MOLTEN-SALT ELECTROLYSIS OF LEAD CHLORIDE IN A 3,000-AMPERE CELL
WITH AN IMPROVED ELECTRODE DESIGN

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ABSTRACT

The Bureau of Mines developed a ferric chloride leaching, molten-salt electrolysis process for producing lead metal from galena concentrates. Previously, the process was demonstrated on a semicontinuous basis in a process development unit (PDU) designed to produce 500 lb of lead metal per day. Electrowinning of lead was accomplished in a 3,000-A cell with horizontal flat-plate electrodes which operated at 450° C using a LiCl-KCl-PbCl₂ electrolyte. Current efficiency averaged 93 pct and the energy required was 0.6 kW·h/lb of lead produced. Since electrolysis was energy-intensive, the present investigation was undertaken to determine if improvements in cell design would significantly decrease energy requirements.

Several bench-scale electrode assemblies were tested to determine electrode efficiency. The design that was chosen for scale-up featured a horizontal sawtooth assembly and was operated at 3,000 and 4,000 A in the PDU cell. The electrode assembly increased electrode surface areas, improved chlorine gas removal, and facilitated electrolyte circulation. With the new electrode system operating under identical conditions as the PDU cell, current efficiency was 99 pct and the energy required at 3,000 A was 0.3 kW·h/lb of lead produced.

INTRODUCTION

Chloride leaching of lead concentrates as an alternative to smelting has been the subject of much interest in recent years because of potential health hazards in the smelter from lead-bearing dusts and vapors. An excellent review of the chloride leaching processes has been presented by Dutrizac (3). The Bureau of Mines investigated ferric chloride leaching of galena followed by molten-salt electrowinning of lead from PbCl₂-LiCl-KCl electrolyte (4-6,8,14-15). The process involved leaching galena with ferric chloride-sodium chloride solution at 95° C,
\[
\text{NaCl} \\
\text{PbS} + 2\text{FeCl}_3 \rightarrow \text{PbCl}_2 + 2\text{FeCl}_2 + S^0 \quad (1)
\]

After liquid-solid separation of the slurry, the solution was cooled to crystallize \(\text{PbCl}_2\) which was dried and fed to a molten-salt electrolytic cell. The cell was operated at 450° C with a LiCl-KCl-PbCl\(_2\) electrolyte. The cell products were lead metal and chlorine gas,

\[
\text{Electrolysis} \\
\text{PbCl}_2 \rightarrow \text{Pb} + \text{Cl}_2(g) \quad (2)
\]

The chlorine was used to regenerate the leaching solution,

\[
2\text{FeCl}_2 + \text{Cl}_2 \rightarrow 2\text{FeCl}_3 \quad (3)
\]

The process was demonstrated in a 500-lb-of-lead-per-day process development unit (PDU) which consisted of a semi-continuous integrated leaching-electrolysis operation (15). ASARCO, AMAX, Cominco, and St. Joe lead companies cooperated with the Bureau in the effort on a cost-sharing basis.

The PDU successfully demonstrated that the process produced high-purity lead metal with minimum health hazards due to the low temperatures of operation and with little environmental pollution because essentially all of the sulfur in the galena can be recovered as elemental sulfur. The leaching operation was subsequently demonstrated on a continuous basis (9).

A cost evaluation by Phillips (10) showed that electrolysis was the most expensive step in the process. The PDU cell operated intermittently for 2 years. The operating data are shown in table 1. The

| TABLE 1. Average operating data for a 3,000-A cell with flat plate electrodes |
|---------------------------------|-----------|
| Current........................A.. | 3,000     |
| Voltage........................V.. | 4.7       |
| Electrolyte temperature.........°C.. | 450      |
| Electrode current density..A/in\(^2\).. | 4.5      |
| Electrode spacing...............in.. | 0.75     |
| Current efficiency........pct.. | 93       |
| Ampere-hours consumed............. | 3,005,064 |
| Lead produced...................lb.. | 23,655    |
| Energy requirement........kW*h/lb.. | 0.60     |
energy requirement given in table 1 is essentially twice that obtained in previous bench-scale work (5). The main reason was that the cell voltage was higher than in bench-scale cells that operated at comparable current densities and electrode spacing. Secondly, a small decrease in current efficiency was experienced in the 3,000-A cell. Using an energy requirement of 0.6 kW*h/lb as found in the 3,000-A PDU electrolytic cell and an electrical energy cost of $0.05/kW*h, the electrolysis cost was $0.03/lb of lead produced. Despite the advantages of the process, the high electrolysis cost coupled with persistently low lead prices make industrial adoption of the process unlikely.

The present investigation was undertaken to determine if the electrolysis cost could be substantially decreased. The objective was to design and operate a 3,000-A cell which would require less energy for electrolysis. Alternative bench-scale electrode assemblies were designed that would promote chlorine removal, maximize the effective electrode area, and allow the interelectrode spacing to be decreased as much as possible.

MATERIALS AND APPARATUS

All reagents used in the bench-scale experiments were reagent grade. Technical grade PbCl$_2$ was used in the 3,000-A cell; other salts used in this cell were reagent grade. The electrolyte composition for all experiments was 6.5 wt pct LiCl, 16.5 wt pct KCl, and 77 wt pct PbCl$_2$, the same as had been used in previous electrolysis work.

In all experiments, the ampere-hour data were obtained by averaging the output from two Curtis 1002 integrating meters. Voltages were measured with a Fluke Model 8026B multimeter calibrated against a potentiometer. Current was measured with a potentiometer and a calibrated shunt.

3,000-A Cell

The 3,000-A cell that was operated in the PDU is shown in figure 1. The overall cell dimensions were 53-in long, 44-in wide, and 30-in high. The enclosure was made of 3/8-in mild steel plate. The cell cavity was 34-in long, 25-in wide, and 18-in deep. The interior walls were constructed of silica brick surrounded by castable refractory and insulating brick. The mild-steel lid had a 3-in layer of lightweight castable insulation. The cell had two graphite plate anodes, 24-in long, 14-in wide, and 3-in thick. A 6-in-diam graphite rod was screwed into each anode and connected to an anode busbar on the other end. The graphite rods were protected from air oxidation by mullite sleeves. The cathode, also of graphite, was 29-in long, 24-in wide, and 2-in thick. The cathode was supported 3 in above the cell bottom by four 3-in-diam graphite rods. The molten lead metal collected beneath the cathode and contacted a 6-in wide by 2-in thick steel plate.
that projected through the sides of the cell. The steel plate served as the cathode bus. The anode and cathode plates were grooved with six 1/4-in-wide channels which served to direct chlorine to one side of the cell and lead metal to the other side. Two auxiliary 3-in-diam graphite electrodes projected through the top of the cell and into the electrolyte to a depth of 2 in. These electrodes were connected to an ac power supply which kept the electrolyte molten when the cell was not in use. During electrolysis no supplemental heat was required.

**Bench-Scale Cells**

A bench-scale cell was designed in which the space between the cell wall and electrodes was minimized so that the effective bath area was essentially the same as the electrode surface area as was the case in the PDU cell. The cell is shown in figure 2. The electrode assembly consisted of two 1/2-in-thick disks of graphite with a diameter of 3-1/8 in. One-half-inch-diameter rods of graphite were screwed into the graphite disks which were held at the desired spacing with 1/8-in-diam alumina rods. The electrode assembly was placed in a 1-L talliform Pyrex glass beaker which had a 3-1/4-in inside diameter. The distance from the sides of the electrode plates to the container walls was 1/16 in. Hence, the effective bath area was very close to the electrode area.

The cell assembly was placed in a stainless steel container and heated to the operating temperature in a temperature-controlled pot furnace. The cell was operated at 450° C with an electrode spacing of 0.75 in to obtain data to compare with the 3,000-A PDU cell.

Three other electrode designs were selected for testing on a bench scale. The results were compared with the horizontal flat plate assembly. An electrode spacing of 0.5 in was selected for all the experiments because Welch and Iwanec (11-12) suggested that 1 cm (0.4 in) was the minimum electrode spacing for lead chloride electrolysis and earlier work by the Bureau of Mines showed that decreasing the electrode spacing from 1 to 0.5 in decreased the energy requirement for lead electrowinning.

The electrode designs are shown in figures 3-5. The electrode assemblies are referred to as vertical flat plate (fig. 3), square wave (fig. 4), and sawtooth (fig. 5). The angles of the triangular cuts in the sawtooth electrodes were 60° which gave the maximum effective electrode area at 1/2-in electrode spacing. Current density-voltage curves were obtained for all electrode designs by increasing the current density incrementally. Electrolysis was continued for 1 min at each selected current density.
EXPERIMENTAL RESULTS AND DISCUSSION

The cell voltage is plotted as a function of the current density in figure 6 for the bench-scale, horizontal flat-plate electrode cell. Also shown in figure 6 are data obtained previously with the 3,000-A PDU cell.

The decomposition voltage was 1.30 V in the PDU cell and 1.33 V in the bench-scale cell. Calculating the decomposition voltage from the free energy of formation of PbCl$_2$ as given by Wicks and Block (13) at 450° C yields a decomposition potential of 1.31 V, which is in good agreement. As the current density increases, the voltage of the 3,000-A cell becomes progressively higher than the bench-scale cell. At 3,000 A, which corresponded to a current density of 4.5 A/in$^2$, the voltage was 4.0 V. At the comparable current density in the bench-scale cell, the voltage was 3.4 V.

The voltage difference between the cells can be explained by the position of the voltage measuring probes. In the 3,000-A cell, voltages were measured outside the cell, from the graphite rod connected to the anode plate to the steel bar that served as the cathode bus. In the small cell, glass-encased tungsten probes were used to measure the voltage directly between the electrodes. The voltage drop between the points of measurements and the electrodes was not measured in the PDU cell during operation at 3,000 A. Subsequently, the voltage losses in the electrode leads were carefully determined in a cell of similar size and design. Subtracting the lead voltage losses from the PDU voltages makes the PDU current density-voltage curve virtually identical to the curve for the bench-scale cell in figure 6.

The cell voltage is the sum of several voltages and is given by:

$$V_{\text{cell}} = V_d + N_a + N_c + R_eI + R_mI$$  \hspace{1cm} (4)

where $V_d$ is the decomposition potential of lead chloride, $N_a$ is the anode overvoltage, $N_c$ is the cathode overvoltage, $R_eI$ is the voltage drop in the electrode leads and the electrodes, and $R_mI$ is the voltage drop in the electrolyte (I is cell current). The cathode overpotential should be very small and will be assumed to be negligible in the analysis of cell potentials. The anode overpotential is probably small but significant (0.1 to 0.2 V).

In the bench-scale experiments, the $R_eI$ term was zero. As stated before, at a current density of 4.5 A/in$^2$, the cell voltage was 3.4 V. Assuming a decomposition voltage of 1.3 V and an anode overvoltage of 0.2 V, the $R_mI$ term can be estimated from equation 4 to be 1.9 V. At 4.5 A/in$^2$ current density in the PDU cell, assuming the $R_eI$ term is 0.6 V, $R_mI$ is also 1.9 V. The $R_mI$ voltage is related to the effective electrolyte conductivity, $K^*$, by (1)
where \( L \) is the electrode spacing and \( I/A \) is the electrode current density. At a current density of 4.5 A/in\(^2\) \( K^* \) is:

\[
K^* = \frac{4.5 \text{ A/in}^2 \times 0.75 \text{ in}}{1.9 \text{ V}} = 1.78 \Omega^{-1} \text{ cm}^{-1} = 0.70 \Omega^{-1} \text{ cm}^{-1}
\]  

\( K^* \), the effective electrolyte conductivity, differs from \( K \), the absolute electrolyte conductivity, because of gas buildup in the electrolyte, chlorine in the present case. According to DeLaRue and Tobias (2), \( K^* \) is related to \( K \) by

\[
K^* = K (1 - E)^{1.5} \tag{7}
\]

where \( E \) is the gas fraction in the electrolyte. Using a \( K \) value of 1.165 \( \Omega^{-1} \text{ cm}^{-1} \) based on the work of Mikhail et al. (7), the gas fraction entrained in the electrolyte is calculated to be 29\%.

The 4.0 V recorded in the 3,000-A PDU cell and used in the foregoing calculation was obtained during momentary operation of the cell. Under the continuous operating conditions shown in table 1, when the cell current is normalized to 3,000 A, the cell averaged 4.7 V. If the 0.7 V difference is accounted for by a buildup of chlorine gas on the anode, the chlorine gas fraction from equation 7 then becomes 42\%.

These calculations show the need for an improved electrode assembly design that would increase the rate of chlorine removal from between the electrodes.

**Bench-Scale Experiments With Other Electrode Designs**

Current density-voltage curves were developed for the other bench-scale electrode assemblies. The results are plotted in figure 7. Also shown in figure 7 is the theoretical current density-voltage relationship based on electrolyte conductivity data and assuming a decomposition voltage of 1.3 V and overvoltages of zero.

The lowest voltages were recorded with the vertical flat-plate electrodes. The voltages were nearly the same as would be expected from the electrolyte conductivity assuming zero electrode overvoltages and no chlorine gas fraction. However, the horizontal surfaces on the top and bottom of the vertical electrodes were neglected in calculating the electrode surface area.

The sawtooth assembly yielded the next lowest voltages followed by the square-wave and horizontal flat-plate assemblies. The relatively poor performance of the square-wave assembly was somewhat surprising because the square wave is really a combination of vertical and horizontal flat plates. A portion of the electrode surface area is
relatively dead to electrolysis with both the square-wave and sawtooth electrodes which helps to explain the poor performance of the square-wave electrodes.

3,000-A Cell Operation With Sawtooth Electrodes

The sawtooth electrode design was chosen for scale-up rather than the vertical-plate design even though the vertical plate design had performed better in the bench-scale tests. One important factor was that the electrode assembly should occupy the same volume in the cell cavity and that the cell would use the same shell as the PDU cell. Thus, it was considerably easier to incorporate the sawtooth electrode design. Equally important, the sawtooth electrodes could be easily fabricated from a rectangular block of graphite and placed in the cell housing with little modification. A photograph of the electrode assembly is shown in figure 8. The two anodes were cut from 24-in by 14-in by 4-in thick graphite plates. As in the bench-scale cell, the angle of the triangles was 60°. The anodes had 1/2-in-diam holes cut in the top of the trough and spaced 3 in apart to permit chlorine escape. The cathodes were similar to the anodes without the holes. The molten lead collected beneath it and made contact with the steel plate, as in the PDU cell. Two auxiliary electrodes were used to provide ac heating.

The sawtooth cell was operated continuously at 3,000 A for 6 days. The results are shown in table 2. The current efficiency of 98.7 pct is similar to the current efficiencies obtained in previous bench-scale tests (5,8). The energy requirement of 0.3 kW·h/lb of lead metal produced is a significant improvement over the 0.6 kW·h/lb obtained in the PDU cell. The voltage of 2.5 V given in table 2 was measured, as in the PDU cell, from the anode connecting rod to the cathode steel busbar. Measuring the voltage between electrodes with glass-encased tungsten rods gave an average voltage of 1.9 V. Thus, the voltage drop in the electrode leads at 3,000-A cell current was 0.6 V. The RmI voltage drop at 3,000 A for the sawtooth electrodes with a decomposition potential of 1.3 V and an anode over-potential of 0.2 V is 0.4 V.

### Table 2. Data for cell operation in a 3,000- and 4,000-A cell with sawtooth electrodes

|                      | 3,000 | 4,000 |
|----------------------|-------|-------|
| Current................| 3,000 | 4,000 |
| Voltage..............| 2.5   | 3.0   |
| Electrolyte temperature......°C... | 450   | 450   |
| Electrode current density..A/in².. | 2.3   | 3.1   |
| Electrode spacing..............in.. | 0.50  | 0.50  |
| Current efficiency..............pct.. | 98.7  | 99.5  |
| Ampere-hours consumed.......... | 426,527 | 230,640 |
| Lead produced...............lb.. | 3,592  | 1,952 |
| Energy requirement......kW·h/lb.. | 0.30  | 0.35  |
This $R_mI$ value agrees closely with a value of 0.39 V calculated by using equation 5. Thus, at 3,000 A in the sawtooth cell, chlorine gas did not influence the electrolyte conductivity very much, while it had played a major role in the PDU cell with horizontal flat-plate electrodes at 3,000 A.

Much less heat was generated by the electrolysis because the potential drop through the electrolyte was dramatically decreased by the sawtooth electrodes. As a result, 6 kVA had to be furnished by the ac power supply during electrolysis to keep the electrolyte at 450° C.

Following cell operation at 3,000 A, the cell was operated at 4,000 A for 58 h. The operational data at 4,000 A is also given in table 2. Current efficiency was excellent at 99.5 pct. The cell voltage increased to 3.0 V which resulted in an energy requirement of 0.35 kW*h/lb. The voltage losses in the leads at 4,000 A increased to 0.9 V. Cell potential from anode to cathode was 2.1 V, which again shows little influence of chlorine gas on the electrolyte conductivity. At 4,000 A, the ac power requirement to keep the electrolyte at 450° C was decreased to 4 kVA.

SUMMARY AND CONCLUSIONS

Lead metal was electrowon from a LiCl-KCl-PbCl$_2$ electrolyte at 450° C at 3,000 and 4,000 A with a sawtooth electrode assembly. At 3,000 A, the energy required was 0.3 kW*h/lb of lead metal produced which is a large improvement compared to the 0.6 kW*h/lb required previously in the PDU cell with horizontal flat-plate electrodes. The decrease in the energy resulted from decreasing the electrode spacing from 0.75 in to 0.5 in, greatly facilitating the removal of chlorine gas from the anode and doubling the electrode surface area. Chlorine gas did not noticeably increase the electrolyte resistance with the sawtooth electrodes at either 3,000 or 4,000 A cell current while chlorine doubled the electrolyte resistance with the flat-plate electrodes.

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FIGURE 1. 3,000-A PDU cell.

FIGURE 2. Bench-scale cell with horizontal flat plate electrodes.
FIGURE 3. Vertical flat plate electrodes.
FIGURE 4. Square wave electrodes.

FIGURE 5. Sawtooth electrodes.
FIGURE 6. Current density versus voltage curves for flat plate electrodes at 0.75 in spacing.

FIGURE 7. Current density versus voltage curves for electrode assemblies at 0.5 in spacing.
FIGURE 8. Sawtooth electrode assembly for 3,000-A cell.