Electrolytic production of metallic cadmium and cadmium–sodium alloys in alkali melts

N.M. BARBIN

Institute of High-Temperature Electrochemistry, Ural Branch RAS, 22 S.Kovalevskaya St., 620219, Ekaterinburg, Russian Federation
(e-mail: N.Barbin@ihte.uran.ru)

Abstract

Reprocessing of cadmium-containing wastes and used storage batteries produces cadmium oxide. Electrowinning of the metal from an alkali melt is proposed for processing of CdO and production of metallic cadmium or cadmium–sodium alloys. The design of a laboratory electrolyzer is discussed. Technological parameters of the electrolysis process are determined. Applied and engineering aspects of the electrowinning of cadmium and cadmium–sodium alloys are considered. Conditions of the electrolytic production of cadmium are optimized. Specific features of the electrochemical production of cadmium–sodium alloys are analyzed. Electrowinning of cadmium from an acid or chloride solution is considered. The comparison of the electrolysis of aqueous solutions and alkali melts is in favor of the latter.

1. Introduction

Metallic cadmium has various technological applications such as in nickel–cadmium and silver–cadmium storage batteries, functional alloys and coatings [1]. Cadmium is used for the synthesis of chalcogenide compounds and the production of semiconductor intermetallics $A^{II}B^{VI}$ and also in control rods in nuclear power plants [2].

Cadmium does not form separate deposits, but is an element associated with zinc and complex ores. Therefore, cadmium production technologies are developing in step with methods for production of zinc and lead. Almost all cadmium producing installations are part of zinc and lead producing facilities [3].

The main starting materials for cadmium are by-products of zinc and lead metallurgical processes (copper–cadmium cakes, dusts left after lead blast smelting, etc.). Cadmium can be extracted from these materials either by the pyrometallurgical (fractional distillation) or hydrometallurgical method or using a combination of these methods. The most widespread technique is the hydrometallurgical method, which consists of the following operations: oxidation of cadmium; leaching; cleaning of the solution and precipitation of the cadmium sponge; oxidation of the sponge, its repeated dissolution and cleaning of the solution; electrowinning; smelting of cathodic cadmium [3, 4].

Electrowinning requires the use of an aqueous electrolyte containing (g l^{-1}) 100–250 Cd, up to 12 H$_2$SO$_4$, up to 80 Zn, 0.001 Cu, 0.02–0.03 Fe, and up to 10 Mn [5].

Electrowinning of cadmium is realized in electrolyzers fitted with insoluble lead anodes and aluminum cathodes. The electrolyte temperature is maintained at 25–40 °C. The current density is 30–50 A m^{-2}. The deposit accumulation time is 24 h, while the current yield is 70–90%. If the electrolyte is circulated, the current density may be increased to 100–200 A m^{-2}. The specific power consumption during the electrolysis is 1400–1600 kW h t^{-1}. The current density may be as high as 250–300 A m^{-2} in electrolyzers with moving cathodes.

Electrowinning of cadmium with cadmium sponge as the product can be accomplished in a chloride solution containing 15–30 g l^{-1} Cd passed through contact and ion-exchange columns. Cadmium is recovered in electrolyzers with graphite anodes and aluminum cathodes at a current density of 100–800 A m^{-2}. The current yield of cadmium is over 90%, while the metal purity is 98–98.5%. The specific power consumption is 2–4 kW h t^{-1} [6, 7].

After the electrolysis procedure about 10% of cadmium is in the form of scrap and debris, which are returned to the dissolution stage. Cadmium cathodes are melted in steel pots under a layer of molten caustic soda. This treatment removes zinc and lead, which form sodium zincate and plumbate. The temperature is 400–500 °C and the cadmium loss is 2–4% [8].

After the remelting operation the cadmium pig contains 0.002–0.005% Pb, 0.001–0.005% Zn, and 0.002–0.003% Cu. The cadmium purity can be improved if the cast metal is refined additionally by electrolysis or distillation [3]. A drawback of electrowinning of cadmium from aqueous solutions is low current density and small current yield.

Secondary raw materials are used increasingly in industry. This is especially important with respect to expensive and scarce rare metals, including cadmium. Therefore, the present study is focused on conditions of electrowinning of cadmium from an alkali oxide melt (the current yield and the metal purity) providing better reprocessing of cadmium wastes.

Cadmium-containing wastes and battery scrap are left after production of alkaline nickel-cadmium batteries. Cycling leaching is used for selective recovery of cadmium from the scrap. This process includes the following main stages:

– the plates are washed to remove the KOH-containing electrolyte;
– calcination at 250–300 °C for oxidation of metallic cadmium and decomposition of cadmium and nickel salts;
– the wastes are leached in an ammonia carbonate solution. The products of this operation are an aqueous solution which contains cadmium, nickel and cobalt as amine complexes, and bottoms containing all the iron present in the starting material;
– treatment of the aqueous solution with a water-insoluble organic solution containing hydroxyoxime, which selectively recovers nickel compounds. Then nickel is separated as nickel sulfate, for which purpose the compounds are treated with an aqueous solution of sulfuric acid;
– ammonium is removed from the solution and cobalt precipitates in the form of carbonate;
– ammonium is removed from the solution and cadmium precipitates in the form of carbonate. Separation cadmium carbonate.

Nickel and cadmium pass to the solution at the leaching stage, while iron remains in the leached material. If conditions are optimal, the yields of nickel and cadmium are >95% and >99% respectively. The method [9] ensures a high purity of final cadmium carbonate. Carbonate is calcined to obtain cadmium oxide.

A method of electrowinning of cadmium from an alkali-oxide melt was proposed [10, 11] for reprocessing of CdO and production of metallic cadmium. It was found [12] that the cadmium precipitation voltage during the electrolysis of a NaOH melt containing 5% CdO at 480 °C was 0.89 V. It was proposed to use a NaOH melt for electrolytic refinement of cadmium, [3, 13]. When cadmium oxide is fused with an alkali at 450–500 °C, sodium cadmiate is formed by the reaction

$$CdO + 2NaOH = Na_2CdO_2 + H_2O \qquad (12)$$
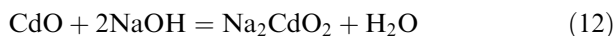
2. Experimental

A laboratory electrolyzer (Figure 1) was placed in an electric resistance furnace with automatic temperature control. The electrolyzer was a beryllium-oxide crucible (1) containing the melt (2). Circular electrodes – the cathode (3) and the anode (4) – were immersed into the melt. The electrode current leads (5, 6) in the form of rods were protected with beryllium-oxide sleeves (7, 8). The current leads were clamped between asbestos-cement plates (9) to ensure a constant distance between the electrodes. A liquid cathode was used in the experiment, for which purpose the electrode (3) was immersed in the layer of molten cadmium (10). Cadmium oxide was charged on the upper surface of the anode (11). The liberated gas mixed the melt, facilitating rapid dissolution of cadmium oxide.

Nickel served as the anode material. Nickel is covered with a thin oxide film and does not corrode at temperatures of up to 600 °C in alkali melts. It is resistant in oxygen atmospheres at temperatures of up to 600 °C and has a high electrical conductivity. Anodic dissolution of nickel does not take place in alkali melts. Oxygen is liberated at the anode. The cathode material was iron or nickel, because these materials dissolve only sparingly in molten cadmium during cathodic precipitation of cadmium.

The solvent melt was a mixture of NaOH or KOH and sodium, potassium or calcium carbonate in an 80:20 percentage ratio of the alkali and carbonate respectively. The reagents were "chemically pure" grade. The melt was allowed to stand for two hours at 500–550 °C to remove most of the moisture. For complete removal of
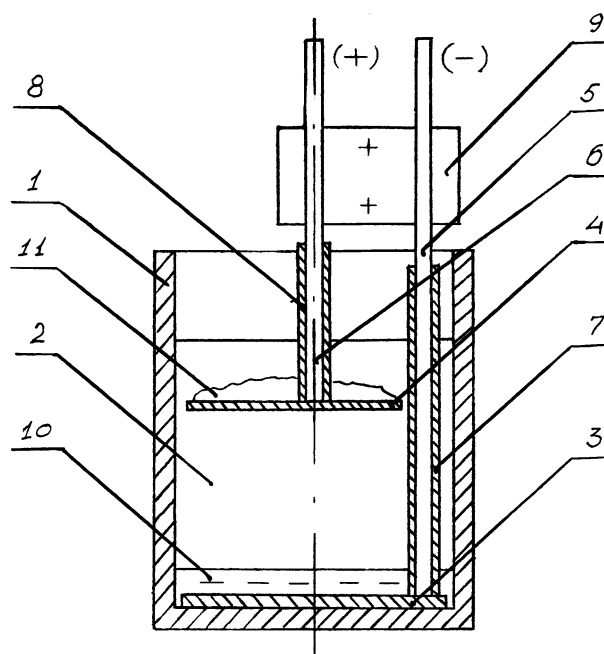

Fig. 1. Laboratory electrolyzer: 1 – beryllium oxide crucible; 2 – melt; 3 – cathode; 4 – anode; 5, 6 – current leads; 7, 8 – protective sleeves of beryllium oxide; 9 – asbestos-cement clamps; 10 – molten cadmium; 11 – cadmium oxide.

water from the melt, the electrolysis was conducted at a current of 1.2 A and a voltage of 1.17 V (that is, not over 100 A m^{-2}). After the moisture was removed, 10–15 g of metallic cadmium and 5 g of CdO were charged into the cell. Then CdO was added at regular intervals. A direct current was passed through the cell. Experiments were performed at different values of the current density. The distance between the electrodes was preset at 2–5 cm, while the melt temperature was adjusted at 450–600 °C.

After the experiment the crucible contents were poured into a graphite mold and were allowed to cool down. The metal was separated from the salt and weighed. The current yield of cadmium was determined and metallic cadmium was analyzed for the concentration of impurities using a PE-404 spectrophotometer.

3. Results and discussion

3.1. *Production of metallic Cd*

Table 1 gives technological parameters and results of experiments on production of cadmium by the electrolysis of a cadmium-containing melt. The best results were obtained at a cathodic current density of 5.10–7.65 kA m^{-2}, an anodic current density of 6.37– 9.55 kA m^{-2}, a temperature of 500 °C, the inter-electrode distance of 4 cm, and a cadmium oxide concentration of 3%.

The interelectrode distance of 3.5–4.5 cm proved to be most reasonable since the current yield was a maximum and the ohmic resistance of the melt was the largest. If the cadmium oxide concentration of the melt was less than 3%, the current yield decreased due to the deficiency of cadmium ions. If the cadmium oxide concentration was over 6%, thick viscous precipitates of undissolved cadmium oxide appeared in the melt.

If the temperature was lower than 450 °C, the melt thickened and the current yield decreased to 20%. At temperatures above 600 °C the melt evaporated considerably and the electrolyzer components corroded increasingly.

The experimental results were processed using a complex method [14] so as to ascertain how several parameters of the process (the melt composition, the cathodic and anodic current densities, the interelectrode distance, the cadmium oxide concentration, and the temperature) influenced the current yield. Acceptable results (current yield of 72–78%) could be obtained if not more than two parameters of the process approached or were equal to maximum (best) values (experiments 5, 9, and 11). The current yield decreased to 36–55% at three limiting parameters and 20% at four limiting parameters of the process (experiments 6 and 7).

The electrolyzer voltage did not exceed 3–3.5 V at a current density of 5–6 kA m^{-2}. The specific power consumption was 1.3–1.5 kW h per kilogram of cadmium. This value is much smaller than that one necessary for the electrolysis of aqueous solutions. The output per 1 m^2 of electrolyzer surface area was tens of times larger than in electrolyzers with aqueous electrolytes.

The chemical composition of cadmium produced in some experiments is given in Table 2. The proposed method allows pure cadmium to be produced in a single electrolysis operation.

Table 1. Technological parameters and results of electrolytic production of cadmium

Exp. No.	Melt composition/mass %	Current density / kA m^{-2}		Inter-electrode distance/cm	T /°C	CdO concentration of melt / mass %	Current yield/%
		i_a	i_c				
1	NaOH(80)–Na$_2$CO$_3$(20)	25.4	2.04	4	500	6.0	54.1
2	NaOH(80)–Na$_2$CO$_3$(20)	3.82	3.06	4	500	3.0	74.2
3	NaOH(80)–Na$_2$CO$_3$(20)	6.37	5.10	4	500	3.0	98.85
4	KOH(80)–Na$_2$CO$_3$(20)	6.25	5.10	3	450	3.0	36.0
5	NaOH(80)–Na$_2$CO$_3$(20)	6.25	5.10	4.5	550	6.0	78.34
6	KOH(80)–Na$_2$CO$_3$(20)	6.25	5.10	5	450	6.0	20.0
7	NaOH(80)–Na$_2$CO$_3$(20)	6.25	5.10	2	450	6.0	35.1
8	NaOH(80)–Na$_2$CO$_3$(20)	7.64	6.12	4	500	3.0	89.0
9	NaOH(80)–Na$_2$CO$_3$(20)	9.37	7.65	5	600	4.0	71.8
10	NaOH(80)–Na$_2$CO$_3$(20)	9.55	7.65	4	500	3.0	82.7
11	NaOH(80)–Na$_2$CO$_3$(20)	9.37	7.65	3.5	600	6.0	71.94
12	NaOH(80)–CaCO$_3$(20)	12.73	10.20	4	500	8.0	42.0
13	NaOH(80)–Na$_2$CO$_3$(20)	19.11	15.31	4	500	10.0	55.52

Table 2. Concentration of impurities in cadmium (mass %)

Exp. No.	Zn/%	Pb/%	Fe/%	Cu/%	Na/%	Ni/%
3	2.3×10^{-4}	3×10^{-4}	1×10^{-3}	2.8×10^{-3}	1×10^{-3}	1×10^{-3}
5	2.5×10^{-4}	3×10^{-4}	1.5×10^{-3}	1.5×10^{-3}	1×10^{-3}	1×10^{-3}
8	1.8×10^{-4}	9×10^{-4}	1×10^{-3}	3.5×10^{-3}	1×10^{-3}	1×10^{-3}

3.2. Production of Cd-Na alloy

The liquid-metal Cd-Na system may be used in thermo-electrochemical converters of the thermal power to electricity [15]. Two congruently melting compounds, namely $NaCd_2$ ($T_m = 657$ K) and Na_2Cd_{11} ($T_m = 637$ K), are formed in the Cd–Na system [16, 17]. Moderate alternating deviations from Raoult's law are observed in liquid alloys of cadmium. These deviations are due to the formation of asymmetric intermetallic compounds [17–19]. The Cd-Na compound is prepared by alloying of the components [20].

An electrolytic method was developed for production of the cadmium-sodium alloy. By this method, sodium and cadmium precipitate simultaneously during the electrolysis of an alkali-carbonate melt containing 0.2–3.0 mass % of cadmium oxide. The process is accomplished using a liquid cadmium cathode at a current density of 1.7–4.0 kA m^{-2} and a temperature of 450–500 °C. Nickel serves as the anode material.

Figure 2 presents the dependence of the concentration of sodium in cathodic cadmium on the total concentration of CdO (dissolved and undissolved) in the electrolyte. The concentration of sodium in cadmium increased when the CdO concentration of the melt was less than 3 mass %.

If the cathodic current density was smaller than 1.7 kA m^{-2}, the sodium concentration of the alloy decreased, because sodium only began to precipitate. If the current density was over 4.0 kA m^{-2}, the sodium concentration of the alloy decreased because of the sodium thermal reduction of CdO (Figure 3).

The simultaneous electrolytic precipitation of sodium and cadmium provides a homogeneous alloy containing 0.1 to 12 mass % sodium. It need not be stirred and the alloy has a uniform composition.

4. Conclusion

A method was proposed for production of pure cadmium or a cadmium-sodium alloy. This method is
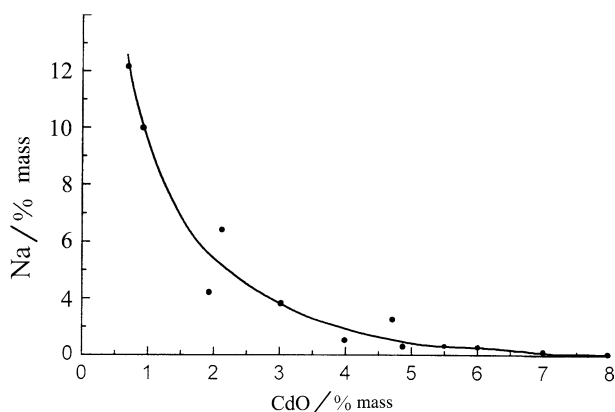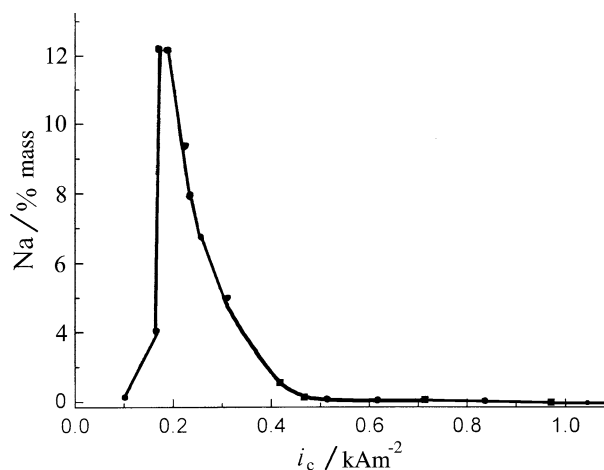

Fig. 3. Dependence of the concentration of sodium in cadmium on the cathodic current density.

reduced essentially to the electrolysis in a NaOH-Na_2CO_3 melt containing cadmium oxide. Optimal conditions for production processes were determined.

References

1. N.P. Lyakishev (ed.), *Encyclopedic Dictionary of Metallurgy* (Intermet Engineering, Moscow, 2000), 320 pp.
2. N.F. Cook, Metals and Miner. *Ann. Rev.* **1** (1992) 87.
3. D.M. Chizhikov, *Cadmium* (Nauka, Moscow, 1967), pp. 230.
4. I.N. Deliev, *Cadmium Metallurgy* (Metallurgizdat, Moscow, 1962), pp. 196.
5. A.L. Rotinyan (ed.), *Applied Electrochemistry* (Khimiya, Leningrad, 1974) 536 pp.
6. W. Schmidt, *Erzmetall* **12** (1979) 522.
7. C. Vladulescu, T. Valea and A. Cornea. C.P.P. Pat. 81200 (1978).
8. N.V. Gudima and Ya.P. Shein, *Handbook of Nonferrous Metallurgy* (Metallurgiya, Moscow, 1975), pp. 536.
9. M. Sitting, *Recovery of Metals and Inorganic Compounds from Wastes* (Metallurgiya, Moscow, 1985), pp. 410.
10. G.F. Kazantsev and N.M. Barbin, R.F. Pat. 2123544 (1994).
11. N.M. Barbin and G.F. Kazantsev, in Proc. XII Conf. "High-Purity Substances and Materials" (N. Novgorod, 2004) p. 96.
12. L. Rolla and R. Salani, *Gazzetta Chim. Ital.* **52** (1922) 286.
13. R.A. Lidin, V.A. Molochko and L.L. Andreeva, *Chemical Properties of Inorganic Substances* (Khimiya, Moscow, 1996), pp. 480.
14. Yu.P. Adler and Yu.V. Granovsky, *Review of Applied Studies on Planning of Industrial Experiment* (Moscow University Publishers, Moscow, 1967), pp. 312.
15. A.G. Morachevsky and I.A. Shesterkin, *Sodium* (Khimiya, St. Petersburg, 1992), pp. 390.
16. H.U. Borgstedt and C.K. Mathews, *Applied Chemistry of the Alkali Metals* (Plenum Press, N.Y.-London, 1987), pp. 450.
17. H.E. Bartlett, A.J. Neethling and P. Crowther, *J. Chem. Thermog.* **4** (1970) 523.
18. K. Hauffe, *Z. f. Elektrochem.* **6** (1940) 348.
19. S. Harada and S. Takahasi, *J. Phys. F: Met. Phys.* **18** (1988) 2559.
20. V.N. Kornienko and N.N. Zhuravlev, *Kristallografia* **4** (1972) 863.

Fig. 2. Dependence of the concentration of sodium in cadmium on the concentration of CdO in the NaOH–Na_2CO_3 (20 mass %) melt.