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(54) **PROCESS FOR RECOVERING COMPONENTS FROM ALKALINE BATTERIES**

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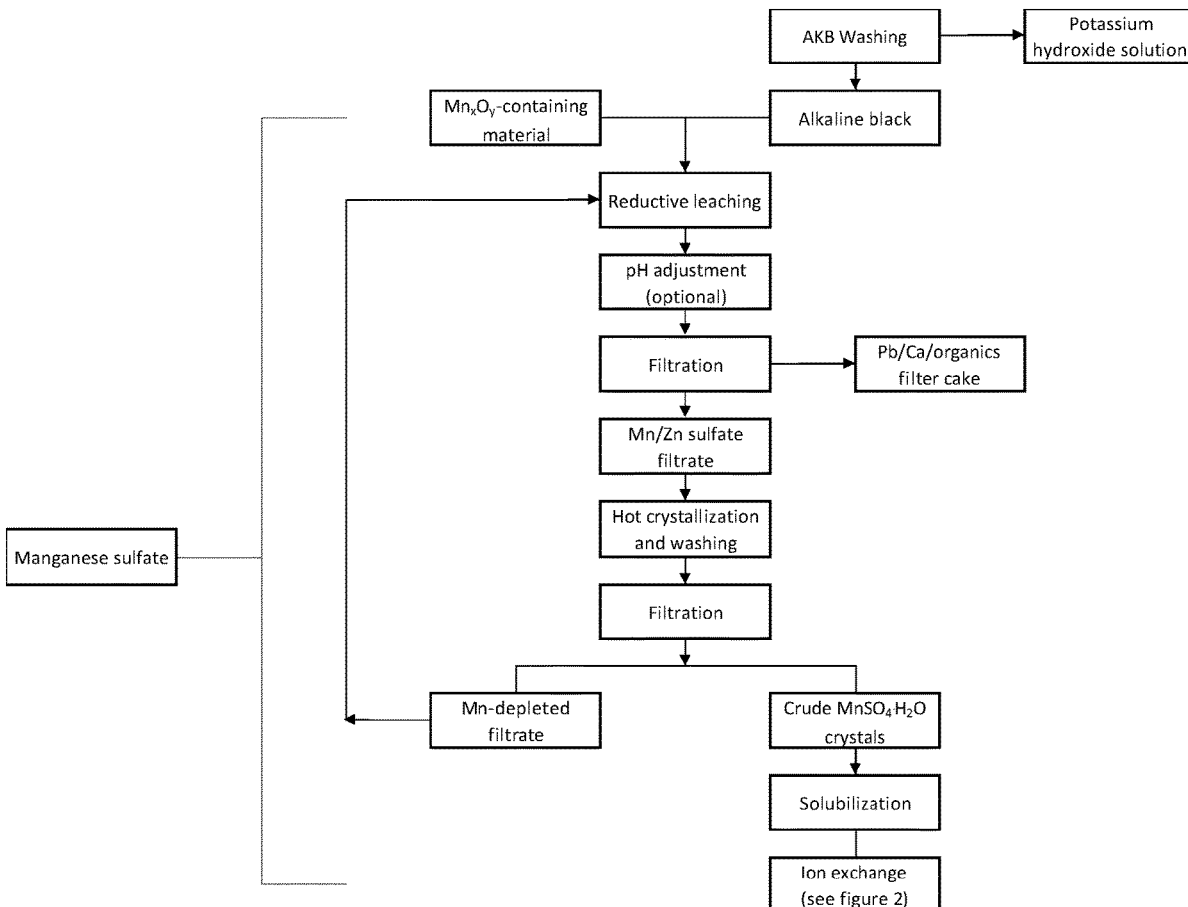
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(57) **ABSTRACT**

The present invention relates to separation and recovery of metals from ground alkaline batteries using anode mud (zinc electrolysis waste) and other manganese and zinc containing materials. The material commonly referred to as alkaline black (AKB) is solubilized into sulfate media and the manganese to zinc ratio is adjusted. The solution containing metals is processed using crystallization and ion exchange methods to produce manganese sulfate and zinc sulfate solutions for several possible applications.



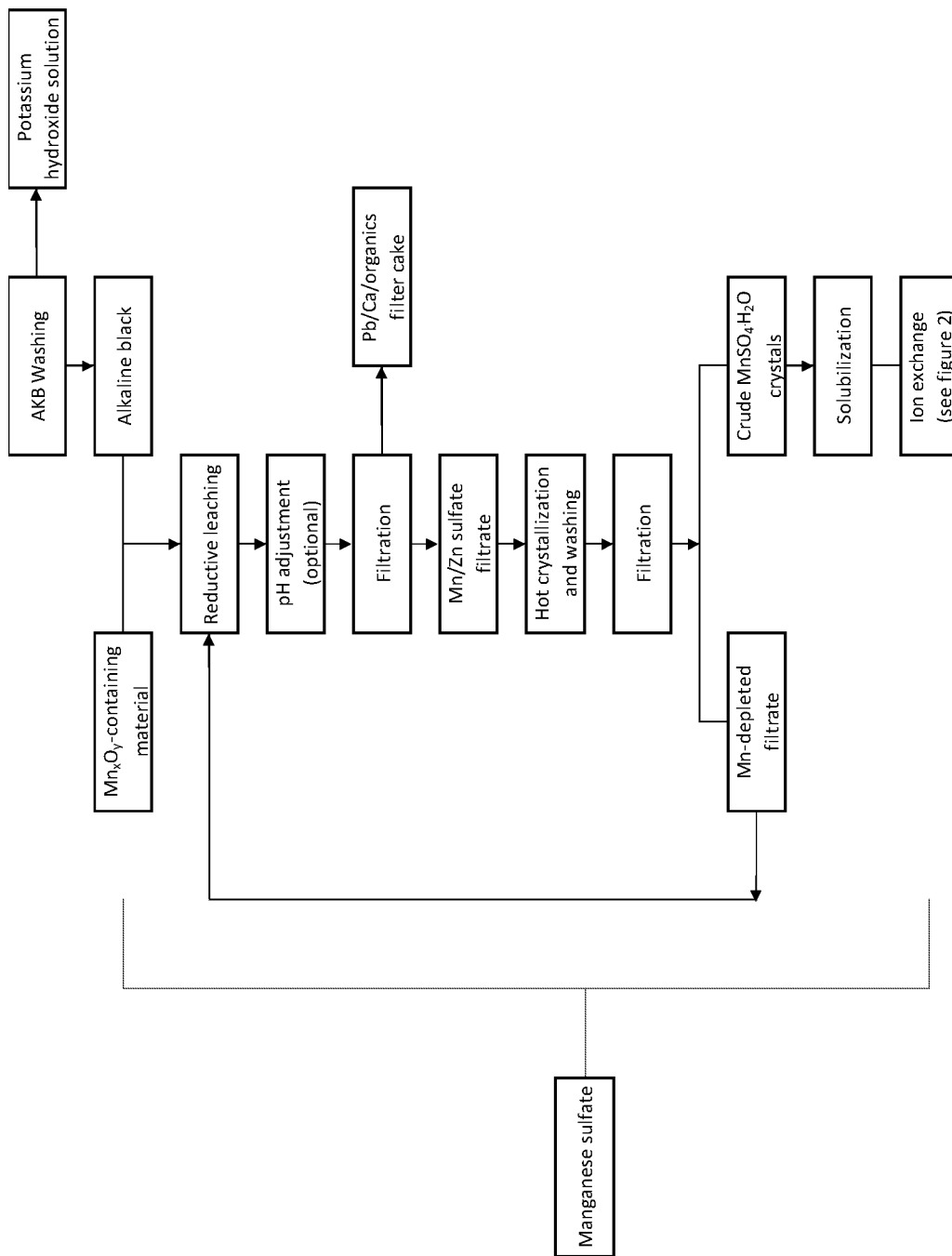


Figure 1.

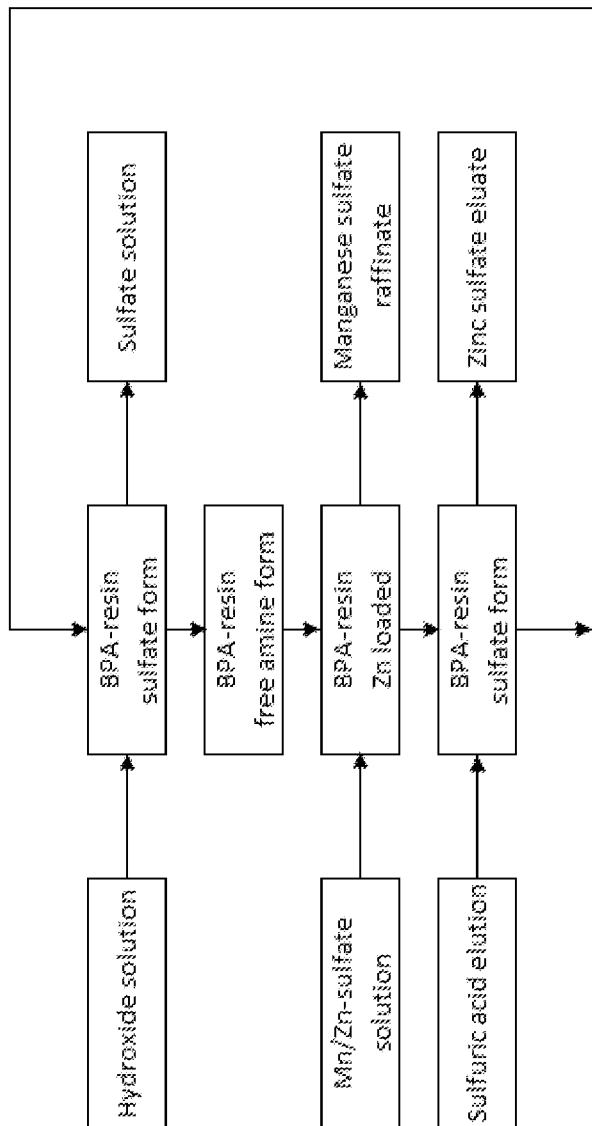


Figure 2.

PROCESS FOR RECOVERING COMPONENTS FROM ALKALINE BATTERIES

FIELD OF THE INVENTION

[0001] The present invention relates to separation and recovery of metals from ground alkaline batteries using anode mud (zinc electrolysis waste) and other manganese and zinc containing materials. The material commonly referred to as alkaline black (AKB) is solubilized into sulfate media, and the manganese to zinc ratio is adjusted. The solution containing metals is then processed using crystallization and ion exchange methods to produce manganese sulfate and zinc sulfate solutions for several possible applications.

BACKGROUND OF THE INVENTION

[0002] Electrification of transport is increasing power storage requirements by volumes and by capacity. Electricity for e.g. electric vehicles is stored in Li-ion batteries, which typically contain lithium, manganese, nickel and cobalt. These metals are currently coming from primary sources, i.e. mining, which are energy intensive and natural resource exhaustive processes. With increased demand for battery metals, the importance of secondary sources for these elements is increasing. Efficient utilisation of secondary metal sources allows cost and energy efficient production of battery metals salts, at the same time saving natural resources. For manganese, there are several secondary sources available.

[0003] A large secondary source for manganese comes from the recycling process of zinc-manganese dioxide batteries, i.e. alkaline batteries. "Black mass" from alkaline batteries (alkaline black, AKB) is generated by crushing the batteries and sieving the resulting material to separate the casing and organics from the cathode and anode material. Currently metals from black mass are recovered by pyrometallurgical routes (smelting) or by combination of thermal and hydrometallurgical treatments. Hydrometallurgical routes typically involve selective solvent extractions and precipitations. According to an international patent application, WO2013124399A1, alkaline black is first washed with water to separate potassium as a hydroxide solution. Then the alkaline black is reduced with hydrogen gas, followed by an ammonia leaching step which selectively leaches zinc from the material. The ammonia is evaporated, and zinc is recovered as a hydroxide filter cake. The zinc-depleted alkaline black then undergoes a reductive leach with sulfuric and citric acid, which dissolves manganese as manganese sulfate, which is then separated by filtration. The filtrate is then mixed with sodium carbonate to precipitate manganese as manganese carbonate and separated from the sodium sulfate wastewater by filtration.

[0004] In the final stage of the zinc refining process, electrolysis, impurities are deposited as solid waste in the vicinity of the anode. This mass is called anode mud (AM) and is removed frequently from the process. Main components of the anode mud are manganese, lead, zinc and minor amounts of other elements such as iron and calcium. Anode mud is classified as hazardous and needs to be landfilled securely. Current utilisation routes typically are based on pyrometallurgy. In hydrometallurgical routes metals can be recovered from anode mud by dissolving with sulfuric acid,

separating lead sulfate and other main impurities as solid residue and purifying dissolved manganese sulfate with further hydrometallurgical steps.

[0005] In a study published 2019 in Journal of Cleaner Production, S. Lannoo et al. describe a process in which ion exchange resins have been used to separate zinc traces from highly concentrated manganese liquor, which was obtained from a solvent exchange process.

[0006] FI127830 discloses a method for preprocessing an alkaline black mass of spent alkaline batteries. The pre-processed alkaline black mass is meant for a leaching process to recover one or more metals from preprocessed alkaline black mass. The invention also relates to a method, device and system for processing a black mass of spent alkaline batteries. In this process, the alkaline black is first calcined to remove graphite and organics, and then the resulting material is leached with sulfuric and citric acid. Impurities are filtered, and the resulting manganese and zinc sulfate solution, containing citric acid, is either used as such as a fertilizer, or zinc is separated as hydroxide by precipitation and filtration.

[0007] In the process according to the present invention the expensive solvent exchange step is avoided by dissolving AKB directly with sulfuric acid to obtain manganese and zinc rich filtrate. The calcination process is also avoided, which results in a lower CO₂-impact as well as the possibility of reusing the graphite. By using ion exchange as a manganese and zinc separation method, filtration steps are also avoided. The manganese to zinc ratio is adjusted with other manganese-containing materials, so that the final ratio is in favour of manganese, for example using anode mud. These liquors are then subjected to a hot crystallization method and an ion exchange process to separate manganese and zinc by capturing zinc with a chelating ion exchange resin and leaving purified manganese sulfate solution. The raffinate containing manganese sulfate is then drained from the column and zinc can be eluted from the resin. Additionally, it is discovered that by preconditioning the ion exchange resin using a hydroxide solution, zinc binding is enhanced.

SUMMARY OF THE INVENTION

[0008] The method for recovering metals from ground alkaline batteries according to the present invention comprises the steps of (a) selectively leaching under reductive conditions manganese and zinc from alkaline black by mixing the alkaline black and a manganese oxide containing material and/or manganese sulfate with a sulfuric acid solution at a leaching temperature of 15-40° C., for 1-5 hours to obtain a mixture; (b) filtering the mixture to obtain a manganese and zinc sulfate filtrate and a Pb/Ca/organics as a filter cake; (c) heating the manganese and zinc sulfate filtrate to a crystallization temperature of 70-100° C. and keeping the crystallization temperature under reflux cooling for at least 30 minutes to precipitate manganese in a form of sulfate crystals; (d) filtrating the sulfate crystals and obtaining a manganese depleted filtrate and finally; (e) solubilizing the sulfate crystals in water to obtain a sulfate solution and separating manganese and zinc by a chelating ion exchange.

[0009] The reductive conditions in the selective leaching step (step a) can be obtained by adding a reducing agent such as hydrogen peroxide or sulfur dioxide during the mixing until manganese and zinc are dissolved.

[0010] According to one embodiment the manganese oxide containing material is manganese dioxide (MnO_2) such as anode mud. In another embodiment the manganese oxide containing material is manganese trioxide.

[0011] According to an embodiment of the recovering method of the present invention the manganese and zinc sulfate filtrate obtained in the filtering step (step b) has a manganese to zinc ratio (Mn:Zn-ratio) between 10:1 and 3.6:1.

[0012] In another embodiment the manganese and zinc sulfate filtrate obtained in the filtering step (step b) has a manganese to zinc ratio (Mn:Zn-ratio) between 7:1 and 5:1.

[0013] According to the present invention manganese sulfate can be added in a stage preceding the chelating ion exchange to adjust the manganese to zinc ratio.

[0014] If the feed manganese materials contain impurities that precipitate at neutral pH, the pH of the mixture to be filtered in the filtering step (step b) is adjusted to be between 1.5 and 7. The pH can be adjusted upwards with a hydroxide solution such as NH_4OH , NaOH or KOH, or downwards with sulfuric acid preceding the mentioned filtering step (step b).

[0015] According to another embodiment the pH adjustment can be done in any stage preceding the chelating ion exchange in step (e). Thus, the sulfate solution, wherefrom manganese and zinc are separated by a chelating ion exchange, has a pH between 1.5 and 7 before entering the ion exchange stage. The pH can be adjusted upwards with a hydroxide solution such as NH_4OH , NaOH or KOH, or downwards with sulfuric acid.

[0016] The alkaline black can be washed before the selective leaching step (step a) by mixing the alkaline black with water at a temperature between 5° C. and 100° C. for at least 30 min. According to one embodiment the alkaline black is mixed with water at a temperature between 20° C. and 25° C. In one embodiment the alkaline black is washed by mixing it with water for 1-2 hours.

[0017] In the method for recovering according to the present invention the manganese depleted filtrate obtained from the filtrating of the sulfate crystals (step d) can be returned to the leaching step (step a).

[0018] According to one embodiment of the present invention a BPA-resin in sulfate form is used in the chelating ion exchange step. The BPA-resin can be preconditioned with ammonium, sodium or potassium hydroxide.

BRIEF DESCRIPTION OF THE DRAWINGS

[0019] FIG. 1. A schematic flow chart of a method according to the present invention for recovering components from alkaline batteries

[0020] FIG. 2. A schematic flow chart of an ion exchange cycle according to the present invention

DEFINITIONS

[0021] AKB means alkaline black i.e. crushed alkaline batteries.

[0022] AM means anode mud that is generated as waste in zinc electrolysis.

[0023] BPA is bis-picoyl amine that is used e.g. as an ion-exchange resin.

[0024] DC means dry content.

[0025] ICP-MS means Inductively Coupled Plasma Mass Spectrometer.

[0026] IEX cycle means the full ion exchange process, including preconditioning, loading, elution and regeneration.

[0027] Mn_xO_y -containing material i.e. manganese oxide containing material, which can be e.g. anode mud or manganese trioxide.

[0028] MP-AES means Microwave Plasma Atomic Emission Spectrometer.

[0029] Room temperature (RT) means temperature, which is in the range of 20° C. and 25° C.

DETAILED DESCRIPTION OF THE INVENTION

[0030] Typically, alkaline black (AKB) is expected to contain 20-40 wt % of graphite and organics that are burned off when calcinating at a temperature greater than 600° C. The calcinated AKB is expected to contain 30-45 wt % zinc oxide, 25-30 wt % manganese oxide and 7-12 wt % potassium hydroxide. It also contains less than 1 wt % of other impurities such as iron, calcium and magnesium also in the form of oxides. The rest can be assumed to be oxygen in the form of metal oxides, as well as moisture. Alkaline mud (AM) contains manganese, zinc and lead in the form of oxides and calcium in the form of sulfate. AM is expected to contain between 25-40 wt % water. In the dry form, AM is expected to contain 30-40 wt % manganese, 3-6 wt % lead, 2-4 wt % calcium and 0.5-1 wt % zinc in the form of oxides. It also contains less than 0.2 wt % of other elements such as iron and magnesium. The rest can be assumed to be oxygen in the form of oxides, as well as moisture.

[0031] The process is now described in detail referring to the schematic flow charts of FIGS. 1 and 2.

[0032] According to the present invention alkaline black can be washed with water (AKB Washing) as an optional pre-step of the recovery process. The wash is done if the manganese sulfate obtained as an end product in the process cannot contain potassium. During this optional washing step potassium hydroxide (KOH) is solubilized from alkaline black when mixing AKB with water at a temperature between 5° C. and 100° C., preferably at a temperature between 20° C. and 25° C. for at least 30 min, preferably 1-2 hours. Washed AKB is then separated from the wash water by filtration, and the wash water (Potassium hydroxide solution) can be reused for washing another batch of AKB. It is possible to circulate this wash water to the following batch to increase the KOH-concentration depending on the final use of the potassium hydroxide solution, such as crystallization.

[0033] The AKB washing step is optional and alkaline black can also be used as such.

[0034] In the first step (step a) of the recovery process according to the invention, manganese and zinc are selectively leached (Reductive leaching) from AKB by mixing AKB and manganese oxide containing material (Mn_xO_y -containing material), e.g. anode mud or manganese trioxide (Mn_2O_3) and/or manganese sulfate, with sulfuric acid solution. The manganese concentration of the resulting filtrate is 100-180 g/l, preferably 140-150 g/l and zinc concentration is 10-50 g/l, preferably 20-30 g/l. The filtrate has a density of 1.38-1.47 g/l, preferably 1.4-1.45 g/l. Thus, the manganese to zinc ratio (Mn:Zn-ratio) is 10:1-3.6:1, preferably 7:1-5:1. A reducing agent such as hydrogen peroxide or sulfur dioxide is added during the mixing until manganese and zinc are dissolved. This can be determined by measuring

the redox potential of the solution. The mixture is kept at 15-40° C., preferably at 20-30° C., during the mixing and the mixing is continued for 1-5 hours, preferably 2-3 hours.

[0035] Then in the second step (step b) the mixture is filtered obtaining a manganese and zinc sulfate solution as a filtrate (Mn/Zn sulfate filtrate) with a pH of 1.5-7, preferably 2-6, and a Pb/Ca/organics as a filter cake. The Pb/Ca/organics filter cake can be used in graphite production as a raw material, or used in a lead smelter to recover lead.

[0036] If pH is not in the correct area, it can be adjusted, optionally, upwards with a hydroxide solution such as NH₄OH, NaOH or KOH, or downwards with sulfuric acid. The pH adjustment is done to ensure that the pH is correct for ion exchange, as well as to precipitate impurities present in the feed material. pH adjustment can be done in any step before ion exchange. In an embodiment, the pH adjustment may be done before filtration of the Pb/Ca/organics-residue, i.e. prior to step (b). This may be advantageous, when the feed manganese materials contain impurities that precipitate at neutral pH.

[0037] In the following step of the recovery process according to the invention (step c), the manganese and zinc sulfate filtrate is heated in a method referred to as hot crystallization and washing which precipitates manganese in the form of sulfate crystals (Crude MnSO₄·H₂O crystals). During this step the mixture is heated to 70-100° C., preferably to 80-100° C., and kept at the required temperature for at least 30 minutes, preferably 1-2 hours, under reflux cooling to avoid water vaporization, which could lead to impurities precipitating into the crystals.

[0038] The crystals are then separated from the process liquid by filtration (step d), obtaining crude MnSO₄·H₂O crystals as a filter cake and Mn-depleted solution as a filtrate, which can be recycled to the reductive leaching step.

[0039] In the following step of the recovery process according to the invention (step e), the MnSO₄·H₂O crystals are solubilized in water to a desired concentration of manganese, preferably 80-100 g/l. Zinc is then separated from the manganese sulfate solution by chelating ion exchange (see FIG. 2.). The bis-picolyl amine resin (BPA-resin; sulfate form) is first preconditioned with ammonium, sodium or potassium hydroxide (Hydroxide solution) and an ammonium, sodium or potassium sulfate solution (Sulfate solution) is received as a product and the resin is transformed into a free amine form (BPA-resin; free amine form). Then the zinc-containing manganese sulfate (Mn/Zn-sulfate solution) is passed through the resin (BPA-resin; Zn loaded). A manganese sulfate raffinate is received as product. Zinc is eluted from the resin (BPA-resin; sulfate form) using a 10-30 wt-%, preferably 15-25%, sulfuric acid solution (Sulfuric acid elution), and a zinc sulfate eluate is received as a product. After zinc elution the resin is ready for another cycle starting with preconditioning.

[0040] According to one embodiment of the invention, other manganese dioxide is used instead of anode mud in the leaching step i.e. in the first step of the recovery process.

[0041] In another embodiment of the invention, manganese sulfate is added to increase manganese sulfate concentration in the process liquor in any step before ion exchange.

[0042] Next, the invention is described with reference to the following examples, which are not intended to limit the scope of the invention.

EXAMPLES

[0043] Metal compositions of alkaline black, anode mud, manganese oxide and manganese sulfate used in disclosed examples are presented in Table 1. Metal compositions of AKB (before and after washing), anode mud (AM), manganese trioxide (Mn₂O₃) and manganese sulfate (MnSO₄·H₂O) analysed with MP-AES and values given in mg/kg.

[0044] 150.76 g of alkaline black was slurried in 100 ml of water and was then left in stirring at room temperature for one and a half hours. After leaching solids were separated from liquid by filtration. The wash water was analysed with MP-AES (microwave plasma atomic emission spectrometer, Agilent Technologies) and is presented in Table 2. It is possible to circulate this wash water to the following batch to increase the KOH concentration.

TABLE 1

Metal compositions of AKB (before and after washing), anode mud (AM), manganese trioxide (Mn ₂ O ₃) and manganese sulfate (MnSO ₄ ·H ₂ O) analysed with MP-AES and values given in mg/kg.					
Element	AKB	AKB, washed	AM	Mn ₂ O ₃	MnSO ₄ ·H ₂ O
Ca	<5000	<5000	20 996	<5000	1 837
K	38 800	8 940	4 669	<5000	620
Mn	311 300	328 600	214 020	652 000	320 000
Pb	<200	<200	28 188	<200	<200
Zn	174 100	150 700	6 032	<5000	<500

TABLE 2

Composition of AKB wash water	
Element	mg/l
K	21 500
Mn	<5
Pb	23
Zn	<250

Example 1

[0045] 51.79 g of AM and 18.85 g of washed and dried AKB were mixed with 50 ml of water and 40 ml of 95 wt % sulfuric acid. 30 ml of 30 wt % H₂O₂ was added gradually during 2 hours, after which the mixture was left to dissolve at room temperature for half an hour. Mixture was filtered, and 130 ml of filtrate and 9.9 g of residue was recovered and analysed with MP-AES. As lead is difficult to measure with MP-AES when manganese is present in large quantities due to overlapping signals, lead was measured with ICP-MS to ensure it does not dissolve into the leachate. In following experiments, it is assumed lead does not dissolve in this step. Results are presented in Tables 3a and 3b.

TABLE 3a

Composition of the Mn/Zn sulfate filtrate	
Element	mg/l
Ca	<500
K	3 090
Mn	97 100

TABLE 3a-continued

Composition of the Mn/Zn sulfate filtrate	
Element	mg/l
Pb	<30
Zn	22 900

TABLE 3b

Composition of the residue i.e. Pb/Ca/organics filter cake.	
Element	mg/kg
Ca	32 100
K	612
Mn	8 480
Pb	43 400
Zn	4 040

[0046] 120 ml of filtrate from the previous step was heated to boiling under continuous mixing and reflux cooling. After 1 hour of boiling, mixture was filtered. The resulting crystals were left to dry at room temperature and analysed with MP-AES. Results are presented in Table 4.

TABLE 4

Composition of manganese sulfate crystals	
Element	mg/kg
Ca	<5 000
K	<500
Mn	235 000
Zn	19 100

[0047] 13 g of manganese sulfate crystals were dissolved in 40 ml water and pH was increased to 2.5 with 24 wt % NH_4OH . 10 ml of Lanxess MonoPlus TP220 (bis-picolyl amine functional group) was washed with 20 ml of 24 wt % NH_4OH and 20 ml of water. The manganese sulfate solution was passed through the resin. 20 ml of 20 wt % H_2SO_4 was used to extract zinc from the resin. Samples were analysed with MP-AES and results are presented in Table 5.

TABLE 5

Composition of the dissolved manganese sulfate liquor, raffinate and eluate.			
Element	Liquor	Raffinate	Eluate
Ca	<500	<500	<60
K	1 040	530	<60
Mn	39 710	27 320	30
Zn	4 900	<50	6 150

Example 2

[0048] 23.02 of washed AKB (DC 88.62%) and 13.03 g of a manganese trioxide (Mn_2O_3) was slurried in 55 ml of water and 20 ml of 95 wt % H_2SO_4 . 30 wt % H_2O_2 was added gradually for three and half hours without additional heating. pH of the mixture was adjusted from 4.74 to 5.50 with 2.11 g of $\text{Ca}(\text{OH})_2$ slurried in water after which the

mixture was filtered. 90 ml of filtrate was recovered, analysed with MP-AES and results are presented in Table 6.

TABLE 6

Composition of filtrate from leaching of AKB and manganese oxide after pH adjustment.	
Element	mg/l
Ca	<500
K	2 990
Mn	123 000
Zn	29 100

[0049] The filtrate from previous step was heated to boiling point. After the mixture started to form crystals the reaction was continued under reflux cooling for one hour. 15.24 g of crystals (DC 83.75%) was recovered by filtration using heated filtration equipment. Samples were analysed with MP-AES and results are presented in Table 7.

TABLE 7

Composition of dried manganese sulfate crystals from crystallization.	
Element	mg/l
Ca	<5 000
K	1 640
Mn	290 000
Zn	27 000

[0050] Crystals from previous step were dissolved in 50 ml of water forming a liquor with pH of 6.46 and volume of 52 ml. Prior to ion exchange, the resin was preconditioned with 40 ml of 10 wt % NH_4OH . The solution was circulated through 30 ml of bis-picolyl amine ion exchange resin for four hours. After ion exchange, 60 ml of raffinate was collected from the column. 40 ml of 20 wt % H_2SO_4 was used to extract zinc from the resin. Samples were analysed with MP-AES and results are presented in Table 8.

TABLE 8

Composition of the dissolved manganese sulfate crystals, the raffinate and eluate.			
Element	Liquor	Raffinate	Eluate
Ca	<500	<500	<500
K	392	210	<50
Mn	48 900	31 000	445
Zn	3 490	<50	3 600

Example 3

[0051] 22.72 of washed AKB (DC 93.56%) and 13.31 g of a manganese trioxide (Mn_2O_3) was slurried in 55 ml of water and 20 ml of 95 wt % H_2SO_4 . 25 ml of 30 wt % H_2O_2 was added gradually during three hours. After reductive leaching pH of the mixture was 2.27. Residual solids were removed from 92 ml of solution by filtration. Samples were analysed with MP-AES and results are presented in Table 9.

TABLE 9

Composition of AKB and manganese oxide leaching.	
Element	mg/l
Ca	<500
K	3 100
Mn	126 000
Zn	28 200

[0052] The filtrate from previous step was heated to boiling point and excess water was removed by means of evaporation. After the mixture started to form crystals the reaction was continued under reflux cooling for one hour. 29.97 g of crystals (DC 75.90%) was removed from 30 ml of mother liquor by filtration with heated filtration equipment. Samples were analysed with MP-AES and results are presented in Table 10.

TABLE 10

Composition of dried manganese sulfate crystals from crystallization.	
Element	mg/l
Ca	<5 000
K	2 730
Mn	284 000
Zn	45 600

[0053] Crystals from previous step were dissolved in 40 ml of water forming a liquor with pH of 3.28 and volume of 45 ml. Prior to ion exchange the resin was treated with 40 ml of 10 wt % NH_4OH . The solution was circulated through 30 ml of Lanxess MonoPlus TP220 for four hours. After ion exchange 52 ml of raffinate was collected from the column. 40 ml of 20 wt % H_2SO_4 was used to extract zinc from the resin and a series of elution samples was collected with volumes of 17 ml, 38 ml, 40 ml and 23 ml respectively. Samples are analysed with MP-AES and results are presented in Table 11.

TABLE 11

Composition of the dissolved manganese sulfate liquor, raffinate and eluates.						
Element	Liquor	Raffinate	Eluate 1	Eluate 2	Eluate 3	Eluate 4
Ca	<500	<500	<500	<500	<500	<500
K	655	469	<50	<50	<50	<50
Mn	72 400	49 000	25	68	14	<5
Zn	10 300	<50	3 570	8 350	1 540	<250

Example 4

[0054] 23.01 g of washed AKB (DC 88.62%) and 30.03 g of technical manganese sulfate hydrate were slurried in 80 ml of water and 10 ml of 95 wt % H_2SO_4 . 12 ml of 30 wt % H_2O_2 was added gradually during one hour. After reductive leaching pH of the mixture was adjusted from 2.61 to 5.58 with 2.18 g of $\text{Ca}(\text{OH})_2$ slurried in water. Residual solids were removed from 100 ml of solution by filtration. Samples were analysed with MP-AES and results are presented in Table 12.

TABLE 12

Composition of leachate from leaching of AKB in presence of technical grade manganese sulfate.	
Element	mg/l
Ca	<500
K	2 810
Mn	120 000
Zn	26 100

[0055] The filtrate from previous step was heated to boiling point, and after the mixture started to form crystals the reaction was continued under reflux cooling for one hour. 19.09 g of crystals (DC 81.88%) was removed from 49 ml of mother liquor by filtration with heated filtration equipment. Samples were analysed with MP-AES and results are presented in Table 13.

TABLE 13

Composition of dried manganese sulfate crystals from crystallization.	
Element	mg/l
Ca	<5000
K	1 480
Mn	287 000
Zn	24 800

[0056] Crystals from previous step were dissolved in 50 ml of water forming a solution with pH of 6.30 and volume of 55 ml. The solution was then circulated through 30 ml of Lanxess MonoPlus TP220 for four hours. Prior to ion exchange, the resin was preconditioned with 40 ml of 10 wt % NH_4OH . After ion exchange 63 ml of raffinate was collected from the column. 40 ml of 20 wt % H_2SO_4 was used to extract zinc from the resin and a series of elution samples was collected with volumes of 16 ml, 40 ml, 40 ml, and 45 ml respectively. Samples were analysed with MP-AES and results are presented in Table 14.

TABLE 14

Composition of the dissolved manganese sulfate liquor, raffinate and eluates.						
Element	Liquor	Raffinate	Eluate 1	Eluate 2	Eluate 3	Eluate 4
Ca	<500	<500	<500	<500	<500	<500
K	517	360	<50	<50	<50	<50
Mn	60 700	42 600	14	144	42	5
Zn	4 160	<50	<250	3 970	1 130	<250

Example 5

[0057] 22.05 of washed AKB (DC 93.56%) was slurried in 80 ml of water and 10 ml of 95 wt % H_2SO_4 . 12 ml of 30 wt % H_2O_2 was added gradually for two hours. After reductive leaching pH of the mixture was adjusted from 5.65 to 6.59 with 4.35 g of $\text{Ca}(\text{OH})_2$ slurried in water. Residual solids were removed from 90 ml of solution by filtration. 30.89 g of technical manganese sulfate hydrate was added to the filtrate and a solution with volume of 100 ml was obtained. The resulting solution was heated to boiling. After the mixture started to form crystals the reaction was con-

tinued under reflux cooling for one hour. 19.97 g of crystals (DC 83.89%) was removed from 37 ml of mother liquor by filtration with heated filtration equipment. Samples were analysed with MP-AES and results are presented in Table 15.

TABLE 15

Composition of the leachate before addition of manganese sulfate, and the dried manganese sulfate crystals from crystallization.		
Element	Leachate	Crystals
Ca	692	<5000
K	620	1 560
Mn	35 800	326 000
Zn	3 880	4960

[0058] Crystals from previous step were dissolved 40 ml of water forming a solution with pH of 7.01 and volume of 40 ml. The solution was then circulated through 30 ml of Lanxess MonoPlus TP220 for four hours. Prior to ion exchange, the resin was preconditioned with 40 ml of 10 wt % NH_4OH . After ion exchange 52 ml of raffinate was collected from the column. 40 ml of 20 wt % H_2SO_4 was used to extract zinc from the resin and a series of elution samples was collected with volumes of 17 ml, 40 ml, 45 ml, and 20 ml respectively. Samples were analysed with MP-AES and results are presented in Table 16.

TABLE 16

Composition of the dissolved manganese sulfate liquor, raffinate and eluates.						
Element	Liquor	Raffinate	Eluate 1	Eluate 2	Eluate 3	Eluate 4
Ca	<500	<500	<500	<500	<500	<500
K	606	330	<50	<50	<50	<50
Mn	92 000	49 500	<50	100	<50	<50
Zn	1 140	<50	<250	900	365	<250

Example 6

[0059] 41.05 g of washed AKB (DC 95%) was slurried in 80 ml of water and 20 ml of 95 wt % H_2SO_4 . 25 ml of 30 wt % H_2O_2 was added gradually for two hours. After reductive leaching pH of the mixture was 4.76. Residual solids were removed from 90 ml of solution by filtration. The filtrate was heated to boiling point and excess water was removed by means of evaporation. After the mixture started to form crystals the reaction was continued under reflux cooling for one hour. 26.24 g of crystals (DC 81.22%) was removed from 30 ml of mother liquor by filtration with heated filtration equipment. Samples were analysed with MP-AES and results are presented in Table 17.

TABLE 17

Composition of the leachate of AKB and the resulting crystals from crystallization.		
Element	Leachate	Crystals
Ca	<500	<5000
K	4 670	8 030

TABLE 17-continued

Composition of the leachate of AKB and the resulting crystals from crystallization.		
Element	Leachate	Crystals
Mn	81 000	225 000
Zn	47 500	93 800

[0060] 6.30 g of crystals from previous step and 10.01 g of technical manganese sulfate hydrate were dissolved in 40 ml of water forming a solution with pH of 6.37 and volume of 44 ml. The solution was then circulated through 30 ml of Lanxess MonoPlus TP220 for four hours. Prior to ion exchange, the resin was preconditioned with 40 ml of 10 wt % NH_4OH . After ion exchange 52 ml of raffinate was collected from the column. 40 ml of 20 wt % H_2SO_4 was used to extract zinc from the resin and a series of elution samples was collected with volumes of 12 ml, 43 ml, 45 ml, and 26 ml respectively. Samples are analysed with MP-AES and results are presented Table 18.

TABLE 18

Composition of the dissolved manganese sulfate liquor, raffinate and eluates.						
Element	Liquor	Raffinate	Eluate 1	Eluate 2	Eluate 3	Eluate 4
Ca	<500	<500	<500	<500	<500	<500
K	430	420	<50	<50	<50	<50
Mn	81 300	59 000	10	110	50	<5
Zn	8 890	<50	<250	8 410	1780	<250

Example 7

[0061] 40.50 g of washed AKB (DC 95%) was slurried in 80 ml of water and 20 ml of 95 wt-% H_2SO_4 . 25 ml of 30 wt % H_2O_2 was added gradually during three to four hours. After reductive leaching pH of the mixture was adjusted from 4.91 to 5.54 with 4.14 g of $\text{Ca}(\text{OH})_2$ slurried in water. Residual solids were removed from 95 ml of solution by filtration. The filtrate was heated to boiling point and excess water was removed by means of evaporation. After the mixture started to form crystals the reaction was continued under reflux cooling for one hour. 17.68 g of crystals (DC 79.36%) was removed from 27 ml of mother liquor by filtration with heated filtration equipment. Samples were analysed with MP-AES and results are presented in Table 19.

TABLE 19

Composition of the leachate from AKB leaching and the resulting crystals from crystallization.		
Element	Leachate	Crystals
Ca	<500	<5000
K	3 710	4 830
Mn	65 400	246 000
Zn	34 100	98 500

[0062] 8.53 g of crystals from previous step and 8.26 g of technical manganese sulfate hydrate were dissolved in 40 ml of water forming a solution with pH of 6.02 and volume of 40 ml. The solution was then circulated through 30 ml of

Lanxess MonoPlus TP220 for four hours. Prior to ion exchange, the resin was preconditioned with 40 ml of 10 wt % NH_4OH . After ion exchange 42 ml of raffinate was collected from the column. 40 ml of 20 wt % H_2SO_4 was used to extract zinc from the resin and a series of elution samples was collected with volumes of 15 ml, 41 ml, 38 ml and 18 ml respectively. Samples were analysed with MP-AES and results are presented in Table 20.

TABLE 20

Composition of the dissolved manganese sulfate liquor, raffinate and eluates.						
Element	Liquor	Raffinate	Eluate 1	Eluate 2	Eluate 3	Eluate 4
Ca	<500	<500	<500	<500	<500	<500
K	920	680	<50	<50	<50	<50
Mn	93 800	64 800	10	110	40	<5
Zn	11 500	<50	500	8 550	1 980	<250

Example 8

[0063] 24.56 g of AKB and 20.36 g of AM were slurried in 55 ml of water and 20 ml of 95% H_2SO_4 . 25 ml of 30 wt % H_2O_2 was added gradually during three to four hours. After reductive leaching pH of the mixture was adjusted from 0.17 to 5.77 with 8.71 g of $\text{Ca}(\text{OH})_2$ slurried in water. Residual solids were removed from 70 ml of solution by filtration. The filtrate was heated to boiling point and excess water was removed by means of evaporation. After the mixture started to form crystals the reaction was continued under reflux cooling for one hour. 9.39 of crystals (DC 84.35%) was removed from 33 ml of mother liquor by filtration with heated filtration equipment. Samples were analysed with MP-AES and results are presented in Table 21.

TABLE 21

Composition of the leachate from AKB leaching and the resulting crystals from crystallization.		
Element	Leachate	Crystals
Ca	<500	<5 000
K	10 700	30 800
Mn	104 000	262 000
Zn	25 100	22 400

[0064] Crystals from previous step were dissolved in 20 ml of water forming a solution with pH of 6.46 and volume of 24 ml. The solution was then circulated through 30 ml of

Lanxess MonoPlus TP220 for four hours. Prior to ion exchange, the resin was preconditioned with 40 ml of 10 wt % NH_4OH . After ion exchange 47 ml of raffinate was collected from the column. 40 ml of 20 wt % H_2SO_4 was used to extract zinc from the resin and a series of elution samples was collected with volumes of 14 ml, 30 ml, 40 ml, and 40 ml respectively. Samples were analysed with MP-AES and results are presented in Table 22.

TABLE 22

Composition of the dissolved manganese sulfate liquor, raffinate and eluates.						
Element	Liquor	Raffinate	Eluate 1	Eluate 2	Eluate 3	Eluate 4
Ca	<500	<500	<500	<500	<500	<500
K	6 870	3 050	<50	<50	<50	<50
Mn	54 300	20 900	50	440	230	100
Zn	4 560	<50	<250	2 850	1 310	<250

Example 9

[0065] 70 mL of a mixed AKB and AM liquor was passed through 40 ml of unpreconditioned bis-picolylamine ion exchange resin, after which 78 ml of solution was recovered from the column. The resin was first rinsed with water and then eluted with 50 ml of 20 wt-% H_2SO_4 and a series of samples in aliquots of approximately 13 ml were collected. Samples were analyzed with MP-AES and the results are in Table 23.

TABLE 23

Composition of the dissolved manganese sulfate liquor, raffinate and eluates.						
Element	Liquor	Raffinate	Eluate 1	Eluate 2	Eluate 3	Eluate 4
Ca	380	240	<60	<60	<60	<60
K	1 040	500	<60	<50	<50	<50
Mn	39 710	23 870	<5	10	8	<5
Zn	4 900	120	60	3 200	2 390	220

[0066] A summary of the relevant parameter differences in Examples 1 to 8 can be found in Table 24.

TABLE 24

Summary of parameters used in the disclosed examples.									
Process step	Ex 1	Ex 2	Ex 3	Ex 4	Ex 5	Ex 6	Ex 7	Ex 8	Ex 9
AKB Washing (optional)	Yes	Yes	Yes	Yes	Yes	Yes	Yes	No	No
Mn containing material	AM	Mn ₂ O ₃	Mn ₂ O ₃	MnSO ₄ •H ₂ O	MnSO ₄ •H ₂ O	MnSO ₄ •H ₂ O	MnSO ₄ •H ₂ O	AM	AM
Mn material added before step	Leaching	Leaching	Leaching	Leaching	Crystallization	Ion Exchange	Ion Exchange	Leaching	Leaching

TABLE 24-continued

Summary of parameters used in the disclosed examples.									
Process step	Ex 1	Ex 2	Ex 3	Ex 4	Ex 5	Ex 6	Ex 7	Ex 8	Ex 9
Leaching									
H2O2 addition time	2 h	3.5 h	3 h	1 h	2 h	2 h	3.5 h	3.5 h	3.5 h
Dissolving time after H2O2 addition	0.5 h	—	—	—	—	—	—	—	—
Temperature	RT	RT	RT	RT	RT	RT	RT	RT	RT
pH adjustment (optional)	No	Yes	No	Yes	Yes	No	Yes	Yes	Yes
Crystallization									
Time	1 h	1 h	1 h	1 h	1 h	1 h	1 h	1 h	1 h
Ion Exchange									
pH adjustment (optional)	Yes	No	No	No	No	No	No	No	No
pH	2.5	6.5	3.3	6.3	7	6.4	6.02	6.46	3
Zn separation	100%	100%	100%	100%	100%	100%	100%	100%	90%

[0067] Based on the above experiments, it can be concluded that the process works with or without washing of AKB, at several pH-areas and better with preconditioning of the resin when comparing examples 1-8 to example 9, which had no preconditioning of the resin. Similarly, the process works with different manganese sources.

1. A method for recovering metals from ground alkaline batteries comprising the steps of:

- selectively leaching under reductive conditions manganese and zinc from alkaline black by mixing the alkaline black and a manganese oxide containing material and/or manganese sulfate with a sulfuric acid solution at a leaching temperature of 15-40° C., for 1-5 hours to obtain a mixture,
- filtering the mixture to obtain a manganese and zinc sulfate filtrate and a Pb/Ca/organics as a filter cake,
- heating the manganese and zinc sulfate filtrate to a crystallization temperature of 70-100° C. and keeping the crystallization temperature under reflux cooling for at least 30 minutes to precipitate manganese in a form of sulfate crystals,
- filtrating the sulfate crystals and obtaining a manganese depleted filtrate, and
- solubilizing the sulfate crystals in water to obtain a sulfate solution and separating manganese and zinc by a chelating ion exchange.

2. The method for recovering according to claim 1, wherein the manganese oxide containing material is MnO₂.

3. The method for recovering according to claim 1, wherein the manganese oxide containing material is manganese trioxide.

4. The method for recovering according to claim 1, wherein the manganese and zinc sulfate filtrate obtained in the filtering step (step b) has a manganese to zinc ratio between 10:1 and 3.6:1.

5. The method for recovering according to claim 4, wherein the manganese and zinc sulfate filtrate obtained in the filtering step (step b) has a manganese to zinc ratio between 7:1 and 5:1.

6. The method for recovering according to claim 4, wherein manganese sulfate is added in a stage preceding the chelating ion exchange to adjust the manganese to zinc ratio.

7. The method for recovering according to claim 1, wherein the mixture to be filtered in the filtering step (step b) has a pH between 1.5 and 7.

8. The method for recovering according to claim 1, wherein the sulfate solution, wherefrom manganese and zinc are separated, has a pH between 1.5 and 7 before entering the chelating ion exchange in step (e).

9. The method for recovering according to claim 7, wherein the pH is adjusted upwards with a hydroxide solution, or downwards with sulfuric acid preceding the filtering step (step b).

10. The method for recovering according to claim 8, wherein the pH is adjusted upwards with a hydroxide solution such, or downwards with sulfuric acid in a stage preceding the chelating ion exchange (step e).

11. The method for recovering according to claim 1, wherein the alkaline black is washed before the selective leaching step (step a) by mixing the alkaline black with water at a temperature between 5° C. and 100° C. for at least 30 min.

12. The method for recovering according to claim 11, wherein the alkaline black is mixed with water at a temperature between 20° C. and 25° C.

13. The method for recovering according to claim 11, wherein the alkaline black is mixed with water for 1-2 hours.

14. The method for recovering according to claim 1, wherein the manganese depleted filtrate from the filtrating of the sulfate crystals (step d) is returned to the leaching step (step a).

15. The method for recovering according to claim 1, wherein in the chelating ion exchange step a BPA-resin in sulfate form is used.

16. The method for recovering according to claim 15, wherein the BPA-resin in sulfate form is preconditioned with ammonium, sodium or potassium hydroxide.

17. The method for recovering according to claim 1, wherein in the selective leaching step (step a) a reducing agent is added during the mixing until manganese and zinc are dissolved.

18. The method according to claim **17**, wherein the reducing agent comprises hydrogen peroxide or sulfur dioxide.

19. The method according to claim **1**, wherein the wherein the manganese oxide containing material is anode mud.

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