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Aqueous Electrolysis of Lead Chloride

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AQUEOUS ELECTROLYSIS OF LEAD CHLORIDE

by

F. P. Haver,[1] D. L. Bixby,[1] and M. M. Wong[2]

ABSTRACT

The Federal Bureau of Mines investigated aqueous electrolysis as a means for reducing lead chloride prepared by ferric chloride leaching of galena concentrate:

$$PbS + 2FeCl_3 \xrightarrow{NaCl} PbCl_2 + 2FeCl_2 + S^\circ .$$

During electrolysis, metal was produced from solid lead chloride in contact with the cathode rather than from lead in solution. Relatively high current densities--up to 300 amp/ft^2--were possible when operating in this way. A very simple cell, having a horizontal lead cathode at the bottom and a vertical graphite anode at the top, was employed. Lead chloride crystals, covering the cathode, were converted to metal powder during electrolysis, and chlorine gas or $FeCl_3$ was produced at the anode, depending on the electrolyte composition. Electrolytes tried included aqueous solutions of HCl, NaCl, NH_4Cl, and $FeCl_2$-NaCl. Optimum results (96-pct current efficiency, 0.23 kwhr/lb Pb) were obtained with 20 pct HCl at 25° C, using a current density of 15 amp/ft^2 and an electrode spacing of 1 inch. When the current density was increased, the energy requirement increased also but only to 0.41 kwhr/lb at 150 amp/ft^2 and 0.58 kwhr/lb at 300 amp/ft^2.

INTRODUCTION

Primary lead is now usually produced from sulfide concentrate by a smelting process that involves sintering, blast furnace reduction with carbon, and refining. Unfortunately, smelting generates gaseous sulfur oxides and particulate lead, which must be controlled to avoid air pollution. Meeting environmental regulations requires production curtailment at times for some smelters, and for others even threatens eventual closure.

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To avoid such problems, the Federal Bureau of Mines has investigated a hydrometallurgical procedure (fig. 1) for producing lead metal from sulfide ores (1-2).[3] In this method, galena concentrate is leached with hot ferric chloride-brine solution to obtain lead chloride and elemental sulfur:

$$PbS + 2FeCl_3 \xrightarrow{NaCl} PbCl_2 + 2FeCl_2 + S^\circ .$$

At 100° C, over 99 pct of the PbS in the concentrate is converted to $PbCl_2$ in less than 15 min. The leach solution, consisting of brine (NaCl) containing the theoretical amount of $FeCl_3$, dissolves the $PbCl_2$ as it is formed, leaving a residue of elemental sulfur and gangue which is easily washed free of entrained liquor. High-purity $PbCl_2$ (>99.9 pct) crystallizes from the leach solution on cooling and may be electrolyzed in a fused-salt cell to obtain high-purity lead (>99.999 pct Pb) and gaseous chlorine, which is used to regenerate the leach solution. Because fused-salt electrolytes can be

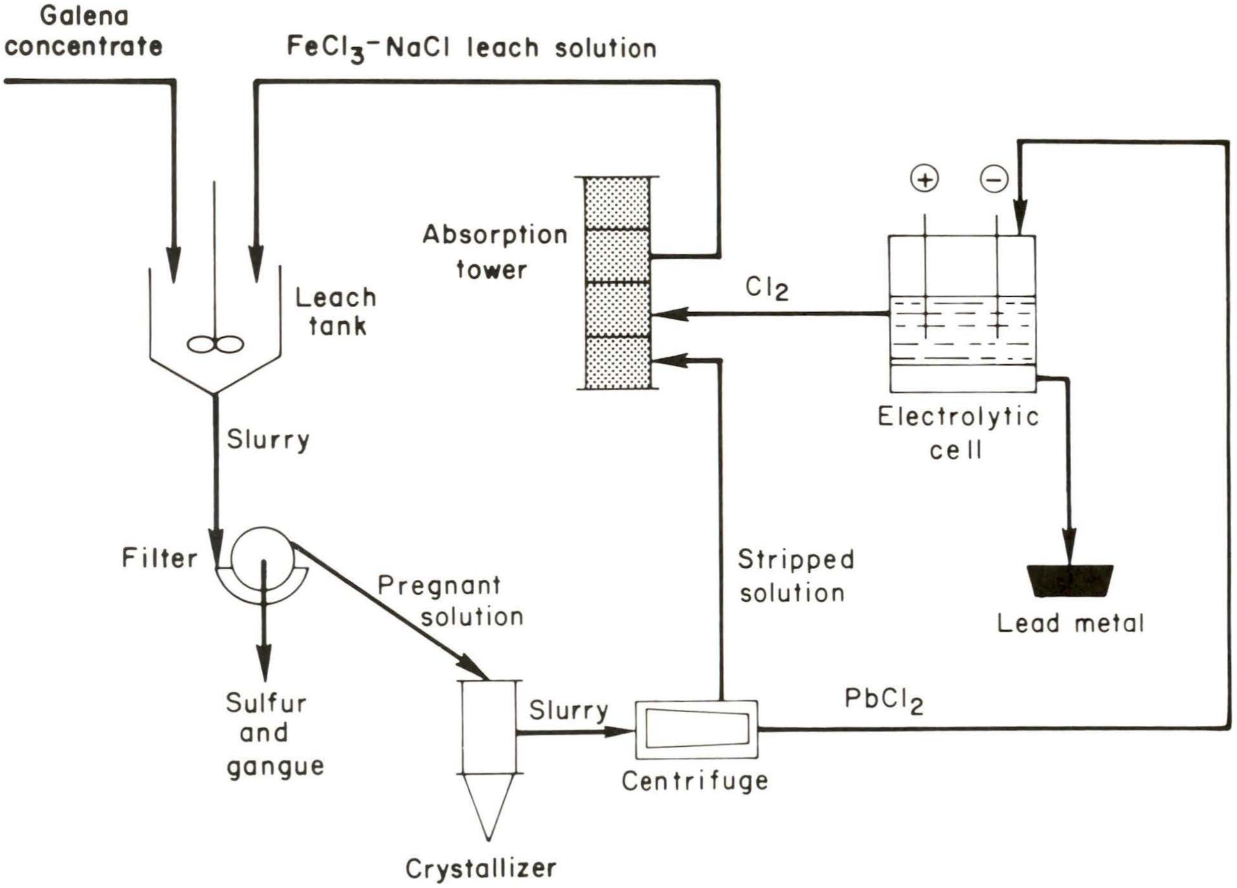

FIGURE 1. - Flowsheet for recovering lead from sulfide concentrate.

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[3] Underlined numbers in parentheses refer to items listed at the end of this report.

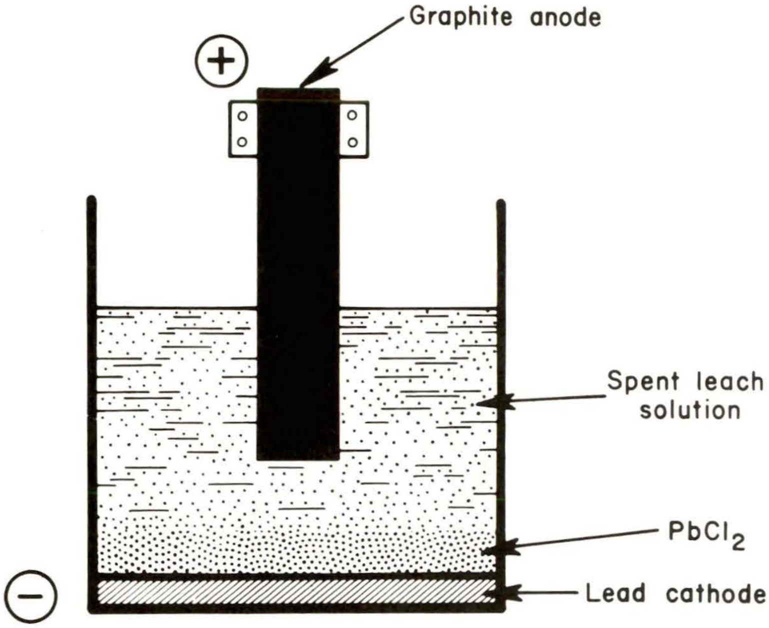

FIGURE 2. - Apparatus for aqueous electrolysis.

operated effectively at high current densities (>1,000 amp/ft^2), a high production rate can be obtained with relatively small equipment. A continuous operation is possible, and energy requirements are low (<1.0 kwhr/lb metal).

Aqueous electrolysis, the subject of the present study, may be more suitable for the small operator, however, because it requires less expensive equipment and can be conducted at ambient temperature with fewer safety hazards. The equipment necessary for the aqueous electrolysis of solid $PbCl_2$ (fig. 2) is extremely simple, merely a tank constructed of some nonconducting material with a horizontal lead cathode at the bottom and a vertical graphite anode at the top. The tank can be filled with hot pregnant solution (fig. 1) which has been purified by passage through a column of lead shot. Lead chloride, crystallizing out on cooling, will then form a layer on the bottom of the tank, covering the cathode. During electrolysis, chlorine produced at the anode reacts with ferrous ions to generate ferric ions in the leach solution, thus eliminating the need for chlorine-handling equipment. At the same time, the $PbCl_2$ is converted to a metallic powder which is not attached to the cathode and can be raked out of the cell, washed, and melted to obtain high-purity lead. While the method is essentially a batch process, very little labor is required. There is also no need for the crystallizer, centrifuge, and absorption tower shown in figure 1.

INVESTIGATION OF VARIABLES

Variables selected for investigation in the electrolysis of $PbCl_2$ were electrolyte composition, temperature, current density, and electrode spacing. Electrolytes tested included spent leach solution ($FeCl_2$-NaCl), HCl, NaCl, and NH_4Cl--these being considered the most practical media. Spent leach solution was prepared by cooling pregnant solution (fig. 1) to room temperature to crystallize out as much $PbCl_2$ as possible. The resulting liquor contained approximately 95 g/l $FeCl_2$, 230 g/l NaCl, and 25 g/l $PbCl_2$ (2). Solutions other than spent leach solution were investigated because they hold the potential of improved electrolytic results. When spent leach solution is electrolyzed, some of the ferric ion formed at the anode is reduced to ferrous ion at the cathode or else reacts with the deposit, lowering the current efficiency and raising the energy requirement. This disadvantage must be weighed against the additional processing required when other electrolytes are used.

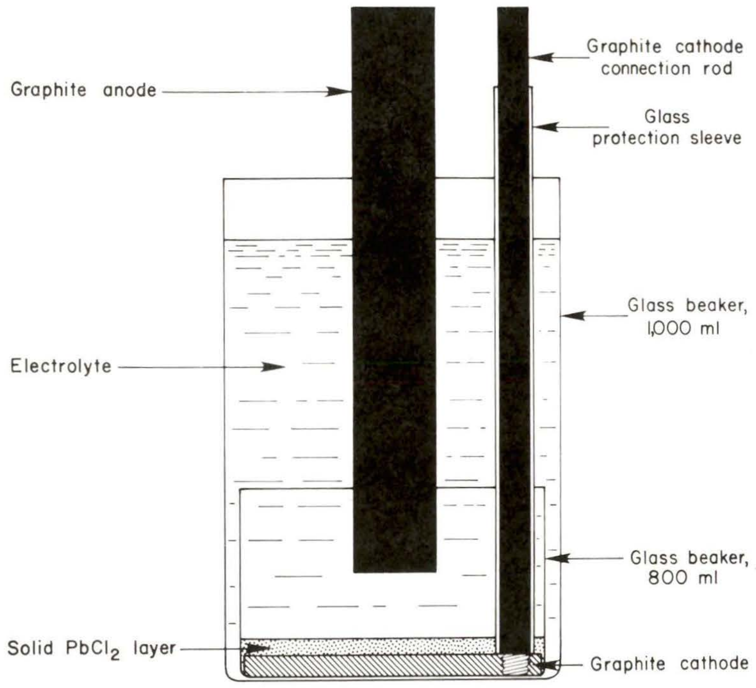

FIGURE 3. - Test cell used in small-scale work.

Experimental Procedure

Small-scale tests were made with the apparatus shown in figure 3. The electrolytic cell consisted of a 1,000-ml beaker containing a 1-inch-diam vertical graphite anode and a cathode assembly made up of a 1/4-inch-thick graphite plate cemented into the bottom of a truncated 800-ml beaker. A 3/8-inch graphite rod protected by a glass sleeve connected the cathode to the dc source. A Hewlett-Packard model 6427B[4] constant-amperage rectifier supplied the dc current, which was measured with a Leeds and Northrup model 8690 potentiometer in conjunction with a 10-amp, 50-mv shunt. Voltage was checked with a Heathkit model 1M-102 multimeter.

In all tests, 35 grams of $PbCl_2$ were placed in the cathode compartment, forming a layer about 1/8 inch thick. After 800 ml of solution was carefully added, electrolysis was started, using a controlled bath composition, temperature, current density, and electrode spacing. Each test was run for 5 amp-hr, equivalent to 75-pct conversion of the $PbCl_2$ to metal. After electrolysis, the deposit was washed, dried in a vacuum oven, and melted at 450° C under an inert salt cover. This eliminated the excess $PbCl_2$, which was mixed in with the lead granules. The button was then weighed to calculate the current efficiency and energy requirement.

Electrolyte Composition

The first series of tests was made to determine the optimum electrolyte composition. Solutions with varying concentrations of HCl, NaCl, and NH_4Cl were electrolyzed at 15 amp/ft^2 using an electrode spacing (anode-to-$PbCl_2$ distance) of 1 inch and a temperature of 25° C. Results are shown in table 1 and figure 4. No investigation was made with spent leach solution because this has a fixed composition as noted previously. However, under the above conditions, spent leach solution gave 67.2-pct current efficiency and an energy requirement of 0.37 kwhr/lb Pb. Of all the electrolytes tried, HCl required the least energy. As expected, the voltage, and therefore the energy

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[4] Reference to specific brands is made for identification only and does not imply endorsement by the Bureau of Mines.

requirement, appeared to be a function of the conductivity of the electrolyte; in general, the energy requirement decreased as the solute concentrate increased.

TABLE 1. - Effect of electrolyte composition on the current efficiency and energy requirement

Electrolyte	Concentration, wt-pct	Cell voltage, v	Current efficiency, pct	Energy requirement, kwhr/lb
HCl....................	1.0	2.61	90.8	0.336
	3.0	2.14	94.0	.266
	5.0	2.05	92.5	.259
	7.5	1.99	96.6	.241
	10.0	1.98	95.5	.239
	12.5	1.91	95.8	.233
	15.0	1.95	96.7	.236
	17.5	1.91	96.2	.233
	20.0	1.91	96.0	.232
NaCl....................	1.0	4.15	93.9	.517
	3.0	3.11	95.3	.382
	5.0	2.70	95.4	.331
	7.5	2.52	96.8	.305
	10.0	2.37	97.0	.286
	12.5	2.31	97.6	.277
	15.0	2.26	97.2	.272
	17.5	2.23	97.8	.267
	20.0	2.20	97.6	.264
NH_4Cl....................	1.0	3.39	94.9	.418
	3.0	2.61	92.3	.333
	5.0	2.37	91.4	.304
	7.5	2.25	94.3	.279
	10.0	2.17	93.8	.271
	12.5	2.12	92.9	.267
	15.0	2.05	90.3	.266
	17.5	2.02	94.4	.251
	20.0	2.00	90.5	.259

The solubility of $PbCl_2$ in all of the electrolytes was low, usually far below that in water (1.0 wt-pct at 20° C) (4). With increasing amounts of HCl, the solubility reached a minimum of 0.1 wt-pct at a concentration of 5 wt-pct HCl and then gradually increased to a maximum of 1.1 wt-pct at 25 wt-pct HCl. With NaCl, the minimum was also 0.1 wt-pct $PbCl_2$ at a concentration of 5 wt-pct NaCl, increasing to a maximum of 1.9 wt-pct at 25 wt-pct NaCl. NH_4Cl gave similar results, the solubility of $PbCl_2$ decreasing to 0.07 wt-pct at 5 wt-pct NH_4Cl and then increasing to a maximum of 0.6 wt-pct at 25 wt-pct NH_4Cl. During electrolysis, the concentration of $PbCl_2$ in the electrolyte remained constant as long as there was an excess of solid $PbCl_2$ in the bottom of the cell. It was noted that if the solid $PbCl_2$

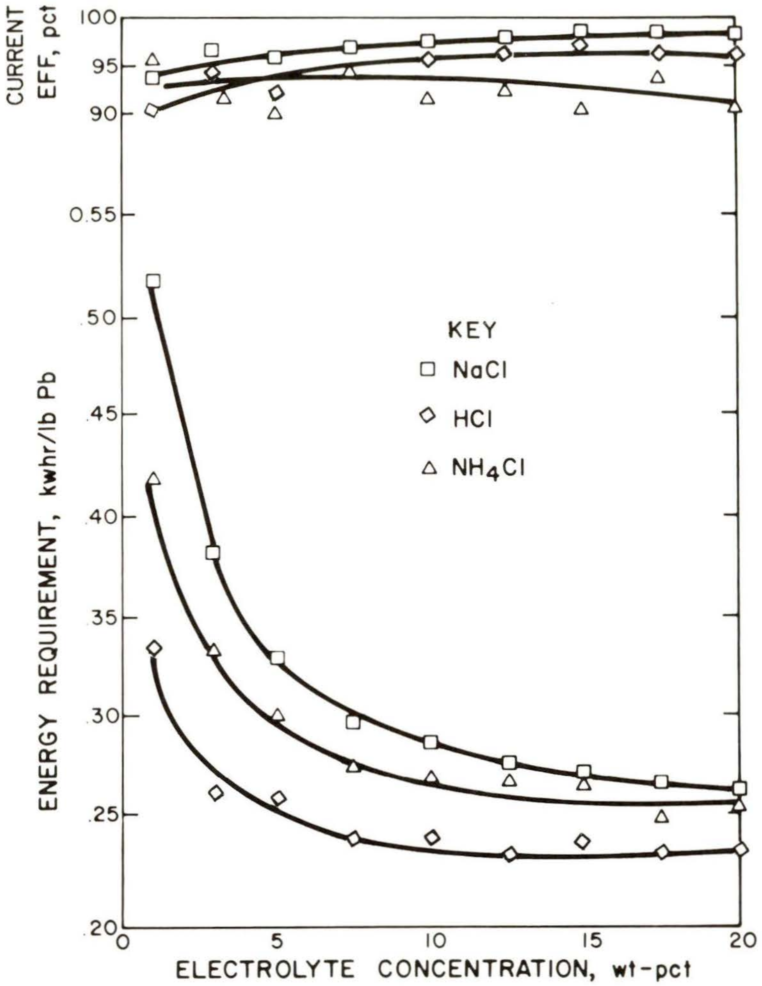

FIGURE 4. - Effect of electrolyte composition on the current efficiency and energy requirement.

was completely converted to metal, the deposit thereafter became black and spongy, indicating that deposition from solution was taking place. At the higher salt concentrations, where more $PbCl_2$ was present in solution, the deposit adhered to the cathode, indicating that reduction of both solid $PbCl_2$ and lead in solution was occurring simultaneously.

Temperature

To determine the effect of temperature, tests were run as before using the electrolyte concentration (20 wt-pct) that gave the lowest energy requirement in the preceding work. The temperature of the solutions was varied from 25° to 75° C, using a constant-temperature water bath to maintain the temperature within ±1° C. No tests were made with spent leach solution because pregnant solution (fig. 1) must be cooled to room temperature to crystallize out as much $PbCl_2$ as possible; otherwise, when it is recycled, its capacity to dissolve $PbCl_2$ is reduced and a greater volume must be used. Electrolysis with spent leach solution is, therefore, preferably conducted only at ambient temperature. Results of the tests are shown in table 2. Increasing the temperature had no significant effect on the energy requirement in the case of HCl and had only a limited effect in the case of NaCl and NH_4Cl.

TABLE 2. - Effect of temperature on the current efficiency and energy requirement

Electrolyte	Temp, ° C	Cell voltage, v	Current efficiency, pct	Energy requirement, kwhr/lb
HCl....................	25	1.91	96.0	0.232
	50	1.80	91.4	.231
	75	1.73	87.7	.230
NaCl...................	25	2.20	97.6	.264
	50	1.94	96.2	.236
	75	1.82	96.4	.222
NH_4Cl....	25	2.00	90.5	.259
	50	1.84	96.3	.224
	75	1.76	96.0	.214

Current Density

Tests were made at current densities ranging from 15 to 750 amp/ft^2, using the conditions found best in the preceding work. Except for spent leach solution, 20.0-wt-pct concentrations of solute were employed. Temperatures were held at 25° C for HCl and $FeCl_2$-NaCl and at 75° C for NaCl and NH_4Cl, using a 1-inch electrode spacing. Results are given in table 3, and the effect of the current density on the energy requirements is shown in figure 5. Even with no external heating, HCl gave the best overall results. As

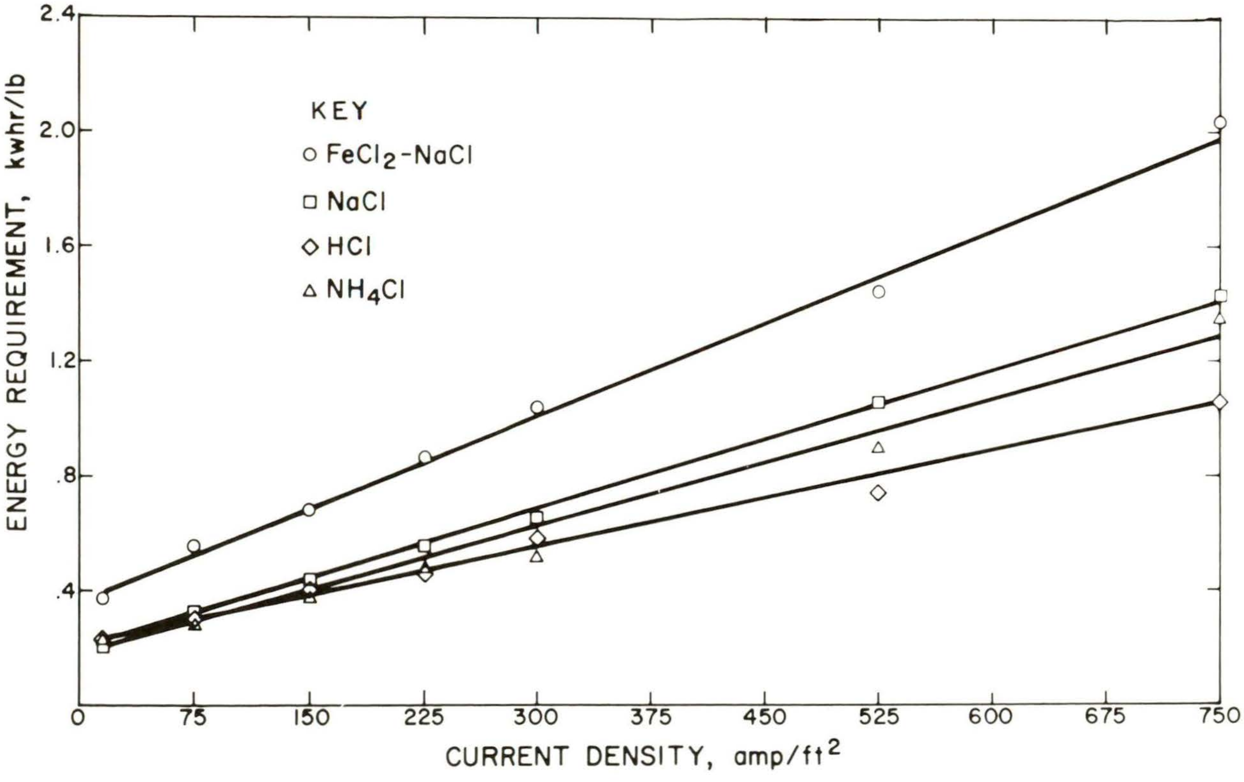

FIGURE 5. - Effect of current density on the energy requirement.

expected, $FeCl_2$-NaCl had the highest energy requirement; however, no chlorine was given off when spent leach solution was electrolyzed, even at the highest current density used. Actually, the results with $FeCl_2$-NaCl were not so different as to preclude its use, considering the other advantages obtained. As the current density was increased in the tests, hydrogen evolution occurred at the cathode, resulting in a rapid reduction in the current efficiency above 300 amp/ft^2. Interaction of ferric ion and the deposit caused a further reduction in current efficiency in the case of spent leach solution.

TABLE 3. - Effect of current density on the current efficiency and energy requirement

Electrolyte and temperature	Current density, amp/ft^2	Cell voltage, v	Current efficiency, pct	Energy requirement, kwhr/lb
HCl, 25° C....................	15	1.91	96.0	0.232
	75	2.47	95.2	.304
	150	3.04	86.6	.411
	225	3.40	86.9	.458
	300	3.85	77.9	.578
	525	4.48	69.9	.745
	750	5.60	62.0	1.060
NaCl, 75° C...................	15	1.82	96.4	.222
	75	2.60	93.7	.325
	150	3.58	93.4	.449
	225	4.18	87.8	.557
	300	4.93	87.2	.662
	525	6.52	71.5	1.070
	750	7.98	65.4	1.430
NH_4Cl, 75° C..................	15	1.76	96.0	.214
	75	2.36	95.3	.290
	150	2.91	86.8	.392
	225	3.57	86.7	.482
	300	3.99	89.9	.519
	525	5.02	64.7	.907
	750	6.43	55.8	1.350
$FeCl_2$-NaCl, 25° C.............	15	2.13	67.2	.370
	75	3.70	77.4	.559
	150	5.02	86.9	.678
	225	5.70	75.9	.870
	300	6.68	75.3	1.040
	525	8.97	72.5	1.450
	750	11.60	66.3	2.050

Electrode Spacing

Conditions used to investigate the effect of electrode spacing were exactly the same as in the previous tests except that the current density was fixed at 15 amp/ft^2 and the electrode spacing was varied from 1/2 to 4 inches. Results are shown in table 4. As would be expected, the cell voltage and energy requirement increased with the spacing; however, the change was surprisingly small. Whereas spacing is a very important factor in fused-salt electrolysis, in this case, the effect was almost negligible.

TABLE 4. - Effect of electrode spacing on the current efficiency and energy requirement

Electrolyte	Electrode spacing, inches	Cell voltage, v	Current efficiency, pct	Energy requirement, kwhr/lb
HCl.................	0.5	1.84	93.4	0.237
	1.0	1.91	96.0	.232
	2.0	1.91	95.8	.233
	3.0	1.98	94.3	.246
	4.0	2.04	93.2	.256
NaCl................	.5	1.75	97.6	.210
	1.0	1.82	96.4	.222
	2.0	1.89	97.6	.227
	3.0	1.98	97.8	.239
	4.0	2.14	95.9	.261
NH_4Cl...............	.5	1.71	99.9	.200
	1.0	1.76	96.0	.214
	2.0	1.81	97.2	.218
	3.0	1.88	97.0	.227
	4.0	1.98	96.2	.241
$FeCl_2$-NaCl..........	.5	2.17	68.6	.353
	1.0	2.13	67.2	.370
	2.0	2.43	75.5	.377
	3.0	2.65	71.3	.434
	4.0	2.93	64.2	.534

Metal Purity

Metal purity was determined by operating the test cell (fig. 3) with spent leach solution ($FeCl_2$-NaCl) at 25° C, using a current density of 15 amp/ft^2 and an electrode spacing of 1 inch. The $PbCl_2$ was obtained by crystallization from pregnant solution (fig. 1) after purification with lead shot. The deposit was washed, dried, melted under an inert salt cover, and analyzed. Results are shown in table 5 together with ASTM specifications for corroding-grade lead. Even though a large amount of iron was present in solution, very little entered the deposit because of the large difference in electrode potential (E_0) for deposition of iron and lead (-0.44 and -0.12 volt, respectively, at 25° C (3)). Elements that fall below lead in the electromotive series include Ag, As, Bi, Cu, and Sb. Arsenic and bismuth did not dissolve in the leach (fig. 1), although they were present in the galena concentrate. Silver, copper, and antimony did dissolve but could be reduced to <1 ppm by passing the pregnant solution, before crystallization, through a bed of lead shot (2). It is apparent that the product met all specifications for corroding-grade metal (>99.94 pct Pb).

TABLE 5. - Purity of $PbCl_2$ and lead product, ppm

Element	$PbCl_2$	Lead product	ASTM specification[1]
Antimony	ND	ND	([2])
Arsenic	ND	ND	<15
Bismuth	ND	ND	<500
Chlorine	-	ND	-
Copper	ND	6	<15
Iron	49	3	<20
Silver	ND	7	<15
Sodium	70	ND	-
Sulfur	33	ND	-
Tin	ND	ND	([2])
Zinc	21	4	<15

ND = Not detected (<1 ppm).

[1] Specification for corroding-grade lead.

[2] Sb + Sn = <95 ppm.

CONCLUSIONS

In conjunction with ferric chloride leaching of galena concentrate, aqueous electrolysis appears to offer the small operator the potential for a simple, inexpensive method for producing lead metal on a limited scale at a reasonable capital cost. While fused-salt electrolysis is more suitable for a large operation, aqueous electrolysis requires less sophisticated equipment and less technical skill. More labor is involved, however, and the energy requirement is higher.

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