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Development of a recycling process for Li-ion batteries

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ABSTRACT

In cooperation with the industrial project partners ACCUREC Recycling and UVR-FIA a recycling process specially dedicated to portable Li-ion batteries was developed combining a mechanical pretreatment with hydro- and pyrometallurgical process steps. Therefore not only the recovery of cobalt but also the recovery of all other battery components, especially of lithium was of interest. Besides the characterization and evaluation of all generated metallic material fractions, the focus of the research work was the development of a pyrometallurgical process step in an electric arc furnace for the carbo-reductive melting of the fine fraction extracted from spent Li-ion batteries. This fine fraction mainly consists of the cobalt and lithium containing electrode material. Since a selective pyrometallurgical treatment of the fine fraction for producing a cobalt alloy has not been done before, the proof of feasibility was the main aim.

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1. Introduction

Within the last two decades the requirements for batteries as mobile energy sources have constantly increased and have become more and more complex. The trend towards improved mobility in the rapidly developing fields of portable computer, communication, video and audio technology has strongly pushed the development of batteries. As supplier of the communications technology industry the battery industry shows an annual double-digit growth rate [1]. At the beginning of the 1990s Li-ion batteries have been regarded as the most promising energy sources for mobile applications. This has been proven true today; for instance, Li-ion batteries have totally replaced NiCd batteries as well as NiMH batteries in mobile phones as they offer a lot of advantages compared to other rechargeable battery systems, such as high operating voltage, high specific energy and long life-time.

The widespread and constantly increasing use of Li-ion batteries also leads to an increased battery scrap generation (in both production as a well as end-of-life), which has to be recycled with regard to environmental and economical sustainability. Ideally a closed-loop recycling should allow for returning back the recycling products to the production of new batteries. Li-ion batteries contain high amounts of valuable metals, such as aluminium, iron, copper, lithium, cobalt, nickel and manganese. The most valuable metal is cobalt, which is contained in the battery electrode material. Hence the cobalt recovery has a strong influence on the economic efficiency of a suitable battery recycling process.

2. Current status of Li-ion battery recycling

2.1. Recycling potential

In 2006 the United States and Europe had the highest proportion, 28.4% respectively 27.2%, of the worldwide Li-ion battery consumption but their proportion of the worldwide Li-ion battery production was only 0.4% and 2.0%, respectively. More than 90% of Li-ion battery cells were produced in Japan, South Korea and China. With 40% Japan was the country with the highest Li-ion battery cell production [2].

Since the mid-1990s the usage of Li-ion batteries has strongly increased. Today's strong market position of Li-ion batteries is reflected by the sales figures. In 2008 more than 3 billion Li-ion battery cells were sold [3]. In the EU sales in 2007 were three and a half times higher than in 2002 (see Table 1). Nevertheless the absolute return flow of spent Li-ion batteries is still low and the collection rate in 2007 was only about 3%. On the one hand this is mainly caused by the long life-time of Li-ion batteries and on the other hand by the end-consumer behaviour, who usually dispose of spent batteries for recycling only after several years.

In Germany Li-ion batteries had a market share of more than 50% for the first time in 2008, but here the collection rate of approximately 9% is comparatively low (see Fig. 1). In spite of the currently low collection rates forecasts show that sales figures will continue

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Table 1
EU sales figures, return flows and collection rates of Li-ion batteries (2002–2007) (source: ACCUREC Recycling).

	2002	2003	2004	2005	2006	2007
Sales in tonnes	3771	4977	6712	8210	9138	13,181
Return in tonnes	17	54	170	175	418	354
Collection in %	0.5	1.1	2.5	2.1	4.6	2.7

to increase up to more than 30,000 tonnes in 2015 and the market share of Li-ion batteries will be far above 50%. As a consequence also a strong increase of the return flow can be expected. That means that suitable recycling processes have to be established, which have the capacities to process the upcoming recycling flow.

In 2006, the European Parliament and the EU Council of Ministers agreed on a compromise to revise the 1991 Battery Directive 91/157/EEC covering batteries and accumulators. Since 2008 the new Battery Directive 2006/66/EC prescribes the currently valid collecting targets and recycling efficiencies. It has been set that member states are obliged to reach a minimum collection rate for spent batteries and accumulators of 25% by 2012 and of 45% by 2016. Furthermore Li-ion battery recycling processes will be obliged to reach a minimum recycling efficiency of 50% by average weight [4–6].

According to the EU Battery Directive the recycling of batteries means the "processing of waste batteries and accumulators for generation of products that can be directly reused in battery production or in other applications or processes" [6]. The definition excludes the possibilities of disposal or energy recovery. Unfortunately a repair and reuse of spent batteries is impossible. Thus the only way of recycling is the recovery of value materials (not only metals).

At least one-third of the production costs for a portable Li-ion battery cell are related to the materials [2,8]. This is due to the fact that Li-ion battery cells contain high amounts of valuable metals which are present in metallic form as well as in the form of inorganic metallic compounds. Examples of metallic battery components are the casing, the electrode foils as well as electronic components. Examples of inorganic metallic components are the active cathode material and the conducting salts contained in the electrolyte. Today's recycling processes mainly aim at metal recovery but also organic battery components, such as the electrolyte and plastics, should be taken into consideration since the additional recovery of such components at least help to increase the total recycling efficiency.

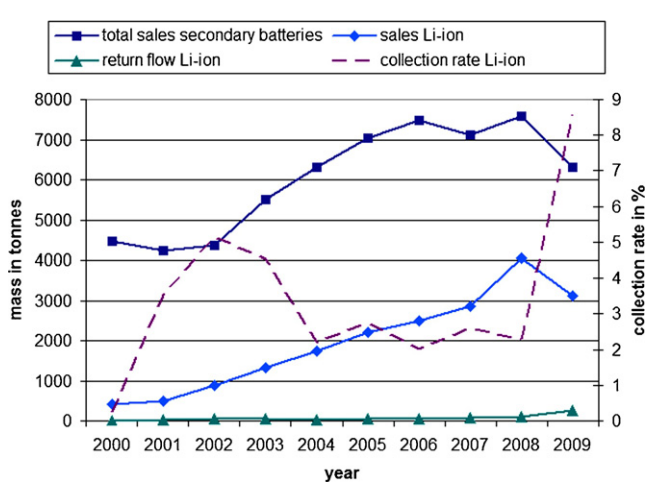

Fig. 1. Sales figures, return flows and collection rates of Li-ion batteries in Germany (2000–2009) [7].

Table 2
Average material content of portable Li-ion batteries.

Battery component	Product data sheets in mass-%	Self-determined
Casing	~20–25	~25
Cathode material ($LiCoO_2$)	~25–30	~25
Anode material (graphite)	~14–19	~17
Electrolyte	~10–15	~10
Copper electrode foil	~5–9	~8
Aluminium electrode foil	~5–7	~5
Separator	–	~4
Others	Balance	Balance

Since all battery producers sell their own specific types of Li-ion batteries it is difficult to specify exact numbers for the material content of a Li-ion battery scrap mixture. In order to give some numbers a study of various product data sheets from different battery producers has been done. Also, Li-ion batteries from a typical production scrap charge have been disassembled by hand and the battery components were separated and weighed. The results are listed in Table 2.

Based on the assumptions that the metal content (self-determined figures) can completely be recovered in metallic form and that the lithium content can completely be recovered in the form of lithium carbonate the monetary value of 1 tonne Li-ion battery scrap is approximately US$ 8500 taking current raw material prices into account. The monetary value of the cobalt content is already about US$ 7200.

2.2. Industrial recycling processes

Various battery recycling processes exist which can basically be divided into pyrometallurgical and hydrometallurgical processes. Some recycling processes combine pyro- and hydrometallurgical steps and often have integrated pre-treatment steps like pyrolysis or mechanical processing, i.e. crushing and material separation. Besides utilisation of specialised battery recycling processes the addition of spent batteries to existing large-scale processes, which are not dedicated to battery recycling (e.g. extractive cobalt or nickel metallurgy) is common practice and very often an economical advantage. Process examples for each category are given as follows.

The company Batrec mainly runs a mechanical processing plant for Li-ion battery cells. The batteries are crushed in CO_2 gas atmosphere. Thereby the volatile organic electrolyte evaporates and is collected as non-usable condensate. A subsequent material separation is done and the different material fractions are sold and represent feedstock materials in other processes [10–17].

Originally the hydrometallurgical Toxco process was developed for the safe recycling of spent lithium primary batteries. Today's facility processes lithium secondary battery scrap as well. The scrap is stored in earth covered concrete storage bunkers. Residual electrical energy is removed from larger and more reactive batteries. If necessary the batteries are treated by Toxco's patented cryogenic process, i.e. they are cooled to about −200 °C. Lithium, although normally explosively reactive at room temperature, behaves almost inert at this temperature. The batteries are then safely shredded and the materials are separated. Metals from the batteries are collected and sold. The lithium components are separated and converted to lithium carbonate for resale. If the batteries contain cobalt it is also recovered for production of $LiCoO_2$ as new battery electrode material [9,11,12,18–20].

The pyrometallurgical Inmetco process was developed for the recycling of spent NiCd, NiMH as well as Li-ion batteries. Thereby only a small amount of Li-ion battery scrap is charged into an electric arc furnace as secondary feedstock besides iron

containing material. The main aim is the recovery of cobalt, nickel and iron for the production of an iron-based alloy. Ignoble metals are slagged and organic materials as well as carbon are burned and used as reducing agents [11,12,21,22]. The Inmetco process is not a dedicated Li-ion battery recycling process, i.e. most of the battery components including the lithium contents are lost during the process.

Since 2001 cobalt and nickel containing battery scrap is added as secondary feedstock material in the extractive cobalt, nickel and copper process routes at Xstrata. Thus only the cobalt, nickel and copper contents of spent Li-ion batteries are of interest. All other battery materials are slagged or used as energy source and as reducing agents. The process includes pyrometallurgical as well as hydrometallurgical process steps [23–26]. Similar to the Inmetco process, the Xstrata process is also not dedicated to Li-ion batteries.

The Umicore VAL'EAS™ process represents a dedicated combined pyro- and hydrometallurgical battery recycling process for spent Li-ion and NiMH batteries. The battery scrap is directly melted down in a purpose-built shaft furnace without any kind of pre-treatment. Umicore is also a producer of cathode material for Li-ion batteries, i.e. the recycling process aims at a closed-loop recovery of cobalt and nickel in form of $LiCoO_2$ and $Ni(OH)_2$. Ignoble metals, such as aluminium and lithium, are lost whereas copper, iron and manganese are recovered in an aqueous solution. Organic materials as well as carbon are burned and used as reducing agents [27–31].

A big disadvantage of all pyrometallurgical recycling processes is the fact that lithium cannot be recovered. Thus a combination of pyro- and hydrometallurgical process steps is necessary as is the case for the Umicore process. However the Umicore process does not aim at the recovery of lithium which is the main disadvantage. Furthermore ignoble metals are slagged and organic materials as well as carbon are lost. Therefore an alternative competing recycling process based on pyro- and hydrometallurgical process steps should also consider an appropriate pre-treatment to recover as many battery components as possible. Especially the increasing use of Li-ion battery technology in (hybrid) electric vehicles and hence the strong growing future demand for lithium call for such recycling solutions.

3. Methods and materials

3.1. Aim, methodology and practical approach

The following research work was done within the joint research project "Recovery of raw materials from Li-ion batteries" with the reference number 01RW0404 funded by the German Federal Ministry of Education and Research. In cooperation with the industrial project partners ACCUREC Recycling GmbH (Mülheim a.d.R.) and UVR-FIA GmbH (Freiberg) a recycling process dedicated to portable Li-ion batteries has been developed combining a mechanical pre-treatment with hydro- and pyrometallurgical process steps to achieve a preferably high recycling efficiency. Therefore it is not only focused on the recovery of cobalt but also on the recovery of all other battery components, especially of lithium.

Besides the characterization and evaluation of all generated metallic material fractions, the main focus is the development of a pyrometallurgical process step in an electric arc furnace for the carbo-reductive melting of the fine fraction extracted from spent Li-ion batteries. This fine fraction mainly contains the cobalt and lithium containing electrode material. Since a selective pyrometallurgical treatment of the fine fraction for producing a cobalt alloy has not been tested before, the proof of feasibility is the main aim.

The processing in the electric arc furnace requires a process slag to keep cobalt losses at a minimum. With help of thermochemical modelling slag compositions are chosen with due consideration of the procedural demands and are evaluated in lab-scale trials (5 kg-scale). The suitability of the prioritized slag composition is finally verified in a 16-h melting campaign in technical-scale (200 kg-scale).

The recycling products of the pyrometallurgical process step are a cobalt alloy as well as lithium containing concentrates. The latter are further treated hydrometallurgically to produce a pure lithium carbonate. Other material fractions generated within the recycling process are an iron-nickel fraction, an aluminium fraction as well as a fraction which contains the aluminium and the copper electrode foils.

By means of a critical mass balance the recycling efficiency is calculated, which has to comply with the legal minimum requirements and, last but not least, with competing industrial recycling processes. Finally the economic efficiency of the process shows that the cost effectiveness is strongly dependent on the cobalt price. The flow chart of the total recycling process is shown in Fig. 2.

3.2. Process description and characterization of single material fractions

Three different charges of Li-ion battery scrap are processed. Two of them are pure production scrap charges with two different manganese contents. Those are used in the lab-scale tests. The third scrap charge represents a mixture of spent Li-ion batteries with no manganese content. This charge is used in the technical-scale melting campaign. During processing different material fractions are generated which are characterized and evaluated.

During pre-treatment the Li-ion battery packs are disassembled and the single battery cells are laid open. Thereby a material fraction which contains electronic parts and plastics is generated. Due to the copper content this material fraction can be regarded as valuable secondary raw material which can be further processed in an ISA/Ausmelt bath melting process. Reselling to companies that are specialized in copper recycling should therefore be the best solution for further processing.

The second process step contains a pyrolysis in a resistance heated retort furnace at temperatures of maximum 250 °C. The battery cells are deactivated safely for further processing and the volatile organic electrolyte evaporates and is caught in a downstream condenser. Both the pre-treatment as well as the thermal treatment are operated by ACCUREC.

At the beginning of the research project it is also aimed at an electrolyte recovery for reuse in batteries but the test set-up turns out to be not practical since the condensate also contains various decomposition products which make a direct reuse of impossible. Nevertheless the main condensate components are ethyl methyl carbonate (71 mass-%) and ethylene carbonate (10 mass-%). With an optimised facility set-up a separate collection of these components is considered as possible. That would mean an electrolyte recovery of approximately 80%.

In the third process step the deactivated cells are crushed safely in a second mill and in a disintegrator. After crushing, a classification and sorting are done by means of vibrating screen, magnetic separation in a drum separator and air separation in a zigzag classifier. The generated material fractions are an iron-nickel and an aluminium fraction (both from battery casings), an electrode foil fraction and a fine fraction which contains the electrode material. All three metal containing material fractions are shown in Fig. 3. The mechanical processing is operated by UVR-FIA [32].

For homogenization and taking of representative samples the iron-nickel fraction is remelted in a vacuum induction furnace. A test melt under salt (as it is standard in aluminium recycling industry) is done with the aluminium fraction in a resistance heated furnace. Due to the very inhomogeneous composition

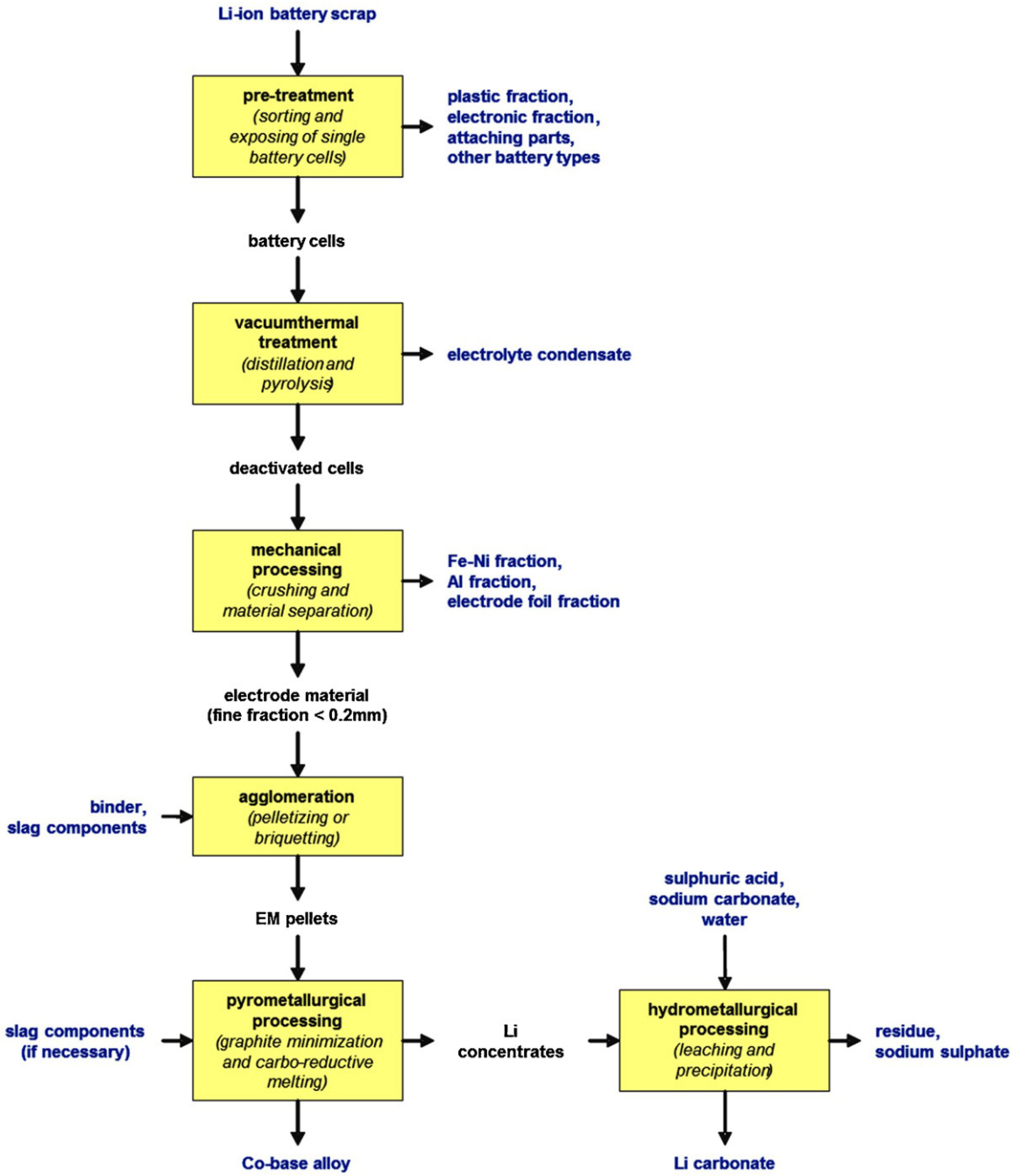

Fig. 2. Alternative recycling process dedicated to portable Li-ion batteries.

Fig. 3. Metal containing material fractions after crushing and material separation (from left to right: iron-nickel fraction, aluminium fraction, electrode foil fraction).

Table 3
Composition of metal containing material fractions.

Fraction	Content in mass-%									
	Al	Co	Cr	Cu	Fe	Li	Mn	Ni	Si	C
Iron-nickel	0.1	0.8	1.0	1.8	89.7	0.3	0.2	3.9	0.3	1.9
Aluminium	97.80	0.01	–	0.30	0.50	–	1.10	0.02	0.20	–
Electrode foil	~25.0	–	–	~60.0	–	–	–	–	–	–

Fig. 4. Electrode material fraction.

of the electrode foil fraction an aqua regia dissolution is done to determine the copper and aluminium contents. All ICP-OES analysis results are listed in Table 3.

The most valuable material fraction is the fine fraction which contains almost all of the cobalt and lithium in form of metal oxides as well as the graphite (see Fig. 4). Measurements with a laser diffraction sensor (Sympatec Helos KFS Oasis) show a density of 2.68 g cm^{-3} and 80% of the particles have a size smaller than 100 μm.

For better handling and charging into the electric arc furnace the fine fraction is agglomerated to pellets using molasses as binding agent. The pellets have a cobalt content of approx. 30 mass-% and a lithium content of approx. 3 mass-%. Due to the high graphite content of approx. 30 mass-% and therefore problems during pyrometallurgical processing a thermal pre-treatment is done. The pellets are charged into a rotary kiln to halve the graphite content to approx. 15 mass-% at a temperature of 800 °C.

4. Theoretical slag evaluation

The carbo-reductive melting of the pellets requires an appropriate process slag that shows a minimum capacity for cobalt and manganese. A simple binary or ternary slag composition is preferred. Looking at the slag systems used in extractive cobalt or manganese metallurgy the slag components Al_2O_3, CaO, MgO and SiO_2 are taken into consideration. The following slag compositions are chosen (see Table 4).

In order to evaluate these slag compositions thermochemical calculations are done with the modelling software FactSage™. Thereby the theoretical distribution coefficient L_{Me} for cobalt and manganese is of interest, which is defined as the ratio between metal concentrations in the slag phase divided by metal concentration in the metal phase. In the calculations cobalt metal phases with increasing manganese contents are set in a chemical equilibrium with all three slag compositions. The temperature is varied in the range between 1500 and 1800 °C in steps of 100 °C.

Slags S1 and S3 show the best calculation results for a manganese-free metal phase. By using these slags the slagging of cobalt is marginal, i.e. the calculations show the lowest distribution coefficients for cobalt. If manganese is present slag S3 shows the lowest distribution coefficient for manganese which makes it the best choice for melting down cobalt as well as manganese containing electrode material pellets. Nevertheless the thermochemical calculations can only give an indication for the evaluation of these slags since kinetic aspects cannot be considered.

5. Experimental procedure and test results

5.1. Pyrometallurgical processing of electrode material fraction

All slags are further evaluated within a test series in a lab-scale DC electric arc furnace powered by a welding transformer with secondary currents of 120–700 A and secondary voltages of 24–44 V (see Fig. 7). The slags are used to melt down electrode material pellets with zero (ZM), low (LM) and high (HM) manganese contents at a temperature within 1700–1750 °C. A slag mass of 1.5 kg and a pellet mass of 3.5 respectively 5.5 kg is used depending on the graphite content of the pellets. In the case of 5.5 kg pellet mass input the graphite content has previously been reduced in a rotary kiln as described above. Examples of the generated metal alloy and slag are shown in Fig. 5. Input and output masses of the lab-scale test series are listed in Table 5 and metal yields are shown in Fig. 6.

The results of the lab-scale test series confirm the results of the thermochemical calculations with FactSage™. The best cobalt and manganese recoveries can be achieved by using slags S1 and S3. But unlike the calculations slag S1 shows better results in terms of metal yields, which can be explained by the better melting behaviour, i.e. the viscosity at process temperature is lower and hence the formation of a coherent metal phase out of single metal droplets is easier. Due to the higher viscosity slag S2 shows a poor melting

Table 4
Physical data of selected slags [33,34].

Slag	Al_2O_3	CaO	MgO	SiO_2	T_m	Density	Viscosity	Electr. conductivity
	in mass-%				in °C	in g cm^{-3}	in g cm^{-1} s^{-1}	in 1 Ω cm^{-1}
S1	–	54.5	–	45.5	~1460	~2.8[a]	<2[a]	~0.5[b]
S2	17.5	45.0	–	37.5	~1450	2.6[a]	~5[a]	~0.6[c]
S3	50.0	45.0	5.0	–	~1350	~3.0[a]	3[a]	~0.9[b]

[a] At T = 1500 °C.
[b] At T = 1600 °C.
[c] At T = 1650 °C.

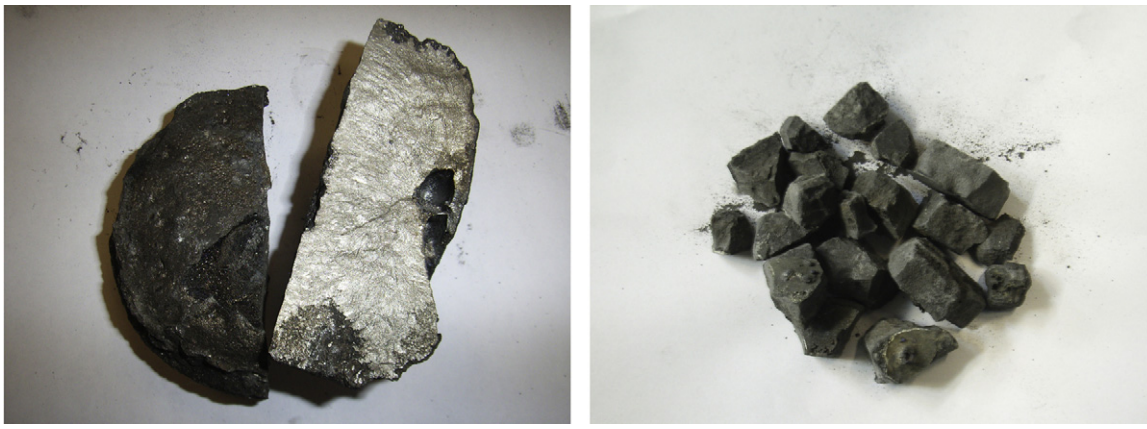

Fig. 5. Metal alloy (left) and slag (right) produced in lab-scale tests.

Table 5
Input and output masses of lab-scale test series.

Test no.	$T_{holding}$ (°C)	Input (g)		Output (g)		Expected metal output[a] (g)
		EM pellets	Slag	Metal	Slag	
V1a	1760	3500 (LM)	1500 (S1)	1130	690	~1000
V1b	1750	3500 (LM)	1500 (S1)	1360	490	~1000
V2a	1750	3500 (LM)	1500 (S2)	1330	750	~1000
V2b	1740	3500 (LM)	1500 (S2)	680	700	~1000
V3a	–	3500 (LM)	1500 (S3)	No melting phase		~1000
V3b	–	3500 (LM)	1500 (S3)	No melting phase		~1000
V4a	1760	5500 (HM)	1500 (S1)	2450	730	~2110
V4b	1730	5500 (HM)	1500 (S1)	2660	850	~2110
V5a	1720	5500 (HM)	1500 (S3)	2060	1110	~2110
V5b	1700	5500 (HM)	1500 (S3)	2080	1640	~2110
V6a	1730	5500 (ZM)	1500 (S1)	2480	740	~1740
V6b	1760	5500 (ZM)	1500 (S1)	2540	670	~1740
V7a	1740	5500 (ZM)	1500 (S3)	1780	1430	~1740
V7b	1720	5500 (ZM)	1500 (S3)	1730	1580	~1740

[a] In case of 100% cobalt and copper reduction and 50% manganese reduction.

behaviour and after cooling down single solidified metal droplets can be found which are entrapped and distributed in the slag phase. The range of metal alloy composition generated during the lab-scale test series is shown in Table 6.

Based on the results of the thermochemical calculations as well as on the lab-scale test series slag S1 is selected for a further test campaign in a technical-scale electric arc furnace. The furnace has a maximum power supply of 450 kVA and can be operated in DC mode (max. 5234 A and 94 V) as well as in AC mode (max. 4290 A and 110 V). The voltage is preset via vertical position of the top electrode which can be changed manually. Current and electric power result out of the given voltage. The copper bottom electrode and the furnace shell are water-cooled. The off-gas is exhausted with a maximum flow rate of 5000 $m^3\ h^{-1}$ and cleaned in a subsequent impact separator and an electrostatic precipitator. The melt temperature is controlled discontinuously via measuring rods. All details of the test campaign are listed in Table 7. The generated metal alloy, slag and flue dust are shown in Fig. 7.

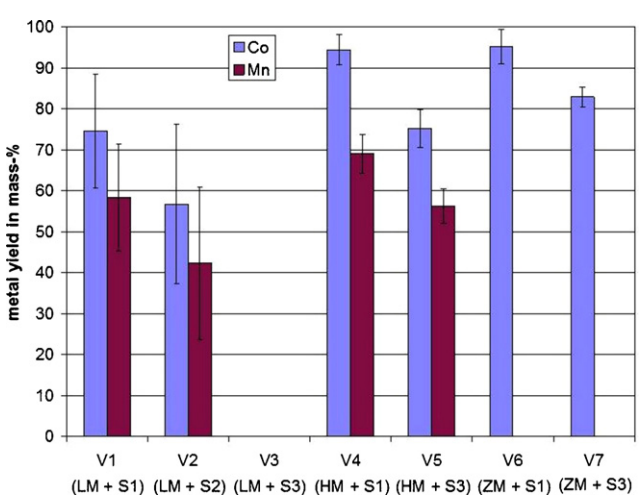

Fig. 6. Cobalt and manganese yields of lab-scale test series.

Zero-manganese type electrode material pellets with a reduced graphite content of 15 mass-% are charged as input material. The cobalt content of the pellets is 30.9 mass-% and the lithium content is 3.9 mass-%. The slag is mixed in advance out of the pure slag components CaO and SiO_2. Pellets and slag are charged alternately and depending on the melt behaviour additional amounts of slag are charged to lower the viscosity. The output masses of the test campaign are listed in Table 8. Since a large amount of the flue dust remains in the electrostatic precipitator the total amount of generated flue dust has to be estimated via mass balance of the single elements (see Table 9).

Table 6
Range of metal alloy composition generated during lab-scale test series.

Co in mass-%	Mn	Si	Al	Cu	C
53–81	0–22	0–22	5–7	1–4	0–5

Table 7
Test campaign in technical-scale electric arc furnace.

Tapping	EM pellets (ZM type) (kg)	Slag (kg)	Others[a] (kg)	$T_{holding}$ (°C)	t_{charge} (h)	$t_{holding}$ (h)	Electric power W (kWh)
1	50	130	12	~1750	~4.0	~0.5	551
2	100	100	12	~1750	~3.5	~1.0	689
3	100	50	12	~1750	~2.5	~0.5	481
4	100	50	12	~1750	~2.5	~0.5	430
Σ	350	330	48	–	–	–	2151

[a] Measuring rods and anchor rests (estimated).

Fig. 7. Metal alloy (left), slag (middle) and flue dust (right) produced in technical-scale test.

Table 8
Output masses of test campaign in technical-scale.

Tapping	$Metal_{out}$ (kg)	$Slag_{out}$ (kg)	Flue $dust_{out}$ (kg)
1	13	96	47[b]
2	32	83	
3	37	60	
4	66 + 25[a]	70	
Σ	173	309	

[a] Metal rest in furnace.
[b] Estimated via mass balance of single elements.

The ICP-OES analysis results of the cobalt alloy as well as of the lithium containing slag and flue dust are listed in Table 10. The metal analysis shows a cobalt-based alloy which contains the same minor elements that are typical for commercial cobalt-based superalloys with trade names like "Stellite", "Haynes" or "Elgiloy" used for production of high temperature turbines. Therefore a possible application for the cobalt-based alloy produced from Li-ion battery scrap could be as a master alloy for these commercial cobalt-based superalloys.

Table 9
Mass balance of single elements.

	Input (kg)			Output (kg)				Difference (mass-%)	Error value (mass-%)	Relative error (mass-%)
	EM	Slag	Others	Metal	Slag	Flue dust	Σ			
Ca	–	128.7	–	–	118.3	10.4	128.7	0.0	0.1	0.0
Co	108.2	–	–	95.7	3.4	9.1	108.2	0.0	0.0	0.0
Cr	–	–	–	0.7	–	–	0.7	0.7	0.7	100.0
Cu	2.2	–	–	1.9	–	0.3	2.2	0.0	0.0	0.0
Fe	–	–	48.0[a]	39.5	3.9	–	43.4	−4.6	4.6	−9.6
Li	13.7	–	–	–	4.3	9.4	13.7	0.0	0.0	0.0
Mn	–	–	–	2.4	–	–	2.4	2.4	2.4	100.0
Ni	2.7	–	–	3.7	–	–	3.7	1.0	1.0	37.0
Si	–	70.1	–	27.1	48.3	–	75.4	5.3	5.3	7.6
C	53.6	–	–	–	22.8	6.2	29.0	−24.6[b]	–	–
Σ	373.6[c]			378.4[c]			4.8[c]	14.1[c]	3.8[c]	

[a] Estimated.
[b] Output as CO resp. CO_2.
[c] Without C.

Table 10
Metal slag and flue dust analysis of test campaign in technical-scale.

	Al in mass-%	Ca	Co	Cr	Cu	Fe	Li	Mn	Ni	Si	C	P
Metal[a]	0.4[b]	n.v.	55.3	0.4	1.1	22.9	n.v.	1.4	2.1	15.7	n.v.	0.6
Slag	n.d.	38.3	1.1	n.d.	n.v.	1.3	1.4	n.v.	n.v.	15.6	7.3	0.1
Flue dust[c]	–	22.3	19.4	–	0.7	–	20.1	–	–	–	13.2	–

n.v.: not verifiable, n.d.: not determined.
[a] After remelting in VIM.
[b] From Al_2O_3 crucible.
[c] From mass balance.

Table 11
Lithium yields of different leaching methods (results from UVR-FIA).

Leaching agent	Lithium yield in mass-%
Hydrochloric acid	45.8
Sodium hydroxide	7.5
Calcium carbonate	2.9
Sulphuric acid	76.7 resp. >90.0

5.2. Hydrometallurgical lithium recovery

The slag and the flue dust (see Fig. 7) are further processed hydrometallurgically to recover the lithium content. Because of its high vapour pressure and its high oxygen affinity lithium leaves the furnace via the off-gas in oxidic form during processing. The flue dust from the test campaign in technical-scale has a lithium content of 20.1 mass-% whereas the slag has a lithium content of 1.4 mass-%. Starting with a lithium content of 3.9 mass-% in the electrode material pellets the lithium content in the flue dust is more than five times higher. It is aimed at a lithium recovery in form of a pure lithium carbonate since from the technical point of view it is the most important lithium compound. Besides the battery production lithium carbonate is mainly used in glass production.

The hydrometallurgical recovery of lithium is developed by UVR-FIA [32]. Different leaching methods are tested with sample masses of 50 g. Before leaching all slag samples are milled to a target particle size of 95% smaller than 100 μm. Due to its particle size the flue dust does not have to be milled and can be leached directly. After leaching the solid is filtered out and then washed and analysed to determine the lithium yield. Table 11 lists all leaching agents and the corresponding lithium yields.

The leaching with sulphuric acid results in the highest lithium yield. Therefore further leaching tests are done using different amounts of sulphuric acid and the lithium yield can even be increased to more than 90%. Finally the total process step is tested with a flue dust mass of 1 kg. A lithium carbonate with a purity higher than 99 mass-% can be generated. An external verification by the glass producer Schott AG (Mainz) has shown that this purity is even high enough for the production of special-purpose glass.

6. Discussion and evaluation of the recycling process

Looking at the extractive metallurgy of cobalt and manganese three slag compositions have been chosen for melting down the electrode material pellets in an electric arc furnace. The thermochemical calculations show that in principle all three slags are suitable but the results are based on a chemical equilibrium, i.e. kinetic aspects cannot be considered.

Therefore the test series in the electric arc furnace is important to evaluate all three slags under realistic melting conditions. It turns out that settling of metal droplets and generation of a metal phase is only possible if a slag phase with a low viscosity is used. That means that kinetic aspects play a decisive role. At the same time the slag protects the metal phase from oxygen and helps to retain heat by acting as a heat insulator. Last but not least the electrical resistance of the slag is important for the processing in the electric arc furnace. Nevertheless the size of the lab-scale electric arc furnace does not guarantee an equal heat balance for each test and thus reproducible test results are hard to achieve. Furthermore mass losses caused by diffuse emissions are high compared to the total input mass. Regardless, with the help of the lab-scale test series it is possible to find the best slag composition for a further test campaign in technical-scale by looking at the melting behaviour in interaction with the electrode material pellets.

The test campaign in technical-scale has successfully proven that the production of a cobalt-based alloy and lithium enrichment in the flue dust is possible, i.e. a positive proof of feasibility has been done since a separate melting of the electrode material extracted from Li-ion batteries has not been published before. The related Sankey diagram of the total test campaign is shown in Fig. 8.

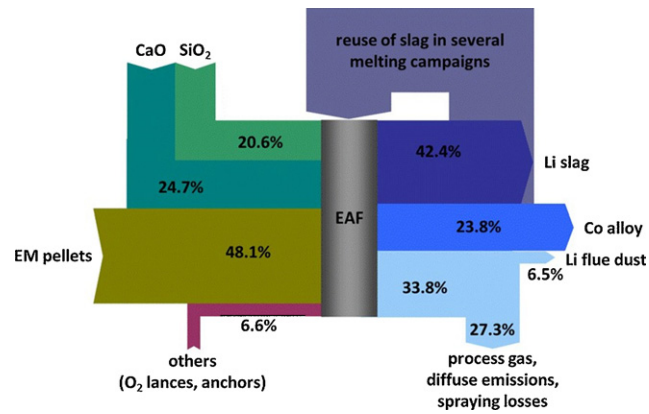

Fig. 8. Sankey diagram of test campaign in technical-scale (incl. improvement by slag reuse).

A lithium enrichment can only be achieved in the flue dust and the slag has to be crushed and milled before leaching. Therefore the lithium recovery from the slag after one use has to be questioned. An improvement might be only to tap the metal and to leave the slag in the furnace for reuse. Thus the slag would be saturated with cobalt and manganese and further slagging of these metals could be minimized.

The high graphite content of the electrode material pellets leads to problems during processing in the electric arc furnace, as already mentioned, although a certain amount of graphite is required for the carbo-reductive melting. To minimize the graphite content to a desired amount the pellets are treated in a rotary kiln. Of course this treatment means an additional extensive and cost-intensive process step. Another possibility to minimize the graphite content could be to run the electric arc furnace similar to a shaft furnace, i.e. to have a submerged electrode in a packed bed inside the furnace whereby the melting takes place in the bottom part and the upward moving heat can be used to partly burn the graphite by adding secondary air.

The Sankey diagram of the total recycling process for portable Li-ion batteries is shown in Fig. 9. Out of an input mass of 100% spent Li-ion battery cells 49.08% of utilisable material fractions for further processing as well as directly utilisable recycling products

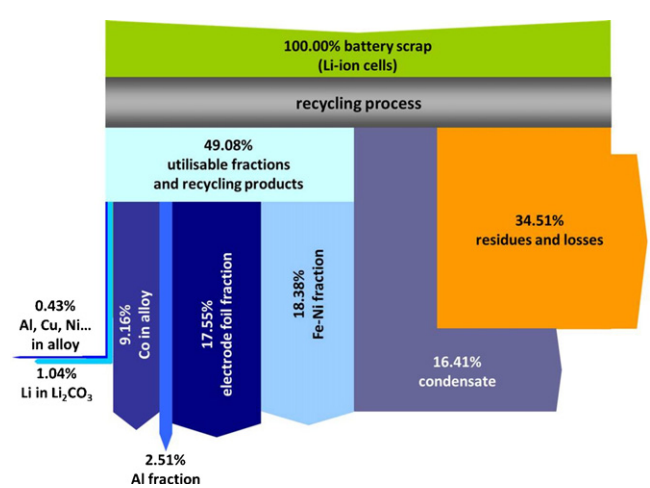

Fig. 9. Sankey diagram of recycling process for portable Li-ion batteries.

Table 12
Calculation of recycling efficiency with estimated metal yields for further processed metal containing material fractions.

	Output in mass-%	Yield (up to marketable product)	Product
Li in Li_2CO_3	1.04	100	1.04
Co in alloy	9.16	100	9.16
Al, Cu, Ni. . . in alloy	0.43	100	0.43
Fe-Ni fraction	18.38	>90	>16.54
Al in electrode foil fraction (25 mass-%)	4.39	>90	>3.95
Cu in electrode foil fraction (60 mass-%)	10.53	>90	>9.48
Al fraction	2.51	>90	>2.26
Σ	46.44	–	>42.86
EMC in electrolyte condensate (70 mass-%)	11.49	>90	10.34
EC in electrolyte condensate (10 mass-%)	1.64	>90	1.48
Σ_{total}	62.85	–	>54.68

can be recovered. The electrolyte condensate accounts for another 16.41% and is marked separately in the diagram because the recovery of pure electrolyte components has not been realized yet but is considered feasible. At the end 34.51% of residues and losses are generated which, amongst others, include CO respectively CO_2, slagged battery components and diffuse emissions like losses during charging or spillings during tapping of the electric arc furnace.

Due to various reasons the recycling efficiency of a process cannot be measured reliably, so that it has to be calculated. But while the recycling targets have been fixed in the EU Battery Directive, it has not been defined how the recycling efficiency is calculated. Up to now no agreement on a calculation method for recycling efficiencies regarding battery recycling processes has been finalized. Critical points that have to be reflected by an equation are, for example, the definition of system boundaries, of battery elements and components to be considered and those to be neglected, of assigning material values to the input and output materials and of ensuring transferability to all related battery systems. However the calculation method will have a major impact on the battery recycling industry in Europe.

Generally the recycling efficiency can be defined as the weight ratio of acceptable recycling products and considered battery scrap mass. The recycling efficiency calculation of the presented recycling process is based on very conservative assumptions regarding estimated metal yields for further processed metal containing material fractions (see Table 12). Only direct utilisable recycling products are taken into account. This also means that the graphite content used for the carbo-reductive melting in the electric arc furnace is not considered because it is used as reducing agent. The graphite is rather lost in form of CO respectively CO_2, which cannot be considered as recycling according to the EU Battery Directive. The recycling definition also excludes the possibilities of disposal or energy recovery. For a comparison with competing recycling processes it has to be mentioned that currently all other battery recyclers include the graphite content in their recycling efficiency calculation.

Another fact is that only those elements in the recycling products have been taken into account which originate from Li-ion batteries and not from other input materials like additives. For instance all elements that exchange from the slag components into the metal phase (e.g. silicon) are taken out for the calculation. This is also not of current practice at competing battery recyclers.

In compliance with EU regulations and based on a conservative calculation a recycling efficiency of approximately 40% is achieved. At this stage a recycling efficiency of at least 50% can only be reached if the main components of the organic electrolyte can be recovered. Therefore it is difficult but not impossible to comply with the legally prescribed recycling efficiency of 50 mass-% for Li-ion batteries.

Currently the only comparable industrial recycling process is Umicore's VAL'EAS^{TM} process. Both the here presented as well as the Umicore process are specially dedicated to Li-ion batteries but the latter is already established with a yearly capacity of 4000 t battery scrap. The main difference is the missing pre-treatment in the Umicore process. That means only noble metals, such as chromium, cobalt, copper and nickel, are recovered. Another disadvantage of the Umicore process is the fact that the electrolyte as well as the lithium content is not recovered. Umicore announces a recycling efficiency of approximately 70 mass-% but the calculation method is not in compliance with the EU Battery Directive since the thermal as well as the material utilisation are taken into account. According to Umicore this adds up to 20 mass-% for plastics and up to 15 mass-% for the graphite. Umicore considers these battery components as recycled. From the economical site of view the process seems to be more cost-effective because of the missing pre-treatment steps. But it has to be mentioned that the metal alloy has to be further processed hydrometallurgically for a separate cobalt and nickel recovery. In contrast the cobalt alloy produced in the electric arc furnace can directly be used as master alloy for cobalt-based superalloys.

7. Conclusions

In combining a pre-treatment with pyro- and hydrometallurgical process steps a recycling process dedicated to portable Li-ion batteries has been developed. Thereby as much battery components as possible are recovered in form of marketable material fractions or as directly utilisable recycling products. The process design aims at the production of a cobalt alloy and a pure lithium carbonate as main recycling products. Nevertheless at the current stage there are still improvements required since the legally prescribed recycling efficiency can only be achieved if the electrolyte is recovered. Furthermore it has to be mentioned that the economic efficiency of the process strongly depends on the cobalt price which is known to be very volatile. None the less an economic evaluation has shown that a minimum cobalt price of 20 € per kg is required if 1000 tonnes of Li-ion battery scrap are processed per year. Since the end of 2003 the cobalt price has never fallen below this limit. In general it is recommended that the annual tonnage of at least 1000 tonnes of scrap is processed in an electric arc furnace with a power supply of approx. 0.5 MVA.

Current battery development focuses on the use of lithium-based secondary batteries in (hybrid) electric vehicles. Since the proportion of automobiles with hybrid drive technology is strongly increasing the return flow of spent Li-ion battery packs will also increase within the near future keeping in mind that approx. 60 million cars are produced per year. Already today it is assumed that new chemical battery systems based on more cost-effective electrode materials, such as $LiFePO_4$, $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$, $LiNi_{0,8}Co_{0,15}Al_{0,05}O_2$, $LiMn_2O_4$, $LiTi_4O_7$ and $LiSi_x$, will be used for this application. The substitution of the valuable cobalt will challenge today's recycling processes with respect to cost-effectiveness as well as recycling technology. With the presented process also new types of Li-ion batteries can be recycled if the pyrometallurgical process step is adjusted to the new chemical systems.

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