THE ELECTROLYTIC RECOVERY OF LEAD FROM BRINE LEACHES

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by

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-:INTRODUCTION AND HISTORY:-

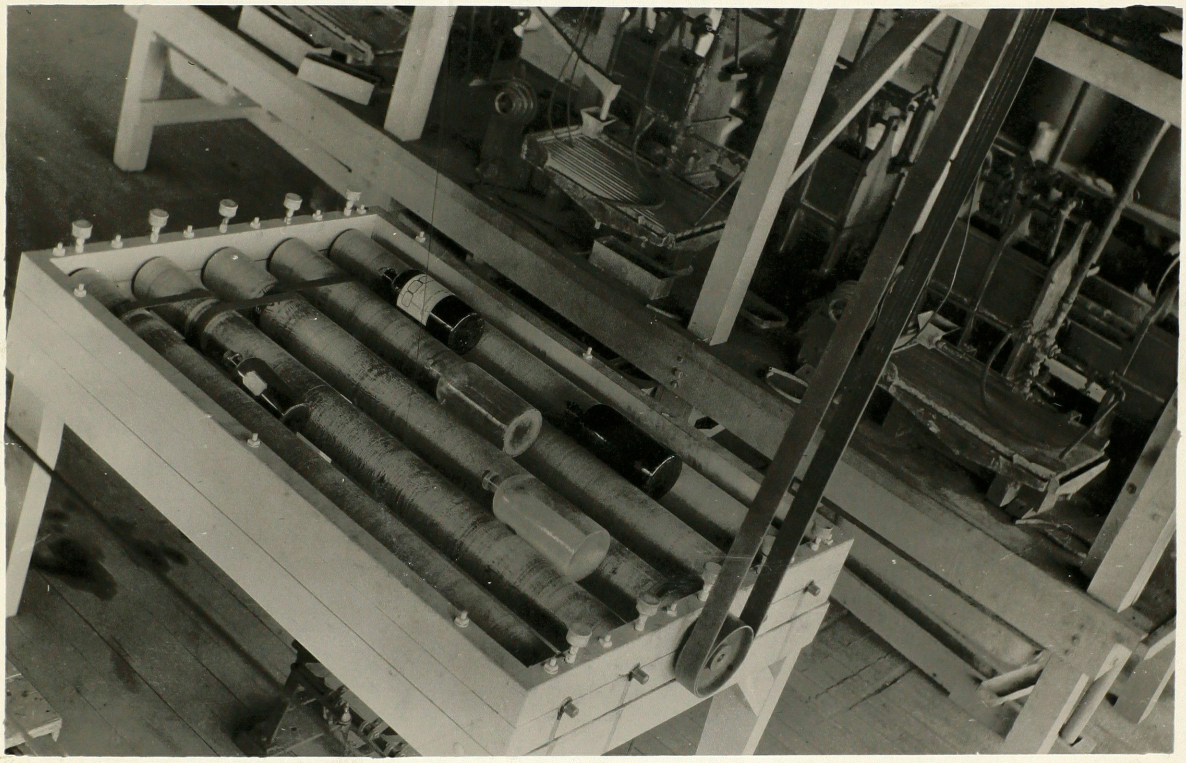
The knowledge that lead sulphate and lead chloride are soluble in a strong brine solution and that lead may be recovered from such a solution by electrolysis, is not new, although certainly not widespread. In fact as long ago as 1854 M. M. Bequerel of Paris reported in Comptes rendus 38: 1095 (1854), of work he had done on lead leaching and electrolysis. In all he treated about 20,000 lb. of ore mostly from South American and Mexican sources. His mthod of procedure was to give the ore a sulphatizing roast in the presence of salt and leach out the lead sulphate and silver chloride with saturated brine. The brine was then electrolysed to recover the metals. The principles of his process are practically identical with those of the work described in the following pages. However, Bequerel could never have made his process commercially practical because of the then existing commercial conditions, which are much changed now. For instance, he obtained his current from the only source he knew of, namely the primary cell.

H. R. Ellis claims to have developed in 1892, a process for leaching oxidized ores of lead with a hot (but not saturated) brine containing some copper sulphate. Mr. Theo. P. Holt at the mill of the Mines Operating Co. at Park City found that on giving his ore a chloridizing roast and leaching with a 20 % brine solution, that lead built up in the solution to about 8 lb. per ton. At the Bunker Hill and Sullivan mill at Kellogg Idaho, lead sulphide ore which has resisted concentration, has been given a chloridizing roast and leached with brine.

But since Bequerel did his work the first (to our Knowledge) to conceive of recovering lead from the brine by electrolysis was Neil C. Christensen working in the Knight-Christensen mill at Silver City. He had been rather successful in recovering it on a laboratory scale and was taking steps to enlarge his experimental plant when the mill burned down.

The following work as described was carried out in the Metallurgical laboratories of the University of Utah in co-operation with the U. S. Bureau of Mines. The University of Utah faculty include Jos. F. Merrill, director of the School of Mines; R. H. Bradford, Professor of Metallurgy; Robt. S. Lewis, Professor of Mining. The Bureau of Mines staff includes Dorsey A. Lyon, Metallurgist in Charge; O. C. Ralston, Assistant Metallurgist, and Jos. F. Cullen, chemist. To these men and also to Mr. Christensen much credit is due for timely suggestions which were gratefully received.

Although as has already been intimated no claim is made that any part of this work is fundamentally new, still it is hoped that it does possess some elements of originality.



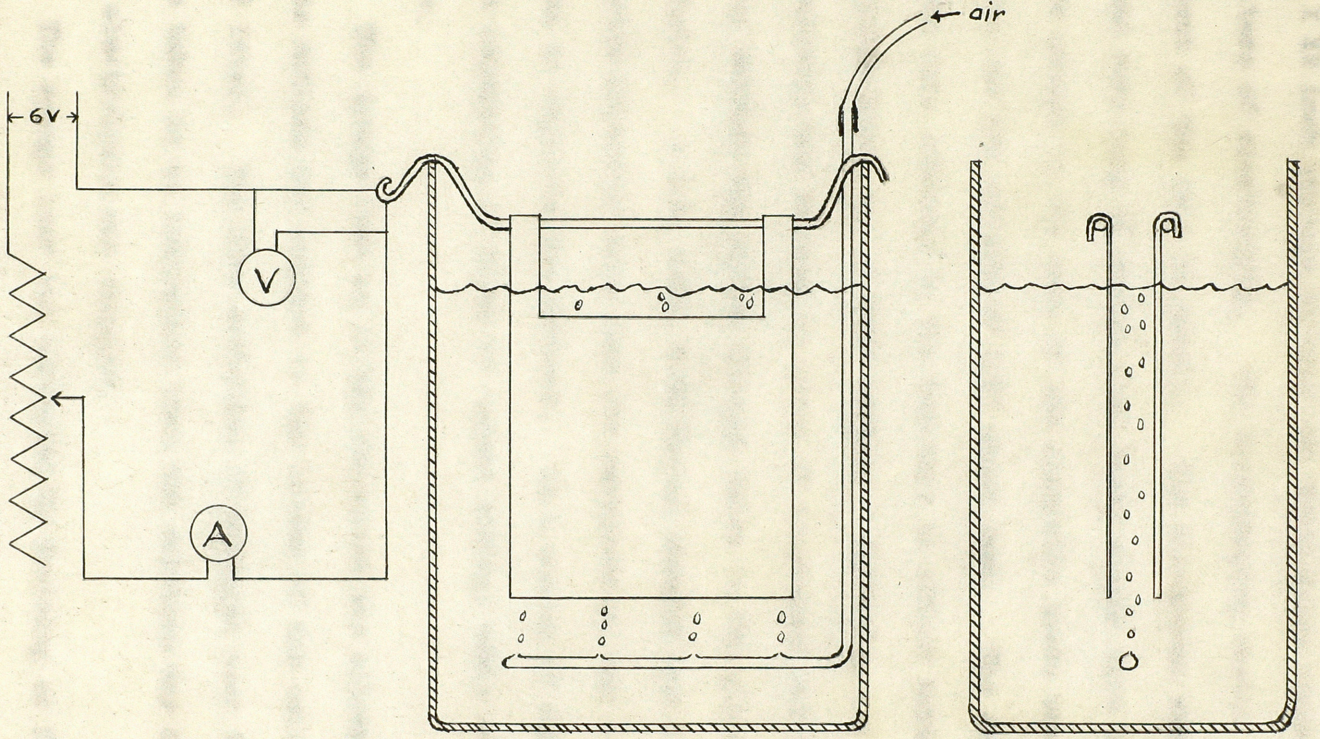
Agitation rolls used in the leaching of the lead ores. These rolls give a large capacity in a small space and give very efficient agitation.

-:METHOD OF EXPERIMENTAL PROCEDURE:-

Leaching. The leaching was done in two-liter acid bottles. Four bottles were used, eight liters of solution being required in all of the runs. The ore and brine were put together in the bottles with enough sulphuric acid to convert all of the lead to sulphate of lead. The bottles were then tightly stoppered and agitated on the rolls, usually from 2 to 5 hours, although at times leaches were allowed to run over night. The type of agitating rolls that were used are shown in the accompanying print. When small amounts of CO_2 were formed due to the action of the acid the stoppers were removed from time to time to relieve the gas pressure. But in ores containing large amounts of carbonate just enough brine was put in with the ore sothat it would not run out of the bottle when lying on its side unstoppered. Then acid was put in and it was filled with saturated brine and put back on the rolls for leaching.

The filtering was done in an eight inch Büchner funnel, using a water suction pump. After the pulp had been drained as thoroughly as possible by this means it was washed with barren brine and then with water. The wash with brine must be given first in order to prevent the reprecipitation of the lead in the ore, because the pregnant brine on being diluted with water precipitates lead

EXPERIMENTAL ELECTROLYTIC CELL.



Side View. End View.

chloride. The water wash is to recover the salt in the ore.

Electrolysis. The electrolysis was carried out in a 6.5 X 9 X 12 inch storage battery jar which holds conveniently eight liters of electrolyte. The accompanying sketch shows the arrangement of the cell in detail. The electrodes were six inches square and were hung by strips over heavy copper wire bus-bars. The anode except in the case of the insoluble anode was of 1/16" sheet iron and the cathode of 1/8" sheet lead. The cathode and anode both were soldered to the bus-bars to afford better connection. The insoluble anode was of 3/8" carbon. Agitation and circulation of the solution was secured by means of compressed air which was bubbled up between the plates through holes in the glass tube shown in the sketch. A 0-3, 0-15, 0-30 Weston ammeter and a 0-3, 0-15, 0-150 Weston voltmeter were used for measurments, and a slide wire resistance to regulate the current. As a source of current two batteries consisting of three 15 ampere storage cells each, were available.

The sponge lead as it was deposited was allowed to drop off of the cathode and collect in the bottom of the cell to be recovered later. The free evolution of hydrogen near the end of a run was taken as an indication that the solution was depleted of lead and electrolysis was stopped.

The sponge lead was collected by draining or filtering off the solution in a small Büchner funnel. While in the funnel it was washed several times, sometimes with hot water, and at times a little acid was added to the first wash. The sponge was then pressed to remove most of the water, after which it was quickly dried on the hot plate. In melting it down to solid lead it was placed in a fire-clay or iron crucible with a light cover of charcoal (to keep a reducing atmosphere) and heated over a gas flame or in a muffle. Samples of the electrolyte were taken with a pipette while the electrolyte was being agitated. Lead analyses were run by the chromate method according to Low's Ore Analysis. Iron was determined by permanganate titration, both zinc and stannous chloride being used at different times for reduction. Zinc was determined by titration with ferrocyanide. Sulphur was run gravimetrically by precipitation as barium sulphate.

-:EFFECT OF CYCLIC RUNS:-

On chlorine content. The series of cyclic runs were started out with eight liters of saturated brine. After agitation with ore it was filtered off pregnant with lead, and was then electrolysed until nearly depleted of lead, when it was run back onto fresh ore for another leach, completing one cycle. Enough fresh brine was added each cycle to replace that lost by evaporation etc., and to keep the volume of solution up to eight liters.

Continuing in this manner it was found that the lead tenor in each succeeding leach was becoming smaller. When some solid salt was put in with the ore at the beginning of the leach, the lead tenor was again raised. Now it is a well known fact that as a saturated brine is diluted its solvent power for lead is decreased rapidly. These two facts apparently prove that the chlorine content (meaning of course, chlorine present as chloride) is lowered somewhat. Some of this chlorine perhaps was precipitated out in the ore along with iron as a basic ferric chloride. But it is more probable that by far the largest part of it was occluded and held mechanically by the ore. This view is strengthened by the observed fact that it is exceedingly difficult and almost impossible to wash a sample of ore tailings free of chlorine; that is, so that the wash water will not give a test for chlorine with silver nitrate. However, if the tailings are well washed, the loss of salt by this means will not be a serious detriment to the process.

Iron builds up slowly in the solution with each cycle until it reaches the neighborhood of 1.5 % when it seems to approach equilibrium. As an amount of iron equivalent to the amount of lead precipitated enters the solution during each electrolysis, then iron must also be thrown out of solution during each cycle. Analysis before and after a leach shows that it is left in the ore. As the leaching solution, although started acid, becomes neutral before the end of each agitation with ore, the iron is probably hydrolysed to either the hydroxide or to a basic chloride. At the end of an electrolysis most of the iron is present as ferrous iron and it is obviously only the ferric iron which is precipitated. However, it is possible in a neutral solution for the ferrous chloride to oxidize to a basic ferric chloride.

When zinc is present in soluble form in the ore it goes into the solution to a small extent. While zinc sulphate is known to be soluble up to at least 10 % of zinc in brine solution, still in the cycles run the zinc always remained below 1 %.

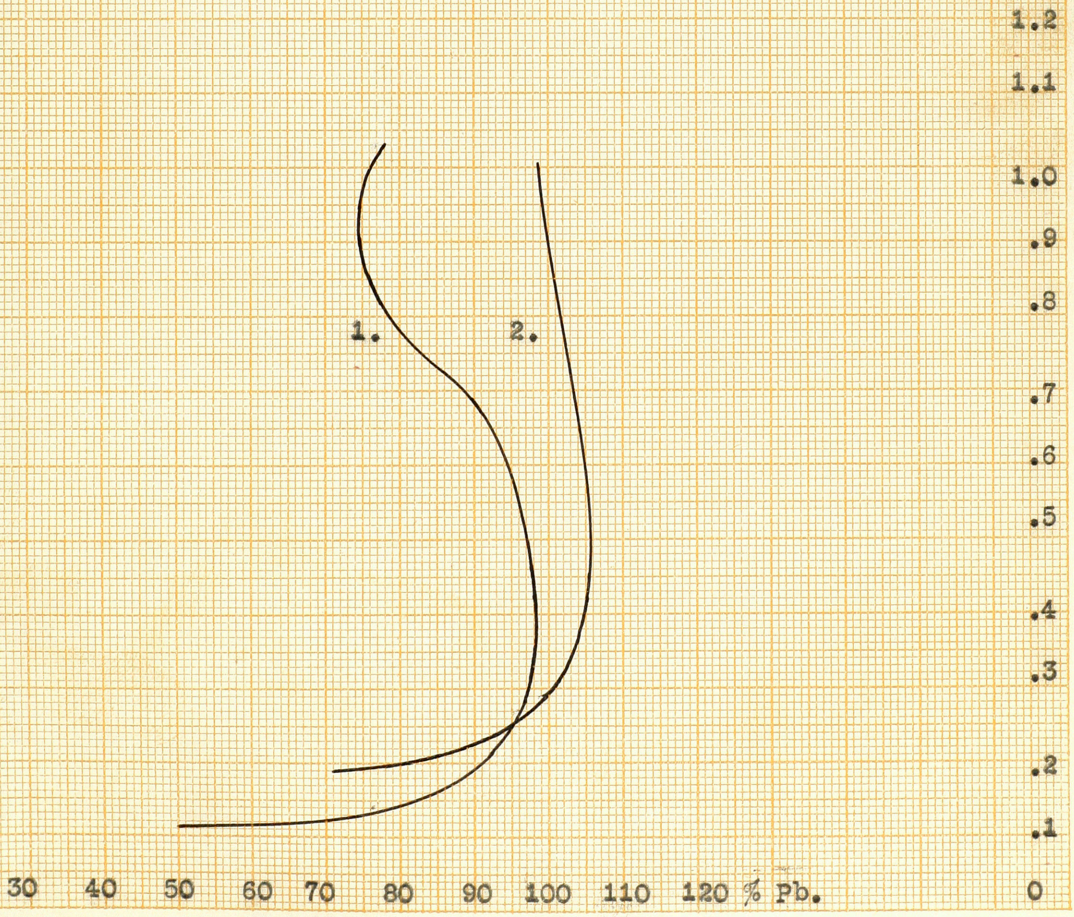
Sulphate builds up slowly and steadily at first. The sulphur of course, is present as sodium sulphate formed by the double decomposition of the salt and the lead sulphate when the latter goes into solution. Sodium sulphate is only slightly soluble in saturated brine, however, and readily crystallizes out when present in anamount equivalent to 1 % of sulphur. Different

SET OF CURVES No. 2.

Showing the relation between the curves obtained from pure and impure electrolytes.

Abscissae, cathode efficiency in %, Ordinates, concentration of Pb.

No. 1. Curve obtained from impure electrolyte.
No. 2. " " " pure "



from other impurities, sodium sulphate is desirable in that it increases the solubility of lead sulphate in brine. The solution of salt and sodium sulphate having the maximum solubility for lead contains about 0.6 % sulphur.

Aside from the effect of the sodium sulphate the solubility of lead in the brine is unaffected by cyclic runs except by lowering the chlorine content as described above.

The cathode efficiency is slightly higher in new brine solution than after the impurities have built up in it. The difference between the cathode efficiency in an old and a new brine is shown in the set of curves No. 2. The cause for the dropping off in the efficiency was not definitely determined, although the iron is probably the chief offender, being oxidized from ferrous to ferric iron at the anode, and reduced to ferrous at the cathode. A search for other causes yielded no results.

SET OF CURVES No. 1.

Showing the relation between cathode efficiency and concentration of lead in the electrolyte at different current densities.

Abscissae, efficiency in percent. Ordinates, concentration of Pb.

Curve No. 1. At a current density of 80 amperes per sq. ft.
" " 2. " " " " " 60 " " " "
" " 3. " " " " " 40 " " " "
" " 4. " " " " " 20 " " " "

-:GENERAL RESULTS:-

The saturated brine after agitation with ore contained from 1.0 % to 1.4 % lead. With proper amounts of ore and brine and enough acid to convert the lead carbonate or oxide to sulphate the pregnant brine will average 1.25 % lead. Under these conditions nearly all of the lead, that is, lead in an oxidized form, will be extracted. A typical example is as follows: Starting with an ore containing 8.68 % Pb with one leach 71 % of the lead was extracted. Then by giving these tailings anotherleach with barren brine a 95 % extraction was obtained. Counter current leaching should always make a 95 % extraction of lead.

Considering the very low concentration of lead in the electrolyte, the current densities it was possible to use, were surprisingly large. That these current densities were not excessive is shown by the fact that with a current density of 80 amperes per sq. ft. and a lead concentration of .4 to .6 %, a cathode efficiency of 80 % was possible; with a current density of 60 amperes per sq.ft. and a lead concentration of 1 %, a cathode efficiency of approximately 100 % was obtained. Set of curves No. 1 gives the relation between lead concentration and cathode efficiency for four different current densities. When the current density reaches much above 60 amperes per sq. ft.

a great deal of hydrogen is evolved from the cathode. Hydrogen is also evolved at lower current densities when the lead tenor of the electrolyte becomes very low.

Interpreting the set of curves No. 1, evidently the best current density to start an electrolysis is 60 amperes per sq. ft. This should be maintained until the lead tenor falls to about .7 % and then it should be dropped 40 amperes per sq. ft. When .3 % of lead is reached the current density should be dropped to 20 amperes per sq. ft., and electrolysis stopped when the lead content falls to .1 %. The cathode efficiency will vary in two different runs having the conditions as nearly alike as possible. One unexplained phenomenon is that the cathode efficiency was always lower at the beginning of an electrolysis than it was a little later in the run. This was also true if the electrolysis was stopped in the middle of a run and started again after an interval of time. It was thought at first that the ferric iron being reduced to ferrous iron at the beginning of the run was the cause of the low efficiency at the start, but it was found that the same thing occurred when no iron was present in the electrolyte. The cathode efficienies on the whole are encouragingly high. In fact during the greater part of most of the runs in which 40 amperes per sq. ft. or less were used the cathode efficiency was somewhat over 100 %., averaging about 104 %. These results may have been due to errors, but the work was carefully done, time measurements and current measurements being accurate and check samples being taken for analysis in each case. These results, therefore, compare very favorably with those obtained by Norman M. Bell who found monovalent lead dissolving from a lead anode during an electrolysis. (See Trans. Faraday Soc. 11: 79-90, 1915).

The voltage is very low, the average voltage for different current densities being as follows:

Curr. den. Amp./sq. ft.	Voltage
80	1.2
60	1.0
40	0.7
20	0.5

The cause of the low voltage is evident. The solution tension for iron is .42 volts and that of lead .12 volts as compared with 0.0 for hydrogen. Therefore, the anodic solution of the iron gives more energy than is necessary to precipitate lead cathodically. In fact there is an initial voltage of .1 volt across the electrolytic cell before the external voltage is impressed. As no gas is formed there is no overvoltage. Therefore, the impressed voltage is needed only to overcome the resistance of the electrolyte.

Owing to the high cathode efficiency, low voltage, and high electrochemical equivalent of lead the power consumption per lb. of lead is very low. With a current density of 20 amperes per sq.ft., which means a voltage of .5 volts and a cathode efficiency of 100 %, as much as 17 pounds of lead per K.W.H. may be produced. This value is not even approached in the electrolysis of any other metal.

Five electrodes were connected in series the same as in the copper series copper refining process, that is, the intermediate electrodes served as both anode and cathode on opposite sides. The comparison of series with multiple connections is as follows:

At a current density of 60 amperes per sq. ft.

	Series	Mutiple
Cathode efficiency	62.2 %	95 %
Lead per K.W.H.	4.59 lb.	6.83 lb.

At a current density of 40 amperes per sq, ft.

	Series	Multiple
Cathode efficiency	68.9 %	95 %
Lead per K.W.H.	7.83 lb.	8.65 lb.

At a current density of 20 amperes per sq. ft.

	Series	Multiple
Cathode efficiency	63.2 %	100 %
Lead per K.W.H.	12.7 lb.	16.1 lb.

In the series connections of the electrodes neither the cathode efficiency nor the power efficiency is as high as in the multiple connections. The advantage obtained by the series connections is (1) a saving of the space taken up by the cathodes and a saving of the cost of the cathodes, and (2) smaller bus-bars because of the higher voltage and lower current required. On the other hand the cathodes and bus-bars are permanent, and it would be only the first cost of installation that would be higher in the case of the multiple connections, while running costs would be lower because (1) more lead would be obtained per K.W.H. and

(2) the cathode efficiency being higher the ratio between the amount of iron consumed and the lead deposited would be greater.

The trials with the insoluble anodes gave very poor results. In the first place the voltage was high. There are two causes for the increase in voltage over that obtained with the iron anodes. First there is no energy obtained by anodic solution, and second there is the high overvoltage of the chlorine on the carbon anode. The voltages were as follows:

Curr. den. amp./sq. ft.	Voltage.
60	2.6
40	2.3
20	2.1

The cathode efficiency near the beginning of a run was around 70 % but fell rapidly. The brine absorbed large quantities of chlorine and became colored a dark greenish-yellow. This dissolved chlorine attacked the deposited lead sponge chemically and dissolved it nearly as fast as it was being deposited.

The deposit of lead sponge is much more compact and more easily recovered when deposited at a lower current density. When a very high current density is employed the lead sponge is fluffy and being filled with bubbles of hydrogen it floats on the surface of the electrolyte. It was also noticed that when the electrolyte was acid rather than neutral that the lead assumed a loose crystalline structure, in which form it could be more easily washed, could be dried more quickly with less oxidation, and could be melted down more readily.

Silver goes along with the lead in electrolysis. When running with Horn Silver ore some of the lead sponge assayed over 100 ounces of silver. This silver could be recovered from the lead by the Parke's process or could be recovered from the solution before electrolysis by precipitation on sponge lead or on iron. A sample of lead obtained from calcined tailings of the Bunker Hill and Sullivan mill after being melted and cast into an ingot was sent to the A. S. & R. Smelter at Midvale. The chemist there analysed it and reported 100 % lead. It seems therefore that silver is the the only substance that stays with the lead through the melting down treatment, and because of the very pure lead obtained it would be good policy to remove the silver before electrolysis and save the desilverizing of the lead bullion.

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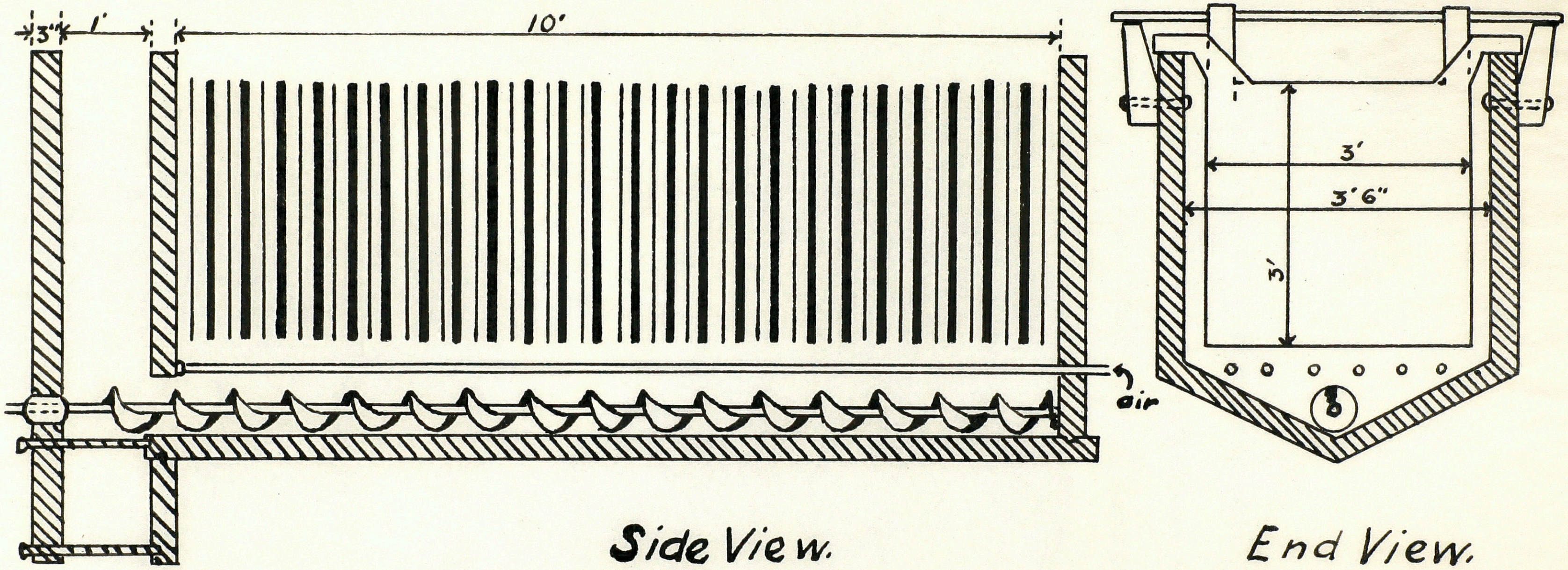
COMMERCIAL-SIZE ELECTROLYTIC CELL.



Side View.

End View.

ESTIMATED COSTS.

The accompanying sketch of a commercial-size electrolytic cell shows how one might be built for the electrolysis of the brine solutions of lead. A cell of this design may be used for either s series or multiple connections of electrodes. The drawing shows the arrangement for multiple connections. The arrangement for series would be the same except that the cathodes would be absent and instead of having bus-bars down the sides only the end plates would be connected with the external circuit. The pregnant solution would flow into one end from a feed launder and overflow at the other into a discharge launder. Agitation would be by air from holes in the six pipes running along under the electrodes. The lead sponge falling off of the plates would collect in the center of the V bottom and be carried to one end by the screw conveyor and then be discharged through the hopper arrangement along with a small amount of barren solution.

Because of the very high current densities used the multiple connections are out of the question owing to the immense size of bus-bars that would be necessary. Therefore, estimates and calculations will be made on series connections of electrodes.

Following is an estimated cost of the erection of an electrolytic plant, exclusive of the leaching plant, to produce

10 tons of pure lead per day. It will be noticed that a margin of from 10 to 20 % excess is allowed in all estimates above calculated figures.

In an electrolytic cell such as is shown, using series connections 41 electrodes may be used. The electrodes being 3 feet square there will be 3 X 3 X 40 = 360 square feet of cathode surface. Using a current density of 40 amperes per sq. ft., which is conservative, and from data obtained assuming a cathode efficiency of 70 % we have

$$\frac{360\text{ ' }40\text{ ' }.70\text{ ' }103.5}{96500\text{ ' }1000} = 38.6\text{ kg. per tank per hour.}$$

38.6 kg. = 85 lb. per tank per hour.

85 X 24 = 2040 lbs. or 1 ton lead per tank per day.

Therefore, ten tanks would produce 10 tons lead per day.

The drop between electrodes will be about .7 volts.

.7 X 40 = 28 volts. 40 volts will be allowed for per tank.

40 X 10 = 400 volts for ten tanks.

Therefore, figures will be made for a 450 volt generator to deliver 400 amperes, 360 amperes being needed.

$$\frac{400\text{ ' }450}{1000} = 180\text{ K.W.}$$

A 200 K.W. ,otor-generator set will therefore be installed. The excess power will generate compressed air and run pumps, etc.

By empirical measurement it was found that about .5 cu.ft. of air per minute is necessary for a three foot length of electrode.

Therefore, 40 X .5 X 10 = 200 cubic feet of air per minute for all of the tanks. 300 cu. ft. will be supplied.

Now that the size and amount of equipment is determined the cost will be as follows:

One 200 K.W. motor-generator set, 450 volt 400 amp. (General Electric estimate)	$3,500.00
One 200 K.W. transformers, 45,000 to 560 volts. (General Electric estimate)	2,100.00
Ten wooden tanks at $100 per board foot including construction, $50.00 apiece	500.00
Copper bus-bars .5 inch diameter. 100 ft. 64 lb. per 100 ft. at $.30 per lb.	30.00
Piping, 800 ft. at $.165 per ft.	130.00
Launders	100.00
Positive pressure blower 300 cu.ft./min. at 3 lb.	420.00
Motor for blower, 25 H.P.	350.00
Small reverberatory for melting down 10 tons lead per day	500.00
Power plant building $8.00 per sq.ft.	3,000.00
Electrolytic plant building $2.00 per sq. ft.	4,000.00
Miscellaneous equipment	2,000.00
Total cost of erection	$16,630.00

OPERATING COSTS.

For operating costs the following figures are approximate. They are made on the assumption that the material used is a mill tailing containing 10 % lead in an oxidized form.

Leaching 100 tons at $.80 per ton	$80.00
Iron figuring 1 lb. iron for 3 lb lead, and $40.00 per ton in anode plates. 3.3 tons	132.00
Power, 200 K.W. at .8 ¢ per K.W.H.	38.00
Labor, one foreman and four helpers on each of three shifts	57.00
Coal, 1 ton per day	3.00
Insurance and interest	20.00
Total for ten tons lead in one day	$330.00

Cost of producing one ton of lead	$33.00
Value of one ton lead at 2 3/4 ¢ lb.	$55.00
Margin for profit	$22.00

CONCLUSIONS.

The investigation on the electrolysis of lead in brine solutions is by no means worked out completely. In the experimental work there is still a great deal to be learned about the causes of low cathode efficiencies; how the iron is thrown out of solution, conditions for obtaining the maximum concentration of lead with the smallest acid consumption, and etc. The working details of a commercial plant have not been worked out thoroughly as yet.

It would seem at the outset that a person must be very optimistic indeed to even think of leaching and electrolysing a metal of as low a value as lead. But when one considers the cheapness of the leaching agent and the high electrochemical equivalent of lead together with the wonderful efficiencies possible, it assumes a different aspect.

Taking a mill tailing or a mine dump as a beginning material the process figures out very nicely at a fair profit. However, considering the low value of the product obtained a 10 % material could not be worked if a mining charge of several dollars a ton was added to the cost, although a surface mining charge(of several dollars) could be stood all right if a 15 to 20 % ore was obtained.