A study of a certain filled-sink ore deposit

Azmon Thurman Dunham

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A STUDY OF A CERTAIN FILLED-SINK ORE DEPOSIT.

BY

AZMON THURMAN DUNHAM

A

THESIS

submitted to the faculty of the
SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI
in partial fulfillment of the work required for the
Degree of
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1916.

Approved by

Professor of Geology and Mineralogy.

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HISTORY.

This mine, which is located about 3-1/2 miles southeast of Sullivan in the extreme northeast corner of Crawford County, Mo., was first known as the Sullivan and Bridell Mine of the old Hamilton Iron Company. It has been operated discontinuously since about 1870. Until 1904 it was worked solely as an iron mine, but at that time development work for copper was started, and from 1905 to 1909 the mine treated only this metal. It is not known how many pounds of copper the mine has produced, but during one 20 day run in 1904 of which there is record, there were produced 22,500 pounds of copper, and the mine has been producing irregularly ever since this date.

STRATIGRAPHY.

The stratigraphy, as indicated by surface outcrops, is identical with that of the general Ozark uplift. In the vicinity of the mine there are only two formations outcropping, the Roubidoux sandstone and, beneath it, the Gasconade dolomite, although Carboniferous rocks occur caping the hills and as fillings in the center of some of the sinks in the near vicinity. The stratigraphy as given for the district by the Missouri Bureau of Geology and Mines is as follows;
Carboniferous

Pennsylvanian

Ordovician

Joachim Limestone.
St Peter Sandstone.

Jefferson City Dolomite.
Roubidoux Sandstone.
Gasconade Limestone.

Cambrian

Elvins Formation.
Acadian.

Archean

Granites and Porphyry
STRUCTURE.

The mine is situated upon the northern side of the Ozark Dome, consequently the formations have a very gentle general dip in a north-eastly direction. The folding within the district is very slight and can only be detected by very careful determination of the elevation of the outcrops of the various formations. In most cases the dips are too low to be determined by the ordinary field methods.

While there have been no faults found in the immediate vicinity of the mine, there are observed cases to the north and east. These are of small displacement and can be traced only a short distance by means of surface outcrops.

The most pronounced structure of the mine, and the one of prime importance, is the typical Ozark sink structure, of which this is one of the largest known examples. As in a great many cases, because of its position near the river, erosion has removed most of the surrounding and overlying rocks so that what was originally the filled sink is in reality a hill. Following is a sketch showing its probable extent and structure.
ORES AND THEIR OCCURRENCE

Iron Ore.- There are three ores of iron present in considerable quantities, the most abundant of which is red hematite. This grades from a soft clay-like ore into one that is hard and porous. It is seldom compact and close-grained, and sometimes shows decided stratification and many pseudomorphic structures after marcasite and pyrite. No exact analysis of the different grades of ore are obtainable, but this ore seems to be too high in silica to be of commercial value, as it is often grades into a highly ferruginous chert.

The best ore is a blue hematite which is rather compact and usually low in silicious matter. While
it sometimes occurs pseudomorphous after marcasite and pyrite, it is low enough in sulphur and other impurities to be a good commercial ore. As mined, the blue hematite is mixed with the red hematite.

Next in the order of importance of the iron ores is limonite. It also grades from clay to porous ore and is usually mixed with varying amounts of clay and silica, so that it does not make a high grade ore. /

Copper Ores.- There have been observed three copper minerals. Others may be present but only in very small quantities. Malachite is the most abundant, occurring as rounded accretions in the clay and soft iron ores where it is also found abundantly along the bedding planes and fractures in the red hematite. There is hardly any part of the ore body in which malachite does not occur, extending even to within four feet of the present surface.

The presence of azurite is usually limited to the bedding planes and fractures in the more compacted iron ores. It is but seldom found in the soft ores and clays.

In the deeper part of the mine and in large masses of unaltered iron sulphides, there are sometimes found black sulphides of copper which probably contain some
chalcopyrite. No analyses have been made on these ores.

Gangue Minerals.- Clay is the most abundant gangue material, and is found in all parts of the ore body. Boulders of silicious gangue and pieces of Roubidoux sandstone are found throughout most of the mine. One of the most peculiar occurrences is that of barite crystals coated with or included in crystals of calcite, both occurring usually as concretions in clay. Small, tabular and slender crystals of selenite are to be found by washing any of the loose material.

ORIGIN.

In discussing the origin of the ores it will be necessary to consider the formation of the filled sink structures in which they occur. These structures in most cases date from pre-Pennsylvanian time, and there is good evidence that this particular sink was at least partly formed previous to that period. This was an unusually large sink and appears to have had several openings to the surface during the course of its formation. In each one of these filled openings are to be found stratified ferruginous sands, sandstones, organic shales and clays that have all the earmarks of the Pennsylvanian rocks that have been
found in the district. The sand grains are very much rounded and water worn and very slightly cemented.

During pre-Pennsylvanian times when erosion had reached the Roubidoux sandstone in places, the surface waters in seeking a downward course were concentrated along the comparatively impervious surface of the Gasconade. Where these waters encountered a fracture in the dolomite which was readily soluble they soon formed solution channel or cave-like opening. Where there was an unusual concentration of the surface water that flowed into the opening, a large amount of solution was possible, and, since the water at the point where it entered the dolomite had a greater dissolving power than elsewhere, due to the contained CO₂, the solution was greatest there. This resulted in the formation of a great opening with one or more smaller channels leading away from it. If the overlying sandstone was strong enough, it formed a natural arch and the enormous cavern thus formed was left open except for a debris cone directly beneath the point at which the water entered. But if the roof would not support the load, it slumped with the solution of the limestone beneath, thus forming a sink open to the surface.

This much of this work, it is believed, was
completed in pro-Pennsylvanian times. The Pennsylvanian series, containing unusual amounts of iron and some copper, lead, and zinc as sulphides, was then laid down.

It will be seen that the theory of origin connects closely with the present theory of the origin of the South-east Missouri Lead district and the South-west Missouri Zinc district.

During the erosion of the Pennsylvanian rocks which now formed the surface, either because the channels of outlet of the sink were stopped up or because the sink was below the ground-water level, it was filled with water not free to circulation. The iron and copper—being the most readily soluble constituents of the overlying rocks, were taken into solution, carried downward and deposited as sulphides in the caves and sinks. The carrying of these sulphides and their depositors is a problem that is worthy of a great deal of investigation, but is without the scope of this article.

As erosion brought these sulphides nearer and nearer the surface, the action of meteoric water oxidized them forming oxides of the iron and carbonates of the copper. The sulphides of copper seem to have been pretty well disseminated through the body of sulphides, for now the copper is found in practically
all parts of the ore body. The presence of copper carbonate within large masses of quite compact hematite suggests that it was originally within the same body and weathered in place.

It seems unusual that the copper should remain within the mass of iron ore from which it was weathered, for in the oxidation of pyrite and marcasite sulphuric acid is usually set free. It would seem more likely that the copper would be carried away as the soluble sulphate instead of being left as carbonate. This would suggest the possibility of the deposition of the copper being subsequent to the alteration of the iron sulphide. However, this may be explained by assuming that the CO₂ of the copper carbonate came from the limestone, instead of the downward moving ground water. The following reaction is suggested.

$$2\text{CuSO}_4 + 2\text{CaCO}_3 + 5\text{H}_2\text{O} = 2(\text{CaSO}_4 \cdot 2\text{H}_2\text{O}) + \text{Cu}_2\text{CO}_3 \cdot \text{H}_2\text{O} + \text{CO}_2$$

Calcium sulphate is found in small crystals all through the deposit. It is said by those who have done some former drifting in the mine that the largest occurrences of copper carbonate have been found near the contact with limestone masses.

There is evidence to show that the deposit is being slowly carried downward even yet. At present a shaft being sunk in the mine has passed through the iron
oxides and copper carbonates and into the dolomite below. Just before the dolomite was encountered, large masses of partly altered pyrite were found. They were unattached crystals and had the appearance of having been weathered from the dolomite. Still lower and within the weathered dolomite more pyrite was found which was less altered. In the deepest part of the shaft where the dolomite was only weathered along small fractures, unaltered pyrite was found.

From this it would seem that the iron is yet being taken into solution above and deposited in the dolomite below. It would also seem that the pyrite was carried and deposited as a sulphide, for if it were carried and deposited as a sulphate the sulphuric acid that was liberated on the formation of the sulphate would dissolve the dolomite and leave a very abundant deposit of gypsum. As a matter of fact gypsum is found, but not in sufficient quantities to account for the deposition of any great amount of the sulphuric acid consequent to the formation of iron oxides from such a mass of sulphides. It would seem probable, then, that the iron was carried and deposited as the sulphide, and the dolomite was dissolved and carried away mainly by the rain water containing very
little sulphuric acid. This would leave the pyrite to be oxidized when erosion had gone deeper and most of the dolomite had been carried away by ground water. The sulphuric acid then set free would not be so active in forming gypsum from the dolomite.

A LEACHING EXPERIMENT ON THE COPPER ORE.

The purpose of this experiment was to determine the amenability of the copper ore to treatment by leaching methods with sulphuric acid.

The ore procured was, as nearly as possible, a sample of the ore just as it came from the steam shovel with which it was mined. The work done on a fifty-pound sample that assayed 4.8 per cent copper and 27.5 per cent iron. This sample was dried and cut into two samples. One lot was crushed through a 1/4 inch mesh screen, while the other was ground through a 20 mesh. The first lot was concentrated to 13 pounds, assaying 7.44 percent, by washing the clay out in tubs.

For the purpose of determining how much acid was needed to effect ready solution of the copper, the same volume of various strength acids was used on equal amounts of ore. Next the effect of different volumes of solvent was determined by using varying amounts of the same strength solution. On the following page is a table showing the results obtained.
<table>
<thead>
<tr>
<th>No. of sample</th>
<th>Wt. of sample</th>
<th>Amount of solution</th>
<th>Strength of solution</th>
<th>% copper in residue</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>29.166</td>
<td>100 cc.</td>
<td>1% H₂SO₄</td>
<td>1.6% Cu.</td>
</tr>
<tr>
<td>2</td>
<td>&quot;</td>
<td>2% &quot;</td>
<td>.40% &quot;</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>&quot;</td>
<td>4% &quot;</td>
<td>.30% &quot;</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>&quot;</td>
<td>6% &quot;</td>
<td>.20% &quot;</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>&quot;</td>
<td>10% &quot;</td>
<td>.01% &quot;</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>&quot;</td>
<td>50 cc.</td>
<td>8% &quot;</td>
<td>no copper</td>
</tr>
<tr>
<td>7</td>
<td>&quot;</td>
<td>75 &quot;</td>
<td>&quot;</td>
<td>trace</td>
</tr>
<tr>
<td>8</td>
<td>&quot;</td>
<td>100 &quot;</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>&quot;</td>
<td>125 &quot;</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>&quot;</td>
<td>150 &quot;</td>
<td>&quot;</td>
<td>.05% Cu.</td>
</tr>
<tr>
<td>11</td>
<td>&quot;</td>
<td>200 &quot;</td>
<td>&quot;</td>
<td>trace</td>
</tr>
</tbody>
</table>

From these experiments it would seem that 100 (or less) cc. of 8% sulphuric acid was the best solvent for the copper. In these cases the time was not considered and they were agitated freely in a beaker.

In order to determine the speed of leaching, amount of acid needed, and percentage of extraction in a somewhat practical manner, small leaching vats were arranged according to the following diagram.
LEACHING SOLUTION TANK.

Cock for regulating flow of solution.

Leaching tank.

Rich solution tank
The above arrangement secured a continuous upward circulation of the solution which prevented packing and insured an intimate contact with every particle of the ore. Four runs were made, the results of which are shown in the following table.

On the first run an attempt was made to continue passing fresh solution through until all of the copper was dissolved. When it seemed that action had ceased the solution was drawn off and the ore was washed, but it was found that much of the ore was still undissolved, so the work was continued. Of course this run used entirely too much acid, 10 percent by volume.

In the second run the wash water from the previous run was used often having been acidified to the proper strength. By this means no dilute solutions were obtained. The same acid solution was passed through the ore twice, the leaching extending over a period of three days. In this case a 10 percent by weight solution was used. Again the amount of acid used was too high, but the extraction was excellent. In the third run an attempt was made to remove the copper by a large amount of weak solution passed through very slowly. The results were poor, only 55 percent of the copper content being taken into solution.
The last run showed good results. With a consumption of 343 pounds of acid per ton a 99.18 percent extraction was obtained. In this case the solution was passed several times through the ore over a period of six days. By so doing the total volume of rich solution and wash-water was kept below two liters. This made a good concentrated solution suitable for the precipitation of the copper.

When sufficient acid was used to combine with the copper, the principal thing seemed the element of time. By using a higher concentration of acid the copper was readily removed in a shorter time, but it would be too expensive. By sacrificing the percentage of extraction the solution could be materially hastened without increasing the acid. It is to be doubted if such an extraction as 99.1+ percent would ever be profitable. The difference in time would not justify it.

In the experiment the exact amount of acid consumed in the solution of the copper was not determined, for it was the purpose of the writer to consider only the electrolytic precipitation of the copper. In this case most of the acid would be regenerated and could be used again.
Commercial Possibilities of the Process.- Until further prospecting is done to determine the exact extent of the ore-body it would be impossible to say whether or not it would be justifiable to build a leaching plant. But from the nature of the ore and ease of access alone, it seems to be a good risk.

The ore-body is in a hill, the lower limit of the ore reaching just to the level of the surface at its foot and the upper limit being just a few feet below the surface at its top. The conditions are ideal for open-cut, steam-shovel methods of mining. The ground requires no blasting. The cost, therefore, of handling the ore would be very small and could be regulated still further by the capacity of the equipment.

Concentration of the ore could be accomplished very cheaply by simply log-washing, or by any method of washing to remove the clay. The removal of clay aids solution and filtration very materially.

Solution could be easily and cheaply accomplished in wooden vats with acid-proof circulating pumps. The number and capacity of these vats would be determined by the size of the plant, but it would probably require five or six for continuous operation, with one steam shovel.

The chief item of cost in the building of a plant
for this property would be an electrolytic precipitation department, unless it would be practical to obtain an electric current from St. Louis. At the present price of sulphuric acid and high grade copper, it would be unfeasable to precipitate the copper by means of iron.

On the whole, the conditions are very favorable at this property for cheap production of copper, but until further prospecting is done and the size of plant determined, even a close estimate of the cost of production per pound of copper could not be made.

**PROBABLE COST PER POUND OF PRODUCING COPPER ELECTROLITICALLY.**

The following calculations are based on a plant with a capacity of 2,000 pounds of copper per day, or one handling approximately 20 tons of ore per day.

Cost per pound.

\[ \begin{align*}
0.0015 & \quad \text{handling of ore by steam shovel.} \\
0.0100 & \quad \text{crushing and washing ore.} \\
0.0150 & \quad \text{leaching.} \\
0.0460 & \quad \text{electrolytic precipitation.} \\
0.0075 & \quad \text{labor.} \\
\hline
0.0700 & \\
\end{align*} \]

The cost of electric current is based upon

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calculations made on the cost of current in a 150 horse power plant at Hamilton, Mo. This cost was 3.83 cents per kilowatt hour. It takes about one ampere to precipitate 1 oz. copper. Assuming that the voltage drop across each cell is about 3 volts with a 10 volt dynamic, we have the following calculation:

\[
1 \text{ ampere day} = 1 \times 3600 \times 24 \text{ amp. for 24 hrs.} \\
\]

\[
\text{The number of kilowatts per 1 oz. copper} = \frac{3 \text{ Volts} \times 3600 \times 24}{1000} \\
\]

Then the number of kilowatts hours per 1 oz. copper

\[
= \frac{3 \text{ Volts} \times 3600 \times 24}{1000 \times 3600} \\
\]

\[
= .072 \times 10 \times 3.83 = 4.5+ \text{ cents per pound.} \\
\]

This figure is probably considerably too low due to not considering varying drop across the cells and loss of current through the presence of iron in the solution. It would not be amiss to double this figure.

The cost of leaching is based on costs at Butte where the percentage of iron and soluble gangue is low. The present abnormal price of sulphuric acid and the high soluble matter would probably double this figure. Also no account was taken of interest on the investment and cost of repairs, so with these revision, the cost would be nearer the following estimate.
$0.0015 - Handling of ore with steam shovel.

$0.0010 - Crushing and washing.

$0.0300 - Leaching.

$0.0900 - Electolytic precipitation.

$0.0075 - Labor.

$0.0050 - Interest on investment.

$0.1350

Therefore it would appear that at the present price of copper this property could be worked at a good profit.
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<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>1000 gms.</td>
<td>275 cc.</td>
<td>1016 lbs.</td>
<td>2225 cc</td>
<td>2500 cc</td>
<td>20.55 gm/l.</td>
<td>2000 cc</td>
<td>900 gms.</td>
<td>.6 32.65 oz.</td>
<td>99.27</td>
</tr>
<tr>
<td>32 oz. 7.5 oz.</td>
<td>468 Used wash</td>
<td>2000 cc</td>
<td>32.25 gm/l.</td>
<td>-</td>
<td>27-1/4 oz.</td>
<td>8.2 31.6 oz.</td>
<td>99.08</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>from leach No.1</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>32 oz. 4.5 oz.</td>
<td>281 cc.</td>
<td>2500 cc</td>
<td>20.55 gm/l.</td>
<td>2000 cc</td>
<td>1.41 gm/l. oz.</td>
<td>3.46 32.1 oz.</td>
<td>55.78</td>
<td></td>
<td></td>
</tr>
<tr>
<td>32 oz. 5.5 oz.</td>
<td>343 cc.</td>
<td>1000 cc</td>
<td>-</td>
<td>1000 cc</td>
<td>27-3/4 oz.</td>
<td>7.1 27.5 oz.</td>
<td>99.18</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

7.44% ore through 1/4" mesh.