

# Fundamental aspects of recycling of nickel–cadmium batteries through vacuum distillation

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Received 27 February 2004; accepted 31 March 2004

Available online 2 July 2004

## Abstract

In spite of the existence of several NiCd batteries treatment processes around the world, little is known about the fundamental aspects of this technology. The objective of this research is to study the most important technological variables of NiCd batteries recycling by vacuum distillation. Laboratory equipment was set up to study vacuum thermal processing of milled batteries. During the tests, the total pressure was maintained at 0.1 mbar while temperatures varied from 700 to 1100 °C. Results obtained show that the distillation process is possible at temperatures above 700 °C. If temperature is raised to the range of 900–1100 °C, treatment time is reduced to less than 2 h. At temperatures higher than 900 °C the recovery of Cd contained in the batteries reached 99.9%.

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*Keywords:* Recycling; Batteries; NiCd

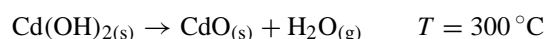
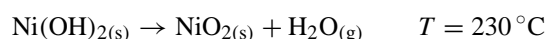
## 1. Introduction

Although pyrometallurgical processes for NiCd batteries recycling have existed in several countries for some years [1,2], there are no indications of scientific research on the subject, as opposed to hydrometallurgical recycling processes for this type of battery [3]. These processes were directly developed by private companies and the literature only showed superficial descriptions of the process, without details.

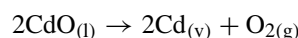
This study presents elements for a better fundamental understanding of the steps regarding Cd distillation from NiCd batteries.

During the distillation process, the decomposition of cadmium and nickel monoxides occurs first, and the products of such decomposition are the oxides of these elements. As the heating continues, there exists the possibility of cadmium oxide decomposition causing the formation of Cd vapor. This decomposition is possible either through partial reduction of the Cd vapor pressure in the atmosphere or through the presence of a reduction agent.

Where distillation occurs without a reduction agent the following reactions describe the process:



After these decomposition reactions, it is expected that [4]:



$$\Delta G^\circ = 174,400 - 96,94T \text{ (cal)}$$

Therefore:

$$(P_{\text{O}_2})(P_{\text{Cd}})^2 = \exp\left[\frac{-\Delta G^\circ}{RT}\right]$$

Thus, it is necessary that the following relation be obeyed in order to have the decomposition:

$$(P_{\text{O}_2}) < \left\{ \frac{\exp[-\Delta G^\circ/RT]}{(P_{\text{Cd}})^2} \right\} \quad (1)$$

Reaction II presents the stoichiometric relationship in the process:

$$P_{\text{O}_2} = \frac{P_{\text{Cd}}}{2} \quad (2)$$

Since:

$$P_{\text{Cd}} + P_{\text{O}_2} = P_T(\text{vacuum}),$$

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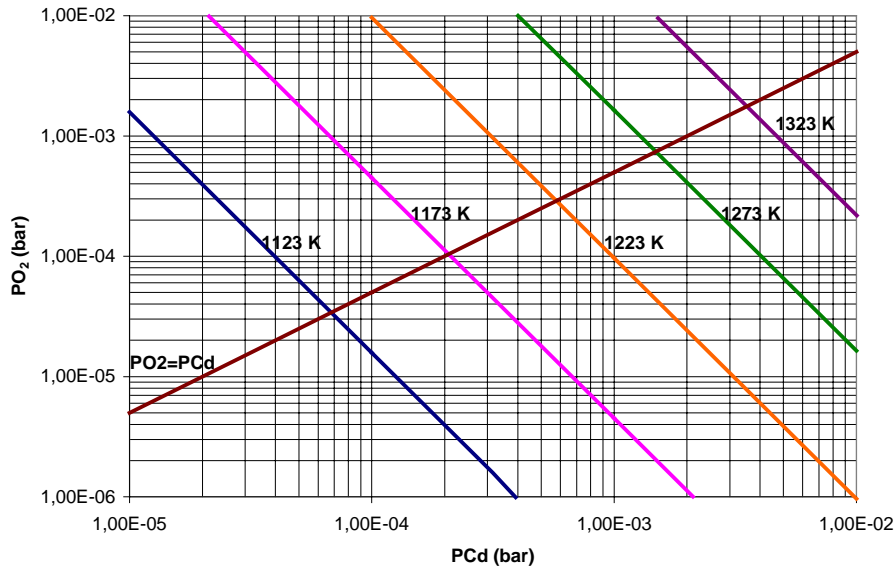


Fig. 1.  $P_{O_2}$  values as a function of  $P_{Cd}$ .

Therefore:

$$P_{T(\text{vacuum})} = 3P_{O_2} \quad \text{or} \quad P_{T(\text{vacuum})} = \frac{3}{2}P_{Cd}$$

Calculating  $P_T$ :

$$P_T = \left[ \frac{27}{4} \exp\left(\frac{-\Delta G^\circ}{RT}\right) \right]^{1/3} \quad (3)$$

Fig. 1 shows the curve obtained from Eqs. (1) and (2) and Fig. 2 shows the curve obtained from Eq. (3).

From the Figs. 1 and 2 one can conclude that the total pressure for the decomposition is in the range of  $10^{-4}$  bar for 850–900 °C.

## 2. Objectives

The objective of the present study is to study the effect of temperature and of reaction time on NiCd batteries evaporation processes and understanding the fundamental aspects of NiCd recycling processes through vacuum distillation.

## 3. Methodology

### 3.1. Equipment for cadmium distillation

In order to study cadmium distillation from NiCd batteries, laboratory equipment was assembled made of a tubular

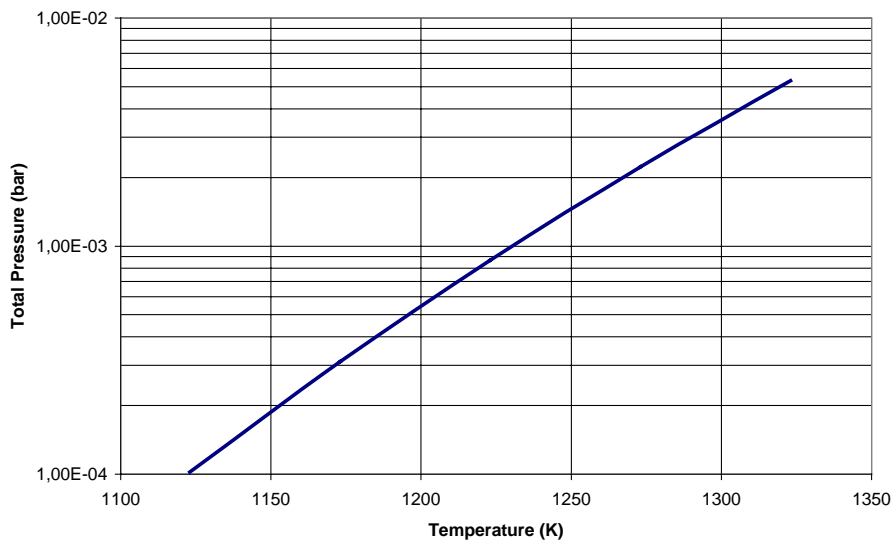


Fig. 2. Total pressure values as a function of temperature.

electric furnace, with a stainless steel retort and a water refrigerated copper condenser. In order to work under vacuum, a vacuum mechanical pump was attached to the condenser. A molecular sieve filter protected the vacuum pump. The entire equipment was arranged inside a structure called *big glove box*, (2 m × 3 m × 2 m) made of steel structure, transparent acrylic walls and a exhaust.

### 3.2. Cadmium distillation

Cadmium distillation studies were done with the equipment described above. Two series of tests on vacuum distillation were carried out. The first tests kept the holding time at set temperature constant and varied the temperature, aiming to determine the minimum temperature for cadmium evaporation (called VT series). For the other series of tests, called VD, two temperatures were chosen and the holding time of the tests at each temperature varied. The objective of this series was to determine the ideal time for decontamination of the material in the crucible, which means maximum evaporation of Cd.

Both in the VT and VD tests the formation of a nickel base alloy was observed. The NiO reduction was not expected, since no reduction agent was used in the tests. A complementary test was performed where the load was a mixture of the active materials that belong to the negative and positive electrodes in the same proportions as in the battery. Therefore the other components of the battery were not fed into the crucible, since it was suspected that some other material (plastic case) could be causing the reduction of the NiO at the positive electrode. This test was named ME 900 and it was carried out at 900° for a period of 2 h.

Except for the ME 900 test, the loads for the experiments were prepared in the following steps. Initially, portable 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.

Thus, the load was essentially shredded batteries without their plastic cases.

Table 1 shows a list of Cd distillation tests.

Table 1  
List of Cd distillation tests performed

Name of the test	Temperature (°C)	Holding time (h)
VT600	600	2
VT700	700	
VT800	800	
VT900	900	
VT1000	1000	
VD7-30	700	0.5
VD7-1		2
VD7-2		3
VD7-4		4
VD9-30	900	0.5
VD9-2		2
VD9-4		3
ME 900	900	2

### 3.3. VT test procedures

The load of each test was obtained through the use of the cone & quartering technique in the original material from physical conditioning step (hammer and knives milling). For each test, approximately 40 g of the material were put in an alumina crucible and placed at the center of the furnace, so that all the materials would be in the hot area of the retort. After closing the retort and reaching the set pressure, e.g. when the pressure in the interior of the retort was around  $10^{-1}$  mbar, the heating process started. During the heating, internal pressure increased reaching a little less than 1 bar, dropping again when the temperature was maintained constant and stable. Timings began when the furnace reached the desired temperature. After cooling, a valve was used to increase the pressure and the system was disassembled. Two types of products were generated: the remaining material in the crucible and the condensed material. The condensed material was collected from the retort and the condenser using a plastic apparatus.

X-ray diffraction analyses were performed in samples of all generated products. Chemical analyses, using atomic absorption spectrophotometry technique were carried out in samples of the materials remaining in the crucible so as to determine the final concentration of Cd.

### 3.4. VD test procedures

A similar procedure was observed in tests in which time varied, except that the vacuum pump was only started when the furnace reached the desired temperature and time counting started. In these tests, the generated products were the same as in the VT tests.

All generated products were identified by X-ray diffraction. Chemical analysis by atomic absorption spectrophotometry technique was also used in the material remaining in the crucible in order to identify the final concentration of Cd.

## 4. Results and discussion

Two series of vacuum tests were carried out. In the first one, temperatures were varied but the holding time in which the material was tested at a given temperature was a constant (VT series). In the other type of test, the temperature remained the same, but the holding time varied (VD series).

### 4.1. VT tests

Tests were carried out at 600, 700, 800, 900 and 1000 °C with a holding time of 2 h at each of these temperatures. Samples were analyzed by X-ray diffraction and samples of what remained in the crucible at the end of the test went through chemical analysis by atomic absorption spectrophotometry.

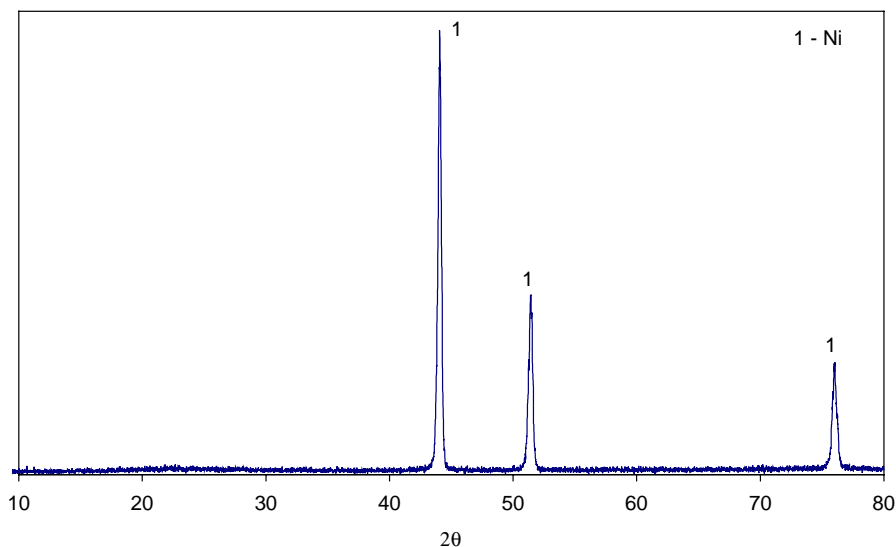


Fig. 3. X-ray diffraction spectrum of the material remaining in the crucible at the end of test VT 900 (900 °C, vacuum and holding time of 2 h).

Fig. 3 shows the X-ray diffraction spectrum for the material remaining in the crucible at the end of the test at 900 °C (VT 900). The peaks of the X-ray diffraction spectrum correspond to the phases: Ni, NiFe<sub>3</sub> and FeNi.

Fig. 4 shows the X-ray diffraction spectrum of the material collected in the condenser. The most important phase identified was metallic Cd.

In all VT tests X-ray diffraction spectra were similar for all condensed material samples. The same behavior was found for samples of materials remaining in the crucible.

For all tests the results of chemical analysis of the material remaining in the crucible are summarized in Table 2.

One can notice that at 600 °C, the total removal of Cd did not occur, but there was a significant reduction of the Cd, in relation to the initial concentration in the samples, since a partial elimination of Cd was obtained even at this

Table 2

Results of the Cd concentration obtained from the chemical analysis of material remaining in the crucible, in the VT tests

Test	Cd (wt.%)
Initial	23
VT600	3.0
VT700	0.01
VT800	0.01
VT900	0.002
VT1000	0.002

temperature. Tests at 700 and 800 °C resulted in a reduction to 100 ppm. As for tests at 900 and 1000 °C, chemical analysis detected the presence of 20 ppm of Cd in the samples.

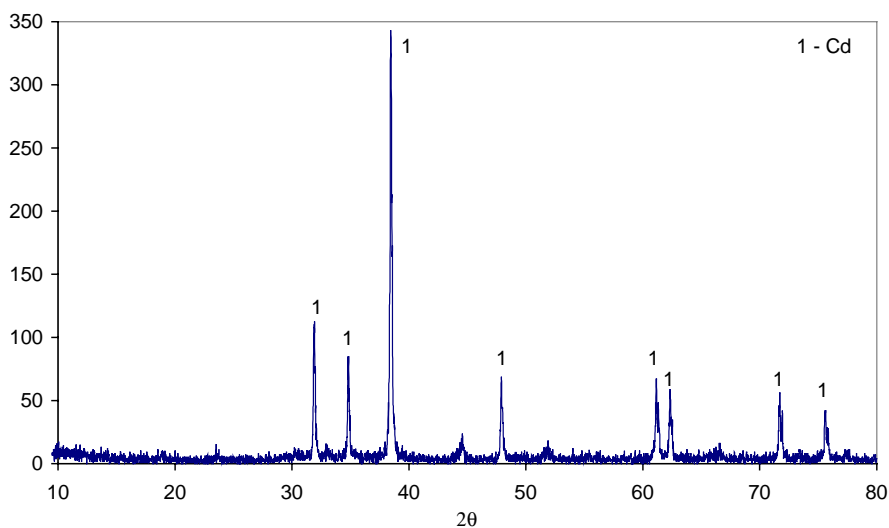


Fig. 4. X-ray diffraction spectrum of condensed material sample in tests VT 900 (900 °C, under vacuum and holding time of 2 h).

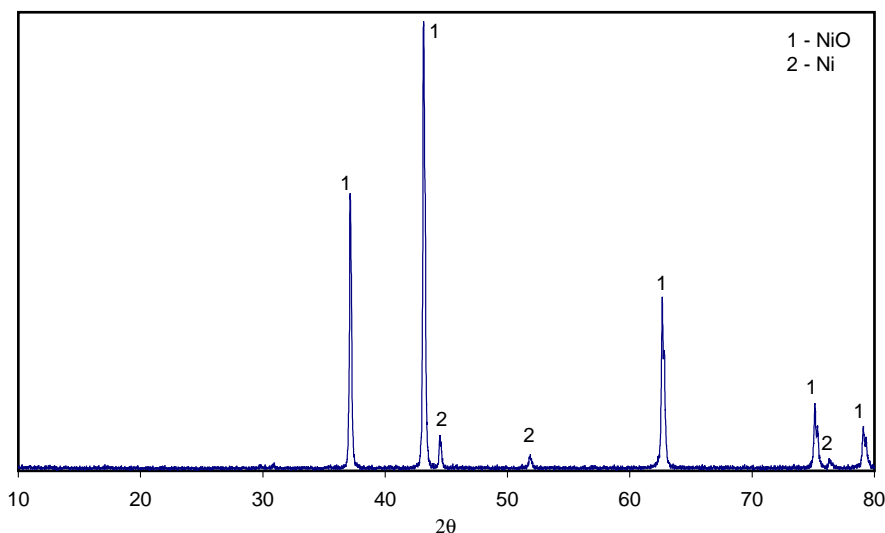


Fig. 5. X-ray diffraction spectrum of material remaining in the crucible in ME 900 tests (900 °C, under vacuum, load of mixture of active materials from electrodes).

Cadmium removal was calculated by dividing Cd's mass in the final sample by Cd's mass in the initial sample and then multiplying the result by 100. For the VT 600 test, cadmium removal was of 93% and for VT tests from 700 to 1000 °C such removal exceeded 99.9%.

#### 4.2. Test using mixtures of electrodes (ME 900)

By analyzing the curves from  $\Delta G^\circ$  as a function of the temperature for the formation of CO, NiO and CdO, NiO could not be reduced if a reduction agent was not added, therefore some component in the battery must be acting as a reduction agent. One hypothesis is that NiO reduction eventually occurred by the presence of metallic Cd itself, since such process could be possible at low temperatures. Thus, a test was made using as a load only a mixture of the two electrodes.

Fig. 5 shows the X-ray diffraction spectrum of the material remaining in the crucible after the test under vacuum and at a 900 °C temperature. The load used in this test was a mixture of the active material of each electrode. The electrodes were separated through manual dismantling from the other components of the battery.

It was observed that Ni hydroxide from the positive electrode was decomposed into oxide, but this oxide was not reduced.

Plastic can act as a reduction agent, and so can the fabric used as a base for the electrolyte. Oxide reduction observed in tests having milled batteries as a load indicates that some of the other components of the battery act as a reduction agent, probably hydrocarbons, hydrogen or CO originated from the pyrolysis of plastics or fabric in the battery. Thus, it is necessary to add a reduction agent in order to obtain metallic Ni in tests under vacuum and using sealed accumulators as a load.

As shown in Fig. 6, the condensed material obtained on this test was identified by X-ray diffraction as basically composed of metallic cadmium.

#### 4.3. VD tests

Tests were also made with different holding time length at the different test temperatures.

In the test with at 700 °C and 30 min holding time (VD7-30), the most important phases identified in the material remaining in the crucible at the end of the test were Ni and NiO. The material condensed in test VD7-30 was characterized as metallic Cd.

In tests with longer periods of time (2, 3 and 4 h) resulting samples were similar to those obtained in VT tests, for example, Ni was the predominant phase identified in the material remaining in the crucible and metallic Cd was the phase identified in the condensed material.

In order to determine if all Cd evaporated during the process, chemical analyses were performed in samples from the material remaining in the crucible and in all tests carried out at 700 °C (VD7). The results for the chemical analysis are shown in Table 3.

Results of chemical analysis show an effective reduction on Cd concentration caused by pyrometallurgical treatment.

Table 3  
Results of chemical analysis of the material remaining in the crucible after each VD7 test

Test	Cd (Wt.%)
Initial	23
VD7-30	3.5
VD7-2	0.6
VD7-3	0.6
VD7-4	0.6

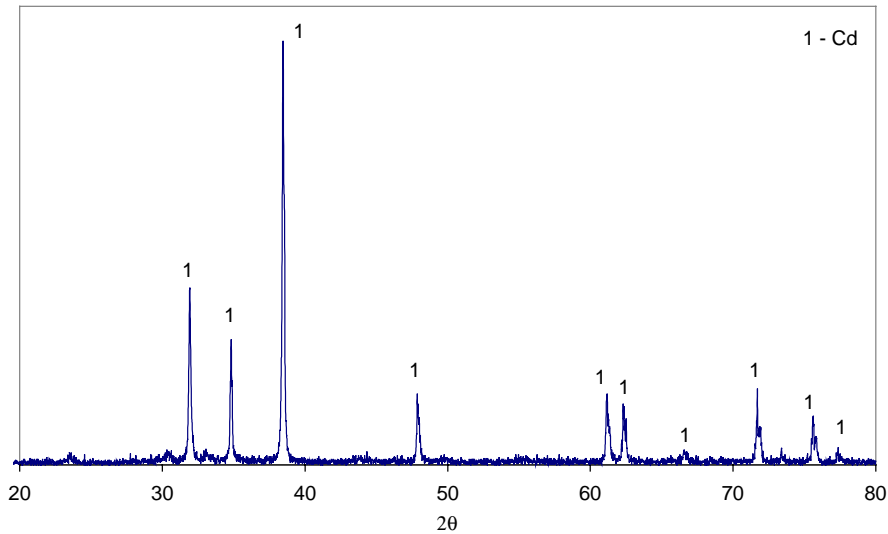


Fig. 6. X-ray diffraction spectrum of condensed material sample from test at 900 °C, under vacuum, using a load of mixture of active materials form electrodes—test ME 900.

It was observed that the VD7-30 treatment (700 °C, 30 min) was not sufficient to remove Cd, since analysis showed 3.5 wt.% remaining Cd. For the tests with longer holding time, Cd concentration diminishes substantially, but the remaining quantities are still too high to consider the sample as decontaminated. Thus, the treatment at 700 °C for up to 4 h was considered not effective for Cd removal.

X-ray diffraction spectra of all tests of the 900 °C series (VD9) showed results similar to those of VT tests.

Chemical analyses were made in VD9 tests, as they were done in the VT7 tests, to verify decontamination of the material remaining in the crucible. The results of such chemical analyses are shown in Table 4.

Data from Tables 3 and 4 could be represented by the curves in Fig. 7.

Table 4

Results of chemical analyses of the material remaining in the crucible after each VD9 test

Test	Cd (Wt.%)
Initial	23
VD9-30	0.03
VD9-2	0.003
VD9-3	0.011

A significant reduction of Cd levels on the sample from 30 min tests was observed. After this time, the rate of Cd removal drops, but both curves seem to present an asymptotic behavior, and the curve tends to zero in the 900 °C.

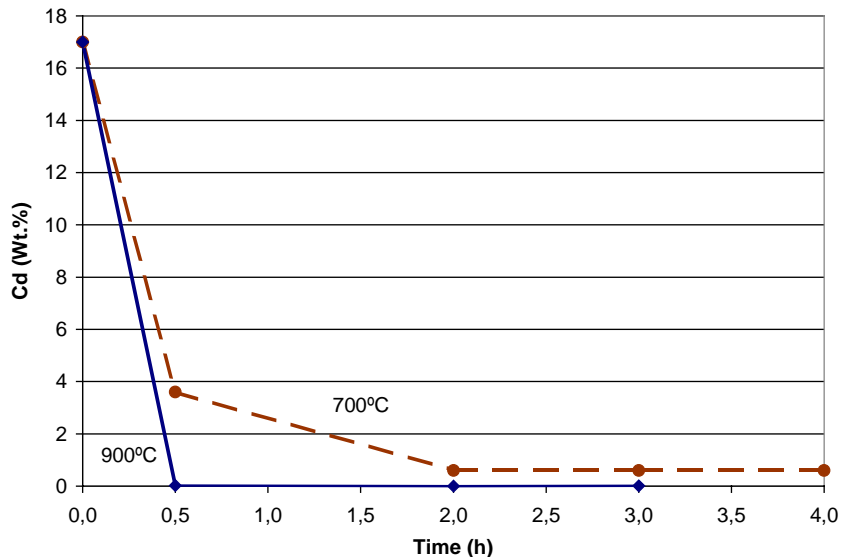


Fig. 7. Cd reduction (wt.%) in VD7 and VD9 tests, as a function of the holding time, respectively at 700 and 900 °C.

The amount of Cd removed in the various tests was calculated from the initial and final masses of each test and the Cd percentage in initial and final samples. Initial Cd quantity was considered to be 23%, value found in the batteries characterization tests [5]. Thus, the amount of Cd removed was calculated through the Eq. (4):

$$\text{Cd removal} = \frac{M_i x \% \text{Cd}_i - M_f x \% \text{Cd}_f}{M_i x \% \text{Cd}_i} \times 100 \quad (4)$$

where  $M_i$  is the initial mass of the load;  $\% \text{Cd}_i$  is the Cd concentration of the load;  $M_f$  is the remaining mass in the crucible after the test;  $\% \text{Cd}_f$  is the Cd concentration in the material remaining in the crucible after the test.

Cd removal in VD7 tests was of around 90% for 30 min and remained constant at about 98.5% for holding times longer than 30 min. As for VD9 tests, Cd removal exceeded 99.9% for all tests, and remained above 99.95% for holding times longer than 30 min.

Pyrometallurgical processes for NiCd batteries recycling use 12–48 h holding time for the Cd distillation phase [1,2]. In this study, it was observed that Cd distillation reaction needed much less time than the applied in the industrial processes.

At temperatures normally used in distillation processes (850–950 °C) the reaction reach more than 99.9% Cd recovery for treatment periods of up to 2 h, and also obtains a metallic material with less than 100 ppm of Cd remaining in the crucible.

The eventual presence of zinc batteries in the load is another factor that must be taken into account in choosing distillation's temperature. Zinc, such as Cadmium, is a volatile metal, which can be reduced by carbon at atmospheric pressure and temperatures around 920 °C. Thus, if Cd distillation is processed at temperatures above 920 °C, zinc contamination of the product would be greater.

The increase in the consumption of household batteries and the regulation and promotion of NiCd portable used batteries' treatment, has caused an increase in its presence in recycled materials, within battery recycling processes.

In NiCd batteries recycling pyrometallurgical processes that existed before, for example, for industrial used batteries, the separation of the batteries' internal components is a simple task. Separation of internal components of sealed batteries is not that easy, since the size and structure of sealed batteries are restricting factors for this operation. It was thus necessary to develop a process for the preparation of the load for sealed batteries distillation treatment.

Household used batteries, such as cell phones, notebook computer and tools batteries are composed of sealed batteries inserted in a shock resistant plastic case. Inmetco, Sab-Nife and Snam processes have an initial phase for the combustion of the plastic case, but there is no information available on the specific methods used for this operation. This work shows that it is possible to separate such plastic containers by using unit operations of mining treatment, which besides recuperating materials that can be recycled, is a much cheaper process than combustion.

## 5. Conclusion

1. It is possible to obtain metallic nickel without the addition of a reduction agent, since the organic material existing in sealed batteries acts as a reduction agent.
2. Cadmium recuperation at tests temperatures above 900 °C is more than 99.9%.
3. For temperatures above 900 °C, increase in temperature has little effect on the rate that Cadmium is eliminated. On the other hand, for temperatures below 900 °C time for Cadmium elimination increases substantially with temperature reduction.
4. It is possible to obtain a metallic material of powder and small fragments (material that remained in the crucible after pyrometallurgical treatment) with less than 100 ppm of Cadmium contamination.
5. The holding time to obtain less than 100 ppm of Cadmium in the material remaining in the crucible was of 2 h, which is substantially less than the holding time used in the main industrial processes.

## References

- [1] A.M. Bernardes, D.C.R. Espinosa, J.A.S. Tenorio, Collection and recycling of portable batteries: a worldwide overview compared to the Brazilian situation, *J. Power Sources* 124 (2) (2003) 586–592.
- [2] A.M. Bernardes, D.C.R. Espinosa, J.A. S Tenorio, Recycling of batteries: a review of current processes and technologies, *J. Power Sources* 130 (1–2) (2004) 291–298.
- [3] C.A. Nogueira, F. Delmas, New flowsheet for the recovery of cadmium, cobalt and nickel from spent Ni–Cd batteries by solvent extraction, *Hydrometallurgy* 52 (1999) 267–287.
- [4] O. Kubaschewski, C.B. Alcock, *Metallurgical Thermochemistry*, fifth ed., Oxford, New York, 1979, pp. 211–240.
- [5] D.C.R. Espinosa, J.A.S. Tenório, The use of unit operations of mining treatment as the first step of NiCd batteries recycling, in: *Proceedings of the TMS Annual Meeting 2001*, New Orleans, Louisiana, EUA, Feb 11–15 2001, TMS, Warrendale, 2001, pp. 173–181.