

**“Ferromanganese production from spent primary  
batteries – Feasibility of an EAF process”**

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## Ferromanganese production from spent primary batteries - Feasibility of an EAF process

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### Summary

In order to improve sustainability and the recycling yield from primary batteries Ferromanganese and metallic Zinc should be produced in a one step process. In the present work the feasibility of producing FeMn from spent primary batteries has been carried out. Through carbothermic reduction in a DC arc furnace at IME Aachen two 0,5 MW pilot tests were done in which a metallic melt was used as starting phase. In the first test steel scrap and FeMn was used in order to form this metallic phase for melting down the batteries. In the second test only FeMn was employed. The results show that it is possible to process spent primary batteries in order to produce FeMn by DC arc furnace technology. Because of the steel scrap in the first test, a high dilution of Mn in FeMn was found. In the second test a manganese content of 45.6 % in FeMn could be obtained. High potential exist to obtain even higher Mn-concentrations. Although these test were carried out without a liquid metal spray condenser this principle was found to be the most effective way to recover Zinc fast and in a metallic stage.

### 1 Introduction

The term "general purpose consumer battery" can be used to describe any portable battery system. This includes both single cells, as those used in torches, radios or other similar devices and "battery packs" used with mobile communication and cordless tools for example. The term covers both rechargeable chemistries as well as the more abundant single use chemistries [1].

The most common primary batteries in use today are the zinc – carbon and the alkaline – manganese battery systems. Together, they constitute in excess of 90 % by weight of the total consumer battery market in Europe. Exemplary the amount of sold batteries for Germany and Switzerland is given in Table 1. Consequently, particularly within the area of battery recycling, the term "primary battery" is often used to describe just these two systems.

Table 1: Overview of battery sale in Germany and Switzerland

year	Alkaline-Manganese, t/a		Zinc-Carbon, t/a	
	Switzerland	Germany	Switzerland	Germany
1994	1700	9300	1400	13000
1995	1850	10740	1500	12460
1996	1800	10740	1250	12220
1997	1870	10950	1320	11640
1998	2035	11432	1375	11770
1999	2170	12160	1225	11730
2000	2110	15080	980	9500
2001	2308	16800	828	9082
2002	2412	17860	756	8455
2003	2564	19340	545	7730

Source: INOBAT, GRs Batterien

## 2 Why recycle primary batteries?

Each and every day important quantity of products which contain metals are thrown away and declared as waste, although they could be recycled in order to use once again the materials contained in these products. The main reasons for recycling metals or products which contain metals are:

- The availability of natural resources is limited, because the mineral deposits get exhausted.
- Metals included in waste can represent an environmental problem (some metals can be toxic, e. g. Hg)

Because of their composition primary batteries are among the materials which can be recycled. Worldwide consumption of primary batteries rises annually. They contain an important quantity of metals, which can be recovered with less energy consumption through a recycling process than would be necessary for winning these metals from the ores. The most important recyclable metals from primary batteries are manganese and zinc.

## 3 Aim of the present work

One characteristic of the primary batteries is that they cannot be recharged, which is a problem after its use. Consequently they produce a considerable amount of pollution because of the accumulation of metals, plastics and organic substances. Due to this the aim of the present work is focused on processing pyrolised spent primary batteries by DC arc furnace technology in order to produce a high manganese-FeMn and to investigate the feasibility of a condensing process attached to the DC-furnace in order to recover commercial Zinc-metal direct as a by-product. The overall target is to safeguard a recovery yield significantly higher than 50 %.

## 4 Fundamentals

In primary batteries the products of the reactions that occur during use are zinc and manganese oxide. These oxides should be reduced by carbothermic reduction. After this reduction the formation of ferromanganese is possible. However, the existing processes are not effective enough, so that it is necessary to improve new processes

or to try to make the current processes more efficient. One proposal is to enhance the existing technologies, so that these metals can be separated better from the waste and can be supplied again not only as a raw material into an industrial process but also as a high quality material.

In Figure 1 the primary batteries are shown on the left side. It is easy to see that along with zinc-carbon and alkaline-manganese batteries there are other battery types as for example mercury oxide, silver oxide, and zinc air cells. Mercury and silver cells show even higher energy densities, but are expensive.

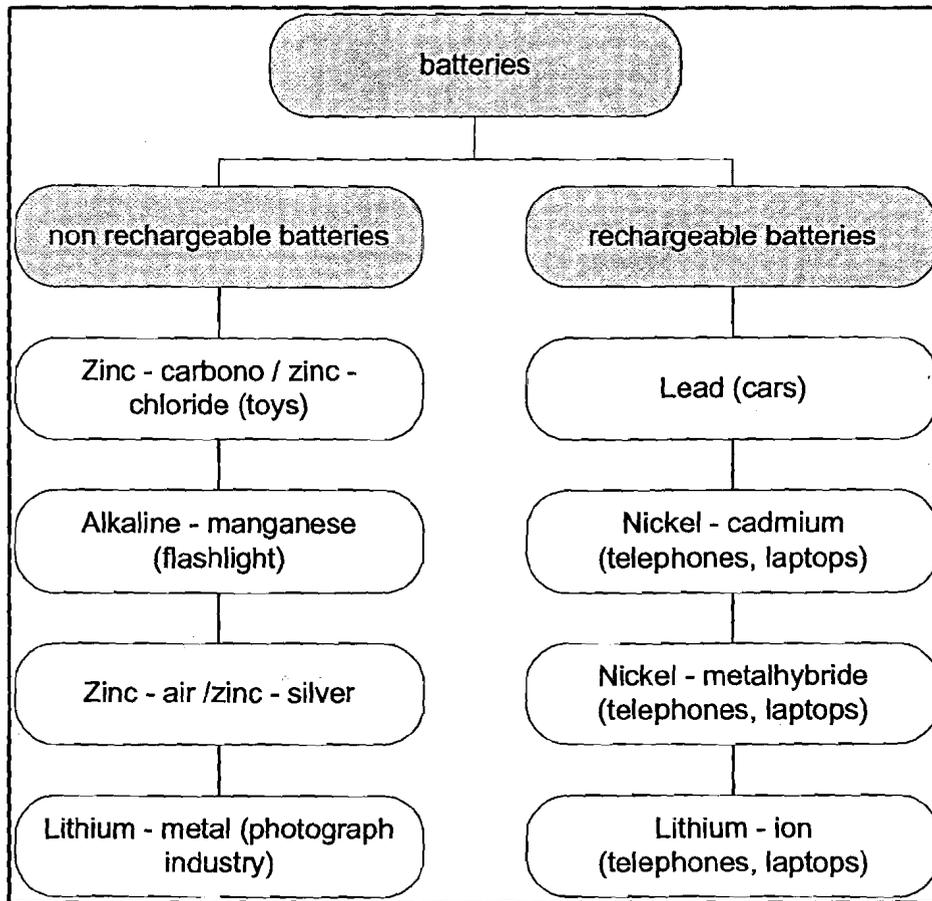


Figure 1: Batteries classification [3]

The present work is focused specially to process zinc-carbon and alkaline - manganese primary batteries, because both can be treated in the similar way due to their constituents.

In Figure 2 the components of these primary batteries are represented. The main components in the regarded primary batteries are zinc, manganese dioxide, iron and electrolytes. Together these constituent build up 85 % of batteries content. It can be seen that the batteries already contain some of the needed reductant. The components of zinc-carbon as well as alkaline-manganese primary batteries are expressed in weight percent. It is clear that both battery types contain about the same materials, but in different amounts, only the applied electrolyte differs from each other. A process which recovers Zinc, Manganese and Iron with a yield of 90 % from a 50:50 mixture of those batteries would lead to a recycling yield of slightly higher than 50 % and

meets the political requirements. This is the driving force for this development that makes the state of the art treatment of ZnO-flue-dusts obsolete.

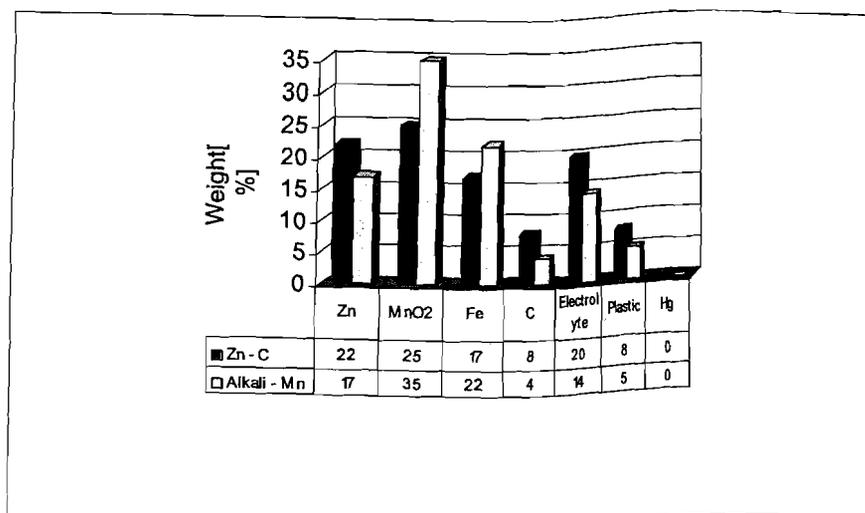


Figure 2: Recyclable materials from primary batteries.[4]

## 5 Experimental

At the IME Process Metallurgy and Metal Recycling, Institute of Aachen University (Germany), two tests at pilot scale in a DC arc furnace have been carried out after an extensive series of lab-tests in a 80 kW-DC-arc furnace. In both pilot-tests a metallic phase was used as premelt. The aim of producing this melt before feeding the batteries into the pilot-furnace is to ensure the total melting of the batteries, but also to make the process start easy and quick. In a production process this step won't be necessary as always a part of the Ferromanganese melt will remain in the furnace after tapping.

### 5.1 Pilot scale DC arc furnace at IME

The pilot scale arc furnace at IME Aachen has an operational power rating of approximately 0.5 MWh. The electric current supply of the furnace is secured by a 0.5 MVA electric rectifier. The furnace is provided with a water-cooled bottom anode of copper and a hollow graphite electrode. The cathode's vertical position is adjustable by an electrical system. The hollow electrode system for charging coke into the furnace has been developed at IME. An exhaust gas system collects the off gas and leads it to a water-cooled spark separator and a bag filter, where the flue dust is separated. The inlet and outlet temperatures of the cooling water, various temperatures of the furnace lining and temperatures on different positions of the bottom electrode and the off gas system are continuously monitored. The melt temperature is measured discontinuously by a thermocouple lance.

Figure 3 shows the flow sheet of the FeMn production process from spent primary batteries by DC arc furnace as it is analysed at IME Aachen. The starting material is pyrolysed batteries. This is necessary to remove the organic materials, water and harmful metals (especially Hg and Cd).

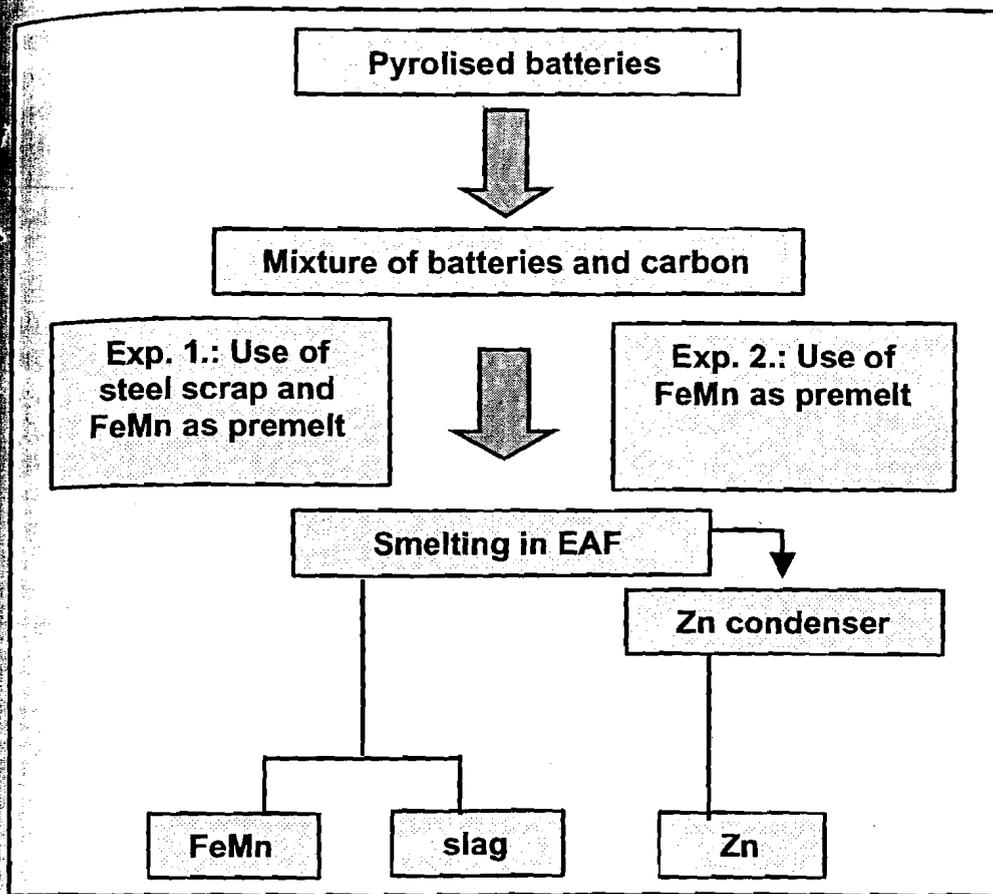


Figure 3: Flow sheet of the FeMn production from spent primary batteries by a DC arc process with attached Zinc-condenser

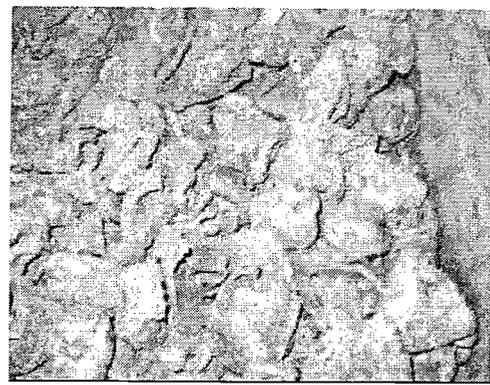
Before charging mixtures of pyrolised batteries and carbon was made, each mixture 2 kg carbon and 10 kg batteries was needed. Depending on the melting rate the next charge mixture is put into the furnace.

## 5.2 Materials

Figure 4 shows the materials which were used during the trials



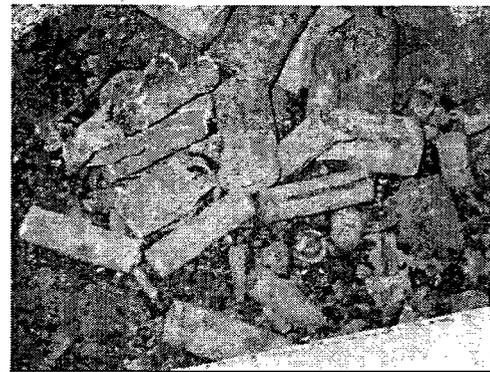
FeMn



steel scrap



slag



Mixture of pyrolised batteries and carbon

Figure 4: Materials used in the FeMn pilot production process (0,5 MW DC-arc-furnace)

### 5.3 Experiment 1

Before the beginning of battery charging in experiment 1 an amount of 40 kg of steel scrap and 100 kg of FeMn was melted in order to have a preheating of the furnace and to maintain a liquid bath. Table 2 shows the materials and amounts which were melted. Additionally slag was feed into the furnace. The batteries could be molten easily and a fluid slag was built up.

Table 2: Charged materials in DC-arc-experiment 1

Materials	Input (kg)
Steel scrap (99%)	40
FeMn40	100
Batteries	152
Slag	60
Carbon	30

The melting velocity of the batteries is rather slow, so the charging process took approximately 150 minutes. In the middle of the test run the bath temperature increased up to 1700°C, which is higher than necessary, but at the end of the process the temperature reached again the target temperature of 1400 °C. The final products of ex-

periment 1 were 155 kg of FeMn, 31.8 kg flue dust including ZnO, and slag. In order to alloy easy access to the melt and to reduce the investments at this stage of process development no gas tight system was employed and no liquid metal condenser was attached to the furnace.

#### 5.4 Experiment 2

After tapping the products of experiment 1 no steel scrap was charged and only an amount of 100 Kg FeMn (with approximately 40 % Mn) was melted as a premeltin order to simulate the production process better. This avoids any dilution of the Mn in the FeMn alloy and should lead to higher Mn-concentrations in the alloy. Table 3 shows the materials which were melted in experiment 2. The process of melting down the batteries could be again conducted easily and a fluid slag was built up.

Table 3: Charged materials in DC-arc-experiment 2

Experiment 2	Input (kg)
FeMn	100
Batteries	138
Slag	30
Carbon	25.6

Because of an electric failure, the process time was 33 minutes longer than in experiment 1. However the experiment 2 was successfully completed. The final products of experiment 2 were 118 kg of FeMn, 25.3 kg flue dust based on ZnO, and 59 kg of slag. Samples of the produced metal, flue dust and slag were taken in order to be analyzed. Figure 5 a) and b) show the FeMn products from experiments 1 and 2 respectively.

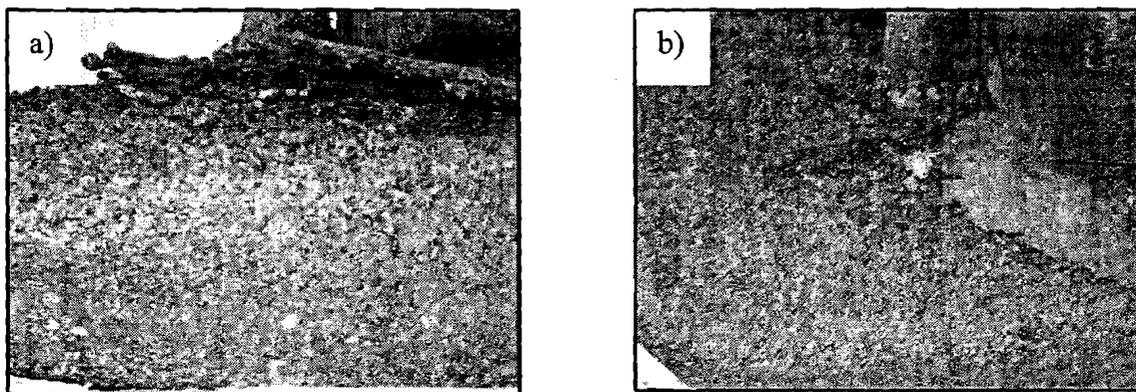


Figure 5: FeMn-ingots from DC-arc-experiments 1 (a: 155 kg) and 2 (b:118 kg)

## 6 Results

In Figure 6 the manganese contents in the actual Batrec-process-metal and the produced metal, flue dust and slag of experiment 1 and 2 are compared.

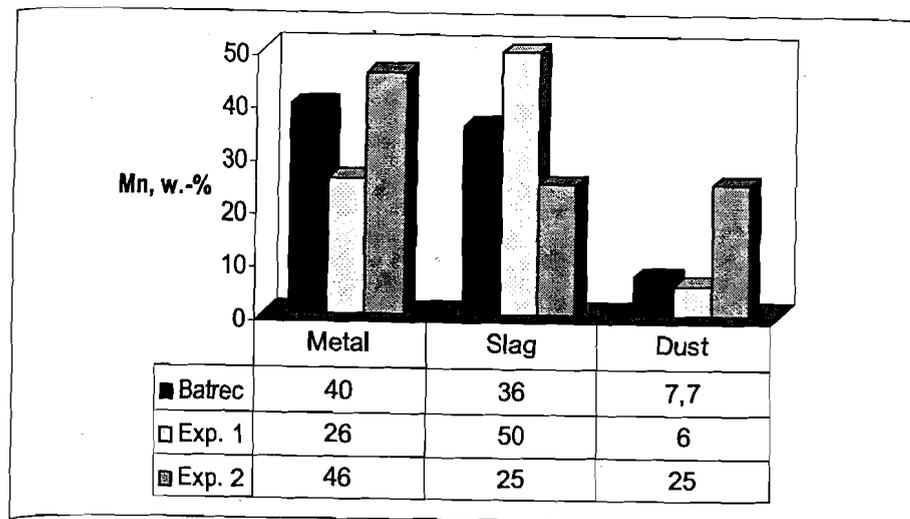


Figure 6: Manganese contents in the products from experiments 1 and 2

The final Mn content in the FeMn produced by the actual Batrec-process is about 40 %. Comparing this with the Mn content of experiment 2 an improvement of the Mn content to 46 % was reached. The lower Mn-content in experiment 1 is attributed to the amount of iron in the premelt which was used for each experiment. The iron has a dilutive effect. The Mn concentration in the slag of experiment 1 is about two times higher than the Mn content in experiment 2. It is very likely that the conditions in the first experiment were more oxidising than in the second one. The high amount of steel is expected having dissolved a significant amount of carbon which is taken away a reductant for MnO. Another important factor was the quantity of slag. In experiment 1 60 kg of Batrec slag was used as fluxing agent while in the experiment 2 only 30 kg was added. Nevertheless a development of the slag system has to be done in order to improve the efficiency of the process. In the experiment 2 about three times more manganese were evaporated and collected as redox product in the flue dust than in experiment 1, again most likely due to the stronger reducing conditions in the process. This show that also the amount of carbon, type of carbon and way of charging (bulk or hollow electrode) must be further investigated. In Figure 7 the iron content in the products metal, and slag of experiment 1 and 2 are shown.

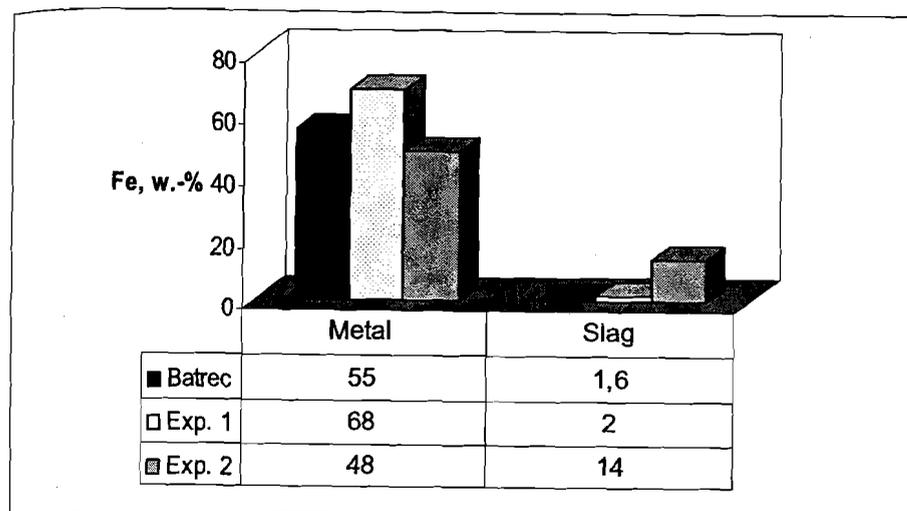


Figure 7: Final iron content in FeMn for Batrec, experiment 1 and 2

As was mentioned previously, the iron content in the FeMn alloy is an important factor, as it reduces price and marketability of the FeMn-product. In experiment 1 the content of iron is about 68 % compared to 48 % in experiment 2. That indicates also the importance of a prior removal Fe from battery scrap by physical processing.

In Figure 8 the zinc content in flue dust of experiment 1 and 2 is given.

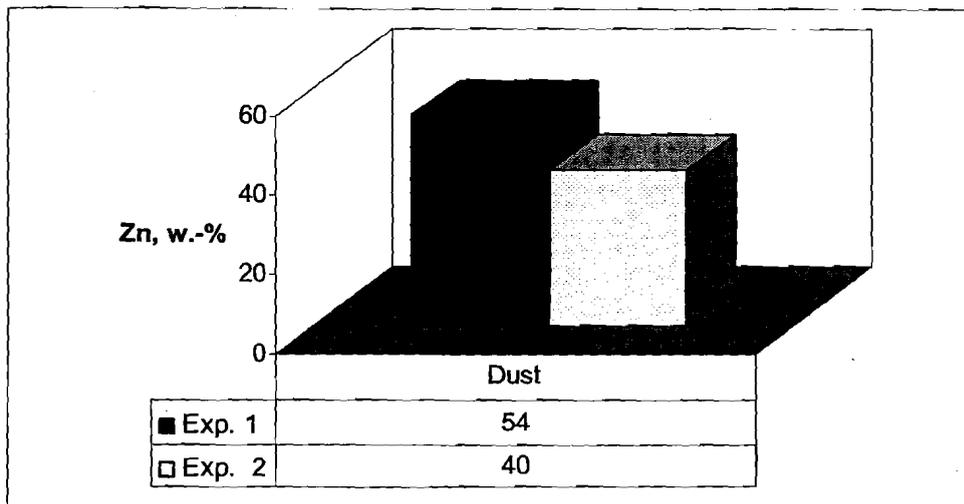


Figure 8: Final zinc content in flue dust of experiment 1 and 2

Another by-product in the process was zinc oxide which was obtained in the flue dust. Zinc is an important component for the economy of the battery recycling process and must be recovered in the production process as liquid metal. Only this allows the "jump" over the 50% value in recycling yield. The zinc content of the flue dust in experiment 1 was higher than in experiment 2 due to the co-evaporation of Manganese.

## 7 Conclusions

- In the DC arc furnace at IME Aachen two pilot scale experiments were successfully carried out in order to produce FeMn from spent primary batteries.
- A metallic premelt was used. In experiment 1 the Mn content in FeMn is diluted to 25% due to the added steel scrap. This procedure is considered to be not ideal for FeMn production from spent primary batteries by means of EAF.
- In experiment 2 FeMn simulating the residue of a continuous process after tapping worked very well as premelt. The Mn content in FeMn is about two times higher compared to experiment 1 and is also higher than the value of the existing Batec process. There is certainly high potential to increase this value above 50%.
- According to the results, the DC arc furnace serves good possibilities to produce FeMn from spent primary batteries. However a further development of the slag system will give important additional information to improve the efficiency of the process.

- The Mn content in the slag declined from 49.5% in experiment 1 to 24.6% in experiment 2. Thermochemical studies as well as experimental validation tests will show how much this value can be decreased in an optimized process leading to high recycling yields and better economy of the process.
- The iron content in FeMn in both experiments is still too high. One proposal could be to reduce the iron content in the batteries before feeding in the furnace by an appropriate treatment and to feed carbon through a hollow electrode in order to reduce more Manganese to the FeMn-melt.
- Zinc was won in oxidic form because it was not feasible at this stage of development to install a zinc-condenser. In future experiments the production of metallic zinc by a condenser will be investigated.

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