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Heavy metals in municipal solid waste incineration residues

Martin Lemann, Rudolf Walder, André Schwyn

Abfuhrwesen Zurich, Hagenholzstrasse 110, 8050 Zurich, Switzerland

Abstract

This report gives general information on the consumption of batteries, and nickel–cadmium storage and handling of spent batteries in Switzerland, followed by detailed battery analyses; it considers finally the environmental impact, due to the heavy metals from nickel–cadmium accumulators and other batteries.

Keywords: Switzerland; Nickel; Cadmium; Battery consumption; Recycling

1. Battery recycling and disposal in Switzerland

The increasing use of nickel–cadmium accumulators has aggravated the environmental problems. Although on 1 January 1992 the preliminary disposal fee was introduced for batteries in Switzerland, the rate of separate collection has stagnated around 55%.

Laziness of the consumer might be the main reason but also the handy shape of the cylindric batteries; they can be easily thrown away with the household waste. In that way still 50% of the spent batteries reach the incineration plants or are disposed in landfills in several regions in Switzerland.

2. Battery consumption in Switzerland

According to the Federal Office of Environment, Forests and Landscape (FOEFL) the consumption of batteries in 1992 is given in Table 1.

For further calculation (Tables 2 and 3) we used the data for zinc–carbon, alkaline manganese and Ni–Cd batteries because most of the sizes are recognizable in municipal solid waste incineration (MSWI) residues. These batteries have a very low mercury content that allowed us to stop further analyses. Based upon these data there are two different ways to calculate the quantity of spent batteries which finally reach the incineration plants in Zurich Hagenholz. One way is to determine the input amount based upon the battery consumption per capita (Table 2), the other way is to calculate these amounts by means of the amount of batteries in the garbage (Table 3). The data of Tables 2 and 3 are based on the assumption that 55% of dry batteries were recycled.

Table 1
Quantity of batteries sold in Switzerland, 1992

Type	Total weight (t)	Mercury (kg)	Cadmium (kg)
Zinc–carbon	1500	22	28
Alkaline manganese	1500	170	6
Mercury button cells	5	1700	0
Silver oxide cells	6	30	0
Zinc–O_2 button cells	1	10	0
Lithium button cells	23	0	0
Lithium accumulators	46	0	0
Ni–Cd	380	0	57000
Total	3461	1932	57034

The results from these two kinds of input calculations into MSWI Hagenholz differ so much (30%) that it has been decided to analyse the slag of the MSWI plant to define the quantity of recognizable battery scrap and to calculate the quantity that reaches the incineration.

3. Element and material balance in the MSWI plant

At the MSWI Hagenholz, analyses of the incineration residues have been made since the end of 1992. Slag, fly ash, ESP dust (ElectroStatic Precipitator) and, since a few months, also the sludge and the effluent of the waste water pretreatment plant have been analysed for metals, anions, organic substances, dioxins and furans.

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Table 2
Calculation of batteries delivered to the incineration, based on the consumption per capita

	Population	Other batteries (t)	Ni–Cd (t)	Cadmium (kg)
Switzerland	6943095	1350	171	25665
Region Hagenholz	396000	77	70	1464

Table 3
Calculation of batteries delivered to the incineration, based on the quantity of household garbage, 1992

	Household waste (t)	Other batteries (t)	Ni–Cd accumulators (t)	Cadmium (kg)
Switzerland	2820000	1350	171	25665
MSWI Hagenholz	210362	100	13	1915

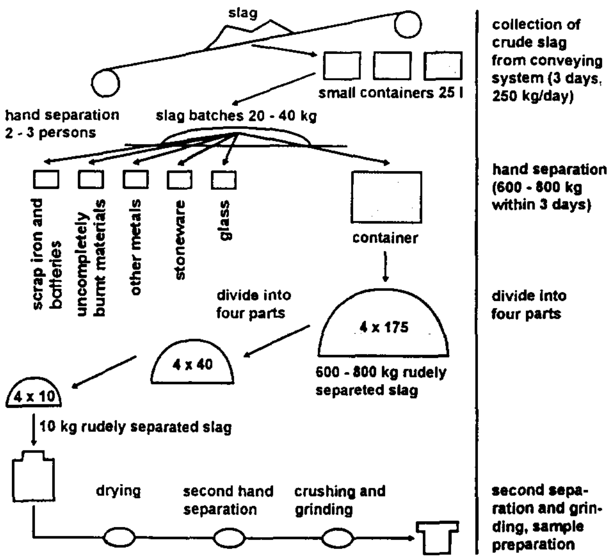

Fig. 1. Sampling procedure for slag samples.

3.1. Slag analysis

From the analytical point of view the slag analyses are the most problematic, because the crude slag contains also heavy iron scrap, stones, etc., which should be separated before the analyses, and usually the coarser fractions are of minor importance. Fig. 1 shows the procedure for the slag separation and sample preparation. First, the scrap iron, unburned materials, nonferrous metals, stones and glass residues are separated. Second, the pretreated slag is divided into four parts and one quarter is again divided into four parts. One part of it is dried and then separated again. Third, the residuary quantity is grinded and milled. A small part of it is analysed. This method is much more extensive than the sample preparation of MSWI slag usually practised. Due to this fact, the results for slag analyses from different waste incineration plants cannot be compared.

3.2. Transfer coefficients

The results in a percentage mass distribution for each element of slag, fly ash, ESP dust, flue gas and water are known as 'transfer coefficients' and gives a complete material/element balance of the whole MSWI system. This allows the build-up of a relationship to the MSWI input and hence a verification of heavy metal input assumptions. Every fraction (slag, fly ash, etc.) must therefore be weighed and chemically analysed.

With a database of 8 analysis of MSWI residues and 1 to 3 clean gas measurements during the last two years, we calculated the transfer coefficients of elements of interest, see Table 4. Table 5 gives the variation in ±% referring to the average values for the analysis of some elements.

The total of the fractions of each element in the slag, ESP dust, flue gas and, if analysed, in the slugde of the waste water pretreatment plant is 100%.

3.3. Influence of heavy metals from batteries on MSWI residues

To show the influence of batteries on the heavy metal content in the residues of an MSWI plant, the waste disposal department of Zurich (AWZ) realized, that even with the extensive method of our own slag analysis the results are not satisfying. One reason is, that with the first separation of

Table 4
Distribution residues in the various fractions in an MSWI plant

Element	Slag (%)	ESP dust (%)	Flue gas (%)	Sludge [a] (%)	Waste water (%)
Lead	58	36	0	6	0
Cadmium	7	89	0	4	0
Chromium	87	12	N.A.	0	0
Copper	95	4	N.A.	0	0
Manganese	83	16	N.A.	1	N.A.
Nickel	89	10	N.A.	1	0
Mercury	1	2	6	91	0
Zinc	37	60	2	3	0
Sulfur	34	36	1	21	8
Chlorine	4	12	0	4	80
Fluorine	31	54	0	13	2

[a] = Sludge from the waste water pretreatment plant of the flue gas treatment system.
N.A. = not analysed.

Table 5
Distribution of some elements of interest in an MSWI plant; variation of the result values

Variation of the values (%)	Slag	ESP dust
Cadmium	± −55	± −65
Zinc	± −50	± −40
Nickel	± −60	± −25
Chlorine, sulfur	± −30	± −35

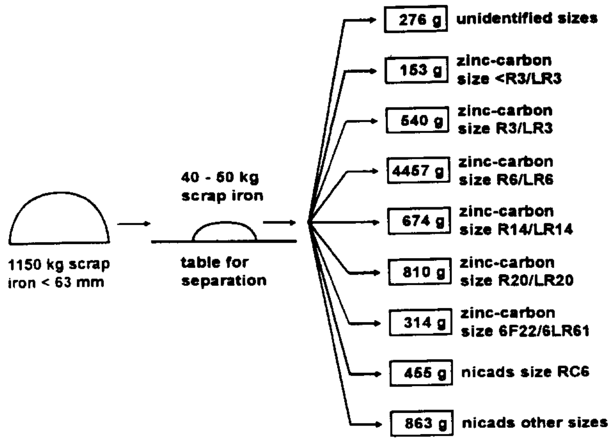

Fig. 2. Classification of batteries found in the slag.

Table 6
Calculation of the production weight of the found batteries

Size	No. of pieces	Dry mass (g)	Production weight [a] (g)	Dry mass/ production weight (%)
Unidentified size	70	276	378	73
< than R3 [b]	25	153	210	73
R3/LR3 [c]	67	540	737	73
R6/LR6	299	4457	6130	73
R14/LR14	22	674	1276	53
R20/LR20	14	810	1610	50
6F22/6LR61 [d]	10	314	420	75
RC6 [e]	30	455	667	68
Other Ni–Cd batteries	36	863	1392	62
Total	573	8542	12820	
Ni–Cd fraction			2059	
Battery fraction			10761	

[a] The number of cells gives the production weight.
[b] R = zinc–carbon.
[c] LR = alkaline manganese.
[d] F = zinc.
[e] RC = nickel–cadmium.

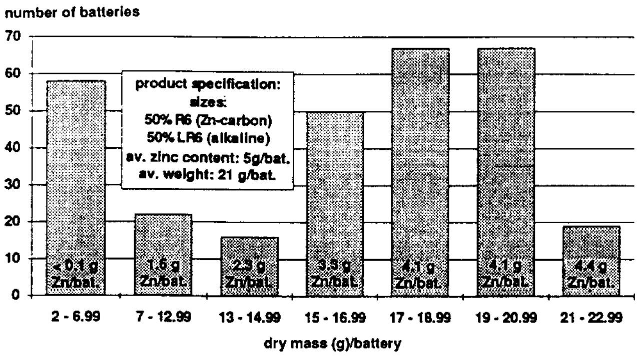

Fig. 3. Distribution of weight and zinc content in battery scrap.

coarse materials, the scrap iron will be separated magnetically and all the batteries with an iron capsule would be removed from the slag.

The heavy metal content of the batteries is mainly zinc. The mercury content in zinc–carbon and alkaline manganese batteries is limited by the Swiss law and today all these batteries are mercury free. The Ni–Cd accumulators contain cadmium and nickel. For this report, AWZ tried for the first time, to analyse and to take regard of all these values for the balancing.

3.4. Slag separation plant

The slag from the AWZ incineration plants is treated in a special plant in order to separate scrap iron from the slag. In this plant, the batteries remain in the scrap iron fraction smaller than 63 mm in diameter. Due to this fact, AWZ used a specific procedure to separate all battery scrap manually from the small scrap iron at the slag separation plant.

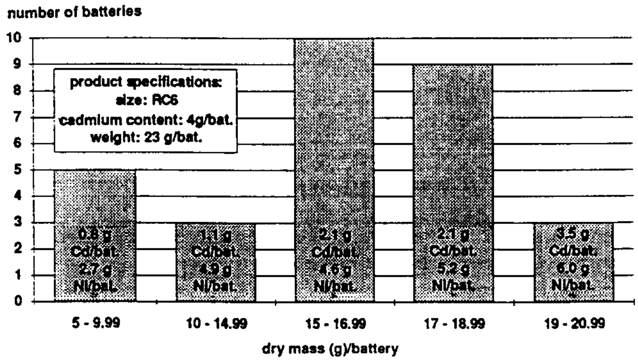

Fig. 4. Distribution of weight and heavy metal content in Ni–Cd accumulator scrap.

Table 7
Results from the manual scrap iron separation

Parameter	Weight (kg)
Separated scrap iron < 63 mm	1146
Other batteries production weight	10.76
Ni–Cd production weight	2.06

Table 8
Database for calculation of the quantity of batteries reaching the incineration

Parameter	Weight
Crude slag (t)	46221
Scrap iron (t)	4410
Scrap iron < 63 mm (%)	46
Scrap iron > 63 mm (%)	54

Table 9
Annual input of batteries into the Hagenholz incinerator

Parameter	Weight (t)
Sum total Ni–Cd accumulators 1994	3.64
Sum total other batteries 1994	19.05
Total	22.69

Table 10
Average battery quantity of FOEFL-battery statistics

Fraction	tons/year	%	Average weight FOEFL region of Zurich (tons/year)
Visible Ni–Cd accumulators scrap in slag	3.64	31.7	11.5
Visible scrap other batteries in slag	19.05	21.5	88.5

Table 11
Calculation of the annual heavy metal input in the Hagenholz incinerator from batteries

Parameter	Weight (t)
Cadmium in Ni–Cd scrap	0.42
Cadmium from Ni–Cd in MSWI-residue	1.65
Sum total cadmium	2.07
Nickel in Ni–Cd scrap	0.70
Nickel from Ni–Cd in MSWI residue	1.86
Sum total nickel	2.56
Zinc in battery scrap	2.37
Zinc from batteries in MSWI residue	15.84
Sum total zinc	18.21

Table 12
Quantity of toxic substances in incinerator

Elements	Mass flow (kg/year)
Lead	82455
Cadmium	2437
Chromium	6641
Copper	66202
Manganese	13639
Nickel	3830
Mercury	299
Zinc	189597
Sulfur	370653
Chlorine	2315643
Fluorine	43816

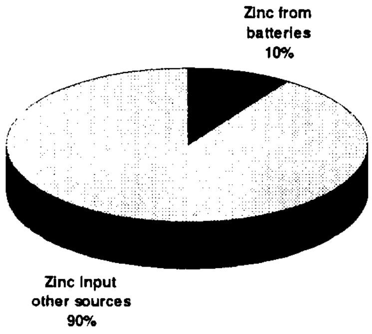

Fig. 5. Percentage of zinc input from batteries in the incineration process.

3.5. Separation of Ni–Cd accumulators from other batteries

The construction features of zinc–carbon, alkaline manganese and Ni–Cd accumulators are not similar. It is therefore possible to separate Ni–Cd accumulators from other batteries. If there was any doubt the top of the battery was opened by pliers to detect if it was really a Ni–Cd accumulator. After this separation, all batteries are weighed. Fig. 2 shows the separation scheme and what sizes of batteries could be recognized. They were divided into several fractions. More detailed results are shown in Table 6.

4. Battery decomposing process during incineration

It is known, from the slag separation, that the batteries were loosing different percentages of weight during the incineration process. The battery size R6/LR6 has been selected because it is the size most used. Fig. 3 shows the ratio of distribution and the remaining zinc content in these batteries. Other analyses also showed that the other battery sizes decompose in the same way.

For the Ni–Cd accumulators, the RC6 size was used to show the ratio of distribution and the remaining cadmium and nickel in the accumulator scrap, see Fig. 4.

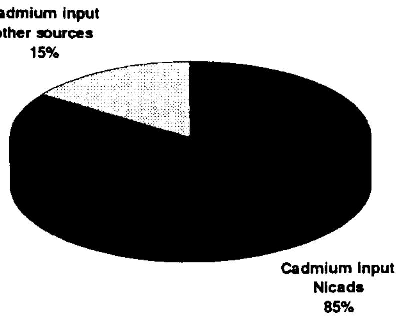

Fig. 6. Percentage of cadmium input from Ni–Cd accumulators in the incineration process.

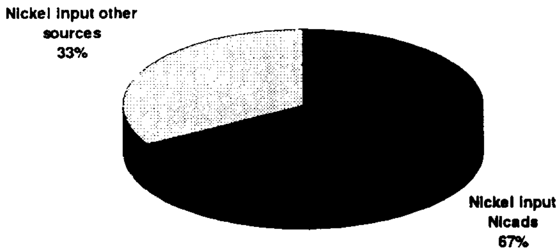

Fig. 7. Percentage of nickel input from Ni–Cd accumulators in the incineration process.

5. Results from the manual scrap iron separation, 1 March 1995

The number of found batteries or their residues multiplied by the production weight of each size gives the results shown in Table 7. Table 8 shows the data bases for the calculation.

6. Calculation of sum total batteries, 1994

With the data from Tables 7 and 8 the annual input of batteries into the Hagenholz incinerator has been calculated, see Table 9.

7. Discussion

If the data from Table 9 are compared with those in Tables 2 and 3 one may find four times less batteries than the estimated mass flows resulting from data of the FOEFL battery statistics from 1992. The data from 1992 with the analyses from March 1995 are compared because the estimated life cycle for Ni–Cd accumulators and other batteries is between one and three years.

In the Zurich area, the whole household waste stream is led to the incineration plant. In this area there are no landfill sites, where household wastes including batteries are deposed of. Could it be possible that in the area of Zurich, the percentage of battery recycling is much higher than the Swiss average value?

To get an answer we asked the biggest chain of supermarkets in Switzerland because it is involved in battery collection and recycling. Their experience is that also in the area of Zurich the percentage of battery recycling is in the range of 50–55%. Respecting this fact we could find only one reasonable explication: more than three quarters of the batteries decompose completely during the incineration process and are therefore unrecognizable in the crude slag. For further calculation the average weights shown in Table 10 were used. Table 11 gives the quantities of cadmium, nickel and zinc in the visible battery scrap and in the MSWI residues.

8. Harmful substances that flow through the Hagenholz incinerator

Table 12 shows the amount of harmful substances per year, which passed through the Hagenholz incinerator in 1994.

Fig. 5 shows the percentage of the zinc input in the MSWI Hagenholz resulting from batteries. Compared with 200 000 tons household waste incinerated in 1994 this very small amount of 88.5 tons batteries is responsible for 10% of the zinc input.

Fig. 6 shows the percentage of the cadmium input in our MSWI Hagenholz caused by Ni–Cd accumulators. The circumstance that a very small amount of 11.5 tons Ni–Cd accumulators causes 85% of cadmium input compared with 200 000 tons household waste incinerated in 1994 is very significant. This fact shows that to cut the cadmium input the most successful act would be a ban on Ni–Cd accumulators.

Fig. 7 shows the percentage of the nickel input in the MSWI Hagenholz caused by Ni–Cd accumulators. Compared with 200 000 tons household waste incinerated in 1994 this very small amount of 11.5 tons Ni–Cd accumulators causes 67% of nickel input.

9. Conclusions

The above investigations show, that the separate collection rate of 50–55% of spent batteries, although the mercury content in batteries is near zero, is still a considerable source of heavy metals in the waste incineration process. These heavy metals, zinc, cadmium and nickel are available in various forms in the slag, i.e. in a very corrosive environment. Therefore, these heavy metals may be easily dissolved and washed out of the slag in any deposit. Consequently, it is still of major importance to collect the different batteries separately from other garbage fractions, and to motivate people for this separate collection by information campaigns and to increase the battery collection rate near 100%. Fortunately, the necessary processes have been recently developed, that these separately collected batteries can be treated and their components recycled. The two battery recycling plants in Switzerland have already the capacity to treat the whole quantity of the batteries consumed annually in Switzerland.

Further research will make it possible to reduce the heavy metals in the MSWI residues in the future, and at the same time to increase recycling of heavy metals.