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Laboratory study on the leaching potential of spent alkaline batteries

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ABSTRACT

Four different leaching tests were carried out with spent alkaline batteries as an attempt to quantify the environmental potential burdens associated with landfilling. The tests were performed in columns filled up with batteries either entire or cross-cut, using either deionized water or nitric acid solution as leachant. In a first set of tests, the NEN 7343 standard procedure was followed, with leachant circulating in open circuit from bottom to top through columns. These tests were extended to another leaching step where leachant percolated the columns in a closed loop process.

Leachate solutions were periodically sampled and pH, conductivity, density, redox potential, sulphates, chlorides and heavy metals (As, Cd, Co, Cr, Cu, Fe, Hg, Mn, Ni, Pb, Sb, Tl and Zn) were determined in the samples.

The results showed that the total amount of substances leached in tests with cross-cut batteries was higher than with entire ones; zinc and sulphates were the substances found the most in the leachate solutions. In general, the amount of substances dissolved in open circuit is higher than in closed loop due to the effect of solution saturation and the absence of fresh solution addition.

Results were compared with metal contents in the batteries and with legal limits for acceptance in landfill (Decision 2003/33/CE and Decree-Law 152/2002). None of the metals were meaningfully dissolved comparatively to its content in the batteries, except Hg. Despite the differences in the experiment procedure used and the one stated in the legislation (mixing, contact time and granulometry), the comparison of results obtained with cross-cut batteries using deionized water with legal limits showed that batteries studied could be considered hazardous waste.

1. Introduction

Since its introduction in the early 1960s, the alkaline-manganese dioxide batteries have gained a dominant position in the portable batteries market due to the advantages of the alkaline system. The total weight of portable batteries sold in the East and West Europe in 2003 was about 164,000 tonnes, of which 50,197 and 99,138 were zinc-carbon and alkaline batteries, respectively (30.5% and 60.3% of the total annual sales) (EPBA, 2008).

Several changes have occurred on these batteries since then, the most significant being the gradual reduction of the mercury content in the anode. Considered as a major source of mercury in municipal solid waste (MSW) in the past, alkaline batteries no longer contain deliberately added mercury and the mercury possibly found on them comes from the impurities of the other components materials. They are therefore called as mercury-free. This trend, which was aided by a substantial improvement in the reliability of cell materials resulting from reduced impurity levels, was driven by worldwide concern over the environmental impact of the materials used in batteries (Linden, 1995).

The disposal of spent batteries became a subject of discussion due to the presence of metals that have been recognized to have negative effects on human health and the environment. Despite recycling having become an important option for spent batteries, they are generally discarded mixed in Municipal Solid Waste (MSW), which is either incinerated or landfilled. In Portugal, between 2004 and 2006, more than 13% of the number of batteries and accumulators existing in the market were collected for recycling (Ecopilhas, 2007), meaning that a significant amount were discarded with MSW. In 2005, about 65% of the mixed waste collected in Portugal were confined in landfills and 20% were incinerated (Instituto do Ambiente, 2006), which means that the main destination of used batteries in Portugal is still the landfill. Environmental impact studies on the disposal of some types of batteries in MSW management systems do not indicate that such

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disposal practices pose significant threat to the environment. This is also the case for alkaline batteries (Xará et al., 2001). Some earlier studies concluded that disposal practices such as incineration and landfilling appear to be safe and adequate (Institute for Risk Research, 1992). However, conditions considered in these evaluations do not cover all the variables of the disposal options. Also, the characteristics of the batteries are not the same as in the past. Therefore, accurate information and up to date data about the behavior of all the types of waste, including alkaline batteries, are required to better evaluate the environmental impact of waste management practices.

The knowledge available on the behavior of products or materials in landfills includes information from field studies, experiments simulating landfill environment or specific processes in landfills, such as leaching or degradation, as well as theoretical modeling of landfills.

Karnchanawong and Limpiteeprakan (2009) evaluated the heavy metal leaching from spent household batteries disposed in municipal solid waste performing bach leaching test and simulated landfill lysimeter tests. The results showed that the type of battery influenced the heavy metal concentration in the leached solutions. The lysimeter experiment results illustrated that at lower pH levels more metals are leached than at higher pH levels. The increasing amount of batteries disposed in landfills can contribute to the leaching of more metals, specially Mn and Zn, in to the environment. These results indicate that the direct disposal of spent households batteries in to MSW landfill can increase the heavy metals contents in the landfill leachate. Agourakis et al. (2006) studied the leaching potential of alkaline batteries, in a soil column, particularly the behavior of zinc and manganese, using a solution simulating acid rain, during one year. The results showed that the leaching of alkaline batteries cause enrichment of 70 and 11 times the Zn and Mn concentration of the topsoil, respectively. Additionally, leaching of electrolyte (KOH) from batteries increased the soil pH in the contaminated column. Slack et al. (2005) focused his work on the assessment of data concerning the presence of hazardous chemicals in leachates as evidence of the disposal of HHW (Household Hazardous Waste) in municipal landfills. In this work, cadmium, nickel, zinc, copper, lead, chromium and mercury were the heavy metals identified in MSW landfill leachates that could be partially traced back to the batteries in the wastes. Panero et al. (1995) performed a releasing test using an acetic acid solution as the extracting liquid, with several batteries samples. Cadmium and nickel levels present in the leaching solution were below the accepted limits for disposal in landfills (0.02 and 2 mg/l, respectively). An opposite situation occurred for the concentrations of zinc and manganese which were greater than the fixed limits (0.5 and 2 mg/l, respectively). The work presented by IRR (1992) discusses the issues relating to used dry-cell battery disposal practices, their potential impact on the environment, the potential risks to humans and offers recommendations for what is considered as acceptable disposal practices for used household batteries. Risks to the environment from battery disposal by landfilling and incineration are not likely to be significant. Thus, most household batteries may be safety disposed of in municipal landfills or municipal incinerators.

This work aims at quantifying the leaching potential of several inorganic substances on most popular alkaline batteries formats in Portugal through laboratorial leaching experiments in order to be able to predict the possible emission factors of those batteries in a landfill and consequently, the associated emission. The tests were carried out in two steps with different conditions. The objectives were to cover the several conditions batteries can experience in a landfill – they can be on the top layers of waste and be contacted by the leachate first or they can be on the lower layers and when the leachate contacts them it has already contacted other batteries, therefore it has already dissolved some components from other batteries. In the last case, a situation of quasi-equilibrium is likely to occur.

The results obtained were used to identify the type of landfill where spent batteries can be deposited according to European and Portuguese legislation, respectively Decision 2003/33/CE and Decree-Law 152/2002. These types of waste are classified as inert, non-hazardous and hazardous, also using information related with the characteristics of their leachate.

The determination of emission factors and emissions associated with the disposal of waste in landfills is important for LCA studies on specific products.

2. Experimental

The batteries used in this work were spent alkaline batteries, format AA, from Duracell®, with expire date of March 2003, from a central collection site in the city of Porto where they were stored in a drum with other different types of household batteries. The batteries in the central collection site come from street collection containers spread all over the city, from collection points located on commercial areas and are also delivered directly there by inhabitants. The target batteries have been characterized using both information from literature and laboratorial tests (Almeida et al., 2006), namely concerning average weight, moisture content, ash content, zinc and zinc oxide on anode, manganese on cathode, other metals, potassium hydroxide on the internal components and heating values for papers, anode and cathode. Before any experiments were carried out, batteries were washed with deionized water and dried to remove external impurities that could exist on the surface.

Four different leaching tests were carried out in cylindrical acrylic columns with 31.0 cm length and 5.4 cm internal diameter, each one filled up with 47 batteries (Fig. 1). Tests 1 and 2 were performed with entire batteries, the first with a nitric acid solution at pH 4, and the second one with deionized water. In Tests 3 and 4, cross-cut batteries were used, respectively, with nitric acid solution at pH 4 and deionized water. The tests were carried out in two steps with different conditions, designated Step 1 and Step 2.

2.1. Step 1 – Leaching tests using NEN 7343 standard

In Step 1, the methodology proposed by NEN 7343 standard was followed. The aim of this column test is to simulate the leaching of inorganic components from powdered and granular materials in an aerobic environment as a function of the ratio between liquid and solid (L/S) over a range varying from 0.1 to 10 l per kg of dry matter. The value L/S can be related to a timescale so that, based on the results of the column test, an opinion can be formed on the time-dependence of the leaching of a material under practical conditions (Nederlands Normalisatie – Instituut, 1995).

In this column test, fresh leaching solution is continuously flowing through each vertical column from bottom to top using a peristaltic pump with a controlled flowrate proportional to dry weight, according to the standard. At the bottom and top of each column there were, respectively, a pre-filter and a pre-filter followed by a 0.45 μm pore size filter, in order to avoid that particles were carried on outside the column.

Samples were collected after set quantities of leaching liquid have passed through the column, corresponding to cumulative L/S ratios of 0.1, 0.2, 0.5, 1.0, 2.0, 5.0 and 10.0 l/kg of dry sample – these leachate fractions were collected in a graduated cylinder that was replaced when the liquid volume reached the defined L/S ratio.

All the samples were characterized in terms of pH, conductivity, density, redox potential, sulphates, chlorides and metal elements –