Recycling Efficiency
of the reprocessing of primary batteries

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1 Introduction

In the New Battery Directive for the European recyclers (draft 11/2003; adoption summer 2006) battery recycling has for the first time been concretised in data. Apart from the requirement, portable batteries and accumulators strengthens to collect (defined Collection Rates) and to intensify material recycling, in article 19 minimum treatment quotas are defined (Recycling Efficiencies). For primary battery systems (zinc-carbon/alkaline-manganese) recycling processes shall recover at least 55 % by average of the battery scrap weight.

Since to date this expected legal threshold was not explicitly defined yet, numerous interpretation possibilities or points of reference for an appropriate computation methodology are offered. In order to provide a strong basis for a constructional suggestion on a methodology, a detailed characterisation of the relevant input-mix is given and comprehensive mass balances are calculated. Based on these calculations, different values for theoretically possible Recycling Potentials (RP) and technically feasible Recycling Efficiencies (RE) are indicated and compared with the targets discussed at present.

2 Characterisation and Recycling Potential (RP) of primary batteries

Against the background of an efficient and thus optimized material recycling, an exact characterisation of the regarded input - as individual material group and/or as representative material mixture - becomes increasingly important.

Depending upon production type and kind of cell, the chemical composition of primary battery systems certain ranges, shown in table 2-1. The main components are zinc, manganese dioxide, iron and electrolytes. Together these constituents build up 70 % (Zn-C) respectively 90 % (Alkaline) of the batteries weight. The content of valuable metals (Fe, Mn, Zn) amount to 60 % (Zn-C) respectively up to 70 % (Alkaline).

Table 2-1: Components of unused primary batteries [1], [2]

component	concentration range [%]	
	zinc-carbon	alkaline-manganese
MnO_2	22 – 34	17 – 38
Zn	16.4 – 28.6	9.9 – 17.5
ZnO	0.3 – 0.4	<0.1 – 0.6
Fe	1 – 25	15 – 59
C	7 – 10.6	0 – 5
Sn	<0.1	n.v.
Cu	<0.2	1 - 3
Ni	n.v.	0 – 0.7
Hg	<0.04	0 – 0.8*1
organics, paper, bitumen	4 - 13	3 - 11
electrolyte	14 – 23 (NH_4Cl a./or $ZnCl_2$)	5 – 16 (KOH, ZnO)

* 1: prismatical and cylindrical cells: 0 % Hg; button cells: 0,6 - 0.8 % Hg

Spent primary batteries enter the metallurgical recycling cycle usually pre-sorted as so-called "market mixtures" (at present approx. 60 % Alkaline and 40 % Zn-C) [3-11]. Different compositions published of such raw material mixtures are shown in table 2-2.

Table 2-2: Components of typical raw material mixtures from primary battery scrap

component	contents of data [%]					average values [%]
	Lit. [9]	**Lit.** [5]	**Lit.** [10]	**Lit.** [8]	**Lit.** [11]	
MnO_x	28.59	(30.62)*1	30.6	(31.64)*1	(31.78)*1	30.6
Mn	(18.07)*1	19.36	(19.34)*1	20	20.09	(19.4)
Zn	12.01	16.72	19.8	20	16.63	18.4*2
$ZnCl_2$	(2.52=1.21 Zn)	(0.32=0.15 Zn)				
ZnO	(6.60=5.30 Zn)					
Fe	16.25	21.62	18.6	15	22.51	18.8
FeO	0.18					0.2
C	9.27	5.91	5.6	10	5.36	7.2
SiO_2	1.43					1.4
CaO	0.74					0.7
Pb	0.08	0.02			0.02	<0.1
Cu	1.05		0.8		0.62	0.8
Ni	0.02	0.32	0.4		0.37	0.3
organics	4.14	3.00	2.5			3.2
paper		0.87	3.9 *3			2.4
bitumen		0.44	1.4			0.9
oxygen(oxides)	(12.84)*4	13.98	(11.27)*4	(11.65)*4	15.01	13.0
moisture(H_2O)	11.50	11.00	9.6		10.77	12.3
electrolyte			6.2			

* 1: calc. via MnO_2; * 2: incl. Zn from $ZnCl_2$ a. ZnO; * 3: acc. 3.3 % C; * 4: calc. via oxide content

The calculated average values for (dry) raw material mixtures add themselves to approx. 100 % (considering oxygen as metal-oxides). Thus it can be assumed, that the percentage composition of the regarded mixtures was recorded as completely as possible. Considering evaporated water having no harm to the environment, the content of the valuable main metals (Fe, Mn, Zn) can generally be called *theoretical (metallurgical) Recycling Potential (RP)*. The following calculations for "market mixtures" lead to RP´s between 57 and 62 % of the (dry) battery weight:

➔ calculation basis: "market mixture" (60 % Alkaline + 40 % Zn-C) acc. to given data for unused batteries (cf. Tab. 2-1):

$$0{,}6 * [17{,}4\,\%\,\mathrm{Mn} + 13{,}7\,\%\,\mathrm{Zn} + (0{,}3 * {}^{65,4}/_{81,4})\,\%\,\mathrm{Zn} + 37{,}0\,\%\,\mathrm{Fe}]$$

$$+\ 0{,}4 * [17{,}7\,\%\,\mathrm{Mn} + 22{,}5\,\%\,\mathrm{Zn} + (0{,}35 * {}^{65,4}/_{81,4})\,\%\,\mathrm{Zn} + 13{,}0\,\%\,\mathrm{Fe}]$$

$$=\ 0{,}6 * [17{,}4\,\%\,\mathrm{Mn} + 13{,}9\,\%\,\mathrm{Zn} + 37{,}0\,\%\,\mathrm{Fe}] + 0{,}4 * [17{,}7\,\%\,\mathrm{Mn} + 22{,}8\,\%\,\mathrm{Zn} + 13{,}0\,\%\,\mathrm{Fe}]$$

$$= 0{,}6 * 68{,}3\,\%\,(\mathrm{Mn, Zn, Fe}) + 0{,}4 * 53{,}5\,(\mathrm{Mn, Zn, Fe})$$

$$= 17{,}5\,\%\,\mathrm{Mn} + 17{,}5\,\%\,\mathrm{Zn} + 27{,}4\,\%\,\mathrm{Fe} = \underline{62{,}4\,\%\,(\mathrm{Mn, Zn, Fe})}$$

➔ calculation basis: typical raw material mixtures from primary battery scrap (cf. Tab. 2-2):

$$19{,}4\,\%\,\mathrm{Mn} + 18{,}4\,\%\,\mathrm{Zn} + 18{,}8\,\%\,\mathrm{Fe} = \underline{56{,}6\,\%\,(\mathrm{Mn, Zn, Fe})}$$

For pure alkaline systems the calculated RP with approx. 68 % definitely outranges that of the pure Zinc-C systems (approx. 54 %). At the current trend - increasing proportion of alkaline batteries in the market mixtures - this will become relevant in the future. Depending on the kind of the respective mixture and the selected reference point of the battery weight, the RP even ranges between 47 and 79 % (tab. 2-3). Considering that within technical processes metal losses are unavoidable, difficulties in realizing the EU-required Recycling Efficiency of at least 55 % become easy obvious. This concerns in particular Zn-C batteries.

Table 2-3: Theoretical (metallurgical) Recycling Potential (RP) and C-content of mixed primary battery systems

reference point:	100 % Zn-C		40 % Zn-C + 60 % Alkaline*		100 % Alkaline	
battery weight incl.	RP [%]	C [%]	RP [%]	C [%]	RP [%]	C [%]
12 % moisture 13 % oxygen (oxides)	47	8	50 – 55	4 – 6	60	2
0 % moisture 13 % oxygen (oxides)	54	9	57 – 62	5 – 7	68	3
12 % moisture 0 % oxygen (oxides)	54	9	57 – 63	5 – 7	69	3
0 % moisture 0 % oxygen (oxides)	61	10	65 – 71	6 – 8	79	3

*: "market mixture"

Additionally, the carbon content can be considered. Depending on the recycling process it can be interpreted as efficiency-relevant as well (substitute for C-containing reducing agents or component in FeMn-master alloy). All other remaining components of the primary batteries cannot be recovered by (metallurgical) recycling processes in efficiency-relevant amounts.

3 Computation methodology of the Recycling Efficiency (RE)

The Recycling Efficiency (RE) represents the result of material flow calculations and thus from mass balances whose system boundaries must be carefully defined. It cannot only be seen against the background of single process units and their optimisation. As an evaluation base it must facilitate also an objective comparison of different recycling technologies. A strong basis for a computation methodology of the RE rather implies a sufficient *comparability of the balancing systems concerned*. This should ensure, that within the recycling processes similar by-products are produced from comparable raw materials. For limiting the calculation effort of this required system expansion, the efficiency-relevant elements and material flows must be identified and selected.

3.1 System scope

For mixed primary battery scrap, the system boundary has to be drawn so far, that the efficiency-relevant metals (Fe, Mn, Zn) can be tracked up to a level at which they represent a *replacable marketable metal product* (crude steel, Ferromanganese, high manganese steel, super high grade Zinc) with the corresponding metallic and non-metallic by-products (other metals, metal-containing residues and concentrates, slag). Therefore the system scope of recycling alternatives for primary batteries should include the production of steel and zinc. Depending on the economic/ecological objectives of the recycling way ("iron route", "zinc route"), the necessary step-by-step modules can be linked differently.

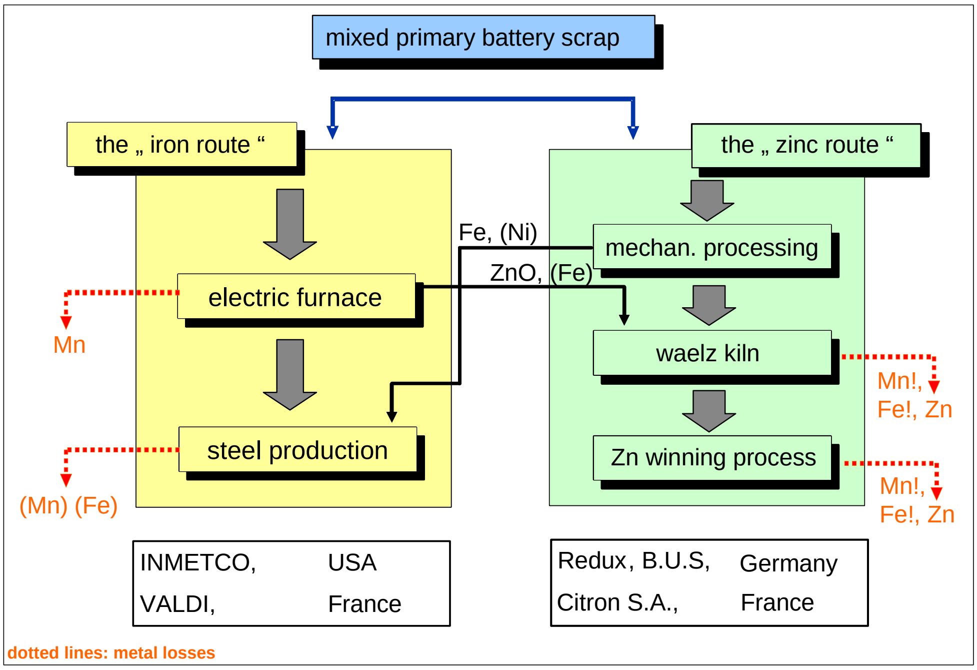

Figure 3-1: System scope of todays recycling alternatives for primary batteries

3.2 System description

In order to determine *technically feasible Recycling Efficiencies* and the *influence of material qualities* as well, the following process alternatives are considered (fig. 3-2):

- ➢ conventional mechanical processing/waelz kiln [module 1 - 4], representing the best available techniques (BAT) of the „zinc route“;
- ➢ virtual extended mechanical processing/waelz kiln [module 1 - 5], improving environmental protection concerning the quality of the produced waelz slag;
- ➢ direct SAF (IME-research project) [module 6, 4], to improve environmental protection concerning the quality of the produced slag in connection with an efficiency increase for Mn and Zn (possible representative of an optimized „zinc-iron route“ in the future).

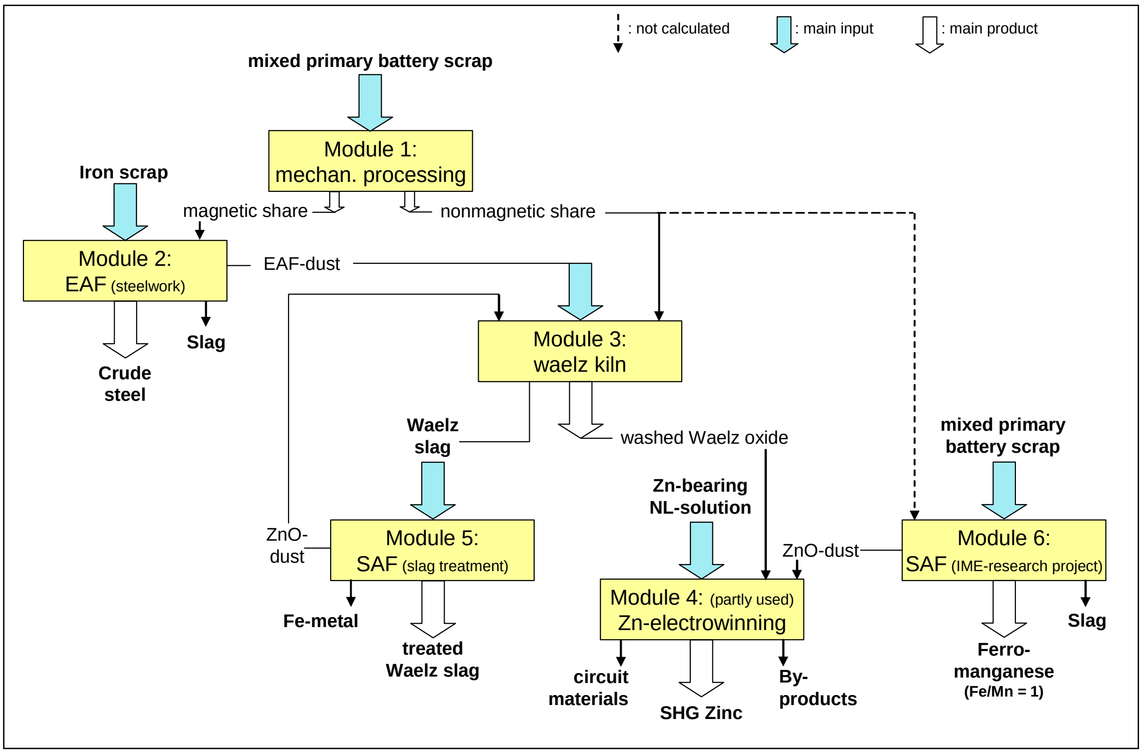

Figure 3-2: Simplified process module flow sheet for the calculated recycling alternatives

For a precise balancing, a brief description respectively definition of the single modules is essential, particularly when only parts of a process are necessary for the recycling of integrated intermediate products (e.g. waelz oxide into Zn-electrowinning):

- module 1: mechanical processing

Pre-sorted Zn-C/Alkaline batteries are firstly shredded in a cutting mill and subsequently magnetically separated into an *iron and a non-magnetic share* rich in zinc. The carbon content of the primary battery scrap is recovered along with the non-magnetic share. Exemplary Redux Dietzenbach (Germany) operates such a completely enclosed equipment.

- module 2: EAF (steelwork)

The *magnetic iron share* is integrated in common steelworks. Together with iron scrap it is melted to *crude steel* in an electric arc furnace (EAF) by adding fluxes under reducing conditions. The resulting *slag* is used in road construction. Arising flue dusts rich in zinc and lead (*EAF-dust*) are generally processed in waelz kilns followed by Zn-electrowinning in order to recover zinc.

- module 3: waelz kiln

The *non-magnetic share* is integrated in common waelz kilns - the world-wide predominant process for the Zn/Pb-enrichment of EAF-dust from steelworks. To feed this large-scale rotary furnace, a homogenous mix of EAF-dust, various zinc-containing residues, coke and fluxes is prepared mostly in form of pellets with an almost constant composition. The main-product of this process is a filter-dust upgraded in volatile metal(-compound)s of zinc and lead (*waelz oxide*), separated in a downstream offgas system. After leaching the alkaline components in a 2-stage countercurrent wash, the waelz oxide can directly feed electrolytic zinc plants. The by-product *waelz slag* contains all non-volatile components as well as the fluxes added. Up to now *waelz slag* is still used for landfill site stabilisation and for road construction.

- module 4: Zn-electrowinning (only partly used)

Most of the EU producing *SHG zinc* facilities use the electrowinning process - a multistage pyro-/hydrometallurgical concept for zinc concentrates with increasing integration of secondary raw materials (e.g. *waelz oxide*). While concentrates pass all process steps - roasting with sulphuric acid plant, (neutral)leaching, leach purification, electrolysis, melting and casting - the feeding of secondary raw materials usually occurs only after a (separate) leaching step. On this account, for the primary battery recycling only sections of this process are to be considered.

- module 5: SAF (slag treatment) [virtual]

The objective of this downstream operation consists in producing an inert and dense slag in a submerged arc furnace (SAF) to meet enforced environmental requirements to be expected for the future. At present the quality of some conventional waelz slags is controversially discussed due to the risk of only partly molten, water-soluble components. In addition to the *treated waelz slag*, an iron-rich metal phase (*Fe-metal*) and a filter dust rich in zinc-oxide (*ZnO-dust*) as by-products will arise only in small amounts. The latter is recirculated in the waelz kiln.

- module 6: SAF (IME-research project)

The objective of this direct mode of operation consists in the production of an inert *slag* in connection with an improvement of the recycling yield from spent primary batteries. Through carbothermic reduction together with addition of fluxes, *Ferromanganese* ($Fe/Mn \leq 1$) and zinc-oxide dust (*ZnO-dust*) - suitable to be treated directly in the usual Zn-electrowinning - should be produced in a single step process. The feasibility of producing a high grade *Ferromanganese* of mixed primary battery scrap in a SAF has already been carried out [12, 13]. In order to achieve this, a (partial) integration of the (zinc rich) non-magnetic share at the mechanical processing step is intended, but not considered in this calculation. Although the tests were conducted without a liquid metal spray condenser, this principle seems to be the most effective way to recover zinc, because it reaches fastly the metallic stage. But preliminary results in a comparable process unit for the treatment of EAF-dust showed strong challenges to operate such a unit [14].

3.3 Boundary conditions of the calculations

The calculations of all mass balances are based on available data from industry, literature and own investigations. In order to limit the necessary calculation effort, an *element-referred cut-off criterion of 1 %* was defined. Thus for (chemical) contents of ≤1 % the appropriate material flow is not continued to pursue concerning this chemical element. This cut-off criterion was used also for dilution effects of particular elements by material integration in usual technical processes with strongly controlled homogenous input mixes.

Establishing a *total material balance conclusive in itself*, all mass flows were closed according to the method of the error square minimization. If necessary, data were adapted to ensure a 100% element yield for the calculated recycling process.

As primary battery mixture the following composition was selected:

% Fe	% Mn	% Zn	% C		**theor. (metallurgical) Recycling Potential** **[0 % moisture; 13 % Oxygen (Oxides)]**
20,4	18,7	18,6	7,5	⇒	RP = 57,7 %

The determination of technically realistic values of the Recycling Efficiency (RE) is based on the *specific recoveries of the efficiency-relevant elements* in each module. Due to following reasons the *carbon content of the spent primary batteries* was not considered for the calculation of the RE:

- The specific carbon-recovery in the selected process alternatives cannot be seen as a material based recycling but more as a partial chemical/energetic recovery. Whereas the energetic part is clearly excluded by the expected New Directive, the chemical part is still under discussion as a substitute for carbon containing reduction agents.
- Up to now no information is available on the degree of carbon utilization within the relevant process modules (Waelz kiln, Direct SAF). This is of particular interest because on the one hand the waelz slag contains less than 1 % remaining carbon. On the other hand using the carbon content of spent batteries within the Direct

SAF-process a very slow chemical reaction rate was already experienced at the IME.

- Due to the lack of process data, no carbon balance can be calculated for the (virtual) Direct SAF-process

4 Results of mass balance calculation

In the following evaluation only the oxygen weight of the input-mix is considered. As details are missing, how much oxygen is recovered as zinc oxide or product slag and how much is lost as waste gas, this effect has been fully neglected (worse case view).

4.1 Process modules of the recycling systems

The calculated *specific element recovery* values for the different modules are summarized in table 4-1. It has to be considered that the investigated efficiency-relevant elements are not necessarily the main elements of the corresponding single process step.

Table 4-1: Calculated average element recovery (η) of single modules of selected recycling possibilities for primary battery scrap

(main, by-, and intermediate) products	η_{Fe} [%]	η_{Mn} [%]	η_{Zn} [%]
module 1: mechanical processing			
Magnetic share	98	nr	nr
Non-magnetic share	nr	99	99
module 2: EAF (steelwork)			
Crude steel	97	nr	nr
Slag	2.5	nr	nr
EAF-dust	nr	nr	nr
module 3: Waelz kiln			
Washed waelz oxide	nr	4	95
Waelz slag	nr	96	5
module 4: Zn-electrowinning (only partly used)			
SHG zinc	nr	nr	98
By-products	nr	nr	nr
Circuit materials*	nr	nr	1.95
module 5: SAF (slag treatment) [virtual]			
Treated waelz slag	nr	90	4
Fe-metal	nr	2	nr
ZnO-dust	nr	8	95.5
module 6: SAF (IME- research project)			
Ferromanganese (Fe/Mn ≤ 1)	88.4	66	nr
Slag	11.5	15	nr
ZnO-dust	nr	19	100

*: due to the necessary consideration of process parts
nr: not relevant for overall mass balance (cut-off criteria ≤1 %)

4.2 Conventional mechanical processing/waelz kiln - process

Summing up all system relevant yields of the different elements it can be seen that the *main elements are clearly distributed to the three products crude steel (Fe), waelz slag (Mn), and SHG zinc (Zn) to a degree of more than 90 % each*. The occurring uncertainties of the mass balance result from dilution and distribution effects (remaining flows below the given cut-off criterion), material circuits (external: EAF-dust; internal: various materials from the Zn-electrowinning process), and rounding errors; they amount to 2.4 % (Fe), 2.8 % (Zn) and 5.0 % (Mn). (fig. 4-1)

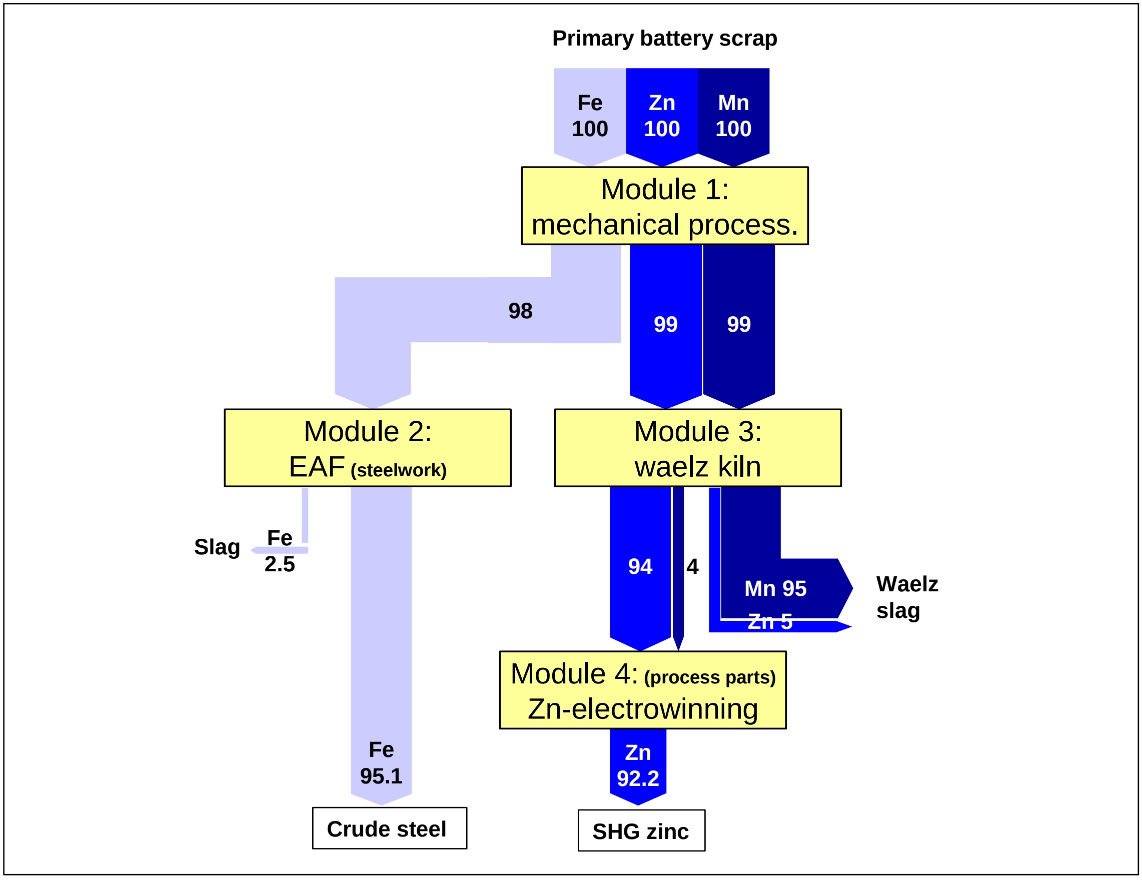

Figure 4-1: Calculated average metal recovery of the conventional mechanical processing/waelz kiln-process

The *overall recovery of the batteries metal content is close to 97 %*. This clearly underlines the high technological standard of the recycling process. On the other hand the related RE of about 56 % of the (dry) battery weight is even sufficient to fulfil the expected legal threshold. Furthermore it has to be assumed that the current practice of using the waelz slag as material for road construction and landfill site stabilisation will be seen more critical in future. Excluding this “by-product” from the calculation of the RE the technically feasible value will be reduced to 37 %. (tab. 4-2)

Table 4-2: Calculated Recycling Efficiency (RE) of the conventional mechanical processing/waelz kiln-process

Input / (main, by-)products	RE_{Fe} [%]	RE_{Mn} [%]	RE_{Zn} [%]
primary battery scrap ***➔ RP***	***20.4***	***18.7***	***18.6***
Crude steel	**19.4**	-	-
Slag (steelwork)	0.5	-	-
EAF-dust (steelwork)	<0.05	-	-
Waelz slag	-	**17.8**	0.9
SHG zinc	-	-	**17.1**
By-products	-	-	<0.05
Circuit materials*	-	-	<0.05
➔ RE **Σ**	**19.9**	**17.8**	**18.0**

theoretical (metallurgical) Recycling Potential: ***Σ_{RP} = 57.7 %***

Recycling Efficiency: - with utilization of slag: Σ_{RE} = 55.7 %

- without utilization of slag: Σ_{RE} = 37.0 %

*: due to the necessary consideration of process parts

Boundary conditions: dry battery weight with 13% oxygen (oxides)

4.3 Virtual extended mechanical processing/waelz kiln-process

In order to simplify the calculation of this study the necessary recirculation of the ZnO-dust from slag treatment is only considered for the first circuit. Under this assumption the *main elements are again clearly distributed to the three products crude steel (Fe), treated waelz slag (Mn), and SHG zinc (Zn) to a degree of 89 to more than 95 %*. The occurring uncertainties of the mass balance result from dilution and distribution effects (remaining flows below the given cut-off criterion), material circuits (external: EAF-dust, simplified recirculation of ZnO-dust; internal: various materials from the Zn-electrowinning process), and rounding errors; they amount to 2.4 % (Fe), 4.0 % (Zn) and 9.5 % (Mn). (fig. 4-2)

The *overall recovery of the batteries metal content is close to 95 %*. This shows again the high technological standard of the recycling process. Compared to the conventional process (mechanical processing/waelz kiln), the loss of valuable metals is marginally higher in this virtual process extension particularly due to dilution (Mn) and distribution (Zn) effects in the Zn-electrowinning. Nevertheless the proposed slag treatment process has to be judged from the viewpoint of an ecologically necessary quality improvement of the waelz slag rather than as a winning process of valuable materials. (tab. 4-3)

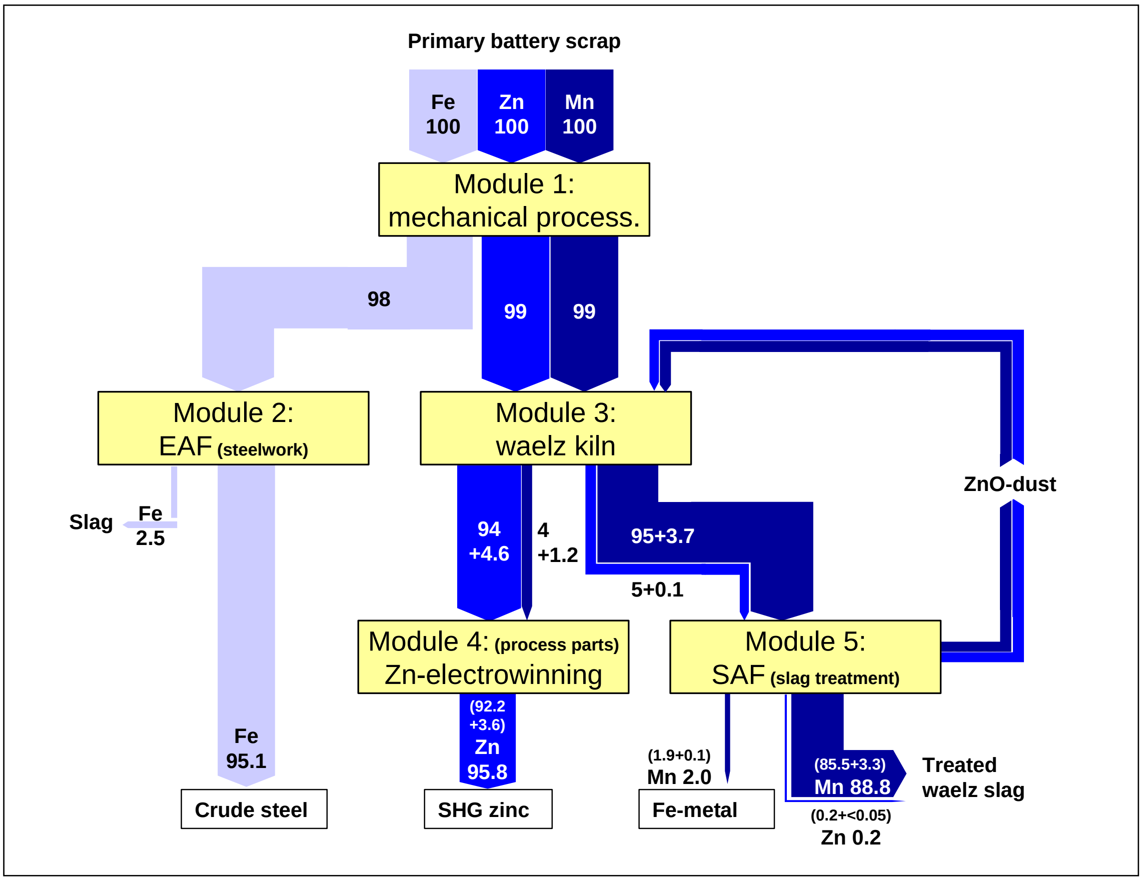

Figure 4-2: Calculated average metal recovery of the virtual extended mechanical processing/waelz kiln-process

Table 4-3: Calculated Recycling Efficiency of the virtual extended mechanical processing/waelz kiln-process

Input / (main, by-)products	**RE_{Fe} [%]**	**RE_{Mn} [%]**	**RE_{Zn} [%]**
primary battery scrap ➔ RP	***20.4***	***18.7***	***18.6***
Crude steel	**19.4**	-	-
Slag (steelwork)	0.5	-	-
EAF-dust (steelwork)	<0.05	-	-
Treated waelz slag	-	**16.6**	<0.05
Fe-metal (slag treatment)	-	**0.4**	<0.05
SHG zinc	-	-	**17.8**
By-products	-	-	<0.05
Circuit materials*	-	-	<0.05
➔ RE Σ	**19.9**	**17.0**	**17.8**

theoretical (metallurgical) Recycling Potential: ***Σ_{RP} = 57.7 %***

Recycling Efficiency: - with utilization of slag: Σ_{RE} = 54.7 %

- without utilization slag: Σ_{RE} = 38.1 %

*: due to the necessary consideration of process parts

Boundary conditions: dry battery weight with 13% oxygen (oxides)

Compared to the conventional process (mechanical processing/waelz kiln) without utilization of the disputable waelz slag, the RE could be increased from 37 % up to 55 % of the (dry) battery weight by waelz slag treatment in a submerged arc furnace. Here it has to be mentioned that the produced slag is nearly inert and therefore an ecologically noncritical by-product. Nevertheless nearly all of the manganese content of the primary battery scrap is lost from a metallurgical point of view. Under this aspect, only the iron and zinc content is actually recycled on a high qualitative level. In case of manganese a downcycling cannot be avoided.

4.4 Direct SAF-process (IME-research project)

Downcycling of metals has to be avoided or limited whenever possible not only under the ecological aspect of resource saving but also for economic reasons. Given that background this process alternative was included in the calculations, which is under current development at the IME at RWTH Aachen: The direct remelting of pre-sorted pyrolized (dry) primary battery scrap in an submerged arc furnace (SAF) [12, 13]. Under ideal conditions with this electro-metallurgical process, the expected environmental problems of the conventional waelz slag would be solvable – besides a meaningful recovery of the manganese content in a commercial FeMn-master alloy. Within a first estimating calculation the planned integration of the non-ferrous metal fraction from the mechanical processing (enhancing the Mn-concentration) to the SAF was kept out of consideration. (fig. 4-3)

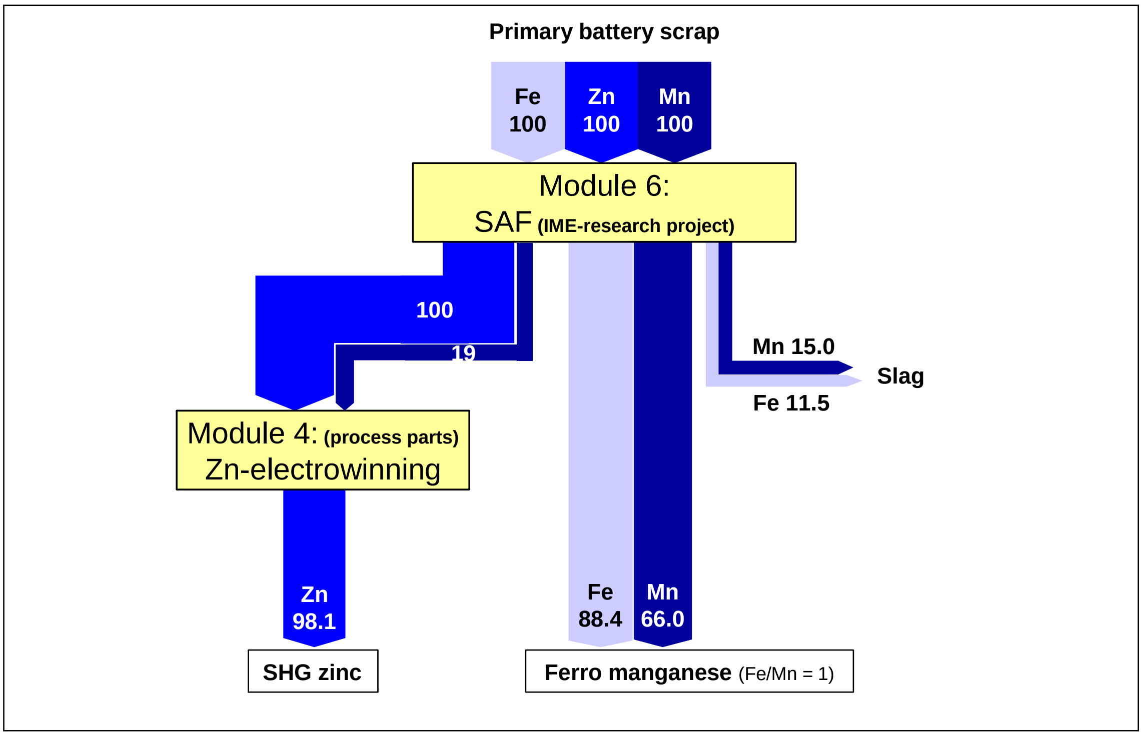

Figure 4-3: Calculated average metal recovery of the virtual Direct SAF-process (IME-research project)

The results in figure 4-3 show a clear distribution of the *main elements to the two products Ferromanganese and SHG zinc with 66 % (Mn) and 88 % (Fe), up to 98 % (Zn)*. The remaining iron content and a major fraction of the manganese content are collected in the inert slag by-product. The occurring uncertainties of the mass balance again result from above mentioned reasons. They amount to at 0.1 % (Fe), 1.95 % (Zn) and 19.0 % (Mn). Latter is particularly due to the dilution and distribution of the manganese content all over the material flows of the Zn-electrowinning.

By now the overall recovery of the main *metallic content are each above 95 % for iron and zinc and above 80 % for manganese*, which are won back in a high-grade quality. (tab. 4-4)

Table 4-4: Calculated Recycling Efficiency of the virtual Direct SAF-Process (IME-research project)

Input / (main, by-)products	**RE_{Fe} [%]**	**RE_{Mn} [%]**	**RE_{Zn} [%]**
primary battery scrap → RP	***20.4***	***18.7***	***18.6***
Ferromanganese (Fe/Mn ≤ 1)	**18.0**	**12.3**	-
Slag	2.3	2.8	-
SHG Zinc	-	-	**18.2**
By-products	-	-	<0.05
Circuit materials	-	-	<0.05
→ RE Σ	**20.3**	**15.1**	**18.2**
theoretical (metallurgical) Recycling Potential:		***Σ_{RP} = 57.7 %***	
Recycling Efficiency: - with utilization of slag:		Σ_{RE} = 53.6 %	
- without utilization slag:		Σ_{RE} = 48.5 %	

*: due to the necessary consideration of process parts

Boundary conditions: dry battery weight with 13% oxygen (oxides)

In contrast to the conventional process (mechanical processing/waelz kiln) without utilization of the waelz slag the RE related to the (dry) battery weight could be increased from 37 % to 54 % by direct remelting in a submerged arc furnace. Nevertheless, additional process improvements and specific investigations of the slag quality and their suitability for further utilization are still under development.

5 Summarizing assessment

By introducing regulations for the battery recycling in form of defined treatment quotas (Recycling Efficiency) a common basis is generated, which limits the possibilities of individual interpretation of the particular EU-Member States. The expected legal threshold of at least 55 % of the (relevant) primary battery weight clearly force recycling activities with optimised material yields. Due to the specific characteristics of primary batteries, their chemical composition and their high amounts of valuable metals (≈ 60 % Fe + Mn + Zn), the field of metallurgy is specifically challenged to meet this limit. Yet, an exact definition as well as a calculation basis for determining this limit value is still lacking.

As a possible input for the discussion on the methodology, in this paper selected process alternatives were balanced concerning the relevant mass flows in order to derive theoretically possible as well as technically realisable (metallurgical) RE´s. Depending on the calculation basis respectively on the reference point, the range and thus the scope for interpreting the results turn out to be rather large, as demonstrated in table 5-1.

Table 5-1: Technically realisable Recycling Efficiencies for primary battery scrap (“market mixtures”) based on Fe, Mn and Zn

reference point*: battery weight incl.	**convent. mechan. process./waelz kiln**	**extended mechan. process./waelz kiln**	**direct SAF (IME-research project)**
with utilization of the produced slags			
12 % moisture **13 % oxygen (oxides)**	49 %	48 %	47 %
0 % moisture **13 % oxygen (oxides)**	56 %	55 %	54 %
12 % moisture **0 % oxygen (oxides)**	56 %	55 %	54 %
0 % moisture **0 % oxygen (oxides)**	64 %	63 %	62 %
without utilization of the produced slags			
12 % moisture **13 % oxygen (oxides)**	33 %	34 %	43 %
0 % moisture **13 % oxygen (oxides)**	37 %	38 %	49 %
12 % moisture **0 % oxygen (oxides)**	37 %	39 %	49 %
0 % moisture **0 % oxygen (oxides)**	43 %	44 %	56 %

The carbon-content was not considered!

The numerous bases of calculation clearly demonstrate one fact: a limit value of at least 55 % for zinc-carbon/alkaline-manganese battery mixtures can today be met only with utilization of the produced slags (calculated without considering the contained carbon and oxygen content). If the reference point is defined “dry battery weight with 13 % oxygen (oxides)” already today mechanical processing/waelz kiln procedures - operating on a large-scale - can exceed RE of 56 %. The RE of the other recycling processes, corporate in the EU and not balanced in detail in this study, are likely to be above this calculated result. In this respect, the recommendations made here should be considered universal.

In order to reduce the computation effort of each battery recycling company in the frame of a legal control of real RE values, weighted factors should be introduced. Such factors should base on above described mass balance calculations and represent the element-recovery-yield on each additionally necessary process module. In the strict sense only this allows a correct and so comparable statement of the *total RE* (of a completely process chain until marketable end-products) without being responsible for subsequent treatment steps.

From ecological-economic points of view also the material quality of the different process chains should be integrated in the recycling evaluation. For this purpose, tab. 7-2 gives an evaluation aid.

Table 5-2: Recycling Efficiency and material quality at the recycling of primary battery scrap ("market mixtures") based on Fe, Mn and Zn

reference point*: battery weight incl.	**convent. mechan. process./waelz kiln**	**extended mechan. process./waelz kiln**	**direct SAF (IME-research project)**
Recycling Efficiency,	56 %	55 %	54 %
therefrom:			
- as metal phase	37 %	38 %	49 %
- as slag phase	19 %	17 %	5 %
quality of slag	ecological critical, slightly to be eluted	ecological uncritical, inert	ecological uncritical, inert
necessary single process modules	4	5	2

*: reference point: dry battery weight with 13 % oxygen (oxides)

Summarizing the presented results of the RE-calculations, the following main statements can be given:

- Many alternative reference points theoretically exist to calculate the Recycling Efficiency (only metals, water content, oxygen and carbon).
- The correct (comparable) calculation of the RE shows high complexity as downstream modules have to be taken into account.
- If only metals and water are considered (reference point: "dry battery weight with 13 % oxygen"), theoretically pure Zn-C batteries can´t reach the legal threshold.
- If the by-product "slag" does not count as recycled material, the Direct SAF-process (still under development) may serve the requirements, as most of the elements are recovered in a metallic stage.

6 Literature

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