

Smelting of Pyrolyzed Battery

With increasing popularity of mobile devices and electromobility, both fields of technology highly dependent on rechargeable batteries, the recycling thereof has become of interest and a field of commercial activity.

- 5 WO 2022/248436 shows a process for the recovery of Ni and Co from Li-ion batteries or their waste, comprising the steps of providing a furnace lined with magnesia-bearing refractory bricks; providing a charge comprising slag formers and Li-ion batteries or their waste, and smelting the charge in reducing conditions, thereby obtaining an alloy containing the major part of nickel,
10 cobalt and a slag.

- Due to oxidation of aluminum in pyrometallurgical battery recycling significant amounts of slag is produced, which requires addition of a flux to decrease its melting point. In addition, the aluminum metal is lost to the slag. Also, process control becomes more troublesome because of the intense heat generation by oxidation of aluminum during the smelting step. Moreover, depending on the carbon content and on how the smelting process is run, intense release of explosive gas (carbon monoxide) is possible during smelting step due to oxidation of remaining plastic and electrolyte in battery, which makes post combustion more difficult.
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- 20 WO 2012/111690 shows a method for recovering metal from waste batteries comprising the steps of a pre-oxidation step wherein the battery is roasted under oxidizing conditions and is consecutively smelted, wherein slag and an alloy of the desired metals is obtained, and the desired metals are separated.

- This method reduces the problem of carbon monoxide evulsion during smelting step by employing a pre-oxidation step, but aluminum recovery still isn't possible.
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JP 7006438 shows a method for recycling of lithium ion batteries comprising the steps of S1: oxidative pretreatment pyrolysis of lithium ion battery, S2: crushing the remains of the lithium ion battery, S3: oxidative pyrolysis step

- to oxidize and remove carbon from the remains of the lithium ion battery followed by S4: reduction melting step to obtain a reduced product. This method allows recovery of aluminum, but requires an additional oxidative pyrolysis step S3 to remove all remaining carbon to achieve better process control in reduction smelting step S4. This will require additional reductant (e.g. cokes) and heat source to reduce carbon-free feed.

Common aluminum separation techniques require physical separation of shredded battery powder, which leads to loss of valuable metals such as nickel, cobalt, and lithium.

- 10 These problems are solved by the method of recovering valuable metals from waste batteries according to the claims. In the method of the subject patent application no second oxidative pyrolysis step is needed.

The method of recovering valuable metals from waste batteries comprises

- a **pyrolysis step** comprising pyrolysis of the waste batteries at a temperature of from about 700°C to about 1300°C, thereby obtaining pyrolyzed batteries;
- a **size reduction step**, comprising size reduction of the pyrolyzed batteries;
- a **smelting step**, comprising smelting the pyrolyzed, size reduced waste batteries at temperatures of 1350°C or higher under oxidizing conditions.

The method may contain additional steps.

Short Description of the Invention

1. Method of recovering valuable metals from waste batteries comprising the steps of -a pyrolysis step comprising pyrolysis of the waste batteries at a temperature of from about 700°C to about 1300°C, obtaining pyrolyzed batteries; -a size reduction step, comprising size reduction of the pyrolyzed batteries; -a smelting step, comprising smelting the

pyrolyzed, size reduced waste batteries at temperatures of 1350°C or higher under oxidizing conditions.

2. The method of item 1, wherein pieces of pyrolyzed, size reduced waste batteries exhibit a diameter of not more than 20 cm and/or the loss of nickel and cobalt metal before the smelting step is less than 2 weight percent.
3. The method of item 1 or 2, wherein during the pyrolysis step air is fed.
4. The method of any of the preceding items, wherein the pyrolyzed, size reduced waste batteries are packed, in particular into paper, plastic or combinations thereof.
5. The method of any of the preceding items, wherein the pyrolyzed, size reduced waste batteries are subjected to extraction of lithium with an aqueous solvent.
6. The method of any of the preceding items, wherein the smelting step yields a lithium-containing slag exhibiting a content of MnO of 10% to 50% or more, based on the weight of the total amount of slag.
7. The method of any of the preceding items, wherein the smelting step yields a lithium-containing slag exhibiting a content of P₂O₅ of from 0,5 weight percent to 10 weight percent.
8. The method of any of the preceding items, wherein the smelting step comprises addition of calcium oxide and alumina and wherein the $(\text{CaO} + 0.4\text{MnO}) / \text{Al}_2\text{O}_3$ ratio is above 0.25.
9. The method of any of the preceding items wherein in the smelting step a metallurgical charge comprising slag formers and the pyrolyzed, size reduced waste batteries containing Co, Ni, metallic Al, and C, and are subjected to a process comprising the steps of:
 - providing a metallurgical smelting furnace equipped with means for the submerged injection of an O₂-bearing gas;

- defining an oxidizing level O_x characterizing oxidizing smelting conditions according to the formula:
$$O_x = p_{CO_2} / (p_{CO} + p_{CO_2}),$$
wherein $0.1 < O_x < 1$, p_{CO} and p_{CO_2} are the partial pressures of CO and CO₂ in contact with the melt;
5 - preparing the metallurgical charge;
 - oxidizing smelting the metallurgical charge by injecting an O₂-bearing gas into the melt to reach the defined oxidizing level O_x , thereby obtaining a first alloy with a major part of Ni, and a slag
10 containing residual Ni and Co;
 - liquid/liquid separation of the alloy from the slag.
- 10. The method of item 10, wherein slag formers are selected from the group consisting of CaO, Al₂O₃, SiO₂ and combinations thereof.
- 15 11. The method of any of the preceding items, wherein the pyrolysis step is carried out at a temperature of from about 700°C to about 1050°C.
- 12. The method of any of the preceding items, further comprising a steps of: - subjecting the pyrolyzed, size-reduced waste batteries with an aqueous solvent, thereby extracting lithium; - applying solid-liquid
20 separation.

Detailed Description of the Invention

Waste batteries may contain end-of-life batteries, off-spec batteries, production scrap, spent lithium ion batteries and may in particular comprise lithium
25 ion batteries. Said products should however contain appreciable amounts of at least Nickel (Ni), Aluminum (Al) and Carbon (C), but may also contain a metal selected from the group consisting of Cobalt (Co), Lithium (Li), Manganese (Mn) and combinations thereof.

The pyrolysis step removes volatile liquids such as a liquid electrolyte and the casing of the waste batteries. The outer casing of the waste batteries is typically made of aluminum. Specifically, the "outer casing" includes module casings as well as cell casings and pack casings and can contain 5 to 50 weight percent of aluminum of the entire waste batteries. This does not mean that there is no aluminum left within the waste batteries.

The pyrolysis step also allows the separation and removal of aluminum, which can be recovered as a valuable resource, and reduces the amount of slag produced and the heat generated in the smelting step by oxidation of the aluminum.

In the pyrolysis step, the aluminum may be separated from the other parts of the waste batteries by, for example, collecting the molten aluminum in a suitable container placed under the waste batteries after it has passed through, for example, a sieve or mesh or other suitable means for retaining the spent lithium-ion batteries and allowing the molten aluminum to pass through the gaps of such means. The aluminum can thus be separated and removed efficiently.

The temperature during the pyrolysis step should be in the range of about 700°C to about 1300°C or higher, or from 700°C to about 1050°C, which is below the melting point of copper, nickel and cobalt. For a brief period of time, namely up to ten (10) minutes, the temperature during pyrolysis can be increased up to a temperature of more than 1050°C, particularly to about 1200°C or even up to 1300°C maximum without

At such temperatures, the aluminum forming the casing or other parts of the waste batteries will melt, as aluminum has a melting point of about 660°C. The upper limit of the pyrolysis temperature is 1300°C, but may be as low as 1050°C or lower because the melting points of copper, nickel, cobalt, etc., which may also be present in the Waste batteries, will only melt at above 1050°C and thus remain as solids and can be recovered later in smelting step. This step is carried out while feeding conventional industrial gas such as air, inert gas such as carbon dioxide or nitrogen or mixtures thereof during the

pyrolysis step. Moreover, natural gas, optionally mixed with air or oxygen, can be injected as well, in particular when used in a burner for heating. In case the natural gas is added in mixture with oxygen, care should be taken to avoid high oxygen amounts to prevent or at least limit oxidation of the aluminum.

In the size reduction step the contents of the battery, from which the aluminum casing and other aluminum parts have been removed, are reduced in size, depending on the scale of the equipment available for further treatment. Usually, reduction to a size of up to about 50 cm is often sufficient, but reduction to a size of less than about 20 cm may be beneficial. A size of 50 cm or 20 cm, respectively, means that object fits within a sphere having a diameter of 50 cm or 20 cm, respectively. For some purposes reduction to a size of 1 cm or less might be useful.

This treatment is useful both for increasing the reaction efficiency by increasing the surface area and for facilitated feeding during the smelting step. The size reduction method is not particularly limited, but can be carried out by crushing, cutting, dismantling by hand or robot or a different means for automated dismantling, sawing or punching using conventionally known machinery such as (preferably automatic) crushers (such as a cutter mixer), punches or saws or any other suitable means for parting or compressing to the desired size.

In dismantling, the cells or modules of pyrolyzed batteries are separated by hand, by robot or by any other automated means of dismantling, which inherently results in a size reduction of the pyrolyzed batteries.

Optionally, after the size reduction the pyrolyzed and size reduced waste batteries can be packed. Suitable packaging material is, in principle, not particularly limited. Suitable packing materials are, for example, paper, plastic, metal or cardboard, either in sheets or as container (e.g. boxes or bags) and can be sealed either by mechanical means such as folding or by other means such as gluing. Plastic or metal sheets can also be soldered or welded. If

metals are used it might be advantageous to use metals present anyway in the batteries or the following process steps.

If the size reduction is carried out by dismantling, for example dismantling by hand, robot or other automated means, the parts obtained by dismantling
5 can be packaged immediately after dismantling, almost as if it was the same process step to avoid formation of dust.

In another embodiment the particle size of 1 cm or less of the pyrolyzed and size reduced waste batteries can be desirable, which can also be achieved by conventional techniques as mentioned before, or conventional means of
10 shredding or milling to generate smaller particles with a size of 1 cm or less.

Optionally, after the size reduction the pyrolyzed and size reduced waste batteries can be extracted with an aqueous, i.e a water containing solvent in order to remove lithium. Consequently, this will result in a method of recovering valuable metals from waste batteries further comprising the steps of: -
15 subjecting the pyrolyzed, size-reduced waste batteries with an aqueous solvent, thereby extracting lithium;- applying solid-liquid separation. Preferably, water is used for the extraction of lithium. The aqueous solvent may be re-used for various batches of the pyrolyzed and size reduced waste batteries, which will reduce the amount of water used and at the same time result in
20 aqueous solutions of lithium compounds with higher lithium concentrations. The solid-liquid separation can be carried out by conventional means such as filtration, centrifugation, decantation, sedimentation or combinations thereof.

Optionally, after the size reduction the pyrolyzed and size reduced waste batteries can be agglomerated in the shape of briquette, extruded, provided that
25 the size has become small enough for such steps, for which sizes of 1 cm or less usually are sufficient.

Optionally, after the size reduction and once the particle size of the pyrolyzed and size reduced waste batteries is sufficiently small, said pyrolyzed and size reduced waste batteries can be delivered with an O₂-bearing gas and injected
30 through a submerged lance during the smelting step.

Optionally, the pyrolyzed and size reduced waste batteries can contain 10 to 50 weight percent of water. The water present can be the result of water addition, filtering of a suspension or other sources.

In a subsequent step the pyrolyzed, size reduced waste batteries are subjected to the smelting step in which they are treated at temperatures of 1350°C or higher under oxidizing conditions.

A suitable smelting process is described, for example, in WO 2022/248436. A suitable smelting furnace is employed in the smelting step. In an embodiment the smelting furnace is equipped with means for submerged injection of an O₂-bearing gas.

In an embodiment of the method, the smelting step is carried out in a way wherein a metallurgical charge optionally comprising slag formers and the pyrolyzed, size reduced waste batteries containing at least Nickel (Ni), Aluminum (Al) and Carbon (C), but optionally also containing a metal selected from the group consisting of Cobalt (Co), Lithium (Li), Manganese (Mn) and combinations thereof, are subjected to a process comprising the steps of:

- providing a metallurgical smelting furnace equipped with means for the submerged injection of an O₂-bearing gas;
- defining an oxidizing level Ox characterizing oxidizing smelting conditions according to the formula:
$$Ox = pCO_2 / (pCO + pCO_2),$$

wherein $0.1 < Ox < 1$, pCO and pCO₂ are the partial pressures of CO and CO₂ in contact with the melt;
- preparing the metallurgical charge;
- oxidizing smelting the metallurgical charge by injecting an O₂-bearing gas into the melt to reach the defined oxidizing level Ox, thereby obtaining an alloy with Ni, and a slag containing at least one of CaO, Al₂O₃ and SiO₂ ;
- liquid/liquid separation of the alloy from the slag;

In this process, the sequence of the steps of "defining an oxidizing level Ox" and of "preparing the metallurgical charge" can be exchanged.

By "slag formers" are meant: one or more of, for example, CaO, Al₂O₃ and
5 SiO₂. Other slag formers, well known to the skilled person, may also be present. The slag forming compounds may be added as such, or they may be obtained in situ from easily oxidized metals present in the charge.

The minimal value of 0.1 for the oxidizing level Ox is determined by the need for the generation of a sufficient amount of CO₂ for heating up and melting a
10 metallurgical charge, as the generation of CO only would generally not suffice. The upper limit of less than 1 corresponds to the avoidance of extremely oxidizing conditions, which would preclude the major part of the Ni to report to the alloy in the smelting step. It is hereby assumed that CO and CO₂ are in contact with the melt, thereby ensuring the control of the redox conditions.

15 The sequential order of the steps that define the oxidizing Ox level and of preparing the metallurgical charge is uncritical as long as the appropriate conditions of the formulae are met.

The oxidizing level of the step is defined by the parameter Ox, i.e., the pCO₂
20 to (pCO+pCO₂) ratio. In practice, this level will result in a major part of the Ni reporting to the alloy. The residual Ni will report to the slag, amounting to a concentration of more than 0.5% by weight, preferably of more than 1%.

According to the above embodiments, the oxidizing operating conditions
25 result in the full oxidation of at least part of the C to CO₂, producing the necessary energy to melt the charge. Thanks to this oxidative smelting step, pyrolyzed battery with carbon content can be processed.

Optionally, applying the formulae for the smelting step shown above leads
30 to an autogenous charge, which means that the step of oxidizing smelting can be performed by making use of the energy contained in the waste batteries. No extra energy needs to be added, nor as fuel, cokes, or other

carbon source, nor as reactive compound in the rest of the metallurgical charge. Nonetheless, in this case, additional heat may still be provided by using cokes or other carbon source, in particular fuel or gas, which may be provided by submerged injection mixed with an O₂-bearing gas. To achieve
5 autogenous smelting, a minimum amount of 3 weight percent, in particular 5 weight percent of aluminum should be contained in the entire pyrolyzed batteries. If the aluminum content in the pyrolyzed batteries is too low, aluminum can be added; for example, waste batteries with a higher aluminum content, such as cells and modules, can be combined with the pyrolyzed
10 batteries.

In an embodiment, the smelting process can be run under conditions wherein the smelting step yields a lithium-containing slag exhibiting a content of MnO of 10% to 50% or more, or 20% to 40% or more, based on the weight of the
15 total amount of slag. It has been observed that amounts of MnO in the specified range in the slag suppress MgO dissolution into the slag from magnesia-bearing refractory bricks lining the furnace. Having at least 20% of MnO in the slag fully shows the effect of suppressing MgO dissolution. The upper limit of 50% MnO in the slag helps to keep the melting point of the slag sufficiently
20 low. Having at most 40% of MnO in the slag is preferred.

In another embodiment, the smelting process can be run under conditions wherein the smelting step yields a lithium-containing slag exhibiting a content of P₂O₅ of from 0,5% to 10%. Phosphorus typically originates from electrolytes in the Li-ion batteries and reports to the slag as P₂O₅. Lithium iron phosphate (LFP) batteries typically contain more phosphorous than NMC batteries,
25 but no cobalt and nickel. In an industrial setup, recyclers may have to deal with charges that contain such LFP batteries mixed with NMC batteries, which would contribute to the overall content of phosphorus in the slag.

In yet another embodiment, the smelting process can be run under conditions
30 wherein the smelting step comprises addition of calcium oxide and alumina and wherein the $(\text{CaO} + 0.4\text{MnO})/\text{Al}_2\text{O}_3$ ratio is above 0.25. This helps to keep the melting point of the slag sufficiently low.

The present method has the technical effect of reducing the amount of slag generated, it will reduce the amount of heat generation and it will suppress the undesirable intense evulsion of gases during the smelting step. In addition, metallic aluminum can be directly recovered as metal without loss of
5 nickel and cobalt.

Examples

Example 1

As waste batteries, spent Li-ion batteries were processed by using the py-
10 rolysis method described in JP6840512B2. Casing material for battery module and cell inside the module are aluminum. Thus, they were melted off and separated from other constituents of battery.

By applying this pyrolysis process, it was confirmed that all of electrolyte and plastics contained in the battery pack were evaporated or oxidized to
15 CO or CO₂ gas and 70 % of total aluminum melted off. No loss of nickel and cobalt was observed during the pyrolysis. The composition of solid battery residue after the heat treatment is shown in table 1.

500 kg of such residue after pyrolysis was fed to a furnace with a diameter
20 of 1 m, lined with chrome-magnesia refractory bricks. 42 kg of limestone were added together with the solid residue. The amount of limestone was chosen to achieve $(\text{CaO}+0.4\text{MnO}/\text{Al}_2\text{O}_3) = 0.74$.

A bath temperature of 1500-1550°C was maintained, which is suitable to maintain both the slag and the alloy sufficiently fluid for easy tapping and
25 handling. The heat was supplied by the oxidation of aluminum and C in the solid residue, using submerged O₂ injection. The injection rate was chosen to guarantee strongly reducing conditions, i.e. pO₂ of 10⁻⁹. Natural gas was added to maintain burner flame temperature above bath temperature.

After 1 h of heating, the produced alloy and slag were separated by tapping.
30 Table 1 shows the analyses of the input and output phases of the process. During processing, small quantities of materials were captured as fume.

Table 1: Input and output phases of the process

Input	Mass (kg)	Composition (%)								
		Ni	Co	Cu	SiO ₂	CaO	Al (Al ₂ O ₃)	Li (Li ₂ O)	Mn (MnO)	C
Battery residue	500	13.9	7.3	9.9	-	-	6.0	3.7	7.8	29.3
Lime-stone	42	-	-	-	4.8	53.3	-	-	-	11.4
Output										
Alloy	155	44.7	22.9	31.3	-	-	-	-	1.1	-
Slag 1	171	0.2	0.8	0.6	1.2	13.0	(32.5)	(22.7)	(27.9)	-

5 **Comparative example 2**

Same battery as one in example 1 was used, although it was fed directly to smelter without pyrolysis. 500 kg of spent Li-ion battery modules were fed to a furnace with a diameter of 1 m, lined with chrome-magnesia refractory bricks. 100 kg of limestone were added together with the battery.

The amount of limestone was chosen to achieve $(\text{CaO}+0.4\text{MnO})/\text{Al}_2\text{O}_3 = 0.51$.

A bath temperature varied between 1450-1600°C due to the intense heat generation by oxidation of aluminum. The heat was supplied by the oxidation of aluminum and C in the battery, using submerged O₂ injection. The injection rate was chosen to maintain a pO₂ of 10⁻⁹. Natural gas was added to maintain burner flame temperature above bath temperature.

Flame from feed port was often observed as the intense release of explosive gas due to oxidation of remaining plastic and electrolyte in battery led to overpressure inside the furnace.

After 1 h of heating, the produced alloy and slag were separated by tapping. Table 2 shows the analyses of the input and output phases of the process. During processing, small quantities of materials were captured as fume.

Table 2: Input and output phases of the process

Input	Mass (kg)	Composition (%)								
		Ni	Co	Cu	SiO ₂	CaO	Al (Al ₂ O ₃)	Li (Li ₂ O)	Mn (MnO)	C
Batter-ies	500	9.9	5.3	6.8	-	-	14.1	2.8	5.7	24.8
Lime-stone	100	-	-	-	4.8	53.3	-	-	-	11.4
Output										
Alloy	108	45.7	23.3	30.5	-	-	-	-	0.5	-
Slag 2	260	0.1	0.4	0.3	1.8	20.3	(50.8)	(11.7)	(13.6)	-

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- Conclusion: The weight ratio of produced slag over alloy is 1.1 for example 1 and 2.4 for example 2. 2.2 times larger weight of slag was produced in order to produce same weight of alloy by processing spent Li-ion battery. In addition, it was more difficult to maintain smelting temperature during smelting
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- example 2, whereas temperature control was easily carried out due to less aluminum content in feed in example 1. In smelting step of example 2, flame from feed port was often observed as the intense release of explosive gas due to oxidation of remaining plastic and electrolyte in battery led to over-pressure inside the furnace, whereas no flame was visible in smelting step of
- 15
- example 1.

Claims

1. Method of recovering valuable metals from waste batteries comprising the steps of -a pyrolysis step comprising pyrolysis of the waste batteries at a temperature of from about 700°C to about 1050°C, obtaining
5 pyrolyzed batteries; -a size reduction step, comprising size reduction of the pyrolyzed batteries; -a smelting step, comprising smelting the pyrolyzed, size reduced waste batteries at temperatures of 1350°C or higher under oxidizing conditions, wherein in the smelting step a metallurgical charge comprising slag formers and the pyrolyzed, size reduced waste batteries containing Co, Ni, metallic Al, and C, and are
10 subjected to a process comprising the steps of:
- providing a metallurgical smelting furnace equipped with means for the submerged injection of an O₂-bearing gas;
 - defining an oxidizing level Ox characterizing oxidizing smelting
15 conditions according to the formula:
$$Ox = pCO_2 / (pCO + pCO_2),$$

wherein $0.1 < Ox < 1$, pCO and pCO₂ are the partial pressures of CO and CO₂ in contact with the melt;
 - preparing the metallurgical charge;
 - 20 - oxidizing smelting the metallurgical charge by injecting an O₂-bearing gas into the melt to reach the defined oxidizing level Ox, thereby obtaining a first alloy with a major part of Ni, and a slag containing residual Ni and Co;
 - liquid/liquid separation of the alloy from the slag.
- 25 2. The method of claim 1, wherein pieces of pyrolyzed, size reduced waste batteries exhibit a diameter of not more than 20 cm and/or the loss of nickel and cobalt metal before the smelting step is less than 2 weight percent.
- 30 3. The method of claim 1 or 2, wherein during the pyrolysis step air is fed.

4. The method of any of the preceding claims, wherein the pyrolyzed, size reduced waste batteries are packed, in particular into paper, plastic or combinations thereof.
- 5 5. The method of any of the preceding claims, wherein the pyrolyzed, size reduced waste batteries are subjected to extraction of lithium with an aqueous solvent.
6. The method of any of the preceding claims, wherein the smelting step yields a lithium-containing slag exhibiting a content of MnO of 10% to 50%, based on the weight of the total amount of slag.
- 10 7. The method of any of the preceding claims, wherein the smelting step yields a lithium-containing slag exhibiting a content of P_2O_5 of from 0,5 weight-% to 10 weight-%.
8. The method of any of the preceding claims, wherein the smelting step comprises addition of calcium oxide and alumina and wherein the $(CaO + 0.4MnO)/Al_2O_3$ ratio is above 0.25.
- 15 9. The method of claim 1, wherein slag formers are selected from the group consisting of CaO, Al_2O_3 , SiO_2 and combinations thereof.
10. The method of any of the preceding claims, further comprising a steps of: - subjecting the pyrolyzed, size-reduced waste batteries with an aqueous solvent, thereby extracting lithium; - applying solid-liquid separation.
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