Construction and operation of a vacuum retort pilot-plant for distillation of alloys

Robert Frederick Doelling
CONSTRUCTION AND OPERATION OF A VACUUM RETORT
PILOT-PLANT FOR DISTILLATION OF ALLOYS

BY
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A
THESIS
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Approved by
Dr. A. W. Schlechten, Chairman, Department of Metallurgical Engineering and Mineral Dressing
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The author wishes to express, also his appreciation to Mr. C. H. Shih for his suggestions and untiring assistance.
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I. INTRODUCTION

The widespread appearance of large scale vacuum systems operating commercially in the micron range of pressures has initiated a new field of industrial endeavor, vacuum engineering. The ever increasing number of applications of vacuo in commercial processes and laboratory research has stimulated the design and improvement of vacuum equipment, and at the present time equipment may be obtained to meet practically any need. In turn, the variety of available tools has directed the engineers attention to improving old processes and developing new ones through the utilization of vacuum techniques.

Reduced pressures may be desirable to the metallurgist for any number of reasons. Distillation processes conducted in vacuo may be carried out at lower temperatures or shorter time. Reduction reactions which yield gaseous products may be attained in lower temperature ranges or may go more nearly to completion in a vacuum. The practical absence of atmospheric gases in a high vacuum lessens fire hazards in the case of magnesium production or makes possible the production of purer metal in the case of titanium and zirconium.


Pressure requirements for the various applications, of course, vary over a rather wide range. In the vacuum desinicing of lead a pressure of 0.5 mm Hg is maintained. In the Pidgeon process


for production of magnesium the pressures are from 0.1 to 0.2 mm Hg, and in laboratory work pressures of 0.001 mm Hg are not uncommon. Maintaining a vacuum becomes increasingly difficult with lowering of pressure; however, pressures down to 0.01 mm Hg are commercially possible and practical.

In the metallurgy of argentiferous lead there have been four important processes for removal of silver which warrant mention:


supellation, Pattinson process, Parkes process, and Betts electrolytic process. The first two are obsolete. The Betts process has the advantage of bismuth removal which the Parkes process does not; however, the cost is high and silver is not removed as completely as by the Parkes process.

In the Parkes process 1 to 2 per cent of zinc is added to the molten bullion and a high zinc-silver material is formed, floats to the top, and may be removed. What the mechanism of the process is is not definitely known. Probably, two immiscible liquids are formed; a high zinc layer saturated with lead and a high lead layer saturated with zinc. The zinc layer has a much greater affinity for silver
than does the lead and there is a silver buildup in the high zinc layer. The high zinc material has a relatively low density and floats to the top. It may then be ladled off as a liquid, or since it has a relatively high melting point, it may be skimmed off as a mushy material if the temperature is low enough. These crusts, as they are called, contain mainly zinc, silver, and lead. Many impurities frequently occur in the crusts also. The major ones are copper and iron.

The zinc additions are generally made in two steps. The first skimmings containing from 2000 to 5000 oz of silver per ton are retained for silver recovery. The second which are lower in silver are used for the first addition of zinc to a new batch of bullion.

The present method of recovering silver from these crusts is a complicated, time-consuming task. The crusts are first distilled at atmospheric pressure to remove the zinc. The residues are then cupelled to crude silver. The crude silver is generally refined again by recupellation or melting with silver sulfate to oxidize impurities. This process has a high initial and operating cost and entails excessive metal losses through oxidation.

The possibility of producing a relatively high purity silver in a single step by distilling off the zinc and lead in a vacuum was suggested as early as 1912 by H. J. Humphries in discussing a paper by Turner but until recently no experimental work on this

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possibility had been published. In 1949, experiments were conducted by Mr. C. H. Shih on the distillation of artificial and commercial \(^{(8)}\) (9) crusts in a small vacuum furnace. Mr. Shih's findings were extremely encouraging and it was decided to carry the investigation


to the pilot plant stage. It is the purpose of this thesis to construct and put into operation the pilot plant for the vacuum distillation of Parkes' process crusts.
II. REVIEW OF LITERATURE

Although there have been rapid strides in the accumulation of know-how in the field of vacuum engineering, the availability of information is relatively meager. The most important commercial application of low pressure in metallurgy is the retort ferrosilicon process for production of magnesium from dolomite. This process involves the removal of magnesium from the smelting zone in the vapor state and subsequent condensation of the metal. Although the process is one of reduction, the problems encountered are similar to those involved in the tentative method of distillation. An excerpt from the paper shows the close resemblance of operational problems.

"The difficulties to be encountered will be evident from a consideration of the fundamental requirements of the reaction. A suitable apparatus must be capable of:

1. Heating calcined dolomite and ferrosilicon in briquetted form to a reacting temperature and maintaining a supply of heat at this temperature sufficient to overcome the endothermic reaction.

2. Receiving a solid charge of briquettes and discharging a residue of similar shape and form. The reaction zone must be in vacuo during evolution of magnesium vapor.

3. Removing magnesium vapor continuously and completely under nonoxidizing conditions.

4. Condensing the magnesium vapor in a form capable of safe
handling and ready conversion to ingots or other marketable form."

Another excerpt from the same paper shows the reason for the design of retorts in use. "The stipulation that the reactive system must be loaded, unloaded and evacuated, suggested a retort or autoclave, with the minimum number of openings, heated at the closed end, with the open end protruding from the hot zone, water cooled and fitted with a vacuum-tight closure. Such an apparatus may be loaded and unloaded as a batch operation, and may readily be evacuated."

For commercial success of the process it was necessary that the retorts be loaded and unloaded at or near operating temperature because of the time element involved in heating and cooling and also because of the excessive strain on the retorts involved in the continual temperature changes. The pyrophoric nature of the condensed metal made this a dangerous process.

There were two main causes of the large number of fires in early runs. It was found that a condensation temperature of about 450°C produced a dense coherent deposit which could be easily handled but in early experiments the metal condensed at varying temperatures along the length of the condenser. The deposit produced in the cold end (below 450°C) was in the form of loose crystals which were readily inflammable. Further aggravation of this was the occurrence in the dolomite of small amounts of alkali metals, which, being quite volatile, condensed in the cold section where the magnesium was loosely deposited. When air was admitted the alkali metals ignited and the fire was transmitted generally to the main deposit.

Figure 1 shows an arrangement which proved to be satisfactory.
Plate A causes the magnesium to deposit in a portion of the condenser where the temperature is high enough to produce a dense deposit. Plate B, being cooler, provides a separate place for the more volatile alkali metals to deposit. Baffle C is a radiation shield which prevents overheating of the front cover and burning of the rubber gasket. The springs shown in the drawing are necessary for tight seating of the condenser. If the condenser fits loosely in the retort, magnesium will condense between the retort and the condenser making removal of the condenser difficult.

It was found that the position and type of deposit was governed in order of importance by:

1. Position of retort in furnace and thickness of furnace wall.
2. Radiation shield position and construction.
4. Position of water cooler.

Since vacuum engineering is a new field and is very important in this work, a brief examination of the vacuum system of the Pidgeon process is of interest.

In any vacuum system two main points should be considered. Minimum pressure required and amount of gas to be handled. There are three main types of pumps which are used in vacuum work: (1) rotary oil-


sealed mechanical pumps, (2) multistage steam jet ejectors, (3) diffusion pumps. Figure 2 gives the speed of various types of pumps over a
wide range of pressure. Figure 3 shows the relative cost of pumping for the various pumps.

The evacuation of a typical retort in the ferrosilicon process can be divided roughly into three periods.

1. Removal of air from the retort.
2. Removal of volatile constituents from the charge.

The first two periods make up the evacuation of the retort. In this part of the cycle the pressures are relatively high (from atmospheric pressure to 0.2 mm. Hg). In the third period the theoretical pumping speed required is zero since the metallic vapors are being condensed and in addition act as getters of the residual atmospheric gases. Actually, considerable pumping speed is needed in the "holding period" due to leaks in the system.

Observation of Figures 2 and 3 shows apparently that the mechanical pumps should be used for period 1 and 2 and steam ejectors for period 3. Actually this system of pumps is little used in the present Pidgeon process plants.

Due to the very large size of steam-jet ejectors and the complicated valving system involved, other schemes have generally proven more attractive. The reasons for selection of the various arrangements are quite numerous and since they pertain directly to the Pidgeon process they will not be included here. Mechanical pumps are used for initial evacuation in all arrangements. Before diffusion
**Fig. 2 Pumping Speeds of Pumps**
(From Leybold Catalogue No. 27)
A. Mechanical pump
B. Jet pump
C. and D. Diffusion pumps

- Cubic Meters per Hour
- Pressure in mm. Hg
Fig. 3 - Pumping Costs Based on 24 Hour Operation

Power @ $0.008 per kw-hr
Water @ $0.02 per 1000 gal.
Steam @ $0.30 per 1000 lb.
Amortization @ 2.0 per cent
and jet pumps were readily available for commercial application, oversized mechanical pumps were used for the holding period. In one plant using a small number of very large retorts, steam-jet ejectors have proven successful. The third option, diffusion pumps in conjunction with suitable backing pumps, has in general been the most satisfactory giving greater speed of evacuation and lower ultimate pressure.

The important considerations in the selection of pumps for any installation are operating efficiency in the desired pressure range, power costs, maintenance, and depreciation. The power costs are large in comparison to maintenance and depreciation and, in general, the power costs and operating efficiency should be the deciding factors in any installation. In some processes involving considerable dust or water vapor an important point may be the pollution of pumping fluid, however, and the necessary frequency of changing pump fluid may be prohibitive for a certain type of pump.

A discussion of the evaporation and melting of metals in general in a recent publication by Kroll is of considerable interest. It was pointed out that the pressure indicated by a pressure gauge connected into the wall of a furnace may be very misleading. We know that the pressure over the charge is greater than that at the condenser because the flow of metal vapor is made possible by this pressure gradient. Due to the nature of the vapors over the evaporating surface, it is extremely difficult to measure the pressure. Factors

causing this increased pressure are the vapor pressure of the material and interference to vapor flow. These effects are greater at higher temperatures and lower pressures.

Consideration of a simple distillation in vacuum shows the amazing volumes of vapors to be handled. If we evaporate 10 pounds of zinc in an hour at 100 microns and 800°C we must handle 27,400 cubic feet per minute of zinc vapor, assuming it to be a perfect gas. It is apparent, then, that any restriction to vapor flow will cause considerable pressure increase.

At lower pressures the ratio of metal vapor to residual gases is greater and the difference in pressure reading to actual pressure over the evaporating surface is increased. These points are important therefore in predicting or interpreting results.

In the case of distillation, evaporation from the molten state, the effect of "hydrostatic head" is important. The effective pressure on a point below the surface is much greater than the surface pressure due to the column of liquid above it and the effective average pressure is greater. With liquids such as water this results in a temperature gradient and "boiling point raising". In the case of metals, where the heat conductivity is relatively high, this temperature gradient is small and boiling, when it occurs, takes place very near the surface of the metal. Dr. Kroll points out that the principle law for vacuum distillation of metals may be deduced from the above, namely that it is exclusively a surface phenomenon. Therefore, for rapid evaporation the greatest possible surface is desirable.

In the case of evaporation from the solid state (sublimation) we
have a large amount of surface available. However, certain disadvantages arise in sublimation. Non-volatile films (oxide, nitride, etc.) may form on the surface or the surface may be depleted of the volatile constituent because of its inability to diffuse. In general the amount of impurities can be used as a first guide in selecting distillation or sublimation.

The vacuum distillation of alloys was considered by Kroll who indicates the work of Leitgeberl in connection with distillation


of alloys at atmospheric pressure. Leitgeberl tried to establish a relationship between the equilibrium diagram and the boiling point composition curves. Several common cases of alloying were pointed out.

In the lead-zinc system no compounds are formed and the metals are only slightly soluble in the liquid state. The boiling point of the alloys increases very gradually until most of the zinc is gone, then the curve rises sharply to the boiling point of lead. The possibility of a separation of zinc and lead is indicated.

In the zinc-cadmium system no compounds are formed but the metals are completely soluble in each other in the molten state. The boiling point of the alloys rises steadily from that of cadmium to that of zinc. Close to pure zinc composition the slope is somewhat steeper. Mixed vapors are probably formed across the diagram and it is doubtful that the metals could be separated by distillation.

Leitgeberl did not mention the case of strong intermetallic com-
pound formation but Dr. Kroll cites numerous examples to show that
strong intermetallic compounds have their own boiling point. Appar-
etly vacuum has less effect on the dissociation of compounds than
has temperature and in his high temperature work, Leitgeb diassoc-
iated the compounds and did not notice their effect.

The effect of operating conditions on the form of the condensate
is discussed by Kroll. The triple point of a substance, the point on
the vapor pressure - temperature curve where liquid, solid, and gas
coexist in equilibrium, is extremely important in this respect. If
the partial pressure of the metal vapor is below the vapor pressure
at the triple point the metal will condense as a solid. In most cases,
for ease of handling, condensation to the solid state is desirable.
If the metal condenses as a liquid, it is necessary that condensation
take place downwards to prevent the molten metal from running back
into the charge.

The pressure in the furnace may affect the form of the condensate
in another way. At higher pressures there are more residual gases
which may react with the metals vapors to cause a loose, even, pow-
dery deposit.

As has been stated, experimental work has been conducted on a
laboratory scale on the vacuum distillation of Parkes' crusts. (15)


The results have been invaluable in this work in indicating directions
of investigation. A summary of the results are shown graphically in
Figures 4, 5, 6, and 7 giving purity of residue and silver loss as
dependent on time, temperature, pressure, and particle size.

The author points out that a practical limit may be set as regards time and temperature. This limit is set by the decrease in partial pressure of a constituent as the activity of that constituent decreases. Thus to completely remove even the highly volatile zinc would require excessive time and high temperature with a resulting high silver loss. Probably then, it would be necessary commercially to provide a subsequent refining operation, but the quality of the residue which could be produced should make this a simple process.

With regard to pressure, Figure 6 shows that the lower is the temperature, the greater is the effect of pressure. This phase warrants considerable investigation because the difficulty of maintaining a vacuum increases rapidly with decrease in pressure. It may very possibly be found that the decrease in temperature and/or time at 10 microns below that at 100 microns does not justify the added difficulty or equipment necessary to maintain the lower pressure.

Figure 7 shows that as particle size decreases to a certain point the purity of silver decreases. The odd result in the finest size is due to excessive volatilization of silver from the very large surface area. Mr. Shih points out, however, that at a temperature of 900°C this tendency will be lessened due to fusing of the charge. Whether or not crushing is desirable depends on the temperature of operation.

The possibility of a partial separation of lead and zinc which has been mentioned was affirmed by Mr. Shih's work. It was found that the condensate could be separated into two parts. The material
from the hot end of the condenser analysed about 60% lead and probably contained practically all of the silver lost from the crust. The cold end condensate assayed about 97 per cent zinc. The latter could be used for desilverization of new bullion while the former could be put back into the desilverization kettles. Silver loss, therefore, may be considered as relatively unimportant since the silver need only return through a small portion of the refinery flow sheet.

One of the most important points brought out by Mr. Shih was that a limit must be placed on the quality of results which could be expected and that this limit depended on the composition of the crust being distilled. The presence of materials of vapor pressure lower than that of silver limits the purity of silver that it is possible to obtain. As is shown in Figures 4 and 5, an increase in temperature or time beyond certain values reduces the purity of the resulting residue because after a certain point the ratio of silver to non-volatile materials begins to fall off. Oxides of lead and zinc have very low vapor pressures and therefore oxidation of the crusts introduces unwanted constituents.

It was indicated, then, that conditions necessary for vacuum distillation of Parkes' crusts may vary considerably from one crust to another. Therefore, examination of the production of Parkes' process crusts should be of interest.

Among the metals encountered in lead refining are the following which should be given consideration: Ag, Au, Cu, Pt, Pd, Te, As, Sb, Sn, and Fe.
Those metals which enter readily into the crust are Ag, Au, Cu, Pt, Pd, and Te. It is believed that addition of zinc to impure lead causes in order the following things:

1. Formation of an Au, Cu, Zn rich layer.
2. Saturation of lead to about 0.7 per cent Zn.
3. Formation of a Zn-Ag rich layer.

These steps are taken advantage of in some refineries in removing an initial "gold crust". Usually the gold content of the bullion does not warrant this practice, however.

As can be seen from the above, the presence of copper in the bullion will increase the consumption of zinc in desilverization. Copper in the crust is undesirable because of its low vapor pressure. It is possible to remove copper suitably by dressing and to reduce it to the extent of 0.005 per cent by addition of sulfur. The sulfur and copper form sulfides which may be skimmed off.

It has been shown that arsenic will not preferentially enter the crust. It does, however, interfere with the entrance of other metals and in the separation of the crust from the underlying lead. The presence of 0.1 per cent arsenic causes production of a mushy crust from which mechanical removal of entrapped lead is difficult. Arsenic also increases the amount of zinc necessary for desilverizing and should therefore be removed as completely as possible. This can be accomplished suitably by careful softening.
Antimony does not complicate the separation of the crust and lead but it does enter into the crust to some degree itself. Antimony is volatile and will probably condense with zinc in vacuum distillation. The antimony would then be reintroduced into the bullion when the zinc is added for desilverization. The antimony might reach an equilibrium concentration between the zinc and bullion which would not be harmful or it might continue to build up in the zinc, in which case it would have to be removed by some means. In any case, antimony can be removed suitably from the bullion by careful softening.

Tin is an undesirable constituent which must be removed by softening. It interferes with desilverization and its low vapor pressure makes it undesirable in a crust to be treated by vacuum distillation.

Iron increases zinc consumption and its presence in the crust is undesirable due to its low vapor pressure. Iron rarely occurs to any extent in lead ores. It is introduced either with the zinc or through corrosion of equipment. Selection of zinc with low iron content will help to alleviate this difficulty and corrosion of equipment can be minimized by avoiding excessive temperatures.

The four metals which interfere principally with desilverization are As, Sb, Sn, and Cu. Copper can be removed suitably by dressing and the other three by softening. Table 1 shows results of softening at the Port Pirie lead refinery. Table 2 shows

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### TABLE 1.

**Port Pirie Continuous Softening**

<table>
<thead>
<tr>
<th>Material</th>
<th>% Sb</th>
<th>% As</th>
<th>% Cu</th>
<th>Ag, oz.</th>
<th>Au, oz.</th>
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<td>Dressed bullion to furnace</td>
<td>0.78</td>
<td>0.29</td>
<td>0.004</td>
<td>53.1</td>
<td>0.039</td>
</tr>
<tr>
<td>Softened bullion from furnace</td>
<td>0.03</td>
<td>0.0004</td>
<td>0.004</td>
<td>54.0</td>
<td>0.040</td>
</tr>
<tr>
<td>Molten slag from furnace</td>
<td>8.10</td>
<td>2.70</td>
<td>0.005</td>
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</tr>
</tbody>
</table>

### TABLE 2.

**Dressing at Bunker Hill Lead Refinery**

<table>
<thead>
<tr>
<th></th>
<th>Au, oz.</th>
<th>Ag, oz.</th>
<th>Cu, %</th>
<th>Sb, %</th>
<th>As, %</th>
<th>Bi, %</th>
<th>Fe, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before dressing</td>
<td>0.48</td>
<td>97.0</td>
<td>0.78</td>
<td>1.19</td>
<td>0.16</td>
<td>0.0012</td>
<td>0.045</td>
</tr>
<tr>
<td>After dressing</td>
<td>0.48</td>
<td>96.7</td>
<td>0.04</td>
<td>1.17</td>
<td>0.10</td>
<td>0.0012</td>
<td>0.008</td>
</tr>
</tbody>
</table>
the effect of dressing.

In general, the removal of silver from lead by the Farikes process is a reasonably standard operation throughout the industry. The crusts do vary, however, and some are much more suitable for vacuum distillation than others. The ideal crust for this process would be pure zinc-silver. This is impractical, of course, so let us consider a method for production of a good crust for vacuum treatment.

One of the best commercial crusts available is produced by the Bunker Hill Lead Smelter at Kellogg, Idaho. The relevant steps in this process are given in the following material.

Bullion from the blast furnace is poured into a dressing kettle and when the kettle is almost full the heavy dress is removed. After the first dressing, the bullion is pumped to another kettle, allowed to cool, and dressed again. By using this double dressing step it is possible to reduce the copper to 0.04 per cent.

After dressing, the lead is heated to about 900°F and pumped to the softening furnaces. The softening is carried out in the usual manner and Sb is reduced to 0.12 per cent.

The next step is the removal of precious metals from the bullion by zinc additions. Here the practice at Bunker Hill differs from other lead refineries in the United States. The Bunker Hill Smelter has reverted to the old custom of making two types of skins, a "gold crust" and a "silver crust". The beauty of this procedure is that the gold crusts, which amount to only 0.8 per cent of the original
bullion, contain practically all of the copper of the bullion and thus the silver crusts are relatively free of this metal. Also, parting of the greater portion of the silver is eliminated since the silver produced from the silver crusts contains only a few cents worth of gold per 1000 oz. Since the big advantage of taking a gold crust is the copper removal, an alternative is removal by sulfur additions. Of course, it is unnecessary to have low copper in the crust but it is desirable because of the higher purity silver possible.

Following the gold crust removal comes desilverization in the usual manner. The subsequent treatment of the silver crust is different, however. The skims are now charged into kettles 18 inches in diameter and 60 inches deep. The kettles are made in two sections, a top half and a bottom half, joined together by bolts through a flange. In a groove in the flange is a one-half inch water pipe to form a seal. In the lower portion of the kettle is a two-inch water pipe which can be brought up to act as a siphon.

The lower portion of the kettle is charged with desilverized lead on to which is added the silver crust. Heat is applied to the top section and when the charge is molten the desired separation has taken place. The major portion of the lead, which is mechanically entrapped in the crust, separates and runs to the bottom and is siphoned off. By this process the lead content of the ensuing crust can be reduced to about 8 per cent.

One disadvantage of this process is that the high temperature required results in corrosion of the liquidation kettle and a relatively high iron content of the crust (about 0.8 per cent).
The alternative method for removal of entrapped lead is by use of the Howard press. This apparatus consists roughly of a perforated basket into which the crusts are placed. A plunger then compresses the mass at a pressure of about 90 psi, causing the molten lead to run back into the desilverization kettle over which the pressing is done. The press, which is on a movable frame, can service dressing kettles as well as desilverization kettles and considerable equipment saving results. However, the Howard Press will not eliminate lead nearly as well as will liquration. Therefore, from a standpoint of vacuum distillation the liquration process is more desirable in spite of the high iron content and the additional equipment required.

Although any type of crust is treatable by vacuum distillation, it is desirable to obtain a crust containing a small amount of impurities having low vapor pressures. We know from previous work that vacuum distillation of Parkes' crusts is possible. With information obtained from previous investigators and operating commercial installations as a guide it is desirable to determine whether this process could compete with the existing method of silver recovery from the crusts.

III. THEORETICAL CONSIDERATIONS

Shih has discussed the mechanism of vacuum distillation of Parkes' crusts in terms of vapor pressures of the constituents. (21)


Probably, a better criterion for such a discussion would be rates of evaporation of the metals under consideration. Actually, a knowledge of both vapor pressure and rate of evaporation is of great importance in guiding the experimenter in logical directions of endeavor and in the interpretation of observed results. (22)

Figure 8 gives the variation of rate of evaporation and vapor pressure with temperature for the five metals commonly encountered in Parkes' crusts. It can be seen that the effect of temperature on rate of evaporation and vapor pressure is practically the same. From a consideration of the mechanics of evaporation we would expect this to be true.

The vapor pressure of a material is the pressure exerted by the atoms or molecules of the material which become detached from the surface and tend to escape to the space surrounding the body. The rate at which the material will evaporate, that is, the rate at which atoms or molecules will permanently leave the surface depends on interference of gas molecules surrounding the body. We would expect, then, that two materials having the same vapor pressure would permanently lose molecules at the same rate if the pressure exerted on
Fig. 8 Variation of Vapor Pressure and Rate of Evaporation for Metals in Parkes' Crusts
both bodies is the same. Actually, there are slight differences in rates of evaporation of materials at the same vapor pressure, probably due to such factors as molecular size and molecular velocity.

At higher pressures (more gas molecules surrounding the body) practically all of the molecules leaving the surface of the body collide with gas molecules and are forced back on to the surface. At ordinary temperatures and pressures the rates of evaporation of most metals are very small and in most cases immeasurable. We may cause a metal to evaporate at a measurable rate by raising its temperature (increasing the internal motion) or by lowering the pressure (decreasing the resistance to resistance to vapor molecules leaving the surface.

Little information is available about the effect of external pressure on rate of evaporation. It is known that below a certain value, given as approximately 1 mm Hg, the effect of pressure is practically eliminated. Probably, below this value of pressure the interference to evaporation is due practically entirely to intercollision of molecules of the material being evaporated and further removal of foreign molecules has little or no effect.

The values which are given for rates of evaporation are only applicable when the effect of pressure is absent. It should be realized that the pressure is made up of residual gas pressure and vapor pressure of the evaporating material. Another point to consider is the partial pressure of the evaporating material. If the space surrounding the body becomes saturated with material being evaporated, that is, if the partial pressure of the material becomes equal to the vapor pressure, evaporation will cease regardless of the total pressure.
Therefore, it is necessary to have ample space for metal vapors to flow away from the evaporating mass.

From Figure 8 we see that the vapor pressures of Pb and Ag at 780°C are $4 \times 10^{-6}$ and $1.5 \times 10^{-7}$ respectively. Since we can use the relative vapor pressures of two materials as a substantially correct measure of the relative rates of evaporation, this means that the Pb should evaporate 2700 times as fast as the silver. If, however, we have an alloy of the two metals it is necessary to again evaluate vapor pressures.

The vapor pressure of a constituent in an alloy is given as the product of the vapor pressure of the pure constituent at that temperature and its activity in the alloy. If we did calculate the vapor pressure in the alloy we would have only an instantaneous value of relative rates of evaporation for as the alloy evaporated the activities of its constituents would change.

Further complicating a mathematical treatment of the problem would be the changing area of evaporation, the rates of diffusion in the alloy, and the lack of knowledge of actual pressure on the evaporating mass. It can be seen, then, that a quantitative treatment of the evaporation of an alloy would be extremely difficult, and at best only an approximation. The value of information about vapor pressure, rate of evaporation, and activity lies in the qualitative treatment of the problem.

From the rates of evaporation shown in Figure 8 and from the activity of zinc in lead-zinc alloys given in Figure 9, we would
expect that most of the zinc is removed before the evaporation of lead begins. This is borne out by the data given in Figure 10 which gives the composition of the vapor, as a function of liquid composition, for lead-zinc alloys at their normal boiling point. This should only be true for evaporation of the molten alloys where the zinc can diffuse to the surface. Even in the sublimation of Parkes’ crusts this should be substantially valid reasoning, however, because the crusts generally contain about 60 per cent zinc and a reasonable quantity of zinc must be evaporated before the depletion of zinc at the surface is such as to halt its evaporation.

Since there are no indications that the other metals in Parkes’ crusts will retard the evaporation of zinc it seems feasible to assume that the evaporation of the crusts will proceed as follows:

1. Zinc vapor given off until most of the zinc (80 to 90 per cent) is removed.

2. Removal of a lead-zinc vapor increasing in lead content from practically pure zinc to pure lead when the zinc is completely removed.

3. Removal of the remaining lead. The vapor will contain increasing amounts of materials of low vapor pressure such as silver, copper, and iron.

As has been stated, the value of vapor pressure and rate of evaporation information is mainly qualitative. We have seen that vacuum
distillation of Parkes' crusts is possible and have gained some insight into what may be happening.
Fig. 9 Activity of Zn in Zn-Pb Alloys

Fig. 10 Composition of Vapor from Boiling Zn-Pb Alloys

Fig. 11 Activities in Pb-Ag Solutions at 1000°C
IV. APPARATUS AND EQUIPMENT

The following list gives the specifications of the equipment used in the experimental work.

1. Motor-generator

   **Motor**: General Electric Corp.
   - Power: 75 Hp
   - 18.2 amps
   - 2200 volts
   - Full load speed: 1140 rpm
   - Temp. rise: 50° C.
   - Three phase, 60 cycle

   **Generator**: General Electric Corp.
   - Capacity: 45 Kw
   - 400 amps
   - 125 volts
   - Speed: rpm
   - Temp. rise: 50° C.
   - Single phase, 60 cycle

   - Power: 15 Kw
   - 268 amps
   - 16/56/125 volts
   - Maximum Temp.: 2600° F.

3. Capacitrol: Wheelco Instrument Company
   - Model: 224
   - Range: 0 to 2000° F.
   - Power consumption: 50 watts maximum
   - Contact rating: 45 amps at 115 volts
   - 35 amps at 230 volts

4. Selector Switch: Wheelco Instrument Company

5. Magnetic Breaker: General Electric Corporation
   - Control Voltage: 110 volts
   - Maximum Kw: 15 at 110 volts
   - 60 at 440 volts
   - 75 at 550 volts
6. Retort: Michiana Products Corp.

Spun cost of 36 ft, 18 Cr. Stainless with 0.15% C max.
8 in. I.D. 10" O.D.
Length - 6 ft 1/8"

7. Mechanical Vacuum Pump: Kinney Mfg. Company

Type VSD 776 - Single Stage
Limiting pressure - 5 microns
Pumping Speed - 27 cfm at 1 atm.
16.8 cfm at 100 microns
7.0 cfm at 10 microns


Power - 1 1/2 HP
220/440 volts.


H - 6, Type 104
Inlet size - 6 in. flange
Outlet size - 2 in. flange
Max. forepressure - 200 microns at 0.1 micron
Charge - 400 cc. Narcom 10, Type 4101


McLeod Type - Fleisch Modification
Type 276 HS
Range - 0 to 500 microns

For purposes of elucidation it is probably desirable to elaborate somewhat on the important features of the equipment.

Power was supplied to the motor-generator set at 2200 volts.
The output of the generator was led to a transformer from which could be tapped 38, 40, 72, 80 and 122 maximum nominal output voltages. The actual voltage on the furnace was regulated by adjusting the current to the generator field by means of a variable resistance.
Operating temperature was maintained by a Wheelco Capacitrol in conjunction with four chromal-alumel thermocouples painted at various positions into the retort. Since the contact rating of the Capacitrol was not large enough, the power supply to the furnace was controlled directly by a magnetic breaker which was in turn actuated by the Capacitrol.

The furnace was of the resistance type with eight silicon carbide Glo-bars in a circle of 18 inch diameter around the retort. The Glo-bars were connected four in parallel in series with four in parallel.

The retort was constructed of a special high Ni-Cr stainless steel so that it would withstand atmospheric pressure at well above operating temperatures and also be resistant to oxidation and corrosion. Several accessories were designed for the retort for purposes of ease of charging and discharging. The crudes were charged in a boat constructed from 1/16 in. sheet iron. A 20-gauge, black iron sheet was used as a liner for the retort on which the metallic vapors condensed. Details of the retort are given in Figure 12.

An oil diffusion pump was connected directly under the retort and was followed by a mechanical rougher pump. The diffusion pump consists of the elements essential to all diffusion pumps, a boiler to vaporize the oil and a chimney for conducting the vapor to the jet. Oil is vaporized and diverted downward by the chimney. The oil vapor entraps gas molecules which diffuse into the pump and carries them to the outlet of the pump. A water jacket cools the vapors causing the oil to condense. The non-condensable gas molecules are released at
the outlet and are pulled away by the rougher pump.

In diffusion pumping the outlet or forepressure is very important. If the forepressure exceeds a certain critical value, characteristic for a given pump, the pump cannot function. A rougher pump, therefore, must be used to reduce the forepressure to a suitable value.

The diffusion pump used in this work had a three-stage jet, thus providing a lower ultimate pressure. The mechanical rougher pump was of sufficient size to lower the forepressure to 150 microns in about one minute.

A McLeod type gauge was used to measure the pressure in the system. The McLeod gauge is simple in principle but quite accurate over a wide range of pressure. By means of a tilting device a reservoir of mercury is caused to seal off a known volume of gas and compress this gas with a constant head of mercury. The final compressed volume is a measure of the pressure in the system.

Photograph 1 shows the arrangement of the apparatus. Figure 13 shows the placement of the retort in the furnace.
Photograph 1. Experimental Apparatus
Fig. 13 - Cross Section of Retort, Furnace, and Diffusion Pump

- Refractories
- Water Jacket
- Glo-bars
- Boat
- Baffle
- 1/8 Rubber Gaskets
- Metal Jacket
- Diffusion Pump
V. Procedure

A. Operation.

In the experimental work two general topics were of concern. One was quality of results obtained (chemical analysis of products) and the other was ease of operation.

The first field can be subdivided rigorously into effect of the following variables:

1. Time
2. Temperature
3. Pressure
4. Amount of charge.

The second general topic was not as specific and results here were obtained on a hit and miss basis. In general then, experiments were performed to best show the effect of the above mentioned variables and a general operating procedure is given in the following.

The retort accessories (liner, boat, and baffles) were cleaned and weighed in preparation for a run. The boat was coated with aluminum by painting it with a suspension of aluminum in water. A weighed portion of crust was placed in the boat and the boat and accessories put in position in the retort.

The retort was then sealed and the cooling water to pumps and retort was turned on. The vacuum pumps were then started. Due to the speed of the pumps it was unnecessary to allow evacuation time and the furnace could be started immediately.

To preserve the Glo-bars, heating was conducted at a slow rate. The heating cycle lasted from three to five hours depending on the
operating temperature.

Operating temperature was maintained automatically by the Capacitrol which had previously been set at the desired temperature, but to eliminate excessive wear of the magnetic breaker the current was regulated as nearly as possible to a value where furnace input equaled output.

The retort was then held at operating temperature for the desired length of time. During this period the operator checked pressure, water flow, condenser temperature, etc., to assure smooth operation.

At the end of the heating cycle the furnace was turned off and the retort allowed to cool to about 200°C (12 to 16 hours) under operating pressure. The diffusion pump was then shut off and when it had cooled sufficiently to avoid oxidation of the pump oil the mechanical pump was stopped.

The retort was then opened and the products removed and weighed. Sampling and analysis of the products will be discussed in the following sections.

B. Sampling of Material.

In any project where a material balance is important, sampling should be given extreme consideration. The materials encountered in this work predicated special attention in this field.

All materials encountered were heterogeneous. Screen analysis of the crusts showed a wide distribution of particle size which would necessitate crushing for good sampling, and crushing was difficult due to the toughness of the crusts.

The best method of sampling materials of this type is to melt
them and either take gum-drop samples of the molten material or drill samples after solidification. This method was eliminated primarily because of oxidation and volatilization of the zinc and secondly because of the amount of material to be handled.

It was finally decided that the best and easiest method of sampling was through the use of the Jones ruffle sampler. A sample of about 10 pounds was obtained from the crusts as received. This was then crushed as fine as possible by numerous passes through a jaw crusher. The crushed mass was then cut to about 100 grams with the Jones's sampler. Samples for charging were obtained by passing the crust as received through the Jones sampler. Due to the size of the charge it was felt that representative samples could be obtained without crushing.

The products of the furnace consisted of a condensate and a residue. The condensate could be subdivided roughly into two sections. A sheet, high in zinc, which stripped easily from the liner and a high lead material from the hot end of the liner. The sheet could be sampled by cutting several thin sheets lengthwise from it. The high lead material, which had condensed in the liquid state, consisted of small droplets and large masses which had run together and solidified. This material alloyed with the liner and was usually difficult to remove. It was broken up as fine as possible and sampled with the Jones's sampler.

The condition of the residue depended on the operating temperature. At lower temperatures (up to 800°C) the residue was granular and broke up easily. At temperatures above 800°C fusing began to occur. Sometimes superficial sintering resulting in weak fusing was
found and sometimes it was found that melting had occurred and the residue was in a solid piece. Whatever its condition, the residue was cut up as fine as possible and sampled on the Jone's sampler.

It should be recognized that even with careful sampling of a very heterogeneous material, large errors can occur and the observed results from chemical analyses must be treated with discretion.

C. Chemical Analysis.

The final samples for chemical analysis were large, 100 to 200 gm. These samples were dissolved and the solution diluted to a known volume. Portions of these solutions were taken for individual analyses. The following analytical methods were used.

Silver:

Titration with standard sodium chloride solution. (Gay-Lussac method).

Lead:

Remove lead from solution as sulfate.
Dissolve sulfate with acid ammonium acetate.
Titrate with standard ammonium molybdate.

Zinc:

Remove lead, silver, copper, and iron.
Titrate with standard potassium ferrocyanide.

Iron:

Titration with standard potassium permanganate.

Copper:

Short iodide method.
VI. EXPERIMENTAL RESULTS

The crusts used in this work were obtained from the Bunker Hill Smelter in Kellogg, Idaho and the St. Joseph Smelter in Herculaneum, Missouri. The crusts were carefully sampled and analyzed. The results given in Table 3 are the mean of numerous analyses made on several samples.

<table>
<thead>
<tr>
<th>Table 3. Composition of Crusts</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crust</td>
</tr>
<tr>
<td>Herculaneum</td>
</tr>
<tr>
<td>Bunker Hill</td>
</tr>
</tbody>
</table>

The results from all the experiments are given in tabular form in the following pages. The compositions given are the results of chemical analyses. The per cent recovery figures are based on the weight of metal charged. In some cases the per cent recovery figures show recoveries of over 100 per cent and in some cases they are much lower than would be expected. These anomalies are probably due to incomplete removal of a product from the retort and to errors in sampling.
### TABLE 4 - RUN 1

**600°C - 3 Hours - 20 Microns - Herculaneum**

<table>
<thead>
<tr>
<th></th>
<th>Wt. (gm)</th>
<th>% Pb</th>
<th>Wt. Pb</th>
<th>% Rec</th>
<th>% Zn</th>
<th>Wt. Zn</th>
<th>% Rec</th>
<th>% Ag</th>
<th>Wt. Ag</th>
<th>% Cu</th>
<th>Wt. Cu</th>
<th>% Rec</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge</td>
<td>4280</td>
<td>33.79</td>
<td>1446</td>
<td>100.0</td>
<td>54.45</td>
<td>2331</td>
<td>100.0</td>
<td>9.45</td>
<td>404.5</td>
<td>100.0</td>
<td>2.00</td>
<td>85.6</td>
</tr>
<tr>
<td>Condensate</td>
<td>1053</td>
<td>0.10</td>
<td>1</td>
<td>0.1</td>
<td>99.9</td>
<td>1052</td>
<td>45.1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Residue</td>
<td>3135</td>
<td>43.22</td>
<td>1355</td>
<td>93.7</td>
<td>37.23</td>
<td>1167</td>
<td>50.1</td>
<td>12.95</td>
<td>406.0</td>
<td>100.4</td>
<td>2.59</td>
<td>81.2</td>
</tr>
<tr>
<td>Loss</td>
<td>92</td>
<td>6.2</td>
<td>90</td>
<td>112</td>
<td>4.7</td>
<td>-</td>
<td>1.5</td>
<td>-</td>
<td>0.45</td>
<td>4.4</td>
<td>-</td>
<td>5.1</td>
</tr>
</tbody>
</table>

### TABLE 5 - RUN 2

**800°C - 3 Hours - 28 Microns - Herculaneum**

<table>
<thead>
<tr>
<th></th>
<th>Wt. (gm)</th>
<th>% Pb</th>
<th>Wt. Pb</th>
<th>% Rec</th>
<th>% Zn</th>
<th>Wt. Zn</th>
<th>% Rec</th>
<th>% Ag</th>
<th>Wt. Ag</th>
<th>% Cu</th>
<th>Wt. Cu</th>
<th>% Rec</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge</td>
<td>3917</td>
<td>33.79</td>
<td>1324</td>
<td>100.0</td>
<td>54.45</td>
<td>2133</td>
<td>100.0</td>
<td>9.45</td>
<td>370.2</td>
<td>100.0</td>
<td>2.00</td>
<td>78.3</td>
</tr>
<tr>
<td>Cold End Sht</td>
<td>1491</td>
<td>3.6</td>
<td>54</td>
<td>4.1</td>
<td>96.5</td>
<td>1439</td>
<td>67.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Hot End Sheet</td>
<td>606</td>
<td>17.07</td>
<td>103</td>
<td>7.8</td>
<td>82.6</td>
<td>506</td>
<td>23.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Granular</td>
<td>293</td>
<td>90.95</td>
<td>271</td>
<td>20.5</td>
<td>11.8</td>
<td>35</td>
<td>1.6</td>
<td>0.8</td>
<td>2.4</td>
<td>0.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Residue</td>
<td>1315</td>
<td>97.03</td>
<td>750</td>
<td>56.6</td>
<td>5.5</td>
<td>72</td>
<td>3.4</td>
<td>25.0</td>
<td>328.7</td>
<td>88.3</td>
<td>6.2</td>
<td>81.5</td>
</tr>
<tr>
<td>Loss</td>
<td>205</td>
<td>14.6</td>
<td>11.0</td>
<td>81</td>
<td>3.8</td>
<td>39.1</td>
<td>10.6</td>
<td>-</td>
<td>3.2</td>
<td>-</td>
<td>4.4</td>
<td>-</td>
</tr>
</tbody>
</table>
### TABLE 6. - RUN 3

900° C - 3 Hours - 21 Microns - Herculaneum

<table>
<thead>
<tr>
<th></th>
<th>Wt. (gm)</th>
<th>% Pb</th>
<th>Wt. Pb</th>
<th>% Rec Pb</th>
<th>% Zn</th>
<th>Wt. Zn</th>
<th>% Rec Zn</th>
<th>% Ag</th>
<th>Wt. Ag</th>
<th>% Rec Ag</th>
<th>% Cu</th>
<th>Wt. Cu</th>
<th>% Rec Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>Charge</td>
<td>3555</td>
<td>33.79</td>
<td>1201</td>
<td>100.0</td>
<td>54.45</td>
<td>1936</td>
<td>100.0</td>
<td>9.45</td>
<td>335.9</td>
<td>100.0</td>
<td>2.00</td>
<td>71.2</td>
<td>100.0</td>
</tr>
<tr>
<td>Sheet</td>
<td>2162</td>
<td>18.24</td>
<td>394</td>
<td>32.8</td>
<td>82.1</td>
<td>1775</td>
<td>91.7</td>
<td>0.64</td>
<td>13.8</td>
<td>4.1</td>
<td>0.12</td>
<td>2.6</td>
<td>3.3</td>
</tr>
<tr>
<td>Granular</td>
<td>831</td>
<td>96.10</td>
<td>799</td>
<td>66.4</td>
<td>3.0</td>
<td>25</td>
<td>1.3</td>
<td>1.78</td>
<td>14.8</td>
<td>4.4</td>
<td>0.43</td>
<td>3.6</td>
<td>4.5</td>
</tr>
<tr>
<td>Residue</td>
<td>420</td>
<td>4.19</td>
<td>18</td>
<td>1.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>69.75</td>
<td>293.0</td>
<td>87.2</td>
<td>16.94</td>
<td>71.1</td>
<td>99.9</td>
</tr>
<tr>
<td>Loss</td>
<td>141</td>
<td>-1.0</td>
<td>-10</td>
<td>-1.0</td>
<td>-</td>
<td>136</td>
<td>5.9</td>
<td>14.3</td>
<td>4.3</td>
<td>-</td>
<td>6.1</td>
<td>-7.7</td>
<td></td>
</tr>
</tbody>
</table>

### TABLE 7. - RUN 4

900° C - 3 Hours - 21 Microns - Herculaneum

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<th>% Pb</th>
<th>Wt. Pb</th>
<th>% Rec Pb</th>
<th>% Zn</th>
<th>Wt. Zn</th>
<th>% Rec Zn</th>
<th>% Ag</th>
<th>Wt. Ag</th>
<th>% Rec Ag</th>
<th>% Cu</th>
<th>Wt. Cu</th>
<th>% Rec Cu</th>
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### TABLE 8. - Run 5

#### 800°C - 5 Hours - 27 Microns - Herculaneum

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<th>% Rec. Pb</th>
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<th>% Rec. Zn</th>
<th>% Rec. Ag</th>
<th>Wt. Ag</th>
<th>% Rec. Ag</th>
<th>% Rec. Cu</th>
<th>Wt. Cu</th>
<th>% Rec. Cu</th>
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### TABLE 9. - Run 6

#### 1000°C - 3 Hours - 21 Microns - Herculaneum

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<th>% Pb</th>
<th>Wt. Pb</th>
<th>% Rec. Pb</th>
<th>% Rec. Zn</th>
<th>% Rec. Zn</th>
<th>% Rec. Ag</th>
<th>Wt. Ag</th>
<th>% Rec. Ag</th>
<th>% Rec. Cu</th>
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<th>% Rec. Cu</th>
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### TABLE 10. - RUN 8

900°C - 3 Hours - 17 Microns - Herculaneum

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<th>Wt. Pb</th>
<th>% Rec</th>
<th>% Pb</th>
<th>% Zn.</th>
<th>Wt. Zn</th>
<th>% Rec</th>
<th>% Zn.</th>
<th>% Ag.</th>
<th>Wt. Ag</th>
<th>Ag</th>
<th>% Cu</th>
<th>Wt. Cu</th>
<th>Cu</th>
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<td>100.0</td>
<td>9.45</td>
<td>1134</td>
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<td>2077</td>
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### TABLE 11. - RUN 9

900°C - 3 Hours - 26 Microns - Herculaneum

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<th>% Rec</th>
<th>% Pb</th>
<th>% Zn.</th>
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<th>% Rec</th>
<th>% Zn.</th>
<th>% Ag.</th>
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<th>Ag</th>
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<th>Cu</th>
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### TABLE 12. - RUN 10

900°C - 7 Hours - 38 Microns - Herculaneum

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<th>Wt. Pb</th>
<th>% Rec.</th>
<th>Pb</th>
<th>% Zn</th>
<th>Wt. Zn</th>
<th>% Rec.</th>
<th>Zn</th>
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<th>Wt. Ag</th>
<th>% Rec.</th>
<th>Ag</th>
<th>% Cu</th>
<th>Wt. Cu</th>
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### TABLE 13. - RUN 19

900°C - 5 Hours - 40 Microns - Herculaneum

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<th>% Rec.</th>
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<th>% Zn</th>
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<th>% Rec.</th>
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<th>% Ag</th>
<th>Wt. Ag</th>
<th>% Rec.</th>
<th>Ag</th>
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<th>Wt. Cu</th>
<th>% Rec.</th>
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**TABLE 14. - RESULTS FROM BUNKER HILL CRUST**

- Run 11. 800°C - 3 Hours - 50 Microns - 5744 cm. Condensate
- Run 12. 800°C - 3 Hours - 10 Microns - 5696 cm. Condensate
- Run 13. 800°C - 3 Hours - 140 Microns - 5637 cm. Condensate
- Run 14. 900°C - 3 Hours - 135 Microns - 5834 cm. Condensate
- Run 15. 900°C - 3 Hours - 28 Microns - 5138 cm. Condensate
- Run 16. 950°C - 3 Hours - 32 Microns - 6227 cm. Condensate
- Run 17. 950°C - 5 Hours - 32 Microns - 6387 cm. Condensate
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<th>% Pb</th>
<th>Wt. Pb</th>
<th>% Zn</th>
<th>Wt. Zn</th>
<th>% Ag</th>
<th>Wt. Ag</th>
<th>% Fe</th>
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<th>% Rec</th>
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<td>9</td>
<td>0.2</td>
<td>79.58</td>
<td>2375</td>
<td>99.9</td>
</tr>
<tr>
<td>Run 21, 900°C - 3 Hours at Temp. - 120 Microns - 5770 g, Condensate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
**Fig. 14**
COMPOSITION OF RESIDUE VS. TIME.
HERCULANEUM CRUST
900°C, 12000 G.M., 17-40 MICRONS

**Fig. 15**
COMPOSITION OF RESIDUE VS. TIME.
BUNKER HILL CRUST
950°C, 8854 G.M., 17-32 MICRONS
**FIG. 16**
Composition of Residue vs. Pressure.
Bunker Hill Crust
8854 Gm., 3 Hrs.

- **900°C**
- **800°C**

**FIG. 17**
Composition of Residue vs. Pressure
Bunker Hill Crust
8854 Gm., 900°C

- Nominal 3 Hr.
- 3 Hr. at Temp.
- **Ag**
- **Pb**
- **Zn**
VII. DISCUSSION

A. Variation of Time.

The time given for the various runs is the length of time which the charge was held at operating temperature except in two cases. With the exceptions of runs 20 and 21 the charge was actually in the sealed retort at operating pressure during the heating and cooling periods in addition to the time at temperature. In runs 20 and 21 the retort was charged at 800°C, sealed and pumped down, brought to 900°C and held for three hours. The retort was allowed to cool to about 850°C and then opened. The products were removed immediately, overall time being about 4 hours.

As can be seen from Figure 17, the results are little different from those obtained in the usual mode of operation. This is to be expected if we consider how rapidly the rates of evaporation decrease with decreasing temperature. Below 800°C the amount of metal evaporated is very small.

Figures 14 and 15 which show the variation of residue composition with time are inconsistent with expected results. Figure 21,

![Graph showing variation of residue composition with time](image)

**Fig. 21** Expected Curves for Time vs. Composition
which concurs with Shih's results, shows the expected curves. The
time required for a given distillation will obviously depend on
the degree of purity we wish to obtain. We see that the removal
of impurities becomes quite slow in the later stages, therefore,
the percentage of impurities which can be tolerated in the final
refining operation should be determined and the distillation stopped
at this point.

B. Variation of Temperature.

The effect of temperature of distillation on residue composition
is shown by Figures 19 and 20. The main objection which has
been raised against using a higher temperature, that is, 1,000°C in-
stead of 800°C, is the increased silver loss. If we desire to evap-
orate an appreciable amount of metal in a reasonable time we must
go to the higher temperature. Since the silver which is evaporated
can be returned with the other condensed metals to the desilverization
kettles, the silver loss seems relatively unimportant. Capacity is
one of the most important commercial considerations, therefore, it
seems desirable to select as high a temperature as possible, with
respect to equipment life and ease of operation, and determine ex-
perimentally the amount of charge which can be distilled at this tem-
perature.

One question which might arise is whether to evaporate from the
solid or liquid state. The melting point of the crusts is not known
but it was observed that at 800°C very little fusion of the residues
from either crust had occurred. Evaporation at 800°C was not as
complete as that at 900°C where the residue was molten, therefore,
it may be concluded that the increased surface available when the mass is in the solid state does not compensate for the decrease in rate of evaporation and the inability of the volatile constituents to diffuse.

C. Amount of Charge.

Figure 18 shows the composition of residues obtained from varying amounts of charge. Table 15 shows what is happening.

### TABLE 15

<table>
<thead>
<tr>
<th>Charge (gm.)</th>
<th>Zn</th>
<th>Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Om. Charged</td>
<td>Om. Evap.</td>
</tr>
<tr>
<td>3555</td>
<td>1936</td>
<td>1936</td>
</tr>
<tr>
<td>8058</td>
<td>4823</td>
<td>4701</td>
</tr>
<tr>
<td>12000</td>
<td>6734</td>
<td>6494</td>
</tr>
<tr>
<td>18028</td>
<td>9810</td>
<td>9481</td>
</tr>
</tbody>
</table>

Apparently the zinc is evaporated mostly in the heating period before the charge becomes molten. Since in the solid state the surface area is a function of amount of charge we obtain about the same degree of zinc removal. The major portion of the lead, however, is evaporated after the temperature is above the melting point of the crust and in this case the surface area is independent of amount of charge except with respect to the cross section of the boat at various depths. The boat which was used apparently had a cross section such that at the operating conditions we could evaporate about 2000 gm. of lead in 3 hours. From the results of the 3555 gm. charge we see that we can evaporate in 3 hours only about 95 per cent of the
lead charged because of the decrease in its activity. From these
data we can then calculate the optimum charge for the given condi-
tions and the boat being used.

The results given in Table 3 suggest the possible advantage
of charging at some intermediate temperature, about 800°C, and
allowing the zinc to evaporate while the charge is solid, then
raising the temperature for lead evaporation. This holding period,
if necessary, should be very short because of the high rate of evap-
oration of zinc.

D. Variation of Pressure.

Figures 16 and 17 show that the pressure of operation has little
effect on the results, at least in the range investigated. The rea-
son for this has been pointed out in the theoretical discussion,
namely, that the main interference to evaporation in this range is
the intercollision of the metal vapor molecules. One might conclude
from this that diffusion pumps are unnecessary, however, this is
misleading for several reasons.

As has been pointed out, at lower pressures a more coherent de-
posit should be formed because less oxidation of the condensate oc-
curs. This is important due to ease of handling in the subsequent
use of the zinc in desilverization. Secondly, the speed of diffusion
pumps and the low cost of operation in the desired pressure range
makes them more attractive than the alternative of using oversize
mechanical pumps. The use of steam-jet ejectors should not be over-
looked but, in general, their speed and capacity is probably greater
than that which would be required.
The main reason for the use of diffusion pumps is that the removal of impurities is very slow in the later stages of distillation. Therefore, in spite of the fact that the increase in purity obtained at lower pressures is only 3 or 4 per cent over that obtained at higher pressures, it would be necessary to evaporate for 1 or 2 hours longer in the range of 120 microns than in the range of 40 microns to obtain the same purity of residue.

It is interesting to note the effect of interference to vapor flow on evaporation. It was postulated that the large flow of metal vapors would cause a pressure increase over the charge and hinder the evaporation. Figure 13 shows that the degree of zinc removal was the same in the three largest charges. Apparently there was no appreciable pressure increase at the greater vapor flow rates, otherwise there would have been an increase in the percentage of zinc in the residue. Certainly, the amount of charge could not be increased indefinitely without producing a prohibitive vapor flow. It is encouraging, however, to note that considerable freedom exists in this phase.

B. Operational Problems.

One of the important phases of this investigation was the study of some of the operational difficulties which might arise in a commercial installation. Numerous minor problems arose but none were encountered of an unsolvable nature.

For ease of charging the crusts and discharging the residues an iron container was used. The containers or boats, constructed from 1/16 inch sheet iron, were cylindrical in shape and had diameters
slightly less than the diameter of the retort. The boats were made with several lengths and depths. Photograph 2 shows two of the boats which were used. Such a container is necessary in order to confine the charge to the hot zone since in operation at 900°C the charge is molten. It was found that the molten charge alloyed with the boat and removal of the residue after solidification was very difficult. Coating the boat with a suspension of alumina in water was found to alleviate this difficulty however, this practice is bothersome and if not done carefully is unsuitable. An alternative would be to melt the residue out of the boat. The best solution to this problem would be to construct the boat from a material which would not react with the residue. The material should be tough enough to stand a certain amount of abuse. Ceramic materials would be largely eliminated on this point.

A 20 gauge black iron sheet was used as a liner for the retort on which the metal vapors could condense. In early experiments the liner extended only over the cooler section, 3 inches from the boat to the open end of the retort. The liner fitted rather loosely in the retort and as the metal vapor rushed out to the condenser section considerable vapor flowed between the liner and the retort. The metal condensed and welded the liner to the retort making removal of the liner extremely difficult. This tendency was increased at greater vapor flows from the larger charges and in some instances the sticking was so bad that the liner had to be ripped out in pieces. It was finally necessary to extend the liner over the full length of the retort. This arrangement was satisfactory. With a retort of the type used in the Pidgeon process, which has a tight fitting con-
denser, this trouble would be largely eliminated.

The form of the condensed metals was interesting. Figure 22 shows the general distribution of metals in the condensate. These zones were generally well defined.

The condensates from runs 1 through 6 were analyzed and the results are given in Tables 4 through 9. The apparent loss of metallics is due mainly to incomplete removal of condensed metal from the liner.

The fact that the high zinc sheet, sections 1 and 2, stripped very easily from the liner was encouraging. It had been expected that the zinc would alloy with the liner but such was not the case. Apparently the zinc vapor will not react with iron and since the zinc condenses to the solid state the easy removal is possible.

Photograph 3 shows two of the condensates. The dark sheet on the left is the result of condensation at too low a temperature. The sheet is black because the surface metal is very finely divided. The sheet on the right is a bright, coherent deposit. These sheets are made up of sections 1 and 2 of Figure 22. The sheet on the right shows that the high zinc portion (upper portion) is brighter than the zinc-lead section.

Some difficulty was experienced with the high lead portion, section 3. The lead in condensing to the molten state had an opportunity to alloy with the condenser and removal of this material was difficult. However, it was found that the lead could be scraped from the liner quite easily when the liner was hot.
**Fig. 22 - Distribution of Metal in Condensate**

- **Sec. 4**: Material which had condensed to liquid state and ran to the bottom of condenser, about 90% Pb.
- **Sec. 3**: High zinc sheet, about 95-100% Zn, stripped easily from liner. Somewhat brighter deposit than section 2.
- **Sec. 2**: Thin layer of shiny material, about 80% Ag.
- **Sec. 1**: Zinc-lead sheet, stripped easily from liner, about 20% Pb and 80% Zn.
Section 4, which was very high in silver, was present in such small quantities that it could not be removed as a strip. A portion scraped from a liner which had been used in numerous runs analyzed about 81% Ag. This portion was only noticeable in runs in which the distillation was quite complete.

In the Pidgeon process the "crowns" of magnesium are rammed out of the condenser by means of a hydraulic press. Split condensers


were also used. A similar scheme should be suitable for removal of condensed metals from Parkes' crusts. If the metals are removed while the condenser is hot they should come out easily.

Several baffle arrangements were tried to obtain a more coherent deposit. The intended purpose of the baffles was to cause metal to condense in a hotter portion of the condenser as is done in the Pidgeon process. The baffles were unsuccessful. No marked improvement of deposit was observed and the tendency for metal to condense behind the liner was increased due to interference of the baffle to vapor flow.

In general, the best deposits were obtained at higher condenser temperatures and lower pressures. The temperature of condensation seemed to have the greatest effect on the deposit. Good deposits should be obtainable by proper adjustment of cooling water flow.

In some of the early runs considerable zinc vapor reached the diffusion pump and condensed there. A vapor baffle placed in the section of the retort leading down to the diffusion pump practically eliminated this trouble.
In runs 20 and 21 the materials were charged and discharged at a temperature of about 850°C. No difficulties were encountered in operation and the only appreciable oxidation observed was that of the residue. In both of these runs the lead removal was incomplete. In a good distillation where the lead content of the residue was low the products could probably be removed at operating temperature with practically no oxidation occurring.

A retort of the Pidgeon type shown in Figure 1 seems to be quite suitable for distillation of Parkes' crusts. The ease of charging and discharging a horizontal retort is attractive and the long heating zone would give considerable capacity. The shorter condenser section should result in a high temperature of condensation and a good deposit. However, the shorter condenser might result in a poorer separation of lead and zinc. This is minor because the condensed metals would probably be returned together to the desilverization kettles.

Several precautions must be observed with respect to lead condensation. Because of the low vapor pressure of lead, it will condense at a high temperature. It is necessary, therefore, that no temperature gradient exist between the hot zone of the retort and the start of the condenser section. Secondly, the retort, or at least the condenser, must slope downwards toward the cold end to prevent molten lead from running back to the hot zone.

Several suggestions for a vertical type retort have been considered but at first glance the design and operational difficulties which are involved are discouraging. The major problem would be
handling the molten lead condensate. In upward condensation a com-
plicated condenser would be necessary with some means of retaining
the molten lead. In downward condensation the charging and discharg-
ing would be difficult since it would have to be done from underneath.

The disposal of the residues has not been investigated but sev-
eral methods have been suggested by Shih. The best method for


production of a high grade silver from the residue seems to be elec-
trolytic refining. With crusts of the Herculaneum type which are
high in copper, an additional refining operation of the residue would
be necessary before electrolysis. Addition of a small amount of
lead and cupellation of this mixture would be satisfactory or oxida-
tion and slagging of impurities in a suitable furnace should be
possible. Residues from crusts of the Bunker Hill could be directly
refined by electrolysis in a suitable cell as described by Allmand.


This author mentions electrolytic refining of anodes containing as
much as 12 per cent base metals resulting in a product over 999 fine.
The electrolyte contained 1.3 per cent silver and 2 per cent nitric
acid and was agitated by means of a propeller. A current density
of 0.65 amps per sq. ft. was used. In the usual industrial electro-
lytic refining of silver the percentage of base metals is about 2
per cent. With a clean crust a residue of 98 per cent silver is
possible but in most cases an intermediate refining of the residues would be necessary to make possible the use of the standard electrolysis.

With the residues which can be obtained from vacuum distillation of Parkes' crusts a relatively simple refining operation should be possible. The lack of equipment and time make it necessary to neglect this problem in the present investigation.
VIII. CONCLUSIONS AND COMMERCIAL POSSIBILITIES

One of the prime considerations in any commercial installation is equipment requirements. From the experiments performed a fair approximation can be made of the equipment which would be needed in vacuum distillation of Parkes’ crusts on a commercial scale.

Let us assume that a certain lead refinery produces crusts of the Bunker Hill type and that the silver output of this refinery is 400,000 troy oz. of silver per month. The crust which would be handled would amount to 3,400 lb. per day. Suppose that we decide to refine the residues in a single step by electrolytic refining as described by Allmand, wherein 12 per cent of base metals can be tolerated in the anodes. In runs 16, 17, and 18 residues of suitable purity were produced in a reasonable time. Let us choose the operating conditions (950°C and about 25 microns) which were used in these runs for the commercial installation. To insure a good residue for electrolysis we decide to evaporate for 5 hours.

The boat which was used gave an evaporating surface of about 55 sq. in. In a retort of the Pidgeon type shown in Figure 1, we could have an evaporation surface of about 520 sq. in. (8 in. x 65 in.). We should therefore be able to evaporate about 9.45 times as much crust with the same resultant residue, or 185 lb. If we allow one hour for charging and discharging a retort, an entire evaporation cycle would take 6 hours, or we could run a retort 4 times in a 24 hour day. One retort could handle 740 lb. per day,
therefore five retorts would be required. The five retorts would give a peak capacity of about 430,000 troy oz. of silver per month.

A possible vacuum system for this arrangement is shown in Figure 23. The retorts are manifolded to a single rougher pump and a single diffusion pump. The operational cycles of the retorts could be staggered and the operating schedule would be as follows. Discharge and charge retort 1. Close the air inlet valve and open the valve to the rougher pump. When a suitable forepressure is reached close the valve to the rougher pump and open the valve to the diffusion pump. The valve to the diffusion pump would be open during the entire evaporating cycle. The charger would then move to retort 2 and repeat the cycle.

The diffusion pump and its forepump would handle all five retorts while the rougher pump would evacuate only one retort at a time.

With crusts of the Herculaneum type the vacuum retorts could be used simply to replace the usual method of retorting. The advantage would be in reducing the time and temperature of retorting. Also, the better removal of lead in vacuum retorting would give less material to be cupelled. Therefore, the capacity of the cupellation furnaces would be increased and the silver loss in cupellation decreased.

The size of retorts which are used in vacuum distillation could be increased, of course. The temperature used in the Pidgeon process, about 1250°C, is prohibitive to larger retort because of the decrease in strength of the retort. In vacuum distillation of Parkes'
Fig. 23 - Tentative Vacuum System

Air Inlet

Valve to diffusion pump

Diffusion pump

Rougher pump

Valve to rougher pump

Fore pump

All valves are special vacuum valves.
crusts the temperature is lower and a bigger retort can be used. This would make possible the use of fewer retorts and perhaps simplify operation.

Because of the difficulties and vagaries involved, no attempt was made to analyze the economics of such a process. However, from an operational viewpoint the possibilities of this process are plentiful and certainly some application of the process to treatment of Parkes' crusts is forthcoming.
In this investigation a pilot plant study of vacuum distillation of Parkes' process crusts was made. Operational problems which were encountered were discussed. No serious difficulties were met which would be prohibitive to the process.

Important operational variables were investigated. A temperature of 900 to 1000°C is necessary in order to evaporate an appreciable amount of material in a reasonable time. The "high" silver loss at the higher temperatures is relatively unimportant since the condensed metals may be returned directly to the desilveryation kettles and the silver can be recovered easily.

Pressure has little effect on results in the range investigated but lower pressures are nevertheless desirable because of the excessive time required to remove impurities in the later stages of evaporation.

The evaporation of lead seems to be mainly from the liquid state. A large heating zone is therefore desirable so that the molten material will have a large evaporation surface. Also, particle size of the crusts is unimportant and crushing is eliminated.

The temperature of condensation seems to have the most effect on the form of the condensate. In general, the more coherent deposits were produced at the higher temperatures of condensation.

A Pidgeon process type retort seems to be suitable for a commercial installation. Such a retort would have reasonable capacity and ease of operation. The most promising method of handling reac-
idues appears to be electrolytic refining. This conclusion is based on published material, not on experimental work with the residues.

The commercial possibilities of the process with respect to operational simplicity and metal recovery have been indicated. Although considerable work remains, it is probable that some application of vacuum distillation to Parkes' process crusts is forthcoming.
BIBLIOGRAPHY


VITA

Robert Frederick Doelling was born on July 29, 1928 in St. Louis, Missouri. He received his elementary education in the public schools of St. Louis.

He entered the Missouri School of Mines and Metallurgy in January, 1945 and in 1948 received the degree of Bachelor of Science in Metallurgical Engineering. Since that time he has worked during two summers in the Research Department of the St. Joseph Lead Co. electrothermic zinc smelter in Monaca, Pa., and has done graduate work in the Metallurgical Engineering Department.