

PRODUCTION OF ELECTROLYTIC LEAD POWDER

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Lead powder has been prepared by electrodeposition from baths of different electrolytic media, e.g., NaCl-PbCl₂; NaCl-KCl-PbCl₂; CaCl₂-PbCl₂ using graphite electrodes and NaOH using lead as electrodes. The limit of the optimum operating variables studied for CaCl₂-PbCl₂ electrolyte were: temperature of bath 50-55°C, current density 5-6 amp/dm²; lead chloride 20 g/l, and pH 5-6.

Use of NaOH as electrolyte (160-180 g/l), lead electrodes at a current density of 5.5-6.2 amp/dm² with the addition of 10-30 ml/l NH₄OH (sp. gr., 0.88) produced an easily detachable spongy deposit at bath temperature 25-27°C.

Lead powder is one of the three low melting metal powders produced in large quantities. It is extensively used for alloying and as an additional agent for those parts or bearings which are required to possess high specific gravity.¹ Large quantity of this powder was used as an ingredient in rounds for target practice. Substantial amount of this powder is also used as an alloying ingredient in nonferrous and ferrous bearings, and as lubricant (5-15% by weight) in the moulding of copper.² It also serves as a protective coating on the surface of various metals. A concise account of the conditions necessary for the production of lead powder by electrolytic methods has been given by various workers.³⁻⁵ In the following investigation an attempt has been made to work out the optimum conditions for the production of pure lead powder using different electrodes, electrolytes, pH values and temperatures of the bath.

Experimental

Apparatus.—The experiments were carried out in a 1-l beaker surrounded by copper jacket and kept in another vessel containing water. The apparatus was heated at the bottom while tap water was kept circulating in the outer jacket to maintain a constant temperature. The distance between the electrodes was kept 4 cm throughout the experiments.

A two-step rectifier of 6-12 volts was used as the source of electrical energy. A rheostat and a voltmeter were used in the circuit to tap out desired amperages and voltages.

Electrolytes.—The electrolytes were prepared from chemically pure reagents. The pH of the bath was adjusted with chemically pure hydrochloric acid, nitric acid or sodium hydroxide.

Electrolysis.—The electrolytic cell was filled with the electrolyte and its pH adjusted to the required value. After adjusting the temperature the current was switched on and each experiment was run for 30 min. The current was, however, interrupted after 15 min to remove the deposit. The rate of the electric current passing through the cell, the temperature and the pH were recorded at regular intervals and adjusted when required. Stirring of the solution was done by means of compressed air.

The powder thus removed was collected in an evaporating dish containing water, washed by decantation until free of the electrolyte, filtered in a sintered glass crucible under vacuum and dried in CO₂ atmosphere in an oven at 50-60°C to obtain a dry, stable and unoxidised product. For a given set of experiments the same cathode was used after washing it with dil HNO₃. In some experiments the powder was found to cake slightly when removed from the oven which could be easily disintegrated by placing it between the sheets of paper and rubbing slightly.

Results and Discussion

The object of the present problem was to obtain the optimum conditions to get pure lead powder. Once the optimum conditions were achieved, it was not very difficult to maintain the same conditions throughout the process. The slight deviation from these conditions was equally compensated for while recording the readings. The particle size of the powder can be varied, if required, by employing different operating conditions. The data obtained from the influence of concentration of electrolyte, temperature and pH of the bath and current density on the current efficiency have been presented in Tables 1-5.

The spongy deposit was obtained by using NaCl-PbCl₂ or KCl-NaCl-PbCl₂ combination

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as electrolytes with graphite electrodes. These gave a low yield of powder as a large amount of chlorine liberated at the anode raised the pH of the bath on the acidic side resulting in partial dissolution of the deposit and low current efficiency. However, in the series of experiments using $\text{CaCl}_2\text{-PbCl}_2$ it was possible to get a spongy deposit with a little liberation of chlorine and with a fairly good current efficiency. Consequently this electrolyte was chosen for further experiments.

Effect of Stirring the Electrolyte.—The observations (Table 1) showed favourable results on current

efficiency when the electrolyte was stirred and the cathode brushed as compared with the experiment eliminating this step. The sponge tends to become bulky when brushing is not done to remove the deposit and is likely to cause shortcircuiting and irregular deposition.

Effect of Variation of Current Density.—The current densities given in all the tables are the cathodic current densities unless otherwise mentioned. Results of the experiments on the effect of variation in current density on the current efficiency are given in Table 2. It can be observed that

TABLE 1.—PREPARATION OF ELECTROLYTIC LEAD POWDER USING CHLORIDE BATH.

Volume of electrolyte, 500 ml; electrodes, graphite; cathode area, 50 cm²; distance of electrodes, 4 cm; time 30 min; temp. 25–27°C.

Expt.	Electrolytes g/l		Current density	Powder obtained g	Current efficiency %	Observation
1	NaCl PbCl ₂	150 5	4	2.13	55.2	Amperage voltage remain constant, deposit spongy, evolution of Cl ₂
2	NaCl PbCl ₂	150 5	6	3.37	58.2	
3	NaCl PbCl ₂	150 5	8	4.64	60.1	
4	NaCl PbCl ₂	150 10	6	3.44	59.5	pH decreases with evolution of Cl ₂ , deposit spongy.
5	NaCl PbCl ₂	150 10	8	4.72	61.2	
6	NaCl KCl PbCl ₂	150 150 10	8	4.98	64.5	Voltage slightly decreased, amperage constant, deposit spongy, evolution of Cl ₂ .
7	KCl PbCl ₂	300 10	6	3.68	63.6	Lead in powder form, evolution of Cl ₂ .
8	CaCl ₂ PbCl ₂	300 10	6	3.84	66.4	Voltage and amperage remain constant. Powder is fine.
9	CaCl ₂ PbCl ₂	300 20	6	3.94	68.1	Voltage slightly decreased, deposit in fine state.
10	CaCl ₂ PbCl ₂	400 20	6	4.02	69.5	
11	CaCl ₂ PbCl ₂	400 20	6	4.12	72.3	Voltage slightly decreased. PbCl ₂ completely soluble in CaCl ₂ solution. Added hydrochloric acid for clarifying the solution.
12	CaCl ₂ PbCl ₂	400 20	6	4.0	70.2	No stirring and brushing was done. Deposit spongy and easily detachable from cathode.
13	CaCl ₂ PbCl ₂	500 10	6	4.08	7.06	Deposit in fine form, somewhat adherent to the cathode.
14	CaCl ₂ PbCl ₂	600 10	6	3.83	66.2	The deposit less spongy, more adherent to the cathode.
15	CaCl ₂ PbCl ₂	700 10	6	3.64	64.7	Voltage increased during deposition. Deposit more adherent and less spongy. Acid was added to clarify the solution.
16	CaCl ₂ PbCl ₂	800 10	6	3.49	60.3	Voltage increased, deposit adherent. More acid was required to clarify the solution.

TABLE 2.—EFFECT OF CURRENT DENSITY ON CURRENT EFFICIENCY

Electrolytes g/l, CaCl₂ 400, PbCl₂ 20; volume of electrolyte, 500 ml; electrodes, graphite; cathode area, 50 cm²; distance of electrodes, 4 cm; time 30 min; temp, 25–27°C.

Expt.	Current density amp/dm ²	Current deficiency %
1	2.0	62.2
2	4.0	77.5
3	6.0	78.1
4	8.0	78.3

TABLE 3.—EFFECT OF TEMPERATURE ON CURRENT EFFICIENCY

Electrolytes g/l, CaCl₂ 400, PbCl₂ 20; volume of electrolyte, 500 ml; electrodes, graphite; average voltage 3.4; average current density 5 amp dm²; cathode area, 50 cm²; distance of electrodes, 4 cm; time 30 min; pH 5–6.

Expt.	Temp °C	Current efficiency %
1	20	52.1
2	30	61.8
3	40	75.0
4	50	82.5
5	60	83.7

TABLE 4.—EFFECT OF pH ON CURRENT EFFICIENCY

Electrolytes g/l, CaCl₂ 400; volume of electrolyte 500 ml; electrodes, graphite; average voltage 3.5; average current density 5 amp dm²; cathode area, 50 cm²; distance of electrodes, 4 cm; time 30 min; temp. 25–27°C.

Expt.	pH	(PbCl ₂ 10 g/l) Current efficiency %	(PbCl ₂ 20 g/l) Current efficiency %
1	2.0	33.7	33.1
2	3.0	45.1	48.3
3	4.0	61.8	65.6
4	5.0	76.1	79.2
5	6.0	73.2	76.1
6	7.0	67.4	70.2

current efficiency gradually rises in the initial stages and remains constant over a range of 4.5–5 amp/dm², other conditions being constant. Current efficiency tends to drop as the concentration of PbCl₂ decreased. It was concluded that high concentrations of PbCl₂ with high current density would give high current efficiency. Though it is not possible to arrive at the optimum current density without the pilot plant studies, it is safe to conclude that 5 amp/dm² is the optimum.

High values even up to 6 amp/dm² do not materially change the nature of the product.

Effect of Temperature.—The results recorded in Table 3 show that increasing the temperature beyond a certain limit has a retarding effect on the deposition of powder. At low temperatures, i.e. 20–25°C, the current efficiency is low. It was not reasonable to increase the temperature beyond 60°C as it decreased the current efficiency. Initiation of deposit was not hindered even at as low a temperature as 20–25°C while actual deposition was convenient and profitable at about 50–55°C.

Effect of pH.—Table 4 shows the effect of pH on the current efficiency at two selected concentrations. The current efficiency attains the maximum at pH 5–6. Further increase in pH would bring about a decrease in the current efficiency. Moreover, the pH shows a tendency to go down with the increase in concentration of PbCl₂. It is thus concluded that pH is related to electrolyte concentration for good deposition efficiency.

Effect of Concentration of PbCl₂ and CaCl₂.—A rise in the current efficiency was observed with the increase in the concentration of CaCl₂ and PbCl₂, attaining its maximum at 400 g/l and 20 g/l, respectively. At higher concentration of CaCl₂ the deposit was not spongy and easily detachable from the cathode as is apparent from the observations in Table 1.

Deposition of Powder from NaOH Electrolyte.—Table 5 shows the effect of variation in the concentration of NaOH on the current efficiency. The cell functions normally when the concentration of NaOH is not below 100 g/l. With the increase in the concentration of NaOH, current efficiency increases and is maximum at 180 g/l at 25–27°C at a current density of 5.5–6 amp/dm². To ensure better strip from the electrolyte a concentration as high as 200 g/l being practicable. The deposit is spongy at room temperature. In the deposition of lead sponge the lead anodes dissolve in the electrolyte to keep the solution approximately constant in composition. This arrangement serves only as a medium for transforming lead anodes into powder. This point is of importance as it should allow the manufacture of lead powder at each mill by casting lead into anodes instead of ingots.

Addition of NH₄OH in small amounts helped in smooth deposition of the spongy lead. Excessive amounts of NH₄OH, however, decreased the current efficiency and was not desirable on this account.

TABLE 5.—PREPARATION OF ELECTROLYTIC LEAD POWDER USING SODIUM HYDROXIDE BATH.

Volume of electrolyte, 500 ml; electrodes, lead; cathode area, 45 cm²; distance of electrodes, 4 cm; time 30 min; temp 25–27°C.

Expt	Electrolytes g/l		Current density/dm ² amp	Powder obtained g	Current efficiency %	Observation
1	NaOH	100	3.33	1.93	68.2	Deposit fine and spongy
2	NaOH	100	3.33	1.88	66.1	Deposit fine, spongy and nonadherent to cathode.
3	NH ₄ OH	30 ml	3.33	2.2	77.0	Deposit as above, initial voltage 1.2, after 6 min 3 and afterwards constant.
	NaOH	120				
4	NH ₄ OH	50 ml	3.33	2.38	82.6	Deposit spongy, voltage constant for 15 min then increased and remained constant.
	NaOH	140				
5	NaOH	140	3.33	2.34	81.2	Deposit spongy, easily detachable than that with no NH ₄ OH. After 6 to 7 min voltage increased then remained constant.
	NH ₄ OH	10 ml				
6	NaOH	160	3.77	2.77	84.6	Deposit fine and spongy. Voltage is lower than with NH ₄ OH.
7	NaOH	160	3.33	2.41	83.4	Vlt increased after 6 min remained constant. Deposit spongy and easily detachable.
	NH ₄ OH	10 ml				
8	NaOH	160	3.33	2.39	82.8	
	NH ₄ OH	30 ml				
9	NaOH	180	3.33	2.43	85.2	
10	NaOH	180	3.33	2.41	84.4	
	NH ₄ OH	10 ml				
11	NaOH	180	3.33	2.39	83.6	
	NH ₄ OH	30 ml				
12	NaOH	200	3.37	2.86	87.2	Deposit similar to that obtained in expt. 6
13	NaOH	200	3.4	2.61	86.3	Deposit similar to that obtained in expt. 9
	NH ₄ OH	10 ml				
14	NaOH	200	3.33	2.44	84.5	
	NH ₄ OH	30 ml				
15	NaOH	180	4.5	3.5	87.4	
	NH ₄ OH	20 ml				
16	NaOH	180	5.5	4.22	89.8	
	NH ₄ OH	20 ml				
17	NaOH	180	6.2	4.85	91.3	
	NH ₄ OH	20 ml				
18	NaOH	180	7.0	5.37	89.5	
	NH ₄ OH	20 ml				

Apparent Density.—In powder metallurgy, the weight of a unit volume of powder, usually expressed as grams per cm³ or grams per inch³ determined by a specific method of loading.

Attempts were made to determine the apparent density of the powder by direct addition into a 5-cm³ weighing bottle. Excess powder forming heaps in the bottle was removed with a scraper after prolonged tapping of the bottle. The powder filling the bottle was weighed to calculate its apparent density. It was found to be in the range of 3.4 to 4.8 g/cm³. The apparent density decreases with the decrease in the particle size. Flaky powders have low density due to the edge-wise positions and bridging tendency of the particles. The particle size of the powder was determined by passing it through a set of sieves; 94–96% of the powder passed through 200 mesh sieve.

Conclusion

Current efficiencies of the order of 83.7% can be obtained using an electrolyte containing 400 g/l

CaCl₂ and 20 g/l PbCl₂ employing graphite electrodes at a temperature of 50–55°C, a pH of 5–6 and current density of 5 amp/dm². Using NaOH 160–180 gm/l as an electrolyte with 10–30 ml/l NH₄OH (sp. gr., 0.88) and lead electrodes, a current efficiency as high as 91% could be obtained.

References

1. G. Goetzel, *Treatise on Powder Metallurgy* (Interscience, New York), Vol. 1, p. 201.
2. G. Goetzel *Treatise on Powder Metallurgy* (Interscience, New York), Vol. 2, p. 545.
3. Kenji Matsuo and Seiji Saito, Japan Patent 40, 828, November 30, 1921.
4. V.S. Lyzlov, G. N. Kalaida and A. Landers, Russian Patent 58, 770, January 31, 1941; *Chem. Abstr.*, **39**, 874 (1945).
5. N.T. Kudryavtsev and E. A. Tereshkooich, *Zhur. Priklad. Khim.*, **23**, 607 (1950); *Chem. Abstr.*, **44**, 7675 (1950).