The Great Falls Zinc Plant

Donald Edward Macknight
Montana School of Mines
Butte, Montana
January 7, 1957

Metallurgy 53
Metallurgical Plant Study

THE GREAT FALLS ZINC PLANT

Submitted to
Dr. F. A. Hames
Metallurgy Department

by
Donald E. Macknight
Montana School of Mines
Butte, Montana
January 7, 1957

Metallurgy 53
Metallurgical Plant Study

THE GREAT FALLS ZINC PLANT

Submitted to
Dr. F. A. Hames
Metallurgy Department

by
Donald E. Macknight
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>TOPIC</th>
<th>PAGE</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>I. Introduction:</strong></td>
<td></td>
</tr>
<tr>
<td>Location and Purposes of the Plant</td>
<td>1</td>
</tr>
<tr>
<td>Scope of this Paper</td>
<td>1</td>
</tr>
<tr>
<td>Acknowledgment</td>
<td>2</td>
</tr>
<tr>
<td>History of the Plant</td>
<td>2</td>
</tr>
<tr>
<td>A Brief Summary of the Zinc Recovery Process</td>
<td>4</td>
</tr>
<tr>
<td><strong>II. A Discussion of the Zinc Plant Operations:</strong></td>
<td></td>
</tr>
<tr>
<td>The Zinc Roasting Department</td>
<td></td>
</tr>
<tr>
<td>Preparation of Concentrates for Roasting</td>
<td>5</td>
</tr>
<tr>
<td>Description of the Roasting Furnaces</td>
<td>5</td>
</tr>
<tr>
<td>Treatment of the Calcine After Roasting</td>
<td>6</td>
</tr>
<tr>
<td>Labor Requirements</td>
<td>8</td>
</tr>
<tr>
<td>Treatment of the Flue Gases</td>
<td>8</td>
</tr>
<tr>
<td>Limitations of Roasting</td>
<td>12</td>
</tr>
<tr>
<td>Difficulties Encountered While Roasting</td>
<td>12</td>
</tr>
<tr>
<td>Thermodynamics of the Process</td>
<td>13</td>
</tr>
<tr>
<td>Conclusion</td>
<td>13</td>
</tr>
<tr>
<td>The Zinc Leaching Department</td>
<td></td>
</tr>
<tr>
<td>Discussion of the Leaching Operation</td>
<td>15</td>
</tr>
<tr>
<td>Description of the Leaching Tanks</td>
<td>15</td>
</tr>
<tr>
<td>Operation of the Leaching Tanks</td>
<td>17</td>
</tr>
<tr>
<td>Flow of Materials</td>
<td>18</td>
</tr>
<tr>
<td>Summary of the Operation</td>
<td>19</td>
</tr>
<tr>
<td>Labor Requirements</td>
<td>19</td>
</tr>
<tr>
<td>Removal of Impurities</td>
<td>20</td>
</tr>
<tr>
<td>Thermodynamics of the Process</td>
<td>20</td>
</tr>
<tr>
<td>Conclusion</td>
<td>20</td>
</tr>
<tr>
<td>The Zinc Electrolyzing Department</td>
<td></td>
</tr>
<tr>
<td>General Data</td>
<td>21</td>
</tr>
<tr>
<td>Power Supply</td>
<td>22</td>
</tr>
<tr>
<td>Distribution and Electrolysis of the Zinc-Sulfate Solution</td>
<td>22</td>
</tr>
<tr>
<td>Labor Requirements</td>
<td>24</td>
</tr>
<tr>
<td>Metallurgical Discussion</td>
<td>24</td>
</tr>
<tr>
<td>Conclusion</td>
<td>26</td>
</tr>
<tr>
<td>The Zinc Casting Department</td>
<td></td>
</tr>
<tr>
<td>Scope of the Department</td>
<td>28</td>
</tr>
<tr>
<td>Treatment of the Gases</td>
<td>28</td>
</tr>
<tr>
<td>Labor Requirements</td>
<td>29</td>
</tr>
<tr>
<td>Summary</td>
<td>29</td>
</tr>
<tr>
<td>Conclusion</td>
<td>29</td>
</tr>
</tbody>
</table>
III. Summary: ........................................... 30

IV. Appendix:
   A Detailed Flow Sheet of the Plant ............ 31
   Bibliography ..................................... 32
I. INTRODUCTION
THE GREAT FALLS ZINC PLANT

INTRODUCTION

In this portion of the report I shall present just the introductory material and shall not discuss the metallurgy or procedure of the individual processes.

Location and Purposes of the Plant

At Great Falls, Montana, on the North bank of the Missouri River, is the Great Falls Reduction Works. This plant is owned and operated by the Anaconda Company of New York City. The main purposes of this plant are twofold: (1) the recovery and purification of zinc from complex sulfide ores; and (2) the purification and fabrication of impure copper anodes received from the Company's great reduction works at Anaconda, Montana.

Recently, an aluminum wire and rod mill has been added to the plant. This mill fabricates pure aluminum, which is received from the Anaconda Aluminum Company's plant at Columbia Falls, Montana.

In addition to the vast quantities of zinc, copper, and aluminum recovered at Great Falls, lesser amounts of cadmium, gold, manganese, indium, and silver are also recovered as by-products in the copper and zinc processes.

Scope of this Paper

This paper will be confined to the processes by which zinc is recovered. In discussing the unit processes and operations, I shall first give a general view of the process and why it is necessary. Next, I shall analyze the process in terms of metallurgy and thermodynamics, showing by calculation, where necessary, certain facts that could not be suitably explained without a knowledge of the fundamental principles of extractive metallurgy.
Acknowledgment

I am deeply indebted to Mr. Clarence V. Saylor (now deceased), General Superintendent of the Great Falls Plant, who furnished me with literature, photographs, and certain metallurgical data in order that my paper be more authoritative. Some data, however, could not be released because of cost or security, therefore, in its place I have estimated the figure shown.

History of the Plant

Early in 1891 the Boston and Montana Consolidated Copper and Silver Mining Company broke ground for a copper reduction works on the North bank of the Missouri River, across from the east end of the City of Great Falls, and about two and one-half miles from the business district of that city. These works were built to treat ore from the Company's mines in Butte, yielding copper and relatively small amounts of silver and gold.

About a year later, a concentrator was in condition to begin operations, and, shortly following, roasting furnaces and reverberatory smelting furnaces were finished. Bessemer converters were also installed about this time. This program completed a chain of operations for the production of blister copper, except that it was found necessary to erect blast furnaces for the re-treatment of converter slag. The blast furnaces were completed and in operation in 1893.

An electrolytic copper refinery and a furnace refinery were built in 1892 and put into operation in 1893, making it possible at that time to carry the treatment from ore to commercial shapes of refined copper. Later, during 1910, the properties of the Boston and Montana Consolidated Copper and Silver Mining Company were taken over by the Anaconda Copper Mining Company, and since then the metallurgical plants at Great Falls have been
known as the Great Falls Reduction Works of the Anaconda Company. The next large step for an increase in production was in 1916 when a plant was completed for the production of electrolytic zinc. In 1918 a mill was finished for the manufacture of copper rods, wire, and cable, which are made from the refined copper produced by the furnace refinery. The completion of this mill brought the copper industry in Great Falls to the point of a product ready for the consumer. In 1929 the mill was transferred to the Anaconda Wire and Cable Company.

During a few years prior to 1918 the work of copper concentrating and smelting, for which the original works were built, was gradually reduced, until, in 1918, this work was discontinued entirely, so that now the operation has changed from copper concentrating and smelting to that of copper refining, copper rod, wire, and cable manufacture, and electrolytic zinc and cadmium production.

A Brief Summary of the Zinc Recovery Process

Zinc at Great Falls is recovered by the electrolytic process. Zinc concentrates from various locations are received at the roasting department of the plant, where they are roasted to zinc oxide and zinc sulfate in furnaces of the Wedge-McDougall type. After roasting, the calcine formed is dissolved by sulfuric acid to form zinc sulfate. This operation is known as leaching. The zinc sulfate solution is then electrolyzed, and the pure zinc is deposited on aluminum cathodes. The pure zinc is next removed from the cathodes and sent to the casting department for melting and subsequent shaping. The final product, usually 50-lb slabs is then shipped by rail to various buyers throughout the world.
II. A DISCUSSION OF THE ZINC PLANT OPERATIONS
A DISCUSSION OF THE ZINC PLANT OPERATIONS

In this portion of the report I shall discuss the "hows" and "whys" of the unit processes by which zinc is recovered; discussing in each case the process itself, the metallurgy of the process, and my conclusion regarding the process.

THE ZINC ROASTING DEPARTMENT

The object of roasting the concentrates is to convert zinc and lead sulfides into sulfates and oxides, expel the excess sulfur and oxidize the iron and other metallic content of the ore, and thus secure a product which is suitable for subsequent treatment in the zinc leaching plant.

Preparation of Concentrates for Roasting

Zinc concentrates, at the rate of 700 tons/day, from Montana, Idaho, California, Utah, Arizona, New Mexico, Canada, Central America, and South America, assaying on the average, 53.0% Zn, 1.5% Pb, 0.30% Cu, 0.25% Cd, 5.0% Fe, 5.0 oz/ton Ag and 0.25 oz/ton Au, are received at Great Falls in 50-ton, bottom-dump, steel railroad cars and delivered to a battery of 19 storage bins, having a total capacity of approximately 3,300 tons. From these bins the material is manually loaded into 56 cu-ft, V-shaped, rocker-dump cars of 36-in. gauge and hauled by an 8-ton electric locomotive to individual feed hoppers directly above the roasting furnaces.

Description of the Roasting Furnaces

Fourteen roasting furnaces of the Anaconda type, a modified Wedge-McDougall furnace, in two rows of seven each are employed at Great Falls. Each furnace consists of a brick-lined steel shell, 25 ft in diameter, which has seven hearths and one open dryer hearth on top. These furnaces also have
a 5-ft brick-lined, hollow, revolving center shaft, which carries 26 water-cooled arms, four for the dryer and first hearths and three for each of the other six hearths. The temperature at the different hearths is as follows: 

#1-440°C, #2-554°C, #3-604°C, #4-632°C, #5-625°C, #6-620°C, and #7-520°C.

The center shaft is turned by a bevel pinion, which is driven by an individual motor belt connected to a series of enclosed reducing gears. The furnaces are also equipped with an apron feeder driven by gearing to the revolving center shaft, and so designed to regulate the rate of feed as desired. The rabbles on the arms are set to move the material from the circumference to the center of the furnace, and vice versa, on alternate hearths, delivering it finally into the calcine hoppers under the furnaces. The water for cooling the arms is delivered through a water column revolving with the center shaft and connected to the water supply mains by a swivel joint.

Treatment of the Calcine After Roasting

From the hoppers, the hot calcine — assaying on the average, 59.5% Zn, 1.7% Pb, 0.34% Cu, 0.28% Cd, 5.6% Fe, 5.6 oz/ton Ag, and 0.28 oz/ton Au — is drawn manually into electrically operated 4-ton, bottom-discharge larry cars, hoisted by means of an 8-ton Otis elevator and discharged into revolving coolers, which in turn discharge into a 400-ton storage bin for shipment by the local electric tram to the zinc-leaching plant. The total time, from when a particle enters the furnace to when it leaves is approximately 24-hr.

The furnaces at Great Falls are designed so that they may be fired with either oil or natural gas. Further data on this subject, however, are unavailable.
Fig. 2. The Wedge-McDougall Roasting Furnaces
Labor Requirements

Data on labor requirements for the Roasting Department were unavailable. I would estimate, however, that approximately 60 man-shifts per 24-hr day would be necessary. With the daily rate of pay at approximately $16.00, this would cost the Company $960.00 per day.

Treatment of the Flue Gases

The gases leaving the furnaces are carried in cross flues to a main flue, through the Cottrell Treaters, and thence to the stack. A small natural draft, the numerical value of which was unavailable, is maintained at the base of the stack to keep the gases flowing.

1. Description of the Cottrell Treater

The Cottrell Treater, where the greater portion of the dust is recovered, is housed in a building 50 ft wide by 75 ft long, including the rectifier room. The precipitator room, 50 ft wide and 60 ft long, is divided into three units, each 16 ft wide and 60 ft long. Each unit is separated from the other by a tile wall, and is a complete unit in itself, having its own inlet and outlet dampers. Each unit is divided into four sections in the direction of the gas flow, each section being made up of alternate curtains of pipes and rods. The high-tension direct current from the rectifiers flows into the rod curtains, and as the dust-laden gases flow past them, the dust particles are charged and attach themselves to the pipe curtains. Periodically, the current is shut off and the curtains are shaken, causing the accumulated dust to fall from the curtains into hoppers directly below them, from where the dust is drawn into cars and fed back to the roasting furnaces.

The Cottrell Treater is connected to the big stack by a brick and steel connecting flue. Steel expansion joints are placed at intervals along the
flue to allow for irregularities in temperature.

2. Description of the Stack

The stack is of brick, 506 ft high, 64 ft in diameter at the bottom, and 50 ft in diameter at the top, inside measurements. Thirteen thousand tons of brick were used in its construction.

3. Calculation for Volume of Flue Gas

Data concerning the quantity and composition of flue gas were unavailable. I have, however (assuming that theoretical conditions are adhered to), made a calculation of the quantity and composition of the gas. This calculation does not include the natural gas burned in the furnaces. The calculation follows:

(Analysis of concentrates is given above)

\[ \begin{align*}
53\% \text{ Zn} & \quad (\text{ZnS}) \\
\quad & = \quad 79\% \text{ ZnS} \\
\quad & = \quad 26.0\% \text{ S} \\
1.5\% \text{ Pb} & \quad (\text{PbS}) \\
\quad & = \quad 1.7\% \text{ PbS} \\
\quad & = \quad 0.2\% \text{ S} \\
5.0\% \text{ Fe} & \quad (\text{FeS}) \\
\quad & = \quad 8.0\% \text{ FeS} \\
\quad & = \quad 3.0\% \text{ S} \\
0.3\% \text{ Cu} & \quad (\text{CuS}) \\
\quad & = \quad 0.45\% \text{ CuS} \\
\quad & = \quad 0.2\% \text{ S} \\
0.25\% \text{ Cd} & \quad (\text{CdS}) \\
\quad & = \quad 0.32\% \text{ CdS} \\
\quad & = \quad 0.02\% \text{ S} \\
\text{Total Sulfur} & = \quad 29.4\% \text{ of the concentrates}
\end{align*} \]

It is desired to have the calcine contain 2.3% elemental sulfur and 2.0% sulfate sulfur.

\[ \begin{align*}
2.0\% \text{ SO}_4 & \quad (\text{S}) \\
\quad & = \quad 0.66\% \text{ S}
\end{align*} \]

Total sulfur in calcine = 2.3 + 0.66 = 3.0%

Sulfur to gas = 29.4% - 3.0% = 26.4%

Therefore, one ton of concentrates will furnish 526 lbs of sulfur to burn to \( \text{SO}_2 \).
Fig. 3. The Stack at Great Falls
528 (SO₂/S) = 1056 lbs SO₂
1056 (359/64) = 5920 ft³ SO₂ per ton of concentrates (STP)
700 (5920) = 4,144,000 ft³ SO₂ per day (STP)

Corrected to actual conditions:
(4,144,000) (823/273) (760/610) = 15,760,000 ft³ SO₂ per day

Air necessary:
528 lbs O₂ (359/32) = 5920 ft³ O₂

Air necessary = 5920/0.21 = 28,200 ft³ air per ton of concentrate

28,200 (0.79) = 22,300 ft³ N₂ per ton of concentrate

22,300 (700) = 15,610,000 ft³ N₂ per day (theoretical)

15,610,000 (760/610) (823/273) = 58,360,000 ft³ N₂ per day (actual)

Assuming 50% excess air:

28,200 (700) = 19,740,000 ft³ air per day

19,740,000 (0.50) = 9,870,000 ft³ air (excess STP)

9,870,000 (0.21) = 2,080,000 ft³ O₂

9,870,000 - 2,080,000 = 7,390,000 ft³ N₂ (excess STP)

2,080,000 (760/610) (823/273) = 7,660,000 ft³ O₂ (excess & actual)

7,390,000 (760/610) (823/273) = 29,400,000 ft³ N₂ (excess & actual)

total N₂ = 29,400,000 + 58,360,000 = 87,760,000 ft³ N₂

Total gas:

SO₂ 15,760,000
O₂ 7,660,000
N₂ 87,760,000

111,180,000 ft³ per day

% composition:

SO₂ 15,760,000/111,180,000 = 14.2%
O₂ 7,660,000/111,180,000 = 6.9%
N₂ 87,760,000/111,180,000 = 78.9%
Limitations of Roasting

As stated previously, the object of roasting is to convert zinc sulfide, as completely as possible, into zinc oxide and zinc sulfate by utilizing the reactions:

\[2\text{ZnS} + 3\text{O}_2 = 2\text{ZnO} + 2\text{SO}_2\]
\[\text{ZnS} + 2\text{O}_2 = \text{ZnSO}_4\]

The amount of zinc sulfate produced, however, should be limited to within the acid requirements of the plant, that is, enough sulfate to satisfy the copper, iron, cadmium, etc, that the concentrates may contain. Any excess acid must be discarded or neutralized to avoid building up acid in the system. Since the acid requirements of the leaching process are rather small, it has been found that 2 to 3 per cent of sulfate sulfur is usually sufficient. The controlling factor for zinc sulfate production was unavailable. I would assume, however, that the \(\text{ZnSO}_4\) in the calcine is possibly from the reaction of zinc oxide with sulfur trioxide.

Difficulties Encountered While Roasting

It is also essential in roasting not to employ too high a temperature, because of the tendency of zinc and iron to form zinc ferrite \((\text{ZnO} \cdot \text{Fe}_2\text{O}_3)\), which is insoluble in warm, dilute sulfuric acid. The formation of this ferrite is dependent upon the iron content of the concentrate, the temperature at which roasting is carried out, the nature and association of the zinc and iron, and the time of roasting. The only rule that can be given is to keep the temperature as low as possible — a maximum of 600-670\(^\circ\)C — particularly if the iron content is high. With concentrates containing high lead, care must also be taken, because galena fuses, forms a hard crust on
the hearth under the rakes, and coats over the particles of zinc ore and prevents complete roasting. Arsenic and antimony, if present, are partially eliminated by volatization, the remainder being eliminated in the leaching operation. A part of the copper combines with the iron in roasting to form a ferrite which is insoluble in dilute sulfuric acid.

Thermodynamics of the Process

The roasting process can be proved to be thermodynamically sound, as follows:

\[
2\text{ZnS} + 3\text{O}_2 \rightarrow 2\text{ZnO} + 2\text{SO}_2
\]

\[
\Delta F = (-124 + -144) - (-88) = -160 \text{ kcal/mole of ZnS}
\]

Therefore, since the change of free energy is negative, this process is thermodynamically sound.

Conclusion

It is evident that no process can operate at 100 pct. efficiency. In this particular case, considering the reaction

\[
2\text{ZnS} + 3\text{O}_2 \rightarrow 2\text{ZnO} + 2\text{SO}_2
\]

it can be seen from the Law of Mass Action that by applying a stress on the left-hand side of the equation, the equilibrium will be shifted to the right and, hence, more ZnO and SO\textsubscript{2} will be produced. The logical way of doing this would be to employ more oxygen which could easily be accomplished by enrichment of the air entering the furnaces. The point of debate on this matter would be cost. Would it be economical? Current figures show that oxygen costs about $5/ton, which is cheap energy. Also, if this figure were too high it could prove economical to erect a plant for SO\textsubscript{2} recovery from the roaster gases for subsequent H\textsubscript{2}SO\textsubscript{4} production. The profits from H\textsubscript{2}SO\textsubscript{4} sales should,
at least, balance the cost of oxygen for air-enrichment. Therefore, even if costs and profits just balanced one another, the roasting process would be more efficient. On the other hand, if more oxygen was present in the roasting furnaces, they would be hotter due to the combustion of the oxygen. Hotter furnaces mean more zinc ferrite produced, and, hence, more zinc not recovered. To recover this zinc ferrite, more concentrated \( \text{H}_2\text{SO}_4 \) would be necessary, which could be gotten from the hypothetical \( \text{SO}_2 \) recovery plant, but, if the \( \text{H}_2\text{SO}_4 \) were used here, it could not be marketed commercially, and the Company would not profit by its manufacture. On the basis of the above discussion, I would recommend that the process be left as it is. The plant is now equipped to handle the calcine capacity of the roasting department, but if calcine of higher \( \text{ZnO} \) content were produced, it is possible that the entire zinc plant operation may have to be altered.

Another suggestion I could offer for better economics is the recovery of waste heat, although I do not know how this could be utilized at the Great Falls Plant. I am sure, however, that if this operation were economical and if the heat could be utilized, the Company would have started recovering it many years ago.
THE ZINC LEACHING DEPARTMENT

The primary object of leaching is to dissolve all zinc oxide and zinc sulfate contained in the roasted concentrates with dilute sulfuric acid from the electrolytic cells. Unfortunately, iron, arsenic, antimony, silicon, aluminum, copper, cadmium, and other metals also dissolve and must be removed before the solution is electrolyzed.

Discussion of the Leaching Operation

The leaching division occupies a brick building 350 ft by 500 ft. The roasted zinc concentrates arrive in standard-gauge steel cars at the highest level in the building and are dumped into steel bins, where they are stored until ready for solution in the leaching tanks.

The leaching solution, containing about 11% sulfuric acid and 2.5% zinc, which is the return solution from the electrolyzing division, is elevated by alloy-steel centrifugal pumps, through lead pipe lines, to the top of the leaching tanks.

Description of the Leaching Tanks

The leaching tanks are of the Pachuca type. The Pachuca agitator (See Fig. 4) operates on the principle of the common air lift, consisting of a fir stave 33 ft high and 10 ft in diameter, with a cone-shaped bottom to facilitate the removal of the residue. At the apex of the cone is a large gate valve, through which the contents of the tank may be discharged at the end of the agitation period. In the center of the tank is the air lift, or standpipe, 10 in. in diameter, open at both ends, and extending from about 2 ft above the apex of the cone to just above the level of the pulp in the tank. At the lower open end is a small pipe, which admits a jet of compressed air. The air lift thus formed raises the pulp in the standpipe and discharges it
Fig. 4
The Pachuca Agitator
at the top of the tank, resulting in a very efficient agitation and circula-
tion.

**Operation of the Leaching Tanks**

The tanks are operated in series, each having a capacity of 30 tons of 
concentrates. There are 21 tanks, operated in three rows of seven each. Acid 
solution is admitted into the first tank, which discharges into the top of 
the second tank. The second tank discharges into the top of the third tank 
and so on through the series to the seventh tank which discharges into Dorr 
classifiers for removal of coarse material. Roasted concentrates are added 
to the leaching tanks until all acid is neutralized, and iron, arsenic, 
silica, alumina, etc., are precipitated. The overflow from the Dorr class-
ifiers goes to the Dorr thickeners for separation of solids and solution. 
This operation is known as the first, or neutral, leach.

The Dorr thickeners are made of fir staves bound together by lead-
covered iron-hoops. There are 22 of these in operation at the Great Falls 
plant. The mechanisms are made of bronze and lead-covered steel, no iron 
or steel being exposed to the solution. The thickened pulp is drawn from 
the bottom of the Dorr tanks and is again treated with acid in the second 
series of seven Pachuca tanks, which discharge into additional Dorr thicken-
ers. The thickened pulp from these thickeners goes to a battery of 2 Moore 
and 10 Oliver filters, the filtrate being returned with the thickener over-
flow to the first leach. The Oliver cake goes to the third set of leaching 
tanks, and then to Dorr thickeners for settling. The thickened spigot from 
these settlers is washed on a Moore filter, dewatered on Oliver filters, and 
the resulting cake, analyzing 14.0% Zn, 0.8% Cu, 6.3% Pb, 29.0% Fe, 11.8% 
insol., 0.05 oz ton Au, and 16.0 oz/ton Ag, is delivered to dryers for sub-
sequent shipment to a lead smelter.

**Flow of Materials**

The overflow from the first set of Dorr thickeners goes to the purification system for removal of copper and cadmium by agitation with zinc dust. The precipitated copper and cadmium and unused zinc dust are filtered from the solution in plate and frame, or as they are more commonly called, Shriver presses. After purification and clarification, the zinc-bearing solution is pumped to storage tanks until it is used in the electrolyzing division. The purification residue product of the filter presses is next treated in a secondary purification plant for the recovery of copper and cadmium.

Spent electrolyte is then added to the second, or acid, leach in sufficient quantity to dissolve all uncombined zinc-oxide residue from the first leach and to insure an excess of acid in the leach discharge. The discharge from this leach goes to the acid thickeners, the overflow being returned to the first leach and the spigot product delivered to filters.

The undried filter cake is sent to mechanically agitated leaching tanks previously filled with hot, spent electrolyte. As the leach progresses, part of the zinc-iron compound is decomposed, giving a solution rich in ferric sulfate and low in free acid. A further reaction between the ferric sulfate solution and zinc ferrite results in solution of the zinc oxide and precipitation of the iron as basic sulfate. While still acid, this leach is discharged to thickeners, the overflow going to the first leach and the spigot to a Moore filter, where the residue is washed nearly free of entrained zinc sulfate solution.
Summary of the Operation

Summarizing, in the first, or neutral, leach: (1) All the calcine enters the process, and approximately three-quarters of the soluble zinc is taken into solution. (2) The iron is oxidized and precipitated. (3) Gelatinous silica is coagulated by excess base and rendered granular. (4) The arsenic and antimony are completely precipitated. (5) Eighty percent of the copper is precipitated as hydioxide by excess base. This operation makes possible the cheap removal of most of the copper, and supplies the iron for removal of arsenic and antimony in the acid leach. (6) A large percentage of the zinc is separated from the residue and is contained in a clear settler overflow (along with 20% of the soluble copper and all the soluble cadmium), which goes to the purification plant. The settler spigot product containing three parts of solids and two parts of solution is elevated to the acid leach. The only heat used in the process is that supplied by the chemical reactions and electric current in the tank room.

The results of the acid-leaching system are as follows: (1) solution of the remainder of the acid-soluble zinc and copper, (2) final separation of the solids from the zinc and copper solutions, (3) roughing out the copper and chlorine, (4) solution of sufficient iron to guarantee removal of arsenic and antimony in the neutral leach step, and (5) elimination of the arsenic and antimony which are only partly redissolved in dilute acid. About 10% of the arsenic and antimony circulates in the acid thickener overflow.

Labor Requirements

Data on labor requirements in the leach were also unavailable. I would estimate, however, that approximately 80 man-shifts per 24-hr day are necessary, thereby making the labor cost approximately $1360.00 per day.
Removal of Impurities

Removing most of the impurities mentioned above as a part of the leaching operation is done by neutralizing the sulfuric acid and precipitating the impurities along with ferric hydroxide and ferric sulfate. Calcine is used for this purpose, but the operation must be carried out carefully; otherwise, there will be a serious loss of zinc in the residue as undissolved zinc oxide. If the calcine does not contain sufficient iron, it is necessary to add the calcine, as well as manganese dioxide, in order to oxidize all ferrous iron to ferric iron. The manganese dioxide for this purpose is recovered from the anode slimes of the electrolyzing department. The chemical reactions involved follow:

\[ 2\text{FeSO}_4 + 2\text{H}_2\text{SO}_4 + \text{MnO}_2 = \text{Fe}_2(\text{SO}_4)_3 + \text{MnSO}_4 + 2\text{H}_2\text{O} \]
\[ \text{Fe}_2(\text{SO}_4)_3 + 3\text{ZnO} + 3\text{H}_2\text{O} = 2\text{Fe(OH)}_3 + 3\text{ZnSO}_4 \]

From the reactions above it is apparent that all sulfuric acid combined with the iron is eventually used to dissolve zinc oxide, and the iron is precipitated as ferric hydroxide, which absorbs the arsenic and antimony or combines with them to form insoluble salts, thus completely removing these elements from the solution.

Thermodynamics of the Process

The main chemical reaction of the leaching process is

\[ \text{ZnO} + \text{H}_2\text{SO}_4 = \text{ZnSO}_4 + \text{H}_2\text{O} \]

Because of the sulfuric acid concentration used in this operation free energy data were unobtainable. The reaction can, however, be proved with the aid of heat content data.

Conclusion

Because of the large capacity of this plant, I believe the "double-leaching" operation as used is very suitable and cannot criticize the process.
The object of this department is to recover, electrolytically, pure zinc from the zinc sulfate solution received from the leaching department.

**General Data**

The Great Falls electrolyzing division is housed in a brick building 252 ft by 395 ft. Inside of this building are eight electrical circuits of 144 cells each, arranged in cascades of 6 and 7 cells each. The general data on this department are shown in the following table:

<table>
<thead>
<tr>
<th>Table No. 1</th>
</tr>
</thead>
</table>

**GENERAL DATA OF THE ZINC ELECTROLYZING DEPARTMENT**

<table>
<thead>
<tr>
<th>Electrolyte:</th>
<th>Anode spacing, in.</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sp. Gr.</td>
<td>1.25-1.30</td>
<td></td>
</tr>
<tr>
<td>Conc. Zn to cell in g/l</td>
<td>110-120</td>
<td></td>
</tr>
<tr>
<td>Conc. Zn from cell in g/l</td>
<td>45</td>
<td></td>
</tr>
<tr>
<td>H₂SO₄ cell discharge in g/l</td>
<td>100-110</td>
<td></td>
</tr>
<tr>
<td>Temp., °C</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>Feed to cells</td>
<td>Cascade &amp; Individual</td>
<td></td>
</tr>
<tr>
<td>Circulation, gal/min</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>Current:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Amp/sq ft</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>Voltage</td>
<td>3.7</td>
<td></td>
</tr>
<tr>
<td>Current Eff. %</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>Current, kw per generator</td>
<td>5,500</td>
<td></td>
</tr>
<tr>
<td>Kwhr/1b Zn</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>Anode: (comp)</td>
<td>Lead</td>
<td></td>
</tr>
<tr>
<td>Length, width, thickness</td>
<td>4.5&quot;x2.24&quot;x3/16&quot;</td>
<td></td>
</tr>
<tr>
<td>Weight (1b)</td>
<td>103</td>
<td></td>
</tr>
<tr>
<td>Mode of suspension</td>
<td>Cast around Cu header</td>
<td></td>
</tr>
<tr>
<td>Construction</td>
<td>Solid, cast</td>
<td></td>
</tr>
<tr>
<td>Life, years</td>
<td>Recast after 3 months</td>
<td></td>
</tr>
<tr>
<td>Cathode (comp)</td>
<td>Aluminum</td>
<td></td>
</tr>
<tr>
<td>Starting sheet, length</td>
<td>1/4&quot;x24&quot;x</td>
<td></td>
</tr>
<tr>
<td>width, thickness</td>
<td>3/16&quot;</td>
<td></td>
</tr>
<tr>
<td>Mode of suspension</td>
<td>Riveted to Cu header</td>
<td></td>
</tr>
<tr>
<td>Removed after (?) hrs</td>
<td>24</td>
<td></td>
</tr>
<tr>
<td>Weight (1b)</td>
<td>2 sheets, each 11</td>
<td></td>
</tr>
<tr>
<td>Deposition tanks:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Number</td>
<td>1,248</td>
<td></td>
</tr>
<tr>
<td>Length, width, depth</td>
<td>10'3&quot;x2'10&quot;x4'9&quot;</td>
<td></td>
</tr>
<tr>
<td>Number anodes, cathodes</td>
<td>33, 32</td>
<td></td>
</tr>
<tr>
<td>Materials of tank construction</td>
<td>Concrete, lead lined</td>
<td></td>
</tr>
<tr>
<td>Tank mud:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Composition</td>
<td>MnO₂</td>
<td></td>
</tr>
<tr>
<td>Amount</td>
<td>22 lb/ton feed</td>
<td></td>
</tr>
<tr>
<td>Removed after (?) weeks</td>
<td>13</td>
<td></td>
</tr>
</tbody>
</table>
Power Supply

Current for the electrolyzing department is received from the Zinc Plant Substation. This substation receives power at 100,000 v, this power being stepped down through nine 6100 kva, 3-phase, 60-cycle, oil-insulated, water-cooled transformers to 406 v, which in turn supply nine 5800 kw, synchronous rotary converters; each converting this alternating current to approximately 580 v, 10,000 amp d. c.. The capacity of the converters is augmented by 8 mercury-arc rectifiers, which also receive power from the 2 incoming 100,000 v lines, through 15,000 kva step-down transformers and their accompanying rectifiers, each of which delivers 3,000 amp d. c. to the tank room circuit, making a total of 13,000 amp d. c. on each of the 8 tank-room circuits.

Distribution and Electrolysis of the Zinc-Sulfate Solution

Zinc sulfate solution is distributed from storage tanks through 6-in. lead pipe lines to individual cascades of cells and is taken from header lines through iron pipes to the individual cells. The flow to each cell is so regulated to maintain a virtually constant acid and zinc concentration in each cell. The electrical resistance of the electrolyte is taken to determine the acid strength, readings so obtained being occasionally checked against a standard chemical test. The feed to the cells amounts to 6,000 tons of purified solution per day. This solution contains approximately 110 g Zn per liter, whereas the cell discharge averages about 105 g sulfuric acid per liter. Spent electrolyte is collected by a system of launders and delivered to storage tanks, from which solution is drawn as needed for the leach and purification residue re-treatment plant.

While zinc is being deposited in the cells, manganese dioxide is formed at the anodes and settles to the bottom of the tanks. This material is
Fig. 5. A View of the Zinc Plant Substation
removed from the tanks and reused in the leaching operation.

The cells are cooled by circulating water which passes through a lead coil placed in each cell. Cell temperatures vary from 37 to 41°C, dependant upon atmospheric and cooling water temperatures. From 8,000 to 15,000 gal of water per ton of cathode material produced are used for cooling purposes.

Labor Requirements

Data on labor requirements were unavailable. I would estimate, however, that approximately 1/40 man-shifts per 24-hr day are necessary, thereby making the labor cost roughly $2400 per day.

Metallurgical Discussion

This discussion will be limited to the effect of metallic impurities, hydrogen overvoltage, and sulfuric acid generation since these are the only reasonable factors which could influence zinc deposition.

1. Effect of Impurities

Antimony is most harmful, for even when 1 mg per liter is present in the electrolyte, sprouts develop on the cathode and current efficiency is lowered. The electrolyte should be so free from antimony that the element is not detectable. Arsenic and cobalt are nearly as dangerous, in that 1 mg per liter of arsenic causes rough deposits. As little as 1 mg per liter of cobalt produces corrosion holes in the deposited zinc; when larger amounts of cobalt are present, honeycombing develops. Copper up to 10 mg per liter has little effect. Larger amounts aid the formation of zinc holes and cathodic corrosion, as well as intensify the bad effect of any antimony or arsenic. The deposition of iron impurities is retarded, but the presence of iron in quantities greater than 20 to 30 mg per liter decreases the current efficiency due to the alternate oxidation of ferrous and reduction of ferric ions.
Lead is probably not harmful at the concentrations reached in zinc sulfate solutions, and cadmium does not affect the deposit unless present in concentrations greater than 500 mg per liter; but for the production of cadmium-free zinc the concentration should be below 50 mg per liter. By itself manganese is not harmful but appears to emphasize the bad effect of other impurities. It is deposited as MnO$_2$ on the anode, and its concentration in the electrolyte is best kept below 350 mg per liter. To allow the production of good cathodic deposits, metals more noble than zinc must be absent.

2. Effect of Hydrogen Overvoltage

Since the decomposition voltage of zinc sulfate solutions, at the concentrations commonly used in electrolysis, is 2.25 v and that of water, 1.70 v, it would apparently be impossible to deposit zinc on the cathode. Actually, the overvoltage of hydrogen on a rough zinc surface is of the order of 0.8 v, with the result that once a thin coating of zinc has been deposited on the aluminum surface the overvoltage abruptly rises, the evolution of hydrogen is prevented, and zinc is deposited at a fairly high current efficiency.

When hydrogen evolution, as the result of hydrogen ion deposition, becomes the major or an important part of the cathodic-deposition process, the electrolyte in the region of the cathode may become alkaline, and insoluble hydroxides of the metal ions may be precipitated. In many industrial processes, however, agents are added to the electrolyte to maintain the pH of the electrolyte. Information on whether a buffer is used in this process was unavailable.

3. Sulfuric Acid Generation

As stated previously, the zinc to be deposited in the tank room enters
the electrolytic cells as zinc sulfate, or to be more specific, zinc ions and sulfate ions. For each mole of zinc deposited, one mole of sulfate ion will be formed. This sulfate ion then releases two electrons and becomes a sulfate molecule. The mole of sulfate then is attracted toward the anode of the tank, where it liberates one oxygen atom to become a sulfite molecule. This sulfite molecule then reacts with the water in the solution to form sulfuric acid. The above may be represented by chemical equations as follows:

\[
\begin{align*}
\text{ZnSO}_4 & \rightarrow \text{Zn}^{\text{++}} + \text{SO}_4^{\text{--}} \\
\text{SO}_4^{\text{--}} & \rightarrow \text{SO}_4^{\text{--}} + 2e \\
\text{SO}_4^{\text{--}} & \rightarrow \text{SO}_3 + 0 \\
\text{SO}_3 + \text{H}_2\text{O} & \rightarrow \text{H}_2\text{SO}_4.
\end{align*}
\]

**Conclusion**

The electrolytic method of recovery, as used at Great Falls, appears to be fairly successful, although some room for improvement is still evident. Current efficiency is 90%, which, considering the position of zinc in the electromotive series, is good. At the present time, I do not feel qualified to discuss the subject of how current efficiency could be raised.

Working conditions are not the best in the tank room. Sulfuric-acid generation within the tanks produces many fumes. Workers must wear gauze masks over their noses and mouths to filter out these fumes. If breathed for long periods of time, the fumes can be injurious to the lungs. The fumes also attack clothing, decomposing it in a few days. The workers, however, receive compensation by a substantial clothing allowance from the Company.
Fig. 7. A View of the Zinc Casting Department
THE ZINC CASTING DEPARTMENT

The object of this department is not really of a metallurgical nature but consists simply of a melting and casting operation.

Scope of the Department

The zinc-casting building is a brick structure 140 ft by 150 ft. Cathodic zinc from the electrolytic tank room is brought here by means of small railroad flat cars, and melted and cast into various industrial shapes and sizes. The principal shapes cast are 50-lb slabs. The analysis of zinc shipped varies to meet customers’ requirements; and zinc is shipped under several brand names denoting the approximate purity — "Anaconda Electric", which is 99.994% zinc; "Anaconda High-Grade", and "Anaconda Intermediate", both of which are of lower grade.

The cathodic zinc is melted in one of four reverberatory furnaces fired with oil or natural gas and attaining a temperature of about 930°F. The zinc is cast from manually operated ladles carried by trolleys on overhead beams, and the cast zinc shapes are stacked on steel trays for subsequent pick-up by storage battery trucks, which take them to the storage docks for shipment.

Also, in this department, zinc dust is produced for use in the leach. Production is accomplished by blowing molten zinc with compressed air, thus atomizing the zinc.

Treatment of the Gases

The gases from the reverberatory furnaces are discharged through brick stacks into a steel flue, through which they pass to a baghouse just east of the casting building. The baghouse contains 96 woollen bags, each 30 ft long and 18 in. in diameter. The zinc-oxide fume in the gases is filtered out in
the bags and recovered for further treatment.

Labor Requirements

Labor requirement data were unavailable. However, I would estimate approximately 55 man-shifts per 24-hr day would be necessary, making the labor cost about $880 per day.

Summary

Since this is only a melting process and no chemical reactions are involved, very little discussion is deemed necessary. The only source of zinc loss is in the dross formed over the molten zinc in the furnaces. This dross is skimmed from the molten zinc, treated in rotating drums, and recharged to the roasting furnaces.

Conclusion

This department of the Zinc Plant operates very efficiently. There is little room for loss of zinc other than in dross. The dross has proved itself necessary, however, because without it, impurities in the molten zinc could not be collected and separated.

The item of waste heat again enters in this department as it did in the Roasting Department. I believe the heat could be recovered, but as in the previous case, how could it be utilized?
III. SUMMARY
The birth of this plant in 1916 gave rise to a totally new industry — zinc production by electrolysis — thus turning many other corporations to this type of zinc recovery. Zinc recovery by retorting is still widely employed in the eastern United States, but here in the west, where hydro-electric power is cheap, this process is indispensable.

The Anaconda Company has produced and marketed zinc for the general public in peace time, and during time of war has geared its industrial machinery to produce products vitally needed on the war-fronts, zinc being one of these products.

Today, the Great Falls Zinc Plant is the largest zinc producer in the world. The plant capacity approaches 1,000,000 lb of zinc per 24-hr day. The author believes that as long as this plant continues its fabulous production, everyone will live a better life: the miner, the plant worker, the industrial engineer, the white-collar boss, and last, but not least, the general public, which uses zinc daily for varied purposes.

SUMMARY
IV. APPENDIX
Fig. 8. A Detailed Flow Sheet of the Plant
BIBLIOGRAPHY


