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Short communication

Use of nitrogen in the recycling of nickel cadmium batteries

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Abstract

The present work considers the fundamental aspects of the NiCd battery recycling process. The objective was to study temperature and atmosphere effects on the decomposition of cadmium oxide in NiCd sealed batteries' electrodes. Initially, cellular phone batteries were physically conditioned so as to obtain a mixture of ground electrodes. This material was submitted to thermal tests in laboratory scale equipment. Tests were conducted using nitrogen as a inert atmosphere, with temperatures from 600 to 1000 °C. Products from the reaction were characterized by X-ray diffraction, atomic absorption spectrophotometry and size particle distribution. High purity Cd was obtained in the condenser and a Ni–Fe–Co alloy with <100 ppm of Cd was also found in the crucible. Zinc was the main impurity in the condensed material.
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1. Introduction

The number of processes for battery recycling has increased over the last few years, mainly because of the environmental impact caused by their disposal. NiCd batteries are considered toxic due to their high Cd concentration. On the other hand, NiCd batteries also count on the most developed and efficient recycling processes. Consequently, NiCd systems may be considered better than other types of batteries regarding sustainable development.

Nevertheless, there is little knowledge about the NiCd battery treatment processes. Available literature only describes industrial development and almost no fundamental aspects.

This paper presents a study on the influence of reduction of oxygen partial pressure contained in the furnace atmosphere, during NiCd recycling process.

From the thermodynamic point of view, the most important reaction to be considered in NiCd battery recycling is:

$$2CdO_{(1)} \rightarrow 2Cd_{(v)} + O_{2(g)}$$

Therefore, cadmium oxide decomposition can be caused by reduction of the total pressure or oxygen partial pressure. Industrial processes for the recycling of NiCd batteries are thus based on this principle. The treatment is either through reduction of total pressure when heating under vacuum is used, or through the reduction of oxygen partial pressure during heating. The reduction of oxygen partial pressure can be achieved in two ways, either by using a reducing agent or using an inert gas.

2. Objective

The objective of the present paper is to study the effects of temperature and of the reduction of oxygen partial pressure on the decomposition reaction of cadmium oxide present in NiCd sealed batteries. Oxygen partial pressure reduction was obtained through the use of nitrogen as an inert gas.

3. Experimental procedure

The loads for the experiments were prepared in the following way. Initially, sealed NiCd batteries were milled in a hammer mill to remove the plastic case. Then, the accumulators were milled in a knives mill to reduce the size and release the components. Consequently, material used in thermal tests was composed of a mixture of milled electrodes.

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Equipment was set up for the study of the decomposition of cadmium oxide in NiCd batteries to work either under vacuum or under controlled atmosphere.

The equipment essentially consisted of a tubular electric furnace, a stainless steel retort and a water-cooled copper condenser. It was assembled within a glove box with transparent acrylic walls and an exhaust.

The gas system was basically composed of a flange with four gas inlets to the condenser, and a gas outlet from the condenser. During the tests, the off-gas coming from the furnace was purged in water before released into the glove box.

A second condenser was developed, called *cold finger*. The cold finger is essentially a water-cooled copper stem, inserted in the interior of the retort, close to the crucible. Thus, vapor formed during the process passes through two different condensers before leaving the set up and being purged in water.

3.1. Inert atmosphere distillation

In all tests, the load was composed of material obtained through physical conditioning of the used batteries, which means milled batteries.

Material was placed in the alumina crucible, which was inserted at the center of the furnace so as to be totally within the hot zone of the furnace. Inert gas was purged in the retort 1 h before starting to heat up the furnace. Standard purity nitrogen was used as an inert gas.

After the cooling period, the furnace was opened and two types of products were collected: the material remaining in the crucible and the condensed material.

Table 1 lists the tests performed with samples coming directly from the batteries physical conditioning step.

Tests were divided in two series. The NT series corresponds to tests with increasing temperatures but with a constant holding time. While in each of the ND series the temperature was kept constant and the holding time varied.

Table 1
Cd distillation tests

Test name	Temperature (°C)	Holding time (h)
NT600	600	2
NT700	700	2
NT800	800	2
NT900	900	2
NT1000	1000	2
ND7-30	700	0.5
ND7-1		1
ND7-4		4
ND9-30	900	0.5
ND9-1		1
ND9-4		4
ND11-30	1100	0.5
ND11-1		1
ND911-4		4

3.2. Products characterization

Characterization of the products was obtained using X-ray diffraction and atomic absorption spectrophotometry. X-ray diffraction was used in both types of samples, and atomic absorption spectrophotometry chemical analysis only on samples from the crucible where only the residual Cd concentration was analyzed.

The material from the crucible was also sent for particle size classification.

Therefore, sieves were used for classification tests in order to determine the size distribution of the product of the reaction found in the crucible. Sieves used in the separation of the product were: 7.93, 2.38, 0.71, 0.30, 0.106, and 0.045 mm.

After going through the sieves, samples for each were sent for chemical analysis. Ni, Co and Cd concentrations were analyzed. The fraction above 2.38 mm was composed only of metallic fragments. All of these fragments were originally from metallic cases and metallic grates.

4. Results and discussion

4.1. NT tests

Tests were done at temperatures from 600 to 1000 °C. In the tests, an inert gas atmosphere was used. The inert gas used was nitrogen.

X-ray diffraction analyses were carried out in the material remaining in the crucible, and in the condensed material. As illustrated in Figs. 1 and 2, metallic Cd was detected as the main phase of the condensed material, and Ni or (Ni, Fe) as the main phase of the material remaining in the crucible.

Chemical analyses were also made in order to determine residual Cd concentration in samples of the material remaining in the crucible. Table 2 shows the results of such analysis.

Fig. 3 shows the curves drawn from the results contained in Table 2.

It is possible to verify that at 600 °C, Cd elimination is only partial for the holding times studied. Cd concentration is still very high in tests conducted at this temperature. Using the same holding time and temperatures of 700 and 800 °C, relatively high Cd concentration remained in the crucible. On the other hand, in the tests at 900 and 1000 °C only 30 ppm of cadmium was detected.

Table 2
Results of chemical analysis of the material remaining in the crucible

Test	Cd (wt.%)
NT600	7.80
NT700	0.19
NT800	0.08
NT900	0.003
NT1000	0.003

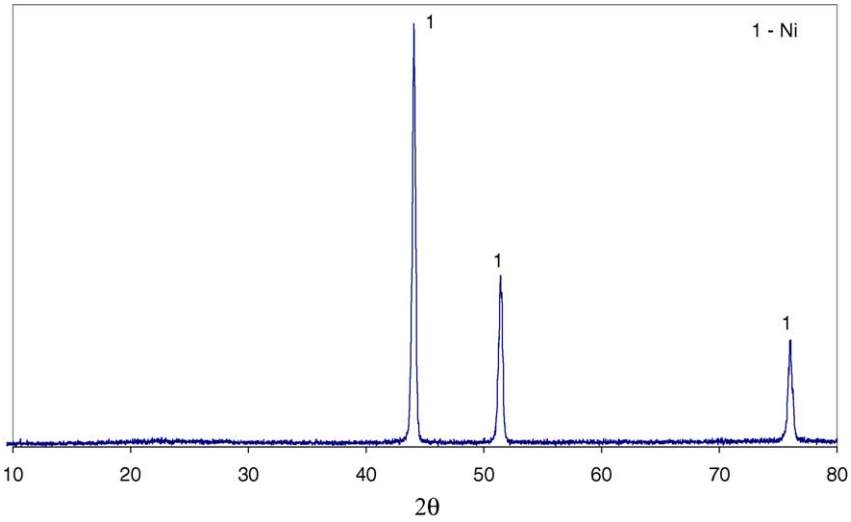

Fig. 1. X-ray diffraction spectrum of material remaining in the crucible.

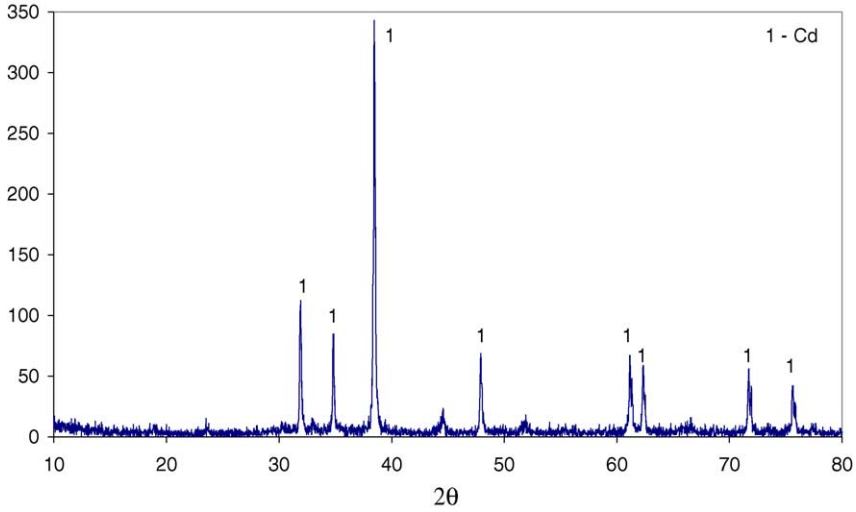

Fig. 2. X-ray diffraction spectrum of condensed material.

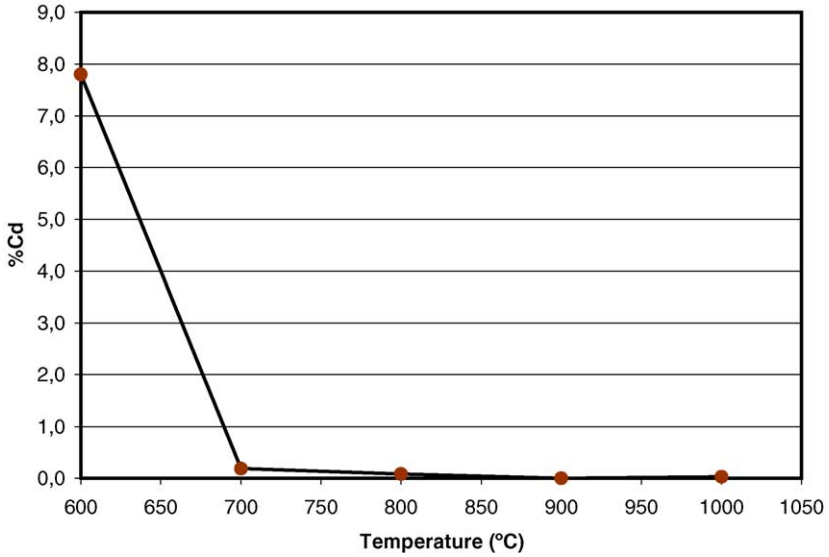

Fig. 3. Results obtained in a nitrogen atmosphere for the decomposition of CdO contained in sealed batteries.

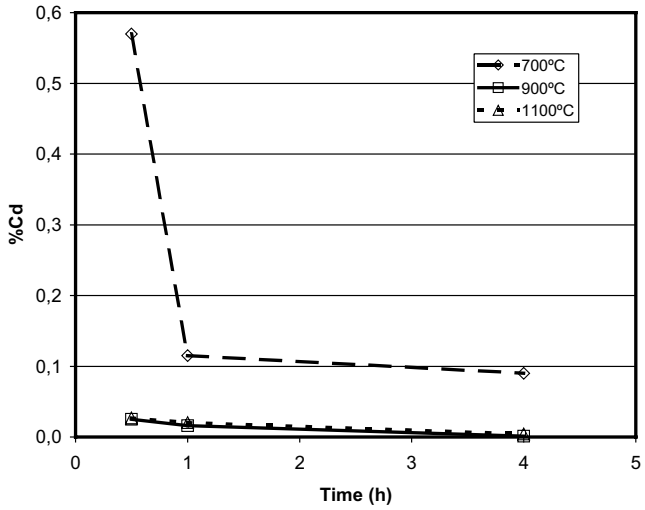

Fig. 4. Residual Cd concentration in the material remaining in the crucible.

4.2. ND tests

Series of tests were performed with different holding times of the samples, but at constant temperatures in each series. Constant temperatures used in each series of test were of 700, 900 and 1000 °C, and in each series the holding time were 30 min, 1 and 4 h.

Condensed samples were identified as composed of metallic Cd. Residual Cd concentration in the samples from what remained in the crucible at the end of each test was determined by chemical analysis by atomic absorption spectroscopy. Results of such analyses are shown in Fig. 4.

As can be observed, even for the lowest temperature and the shortest time, final Cd concentration showed drastic reduction as compared to the initial concentration (23%). Even for the ND7-30 test, carried out at 700 °C during only 30 min, Cd final concentration was only 3% of the initial value.

From the data related to the loss of mass of the sample and of Cd content, the percentage of the cadmium removed can be calculated by dividing the final quantity of Cd remaining in the crucible by the initial quantity, and multiplying the result by 100, and subtracting the obtained value from 100. Consequently, the total Cd removal was of around 98.7% for the ND7-30 test.

For the other tests at 700 °C, ND7-1 and ND7-4, removal calculated by the same way was around 99.7%.

The results of tests at 900 and 1000 °C were similar. Both showed Cd contents lower than the samples from the ND7 series of tests, even for the 30 min holding time, indicating that the reaction of Cd removal is fast under these conditions.

In the ND9 and ND11 tests, respectively, conducted at 900 and 1100 °C, Cd removal exceeded 99.9%.

Table 3 shows the results of chemical analyses. The calculated purity of the Cd obtained is of around 99.92%. Main contaminants found were zinc (200 ppm) and iron (380 ppm). Fig. 5 shows a picture of the condensed material.

Table 3
Results of the chemical analysis of Cd obtained in a test at 900 °C

Element	Concentration (ppm)
Aluminum	<0.01
Calcium	<0.01
Plumb	42
Cobalt	<0.01
Copper	45
Chromium	<0.01
Tin	<0.01
Iron	380
Lantanium	<0.01
Lithium	<0.01
Magnesium	2.0
Manganese	<0.01
Mercury	<0.01
Nickel	<0.01
Potassium	100
Silicon	<0.01
Sodium	1.0
Titanium	<0.01
Zinc	200

The presence of zinc in the condensed material is expected since both positive and negative electrodes have zinc in their composition, as described by Espinosa et al. [1] showing the chemical analysis of components of NiCd batteries. Similarly to cadmium, zinc shows volatility at the studied temperatures. The other contaminants are iron and copper, intrinsic to the laboratory process and that can be avoided by using industrial process.

Material remaining in the crucible went through particle size classification. Chemical analyses of the fractions by atomic absorption spectroscopy were carried out so as to verify nickel, cobalt and cadmium concentrations.

Fig. 6 shows the results of particle size distribution of the material remaining in the crucible. Results presented refer to the arithmetic average of the results obtained in each type of test.

Around 60% of the material is composed of particles >2.38 mm. This fraction is composed only of metallic

Fig. 5. Image of the condensed material.

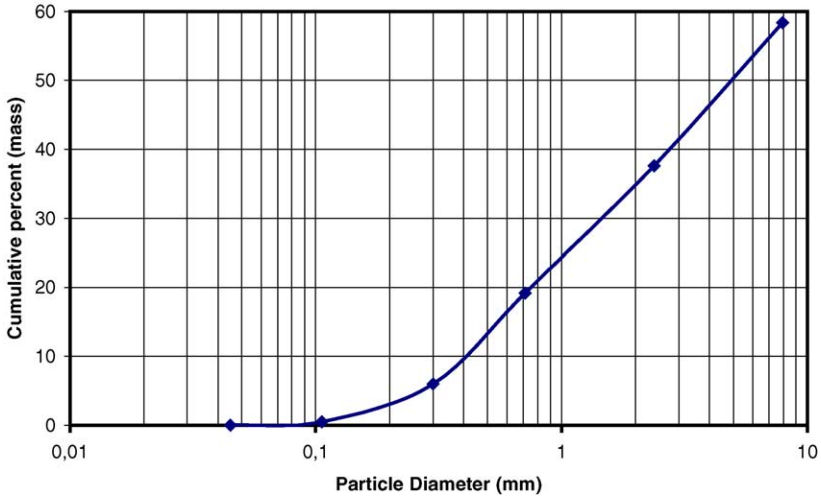

Fig. 6. Particle size analysis of the material remaining in the crucible.

Table 4
Chemical analyses of material obtained in the particle size classification of the product remaining in the crucible

Fraction	Ni (wt.%)	Co (wt.%)	Cd (wt.%)
−2.38 + 0.71	66.8	18.0	0.02
−0.71 + 0.30	79.1	20.5	0.02
−0.30 + 0.106	78.1	20.5	0.06
−0.106	71.0	19.0	0.21

fragments from the metallic cases and the metallic grates. In all tests, the average quantity of powdered material accumulated in sieves <0.3 mm was around 7%.

Table 4 presents the results of the chemical analyses for Ni, Co and Cd contents in the fractions obtained in the particle size classification tests. As can be observed, the remaining Cd concentrates in the powdered fraction of the material.

Fractions of <2.38 mm were briquetted, and the briquettes presented good resistance. The composition of these briquettes is approximately Ni-20% Co.

5. Analysis of the results

The same kind of tests performed under vacuum showed the same results [2]. Consequently, the choice of the best process for NiCd batteries recycling should thus be made taking into account mainly the economic factors and local legislation.

From a thermodynamic point of view, just the use of inert atmosphere with low oxygen partial pressure should be sufficient for cadmium distillation. Thus, to avoid the need of adding a reducing agent to the load, it would be necessary to use high purity nitrogen or argon, which would substantially increase the cost of the process. A reactive material could also be used to consume oxygen within the furnace, and thus reduce oxygen partial pressure during the treatment. In this case, the cheapest material for this purpose should be carbon, which would assure the oxygen potential lower than needed for CdO decomposition. The effect would be the same of a reducing agent.

In the closed furnace processes, metallic cadmium and an alloy containing iron and nickel were obtained as products of the recycling. The literature is not clear about cadmium contamination in such alloy. Results obtained in this work show that this alloy had a maximum of 100 ppm of cadmium after distillation treatment at 900 °C.

6. Conclusions

1. Cadmium recuperation is possible at temperatures above 600 °C, but an increase in the temperature caused a strong decrease in the holding time for the decomposition of cadmium oxide.
2. Temperatures above 900 °C promoted little cadmium oxide decomposition.
3. Zinc is the main contaminant in the Cd vapor produced under nitrogen atmosphere. The Zn concentration in the condensate was 200 ppm.
4. At 900 °C, the total amount of Cd in the crucible was below 100 ppm.
5. Cd concentrates in the powdered material present in the crucible. The material obtained in the crucible is essentially a Fe–Ni–Co alloy.

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