CUPELLATION IN CONTACT WITH COMBUSTION GASES

BY

LEONARD L. SUTKER

THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMICAL ENGINEERING

COLLEGE OF LIBERAL ARTS AND SCIENCES

UNIVERSITY OF ILLINOIS

1926
UNIVERSITY OF ILLINOIS

May 27, 1926

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

LEONARD L. SUTKER

ENTITLED CUPELLATION IN CONTACT WITH COMBUSTION GASES.

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF Bachelor of Science in Chemical Engineering.

W. M. Austin
Instructor in Charge

W. A. Negre

HEAD OF DEPARTMENT OF CHEMISTRY

605867
This work is respectfully dedicated to Dr. M.M. Austín in appreciation of his willing help and his constant interest in the problem.
CONTENTS.

I- INTRODUCTION

II- HISTORY
   (a) RESUME OF HISTORY OF GOLD AND SILVER
   (b) HISTORY OF CUPellation
   (c) HISTORY OF THE TYPES OF FURNACES.

III- EQUIPMENT MATERIALS AND METHODS.

IV- CUPellation EXPERIMENTS
   (a) UNIFORMITY OF TEMPERATURE OVER HEARTH AREA
   (b) DEGREE OF OXIDATION OF FURNACE ATMOSPHERE
   (c) DIFFICULTIES ARISING FROM RAPID CIRCULATION
       OF THE GASES OVER THE CUPEL
   (d) TIME OF CUPellation AND CUPellation LOSSES
   (e) FUEL EFFICIENCY

V- CONCLUSION

VI- BIBLIOGRAPHY.
I

INTRODUCTION.

THE CUPELLATION PROCESS.

Cupellation is the rapid oxidation of impurities from a mixture of baser metals and the noble metals. Lead and copper usually contain small amounts of gold and silver, as also do antimony, bismuth and several other metals. To obtain the gold and silver from these alloys it is necessary to remove the base metals by a rapid oxidation in a manner which will leave most of the noble metals behind in a pure state.

Cupellations which have been carried out in the laboratory as a part of gold and silver assays, have always been conducted in muffle type furnaces which completely protected the cupellations from the furnace atmosphere. Good practice is to place a bone ash cupel onto the muffle floor and heat it to a certain definite temperature. Commercially, cupellations have always been carried out in contact with combustion gases with an auxiliary blast of air.

Here at the University of Illinois all cupellations have been carried out in the muffle type of furnace. Recently, however, the coal fired furnaces which had been in use in this laboratory, were replaced by gas heated furnaces. These furnaces were not designed specifically for use in assaying and instead of being provided with completely enclosed muffles, they were equipped with carborundum hearths. If these furnaces were to be used in the way in which they were intended with carborundum hearths in place, not only would the crucible fusions have to be
carried out in contact with combustion gases, but cupellations as well. From a description of the cupellation process, it is evident that there must be an oxidizing atmosphere present. If the cupels are in contact with the combustion gases, which may or may not give an oxidizing atmosphere, will cupellation proceed as it should? Since the design of these furnaces allows for an atmosphere of any degree of oxidation, and since the furnaces would be expected to operate more efficiently using the hearths for which they were designed, it seemed desirable to make a study of the cupellation behavior in these furnaces. A search of the literature reveals that little work has been done in this direction. The only suggestion that the idea is feasible is the fact that commercial cupellations are carried out in a similar manner.

As a trial run several samples of test lead were taken and then placed into cupels on the hearth. Although cupellation was slow, taking over an hour and a half to cupel twenty five grams of test lead, it was found that cupellation could be carried out in contact with the combustion gases. It was further found that all of the phenomena of cupellation in the muffle type were also present in this cupellation. The brightening and the play of colors were especially pronounced. The next factor in the problem was to try and correct cupellations in the open hearth type of gas fired furnace so as to compare favorably with results in the muffle types, to determine whether cupels located in various parts of the furnace behave similarly, to check losses of silver with those losses encountered in good muffle practice and in general to determine the conditions for satisfactory cupellation in this type of furnace.
One of the most interesting observations in connection with gold and silver is the fact that the eager search which has been made for them has led to practically every exploration and voyage of discovery known to history. It has also furnished the impulse behind the discovery and settlement of many pieces of territory, as for instance, California, Alaska, South Africa etc. The process for recovery of gold and silver by cupellation was known by the early workers in these metals, and in searching the literature for material on the subject one encounters very interesting human side lights.

The suffering and pains which used to accompany the ever increasing demand for more gold and silver even in ancient times can be seen from the following excerpt (BC59); (1) "The parts of Egypt----are rich in gold mines. The ore is a black mineral marked with white veins(probably silver) and shiny specks. The chiefs of the undertakings employ a great number of workmen who are all either condemned criminals or prisoners of war. Even the parents of the condemned are summoned, -------. They work day and night------under the surveillance of barbarous soldiers.

The workmen never cease from their toil, they are forced incessantly to the work by bad treatment and by blows of the whip."

Gold and silver are mentioned in the bible, and we know now that gold has been known for ages. The ever increasing demand for gold continued throughout the ages and at one period in history chemists tried to make gold from base materials, but of
course they failed. Recently the attempted transmutation of mercury to gold attracted considerable attention, but has not been definitely proven possible. Gold itself does not require cupellation to be purified, and neither does silver unless it is contaminated with base metals. Gold is separated from silver by a process known as parting.

Cupellation was known back as far as 1000 A.D. In fact here are some directions given at the time. (translated here.) (2) "If you should break any kind of gilded copper or silver vessel, you may recover the gold by this method; take the bones of any animal, such as you may find in the street and burn them. When cooled, grind them very fine and mix with a third part of beechwood ashes and make testas (cupels). Then carefully scrape the gold from the copper and wrap these scrapings in lead hammered thin etc." The directions given above although crude are quite like our directions today.

The chief method of cupellation, as mentioned before, has been carried out in the muffle. The muffle has kept the cupels out of contact of the flames and the combustion gases. Only one reference was found in literature to any other type of furnace used. In 1898 (3) George A Koenig reported that he did not think that the muffle was necessary, and he described a method of his, in which he placed the cupel onto a stand and using a gasoline furnace having the heat passing underneath the stand, and he blew a blast of air directly onto the cupel. He claimed that the losses of silver by cupelling this way were not any larger than those in the muffle type.

The first furnaces were heated, of course with the old reliable wood fire. Then came the introduction of
bellows to increase the temperature of the flame, the first reference to such a furnace is where they used mouth blow pipes. Later came the Egyptian furnace closely resembling a campfire, but fitted with bellows, to which oftimes men were tied and forced to jump up and down to furnish air to the furnace. What an advancement there has been made, first to the coal type of furnace with almost no control of the temperature, and now to the gas fired type of furnace with such delicate control of the temperature possible.
III
EQUIPMENT, MATERIALS, AND METHODS.

Perhaps it is best at this point to describe the muffle and the hearth type of furnaces which are under comparison in this research.

Muffle furnaces are arranged so that the charge is placed in a space known as a muffle. The muffle is a semi-cylindrical receptacle of any suitable refractory, set horizontally and so arranged that the fuel or products of combustion pass around and under it. Thus, the material to be heated is entirely separated from the products of combustion.

Figure 1
Muffle in place in the furnace

The following figure 2 illustrates the arrangement of parts in the hearth type of furnace. The hearth, as well as the muffle, occupies a horizontal position in the furnace. It is heated by means of four gas ports, two above the hearth and two below it. The hearth is made of a carborundum mixture and is highly refractory. In the following chapters the word hearth will be used to refer to the open hearth type.
The different types of fuels that are used in cupellations are numerous. However, the gaseous fuels are much more advantageous than are the solid types of fuels. In using gas the fire is kindled instantly and the temperature is easily controllable. A high efficiency is possible and gas furnaces are much cleaner to operate.

The furnace used throughout all the experiments on this problem is a surface combustion furnace. It is made by the Surface Combustion Company of New York and is 56 inches high, 28 1/2 inches wide, and 26 1/2 inches deep. The gas supply is at a pressure of about 15 pounds. This gas is supplied by an electrically operated pump in the gas line to a reservoir, which is followed by a high pressure gas meter. Plate 1 and 2 show the heating chambers of the hearth and muffle types. Plate 3 shows the group of five furnaces that are used in regular assay work. Plate 4 shows the gas equipment for furnishing gas to the furnaces.

The cupels are shallow, porous dishes made of bone ash, Portland cement, magnesia or other refractory and non-corrosive material. The early assayers used cupels of wood ashes.
Today it is generally thought that the ash from sheep's bones are best suited for cupels. The cupels are made by first moistening the dust slightly with water, and later pressing it in a mold to the proper shape. Then it is allowed to dry for several months before using. The cupels used in this work were made of bone ash in which no binding material was used.

The cupellation method is rather interesting. First the hearth or muffle is heated up to a red color, and several dried cupels are placed onto the floor. The cupel is allowed to heat up and then the lead button containing the silver and gold is placed into the shallow portion of the cupel. The door of the furnace is closed momentarily to allow the lead button to melt. Then the door is opened and it is seen that the molten lead in the cupels appears very bright. Then it is noticed that the lead is being partly volatalized and partly absorbed by the cupel. This continues until all of the lead is oxidized and then the pure button containing the noble metals is left. This button is removed, cooled and weighed.
IV

CUPELLATION EXPERIMENTS.

In contemplating cupellation in this type of furnace some of the factors which need to be studied are;-(1) Uniformity of temperature over the hearth area;(2) Degree of oxidation of furnace atmosphere;(3) Difficulties arising from the rapid circulation of gases over the cupel;(4) Time of cupellation and cupellation losses;(5) Fuel efficiency.

Observation of the cupels as they were placed in the furnace showed that the rate of heating over the hearth area was somewhat uneven. The tops of the cupels appeared to get much hotter than the bottoms, in fact anything projecting up into the atmosphere above the hearth was heated much more rapidly by contact with the heated gases than it was by radiation from the hearth. This fact is very clearly shown by the behavior of the pyrometer which reads many degrees higher when the thermocouple is suspended in the atmosphere above the hearth than when buried in the bone ash or lying on the hearth. Although the hearth itself appeared to be of a uniform temperature over a considerable portion of its area, cupels that were placed farthest from the upper pair of gas ports were much hotter than were those placed near the ports and beneath the flames.

The influence of the degree of oxidation of the furnace was studied in the following ways. To determine whether the furnace would be satisfactory for cupellations without any modifications, several cupellations were carried through using the same technique as would have been used in a muffle.
Time of cupellation................. 1 hour and 30 minutes.

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight of silver before cupellation</td>
<td>.05382gr.</td>
<td>.06399gr.</td>
</tr>
<tr>
<td>Weight of silver after cupellation</td>
<td>.05265</td>
<td>.06283</td>
</tr>
<tr>
<td>Loss in weight</td>
<td>.00117</td>
<td>.00116</td>
</tr>
<tr>
<td>Percent loss of silver</td>
<td>2.17%</td>
<td>1.81%</td>
</tr>
<tr>
<td>Average percent loss</td>
<td>1.99%</td>
<td></td>
</tr>
</tbody>
</table>

In an effort to increase the amount of air in the furnace without disturbing the combustion efficiency, which was adjusted for maximum, an attempt was made to conduct cupellations under a jet of air directly onto the cupel. This resulted in a very rapid cupellation, but was accompanied by prohibitive losses of silver. Several trial runs were made and two runs will be given as evidence.

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight of silver before cupellation</td>
<td>.03924</td>
<td>.04184</td>
</tr>
<tr>
<td>Weight of silver after cupellation</td>
<td>.03393</td>
<td>.03783</td>
</tr>
<tr>
<td>Loss in weight</td>
<td>.00521</td>
<td>.00401</td>
</tr>
<tr>
<td>Percent loss of silver</td>
<td>13.3%</td>
<td>9.52%</td>
</tr>
</tbody>
</table>

The second attempt to increase the air in the furnace was by the use of an aspirator, the purpose of which was to create a gentle draft of air over the hearth.

Sketch of the aspirator.
After the aspirator has been placed on the back port of the furnace another set of trial runs were made, using the aspirator.

Time of cupellation................. 31 minutes.

<table>
<thead>
<tr>
<th></th>
<th>I</th>
<th>II</th>
<th>III</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight of silver before cupellation</td>
<td>.04371</td>
<td>.04184</td>
<td>.03993</td>
</tr>
<tr>
<td>Weight of silver after cupellation</td>
<td>.04292</td>
<td>.04093</td>
<td>.03914</td>
</tr>
<tr>
<td>loss in weight</td>
<td>.00080</td>
<td>.00091</td>
<td>.00079</td>
</tr>
<tr>
<td>Percent loss of silver.</td>
<td>1.83%</td>
<td>2.17%</td>
<td>1.98%</td>
</tr>
<tr>
<td>Average percent loss</td>
<td>1.99%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The next method tried, of introducing air into the furnace was by shooting a jet of air into the gas going into the furnace at the air inlet to the furnace burner. Although this method also cut down the time of cupellation, and the silver losses were quite satisfactory, the furnace was cold and the combustion of the gases was not exactly as it should have been. This method of hurrying the cupellation is, of course, unfeasible, and not much work has been done in that direction. A refinement on this method of introducing air into the burner in excess of that needed for proper combustion of the gases was by the use of a spudd having a smaller hole.

Sketch of a spudd.

The spudd usually used in this type of furnace is number 29 or having an opening of .136 inches. This spudd needs the aspirator to hurry the cupellations. The other size spudd used was number 31, having an opening of .120 inches, this spudd does not need the aspirator, but it is not as efficient in its fuel.
consumption, however that will be taken up later.

One reason for using a muffle is the fact that the cupellation proceeds in a very quiet atmosphere, while in the furnace used in these experiments, there is a violent circulation of gases. It has already been pointed out that this circulation of the gases results in a very rapid heating of objects projecting above the hearth. Another disadvantage resulting, is the fact that the oxidation of lead and the general behavior of the cupellation cannot be determined by observation as it is possible in the muffle type. No difficulty has been encountered through contamination of the cupellations by particles of bone ash or refractory.

Losses of silver due to volatalization as well as absorption into the cupel is something which cannot be overlooked in any cupellation. There have been many experiments performed to determine the losses of silver in muffle cupellations at various temperatures, and one table of results that gives average results as to cupellation losses is offered here. This table is taken from 'Notes on Assaying' by R W Lodge.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>% Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>700 °C</td>
<td>0.99-1.05</td>
</tr>
<tr>
<td>775</td>
<td>1.18-1.76-1.41</td>
</tr>
<tr>
<td>850</td>
<td>1.75</td>
</tr>
<tr>
<td>870</td>
<td>1.80</td>
</tr>
<tr>
<td>925</td>
<td>2.59-3.53-3.78</td>
</tr>
<tr>
<td>1000</td>
<td>4.78-4.97</td>
</tr>
</tbody>
</table>

In general the losses of silver in the muffle type varies as the temperature, as it also does in the
hearth type. The temperature at which it is possible to cupel, that is, the lowest temperature at which it is possible to cupel in the muffle type varies somewhat with the size of the furnace, and the method of heating, but usually it is possible to cupel in the muffle type as low as 700° Centegrade, except at the end of the operation when the temperature must be raised slightly.

From preliminary runs it was indicated that the aspirator was effective, accordingly many tests were run on the open hearth type of gas fired furnace with the aspirator in operation and a table of losses at various temperatures, compiled. In making this table the loss of silver at the temperature shown is the average loss of the ten or twelve samples that were run at the same time.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>% Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>850°C</td>
<td>1.32</td>
</tr>
<tr>
<td>920</td>
<td>1.39</td>
</tr>
<tr>
<td>930</td>
<td>2.13</td>
</tr>
<tr>
<td>940</td>
<td>2.72</td>
</tr>
<tr>
<td>980</td>
<td>2.53</td>
</tr>
<tr>
<td>1000</td>
<td>2.78</td>
</tr>
<tr>
<td>1025</td>
<td>3.74</td>
</tr>
</tbody>
</table>

It was found that it was possible to easily control the gas heated furnace so as to get any one temperature desired. In general the losses of silver seem to be lower than the losses in the muffle type at the same temperature. There seems to be a difference, however, in the temperature at which it is possible to cupel in the two types. In the muffle type it is possible to cupel at 700°C, but it was found that the lowest temperature at which it is possible to cupel in the hearth type...
was 850°C.

As a confirmatory test two special runs were made, one each in the two types, cupelling at the same temperature. The losses of silver, average for the twelve cupellations, in each case was,

- Muffle type..... 1.19%
- Hearth type..... .94%

The hearth type seems to give a lower loss of silver, although the losses of silver at different points on the hearth vary, while the losses in the muffle type is generally constant over the entire muffle floor.

An average loss of silver, taken from a special test on a muffle type coal fired furnace, an average of the work of thirty men, gave a silver loss of 2.06% at 800°C.

The efficiency of a furnace is of considerable importance. It was found in working on the hearth furnace that the use of spudds of different sizes can hurry or retard the cupellation time. The important matter to notice is the amount of gas required to heat up the furnace. In using a small spudd, where it is possible to cupel without the use of an aspirator, it used over 400 cubic feet of gas to get the furnace hot enough to cupel in, whereas in using a spudd with a larger opening only 314 cubic feet of gas was necessary.

In a similar manner, the amount of gas necessary to heat up the muffle type was determined, and it was found that it required 424 cubic feet of gas. This would make it appear that the efficiency of the hearth type was better than that of the muffle type, in getting the furnace up to the cupelling temperature.

Another matter of importance that must be
considered is the initial cost. The initial cost of both the muffle or the hearth does not leave any room for argument, for the cost of the two is practically the same, but however, the cost of repairs, and the upkeep is less for the hearth than for the muffle. The muffle is built of a brittle fireclay that breaks easily and must be handled carefully, and repaired quite frequently. The hearth is built of a carborundum mixture and is solid, can stand shocks easily, is almost foolproof, and it is sturdy and will last indefinitely.

There is one matter of difference that is quite noticeable, and that is; cupellation in the muffle type proceeds quite regularly over the entire muffle floor and volatalization of lead can be noticed all over the furnace, but in the hearth type, cupellation is not regular over the furnace, and volatalization of lead can only be noticed under the flames.
CONCLUSIONS.

1. Cupellation in contact with combustion gases of a hearth type of furnace is impracticable without the introduction of more air than should be used for efficient combustion.

2. Effort to increase the speed of cupellation by introducing a blast of air directly upon the cupel results in excessive silver losses.

3. Introduction of excess air through the burner improves cupellation time and behavior, but lowers the fuel efficiency.

4. A gentle draft of air drawn over the hearth by means of an aspirator resulted in good cupellation behavior without noticeable loss in fuel efficiency.

5. Cupellation losses vary over a wide range depending on the position of the cupel on the hearth. Only when the cupels are placed on a small area of the hearth beneath and adjacent to the gas ports are satisfactory results obtained.

6. The substitution of a muffle for the hearth in these furnaces does not result in excess fuel consumption.

7. In general the use of the hearth for cupellations is impracticable.
VI

BIBLIOGRAPHY.

(1) The precious metals
    Sir T Kirke Rose

(2) The Story of Early Chemistry
    John M Stillman

(3) Transactions of the American Institute of Mining Engineers
    Volume 28 page 271 George A Koenig

(4) Textbook of Fire Assaying
    Bugbee.