Recovery of Zinc from Spent Batteries by the Treatment in a Shaft Furnace

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The increasing amount of collected spent batteries demands processes for the material utilization. Since several years, the batteries are treated in the blast furnace of the DK process, transferring the components of the batteries to the several products, such as pig iron, zinc concentrate and slag.

Keywords:

Recycling – Material utilization – Batteries – Pig iron – Zinc

Zinkgewinnung aus Altbatterien im Hochofen

Die steigende Menge an über Rücknahmesysteme gesammelten Altbatterien erfordert entsprechende Prozesse zur stofflichen Verwertung. Ein langjährig etablierter Weg ist dabei der DK-Prozess, in dem die einzelnen Inhaltsstoffe der Batterien über den Hochofen in die verschiedenen Produkte Roheisen, Zinkkonzentrat und Schlacke überführt werden.

Schlüsselwörter:

Recycling – Stoffliche Verwertung – Batterien – Roheisen – Zink

Récupération de zinc des piles et accumulateurs usagés dans un four à cuve

Recuperación de cinc de pilas usadas por el tratamiento en un horno de cuba

1 Introduction

Most of the 32,400 t of batteries sold each year in Germany can be recycled to reclaim valuable metals. About 15,000 t of spent batteries have been collected by the German collecting system “GRS” in 2013. Out of this amount, 80 % or 11,900 t were of the type zinc/carbon and alkaline-manganese respectively [1]. This paper describes one option for the recycling of such types of spent batteries.

2 The DK process

DK Recycling und Roheisen GmbH, founded in 1876 as Duisburger Kupferhütte, changed its process in 1982 from the recycling of pyrite cinders to the recycling of iron containing waste oxides, mainly dusts and sludges from Basic Oxygen Furnace (BOF) steelmaking. Today DK processes about 460,000 t/a of different dusts and sludges using a sinter plant to transform the waste oxides into a form that meets the requirements for processing in a blast furnace. The liquid iron from the blast furnace is cast into pigs on a casting machine. The pig iron (280,000 t/a) is sold in Germany, Europe and overseas to iron foundries.

The production of pig iron from waste oxides is a two-step process. After burden preparation and agglomeration, the agglomerated oxides (sinter) are reduced in a blast furnace to liquid iron. The agglomeration of the fine oxides is done on a sinter plant at DK (Table 1).

The most important steps in the sinter process are shown in Figure 1.

After the agglomeration of the fine oxides, the sinter is reduced in the blast furnace to liquid iron. Although DK has two blast furnaces (Table 2), only BF # 3 is operated. The main steps in the blast furnace process are shown in Figure 2.

Table 1: Sinter plant data

Year of construction	1981
Manufacturer	Lurgi
Nominal Capacity	500,000 t/a
Strand length	32 m
Strand width	2.5 m
Effective suction area	60 m²
Number of suction boxes	16
Waste gas cleaning	Electrostatic precipitator Semi-dry spray absorber Fabric filter
Production	1450 t/d

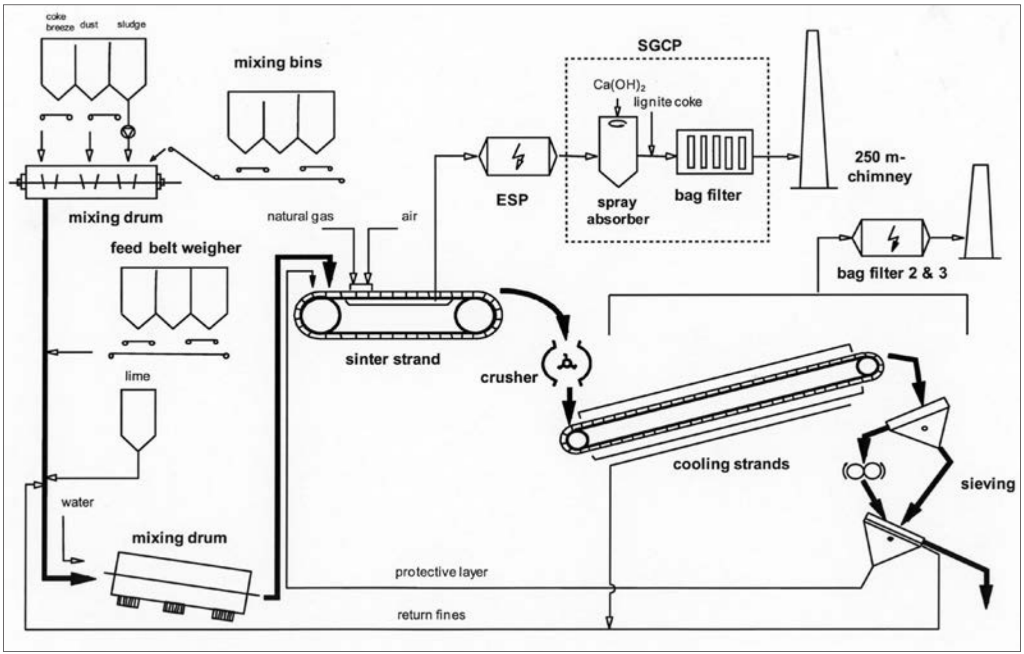

Fig. 1:
Sinter plant flow sheet

3 Zinc recovery from batteries

Due to increasing zinc contents in the filter dusts and sludges, the DK process has to cope with an extremely high zinc load. Since the sintering process does not remove notable quantities of zinc, the zinc input into the blast furnace amounts to 35 to 40 kg per ton of hot metal. Compared to a "normal" blast furnace, this is 250 times higher.

Due to intensive work on the process, it is possible to recover the zinc separately from the iron. Consequently it appeared to be reasonable, to recover zinc from spent batteries as well.

Table 2: Blast furnace plant data

	BF No. 3	BF No. 4
Year of construction	1974	1959
Working volume	580 m³	460 m³
Tuyeres	12	9
Blast volume	60,000 Nm³/h	45,000 Nm³/h
Production	1000 t/d	550 t/d
Last relining	2011	1998
Blast pressure	0.8 bar	0.8 bar
PC injection	yes	no
Oxygen in blast	25 %	21 %
Blast temperature	1100 °C	1050 °C

3.1 Types of batteries

Collected spent batteries consist of 80 % non-rechargeable (primary) batteries. In 2013 the quantity of this type of spent battery in Germany had been 11,900 t [1]. Alkaline-manganese batteries account for more than 86 % of

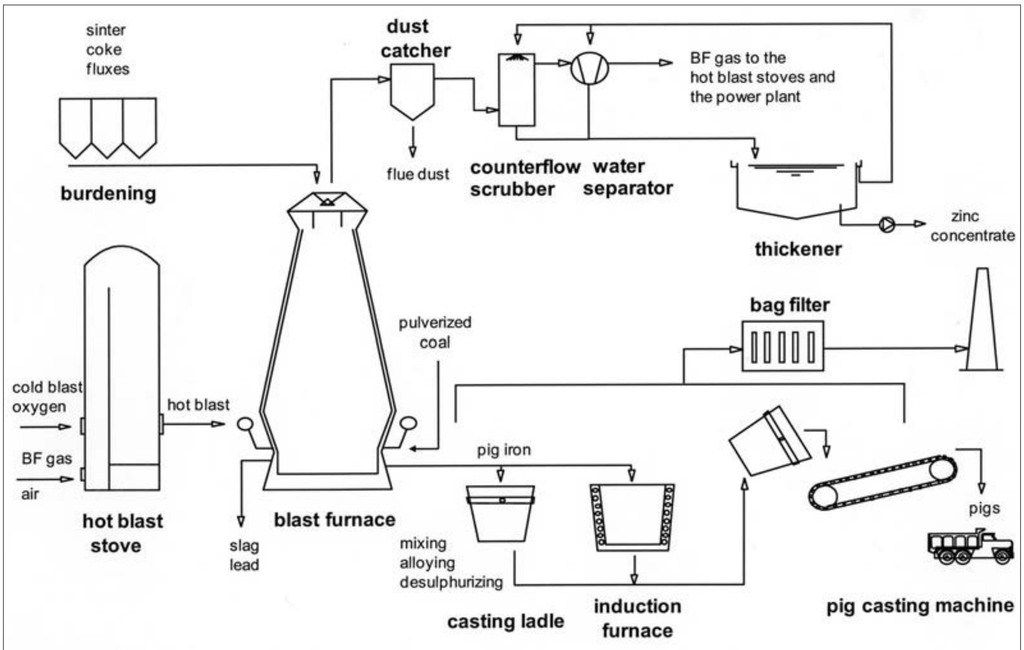

Fig. 2:
Blast furnace flow sheet

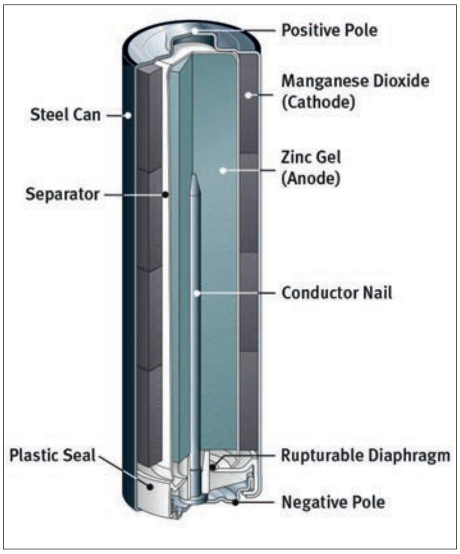

Fig. 3: Alkaline-manganese battery [2]

Fig. 4: Composition of an alkaline-manganese battery [1]

Fig. 5: Zinc/carbon battery [2]

Table 3: Delivered batteries to DK in 2013 [t]

Degraded batteries	958
Zn/C	568
Alk/Mn	2899
Total	4425

this quantity. The construction of an alkaline-manganese battery can be seen in Figure 3.

Alkaline-manganese batteries contain valuable metals like manganese, zinc and iron (Figure 4).

Besides the alkaline-manganese batteries, zinc/carbon batteries represent the second largest type of collected primary batteries. The construction of a zinc/carbon battery can be seen in Figure 5.

During the collection and separating process it is assured that no mercury containing batteries are delivered to DK. Besides the spent batteries, DK also processes some quantities of degraded material from battery producers. Table 3 shows the delivered quantities of the various battery types in the last year.

The quantity of processed batteries in the blast furnace can be seen in Figure 6.

3.2 Process of zinc recovery

Without any additional preparation, the batteries are charged together with sinter and coke directly to the blast furnace. While iron is converted to nearly 100 % to pig iron, about 80 % of the manganese can be found in the pig iron.

Fig. 6: Usage of Alk/Mn and Zn/C-batteries in the blast furnace [t/a]

Zn	65-68
Pb	1-2
C	<2.0
Fe	<1.5
F	<1.0
Cl	<1.0
Na	<0.10
K	<0.15

Table 4: Analysis of DK zinc concentrate [wt.-%]

The remaining part of the manganese as well as the alkalies are transferred to the slag.

The zinc leaves the furnace with the blast furnace gas and is collected in the gas cleaning. The gas cleaning consists of two steps: a dry precipitation of coarse dust in the dust catcher and a wet one with the separation of fine and zinc carrying particles. The sludge of the wet gas cleaning is collected in the thickener and forms the second product of DK, the zinc concentrate.

3.3 Zinc product

The sludge from the thickener is dried in a filter press and appears as a concentrate with 65 to 68 % of zinc and very little impurities (Table 4). Compared to other secondary zinc raw materials the low contents of fluor and chloride are an advantage. The annual production of 15,000 t is sold to various European zinc smelters.

4 Summary

DK has widened its capability for the processing of industrial residues by the recycling of spent batteries. Like the whole DK process, the recycling efficiency for the batteries shows excellent values with more than 98 % (Figure 7).

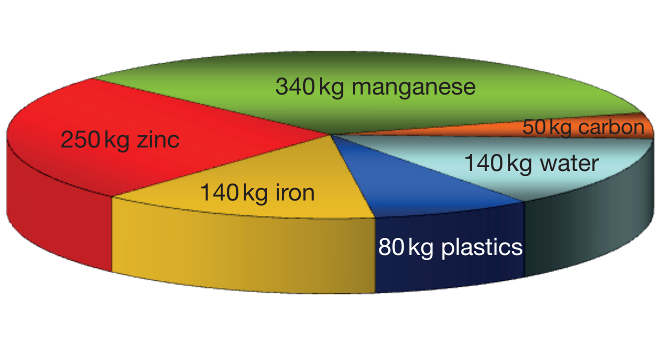

Fig. 7: 1 ton of batteries contains …

References

[1] Stiftung Gemeinsames Rücknahmesystem Batterien: Erfolgskontrolle 2013; www.grs-batterien.de

[2] Stiftung Gemeinsames Rücknahmesystem Batterien: Die Welt der Batterien 2007

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