The article entitled "Acid leaching of mixed spent Li-ion batteries" by Nayl et al, Arabian Journal of Chemistry, 2017, 10, S3632-S3639 also describes a leaching method for lithium batteries, in which diluted sulphuric acid and hydrogen peroxide are used. It has been found that the degree of leaching initially increases with an increasing concentration of sulphuric acid and then declines from 3 M. The highest examined concentration is 4 M.

Summary

According to a first aspect, the present disclosure refers to a method for recycling lithium batteries containing the steps:

(a) digesting comminuted material, which contains comminuted components of electrodes of lithium batteries, using concentrated sulphuric acid at a digestion temperature (T_A) of at least 100°C, in particular at least 140°C, so that hydrogen fluoride containing waste gas and a digestion material are produced,

(b) discharging the waste gas and

(c) the wet chemical extraction of at least one metallic component of the digestion material.

According to another aspect, the present disclosure refers to a recycling installation for processing lithium batteries with

(a) a comminution unit for comminuting the lithium batteries such that shredded material is obtained,

(b) a deactivation unit for deactivating the batteries such that shredded material is obtained,

(c) a reactor, especially a heated forced action mixer or rotary kiln, for digesting comminuted material, which contains components of electrodes of the lithium batteries, with concentrated sulphuric acid at a digestion temperature (T_A) of at least 100°C,

(d) a sulphuric acid supply device for adding sulphuric acid to the comminuted material and

(e) a discharge device which is arranged to discharge waste gas out of the reactor and is hydrogen fluoride-proof.

Patent claims

1. A method for recycling lithium batteries containing the steps:

(a) digesting comminuted material, which contains comminuted components of electrodes of lithium batteries, using concentrated sulphuric acid at a digestion temperature (T_A) of at least 100°C, in particular at least 140°C, so that hydrogen fluoride containing waste gas and a digestion material are produced,

(b) discharging the waste gas and

(c) the wet chemical extraction of at least one metallic component of the digestion material.

2. The method according to claim 1, characterized in that the comminuted material has not been subjected to calcination or combustion.

3. The method according to claim 1, characterized in that the digestion of the comminuted material comprises the following steps:

(a) mixing concentrated sulphuric acid and comminuted material, resulting in a mixture,

(b) detecting a mixture temperature (TM) of the mixture and

(c) controlling or regulating

(i) a dosage mass flow (q_m) of the sulphuric acid and/or

(ii) an addition mass flow (q_{10}) of the comminuted material,

so that the mixture temperature (T_M) remains within a predetermined mixture temperature range (I).

4. The method according to claim 1, characterized in that the digestion of the comminuted material comprises the following steps:

(a) dosing concentrated sulphuric acid to the comminuted material with a dosage mass flow (q_m) so that the mixture is created,

(b) detecting the mixture temperature (T_M) of the mixture and

(c) regulating the dosage mass flow (q_m) so that the mixture temperature (T_M) remains within the predetermined mixture temperature range (I).

5. The method according to one of the preceding claims, characterized by the steps:

(a) leaching the digestion material, especially with an aqueous fluid, and

(b) prior to the wet chemical extraction of at least one metallic component of the digestion material, particularly following the leaching of the digestion material, conducting an ion exchange during which metallic impurities, especially zinc and/or copper and/or iron and/or aluminium, are removed.

6. The method according to one of the preceding claims, characterized by the step: prior to the wet chemical extraction of at least one metallic component of the digestion material, particularly following the leaching of the digestion material, conducting an ion exchange during which cobalt and/or nickel and/or manganese and/or lithium are not removed.

7. The method according to one of the preceding claims, characterized by the step:
prior to the wet chemical extraction of at least one metallic component of the digestion material, particularly following the leaching of the digestion material, absorbing organic components, particularly by means of activated carbon.

8. The method according to one of the preceding claims, characterized by the steps:

(a) separating, especially filtering out, graphite, thereby producing a raw fluid, and

(b) purifying the graphite so that the content of non-metallic impurities, especially binders and silicon, is reduced.

9. The method according to claim 7, characterized in that purification comprises a heating to a decomposition temperature T_Z of the binder of at least 250°C and/or at most 700°C, in particular at most 430°C.

10. The method according to claim 8, characterized in that heating occurs

(a) under an oxidizing atmosphere,

(b) a inert atmosphere or

(c) a reducing atmosphere.

11. The method according to claim 7 or 8, characterized by the steps:

(a) classifying the graphite so that

at least one fine fraction and one coarse fraction are obtained,

wherein a binder content of binder in the fine fraction is at least twice as large as in the coarse fraction and/or

(b) floating the graphite or the binder, particularly in an aqueous flotation fluid.

12. The method according to one of the claims 7 to 10, characterized in that the purification comprises dissolving a binder out of the graphite using a solvent.

13. The method according to one of the claims 7 to 11, characterized in that

(a) purification comprises a rinsing and/or washing with acid, in particular sulphuric acid, and

(b) purification is carried out until a concentration of metallic impurities is at most 10 000 ppm.

14. The method according to one of the claims 7 to 12, characterized in that

(a) purification comprises a leaching and/or washing with an oxidation agent, and

(b) purification is carried out until a concentration of metallic impurities is at most 10 000 ppm.

15. The method according to one of the preceding claims, characterized by the step:

(a) separating copper from the raw fluid, so that a de-copperized raw fluid is obtained,

(b) wherein the ion exchange is conducted after the copper has been separated.

16. The method according to one of the preceding claims, characterized by the steps:

(a) removing, especially solvent extraction, of cobalt by means of a cobalt complexing agent, and/or

(b) removing nickel, especially solvent extraction of nickel, by means of a nickel complexing agent, and/or

(c) removing manganese, especially solvent extraction of manganese, by means of a manganese complexing agent,

so that a target fluid is obtained.

17. The method according to one of the preceding claims, characterized in that during wet chemical extraction

(a) manganese is extracted before cobalt and/or

(b) cobalt is extracted before nickel.

18. The method according to one of the preceding claims 15 to 16, characterized in that the removal of nickel comprises a precipitation of alkaline nickel carbonate from the pure fluid.

19. The method according to one of the preceding claims 15 to 17, characterized by the step: extracting lithium by means of solvent extraction from the target fluid, particularly by means of a lithium complexing agent.

20. The method according to one of the preceding claims, characterized by the step: following comminution, heating the comminuted material to an electrolyte removal temperature (T_E) of over 80°C, so that electrolyte in the comminuted material evaporates.

21. A recycling installation for processing lithium batteries with

(a) a comminution unit for comminuting the lithium batteries such that shredded material is obtained,

(b) a deactivation unit for deactivating the batteries such that shredded material is obtained,

(c) a reactor, especially a heated forced action mixer or rotary kiln, for digesting comminuted material, which contains components of electrodes of the lithium batteries, with concentrated sulphuric acid at a digestion temperature (T_A) of at least 100°C,

(d) a sulphuric acid supply device for adding sulphuric acid to the comminuted material and

(e) a discharge device which is arranged to discharge waste gas out of the reactor and is hydrogen fluoride-proof.

22. A recycling installation according to claim 20, characterized by

(a) a dosing device for dosing a dosage mass flow (q_m) of concentrated sulphuric acid to the comminuted material so that the mixture is created, and
a mixture temperature detection device for detecting a mixture temperature (T_M) of the mixture,
wherein the dosing device is configured to regulate or control the dosage mass flow (q_m), so that the mixture temperature (T_M) remains within a predetermined mixture temperature range (I), and/or

(b) a conveyor for adding comminuted material to the sulphuric acid, and
a mixture temperature detection device for detecting a mixture temperature (T_M) of the mixture,
wherein the conveyor is configured to regulate or control an addition mass flow (q_m), so that the mixture temperature (T_M) remains within a predetermined mixture temperature range (I).

23. A recycling installation according to claim 21, characterized by

(a) a precipitation material separator for separating, especially filtering out, precipitated Cu or Cu compounds and/or

(b) a Fe/Al/Ti precipitation material separator for separating, especially filtering out, precipitated iron and/or aluminium and/or titanium compounds.

24. A recycling installation according to claim 21, characterized by a transition metal extraction device for

(a) removing cobalt and/or

(b) removing nickel and/or

(c) removing manganese

from a pure fluid, so that a target fluid is obtained.

25. A recycling installation according to claim 23, characterized in that the transition metal extraction device comprises a solvent extraction device for

(i) the solvent extraction of cobalt, especially from the pure fluid, especially by means of a cobalt complexing agent, and/or

(ii) the solvent extraction of nickel, especially from the pure fluid, especially by means of a nickel complexing agent, and/or

(iii) the removal of manganese, especially from the pure fluid, particularly the solvent extraction of manganese by means of a manganese complexing agent, which is arranged behind the graphite separation device in the direction of material flow (M).

26. The recycling installation according to one of the claims 20 to 24, characterized by

a graphite purification installation for reducing a content of binder on the graphite which comprises

(a) a classifier for classifying the graphite, so that
at least one fine fraction and one coarse fraction are obtained,
wherein a binder content of binder in the fine fraction is at least twice as large as in the coarse fraction and/or

(b) a washer for dissolving the binder out of the graphite using a solvent and/or

(c) a leaching reactor for purifying the graphite through rinsing and/or washing with acid, especially sulphuric acid, and/or an oxidation agent.