof of the above concept is lacking, however.

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Paper 3

Preparation of Cerium by Chemical Reduction in Open Crucibles in an Inert Atmosphere*

E. D. EASTMAN, W. D. GWINN, and D. D. CUBICCIOTTI

ABSTRACT

The production of metallic cerium has been studied. A 99 per cent yield of metallic cerium has been obtained by reduction of pure cerium chloride with metallic calcium in an open crucible under an inert atmosphere. Of the 1 per cent cerium which was lost, some was unreduced cerium chloride in the salt, some was metallic cerium dissolved in the excess metallic calcium, some was metallic cerium which was dissolved by the wash water, and some was probably finely divided cerium dispersed in the salt. Reduction in the crucibles has the advantage of being simpler and more convenient than the bomb method.

* * * * *

When this work was undertaken, the bomb methods being used for metal production were giving low yields, and it was desirable to find a process which would give a better yield. While this method was being developed, the bomb methods were improved. Now the yields from this method and the improved bomb methods are comparable. However, the method to be described possesses several advantages of simplicity and convenience over the bomb methods. The reduction is carried out in an open crucible instead of a bomb; it is not necessary to grind the calcium metal for the reduction; and it is easier to recover the cerium which does not find its way into the ingot.

A study of the free energy of reduction¹ suggests that cerium chloride can be reduced with calcium, strontium, barium, lithium, sodium, or potassium. It should be impossible to reduce it with magnesium or aluminum. The high volatility of sodium and potassium make them undesirable for use in an open crucible.

When calcium is used as the reducing agent, the heat of reaction is high—about 26 kcal per mole of cerium chloride.¹ The heat of reaction is even higher when strontium, barium, or

*Work done at the Department of Chemistry, University of California, Berkeley. Paper written by W. D. Gwinn. Prepared for publication August 1945, as ANL-HDY-66.

lithium is used. If the reduction took place very rapidly, or if no heat were lost during the reduction and the heat capacity of the crucible were negligible, the temperature rise would be about 600°C. Since the reduction does not start until the temperature of the reactants reaches 700 or 800°C, the final temperature would be between 1300 and 1400°C. Since at this temperature there would be much volatilization from an open crucible, it was desirable to lower this maximum temperature.

Several methods may be used to prevent this high temperature. One method is to add an inert salt to the reaction mixture. This would raise the heat capacity of the system and lower the maximum temperature. Another method is to slow down the reaction so that the heat may be dissipated as it is produced. In the reduction of cerium it is possible to slow down the reaction by adding the calcium in a few large pieces.

The first method to be tried, later to be discarded, was the addition of an inert salt, usually a eutectic of potassium chloride and lithium chloride. The reductions were carried out in the apparatus shown in Fig. 3.1. The reactants were placed in the crucible and heated to 700°C in an induction furnace. After the reaction was complete, the crucible was heated to 900°C for 5 or 10 min to melt the cerium metal. The reaction took place slowly and the temperature rise during the reaction was small. At the highest temperature (900°C) there was considerable fuming due to the reduction and volatilization of potassium. In spite of the fuming there was no loss of cerium by spattering or volatilization.

The initial cerium chloride concentration in the salt was varied between 5 and 20 mole %. The amount of calcium was varied from 20 to 70 per cent excess. The yields in this process were high if powdered metal were included as part of the yield. The yield was always at least 99 per cent and usually 99.6 per cent. Unfortunately, while some of the trials did produce single ingots, the majority of them produced some powdered metal. No differences were found when the heating was done with a resistance furnace.

The second method tried was much more successful. Calcium in the form of several large pieces was added to pure cerium chloride, and the mixture was heated; the reaction was slow enough to allow the heat to be dissipated. The apparatus shown in Fig. 3.1 was used. There was a slight increase in temperature at the surface between the molten cerium chloride and the calcium, but this temperature rise was less than 200°C. After the main reaction was over, the mixture was held at 950°C for 5 or 10 min and then was allowed to cool slowly. At 950°C there was a little volatilization of calcium, but no cerium could be detected on the walls of the glass jacket. After cooling, the calcium chloride and the excess calcium were washed out with water. In all of the trials using this method, the metallic cerium produced was in the form of a single ingot. Any powdered cerium was washed out with the salt, and was not considered as being in the yield. Table 3.1 gives a summary of the results obtained with this method. In Experiments 1, 3, and 4, the heating was done with a resistance furnace instead of an induction furnace. No differences could be noticed when resistance heating was used.

Since cerium and calcium are not very soluble in each other, the cerium produced contains only about 1 per cent calcium by weight. (The solubility of calcium in cerium is higher than 1 per cent, but apparently equilibrium is not reached. See Table 3.2.) Part of the excess calcium metal dissolves in the calcium chloride melt, and the rest floats on top of the melt. As a result of the calcium dissolving in the calcium chloride, the rate of solution of the melt is much faster than it would be if the melt were pure fused calcium chloride.

Molybdenum crucibles were usually used because they were not attacked during the reduction. They have the disadvantage that cerium "wets" a molybdenum surface and makes the metal difficult to remove. To offset this, when it was desirable to prepare a large amount of pure cerium, several reductions were carried out in the same crucible without removing the cerium produced. The salt phase was washed out with water between each reduction. The reductions were continued until the crucible was half full of metallic cerium. If very pure cerium was desired, the cerium was vacuum heated at this point to remove the calcium. The crucible was then turned upside down over a ceramic crucible or mold and heated until the cerium ran out. The molybdenum crucible was then used again without cleaning, so that the cerium metal remaining in the crucible was not lost.

Table 3.1—A Summary of the Yields Obtained from the Reduction of CeCl_3 by Calcium

Exp. No.	Grams of CeCl_3 reduced	Calcium excess	Yield, %
1*	8	84	98.6
2	14	80	98.2
3*	13	80	98.8
4*	7	70	98.8
5	7	70	98.2
6	40	70	98.7
7	14	61	98.1
8	26	60	99.1
9	65	55	99.2
10	16	50	99.3
11	13	50	99.3
12	7	44	98.8
13	14	40	99.0
14	14	40	99.1
15	28	36	98.5
16	14	30	99.2
17	29	28	99.7
18	11	26	98.4
19	12	23	98.2
20	14	20	99.0
21	13	16	98.9
22	16	15	98.9

*Heating was done in a resistance furnace instead of an induction furnace.

Table 3.2—Analysis of the Two Phases Obtained by Heating Metallic Cerium and Metallic Calcium Together and Cooling Suddenly

Temperature, °C	Mole fraction of cerium	
	Top phase	Bottom phase
920	0.052	> 0.80
930	0.035	0.86

The data in Table 3.1 show that the best yields were obtained using a 40 to 50 per cent excess of calcium. If more calcium were used, the amount of cerium dissolved in the excess calcium would be appreciable and the yield would be lowered. To find out how much cerium was lost in the salt and how much was lost in the excess calcium metal, three reductions were carried out, and the salt was separated from the metallic cerium and excess calcium by breaking the crucible. The salt was analyzed and was found to contain about 0.3 per cent (0.25, 0.27, and 0.47 per cent in the three trials) of the cerium. The calcium was dissolved in water and was found to contain 1 to 2 per cent of the cerium, depending upon how much excess calcium was present. In one trial the cerium mole fraction in the calcium was determined and was found to be 0.018 (see Table 3.2).

On the basis of the above experiments, it would be expected that the maximum yield of metallic cerium would be 99.6 or 99.7 per cent and that it would occur with only a 25 per cent excess of calcium, since the solubility² of calcium in calcium chloride is only 20 per cent at these temperatures and not more than 5 per cent is lost by volatilization. In the actual reductions the maximum yield was only 99.3 per cent, and this occurred with a 50 per cent excess of calcium. This discrepancy has not been explained.

There are several factors which will cause the cerium to remain in the salt phase: the equilibrium concentration of cerium chloride in the presence of calcium, cerium, and calcium chloride may be high enough to be of significance; the metallic cerium may be soluble in calcium chloride; and part of the metal may be formed as a fog dispersed in the calcium chloride.

Brewer, Bromley, Gilles, and Lofgren¹ give the free energy of the reaction

to be +28 kcal at 1200°K. The corresponding equilibrium constant would be 7×10^{-6} . After a reduction there is both metallic cerium and calcium; therefore, both the cerium and calcium activities would be unity. The CaCl_2 activity would be less than unity, but for the purposes of the calculations we will assume it to be unity.

$$(\text{CeCl}_3) = 7 \times 10^{-6} \times (\text{CaCl}_2) = 7 \times 10^{-6}$$

A CeCl_3 mole fraction of 7×10^{-6} would be negligible, corresponding to a 0.0004 per cent loss. If cerium subhalides were formed, this value would be higher.

To measure the equilibrium concentration of CeCl_3 in the CaCl_2 , and also to measure the solubility of cerium in CaCl_2 , the following experiments were performed. A molybdenum crucible containing pure metallic cerium and CaCl_2 was heated to 900°C, under helium, in a sealed quartz tube for 2 hr, and then cooled suddenly. The crucible was broken, and the total cerium contained in the salt was determined. The data from these experiments are given in Table 3.3. The amount of calcium in the cerium metal was undetectable. In some of the trials calcium was added to the CeCl_3 and cerium. The amount added is given in Column 3. The equilibrium constants were calculated by assuming the cerium and CaCl_2 activities to be unity, the CeCl_3 activity to be equal to its mole fraction, and the calcium activity to be equal to its mole fraction divided by the mole fraction of calcium in a solution of CaCl_2 saturated with calcium. This solubility² of Ca in CaCl_2 at the temperature of the trial is given in Column 5. The mole fraction of the calcium was computed from the amount of calcium added and the amount of cerium found in the salt. In several of these experiments and a number of similar experiments the hydrogen evolved when the salt was dissolved in acid was measured. The hydrogen evolved was found to be within 15 per cent of being equivalent to the calcium added and the cerium found in the salt. This is not very good agreement, but the nature of the experiments makes it difficult to obtain better results.

The values of the equilibrium constants in Column 6 increase, and the corresponding free energies in Column 7 decrease as the calcium concentrations is increased. This may be due to experimental error, or it may be due to a small solubility of cerium in CaCl_2 , or, and more likely, it may be due to the formation of cerium subhalides. Columns 8 and 9 give the equilibrium constants and corresponding free energies, calculated with the assumption that 0.001 mole of cerium per mole of CaCl_2 found in the salt was present as cerium metal dissolved in the calcium chloride. The values so obtained fluctuate due to the experimental error, but they show no trend with the calcium concentration. The average value of the free energy of reaction was 23 kcal and is in satisfactory agreement with the value of 28 kcal computed by Brewer, Bromley, Gilles, and Lofgren¹ from thermal data.

The values given in Columns 10 and 11 likewise show no trend with the calcium concentration. They were calculated assuming the formation of a cerium subhalide, according to the equation:

Table 3.3—Summary of Results Obtained After Heating Metallic Cerium and CaCl_2 Together

Exp. No.	Temp., °C	Mole of Ca added/mole of CaCl_2	Mole of Ce in salt/mole of CaCl_2	Solubility of Ca in CaCl_2 (mole fraction)	$\text{Ce} + 3/2 \text{CaCl}_2 = \text{CeCl}_3 + 3/2 \text{Ca}$		Solubility of Ce in $\text{CaCl}_2 = 0.0001$ mole/mole CaCl_2		$\text{CaCl}_2 + \text{Ce} =$ $\text{Ca} + \text{CeCl}_2$ (subhalide formation)	
					Solubility of Ce in $\text{CaCl}_2 = 0$					
					K	ΔF	K	ΔF	K	ΔF
1	850	0	4.29×10^{-3}	0.21	2.3×10^{-5}	23.7	1.8×10^{-5}	25.8	1.3×10^{-4}	20.0
2	940	0	7.62×10^{-3}	0.153	1.4×10^{-4}	21.3	8.9×10^{-5}	22.2	5.2×10^{-4}	18.1
3	930	0	3.43×10^{-3}	0.157	1.9×10^{-5}	26.0	8.1×10^{-6}	26.4	1.2×10^{-4}	21.4
4	930	0	5.63×10^{-3}	0.157	6.8×10^{-5}	22.8	4.1×10^{-5}	23.0	3.0×10^{-4}	19.5
5	925	2.67×10^{-2}	4.51×10^{-3}	0.159	3.1×10^{-4}	19.2	2.2×10^{-4}	20.0	9.1×10^{-4}	16.6
6	906	4.66×10^{-2}	1.44×10^{-3}	0.164	2.2×10^{-4}	18.0	7.3×10^{-5}	22.3	4.3×10^{-4}	18.4
7	915	5.99×10^{-2}	2.12×10^{-3}	0.161	4.7×10^{-4}	18.2	2.5×10^{-4}	19.7	7.9×10^{-4}	17.4
8	920	0.111	1.34×10^{-3}	0.160	7.8×10^{-4}	17.0	3.1×10^{-5}	24.4	9.3×10^{-4}	16.6
9	920	0.112	1.77×10^{-4}	0.160	1.0×10^{-4}	22.0			1.2×10^{-4}	21.4
10	940	0.123	9.29×10^{-4}	0.153	6.6×10^{-4}	17.6			7.4×10^{-4}	17.2
							Av. 23.0		Av. 18.7	

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This assumption is self-consistent in that the free energy of formation of CeCl_2 would be $150^1 - 18.7$ (Column 7, Table 3.3) = 131.3 kcal. Then the free energy of the reaction at 1200°K:

would be -1 kcal, and the equilibrium constant would be 1.5. At the highest concentration of cerium chlorides encountered, the CeCl_3 concentration would be about 5 per cent that of the CeCl_2 , and it would be less at the lower concentrations. Therefore, no large errors were introduced by assuming the CeCl_2 concentration in the salt to be equal to the total cerium concentration in the salt.

While these data are not accurate enough to decide between the three possibilities stated in the preceding paragraphs, they do show that the cerium concentration in the salt, after a reduction, could not be less than 0.1 to 0.2 per cent. Since the cerium content of the salt after a reduction is only 0.3 per cent, there is not much chance of reducing this loss.

Several reductions have been carried out using barium, lithium, or potassium as the reducing agent, but in all cases the metal produced was either powdered or had been alloyed with the excess reducing agent. In no case was a good ingot obtained. Experiments attempting to reduce cerium oxide were also unsuccessful. The reduction was not complete, and the small amount of metal formed was either powdered or in the form of small pellets. This was also true when calcium chloride was added to the cerium oxide to serve as a flux.

The presence of cerium oxide as an impurity in the cerium chloride will cause the yield in reduction to be low. Since at high temperature cerium chloride reacts with any moisture present to form cerium oxide and hydrogen chloride, it is very important to have the cerium chloride dry and to keep it dry. Otherwise, the yield from the reduction will be low.

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A - CERAMIC STAND

B - MOLYBDENUM CRUCIBLE

C - CERAMIC RADIATION SHIELD
(seldom used)

Fig. 3.1—Apparatus used for reductions.

Paper 4

The Production of Cerium in the Massive Metallic State*

W. H. KELLER, ROBERT P. ERICSON, and CLIFFORD HACH

ABSTRACT

The optimum conditions for the production of metallic cerium by bomb reductions of cerous chloride with magnesium or calcium were found to include the use of 0.5 mole of dry iodine per mole of cerium chloride as a "booster," giving yields of 85 to 95 per cent, or the use of 0.3 mole of iodine and 0.0625 mole of potassium perchlorate per mole of cerous chloride (to save iodine), giving yields of 90 per cent. Bomb construction and operation and the preparation of cerous chloride are described.

1. INTRODUCTION

A need for massive cerium metal for use in making ceramic materials led to a request for the production of the metal.

Mosander¹ prepared cerium by the reduction of the chloride with sodium or potassium and obtained poor yields of powdered metal contaminated with sodium and sodium chloride. Wohler, Marignac, and others used similar procedures. Moldenhauer² obtained alloys of the metal by reducing the fluoride with calcium or aluminum. Cerous oxide has been reduced with magnesium,^{3,4} aluminum,^{2,4,5} calcium, silicon, or carbon⁵ to yield alloys, carbides, or silicides of cerium. However, most of the cerium produced prior to our work was prepared by the electrolysis of the chloride or fluoride, a process used by Hillebrand and Norton,⁶ Muthmann and associates,⁷ Hirsch,⁵ Kremers and Beuker,⁸ Tromb,⁹ and Eastman, Fontana, Thurmond, and Wilmarth.¹⁰

In spite of the greater success of electrolytic processes over those based on thermal reductions by metals, the bomb process of making metals developed by Spedding, Wilhelm, and Keller appeared to offer an ideal procedure for making a low-melting metal like cerium. This procedure consists of lining a steel bomb with a refractory material such as calcium oxide, or magnesia, placing therein a charge consisting of a salt of the metal to be produced, a reducing agent such as calcium or magnesium and, in some cases, an auxiliary oxidant or "booster" to supply additional heat, and then heating the bomb and its contents or a portion of the charge until reaction occurs.

*Work done at the Metallurgical Laboratory at Ames, Iowa. Prepared for publication February, 1945; based on Metallurgical Project Report CT-2396, and also, in part on ISC-75, a declassified version of which was issued as AECD-3208, July 24, 1951.

2. PROCEDURE

Bombs were constructed of standard black steel pipe with a welded bottom on one end and threads on the other. The bombs were closed with standard pipe caps. Liners were installed either by jolting lime by a pneumatic jolting table into the annular space between the pipe and a cylindrical mandrel inserted in the pipe (Fig. 4.1), or by placing sintered lime crucibles in the pipe and filling the space between crucible and pipe with loose lime (Fig. 4.2). The crucibles were made by jolting lime as above in graphite crucibles and sintering in the induction furnace at 1850°C. Such crucibles are dense, smooth surfaced, mechanically strong, and fairly resistant to thermal shock. They do absorb water to some extent, however, and have to be kept in a dry atmosphere.

The charge was mixed in a MacLellan batch mixer, poured into the bomb by means of a funnel of paper or metal, and covered by a sintered refractory disk or by a graphite disk. In the case of cerium, graphite disks have proved usable and very convenient.

Next, the pipe cap was screwed on. In case a volatile component such as iodine or sulfur is present, the cap must be made gas-tight by the use of a plumber's seal (litharge and glycerine, or its equivalent) on the threads of the pipe. Good threads are very essential in this case.

The loaded and closed bomb was then placed in a resistance furnace, gas-heated soaking pit, or high-frequency induction furnace to be heated to the reaction temperature. After reaction the bomb was cooled and opened, and the ingot was removed for casting.

3. REAGENTS

Cerous chloride, obtained in the hydrated state, was dried by heating in an atmosphere of hydrogen chloride at reduced pressure. For the first reductions, the hydrate was heated gradually for 10 hr to 350°C in a pyrex or quartz tube in an atmosphere of hydrogen chloride in a resistance furnace and held at that temperature for 2 hr.* Subsequently, the salts were dried by heating gradually to 350°C for 12 hr, then raising the temperature to 450°C and holding for 12 hr. The pressure was reduced by means of water aspirators, and hydrogen chloride was fed into the drying chamber from a tank. The pressure during most of the operation was about 20 to 30 mm. Water losses amounted to 32 to 37 per cent by weight. By this procedure the water content of the salt is reduced to 0.2 to 0.4 per cent. The resulting salt is so slightly hygroscopic that it can be weighed and mixed in air.

The drying of the cerous chloride is necessary because (1) the presence of more than a few tenths of 1 per cent of water decreases the yield in a bomb reduction; (2) water is likely to cause an explosion due to reaction to form hydrogen, or to expansion of the water vapor with rising temperature.

The purity of the reagents used in the bomb process is of utmost importance as impurities in the reagents will be present in the product. The content of a given contaminant in the final product may be decreased by separation in the slag (calcium or magnesium may be removed in the slag as halides), or by vacuum casting if the contaminant is a more volatile metal. Many impurities go through the entire process, however, unless they are removed from the reagents before reaction occurs.

4. FLUX

Other investigators had achieved some success in small-scale attempts by heating the bomb in an induction furnace to temperatures above the melting point of the metal following reaction, on the assumption that such heating would melt the metal and slag to assure separation.

When the same procedure was first attempted in our work, it was found that the prolonged heating produced a boiling action which resulted in continued admixture of slag and metal, and in greater wetting and penetration of the liner by the metal. This effect produced badly formed

*Dried by Dr. Amos Newton and co-workers at the Ames Laboratory.

ingots, highly contaminated with included slag and lime, and with tightly adhering deposits of slag on the top and of lime on the sides.

To prevent this boiling of the metal and wetting of the liner the operating temperature was lowered by adding a flux to reduce the melting point of the slag so that the metal and slag could be separated at lower temperatures. When 20 mole % of potassium chloride was added and the holding temperature dropped to about 850°C, yields rose to between 50 to 78 per cent and much cleaner metal was obtained.

5. BOOSTERS

For large-scale production, it appeared that two factors created difficulties, (a) the unnecessarily high temperatures of the post-heat stage, and (b) the difficulty of exact control of heating in the induction furnace. To obtain the temperatures necessary for melting the components of the system, it was decided to use materials that would momentarily increase the temperature of the reaction mixture within the bomb rather than to apply excessive external heat after the reaction had taken place.

5.1 Iodine

Iodine was first investigated as a booster. Charges of 150 g of anhydrous cerous chloride with 5 per cent excess calcium and 1 mole of iodine per mole of cerous chloride were heated in $2\frac{1}{2} \times 8$ in. bombs with sintered lime crucibles. Yields of 58 to 78 per cent of fairly clean, castable metal were obtained with an average of 65 per cent for seven runs.

A study of the effect of the ratio of iodine to cerous chloride was then made; the results are given in Table 4.1.

The reaction was brought to the stage where 85 to 95 per cent yields were consistently obtained with a charge of 1600 g of fully dried cerous chloride, and dry iodine in a ratio of 0.5 mole iodine per mole of CeCl_3 , in sintered-lime bomb liners (Fig. 4.2), with graphite caps over the top. This reaction was carried out in a steel bomb, 4 in. in diam and 24 in. long.

(a) Iodine Recovery. Since iodine is expensive and not readily available in great quantity, its recovery from the slag seemed desirable. Several methods were tried. The simplest and most successful was the passage of oxygen gas through the crushed slag in a steel bomb heated to about 300°C, so that the iodine was displaced by the oxygen. The effluent gas, including iodine vapor, was led out through a steel pipe in the top of the bomb and into a cooled flask which served as a condenser. The iodine thus collected contained a small amount of water vapor. This was removed by fusion of the iodine in a flask fitted with a water-cooled condenser. Some iodine vapor was lost with the water but recovered in the condenser and recycled for drying. The fused product was quite dry.

Table 4.1—Production of Cerium Metal

Charge, g	Mole I_2 per mole CeCl_3	Excess Ca, %	Yield range, %	Yield average, %
150	1.0	5	58-78	65
150	0.75	10	62-65	64
300	0.75	10	73-88	84
420	0.625	10	70-91	82
1600	0.625	5	76-91	84
1600	0.5	5	90-97	94

5.2 Sulfur

In an effort to reduce the costs due to the heavy iodine requirement, other boosters were investigated. Sulfur was tried in the range of 0.5 to 2 mole of sulfur per mole of cerous

chloride. Although sufficient heat was generated, as evidenced by the outside temperature of the bomb, no separation of metal and slag occurred. Apparently, the sulfides produced were miscible with the metals present.

5.3 Potassium Perchlorate and Potassium Perchlorate and Iodine

Fairly satisfactory results were obtained with potassium perchlorate as a booster. The range from 0.10 to 0.61 mole of potassium perchlorate per mole of cerous chloride was investigated. The optimum yield of 83 per cent was obtained with 0.11 mole potassium perchlorate per mole of cerous chloride, but even under its best conditions, potassium perchlorate did not produce a yield comparable to that produced by iodine. However, 0.11 mole potassium perchlorate plus 0.33 mole calcium, as compared with 0.5 mole iodine plus 0.5 mole calcium, represents a savings in both calcium and iodine more significant than the loss of yield of 0.1 mole of cerous chloride. The metal produced by the use of potassium perchlorate, however, was never as clean as that produced by the use of iodine, neither externally with respect to adhering slag nor internally with respect to inclusions. Hence, the effort was made to save the cost of a part of the iodine by the use of both iodine and potassium perchlorate. Almost half the required iodine was saved by the use of 0.3 mole of iodine and 0.0625 mole of potassium perchlorate per mole of cerous chloride. By this combination, 90 per cent yields have been obtained.

6. CASTING

The cerium produced by this method contained about 0.5 per cent calcium and 0.5 per cent magnesium. In order to remove these and other volatile components, as well as to shape the metal, it was cast by melting in magnesia crucibles and pouring into cooler graphite molds. After casting, the calcium content had dropped to 0.3 per cent, magnesium to 0.1 per cent and other volatile contaminants had also been decreased. The details of the casting procedure and the composition of the final product are presented in Paper 5 of this volume.

Considerable quantities of cerium were produced by the above methods for use in the different Project Laboratories.

7. LANTHANUM PRODUCTION

Lanthanum has also been produced by this method. Since its melting point was reported to be fairly close to that of cerium, the same conditions used for the reduction of cerium chloride were applied, with an average yield of 91 per cent in three reductions. These conditions should apply equally well to the production of any metal of about the same melting point and wetting properties whose compounds have approximately the same energy contents as those of cerium.

ACKNOWLEDGMENTS

The writers wish to thank Dr. F. H. Spedding and Dr. H. A. Wilhelm who closely followed this work and who contributed to its success by many helpful discussions.

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$2 \frac{1}{2}$ in. iron pipe
and cap

Fig. 4.1 — Cross Section of Reduction Bomb.

$2 \frac{1}{2}$ in. iron pipe
and cap

Fig. 4.2 — Cross Section of Reduction Bomb.

Paper 5

The Casting of Cerium and Some Properties of the Cast Metal*

DAVID PETERSON, WARD LYON, and W. H. KELLER

ABSTRACT

Cerium metal produced by the reduction of anhydrous cerium chloride by calcium with iodine as an auxiliary oxidant was cast in vacuo for purification and shaping. The metal was melted in crucibles of lime, magnesia, or beryllia (usually lime) and cast into graphite molds. The metal was cast at 900°C into a mold at 650°C. A multiple mold of graphite capable of casting 19 billets per cast was developed. Density, hardness, and melting point of cast cerium are discussed. Some methods of shaping and fabrication are described.

* * * * *

Cerium metal was produced at Iowa State College for use in the ceramic program of the Project by the reduction of anhydrous cerium chloride with calcium using iodine as an auxiliary oxidant or "booster."¹ The crude ingots of metal thus produced contained a certain amount of included slag and calcium. The latter is virtually insoluble in cerium in the solid state and existed in the form of pellets on the outside of the ingot, especially on the top. For the use intended, it was necessary that the cerium be purified and put into shapes of the proper size. These objectives were achieved by casting in vacuo.

1. CRUCIBLE AND MOLD REFRACTORIES

Refractory materials for use in fabricating melting crucibles and molds were first selected by making melts in bodies made of various refractories.

1.1 Melting Crucible

Because of availability and ease of fabrication, graphite would have been very desirable as a melting crucible. However, at its melting point, cerium reacts readily with graphite to form the carbide,^{2,3} hence graphite was not usable as the melting medium.

*Work done at the Metallurgical Laboratory at Ames, Iowa. Prepared for publication October 5, 1945; based on Metallurgical Project Report CT-2952. The declassified version was issued as MDDC-608.

Oxide refractories were next investigated, and those of magnesium, calcium, and beryllium were found satisfactory.² Crucibles of these oxides were made by jolting the powdered refractory in graphite forms with graphite mandrels and firing by induction heating at 1700 to 1850°C.⁴ Of the above, calcium oxide, being the cheapest and one of the purest available, was used for casting the major portion of the cerium produced.

1.2 Mold

While graphite could not be used as the melting chamber, it could be used as the mold by pouring the molten metal into the mold below the melting point of the metal. This was done by maintaining the mold at a temperature of 650°C at the time of pouring. Oxide refractories were used as molds for some purposes, but most of the metal was cast into molds of graphite because of its ease of shaping.

2. CASTING CONDITIONS AND PROCEDURE

2.1 Temperature

The melting point of cerium has been variously reported as 635 to 840°C (Sec. 3.2). Most of the metal used in the studies reported in the literature was probably not sufficiently pure for a good determination. The authors have not produced metal of greater than 99 per cent purity, and the best value obtained with metal of 98 to 99 per cent purity is 780 to 790°C. The low heat of fusion causes difficulty in obtaining a sharp melting point. Because the metal does not flow freely until a temperature of 900°C is reached, this temperature was adopted for casting.

2.2 Pressure

The pressure of casting was not too critical, but a good vacuum prevented loss of metal by oxidation and was helpful in maintaining free flow. Most of the melting and casting was done at the low pressures obtainable with Cenco Hypervac pumps.

2.3 Heating and Insulation

Heating was achieved by graphite induction heaters. The mold itself acted as a heater while a graphite cylinder was used as the heater for the crucible. The insulation of a system at a temperature as low as 900°C is quite simple; a single sillimanite shield proved adequate.

2.4 Casting Procedure

The casting of simple shapes was done by melting in calcium oxide, magnesia, or beryllia crucibles with a pour hole in the bottom, with or without a valve, and casting into similar materials or graphite.

The major portion of the cerium produced, however, was cast into rods $\frac{3}{4}$ in. in diameter by about 4 in. long for use in hydrogenation chambers. Since these rods were relatively small, it was uneconomical to cast singly, and a multiple mold was developed by which 19 rods were cast at one time. This apparatus is presented in Fig. 5.1.

The metal was melted by induction heating in the crucible (E) of sintered lime by a graphite heater (D). The calcium oxide crucible had a $\frac{1}{2}$ in. hole in the bottom at the center fitted with a sintered beryllium plug (F). The mold (H) consisted of a cylinder of graphite with 19 holes $\frac{43}{64}$ in. in diameter drilled in two concentric rows about the center. A hole $\frac{5}{16}$ in. in diameter was drilled through the center of the mold to permit passage of the push rod (J) used to push the plug (F) from the hole in the bottom of the crucible. The crucible was supported $\frac{1}{4}$ in. above the mold by a graphite collar, and both were surrounded by a graphite induction heater (D). The induction coil was so placed that the crucible and the mold were each heated to the desired temperature, which was measured by thermocouples in wells (A) and (I). About 15 min were required to heat the charge to the proper temperature (900°C) for pouring. The mold

was held at 650°C by raising or lowering the coil. At the proper temperature, the metal was poured by pushing the beryllia plug from the bottom of the crucible by a beryllia rod (G) passing down into the center hole in the mold. The beryllia rod was pushed up by a graphite rod (J) which passed through the water-cooled vacuum base by means of a Wilson seal. The vacuum was not critical; a Cenco Hypervac or Megavac had sufficient capacity to produce good results. When the metal had cooled after pouring, the system was opened, the mold removed, and the graphite broken away from the rods. Any excess metal on top of the mold was cropped and recast in subsequent castings. The rods were leached in hot water for several hours to remove adhering carbide and graphite. The billets were then cleaned by buffing with a wire brush. Each casting produced 19 ingots about 4 in. long, the whole charge weighing from 5½ to 6 lb.

3. PROPERTIES

3.1 Hardness and Density

Cast cerium is a bright silver-white metal which tarnishes fairly rapidly on standing in air. It is relatively soft and has a hardness of 60 on the Rockwell M scale. On cold rolling, the hardness increases to 92 R_M with 25 per cent reduction, which is about the same hardness as that of rolled magnesium. Further cold working does not increase the hardness; 50 per cent reduction on cold rolling produces a hardness of 93 R_M. The specific gravity of the cast metal ranged from 6.57 to 6.65, the latter value being most frequently obtained. Because of the rapid corrosion of the metal by water, the density was determined with the Westphal balance and checked by direct measurement of the mass and volume of an exactly machined piece.

3.2 Melting Point

As mentioned above (Sec. 2.1) the values of the melting point of cerium reported in the literature are extremely discrepant, ranging from 675°C, reported by Mazza⁵ who claimed 99.8 per cent pure electrolytic cerium, to 775°C, given by Vogel⁶ for 95.6 per cent cerium containing 4.3 per cent other rare earths. Vogel also reported 840°C, arrived at by extrapolation of phase diagrams of cerium alloys. Other investigators have reported intermediate values, mostly based on determinations on quite impure metal. The authors obtained thermal breaks ranging from 728 to 802°C with various samples of metal containing as much as 5 per cent of other rare earths and alkaline earth metals. However, with samples of the purer part of the regular metal produced in quantity, 764 and 770°C were obtained. These samples contained 98.5 per cent cerium, 1 per cent other rare earths, and 0.1 per cent carbon, the residue consisting of undetermined alkali and alkaline earth metals.

A melting point of 780°C was obtained with the purest metal produced by the writers from especially purified cerous chloride. This metal assayed 99.3 per cent cerium, 0.15 per cent alkaline earth metals, 0.12 per cent carbon, and less than 0.4 per cent other rare earths. On the basis of these data, the melting point of pure cerium appears to lie between 780 and 790°C.

4. WORKING AND FABRICATION

4.1 Machining

Cerium is a tough, soft metal which can be machined easily with steel tools. It must be machined under a coolant, as the metal and turnings ignite easily. It can be sawed and drilled readily, with a coolant, and can be surface-cleaned by buffing with a wire brush.

4.2 Rolling

Cerium can be cold-rolled without difficulty. The hardness increases on cold working from 60 R_M as cast to 92 R_M on 25 per cent reduction. Further reduction does not seem to increase the hardness.

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Fig. 5.1—Assembly for multiple casting of cerium rods.

A. Thermocouple Well	F. BeO Valve Plug
B. Quartz Tube	G. BeO Push Rod
C. Sillimanite Shield	H. Graphite Multiple Mold
D. Graphite Heater	I. Thermocouple Well
E. Lime or MgO Crucible	J. Graphite Push Rod
K. Insulation Brick Support	

Paper 6

Recovery of Iodine from Cerium Slag*

J. E. POWELL, CLIFFORD HACH, and R. W. NOTTORF

ABSTRACT

The recovery of iodine, used as a booster in the production of cerium metal, was investigated. Wet and dry methods of recovery are described.

* * * * *

Iodine was used in the Ames Laboratory as a booster¹ in the production of cerium metal from cerous chloride and calcium. The iodine content of the resulting slag was generally 10 to 12 per cent since half a mole of iodine was required per mole of cerous chloride for the optimum yield. The high cost of iodine warranted its recovery and it was desirable that the recovered iodine be free from moisture.

The first method of recovery attempted was a wet method. The slag, consisting largely of calcium oxide, calcium chloride, and calcium iodide along with small amounts of cerous chloride, cerium, calcium, and iron scale from the bomb, was leached with water. The water solution of calcium iodide and calcium chloride was acidified with nitric acid and treated with chlorine. The liberated iodine was recovered by decantation and filtration. Three procedures were used for drying this wet product.

The first procedure for drying iodine consisted of subliming the product down a long glass tube. The apparatus used was a 4-in. Pyrex tube, 4 ft long, closed at both ends with one-hole rubber stoppers. The wet iodine was placed in a boat at one end of the tube, and a glass wool plug was placed at the other end. The iodine was heated while air was drawn over it. Water first condensed on the inside surface of the tube just outside the furnace and was driven off by gently warming the glass with a soft flame. Iodine then sublimed and collected on the cool walls of the tube, from which it was removed from time to time. The final product was suitable for use as a booster in the reduction of cerous chloride.

In the second procedure, the wet product was steam distilled to remove occluded impurities. The moist iodine was then placed in a still and heated until the water had been driven off and pure dry iodine began to collect in the condenser. At this point the molten iodine was poured into a cool mortar for grinding. The product obtained by this procedure was also suitable for use as a booster.

*Work done at the Metallurgical Laboratory at Ames, Iowa. Prepared for publication June 19, 1945; based on Metallurgical Project Report CC-2936.

The third method involved the principle of steam distillation. The wet iodine was placed in a still and covered with carbon tetrachloride. The distillate was collected in a reservoir where the phases were allowed to separate. The heavy carbon tetrachloride phase was automatically returned to the still, while the water phase was allowed to overflow (Fig. 6.1). After the water was completely removed, the reservoir was lowered by tilting the still in order to permit the removal of the carbon tetrachloride by distillation.

The dry method for the recovery of iodine from slag consisted of oxidizing the calcium iodide in the slag with air or oxygen. Crushed slag was heated to 300 to 550°C in a steel bomb, oxygen was passed in at the bottom and the effluent gas was led through a steel pipe in the top of the bomb into a cooled flask. The iodine thus collected contained a small amount of water, which was removed by fusion of the iodine. The fusion was carried out in a flask fitted with a water-cooled condenser. Some iodine was lost with the water, but was recovered from the condenser and recycled.

Of the two types of recovery procedures discussed, the dry technique is the most advantageous, since the iodine is obtained nearly dry. The leaching of calcium slag, moreover, is rather messy due to the bulk of calcium hydroxide formed by the reaction of lime with water.

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Fig. 6.1—Apparatus for drying iodine.

- A. Wet iodine covered with carbon tetrachloride.
- B. Water-cooled condenser.
- C. Water phase of distillate.
- D. Carbon tetrachloride phase of distillate.
- E. Carbon tetrachloride return.
- F. Water overflow.
- G. Graduated cylinder for collecting overflow.

Paper 7

The Production of Beryllium by the Metallothermic Reduction of Beryllium Fluoride*

F. H. SPEDDING, H. A. WILHELM, W. H. KELLER, and CHARLES NEHER

ABSTRACT

The production of beryllium by the metallothermic reduction of its fluoride has been attempted, both in closed bombs and in open reaction chambers. Reduction of BeF_2 with Ca or Mg alone in closed bombs failed to fuse the products. The use of ZnCl_2 and PbCl_2 as boosters fused both metal and slag and resulted in separation of the metals from each other and from the slag. However, the beryllium in neither case was as free of inclusions as was desirable. Sulfur as the booster with mixtures of Ca and Mg produced clean, massive metal, but frequent burn-outs at the gasket of the bomb caused the process to be dangerous and wasteful.

The use of magnesium as the reductant was very desirable economically, and the open reaction chamber was mechanically more convenient and safer than the closed bomb. Charges of BeF_2 and Mg reacted smoothly when heated by induction in graphite crucibles and on continued heating the metal and slag separated fairly well. It was found that an addition of CaCl_2 to the top of the charge facilitated the separation a great deal. Very clean, massive metal has been produced by this procedure.

1. LITERATURE SURVEY

The production of beryllium by the metallothermic reduction of beryllium halides has been widely investigated. Wöhler¹ first produced the metal by the reduction of BeCl_2 by Ca which yielded the metal as a dark gray powder on leaching. Granular metal was also produced by reduction of BeCl_2 by sodium.^{2,3} Mixed fluorides were also reduced, K_2BeF_4 with Na by Kruss and Morath,⁴ $\text{NaF} \cdot \text{BeF}_2$ with Na by Engle and Hopkins⁵ and $\text{BeF}_2 \cdot \text{NaF}$ with Mg or Na by the Dow Chemical Company.⁶ The Brush Beryllium Company⁷ has reduced the fluoride with Mg.

The oxide has produced only low yields of impure metal on metallothermic reduction. Electrolytic methods have yielded satisfactory metal and are now in production, as at Clifton Products, Incorporated. The history of the production of beryllium by these and other methods

*Work done at the Metallurgical Laboratory at Ames, Iowa. Prepared for publication September 30, 1954; partially based on Metallurgical Project Reports CT-2953, CT-1982, and CT-1985. A declassified version of CT-2953 was issued as AECD-3315.

is fully summarized in the report by the Siemens Company on the production and applications of beryllium and its alloys.⁸

2. METALLOTHERMIC REDUCTION

2.1 Possible Reactants

In attempting production by metallothermic reduction, the fluoride of beryllium was selected for investigation because it was commercially available in quantity and because it was less hygroscopic than the chloride. Of the many possible reducing metals only Ca, Mg, Al, and Na are of interest from the point of view of availability and purity. Of these, Al alloys with Be and cannot readily be removed by vacuum distillation. The heats of formation at 298°K of the compounds involved are such that the reaction would not be expected to give the products in the liquid state without the addition of heat to the system.

2.2 Energies of Reactions

The heats of formation at 298°K of the compounds of interest in the metallothermic production of beryllium are as follows:

$\frac{1}{2}$ BeF ₂ , -118 kcal/equiv	$\frac{1}{2}$ BeCl ₂ , -56 kcal/equiv
$\frac{1}{2}$ MgF ₂ , -132 kcal/equiv	$\frac{1}{2}$ MgCl ₂ , -77 kcal/equiv
$\frac{1}{2}$ CaF ₂ , -143 kcal/equiv	$\frac{1}{2}$ CaCl ₂ , -95 kcal/equiv
$\frac{1}{3}$ AlF ₃ , -110 kcal/equiv	$\frac{1}{3}$ AlCl ₃ , -56 kcal/equiv
1 NaF, -136 kcal/equiv	1 NaCl, -98 kcal/equiv

Aluminum will not be considered for the reasons stated above. Sodium is undesirable for metallothermic work because of the mechanical difficulties of handling due to its extreme reactivity with atmospheric moisture. Calcium has the advantages over magnesium of higher heat production and less volatility, but magnesium is much cheaper. Both are available in sufficient purity.

3. CLOSED BOMB PROCEDURE

Work was begun using a bomb procedure by which cerium had been produced at Iowa State College.⁹ Sufficient heat to fuse the products and bring about the separation of metal and slag was not produced by the use of either Ca or Mg as the reducing metal with BeF₂ as the source. It was apparent that additional heat would have to be supplied. For this purpose auxiliary oxidants of boosters could be used, as was done with cerium.⁹

3.1 Iodine as Booster

The use of iodine as the booster with calcium as the reductant was first investigated. The reaction was attempted in the range of 0.05 to 0.1 moles of I₂ per mole of BeF₂. Since within these limits sufficient heat should have been produced, it appeared that slag composition, surface tensions, and other properties were responsible for the lack of agglomeration of the metal and separation of the metal and slag. Potassium chlorate and other oxysalts failed to produce separation of the beryllium, although reduction seemed to be fairly complete in all cases.

3.1 Halides of Volatile Metals as Boosters

The use of ZnCl₂ and PbCl₂ as boosters was tried. Since both of these metals are more volatile than Be they could be removed from the Be, if they formed alloys, by melting in vacuo, provided stable compounds were not formed.

The first efforts in the use of ZnCl₂ were unsuccessful;¹⁰ no separation of metal and slag

was achieved. In later attempts, however, separation of the Be, Zn, and slag into three phases was achieved, Zn appearing to be virtually insoluble in Be. The use of ZnCl_2 was investigated in the range of 0.05 to 0.1 moles of ZnCl_2 per mole of BeF_2 . Maximum yields of 50 to 70 per cent were obtained with 0.05 mole ZnCl_2 per mole BeF_2 , but the metal was not clean enough for successful casting, minute slag inclusions occurring throughout.

Lead chloride was next tried as the booster^{10,11} with results similar to those obtained with ZnCl_2 . The two metals appear to be immiscible and separate from each other and from the slag to form three phases, the heavy lead sinking to the bottom of the slag and the beryllium rising to the top. The range of 0.05 to 0.1 moles of PbCl_2 per mole of BeF_2 was investigated. Best results were obtained with 0.05 mole PbCl_2 per mole of BeF_2 , which produced yields of 50 to 80 per cent of fairly clean metal. As in the case of ZnCl_2 , sufficient slag was included to interfere with casting, and further efforts to use the metallic halides as boosters were discontinued for the time being.

3.3 Sulfur as Booster

It appeared that a volatile elementary substance which could leave no residue in the metal would be desirable as a booster. Iodine appeared to be necessary in uneconomical quantities. Sulfur, however, because of its low equivalent weight, would be required in a much smaller quantity and was much cheaper and available in any desired quantity. Heats of formation at 298°K indicated that its use would be feasible. Heats of formation of sulfides and iodides per equivalent at 298°K are as follows: $\frac{1}{2} \text{CaS}$, -57 kcal; $\frac{1}{2} \text{CaI}_2$, -64 kcal; $\frac{1}{2} \text{MgS}$, -41 kcal; $\frac{1}{2} \text{MgI}_2$, -43 kcal.

Thus only 64/127, or 0.5 kcal are obtained per gram of iodine used as booster with calcium as the reductant, while 57/16 or 3.56 kcal are obtained per gram of sulfur, or sulfur produces seven times as much heat per gram as does iodine but is less dense and so produces only three times as much heat per volume used. However, this saving of volume and consequent economy of heating of the slag, together with the cheapness and availability of sulfur, made its use very desirable.

(a) Sulfur as Booster with Ca or Mg Alone. Attempts to use Ca alone as the reductant with S as the booster resulted in reaction but no separation of the metal. Although considerable heat was produced the slag appeared to be too viscous to permit flow of the metal. In the range of 0.05 to 0.1 mole of S per mole of BeF_2 no separation occurred. Efforts to use Mg alone with sulfur as the booster indicated no reaction of Mg with S under the conditions employed and thus no booster action on the part of the sulfur.

(b) Sulfur with Mixture of Ca and Mg. It appeared that a slag of three components might be more fluid, and it was desirable to replace all or a part of the very expensive calcium by inexpensive magnesium. Experiments were begun using about 50 mole % of each reductant with 0.5 mole of S per mole of BeF_2 . Separations of Be and slag were obtained. A comprehensive investigation of the ratios of Ca, Mg, and S was made with the discovery that the ratio of Ca to Mg could be decreased, which was desirable economically, by increasing the booster ratio. Metal was obtained with Ca-Mg ratios from 50 mole % Ca, 50 mole % Mg to 20 mole % Ca, 80 mole % Mg. The booster ratio was increased from 0.5 mole of S per mole of BeF_2 in the former case to 0.75 mole of S per mole of BeF_2 in the latter case. The highest yields and best separation of metal were consistently obtained using 0.75 mole S per mole BeF_2 with 80 mole % Mg and 20 mole % Ca. (In other words, 80 per cent of the total number of moles of reductant necessary to react with both the BeF_2 and S are Mg and 20 per cent are Ca.) These ratios have been found to be the optimum regardless of the scale of reduction up to an including the 6-in. bomb. Yields of 85 to 90 per cent of relatively clean massive metal were obtained under these conditions.

(c) Conditions. The particle size of the various components was found to be significant within a range but not highly critical. Beryllium fluoride of about 100 mesh gave good results. Finer grinds than this showed no advantages whatever and only added to the difficulty of grinding and handling since BeF_2 in the finely ground state is very hygroscopic. Magnesium and Ca of 10 to 40 mesh were found very suitable. The particle size of the S is least important of all, although it should be fine enough (about 40 mesh) to mix well with the charge.

In small bombs a gas-tight seal on the bomb was not absolutely necessary, and a metal to metal seal obtained by bolting a cover to the flange on the bomb was sufficient. However, since there was considerable Mg pressure in the Be bomb at the moment of reaction, it was necessary in the 6-in. bomb to use a gasket and plumber's seal to make a tight closure. An oil-impregnated, compressed asbestos gasket known as "Durable" was found satisfactory.

The preheating temperature of the Be bomb was not critical. Good results have been obtained when the soaking pit temperature was from 1000 to 1200°F. A temperature of 1050°F was employed in the majority of shots with good results.

(d) Procedure. The procedure was similar to that employed for Ce⁹ and may be summarized as follows:

The bomb consisted of standard 4- or 6-in. pipe, with bottom of steel plate and upper companion flange welded on. It was closed by a blind flange attached by bolts and sealed by a gasket. The bomb was lined with a refractory oxide such as high-calcium lime or electrically fused dolomitic lime jolted into the bomb around a concentrically placed steel or wooden mandrel to form a wall $\frac{1}{4}$ in. thick in the 4-in. bomb and $\frac{1}{2}$ in. thick in the 6-in. bomb. The charge for the 4-in. bomb consisted of the following: BeF₂, 1080 g; S, 550 g; Mg, 785 g; Ca, 320 g.

The materials were weighed out, the BeF₂ last because it is hygroscopic, and intimately mixed. The charge was packed into the bomb with a $\frac{1}{2}$ -in. wooden dowel stick. A graphite disk $\frac{1}{2}$ in. thick was placed on top of the charge and then lime was packed tightly to the top of the bomb. Plumber's seal was spread on both sides of the gasket and the cover was bolted on. At a temperature of 1050°F in preheating, the bombs fired in about 18 min on the average. They were allowed to remain in the furnace for 2 min after firing, then withdrawn and jolted about 10 times against the floor to bring about a better separation and more compact metal. The billet of Be metal was then found on top of the slag usually coated with a light film of Mg which was removed with concentrated HNO₃ without any noticeable attack on the Be. The metal thus cleaned was ready for casting.

(e) Pressure. Possibly due to sudden vaporization of Mg at the high temperature produced by the very rapid Ca-S reaction a much higher pressure is developed in the BeF₂-Ca-Mg-S bomb reaction than in any of the others investigated. As a result several of the bombs burned through at the gasket with explosive violence, and the greatest care in the application of the gasket and cover failed to prevent such burn-outs in some cases. For this reason further investigation of the reaction was suspended in order that open chamber procedures might be investigated.

4. REDUCTION IN OPEN CHAMBER

The production of beryllium by the reduction of BeF₂ by Ca or Mg in an open chamber heated in the induction furnace appeared feasible. It was first necessary to determine a suitable refractory from which to build the reaction chamber.

4.1 Reaction Chamber

Crucibles made of BeO and sintered at about 1950°C were first tried. This material proved to be almost ideal since it withstood the thermal shock well and showed little or no reactivity toward any of the components of the reaction. However, the cost of this material and the work necessary for its fabrication made its use undesirable. Other refractories tried were sintered CaO, MgO, and Al₂O₃. None of these proved satisfactory for various reasons—thermal cracking, reaction with materials used in the reduction, etc. In every case, the heating procedures were the same, namely, electrical induction heating using a graphite element as the heater.

When Be metal is heated to its melting point in a graphite crucible, there is a considerable and fairly vigorous reaction between the metal and the graphite, with the formation of Be₂C. However, under proper conditions, graphite has been found a suitable material in which to carry out the reduction because the metallic Be formed has a strong surface tension which tends

to pull it together in globules which migrate to the top center of the charge, thus effectively preventing extensive contact between the metal and graphite. At the final temperature of the reduction there is evidence of some reaction between the slag and the graphite, but if the heating rate is properly controlled this is not excessive.

4.2 Post-Heating

The reaction

is not sufficiently exothermic to produce a temperature great enough to melt the Be metal and the slag formed without a booster or additional heating. A volatile booster cannot be used in the open chamber procedure but a "post heating period" can be employed to bring about agglomeration of the metal and fusion of the slag, permitting separation.

Observations have shown that when finely ground BeF_2 and Mg are intimately mixed and heated, the reaction begins at about 700°C and increases rapidly to about 1000°C . It is then necessary to continue heating until a final temperature of 1350 to 1400°C is reached. This requires considerable time since at a temperature of about 1100°C unused Mg is boiled off and a thermostating effect is produced. There is considerable difficulty in determining when the final temperature has been reached. Cutting off the power and allowing the Mg vapors to subside permits a fairly accurate reading with the optical pyrometer. If the heating rate is carefully controlled, the length of time of heating for a specific size charge can easily be determined by experiment and repeated quite consistently.

4.3 Conditions

The particle sizes of the BeF_2 and the reductants (whether Mg or a mixture of Mg and Ca) are important. If the particle sizes are too large, considerable sputtering and spewing occurs when the reaction starts. Best results have been obtained when the BeF_2 is crushed to approximately 5 to 10 mesh and the Mg and Ca to 10 to 40 mesh. Finer grinds than this give no advantage and only add to the difficulty of processing and handling.

The reduction of BeF_2 with Mg alone presents some difficulties. The main one is that MgF_2 slag formed has a very high melting point—about 1400°C . Thus it requires longer heating to effect separation and some of the Be metal is lost by a reversal of the reaction at this high temperature. Since slag consisting of 42 mole % CaF_2 and 58 mole % MgF_2 constitutes a eutectic mixture melting at 950°C , the use of these mixed reductants in the above ratio has given good results. It has also been found that Mg can be used alone quite successfully if a considerable amount of desiccator grade of CaCl_2 is packed on top of the charge as a flux. This layer of CaCl_2 prevents oxidation of the materials while they are being heated to the reaction temperature, and since it has little tendency to mix with the MgF_2 slag, it provides a very good medium on top of the charge in which the Be metal can agglomerate.

4.4 Equipment and Charge

The equipment used is described and a typical charge given as follows:

Crucible: graphite, 5-in. inside diameter, 13-in. outside length, $\frac{1}{4}$ -in. wall thickness and $\frac{1}{2}$ -in. bottom thickness. Cover to fit is $\frac{1}{4}$ in. thick with a $1\frac{1}{2}$ -in. hole in the center.

Quartz tube: $8\frac{1}{4}$ -in. inside diameter, 20 in. long. A graphite heater with $\frac{1}{8}$ -in. walls and bottom and of suitable dimensions to allow free insertion of the graphite crucible is placed in the center of the quartz tube and insulated with "Norblack."

Induction coil: 9-in. inside diameter with 20 turns per foot; 16 in. of the coil are used.

Charge (using all Mg): BeF_2 , 5 lb (5 to 10 mesh); Mg, 2.6 lb (10 to 40 mesh).

Charge (using 42 mole % Ca and 58 mole % Mg): BeF_2 , 5 lb (5 to 10 mesh); Ca, 1.8 lb (10 to 40 mesh); Mg, 1.35 lb (10 to 40 mesh).

4.5 Procedure. (Described for reduction with Mg alone. Procedure for using mixed reductants is identical.)

The BeF_2 and Mg are weighed out, intimately mixed, and packed tightly into the graphite crucible using a $\frac{1}{2}$ -in. wooden dowel stick. Firm packing of the charge is essential for a smooth reaction. The charge is then covered to the top of the crucible with desiccator grade CaCl_2 , usually about a 2-in. layer. The cover is put on and the crucible is placed in the graphite heater. Porous bricks cut to fit the quartz tube, with $1\frac{1}{2}$ -in. holes in the centers to coincide with those in the crucible lid, are placed on top for insulation. The whole assembly should be so placed that it can be shielded and is near an air duct to remove the fumes, which are very irritating and highly toxic.

Power is turned on to 12.5 kw on the 30 kv amp Ajax Converter. At this rate the reaction begins in 23 to 25 min, as evidenced by glowing of the charge in the crucible, and about 15 min later considerable Mg fumes begin to come off. Heating is continued at the same rate until a total heating time of 80 to 85 min has elapsed. In the later stages of heating it may be necessary occasionally to remove the cone of MgO that builds up over the center hole of the crucible cover. This can be done by cutting off the power for a minute and breaking away the cone of oxide with a suitable instrument.

After cooling, the crucible is removed from the heater and broken to recover the metal, which is cleaned by leaching in hot water and by sand blasting. The cleaned metal is then ready for remelting or casting.

5. PURITY

The purity of the beryllium produced by these procedures is a function of the purity of the reagents as no significant contaminants are introduced during the reactions.

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Paper 8

The Extrusion of Beryllium*

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ABSTRACT

A method for the extrusion of beryllium into rods and tubing has been developed. The operation is carried out between 1500 and 1900°F and the billet is clad in a layer of soft iron to prevent contact between it and the die steels. Extruded beryllium has much more strength and ductility than cast metal due to the crystal refinement which occurs as a result of the fabrication operation.

* * * * *

The early investigators of beryllium have all agreed that the metal is extremely brittle and that the elongation in tension, for example, is less than 0.1 per cent. Most of these results were obtained on cast specimens since almost all efforts at large-scale fabrication of the material had led to failure. There is one reference in the literature to a successful forging¹ of beryllium (which never could be repeated) and the ductility of this sample after annealing was given as 0.0 per cent elongation in 4 in. Small pieces of beryllium have been satisfactorily rolled by a special technique but the samples were too small to allow physical tests to be made on them.^{2,3} The cast metal is characterized by extremely large crystals and this undoubtedly contributes to the lack of ductility. There have been numerous attempts at purifying the beryllium, but these have given no promising results since there is no apparent increase in ductility with decrease of impurities, and even metal which is alleged to be 99.9 per cent Be is still brittle. Some investigators believe there is a possibility that minute amounts of certain elements such as oxygen could cause the brittleness, but all recent attempts to follow this line of attack or even to determine the oxygen content of the metal have accomplished very little.

An unsuccessful attempt was made to extrude beryllium in June of 1943 at the Battelle Memorial Institute.⁴ The work was carried out with a 1¼-in. diameter billet and a highly heated die and container. The available press did not give sufficient force for extrusion at 1800 and 2150°F, and at 2300°F the steel container expanded without any appreciable amount of beryllium having come through the aperture. On the basis of these results, it was concluded that with present-day steels the extrusion of beryllium would not be possible.

*Work done at the Metallurgical Laboratory at the Massachusetts Institute of Technology, Cambridge, Mass. Paper written by A. R. Kaufmann. Prepared for publication January, 1946, and issued as AECD-2883 (ANL-HDY-675).

The next attempts to extrude beryllium were carried out between May and November of 1944 under the direction of E. C. Creutz⁵ of the Metallurgical Laboratory, University of Chicago. The work was done on the 680-ton vertical press of the Wolverine Tube Division of Calumet & Hecla Consolidated Copper Co., Detroit, Michigan, using thin shells of graphite around the billet as a "lubricant." Both 2- and 4½-in. diameter billets were pushed through the dies at about 2000 to 2100°F and in a number of instances fairly satisfactory rods were obtained, as well as some tubing of 1-in. I.D. and 1⅜-in. O.D. The general technique consisted of using a hardened and polished die of high-speed steel with a conical surface leading to the aperture and with the extrusion ram pointed to conform to the cone in the die. Some work was done to determine the best shape for the cone and it was concluded that flat dies or cones with an included angle of more than 160° were not satisfactory, while 120° and 90° dies gave good results. All of the billets used in this work were flat at both ends. These billets were placed inside a 0.020-in. thick graphite shell and were then heated to the extrusion temperature while inside a heavy graphite crucible which prevented oxidation. After heating, the billet and thin graphite shell were dropped into the container of the press. An effort was made to preheat the container and die by means of a gas fire around the container and by a preliminary extrusion of brass. However, the actual temperature of the die was indefinite and was certainly below 500°C. Before each extrusion the container and die were swabbed with a mixture of heavy oil and powdered graphite with the hope that this would do some good. In the extrusion itself the motion of the ram was fairly rapid with not more than about 2 sec being required to expel a 4- to 6-in. long billet. In general, all of these techniques, with the exception of the thin graphite shell around the billet, were about the same as those used by the Wolverine Company to extrude brass and copper. It seems likely that the use of this shell is what made the process at all possible since it partially prevented alloying and sticking between the billet and the die.

The extruded rods produced with the use of a graphite "lubricant" were characterized by a rough and fibrous looking surface. In addition the occurrence of the "rattlesnake" or "Christmas tree" type of defect was quite frequent and erratic so that the production of good material seemed almost a matter of chance. Part of these difficulties probably could be attributed to the inferior billets which were the only material available at that time. Even with good billets, however, it hardly seems likely that the use of a graphite shell would have given consistently good results when a large number of billets were pushed through the same die. The tensile properties of beryllium extruded in this way will be described in Sec. 4.

The next work on extrusion of beryllium was started in February, 1945, on the 100-ton press available at the Metallurgical Laboratory of the University of Chicago.⁶ A number of specimens ¾ in. in diameter by 2 in. long were covered on the bottom and side with a layer of copper 30 mils thick and extruded into ½-in. and ¼-in. rods at temperatures between 1100 and 1800°F. The dies were conical with a 60° included angle. This work met with considerable success and it was concluded that the use of a copper layer around the billet prevented scoring and charging of the die and had no objectionable effect on the beryllium itself.

On the basis of this work an extrusion operation was carried out on March 14, 1945, at the Wolverine Plant using both 2-in. and 4-in. diameter billets. These billets were all made at MIT using a vacuum melting and casting technique which yielded sound metal free of blow holes and cracks. The large billets were encased in a ⅜-in. shell of copper on the side and bottom while the smaller ones had a ⅜-in. shell on the side only. All of the billets were flat at each end. The details of the extrusion operation were about the same as described above for the earlier work at Wolverine including the use of a 120° conical die. It was discovered that there was a considerable amount of alloying between the beryllium and copper with the formation of a liquid phase which dripped off the extruded rods. This alloying was particularly bad at 1650°F on ¼-in. diameter bars and appeared to be less serious at about 1500°F. Attempts to make 1-in. rods from the 4-in. billets at about 1550°F led to only partial extrusion before the press stalled, while the extrusion of a 2¼ × ½ in. flat through a shear die at 1550°F stalled the press completely. Two attempts were made to produce 2-in. O.D. × ⅝-in. I.D. tubes from drilled billets lined with copper inside and out, and the resulting material was so badly split and deformed as to be worthless. The 2-in. diameter billets were successfully extruded to ½-in. diameter bars at temperatures of about 1400°F and in two cases at 1250°F without serious alloying with the

copper jacket. These specimens contained various alloying elements in amounts up to 1 per cent by weight, none of which appeared to have any effect on the extrusion properties.

Examination of the rods extruded from the 4-in. billets revealed the presence of deep longitudinal cracks in almost all cases. It was concluded that these were formed by splitting of the square end billet by the pointed ram during the early stages of the extrusion and that these cracks then filled with copper. This condition was more serious than the surface alloying with copper but it was felt that both problems needed to be solved.

During the month of March, 1945, further extrusions on the 100-ton laboratory press were made with 60, 90, and 120° conical dies at temperatures between 1500 and 1800°F using 30- and 5-mil copper jackets. Some alloying with the copper was noted but not nearly to the extent that it occurred on the 4-in. billet extrusions. A number of bare beryllium billets were extruded at 1100°C with good results except for a progressive charging of the die.

The next extrusion at the Wolverine Plant took place on April 12, 1945, and this operation was intended primarily to convert 2-in. billets to $\frac{3}{8}$ - and $\frac{5}{8}$ -in. diameter rods. This was carried out satisfactorily at 1500°F using a 30-mil copper jacket. Four of the 4-in. billets were extruded into $1\frac{1}{8}$ -in. rods in order to study methods of overcoming the previously noted difficulties. Two of these were encased in 20-mil graphite and extruded at 2100 and 1950°F, respectively. Both of the rods were seriously "rattlesnaked" along almost the entire length. It was later discovered that in all probability the thin graphite shells did not follow the billet into the press so that these were bare beryllium extrusions. The remaining two billets had 30-mil copper jackets and each was put into the press at about 1500°F. In both cases the press stalled. This indicated that higher temperatures would be needed to carry out the extrusion.

Operations on the 100-ton press were continued during April, 1945, still using copper jacketed or bare billets. It was found that a copper layer less than 10 mils thick was unsatisfactory, while for the bare billets, it was observed that neither silicone, powdered graphite, nor pipe lubricant was successful in preventing charging of the dies.

The next extrusion at the Wolverine Plant took place on May 18, 1945. This time a 30° cone was machined into the back end of the $4\frac{1}{2}$ -in. billets to accommodate the pointed ram. It was hoped that this precaution would reduce the tendency for splitting of the billets which actually turned out to be the case. In an effort to avoid alloying with the jacket metal, the billet cans were prepared from a number of materials including low carbon steel, monel, nickel, and copper with a 5-mil layer of iron on the inside. The latter composite can was prepared at the last minute because some work on the 100-ton press a few days earlier had indicated that an iron can would extrude satisfactorily although a somewhat larger force was required than when a copper can was used. All of these cans were $\frac{1}{16}$ in. thick and they covered the bottom and side of the billets. A number of $4\frac{1}{2}$ -in. diameter billets were extruded to $1\frac{1}{4}$ -in. rod at 1830°F and it was observed that the iron can give the most satisfactory results. No greater force was required to extrude these large billets with an iron can than when copper lined with 5 mils of iron was used as the can, and in the latter case there still was some alloying with the copper. The nickel and monel covered rods were badly "rattlesnaked" and it is believed that this was due to the greater stiffness of these materials at the extrusion temperature. None of the cans other than that of copper showed any appreciable alloying with the beryllium.

In addition to the extrusion of rods there have been several attempts to produce tubing and flat stock on the Wolverine press. Each of these operations was carried out using the $\frac{1}{16}$ in. thick iron jacket and for the production of tubes the drilled hole in the billet was also lined with iron. The arrangement of die and mandrel for tube work is shown in Fig. 8.2. Tubes of 2-in. O.D. and $1\frac{1}{2}$ -in. I.D. have been successfully made. A $\frac{1}{2} \times 3$ in. flat was extruded through a shear die but without a satisfactory flow of the iron jacket. Two attempts to make flat stock with dies of a conical shape led to failure due to splitting of the dies.

The use of $\frac{1}{16}$ -in. thick iron cans on $4\frac{1}{2}$ -in. billets has become standard practice for the extrusion of beryllium rods on the Wolverine press. The billets for rod production are prepared with a 30° point to correspond to the 120° included angle conical die and have a 20° cone machined into the back end to accommodate the pointed ram. Billets of 2-in. diameter usually have a $\frac{1}{32}$ -in. thick iron can and are flat at each end. The large billets are extruded at about 1800°F but this temperature is not at all critical as far as the metal itself is concerned. Lower

temperatures down to 1400°F would be possible if the press had sufficient power and such extrusions have actually been made with 2-in. diameter billets. The types of dies used and the arrangements of these in the extrusion press are shown in Figs. 8.1 to 8.3. A noteworthy feature of this arrangement is the automatic centering of the die in the container. This centering allows the iron jacket to flow uniformly over the surface of the die and to emerge as a continuous jacket on the extruded rod. This flow of the iron is shown in the sectioned extrusion butt shown in Fig. 8.4. The remaining details of the extrusion operation such as billet heating, die lubrication, container heating, and rate of extrusion are closely similar to the description given above of the earlier extrusion work by Creutz.

In June, 1945, an experimental extrusion of beryllium was carried out at the Detroit plant of the Revere Copper and Brass Company. This work was done on an 1100-ton horizontal press using a flat-faced die which was held against the exit end of the container, and a dummy block which was between the billet and the ram. The die was preheated to 800°F before being placed in the machine and the container was given an indefinite heating to perhaps 500 to 800°F by means of a gas flame. The billets, which were 4.33 in. in diameter by 8 in. long were flat at both ends, and had an iron jacket $\frac{1}{16}$ in. thick on the sides and bottom. Heating was carried out in a muffle furnace with the billets inside of graphite shells to prevent oxidation. In general this technique was the same as that used at Wolverine except for the difference in die shape and in the method of holding the die in the machine.

At this operation four billets were extruded at 1800°F, each one through a differently shaped die. Three of the dies had a round hole and varied in the amount of radius leading to the aperture and the fourth had a $\frac{1}{2} \times 3$ in. rectangular opening with about a $\frac{5}{8}$ -in. radius bell mouth at the entrance. The rods which were produced had a rough surface due to a poor flow of the iron jacket but it was apparent that this difficulty became less as the radius of the bell mouth became greater. The flat bar was fairly well covered with iron since it had a large bell mouth radius.

On the basis of these results it was decided to make up new dies with bell mouth radii of $\frac{3}{4}$ in. and $1\frac{1}{8}$ in. and also a die with a 120° cone leading from the container walls to the hole. Drawings of these dies and of a $\frac{1}{2} \times 4$ in. rectangle die are shown in Figs. 8.5 to 8.8. It was hoped that observation of extrusion pressures for the various dies as well as a study of the rods produced would indicate which type of die gave the best results.

The new dies were tested with a large-scale extrusion of about 2 dozen billets heated to 1800°F and it was found that the extrusion pressure readings were too erratic to give significant differences for the various shapes of die. The two shapes of bell-mouthed die both gave fairly good rods, but the conical die produced badly "rattlesnaked" material. It was observed that with both round and flat stock the surface became progressively rougher as successive billets were pushed through a given die and that this difficulty was due to material which built up on the surface of the die. An attempt was made to extrude a $1\frac{1}{16}$ -in. diameter rod at a series of temperatures below 1800°F, but this was successful only at about 1620°F since the press stalled when the billet temperature was dropped to 1400°F.

Examination of the extruded stock and the extrusion butts revealed that the die charging occurred because the iron jacket on the billet was not flowing continuously over the flat die face and into the aperture. Instead the iron preferred to follow the flow lines from higher up in the billet and this led to the formation of a beryllium pocket at the periphery of the die which was able to feed in slowly and form a layer of beryllium between the iron jacket and the die. This behavior is shown by the photographs of sectioned butts which are given in Figs. 8.9 and 8.10. A similar section of a Wolverine butt, Fig. 8.4, shows that the iron flow can be quite satisfactory with a 120° conical die. Two other conditions were observed which contributed to the poor flow of iron. These were the development of a heavy flash at the interface between container and die and the eccentric alignment of the die and container axes. The poor behavior of the 120° die in the Revere press is at least partially due to these latter causes.

The use of flat-faced dies with a bell mouth appears to be necessary for the production of flat stock, since conical dies for this purpose are prone to cracking. Therefore, it was felt that further experimentation on flat dies to overcome the formation of a beryllium pocket at the periphery was desirable. For this purpose an extrusion was carried out using soft iron (SAE

1020) disks or cones $\frac{3}{4}$ in. thick at the bottom of the billet inside the cans as shown in Fig. 8.11. This iron was to fill the dead space at the periphery and prevent the beryllium from getting outside the iron jacket on the rod. A number of rods and some flat stock were produced by this method at 1800°F and it was apparent that the iron jackets on the rods were much more continuous than before. There was some slight charging of the dies, however. Examination of the butts showed that the flow of iron was quite satisfactory (Fig. 8.12) although occasionally some beryllium still was trapped at the periphery of the die (Fig. 8.13). It is thought that the use of more iron at the front of the billet or the elimination of the flash, which consumes iron, would further reduce this difficulty. The use of a stiffer metal, such as stainless steel, for the disks or cones probably also would be helpful. The butt obtained on a 120° cone die using an iron cone at the front of the billet is shown in Fig. 8.14.

It is apparent that the iron flow was very satisfactory and it seems likely that the flash shown here did not develop until the end of the operation. The rod produced with this die was slightly "rattlesnaked" but this is probably due to some detail of the die design rather than to poor iron flow.

The extrusion of round or flat stock through bell-mouthed dies at Revere is in a fairly satisfactory state when using the technique described above and further experimentation combined with elimination of the flash should lead to a solution of all the difficulties.

1. EXTRUSION OF FLAKE BERYLLIUM

The electrolytic flake beryllium produced by the Clifton Products Company has been shaped into sound metal by extruding it in the usual way at both Wolverine and Revere. The technique is to compact the metal in the $\frac{1}{16}$ -in. thick iron cans at a pressure of about 15 tons in⁻² and then weld a cover on the open end. The density of the compact is about 70 per cent of the theoretical and hence there is a further compacting of the metal in the initial stages of extrusion. The extruded stock is about as strong and dense as that made from melted metal but there are subtle differences in such properties as grain structure and corrosion resistance.

2. EXTRUSION PRESSURES

The beryllium extrusion operations which have been carried out on commercial presses have not been extensive enough to allow the accumulation of systematic data on extrusion pressures as a function of temperature, velocity of extrusion, or die shape. Pressure readings have been taken, however, and the results should be of interest in indicating the order of magnitude as compared with the values for other metals. The results for a number of sizes of rod are shown in Table 8.1 both for the work at Wolverine and at Revere. The basis for comparison is the pressure on the billet divided by the natural logarithm of the ratio of billet to rod area as shown in the last column. The reason for the great discrepancy between values obtained at the two companies is not known. It does not seem to be a question of cone dies at Wolverine as compared with bell-mouthed dies at Revere since the former type give the largest values at Revere. Representative values obtained on 70-30 brass⁷ at the extrusion temperature of 800°C are about 16,000 to 18,000 lb in⁻². When extruding compacted flake metal the starting pressure is low but it builds up to the usual value during the actual extrusion.

The use of soft iron disks or cones at the front of the billet does not seem to increase the extrusion pressure very greatly over that needed on normally jacketed billets. The solid disks seem to lead to a somewhat greater pressure than the cones but the evidence is not conclusive.

3. QUALITY OF EXTRUDED BERYLLIUM

Because of the brittleness of beryllium there is a great tendency for the extruded bar stock to have cracks which are usually longitudinal. This difficulty has been gradually overcome so that at the present time at least 95 per cent of the extruded bars made at Revere are sound. In

Table 8.1—Extrusion Pressure Data for Beryllium on Commercial Presses

Wolverine Press, 24-in. ram, 4.62-in. container, 8-in. long billet

Temperature, °F	Rod size, in.	Type die	Water pressure, lb in ⁻²	Pressure on billet, lb in ⁻²	$\frac{A}{a}$	$\frac{A}{\ln a}$	$\frac{P^*}{\ln \frac{A}{a}}$
1830	1 $\frac{1}{8}$	30° cone	2300	62,000	16.8	2.82	22,000
1650	1 $\frac{1}{8}$	30° cone	2700	73,000	16.8	2.82	26,000
1800	$\frac{1}{2} \times 3$ round ends	shear	2400	65,000	14.2	2.65	23,500
1830	2	30° cone	1100	30,000	5.3	1.67	18,000

Revere Press, 26-in. ram, 4.62-in. container, 8-in. long billet

1880	1 $\frac{1}{16}$	1 $\frac{1}{8}$ -in. radius bell mouthed	2800	89,000	18.8	2.93	30,000
1900	1 $\frac{1}{16}$	30° cone	3600	114,000	18.8	2.93	39,000
1620	1 $\frac{1}{16}$	1 $\frac{1}{8}$ -in. bell	4000	126,000	18.8	2.93	43,000
1870	$\frac{1}{2} \times 4$	bell mouth	2700	86,000	8.4	2.13	40,000
1890	$\frac{1}{2} \times 3$	bell mouth	2900	92,000	10.2	2.32	39,500
1780†	1 $\frac{1}{8}$	$\frac{3}{4}$ -in. radius bell	3000	95,000	16.8	2.82	33,500
1780†	1 $\frac{3}{16}$	$\frac{3}{4}$ -in. radius bell	2700	89,000	15.1	2.71	33,000
1810†	1 $\times$ 4	bell mouth	1300	41,000	4.2	1.43	29,000

*Extrusion Pressure = $\frac{P}{\ln \frac{A}{a}}$, where P = pressure on billet, A = container area, a = rod area.

†Soft iron cone on billet.

spite of this improvement, however, it is still desirable to inspect all of the material that is produced.

A large part of the difficulty with longitudinal cracks is probably due to the presence of radial cracks in the cast billet. Proper casting technique and careful radiographic inspection of the billets from a number of angles are necessary in order to have good starting material for extrusion.⁸ The use of a pointed ram, such as is employed at Wolverine, tends to split the billet in the early stages of extrusion and the machining of an inverted cone into the back of the billet relieves this condition only partially. At Revere almost no trouble with cracking of the billet is encountered when using the flat ram.

The extrusions at Revere are stopped when about a 1-in. thick butt still remains, but at Wolverine practically all the metal is forced through the die. This difference in practice results in about a 2-ft extrusion defect at the back of the bar in the latter case, while sound material is found all the way up to the butt in the former. The amount of lost material is roughly the same in each case.

The presence of longitudinal cracks in extruded beryllium cannot always be revealed by direct inspection of even a polished section of the bar. A deep etch in 5 per cent sulphuric acid by weight for one-half hour will make any minute cracks easily visible. The results of this technique are illustrated in the macrographs shown in Fig. 8.15.

The iron jacket on a round rod will be thinner than the jacket on the billet by the ratio of the diameters of bar to billet if the iron flow is uniform throughout. This actually occurs when a cone die is used, but with flat-faced dies the iron jacket becomes progressively thinner to-

ward the back of the bar. When using an iron disk or cone at the front of a billet, the iron jacket is quite thick at first but reduces to about $\frac{1}{32}$ in. after the first foot. The beryllium is apparently harder than iron at the extrusion temperature and hence the interface between the two metals is usually quite irregular as shown in Fig. 8.15. The surface of the beryllium rod becomes smoother as the thickness of the iron jacket is decreased. Due to the serrated surface of the rods and to the presence of micro defects just below this surface, it is necessary to machine about $\frac{1}{16}$ in. off the radius of the rough bars (including iron) to get to really sound metal.

4. PHYSICAL PROPERTIES OF EXTRUDED BERYLLIUM

A general survey of the properties of beryllium including extruded metal has been reported.⁹ It seems worthwhile, however, to summarize the results of tensile tests which illustrate the beneficial effects of extrusion. The first work of this kind was carried out by Creutz¹⁰ who showed that the tensile strength increased progressively as the reduction of area by extrusion became greater. For example, cast beryllium had a tensile strength of about 25,000 lbs in⁻² with zero elongation while after 16 and 64 times reduction in area at about 2000°F the strength was about 42,000 and 53,000 lbs in⁻², respectively, with elongations up to 0.9 per cent. A few scattered attempts at annealing indicated that the tensile properties were always decreased by such treatment. A more extensive investigation was carried out at MIT¹¹ on beryllium and on binary alloys of beryllium with about 1 wt. % of Ti, Zr, Ce, Ca, and Al. This material was extruded at about 1400°F with a reduction of 16 times in area. The metal was in a cold worked condition after extrusion and had tensile strengths between 40,000 and 50,000 lbs in⁻² with elongations at fracture between 0.1 to 0.4 per cent. The aluminum alloy had the best properties, while the other alloys showed no obvious superiority over the pure beryllium. Annealing at about 700 to 750°C led to no great change in tensile strength but did increase the elongation at fracture up to about 2 to 2.7 per cent with the pure beryllium showing up better than most of the alloys. This is the greatest amount of ductility so far observed in beryllium. The annealed specimens exhibited a definite yield point between 25,000 and 30,000 lbs in⁻².

It is believed that the improvement in tensile properties as a result of extrusion is due to grain refinement and also to a preferred orientation which has been shown to exist by means of x-ray studies. Recent investigations have shown that in extruded flat stock the strength perpendicular to the direction of extrusion is only about one-third as great as in the parallel direction. It is not known as yet whether this directionality can be removed by annealing. In any case where fabricated beryllium is to be used as a structural member, the possibility of extremely poor physical properties perpendicular to the direction of working should be kept in mind.

5. CONCLUSION

The extrusion of beryllium into round or rectangular shapes or into tubing can be accomplished on a commercial scale and the resulting material is sound and slightly ductile.

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Fig. 8.1—Wolverine extrusion assembly, 4½-in. billets, rod.

Fig. 8.1a—Wolverine extrusion assembly, 2-in. billets, rod.

Fig. 8.2—Wolverine extrusion assembly, 4½-in. billets, tube.

Fig. 8.2a—Wolverine extrusion assembly, 2-in. billets, tube.

Fig. 8.3—Wolverine extrusion dies.

Fig. 8.4—Butt from Wolverine extrusion. The ragged hole at the center occurs where the rod was punched from the butt.

Fig. 8.5— $\frac{3}{4}$ -in. radius bell-mouth die for Revere press.

Fig. 8.6— $1\frac{1}{8}$ -in. radius bell-mouth die for Revere press.

Fig. 8.7—120° cone die for Revere press.

Fig. 8.8—Slab die for Revere press.

Fig. 8.9—Butt from $1\frac{1}{16}$ -in. round bar showing Be pocket.

Fig. 8.10—Butt from $\frac{1}{2} \times 4$ in. flat showing Be pocket.

EXTRUSION ASSEMBLIES 1/2 of Jacket Removed

Type 1 - Flat Plug.

Type 2 - Taper Plug

Note:
All billets are
4.330" diameter.
Leading end and
sides are jacketed
with 1/16" S.A.E.
1020 steel plugs
are S.A.E. 1020.

Fig. 8.11—Billet assemblies showing soft iron nose at front end.

Fig. 8.12 — Butt from 1 x 4 in. flat using iron cone at front of billet.

Fig. 8.13 — Butt from $1\frac{1}{8}$ -in. round bar using soft iron cone on billet.

Fig. 8.14—Butt from $1\frac{1}{8}$ -in. round bar using soft iron nose. The flash probably developed at the end of the extrusion.

As polished

After deep acid polish

Fig. 8.15—Cross-sections of extruded bars before and after etch inspection. The bar on the left is sound, the one in the middle shows a fine crack, while the one on the right has a big defect.

Paper 9

Production of Beryllium Metal Ingots for Extrusion*

C. B. SAWYER and C. H. TOWER

ABSTRACT

Beryllium oxide crucibles were found satisfactory for the reduction of beryllium fluoride with magnesium. The metal was degassed with anhydrous sodium sulfide in an atmosphere of argon. A furnace and technique were developed for melting, pouring, and cooling the metal in a vacuum. Two centrifugal casting machines were also constructed, one for vertical and one for horizontal castings. Good quality castings are produced by centrifugal casting, but the purity of metal is not as high and its mechanical characteristics are not as good as those of metal produced by vacuum casting. However, more intricate pieces may be cast by the centrifugal method. The metal produced by both methods is superior to air-cast metal.

* * * * *

The purpose of this work was to produce sound, high-density beryllium ingots suitable for extrusion and machining. All the beryllium used in this work was made by reducing beryllium fluoride (BeF_2) with magnesium. (U.S. Patent No. 2,381,291.) At the time this work was undertaken, it had been demonstrated that by proper fusing with beryllium fluoride, flux billets could be produced which could be swaged. It was known that undesirable compounds of beryllium with carbon, nitrogen, and oxygen were formed under some conditions. These compounds were very stable or highly refractory and constituted undesirable impurities which were difficult to eliminate. Hydrogen also appeared as an undesirable constituent under some conditions.

In 1939 Sawyer and Kjellgren¹ had cast a billet 0.62 in. in diameter which was swaged down to a rod 0.36 in. in diameter and 40 in. long. It had also been observed that vacuum melting and solidification of beryllium resulted in a metal which was superior in quality both as to soundness and resistance to cracking and had a high density and purity.

In the early work graphite crucibles were used for melting. This tended to introduce slight amounts of impurities from the graphite crucible into the metal and to form beryllium carbide (sometimes with a violent exothermic reaction). To overcome this, the later work employed beryllium oxide crucibles produced by tamping and firing at a little over 1500°C. These

* Contribution from The Brush Beryllium Company, Cleveland, Ohio. Prepared for publication June 30, 1946. (M-4516)

crucibles would stand thermal shock and were quite satisfactory for melting beryllium. A 20 kw Ajax Northrup sparkgap furnace was used for this at a frequency of about 15,000 cycles. The heating element consisted of a graphite sleeve around the beryllium oxide crucible containing the metal. Under these conditions the stirring action of the high-frequency currents in the metal was negligible and the melt was therefore stirred briefly at intervals with a beryllium or graphite rod to insure mixing and to detect unmelted lumps in the metal.

Further improvements were introduced by degassing the metal with anhydrous sodium sulfide and surrounding the top of the melt by an atmosphere of argon gas to prevent oxidation of the metal by the outside atmosphere. In using the sodium sulfide the usual procedure was to place a small piece (about 1 g) in the bottom of the crucible before heating and then to add similar small pieces whenever more metal was added. It was necessary for good results to use CP sodium sulfide free from moisture. If the sulfide were not completely anhydrous little or no improvement was obtained. Under these conditions the sodium sulfide degasified the metal quite thoroughly and reduced the magnesium content. Finely divided sulfur added to the melt in place of sodium sulfide also produced good results. Bubbling chlorine gas through the melt was also tried and made some improvement in the metal. The aluminum content was reduced, the silica content remained unchanged and there was a tendency for the iron content to increase probably because of impurities in the graphite tube used to introduce the chlorine into the melt.

A further improvement in the quality of the metal was made by melting, pouring, and cooling in a vacuum. A special furnace and technique were developed for this work.

A furnace was constructed which consists essentially of a quartz tube closed at one end and having a water-cooled cover clamped to the other end. A window of quartz or heat-resistant glass in the cover permits observation of the melt and reading the temperature by an optical pyrometer. The beryllium oxide crucible in the lower part of the tube, held in place and separated from the walls by packed insulation, has a capacity of about two kilograms of melted beryllium. A graphite sleeve about $\frac{5}{16}$ in. thick and 9 in. long, fitting rather closely around the crucible, provides the heating element. The mold, usually of graphite, is positioned on top of the crucible and held in place by a shoulder engaging the crucible and a steel pin in the mold bottom engaging the water-cooled cover. A sight hole drilled through the mold at one side but in line with the window in the cover permits observation of the metal in the crucible. The high-frequency coil is outside the quartz tube. One advantage of having the mold above the crucible and in close contact with it is that during the operation of the furnace the heat radiated from the molten metal in the crucible preheats the graphite mold for casting. Furthermore, the vacuum acts on both the molten metal and the heated mold, giving a strong degasifying action.

The whole assembly is mounted on trunnions so that the furnace may be rotated through 180° to bring the crucible on top and the mold on the bottom. Flexible connections are provided for the electrical power supply, the water supply, and to the vacuum pump. Figs. 9.1 and 9.2 illustrate this furnace.

The operation of the furnace is as follows: The beryllium to be used in the furnace is first premelted with sodium sulfide under an argon atmosphere and after being melted, is usually allowed to cool in the melting crucible. The crucible is about $3\frac{1}{2}$ in. I.D. and $8\frac{1}{2}$ in. deep and the resulting beryllium slug will just fit the crucible in the vacuum furnace. The metal may, however, be cast in graphite molds of suitable size which is advantageous when several castings are to be made.

The slug is placed in the crucible of the vacuum furnace and the graphite mold positioned on top of the crucible and the water-cooled cover clamped on.

The air pump is now started and when a vacuum of one millimeter of mercury or better is obtained, the high-frequency furnace is started with the pump still running. Sufficient electrical power is supplied to the high frequency coil to heat up the crucible and melt the beryllium in about 30 to 60 min. The temperature of the melt is then raised slowly to 1500°C and held there for a few minutes while the entire furnace is rotated back and forth slightly on its trunnions to agitate the metal.

At the moment of fusion a violent evolution of vapor and the ejection of small particles of metal takes place. When the surface of the liquid metal is smooth and without indication of bubbles, the power is reduced; when the temperature of the melt has reached about 1400°C, the power is shut off; the metal is poured from the crucible into the mold by slowly rotating the furnace until the mold is on the bottom and the crucible on top. Before the metal in the mold has had a chance to solidify, the vacuum may be broken by admitting air or argon into the furnace so that the metal solidifies under pressure. Very little oxidation is produced when using air as only the top of the metal in the mold is exposed to the atmosphere and this solidifies so quickly that there is no appreciable penetration of oxygen into the melt proper. The resulting castings are of high density and purity. A casting made by this method was extruded elsewhere into rods.

A larger vacuum furnace was constructed differing in some features from the furnace described above. This consisted essentially of an iron shell capable of being tilted through a little more than 90°. The mold in this case was placed at right angles to the crucible so that a pouring action similar to that in an ordinary furnace would be obtained. The turning axis was approximately in line with the lip of the crucible. The crucible was about 6 in. in diameter by 9 in. deep and heated by a coil of molybdenum wire wound on the outside. Windows of quartz or heat-resistant glass were provided so that the temperatures of the molybdenum winding, the crucible, and the top of the metal in the crucible could be read by an optical pyrometer. Fig. 9.3 shows this furnace open with the cover adjacent.

Both graphite and chilled copper molds were used in this furnace depending upon the shape of the piece and grain structure desired. Water cooling was provided for the bottom of the mold and the sides of the shell. A vacuum of from 0.1 to 1.0 mm of mercury could be maintained on this furnace and the casting procedure was the same as that previously described.

Two centrifugal casting machines were constructed, one for vertical and one for horizontal castings. The vertical casting machine consists of a steel drum 10 in. in diameter and 10 in. deep mounted on the top end of a vertical shaft running in ball bearings. This is driven by a 2 hp 1800 rpm induction motor. Speed regulation is obtained by means of an adjustable Reeves pulley mounted on a motor shaft driving the vertical shaft by means of a V-belt. A graphite mold is inserted in the steel drum and held in place by a flange screwed down into the top of the drum. Balancing is accomplished by drilling holes in the mold in place in the drum. For smaller castings a graphite holding ring is first centered in the drum, and then the mold, which has been closely machined to fit the inside after the ring is in place, is inserted. No special cooling means are provided as it has been found that heat absorption of the graphite and the cooling by the air currents induced by the drum rotation are sufficient to dissipate the heat from the amount of metal that may be used for this machine.

The horizontal casting machine consisted of a steel drum 2 ft in diameter and 2 ft long mounted on the end of a 9 ft 6 in. diameter hollow shaft. The shaft was supported by SKF ball bearings and driven by a 15 hp woundrotor induction motor through a step pulley. The mold was made of graphite and inserted in the 2 in. drum and locked in position by radial bolts. A space was always left between the mold and the inner surface of the drum and a fan attached to the drum drew air at high velocity around the outer surface of the graphite mold for cooling purposes. The pouring hole was in the center and was fed by a specially constructed beryllium oxide lined graphite feeding trough. The casting procedure was as follows:

The graphite mold was mounted in the 2-ft iron cylinder and locked in place. The machine was then brought up to a speed somewhat higher than the speed that was to be used in casting and sufficient to develop an appreciable vibration. The rotating drum was then touched by a piece of chalk in a mechanical holder brought just close enough to the drum during rotation to leave a light line on the side that was being drawn away from the center by the centrifugal action. This was noted and weight was removed from the graphite mold on this side. This procedure was continued until the mold balanced dynamically and could be rotated without appreciable vibration several hundred revolutions faster than intended for the casting operation. To cast the metal the removable pouring spout, preheated to 800 to 1000°C, was placed in position to feed metal into the center opening. With the machine at speed, the molten

beryllium which had been heated in the furnace to about 1500°C was poured into the spout, either from a transfer ladle or directly from the furnace according to the amount required for the casting.

For most castings a speed of rotation which would give a centrifugal force of about 110 times gravity was utilized. Experience showed that if the speed was such as to give much more than 110 times gravity, the graphite mold had a tendency to spread and crack. The one exception to this was when casting a beryllium ring. In this case it is usually necessary to use a lower speed of rotation. If the speed of rotation is too high after a ring has been poured and started to cool as the thermal contraction tended to separate it slightly from the sides of the mold, the centrifugal force would cause it to expand against the sides of the mold, thus producing cracks in the metal since it had not been allowed to contract normally in cooling.

Castings produced by this method are sound and of good quality but the purity of the metal is not as high as that of the metal produced by vacuum casting, and neither the machinability nor the general mechanical characteristics are quite as good as when the metal has been properly cast in a vacuum. However, larger and more intricate pieces may be produced since it is possible to force the metal into smaller apertures by the centrifugal method than can be done in vacuum casting.

The metal produced by the above methods was superior to ordinary air-cast metal in physical characteristics and chemical purity. The air-cast metal is turned on the lathe with some difficulty and the chips tend to detach themselves in small separate particles as if they had very little coherence at the grain boundaries.

In the centrifugal cast metal the chips are much more coherent and with the tool properly adjusted show a tendency to curl. In good vacuum cast metal the curly appearance of the chips is quite pronounced if the tool is sharp and properly adjusted and in one or two cases they have even come off in the form of a helix. The surface of a vacuum cast metal after turning is much smoother than that of air-cast metal or even centrifugally cast metal.

Castings are always examined by x rays for piping or large voids. Circular disks or small sections, when made from vacuum cast metal, are usually photographed by x rays and the photographs examined under a magnification of about 30 diameters to determine the existence of minute blowholes or cracks which might render them porous. They are superior in this respect to the air-cast or centrifugally cast metal.

In general, castings of beryllium can be forged and extruded when made by the vacuum cast process, and they machine comparatively well. Large solid castings free from blowholes and cavities and having a specific gravity of 1.8 or better have been made by both vacuum casting and centrifugal casting.

About 300 lb of finished castings were produced. Some of these were extruded. Vacuum melting and vacuum casting and beryllium oxide crucibles were shown to be useful and to produce a superior grade of metal. Degassing with chlorine and sodium sulfide and protection with argon were also found useful.

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Fig. 9.1 — High-frequency furnace.

Fig. 9.3 — Large low-frequency (60 cycle) furnace.

Paper 10

Fused Beryllium Oxide and Refractory Shapes*

C. B. SAWYER and C. H. TOWER

ABSTRACT

Methods were developed to produce the beryllium oxide with a reasonable degree of purity and in adequate quantity for large-scale production.

In the preparation of furnace "cake" or feed the use of glucose instead of the potentially toxic beryllium sulfate as a binder was developed and more efficient acid washing and carbon removal by whitening was perfected.

* * * * *

The stability of beryllium oxide, its strength, high melting point of about 2500°C, and high thermal conductivity indicated that it would be very suitable as a refractory material for crucibles and other shapes to withstand high temperatures in firing and in use with a minimum of shrinkage and deterioration. Fused beryllium oxide had been produced in the Brush Beryllium Company laboratories by means of the electric arc, by the combustion of carbon in an oxygen atmosphere, and by the combustion of hydrocarbon gases in oxygen.

When fused by the electric arc some of the oxide reacts with the carbon of the electrodes to form beryllium carbide (Be_2C). The separation of this carbide from the beryllium oxide is difficult. The formation of carbide is minimized when the oxide is fused by firing with oxygen and hydrocarbon gas or oxygen and carbon. As finally developed the process of fusing the oxide by the combustion of carbon with oxygen proved to be quite satisfactory. Acheson graphite or the AGT grade was first used as a source of carbon; later petroleum coke was substituted. The graphite has about 0.08 per cent ash content and about 0.01 per cent iron content. Comparative values for the coke were 0.20 per cent ash content and 0.02 per cent iron content.

This process consists of making the oxide into a cake with carbon, charging it into a special furnace and fusing by burning the carbon contained in the cake with oxygen and then pulverizing the cake and purifying the fused oxide.

The furnace for fusing the beryllium oxide consists of a sheet metal tube or shell about 24 in. in diameter and 36 in. long. The bottom is closed by a sheet metal through the center of which projects a pipe for supplying gas to the burner. The burner is simply a bowl-shaped piece of steel perforated with holes and positioned over the gas inlet. The furnace (Fig. 10.1)

* Work done at The Brush Beryllium Company, Cleveland, Ohio. Prepared for publication May 15, 1946.

is mounted on trunnions so that it can be tipped for emptying and cleaning. The furnace must be carefully lined before being used. For this purpose G28 insulation brick is laid flat on the bottom around the burner in a ring about 12 to 14 in. in diameter and $2\frac{1}{4}$ in. high. In laying this brick, care should be used to avoid forming brick fragments or powder. Next a core of wood or sheet metal about 12 in. in diameter and a little longer than the shell is carefully centered in the shell. A lining mixture of beryllium oxide mixed with 7 to 12 per cent its weight of glucose and just enough water to permit easy tamping (5 to 10 per cent) is then tamped in between the core and the furnace shell until the space is filled to the upper brim. The core is removed and the lining is dried with a gas flame for about 24 hr. If the time required for drying is much longer, too much water was added to the mixture of beryllium oxide and glucose.

The furnace is put in operation after the lining has dried by first covering the burner with a 4-in. layer of high-fired oxide about walnut size. Broken crucible ware or scrap pieces of lining may be used, but it should be free from graphite.

The furnace is then loaded with oxide cake for firing. The cake may be made from standard grade beryllium oxide, from oxide which has been fired but not fused, or from pieces of used furnace lining. The cake is made from a mixture of beryllium oxide from the previously mentioned sources, glucose, water, and graphite or coke which has been crushed into pieces which will just pass through a 1-in. mesh screen.

A typical formula for making the cake is as follows:

Relative proportions	
Glucose*	4 kg
Beryllium oxide	15 kg
Coke lumps	9 kg
Water	about 15 liters

* The glucose is first mixed with the water and then added to the mixture of beryllium oxide and coke. More water may be used if necessary.

In making the cake for the high-firing process, slight variations in the formula are advantageous according to whether the cake is to be made from soft high-fired oxide, fluffy oxide, cake fines, or used insulation.

The ingredients are placed in the wooden tub of the mixing machine and stirred with a stainless steel stirrer. When thoroughly mixed, the contents of the mixing machine are poured into stainless steel trays lined with large sheets of filter paper.

The tray is then put in a drying oven and slowly heated until the charge is thoroughly hard and dry. The cake is carefully removed from the tray and broken up into pieces about 4 in. square. Care should be taken to avoid breaking the cake into finely divided powder.

Large lumps of kerosene-soaked coke are put in the bottom of the fusing furnace to form a layer about 4 to 6 in. deep and ignited. A slow stream of oxygen is started. When the coke is cherry red, the flow of oxygen is increased to about 44 cu ft/hr. The first charge of cake (about 9 kg) is added. As smoke forms, the amount of oxygen should be increased until a flame begins to show. About 2 kg of dry coke is added. After about 15 to 20 min a very brilliant white light will be observed in the furnace. Then add the second charge of cake (about 9 kg). The charge should be tamped down with a graphite rod if the oxygen shows signs of channeling through it. Channeling causes insufficient heating of some portions of the charge and results in an undesirably large proportion of the charge coming out as a soft fluffy powder which is only partially fused. The oxygen flow is decreased before a charge is added and increased after a charge is added. There should be at least 15 min between each charge. The hotter the furnace, before a charge is added, the more charges may be made in a single run. The oxygen flow should be reduced if it begins to throw out some of the oxide. After the third charge of cake is heated to incandescence, it should be possible to hear a bubbling sound of the oxygen

passing through the melted oxide. As the furnace begins to fill up, the charge is reduced to 7 kg or less per charge as necessary. After the furnace is full, the oxygen flow should be continued (usually $\frac{1}{2}$ to 1 hr) until the color of the flame indicates that all the carbon is consumed. It may be necessary to add a small amount of cake occasionally if channeling is noticed. It is sometimes necessary to add some coke between charges to maintain the temperature. After the firing is complete, the oxygen is turned off and a stream of compressed air passed through the furnace to hasten the cooling. This takes from 8 to 12 hr. About 130 kg of oxygen is required for a run.

When cool, the furnace is unloaded. In a successful run the core of fused beryllium oxide is so solid that the lining is removed first. An electric hammer is used to break it. The fused charge usually comes out in one large piece weighing from 60 to 100 kg.

The material from the furnace is carefully inspected and sorted. The thoroughly fused oxide is separated from that which has not been heated to the melting point. This soft non-fused or partially fused oxide may subsequently be refired. It is desirable to make the separation as complete as possible since the soft oxide dissolves appreciably in the subsequent washing treatment and is lost. The pieces of coke or graphite must also be carefully separated from the soft non-fused oxide if the latter is to be used as a lining. The coke or graphite is likely to cause the soft oxide to fuse through to the shell and to melt a hole in the furnace.

The fused cake is next reduced to a powder by crushing and grinding. It is first broken into pieces small enough to enter the jaws of a crusher and then to about $\frac{1}{4}$ in. mesh. If a powder having a mesh size from -20 to +200 mesh is wanted, the best procedure is to crush the fused oxide through rolls. The material should be screened after each pass and only the coarse particles recrushed. If this is done, the amount of material worked can be kept to a minimum; likewise the iron contamination and the fines will be a minimum. If done efficiently, it is possible to crush the oxide to 100 mesh in steel rolls without raising the iron content of the crushed oxide over 0.08 per cent. If such is the case, acid washing will not be required.

If sizes of 150 mesh or smaller are desired, it is necessary to ball mill the fused oxide. A charge of about 250 kg of iron balls to 25 kg of $\frac{1}{4}$ -in. lumpy fused oxide is usually used. The mesh size and particle size distribution is determined by the milling time.

The crushed and ground oxide is separated into various mesh sizes by screening. Dry screening can be done in the shaker type sifter only if about one-half the material to be sifted is coarser than 60 mesh. Screening is most easily done in the wet state. A rotary wet screener is very efficient.

After the screening, and especially if the material has been ball milled, it is necessary to remove the iron by acid washing. Fully high-fired beryllium oxide is quite insoluble in a dilute HCl solution at 65°C, but incompletely fired oxide is more soluble. Thus, as pointed out previously, a very careful sorting of the soft high-fired from the lumpy fused high-fired oxide should be made to prevent loss by solution.

Thorough removal of the iron is very important and the detailed procedure is as follows:

About 36 kg of the oxide is added to about 115 liters of water in a wooden barrel or crock and stirred until the oxide is in suspension without lumps. Two liters of 10N HCl and 1 liter of HNO_3 are added and the mixture is heated to 65°C by steam introduced through a rubber hose. The hose is removed and the oxide is allowed to settle while the mixture cools to room temperature. When cool the acidified water is siphoned off as completely as possible.

The barrel is now filled with cold water, 200 cc of HCl is added, and the whole is stirred until the slurry is in suspension. The solution is allowed to settle, the liquid is siphoned off, and the process repeated. It is necessary that the solution be kept acidic. For insurance, the solution is tested with litmus paper about an hour after the precipitate has begun to settle. If necessary, more HCl is added. This procedure is repeated several times.

The acid-washed oxide is next pumped into a filter press. The solution is removed by compressed air introduced through the press inlet. An acid solution (100 cc HCl to 50 liters of water) is then pumped through the press until the discharge liquor does not show an iron reaction by the following test:

To 25 cc of discharge water from the press 2 cc of HCl is added in a white porcelain dish.

If a coloration appears when 2 drops of potassium sulfocyanide is added, the amount of iron is too high and more acid wash water must be pumped through.

After the discharge water test shows freedom from iron, the water is blown out of the press by compressed air, and the air flow is continued for about one hour after the water has stopped running to dry the cake. The condition of the cake obtained by the continued air flow facilitates the subsequent unloading of the press.

The oxide is next transferred to a stainless steel tray lined with filter paper and placed in the drying oven. A fan type gas heater has been found satisfactory for drying. When the oxide is dry, the lumps formed in the drying operation are broken up.

A tumbling barrel with a lining which will not contaminate the oxide is usually used for this operation. At this stage the oxide is usually greyish in color due to residual graphite in the oxide. The graphite is removed in the whitening operation which is done in a rotary furnace. This furnace (Fig. 10.2) consists of a silica tube about 8 in. in diameter and 6 ft. long. It rotates on trunnions placed about 7 in. from each end and is inclined about 5° from the horizontal. The rotational speed is about 2 rpm. Between the trunnions the tube is surrounded by a brick furnace heated by four burners fed with gas and compressed air. An indicating pyrometer measures the temperature of the outside of the silica tube; the temperature inside the tube is checked by an optical pyrometer. Oxygen is fed into the exit end of the tube. The beryllium oxide is fed into the upper end of the tube from a vibrating hopper. The rate of feed is regulated by a sliding gate opening. The temperature of the tube is maintained at about 900°C. If the oxide is free from iron, it will come out of the furnace with a white color. Traces of iron produce a pinkish tint in the white oxide.

The whitened beryllium oxide may be formed into various refractory shapes by pressure molding, slip casting, jigging, or tamping. The shapes made by tamping have the highest density and the greatest durability under high temperatures and thermal shock. In the tamping process a mold is made of either graphite or steel and, to facilitate removal and avoid contamination, is frequently lined with celluloid. A shrinkage allowance of about 0.40 in. to 1 ft is a reasonable allowance in making the mold.

When the beryllium oxide refractory pieces are made by tamping, the oxide is mixed with about 10 wt. % of a nearly saturated beryllium sulfate solution and forced into the mold a little at a time by an air-driven tamper. When the mold is full, it is exposed to the heat of infra-red lamps until it is dry enough to be handled. When this has occurred, enough shrinkage will have taken place so that the piece may be easily removed from the mold. It is oven dried for about 6 hr and then placed in an electric furnace. The temperature is raised to 1500°C during a period of about 24 hr. The piece is then removed from the furnace and inspected for incipient cracks and flaws. If any of these have occurred, they may be repaired by filling them with a slurry of beryllium sulfate and water and high-fired oxide. A second firing is then necessary. Densities in the neighborhood of 2.8 g/cc are obtainable by this process. Where crucibles are to be used at very high temperatures, or exposed to high thermal shock, they are sometimes fired at 2000°C. This requires a second firing, i.e., the crucibles are fired first at 1500°C, inspected, and then fired at a temperature of 2000°C. Three or four hours may be needed to reach the higher temperature which is maintained for $\frac{1}{2}$ to 1 hr. The crucible may be removed from the furnace and allowed to cool or it may be left in the furnace and allowed to cool with the furnace. The heating and cooling times are dependent upon the size of the crucible and furnace conditions. After the first firing at 1500°C they are not critical, it being only necessary to make sure the time is sufficient to assure an even distribution of heat through the crucible.

Fig. 10.1 — Furnace for fusing beryllium oxides.

Fig. 10.2 — Furnace for whitening beryllium oxide.

Paper 11

Geochemistry of Beryllium*

MICHAEL FLEISCHER and E. N. CAMERON

ABSTRACT

This is a review, with annotated bibliography, of the mode of occurrence of the element beryllium. It is not a list of specific ore deposits, but a summary of the types of minerals and rocks in which beryllium has been reported to occur. In addition, the unpublished spectrographic studies of the Geological Survey on mill products are summarized, and data are given on domestic production and reserves and on foreign production.

Beryllium is now obtained solely from beryl, mined from granitic pegmatites. Other beryllium minerals, all confined to granitic and syenitic pegmatites, are not likely to be possible sources, but contact metamorphic deposits of helvite of commercial grade might possibly be found. Suggestions are made for further investigations, particularly of methods of concentrating low-grade beryl ores, and of the occurrence of beryllium in American coals.

1. INTRODUCTION

This report on the occurrence of beryllium is one of a series of similar reports prepared by the Geological Survey discussing possible sources of rare or uncommon elements that had special war uses.

Beryllium is a chemical element with atomic number 4, and atomic weight 9.02. It belongs to the second group of the periodic table and is bivalent in its compounds.

2. GEOCHEMICAL CONSIDERATIONS

2.1 General Statement

Beryllium is a relatively rare element. Recent estimates^{1,6,13} give 0.0005 to 0.0006 per cent Be for the content in the earth's crust. Earlier estimates⁴ were somewhat higher, but were based on few data. Beryllium is a lithophilic element, found almost exclusively in igneous and sedimentary rocks. In contrast to dispersed elements such as gallium or indium, beryllium is so concentrated during the process of magmatic differentiation that it is a major

*Contribution from the Geological Survey, U. S. Department of the Interior, Washington, D. C. Prepared for publication June 1946 and issued as MDDC-643.

constituent of many minerals. These minerals, almost without exception, occur in granitic or syenitic pegmatites, or in contact metamorphic deposits.

The empirical ionic radius of beryllium is 0.34A, so much lower than those of most metals that there is little possibility of isomorphous substitution by beryllium excepting for such high valence atoms as Si^{+4} (0.39A) or V^{+5} (0.4A). Such possible substitutions involve complex valency adjustments within the crystal lattice. It is therefore not surprising that beryllium is present in appreciable amounts only in the late residual phases of magmatic activity.

2.2 Occurrences in Specific Minerals and Rocks

The following list includes all the minerals that have been reported to contain as much as 0.004 per cent Be (0.01 per cent BeO). The mineral beryl is the only commercial source at present and is therefore discussed first under (a). The other minerals have been divided into two groups: (b) Minerals in which beryllium is an essential constituent, and (c) Minerals in which beryllium is an accessory constituent. Within each group the minerals are subdivided into chemical classes and are listed alphabetically within each class. Unless otherwise indicated, the data given are from Volume 1 of the Seventh Edition of Dana's System of Mineralogy and from the mineralogical file of the Section of Chemistry and Physics, Geological Survey.

Index of minerals listed

Mineral	Page	Be, %	Type of occurrence
Aegirite	10	Up to 0.04	Syenitic pegmatite
Allanite	10	Up to 2	Various
Alvite	10	Up to 5	Granitic pegmatite
Aminoffite	7	2.2	Contact metamorphic?
Arfvedsonite	10	Up to 0.01	Syenitic pegmatite
Axinite	10	Up to 0.04	Pneumatolytic
Barkevikite, see Arfvedsonite	10		
Barylite	7	5.7	Contact metamorphic
Bavenite	7	1.1	Granitic pegmatite
Bertrandite	7	15.1	Granitic pegmatite
Beryl	6	3.0-5.0	Granitic pegmatite
Beryllonite	7	7.1	Granitic pegmatite
Bityite	7	0.8	Granitic pegmatite
Bromellite	6	36.0	Contact metamorphic
Cassiterite	9	Traces	Granitic pegmatite
Chkalovite	8	4.1-4.6	Syenitic pegmatite
Chrysoberyl	6	7.1	Granitic pegmatite
Clinohumite	10	Up to 0.6	Contact metamorphic
Danalite, see Helvite Group	8		
Epididymite	8	3.7	Nepheline syenite
Erdmannite	10	1 to 1.5	Nepheline syenite
Euclase	8	6.1	Granitic pegmatite
Eudidymite	8	3.7	Nepheline syenite
Euxenite	9	Up to 0.03	Granitic pegmatite
Fergusonite	9	Up to 0.14	Granitic pegmatite
Fluorite	9	Traces	Granitic pegmatite
Foresite	10	0.25	Granitic pegmatite
Gadolinite	8	3.2-4.7	Granitic pegmatite
Garnet group	10	Up to 0.04	Contact metamorphic
Genthelvite, see Helvite Group	8		
Hambergite	6	19.2	Granitic and syenitic
Harstigitite	8	4.0	Contact metamorphic
Helvite Group	8	3.8-5.4	Various

Index of minerals listed (cont'd)

Mineral	Page	Be, %	Type of occurrence
Herderite	7	5.6-5.9	Granitic pegmatite
Hyalotekite	11	0.27	Contact metamorphic
Idocrase	11	Up to 0.39	Contact metamorphic
Kolbeckite	7	3.1	Hydrothermal
Leucophanite	8	4.0	Syenitic pegmatite
Meliphanite	8	3.4-5.0	Syenitic pegmatite
Mica Group	11	Up to 0.04	Granitic pegmatite
Microlite	9	0.12	Granitic pegmatite
Milarite	9	1.8	Granitic pegmatite
Nepheline	11	Up to 0.014	Nepheline syenite
Phenakite	9	16.4	Granitic pegmatites
Rhodizite	6	3.6-5.4	Granitic pegmatites
Samarskite	9	Up to 0.11	Granitic pegmatites
Steenstrupine	11	0.43 to 0.68	Syenitic pegmatite
Swedenborgite	7	12.6	Contact metamorphic
Tengerite	6	3.5	Granitic pegmatite
Thorite	11	Up to 0.01	Granitic pegmatite
Tourmaline	11	Up to 0.04	Granitic pegmatite
Trimerite	9	6.1	Contact metamorphic
Tscheffkinite	11	Up to 0.7	Granitic pegmatite
Uraninite	9	Up to 0.004	Granitic pegmatite
Vesuvianite, see Idocrase	11		
Wavellite	9	0.10	Secondary mineral
Yttrotantalite	9	Up to 0.21	Granitic pegmatite

(a) Beryl. Beryl, the only source of beryllium at present, has the ideal composition $\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$ with 5.0 per cent Be (14.0 per cent BeO). Complex isomorphous replacement, including the introduction of water and the alkalis, causes the beryllium content of the mineral to be lower than this, down to a minimum of about 3 per cent Be. The common range of beryllium content in beryl is 3.8 to 4.6 per cent Be.

Beryl occurs in minable amounts almost exclusively in granitic pegmatites. A review of world deposits has recently been published in Russian.²³

(b) Minerals in which beryllium is an essential constituent. (1) Oxides. Bromellite, BeO , containing 36 per cent Be, is a very rare mineral that occurs in a contact metamorphic skarn.

Chrysoberyl, BeAl_2O_4 , containing 7.1 per cent Be, is an uncommon mineral that occurs in small amounts in granitic pegmatites and placers derived from them, also in mica schists.

(2) Carbonate and borates, Hambergite, $\text{Be}_2(\text{OH})\text{BO}_3$, containing 19.2 per cent Be, is a rare mineral that occurs in small amounts in granitic and syenitic pegmatites.

Rhodizite, perhaps $(\text{Na}, \text{K})_2\text{Li}_4\text{Al}_4\text{Be}_3\text{B}_{10}\text{O}_{27}$, containing 3.6 to 5.4 per cent Be, is a very rare mineral that occurs in small amounts in granitic pegmatites.

Tengerite, a hydrated carbonate of yttrium and beryllium, containing 3.5 per cent Be, occurs rarely in granitic pegmatites as an alteration product of gadolinite.

(3) Phosphates, Antimonate. Beryllonite, NaBePO_4 , containing 7.1 per cent Be, is a rare mineral that occurs in small amounts in granitic pegmatites.

Herderite, $\text{CaBePO}_4 (\text{OH}, \text{F})$, containing 5.6 to 5.9 per cent Be, is an uncommon mineral that occurs in small amounts in granitic pegmatites.

Kolbeckite is a very rare hydrated silicophosphate of beryllium, calcium, and aluminum, containing 3.1 per cent Be. The only known occurrence is in a quartz-wolframite vein.

Swedenborgite, $\text{NaBe}_4\text{SbO}_7$, containing 12.6 per cent Be, is a very rare mineral that is found at one locality in a contact metamorphic deposit.

(4) Silicates. Aminoffite, a calcium beryllium aluminum silicate containing 2.2 per cent Be, is a very rare mineral that occurs in veins in magnetite in a contact metamorphic deposit.

Barylite, $\text{BaBe}_2\text{Si}_2\text{O}_7$, containing 5.7 per cent Be, is a very rare mineral that occurs in small amounts in contact metamorphic deposits.

Bavenite, $\text{Ca}_4\text{BeAl}_2\text{Si}_9\text{O}_{28} \cdot \text{H}_2\text{O}$, containing 1.1 per cent Be, is a very rare mineral that occurs in small amounts in granitic pegmatites.

Bertrandite, $\text{Be}_4\text{Si}_2\text{O}_7(\text{OH})_2$, containing 15.1 per cent Be, is an uncommon mineral that occurs in very small amounts as an alteration product of beryl in granitic pegmatites.

Bityite, perhaps $\text{Li}_2\text{BeCa}_3\text{Al}_3\text{Si}_6\text{O}_{27}(\text{OH})_7$, containing 0.8 per cent Be, is a very rare mineral. The only known occurrence is in a granitic pegmatite.

Chkalovite, $\text{NaBeSi}_2\text{O}_6$, containing 4.1 to 4.6 per cent Be, is a very rare mineral. The only known occurrence is in a syenitic pegmatite.

Epididymite and its dimorph eudidymite, $\text{HNaBeSi}_3\text{O}_8$, containing 3.7 per cent Be, are rare minerals that occur in small amounts in nepheline syenites.

Euclase, $\text{BeAlSiO}_4(\text{OH})$, containing 6.1 per cent Be, is an uncommon mineral occurring in small amounts in granitic pegmatites and in placers.

Gadolinite, $\text{Be}_2\text{Y}_2\text{FeSi}_2\text{O}_{10}$, containing 3.2 to 4.7 per cent Be, is an uncommon mineral that occurs in granitic pegmatites, but only rarely in large amounts.

Harstigit, $(\text{Ca}, \text{Mn})_7\text{Be}_4\text{Si}_6\text{O}_{21}(\text{OH}, \text{F})_4$, containing 4.0 per cent Be, is a very rare mineral that occurs in contact metamorphic deposits.

The helvite group, $(\text{Mn}, \text{Fe}, \text{Zn})_4\text{Be}_3\text{Si}_3\text{O}_{12}\text{S}$, including helvite, danalite, and genthelvite, and containing 3.8 to 5.4 per cent Be, are uncommon minerals that occur, generally in small amounts, in granitic and syenitic pegmatites.⁵ A recently discovered contact metamorphic deposit contained sufficient helvite to be considered as a possible commercial source of beryllium,¹⁰ and other similar deposits may have been overlooked.

Leucophanite, $(\text{Ca}, \text{Na})_2\text{BeSi}_2(\text{O}, \text{OH}, \text{F})_7$, containing 4.0 per cent Be, is a very rare mineral that occurs in small amounts in augite-syenite pegmatites. The chemically similar mineral, meliphanite, $(\text{Ca}, \text{Na})_2\text{Be}(\text{Si}, \text{Al})_2(\text{O}, \text{F})_7$, containing 3.4 to 5.0 per cent Be, is a very rare mineral that occurs in small amounts in syenitic pegmatites.

Milarite, $\text{K}_2\text{Ca}_4\text{Be}_4\text{Al}_2\text{Si}_{24}\text{O}_{60} \cdot \text{H}_2\text{O}$, containing 1.8 per cent Be, is a very rare mineral that occurs in small amounts in granitic pegmatites.

Phenakite, Be_2SiO_4 , containing 16.4 per cent Be, occurs rather commonly, but only in very small amounts, in granitic pegmatites.

Trimerite, $\text{Be}(\text{Mn}, \text{Ca})\text{SiO}_4$, containing 6.1 per cent Be, is a very rare mineral that occurs in small amounts in contact metamorphic deposits.

(c) Minerals in which beryllium is a minor, accessory constituent. (1) Oxides. Cassiterite, SnO_2 , has been reported^{2,11} to contain spectrographic traces of beryllium.

Uraninite has been reported to contain beryllium,¹⁴ but no sample tested contained more than 0.004 per cent Be.

Microcline, $\text{Ca}_2\text{Ta}_2\text{O}_7$, has been reported to contain up to 0.12 per cent Be. Euxenite, fergusonite, samarskite, and yttrantalite, which are complex columbate-tantalates of the rare earths, have been reported to contain up to 0.2 per cent Be. They occur in granitic pegmatites.

(2) Halides. Fluorite, CaF_2 , does not generally contain beryllium, but some samples from granitic pegmatites have been found to contain traces of beryllium.²⁶

(3) Phosphates. Wavellite, $\text{Al}_6(\text{PO}_4)_4(\text{OH}, \text{F})_8 \cdot 9\text{H}_2\text{O}$, has been found²⁶ to contain beryllium. Material from Tennessee contained 0.10 per cent Be; some from Arkansas may contain even more beryllium.²⁶ Wavellite is a common mineral that occurs, usually in small amounts, as a secondary mineral.

(4) Silicates. Aegirite, approximately $(\text{Na}, \text{Ca})(\text{Mg}, \text{Fe}''')\text{Si}_2\text{O}_6$, a pyroxene from syenitic pegmatites has been reported⁷ to contain up to 0.04 per cent Be.

Allanite, $(\text{Ca}, \text{Ce})_2(\text{Al}, \text{Fe})_3\text{Si}_3\text{O}_{12}(\text{OH})$, is widely distributed in various rock types, generally in small amounts. Most samples contain a few hundredths of a per cent of beryllium, but exceptional samples have been reported to contain up to 2 per cent Be.

Alvite, is a rare, dubious, zirconium silicate that contains up to 5 per cent Be, according to old analyses.

Arfvedsonite and barkevikite, soda-rich amphiboles that occur in syenitic rocks, are reported⁷ to contain up to 0.01 per cent Be.

Axinite, a complex borosilicate, has been reported⁷ to contain 0.04 per cent Be. It is a common mineral that occurs in small amounts in pneumatolytic deposits and in the contact zones of some granites.

Clinohumite, $\text{Mg}_3\text{Si}_4\text{O}_{16}(\text{OH},\text{F})_2$, is an uncommon mineral that occurs in small amounts in contact metamorphic deposits. Material from one deposit is reported²² to contain 0.6 per cent Be.

Erdmannite is a dubious rare silicate of the rare earths reported to contain 1 to 1.5 per cent Be.

Foresite is a dubious rare zeolite that occurs in a granitic pegmatite. Two analyses show 0.25 per cent Be.

Garnet, $\text{Ca}_3(\text{Al}, \text{Fe})_2\text{Si}_3\text{O}_{12}$, is a very common mineral. Garnet from contact metamorphic deposits may contain traces to 0.04 per cent Be.^{5,26}

Hyalotekite is a very rare complex borosilicate of lead and barium known only from one contact metamorphic deposit. It contains 0.27 per cent Be.

Idocrase (vesuvianite), a complex calcium aluminum silicate, is a common mineral that occurs in moderate amounts in contact metamorphic deposits. Beryllium has been determined in a number of samples,^{5,7,15,20,26,28} Nearly all contain a few hundredths of a per cent or less of beryllium; a few contain more. The highest verified content is 0.39 per cent Be⁵; the report¹⁵ of a sample with 3.3 per cent Be is questionable.

Mica Group—Various members (muscovite, biotite, zinnwaldite, lepidolite) of the mica group that occur in granitic pegmatite have been found^{7,26} to contain traces to 0.04 per cent Be.

Nepheline, $\text{NaAlSi}_3\text{O}_8$, is a common mineral that is one of the principal constituents of nepheline syenite rocks. Analyses^{7,25} show that most nephelines contain beryllium, the maximum percentage found being 0.014 and the average 0.005 per cent Be.

Steenstrupine is a very rare complex phosphate-silicate of the rare earths, sodium, and calcium, that occurs in syenite pegmatite and is reported to contain 0.43 to 0.68 per cent Be.

Thorite, essentially ThSiO_4 , is a rare mineral that occurs in granitic pegmatites. It is reported¹⁴ to contain up to 0.01 per cent Be.

Tourmaline, a complex borosilicate, is a very common mineral that occurs in granitic pegmatites. It contains traces to 0.04 per cent Be.^{7,26}

Tacheffkinite (chevkinite) is a rare, complex silicate of cerium, lanthanum, and titanium that occurs in granitic pegmatites. It is reported to contain up to 0.7 per cent Be.

(d) Rocks. The average content of beryllium in the earth's crust has been estimated to be 0.0005 to 0.0006 per cent Be. Most rocks have lower beryllium contents than this. The average content of all eruptive rocks may be 0.0002 per cent Be.⁷ Higher concentrations are shown by granites, which average perhaps 0.0007 per cent Be^{7,9,17-21} and by nepheline syenites, which may average 0.001 to 0.004 per cent Be.^{7,9,19} Contact metamorphic deposits containing pneumatolytic minerals show a concentration of beryllium⁵ but few quantitative data are available. Beryllium apparently follows aluminum in sedimentary processes, as bauxites generally contain a few thousandths of a per cent.^{7,21} Clays and clay schists appear to have slightly lower beryllium contents than bauxite,⁹ but bentonite may contain a few hundredths of a per cent of beryllium.²⁶

(e) Coal ashes. The ash of coal samples commonly contains detectable amounts of beryllium. Spectrographic study of the ash of 12 English and German Coals⁸ showed up to 1 per cent Be and 10 of the 12 examined had 0.01 per cent Be or more. Studies of the ashes of Russian coals^{12,29} give much lower figures for the beryllium content. Beryllium has been detected in the ash of certain American coals,²⁶ but no quantitative data are available.

3. RESULTS OF MILL PRODUCT STUDIES

The beryllium content of more than 1000 samples from over 200 mines, mills and geological occurrences was determined spectrographically by Rabbit²⁶ as part of the Geological Survey's Trace Elements investigations. One sample of ore from a tungsten prospect in Yavapai County, Arizona, contained 0.2 per cent BeO. Two others, both contact-altered limestones in the vicinity of alkali-syenite intrusives, contained 0.2 per cent and 0.3 per cent BeO, respectively. Fifteen other samples contained BeO in amounts ranging from 0.02 to 0.08 per cent BeO. All the samples are listed in Table 11.1.

Taken together with the investigations of beryllium occurrences made during the war, the results corroborate long-standing conclusions regarding the distribution of beryllium in minerals and rocks. Beryllium is concentrated chiefly in granitic pegmatites, and is rarely found elsewhere in significant amounts. The high values obtained for the two samples of contact-altered limestone, however, are of interest because they indicate that concentrations of beryllium in contact metamorphic deposits may be less rare than a perusal of the literature would suggest and that contact aureoles around alkali-syenite intrusives should receive the same attention as those around granitic intrusives. Hydrothermal deposits in general appear to carry only traces of beryllium. BeO to the extent of 0.02 per cent or more was found in samples of hydrothermal ores from only four mills or localities out of a large number examined. A single sample of a manganese concentrate showed 0.02 per cent BeO, but other samples of manganese ores, concentrates, and tailings showed only traces of beryllium.

4. BEST SOURCES OF BERYLLIUM

At present, beryllium is produced entirely from beryl, and all commercial deposits are in granitic pegmatites. During the war there was considerable interest in the contact-metamorphic beryllium deposits of Iron Mountain, New Mexico, in which beryllium occurs largely in the form of helvite,^{5,10} but investigation has shown that the grade of much of the beryllium-bearing rock is low, and the tonnage of beryllium present probably is only moderately large. In addition, metallurgical difficulties in treating the ore remain to be solved.

Figures for domestic production of beryl and for amounts of beryl and helvite present in known domestic deposits are given in Table 11.2. Domestic beryl has been produced almost entirely as a byproduct of operations for feldspar, mica, or lithium minerals. Estimates of tonnages of beryl present in known deposits are given under two headings—hand-separable beryl, and milling beryl; i.e., beryl recoverable only by milling and flotation. Only the hand-separable beryl can be classified as reserves at the present time. The figures were furnished by various members of the Geological Survey. They are based in part on records of past production, but in large part on measurements of crystals in exposure of pegmatites and on calculation of the ratios between the areas occupied by beryl crystals and the total areas of the exposures. Some of the figures for grades and tonnages of beryl-bearing material are based on exploration and sampling by the U. S. Bureau of Mines.

Figures for foreign production of beryl are given in Table 11.3. The data are mostly from Minerals Yearbook, Mineral Trade Notes, and from information furnished by the Foreign Economic Administration, War Production Board, the Department of State, and other federal agencies. All production figures are for beryl concentrates with a minimum average content of 8 per cent BeO. Most of the concentrates are reported to have averaged 10 per cent BeO or more. Foreign production is partly byproduct, partly from operations conducted primarily for beryl. Few data on grades are available. According to local report, the productive deposits of northeastern Brazil showed an average recovery of about 0.3 per cent beryl from rock mined. The few data available for Indian deposits suggest grades, in terms of beryl recovered from rock mixed, of 0.5 to 8 per cent. Rock mined from the remarkable deposit of Las Tapias, the principal source of Argentine beryl, and probably the most productive single beryl deposit in the world, appears to have yielded in excess of 9 per cent beryl, if a mining width of 6 ft is assumed for purposes of calculation.

The only guides to reserves in foreign countries are production and import figures, together with comments and rough estimates contained in reports of various government agencies. Brazil and Argentina furnished the bulk of pre-war production and, together with Australia and India, supplied the bulk of war requirements. In early 1945, reserves in Australia, Argentina, Madagascar, and Union of South Africa were reported to be virtually exhausted. India and Brazil appear to have the largest known reserves of hand-separable beryl, but reserves and production for U.S.S.R., China, and Korea, have not been published. Canada may have sizeable reserves, but production to date is very small.

5. SUGGESTIONS FOR FURTHER INVESTIGATIONS

Further investigations should be directed first toward increasing our knowledge of the beryl supplies present in domestic deposits. During the war most of the known domestic beryl-bearing pegmatites were examined by the Geological Survey. A large number were mapped and studied in detail, and some were explored by the Bureau of Mines and other agencies, but in several parts of the country there are large pegmatite-bearing areas that have not been investigated adequately for beryl. Wartime investigations indicate, however, that the largest amounts of beryl are in deposits of milling grade, hence the development of techniques for milling beryl-bearing pegmatite and concentrating the beryl by flotation is a prerequisite to sizeable beryl production. At the present time, operations would have to be supported largely by recovery of feldspar and other minerals from the pegmatites.

The long range outlook for beryl production is involved with the trend in the feldspar industry toward recovery of feldspar by flotation. If, despite the development of this process, the industry continues to rely on pegmatites for raw material, certain pegmatites containing milling beryl may ultimately be mined in the course of feldspar operations, but if granites supplant pegmatites as the principal sources of commercial feldspar, only a large increase in the price of beryl or the development of low-cost processes for concentration is likely to bring the pegmatites containing milling beryl into production. Even granting the development of the necessary techniques, the immediate outlook for mass milling of beryl-bearing pegmatites in general is not bright, as these pegmatites appear unable to compete with other pegmatites that are larger, richer in feldspar, and structurally more favorable to low-cost mining.

In addition to studies of resources of beryl, certain other potential sources of beryllium should be investigated. The fate of beryllium in the production of aluminum from bauxite should be studied to determine whether beryllium is concentrated in the waste products. Nepheline syenite has been suggested as a raw material for the production of aluminum. If a plant is built for extraction of aluminum from nepheline syenite, or from clay, the fate of the beryllium present should be studied. Systematic studies of the beryllium content of American coal ashes should be made. Contact metamorphic deposits should be examined for the presence of helvite and associated beryllium-bearing minerals. Garnet-bearing contact deposits should be examined carefully, as helvite is readily mistaken for garnet.

ANNOTATED BIBLIOGRAPHY OF OCCURRENCES OF BERYLLIUM

Note: Descriptions of individual deposits are not included. The original papers were seen except those for which reference to an abstract journal is given.

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A summary. The earth's crust is estimated to contain 0.0005 per cent Be. This would place beryllium forty-first in abundance of the elements.

2. Borovick, S. A. and Gotman, J. D., Content of rare and other elements in the cassiterites of different genesis from U.S.S.R. deposits according to spectrum analysis data, Compt. rend. acad. sci. U.R.S.S., 23: 351-354 (1939).

Beryllium was detected in small amount in some cassiterites, but was absent in most.

3. Brandes, W., Das natürliche Vorkommen des Berylliums. (Occurrence of beryllium in nature.) Z. prakt. Geol. 41:35-39 (1933).

A brief review, with a list of beryllium minerals and their temperatures of formation.

4. Clarke, F. W. and Washington, H. S., The composition of the earth's crust, U. S. Geol. Survey Prof. Paper 127:117 pp. (1924)

The beryllium content of the earth's crust was estimated on very little evidence to be 0.001 per cent Be.

5. Glass, J. J., Jahns, R. H., and Stevens, R. E., Helvite and danalite from New Mexico and the helvite group, Am. Mineral. 29:163-191 (1944).

Contains a summary of available data on the occurrence of the minerals of the helvite group and on the beryllium content of various minerals from Iron Mt., New Mexico.

6. Goldschmidt, V. M., Geochemische Verteilungsgesetze der Elemente. IX. Die Mengenverhältnisse der Elemente und der Atom-Arten. (The principles of the geochemical distribution of the elements. IX. Abundance of the elements and isotopes.) Skrift. Norsk. Videnskaps-Akad, Oslo, Mat.-Nat. Klasse 1937, No. 4, 148 pp.

The earth's crust, including the sedimentary rocks, is estimated to contain 0.0006 per cent Be.

7. Goldschmidt, V. M. and Peters, Cl., Geochemi des Berylliums. (Geochemistry of beryllium.) Nachr. Ges. Wiss. Göttingen, Math.-Phys. Klasse 1932, Heft 4:360-376.

A detailed spectrographic study of a large number of samples. The average content for all eruptive rocks is probably about 0.0002 per cent Be. Granites average perhaps 0.0004 per cent Be, nepheline syenites 0.004 per cent Be; other rocks have much lower beryllium contents. Beryllium is notably high in contact metamorphic deposits. In sedimentary processes, beryllium follows aluminum. Two bauxites had 0.0004 and 0.004 per cent Be. Many minerals were analyzed; the following contained up to 0.04 per cent Be; muscovite, biotite, zinnwaldite, tourmaline, nepheline, aegirine, barkevikite, axinite, and idocrase (vesuvianite).

8. Goldschmidt, V. M. and Peters, Cl., Ueber die Anreicherung seltener Elemente in Steinkohlen. (The enrichment of rare elements in coals.) Nachr. Ges. Wiss. Göttingen, Math.-Phys. Klasse 1933, Heft 4:371-387.

Spectrographic analysis of the ashes of twelve English and German coals. Three had 0.1 to 1.0 per cent Be, 4 had 0.1 per cent, 2 had 0.01 to 0.1 per cent, 1 had 0.01 per cent, 2 had 0.001 per cent. The ashes of lignites had lower contents of beryllium.

9. Goldschmidt, V. M., Hauptmann, H., and Peters, Cl., Ueber die Berücksichtigung "seltener" Elemente bei Gestein-Analysen. (Consideration of "rare" elements in rock-analyses.) Naturwissenschaften 20:362-365 (1933).

The following new determinations are given: (1) A mixture of 11 German gabbros 0.0001 per cent Be. (2) A mixture of 14 German granites 0.0007 per cent Be. (3) A mixture of 22 nepheline syenites 0.001 per cent Be. (4) A mixture of 24 greisens 0.0003 per cent Be. (5) A mixture of 36 clay schists 0.0005 per cent Be.

10. Jahns, R. H. and Glass, J. J., Beryllium and tungsten deposits of the Iron Mt. district, Sierra and Socorro Counties, New Mexico, U. S. Geol. Survey Bull. 945-C:45-79 (1944).

A study of the helvite deposits.

11. Larionov, J. and Tolmacev, J. M., On the chemical composition of cassiterites, Compt. rend. acad. sci. U.R.S.S. 14:303-306 (1937).

Qualitative spectrographic study showed the presence of beryllium in 5 pegmatite cassiterites and its absence in two hydrothermal cassiterites.

12. Nazarenko, V. A., The occurrence of vanadium, beryllium, and boron in the ash of some coals, Trav. lab. biogeochem. acad. sci. U.R.S.S. 4:265-270 (in German 271) (1937); Chem. Abstracts 32:7770 (1938).

Very small amounts of beryllium were found in 4 of 21 samples examined.

13. Noddack, Ida and Noddack, Walter, Die geochemischen Verteilungskoeffizienten der Elemente. (Geochemical distribution of the elements.) Svensk. Kem. Tidskr. 46:173-201 (1934).

The earth's crust is estimated to contain 0.0005 per cent Be.

14. Oftedal, Ivar, Beryllium in radioactive minerals, Norsk. Geol. Tids. 19:341-342 (1939).

Beryllium was present (less than 0.01 per cent Be) in thorites, uraninites and other radioactive minerals. This may be a source of neutrons, hence suggests the possibility of nuclear fission as a natural phenomenon.

15. Palache, Charles and Bauer, L. H., The occurrence of beryllium in the zinc deposits of Franklin, N. J., Am. Mineral., 15:30-33 (1930).

An analysis of idocrase is given that shows 9.2 per cent BeO. This figure has been stated (private communication from Prof. E. S. Larsen) to be in error.

16. Pieruccini, Renzo, Spectrographic determination of beryllium in some sedimentary rocks of the Toscan-Emilian Apennines (in Italian) Spectrochim. Acta 2:269-290 (1943); Chem. Abstracts 39:471(1945)

Some sedimentary rocks contained 0.0001 to 0.00002 per cent Be.

17. Rankama, Kalervo, The geochemical differentiation in the earth's crust, Bull. comm. géol. Finlande No. 137:39 pp. (1946).

A discussion of the concentration of certain elements, including beryllium, in the refusion of granitic rocks, with the conclusion that the beryllium content might be expected to increase in the youngest granites. A compilation of analyses of granites for Be is included.

18. Sahama, Th. G., The chemistry of the East Fennoscandian rapakivi granites, Bull. comm. géol. Finlande No. 136:15-67 (1945).

Spectrographic analyses of ten rocks. Beryllium was not detected in 5, 0.0003 per cent BeO was reported in 3, and 0.001 per cent BeO in 2, including a sample representing a mixture of 54 granites.

19. Sahama, Th. G., Spurenelemente der Gesteine im südlichen Finnisch-Lapland. (Trace elements in the rocks of southern Finnish Lapland.) Bull. comm. géol. Finlande, No. 135:86 pp. (1945).

Average beryllium contents (spectrographic) are given for 22 types of rocks. Granitic rocks averaged 0.0003 per cent BeO, syenitic rocks 0.0006 per cent BeO. Basic rocks contained less beryllium. Certain aluminous schists contained 0.0003 per cent BeO.

20. Sandell, E. B., Determination of small amounts of beryllium in silicates, Ind. Eng. Chem., Anal. Ed. 12:674-675 (1940).

This includes the following determinations: a granite contained 0.0005 per cent Be, an idocrase 0.06 per cent Be, a nepheline syenite less than 0.0002 per cent Be.

21. Sandell, E. B. and Goldich, S. S., The rarer metallic constituents of some American igneous rocks, J. Geol. 51:99-115, 167-189 (1943).

Chemical analyses of 7 granites, 1 rhyolite, and a composite of 5 granites gave 0.0002 to 0.0014 per cent Be, average 0.0007 per cent Be.

22. Schäfer, Raimund William, Ueber die metamorphen Gabbrogesteine des Allalingsbieten im Wallis zwischen Zermatt und Saasthal. (Metamorphic gabbro rocks of the Allalings region, Wallis.) Mineralog. petrog. Mitt. 15:91-134 (1896).

Analyses are given of two humites that contained 1.68 and 1.04 per cent BeO.

23. Sinegub, E. S., Beryl (in Russian), Nemetallicheskie Iskopaermye S.S.S.R., Acad. Sci. Vol. 2: 129-161 (1943); Chem. Abstracts 39:3226 (1945).

A review of beryl deposits of the world and their genetic types.

- 23a. Sullivan, C. J. and Ludbrook, N. H., Min. Res. of Australia, Summary Report No. 18, Comm. of Australia, Min. Res. Surv., Aug. 1945

24. Szelényi, Tibor, Beryllium in bauxites, Math. Naturw. Anz. ungar Akad. Wiss 56:231-246 (1937); Chem. Abstracts 32:1616 (1938).

Spectrographic determination showed 0.002 to 0.004 per cent Be in Hungarian bauxites. Some clays had beryllium contents equal to or lower than those of the bauxites.

25. Tolmacev, J. M. and Filippov, A. N., Presence of rubidium, beryllium, gallium, and strontium in nephelites. *Compt. rend. acad. sci. U.R.S.S.* 3:366-369 (in English 368-369) (1934).

Spectrographic study following chemical concentration showed 0.0003 to 0.012 per cent Be, average 0.005 per cent Be, in 8 nephelines.

26. U. S. Geological Survey, Section of Chemistry and Physics. Unpublished data.

27. Washington, H. S., Beryllium in minerals and igneous rocks, *Am. Mineral.* 16:37-41 (1931).

It is suggested that beryllium is more common, especially in nepheline syenites, than is generally supposed.

28. Zilbermintz, V. A. and Roshkova, E. V., Zur Frage des Vorkommens von Beryllium in Vesuvianen. (The occurrence of beryl in vesuvianites.) *Centralbl. Mineral., Geol.* 1933A:249-254.

Beryllium was found to be present in 6 of 14 idocrases (vesuvianites) tested; quantitative determinations on three of these gave 0.065, 0.033, and 0.003 per cent Be.

29. Zilbermintz, V. A. and Rusanov, A. K., The occurrence of beryllium in fossil coals, *Compt. rend. acad. sci. U.R.S.S.* 2: 27-31 (1936).

Spectrographic study of the ash of 602 Russian coals. Only 39 contained more than 0.0004 per cent Be, and only 3 contained over 0.004 per cent Be, the maximum found being 0.04 per cent Be.

Table 11.1—Best Beryllia Values from Spectrographic Testing of Mill Products and Other Samples

Occurrence	Location	Product	Beryllium-bearing material	BeO, %
Mill product		Pb-Zn concentrates	Mill heads	0.02
Mill product		Pb-Zn concentrates	Mill tailings	0.03
Mill product		Manganese concentrates	Coarse concentrate from double log washer	0.02
Mill product		Gold silver	Tailings from cyanidation	0.02
Mill product		Gold	Composite of tailings	0.02
Mill product		Gold	Composite of heads oxidized ore	0.02
Mill product		(Lepidolite, muscovite)	Lepidolite flotation concentrate	0.05
		(Columbite-tantalite, microlite)	Muscovite flotation concentrate	0.05
		(Cassiterite: from pegmatite)	Tailings from flotation	0.06
			Ta-Ch-Sn table concentrates	
			(a) from muscovite ore	0.04
			(b) from lepidolite ore	0.04
Mill product		Cu, Pb, Zn alloys and metals	Slag from treatment of scrap metal	0.05
Wind River intrusive	Cornudas Peaks, N. Mex.	None	Altered limestone at contact with nepheline syenite	0.2 (0.14, chem analysis)
Sierra Diablo intrusive	Sierra Diablo, N. Mex.	None	Altered limestone at contact with nepheline syenite	0.3
Sierra Diablo intrusive	Sierra Diablo, N. Mex.	None	Gray-green prophry	0.02
Mill product		Tin	Tin-spodumene pegmatite	0.08
Wolframite prospect	Near Bagdad, Arizona	Wolframite	Tungsten ore	0.05
Wolframite prospect	Near Bagdad, Arizona	Wolframite	Tungsten ore	0.2

Table 11.2—Beryllium-bearing minerals—production and resources

a. Beryl—production and resources, U. S.

Amounts of beryl in known deposits									
Mostly beryl separable by hand					Mostly milling beryl				Total beryl
State	Production		Measured and indicated short tons	Inferred short tons	Grade of beryl-bearing pegmatite, in per cent beryl*	Measured and indicated short tons	Inferred short tons	Grade of beryl-bearing pegmatite, in per cent beryl	Short tons
	Period covered	Weight short tons							
Maine	thru 1944	200±	220	220	0.2 to 1.0	30	355	0.16 to 0.5	825
New Hampshire	thru 1944	100±	40	15	0.1 to 47.0†	30	25		110
Massachusetts	thru 1944	6±		5					5
Connecticut	thru 1944	20±				720	140	0.04 to 1.14	860
Virginia	1929-43	9±		45					
Idaho						76	280+	0.2 to 3.0	356
South Dakota	1879-1943	1229		540 to 1460	0.05 to 2.0		2600 to 2900	0.05 to 2.0	3140 to 4360
Wyoming	to 1943	<1		5			54	Low	
Colorado	to Jan. 1945	450+	53	300+	0.5 to 2.0	1000	2000+	0.5 to 2.0	3353+
New Mexico	to 1943	37+	365	320					685
Grand total 9334 to 10554									

*Estimates of grades are mostly rough approximations.

†This figure applies only to a remarkable beryl-rich shoot within a pegmatite at one locality.

b. Resources of helvite and associated beryllium-bearing minerals, and grades of beryllium-bearing material

	Indicated resources of beryllium- bearing rock—short tons	Inferred resources of beryllium- bearing rock—short tons	Grade in per cent Be
Iron Mtn., N. Mex.	3,500	1,000	0.7
	84,000	100,000	0.2

Table 11.3 — Foreign Production of Beryl

Country	1939	1940	1941	1942	1943	1944
Anglo-Egyptian Sudan	Very small	Very small	Very small	Very small	Very small	Very small
Argentina	299	520	2,186	925	530	275*
Australia	6	2	3	?	524†	414†
Brazil	276	1,472	1,703	1,634	2,027	1,185
British E. Africa						11*
Canada	Very small	Very small	Very small	Very small	Very small	Very small
India and dependencies‡	9	52		119	1,463	1,000§
Madagascar	?	?	?	?	67	?
Portugal	?	?	35	?	14	60*
Spain		4	?	?	?	?
Southern Rhodesia	Very small	Very small	Very small	Very small	Very small	Very small
Southwest Africa	?	?	20	39	36	11
Union of S. Africa	?	5	?	34	78	?
United States	86	110	143	244	323	352

From Minerals Yearbook, except as noted under † and ‡ below.

*Estimate.

†Figures from Commonwealth of Australia, Mineral Resources Survey, Mineral Resources of Australia, Summary Report No. 18; Beryllium, C. J. Sullivan and N. R. Ludbrook, August, 1945.

‡From records of Geological Survey of India, Mineral Trade Notes, March 20, 1946.

§Estimated from U. S. imports.

Paper 12

Geochemistry of Germanium*

MICHAEL FLEISCHER and JAMES O. HARDER

ABSTRACT

This is a review, with annotated bibliography, of the mode of occurrence of the element germanium. It is not a list of specific ore deposits, but a summary of the types of minerals and rocks in which germanium has been reported to occur. Best sources for germanium are indicated, based on the data in the literature and on the unpublished spectrographic studies of the Geological Survey on mill and smelter products. Suggestions are made for further investigations.

Germanium occurs most abundantly in sphalerites of low temperature deposits. The amount ranges from traces to tenths of a per cent. Cinnabar sometimes contains germanium in tenths of a per cent and enargites contain up to 0.1 per cent. Pyrargyrite contains up to 1.0 per cent and some tin-bearing sulfides have 0.5 per cent germanium. Many other minerals have germanium in hundredths of a per cent.

Some residues in zinc smelting contain more than 1.0 per cent germanium. Dusts and ashes from the burning of certain coals contain germanium in amounts from tenths to more than 1.0 per cent. Zinc smelter residues are believed to offer the best immediate chance for recovery of germanium, but copper smelters, and plants burning large quantities of coal should be investigated.

1. INTRODUCTION

This report on the geochemistry of germanium is one of a series of similar reports prepared by the Geological Survey discussing possible sources of several rare or uncommon elements for which there were war uses.

Germanium is a chemical element with the atomic number 32 and the atomic weight 72.60. It belongs to the fourth group of the periodic table, midway between silicon and tin, and in its chemical behavior shows many similarities to these elements. Germanium may be quadrivalent, as in GeO_2 , or bivalent as in GeO . The element's history, its properties and those of its compounds are summarized by Mellor.⁵⁴

*Contribution from the Geological Survey, U. S. Department of the Interior, Washington, D. C. Prepared for publication [June 1946] as TEI-31I and issued as MDDC-645.

2. GEOCHEMICAL CONSIDERATIONS

2.1 General Statement

Germanium was formerly regarded as a very rare element. Clarke and Washington¹⁵ estimated in 1924 that the earth's crust contained $n \times 10^{-9}$ per cent Ge, a value in good agreement with earlier estimates. Spectrographic study since then has shown that this estimate was much too low. The most recent estimates^{3,22,36,37,40,58,60} range from 1×10^{-4} per cent to 7×10^{-4} per cent Ge in the earth's crust, and 4×10^{-4} per cent may be taken as a fair average. This may be compared to the following estimates³⁷ for the percentage of more familiar elements in the earth's crust: 100×10^{-4} per cent Cu; 40×10^{-4} per cent Zn; 16×10^{-4} per cent Pb; 0.1×10^{-4} per cent Ag; and 0.005×10^{-4} per cent Au.

Studies of the distribution of germanium among the metallic, sulfide, and silicate portions of meteorites^{40,41,59} show that germanium is, according to Goldschmidt's classification, siderophilic and chalcophilic, i.e., it tends to be concentrated in the metallic and sulfide phases rather than in the silicate phase. The outer crust of the earth should therefore have a lower content of germanium than the earth's interior. Furthermore, sulfide ores should be richer in germanium than silicate rocks, and this has been found to be true.

From the size of the ionic radii, it might be predicted that quadrivalent germanium would occur as an isomorphous replacement of silicon in silicates, of quadrivalent tin, and of quinquevalent arsenic, antimony, and vanadium. The first three replacements have been observed and data are lacking for the others. However, the occurrence of germanium in sphalerite and cinnabar is not explicable on this basis, but would fit well with the assumption that germanium is present in these minerals as bivalent germanium.

2.2 Occurrences in Specific Minerals and Rocks

Germanium is an essential constituent of only two minerals, argyrodite-canfieldite and germanite (see under Sulfosalts below). Associations in which germanium has been reported are discussed below.

(a) Native metals. Germanium^{28,37,40,41,46,58,59} is relatively concentrated in the nickel-iron of meteorites whose average content is reported to be 0.02–0.05 per cent Ge. Terrestrial native iron also is relatively high in germanium.⁴⁰ Native arsenic⁵⁹ was reported to contain 0.01 per cent Ge and native copper to contain traces.^{34,65}

(b) Sulfides. Germanium has been detected spectrographically by many workers^{2,8,9,11,12,18,21,43,45,48,70-72,76,84,85,87,89} in sphalerite and wurtzite from many localities. Quantitative spectrographic determinations are given for many sphalerites by Oftedal,⁶² by Stoiber,⁷⁹ and by Goldschmidt and Peters,⁴⁰ and there are individual determinations by others.^{14,59,80} A summary of the results on 237 Russian sphalerites has been published.¹ The germanium contents determined range from traces to tenths of a per cent. There is general agreement^{9,18,43,62,79} that the germanium content is highest in sphalerites of low-temperature deposits such as those of the Tri-State district and Wisconsin.

Unpublished spectrographic determinations in the Chemical Laboratory of the U. S. Geological Survey show that germanium is present in many samples of cinnabar and meta-cinnabar in amounts up to tenths of a per cent. No examination of these minerals for germanium has been reported previously.

Chalcocite⁵⁹ from Butte has been reported to contain 0.03 per cent Ge. Secondary chalcocite from Tsumeb, South West Africa, contained up to 0.02 per cent Ge, whereas primary chalcocite from the same deposit contained no germanium.⁵⁸ Germanium has been detected in chalcopyrite,^{40,59,70,87} the maximum content recorded being 0.009 per cent Ge. Gersdorffite⁵⁹ from Loos, Sweden, contained 0.03 per cent Ge, marcassite⁵⁹ from Westphalia was reported to contain 0.009 per cent Ge; many other sulfides and arsenides examined^{40,59} had less than 0.005 per cent Ge or none.

(c) Sulfosalts. The only two minerals known in which germanium is a major constituent are sulfosalts. These rare minerals are the argyrodite-canfieldite series (Ag_8GeS_8 – Ag_8SnS_8) and germanite [perhaps $(\text{Cu,Ge,Fe})(\text{As,S})$]. A third mineral, ultrabasite, reported to contain

germanium, has been discredited.¹⁷ Argyrodite-canfieldite occurs at several mines in Bolivia and near Freiberg, Saxony,¹⁷ and perhaps in Switzerland.⁴ Germanite is known only from Tsumeb, South West Africa.¹⁷ All these occurrences are from low-temperature sulfide deposits.

Quantitative spectrographic determinations have been reported for sixteen enargites.^{40,59,67} Most contain 0.01–0.1 per cent Ge, including samples from Butte, Montana, Central City and Red Mountain, Colorado, and Tintic, Utah. A sample from the Santa Fe mine, Chiapas, Mexico, contained more than 0.1 per cent Ge. The tin-bearing sulfosalts franckeite, cylindrite, and teallite from Bolivia have been reported^{2,59} to contain up to 0.5 per cent Ge, but stannite contained only 0.01 per cent or less. Chalcostibite² from Colquechaca, Bolivia, contained 0.64 per cent Ge. Of seven pyrargyrites⁶⁵ examined, five contained no germanium, one contained 0.07 per cent and one contained more than 1 per cent Ge. Tetrahedrite^{40,59} contained traces to 0.02 per cent Ge. The rare tin-bearing mineral colusite⁸⁹ from Butte, Montana, was recently found spectrographically to contain germanium.

(d) Oxides. Germanium has been reported^{7,25,40,44,52,64,67} to occur in cassiterite, especially in pegmatite cassiterite,⁵² but none has been found to contain as much as 0.01 per cent, and most contain less than 0.005 per cent Ge. Many other oxide minerals contain traces of germanium,^{40,59,83} but the percentages reported are less than 0.005 per cent Ge, except for the columbium-tantalum minerals blomstradine (0.008 per cent) and euxenite (0.015 per cent),⁵⁹ a sample of rutile (0.01 per cent)⁵⁹ and some hematites (0.001–0.01 per cent).⁴⁰ Chromite⁵⁹ was reported to contain up to 0.45 per cent Ge, but this has not been verified by later work.^{40,85} Silica sinters and iron-manganese-rich deposits⁴⁰ from hot springs may contain up to 0.01 per cent Ge, exceptionally 0.05 per cent Ge.

(e) Carbonates, Halides, Sulfates, Phosphates, etc. There are few data on these minerals.⁵⁹ With few exceptions, the samples examined contained 0.001 per cent Ge or less. The germanium content of smithsonite is apparently lower than that of sphalerite;^{48,59} the highest content reported is 0.01 per cent Ge in smithsonite from Marion County, Kentucky.⁵⁷ Vanadinite⁵⁹ from Arizona is reported to contain 0.007 per cent Ge, huebnerite⁵⁹ from Gladstone, Colorado, to contain 0.009 per cent Ge.

(f) Silicate Minerals. Many silicates have been analyzed quantitatively for germanium,^{40,59} and many qualitative tests have been made.^{66,85} The only minerals found to contain appreciable percentages of germanium are some of pneumatolytic or pegmatitic origin. Qualitative tests^{64,66,85} show that most topazes contain germanium. Quantitative determinations^{6,25,40,61,63,85} showed contents of more than 0.01 per cent Ge in 23 of 35 topazes studied; the maximum percentage recorded is 0.1 per cent Ge. Lepidolite,^{40,66,85} spodumene,^{40,66,85} tourmaline^{40,66} and garnet,^{40,61,85} all from pegmatite, show appreciable germanium contents, 0.01 per cent Ge being the highest percentage recorded. Most hemimorphites (calamine) examined gave negative or weak tests for germanium, but a few gave good tests.⁶⁵ Two samples of diopase³⁹ contained about 0.01 per cent Ge.

(g) Rocks. Germanium is similar to silicon in its chemistry and in ionic radius,^{31,32,75} so that it might be expected to occur in silicates. It is, however, rather evenly distributed and no very high concentrations have been reported. The germanium content of igneous rocks increases with increasing silicon content, gabbros averaging 0.00014 per cent Ge, granites^{34,38,40,49,59,74,88} perhaps 0.00035 per cent Ge. Greisen^{38,40} from cassiterite veins is distinctly enriched in germanium and may contain up to 0.005 per cent. Clays and schists have a slightly higher average germanium^{38,40,59} content than the igneous rocks, but none is reported to contain over 0.005 per cent Ge.

(h) Coal, Coal Tar, Coal Ashes, and Flue Dusts. Since 1930, when Goldschmidt²⁹ reported that coal ashes were enriched in germanium, many analyses have been published of coals and ashes from Germany,^{35,40,42} England,^{40,55} Bohemia,⁷⁸ Russia,^{20,51,73,86,90,91} and Australia.¹⁶ No data on American coals have been published, but germanium has been detected in coal from Clymer, Pennsylvania.⁸⁵ A review of the literature has recently been published.²⁷

There is general agreement that the germanium content is highest in coals with the lowest ash content, and that lignites are low in germanium. Vitrain and clarain are highest in germanium.^{20,73} The behavior of germanium during the burning of the coal varies with the conditions of burning. Germanium is concentrated in the ash, whose germanium content is

for most samples a few hundredths of a per cent, although up to 1.2 per cent Ge has been reported. Flue dust is also enriched in germanium;^{40,42} a study⁵⁵ of 72 flue dusts from English gas works showed that many contained tenths of a per cent of germanium. The tarry residues left in coking also may contain germanium concentrations up to one per cent.^{40,51,80}

3. RESULTS OF MILL PRODUCT STUDIES

Germanium has been found in several smelter products, particularly in zinc smelters. The residues from spelter retorts, in which zinc is reduced to metal and volatilized, are particularly enriched in germanium^{12,23,48} and may contain up to 0.5 per cent Ge. Under oxidizing treatment, germanium^{12,18} is concentrated in the zinc oxide^{12,57} which may contain up to 0.18 per cent Ge. Data on the occurrence of germanium in products of zinc smelters are also given in other papers.^{8,13,82}

Products of many American zinc smelters have been studied spectrographically by the Geological Survey.⁸⁵ Some spectrographic results are shown in Table 12.1. The germanium

Table 12.1—Best Germanium Values Resulting from Mill Products Spectrography
(Unpublished Data of the U. S. Geological Survey)

Samples from many smelters of zinc ores*	
Germanium-bearing product	Germanium per cent
Special residue—Dwight-Lloyd flue dust	1.0
Cadmium plant lead sludge	0.5
Waelz, zinc oxide	0.5
Cadmium furnace residue	0.2
Waelz, zinc oxide	0.2
Waelz, zinc oxide	0.2
Dwight-Lloyd Cottrell dust	0.08
Ozark calcines	0.08
Zn furnace residue	0.06
Moore filter cake	0.05
Fresnillo calcine	0.05
Herreshoff furnace—Cottrell dust	0.05
Car residue	0.04
Calcine from Ti pigment	0.04
Zn concentrates	0.04

* More than 100 samples of zinc concentrates from many mills, mostly Tri-State, contain 0.01 to 0.002 per cent Ge.

contents of various types of mill products vary, as would be expected, with different sources of ore, but some generalizations can be made. The best sources of germanium appear to be residues from cadmium furnaces (up to 0.5 per cent Ge), lead sludge from the cadmium plant (up to 0.4 per cent Ge) and zinc oxide from the Waelz process (up to 0.5 per cent Ge). Some Cottrell dusts are rich in germanium (up to 0.06 per cent Ge). Coarse zinc and flotation zinc concentrates from the Tri-State district contain 0.01 to 0.02 per cent Ge; Waelz zinc oxide from the Tri-State smelters averages about 0.14 per cent Ge.

Copper smelters^{5,65} yield flue dusts and slags which contain germanium. It is also reported in mill products of non-ferrous metallurgy^{8,82} and in the waste products of sulfuric acid plants.⁸¹

Two gold mines in South Dakota produced concentrates⁸⁵ which contained 0.014 per cent Ge.

4. RECOVERY OF GERMANIUM

The literature contains many references to methods for recovering germanium. Most of the work has been done on a laboratory scale, but many of the proposed methods are relatively simple and probably could be adapted to large-scale operations. Methods of recovering germanium from spelter and zinc oxide have been published,^{12,13,19,24,48,57} and it has been stated⁴⁷ that workable methods for the recovery of germanium from zinc-plant residues have been developed at the Anaconda plant at Great Falls, Montana.

The extraction of germanium from germanite has been studied; the most recent reports^{23,50,68,77} give references to earlier work. Possible methods of recovery have also been discussed for flue dusts of gas works,^{16,55} for coal by-products such as tars,⁵¹ and for waste products of a sulfuric acid plant.⁸¹

5. BEST SOURCES OF GERMANIUM

The by-product of zinc smelters should be the best source of germanium and would also yield gallium and thallium. Cadmium and indium are now being recovered from this source. The percentage of germanium contained in the best of the zinc smelter by-products ranges from 0.2 per cent to more than 1 per cent. No quantitative data are available regarding amounts of such material; but since most are residues and sludges, the amounts are probably not large. It is not known whether or not germanium is now being recovered from these sources.

6. SUGGESTIONS FOR FURTHER INVESTIGATIONS

Flue dusts from the manufacture of producer gas is a possible source, if American coals are similar to other coals in their germanium content. Only a few coals have been examined in the mill products study investigation of the U. S. Geological Survey.⁸⁵ No germanium was found in them. Tarry residues from coke ovens are also worth more investigation.

Some cinnabar contains germanium and it is possible that flue dusts from mercury retorts might contain concentrations of germanium; but none of the few tested by the Geological Survey (Arkansas, Arizona, and California) have shown any germanium concentration.

Copper smelting waste and by-products should be investigated, particularly in the Butte district, where enargite is common.

Waste products of smelters handling Bolivian tin sulfide ore would also be worth study.

Flue dust and ashes from oil burners might be worth investigation.

ANNOTATED BIBLIOGRAPHY OF OCCURRENCES OF GERMANIUM

Note: The original papers were seen except those for which reference to an abstract journal is given.

1. Abramov, F. I. and Rusanov, A. K. Spectroscopic investigation of sphalerites for germanium, indium, cadmium and gallium. (In Russian.) Problem. Soviet Geol. 8, No. 5, 64-73 (1938).

Of 237 samples studied, 30 had 0.1 per cent Ge, 7 had 0.01 to 0.1 per cent Ge, 61 had 0.01 per cent Ge. The germanium content was slightly higher in light-colored varieties, and particularly high in the "schalenblende" type of sphalerite (or wurtzite). The samples studied are classified according to type of deposit; those from "sulfide-magmatic" and "metasomatic" deposits have the highest germanium contents.

2. Ahlfeld, Friedrich and Moritz, H. Beitrag zur Kenntniss der Sulfostannate Boliviens. (The sulfostannates of Bolivia.) Neues Jahrb. Mineral. Geol., Beil.-Bd. 66A, 179-212 (1933).

Chemical and spectrographic analyses are given of wurtzite, stannite, chalcostibite, teallite, franckeite, cylindrite, and argyrodite from Bolivia. The occurrence and paragenesis of argyrodite-canfieldite are described.

3. Anderson, J. S. Chemistry of the earth. J. Proc. Roy. Soc. New South Wales 76, 329-345 (1942).

A general account, including a table of the abundance of the elements. Germanium is estimated to be 0.0001 per cent of the earth's crust.

4. Beck, G. Der Nachweise seltener Elemente in dem Amsteger und Walliser Erzen! (Detection of rare elements from Amsteg and Wallis.) Abstr. in Mitt. naturforsch. Ges. Bern 1937, V-VI.

Ore from Amsteg, Switzerland, contained germanium corresponding to 0.5 per cent argyrodite (= 0.03 per cent Ge). Lead-zinc ores from mines in Wallis contained germanium and about 0.2 per cent indium.

5. Borovick, S. A. Spectroscopic investigation of the products of an arsenic plant. Compt. rend. acad. sci. U.R.S.S. 25, 210-21 (1939).

Samples, collected from the arsenic recovery plant of a copper smelter, included Cottrell dust, bag filter material obtained after removing As_2O_3 , dross from roasting Cottrell dust, coal dust, boiler dust, etc. Germanium was found to be concentrated (no figures given) in all the samples excepting the Cottrell dust.

6. Borovick, S. A. On the content of germanium and other rare elements in topazes and beryls of the U.S.S.R. Compt. rend. acad. sci. U.R.S.S. 31, 24-26 (1941).

Twenty-seven topazes were examined. Seven contained 0.04 to 0.03 per cent Ge, four contained 0.03 to 0.02 per cent Ge, six contained 0.02 to 0.01 per cent Ge, seven contained 0.01 to 0.001 per cent Ge, three contained no germanium.

7. Borovick, S.A. and Gotman, J.D. Content of rare and other elements in the cassiterites of different genesis from U.S.S.R deposits according to spectrum analysis data. Comp. rend. acad. sci. U.R.S.S. 23, 351-354 (1939).

Qualitative spectrographic study of 27 cassiterites. Only one wood-tin contained germanium and that one only traces.

8. Borovick, S. A. and Kalinin, S. K. Detection of germanium in ores and industrial wastes. (In Russian.) Problem. Soviet Geol. 9, Nos. 4-5, 140-141 (1939); from English abstract by T. Stadnichenko.

Spectrographic data are given for ores and for products of zinc, lead, copper, and cadmium smelters. Only 8 of 204 samples contained germanium. "Speise" from a zinc plant had strong germanium lines.

9. Borovick, S. A. and Prokopenko, N. M. Germanium in some sulfide ores in U.S.S.R. (In Russian.) Bull. acad. sci. U.R.S.S., ser. geol. 1938, No. 2, 341-346; Chem. Abstr. 34, 691 (1940).

Qualitative spectrographic study. Of 58 sphalerites examined, 19 contained germanium in small amounts. Sphalerites containing germanium are mostly found with low-temperature meso- and epithermal deposits. These are usually light-colored and contain very little or no indium. In zones of oxidation, no germanium was found.

10. Brandes, Wilhelm and Geller, Adolf. Seltener Elements (Rarer elements). Z. prakt. Geol. 41, 153-163 (1933).

A brief review of occurrences of germanium is included.

11. Buchanan, G. H. The occurrence of germanium in zinc materials, Ind. Eng. Chem. 8, 585-586 (1916).

Germanium was found in Joplin ores and in some Mexican ores, but none in Franklin ore. A by-product of Wisconsin sphalerite (see 12, below) contained 0.18 per cent Ge.

12. Buchanan, G. H. The occurrence of germanium in Missouri and Wisconsin blends. Ind. Eng. Chem. 9, 681-683 (1917).

Germanium is concentrated in the residue left in spelter retorts. When these residues are heated under oxidizing conditions to recover ZnO, germanium accompanies the oxide which may contain 0.18 per cent Ge (see 11, above). A method is given for recovering the germanium.

13. Burkser, E. S. Rare elements in the wastes of sulfuric acid and zinc plants. (In Russian.) Redkie Metally 6, No. 4, 34-36 (1937); Chem. Abstr. 32, 3099 (1938).

"The recovery of tellurium and bismuth from the Cottrell dust of H_2SO_4 plants and of germanium, indium, and thallium from zinc retorts is discussed."

14. Cambi, L. and Malatesta, L. Germanio, gallio, indio, nella blende di Sardegna. (Germanium, gallium, indium in sphalerite from Sardinia.) Rend. Ist. Lombardo Sci. Lett. Milano 69, 369-374 (1936); Mineralog. Abstr. 7, 107 (1938).

Spectroscopic analysis of calcined sphalerite from Sardinia gave 0.009 to 0.016 per cent Ge, 0.007 to 0.012 per cent In.

15. Clarke, F. W. and Washington, H. S. The composition of the earth's crust. U. S. Geol. Survey Prof. Paper 127, 117 pp. (1924).

A summary.

16. Cooke, W. T. The occurrence of gallium and germanium in some local coal ashes. Trans. Roy. Soc. South Australia 62, 318-319 (1938).

Chemical analyses showed up to 0.03 per cent Ge in flue dusts from coal burners. The germanium can be leached out of the flue dusts by hot caustic soda, but too much silica accompanies it.

17. Dana's System of Mineralogy, Seventh Edition, Volume I. John Wiley and Sons (1944).

For an account of the occurrences of argyrodite-canfieldite, see pp. 356-358; for the occurrence of germanite, see pp. 385-386; on ultra-basite, see p. 415.

18. DeLaunay, L. and Urbain, G. Recherches sur la métallogénie des blendes et des minéraux qui en dérivent. (The metallogeny of sphalerite and of minerals derived from it.) Bull. Geol. Soc. France (4) 10, 787-795 (1912).

Qualitative spectrographic study of sphalerite with the conclusion that germanium is highest in sphalerite from low-temperature deposits.

19. Dennis, L. M. and Johnson, E. B. Germanium V. Extraction from germanium-bearing zinc oxide. Direct preparation of germanium dioxide free from arsenic. Detection of minute amounts of arsenic in germanium dioxide. J. Am. Chem. Soc. 45, 1380-1391 (1923).

Crude ZnO from the New Jersey Zinc Co. contained 0.18 per cent Ge (compare 12).

A method for the extraction of germanium is given.

20. Egorov, A. I. and Kalinin, S. K. Distribution of germanium in Compt. rend. acad. sci. U.R.S.S. 26, 925-926 (1941).

Germanium was present in the ashes of coal from eleven of thirty-five deposits studied, the highest concentration being 0.5 per cent Ge. Coals with low ash had the highest germanium content. Vitrain and clarain were much higher in germanium than other coal constituents.

21. Evrard, Pierre. Minor elements in sphalerites from Belgium. Econ. Geol. 40, 568-574 (1945).

Qualitative spectrographic analyses of 21 sphalerites from Belgium. Germanium was present in all. Marcasite from the same deposits contained only traces of germanium, galena contained none.

22. Fersman, A. E. Geokhimiya (Leningrad, 1933), quoted by Wells, R. C., U. S. Geol. Survey Bull. 878, p. 4 (1937).

The earth's crust is estimated to contain 0.0001 per cent Ge.

23. Foster, L. S. and Tompson, R. Y. The extraction of germanium and gallium from germanite. III. The recovery of germanium from the arsenious sulfide sublimates. J. Am. Chem. Soc. 61, 936-937 (1939).

24. Gable, H. S. The extraction of germanium from germanium-bearing spelter retort residues. Rec. trav. chim. Pays-Bas 52, 225-228 (1933).

Spelter residues from Missouri zinc ores contain fused silicates, much coke, and iron sulfide. The germanium, apparently present as metal, varies from 0.1 to 0.5 per cent Ge. It can be recovered by a simple distillation with HCl.

25. Geilmann, W. and Brünger, K. Zum Nachweis von Germanium. (Determination of germanium.) Z. anorg. allgem. Chem. 196, 312-320 (1931).

Details are given of methods of chemical concentration and spectrographic determination. Analyses for germanium are listed for topaz, cassiterite, and native copper.

26. Geilmann, W. and Brünger, K. Die Aufnahme von Germanium durch Pflanzen. (Utilization of germanium by plants.) Nachr. Ges. Wiss. Göttingen, Math.-Phys. Klasse, 1932, Heft 3, 249-253.

Authors found that plants grown on soil to which germanium had been added contained appreciable amounts of germanium in their ashes. This may explain the concentration of germanium in coal.

27. Gibson, F. H. and Selvig, W. A. Rare and uncommon chemical elements in coal. U. S. Bur. Mines, Techn. Paper 669, 23 pp. (1944).

A review, with bibliography, including a section on germanium.

28. Goldschmidt, V. M. Ueber das Vorkommen des Germaniums in Meteoriten von Cranbourne. (Occurrence of germanium in the Cranbourne meteorite.) Z. physikal. Chem. A 146, 404-405 (1930).

Troilite from this meteorite contained approximately 0.1 per cent Ge.

29. Goldschmidt, V. M. Ueber das Vorkommen des Germaniums in Steinkohlen und Steinkohlen-Produkten. (Occurrence of germanium in coal ashes.) Nachr. Ges. Wiss. Göttingen, Math.-Phys. Klasse, 1930, Heft 3, 398-401.

Germanium occurs in many coals in percentages of 0.001 to 0.01 per cent Ge. Germanium is also concentrated in the flue dust, which contains much arsenic.

30. Goldschmidt, V. M. Geochemische Verteilungsgesetze und kosmische Häufigkeit der Elemente. (Laws of geochemical distribution and cosmic abundance of the elements.) Naturwissenschaften 18, 999-1013 (1930).

A general review of geochemical principles with some data on germanium.

31. Goldschmidt, V. M. Ueber die Kristallchemischen Beziehungen zwischen Gallium und Aluminum, Germanium und Silicium. (Crystallochemical relations between gallium and aluminum, germanium and silicon.) Norsk Geol. Tids. 12, 247-264 (1931).

Nearly the same as 32 below.

32. Goldschmidt, V. M. Kristallchemie des Germanium. (Crystal chemistry of germanium.) Nachr. Ges. Wiss. Göttingen, Math.-Phys. Klasse, 1931, Heft 2, 184-190.

The close similarity between silicon and germanium, which have ionic radii respectively 0.39 and 0.44 Å., is further shown by synthesis of various germanium compounds which have crystal structures close to those of the analogous silicates.

33. Goldschmidt, V. M. Grundlagen der quantitativen Geochemie. (Foundations of quantitative geochemistry.) Fortschr. Mineral., Krist., Petrog. 17, 112-156 (1933).

A review of geochemical principles, with some applications to the occurrence of germanium.

34. Goldschmidt, V. M. Drie Vorträge ueber Geochemie. (Three lectures on geochemistry.) Geol. För. Förh. (Stockholm) 56, 385-427 (1934).

A general review. The germanium content of silicate rocks is roughly proportional to the content of silica. Gabbros average 0.00014 per cent Ge, nepheline syenites 0.00021 per cent, granites 0.00035 per cent.

35. Goldschmidt, V. M. Rare elements in coal. Ind. Eng. Chem. 27, 1100-1102 (1935).

About the same as 42 below.

36. Goldschmidt, V. M. The principles of distribution of chemical elements in minerals and rocks. J. Chem. Soc. (London) 1937, 655-673.

A general account, with a table of the content of the earth's crust for all the elements.

37. Goldschmidt, V. M. Geochemische Verteilungsgesetze der Elemente. (IX). Die Mengenverhältnisse der Elemente und der Atom-Arten. (Laws of geochemical distribution of the elements (IX). The relative amounts of the elements and of the isotopes.) Skrift. Norsk. Videnskaps-Akad. Oslo, Mat.-Nat. Klasse 1937, No. 4, 148 pp.

The most detailed recent work giving a discussion of the occurrences of the elements and the content of the earth's crust for all the elements.

38. Goldschmidt, V. M., Hauptmann, H., and Peters, Cl. Über die Berücksichtigung "seltener" Elemente bei Gesteine-Analysen. (Consideration of the "rarer" elements in rock analyses.) *Naturwissenschaften* 20, 362-365 (1933).

A discussion of the distribution of various elements in types of rocks. The following new determinations are given: a mixture of 11 gabbros from Germany contained 0.00014 per cent Ge, a mixture of 14 granites from Germany contained 0.00035 per cent Ge, a mixture of 22 nepheline syenites contained 0.00021 per cent Ge, a mixture of 24 greisens from the Erzgebirge contained 0.00035 per cent Ge, a mixture of 36 clay schists contained 0.0007 per cent Ge.

39. Goldschmidt, V. M. and Peters, Cl. Geochemie des Galliums. (Geochemistry of gallium.) *Nachr. Ges. Wiss. Göttingen, Math.-Phys. Klasse*, 1931, Heft 2, 165-183.

A detailed spectrographic study, with some data on germanium. Two samples of diopside contained about 0.01 per cent Ge. Determinations of germanium are given for a number of meteorites. Germanium is highest in the metallic portion, lowest in the stony portion of meteorites. Sedimentary iron oxide ores nearly always show enrichment in germanium, with contents of 0.001 to 0.004 per cent Ge.

40. Goldschmidt, V. M. and Peters, Cl. Zur Geochemie des Germaniums. (Geochemistry of germanium.) *Nachr. Ges. Wiss. Göttingen, Math.-Phys. Klasse*, 1933, Heft 2, 141-166.

An elaborate study, with spectrographic determinations of the germanium content of two hundred or more rocks and minerals of all types. The highest values for these are cited in section 2.2 on Occurrences in Specific Minerals and Rocks.

41. Goldschmidt, V. M. and Peters, Cl. Zur Kenntniss der Troilit-Knollen des Meteoriten. Ein Beitrag zur Geochemie von Chrom, Nickel und Zinn. (The troilite nodules of meteorites. A contribution to the geochemistry of chromium, nickel and tin.) *Nachr. Ges. Wiss. Göttingen, Math.-Phys. Klasse*, 1933, Heft 3, 278-287.

Data are given on the germanium content of metal and troilite phases of several meteorites.

42. Goldschmidt, V. M. and Peters, Cl. Ueber die Anreicherung seltener Elemente in Steinkohlen. (The enrichment of rare elements in coal ashes.) *Nachr. Ges. Wiss. Göttingen, Math.-Phys. Klasse*, 1933, Heft 4, 371-387.

Data on many elements. The germanium determinations on coal ashes are repeated from 40. Coal ashes average 0.05 per cent Ge. The mode of concentration of germanium in coal is discussed.

43. Graton, L. C. and Harcourt, G. A. Spectrographic evidence on origin of ores of Mississippi Valley type. *Econ. Geol.* 30, 800-824 (1935).

Qualitative spectrographic data are given for 18 sphalerites. Conclusion that the germanium content is highest for low-temperature deposits.

44. Hadding, Assar. Ueber das Vorkommen des Germaniums im Kassiterite. (The occurrence of germanium in cassiterite.) *Z. anorg. allgem. Chem.* 123, 171-173 (1922).

Qualitative spectrographic study of four cassiterites showed that two contained traces of germanium.

45. Hassler, E. L. and Roys, H. C. Rare elements in Oklahoma sphalerite. *Proc. Okla. Acad. Sci.* 14, 67-68 (1934).

Germanium was detected in Oklahoma sphalerite.

46. Heide, F., Herschkowitz, E., and Preuse, E. Ein neuer Hexahedrite von Cerros del Buei Muerte, Chile. (A new hexahedrite from Cerros del Buei Muerte, Chile.) *Chem. Erde* 7, 483-502 (1932).

Germanium was detected in the iron of this meteorite.

47. Hess, F. L. Rare metals and minerals. *Mining and Metallurgy* 19, 5-9 (1938).

A brief review. The statement is made, "Workable methods for the recovery of indium and germanium from zinc-plant residues have been developed at the Anaconda plant at Great Falls, Montana."

48. Hillebrand, W. F. and Scherrer, J. A. Recovery of gallium from spelter in the United States. *Ind. Eng. Chem.* 8, 225 (1916).

Qualitative spectroscopic tests for germanium were made on four zinc sulfide ores and three zinc carbonate ores.

49. Hybinette, A. G. and Sandell, E. B. Determination of germanium in silicate rocks. *Ind. Eng. Chem., Anal. Ed.* 14, 715-716 (1942).
A method is given for chemical concentration and colorimetric determination of traces of germanium. A granite contained 0.00026 per cent, a diabase contained 0.00014 per cent Ge.
50. Johnson, W. C., Foster, L. S., and Kraus, C. A. The extraction of germanium and gallium germanite. I. The removal of germanium by the distillation of germanous sulfide. *J. Am. Chem. Soc.* 57, 1828-1832 (1935).
This includes references to previously suggested methods for recovery of germanium.
51. Kostrikin, V. M. Germanium in the tar by-products of the coking process. (In Russian.) *J. Applied Chem. U.S.S.R.* 12, 1449-1454 (1939); from English abstract by T. Stadnichenko.
Germanium is generally present in the light ash found in gas flues. All samples of coal tar and carbonaceous residues left after distilling tar are enriched in germanium. Two methods of extracting germanium from these products are described.
52. Larionov, J. and Tolmacev, J. M. On the chemical composition of cassiterite. *Compt. rend. acad. sci. U.R.S.S.* 14, 303-306 (1937).
Qualitative spectrographic study showed germanium to be present in five cassiterites from pegmatites and absent in two cassiterites from hydrothermal deposits.
53. López de Azcona, J. M. Geochemical study of the lead minerals. (In Spanish.) *Ion (Revista española de química aplicada)* 2, 446-457 (1942); *Chem. Abstr.* 37, 1670 (1943).
Qualitative spectrographic tests were made of 924 samples of lead ores, mostly from Spain. Germanium was present in 3 per cent of the samples.
54. Mellor, J. W. A comprehensive treatment on inorganic and theoretical chemistry. Vol. VII, Longmans, Green and Co. (1927).
Pages 254-275 deal with germanium.
55. Morgan, Gilbert and Davies, G. R. Germanium and gallium in coal ash and flue dust. *J. Soc. Chem. Industry* 56, 717-721 (1937).
Germanium is present in the ashes of many English coals, also in tarry residues from coke ovens. It is particularly concentrated in the flue dusts of gas works. Many analyses are given, with a discussion of possible methods of recovery of germanium and gallium.
56. Moritz, H. Die sulfidische Erze der Taumeb-Mine von Ausgehenden bis zur XVI Sohle. (Sulfide ores of the Tsumeb mine.) *Neues Jahrb. Mineral. Geol., Beil.-Bd.* 67A, 118-153 (1933).
Secondary chalcocite from Tsumeb, South West Africa, contained 0.005 to 0.02 per cent Ge, primary chalcocite and other sulfides contained none.
57. Müller, J. H. Germanium in smithsonite and mine waters from the Hudson mine, Livingston Co., Kentucky. *Ind. Eng. Chem.* 16, 604-605 (1924).
Chemical analysis showed 0.01 per cent Ge in smithsonite and 0.3 parts per million Ge in the mine waters. At the Trenton, N. J., plant that treated this ore, the furnace clinker contained 0.006 per cent, the flue deposit 0.003 per cent, ZnO from pipes near the bag house 0.007 per cent, and the finished product (ZnO) 0.011 per cent Ge. Recovery of germanium from zinc oxide is described.
58. Noddack, Ida and Noddack, Walter. Die Häufigkeit der Chemischen Elemente. (Abundance of the chemical elements.) *Naturwissenschaften* 18, 757-764 (1930).
Tables are given of the occurrence of the elements in the earth's crust and in meteorites. The percentage of germanium in the earth's crust is given as 0.0001 per cent Ge.
59. Noddack, Ida and Noddack, Walter. Die Geochemie des Rheniums. (Geochemistry of rhenium.) *Z. physikal. Chem.* A154, 207-244 (1931).
Quantitative spectrographic determinations are given of the germanium content of about 200 rocks and minerals.
60. Noddack, Ida and Noddack, Walter. Die geochemischen Verteilungskoeffizienten der Elemente. (Geochemical distribution of the elements.) *Svensk Kemisk Tidsskrift* 46, 172-201 (1934).

A general discussion. Tables are given of the occurrence of germanium in the earth's crust, in meteorites, and in minerals.

61. Oftedal, Ivar. On the occurrence of tin in Norwegian minerals. *Norsk Geol. Tids.* 19, 314-325 (1939).

A spectrographic study. A sample of topaz contained 0.1 per cent Ge, spessartite garnet from the same locality contained somewhat less germanium.

62. Oftedal, Ivar. Untersuchungen über die Nebenbestandteile von Erzmineralien norwegischer zinkblendeführender Vorkommen. (Study of the accessory constituents of ore minerals from the Norwegian sphalerite-bearing deposits.) *Skrift. Norsk. Videnskaps. Akad. Oslo, Mat.-Nat. Klasse*, 1940, No. 8, 1-103 (1941).

A very careful quantitative spectrographic study of many minerals from Norwegian sphalerite deposits. Germanium was found only in sphalerite, and was highest in those from low-temperature deposits.

63. Oftedal, Ivar. Lepidolite- og tinnsteinførende pegmatitt i Tordal, Telemark. (Lepidolite- and cassiterite-bearing pegmatites of Tordal, Telemark.) *Norsk Geol. Tids.* 22, 1-14 (in English 13-14) (1942).

A topaz contained 0.05 per cent Ge, by spectrographic analysis.

64. Papish, Jacob. Occurrence of germanium in topaz. *Science* 68, 350-351 (1928).

Qualitative spectrographic tests showed germanium to be present in many topazes, in appreciable amounts in some. Cassiterites contained only traces of germanium.

65. Papish, Jacob. New occurrences of germanium. I. *Econ. Geol.* 23, 660-670 (1928).

Qualitative spectrographic tests. Four samples of stannite contained traces of germanium. Five samples of pyrargyrite gave negative tests, one contained 0.07 per cent Ge, and one over 1 per cent Ge. Seven samples of native copper contained traces of germanium. Five hemimorphites gave negative tests, six gave weak tests, and four gave tests for germanium. It is stated that some flue dusts and slags from copper smelters contained germanium.

66. Papish, Jacob. New occurrences of germanium. II. The occurrence of germanium in silicate minerals. *Econ. Geol.* 24, 470-480 (1929).

Qualitative spectrographic tests on nearly two hundred silicates. Germanium was found especially in topaz, tourmaline, lepidolite, spodumene, and some muscovites.

67. Papish, Jacob, Brewer, F. M., and Holt, D. A. Germanium. XXV. Arc spectrographic detection and estimation of germanium. Occurrence of germanium in certain tin minerals. Enargite as a possible source of germanium. *J. Am. Chem. Soc.* 49, 3028-3033 (1927).

Spectrographic analyses of twelve cassiterites showed two with 0.005 per cent Ge or more. Of fourteen enargites, two contained 0.1 per cent Ge or more; six additional contained 0.01 to 0.1 per cent Ge.

68. Patnode, W. I. and Work, R. W. Germanium XXXVI. Extraction of germanium and gallium from germanite. *Ind. Eng. Chem.* 23, 204-207 (1931).

69. Petar, A. V. Gallium, germanium, indium and scandium. *U. S. Bur. Mines, Inf. Circ.* 6401, 17 pp. (1930).

Brief reviews of occurrences and uses of these elements. Bibliography.

70. Pilipenko, P. P. Investigations of the paragenesis of chemical elements in the sulfide ores of copper, lead and zinc. (In Russian.) *Trudy Moskov. Geol.-Razved Inst.* 8, 3-16 (1937) *Chem. Abstr.* 33, 7240 (1939).

Germanium was found in traces in some chalcopyrites.

71. Pina des Rubies, S. and López de Azcona, J. M. Análisis espectral de la Blende por concentración piroeléctrica. (Spectrographic analysis of sphalerite.) *Anal. Soc. Espan. fís. quím.* 34, 307-314 (1936); *Neues Jahrb. Mineral. Geol.* 1938, Ref. I. 166.

Qualitative spectrographic detection of germanium in sphalerite.

72. Pina des Rubies, S. and López de Azcona, J. M. The relation between color and spectrochemical composition of sphalerite from Aliva, Picos de Europa. (In Spanish.) *Anales. soc. Espan. fís. quím.* 35, 180-186 (1937); *Chem. Abstr.* 32, 2462 (1938).

Qualitative spectrographic detection of germanium in sphalerite.

73. Ratynsky, V. M. Accumulation of germanium in coals. *Compt. rend. acad. sci. U.R.S.S.* 40, 198-201 (1943).

Analyses of about 100 Russian coals show 0.001 to 1 per cent Ge in the ashes. Low-ash material is, in general, highest in germanium content but there is much variation even within a single field. Vitrain coals contain 10 to 100 times as much germanium as average coals.

74. Sahama, Th. G. On the chemistry of the East Fennoscandian rapakivi granites. *Bull. Comm. géol. Finlande.* No. 136, 15-67 (1945).

Spectrographic analysis of a mixture of 54 granites from Finland gave 0.00007 per cent Ge.

75. Schütz, Wolfram. Kristallchemische Beziehungen zwischen Germanium und Silicon. (Crystallochemical relations between germanium and silicon.) *Z. physikal. Chem.* B31, 292-308 (1936).

X-ray study of some germanates shows them to correspond closely in crystal structure to the analogous silicates.

76. Scutt, Walter. Germanium in a British mineral. *Phil. Mag.* (7) 1, 1007-1009 (1926).

Qualitative spectrographic detection of germanium in sphalerite from Wales.

77. Sebba, F. and Pugh, W. Gallium. II. The extraction of gallium and germanium from germanite. *J. Chem. Soc. (London)* 1937, 1371-1373.

78. Simek, B. G. The germanium content of coals of the Ostrau-Karwin basin. *Chem. Listy* 34, 181-185 (1940); *Chem. Abstr.* 37, 4036 (1943).

Spectrographic determinations on coal ashes gave 0.0001 per cent Ge for most of the coals, 0.001 per cent Ge for some.

79. Stoiber, R. E. Minor elements in sphalerite. *Econ. Geol.* 35, 501-519 (1940).

Spectrographic determinations on seventy-five sphalerites gave: 0.01 to 1 per cent Ge two, 0.01 to 0.1 per cent Ge nine, less than 0.01 per cent Ge thirty-two, not detected thirty-two. Germanium is highest in sphalerite from low-temperature deposits.

80. Strock, Lester W. Quantitative spectrographic determination of minor elements in zinc sulfide ores. *Am. Inst. Mining Met. Engineers, Tech. Publ. No. 1866*, 1-22 (1945).

Mainly devoted to methods. One commercial zinc ore concentrate contained 0.02 per cent Ge, others contained less than 0.001 per cent Ge.

81. Syrokonsky, V. S. and Sharova, A. K. The presence of the rare elements thallium and germanium in the waste products from sulfuric acid factories. (In Russian.) *J. Chem. Ind. U.R.S.S. (Zhurnal Khimicheskoi Promishlennosti)* 15, No. 2, 22-30 (1938); from an abstract prepared by Taisia Stadnichenko.

The thallium and germanium contents of waste products of sulfuric acid plants are low when flotation tailings are used as a source of sulfur. Cottrell dusts may contain 0.01 to 0.03 per cent Ge. Leaching these dusts with 35 per cent H_2SO_4 dissolves only 25 to 40 per cent of the germanium content. The recovery of germanium would be profitable since other elements would be recovered. It is mentioned that Cottrell dust from the Chelyabinsk zinc plant (7 tons daily) contained 0.004 to 0.005 per cent Ge.

82. Syrokonsky, V. S. and Sharova, A. K. The content of the dispersed rare elements thallium, indium, gallium, and germanium in the intermediate and the waste products of the non-ferrous metallurgy of Ural. (In Russian.) *Tsventye Metally* 1938, No. 11, 23-27; *Chem. Abstr.* 34, 695 (1940).

No specific data are given.

83. Ulrich, Frantisek. Brookite from Bobrovka. *Rozpravy Ceske Akad., Classe 2*, 31, No. 8 (1922); *Mineralog. Abstr.* 2, 141 (1923).

Brookite from albite pegmatite contained germanium.

84. Urbain, G. Analyse spectrographique des blendes. (Spectrographic analysis of sphalerites.) *Compt. rend.* 149, 602-603 (1909).

Qualitative spectrographic study showed that germanium was present in thirty-eight of sixty-four sphalerites examined.

85. U. S. Geological Survey. Unpublished spectrographic data by George Steiger, K. J. Murata, Cyrus Feldman and J. C. Rabbitt.

86. Vakhrushev, G. V. Exploration of rare elements in Bashkiriya (southern Ural). (In Russian.) Uchenye Zapiski Saratov Gosudarst Univ. N. G. Chernyshevskogo 15, No. 1, 124-146 (1940); Chem. Abstr. 35, 6541 (1940).

The upper horizon of the Ermolaevka coal deposits contains 0.05 to 0.2 per cent V_2O_5 and approximately 0.1 per cent Ge.

87. Veselovsky, B. K. High-vacuum sublimation as a method for detecting and concentrating rare elements. (In Russian.) Zavodskaya Lab. 10, 372-374 (1941); Chem. Abstr. 35, 7873 (1941).

A method is described for fractional sublimation of mineral sulfides under high vacuum. A sphalerite contained 0.0001 per cent Ge, a chalcopyrite 0.001 per cent Ge.

88. Wager, L. R. and Mitchell, R. L. Preliminary observations on the distribution of trace elements in the rocks of the Skaergaard intrusion, Greenland. Mineralog. Mag. 25, 283-296 (1943).

The germanium content of average gabbro is listed as 0.00014 per cent Ge, of average granite as 0.00035 per cent Ge.

89. Warren, H. V. and Thompson, R. M. Sphalerites from Western Canada. Econ. Geol. 40, 309-335 (1945).

Qualitative spectrographic study of 164 samples of sphalerite, mostly from British Columbia. Germanium was not detected in most and was present in very small amount in others. Germanium was detected in colusite from Butte, Montana.

90. Zilbermintz, V. A. Germanium in the coals of the Donetz Basin. (In Russian.) Mineral. Syre 11, No. 6, 16-26 (1938); from an English abstract by Taisia Stadnichenko.

Nearly 300 samples from 250 coal fields were studied. The percentage of germanium varies, even in a single bed. Of the samples studied, the ashes of 7 per cent of the samples had 0.1 to 1 per cent Ge, of 12 per cent had 0.01 to 0.1 per cent Ge. The ashes of carbonaceous residues and pitch from coke ovens contained about 1 per cent Ge.

91. Zilbermintz, V. A., Rusanov, A. K., and Kostrikin, V. M. The question of the distribution of germanium in fossil coals. (In Russian.) Akad. V. I. Vernadskomu Pyatidessyatiletiiyu Nauch. Deyatelnosti 1, 169-190 (1936); Chem. Abstr. 33, 8384 (1939).

Spectrographic determinations of germanium in the ashes of coals from all over the U.S.S.R. Thirty-four had 0.1 to 1 per cent Ge, fifty-eight had 0.01 to 0.1 per cent Ge. Most coals rich in germanium had low ash content.

Paper 13

The Geochemistry of Indium*

MICHAEL FLEISCHER and JAMES O. HARDER

ABSTRACT

This is a review, with annotated bibliography, of the mode of occurrence of the element indium. It is not a list of specific ore deposits, but a summary of the types of minerals and rocks in which indium has been reported to occur. In addition, the unpublished spectrographic studies of the Geological Survey on mill and smelter products are summarized, best sources of indium are indicated, and suggestions are made for further investigations.

Indium has been found to occur most abundantly in sphalerites, the amount ranging from traces to a maximum of 1.0 per cent. Dark sphalerites are reported richer in indium than light-colored sphalerites. Up to 0.1 per cent indium has been reported in chalcopyrite and bornite, but these minerals generally contain very little indium. Some sulfosalts of tin from Bolivia contain up to 1.0 per cent indium. There is an unverified report of a pegmatite in Utah containing 1.0 to 2.8 per cent indium.

Some residues in zinc smelting contain more than 1.0 per cent indium and are the present source of indium. No better source can be suggested but steps should be taken to ascertain that this source is being fully exploited. Tin sulfide smelter products should be checked. An effort should be made to check the Utah pegmatite occurrence.

1. INTRODUCTION

This report on the occurrences of indium is one of a series of similar reports prepared by the Geological Survey, discussing possible sources of several rare or uncommon elements for which there were war uses.

Indium is a chemical element with the atomic number 49 and the atomic weight 114.76. It belongs to the third group of the periodic table, midway between gallium and thallium, and is similar in its chemical behavior to these elements. Indium is trivalent in most of its compounds. The element's history, its properties, and those of its compounds are summarized in detail by Gmelin³⁰ and Mellor,⁵³ briefly by others.^{27,29,47,64} Several bibliographies of indium are available.^{16,50,56,65}

*Contribution from the Geological Survey, U. S. Department of the Interior, Washington, D. C. Prepared for publication June 1946 as TEI-31 H and issued as MDDC-646.

2. GEOCHEMICAL CONSIDERATIONS

2.1 General Statement

Indium is one of the very rare elements. All the recent estimates^{2,20,26,32,58,59} give 1×10^{-5} per cent In for its abundance in the earth's crust, which makes it sixty-fourth in abundance of the ninety known elements. These estimates were, however, based on very scanty data. Indium is a dispersed element, and is not a major constituent of any mineral, 1 per cent In being the maximum recorded percentage. It is a strongly chalkophilic element, concentrated almost exclusively in sulfides.

The empirical ionic radius of trivalent indium is given by Goldschmidt as 0.92. One might therefore expect that indium might be associated with the following elements, whose ionic radii are close to 0.92: divalent manganese 0.91, zinc 0.83, divalent iron 0.83, cobalt 0.82, cadmium 1.03, and trivalent thallium 1.05. Zirconium and scandium have ionic radii in this range, but do not occur in sulfide deposits. Actually, indium is found to be associated especially with zinc, also with divalent iron, quadrivalent tin (ionic radius 0.74), and copper, and only very rarely with divalent manganese. This suggests that the ionic radius of indium is lower than 0.92, perhaps about 0.85.

2.2 Occurrences in Specific Minerals and Rocks

(a) Sulfides. Indium was first detected in 1863 in sphalerite from Freiberg, Germany, and has since been detected in sphalerite from many localities. The early work is summarized by Mellor.⁵³ Qualitative data have been published by many workers.^{2,4,9,10,21,34,37,39,43,52,60,66-68,77-81} Quantitative determinations have been published for many sphalerites, with studies of paragenesis and associations.^{1,12,19,25,62,71,72,74} The indium content of sphalerite varies from none to 1 per cent. About 5 per cent of the analyses reported, including one sample from Leadville, Colorado, show over 0.1 per cent In, and about 30 per cent, including samples from Georgetown, Colorado, Nevada City, Colorado, and Bingham Canyon, Utah, show 0.01 to 0.1 per cent In. There is general agreement in the literature^{1,10,12,62,67,72,78} that sphalerite from low-temperature deposits is low in indium, whereas sphalerite from mesothermal to hypothermal deposits is likely to contain appreciable indium. However, this does not check with results from the Geological Survey mill products study which indicates no such correlation (see Section 3). Sphalerite from contact deposits of scheelite or magnetite and sphalerite from wolframite deposits are likely to have high indium contents.^{12,67} Dark-colored, i.e., iron-rich sphalerites are generally richer in indium than light-colored sphalerites.^{1,12,25,60}

Indium has been detected^{9,12,25,37,52,60,67,68} in many other sulfides including chalcopyrite, stannite, chalcocite, covellite, bornite, galena, pyrite, pyrrhotite, cobaltite, and bismuthinite. The concentrations of indium in these minerals are generally very low, in the thousandths of a per cent, but up to 0.1 per cent In has been reported in chalcopyrite and bornite. The statement in a recent paper⁵² that the indium content of galena is higher than that of associated sphalerite contradicts the findings of all other workers,^{25,62} and cannot be accepted without further quantitative study.

(b) Sulfosalts. The tin-bearing sulfosalts, cylindrite and francheite, from Bolivia have been reported to contain 0.1 to 1.0 per cent In.^{14,15} Indium has been detected in traces in tetrahedrite,²⁵ in germanite⁵¹ and in teallite.¹⁴

(c) Oxides. Indium has been detected in cassiterite^{7,14,25,32,37,46,48,60,66-68,77,81} from many localities, but the concentration is always very low, perhaps 0.01 per cent In as a maximum. Commercial tin metal likewise contains traces of In.^{14,15,23,28,35,77} Other oxides that have been reported to contain traces of indium include columbite (up to 0.01 per cent In), hematite, limonite, magnetite, Mn ores, zincite, and samarskite.

(d) Carbonates, Phosphates. Indium has been reported to occur in traces and small amounts (no figures given) in cerussite,⁹ rhodochrosite,¹⁰ smithsonite,^{14,52,75} siderite,^{31,37,66} and in triplite.³² One sample of siderite gave a strong test for In.³⁷

(e) Tungstates, Sulfates. Indium has been reported^{3,10,32,42,66-68,79,81} to occur in wolframite from many localities, but apparently is generally present in very low percentage. The only quantitative analysis⁴² gave 0.02 per cent In. Indium has also been reported to occur in traces in alunite⁸⁰ and in jarosite.^{9,68}

(f) Silicate minerals. The indium content of most silicates examined²⁵ has been very low. Hemimorphite,^{21,52,75} rhodonite,⁸⁰ muscovite,³² garnet,²⁵ vesuvianite,²⁵ and allanite,²⁵ the last three from an ore deposit at Pitkäranta, Finland, unusually rich in indium, have been reported to contain traces of indium. Helvite from Pitkäranta contained up to 0.005 per cent In, serpentine from Pitkäranta up to 0.05 per cent In, and an unusual tin-bearing amphibole from Pitkäranta contained 0.1 to 1.0 per cent In,²⁵ although other amphiboles contained none. Cordierite has been reported⁷⁰ to contain probably several per cent of indium, but this has not been substantiated.

(g) Rocks. The few published determinations^{11,31,32,38,67,70} of the indium contents of rocks are all below 0.001 per cent In, excepting the unverified report⁷⁰ that a pegmatite dike in western Utah contained 1.0 to 2.8 per cent In.

3. RESULTS OF MILL PRODUCT STUDIES

The indium content of zinc smelter products varies with varying sources of ore, and also depends on the metallurgical treatment. However, some generalizations can be made from the published data.^{5,8,13,17,24,40,41,45,54,73,76} Indium is concentrated in the residues from spelter retorts,^{17,24,40} which may contain up to 1 per cent In, in the sludge precipitated in purifying zinc sulfate in the manufacture of lithopone,⁴¹ in flue dusts (up to 0.1 per cent In),^{13,54,60,61,76} in residues from cadmium recovery,^{8,45,63} and in certain ore slimes whose exact nature is not specified.^{8,60,61}

Appreciable percentages of indium have been reported in various products of lead smelters^{8,60} and copper smelters.^{6,9,38} Traces of indium have been reported in the flue dust of gas works,^{38,55} in coal ashes,³¹ in flue dust of iron works,³⁸ in commercial aluminum and alumina,³⁶ and in metallic tin. (See Section 2.2c.)

Over 1000 samples from more than 200 mines and mills have been tested for indium by the Geological Survey as part of the mill products study. Table 13.1 lists 29 of the samples which contained 0.01 per cent or more indium. It is noteworthy that all but one of the samples came from zinc producing plants. The exception is a calcine from titanium pigment and it is not clear whether it also contains zinc or not. There are many more samples containing indium in the range of 0.002 to 0.005 per cent which have not been listed, almost all of which are from zinc plants. The information available to us does not indicate specific quantities of the indium-bearing products. However, in the case of flue dusts and comparable smelter by-products which are comparatively rich in indium the amounts are certain to be relatively small, probably considerably less than one ton per day even in smelters of moderate size. The sphalerite concentrates would, of course, be available in large tonnages but they contain rather small quantities of indium. The concentration of indium comes in the smelting process.

The experience in the mill products testing does not clearly support the indication from the literature that high-temperature sphalerite contains more indium than low-temperature sphalerite. However, the mill products testing is on various zinc concentrates with no knowledge of the degree of concentration of the product by various mines.

Concentrates from the Wisconsin area were lowest (0.002 per cent In) but concentrates from the Metairie district in Washington, where the ore is a relatively low-temperature type, contained the most (up to 0.020 per cent In) of any zinc concentrates. Only certain smelter products were higher, notably special residues such as Cottrell dust from Dwight-Lloyd furnaces, some of which contained more than 1.0 per cent In. Concentrates from the Tri-State area, which is a very low-temperature deposit, contain about 0.004 per cent In, whereas concentrates from Britannia, B. C., at 4000 feet depth and presumably a relatively high-temperature deposit, also contain 0.004 per cent In. Thus, there seems to be no general agreement.

Table 13.1—Best Indium Values Resulting from Mill Products Spectrography
(Unpublished Data of the Geological Survey)

Material treated	Indium-bearing product	In ₂ O ₃ , %
Zn ore	Special residue	1.0
	Dwight-Lloyd flue dust	
..Do..	Blackwell Cottrell dust	1.0
..Do..	Cadmium plant, lead sludge	0.4
..Do..	Cottrell dust (D-L)	0.4
..Do..	Zinc concentrate (Ozark)	0.01
..Do..	Zinc concentrate (Petosi)	0.01
..Do..	Flue dust	0.06
..Do..	Car residue	0.05
..Do..	Pb residue	0.04
..Do..	Zn furnace residue	0.04
..Do..	Herreshoff Cottrell dust	0.03
..Do..	Cottrell dust	0.02
..Do..	Cd furnace residue	0.02
..Do..	Waelz clinker	0.01
..Do..	Ozark calcines	0.02
..Do..	Moore filter cake	0.02
	Potosi calcine	0.02
	Calcine from Ti pigment	0.02
Zn ore	Fresnille calcine	0.01
..Do..	Zinc concentrate	0.02
*	Flue dust (some Zn)	0.02
Zn ore	Flue dust	0.01
	Cottrell dust	0.01
†	Zn concentrate and molybdenum conc.	0.01
..Do..	Clinker from oxide plant	0.01
..Do..	Flue dust	0.01
..Do..	Zinc concentrate	0.01
..Do..	Zinc concentrate	0.01

*Various ores.

†Pb-Zn-Mo-ore.

No other source than by-products of zinc treatment has so far been indicated by the mill products work. Manganese samples tested were very low and copper ores and concentrates in general were also very low. However, some large plants have not yet been tested. Tungsten concentrates tested in the mill products study did not contain any indium.

4. RECOVERY OF INDIUM

Indium is now being recovered from some plants by several of the largest American companies, namely, American Metal Co., Ltd., American Smelting and Refining Co., Anaconda Copper Mining Co., and National Zinc Co., Inc. Early work on the recovery of indium is summarized by Mellor;⁵³ more recent methods have been reviewed briefly.^{24,27,47} A number of other papers are concerned with the recovery of indium from various types of zinc by-products.^{13,15,18,22,44,45,57}

5. BEST SOURCES OF INDIUM

The best-known source for indium continues to be zinc smelter by-products, particularly some of the residues and flue dusts. For the present, the only apparent way to increase supplies of indium is by more complete recovery from these by-products at all zinc smelters. Data are not available to indicate the possibilities of such a plan which may already have reached fulfillment. No supplementary source is so far suggested in the mill products study.

6. SUGGESTIONS FOR FURTHER INVESTIGATIONS

Waste products of smelters handling Bolivian tin sulfide ores should be worth study, in view of the reported high indium content of cylindrite.

Waste and by-products of copper smelters might be worth investigation, especially those handling ore that contains much covellite or secondary chalcocite.

The fate of the small indium content of wolframite during the recovery of tungsten metal is not known. Possibly indium could be recovered from these operations. However, no indium was found in tungsten concentrates tested in the mill products study.

Steps should be taken to ascertain that all zinc smelters are making all the indium recovery that is possible or practicable.

Some large copper smelters have not been tested in the mill products program, and although some of the copper tested has not been of interest, these large plants should be tested.

The reported indium-bearing pegmatite in Utah should be investigated.

ANNOTATED BIBLIOGRAPHY OF OCCURRENCES OF INDIUM

Note: The original papers were seen except those for which reference to an abstract journal is given.

1. Abramov, F. I. and Rusanov, A. K., Spectroscopic investigation of sphalerites for germanium, indium, cadmium and gallium. (In Russian.) *Problem. Soviet Geol.* 8, No. 5: 64-73 (1938).

A summary of results on 236 sphalerites from the U.S.S.R. Of these, 2 contained 0.1 to 1.0 per cent In, 12 contained 0.1 per cent, 7 contained 0.01 per cent, 54 contained 0.01 per cent, 31 contained less than 0.01 per cent, 36 contained traces and indium was not detected in 94. Sphalerites of hypothermal, mesothermal, and sulfide-magmatic deposits were, in general, highest in indium content. Dark sphalerites generally contained more indium than light-colored sphalerites.

2. Anderson, J. S., Chemistry of the earth, *J. Proc. Roy. Soc. New South Wales* 76: 329-345 (1943).

A general account, including a table of the abundance of the elements. Indium is estimated to be 1×10^{-5} per cent of the earth's crust which places it as sixty-fourth in order of abundance of the elements. Sphalerite and galena from Broken Hill, New South Wales, contain minute but detectable amounts of indium. It is estimated that about one ton of indium annually passes through this one smelter.

3. Atkinson, E. A., Indium in tungsten minerals, *J. Am. Chem. Soc.* 20: 811-813 (1898).

Indium was detected in wolframite from Zinwald, Bohemia, but not in two other wolframites or in two scheelites.

4. Beck, G., Der Nachweis seltener Elemente in dem Amsteger und Walliser Erzen. (The detection of rare elements in ores from Amsteg and Wallis.) Abstract in *Mitt. naturforsch. Ges. Bern* 1937. V-VI.

Lead-zinc ores from two Swiss localities contained approximately 0.2 per cent In.

5. Bibikova, V. I. and Gornova, Z. A., Investigation of the products and the wastes of the Chelyabinsk zinc plant for minor elements. (In Russian.) *Tsvetnye Metal.* 1940, No. 5-6: 121-123. (From an English summary by T. Stadnichenko.)

Spectroscopic study of various mill products. The ore concentrates treated were all low in indium (0.004 per cent maximum), and most of the products studied had very low indium contents, the maximum recorded being in ZnO (0.007 to 0.01 per cent In).

6. Borovick, S. A., Spectroscopic investigation of the products of an arsenic plant, *Compt. rend. acad. sci. U.R.S.S.* 25: 210-211 (1939).

Five samples from the arsenic plant of a copper smelter were studied. Four samples of Cottrell and bag-filter dusts contained small quantities of indium (no figures given).

7. Borovick, S. A. and Gotman, J. D., Content of rare and other elements in the cassiterites of different genesis from U.S.S.R. deposits according to spectrum analysis data, *Compt. rend. acad. sci. U.R.S.S.* 23: 351-354 (1939).

Spectrographic study of 27 cassiterites. Indium lines were absent in most samples, weak in cassiterite from sulfide-cassiterite veins, strong in two wood-tin samples.

8. Borovick, S. A. and Kalinin, S. K., Spectroscopical analysis of the products of lead and zinc plants, *Compt. rend. acad. sci. U.R.S.S.* 19: 257-258 (1938).

Indium was found (figures not given) in Cottrell dusts and in dry ore slime of the Chimkent lead works. Copper-cadmium cake from the Ridder plant contains about 0.005 per cent In; slimes and spongy cadmium from this plant contained somewhat less indium.

9. Borovick, S. A. and Prokopenko, N. M., New data on the distribution of indium in Kazakhstan, *Compt. rend. acad. sci. U.R.S.S.* 24: 925-928 (1939).

Indium was detected in sphalerites from several deposits, in some pyrite, chalcocite, and chalcopyrite (thousandths of a per cent). Traces of indium were found in some jarosite and cerussite. Traces of indium were found in the slag and dust of the reverberatory furnace flue, in Dorr thickener tailings, and in black copper, all from the Karsakpai copper smelter. In the Kyzyl-Espe deposit, the indium content varies directly with the tin content.

10. Borovick, S. A. and Prokopenko, N. M., Distribution of indium in Ural ore deposits, *Compt. rend. acad. sci. U.R.S.S.* 31: 22-23 (1941).

No quantitative data are given. Indium was found spectroscopically in many sphalerites, especially in those from high-temperature deposits. Indium was noted in low concentrations in chalcopyrite, rhodochrosite, wolframite and native gold.

11. Borovick, S. A., Prokopenko, N. M., and Pokrovskaya, T. L., Distribution of indium in rocks, *Compt. rend. acad. sci. U.R.S.S.* 25: 618-621 (1939).

Spectrographic analysis following chemical concentration was used. A mixture of 12 Russian granites contained 5×10^{-6} per cent In. Another granite contained 1.5×10^{-4} per cent In, a nepheline syenite contained 9×10^{-6} per cent In and a monzonite contained 1.9×10^{-4} per cent In. No indium was detected in gabbros and dunites. Traces of indium were detected in clays and in one sample of pyrrhotite.

12. Borovick, S. A., Vlodavets, N. I., and Prokopenko, N. M., The occurrence of indium in the lead-zinc deposits of Middle Asia, *Bull. acad. sci. U.R.S.S., Classe sci. math. nat., Sér. géol.* 1938, 335-339 (in Russian), 339-340 (in English).

Spectrographic analyses of 52 minerals are given. Up to 0.3 per cent In was found in sphalerite. Sphalerites containing much iron and little germanium and cadmium were highest in indium and tin. Sphalerites richest in indium were those from hypothermal deposits, also those from skarn scheelite deposits and from wolframite deposits. Indium was also detected in chalcopyrite, arsenopyrite and pyrite.

13. Boettger, R., Ueber das Vorkommen des Indiums in sogenannten Ofenrauche der Zink-Rostofen auf Julius-Hütte bei Goslar am Harz. (The occurrence of indium in the furnace fumes of the zinc-roasting furnaces of the Julius smelter near Goslar in the Harz.) *J. prakt. Chem.* 98: 26-29 (1866).

Flue dusts from furnaces roasting Rammelsberg ore contained 0.1 per cent In_2O_3 . The extraction of indium from these dusts is described.

14. Brewer, F. M. and Baker, Enid, Arc spectrographic determination of indium in minerals, and the association of indium with tin and silver, *J. Chem. Soc. (London)* 1936: 1286-1290.

Spectrographic determinations of indium in many minerals. Traces were found in metallic tin (up to 0.01 per cent In), in some cassiterites, in zincite from Franklin, N. J.,

in argentite, in teallite and in smithsonite. Cyndrite from Bolivia contained 0.1 to 1.0 per cent In, franckeite from Bolivia 0.1 per cent In. Two chalcopyrites contained approximately 0.1 per cent In; two others contained none.

15. Brewer, F. M. and Baker, Enid, Extraction of indium from cyndrite, chalcopyrite and metallic tin, J. Chem. Soc. (London) 1936, 1290-1294.

Laboratory-scale extraction is described. Spectrographic analysis after chemical concentration gave 0.003 per cent In in metallic tin and 0.1 per cent In in cyndrite from Bolivia.

16. Browning, P. E., Index to the literature of indium (1863-1903), Smithsonian Misc. Coll. 46: 1-15 (1905).

17. Browning, P. E. and Uhler, H. S., On a gallium-indium alloy, Am. J. Sci. 41: 351-354 (1916).

The alloy, containing 10 per cent In, was found as liquid globules on the surface of the residue from the distillation of zinc spelter in the Tri-State district. The residue contained 95.6 per cent Pb, 1.2 per cent Zn, 3 per cent Ga plus In and a little copper.

18. Burkser, E. S., Rare elements in the wastes of sulfuric acid and zinc plants. (In Russian.) Redkie Metally 6, No. 4: 34-36 (1937); through Chem. Abs. 32: 3099 (1938).

The recovery of indium from zinc retorts is discussed.

19. Cambi, L. and Malatesta, L., Germanio, gallio, indio nella blende di Sardegna. (Germanium, gallium, and indium in Sardinian sphalerite.) Rend. Ist. Lombardo Sci. Lett. Milano 69: 369-374 (1936); through Mineralog. Abs. 7: 107 (1938).

Calcined sphalerite from Sardinia contained 0.007 to 0.012 per cent In.

20. Clarke, F. W. and Washington, H. S., The composition of the earth's crust, U. S. Geol. Survey Prof. Paper 127, 117 pp. (1924).

The indium content of the earth's crust was estimated, from very few data, to be 10^{-9} per cent.

21. DeLaunay, L. and Urbain, G., Recherches sur la métallogénie des blendes et des minéraux qui en dérivent. (Research on the metallogeny of sphalerite and minerals derived from it.) Bull. Geol. Soc. France 10: 787-795 (1912).

Qualitative spectrographic study. Indium was detected in many sphalerites and in some hemimorphites (calamines).

22. Druce, J. G. F., Occurrence of indium in commercial iron sulfide and its extraction. (In German.) Z. Angew. Chem. 41: 79 (1928); through Chem. Abs. 22: 3022 (1928).

Commercial iron sulfide contained about 0.006 per cent In.

23. Eastman, E. D., Indication of a genetic relation between indium and tin, Phys. Rev. 52: 1226-1227 (1937).

A review of the literature indicates marked association of indium with tin. Possible transitions are discussed.

24. Ensslin, Fritz, Gewinnung des Indiums aus den Zwischenprodukten des Zinkhüttenprozesses. (Recovery of indium from the intermediate products of zinc smelting.) Metall. u. Erz. 37: 401-403 (1940).

Previous methods for extracting indium are reviewed. In the distillation of zinc, indium is concentrated in the residue (Waschzink), a lead-zinc alloy that separates into two layers. The lead-rich layer contains 0.5 to 1.0 per cent In, the zinc-rich layer 0.05 to 0.1 per cent In.

25. Erämetsä, Olavi, Ueber die Verbreitung in finnischen Mineralen und ueber seine Trennung von anderen Metallen. (The distribution of indium in Finnish minerals and its separation from other metals.) Annales Acad. Sci. Fennicae (Suomalaisen Tiedeakatemia Toimituksia) A51, No. 1, 92 pp. (1938).

Spectrographic determinations of indium are given for several hundred mineral specimens. Forty sphalerites contained from 0 to 1 per cent In, the mineral from Pitkäranta being especially rich in indium. In general, dark-colored and coarsely crystallized sphalerites were highest in indium. Most chalcopyrites contained little or no indium, but four samples from Pitkäranta contained 0.05 to 0.1 per cent In. Bornite from this deposit contained 0.1 per cent In. Traces of indium (up to 0.001 per cent) were found in some tetrahedrites and cassiterites. Columbites contained up to 0.01 per cent In. All silicates tested

contained no indium except for samples from Pitkäranta. Garnet, vesuvianite, and allanite from this deposit contained up to 0.001 per cent In, helvite up to 0.005 per cent In, serpentine up to 0.05 per cent In, and a single unusual amphibole contained 0.1 to 1.0 per cent In, although other amphiboles contained only traces of indium.

26. Fersman, A. E., *Geokhimiya* (Leningrad, 1933), quoted by Wells, R. C., U. S. Geol. Survey Bull. 878: p. 4 (1937).

The indium content of the earth's crust is estimated to be 1×10^{-5} per cent.

27. French, S. J., A story of indium, *J. Chem. Education* 11: 270-272 (1934).

A popular general account, including a highly glamorized account of the search for indium ore by W. S. Murray of the Indium Corporation of America. It is stated that at an unnamed locality (stated elsewhere to be near Kingman, Ariz.), 35,000 tons of ore have been blocked out that contain an average of 1.93 oz/ton In (0.006 per cent In). Methods of treatment of the ore are described.

28. Garrett, M. W., Experiments to test the possibility of transmutation by electronic bombardment, *Proc. Roy. Soc. London* 114A: 289-292 (1927).

It is stated that "considerable difficulty was experienced in obtaining tin free from all traces of indium."

29. Geckler, R. P. and Marchi, L. E., Indium., *J. Chem. Education* 21: 407-411 (1944).

A general review.

30. Gmelin's *Handbuch der Anorganische Chemie*. System No. 37, Indium, 116 pp. (1936).

31. Goldschmidt, V. M., The principles of distribution of chemical elements in minerals and rocks, *J. Chem. Soc. (London)* 655-673, (1937).

A general account. The indium content of the earth's crust is estimated to be 1×10^{-5} per cent In. It is stated without details that indium has been found to be somewhat concentrated in oceanic phosphate sediments, in sedimentary and hydrothermal siderite and in some coal ashes (up to 2×10^{-4} per cent).

32. Goldschmidt, V. M., *Geochemische Verteilungsgesetze der Elemente (IX)*. Die Mengenverhältnisse der Elemente und der Atom-Arten. (The principles of the geochemical distribution of the elements. (IX). The abundance of the elements and isotopes.) Skrift. Norsk. Videnskaps-Akad. Oslo, Mat.-Nat. Klasse 1937, No. 4, 148 pp.

The most detailed recent account. It is stated that unpublished work shows indium to be somewhat concentrated in basic pyroxene-rich rocks (5 to 10×10^{-5} per cent In), in muscovites (about 5×10^{-5} per cent In), especially high in tin and tungsten minerals of pneumatolytic origin (5×10^{-5} per cent to 1×10^{-3} per cent In), also in stannite, cassiterite, wolframite and triplite (no figures given). Indium is also concentrated in iron and manganese-rich sediments (no figures given).

33. Goldschmidt, V. M., Barth, T. F. W., and Lunde, G., *Geochemische verteilungsgesetze der Elemente. V. Isomorphie und Polymorphie der Sesquioxyde. Die Lanthanide-Kontraktion und ihre Konsequenzen*. (The principles of the geochemical distribution of the elements. V. The lanthanide contraction and its consequences.) Skrift. Norsk. Videnskaps-Akad. Oslo, Mat.-Nat. Klasse 1925, No. 7, 59 pp.

Indium has close crystallochemical relations with scandium, less close relations with thallium and gallium. Indium might be expected to be present in rare earth minerals, especially those high in scandium.

34. Graton, L. C. and Harcourt, G. A., Spectrographic evidence on origin of ores of Mississippi Valley type, *Econ. Geol.* 30: 800-824 (1935).

Qualitative spectrographic study of 18 sphalerites. Indium was present in some.

35. Green, J. R., Occurrence of indium in tin, *Nature* 119: 893 (1927).

Nearly all samples of metallic tin examined contained indium.

36. Hartley, W. N. and Ramage, Hugh, On the spectrographic analysis of some commercial samples of metals, of chemical preparations, and minerals from the Stassfurt potash beds, *J. Chem. Soc. (London)* 71: 547-550 (1897).

Commercial Al_2O_3 and aluminum metal contained traces of indium.

37. Hartley, W. N. and Ramage, Hugh, The wide dissemination of some of the rarer elements, and the mode of their association in common ores and minerals, J. Chem. Soc. (London) 71: 533-547 (1897).

Qualitative spectrographic study. Indium was detected in 9 of 14 sphalerites, 3 of 9 pyrites, 1 of 2 pyrrhotites, 1 of 1 chalcopyrite, 1 of 1 stannite, 4 of 4 cassiterites, 1 of 6 brown hematites (limonites?), 3 of 18 red hematites, 1 of 7 magnetites, 1 of 12 manganese ore, 5 of 5 siderites (strong test in one).

38. Hartley, W. N. and Ramage, Hugh, The mineral constituents of dust and soot from various sources, Proc. Roy. Soc. London 68: 97-109 (1901).

Qualitative spectrographic study. Indium was detected in the flue dust of a copper works, in the flue dust of a gas works, in traces in flue dust of four iron furnaces, and in pumice from Krakatoa.

39. Henrich, F., Laubmann, H., and Prell, Ueber eine indiumhaltige Zinkblende aus dem Oberpfälzer Walde (Bayern). (An indium-bearing sphalerite from the Oberpfalz Forest, Bavaria.) Z. angew. Chem. 37: 877-878 (1924).

A black sphalerite from pegmatite at Hagendorf contained somewhat less than 0.1 per cent In.

40. Hillebrand, W. F. and Scherrer, J. A., Recovery of gallium from spelter in the United States, Ind. Eng. Chem. 8: 225 (1916).

The presence of indium was noted in a spelter residue from the Tri-State district.

41. Hirschel, W. N., Cadmium, thallium, indium and gallium as by-products of the lithopone industry, Chemistry and Industry, 797-798, (1933).

Zinc sulfate solutions to be used in manufacturing lithopone are treated with metallic zinc to remove elements whose sulfides are colored. The precipitate obtained may contain 10 to 30 per cent Cd, also thallium, gallium, and indium. One such precipitate contained 0.15 per cent In.

42. Hoppe-Seyler, E., Ueber das Vorkommen von Indium in Wolfram. (The occurrence of indium in wolframite.) Annalen der Chemie 140: 247-248 (1866).

Wolframite from an unknown locality contained 0.023 per cent In_2O_3 . Wolframite from Zinnwald also contained indium.

43. Imaizumi, Yoshio, Occurrence of indium in Japan. (In Japanese.) J. Chem. Soc. Japan 54: 771-772, 1009-1010 (1933); through Chem. Abs. 28: 583 (1934).

Indium was present in many Japanese sphalerites, the maximum percentage found being 0.006 per cent In.

44. Izbekov, V. O. and Vovk, M. V., The separation of indium from the dust of the Konstantinovskiy zinc plant. Univ. etat. Kiev, Bull. sci., Rec. chim. 2, No. 2, 21-27 (1937) (In Ukrainian, 21-25; in Russian, 25-26; in English, 26-27.)

In the electrolysis of furnace dust, cadmium, lead, and indium remain in the slime and can be recovered chemically. The recovery from 1.5 kg of dust was 0.156 g In_2O_3 or 0.008 per cent In.

45. Kasatkina, N. A., Recovery of indium from the waste products in cadmium production. (In Russian.) Novosti Tekhniki 1940, No. 17-18, 27-28; through Chem. Abs. 37: 5317 (1943); see also Russian Patents 50,448 and 50,479 (1937); Chem. Abs. 31: 8848 (1937); 32: 1415 (1938).

Chemical and electrolytical recovery of indium is described for secondary cadmium sponge containing 29.7 per cent Cu, 14.4 per cent Cd, and 0.045 per cent In.

46. Larionov, J. and Tolmacev, J. M., On the chemical composition of cassiterites Compt. rend. acad. sci. U.R.S.S. 14: 303-306 (1937).

Qualitative spectrographic study. Indium was present in five pegmatite cassiterites.

47. Lawrence, R. E. and Westbrook, L. R., Indium—occurrence, recovery, and uses. Ind. Eng. Chem. 30: 611-614 (1938).

A review.

48. Liebisch, Th., Ueber den Schichtenbau und die elektrischen Eigenschaften des Zinnerzes. (The zonal structure and electrical properties of cassiterite.) Sitzber. Kon-Preuss. Akad. Wiss., 414-422 (1911).

Qualitative spectrographic study. Indium was detected in one of five cassiterites.

49. Lopez de Azcona, J. M., Geochemical study of the lead minerals. (In Spanish.) *Ion (Revista espanola de quimica aplicada)* 2: 446-457 (1942); through *Chem. Abs.* 37: 1670 (1943).
Qualitative spectrographic study. Indium was detected in 18 per cent of the 924 lead ores examined.
50. Ludwick, M. T., A bibliography of indium, 1934-1940. Supplement to the bibliography of indium, 1941-1942. Indium Corporation of America, Utica, N. Y.
51. Lunt, Joseph, A spectrographic analysis of the new germanium-gallium mineral germanite, *S. African J. Sci.* 20: 157-165 (1923).
Indium was detected spectrographically in germanite.
52. McLellan, Roy D., The occurrence and hardness of indium, *Am. Mineral.* 30: 635-638 (1945).
Spectrographic study on picked material indicated that indium occurs mainly in galena, with less present in sphalerite. Traces to moderate amounts of indium were found in hemimorphite and smithsonite.
53. Mellor, J. W., A comprehensive treatise on inorganic and theoretical chemistry, Volume V, Longmans, Green, and Co. (1924).
Pages 387-405 deal with indium.
54. Meyer, R. E., Zur Kenntniss des Indiums, *Annalen der Chemie* 150: 137-160 (1869).
Flue dust of a lead-zinc furnace contained very little indium. Sphalerite from Freiberg contained 0.014 per cent In.
55. Morgan, Gilbert and Davies, G. R., Germanium and gallium in coal ash and flue dust, *Chemistry and Industry* 56: 717-721 (1937).
Traces of indium were detected in flue dusts of gas works.
56. Murray, W. S., A preliminary indium bibliography (1863-1932). W. S. Murray, Inc., Utica, N. Y., 25 pp. (1933).
57. Nizhnik, O. T., Thermal method of enriching cadmium dust, *Zapiski Inst. Khim., Akad. Nauk U.R.S.R.* 7: 179-191 (1940); 179-189 in Ukrainian, 190 in Russian, 190-191 in German.
The cadmium and indium contents of zinc furnace dust were increased by proper control of addition of NaCl.
58. Noddack, Ida and Noddack, Walter, Die Haufigkeit der chemischen Elementen. (The abundance of the chemical elements), *Naturwissenschaften* 18: 757-764 (1930).
A general account. The indium content of the earth's crust was estimated to be 1×10^{-6} per cent In.
59. Noddack, Ida and Noddack, Walter, Die geochemischen Verteilungskoeffizienten der Elemente. (The geochemical distribution coefficients of the elements.) *Svensk Kemisk Tidsskrift* 46: 173-201 (1934).
A general account. The indium content of the earth's crust was estimated to be 8×10^{-6} per cent In.
60. Novokhatsky, I. P. and Kalinin, S. K., Indium and its distribution. (In Russian.) *Redkie Metally* 1937, No. 5-6, 24-28. (From an abstract by T. Stadnichenko.)
Many ores and minerals from Kazakhstan and Northern Kirgisia were examined. Dark-colored sphalerites generally are highest in indium (up to 0.07 per cent In). Indium was also detected in cassiterite and stannite. Chalcopyrite contained up to 0.01 per cent In. A study was made of the products of the Chimkent lead works, which was treating ore containing less than 0.001 per cent In. Indium was found to be concentrated in Cottrell dusts (up to 0.1 per cent In) and in dry slimes (over 0.1 per cent In).
61. Novokhatsky, I. P. and Kalinin, S. K., Indium in the waste of the Chimkent lead works, *Compt. rend. acad. sci. U.R.S.S.* 22: 425-426 (1939).
See No. 60 above.
62. Oftedal, Ivar, Untersuchungen über die Nebenbestandteile von Erzmineralien norwegischer zinkblendeführender Vorkommen. (Studies of the accessory elements in ore minerals from Norwegian sphalerite-bearing deposits.) *Skrift. Norsk. Videnskaps-Akad. Oslo, Mat.-Nat. Klasse*, 1940, No. 8, 1-103 (1941).
Very careful quantitative spectrographic analyses of many minerals. Indium was found only in sphalerite; none was found in galena. Most sphalerites examined contained

0.001 to 0.01 per cent In, the highest concentration found being 0.07 per cent In. The indium content is low in high- and low-temperature deposits, highest in intermediate-temperature deposits.

63. Papish, Jacob and Holt, D. A., Indium (I). Detection and estimation of indium from the arc spectrum. (In German.) Z. anorg. allgem. Chem. 192: 90-96 (1930), through Chem. Abs. 24: 5619 (1930).

A commercial sample of cadmium oxide contained about 0.1 per cent In.

64. Petar, A. V., Gallium, germanium, indium and scandium. U. S. Bur. Mines Inf. Circ. 6401: 17 pp. (1930).

A brief review of occurrences and uses with an incomplete bibliography.

65. Potratz, H. A. and Ekeley, J. B., A bibliography of indium, 1863-1933. Univ. Colorado Studies 21: 151-187 (1934).

66. Prokopenko, N. M., Occurrence of indium in various metallogenetic cycles of the U.S.S.R., Compt. rend. acad. sci. U.R.S.S. 31: 19-21 (1941).

No numerical data are given. Indium occurs in young, as well as in old, metallogenetic cycles. It has been found in sphalerites from many deposits, in cassiterite and wolframite from high-temperature tin deposits, and in mangansiderite.

67. Prokopenko, N. M., Principal stages in the history of indium in the earth's crust, Compt. rend. acad. sci. U.R.S.S. 31: 903-906 (1941).

A discussion of the occurrence of indium as related to genesis. No numerical data are given and high, low, and trace concentrations are not defined. Magmatic State (see No. 11 above). Indium is found only in traces in sulfides genetically related to basic and alkaline rocks, whereas some sulfides genetically related to intermediate and acid rocks may have appreciable indium contents. Pegmatitic Stage. Indium is not typical of pegmatites. It occurs in low concentrations in several silicates from pegmatites. Pneumatolytic Stage. Few data are available. Indium may be present in low concentration in cassiterite, wolframite, and zinnwaldite. Ore Deposits. (a) Contact Type. Sphalerite from contact deposits of scheelite-molybdenite, magnetite, lead-zinc, and tungsten-tin-arsenic are rather high in indium. Chalcopyrite and arsenopyrite from such deposits generally have low concentrations of indium, (b) Lead-zinc deposits. The indium content of sphalerite varies widely, but, in general, Sphalerite from sphalerite hypothermal and hypo-mesothermal deposits is rich in indium, from mesothermal deposits is low in indium; sphalerite from epithermal deposits contains none or very little indium. Cobaltite from a hypothermal deposit was enriched in indium. (c) Tin deposits. Indium is typically associated with tin in tin sulfide deposits. It may also be present in cassiterite and wolframite and in sulfides of metals other than tin. (d) Tungsten-molybdenum deposits. Indium is generally present in wolframite, usually in low concentrations, but sometimes in increased concentrations. Sulfides associated with tungsten deposits, such as galena, sphalerite, and chalcopyrite, may contain increased concentrations of indium. Supergene Stage. Indium seldom accumulates in the oxidation zone of sulfide deposits, but is further disseminated. It occurs in traces and small concentrations in minerals such as hemimorphite, cerussite, and jarosite. However, indium appears to be precipitated at places where acid waters of the oxidation zone are neutralized, and should be looked for in zones of secondary sulfide enrichment, particularly in covellite and chalcocite. Sedimentary Rocks. Indium has been found in low concentrations and traces in some manganese ores, bauxites, and clays.

68. Prokopenko, N. M., Distribution of indium in Transbaikal, Compt. rend. acad. sci. U.R.S.S. 31: 907-908 (1941).

Qualitative data on minerals from many deposits. Indium was detected in sphalerite, pyrite, chalcopyrite, covellite, cassiterite, wolframite, stannite, galena, bismuthinite, and jarosite.

69. Ramage, Hugh, Gallium in flue dust, Nature 119: 783 (1927).

Indium was detected in flue dust from a gas works.

70. Romeyn, Hendrik, Jr., Indium and scandium in pegmatite, J. Am. Chem. Soc. 55: 3899-3900 (1933).

Analyses of samples taken at random along a pegmatite dike in Western Utah indicated 1.0 to 2.8 per cent In and 0.5 to 1.2 per cent Sc. The chief minerals of the deposit were cordierite, actinolite, antigorite, calcite, and molybdenite. Apparently indium occurred as a partial replacement of the aluminum in cordierite. (Note - This brief note has never been substantiated and must be regarded with suspicion - Abstractor).

71. Siniakova, S. I., Polarographic determination of indium and cadmium. *Compt. rend. acad. sci. U.R.S.S.* 29: 376-379 (1940).

Four sphalerites from Kirghisia contained 0.026 to 0.083 per cent In.

72. Stoiber, R. E., Minor elements in sphalerite. *Econ. Geol.* 35: 501-519 (1940).

Spectrographic study of 75 sphalerites, of which 2 contained 0.1 to 1 per cent In (one of these from Leadville, Colo.), 11 contained 0.01 to 0.1 per cent In, 26 contained less than 0.01 per cent, 36 contained no indium. The indium content was lowest in sphalerites from low-temperature deposits, highest in sphalerites from intermediate-temperature deposits.

73. Streng, A., Ueber das Vorkommen von Thallium und Indium in einigen Erzen und Hüttenprodukten des Harzes. (The occurrence of thallium and indium in some ores and furnace products of the Harz.) *Berg. - u. Huttenmann Ztg.* 24: 191 (1865).

In a mill treating Rammelsberg ore, much thallium and indium present in (1) the mother liquor of vitriol preparation from furnace residues, (2) the mother liquor of copper sulfate manufacture and (3) the gold- and silver-rich slime left after solution of copper in dilute sulfuric acid.

74. Strock, L. W., Quantitative spectrographic determination of minor elements in zinc sulfide ores, *Am. Inst. Mining Metallurgical Eng., Tech. Publ. No. 1866*, 22 pp. (1945).

Mainly devoted to methods. Zinc concentrates contained 0.0005 to 0.2 per cent In.

75. Tanner, J. A., Examination for indium of smithsonite from southwestern Virginia and eastern Tennessee, *Chem. News* 30: 141-142 (1874).

Traces of indium were found in ore containing smithsonite and hemimorphite.

76. Thiel, A., Studien ueber das Indium. *Z. Anorg. allgem. chem.* 40: 280-336 (1904).

The lead fumes from tapping lead-zinc slag contained 0.2 per cent In.

77. Tongeren, W. van, Contributions to the knowledge of the chemical composition of the earth's crust in the East Indian Archipelago. II. On the occurrence of rarer elements in the Netherlands East Indies, Amsterdam, 1938, pp. 122-181.

Zinc ore from West Borneo contained 0.008 per cent In. Malayan cassiterite contains somewhat less than 0.01 per cent In, and indium is always present in commercial tin.

78. Urbain, G., Analyse spectrographique des blends. (Spectrographic analysis of sphalerites.) *Compt. rend.* 149: 602-603 (1909).

Indium was detected in 41 of 64 sphalerites examined. It was lowest in those samples containing much germanium.

79. U. S. Geological Survey. Unpublished spectrographic data by George Steiger, K. J. Murata, and J. C. Rabbitt.

80. Vernadsky, V. I., Notes on the distribution of the chemical elements in the earth's crust. (In Russian.) *Bull. acad. sci. St. Petersburg* 4: 1129-1148 (1910); 5: 187-193 (1941).

Qualitative spectrographic study of many minerals. Indium was detected in sphalerite, pyrrhotite, franklinite, rhodonite, tantalite, wolframite, samarskite, and alunite.

81. Warren, H. V. and Thompson, R. M., Sphalerites from Western Canada, *Econ. Geol.* 40: 309-335 (1945).

Qualitative spectrographic study of 164 samples, mostly from British Columbia. Indium was present in many. The results agree well with those of Stoiber.⁷² Indium was also found in ores of iron, manganese, tin, and tungsten.

Paper 14

The Geochemistry of Columbium and Tantalum*

MICHAEL FLEISCHER and JAMES O. HARDER

ABSTRACT

This is a review, with annotated bibliography, of the mode of occurrence of the elements columbium and tantalum. It is not a list of specific ore deposits, but a summary of the types of minerals and rocks in which these elements have been reported to occur. In addition, the unpublished spectrographic studies of the Geological Survey are summarized, best sources for columbium and tantalum are indicated, and suggestions are made for further investigation.

Columbium and tantalum occur most abundantly in certain minerals which form late in the general process of magmatic differentiation, including the late hydrothermal stages. These minerals occur almost without exception in granitic and syenitic pegmatites and placers derived therefrom. Among the metallic elements, columbium and tantalum are most closely associated with titanium and zirconium, and to some extent with tungsten and tin, as might be expected from their ionic radii. The $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$ content of the minerals varies from a trace to 86 per cent. The high value is for columbite-tantalite, the most common ore mineral of columbium and tantalum.

The domestic reserves of columbium-tantalum minerals are estimated to be 875,800 pounds of all minerals as of January 1, 1945. No grade figures are reported.

Products of tin smelters and plants which treat minerals chemically for elements such as titanium and tungsten should be investigated for columbium on the basis of association.

1. INTRODUCTION

This report on the geochemistry of columbium and tantalum is one of a series of similar reports prepared by the Geological Survey, discussing possible sources of several rare or uncommon elements for which there were war uses.

Columbium† and tantalum are chemical elements with atomic numbers 41 and 73, and atomic weights 92.91 and 180.88, respectively. They belong to the fifth group of the periodic table and are quinquevalent in most of their compounds. The history of these elements, their

*Contribution from the Geological Survey, U. S. Department of the Interior, Washington, D. C. Prepared for publication June 1946 as TEI-31J and issued as MDDC-644.

†Niobium (Nb) is generally used in place of columbium (Cb) in the European literature.

properties and those of their compounds, are summarized by Mellor.²¹ Their chemistry and metallurgy have been summarized recently.^{1,22}

2. GEOCHEMICAL CONSIDERATIONS

2.1 General Statement

Columbium and tantalum are relatively rare elements, whose exact position in the order of abundance of the elements is uncertain. Analysis for these elements is unusually difficult, which may explain the paucity of data on their distribution and the widely varying estimates of their abundance. Thus Clarke and Washington in 1924⁶ gave 0.003 per cent as the average columbium plus tantalum content of igneous rocks, whereas two years earlier they had given it as $n \times 10^{-6}$ per cent. More recently, von Hevesy and co-workers^{15,16} gave 3.2×10^{-5} per cent Cb and 2.4×10^{-5} per cent Ta for the average contents of eruptive rocks, Goldschmidt¹³ gave 0.002 per cent Cb and 0.0015 per cent Ta, and van Tongeren²⁹ estimated 0.001 per cent Cb to be the average content of the rocks of the Dutch East Indies. Recent careful study by Rankama²⁵ gave 0.00021 per cent Ta for the average content of the igneous rocks, and indicates that the Cb/Ta ratio is more probably 9:1 or 10:1 than the 3:2 figure of the previous workers.

Columbium and tantalum are lithophilic elements that occur almost exclusively in igneous rocks. In contrast to dispersed elements such as gallium and indium, columbium and tantalum are so concentrated during the processes of magmatic differentiation that they are major constituents of many minerals. These minerals, almost without exception, occur in granitic and syenitic pegmatites.

The empirical ionic radius of columbium is given as 0.69 Å, and that of tantalum must be nearly the same. Columbium and tantalum are associated closely with titanium and zirconium, and to some extent with tin and tungsten. These associations would be anticipated from the ionic radii (titanium 0.64, tin 0.74, and tungsten approximately 0.6), except for zirconium, whose ionic radius is given as 0.87 Å, but may well be smaller. Molybdenum minerals have apparently not been tested for the presence of columbium and tantalum, although the ionic radius of molybdenum (0.6 to 0.7) suggests a possible association, especially in molybdenite from pegmatites. Some molybdenum ores tested spectrographically by Rabbitt³⁰ did not contain measurable amounts of columbium, nor did molybdenite from Pitkäranta, Finland.²⁵

2.2 Occurrences in Specific Minerals and Rocks

The following list includes all the minerals that are reported to contain columbium or tantalum, that are recognized as valid species and some that are of dubious validity. The complexity of composition and the difficulty of analysis make it impossible to systematically classify all these minerals accurately. They have been divided into two groups: (a) Minerals in which columbium or tantalum is a major constituent and (b) Minerals in which these elements are minor constituents. Within each group, the arrangement is roughly in order of possible importance as a source of columbium and tantalum. For the many rare and ill-defined species, a rough grouping of like minerals has been attempted. Unless otherwise indicated, the data given are from Volume 1 of the Seventh Edition of Dana's System of Mineralogy⁷ and from the mineralogical file of the Section of Chemistry and Physics, Geological Survey, Department of the Interior.

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(a) Minerals in Which Columbium and/or Tantalum Is a Major Constituent. Columbite-Tantalite Series, $(\text{Fe, Mn}) (\text{Cb, Ta})_2\text{O}_6$, varying from columbite containing little tantalum to tantalite containing little columbium. The $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$ content is 75 to 86 per cent. This is the principal ore of columbium and tantalum. Columbite-tantalite and tapiolite are the ores from which 95 per cent or more of these metals are produced outside the U.S.S.R. (See Loparite, below.) Columbite-tantalite occurs almost exclusively in granite pegmatites, especially in those rich in lithium minerals. Although of widespread occurrence, it is generally sparsely disseminated, and relatively few of the occurrences contain large amounts. It has also been found in some placer deposits, and occurs in the cryolite deposits at Ivigtut, Greenland. A summary account of columbite-tantalite deposits has been published by Mathieu,²⁰ and an account of the Russian deposits by Gerasimovsky.¹¹

Tapiolite-Mossite Series, $(\text{Fe, Mn}) (\text{Ta, Cb})_2\text{O}_6$, varying from tapiolite with little columbium to mossite with Cb:Ta approximately 1:1. The $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$ content is 79 to 85 per cent. This tetragonal dimorph of orthorhombic columbite-tantalite is generally considered to be a rare mineral, but is actually of common occurrence. Much of the so-called tantalite has been found by x-ray study to be tapiolite.³⁰ It occurs in granitic pegmatites, generally associated with tantalite.

Loparite, essentially $(\text{Ce, Na, Ca})_2 (\text{Ti, Cb})_2\text{O}_6$, is a member of the perovskite group. The $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$ content is 9 to 11 per cent, with columbium predominating over tantalum. Loparite is a rare mineral, known only from nepheline syenite pegmatites of the Kola Peninsula, U.S.S.R. where, however, it occurs in large amounts and may be an important source of columbium. The deposits have been described.⁹⁻¹¹

Perovskite, CaTiO_3 , with columbium and tantalum substituting for titanium, and rare earths and sodium for calcium (compare loparite). The columbian variety is called dysanlyte. The $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$ content ranges from traces to 26 per cent and is particularly high in samples from contact zones of nephelinitic rocks. (For analyses, see Refs. 4, 15, and 25.) The columbian variety of perovskite is an uncommon mineral that generally occurs in small amounts.

Pyrochlore-Microlite Group (including the varieties columbomicrolite, koppite, hatchetolite, and ellsworthite). Formula essentially $(\text{Na}, \text{Ca})_2 (\text{Cb}, \text{Ta})_2 \text{O}_6 (\text{O}, \text{OH}, \text{F})$, but with variable amounts of uranium and rare earths replacing calcium and with various elements, especially titanium, replacing columbium and tantalum. The $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$ content is generally 56 to 78 per cent, but may be as low as 40 per cent, particularly in uranium varieties. Tantalum commonly predominates over columbium. These minerals are of uncommon occurrence and are present in small amounts in most occurrences. However, at a few localities, they occur in sufficient amounts to be mined as a source of tantalum. They occur in granitic pegmatites and in nepheline syenites and related rocks, also in placers derived from such rocks.

Scheteligite is a very rare complex mineral related to the Pyrochlore-Microlite Group. It contains 29 per cent $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$. It occurs in granitic pegmatite.

Hjelmite is a very rare, chemically complex mineral similar to microlite in composition and containing 62 to 70 per cent $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$. It occurs in granitic pegmatites.

Rutile, TiO_2 (columbian and tantalian varieties, also called ilmenorutile and strueverite). These are solid solutions of TiO_2 containing variable amounts of the tapiolite-mossite molecules, $\text{Fe}(\text{Ta}, \text{Cb})_2\text{O}_6$. The $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$ content ranges from traces to 47 per cent. (For analyses see Refs. 4, 15, and 25.) The varieties of rutile that contain appreciable percentages of columbium and tantalum are rare minerals, occurring in granitic and syenitic pegmatites. Most rutiles contain less than 0.1 per cent Ta_2O_5 .

Tantalum, Ta. Tantalum metal, containing 1.5 per cent Cb, has been reported to occur as a rarity in some placers, but the occurrences need verification.

Simpsonite, $\text{Al}_6\text{Ta}_4\text{O}_{18}$, containing up to 6 per cent Cb_2O_5 . The $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$ content is 70 to 75 per cent. A rare mineral occurring in granitic pegmatites. It has been reported to occur in placers in sufficient amount to serve as a minor source of tantalum.

Stibiotantalite-Stibiocolumbite Series, $\text{Sb}(\text{Cb}, \text{Ta})\text{O}_4$, nearly the entire series being known. The $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$ content is 50 to 60 per cent. It is a rare mineral, occurring in small amounts in lithium-rich granitic pegmatites and in some placers derived therefrom.

Bismutotantalite, $\text{Bi}(\text{Ta}, \text{Cb})\text{O}_4$, with tantalum predominating. The $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$ content is 45 to 47 per cent. It is a very rare mineral that occurs in granitic pegmatite.

Thoreaulite, SnTa_2O_7 , containing Cb_2O_5 trace, Ta_2O_5 73 per cent. It is a very rare mineral, occurring in granitic pegmatite.

The following is a group of complex, poorly defined columbates and tantalates of the rare earths.

Euxenite-Polycrase Series, essentially AB_2O_6 , with (a) chiefly yttrium and calcium, also cerium, uranium, and thorium; (b) chiefly columbium, tantalum, and titanium. The $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$ content ranges from 20 to 51 per cent. It is an uncommon mineral occurring in granitic pegmatites, but only rarely in appreciable amounts. It has also been found in placers.

Khlopinite and **Eschwegeite** are very rare minerals similar to euxenite in composition and occurrence.

Eschynite-Priorite Series, including blomstrandine. These minerals are similar to the euxenite-polycrase series in composition, but differ in crystal structure. The $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$ content ranges from 16 to 37 per cent. Columbium generally predominates over tantalum. These are uncommon minerals that occur, generally in small amounts, in nepheline-syenite and related rocks and in granitic pegmatites.

Samarskite is similar in composition to euxenite, but differs in crystal structure. The $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$ content ranges from 43 to 60 per cent. Columbium generally predominates over tantalum. Samarskite is an uncommon mineral that occurs, generally in small amounts, in granitic pegmatites.

Fergusonite-Formanite Series, essentially $\text{Y}(\text{Cb}, \text{Ta})\text{O}_4$, with variable amounts of calcium, cerium, and uranium substituting for yttrium, and with titanium and other elements substituting for columbium and tantalum. Columbium generally predominates over tantalum. The $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$ content ranges from 42 to 58 per cent. Fergusonite is an uncommon mineral that occurs, generally in small amounts, in granitic pegmatites, and in placers derived therefrom.

Yttrotantalite is similar to fergusonite in composition, but differs in crystal structure. The $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$ content is 55 to 60 per cent. It is a very rare mineral that occurs in granitic pegmatites.

Ishikawaite is a very rare mineral similar to yttrotantalite in composition and occurrence. The $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$ content is 52 per cent.

Polymignite and Loranskite are very rare, ill-defined minerals similar to yttrotantalite in composition, but containing much zirconium. The $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$ contents reported range from 13 to 48 per cent. These are very rare minerals, occurring in small amounts in granitic pegmatites, nepheline-syenites, and augite-syenite pegmatites.

Betafite Group (including betafite, samiresite, djalmaite, and amfangabeite). A group of complex, ill-defined minerals of doubtful formula, containing chiefly columbium, tantalum, titanium, calcium, and uranium. The $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$ content ranges from 18 to 73 per cent. These rare minerals all occur in granitic pegmatites.

Fersmanite, $(\text{Ca}, \text{Na})_2 (\text{Ti}, \text{Cb}) \text{SiO}_5 \text{F}$. The $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$ content is about 15 per cent, nearly all of which is columbium. It is a rare mineral that occurs in nepheline syenite pegmatite.

Murmanite, approximately $(\text{Na}, \text{Ca})_3 (\text{Ti}, \text{Cb})_5 \text{Si}_5\text{O}_{19} (\text{OH})_7 \cdot 4\text{H}_2\text{O}$. It contains about 8 per cent Cb_2O_5 and 1 per cent Ta_2O_5 . It is a rare mineral that occurs in nepheline syenite pegmatite with loparite and fersmanite and is therefore a minor source of columbium in the treatment of loparite.

Epistolite is a sodium columbium silicate of uncertain formula. The only analysis gave 34 per cent Cb_2O_5 . It is a very rare mineral that occurs in nepheline syenite pegmatite.

Wöhlerite, perhaps $\text{NaCa}_2 (\text{Zr}, \text{Cb}) \text{Si}_2\text{O}_7 (\text{O}, \text{OH}, \text{F})_2$. The $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$ content is 13 to 15 per cent, with columbium predominating over tantalum. Wöhlerite is a very rare mineral that occurs in nepheline syenite pegmatites.

Lavenite and Hiortdahlite are sodium calcium zirconium silicates, like wöhlerite, but are reported to contain up to 5.2 and 2 per cent, respectively, of $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$. They are very rare minerals that occur in nepheline syenite pegmatites.

(b) Minerals in which columbium or tantalum is a minor constituent. Wolframite, $(\text{Fe}, \text{Mn})\text{WO}_4$. Few analyses of wolframite report columbium or tantalum, but these may have been overlooked.¹⁸ The content of columbium and tantalum is usually low,²⁵ except for samples from pegmatites, but the data in the literature are too few to allow any estimate of average content. The maximum content recorded is 2.2 per cent $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$.

Scheelite,⁵ CaWO_4 , has been reported to contain 0.10 per cent $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$, but the method of analysis used has been challenged.²⁷ No other analysis of scheelite shows columbium or tantalum.

Ilmenite, FeTiO_3 . Columbium and tantalum have been reported in only a few analyses of this very common mineral, but may not have been looked for. The maximum content of $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$ reported is 1.3 per cent from syenitic pegmatite, which would be expected to be relatively high in columbium + tantalum content.^{15,23,25,31,32} Two black sands¹⁵ from Norway and India contained 0.18 and 0.02 per cent, respectively, of $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$. These were presumably the "ilmenite" sands of commerce, which may be ilmenite, arizonite, or amorphous material. The only analysis of arizonite shows neither columbium nor tantalum, but the similar mineral kalkowskite contains 1.7 per cent $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$.

Cassiterite, SnO_2 . This very common mineral has been reported to contain columbium and tantalum in amounts ranging from spectrographic traces to over 10 per cent $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$. (For analyses see Refs. 4 and 25.) Some of the samples analyzed probably were not homogeneous and contained intergrown columbite-tantalite or tapiolite, but there is evidence that cassiterite may contain columbium and tantalum in solid solution.⁸ Cassiterite from pegmatite veins contains more columbium than cassiterite from hydrothermal sulfide-bearing veins.^{3,19}

Brookite and anatase, both TiO_2 , have been reported to contain spectrographic traces of columbium and tantalum,²⁵ up to 0.03 per cent Ta_2O_5 .

Zircon, ZrSiO_4 . Most analyses of this very common mineral do not report columbium or tantalum, which probably was overlooked, since most of the zircons that have been examined spectrographically contain columbium and tantalum,^{4,18,25} generally 0.05 to 0.5 per cent $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$. Zircons that contain appreciable amounts of rare earths and uranium also generally contain columbium and tantalum, the maximum content reported being 7.7 per cent $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$. This variety of zircon (to which several special names such as cyrtolite, naegite, and hagatelite have been given) is of rare occurrence in granitic pegmatites.

Sphene, CaTiSiO_5 commonly contains columbium and tantalum^{2,4,15,25} in amounts ranging from traces to about 2 per cent $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$. The highest percentages reported are for samples from nepheline syenite pegmatites. Columbium generally predominates over tantalum.

Astrophyllite, $(\text{K}, \text{Na}) \text{Fe}_3\text{TiSi}_3\text{O}_{11} (\text{OH})$, has been reported to contain up to 0.8 per cent Ta_2O_5 . It is a very rare mineral that occurs in nepheline syenite pegmatites.

Lamprophyllite, approximately $\text{Na}_5\text{Sr}_2\text{Ti}_4\text{Si}_5\text{O}_{22}\text{F}$, has been reported⁴ to contain up to 0.4 per cent $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$. It is a very rare mineral that occurs in nepheline syenite pegmatites.

Eudialyte, approximately $(\text{Na}, \text{Ca})_5 (\text{Zr}, \text{Fe})_2 \text{Si}_4\text{O}_{18} (\text{OH}, \text{Cl})$. It has been reported to contain up to 3.5 per cent $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$, but most analyses show 0.2 to 1.0 per cent.^{4,18,25} Eudialyte is a rare mineral that occurs in nepheline syenite pegmatites.

Catapleite, $(\text{Na}_2, \text{Ca}) \text{ZrSi}_3\text{O}_9 \cdot 2\text{H}_2\text{O}$, has been reported^{4,25} to contain up to 0.1 per cent $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$. It is a rare mineral that occurs in nepheline syenite pegmatites.

Lorenzenite (including the variety ramsayite), $\text{Na}_2 (\text{Ti}, \text{Zr}) \text{Si}_2\text{O}_6$, is reported⁴ to contain up to 3 per cent $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$. It is a very rare mineral that occurs in granitic and nepheline syenite pegmatites.

Thortveitite, $\text{Sc}_2\text{Si}_2\text{O}_7$, is reported²⁵ to contain up to 2 per cent Ta_2O_5 . It is a very rare mineral that occurs in granitic pegmatites.

Tritomite, a complex borosilicate of cerium, lanthanum, thorium, and calcium, is reported to contain up to 3.1 per cent Ta_2O_5 . It is a very rare mineral that occurs in nepheline syenite pegmatites.

Caryocerite-Melanocerite, a complex borosilicate of the rare earths and calcium, is reported to contain up to 3.5 per cent $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$. It is a very rare mineral that occurs in nepheline syenite pegmatites.

Steenstrupine, a complex phosphate-silicate of the rare earths, thorium, iron, and calcium, is reported to contain up to 4 per cent $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$. It is a very rare mineral that occurs in nepheline syenite pegmatites.

Polyolithionite, $\text{KLi}_2\text{AlSi}_4\text{O}_{10}\text{F}_2$, contains up to 1.5 per cent Cb_2O_5 .²⁸ It is a very rare mica that occurs in granitic pegmatites. Other micas contain traces of columbium and tantalum, and one biotite²⁵ is reported to contain 0.1 per cent Ta_2O_5 .

2.3 Rocks

As stated under Geochemical Considerations, p. 119, data on the columbium and tantalum content of rocks are not in good agreement. The recent published values^{12,13,16,24,26,29} range from 3.2×10^{-5} per cent Cb to 0.002 per cent Cb for the average content of igneous rocks. The highest values reported are 0.005 per cent Cb for granite, 0.02 per cent Cb for nepheline syenite.¹² The best value at present appears to be about 0.001 per cent Cb for the average content of igneous rocks. The very recent work of Rankama²⁵ gave 0.00021 per cent Ta for the average content of igneous rocks.

3. RESULTS OF MILL PRODUCT STUDIES

The columbium content of more than 1000 samples from over 200 mines, mills, and geological occurrences was determined spectrographically by Rabbitt²⁵ as part of the Geological Survey's Trace Elements investigations. Three of the samples each contained 0.2 per cent Cb_2O_5 . Two of these were from areas of alkali-syenite intrusives, some of which contain eudialyte. The third of these three samples is a placer concentrate from the Yentna district in Alaska. In addition to the three samples described above, 22 samples contained columbium in amounts ranging from 0.005 to 0.008 per cent Cb_2O_5 . All of these samples are listed in Table 14.1.

It is noteworthy that excepting the placer sample the highest content of columbium was in the samples from alkali-syenite intrusive areas. This is in accord with previous experience which has shown columbium to be generally concentrated in the late differentiates of the magma. The only other important conclusion to be drawn from the mill product spectrographic study is a negative one. The remaining thousand odd samples which were examined and found to contain less than 0.005 per cent Cb_2O_5 included products from nearly every type of valuable mineral deposit and a variety of other geological occurrences. This evidence strengthens the

Table 14.1 — Best Columbium Values Resulting from Mill Products Spectrography
(Unpublished data of the Geological Survey)

Name of plant or occurrence	Location	Product	Columbium-bearing material	Cb ₂ O ₅ , %
Sierra Diablo Intrusive	Van Horn, Texas	None	Gray porphyry	0.2
Wind Mtn. Intrusive	Cornudas Peaks, N. Mex.	None	Altered limestone cut by dikes	0.2
Alaskan placer	Yentna dist., Alaska	Gold	Placer concentrates	0.2
Sierra Diablo Intrusive	Van Horn, Texas	None	Gray-green porphyry	0.08
Sierra Diablo Intrusive	Van Horn, Texas	None	Purplish-gray porphyry	0.06
Sierra Diablo Intrusive	Van Horn, Texas	None	Manganese-bearing vein	0.05
Mill product		Radium	Radioactive sludge	0.02
Alaskan placer	Yentna dist., Alaska	Gold	Placer concentrates	0.01
Mill product		Coal	Quartz-carnotite veins	0.01
Mill product		Tungsten	Composite conc. (scheelite)	0.01
Mill product		Aluminum	Slimes from filter	0.01
Mill product		Titanium	Rutile concentrates	0.01
Mill product		Titanium	Rutile concentrates	0.01
Mill product		Coal	Siliceous coal	0.008
Mill product		Titanium	Tails, magnetic separation	0.008
Mill product			PbS sludge (African ore)	0.008
Mill product		Phosphate	Pebble concentrates	0.007
Jacksonville Beach	Jacksonville, Fla.	None	Rutile, from black sand	0.007
Mill Product		Coal	Grab sample from dump	0.007
Mill Product		Aluminum	Iron tails	0.006
Mill Product		Aluminum	Sand from thickener	0.006
Alaskan placer	Yentna dist., Alaska	Gold	Placer concentrates	0.005
Mill product		Aluminum	Iron tails	0.005
Jacksonville Beach	Jacksonville, Fla.	None	Ilmenite	0.005
		Tungsten	Sulfide flotation tails	0.005

relationship between columbium and late magmatic differentiates and makes hydrothermal deposits appear unattractive as possible columbium sources.

4. BEST SOURCES OF COLUMBIUM AND TANTALUM

At present, columbium and tantalum are produced almost entirely from columbite-tantalite and tapiolite, with minor amounts from microlite and simpsonite, all from granitic pegmatites. The minerals, such as loparite, associated with nepheline syenites appear to have been utilized only in the U.S.S.R., where the deposits are large. These minerals have low columbium + tantalum contents and are probably not attractive sources, even if titanium is also recovered.

Some production and reserve figures on the domestic columbium-tantalum supply were obtained by the Geological Survey. The figures were assembled from data supplied by various men. All of the figures are production or reserves for granitic pegmatites in the states indicated.

The production is given in pounds of mineral produced. Records are not available, and probably not existent, to show the proportion of columbium to tantalum in the various minerals listed and there are no figures to show the amount of pegmatite material from which the minerals were obtained. In nearly all cases the columbium-tantalum minerals are produced as by-products of the mining of a pegmatite body for other valuable minerals such as mica, feldspar, and spodumene. With one possible exception, it is doubtful if there is a single domestic mine which could operate for columbium-tantalum alone.

Reserve figures given in pounds of mineral are in part based on production records and estimates of volumes of pegmatite. Neither grade figures to show percentage of mineral in the pegmatite nor figures to show the ratio of columbium to tantalum have been included. As in past production, the reserves are chiefly dependent on the chance that they can be recovered as a by-product of pegmatite mining for other minerals.

Tabulation of domestic production and reserves of columbium-tantalum minerals:

Columbite—Production and reserves (U. S.)

(Jan. 1, 1945)

State	Production		Reserves (lb columbite)		
	Period	Wt. lb	Measured	Indicated	Inferred
Arizona					500
Colorado	1943	1,422		200	
New Mexico	1943	1,500			2,000
North Carolina	1943	4,219			6,000
South Dakota	1903-1908	66,000			120,000
Virginia	1934	50			
Totals		73,191		200	128,500
			TOTAL	128,700	

Microlite—Production and reserves (U. S.)

(Jan. 1, 1945)

State	Production		Reserves (lb columbite)		
	Period	Wt. lb	Measured	Indicated	Inferred
Colorado				6,193	2,347
New Mexico			500	400,000	200,000
South Dakota					3,000
Totals			500	406,193	205,347
TOTAL				612,040	

Tantalite—Production and reserves (U. S.)

(Jan. 1, 1945)

State	Production		Reserves (lb tantalite)		
	Period	Wt. lb	Measured	Indicated	Inferred
New Mexico	1942-1944	800	300	750	750
South Dakota	Incomplete	1,381		30,000	60,750
Virginia	1929-1941	1,390		19,900	
Wyoming	1942	85		13,780	830
Totals		3,656	300	64,430	62,330
TOTAL				127,060	

Mixed ores—Production and reserves (U. S.)

(Jan. 1, 1945)

(Columbite, tantalite, microlite, hatchettolite, samarskite, etc.)

State	Production		Reserves (lb tantalite)		
	Period	Wt. lb	Measured	Indicated	Inferred
Idaho	?	500			
New England	1930-1942	<100			
New Mexico	?	700			2,000
North Carolina	1930-1942	4,000			6,000
South Dakota	1943	630			
Totals		5,930			8,000

Summary—Production and reserves (U. S.) of all columbium and tantalum minerals
(Jan. 1, 1945)

Mineral	Production		Reserves (lb of ore mineral)		
	Period	Wt. lb	Measured	Indicated	Inferred
Columbite		73,191		200	128,500
Microlite		10,250	500	406,193	205,347
Tantalite		3,956	300	64,430	62,330
Mixed ore		5,930			8,000
Totals		93,327	800	470,823	404,177
			TOTAL	875,800	

5. SUGGESTIONS FOR FURTHER INVESTIGATIONS

Further investigation should be directed to those minerals that contain columbium and tantalum, and that are treated chemically. Such minerals as rutile and zircon, that are marketed as such, are not possible sources.

Products of tin smelters should be investigated to learn the fate of the columbium and tantalum content of cassiterite during smelting, although the Bolivian ore used at the Longhorn Smelter is presumably low in columbium and tantalum.

The fate of the columbium and tantalum content of wolframite during the recovery of tungsten should be studied.

Products of plants producing titanium dioxide from "ilmenite" sands should be studied, though it seems likely that the columbium and tantalum would probably be concentrated in the final titanium dioxide product.

However, none of the foregoing possibilities appears now to offer a good chance for supplying important quantities of columbium. No better source is evident than the granitic pegmatites, such as now supply nearly all of the columbium. Furthermore the general distribution and mode of occurrence of these rocks in the United States appear to be quite well-known and their content of columbium-bearing minerals is seldom more than one pound of mineral per ton of pegmatite material. In most cases it is much less. Therefore, the prospect for finding large quantities of columbium is not good. Probably an increase of price would stimulate production from known sources but, because most columbium is a by-product anyway, the effect would undoubtedly be limited unless the price increase was very great.

ANNOTATED BIBLIOGRAPHY OF OCCURRENCES OF COLUMBIUM AND TANTALUM

Note: Descriptions of individual deposits are not included. The original papers were seen except those from which reference to an abstract journal is given.

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A brief review of methods of extraction from ores is included.

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Eight analyses of sphene from nepheline syenites of the Kola Peninsula, U.S.S.R., show Cb_2O_5 contents up to 2 per cent.

3. Borovick, S. A. and Gotman, J. D., Content of rare and other elements in cassiterites of different genesis from U.S.S.R. deposits according to spectrum analysis data, Compt. rend. acad. sci. U.R.S.S. 23, 351-354 (1939).

Qualitative spectrographic study of 27 cassiterites showed strong tests for columbium in pegmatite vein samples, moderate to none in samples from sulfide-cassiterite veins.

4. Borowsky, I. B. and Blochin, M. A., The analysis of minerals by the x-ray spectroscopical method, *Bull. acad. sci. U.R.S.S., Ser. geol.* 1937, No. 5, 929-936 (Russian, with English summary).

Analyses for columbium and tantalum are given for cassiterite, catapleite, eudialyte, ilmenite, lamprophyllite, lorenzenite, perovskite, sphene, and zircon.

5. Carobbi, G., Ricerche analitiche sulla scheelite di Traversella, *Gazz. chim. Ital.* 54, 59-64 (1924); *mineralog. Abstracts* 3, 105 (1926).

Analysis of scheelite from Traversella, Piedmont, gave Cb_2O_5 0.08, Ta_2O_5 0.02 per cent, but these results have been questioned, see (27).

6. Clarke, F. W. and Washington, H. S., The composition of the earth's crust, U. S. Geol. Survey, Prof. Paper 127, 117 pp. (1924).

The average content of igneous rocks is estimated, from scanty data, to be 0.003 per cent Cb + Ta. Earlier, widely diverging, estimates are summarized.

7. Dana's System of Mineralogy, Seventh Edition, Volume I, John Wiley and Sons (1944).
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9. Eliseev, N. A. and Nefedov, N. K., The loparite deposits of luyavrite. *Proizvod. Sil'y Kol'skoge Poluostrove* 1940, No. 1, 77-118; *Chem. Abstracts* 37, 1679 (1943).

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A description of the loparite deposits.

11. Gerasimovsky, V. I., Columbium and tantalum in the U.S.S.R., *Trudy Inst. Geol. Nauk.,* No. 39, Mineral.-Geokhim. Ser. No. 8, 49-57 (1940); *Chem. Abstracts* 37, 6602 (1943).

A summary of data on Russian deposits, including the loparite deposits, syenite pegmatites containing ilmenorutile and ilmenite, and columbite-tantalite deposits.

12. Goldschmidt, V. M., The principles of distribution of chemical elements in minerals and rocks, *J. Chem. Soc. (London)* 1937, 655-673.

A general account. The average content of columbium in the earth's crust is stated to be 0.0015 per cent, from unpublished work. The following data on the Cb_2O_5 content of rocks are also from unpublished work: gabbro 0.001 per cent, diorite, 0.003 per cent, granite 0.005 per cent, and nepheline syenite 0.02 per cent.

13. Goldschmidt, V. M., *Geochemische Verteilungsgesetze der Elemente. IX. Die Mengenverhältnisse der Elemente und der Atom-arten.* (The principles of the geochemical distribution of the elements. IX. The relative abundance of elements and isotopes.) *Skrift. Norsk. Videnskaps-akad. Oslo, Mat.-Nat. Klasse* 1937, No. 4, 148 pp.

The estimates by von Hevesy¹⁸ of the columbium and tantalum contents of the igneous rocks are considered to be too low. Unpublished work gives approximately 0.002 per cent columbium for eruptive rocks and for clay-sand sediments. No data were obtained for tantalum, but if von Hevesy's Cb:Ta ratio is accepted, the content of tantalum would be 0.0015 per cent. In many rocks, the columbium content varies with the zirconium content.

14. Hevesy, G. von and Würstlin, K., Über das Häufigkeitsverhältnis Zirkonium/Hafnium und Niob/Tantal. (The abundance ratios Zr/Hf and Cb/Ta.) *Z. physikal. Chem.* 139A, 605-614 (1928).

From a discussion of the data in the literature, it is concluded that the amounts of columbium and tantalum in the earth's crust are approximately equal, and are related most closely to the titanium content.

15. Hevesy, G. von, Alexander, E., and Würstlin, K., Über die Häufigkeitsverhältnis Niob-Tantal in Titanmineralien. (The abundance ratio Cb/Ta in titanium minerals.) *Z. anorg. allgem. Chem.* 181, 95-100 (1929).

Analyses were made by chemical concentration followed by x-ray spectroscopic determination of 6 rutiles (0.22 to 3.1 per cent $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$), 10 sphenes (1.37 to less than 0.006 per cent $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$), 1 brookite (0.23 per cent $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$), perovskite (0.095 per cent $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$), 3 ilmenites (0.006 to 0.001 per cent $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$) and two "black sands" (0.18 and 0.02 per cent $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$).

16. Hevesy, G. von, Alexander, E., and Würstlin, K., Die Häufigkeit der Elemente der Vanadiumgruppe in Eruptivgesteine. (The abundance of the elements of the vanadium group in eruptive rocks.) Z. anorg. allgem. Chem. 194, 316-322 (1930).

A "synthetic" eruptive rock was made by mixing 133 granites, 9 quartz-diorites, 35 diorites, 82 gabbros and norties, and 23 ultrabasic rocks. Analysis by chemical concentration followed by x-ray spectroscopic determination gave 3.2×10^{-5} Cb, 2.4×10^{-5} Ta. Biotite from Hittero, Norway, contained 6×10^{-5} Cb + Ta; phlogopite from Bamle, Norway, contained 3.2×10^{-5} per cent Cb + Ta.

17. Hodge-Smith, T., Mineralogical notes. No. 6. Rec. Australian Museum 21, 244-256 (1943).

Analyses of 9 wolframites from New South Wales showed that 6 contained $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$, the contents being 0.26 to 1.95 per cent. It is suggested that most earlier analysts missed the presence of columbium and tantalum.

18. Kunitz, Wilhelm, Die Rolle des Titans und zirkoniums in den gesteinsbildenden silikaten. (The role of titanium and zirconium in rock-forming silicates.) Neues Jahrb. Mineral. Geol., Beil.-Bd. 70A, 385-466 (1936).

The substitution of titanium and zirconium by columbium and tantalum is discussed. Analyses are given of lavenite, eudialyte, and zircon, with determinations of the $\text{Cb}_2\text{O}_5 + \text{Ta}_2\text{O}_5$ content.

19. Larionov, J. and Tolmacev, J. M., On the chemical composition of cassiterites, Compt. rend. acad. sci. U.R.S.S. 14, 303-306 (1937).

Qualitative spectrographic study showed columbium to be present in 5 pegmatitic cassiterites, present in traces in 2 hydrothermal cassiterites.

20. Mathieu, F. F., Les gisements des minerais de tantale et de niobium. (Deposits of columbium and tantalum minerals.) Publ. assoc. ing. faculté polytech. Mons, No. 64, 47-139 (1938).

A review of occurrences of columbium and tantalum minerals.

21. Mellor, J. W., A comprehensive treatise on inorganic and theoretical chemistry. Vol. IX. Pages 837 to 925 deal with columbium and tantalum.
22. Myers, R. H., A review of the literature on the chemistry and metallurgy of tantalum and columbium, Proc. Australasian Inst. Mining and metallurgy No. 129, 55-79 (1943).
23. Panteleev, P. F., Titanium, columbium and tantalum in the alkaline complex of the Ilmensky Mountains in the Urals, Bull. acad. sci. U.R.S.S., classe sci. math. nat., Ser. geol. 1938, 827-835 (in English 835-836).

The deposits are described. They contain rutile (ilmeno-rutile) with 6-17 per cent Cb_2O_5 , 1-3 per cent Ta_2O_5 , and ilmenite with 0.6-1.3 per cent Cb_2O_5 and 0.1 per cent Ta_2O_5 . The occurrences of columbium and tantalum are discussed, with the general conclusions that they are most closely related to titanium in occurrence, and that the greatest concentrations occur in pegmatite veins of syenitic and miasskitic magmas.

24. Rankama, Kalervo, The columbium and tantalum content of three Finnish Archean granites (a preliminary report), Bull. comm. geol. Finlande No. 128, 34-38 (1941).

X-ray spectroscopic analysis, after chemical concentration, gave Cb_2O_5 0.010, 0.0045, 0.0011 per cent; Ta_2O_5 0.0026, 0.0021, 0.0002 per cent.

25. Rankama, Kalervo, The geochemistry of tantalum, Bull. comm. geol. Finlande No. 133, 1-78 (1944).

An elaborate study. Analyses for tantalum, made by the x-ray spectrographic method after chemical concentration, are given for 237 mineral samples, 41 ore samples, 136 rocks, and 10 meteorites. Tantalum was found to occur in appreciable amounts in titanium minerals (rutile, brookite, anatase, perovskite, ilmenorutile, and sphene); in zirconium minerals (zircon, eudialyte, catapleite); in cassiterite, wolframite, and thortveitite, also in small amounts in some micas. In rocks, tantalum is concentrated in the late magmatic

stages of differentiation. Very little tantalum is present in the ultra-basic and basic rocks, perhaps 0.0001 per cent Ta_2O_5 . The granites are richest in tantalum, averaging 0.0005–0.0009 per cent Ta_2O_5 . The syenites and nepheline syenites probably have tantalum contents somewhat lower than that of granites. The ratio Ta/Ti increases with progressive differentiation. In the weathering cycle, tantalum is readily precipitated and is therefore not found in deep sea sediments, but occurs in small amounts, perhaps 0.0002 per cent Ta_2O_5 , in coastal sediments. The content of igneous rocks is estimated to be 0.00021 per cent Ta as a maximum; this may be 2 to 3 times the true figure.

26. Sahama, Th. G., The chemistry of the East Fennoscandian rapakivi granites, *Bull. comm. geol. Finlande* No. 136, 15-67 (1945).

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27. Schoeller, W. R. and John, C., Investigations into the analytical chemistry to tantalum, niobium, and their mineral associated VIII. The separation of tungsten from tantalum and niobium, *Analyst* 52, 506-514 (1927).

Chiefly analytical chemistry. The determination of 0.1 per cent $Cb_2O_5 + Ta_2O_5$ in scheelite by Carobbi (5) is doubted, because he used an unreliable method of analysis.

28. Stevens, R. E., New analyses of lepidolite and their interpretation, *Am. Mineral.* 23, 607-628 (1938).

Two analyses of polylithionite showed 0.14 and 1.52 per cent Cb_2O_5 .

29. Tongeren, W. Van, Contributions to the knowledge of the chemical composition of the earth's crust in the East Indian Archipelago. II. On the occurrence of rarer elements in the Netherlands East Indies. pp. 122-181. Amsterdam, 1938.

Quantitative spectrographic study of many samples. No details are given, but it is stated that as far as evidence is available, the columbium content parallels the zirconium content. A rough approximation is $Zr : Cb = 10 : 1$, which gives 0.001 per cent Cb_2O_5 , for the average content.

30. U. S. Geological Survey Laboratory. Unpublished X-ray data by W. E. Richmond and J. M. Axelrod; unpublished spectrographic data by K. J. Murata, J. C. Rabbitt, and George Steiger.
31. Yurk, Y. Y. and Bresler, V. M., Geochemistry of rare elements in the granitic pegmatites of the western Azov seacoast region, *J. Geol., Acad. sci. Ukrain. S.S.R.* 6, No. 4, 131-161 (in English 161-163) (1940); *Chem. Abstracts* 35, 416 (1941).

The ilmenite sands of the Azov seacoast contain 0.25 per cent Cb_2O_5 and traces of Ta_2O_5 . Recovery and utilization are discussed.

32. Yurk, Y. Y. and Tsarovsky, I. D., Black-ore minerals of the Mariupol alkaline massif, *J. Geol., Acad. sci. Ukrain. S.S.R.* 7, Nos. 1-2, 151-160 (in English 161-162) (1940); *Chem. Abstracts* 35, 3198 (1941).

Ilmenite from syenite pegmatite contained up to 0.4 per cent $Cb_2O_5 + Ta_2O_5$.

Paper 15

Remote Control for Continuous Liquid Extractors*

REMSEN T. SCHENCK

ABSTRACT

An electronic device has been developed for indication at a distance and simultaneous automatic correction of changes in density, temperature, and interface level of polyphase solutions.

1. INTRODUCTION

1.1 Automatic Control of Extractors

Procedures for the separation of ions by continuous or semicontinuous extraction of aqueous solutions of the salts with immiscible solvents involve a series of unique problems of control particularly if part of the material in solution is a highly radioactive species. Constant attention is imperative to keep the process running smoothly and to minimize the fire hazard attendant on the use of inflammable organic solvents yet direct observation is impeded by the necessity of manipulation from behind a biological shield because the radiation level is too high for direct handling of the extractor.

Working by reflection, sometimes multiple reflection, from plane mirrors, although awkward, is possible until the glass of the extractor becomes so darkened by radiation that vision is obscured. Some system of signalling any change in conditions to a protected observer is evidently desirable and in large-scale equipment indispensable. Electronic devices inherently fit the specifications of perpetual vigilance, immunity to radiation, and ability to function efficiently over considerable distances. Additional advantages are the facts that corrections may be applied automatically to the process tripping the circuit, and that the operator may relax his attention and merely supervise the system.

The fundamental principles of the control described in this note should prove of universal utility for solvent extractors. A schematic circuit diagram is shown in Fig. 15.1.

*Work done at the Metallurgical Laboratory, University of Chicago. Report AECD-2610; based on Metallurgical Project Reports CC-1204 and CP-1789.

1.2 Choice of Actuating Means

Electronic regulators are commonly energized by one of three types of trigger mechanism: direct contact, photoelectric, and tuned-circuit. In the present instance, the first type is unsuitable chiefly because some electrolysis of the solution would result, and the second type is unsuitable because of progressive darkening of the glass. The third method is quite satisfactory; no direct connection with the extraction system is necessary, a reasonably long line can be interposed between the trigger and the balance of the circuit, and almost any desired degree of sensitivity can be attained.

The tuned-circuit trigger mechanism is applicable in two of the three danger points of an extraction apparatus where automatic control is needed—at the density regulator and at the interface locator. The former device prevents the salt concentration in a recycled aqueous solution from rising to the crystallization point; the latter holds an ether-water or other interface in the extractor proper within the correct vertical limits. The third danger point is the boiler for the non-aqueous solvent, such as ether, in which the extracted salt solution is heated to concentrate the non-aqueous solvent before its return to the extractor. Water flows continuously through this part of the equipment to remove the salt; should the circulation stop, the temperature could increase to a dangerous degree. To guard against difficulty in this stage, a simple mercury-expansion contact may be utilized, which, on closing with an increase in temperature, operates a relay to sound an alarm and to either increase the flow of water or out off the power to the non-aqueous solvent evaporator.

2. THE CONTROL MECHANISM

2.1 The Basic Circuit

The basic circuit consists of a triode oscillator, a pentode amplifier, a diode rectifier, and a pentode relay tube. As designed, the first and last stages were combined in one envelope by choosing type 6AD7G, followed by a 6SK7 and 6H6. The triode section of the 6AD7G oscillates at fixed frequency and an amplitude of some 4 v; the signal is inductively fed to the 6SK7, there amplified and transferred, again inductively, to the diode, where it is rectified and appears across a 10^5 ohm load as a DC potential of about 21 volts. By placing the load in the diode plate ground-return circuit this potential is made to lie below ground and serves to bias the power pentode, which is thus cut off, holding the plate-circuit relay open as long as oscillation is maintained at the prescribed frequency and amplitude.

2.2 Trigger Devices

Introduction of core steel into the field of the oscillator coil radically alters the frequency of the tuned circuit by increasing the inductance. (It is also possible thus to quench oscillation completely in a loosely coupled circuit, if the losses in the coil are thereby made greater than the amount of feedback from the plate circuit.) Since both stages of inductive coupling are sharply tuned to the fundamental frequency, the new signal can no longer pass, the power pentode grid returns to ground potential, and the relay closes.

Silicon core steel, in the form of strips rather than as a powder, was found to be the best material for actuating the circuit. About 2 g is necessary to cause the bias to fall to zero. It is improbable that this quantity could be substantially reduced by refinement of other specifications without operating at much higher frequencies. The metal is contained in two hollow glass floats. The float used in the density control is so constructed that it floats in a solution of the limiting concentration of the salt being extracted and sinks in one of lower density. The coil is in such a position that when the density increases enough to raise the float within the coil, the circuit is tripped. The interface float floats in dilute aqueous salt solutions but sinks in an equilibrated ether solution. The two corresponding oscillator coils are placed above and below the desired normal interface level, so that excessive movement of the float in either direction will trip the appropriate circuit.

The oscillation frequency selected was 455 kc, the highest (and therefore the most easily altered by small changes in the inductance) for which standard double-tuned coupling transformers are easily available. The coil for the density float must encircle 12 to 15 mm glass tubing, while those in the interface level control must pass 20 mm tubing. The coils were therefore wound on 1 in. lengths of $\frac{3}{4}$ -in. and 1-in.-O.D. bakelite tubing, respectively (I.D. $\frac{5}{8}$ and $\frac{7}{8}$ in.). It was necessary to provide a narrow-range trimmer condenser of about 200 $\mu\mu$ fd capacity across each input circuit to allow adjustment for variations in the distributed capacity of the leads; the two types of coils were therefore wound so that the 455 kc resonance point lay within this tuning range. Seventy-one turns of No. 30 B and S enameled on the 1-in. form and 97 turns of No. 32 B and S enameled on the $\frac{3}{4}$ -in. form, close-wound in two layers in each case, fit the respective specifications. The plate winding is not critical since it is untuned; any convenient number of turns were applied over the grid winding, in two layers to ensure adequate energy transfer.

2.3 Adjustment

A cathode-ray "magic eye" tube was provided conveniently close to the trimmer bank to assist in setting at resonance when installing the system. The tube is switched into the appropriate circuit and the associated padder tuned to maximum "eye" closure; when adjustment is complete the entire tuning assembly can be turned off to preserve the brilliancy of the fluorescent screen.

2.4 Alarm Circuits

The relays operated in the pentode plate circuits are all 4-pole double throw. In each case, one set of points, on relay closure, illuminates a warning pilot light. Two more sets provide in addition an audible alarm by actuating an audio-frequency oscillator consisting of a 6V6 pentode in an electron-coupled inductive circuit. A 6-in. permanent magnet speaker is thereby driven at a maximum of 4 w output; a T-pad is provided with which to moderate the volume to nearly zero if desired. Each relay sets up oscillations of a distinctive frequency, so that from a distance the circuit which has been disturbed may be identified by the pitch of the note emitted. A separate switch on the front panel for each circuit permits the oscillator to be silenced without affecting either the other functions of that circuit or any function (including the oscillator) of the other circuits.

2.5 Automatic Correction

The fourth set of relay points controls in each case the automatic corrective device associated with the circuit. In the density control system, a supplementary power relay with a 110 volt AC coil is caused to close together with the plate-circuit relay, thereby cutting off the power to the heater under the water evaporator.

Restoration of the non-aqueous water interface to the proper level is a slightly more complicated matter. The operating point is fixed by an automatic siphon from the reservoir; the constant hydrostatic head is determined by the pressure of the atmosphere over the solution in the closed system. Adjustment of the head must therefore be achieved by regulating the air pressure; because very delicate control is necessary, the chief consideration is to avoid overshooting. Two connections to the space over the liquid in the reservoir lead, through fine capillaries closed by solenoid valves, to the open air and to a source of slight suction (for example, a water aspirator with a large air-leak). By momentarily opening one or the other of the solenoids a very small change in the pressure can be obtained.

A special circuit had to be designed to provide electronic operation of the valves in the manner required (very short periods of energization at long intervals). A gas triode, type 884, in a conventional saw-tooth sweep circuit of long time-constant is so coupled to a power pentode (type 6V6) that the pentode cathode is about 5 volts less positive than the 884 plate-supply voltage, while the pentode grid is at the same potential as the 884 plate.

Assuming the initial state to be the instant after the gas triode has fired, the cycle proceeds as follows: the triode plate and the pentode grid are far below the plate-supply voltage, approaching the triode cathode potential, since the condenser across the triode has just discharged through the tube. Hence, the pentode is cut off and its plate-circuit relay is open. The condenser at once commences to recharge through the series resistor, bringing the pentode grid gradually nearer the cathode. When the bias has thus been sufficiently reduced the pentode conducts, closing the relay, which in turn actuates the proper solenoid valve. Almost as soon as this state is reached, however, the triode fires and its plate drops sharply toward cathode potential again, cutting off the pentode and permitting the valve to reclose.

Two variable-resistor controls are provided in each circuit to permit setting the two components of the cycle; the series resistor in the triode plate circuit determines the over-all length of the cycle, while adjustable bias for the triode fixes the voltage at which the tube fires and thereby controls the fraction of each cycle during which the pentode conducts. The cycle length can be varied from a fraction of a second to half a minute or more, and the "valve open" period from zero to several seconds. With the primary relay in the open position the fourth set of points shorts the 884 plate and cathode, inactivating the time circuit. Auxiliary pilot lights across the solenoid coils indicate their operation.

The remaining, non-tuned circuit is much simpler than the preceding three. Here only a single power pentode (6V6) is necessary, driving in its plate circuit the same type of 4-pole relay as already described. The control grid is supplied with cut-off bias (20-30 volt) through a resistor of the order of one megohm. Grid and ground are connected to the two sides of a mercury expansion contact immersed in the ether solution being concentrated. If the non-aqueous solvent temperature exceeds a safe value the circuit is closed through the mercury, bias is removed from the grid, the tube conducts, and the relay closes. Besides illuminating the pilot and sounding the characteristic audible alarm, this relay closes another power relay which opens the power line to the hot plate under the non-aqueous solvent still. Since a fourth set of points is available on the primary relay, it is also possible to actuate a solenoid valve simultaneously and increase the rate of flow of extracting water through the non-aqueous solvent.

REFERENCE

1. C. V. Cannon, G. Jenks, and J. W. Boyle, reported in CC-1204, p. 37, January 11, 1944.

Fig. 15.1

Fig. 15.1 (continued)

Paper 16

Solubility of Xenon and Nitric Oxide in Various Solvents*

W. L. KAY and R. A. PENNEMAN

ABSTRACT

The solubility of xenon in air-free carbon tetrachloride has been determined. Nitric oxide solubilities have been measured in aqueous solutions of various reagents.

1. INTRODUCTION

It was desired to recover radioactive Xe^{133} (5.5d) from neutron-bombarded uranium metal containing fission products. Dissolving such metal in nitric acid results in the evolution of gas consisting largely of nitric oxide, with other oxides of nitrogen, air, and a small amount of active xenon. In devising a scheme for separation of these gases, data on the solubility of xenon in carbon tetrachloride and of nitric oxide in various absorbing reagents were required.

2. EXPERIMENTAL

The method, essentially that described by McDaniel,¹ involved measurement of the volume of gas dissolved at constant pressure in a known volume of solvent. Pure xenon (analysis not given) was obtained from the General Electric Company and was used without additional purification. The nitric oxide was prepared by the method of Giaque.² In a typical run, a known volume of xenon saturated with carbon tetrachloride vapor was put into contact with a definite volume of the air-free solvent (boiled and cooled under reduced pressure). The solvent was agitated until equilibrium was obtained. The volume decrease divided by the volume of the solvent gave the Ostwald solubility coefficient α . This coefficient is not pressure dependent for a perfect gas and is practically independent of pressure over the range of a few atmospheres for any gas.

The values reported in Table 16.1 include solubilities that were previously available³ but which were checked to evaluate the apparatus and to establish the purity of the xenon and nitric oxide.

*Work done at the Metallurgical Laboratory, University of Chicago. Paper written by R. A. Penneman, and prepared for publication July, 1945. Report MDDC-495; ANL-HDY-71.

Table 16.1—Xenon and Nitric Oxide Solubilities

Gas	Temp., °C	Solvent	1	Remarks
Xe	31	H ₂ C	0.097	Lit. values ³ 0.100, 0.107
	28	CCl ₄	2.4	
	31		2.3	
	31		2.9	
	32		2.4	
NO	32	CCl ₄	0.380	Lit. value ³ 0.37
	32		0.387	
	30	20 g CrO ₃ in 100 g 40 per cent H ₂ SO ₄	60	End soln. showed complete reduction to Cr ⁺⁺⁺ . No ppt. formed
	30		57	
	31	25 g FeSO ₄ in 100 g H ₂ O	9.0	NO causes some oxidation to Fe ⁺⁺⁺
	31		9.4	
	27	15 g FeSO ₄ in 100 g 2.25 N H ₂ SO ₄	7.2	NO readily expelled to yield original soln.
	30		6.6	
	31		6.8	
	28	33 g Fe ₂ (SO ₄) ₃ in 100 g 2.25 N H ₂ SO ₄	0.2	

3. DISCUSSION

The expression of Raoult's law for a volatile solute is

$$P_2 = x_2 P_2^0 \quad (1)$$

where P_2 is the partial pressure of the solute, x_2 is its mole fraction in the solution, and P_2^0 is the vapor pressure of the pure solute. Extrapolating by means of the Clausius-Clapeyron equation, the vapor pressures of xenon and nitric oxide at 30°C are 72.5 and 2140 atm, respectively. Setting P_2 equal to 1 atm in Eq. 1, the ideal solubility of xenon expressed as a mole fraction is $1/72.5$. This results in a value for "1" of 3.56 in carbon tetrachloride at 30°C. A similar calculation for nitric oxide yields 0.120 for the coefficient. The experimental solubility of xenon in carbon tetrachloride agrees rather closely with the predicted value. The discrepancy between the experimental and calculated values in the case of nitric oxide may be attributed to the uncertainty in extrapolating its vapor pressure so far above its critical temperature, or to the failure of Raoult's law for mixtures of dissimilar molecules.

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Paper 17

Infrared Spectrum of Benzene*

JOHN FLANAGAN, R. GARDNER, FRANCES McKEE, and RICHARD SCHLEGEL

ABSTRACT

Benzene shows weak absorption bands in the 3μ aliphatic C-H region of the spectrum. The peaks of these bands are at 3.439μ , 3.459μ , 3.504μ , and 3.545μ .

* * * * *

In connection with the study of the infrared spectrum of irradiated benzene an intensive study was made of the spectrum of pure benzene in the 3μ aliphatic C-H region. It was found that pure benzene shows some absorption in that region. "Aliphatic" peaks were found at wavelengths 3.439μ , 3.459μ , 3.504μ , and 3.545μ . (See Fig 17.1) The absorption coefficients[†] of the very strong benzene bands around 3.26μ (the aromatic C-H region) compare with those of the "aliphatic" peaks shown in Table 17.1.

At first it was assumed that the absorption bands in the aliphatic region were the result of aliphatic impurities in the benzene. Cyclohexane, with freezing and boiling points close to those of benzene, seemed a possible impurity. However, the frequencies of the three cyclohexane bands are sufficiently different from the observed benzene bands to eliminate the chance that the latter arise from cyclohexane. An actual study of a mixture of benzene and cyclohexane corroborated this conclusion.

Table 17.1 — Absorption Coefficients of Benzene Bands

"Aromatic" region		"Aliphatic" region	
Wave length, μ	Absorption coefficient	Wave length, μ	Absorption coefficient
3.232	43.8	3.439	0.4
3.253	36.5	3.459	1.2
3.290	54.2	3.504	0.3
		3.545	0.9

Next a study of samples of benzene of extremely high purity was made. One sample was prepared by the method of Richards and Shipley,¹ which is now in general use for the prepara-

*Work done at the Metallurgical Laboratory, University of Chicago. Paper written by Richard Schlegel. Report MDDC-663; ANL-HDY-69.

[†]The absorption coefficient k is here defined by the expression $I = I_0 \exp(-kcd)$ where c is the concentration in moles per 1000 g of CCl_4 and d is the path length in centimeters.

tion of benzene for thermodynamic and physical studies. The method involves various chemical washings, and is completed with six recrystallizations and fractional distillation. With this very pure sample (derived from Baker's c.p. thiophene-free reagent) no decrease in infrared absorption in the aliphatic region was found. Benzene was also prepared from benzoic acid and calcium oxide, CaO. This benzene was recrystallized four times and fractionally distilled. Again, no decrease in the aliphatic absorption was found.

Finally, carbon disulfide was used in place of carbon tetrachloride, the solvent in which the benzene absorption is usually studied. The possible effect of a glyptal glue (used in the cell and normally impervious to the solvents used) on the dilute solutions of benzene was also studied. None of these studies indicated that the absorption was caused by materials extraneous to benzene. It was concluded that the bands observed are proper to the benzene spectrum.

These investigations were made with the University of Illinois echelette type grating spectrometer, ruled 3600 lines to the inch, which was made available through the courtesy of Professor W. H. Rodebush.

The only previous work found on the presence of benzene absorption bands in the aliphatic C-H region is that of Barnes,² done with the Johns Hopkins grating in 1930. There seems to have been uncertainties, however, in Barne's method; he does not report the bands in later papers.

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Fig. 17.1 — Infrared absorption in benzene.

Paper 18

**Minimum Hydrogen Peroxide Concentration Required
for Precipitate Formation from 50 Per Cent
Uranyl Salt Solutions***

RALPH LIVINGSTON

ABSTRACT

Tests showed the threshold concentration of hydrogen peroxide for precipitate formation in 50 per cent solutions of uranyl nitrate and uranyl sulfate with varying amounts of excess anion as acid is higher for nitrate than for sulfate and is raised by addition of excess acid.

* * * * *

The purpose of this study was to estimate the minimum hydrogen peroxide concentrations required for formation of a precipitate in 50 per cent solutions of uranyl nitrate and uranyl sulfate (per cent based on weight of anhydrous salt) containing various concentrations of excess anion as acid.

Thirty-six tests were carried out simultaneously in 3-ml corked pyrex test tubes at room temperature. The results are given in Table 18.1. In each test, 2 ml of the 50 per cent uranyl solution was placed in the tube and the proper volume of 70 per cent nitric acid or 96 per cent sulfuric acid was added to give the per cent by weight of additional acid indicated in the table. Chemical analysis showed that the uranyl sulfate solution initially contained 0.26 per cent free sulfuric acid, while a less satisfactory analysis of the uranyl nitrate indicated essentially no free acid. Six dilutions of "Superoxol" H_2O_2 solution were standardized iodometrically for H_2O_2 . H_2O_2 was introduced into the test solution by addition of 0.1 ml of one of the diluted H_2O_2 solutions to give the concentrations indicated in the table. In each case, a precipitate formed (sometimes only momentarily) on addition of H_2O_2 , due to local saturation. Table 18.1 gives the results after the tubes had been shaken and allowed to stand for 3 hr. After several days the only change noted was a decrease in the opalescence in some of the tubes accompanied by the formation of more precipitate. The results indicate that the threshold concentration of H_2O_2 for precipitate formation is higher for nitrate than for sulfate, and is raised by the addition of excess acid.

*Work done at the Metallurgical Laboratory, University of Chicago. Report MDDC-493; ANL-HDY-70.

Table 18.1—Effects of Hydrogen Peroxide Concentration on Precipitate Formation in 50 Per Cent Uranyl Nitrate and 50 Per Cent Uranyl Sulfate Solutions

Solution composition	Approximately H_2O_2 concentration					
	0.11N	0.055N	0.045N	0.028N	0.022N	0.011N
50% uranyl nitrate; no additional acid	Opalescent Very heavy ppt.	Opalescent Moderate ppt.	Opalescent Some ppt.	Very weakly opalescent No ppt.	Clear	Clear
50% uranyl nitrate; 1% additional HNO_3	Opalescent Heavy ppt.	Opalescent Some ppt.	Opalescent Some ppt.	Opalescent Some ppt.	Clear	Clear
50% uranyl nitrate; 4% additional HNO_3	Opalescent Heavy ppt.	Opalescent Small ppt.	Opalescent Small ppt.	Clear	Clear	Clear
50% uranyl sulfate; 0.26% free H_2SO_4	Opalescent Very heavy ppt.	Strongly opal. Very heavy ppt.	Strongly opal. Very heavy ppt.	Strongly opal. Moderate ppt.	Strongly opal. Some ppt.	Strongly opal. No ppt.
50% uranyl sulfate; 1.26% free H_2SO_4	Opalescent Very heavy ppt.	Strongly opal. Very heavy ppt.	Strongly opal. Very heavy ppt.	Strongly opal. Moderate ppt.	Strongly opal. No ppt.	Very weakly opal.
50% uranyl sulfate; 4.26% free H_2SO_4	Strongly opal. Very heavy ppt.	Strongly opal. Heavy ppt.	Strongly opal. Heavy ppt.	Slightly opal. No ppt.	Slightly opal. No ppt.	Clear

TTD-5212

Paper 19

The System Nitric Acid-Water-Methyl Isobutyl Ketone*

J. E. POWELL and AMOS S. NEWTON

ABSTRACT

A ternary diagram for the system nitric acid-water-methyl isobutyl ketone has been drawn. Distribution data for nitric acid between water and hexone is presented.

* * * * *

The system water-nitric acid-methyl isobutyl ketone has been studied at 25°C.

The hexone used was Eastman Practical Grade. In the distribution experiments it was used as received, but in determining the ternary solubility curve the hexone was purified by drying with anhydrous potassium carbonate overnight, then refluxing with metallic calcium for 4 hr and finally distilling from metallic calcium. The hexone has a b.p. of 114°C at 730 mm of Hg.

The distribution coefficients for nitric acid between water and hexone were determined as follows:

Various concentrations of nitric acid in water were shaken with an equal volume of hexone in a glass-stoppered graduate. The volume of both the phases formed was recorded and the layers were separated. The concentration of nitric acid in each phase was determined by titration of aliquots with standard sodium hydroxide solution (Table 19.1).

When the concentration of nitric acid in the water-rich layer (C_1) was plotted against the concentration of nitric acid in the hexone-rich layer (C_2) on log-log graph paper (Table 19.2 and Fig. 19.1), it was found that a straight line could be drawn through the points representing nitric acid concentrations between 3.5N and 11N in the water layer or 1.5N and 7N in the hexone layer. The line can be represented by the following equations: (See Table 19.2 and Fig. 19.1)

*Work done at the Metallurgical Laboratory, University of Chicago. Based on report CC-2394, and prepared for distribution February 19, 1945.

$$\begin{aligned}
 \log C_2 &= m \log C_1 + \log B \\
 m &= 1.28 \\
 B &= 0.308 \\
 \log C_2 &= 1.28 \log C_1 + \log 0.308 \\
 C_2 &= 0.308 C_1^{1.28} \\
 C_2/C_1^{1.28} &= 0.308 \\
 K_e &= C_1^{1.28}/C_2 = 3.25 \pm 0.05
 \end{aligned}$$

Another straight line can be drawn through the points representing nitric acid concentrations below 3.5N in the water phase and 1.5N in the hexone phase. The slope of this line is somewhat greater than the first and the following equation represents the data:

$$\begin{aligned}
 \log C_2 &= m \log C_1 + \log B \\
 m &= 1.84 \\
 B &= 0.156 \\
 \log C_2 &= 1.84 \log C_1 + 0.156 \\
 C_2 &= 0.156 C_1^{1.84} \\
 C_2/C_1^{1.84} &= 0.156 \\
 K_e &= C_1^{1.84}/C_2 = 6.4 \pm 0.5
 \end{aligned}$$

The slope changes very rapidly with nitric acid concentrations above 11N in the water phase and 7N in the hexone phase. Very low concentrations of nitric acid gave erratic results.

By titrating mixtures of water and hexone with concentrated nitric acid until a single phase formed, and by adding hexone to aqueous nitric acid until first two phases were formed and finally until these two phases formed a single phase, a ternary solubility curve was obtained (Table 19.3 and Fig. 19.2). A few tie lines were determined by analyzing the phases for nitric acid and determining the densities in a pycnometer (Table 19.5). Other tie lines were determined from the distribution data (Table 19.1) by calculating the density of the water phase from data available from other experiments (Table 19.4 and Fig. 19.3). The dotted line on the ternary diagram is the conjugate curve from which any tie line can be determined. It has been extrapolated to give the plait point.

Table 19.1—Distribution of Nitric Acid Between Water and Hexone

Vol. of aqueous acid (start)	50	50	50	50	50	50	50	50	50
Vol. of hexone (start)	50	50	50	50	50	50	50	50	50
Vol. of aqueous layer (end)	18.7	25.6	30.4	34.0	36.9	40.9	43.4	48.5	49.5
Vol. of hexone layer (end)	18.3	74.4	69.9	66.0	63.1	59.1	56.6	51.5	50.5
Conc. HNO_3 in aqueous layer	11.30	10.13	9.17	8.03	6.91	5.72	4.74	2.71	1.29
Conc. HNO_3 in ketone layer	7.11	6.02	5.20	4.39	3.64	2.87	2.26	0.97	0.257
Moles HNO_3 in aqueous layer	0.212	0.260	0.279	0.273	0.255	0.234	0.206	0.131	0.064
Moles HNO_3 in ketone layer	0.578	0.448	0.363	0.290	0.230	0.170	0.128	0.0499	0.013
Total moles HNO_3	0.790	0.708	0.642	0.563	0.485	0.404	0.334	0.181	0.077
Normality of original aq. acid	15.8	14.2	12.8	11.3	9.70	8.08	6.68	3.62	1.54
Density orig. acid soln. (Handbook)	1.415	1.389	1.363	1.331	1.293	1.251	1.213	1.118	1.050
Wt. of original acid soln.	70.8	69.5	68.2	66.6	64.8	62.6	60.7	55.8	52.5
Wt. of Hexone	40.1	40.1	40.1	40.1	40.1	40.1	40.1	40.1	40.1
Total wt. of soln.	110.9	109.6	108.3	106.7	104.9	102.7	100.8	95.9	92.6
Density of hexone layer (graph)	1.060	1.023	0.995	0.968	0.944	0.917	0.895	0.843	0.813
Wt. of Hexone layer	86.2	76.1	69.5	63.9	59.5	54.2	50.6	43.4	41.0
Wt. of aqueous layer	24.7	33.5	38.8	42.8	45.4	48.5	50.2	51.5	51.6
Density of aqueous layer	1.32	1.31	1.28	1.26	1.23	1.19	1.16	1.06	1.04
Wt. HNO_3 in aqueous layer/cc.	0.712	0.639	0.577	0.506	0.435	0.360	0.298	1.71	0.0815
Wt. HNO_3 in hexone layer/cc.	0.448	0.379	0.328	0.277	0.229	0.181	0.142	0.0611	0.0162
% HNO_3 by wt. in aqueous soln.	53.9	49.9	45.8	40.1	35.3	30.3	25.6	16.1	7.8
% HNO_3 by wt. in hexone soln.	42.3	37.0	33.0	28.6	24.3	19.8	15.9	7.3	2.0

Table 19.2—Distribution of Nitric Acid Between Water and Hexone

Conc. of HNO ₃ in H ₂ O phase C ₁	Conc. of HNO ₃ in Hexone phase C ₂	C ₁ /C ₂	C ₁ ^{1.28} /C ₂	C ₁ ^{1.84} /C ₂
11.76	9.56	1.86	2.45	
11.98	8.68	1.38	2.77	
11.3	7.11	1.59	3.13	
10.13	6.02	1.68	3.22	
9.17	5.20	1.76	3.28	
8.03	4.39	1.83	3.28	
5.91	3.64	1.90	3.26	
5.72	2.87	1.99	3.24	
4.74	2.26	2.10	3.24	
3.65	1.57	2.32	3.34	6.90
2.71	0.970	2.79	3.69	6.31
2.42	0.802	3.02	3.87	6.33
1.29	0.257	5.05	5.41	6.23
0.673	0.0682	9.87	8.83	7.09
0.297	0.0167	17.8	12.63	6.41
0.0653	0.00152	42.9		

Table 19.3—Ternary Solubility Data

% H ₂ O by wt.	% anh. HNO ₃ by wt.	% Hexone by wt.
98.1	0	1.9
32.0	58.5	9.5
30.1	58.2	11.7
42.0	53.1	4.91
11.0	24.8	64.2
58.9	37.6	3.5
24.8	55.8	19.4*
2.3	0	97.7

*A mixture containing 20.4 per cent hexone, 55.1 per cent HNO₃ and 24.5 per cent water gave 2 phases in about equal proportions.

Table 19.4—Densities of Hexone Solutions of Aqueous Nitric Acid*

Conc. of HNO ₃	9.56	8.68	7.01	5.16	3.56	2.15	0.797	0.257	0.0405
Density	1.169	1.130	1.057	0.992	0.941	0.890	0.834	0.811	0.801

*The solutions were obtained by shaking various concentrations of nitric acid in water with equal volumes of hexone.

Table 19.5—Tie Line Data

	(1)	(2)
Conc. HNO_3 in water phase	11.98	11.76
Conc. HNO_3 in hexone phase	8.68	9.56
Density of water phase	1.306	1.279
Density of hexone phase	1.130	1.169
% HNO_3 in water phase	57.8	57.9
% HNO_3 in hexone phase	48.3	51.6

Fig. 19.1—Distribution of nitric acid between water and methyl isobutyl ketone (hexone) at 25°C.

Fig. 19.2—Ternary diagram of water-hexone-nitric acid system at 25°C. Percentages are based on weight.

Fig. 19.3—Density of hexone-water-nitric acid solutions at 25°C.

The Preparation of Tungsten Hexafluoride*

HOMER F. PRIEST and R. COLTON

ABSTRACT

A method for preparing tungsten hexafluoride by direct combination of the elements was developed, and preliminary tests were made to determine the solubility of UO_3 , UF_4 , UO_2 , UO_2F_2 , and NaF in tungsten hexafluoride.

* * * * *

Because of the possibility that tungsten hexafluoride might occur as an impurity in uranium hexafluoride, it seemed worthwhile to prepare some of the material in order to become familiar with its mode of preparation, reactions, etc.

A sample of 100-mesh tungsten powder was obtained, and because of the volatility of the fluoride (b.p. 19°C) it seemed likely that direct combination with fluorine would be the simplest mode of preparation.

A 100-gram sample of tungsten metal was weighed into a nickel boat and placed in a nickel reactor 2 in. in diameter and 14 in. long. The reactor was fitted with heaters and controls for maintaining the temperature at any desired level.

The outlet of the furnace was connected to a nickel trap immersed in dry ice-trichloroethylene slush, and thence to the vent stack. Fluorine was provided from a pot type, high temperature fluorine cell. The experimental set-up is shown schematically in Fig. 20.1.

With the furnace at 100°C the flow of fluorine was started. The reaction started immediately and the temperature of the reactor went immediately to 400 to 500°C indicating a strongly exothermic reaction. No gas passed through the sulfuric acid bubbler indicating that all products were condensed in the dry ice trap.

After a 2-hr run the flow of fluorine was stopped, the valves on the trap were closed, and the trap was removed. Upon warming to room temperature and shaking, the trap was found to be approximately half full of liquid.

No quantitative experiments were carried out, but several qualitative experiments were run using this material.

*Work done at Columbia University, Division of War Research, Project SAM. Prepared for publication June, 1942. Report MDDC-574.

The trap containing the tungsten hexafluoride was cooled to 0°C in an ice bath and water white liquid was poured into a platinum thimble. A striking difference between UF_6 and WF_6 was noted in that only slight fuming of the WF_6 was noticed on exposure to moist air whereas UF_6 fumes copiously.

Using platinum apparatus and maintaining the temperature of the liquid as close to 0°C as possible, solubility experiments were run to ascertain the solubility of UO_3 , UF_4 , UO_2 , UO_2F_2 , and NaF in WF_6 . While the tests were rough and little more than qualitative, one can say as a result of the experiments that the solubility of each of these components is so small as to be undetectable by the method used. The procedure was simple. About 5 ml of the WF_6 was put in a platinum test tube and 1 gram of the potential solute added. Vigorous stirring was carried out for 10 min and the suspended material allowed to settle. The supernatant liquid was then poured into a clean bright platinum dish and the WF_6 allowed to evaporate. The quantity of residue was taken as a measure of the solubility and in no case was a residue observable.

The work reported above was incomplete and not conclusive, yet it served a definite purpose in providing a knowledge of the general characteristics of compounds of this type.

Fig. 20.1

The Preparation of Molybdenum Hexafluoride*

H. A. BERNHARDT, H. W. BISHOP, and J. P. BRUSIE

ABSTRACT

An all-nickel reaction tube was devised for the preparation of MoF_6 . Molybdenum under vacuum and at an initial temperature of 315°C was treated with fluorine under pressure. The yield of MoF_6 was 78 per cent of the theoretical.

1. INTRODUCTION

Molybdenum hexafluoride was first prepared according to the method described by Ruff,¹ who treated finely divided molybdenum metal with fluorine at a temperature of 60°C . This attempt, however, produced very minute quantities of MoF_6 . It was concluded that the temperature used was too low and that the purple products obtained in the reaction tube were lower fluorides of molybdenum.

2. EXPERIMENTAL

The reaction was repeated at a temperature of about 315°C . The all-nickel apparatus used is shown in Fig. 21.1. All nickel parts of the apparatus were well degreased with trichloroethylene. The reaction tube had nickel screw caps that were made vacuum tight by the use of Teflon gaskets. Since Teflon is consumed by fluorine at temperatures above 125°C , it was necessary to cool the ends of the reaction tube by wrapping them with asbestos and allowing cool water to run over them.

Twenty grams of finely divided molybdenum metal were placed in the reaction tube and a tube furnace was used to supply the heat for the reaction. The metal system was well flamed and pumped down to a vacuum of 0.06 micron with a leak rate of 0.02 micron per minute. The reaction tube was then heated up to 315°C . Valve 1 was opened, and the molybdenum was treated with fluorine at a pressure of about 5 lb gauge. As soon as fluorine was allowed to enter the reaction tube, the temperature rose to 480°C (as measured by means of a thermocouple). The molybdenum hexafluoride formed was condensed in the metal trap which was cooled in a

*Work done at the Carbide and Carbon Chemicals Corporation, Laboratory Division, Clinton Engineer Works. Prepared for publication December 11, 1945. Report MDDC-1528.

dry ice trichlorethylene mixture. The fluorine was added as long as there was any consumption (about 8 hr). When fluorine was no longer being consumed, valve 1 was left open, the metal trap containing the MoF_6 was cooled down with liquid nitrogen, and the excess fluorine was pumped off by means of a disposal system. Valve 1 was then closed, and the second metal trap was cooled down with liquid nitrogen. Valve 2 was opened and the first trap was heated to about 60°C with a burner in order to distill the product over to the second metal trap. This step seemed to separate the MoF_6 from any lower fluoride of molybdenum that may have been formed.

3. DISCUSSION OF RESULTS

The product obtained was a white crystalline solid which turned to a light yellow liquid at room temperature. Molybdenum hexafluoride decomposes at once if it is allowed to come in contact with moist air. It melts at about 17°C and boils at about 35°C . The yield of product obtained was 78 per cent of the theoretical.

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Fig 21.1

Paper 22

Production of High Boron Steel*

G. D. BAGLEY and F. E. BACON

ABSTRACT

A series of 21 heats was made in a laboratory induction furnace to see what per cent of boron could be added to steel without making it unforgeable. It was found that 1.5 per cent boron steels could be produced from ferroboration, with good recovery, and rolled to $\frac{1}{4}$ -in. strips.

* * * * *

High-boron steel was desired for use in metallurgical studies on the Manhattan Project. Although boron had been added to steel as an alloying agent, it was not too clear from prior research what recoveries of boron could be expected from the ferroboration added, and whether or not steels containing several per cent of boron could be forged and rolled to $\frac{1}{4}$ -in. strip. For example, Guillet¹ made and worked steels with 0.15 to 1.51 per cent boron. When he tried to prepare steels with a higher boron content he found that they could not be forged. He did not study the higher boron steels further to learn the cause of the forging difficulties which may have been due to the limited solubility of boron in iron at all temperatures. According to Wever and Mueller,² the maximum solubility of boron in iron is 0.15 per cent. If the iron contains more than 0.15 per cent boron the compound Fe_2B separates as a second phase. The formation of this compound probably accounts for the forging difficulties encountered by Guillet.

In view of these results it was thought desirable to make a series of experimental heats to see what percentage of boron could be added to a steel without rendering it unforgeable. A total of 21 heats was made in a small laboratory induction furnace. These varied from 6-lb to 80-lb heats. The raw materials were ingot iron, ferroboration, ferrosilicon, and ferromanganese. The steels were melted in a magnesia-lined crucible and cast into small ingots. Steels ranging from 0.44 to 3.34 per cent boron were made and cast successfully. They were made to contain 0.75 per cent manganese and 0.25 per cent silicon. The recovery of ferroboration was satisfactory; for example, 1.67 per cent boron was added to one heat as ferroboration

*Work done at the Electro Metallurgical Company, New York. Paper written by R. M. Fowler. Report MDDC-567.

and 1.45 per cent was recovered. The ferroboron used contained 17.74 per cent boron. The ingots were reheated to 1000°C and forged to 1-in. square bars. The steel containing 3.34 per cent boron was forged to 1-in. bars and flattened to $\frac{1}{2}$ -in. strip, but when the strip was reheated to 1000°C and an attempt made to roll it, the material broke up on rolling. The 1.5 per cent boron steels were heated to 1000°C and rolled to $\frac{1}{4}$ -in. strip without difficulty. Several 80-lb heats of this analysis were made, forged, and rolled, and utilized in experimental work, showing that 1.5 per cent boron steels could be produced from ferroboron with good recoveries and worked to $\frac{1}{4}$ -in. sheet in conventional steel-making equipment.

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Paper 23

**The Crystal Structure of Trichlorides, Tribromides,
and Trihydroxides of Uranium and of Rare Earth Elements***

W. H. ZACHARIASEN

1944-1946

ABSTRACT

The compounds UCl_3 , UBr_3 , LaCl_3 , LaBr_3 , $\text{La}(\text{OH})_3$, CeCl_3 , CeBr_3 , PrCl_3 , PrBr_3 , $\text{Pr}(\text{OH})_3$, NdCl_3 , and $\text{Nd}(\text{OH})_3$ are shown to be isomorphous. They have hexagonal structures with two molecules per unit cell. The complete structures are determined and described.

1. INTRODUCTION

This paper gives an account of complete crystal structure determinations for the following series of isostructural substances: UCl_3 , UBr_3 , LaCl_3 , LaBr_3 , CeCl_3 , CeBr_3 , PrCl_3 , PrBr_3 , NdCl_3 , $\text{La}(\text{OH})_3$, $\text{Pr}(\text{OH})_3$, and $\text{Nd}(\text{OH})_3$.

UCl_3 is the first compound of the set for which the structure was found. Since the structure is of a new kind the structure type should thus properly be referred to as the UCl_3 -type of structure.

It should be mentioned that the lattice dimensions of UBr_3 were first obtained in the Ames Laboratory.

The various samples which were used in the investigation came from several sources. The material of UCl_3 was obtained from C. A. Kraus at Brown University while F. H. Spedding of Iowa State College supplied the sample of UBr_3 . The samples of the rare earth trihalides were procured from the University of Illinois through the kind cooperation of H. B. Arnold. The writer prepared the trihydroxides.

2. THE LATTICE PERIODS

All the preparations were in finely divided form so that single crystal diffraction patterns could not be obtained. The halides are all quite hygroscopic and thin-walled pyrex capillaries were therefore used as specimen containers.

*Work done at the Metallurgical Laboratory, University of Chicago. Report AECD-2091: ANL-HDY-499.

The powder diffraction patterns were taken with CuK-radiation filtered through nickel foil. The following tables give a small part of the diffraction data for UCl_3 , UBr_3 , CeCl_3 , CeBr_3 , and $\text{La}(\text{OH})_3$. Except for small shifts in the positions of the diffraction lines the patterns LaCl_3 , PrCl_3 , and NdCl_3 are identical with those of CeCl_3 , the patterns of LaBr_3 and PrBr_3 with CeBr_3 , and the patterns of $\text{Pr}(\text{OH})_3$ and $\text{Nd}(\text{OH})_3$ with $\text{La}(\text{OH})_3$.

The data given in Tables 23.1 to 23.3 show that the observed sine square values correspond to hexagonal unit cells. The lattice periods given in Table 23.4 were deduced from observations in the back-reflection region.

The densities reported in the literature for the trichlorides show that the unit cell contains two stoichiometric molecules. The calculated densities are listed in Column 4 of Table 23.4.

3. DETERMINATION OF THE ATOMIC POSITIONS

The reflections ($00H_3$) are absent if H_3 is odd, but this is the only regularity among absent reflections. It will be noted, however that reflections ($H_1H_2H_3$) with $2H_1 + H_2 = 3n$ and H_3 odd are consistently weak or missing.

One of the space groups $C6_3$, $C6_3/m$, or $C6_3/2$ is thus indicated. $C6_3$ is a subgroup of the other two and accordingly it suffices to consider this space group. The atomic positions for the compounds AB_3 compatible with the observed intensities are:

$$2A \text{ in } \pm (\frac{1}{3}, \frac{2}{3}, \frac{1}{4})$$

$$6B \text{ in } (x, y, z) (\bar{y}, x - y, z) (y - x, \bar{x}, z) (\bar{x}, \bar{y}, z + \frac{1}{2}) (y, y - x, z + \frac{1}{2}) (x - y, \bar{x}, z + \frac{1}{2})$$

The symmetry is raised to that of $C6_3/M$ if $z = \frac{1}{4}$ and to that of $C6_3/2$ if in addition $y = 2x$, or if $x = y$ and $z = 0$. The latter space group must, however, be ruled out since the reflection (1 1 1) occurs in the diffraction patterns.

The unknown parameters x , y , z are readily determined from detailed intensity calculations. The values finally arrived at are:

$$x = 0.375 \pm 0.014 \quad y = 0.292 \pm 0.014 \quad z = 0.25 \pm 0.03$$

Normally one would expect some variation in parameter values from one compound to the next. Undoubtedly there are such variations, but they are so small as to fall within the limits of error given above for parameter values.

There is no evidence that the parameter is $z \pm \frac{1}{4}$; therefore the conclusion is that the space group symmetry is $mC6_3/(C6h^2)$.

In Tables 23.5 to 23.7 the observed intensities are compared with calculated values $1F1^2p$ where F is the structure factor and p the multiplicity factor. The quantities $1F1^2p$ should be proportional to the observed intensities as long as care is taken to compare only neighboring reflections. In comparing intensities of reflections occurring at widely different scattering angles, allowance should be made for the effects of absorption, Lorentz-polarization factor, and heat motion.

The agreement between observed intensities and calculated quantities $1F1^2p$ is seen to be satisfactory so that the deduced structure can be regarded as essentially correct.

5. DISCUSSION OF THE STRUCTURE

The structure is of a new type. However, there is no feature in the structure not compatible with the assumption that the bonds are chiefly ionic in nature. Each cation is bonded to nine anions, three of which are at a slightly different distance than are the other six. Each anion is conversely linked to three cations. This fact explains the relatively high sublimation points of the tri-halides. The cation-anion distances and the closest approach of the anions are listed in Table 23.8.

The results given in Tables 23.4 and 23.8 show that U^{+3} is almost identical in size with Ce^{+3} in the trichlorides and tribromides. In the trifluorides on the other hand U^{+3} corresponds to La^{+3} in size. Similarly U^{+4} is larger than Ce^{+4} in tetravalent oxygen and fluorine compounds. This apparent discrepancy can be attributed to the greater polarizability of Cl^- and Br^- as compared to F^- and to a slightly greater admixture of covalent nature in the bonds than for the lanthanide ions.

It is of interest to deduce the ionic radii of U^{+3} , La^{+3} - Nd^{+3} from the results given in Table 23.8 and from the results for the tri-fluorides. For that purpose the ionic radii of Cl^- , Br^- , and F^- will be taken as 1.81 Å, 1.96 Å, and 1.33 Å. Table 23.9 gives the radii so obtained, all reduced to the standard coordination number of six.

The UCl_3 -type of structure becomes unstable if the ratio of cation to anion radius becomes too small. Thus $NdBr_3$ and the tri-iodides crystallize with a different structure which is of the layer-structure type.

It is seen that there is a steady decrease in lattice dimensions and interatomic distances as one goes from the lanthanum to the neodymium compounds. This illustrates the lanthanide contraction due to added electrons going into the 4f-shell.

The x-ray diffraction patterns were taken by Miss Anne Plettinger and some of them were measured by Wallace C. Koehler.

Table 23.1—Powder Diffraction Data for UCl_3 and $CeCl_3$

UCl_3		$CeCl_3$		$H_1H_2H_3$
Intensity	$\sin^2\theta$	Intensity	$\sin^2\theta$	
MS	0.0144	M	0.0151	100
M	0.0430	W^+	0.0436	110
S	0.0462	MS	0.0471	101
VW^+	0.0575	W^-	0.0584	200
VW^-	0.0752	W	0.0761	111
S^+	0.0894	S	0.0907	201
VW^+	0.1005	W^-	0.1022	210
W	0.1291	M	0.1301	300, 002
S^+	0.1325	S^-	0.1337	211
VW	0.1420	VW	0.1434	102
W	0.1711	W^+	0.1728	220, 112
W^-	0.1859	W^+	0.1877	310, 202
M	0.2182	W	0.2201	311
W^-	0.2283	W	0.2297	400, 212
M	0.2562	M	0.2582	302
VVW	0.2613			401
VW^-	0.2725	VVW	0.2733	320
MS	0.3008	MS	0.3039	222, 410, 103
MS	0.3037			
VW	0.3137	VW	0.3155	312
		Trace	0.3316	113
W^-	0.3438	W	0.3463	203
VW	0.3575	VW	0.3590	500, 402
W	0.3858	M	0.3894	330, 213
VW	0.3889			
VW^-	0.4005	VW^+	0.4019	420, 322
W	0.4278	M	0.4302	412
W	0.4321	M	0.4355	421
VW^-	0.4716	M^-	0.4770	313
W^-	0.4752			
		Trace	0.4869	502

Table 23.2—Powder Diffraction Data for UBr_3 and CeBr_3

UBr_3		CeBr_3		$\text{H}_1\text{H}_2\text{H}_3$
Intensity	$\text{Sin}^2\Theta$	Intensity	$\text{Sin}^2\Theta$	
WM	0.0390	VW	0.0372	110
M^-	0.0441	W^+	0.0432	101
W	0.0519	W	0.0505	200
M^-	0.0699	S	0.0688	111
S^+	0.0828	S^+	0.0814	201
M^-	0.0902	M	0.0888	210
MT	0.1158	M	0.1142	300
S	0.1208	S	0.1189	211
W^-	0.1225	W	0.1214	002
VW^+	0.0355	VW^+	0.1336	102
W^-	0.1538	VVW	0.1522	220
VW	0.1607			112
W	0.1665	VW^+	0.1648	310
VW^-	0.1736	VW^-	0.1718	202
W	0.1963	VW	0.1936	311
W	0.2047	VW	0.2020	400
W	0.2114	M	0.2092	212
MS	0.2364	MS	0.2340	302
W	0.2420	VW	0.2401	320
W^+	0.2671	VW	0.2653	410
S^+	0.2725	S	0.2700	321, 322
W^+	0.2874	W^-	0.2840	312, 103
VVW	0.3122	VW	0.3088	113
VVW	0.3184			500
WM	0.3246	M	0.3216	402, 203
VVW	0.3423			330
W	0.3477	VW^+	0.3442	501
M	0.3619	M	0.3600	322, 213
MS	0.3870	M	0.3841	421, 412
M	0.4235	M^-	0.4194	511
W^-	0.4382	W^-	0.4337	502, 313

Table 23.3—Powder Diffraction Data for $\text{La}(\text{OH})_3$

Intensity	$\sin^2\theta$	$H_1H_2H_3$
M	0.0186	100
M ⁻	0.0560	110
M ⁺	0.0591	101
W ⁻	0.0754	200
VW	0.0958	111
M	0.1159	201
VW	0.1315	210
VW ⁺	0.1607	002
M ⁺	0.1713	300, 211
VW	0.1798	102
W ⁺	0.2168	112
VW	0.2240	220
Trace	0.2428	310
W ⁺	0.2832	311
VW	0.2906	212
W ⁺	0.3283	302
VW	0.3389	401
VW	0.3828	222, 103
W ⁺	0.3947	410, 321
VW ⁺	0.4354	203
VW ⁺	0.4901	213
VW ⁻	0.5054	330, 501
VW ⁺	0.5512	412
VW	0.5611	421
VW	0.6041	313
VW	0.6181	511

Table 23.4—Lattice Periods and Densities

	a_1	a_3	Calculated	Observed
U Br_3	7.926 ± 0.002 A	4.432 ± 0.002	6.53	
La Br_3	7.951 ± 0.003	4.501 ± 0.003	5.07	
Ce Br_3	7.936 ± 0.003	4.435 ± 0.003	5.18	
Pr Br_3	7.92 ± 0.01	4.38 ± 0.01	5.26	
U Cl_3	7.428 ± 0.003	4.312 ± 0.003	5.51	5.44
La Cl_3	7.468 ± 0.003	4.366 ± 0.003	3.84	3.842
Ce Cl_3	7.436 ± 0.004	4.304 ± 0.004	3.95	3.92
Pr Cl_3	7.41 ± 0.01	4.25 ± 0.01	4.02	4.02
Nd Cl_3	7.381 ± 0.004	4.231 ± 0.003	4.14	4.134
La $(\text{OH})_3$	6.510 ± 0.005	3.843 ± 0.005	4.44	
Pr $(\text{OH})_3$	6.47 ± 0.03	3.76 ± 0.03	4.63	
Nd $(\text{OH})_3$	6.42 ± 0.02	3.74 ± 0.02	4.81	

Table 23.5

$H_1H_2H_3$	UCl_3		$CeCl_3$	
	Observed intensity	$1F1^2p$	Observed intensity	$1F1^2p$
100	MS	4.1	M	3.4
110	M	8.9	W^+	5.0
101	S	14.9	MS	9.3
200	VW^+	4.1	W^-	3.6
111	VW^-	2.5	W	5.0
201	S^+	27	S	25
210, 120	VW^+	$5.0 + 0.4$	W^-	$4.9 + 0$
300	W	15.9	M	{ 14.4
002		7.4		{ 7.8
121	S^+	$19.4 + 16.9$	S^-	$16.0 + 12.8$
102	VW	5.6	VW	4.2
301	nil	0	nil	0.1
112	W	14.0	W^+	7.2
220		8.7		5.5
202	W^-	6.1	W^+	{ 4.8
310, 130		$4.6 + 1.1$		{ $4.5 + 0.3$
221	nil	0.3	nil	0.5
311, 131	M	$6.1 + 13.0$	W	$1.7 + 7.0$
122	W^-	$7.6 + 0.8$	W	{ $7.0 + 0$
400		3.8		{ 3.5
302	M	25	M	21
401	VVW	6.9	nil	2.6
320, 230	VW^-	$1.6 + 4.2$	VVW	$0.9 + 4.2$

Table 23.6

$H_1H_2H_3$	U Br_3		Ce Br_3	
	Observed intensity	1F1 ² p	Observed intensity	1F1 ² p
110	WM	4.2	VW	0.8
101	M ⁻	9.2	W ⁺	3.6
200	W	5.3	W	5.2
111	M ⁻	13.7	S	27
201	S ⁺	44.1	S ⁺	50
210, 120	M ⁻	8.6 + 0.8	M	10.2 + 4.9
300	M ⁺	24.0	M	26
211, 121	S	23.7 + 17.7	S	22 + 13.7
002	W ⁻	14.8	W	19.2
102	VW ⁺	6.1	VW ⁺	4.8
301	nil	0.4	nil	0.8
220	W ⁻	7.0	VVW	3.6
112	VW	7.2	nil	1.5
310, 130	W	8.9 + 0.1	VW ⁺	10.8 + 0.2
202	VW ⁻	7.9	VW ⁻	7.2
221	nil	1.5	nil	3.0
311, 131	W	1.4 + 11.7	VW	1.7 + 7.0
400	W	6.4	VW	7.2
212, 122	W	12.8 + 0.9	M	14.4 + 6.7
401	nil	1.6	nil	0.1
302	MS	37.3	MS	38
320, 230	W	1.0 + 8.3	VW	0.6 + 10.4
410, 140	W ⁺	13.5 + 4.2	VW	12.1 + 2.9
321, 231 } 222 }	S ⁺	11.9 + 46.6 11.0	S	{ 8.4 + 59 5.6

Table 23.7

La(OH) ₃		
H ₁ H ₂ H ₃	Observed intensity	1F1 ² p
100	M	3.1
110	M ⁻	6.4
101	M ⁺	10.6
200	W ⁻	2.9
111	VVW	1.3
201	M	17.0
210, 120	VW	1.0 + 0.4
002	VW ⁺	4.4
300	M ⁺	9.6
211, 121		12.1 + 11.0
102	VW	3.6
112	W ⁺	9.0
220	VW	5.5
202	VVW	3.4
301	nil	0

Table 23.8—Interatomic Distances

AB ₃	A-B (3)	A-B (6)	B-B
UBr ₃	3.15 A	3.10 A	3.64 A
LaBr ₃	3.16	3.13	3.67
CeBr ₃	3.15	3.10	3.64
PrBr ₃	3.14	3.08	3.61
UCl ₃	2.95	2.96	3.45
LaCl ₃	2.97	2.99	3.48
CeCl ₃	2.96	2.96	3.45
PrCl ₃	2.94	2.94	3.43
NdCl ₃	2.93	2.92	3.42
La(OH) ₃	2.59	2.62	3.05
Pr(OH) ₃	2.57	2.58	3.01
Nd(OH) ₃	2.55	2.56	2.98

Table 23.9—Ionic Radii

	Chlorides	Bromides	Fluorides
U ⁺³	1.03	1.04	1.06
La ⁺³	1.05	1.06	1.06
Ce ⁺³	1.03	1.04	1.04
Pr ⁺³	1.01	1.02	1.03
Nd ⁺³	0.99		1.01

Identification and Crystal Structure of Barium Hydrogen Phosphate*

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ABSTRACT

The complete structure of barium hydrogen phosphate, BaHPO_4 , as determined by means of x-ray diffraction is described.

The crystal is orthorhombic, with cell dimensions given by: $a = 5.71 \text{ \AA}$; $b = 7.05 \text{ \AA}$; $c = 4.61 \text{ \AA}$. The calculated density is 4.15 g/cm^3 for two molecules in the unit cell.

The space group is C_{2v}^1 -Pmn. The barium, phosphorus, and two sets of oxygen lie in the plane of symmetry. The third set of oxygens are in general positions. Parameters for these atoms have been found, and interatomic distances calculated. The positions of the hydrogens are indicated by the characteristic O-H-O distance ($2.58 \text{ \AA}$) between two oxygens.

1. INTRODUCTION

In connection with investigations on the carrying of fission products, a fairly extensive X-ray structural study of the indicated phosphates has recently been undertaken. These first results are concerned with barium phosphate precipitate.

Eight preparations of barium precipitated by phosphate ion in acid solution were used. These were prepared by the Chemistry Division of the Metallurgical Laboratory under the supervision of W. Robinson. Six of these, which had been allowed to precipitate slowly, gave identical X-ray powder patterns. Two, made by rapid precipitation, gave a different pattern, although the first compound was present to the amount of 15 per cent. The nature of the second phase is as yet unknown. The first compound, which formed by slow precipitation, has been identified as BaHPO_4 , and its complete crystal structure determined by X-rays.

2. POWDER DATA

The powder pattern used in the cell size determination was taken in a 19 cm Bradley type camera with copper radiation filtered through nickel foil. The indexed observations are recorded in Table 24.1, along with calculated and observed values of $\sin^2\theta$.

*Work done at the Metallurgical Laboratory, University of Chicago. Report MDDC-607; based on report CC-1963(A-2840) and prepared for publication August 8, 1944.

Table 24.1—Powder Diffraction Data for BaHPO_4
(19 cm Bradley camera, $\text{CuK}\alpha$)

$\text{Sin}^2\theta$, observed	Intensity	Index	$\text{Sin}^2\theta$, calculated
0.0302	M	110	0.0301
0.0403	M^-	011	0.0398
0.0460	VS	101	0.0461
0.0475	S	020	0.0477
0.0578	VW	111	0.0580
0.0659	M^+	120	0.0659
0.0728	M^+	200	0.0728
0.0755	VW	021	0.0756
0.0936	S^+	121	0.0938
0.1074	W^+	030	0.1073
0.1123	S	211, 002	0.1126, 0.1116
0.1206	W^+	220	0.1205
0.1252	W	130	0.1255
0.1419	VW	112	0.1417
0.1484	M^+	221	0.1484
0.1537	W	131	0.1534
0.1586	W	022	0.1593
0.1758	W^-	310	0.1757
0.1848	VW	202	0.1844
0.1913	W	301-040	0.1917, 0.1907
0.2091	M^-	231	0.2080
0.2188	W	041, 032	0.2185
0.2321	VW	222	0.2321
0.2392	M^-	321	0.2394

Constants: $A_1 = 01820$ $a_1 = 5.71 \text{ \AA}$
 $A_2 = 01192$ $a_2 = 7.05 \text{ \AA}$
 $H_3 = 02790$ $a_3 = 4.61 \text{ \AA}$

3. SINGLE CRYSTAL DATA

Some of the samples contained crystals visible under a low power microscope. In form, they are thin 6-sided plates. Only very small ones, of 0.1 to 0.3 mm dimensions, were found to be single, the tendency being for the crystals to grow one upon the other in stacks. However, it was possible to mount single crystals suitably so as to obtain rotation photographs about the two axes lying in the plane of the plate (a and c), and Weissenberg photographs of layers perpendicular to these. The cell dimensions as obtained from the powder photograph were thereby confirmed, and a good set of single crystal intensity data obtained. Some of these data, showing the observed intensities and calculated structure amplitudes from the completed structure, are recorded in Table 24.2.

4. CELL SIZE, SPACE GROUP, AND IDENTIFICATION OF THE COMPOUND

The X-ray data establish that the crystal is orthorhombic, with cell dimensions given by: $a = 5.71 \pm 0.01 \text{ \AA}$; $b = 7.05 \pm 0.01 \text{ \AA}$; $c = 4.61 \pm 0.01 \text{ \AA}$. Consequently, the volume is $185.58 \text{ \AA}^3$.

The X-ray data also show that the crystal symmetry must be either that of the holohedral space group, D_{2h}^{13} (Pmnm) or that of the hemihedral space group, C_{2v}^I (Pmn); for all planes h are absent unless $h + 1$ is even.

The space group D_{2h}^{13} , provides eightfold general positions; two types of fourfold special positions, with symmetry m or $\bar{1}$; and twofold special positions with symmetry mm .

Table 24.2—Observed Intensities and Calculated Structure Amplitudes

Index	$\sin \theta/\lambda$	Observed intensity*	F, calculated
010	0.071	W	17
110	0.112	M	26
011	0.130	M	32
101	0.139	S ⁺	59
020	0.142	S ⁺	54
111	0.157	W ⁻	16
120	0.167	S ⁻	32
200	0.175	S ⁺	57
021	0.179	W ⁻	14
210	0.189	nil	2
121	0.199	S	50
030	0.213	S	41
211	0.218	M ⁺	44
220	0.225	S	45
130	0.230	M ⁻	21
031	0.239	M	32
221	0.251	W ⁺	32
131	0.251	W ⁺	49
310	0.272	W ⁺	28
230	0.276	W	22
040	0.284	W	18
301	0.285	M	43
311	0.293	nil	7
140	0.297	M	35
231	0.297	W	20
141	0.317	M	24
321	0.318	M	35
400	0.350	S ⁺	55
241	0.351	M	29
050	0.355	M	31
331	0.356	W	33

*W = weak; M = medium; S = strong

The space group C_{2v}^I provides fourfold general positions, and twofold special positions with symmetry m .

This information, along with intensity and spatial considerations, leads to the identification of the compound, if it can be assumed, from the conditions of preparation, that it really is a phosphate. Within this limitation, several possibilities have to be considered, namely, that the compound may be (a) the orthophosphate, $Ba_3(PO_4)_2$; (b) one of the acid phosphates, $BaHPO_4$ or $BaH_2(PO_4)_2$; or (c) a hydrate of any one of these.

Fortunately, the cell is small. There cannot possibly be four barium atoms in it, and the known symmetry forbids the presence of three or of one.

There are therefore two barium atoms in the cell. Consequently, they must lie in the special twofold positions of one or the other of the possible space groups.

These positions are:

$$\begin{aligned} D_{2h}^{18} - Pmnm \quad (a) \quad & 0 \ y \ 0; \ \frac{1}{2} \ \bar{y} \ \frac{1}{2} \\ C_{2v}^7 - Pmn \quad (a) \quad & 0 \ y \ z; \ \frac{1}{2} \ \bar{y} \ \frac{1}{2} + z \end{aligned}$$

These positions are identical if one considers barium alone, but the distribution of the other atoms in the cell leads to a choice of the lower symmetry space group.

The parameters for barium, in angular measure, have been fixed at: $y = 73.5^\circ$; $z = 72^\circ$.

With the barium atoms placed, the remaining space in the cell is sufficient for only two phosphate groups. Therefore, it must be concluded that the crystal is $BaHPO_4$, with two molecules in the unit cell. The calculated density is then 4.15 g/cm^3 .

The two phosphorus atoms as well as the hydrogen must also be in special positions in the reflection planes; the eight oxygens may occupy two sets of fourfold positions, or may fall into two twofold and one fourfold set. The second distribution has been found to be the correct one.

Since only the intensities of weak planes are affected by the comparatively small oxygen-phosphorus contributions, the remainder of the structure was deduced on the basis of the known size and configuration of the phosphate group, and known interatomic distances. The results are confirmed by the agreement between observed intensities and calculated structure amplitudes; for the phosphorus-oxygen contribution does affect the intensity of low-value planes. The data are tabulated in Table 24.2. No corrections have been made for Lorentz and polarization factors, so only planes which have nearly the same scattering angle are strictly comparable.

The symbols used to indicate the visually estimated intensities are, in descending order of intensity, S^+ , S , S^- ; M^+ , M , M^- ; W^+ , W , W^- , nil.

5. STRUCTURAL DATA

Barium hydrogen phosphate has two atoms in a cell of dimensions: $a = 5.71 \text{ \AA}$; $b = 7.05 \text{ \AA}$; $c = 4.61 \text{ \AA}$.

The density is 4.15 g/cm^3 .

The space group is $C_{2v}^7 - Pmn$.

The equivalent positions are:

2-fold (a) $0 \ y \ z; \ \frac{1}{2}, \ \bar{y}, \ \frac{1}{2} + z$.

4-fold (b) $x \ y \ z; \ \bar{x} \ y \ z; \ \frac{1}{2} - x, \ \bar{y}, \ \frac{1}{2} + z; \ \frac{1}{2} + x, \ \bar{y}, \ \frac{1}{2} + z$

The distribution of the atoms in these positions and the parameters expressed as fractions of the unit cell dimensions are given in the following table:

Table 24.3— $BaHPO_4$ Parameters

	Position	x	y	z
Barium	(a)	0	0.204	0.200
Phosphorus	(a)	0	0.752	0.271
Oxygen I	(b)	0.223	0.865	0.179
Oxygen II	(a)	0	0.567	0.087
Oxygen III	(a)	0	0.702	0.607

6. INTERATOMIC DISTANCES AND DISCUSSION OF THE STRUCTURE

Figure 24.1 is a projection of the structure on the 100 plane. The circles, in descending order of size, represent barium, oxygen, phosphorus, and hydrogen. Atoms lying in the plane $x = \frac{1}{2}$ are open circles, while those lying in the plane, $x = 0$, are hatched. Oxygens of set I are the only atoms in the structure which do not lie in these planes. Their distances above or below are given on the diagram.

The coordination for one barium is shown by dashed lines, while the phosphorus-oxygen and oxygen-hydrogen bonds are shown by full lines.

It will be noted that hydrogen positions are shown on the diagram, although no parameters are given in the table. Obviously, hydrogen positions cannot be found directly from x rays. However, the hydrogen must be lying somewhere between O_2 and O_3 on the following considerations.

Except for the distance between O_2 and O_3 , the closest oxygen-oxygen distances between phosphate tetrahedra are between 2.85A and 3.16A, as would be expected. Between these two oxygens, the distance is only 2.57A, much too small unless the hydrogen lies in between. The O-H-O distance has previously been measured, in potassium dihydrogen phosphate and in sodium bicarbonate. The distances, respectively, are 2.54A and 2.55A, values in good agreement with ours.

Barium is surrounded by an irregular coordination sphere consisting of nine oxygens at the following distances:

1 O_2 at 2.61 A
2 O_1 at 2.73 A
2 O_1 at 2.76 A
2 O_1 at 2.91 A
2 O_3 at 2.96 A

The irregularity of the barium to oxygen distances can be expected because of the non-equivalence of the oxygen atoms, only half of which are hydrogen coordinated.

The atomic surroundings of each phosphate tetrahedron are as follows. Oxygens of the first set (fourfold) are each coordinated to three barium atoms at an average distance of 2.80A. The oxygens of set two are coordinated to one barium atom at a shorter distance, 2.61A and to one hydrogen; while the oxygens of set three are coordinated to two bariums at rather long distances (2.91) and to one hydrogen.

This, as far as we know, is the first phosphate of a divalent cation which has been structurally analyzed.

Fig. 24.1 — Barium Hydrogen Phosphate.

Bibliography

NOTE: These papers were originally intended for this report but have been omitted because they have already appeared in scientific journals.

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