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(54) METHOD OF PRODUCING PURIFIED GRAPHITE

(71) Applicant: **ECOGRAF LIMITED**, West Perth (AU)

(72) Inventor: **Christoph FREY**, West Perth (AU)

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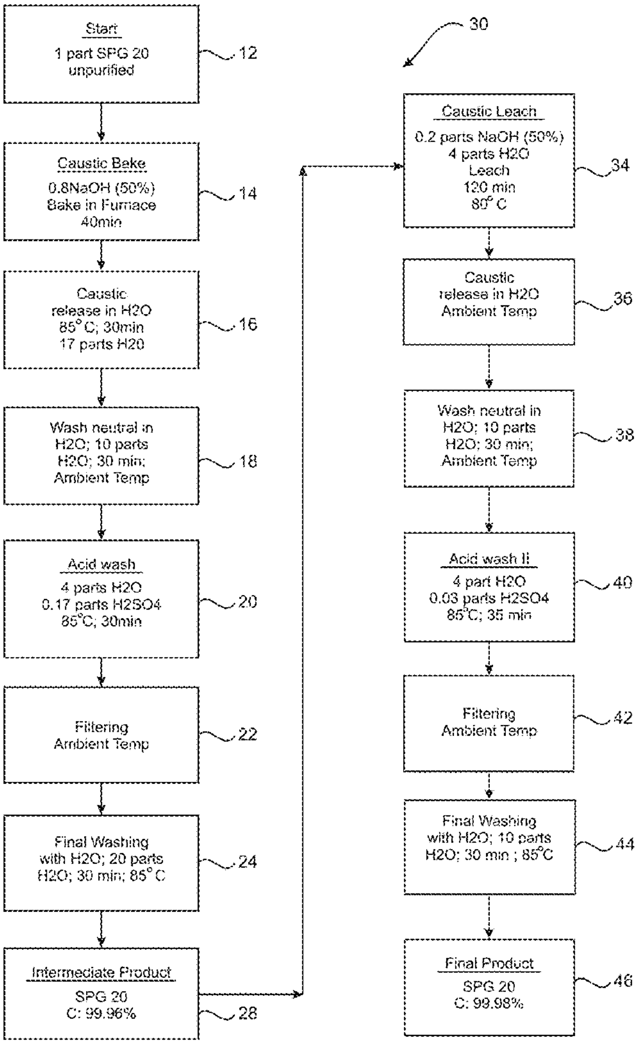
(57) ABSTRACT

A two-stage method of producing purified graphite is described. The first stage of the method comprises the steps of subjecting graphite material to a caustic bake and releasing any remaining caustic using water. The graphite material is then subjected to a first acid wash. Neutralising and washing the acid washed graphite material is then performed to deliver an intermediate purified graphite product. In the second stage the intermediate purified graphite product is subjected to a low temperature caustic leach. Any remaining caustic in the intermediate purified graphite product is released using water, and the intermediate purified graphite product is subjected to a second acid wash. Finally, neutralising and washing the intermediate purified graphite product is performed to deliver a final purified graphite product with a purity of 99.95% C and above.



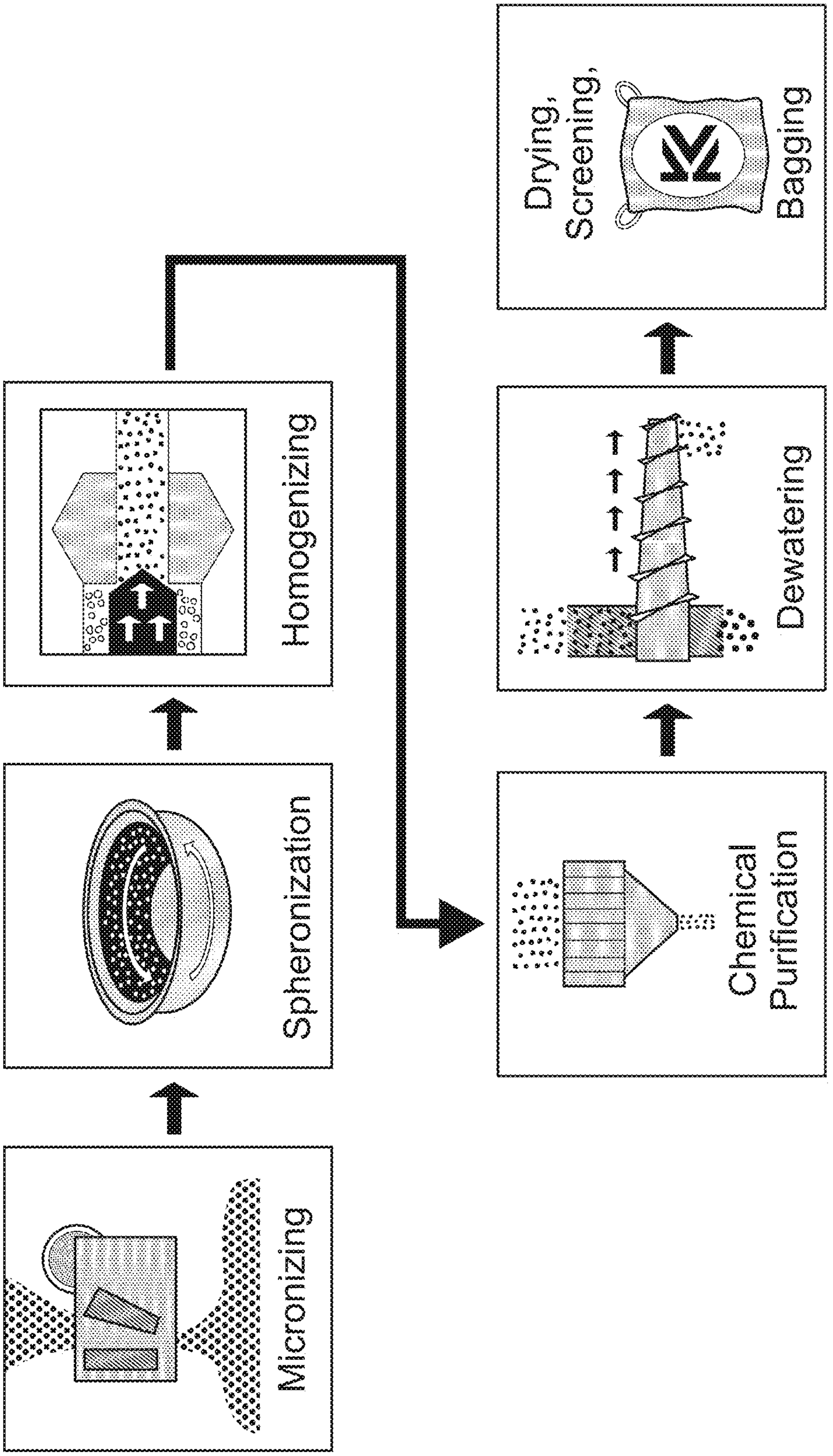

Micronizing
Spheronization
Homogenizing
Chemical
Purification
Dewatering
Drying,
Screening,
Bagging

FIGURE 1

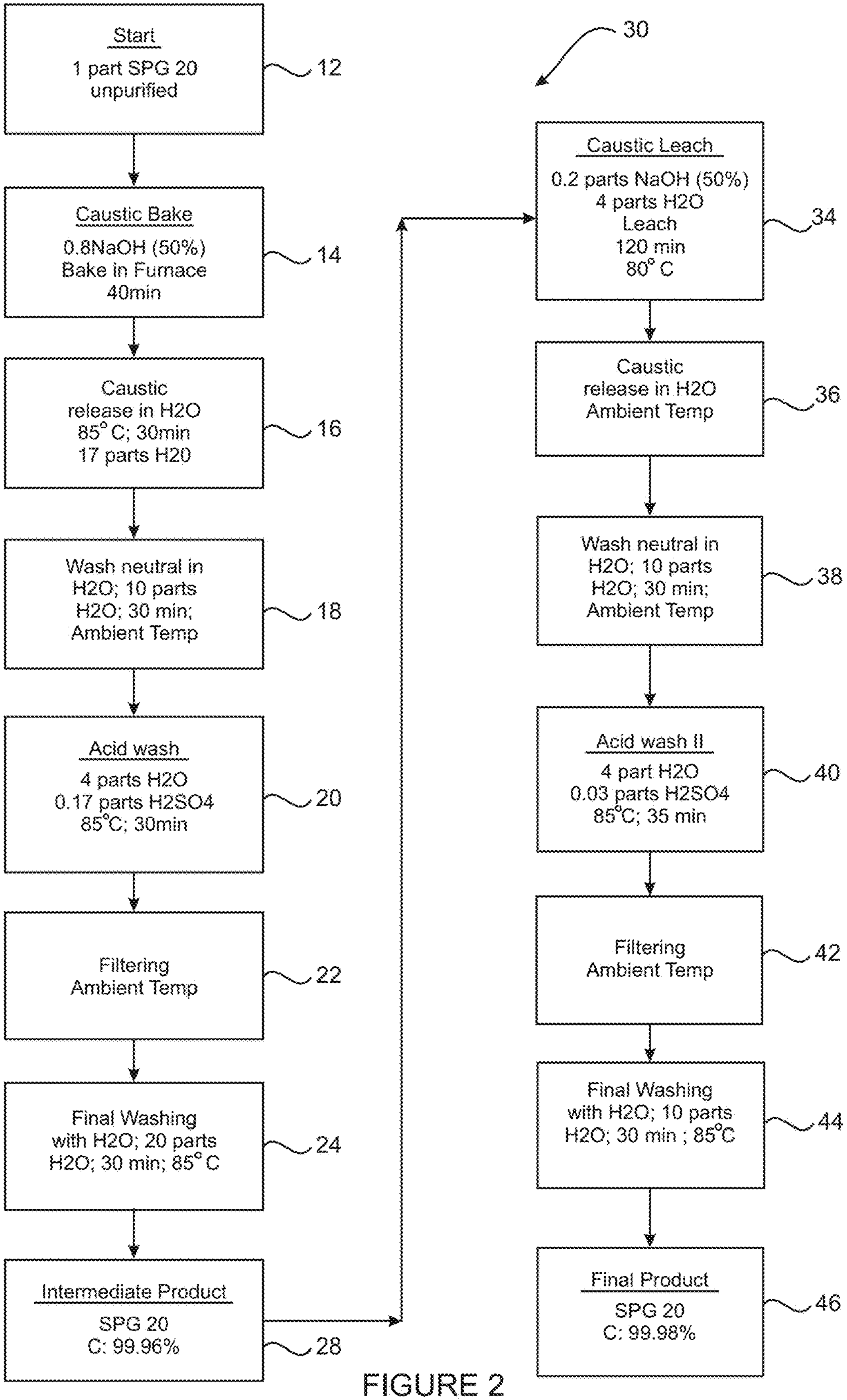

Start
1 part SPG 20 unpurified
12
Caustic Bake
0.8NaOH (50%) Bake in Furnace 40min
14
Caustic release in H2O 85° C; 30min 17 parts H20
16
Wash neutral in H2O; 10 parts H2O; 30 min; Ambient Temp
18
Acid wash
4 parts H2O 0.17 parts H2SO4 85°C; 30min
20
Filtering Ambient Temp
22
Final Washing with H2O; 20 parts H2O; 30 min; 85° C
24
Intermediate Product
SPG 20 C: 99.96%
28
30
Caustic Leach
0.2 parts NaOH (50%) 4 parts H2O Leach 120 min 80° C
34
Caustic release in H2O Ambient Temp
36
Wash neutral in H2O; 10 parts H2O; 30 min; Ambient Temp
38
Acid wash II
4 part H2O 0.03 parts H2SO4 85°C; 35 min
40
Filtering Ambient Temp
42
Final Washing with H2O; 10 parts H2O; 30 min ; 85°C
44
Final Product
SPG 20 C: 99.98%
46

FIGURE 2

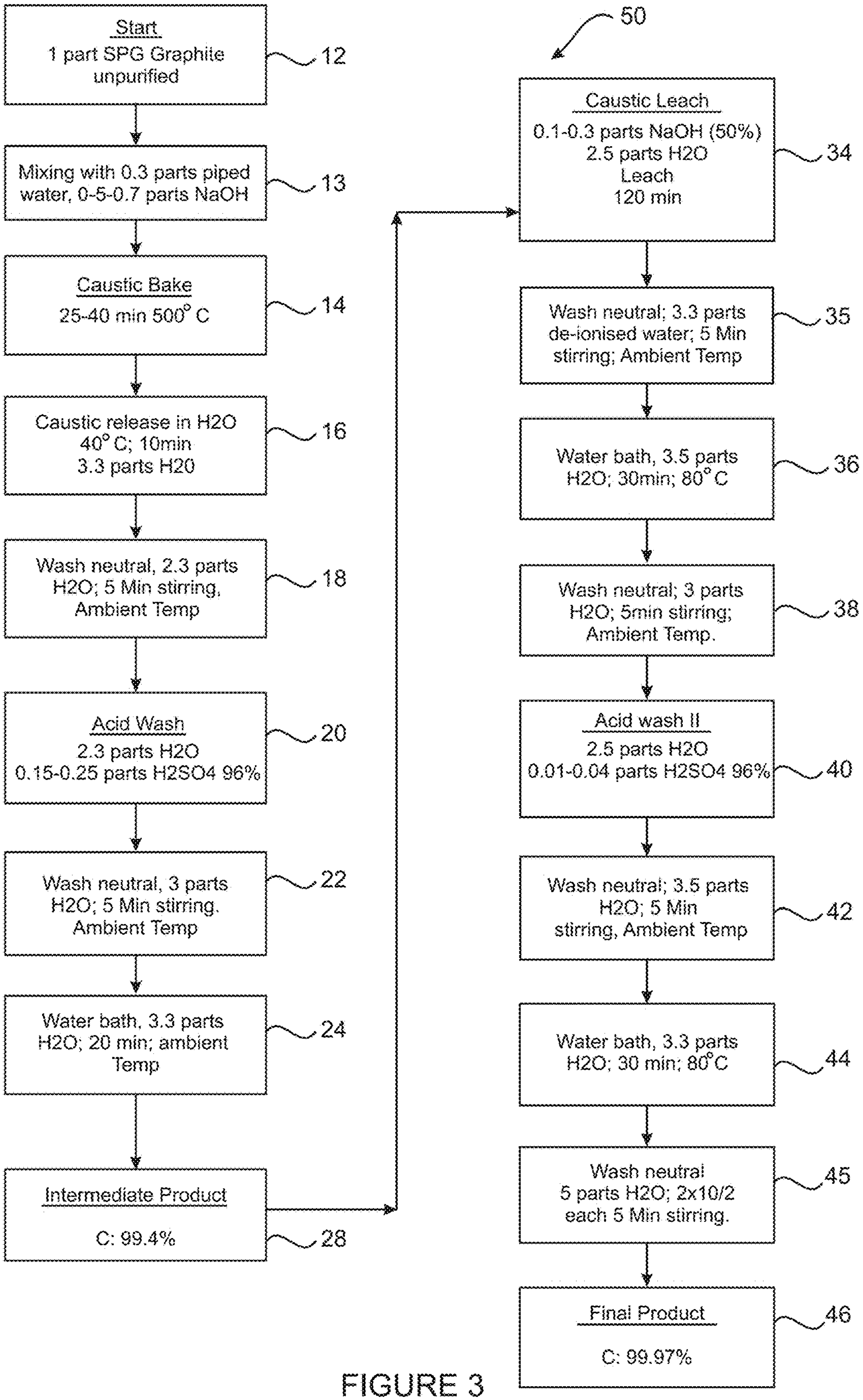

Start
1 part SPG Graphite unpurified
12
Mixing with 0.3 parts piped water, 0-5-0.7 parts NaOH
13
Caustic Bake
25-40 min 500° C
14
Caustic release in H2O
40° C; 10min
3.3 parts H20
16
Wash neutral, 2.3 parts H2O; 5 Min stirring, Ambient Temp
18
Acid Wash
2.3 parts H2O
0.15-0.25 parts H2SO4 96%
20
Wash neutral, 3 parts H2O; 5 Min stirring, Ambient Temp
22
Water bath, 3.3 parts H2O; 20 min; ambient Temp
24
Intermediate Product
C: 99.4%
28
50
Caustic Leach
0.1-0.3 parts NaOH (50%)
2.5 parts H2O
Leach
120 min
34
Wash neutral; 3.3 parts de-ionised water; 5 Min stirring; Ambient Temp
35
Water bath, 3.5 parts H2O; 30min; 80° C
36
Wash neutral; 3 parts H2O; 5min stirring; Ambient Temp.
38
Acid wash II
2.5 parts H2O
0.01-0.04 parts H2SO4 96%
40
Wash neutral; 3.5 parts H2O; 5 Min stirring, Ambient Temp
42
Water bath, 3.3 parts H2O; 30 min; 80°C
44
Wash neutral
5 parts H2O; 2x10/2 each 5 Min stirring.
45
Final Product
C: 99.97%
46

FIGURE 3

METHOD OF PRODUCING PURIFIED GRAPHITE

FIELD OF THE INVENTION

[0001] The present invention relates to a method of producing purified graphite and relates particularly, though not exclusively, to such a process for producing battery-grade spherical purified graphite (SPG).

BACKGROUND TO THE INVENTION

[0002] Spherical graphite is manufactured from flake graphite concentrates in which the flakes have to be rounded to produce spherical particles of graphite. The spherical graphite can be spread thinly and uniformly during the manufacturing process and is used for the anode material in lithium ion batteries. Spherical purified graphite (SPG) is sold as either a coated or uncoated product. Uncoated SPG is manufactured by micronizing, rounding and purifying flake graphite. The bulk of natural, uncoated SPG is currently manufactured in China due to low labour costs and weak environmental regulations. The micronized, rounded graphite is chemically purified from 94% to 99.95% C using strong hydrofluoric and other acids. Impurities will have a deleterious effect on battery performance.

[0003] Apart from the environmental concerns, the hydrofluoric acid typically employed in the prior art purification process is also highly toxic and hazardous to use. A great deal of effort is therefore being expended to find a more cost-effective, non-toxic and environmentally sustainable process for the purification of spherical graphite.

[0004] With the widespread use of lithium-ion batteries, there is now also a significant market for the recycling of these kinds of batteries. In typical prior art recycling plants, the lithium-ion batteries are first made safe for further treatment, by separating the plastics, aluminium and copper components and directing them to their own recycling processes. The remaining components of the battery after these processes are the chemical and mineral components. “Black mass” is the residue remaining from existing hydrometallurgical processes that recover the valuable metals. The black mass typically consists of a mixture of carbon, lithium, manganese, cobalt and nickel in various ratios, including anode material which consists of natural battery graphite, synthetic graphite and silicon. As graphite comprises almost 50% of the mass of a typical lithium-ion battery, there is a significant benefit to be gained in being able to purify the black mass material for the recovery of high purity graphite.

[0005] The present invention was developed with a view to providing a cost-effective and environmentally sustainable method of producing purified graphite with carbon content higher than 99.9%. Although the present invention is described with particular reference to producing battery-grade SPG it will be understood that the method of producing purified graphite may also have wider applications.

[0006] References to prior art in this specification are provided for illustrative purposes only and are not to be taken as an admission that such prior art is part of the common general knowledge in Australia or elsewhere.

SUMMARY OF THE INVENTION

[0007] According to one aspect of the present invention there is provided a method of producing purified graphite, the method comprising the steps of:

[0008] subjecting graphite material to a sodium hydroxide (NaOH) bake;

[0009] releasing any remaining NaOH using water;

[0010] subjecting the graphite material to a first acid wash;

[0011] neutralising and washing the acid washed graphite material to deliver an intermediate purified graphite product;

[0012] subjecting the intermediate purified graphite product to a NaOH leach;

[0013] releasing any remaining NaOH in the intermediate purified graphite product using water;

[0014] subjecting the intermediate purified graphite product to an acid wash; and,

[0015] neutralising and washing the intermediate purified graphite product to deliver a final purified graphite product.

[0016] Preferably the step of subjecting the graphite material to a NaOH bake comprises mixing the graphite material with liquid NaOH (50%) and heating the mixture in a furnace. Typically the mixture is heated to a temperature of between 450° C. and 550° C. Advantageously the mixture is heated for between approximately 25 to 45 minutes. Preferably the mixture is heated to 500° C. for 30 minutes.

[0017] Preferably the step of releasing any remaining NaOH comprises immersing the material in hot water. Preferably after the step of releasing any remaining NaOH, the material is washed and filtered. Typically the material is washed and filtered in a wash neutral step at ambient temperature, for about 5 to 10 minutes, using 2.0 to 7.0 parts H_2O.

[0018] Preferably the step of subjecting the material to a first acid wash comprises washing the material with a diluted acid mixture comprising water and H_2SO_4. Typically the diluted acid mixture comprises between 2.0 to 5.0 parts H_2O and between 0.15 and 0.25 parts H_2SO_4 96%. Advantageously the diluted acid mixture comprises 4.0 parts H_2O and 0.17 parts H_2SO_4 96%. Preferably the first acid wash is performed at elevated temperatures in the range of approximately 70° C. to 90° C. to increase reactivity. Typically the first acid wash is performed at an elevated temperature of 80° C. for between about 25 to 45 minutes.

[0019] Preferably the step of neutralising and washing the acid washed graphite material comprises filtering the material at ambient temperature and final washing with water at elevated temperatures respectively. Typically the final washing with water occurs at 85° C. for 30 minutes using 20 parts H_2O. Preferably the step of neutralising and washing the material comprises washing the acid washed graphite material in 3 to 7 parts H_2O for 3 to 7 minutes while stirring, at ambient temperature.

[0020] Preferably the step of subjecting the intermediate purified graphite product to a NaOH leach comprises immersing the intermediate purified graphite product in 0.1 to 0.3 parts NaOH (50%) with 2.0 to 4.0 parts H_2O at low temperature. Typically the NaOH leach takes place at temperatures in the range of 72° C. to 88° C. Preferably the residence time for the NaOH leach is about 1.5 to 2.5 hours.

[0021] Preferably the intermediate purified graphite product is preferably neutralized and washed, before it is subject to the acid wash step.

[0022] Advantageously the only reagents used are NaOH in the NaOH bake and NaOH leach steps, and H_2SO_4 in the acid wash steps.

[0023] Preferably the intermediate purified graphite product is finally washed in a water bath and neutralized with water after the acid wash step.

[0024] Preferably the acid wash of the intermediate purified graphite product is performed with a diluted acid mixture comprising between 2.0 and 4.0 parts H_2O and 0.01 to 0.04 parts H_2SO_4 96%. Typically the diluted acid mixture comprises 2.5 parts H_2O and 0.03 parts H_2SO_4 96%, and the acid wash is performed at elevated temperatures in the range of approximately 77° C. to 93° C. to increase reactivity. Preferably the acid wash is performed at an elevated temperature of 80° C. for approximately 35 minutes.

[0025] By incorporating the second stage NaOH leaching step, with low consumption of chemicals, carbon content of the final purified graphite product can be increased to 99.98%.

[0026] Throughout the specification, unless the context requires otherwise, the word "comprise" or variations such as "comprises" or "comprising", will be understood to imply the inclusion of a stated integer or group of integers but not the exclusion of any other integer or group of integers. Likewise the word "preferably" or variations such as "preferred", will be understood to imply that a stated integer or group of integers is desirable but not essential to the working of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0027] The nature of the invention will be better understood from the following detailed description of several specific embodiments of the method of producing purified graphite, given by way of example only, with reference to the accompanying drawings, in which:

[0028] FIG. **1** illustrates a typical manufacturing process for producing purified graphite;

[0029] FIG. **2** is a process flow diagram illustrating a first embodiment of the method of producing purified spherical graphite according to the present invention; and,

[0030] FIG. **3** is a process flow diagram illustrating a second embodiment of the method of producing purified spherical graphite according to the present invention.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

[0031] The process of manufacturing purified spherical graphite (SPG) involves the steps of micronizing, rounding, homogenising and purifying flake graphite, as illustrated in FIG. **1**. Purification is traditionally done by means of chemical purification, which is followed by dewatering, drying, screening and bagging of the finished SPG product.

[0032] A first embodiment of the method **10** of producing purified graphite in accordance with the invention, as illustrated in FIG. **2**, comprises the step of subjecting spherical graphite material **12** to a caustic bake, as shown at **14**. The starting material **12** is typically 1 part SPG to 20 parts un-purified spherical graphite material. Preferably the step of subjecting the spherical graphite material to a caustic bake comprises mixing the spherical graphite material with liquid NaOH (50%) and heating the mixture in a furnace or kiln. Typically the mixture comprises 0.3 parts water and 0.66 parts NaOH. Preferably the mixture is heated to a temperature of between 400° C. and 550° C., for approximately 25 to 45 minutes. The weight of the material was checked before and after the heat treatment at different temperatures. The results indicate that no graphite burns at a process temperature of 500° C., if the dwelling time does not exceed about 40 minutes. More preferably the mixture is heated to 500° C. for 30 minutes. After the caustic bake the material has a solid consistency (the H_2O from the NaOH has evaporated).

[0033] The method further comprises the step of releasing any remaining caustic, at step **16**, using water. Preferably the step of releasing any remaining caustic comprises immersing the solid material in water and dissolving any remaining caustic for about 10 to 45 minutes. Typically this is done in warm water, for example, water heated to between 40° C. to 85° C. Typically 1 part spherical graphite material is immersed in from between 3 to 20 parts H_2O. In this embodiment 1 part spherical graphite material is immersed in 17 parts H_2O, at about 85° C., for 30 minutes.

[0034] Preferably, after the step of releasing any remaining caustic, the material is washed and filtered at step **18**. Typically this is done at ambient temperature for about 30 minutes using ten parts H_2O.

[0035] The method further comprises the step of subjecting the material to an acid wash at step **20**. Typically the step of subjecting the material to an acid wash comprises washing the material with a diluted acid mixture comprising water and H_2SO_4. Typically the diluted acid mixture comprises 4 parts H_2O, and 0.17 parts H_2SO_4. Preferably the acid wash is performed at elevated temperatures in the range of approximately 77° C. to 93° C. to increase reactivity. More preferably the acid wash is performed at an elevated temperature of 85° C. Typically the material is subjected to an acid wash for about 30 minutes.

[0036] The method further comprises the step **22** of filtering and the step **24** of final washing the material to deliver an intermediate spherical purified graphite (SPG) product **28**. Preferably the steps of filtering and washing the material comprise filtering the material at ambient temperature and washing with water at elevated temperatures respectively. Typically the final washing with water occurs at 85° C. for 30 minutes using 20 parts H_2O.

[0037] Advantageously this process delivers an intermediate spherical purified graphite (SPG) product at step **28** with a final purity of 99.96% C.

[0038] The method of FIG. **2** further comprises a second stage which begins with the step of subjecting the intermediate SPG product **28** to a caustic leach, at step **34**. Preferably the caustic leach step **34** comprises immersing the intermediate SPG product **28** in 0.2 parts NaOH (50%) with four parts H_2O. Preferably the caustic leach step **34** is performed at relatively low temperatures in the range of approximately 77° C. to 93° C. for about 1.5 to 2.5 hours. More preferably the caustic leach step is performed at 80° C. for about 120 minutes.

[0039] The method further comprises the step of releasing any remaining caustic, at step **36**, using water. Preferably the step of releasing any remaining caustic comprises immersing the material in H_2O for about 30 minutes at ambient temperature.

[0040] Preferably, after the step of releasing any remaining caustic, the material is washed and filtered at step **38**. Preferably the neutral wash at step **38** is done at ambient temperature for about 30 minutes, using ten parts H_2O.

[0041] The method further comprises the step of subjecting the intermediate SPG product to a second acid wash at step **40**. Typically the step of subjecting the material to a second acid wash comprises washing the material with a diluted acid mixture comprising water and H_2SO_4, where a very low concentration of H_2SO_4 is sufficient (preferably between 0.01 to 0.04 parts H_2SO_4 and 4 parts water). Typically the diluted acid mixture comprises 4 parts H_2O and 0.03 parts H_2SO_4. Preferably the second acid wash is performed at elevated temperatures in the range of approximately 77° C. to 93° C. to increase reactivity. More preferably the second acid wash is performed at an elevated temperature of 85° C. for approximately 35 minutes.

[0042] The method further comprises the step of filtering the intermediate SPG product, at **42**, and final washing and neutralization with water at step **44**, to deliver a final SPG product at **46**. Preferably the steps of filtering and washing the material comprise filtering the material at ambient temperature and washing with water at elevated temperatures respectively. Typically the final washing with water occurs at 85° C. for 30 minutes using 10 parts H_2O.

[0043] By incorporating the second stage caustic leaching step **34**, with low consumption of chemicals, the carbon content of the final SPG product at **46** can be increased to 99.98%.

[0044] Test Work

[0045] The parameters listed in Table 1 are for the first embodiment of the method **30** of purifying SPG illustrated in FIG. **2**.

[0046] The method of FIG. **2** is in two parts, and the table of parameters in Table 1 is therefore shown in two parts. Part **1** corresponds to the first stage of the method in FIG. **2**. Part **2** corresponds to the second stage of the method in FIG. **2**, which includes the caustic leach.

TABLE 1

Preferred parameters for method 30 of FIG. 2

Part 1

Test#	TW 10 part 11
Sample #	S#1080
([g] Graphite)	60.28
NaOH (50%) [g]	48.03
ratio NaOH:Graphite	0.80
Temperature	500
duration (min)	38
cool down	yes
Water (g)	1000
ratio Water:Graphite	17
Temperature (° C.)	75
duration (min)	60
“neutral” washing	yes
Water (g)	850
Ratio	14
Water (g)	241.95
Ratio	4.01
H2SO/HNO3 (g)	10.06
ratio H2SO4:Graphite	0.17
Temperature (° C.)	80
duration (min)	35
filtering	yes
Water (g)	1000
Ratio	16.6
Temperature (° C.)	98
duration (min)	40
C-content (%)	99.96
sample material	ca 55 g
Sample #	S#1080

Part 2

Test #	TW 10 part 2
Sample #	S#1083
NaOH (50ig %) [g]	11.03
ratio NaOH:Graphite	0.20
Temperature	88
duration (min)	120
Water (g)	221.76
Ratio	3.696
“neutral” washing	Yes
Water (g)	600
Ratio	10
Water (g)	600
	10
Temperature (° C.)	78
duration (min)	30
Water (g)	220.23
Ratio	3.67
H2SO 96% (g)	1.6
ratio H2SO4:Graphite	0.029
Temperature (° C.)	90
duration (min)	35
filtering	yes
Water (g)	600
Ratio	10
Temperature (° C.)	98
duration (min)	80
Sample #	S#1083
C-content (%)	99.98
sample material	ca 50 g

[0047] FIG. **3** illustrates a second embodiment of the method **50** of producing purified spherical graphite. This second embodiment of the method of the invention is similar in many respects to the method of FIG. **2**, and therefore the like reference numerals will be used to identify what are essentially the same method steps, and these will not be described again in detail. As with method **30** of FIG. **2**, this is also a two stage process, but with lower chemical consumption and lower water consumption.

[0048] As with the first embodiment, the second embodiment of method **50** of FIG. **3** starts with 1 part unpurified SPG graphite, at step **12**. This is followed by a mixing step **13**, which involves mixing the graphite with NaOH. Preferably the mixture comprises from between 0.5 to 0.7 parts NaOH, and from between 0.2 to 0.4 parts piped water. More preferably the mixture comprises 0.3 parts of piped (tap) water and 0.66 parts of NaOH. The method **50** also comprises the step **14** of subjecting spherical graphite material to a caustic bake in which a mixture of the spherical graphite material and NaOH is heated to a temperature of between 400° C. and 550° C., for approximately 25 to 45 minutes. More preferably in the caustic bake step **14** the mixture is heated to 500° C. for about 30 minutes.

[0049] The caustic bake step **14** is followed by a caustic release step **16** of dissolving any remaining caustic in a water bath, in order to cool down and to release the impurities, which are soluble in water. Preferably the caustic release step **16** in this embodiment comprises immersing the solid material in water and dissolving any remaining caustic for about 5 to 15 minutes. Typically this is done in warm water, for example, water heated to between 35° C. to 45° C. Typically 1 part spherical graphite material is immersed in from between 2 to parts H_2O. In this embodiment 1 part spherical graphite material is immersed in 3.3 parts H_2O, at about 40° C., for 10 minutes.

[0050] Preferably, after the caustic release step **16**, the material is washed and filtered at wash neutral step **18**. Typically this is done at ambient temperature, for about 5 to

10 minutes, using 2.0 to 7 parts H_2O. In the illustrated example, the wash neutral step **18** is done at ambient temperature, for about 5 minutes stirring, using 2.3 parts H_2O. After 10 minutes the slurry is filtered until the pH value is neutral. After the caustic bake the material has a solid consistency, which is then subject to a first acid wash at step **20**. The filter cake material is put in a moist condition into a stirred reactor, filled with diluted acid. Gentle stirring supports the process of dissolving impurities. The first acid wash is preferably performed with a mixture of between 2.0 to 5.0 parts H_2O and between 0.15 and 0.25 parts H_2SO_4 96% at elevated temperatures. Preferably the filter cake material remains in the stirred reactor for 25 to 45 minutes, and the temperature is kept at between 70° C. and 90° C. More preferably the first acid wash step **20** is performed with 4.0 parts H_2O and 0.17 parts H_2SO_4 96% at 80° C. for 35 minutes.

[0051] Wash neutralization of the material at step **22** is used to separate the acid and the dissolved impurities. The wash neutralization step **22** preferably comprises washing the acid washed graphite material in 3 to 7 parts H_2O for 3 to 7 minutes while stirring, at ambient temperature. Typically the wash neutralization step **22** comprises washing the acid washed graphite material in parts H_2O for 5 minutes, while stirring at ambient temperature. Afterwards the material is subject to a water bath, having between 2 to 8 parts H_2O, for 20 to 40 minutes, at ambient temperature, to further eliminate impurities, at step **24**. Preferably the water bath **24** is performed with 7 parts H_2O, for 40 minutes, at ambient temperature. The wash neutralization step **22** should be repeated until the pulp is pH neutral. The end result of this first stage of the method **50** is to deliver an intermediate spherical purified graphite (SPG) product **28** with a purity of 99.4% C to 99.9% C.

[0052] The first stage of method **50** is basically the same as in the first embodiment (method **30** in FIG. **2**), except that in this case an additional mixing step **13** was introduced prior to the caustic bake. The first stage is done with tap water, the second stage is done with de-ionised water.

[0053] In the second stage, the method **50** of FIG. **3** further comprises the step of subjecting the intermediate SPG product **28** to a caustic leach, at step **34**. Preferably the caustic leach step **34** comprises immersing the intermediate SPG product **28** in 0.1 to 0.3 parts NaOH (50%) with 2.0 to 4.0 parts H_2O. More preferably the caustic leach step **34** comprises immersing the intermediate SPG product **28** in 0.2 parts NaOH (50%) with 2.5 parts H_2O. Preferably the caustic leach step **34** is performed at relatively low temperatures in the range of approximately 77° C. to 93° C. for about 1.5 to 2.5 hours. More preferably the caustic leach step is performed at 80° C. for about 120 minutes. The concentration of NaOH is low, however there is still sufficient for the low amount of remaining impurities in the graphite to be removed. The process is probably supported by the liquid phase, which enables a better mobility of the Na+ ions. Due to the lower temperature, the reactivity is slower; therefore 2 hours reaction time was identified as a suitable duration.

[0054] After the caustic leach, the caustic water with the dissolved impurities needs to be neutralised by washing and filtering at step **35**. The wash neutralisation step **35** preferably comprises washing the leached graphite material in 3 to 7 parts H_2O for 3 to 7 minutes while stirring, at ambient temperature. Typically the wash neutralization step **35** comprises washing the acid washed graphite material in 5 parts de-ionised H_2O for 5 minutes, while stirring at ambient temperature. Afterwards the material is subject to a water bath, having between 2 to 8 parts H_2O, for 20 to 40 minutes, at elevated temperatures, to further eliminate impurities, at step **36**. Preferably the water bath **36** is performed with 3.5 parts H_2O, for 30 minutes, at 80° C. The water bath **36** supports the dissolution of more-slowly dissolving impurities and the releasing of any remaining caustic. The wash neutralization step may need to be repeated until the pulp is pH neutral (see further wash neutralization step **38**).

[0055] The method **50** further comprises the step of subjecting the intermediate SPG product to a second acid wash at step **40**. Typically the second acid wash step comprises washing the material with a diluted acid mixture comprising water and H_2SO_4, where a very low concentration of H_2SO_4 is sufficient. The filter cake is put in a moist condition into a stirred reactor, filled with diluted acid. The acid concentration is very low, as the amount of impurities to dissolve is very low. Stirring supports the process of dissolving impurities. Preferably the diluted acid mixture comprises between 2.0 and 4.0 parts H_2O and 0.01 to 0.04 parts H_2SO_4 96%. Typically the diluted acid mixture comprises 2.5 parts H_2O and 0.03 parts H_2SO_4 96%. Preferably the second acid wash is performed at elevated temperatures in the range of approximately 77° C. to 93° C. to increase reactivity. More preferably the second acid wash is performed at an elevated temperature of 85° C. for approximately 35 minutes.

[0056] The method **50** further comprises a further step of wash neutralization of the intermediate SPG product, at **42**, and final washing and neutralization with water at steps **44** and **45**, to deliver a final SPG product at **46** with a purity of 99.95% C and above. Preferably the steps of neutralization and washing the material comprise a wash neutralising step **42** of the material at ambient temperature and a water bath **44** at elevated temperatures respectively. The wash neutralisation step **42** preferably comprises washing the graphite material in 3 to 10 parts H_2O, 3×10/3 each 1 minute stirring, at ambient temperature. Typically the wash neutralization step **42** comprises washing the acid washed graphite material in 3.5 parts H_2O for 5 minutes, while stirring at ambient temperature. Afterwards the material is subject to another water bath **44**, having between 2 to 10 parts H_2O, for 20 to 40 minutes, at elevated temperatures, to further eliminate impurities. Preferably the water bath **42** is performed with 3.5 parts H_2O, for 30 minutes, at 80° C.

[0057] A further wash neutralization step **45** may be needed until the graphite material is pH neutral. The wash neutralisation step **45** preferably comprises washing the graphite material in 3 to 10 parts H_2O, 2×10/2 each 5 minute stirring, at ambient temperature.

[0058] The final filtration is also the dewatering step before the graphite is put into a dryer. Recommended temperatures for drying are relatively low (below 150° C.) to prevent any damage to the particles which could occur if higher temperatures are applied.

[0059] The second stage of this method **50** is basically the same as for the first method **30** above, except that additional wash neutralization steps **35**, **42** and have been introduced.

[0060] Although the above described embodiments describe a method of purifying graphite using purified spherical graphite (SPG) as the starting material, the same chemical purification process can also be used with flake graphite as the starting material or for purifying black mass, a residue produced in the recycling of Lithium-ion batteries.

Black mass is the residue remaining from existing hydrometallurgical processes that recover the valuable metals. The purification process increases the grade from 30-50% carbon to +99% carbon to re-use in graphite markets.

[0061] Now that preferred embodiments of the method of purifying SPG have been described in detail, it will be apparent that the described embodiments provide a number of advantages over the prior art, including the following:

- **[0062]** (i) The method is relatively simple, using standard industrial process steps, and yet is capable of achieving a purity of 99.95% C and above.
- **[0063]** (ii) The amount of caustic and acid used for the purification process is significantly reduced compared to prior art methods, and the process time is also shortened.
- **[0064]** (iii) The chemicals used in the method are more environmentally sustainable than prior art methods and do not harm the spherical graphite product.

[0065] It will be readily apparent to persons skilled in the relevant arts that various modifications and improvements may be made to the foregoing embodiments, in addition to those already described, without departing from the basic inventive concepts of the present invention. For example, the method comprises a multi-step and multi-parameter (temperatures, residence time, concentration of acids and caustic, volume of wash water, etc.) process, and therefore sophisticated optimization will undoubtedly yield further improvements in purity and cost savings. Furthermore although the process is described applied unpurified SPG, it is not limited to spherical graphite but could also be applied using other types of flake graphite as a precursor material, such as screened fractions of a flake graphite concentrate or a by-product from spherical graphite production. Therefore, it will be appreciated that the scope of the invention is not limited to the specific embodiments described.

1. A method of producing purified graphite, the method comprising the steps of:

subjecting graphite material to a sodium hydroxide (NaOH) bake;
releasing any remaining NaOH using water;
subjecting the graphite material to a first acid wash;
neutralising and washing the acid washed graphite material to deliver an intermediate purified graphite product;
subjecting the intermediate purified graphite product to a NaOH leach;
releasing any remaining NaOH in the intermediate purified graphite product using water;
subjecting the intermediate purified graphite product to an acid wash; and,
neutralising and washing the intermediate purified graphite product to deliver a final purified graphite product.

2. A method of producing purified graphite as defined in claim **1**, wherein the step of subjecting the graphite material to a NaOH bake comprises mixing the graphite material with liquid NaOH (50%) and heating the mixture in a furnace.

3. A method of producing purified graphite as defined in claim **2**, wherein the mixture is heated to a temperature of between 450° C. and 550° C.

4. A method of producing purified graphite as defined in claim **3**, wherein the mixture is heated for between approximately 25 to 45 minutes.

5. A method of producing purified graphite as defined in claim **4**, wherein the mixture is heated to 500° C. for 30 minutes.

6. A method of producing purified graphite as defined in claim **1**, wherein the step of releasing any remaining NaOH comprises immersing the material in hot water.

7. A method of producing purified graphite as defined in claim **1**, wherein, after the step of releasing any remaining NaOH, the material is washed and filtered.

8. A method of producing purified graphite as defined in claim **7**, wherein the material is washed and filtered in a wash neutral step at ambient temperature, for about 5 to 10 minutes, using 2.0 to 7.0 parts H_2O.

9. A method of producing purified graphite as defined in claim **1**, wherein the step of subjecting the material to a first acid wash comprises washing the material with a diluted acid mixture comprising water and H_2SO_4.

10. A method of producing purified graphite as defined in claim **9**, wherein the diluted acid mixture comprises between 2.0 to 5.0 parts H_2O and between 0.15 and 0.25 parts H_2SO_4 96%.

11. A method of producing purified graphite as defined in claim **10**, wherein the diluted acid mixture comprises 4.0 parts H_2O and 0.17 parts H_2SO_4 96%.

12. A method of producing purified graphite as defined in claim **9**, wherein the first acid wash is performed at elevated temperatures in the range of approximately 70° C. to 90° C. to increase reactivity.

13. A method of producing purified graphite as defined in claim **12**, wherein the first acid wash is performed at an elevated temperature of 80° C. for between about 25 to 45 minutes.

14. A method of producing purified graphite as defined in claim **1**, wherein the step of neutralising and washing the acid washed graphite material comprises filtering the material at ambient temperature and final washing with water at elevated temperatures respectively.

15. A method of producing purified graphite as defined in claim **14**, wherein the final washing with water occurs at 85° C. for 30 minutes using 20 parts H_2O.

16. A method of producing purified graphite as defined in claim **1**, wherein the step of neutralising and washing the material comprises washing the acid washed graphite material in 3 to 7 parts H_2O for 3 to 7 minutes while stirring, at ambient temperature.

17. A method of producing purified graphite as defined in claim **1**, wherein the step of subjecting the intermediate purified graphite product to a NaOH leach comprises immersing the intermediate purified graphite product in 0.1 to 0.3 parts NaOH (50%) with 2.0 to 4.0 parts H_2O at low temperature.

18. A method of producing purified graphite as defined in claim **17**, wherein the NaOH leach takes place at temperatures in the range of 72° C. to 88° C.

19. A method of producing purified graphite as defined in claim **18**, wherein the residence time for the NaOH leach is about 1.5 to 2.5 hours.

20. A method of producing purified graphite as defined in claim **1**, wherein the intermediate purified graphite product is preferably neutralized and washed, before it is subject to the acid wash step.

21. A method of producing purified graphite as defined in claim **1**, wherein the only reagents used are NaOH in the NaOH bake and NaOH leach steps, and H_2SO_4 in the acid wash steps.

22. A method of producing purified graphite as defined in claim **21**, wherein, the intermediate purified graphite product is finally washed in a water bath and neutralized with water after the acid wash step.

23. A method of producing purified graphite as defined in claim **1**, wherein the acid wash of the intermediate purified graphite product is performed with a diluted acid mixture comprising between 2.0 and 4.0 parts H_2O and 0.01 to 0.04 parts H_2SO_4 96%.

24. A method of producing purified graphite as defined in claim **23**, wherein the diluted acid mixture comprises 2.5 parts H_2O and 0.03 parts H_2SO_4 96%, and the acid wash is performed at elevated temperatures in the range of approximately 77° C. to 93° C. to increase reactivity.

25. A method of producing purified graphite as defined in claim **24**, wherein, the acid wash is performed at an elevated temperature of 80° C. for approximately 35 minutes.

26. A graphite product produced according to the method of claim **1**.

27. The graphite product as defined in claim **26**, wherein the graphite product has a purity of at least 99%.

28. A battery or battery product including a graphite product, the graphite product produced according to the method of claim **1**.

29. The battery or battery product as defined in claim **28**, wherein the graphite product has a purity of at least 99%.

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