

# Recycling of nickel–cadmium batteries using coal as reducing agent

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## Abstract

The objective of this work is to study the recycling of sealed nickel–cadmium batteries through cadmium distillation using a carbonaceous material as reducing agent. In spite of the existence of some industrial processes for nickel–cadmium batteries recycling, there are few fundamental studies about this subject. For the study of the reducing process, coal was added to the material of electrodes. Reduction process was performed from 700 to 1000 °C with different quantities of reducing added to the load. Results showed that cadmium purity is of approximately 99.92% and the main impurity found was zinc at around 200 ppm. A Ni–Co alloy containing 100 ppm cadmium was also obtained.

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*Keywords:* Nickel–cadmium Batteries; Recycling; Coal

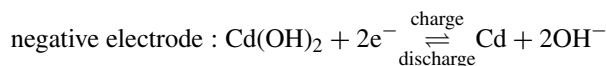
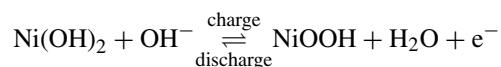
## 1. Introduction

Jungner developed nickel–cadmium alkaline cell technology in 1899. The materials to produce the batteries were scarce and expensive at that time, thus limiting the use of such batteries to very special situations, in which price was not a determining factor. In 1932 Shlecht and Ackermann invented porous nickel electrodes where the active materials of the batteries were deposited. This increased the contact area of the electrodes, allowing a higher velocity in the reactions of charge and discharge. This advance on the material of the electrodes was significant for the development of sealed batteries [1].

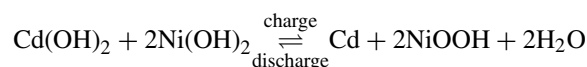
In 1947 Neumann succeeded in re-combining gases from the reaction of batteries, thus allowing the creation of sealed nickel–cadmium batteries. Up to then, vented (open) batteries were used to allow the exhausting of gases that were formed in the reaction. These advances allowed the evolution of this type of battery to their present state [1].

Nickel–cadmium batteries have a cadmium cathode which transforms to Cd(OH)<sub>2</sub>, and a NiOOH anode which transforms to Ni(OH)<sub>2</sub>. Charge and discharge reactions could thus be described in a simplified way [2–4]:

positive electrode :



global reaction :

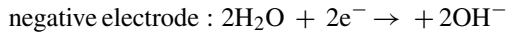
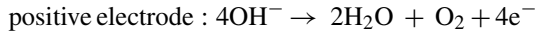


This reaction can be reverted by passing an electric current in the system, during the charging period of the battery.

Nickel–cadmium batteries can be classified in two types: vented (open) and sealed. Vented batteries are normally used for industrial applications. Industrial batteries need high rates of charge and discharge and may eventually need electrolyte or water reposition.

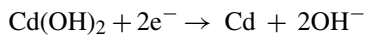
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In order to maintain their capacity, cells need to be overcharged at a level of at least approximately 10% above their limit. As a result,  $\text{Cd}(\text{OH})_2$  of the negative electrode is completely consumed. During the overcharge, oxygen is generated in the negative electrode, while hydrogen is liberated in the positive electrode, as represented by the following equations [5]:



For eventual periods of overcharge in sealed batteries, the formation of hydrogen should be avoided and the reaction of oxygen with cadmium should be promoted. Hydrogen evolution is prevented by keeping an excess of cadmium hydroxide in relation to the nickel hydroxide. In the case of oxygen, the gas diffusion is increased by the use of high porosity electrodes, and limiting the quantity of water in the electrolyte, and finally increasing the quantity of cadmium. Hydrogen formation must be prevented because the hydrogen combination in the negative electrode is an extremely slow reaction.

Another method to prevent hydrogen formation is the addition of  $\text{Cd}(\text{OH})_2$  to the positive electrode. Thus, instead of the formation of hydrogen, the following reaction would occur:



The result of the overcharge process is the evolution of oxygen in the positive electrode, followed by its diffusion and the oxidation of cadmium in the negative electrode.

Sealed batteries usually are applied in household applications. Sealed batteries are classified by their format: button, rectangular and cylindrical [6].

Regarding nickel–cadmium batteries for mobile phones, the most common shape is the cylindrical one. A group of cylindrical batteries is inserted in a shock resistant plastic case. An example of plastic is the ABS type, a copolymer composed of acrylonitrile, butadiene and styrene. These batteries are formed by sintered electrodes rolled from the nucleus.

The main materials in batteries formation are: isolators, positive electrodes, separators, negative electrodes and metal cup [3].

The metal cup is made of nickel-plated steel. The negative electrode is made of a cadmium and  $\text{CdO}$  mass or  $\text{Cd}(\text{OH})_2$ . The positive electrode is made of a nickel plate with holes on it, and a paste made of nickel, cobalt and cadmium hydroxides. Graphite and iron oxide powder are normally added to increase electric conductivity of the nickel and cadmium hydroxide powders [3,5,7].

Cobalt powder, cobalt hydroxide or other forms of cobalt are added to nickel electrodes to improve the performance of the accumulator. These electrodes are used in nickel–cadmium, nickel–metal hydride and nickel hydrogen accumulators. These cobalt compositions are used to cover nickel hydroxide particles, thus causing an increase in the potential difference between the desired nickel hydroxide

oxidation reaction and the undesired oxygen discharge reaction [8].

The electrolyte is a  $\text{KOH}$  25–35% solution imbibed in a separator. This separator is made of a material that remains stable at operation temperatures and presents sufficient mechanical resistance for the operation of battery fabrication. Another important characteristic of the separator is its permeability to oxygen. In sealed batteries, the separator must be permeable to oxygen, while in open batteries it must be non permeable to the passage of oxygen. In general, polyamide screens, such as nylon, polyethylene or polypropylene are used in sealed batteries. In open batteries, the separator is composed of cellophane with nylon or micro porous polypropylene or polyethylene [9,10].

A review of the current processes and technologies to recycle nickel–cadmium batteries was recently published [11,12].

## 2. Thermodynamics of cadmium distillation

During batteries distillation process the decomposition of cadmium and nickel hydroxides occurs first. The products from this decomposition are the oxides of the same elements. As heating proceeds, there is the possibility of decomposition of cadmium oxide, with the formation of cadmium vapor. This decomposition is achieved by the reduction of the partial activity of cadmium vapor in the atmosphere, or by the presence of a reducing agent.

During the heating of a load containing cadmium and nickel hydroxides, the decomposition of the hydroxides occurs first. In the presence of a carbonaceous reducing agent, the system should be analyzed through the following equations:

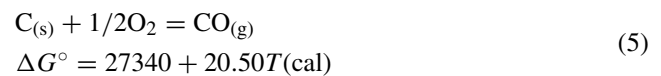
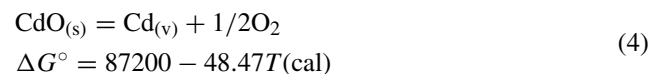
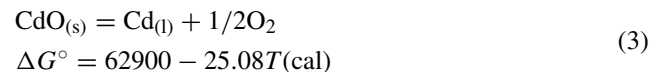
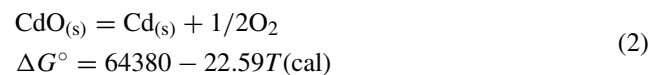
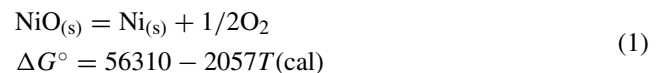


Fig. 1 shows the  $\Delta G^\circ$  curves as a function of temperature for the Eqs. (1)–(5). The reduction through carbon is thermodynamically feasible at significantly low temperatures, either for  $\text{NiO}$  or  $\text{CdO}$ . For  $\text{NiO}$ , the reduction is possible starting from  $435^\circ\text{C}$  (708 K), while the  $\text{CdO}$  reduction, generating liquid cadmium occurs at temperatures above  $507^\circ\text{C}$  (780 K). Above the temperature of  $767^\circ\text{C}$ , and under atmospheric pressure, cadmium is produced in the form of vapor.

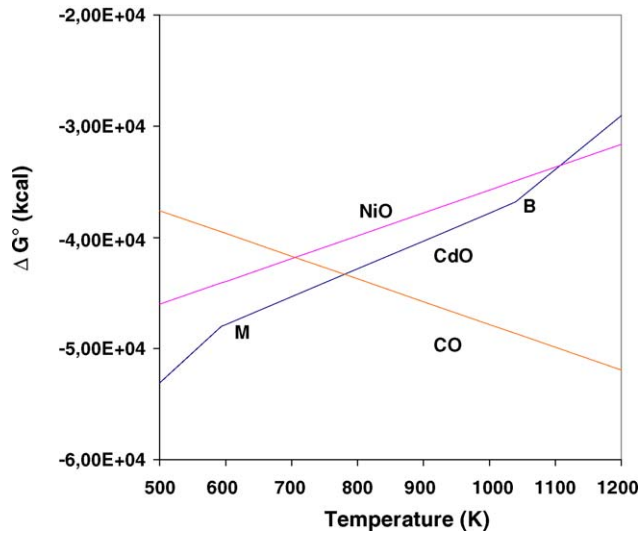


Fig. 1.  $\Delta G^\circ$  curves as a function of temperature for CO, NiO and CdO formation. Indications M and B on CdO curve respectively indicate passage of cadmium from solid to liquid, and from liquid to vapor.

### 3. Objectives

The objective of this work is to study the recycling of nickel–cadmium sealed batteries through a pyrometallurgical process through cadmium distillation by using a carbonaceous reducing agent.

### 4. Materials and methods

Discharged batteries from portable phones were collected by a manufacturer of electronic equipment, and were used in this study. The characterization of the used nickel–cadmium batteries and the initial stages of separation of the scrap were previously described. The reduction tests were carried out using essentially the same procedures described elsewhere [13,14].

Anthracite was used as the reducing agent. The particle size of the anthracite was below  $106 \mu\text{m}$  and the fixed carbon was 83.83%.

The anthracite quantity added to the milled accumulator load was calculated based on chemical analysis. The amount added was sufficient for reduction of cadmium, nickel and cobalt oxides. Two series of tests were carried out. In one of the series, anthracite was added in the stoichiometric quantity for the oxides reduction; in the second series, anthracite was added using 20% excess to the stoichiometric quantity. Tests executed in this phase are listed in Table 1.

The products of the reaction are the material remaining in the crucible and on the condenser. The condensed material was submitted to chemical analysis, where atomic absorption spectrophotometry was the technique applied, while the material in the crucible was sent to the determination of particle size distribution.

Table 1  
Cadmium distillation: list of tests

Test	Quantity of reducing agent	Temperature (°C)	Period of time (h)
RDe7–30	Stoichiometric	700	0.5
RDe 7–1			1
RDe 7–2			2
RDe 7–4			4
RDe 9–30	Stoichiometric	900	0.5
RDe 9–1			1
RDe 9–2			2
RDe 9–4			4
RD7–30	20% excess	700	0.5
RD7–1			1
RD7–2			2
RD7–4			4
RD9–30	20% excess	900	0.5
RD9–1			1
RD9–2			2
RD9–4			4
RD11–30	20% excess	1100	0.5
RD11–1			1
RD11–2			2
RD11–4			4

After screening, samples of fractions under 2.38 mm were sent to chemical analysis. The concentration of nickel, cobalt and cadmium were determined through chemical analysis. Fractions of the material which were above 2.38 mm were essentially composed of metal fragments, originated from the metal wrap, and metal screens.

### 5. Results and discussion

The percentages of cadmium removed at the different tests were calculated from the initial and final masses in each test and from the cadmium concentrations in the initial and final samples. The initial cadmium quantity was considered as 23 wt.% as found in the characterization of accumulator step [15]. Therefore, the removed percentage of cadmium was calculated by the following expression:

$$\text{Cd removal} = \frac{M_i \times \% \text{Cd}_i - M_f \times \% \text{Cd}_f}{M_i \times \% \text{Cd}_i} \times 100$$

where  $M_i$  is the load's initial mass,  $\% \text{Cd}_i$ , the initial cadmium concentration (wt.%),  $M_f$ , the mass of the material remaining at the crucible after the test and  $\% \text{Cd}_f$  is the final cadmium concentration (wt.%) in the crucible.

Two mixtures were performed of the material coming from physical conditioning and reducing agent. One of the mixtures contained the stoichiometric quantity of reducing agent for the reduction of cadmium, nickel and cobalt oxides present in the sample. The other mixture was prepared using 20% excess of reducing agent. The reducing agent used was anthracite, with particle size 100% under  $106 \mu\text{m}$ , and presenting 83.83% of fixed carbon.

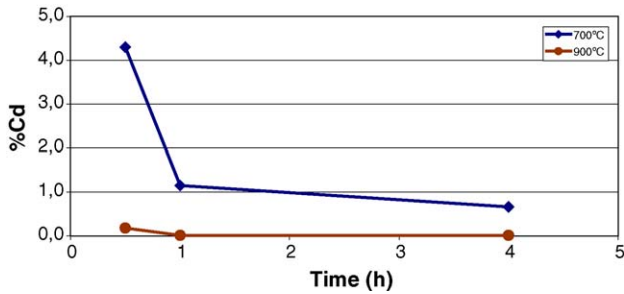


Fig. 2. Cadmium concentration in the samples remaining in the crucible at the end of the RDe tests.

Tests were carried out in a nitrogen atmosphere to avoid the oxidation of cadmium vapor formed during the distillation process. Test temperatures were of 700 and 900 °C for the mixture with stoichiometric reducing agent and 700, 900 and 1100 °C for the mixture using 20% excess of carbon.

The cadmium quantity of the sample that remained in the crucible after the end of each test was analyzed by atomic absorption spectrophotometry. The results related to RDe tests (with stoichiometric reductor) are shown in Fig. 2. The results related to RD tests (samples with 20% reductor excess) are shown in Fig. 3.

Tests at 700 °C were less efficient than at 900 °C.

For the RDe7 test (700 °C, stoichiometric reducing agent) and for the RD7 tests (20% reducing agent excess and temperature of 700 °C) the maximum cadmium removal was of approximately 98%.

For the RDe9 tests (900 °C and stoichiometric reducing agent), the cadmium removal was calculated at over 99.95% after 1 h of reduction. For the RD9 tests the cadmium removal was of 99.9% with only 30 min, recoveries of 99.99% were obtained after 4 h of reaction. All tests at 1100 °C presented a cadmium removal of 99.99%.

The material condensed in the tests was directly sent to chemical analysis, and the result was identical to what was obtained using an inert atmosphere [14]. Cadmium purity is of approximately 99.92% and the main impurity found was zinc at around 200 ppm.

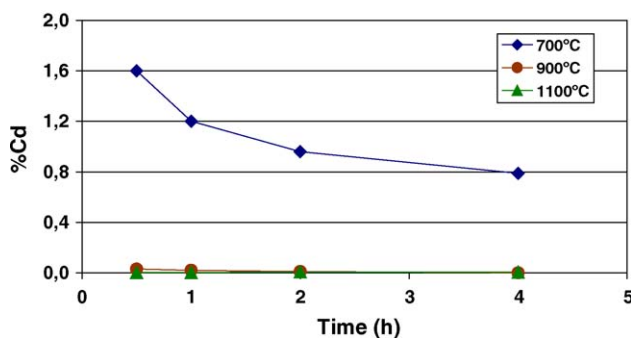


Fig. 3. Cadmium concentration in the samples remaining in the crucible in the RD tests.

The presence of zinc in the condensed material was expected, since both positive and negative electrodes have zinc in their composition [15].

The result of chemical analysis for the evaluation of the amount of nickel, cobalt and cadmium in the fractions obtained in the separation by particle size showed that cadmium concentrates in the smaller particles and the material is basically composed by a Ni–20% Co alloy. The same behavior was found in a recycling process under vacuum [13].

Some differences between the processes must be considered in the choosing of a process to recycle batteries, for example, the vacuum process in which there is no need of reducing agent to execute the treatment. The pyrometallurgical processes that recycle nickel–cadmium batteries were initially developed to recycle industrial batteries. Even now, these processes still operate with loads mainly composed of material from industrial nickel–cadmium batteries. These batteries are previously opened, the electrolyte is drained and nickel is extracted from its interior, and the plastics are also separated. Thus, only the material from the negative electrode (specially cadmium hydroxide) that goes through the pyrometallurgical process of cadmium distillation.

From the thermodynamic point of view, just the use of an inert atmosphere, with low partial oxygen pressure, should be sufficient for cadmium distillation [14]. Therefore, in order to avoid reducing agent addition in the load, the use of high purity nitrogen or argon would be necessary, which would make the process very expensive. The use of some material to consume the oxygen inside the furnace is a way to reduce the partial oxygen pressure during treatment. In this last example, the cheaper material would be carbon, which would cause the reduction of oxygen potential below the necessary level for the CdO decomposition. The presence of the electrolyte fabric could help in the reduction causing the lowering of the oxygen potential. Tests executed afterwards showed that nickel and cadmium oxides reductions occur even without the presence of a reducing agent. This effect was attributed to the presence of the polymer (fabric) between the electrodes, which was not separated during the scrap milling.

## 6. Conclusions

For the tests conditions presented on this research, the achieved results led to the following conclusions:

1. Cadmium recovery is possible at 900 °C. At lower temperatures the reaction rates are too slow.
2. The major impurity found in the condensate material was Zn in the range of 200 ppm. The cadmium purity was about 99.92 wt.%.

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