

# Optimization of the Ferromanganese Production from Spent Primary Batteries – Design of the Process Slag

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In order to improve the recycling efficiency and especially the manganese recovery yield in the ferromanganese production from spent primary batteries process, slag-metal equilibrium experiments were conducted in a closed MoSi<sub>2</sub>-resistance furnace above argon atmosphere. Four synthetic slag-series: CaO-SiO<sub>2</sub>, CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, CaO-SiO<sub>2</sub>-MgO and CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-MgO in different compositions were brought into contact with two different Fe-Mn alloys (50 and 90 wt.-%Mn), using alumina crucibles at 1470 °C. The equilibrium computations were carried out with the computer software FactSage using the FACT compound 5.0 databases. The theoretical and experimental results clearly showed the same tendency and an acceptable agreement.

Five slag systems were found allowing keeping more than 80 wt.-%Mn in the metallic alloy. The most important factor to increase the manganese fraction in the Fe-Mn-alloy is the CaO-content in the slag, together with the concentration of MgO improving the basicity of the slag. The initial slag basicity must be near to or higher than 1. The best results were obtained using a slag composition of 54 wt.-% CaO, 6 wt.-% SiO<sub>2</sub>, 37 wt.-% Al<sub>2</sub>O<sub>3</sub> and 3 wt.-% MgO. This recovered more than 90 wt.-% of the Mn-input in the alloy.

**Keywords:**

Recycling efficiency – Ferromanganese – Slags – Distribution coefficient – Basicity – Primary batteries

## Optimierung der Ferromanganherstellung aus Primärbatterieschrott – Aufbau des Schlackenprozesses

Um die Manganausbeute im Zuge der Ferromangan-Produktion aus gebrauchten Primärbatterien zu erhöhen, wurden Versuche zum Schlacke-Metall-Gleichgewicht in einem geschlossenen MoSi<sub>2</sub>-Widerstandsofen unter Argon-Atmosphäre durchgeführt. Vier synthetische Schlackenserien – CaO-SiO<sub>2</sub>, CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, CaO-SiO<sub>2</sub>-MgO und CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-MgO – wurden in verschiedenen Zusammensetzungen mit zwei verschiedenen synthetischen Fe-Mn-Legierungen (50 und 90 Masse-% Mn) in Aluminiumoxid-Tiegeln bei 1470 °C zur Reaktion gebracht. Thermochemische Gleichgewichtsberechnungen mit der Software FactSage begleiteten die Experimente. Der Vergleich von theoretischen und experimentellen Ergebnissen zeigte ausreichende Übereinstimmungen. Fünf Schlacken-zusammensetzungen wurden gefunden, die es ermöglichten,

mehr als 80 Masse-% Mn in der Legierung zu halten. Der wichtigste Faktor zur Steigerung des Mangananteils in der FeMn-Legierung ist der CaO-Gehalt in der Schlacke bei gleichzeitig geringen Konzentrationen an MgO, die die Basizität der Schlacke verbessern. Die anfängliche Schlackenbasizität muss annähernd oder höher als 1 sein. Die besten Ergebnisse wurden mit einer Schlackenzusammensetzung von 54 Gew.-% CaO, 6 Gew.-% SiO<sub>2</sub>, 37 Gew.-% Al<sub>2</sub>O<sub>3</sub> und 3 Gew.-% MgO erzielt. Dies ermöglicht es, sogar mehr als 90 Gew.-% des Mn in der Legierung zu halten.

**Schlagwörter:**

Recyclingeffizienz – Ferromangan – Schlacke – Verteilungskoeffizient – Basizität – Primärbatterien

## Optimisation de la fabrication du ferro-manganèse de riblons de batteries primaires – formation d'un procédé en scorie

## Optimización de la producción de ferromanganeso de baterías primarias desgastadas – Diseño de la escoria del proceso

### 1 Background and aim of the project

Industrial and domestic waste has continuously increased in the last 30 years. The storage capacity of landfills and special waste dumpsites is limited, and disposal costs become high. Therefore concepts for recycling emerge for minimizing the wastes and sometimes they offer economical benefits through the reuse of possible valuable materials present in them. In other words: minimizing the production costs via substituting raw materials by cleaned recyclable products leads to the preservation of resources on earth

and is a social goal, since they are limited. Recycling is a major aspect of environmental protection.

Manganese is the fourth most used metal in terms of tonnage, being ranked behind iron, aluminium and copper, with in the order of 29 million tons of ore being mined annually (2004). Manganese has numerous applications which impact on our daily lives as consumers, whether it is of parts made of steel, portable batteries, or aluminium beverage cans. After steel, the second most important market for manganese, in dioxide form, is that of portable primary dry batteries [1].

The most common primary batteries in use today are based on the zinc-carbon and the alkaline-manganese system. Together, they constitute more than 85 % by weight of the total consumer battery market in Europe. The primary batteries are lightweight and convenient, relatively inexpensive and, consequently, are used in households throughout the world to power portable electrical and electronic devices, radios, torches, toys and a whole host of other everyday appliances. One characteristic of the primary batteries is that rechargeability is almost not given their usage. Thus, they produce a considerable amount of waste with an accumulation of metals, plastics and organic substances. On the other hand primary batteries represent a good opportunity to be recycled, because their chemical composition is more or less homogeneous, with reduced "mineralogical" problems like those of ores. They have an ideal ratio of weight and size, a high metal content and a regular form. Therefore, they are capable of being easily pre-treated or classified. This project focuses on the treatment of spent primary batteries by the Direct Current-Submerged Arc Furnace route (DC-SAF), whereas the contained manganese oxide is reduced by a carbothermic process. Together with (a part of) the iron contained in the steel cane, manganese is melted down to form a Fe-Mn alloy (Figure 1 shows the binary system Fe-Mn, showing the expected melting temperatures slightly below 1400 °C), while the zinc oxide is evaporated, reduced and recovered as metallic Zn in an attached zinc condenser or as oxidized flue dust. This process has been recently compared with today's used recycling technologies with regard to its recycling efficiency [2].

This work presents the first part of the investigations focussing on slag-metal equilibrium experiments in order to reduce losses in slag and such to improve the manganese recovery yield. An average chemical composition of zinc carbon and alkaline batteries is given in Table 1, and an exemplary average composition of a dry black powder from spent alkaline batteries after dismantling is presented in Table 2.

The recycling technology selected depends mainly on its economy and the legislative frame at the time. In order to improve the sustainability and the recycling efficiency from

Tab. 1: Average primary battery composition [wt.-%] [3]

Battery component	Zn-C	Alkaline-Mn
Zn	16.4 – 28.6	5.4 – 17.5
ZnO	0.3 – 0.4	0 – 0.6
Hg <sub>total</sub>	max. 0.04	max. 0.04
MnO <sub>2</sub>	22 – 34	17 – 38
Plastic	7 – 10.6	3 – 5
Fe	14 – 21	15 – 26
Cu	0 – 0.2	1 – 3
Miscellaneous parts	4 – 13	4 – 11
Electrolyte	14 – 23	5 – 16

Tab. 2: Average dry powder composition of alkaline batteries after dismantling [4]

Compounds	Composition [wt.-%]
ZnO	25.6
Mn <sub>total</sub>	44.2
K <sub>2</sub> O	8.6
Fe <sub>2</sub> O <sub>3</sub>	1.4
Pb <sub>total</sub>	0.06
Hg <sub>total</sub>	0.0001
Cd <sub>total</sub>	0.000006
Others, miscellaneous parts	20.5

primary batteries, ferromanganese and a zinc concentrate should be produced in a one step process. Since the mercury content in primary batteries has been dramatically diminished, the use of pyrometallurgical instead of hydro-metallurgical processes offers higher potential due to a reduced waste formation (almost no waste water and no wet leach residues). According to the European Portable Batteries Association (EPBA), among the pyrometallurgical processes, the electric arc furnace (SAF) route represents the best way to recycle primary batteries. The strengths of this route are: 1) Large batches of primary batteries can be treated in one step with high productivity; almost all metallic element as well as the carbon content of the batteries are recovered or used, the latter as reducing agent and 2) The metals are recovered in form of two secondary products: metallic condensed zinc (ingots) or oxidic zinc concentrate and a high-grade ferromanganese master-alloy. Both qualities are similar to the primary products used in the stainless steel industry or in the chemical and metallurgical Zn-industry.

Nevertheless, the treatment of primary batteries through a standard SAF-process alone is not capable of attaining a sufficient manganese recovery. In fact, in the recycling process of primary batteries manganese is found in high proportions in the slag, resulting in a decreased efficiency and economic losses for the process. Thus, the SAF-route requires modifications in order to improve this situation. As manganese has a vapour pressure approximately 250 times higher than iron at 1600 °C, the process temperature has to be as low as possible. A second requirement is a suitable slag system serving the following characteristics at process conditions in order to achieve a high manganese recovery yield: molten condition (sufficient superheat) at process

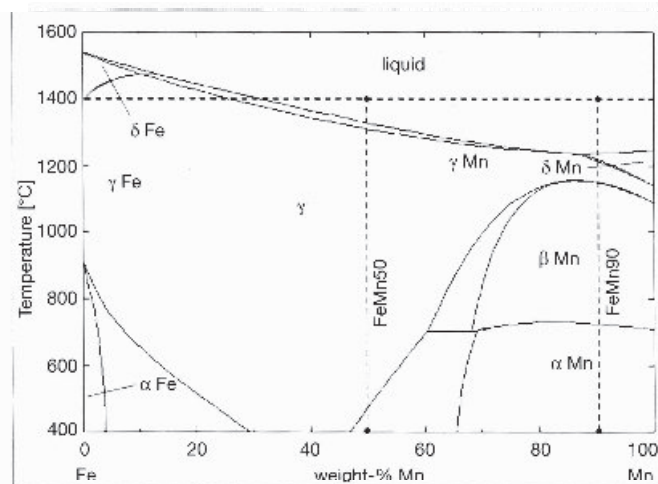
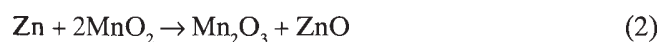
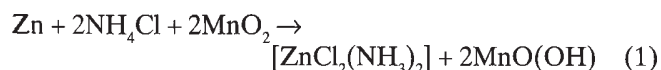


Fig. 1: Fe-Mn binary diagram calculated in Factsage™ 3.5.1



temperatures of 1470 °C; low evaporation pressures of the slag components; manganese solubility significant less than 20 wt.-%; low viscosity to allow metal drop settling and high density difference between the metal and slag phase.

During discharging all batteries change their original chemical composition resulting from anode and cathode reaction mechanisms. The overall chemical reactions of the Zn-C and alkaline-Mn systems can be expressed as:



These are the most probable reactions. Yet sometimes the reaction products change depending on the battery discharging conditions.

According to the chemical compositions presented in Table 1, a direct recycling process will result in a Fe-Mn-alloy of max. 30 wt.-% Mn. Without any pre-treatment of the spent primary batteries the ratio between manganese and iron cannot reach the target value of 1 (industrial commodities). But applying of an appropriate mechanical processing separation technique, iron can be separated. This is implemented in most of the hydrometallurgical and pyrometallurgical recycling routes. The concentrated and de-ironed product is called black mass, being rich in Mn- and Zn-oxides can directly be fed into a SAF-furnace. If purely charged, e.g. without addition of only pyrolyzed battery scrap, a high-content manganese alloy will form, which contains according to Table 2 theoretically more than 80 wt.-% Mn.

The major components of slags produced in ferromanganese smelting processes are MnO, CaO, MgO, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> [5]. The content of each oxide depends on the composition of the original ore and the plant practice adopted. Only limited information about ferromanganese alloys processes, their thermodynamics and kinetics can be found in literature. However, the chemical and “mineralogical” composition of spent primary batteries is different compared to manganese ores. Therefore, on the basis of slag compositions commonly used to produce ferromanganese, four different synthetic slag systems with expected liquidus temperatures below than 1500 °C are fundamentally investigated in this work. The aim is to minimize the manganese losses as oxide and to improve the manganese recovery yield for the proposed pyrometallurgical recycling route in SAF-furnaces.

## 2 Thermochemical analysis

In ferromanganese production, either in blast furnaces or in electric furnaces, the gas-slag-metal reactions are of vital industrial interest, as they determine the economy of the process (metal losses, waste gas composition). An understanding of these reactions is absolute necessary to predict and control the mass flow of elements such as Mn, Si and K, (e.g. distribution between phases). Because the metal components are non-ideal, solution models are needed to calculate activities for slag and metal phases. The thermodynamic properties of solutions play an important role in

pyrometallurgical processes. The thermodynamic database available in the software FactSage (Facility for the Analysis of Chemical Thermodynamics) accesses species data in-form real solutions, allowing to determine equilibria compositions of this multiphase and multicomponent system at given temperatures, pressures and initial compositions. The software uses unified interaction parameters proposed by BALE & PELTON [6] for the metallic molten phase and a quasi-chemical approximation for the slag. The derived unified interaction parameter (UIPM) describes the thermodynamic behavior of components in liquid dilute alloys; the method was subsequently extended by LUPIS & ELLIOTT [7]. PELTON & BALE [8] proposed a formalism that combines or unifies the standard first-order interaction parameter formalism, the standard second-order interaction parameter formalism, the quadratic formalism and the polynomial expression. This improved model was named UIPM. This model is thermodynamically self-consistent at both infinite dilution and finite concentrations and has been used successfully for molten iron.

The quasichemical model describes the thermodynamic properties of a system taking the structural ordering into account. In order to apply this model to a highly order system, the model was modified to the basic quasichemical model by: a) providing an expression of the entropy and enthalpy, that exhibits ordering at any desired composition; b) introducing a composition-dependent energy change for the formation of pairs; and c) extending this model to ternary and multicomponent systems. ERIKSSON et al. [9] have evaluated binary slag-subsystems of eleven components: SiO<sub>2</sub>-CaO-Al<sub>2</sub>O<sub>3</sub>-FeO-MgO-MnO-Na<sub>2</sub>O-K<sub>2</sub>O-TiO<sub>2</sub>-Ti<sub>2</sub>O<sub>3</sub>-S. But not all ternary combinations have been investigated in detail and only a few higher order systems have been studied. Since the model parameters for the SiO<sub>2</sub>-CaO-Al<sub>2</sub>O<sub>3</sub>-MgO-MnO-K<sub>2</sub>O system have been integrated into FACT database, the modified quasichemical model was applied to the ferromanganese slag of this study. Using the equilib module in the software Factsage™ 5.3.1, equilibria computations were performed in order to analyze the impact of slag components (kind) and reducing elements (Ca, Mg, Si, Al) on the distribution constant. Always the main target

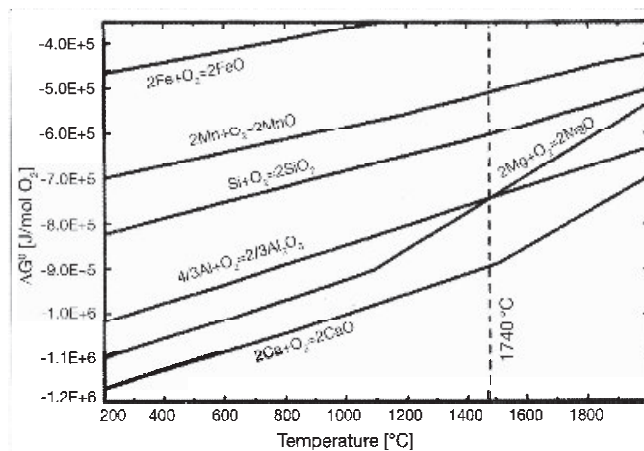


Fig. 2: Richardson-Ellingham diagram for the reactions of oxidation in the analyzed metal-slag system, calculated with the software Factsage™ 5.3.1 (standard conditions and pure substances).

Tab. 3:  
Experimental plan; composition  
and initial basicity of the tested  
slags.

In Fig. 3 or 4	Heat Nr.	Slag- series	FeMn- alloy	Alloy weight [g]	CaO [wt.-%]	SiO <sub>2</sub> [wt.-%]	Al <sub>2</sub> O <sub>3</sub> [wt.-%]	MgO [wt.-%]	Initial slag basicity
a	1	I	FeMn50	183.1	56.3	43.7	—	—	1.29
	2		FeMn90	183.7	56.3	43.7	—	—	1.29
b	3		FeMn50	185.2	37.0	63.0	—	—	0.59
	4		FeMn90	182.5	37.0	63.0	—	—	0.59
c	5	II	FeMn50	186.2	46.7	38.3	15.0	—	0.88
	6		FeMn90	190.2	46.7	38.3	15.0	—	0.88
d	7		FeMn50	181.0	43.0	38.3	18.7	—	0.75
	8		FeMn90	184.7	43.0	38.3	18.7	—	0.75
e	9		FeMn50	179.2	43.0	42.0	15.0	—	0.75
	10		FeMn90	193.0	43.0	42.0	15.0	—	0.75
f	11		FeMn50	177.1	31.6	38.3	30.1	—	0.46
	12		FeMn90	186.7	31.6	38.3	30.1	—	0.46
g	13		FeMn50	192.8	31.6	53.4	15.0	—	0.46
	14		FeMn90	186.0	31.6	53.4	15.0	—	0.46
h	15		FeMn50	201.9	22.0	63.0	15.0	—	0.28
	16		FeMn90	187.0	22.0	63.0	15.0	—	0.28
i	17		FeMn50	179.4	16.5	68.5	15.0	—	0.20
	18		FeMn90	191.2	16.5	68.5	15.0	—	0.20
j	19		FeMn50	180.5	50.0	7.0	43.0	—	1.00
	20		FeMn90	196.4	50.0	7.0	43.0	—	1.00
k	21		FeMn50	172.1	55.0	7.0	38.0	—	1.22
	22		FeMn90	191.7	55.0	7.0	38.0	—	1.22
l	23	III	FeMn50	162.2	44.4	46.8	—	8.8	1.14
	24		FeMn90	191.7	44.4	46.8	—	8.8	1.14
m	25		FeMn50	190.0	36.4	46.8	—	16.8	1.14
	26		FeMn90	187.0	36.4	46.8	—	16.8	1.14
n	27		FeMn50	182.9	29.9	46.8	—	23.3	1.14
	28		FeMn90	194.7	29.9	46.8	—	23.3	1.14
	29	IV	FeMn50	185.9	45.7	37.3	14.0	3.0	0.95
	30		FeMn90	190.2	45.7	37.3	14.0	3.0	0.95
	31		FeMn50	186.0	54.0	6.0	37.0	3.0	1.33
	32		FeMn90	182.4	54.0	6.0	37.0	3.0	1.33

of this study identifying a slag basicity/composition that minimizes the loss of manganese as oxide in the slag determined the methodology. The results of the thermochemical calculation based on the slag and metal composition data shown in Table 3 will be presented in direct comparison with the experimental outcome in graphic form.

Figure 2 shows the Richardson-Ellingham-Diagram for the selected metal-oxide systems. The diagram was theoretically calculated with the software Factsage™ 5.3 from 200 to 2000 °C. At 1470 °C, CaO is the most stable oxide followed for Al<sub>2</sub>O<sub>3</sub> and MgO with about the same chemical stability. SiO<sub>2</sub> is close to MnO, FeO is situated in the top area of the diagram.

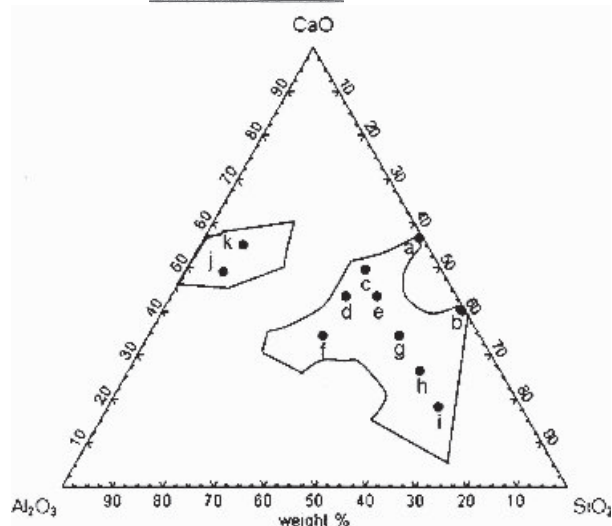
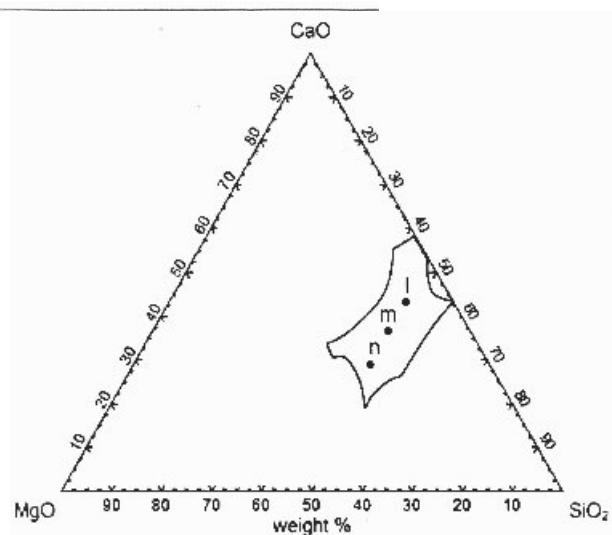
### 3 Materials and experimental procedures

Two binary alloys were prepared from electrolytic iron and electrolytic manganese in an induction furnace under 800-mbar-argon atmosphere at 1500 °C. The compositions in mass-% were FeMn50 and FeMn90 and selected, as they can be the expected min-/max-values from an optimized recy-

cling process of spent primary batteries. The melted quantities were 10 kg of each alloy, using cylindrical low-porosity alumina crucibles with a capacity of 1000 ml. The prepared alloys were cast in cylindrical steel moulds of 45 mm diameter and 250 mm height. Subsequently, they were analyzed by an atomic absorption spectrometer and cut into small discs of about 20 mm thickness. Synthetic slags were prepared from pure oxides (CaO, MgO, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>), the corresponding quantities for each experiment were weighted, mechanically mixed and dried during 24 hours at 200 °C. The compositions are listed in Table 3. The initial mass ratio between alloy and slag was 2 : 1 for each experiment.

The basicity of the slags was considered as  $B = \text{wt.-% basic oxides (CaO+MgO) / wt.-% acidic oxides (SiO}_2\text{+Al}_2\text{O}_3\text{)}$ . Figures 3 and 4 represent the liquidus lines of the CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>- and CaO-SiO<sub>2</sub>-MgO-slag systems at 1470 °C. In the diagrams, the points indicate the investigated ternary slag compositions. A quaternary slag-series IV was performed based on the best results obtained from the ternary slag-series.



Fig. 3: CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> isotherms at 1470 °CFig. 4: CaO-SiO<sub>2</sub>-MgO isotherms at 1470 °C

Experimentally the metal-slag equilibria were determined in a resistance furnace using MoSi<sub>2</sub>-heating elements. The experiments were conducted at 1470 °C combining the two different Fe-Mn alloys and the four slag-series. A metallic and slag sample was placed into an Al<sub>2</sub>O<sub>3</sub>-low porosity crucible, 70 mm in height and 50 mm in inside cylindrical diameter. The crucible with slag and metal samples was placed onto an Al<sub>2</sub>O<sub>3</sub>-billet. The insertion and the final positioning of the crucible in the furnace were executed by means of a piston.

The furnace temperature was controlled by a Euro-therm phase angle thyristor unit connected to a PtRh6/PtRh30-thermocouple. This was positioned between crucible and heating elements nearing height of the phase boundary metal and slag. The top and the bottom of the furnace were closed by ceramic lids and argon gas was introduced through the bottom of the furnace at a flow rate of 2 l/min in order to maintain a quasi inert atmosphere. The used equipment is shown in Figure 5, details of the furnace are illustrated in Figure 6. The heating process was computer

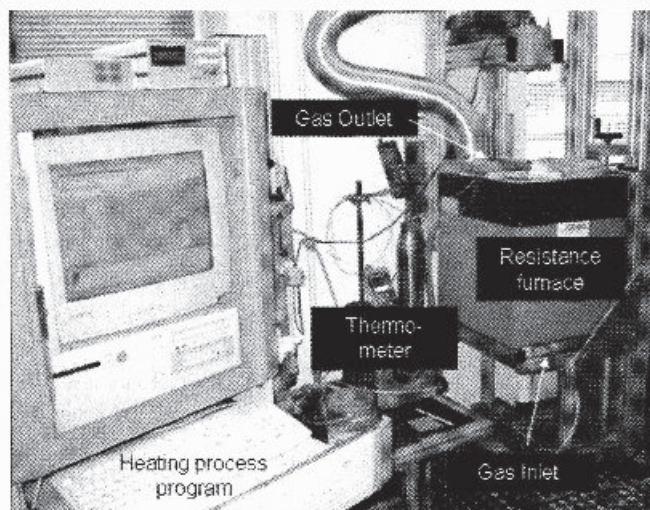
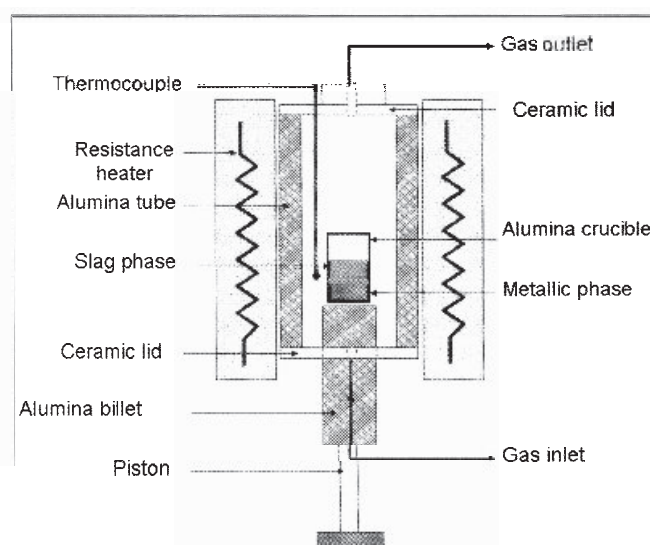


Fig. 5: Equipment used for metal slag equilibria experiments

Fig. 6: MoSi<sub>2</sub>-resistance furnace used for metal/slag equilibria measurements of the Fe-Mn alloys

controlled to maintain 1470 °C for 6 hours, it took approx. 2 hours to reach thermal equilibrium. Subsequently the heating power was turn off and the furnace was cooled down for 2 hours to reach room temperature. The crucibles were taken out, weighted together with the contained metal/slag-phases and finally manually broken. The metallic and slag phases were carefully separated, weighted individually and analyzed (metal on Mn and Fe by atomic absorption, slag on Mn, Ca, Al, Si and Mg by ICP-spectrometer).

## 4 Results

The weights of metal and slag as well as their manganese contents are listed in Table 4. In order to assess the results a distribution coefficient, e.g. the ratio between the final manganese content in the slag (weight-%) and the final manganese content (weight-%) in the Fe-Mn alloy was used and for the present work it is expressed as:

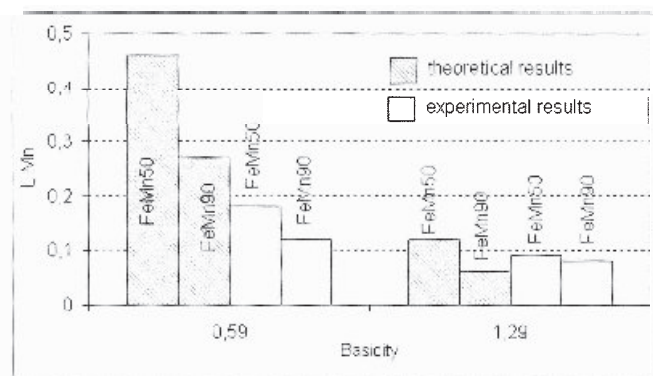
$$L_{Mn} = [Mn]_{Slag} / [Mn]_{Metal} \quad (3)$$

Tab. 4: Metal/slag weight and manganese content after equilibria experiments.

Heat Nr.	FeMn-alloy	Slag-series	Final metal weight [g]	Final slag weight [g]	[Mn] <sub>Metal</sub> [%]	[Mn] <sub>Slag</sub> [%]
1	FeMn50	I	177.5	75.8	47.4	10.1
2	FeMn90		175.0	79.3	84.0	14.5
3	FeMn50		173.7	89.6	44.6	15.2
4	FeMn90		167.7	92.8	81.0	17.5
5	FeMn50	II	179.6	82.0	45.9	10.0
6	FeMn90		181.4	84.5	88.3	7.7
7	FeMn50		174.5	79.9	46.1	9.6
8	FeMn90		177.1	83.4	85.0	8.2
9	FeMn50	III	172.9	79.5	47.2	10.1
10	FeMn90		183.7	88.4	87.5	8.3
11	FeMn50		171.9	81.3	44.4	10.2
12	FeMn90		180.1	87.2	86.2	7.4
13	FeMn50	IV	183.8	92.5	46.5	8.5
14	FeMn90		178.3	89.8	82.0	9.8
15	FeMn50		189.1	103.0	45.7	9.8
16	FeMn90		167.2	104.9	87.1	4.3
17	FeMn50	V	163.8	90.1	40.9	16.6
18	FeMn90		167.3	112.2	88.8	11.3
19	FeMn50		176.1	75.9	48.5	4.7
20	FeMn90		188.7	84.9	88.6	6.0
21	FeMn50	VI	167.5	71.1	47.6	4.7
22	FeMn90		182.0	83.4	89.8	6.4
23	FeMn50		157.2	75.6	46.8	8.5
24	FeMn90		183.8	84.9	88.4	6.1
25	FeMn50	VII	185.5	83.7	47.0	5.2
26	FeMn90		182.3	83.5	88.2	4.2
27	FeMn50		180.2	81.5	47.4	2.7
28	FeMn90		183.0	96.5	88.1	3.1
29	FeMn50	VIII	178.6	80.8	47.6	12.6
30	FeMn90		180.2	88.2	88.5	8.3
31	FeMn50		182.9	74.6	49.8	2.8
32	FeMn90		178.2	82.3	89.1	2.5

#### 4.1 Metal-Slag equilibria in the CaO-SiO<sub>2</sub>-system

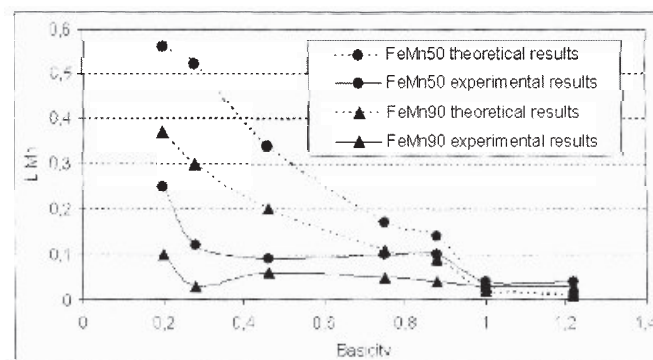
The manganese distribution ratio according to (3) decreases with increasing slag basicity, as shown Figure 7. This is in good agreement with the results of BARCZA [5] as well as of DING & ERIC [10], who showed that the manganese content

Fig. 7: Effect of the basicity on the  $L_{Mn}$  (Mn concentration ratio slag/metal) at 1470 °C, Ar-atmosphere for the CaO-SiO<sub>2</sub> slag-series

in the Fe-Mn-alloy can be attributed to the direct influence of basicity on the activity coefficients of manganese. At a basicity value of 0.59,  $L_{Mn}$  is about 0.18 for the FeMn50-alloy and 0.12 for the FeMn90-alloy, rising the basicity to 1.29  $L_{Mn}$  decreases for FeMn50 to 0.09 and for FeMn90 to 0.08. The theoretical- and experimental-tendencies of the coefficient distribution values showed the same sinking behavior as the basicity value of the initial slag rises for the two tested alloys.

#### 4.2 Metal-Slag equilibria in the CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-system

Figure 8 illustrates the experimental and theoretical  $L_{Mn}$ -values obtained for the system CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>. Theoretically  $L_{Mn}$  decreases continuously from basicity values of 0.2 to 0.9 for both Fe-Mn-compositions, followed by a significant drop with the result of more than 85 % Mn in metal. The figure also demonstrates a reasonable accordance between theoretical prognosis and experimental results. They can be divided into three regions. Decreasing

Fig. 8: Effect of the basicity on the distribution coefficient  $L_{Mn}$  at 1470 °C, Ar-atmosphere for the CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-series

values are found at low basicity values (from 0.2 to 0.46), but between 0.75 and 1 constant values were measured. In a third region at high basicities ( $B > 1$ ) theoretically and experimentally the lowest values with similar results were obtained. The addition of alumina partially replacing the initial content of silica results in a considerable decrease of  $L_{Mn}$ , which means that alumina in the given slag system acts as more basic component than silica does from the standpoint of the Mn-distribution. However experimentally was found that more than 18.7 wt.-% alumina in the initial slag system promotes the presence of metallic drops in the slag at the end of the heating process. Generally the achieved  $L_{Mn}$ -values for FeMn50 were again higher than for FeMn90. A slight improvement can be detected while changing from the CaO-SiO<sub>2</sub> to the CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> slag system.

#### 4.3 Metal-Slag equilibria in the CaO-SiO<sub>2</sub>-MgO-system

In slag series III (CaO-SiO<sub>2</sub>-MgO) the initial basicity was kept constant at 1.14 and the MgO/CaO-ratio were varied. The results are presented in Figure 9. For all tested slags it was experimentally possible to achieve an  $L_{Mn}$ -value lower than 0.1 after a running time of 6 hours, the theoretical results obtained by FACT forecasted higher values of



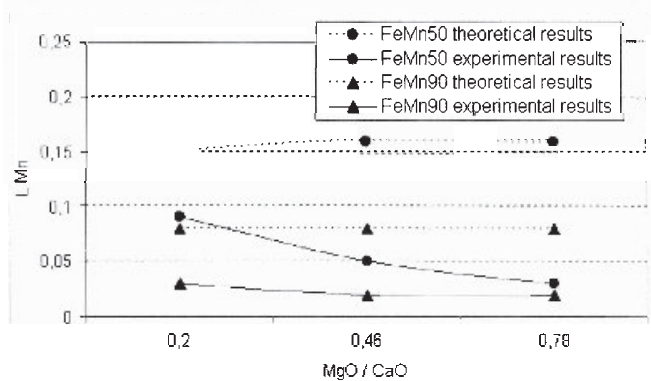


Fig. 9: Effect of the MgO/CaO-ratio on the manganese distribution coefficient at 1470 °C, Ar-atmosphere for the CaO-SiO<sub>2</sub>-MgO-series

$L_{Mn}$  for FeMn50 than for FeMn90, always lower than 0.2. Experimentally and theoretically no significant effect by improving the MgO/CaO-ratio was found for FeMn90, and  $L_{Mn}$ -values could be reached less than 0.03. FeMn50 shows a different picture:  $L_{Mn}$  decreases experimentally from 0.09 to approximately 0.03, as the ratio of MgO/CaO increases, theoretically a small increase was expected.

A partial replacement of CaO by MgO seems to be helpful to increase the manganese content in the Fe-Mn alloy, as shown Figure 10. This was already explained by CHANON & SEE [11] and WOLLACOTT et al. [12]. The cations Ca<sup>2+</sup>, Mg<sup>2+</sup> become associated with the larger ionic groups of SiO<sub>2</sub>, are resulting in very few free O<sup>2-</sup> anions. MnO therefore has a reduced activity coefficient. As the content of basic oxides is increased, the SiO<sub>2</sub>-network is broken down into smaller anionic groups and more free O<sup>2-</sup> ions become present. The role of these two basic oxides in breaking up the silicate network is even more important when secondary SiO<sub>2</sub> is formed as a product of the reaction. The molecular weight of MgO is lower than that of CaO, and there is an overall increase in the wt.-% of the basic oxides. On the other hand only few quantities of MgO are necessary to increase the liquidus temperature of the slag, and the CaO/MgO-ratio should not be less than three for the tested slag to maintain a sufficient low viscosity.

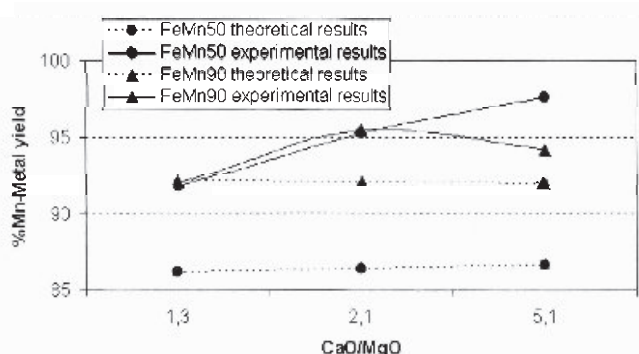


Fig. 10: Effect of the ratio CaO/MgO on the manganese metal yield at 1470 °C, Ar-atmosphere for the CaO-SiO<sub>2</sub>-MgO-series

#### 4.3 Metal-Slag equilibria in the CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-MgO-system

Slag series IV was designed on the basis of the best results obtained from the previous tests, the MgO addition was

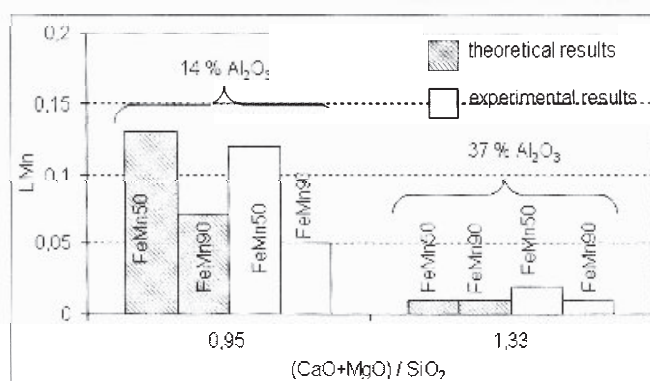


Fig. 11: Effect of the basicity on the Mn-distribution coefficient  $L_{Mn}$  at 1470 °C, Ar-atmosphere, CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>-MgO slag

fixed to 3 %. Two experiments were conducted at a basicity of 0.95 with 37.7 wt.-% SiO<sub>2</sub> and 14.0 wt.-% Al<sub>2</sub>O<sub>3</sub>, a second set was run at a basicity of 1.33 with 6.0 wt.-% SiO<sub>2</sub> and a Al<sub>2</sub>O<sub>3</sub>-content of about 37.0 wt.-%. The results are shown in Figure 11. At an initial basicity of 0.95, the experimental and theoretical  $L_{Mn}$ -values were below 0.15, the values of  $L_{Mn}$  for FeMn50 about two times higher than those for the FeMn90-alloy. Significant better distribution coefficients lower than 0.013 were achieved at a basicity value of 1.33. The benefit of a high basicity as well as of a relative high Al<sub>2</sub>O<sub>3</sub>-content to recover as much manganese in the alloy as possible can again be seen. However, at high Al<sub>2</sub>O<sub>3</sub>-contents, experimentally was observed a considerable amount of metallic drops in the slag for both tested alloys. The theoretical and experimental-results showed a good agreement for both alloys.

## 5 Summarizing assessment and conclusions

On the basis of standard slags used in ferromanganese production, four "low temperature" slags series were tested to optimize the Mn-recovery yield in spent primary batteries recycling, e.g. to minimize the manganese loss in the slag. The slag/metal equilibria were investigated with two possible Fe-Mn alloys expectable from a SAF process. The experimentally determined distribution coefficient-values ( $L_{Mn}$ ) for both alloys are shown in Figure 12. The range from 0.01 up to 0.25 indicate that the initial slag system has a strongly influence in the final manganese content of the alloys.

As elevated contents of CaO and MgO improve the Mn-yield, but have a negative impact on the liquidus temperature of the slags, a basicity window of 0.95 to maximum 1.33 is recommended with max. 3 wt.-% of MgO in the initial slag.

The partial replacement of SiO<sub>2</sub> by Al<sub>2</sub>O<sub>3</sub> could significantly reduce  $L_{Mn}$  at the given (CaO+MgO)/(SiO<sub>2</sub>+Al<sub>2</sub>O<sub>3</sub>) ratio. Al<sub>2</sub>O<sub>3</sub>-contents between 14.0 and 18.7 wt.-% in the initial slag is recommended and also help to avoid metallic drops in the slag at the end of the process. On the other hand high SiO<sub>2</sub>-contents in the slag promote the binding of manganese in the slag as oxide. The effectiveness to avoid the presence of manganese in the slag was found in the following sinking order: CaO, MgO, Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub>.

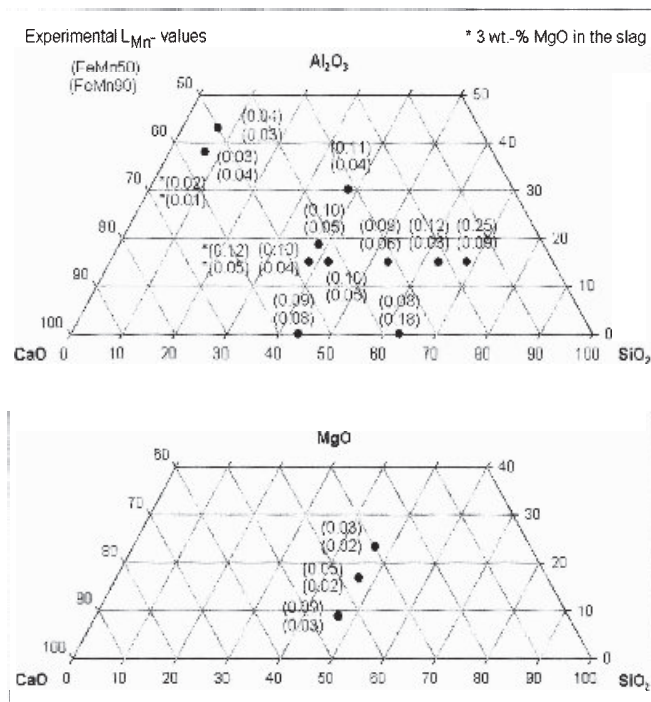


Fig. 12: Experimentally determined  $L_{Mn}$ -values for FeMn50 and FeMn90, 1470 °C, and Ar-atmosphere.

The results from equilibria calculation show good or reasonable accordance. To achieve a better agreement between theoretical and experimental results, the experimental time must be probably longer than six hours and all ternary systems in the FACT-database must be optimized. Better agreements generally were found for slags with basicity higher than 0.80. According to the obtained results the following slags systems are judged to be suitable and will be intensive tested in a laboratory-scale DC-SAF process to fix the operation parameters for pilot-recycling tests of spent primary batteries in Aachen.

- Slag 1: 56.3 % CaO and 43.7 % SiO<sub>2</sub>  
Slag 2: 46.7 % CaO, 38.3 SiO<sub>2</sub> and 14.7 % Al<sub>2</sub>O<sub>3</sub>
- Slag 3: 45.7 % CaO, 37.3 SiO<sub>2</sub>, 14% Al<sub>2</sub>O<sub>3</sub> and 3 % MgO

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#### Literature

- [1] Manganese International Institute. (2006): Homepage.
- [2] ROMBACH, E., FRIEDRICH, B. & BERGER, M. (2006): Efficiency of the reprocessing of primary batteries. Intern. Conference of Battery Recycling ICBR 2006, Interlaken, Swiss.
- [3] MUTH, B. (1996): Daten und Fakten zum Umweltschutz: pp. 18-19; Springer.
- [4] TENORIO, J. OLIVEIRA, D.C. & CHAVES, A.P. (1999): Carbon-zinc batteries treatment by ore processing methods. Proc. of the Global Symposium on Recycling Waste Treatment and Clean Technology (REWAS'99): Vol. II, pp. 1153-1160; TMS.
- [5] BARCZA, N.A. (1979): Slag-metal equilibrium in the production of low-carbon ferromanganese. – Journal of South African Institute of Mining and Metallurgy: 269-280.
- [6] BALE, C.W. & PELTON, A.D. (1990): The Unified Interaction Parameter Formalism: Thermodynamic Consistency and Applications. – Metall. Trans. Act., 21A: 1997.
- [7] LUPIS, C.P. & ELLIOTT, J.F. (1966): Generalized Interaction Coefficients: Part I: Definitions. – Acta Metall., 14: 529-538.
- [8] PELTON, A.D. & BALE, C.W. (1986): A Modified Interaction Parameter Formalism for Non-Dilute Solutions. – Metal. Trans. Act., 17A: 1211-1215.
- [9] ERIKSSON, G. et al. (1994): Critical Evaluation and Optimization of the Thermodynamic Properties and Phase Diagrams of the MnO-S. – Can. Metall. Q., 33: 13-21.
- [10] DING, K. & ERIC, R.H. (2004): The Thermodynamic Activity of MnO in Stainless steel Type Slags. VII International Conference on Molten Slags Fluxes and Salts: pp. 25-29. The South African Institute of Mining and Metallurgy.
- [11] CHANNON, B.P. & SEE, J.B. (1977): The Reduction of Fluxed and Non-fluxed Manganese Ores by Ferromanganese Silicide. – J. S. Afr. Inst. Min. Metall., 77, 8: 151-162.
- [12] WOLLACOT, L.C., JOCHENS, P.R. & HOWAT, D.D. (1975): The Viscosities and Electrical Conductivities of Slag Associated with the Production of High-carbon Ferromanganese Alloys. Proc. Infacon 74, Johannesburg: pp. 227-232; The South African Institute of Mining and Metallurgy.

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