FEUP LEPAE

FCT Fundação para a Ciência e a Tecnologia

UNIVERSIDADE CATÓLICA PORTUGUESA
ESCOLA SUPERIOR DE BIOTECNOLOGIA

Preliminary inventory of alkaline batteries landfilling

Susana Xará
Manuel F. Almeida
Margarida Silva
Carlos Costa

ISWA World Environment Congress & Exhibition
Istanbul-Turkey, July 8-12, 2002

FEUP LEPAE

Presentation plan

- Introduction
  - Why this inventory?
  - Life Cycle Assessment (LCA) technique
- Method of approach
  - Batteries characterization
  - Preliminary inventory using theoretical model
  - Laboratorial leaching experiments
- Results and conclusions

FEUP LEPAE

Why this inventory?

- **part of a project**
  - to compare the environmental impact of **incineration**, **landfilling** and **recycling** alkaline batteries using Life Cycle Assessment (**LCA**) technique
- **present and discuss the preliminary inventory of batteries landfilling**
  - in terms of consumption of **materials** and **energy**, **emissions** to air and water and, solid waste

FEUP LEPAE

Why this inventory?

- **performed in two parts**
  - a **theoretical model** was used to estimate resources and emissions resulting from batteries landfilling based on batteries characterization
  - results from **leaching laboratorial experiments** made with the target batteries were compared with the theoretical model approach
- **result of this preliminary inventory shows**
  - the **potential contribution of landfilled batteries** to the environmental burdens of a landfill
  - allows an evaluation of the **relative contribution of the different batteries components** to these burdens

FEUP LEPAE

Life Cycle Assessment (LCA)

- Technique for assessing the **environmental aspects and potential impacts** associated with a product by:
  - **Compiling an inventory of relevant inputs and outputs of a product system**
  - Evaluating the potential environmental impacts associated with those inputs and outputs
  - Interpreting the results of the inventory analysis and impact assessment phases in relation to the objectives of the study

Product system

Collection of materially and energetically connected unit processes which performes one or more defined functions

FEUP LEPAE

Method of approach

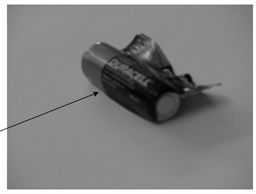
1. **Batteries characterization**
   - **Strutural** components
   - **Chemical** composition
2. **Preliminary inventory of batteries landfilling using a theoretical model**
   - Landfill **characterization**
   - Landfilling process **modelling**
3. **Laboratorial leaching experiments**
   - Tests description

Batteries characterization

- **alkaline zinc-manganese dioxide batteries, format AA**
  - **alkaline batteries**
    - powdered zinc as the negative electrode (anode)
    - manganese dioxide (MnO_2) with graphite as the positive electrode (the cathode)
    - potassium hydroxide (KOH) as the electrolyte
  - **format AA**
    - cylinder with 50mm length, 14mm diameter and approximately 23.5g of weight

Batteries characterization

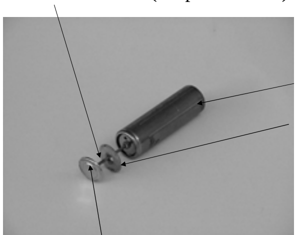
AA alkaline batteries



Outer plastic sleeve (PVC)

Batteries characterization

Anode collector (tin-plated brass)

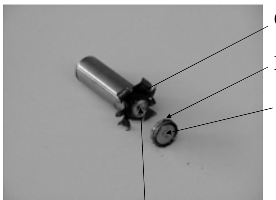


Cathode collector/can (steel)

Insulator (cardboard)

Anode cap (steel)

Batteries characterization

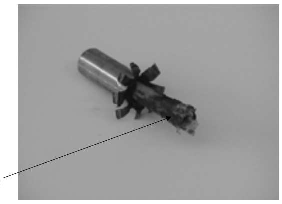


Cathode (MnO2, C, KOH)

Plastic grommet (PA)

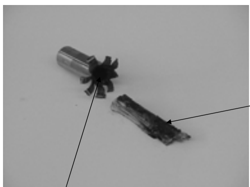
Metal separator

Anode
(Zn, ZnO, KOH)



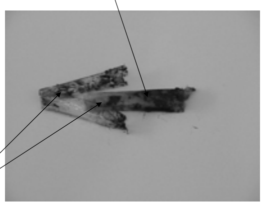
Separators (paper)

Batteries characterization



Anode
(Zn, ZnO, KOH)

Cathode (MnO2, C, KOH)



Separators (paper)

Batteries characterization

- **Average weight: 23.5 g**
- **Moisture: 2 g**
- **Lower heating value: 121 kJ**
  - **Steel: 4.7 g**
  - **Tin-plated brass: 0.44 g**
  - **PVC: 0.23 g**
  - **PA: 0.22 g**
  - **Cardboard: 0.060 g**
  - **Paper: 0.11 g**
  - **Cellophane: 0.045 g**
  - **Mn (cathode): 5.4 g**
  - **C (cathode): 0.71 g**
  - **Zn (anode): 3.2 g**
  - **KOH: 0.92 g**
  - **Others: 7.5 g**

- **Trace elements (mg/battery)**
  - **As: 0.021**
  - **Cd: 0.060**
  - **Co: 0.84**
  - **Cr: 9.5**
  - **Cu: 281**
  - **Hg: 0.0038**
  - **Mn (except cathode): 11**
  - **Ni: 65**
  - **Pb: 1.2**
  - **Sb: 0.44**
  - **Si: 0.84**
  - **Tl: 1.4**
  - **Zn (except anode): 265**

FEUP LEPAE

Theoretical model

Landfill characterization

- **MSW landfill**
  - **spread of waste, compaction**
  - **soil covering (daily and final)**
  - **gas extraction system**
    - **collection efficiency assumed as 50%**
    - **collected gas is flared on the site**
    - **methane oxidation on the soil cover (15%)**
  - **leachate collection system**
    - **treatment not considered**

FEUP LEPAE

Theoretical model

Landfilling process modelling

- **Surveyable time period (STP*)**
  - **time period until the landfill reaches some kind of pseudo-steady-state**
  - **period until the later part of the methanogenic phase**
  - **magnitude of one century**
- **Infinite time period (ITP*)**
  - **when all landfilled material has been released to the environment**

*** Sundqvist, J.-O., 1999**

FEUP LEPAE

Theoretical model

Landfilling process modelling

- **INPUTS**
  - **Diesel for the compactor**
    - 1 L/ton
    - allocation by weight
  - **Daily and final soil cover**
    - 0.08 + 0.125 m^3/ton
    - allocation by weight
- **OUTPUTS**
  - Landfill gas
  - Leachate
  - Final stabilized solid waste
  - **Decomposition**
    - **Organic components**
      - PVC, PA, paper, cardboard and cellophane
    - **Metals**
      - Metal components
      - Metallic materials

FEUP LEPAE

Theoretical model

Landfilling process modelling

- degradation yield of **organic materials** (STP)
  - 3% for PVC and PA
  - 70% for paper, cardboard and cellophane
- degraded **carbon** outflow:
  - 99% via the landfill **gas** (as CH_4 and CO_2)

$$C_aH_bO_cN_dS_e + \left(a - \frac{b}{4} - \frac{c}{2} + \frac{3d}{4} - \frac{e}{2}\right)H_2O \longrightarrow \left(\frac{a}{2} + \frac{b}{8} - \frac{c}{4} - \frac{3d}{8} - \frac{e}{4}\right)CH_4 + \left(\frac{a}{2} - \frac{b}{8} + \frac{c}{4} + \frac{3d}{8} + \frac{e}{4}\right)CO_2 + dNH_3 + eH_2S$$

  - 1% weight via **leachate** (mainly as fatty acids, TOC)
    - 1g of total organic carbon (TOC) corresponds to 3g of chemical oxygen demand (COD)
    - BOD/COD = 0.25 during the STP
  - On the ITP a complete degradation of the materials occurs and the major degradation product is assumed to be CO_2

FEUP LEPAE

Theoretical model

Landfilling process modelling

Emission factor for metals (kg emitted/kg landfilled)

	STP	ITP	
As	**2×10^{-3}**	**1**	leachate
Cd	**5×10^{-4}**	**1**	10% gas, 90% leachate
Cr	**7×10^{-4}**	**1**	leachate
Cu	**7×10^{-5}**	**1**	leachate
Fe	**1×10^{-4}**	**1**	leachate
Hg	**1×10^{-4}**	**1**	50% gas, 50% leachate
Ni	**5×10^{-3}**	**1**	leachate
Pb	**6×10^{-5}**	**1**	leachate
Zn	**2×10^{-4}**	**1**	leachate

FEUP LEPAE

Theoretical model

Results (1 battery)

Inputs

- **Diesel (L):** 2.35×10^{-5}
- **Soil cover (m^3):** 4.82×10^{-6}

Outputs	STP	ITP
Air emissions (mg)		
CO_2	195.7	1078
CH_4	19.9	19.9
HCl	3.9	3.9
NH_3	0.96	0.96
Cd	3.00E-06	6.00E-03
Hg	1.90E-07	1.90E-03
Water emissions (mg)		
TOC	0.69	0.69
COD	2.1	2.1
BOD	0.52	0.52
As	4.20E-05	2.10E-02
Cd	2.70E-05	5.40E-02
Cr	6.65E-03	9.50E+00
Cu	1.97E-02	2.81E+02
Fe	4.66E-01	4.66E+03
Hg	1.90E-07	1.90E-03
Ni	3.25E-01	6.50E+01
Pb	7.20E-05	1.20E+00
Zn	7.14E-01	3.57E+03

FEUP LEPAE

Leaching experiments

- Based on the standard **NEN 7343**

- **Column 1**
  - entire batteries
  - nitric acid solution
  - 25 days
- **Column 2**
  - entire batteries
  - deionised water
  - 25 days
- **Column 3**
  - cross-cut batteries
  - nitric acid solution
  - 21 days
- **Column 4**
  - cross-cut batteries
  - deionised water
  - 21 days

FEUP LEPAE

Leaching experiments – Results (1 battery)

Metal	Entire batteries nitric acid solution 25 days	Entire batteries deionised water 25 days	Cross-cut batteries nitric acid solution 21 days	Cross-cut batteries deionised water 21 days
	Amount leached (mg/battery, except As and Hg expressed as μg/battery)			
As	< LD	< LD	0.0242	0.0217
Cd	< LD	< LD	0.0001	< LD
Co	< LD	< LD	< LD	< LD
Cr	0.0130	0.0083	0.0017	0.0013
Cu	< LD	< LD	0.0058	0.0067
Fe	0.1897	0.0653	0.0493	0.0075
Hg	< LD	< LD	0.2156	0.1001
Mn	0.0021	0.0008	0.0491	0.0235
Ni	0.0266	0.0001	0.0102	0.0153
Pb	< LD	< LD	0.024	0.0072
Sb	< LD	< LD	< LD	< LD
Tl	< LD	< LD	< LD	0.0008
Zn	0.0092	0.0350	8.9301	9.7397

FEUP LEPAE

Results and conclusions

- **Theoretical model**
  - **most of the emissions (CO2 from the organic fraction and metals) will occur after the surveyable time period**
    - this conclusion is expressive for all metals where Zn, Fe and Ni show the highest release on the surveyable time period
- **Leaching tests**
  - **cross-cut vs. entire**
    - metals are more strongly leached from cross-cut batteries than the entire ones, except for Cr and Fe, and Ni with nitric acid solution
    - the larger difference between metals released from entire and cross-cut batteries is for Zn that shows appreciable values only for cross-cut batteries where anode is exposed to the leaching solution
  - **nitric acid solution vs. deionised water**
    - on entire batteries the extraction with nitric acid solution was higher than with deionised water for Cr, Fe, Mn and Ni, but lower for Zn
    - with the cross-cut batteries this difference is sensible for Fe, Hg and Pb. Again for Zn, extraction with deionised water on cross-cut batteries was higher than with nitric acid solution.

FEUP LEPAE

Results and conclusions

- **Theoretical model vs. Leaching tests**
  - **Lower emissions estimated by theoretical model**
    - Cross-cut batteries: **Hg**, **As**, **Pb**, **Zn** and Cd
  - **Higher emissions estimated by theoretical model**
    - Cu, Fe, Ni
  - the state of the metals on batteries strongly conditionates its release
  - neither the nitric solution nor the deionised water are expected to be the leachant at the MSW landfill, thus the amounts of metals leached could not be the same
  - the oxidation potential of both types of solutions are not equal, and, clearly, 21 days is not the same as 100 years
  - whether or not the batteries are damaged strongly influences the metals released
  - when entire batteries are landfilled they must be seriously corroded before releasing significant amounts of metals.

FEUP LEPAE

Acknowledgements

- Authors acknowledge the financial support from **Fundação para a Ciência e a Tecnologia**, under the research project **POCTI/1999/CTA/35616**.
- Susana Xará acknowledges to **Fundação para a Ciência e a Tecnologia** for the PhD grant under the program **Praxis XXI (BD/20315/99)**.