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(54) Title: PROCESS FOR PURIFYING A SODIUM SULFATE RESIDUE

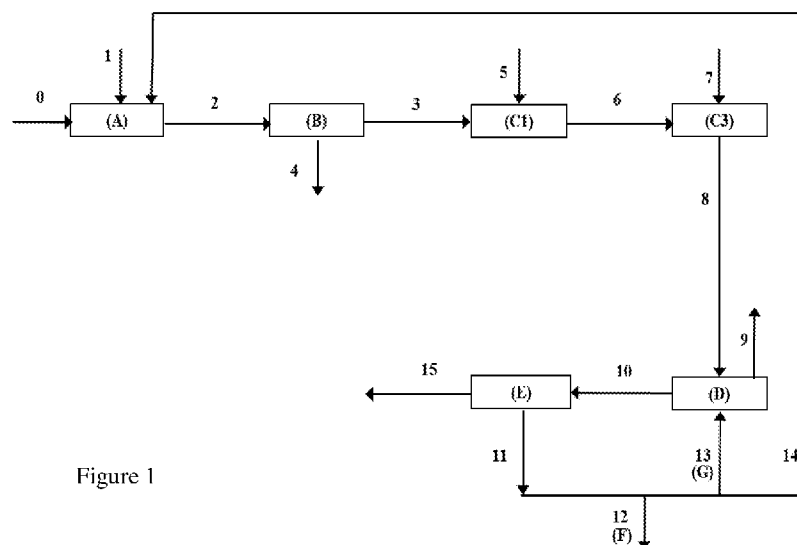


Figure 1

(57) **Abstract:** Provided is a process for purifying a sodium sulfate residue comprising sodium sulfate, sodium carbonate and sodium chloride, and optionally insoluble matter. The process comprises: (a) dissolving the residue with a first aqueous solution to obtain a first aqueous suspension comprising at least 5 wt% and at most 32 wt% of sodium sulfate; (b) optionally separating the insoluble matter from the first aqueous suspension to obtain a separated insoluble matter and a second aqueous solution; (c1) acidifying the second aqueous solution with sulfuric acid to a pH of less than 6 so as to transform at least part or all of dissolved sodium carbonate to sodium sulfate; (c2) optionally aerating the acidified second aqueous solution with oxygen or air to convert sulfites to sulfates; (c3) alkalinizing the acidified second aqueous solution to a pH of about 7 or more with an alkali; (d) removing part of the water from the second aqueous solution to obtain a mother liquor and to crystallize sodium sulfate; (f) purging part of the mother liquor and recycling part of the non-purged mother liquor in at least one of the steps (a) to (d), wherein a weight ratio of the purged separated mother liquor to the non-purged separated mother liquor is at most 0.20 t/t. Also provided is a use of sodium sulfate particles obtained from the process.

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Process for purifying a sodium sulfate residue**TECHNICAL FIELD**

The present invention relates to a sodium sulfate recovery plant from sodium sulfate residue comprising sodium sulfate, sodium carbonate or sodium bicarbonate, and insoluble matter. Many processes produce flue gases containing sulfur oxides and other organics. Most of said flue gases are generated by the combustion of carbonaceous products such as: coal, coke, oil, or organic material such as wood or agriculture wastes, paper wastes, municipal and industrial wastes. Most of those flue gases contain also heavy metals, in particular the ones that are volatile at high temperatures of combustions (such as above 800°C or above 1100°C).

In particular the steel industry, including coke plants and sinter plants also produces flue gases that are to be treated before being released to the atmosphere, needing acidic gases mitigation in particular SO_x (as SO₂ or SO₃) mitigation, but also organic mitigation (such as aromatics compounds, benzols, dioxines and furanes), and in less quantity HX halogenated compounds mitigation (as HCl, HF, HBr, HI), and NO_x mitigation. This is important to reduce hazards for the health nearby living population, and for nature preservation.

Most of SO_x mitigation is done worldwide using either calcium alkaline compounds (such as limestone, or lime) or using sodium compounds (such as sodium hydroxide, sodium bicarbonate, and trona).

The use of sodium alkaline compounds is one of those uses that is developing fast, as very efficient. In particular dry-sorbent injection (DSI) using trona or sodium bicarbonate is an interesting way to mitigate acidic gases as it produces less vapor clouds and dryer gases when released to atmosphere, compared to wet mitigation processes, and less residues byproducts compared to calcium alkaline compounds.

For DSI with sodium alkaline compounds, trona or sodium bicarbonate are injected directly in the flue gas at temperatures of more than 100°C generally, and preferably at temperatures of more than 140°C, alone or with co-sorbents such as active carbon or lignite-coke. With hot fumes, trona or sodium bicarbonate are transformed into high specific porous sodium carbonate particles that react rapidly with acidic gas. The generated salts such as sodium sulfate

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(SO₂ and SO₃ mitigation) or sodium chloride (HCl mitigation), are then recovered on electrostatic filters or preferably on bag filters, constituting sodium sulfate residues.

Though amounts of said sodium sulfate residues are now increasing
5 (several thousand tons per year), and are generally stored in ponds or underground as wastes, and may leak out and contaminate subsoil of the disposal site.

Little of it is presently recovered and valorized in other industrial uses.

BACKGROUND

10 US5135734 discloses a sodium sulfate residue treatment process wherein sodium sulfate is reacted with calcium chloride to generate calcium sulfate that is stored underground in salt cavity, and co-generating sodium chloride that can be valorize in ammonia soda ash plant to produce sodium carbonate. Though the amounts of volume of calcium sulfate exceeds the volume of sodium sulfate
15 residues, and so does not solve the problem linked to the disposals and leaks.

US6180074 discloses a process using a sodium sorbent made of sodium bicarbonate and sodium ammonium compounds. The sodium sulfate residues from flue gas mitigation, is dissolved, optionally treated with reactants to precipitate heavy metals on the main streams, but is silent on other compounds
20 that built up in the circuits and how to decrease the purge volumes. Moreover some of the ammonium compounds form complex with specific heavy metals such as copper and give blue coloration on the produced sodium sulfate that is then hardly accepted by other industrial users.

Therefore there is still the need to improve the existing technologies, so
25 that to reduce the purge volumes, and still give good quality sodium sulfate crystals usable for instance by demanding industries, such as the detergent industry, the dye and textile industry and others such as the glass industry.

The inventors of present invention, have discovered that sodium sulfate residues, in particular those for flue gas SO_x mitigation, may effectively be
30 processed and purified, while minimizing the purge to obtain salable sodium sulfate, and minimizing the amount of final wastes to be disposed of, that represents a noticeable progress compared to existing technologies.

SUMMARY

The present invention relates to a sodium sulfate recovery plant and to a sodium
35 sulfate recovery process from sodium sulfate residue, said sulfate residue comprising sodium sulfate, sodium carbonate and/or sodium bicarbonate,

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insoluble matter, and optionally: organics, sodium sulfite, and/or sodium nitrite, said recovery plant comprising:

- (a) a dissolver (A) for dissolving the sodium sulfate residue with a first aqueous solution to obtain a first aqueous suspension comprising sodium sulfate;
- 5 (b) a separation equipment (B) such as: a filter, a decanter, or a centrifuge, for separating insoluble matter by filtration, decantation, or centrifugation from the first aqueous suspension for obtaining:
 - a separated insoluble matter, and
 - a second aqueous solution;
- 10 (c1) an acidifying reactor (C1) for acidifying the second aqueous solution with sulfuric acid to a pH less than 6 so that to transform at least part, or all, dissolved sodium carbonate and/or sodium bicarbonate to sodium sulfate;
- (c2) an optional oxidizing reactor (C2) for oxidizing the second aqueous solution with oxygen or air;
- 15 (c3) an alkalizing reactor (C3) having a feeding inlet for an alkali solid or an alkaline solution such as sodium carbonate solid or solution, or sodium hydroxide solid or solution, for alkalizing to a pH of about 7 or more the aqueous solution exiting the acidifying reactor (C1) or the optional oxidizing reactor (C2);
- 20 (d) an evaporator-crystallizer (D) for removing at least part of the water from the alkalized aqueous solution exiting the alkalizing reactor (C3) and to obtain a mother liquor and to crystallize sodium sulfate particles within said mother liquor;
- (e) a separation equipment (E) for separating sodium sulfate particles from the mother liquor, and sodium sulfate particles being recovered;
- 25 (f) a purge mean (F) within the evaporator-crystallizer (D) or within the separation equipment (E) for purging at least part of the mother liquor; and
- (g) a recycling mean (G) such as a gravity pipe outlet or a pump, for recycling at least part of the non-purged mother liquor in at least one of the devices
- 30 (A) to (D);

characterized in that the purge mean (F) provides a purge weight ratio of the purged separated mother liquor to the non-purged separated mother liquor of at least 0.005 t/t and at most 0.20 t/t.

- A first advantage of the present invention is that the purge is reduced by a
- 35 factor 4 to 10 compared to previous technology processing such residues.

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A second advantage of the present invention is that the solids to be disposed of, for instance in underground mines, is also reduced by a factor 4 to 10 compared to previous known technology.

5 A third advantage of the present invention, is that it enables to reduce equipment size by treating mother liquors where impurities are concentrated rather than treating the main stream after dissolution of sodium sulfate residues.

10 A forth advantage of present invention is that it enables the production of high purity sodium sulfate with a low content in organics and heavy metals, in particular when the sodium sulfate residues are from DSI of steel industry, coke industry and sinter plants, and particularly suitable for the detergent industries and textile industries, while minimizing purge volumes.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 shows a representative scheme of the sodium sulfate recovery plant according one embodiment of present invention.

15 DETAILED DESCRIPTION

In the present specification, the plural form and the singular form are used interchangeably. Thus, it should be understood that the plural form also includes the singular form and vice-versa.

20 The term "comprising" includes "consisting essentially of" and "consisting of".

The sign "wt. %" refers to "percent by weight" and the sign "vol. %" refers to "percent by volume". When vol. % is used for gas concentrations, it refers in present application to dry gas concentrations (therefore without water vapor content).

25 The term "ppm" means parts per million, expressed by weight (e.g., 1 ppm = 1 mg/kg).

30 In the present specification, the description of a range of values for a variable, defined by a bottom limit, or a top limit, or by a bottom limit and a top limit, also comprises the embodiments in which the variable is chosen, respectively, within the value range: excluding the bottom limit, or excluding the top limit, or excluding the bottom limit and the top limit.

In addition, if the term "about" is used before a quantitative value, the present teachings also include the specific quantitative value itself, unless specifically stated otherwise.

35 As used herein, the term "about" refers to a $\pm 10\%$ variation from the nominal value, unless specifically stated otherwise.

The term "soluble" and "insoluble" used herein means soluble or insoluble in aqueous solution, unless indicated otherwise. The term "soluble" denotes salts having solubility in water of equal to more than 0.05 g/liter at 20°C. The term "insoluble" denotes salts having solubility in water of less than 0.05 g/liter at 20°C.

The different embodiments of the present invention, related to a sodium sulfate recovery plant (items 1 to 13) and related to a process for purifying a sodium sulfate residue (items 101 and subsequent items), are defined hereafter. All Items 1 to 13 and 101 to 123 of present invention are combinable together.

Item 1. A sodium sulfate recovery plant from sodium sulfate residue, comprising sodium sulfate, sodium carbonate and/or sodium bicarbonate, insoluble matter, and optionally: organics, sodium sulfite, and/or sodium nitrite, said recovery plant comprising:

- (a) a dissolver (A) for dissolving the sodium sulfate residue with a first aqueous solution to obtain a first aqueous suspension comprising sodium sulfate;
- (b) a separation equipment (B) such as: a filter, a decanter, or a centrifuge, for separating insoluble matter by filtration, decantation, or centrifugation from the first aqueous suspension for obtaining:
 - a separated insoluble matter, and
 - a second aqueous solution;
- (c1) an acidifying reactor (C1) for acidifying the second aqueous solution with sulfuric acid to a pH less than 6 so that to transform at least part, or all, dissolved sodium carbonate and/or sodium bicarbonate to sodium sulfate;
- (c2) an optional oxidizing reactor (C2) for oxidizing the second aqueous solution with oxygen or air;
- (c3) an alkalizing reactor (C3) having a feeding inlet for an alkali solid or an alkaline solution such as sodium carbonate solid or solution, or sodium hydroxide solid or solution, for alkalizing to a pH of about 7 or more the aqueous solution exiting the acidifying reactor (C1) or the optional oxidizing reactor (C2);
- (d) an evaporator-crystallizer (D) for removing at least part of the water from the alkalized aqueous solution exiting the alkalizing reactor (C3) and to obtain a mother liquor and to crystallize sodium sulfate particles within said mother liquor;
- (e) a separation equipment (E) for separating sodium sulfate particles from the mother liquor, and sodium sulfate particles being recovered;

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- (f) a purge mean (F) within the evaporator-crystallizer (D) or within the separation equipment (E) for purging at least part of the mother liquor; and
(g) a recycling mean (G) such as a gravity pipe outlet or a pump and pipes, for recycling at least part of the non-purged mother liquor in at least one of the devices (A) to (D);

characterized in that the purge mean (F) provides a purge weight ratio of the purged separated mother liquor to the non-purged separated mother liquor of at least 0.005 t/t and at most 0.20 t/t.

- Item 2. The sodium sulfate recovery plant of item 1, characterized in that the purge mean (F) provides a purge weight ratio of the purged separated mother liquor to the non-purged separated mother liquor of at most 0.10 t/t.

Item 3. The sodium sulfate recovery plant of item 2 characterized in that the purge outlet mean (F1) provides a purge weight ratio of the purged separated mother liquor to the non-purged separated mother liquor of at most 0.05 t/t.

- Item 4. The sodium sulfate recovery plant of any one of preceding items, suitable for treating sodium sulfate residue comprising a residual salt from flue gas SO_x mitigation, said flue gas being selected from: a coke plant, a sinter plant, a steel plant, a cement plant, a glass plant, an oil refinery, a petro-chemical plant, a power plant, a lime kiln, a waste incinerator, preferably selected from: a coke plant, a sinter plant, a steel plant, more preferably from: a coke plant.

Item 5. The sodium sulfate recovery plant of any one of preceding items, suitable for treating sodium sulfate residue obtained from flue gas mitigation using a dry sodium sorbent injection, such as: sodium bicarbonate dry sorbent injection or trona dry sorbent injection.

- Item 6. The sodium sulfate recovery plant of any one of the preceding items, further comprising at least one of the following devices:

- (h1) an adsorption device (H1) for adsorbing at least part of organics from the non-purged separated mother liquor before being recycled in at least one of the devices (A) to (G), and/ or
(h2) a reactor (H2) for oxidizing at least part of organics with an inlet mean for introducing hydrogen peroxide or sodium hypochlorite, to discolor and/or decrease total organic carbon (TOC) or the COD of the non-purged separated mother liquor before being recycled in at least one of the devices (A) to (G).

- Item 7. The sodium sulfate recovery plant of item 6, comprising an adsorption device (H1) for adsorbing at least part of organics from the non-

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purged separated mother liquor before being recycled in at least one of the devices (A) to (G), and wherein said adsorption device (H1) comprises active carbon.

Item 8. The sodium sulfate recovery plant of any one of the preceding items, further comprising:

(i) at least one addition mean (I) to the dissolver (A) and/ or an addition mean to the non-purged separated mother liquor before being recycled in at least one of the devices (A) to (H2), such as a solid screw feeder or a pump for adding to the at least one of the following reactant in solid form or in solution:

- an hydroxide salt such as: hydrated lime ($\text{Ca}(\text{OH})_2$), or caustic soda (NaOH);
- a silicate such as sodium silicate or sodium metasilicate;
- a calcium salt such as one chosen among: lime (CaO), portlandite ($\text{Ca}(\text{OH})_2$), calcium sulfate (CaSO_4) anhydrous or hydrated (in particular: calcium sulfate hemihydrate or calcium sulfate dihydrate ie.: gypsum), calcium chloride (CaCl_2), calcium nitrate ($\text{Ca}(\text{NO}_3)_2$);
- a sulfide salt such as sodium sulfide (Na_2S) or an organic sulfide compound such as TMT15;
- a ferrous salt such as ferrous sulfate (FeSO_4), or a ferric salt such as ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3$);
- a phosphate salt such an alkaline metal phosphate salt or an alkaline earth metal phosphate salt; advantageously in combination with a calcium salt as listed above;
- a lead salt, such as lead carbonate (PbCO_3);

or mixtures thereof,

for precipitating at least part of heavy metals or chemical elements such as aluminum (Al), arsenic (As), boron (B), barium (Ba), cadmium (Cd), chromium (Cr), iron (Fe), manganese (Mn), mercury (Hg), nickel (Ni), lead (Pb), antimony (Sb), selenium (Se), titanium (Ti), vanadium (V), or zinc (Zn), from the non-purged separated mother liquor.

Item 9. The sodium sulfate recovery plant of item 8, wherein the separation equipment (B) is suitable for separating heavy metal precipitates or chemical element precipitates generated by the addition mean (I) of the at least one reactant when said reactant is added to the dissolver (A) and/ or added to the non-purged separated mother liquor before being recycled in at least one of the devices (A) to (H2).

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Item 10. The sodium sulfate recovery plant of any one of the preceding items, wherein the evaporator-crystallizer (D) is of a forced circulation evaporator-crystallizer type, or is of a draft-tube baffled evaporator-crystallizer type, and preferably equipped with a mechanical vapor recompression device,
5 preferably also operating under vacuum, and generally operating at temperatures from 50°C to 120°C.

Item 11. The sodium sulfate recovery plant of any one of the preceding items, for treating a sodium sulfate residue that further comprises sodium chloride, and said sodium sulfate recovery plant further comprising:
10 (j) a chloride analyzer mean of the aqueous solution that is present in, or that exits from, any device or piece of equipment (A) to (I), and the weight ratio of the purged separated mother liquor to the non-purged separated mother liquor is controlled so that sodium chloride solution present in the mother liquor present in the crystallization device (D) or exiting the crystallizing device (D) is at most
15 250 g NaCl/ kg of mother liquor, preferably at most 220 g NaCl/ kg of mother liquor.

Item 12. The sodium sulfate recovery plant of item 11, wherein the weight ratio or the volume ratio of the purged separated mother liquor to the non-purged separated mother liquor is controlled so that the weight ratio of sodium chloride
20 to sodium sulfate in the purged separated mother liquor is at least 1.5 and at most 6, preferably at least 2.5 and at most 4.

Item 13. The sodium sulfate recovery plant of any items 1 to 11, wherein the purged separated mother liquor volume or flow is controlled so that the concentration of at least one of the following salt: sodium chloride, sodium
25 nitrate, sodium borate, sodium phosphate, is maintained in a defined range of salt concentration in the mother liquor or in the sodium sulfate particles.

Item 14. The sodium sulfate recovery plant of item 13, wherein the defined range of salt concentration is defined with a lower concentration limit and an upper concentration limit of said salt(s).

30 Item 15. The sodium sulfate recovery plant of items 13 or 14, wherein the lower concentration limit of said salt(s) multiply by the flow of the purged separated mother liquor is at least 60%, preferably at least 80%, of the flow of said salt entering the sodium sulfate recovery plant by the sodium sulfate residue.

Item 16. The sodium sulfate recovery plant of any one of the preceding
35 items, further comprising:

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k) a dryer (K), such as a spray dryer, for drying the purged separated mother liquor into a salt powder.

Item 17. The sodium sulfate recovery plant of any one of the preceding items, wherein the evaporator-crystallizer (D) comprises a condenser (L) for
5 condensing at least part of the water removed from the alkalinized aqueous solution as vapor into a condensate, and the condenser (L) comprises a pipe (M) for hydraulic connection to dissolver (A), for recycling at least part or totally the condensate to the dissolver (A) for dissolving the sodium sulfate residue.

- 10 Item 101. A process for purifying a sodium sulfate residue comprising:
sodium sulfate, sodium carbonate and/or sodium bicarbonate,
and sodium chloride, and optionally insoluble matter, said process comprising :
- (a) dissolving the residue with a first aqueous solution to obtain a first aqueous suspension, comprising at least 5 wt% and at most 32 wt% sodium sulfate;
 - 15 (b) optionally separating insoluble matter by filtration, decantation , or centrifugation from the first aqueous suspension to obtain:
 - a separated insoluble matter, and
 - a second aqueous solution;
 - (c1) acidifying the second aqueous solution with sulfuric acid to a pH less than 6
20 so that to transform at least part, or all, dissolved sodium carbonate and/or sodium bicarbonate to sodium sulfate;
 - (c2) optionally aerating the second aqueous solution with oxygen or air to convert sulfites to sulfates;
 - (c3) alkalinizing the acidified second aqueous solution obtained at step (c1) to a
25 pH of about 7 or more, using an alkali or an alkaline solution such as sodium hydroxide or part of the second aqueous solution obtained at step (b);
 - (d) removing at least part of the water from the second aqueous solution from any step (c1) to (c3) to obtain a mother liquor and to crystallize sodium sulfate particles within said mother liquor,
 - 30 (e) separating sodium sulfate particles from the mother liquor
 - (f) purging at least part of the mother liquor and recycling at least part of the non-purged mother liquor in at least one of the steps (a) to (d),
- characterized in that the weight ratio of the purged separated mother liquor to the non-purged separated mother liquor is at most 0.20, preferably at most 0.10,
35 more preferably at most 0.05 t/t, or at most 0.005 t/t.

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Item 102. The process of Item 101 wherein the sodium sulfate residue comprises:

- at least 70 wt% sodium sulfate,
 - from 0.01 to 30 wt% insoluble matter,
 - 5 - from 0.01 to 30 wt% sodium carbonate and/or sodium bicarbonate,
 - from 0.01 to 30 wt% sodium chloride,
- expressed on the total weight of the sodium sulfate residue.

Item 103. The process of Item 101 or Item 102 wherein the sodium sulfate residue comprises:

- 10 - from 0.05 to 10 wt% sodium sulfite,
- reported to the total weight of the sodium sulfate residue.

Item 104. The process of any one of the preceding Items wherein the sodium sulfate residue comprises:

- from 0.01 to 10 wt% sodium nitrite and/or nitrate,
- 15 reported to the total weight of the sodium sulfate residue.

Item 105. The process of any one of the preceding Items wherein the sodium sulfate residue comprises:

- from 0.001 to 1 wt% aluminum,
- from 0.001 to 1 wt% iron,
- 20 reported to the total weight of the sodium sulfate residue.

Item 106. The process of any one of the preceding Items wherein the sodium sulfate residue comprises:

- from 1 to 500 ppm lead, and/or
 - from 1 to 500 ppm selenium, and/or
 - 25 - from 1 to 500 ppm zinc, and/or
 - from 1 to 100 ppm arsenic, and/or
 - from 1 to 50 ppm mercury, and/or
 - from 1 to 100 ppm vanadium,
- expressed as part per million (ppm) in weight and reported to the total weight of
- 30 the sodium sulfate residue.

Item 107. The process of any one of the preceding Items wherein step (a) is operated per batch operation or in a continuous or semi continuous operation, and when operated in continuous operation is preferably operated in at least two dissolver devices in series.

- 35 Item 108. The process of any one of the preceding Items wherein steps (c1) and (c2) are both operated in a same device.

Item 109. The process of any one of the preceding Items wherein the weight ratio of the purged separated mother liquor to the non-purged separated mother liquor is at least 0.001, preferably at least 0.002 t/t.

5 Item 110. The process of any one of the preceding Items, wherein the sodium sulfate residue comprises a residual salt from flue gas SO_x mitigation, said flue gas being selected from: a coke plant, a sinter plant, a steel plant, a cement plant, a glass plant, an oil refinery, a petro-chemical plant, a power plant, a lime kiln, a waste incinerator.

10 Item 111. The process of the preceding Item, wherein the sodium sulfate residue comprises a residual salt from flue gas SO_x mitigation, said flue gas being from: a coke, or a steel plant or a sintering plant, preferably from a coke plant.

15 Item 112. The process of any one of the preceding Items, wherein the sodium sulfate residue is a salt residue obtained from a flue gas mitigation using a dry sodium sorbent injection, such as sodium bicarbonate dry sorbent injection or trona dry sorbent injection.

20 Item 113. The process of the preceding Item, wherein the the flue gas mitigation uses sodium bicarbonate dry sorbent injection wherein the sodium bicarbonate dry sorbent has a particle size distribution so that at least 90% in weight of the particles have a particle size of less than 30 μm, preferably less than 20 μm, more preferably less than 15 μm.

25 Item 114. The process of any one of the preceding Items, wherein the sodium sulfate residue is a salt residue obtained from a flue gas mitigation using a dry sodium sorbent injection, using a sodium sorbent injection operating at temperatures between 150°C and 400°C, preferably between 160 and 270°C, more preferably between 170 and 220°C.

30 Item 115. The process of any one of the preceding Items, wherein the sodium sulfate residue comprises from 0.05 to 10wt.% sodium sulfite, and wherein step (c2) is performed so that to oxidize at least part of sodium sulfite into sodium sulfate.

Item 116. The process of any one of the preceding Items, wherein the sodium sulfate residue comprises from 0.01 to 10wt.% sodium nitrite, and wherein step (c2) is performed so that to oxidize at least part of sodium nitrite into sodium nitrate.

35 Item 117. The process of any one of the preceding Items, wherein after acidifying step (c1) or during aerating step with oxygen or air (c2) or after step

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(c2), an oxidant selected among: hydrogen peroxide, ozone and sodium hypochlorite, or mixture thereof, is (are) added to the acidified second aqueous solution, and then after alkalization step (c3) of pH about 7 or more, the alkalized aqueous solution is filtered to discolor (decrease the aqueous solution coloration measured with ASTM D1209 standard) or to improve the transparency of the aqueous solution.

Item 118. The process of the preceding Item, wherein the acidified second aqueous solution after step (c1) has an APHA color measured with ASTM D1209 standard of at least 100, and wherein after filtration the aqueous solution comprising sodium sulfate has an APHA value of less than 60, preferably less than 20.

Item 119. The process of any one of the preceding Items, wherein the non-purged separated mother liquor, before being recycled to any one of steps (a) to (d) is treated with at least one of the following treatments:

- adsorption of at least a part of dissolved organic matter on an adsorbent such as active carbon;
- addition of an oxidant selected among: hydrogen peroxide, ozone, sodium hypochlorite, or mixture thereof, is (are) added to mother liquor at acidic pH of less than 6, preferably at pH about 3 to 4 and then the obtained mother liquor is alkalized to pH about 7 or more with an alkaline solution, such as of sodium hydroxide or of calcium hydroxide, to obtain an alkalized mother liquor, and the alkalized mother liquor is filtered to discolor (decrease the aqueous solution coloration measured with ASTM D1209 standard) and/ or to improve the transparency of the aqueous solution, and/or decrease total organic carbon (TOC) content, and/or decrease the chemical oxygen demand(COD).

Item 120. The process of any one of the preceding Items, wherein the the first aqueous suspension on step (a), or the second aqueous solution from any steps (b) to (c3), or the mother liquor from any step (d) to (f), or the non-purged separated mother liquor before or when being recycled to any one of steps (a) to (d), is treated with at least one of the following chemical agent in solid form or in solution:

- an hydroxide salt such as: hydrated lime ($\text{Ca}(\text{OH})_2$), or caustic soda (NaOH);
- a silicate such as sodium silicate or sodium metasilicate;

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- a calcium salt such as lime (CaO), calcium hydroxide (Ca(OH)_2), calcium sulfate (CaSO_4) anhydrous or hydrated (such as: calcium sulfate hemihydrate or calcium sulfate dihydrate i.e.: gypsum), calcium chloride (CaCl_2), calcium nitrate ($\text{Ca(NO}_3)_2$);
- 5 - a sulfide salt such as sodium sulfide (Na_2S) or an organic sulfide compound such as: trimercapto-s-triazine, trisodium salt (such as TMT15 from Evonik®);
- a ferrous salt such as ferrous sulfate (FeSO_4), or a ferric salt such as: ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3$) or iron chloride (FeCl_3);
- 10 - a phosphate salt such an alkaline metal phosphate salt or an alkaline earth metal phosphate salt, preferably in presence of calcium salt listed above;
- a calcium phosphate solid chosen among: hydroxyapatite, apatite, tricalciumphosphate, whitlockite, phosphate octacalcium, brushite, monetite, preferably: apatite;
- 15 - a lead salt, such as lead carbonate (PbCO_3);
- or mixtures thereof,
- for precipitating at least part of heavy metals or chemical residue elements such as: aluminum (Al), arsenic (As), boron (B), barium (Ba), cadmium (Cd), chromium (Cr), cobalt (Co), iron (Fe), manganese (Mn), mercury (Hg),
- 20 molybdenum (Mo), nickel (Ni), lead (Pb), antimony (Sb), selenium (Se), titanium (Ti), vanadium (V), or zinc (Zn), or mixtures thereof, from the non-purged separated mother liquor.

Item 121. The process of the preceding Item, wherein the treatment with at least one of the chemical agent selected from: the silicate salt, the calcium salt,

25 the sulfide salt, the ferrous salt, the phosphate salt, the calcium phosphate solid, and mixtures thereof is operated at a pH of 7 to 13, or more preferably at a pH 8 to 10.5.

Item 122. The process of Item 120, wherein the treatment of the first aqueous suspension on step (a), or of the second aqueous from steps (b) or (c3),

30 or of the mother liquor from any step (d) to (f), or of the non-purged separated mother liquor is done with an hydroxide salt and is operated at a pH of at least 12, and is followed by a separation step of insoluble matter so that to discolor (decrease the aqueous solution coloration measured with ASTM D1209 standard) corresponding solution after said separation step.

35 Item 123. The process of the preceding Item, wherein the treatment of the first aqueous suspension on step (a), or of the mother liquor from any step (d) to

(f), or of the non-purged separated mother liquor with the hydroxide salt operated at a pH of at least 12 is done at step (a) so that to discolor the second aqueous solution from step (b).

Item 124. The process of Items 123 or 124, wherein the pH is at most 13.

5 Item 125. The process of any Items 120 to 124, wherein the treatment with the hydroxide salt, the silicate salt, the calcium salt, the sulfide salt, the ferrous salt, the phosphate salt, the calcium phosphate solid, and mixtures thereof is operated before or when recycling the non-purged mother liquor at step (a) or (b).

10 Item 126. The process of any Items 120 to 125, wherein the treatment with at least one of the chemical agent selected from: the hydroxide salt, the silicate salt, the calcium salt, the sulfide salt, the ferrous salt, the phosphate salt, and mixture thereof is performed before or when recycling at step (a) or (b), and preferably at a pH of 7 to 13, or more preferably at a pH 8 to 10 (pH 8 to 10 being particularly preferred when the solutions comprise more than 2 ppm Pb).

15 Item 127. The process of any Items 120 to 125, wherein the treatment with at least one of the chemical agent selected from: the ferric salt, or the lead salt is the hydroxide salt, the silicate salt, the calcium salt, the sulfide salt, the ferrous salt, the phosphate salt, and mixture thereof is performed before or when recycling at step (c) or (d), and preferably at a pH of 3 to 7, more preferably at a
20 pH of 4 to 6.

Item 128. The process of any one of the preceding Items, wherein the purged mother liquor has a sodium sulfate concentration of at most 15 wt%, preferably at most 10 wt%, more preferably at most 8 wt%.

25 Item 129. The process of any one of the preceding Items, wherein the purged mother liquor has a sodium chloride concentration of at least 5 wt%, preferably at least 10 wt%, or at least 15 wt%.

Item 130. The process of any one of the preceding Items, wherein the purged mother liquor has a sodium chloride concentration of at most 28 wt%, preferably at most 25 wt%, or at most 20 wt%.

30 Item 131. The process of any one of the preceding Items, wherein the purged mother liquor is then sprayed-dried.

Item 132. The process of any one of the preceding Items, comprising further:

(f) drying the sodium sulfate particles separated from mother liquor at step (e).

35 Item 133. The process of any one of the preceding Items, wherein the sodium sulfate particles obtained at step (d) is anhydrous sodium sulfate.

Item 134. The process of any one of Items 101 to 131, wherein the sodium sulfate particles obtained at step (d) is sodium sulfate decahydrate crystals.

Item 135. The process of any one of the preceding Items, wherein the sodium sulfate particles are further used in a soda ash plant as a sodium raw
5 material.

Item 136. The process of the preceding Item, wherein the sodium sulfate particles are further dissolved and reacted with residual distillation liquid comprising calcium chloride from an ammonia soda ash process, to produce sodium chloride and calcium sulfate, and said sodium chloride is further recycled
10 to produce sodium carbonate or sodium bicarbonate.

Item 137. Use of the sodium sulfate particles obtained from steps (e) or (f) of any one of the preceding Items, in detergent powder or detergent tablet.

Item 138. Use of the sodium sulfate particles obtained from steps (e) or (f) of any one Items 101 to 136, in glass furnace.

Item 139. Use of the sodium sulfate particles obtained from steps (e) or (f) of any one Items 101 to 136, in dyeing and/or textile processes.

Figure 1 illustrates an embodiment of the sodium sulfate recovery plant of present invention. A sodium sulfate residue **0**, comprising sodium sulfate, sodium carbonate, and insoluble matter, is dissolved in a dissolver (A) for
20 dissolving the sodium sulfate residue with a first aqueous solution **1** to obtain a first aqueous suspension **2** comprising sodium sulfate and sodium carbonate and is injected in a press filter or disk filter (B), to separate a separated insoluble matter **4**, and a second aqueous solution **3**; said second aqueous solution **3** is then directed in an acidifying reactor (C1) for acidifying the second aqueous
25 solution with sulfuric acid **5** to a pH less than 6, so that to transform all dissolved sodium carbonate to sodium sulfate; the generated CO₂ from the acidifying of the carbonate is removed from the reactor (C1) by an outlet placed on the reactor; the acidified second aqueous solution **6** is fed then into an alkalinizing reactor (C3) having a feeding inlet for an alkali solid or an alkaline solution such
30 as sodium carbonate solid or solution, or sodium hydroxide solid or solution **7**, for alkalinizing to a pH of about 7 or more the aqueous solution exiting the acidifying reactor (C1); an evaporator-crystallizer (D) for removing at least part of the water **9** from the alkalinized aqueous solution exiting the alkalinizing reactor (C3) and to obtain a mother liquor and to crystallize sodium sulfate
35 particles within said mother liquor; a separation equipment (E) for separating sodium sulfate particles **15**, from the mother liquor **11**, and sodium sulfate

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particles **15** being recovered; a purge mean (F) such as a pump enables to purge part of mother liquor to maintain level of soluble impurities in the crystallizer at a targeted value, said purge mean (F) being placed on the pipe from the press filter (E) to the evaporator-crystallizer (D) for recycling mother liquor **13**, and
5 for recycling mother liquor **14** to the dissolver (A); the pump (F) is selected to provide a purge weight ratio of the purged separated mother liquor **12** to the non-purged separated mother liquor (**13** + **14**) of at least 0.005 t/ t and at most 0.20 t/t.

Typically the ratio of the recycling mother liquor **13** to the evaporator-crystallizer (D) to the non-purged separated mother liquor (**13** + **14**) is 0.2 to 1.0
10 t/t in weight. Preferably this ratio is 0.6 to 0.98 t/ t in weight. Therefore preferably, the recycled mother liquor **13** to the evaporator-crystallizer (D) to the recycled mother liquor **14** to the dissolver (A) is 1.5 to 49 t/t in weight, more preferably 4 to 10 t/t in weight; This enables to make part of secondary
15 impurities treatment (aside sodium chloride impurity that is generally controlled by the purge flow **12** for removing NaCl and for removing other soluble salts such as: NaF, NaBr, NaI, NaNO₂, NaNO₃) when removed in dissolver (A) with additives to make them precipitate as insoluble salts with one of the reactant listed in Item 120, and to remove them on a filtration step b) of above described
20 process.

Should the disclosure of any patents, patent applications, and publications which are incorporated herein by reference conflict with the description of the present application to the extent that it may render a term unclear, the present description shall take precedence.

EXAMPLES

EXAMPLE 1

The following examples are intended to illustrate the present invention without limiting the scope of the present invention.

30 The samples used here after have been selected from 3 different steel and coke plants using dry sorbent injection flue gas mitigation, using technical grade sodium bicarbonate.

Typical analysis of sodium sulfate residues present on the market (such as coking flue gas mitigation residues).

Table 1 - Main components ranges in coking residue

Components	Na ₂ SO ₄	Na ₂ CO ₃	NaCl	Insoluble
Composition (wt%)	80-90	10-15	1-5	<1

As shown in table 1, the sulfate residues belongs to inorganic residue and most of the content in the residue is Na₂SO₄. There is still 10 to 15% of Na₂CO₃ in the residue due to insufficient reaction. However, to change the Na₂CO₃ to Na₂SO₄ acid attack with H₂SO₄, is operated and thus obtaining a Na₂SO₄ content higher than 95%.

Residue analysis of sample tested for exemplifying present invention, in following examples.

Table 2 - Values of key components in three batches of residue
(composition in wt%).

Sample A		Sample B		Sample C	
Na ₂ SO ₄ %	92.7	Na ₂ SO ₄ %	82.6	Na ₂ SO ₄ %	89.6
Na ₂ CO ₃ %	3.9	Na ₂ CO ₃ %	18	Na ₂ CO ₃ %	11.2
NaCl %	4.9	NaCl %	2.5	NaCl %	0.8
Insoluble %	0.45	Insoluble %	0.9	Insoluble %	0.02
Total %	102	Total %	104	Total %	101.7

The following steps were performed at lab scale on reactors of 1.5 liters volumes:

Dissolution → filtration → acidification → crystallization → drying

The sodium sulfate residue is dissolved in water first and form a yellow liquid with black insoluble particles (ie first aqueous suspension). The solution concentration was 25 wt% in salts, close to saturation at room temperature and included Na₂CO₃, Na₂SO₄, NaCl and insoluble particles. The filtration step was performed on lab filter to remove insoluble particles, so the resultant solution (ie. 'second aqueous solution') included Na₂CO₃, Na₂SO₄, and NaCl.

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Then, H_2SO_4 was added into the solution at a pH value under 3.7 in order to change all the Na_2CO_3 to Na_2SO_4 , and then NaOH was added to adjust pH value back to 7-8 so that after acidification and neutralization process the solution has its sodium carbonate transformed in sodium sulfate, and thus
5 includes mainly Na_2SO_4 , NaCl .

After above steps, the second aqueous solution was injected into flask for the crystallization process. The crystallization process was kept at 50 °C and under the pressure of 100 mbar. The evaporation rate was 100 g water/ h. During the evaporation, the Na_2SO_4 crystallized when saturation is reached.

10 After a certain period of crystallization, the crystal particles were removed out of the solution and then dried in an oven after washing. The purified Na_2SO_4 produced showed a very light color.

Moreover, COD (Chemical Oxygen Demand) content and Na_2SO_3 were also considered during the whole process. Na_2SO_3 was low in the solution due to
15 its oxidation at acidic pH into Na_2SO_4 . The COD content in solution before crystallization was 150-300 ppm of equivalent carbon. The COD from organics, does not evaporate in the crystallization step, therefore it accumulates when recycling the mother liquors of the crystallization to dissolve again sodium sulfate residues. Rather than purging a high quantity of crystallization mother
20 liquor, to avoid high concentration of impurities such as sodium chloride, or organics, the purge is oxidized with H_2O_2 or hypochlorite at pH , to remove part of the organics (measured as COD or as TOC). And part of this treated mother liquor is recycled back to the dissolution of sodium sulfate residues according the present invention.

25 The obtained purified sodium sulfate is non-colored, as when the purge from crystallizer is not treated the obtained sodium sulfate particles become more and more brownish.

Also a check on heavy metals concentration in final sodium sulfate, on listed elements with reactants such as sodium silicate or sodium sulfide, shows that the
30 removal of heavy metals on the concentrated crystallization mother liquor is more efficient on total heavy metal removal than doing it on the main dissolution flow stream and reduces.

The treatment of the purge enables to decrease sensitively the purge volume, and increases the yield for recovering the sodium sulfate from the residues, and
35 decrease the purge brine to be disposed of.

The final crystallized sodium sulfate meets Chinese national standard (Class II first grade).

Another trial was made with higher temperature difference (60°C) to heat the crystallizer, with a higher evaporative rate of 300g water/h (compared to 100g/h with lower temperature difference: 25 °C). The obtained crystals were of smaller size compared to previous test but still meeting Chinese national standard (Class II first grade).

Tests on other sodium sulfate residues of similar compositions but from other industrial flue gases (power steam generator, tires incinerators, ...), show similar behavior in regards of limiting purge amount possibility, when purifying part of the purge of mother liquors before recycling them either in the crystallizer or in the dissolution step. Though impurities level varies in sulfate residues according to the flue gas type and therefore quantity of sorbent or reactants to remove impurities are adapted consequently. Steel and coke residues among said sulfate residues present favorable conditions for obtaining high grade purified sodium sulfate particles.

EXAMPLE 2

Three other samples of sodium sulfate residues selected from 3 other different coke plants (different from Example 1) and also using dry sorbent injection flue gas mitigation, using technical grade sodium bicarbonate, Said three samples were within the composition limits from table 3 infra.

Table 3 - Typical composition of sodium sulfate residues from flue gas SOx mitigation

Component	Na ₂ SO ₄	Na ₂ CO ₃	NaHCO ₃	NaCl	Insoluble
Composition (wt%)	70~90	5~35	0~3	0.05~10	<2

The three above samples were mixed so that to make one homogeneous sample of sodium sulfate residue.

As shown in the table 3, the residues are Na₂SO₄-enriched solid wastes. The incomplete reaction between the flue gases to be treated and the injected sodium bicarbonate explains the remaining amount of Na₂CO₃ (resulting from the thermal activation of NaHCO₃) and NaHCO₃. However, when dissolved in an aqueous solution, these salts can be easily transformed into Na₂SO₄ by means of a treatment of pH adjustment.

Table 4 - Values of key components of the mixture sample
of sodium sulfate residue of Example 2

Component	Composition (wt%)
Na ₂ SO ₄	79,8
Na ₂ CO ₃	15,6
NaHCO ₃	0,87
NaCl	4,49
NaNO ₃	0,12
Insoluble	1,31
COD	0,07

Table 5 - Values of secondary impurities and heavy metals
of the mixture sample of sodium sulfate residue of Example 2

Element	ppm (mg/ kg)
Mg	65
Al	50
Si	9
K	44
Ca	134
Ti	3
V	7
Cr	2
Fe	205
Zn	14
Pb	441
Mn	2
P	79
Se	2

5 Description of the tests performed at laboratory scale simulating the Figure 1 process

Similar conditions as the ones performed in Example 1 were used
consisting mainly in:

- a pretreatment process comprising steps (a) to (c3) and
- 10 - a crystallization process comprising steps (d) to (f).

The mixture of residues (1200 g) were dissolved in water (5000 g) at 25°C, forming a yellow liquid with black insoluble materials (i.e. the first aqueous suspension). The liquid comprised 20 wt% of soluble salts (close to the saturation at room temperature of sodium sulfate and other soluble salts from the sodium sulfate residues (i.e. including 16 wt% Na₂SO₄, 2.7 wt% Na₂CO₃, 0.5 wt% NaHCO₃, 0.9 wt% NaCl and 0.03 wt% NaNO₃, and 0.07 wt% COD, as main components of soluble salts and compounds, and 0.2 wt% insolubles). pH of the suspension was 10.5.

25 g of solid sodium hydroxide was added to rise pH to 12.5 of the suspension, and the suspension was filtered on a stainless filter (membrane of 0.22 µm) coupled with a vacuum pump to remove the insolubles and formed precipitate of some of the heavy metals.

The rise of the pH to 12.5 had the advantage to decrease sensitively the color of the second aqueous solution obtained after filtration.

Indeed without pH adjustment (original pH = 10.5) the second aqueous solution after removal of insolubles had a strongly yellow color. When pH was raised to 12.5 with sodium hydroxide addition, the second aqueous solution after filtration had a very light yellow color.

Sulfuric acid (167 g) was then added to the second aqueous solution to reach a pH value of 3.8. The acidified solution was bubbled with compressed air during 30 minutes to ease the stripping of the carbon dioxide gas (therefore reacting on sodium carbonate to produce sodium sulfate, water and CO₂ gas), using an air flow of about 8 liters of air per minute and per liter of the aqueous solution to bubbled. The acidified second aqueous solution had the following composition: 21.4 wt% Na₂SO₄, 0 wt% Na₂CO₃ & NaHCO₃, 0.8 wt% NaCl and 0.03 wt% NaNO₃ and a COD value of 0.03 wt%.

Then pH was raised back to about 7 with the addition of 1.8 g solid NaOH.

One kilogram of this neutralized second aqueous solution was then introduced into a glass reactor of 2 liters, fitted with an impeller with 4 pitched blades and a heating jacket for the evaporative crystallization. The pressure was maintained at atmospheric pressure (at about 1 bar), a temperature of 104 to 109°C, and a rotation speed of 350 RPM. The evaporation rate was controlled between 200 and 250 g of water / hour. During this step, Na₂SO₄ crystals were formed and accumulated in the reactor.

After about 2 hours of evaporation and removal of 550 g of water (to limit the solid content in the slurry of less than 30% in weight), the formed Na₂SO₄

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crystals were separated from the mother liquor by a filtration step performed thanks to a stainless filter (paper membrane) coupled with a vacuum pump.

The mother liquor after separation of the sodium sulfate crystals had the following composition: 25.1 wt% Na₂SO₄ and 2.1 wt% NaCl, and 0.06 wt%
5 NaNO₃ and 0.05 wt% COD.

The sodium sulfate crystals were dried at 100°C and had the following characteristics: particle size distribution: D₉₀= 376 μm, D₅₀= 99μm, D₁₀ = 6 μm. And the crystals had the following composition: 99.1 wt% Na₂SO₄, 0.09 wt% NaCl, 0.02 wt% NaNO₃ and 0.01 wt% COD.

10 The first mother liquor obtained after filtration was mixed back with a part of part of remaining pretreated solution (a sufficient quantity of the pretreated solution was prepared for five crystallization cycles) to simulate the recycling of mother liquors and the resulting solution was adjusted before each crystallization cycle by keeping the quantity of the solution and the concentration of Na₂SO₄
15 constant (addition of water).

A washing step of the wet cake with a Na₂SO₄ saturated solution was carried out to simulate a better removal of mother liquors (i.e. be close to the efficiency of a centrifuge). Thus, a second filtration step was achieved by means of a stainless filter (paper membrane) coupled with a vacuum pump to recover
20 the washed wet cake that was dried in an oven at 100°C to produce purified Na₂SO₄.

Results of the tests performed at laboratory scale.

According to the results of the five crystallization cycles, it was possible to note that the accumulation of impurities associated with a limited purge related
25 to the sample that were analyzed, enabled to build up the impurities, including the salts (NaCl and NaNO₃) as well as the organic materials, impacted in a limited way the quality of the final product.

The sodium chloride content in the dried crystals raised gradually to the following values: 0.09 wt%, 0.15 wt%, 0.12 wt%, 0.16 wt%, 0.31 wt%.
30 The NaNO₃ content in the dried crystals raised gradually to the following values: 0.016 wt% to 0.025 wt%. The COD content in the dried crystals raised gradually from 0.08 wt% to 0.017 wt%. Whiteness* decreased gradually from 91.8% for the first crystallization, then to the following values: 90.5%, 92.3%, 91.8%, 92.7%

35 In fact, the crystals of Na₂SO₄ resulting from each crystallization cycle meet the intended quality of the final product in terms of purity (including

insoluble matter and metals) and whiteness according to *GB/T 6009-2014 Chinese specifications regarding anhydrous sodium sulfate (Whiteness to be > 82% for standard II 1st grade).

Analysis of the 5th sample of sodium sulfate crystallized is given in Table

5 Though, the amount of NaCl and NaNO₃ as well as the COD (Chemical Oxygen Demand) content in each first filtrate that is recycled at the next crystallization cycle increase linearly. On the contrary, the quantity of NaCl, NaNO₃ and COD contained in the final product does not follow a clear tendency, probably due to the efficiency of the washing step which is highly dependent on
10 the properties (size and porosity) of the crystals of Na₂SO₄. In addition, the amount of moisture and the insoluble matter content measured in the final product seems to change in the same way, indicating that the higher the humidity, the greater the insoluble matter content. Finally, the quantity of metals
15 in the final product, and especially the amount of Mg, Ca and Fe entering into the specifications of above cited standard, appears globally constant and well below the standard limits. Therefore enabling the use of said sodium sulfate in detergent application, and also in glass industry, and textile industry.

Table 6 - Values of main components and impurities
of the mixture sample of final sodium sulfate crystals of Example 2
20 with simulation of impurities build-up

Comparison with the specifications (Class II - First grade - GB/T 6009-2014)		
Element	Specifications (% w)	Product (% w)
Na ₂ SO ₄	≥ 98	98.7
Cl	≤ 0.70	0.19
Moisture	≤ 0.50	0.10
Insoluble	≤ 0.10	0.08
Ca	≤ 0.30	0.0043
Mg	≤ 0.30	0.0001
Fe	≤ 0.01	0.0001
Whiteness	≥ 82	92.7

EXAMPLE 3

As the aqueous solution obtained after dissolution of the sodium sulfate residues coming from gas mitigation, has a yellow color coloration depending sensitively on the plant delivering such salt residues, as this is linked to the raw materials used in coke plant, sintering plant and steel plants, and the impurities of said raw materials (coal, iron ore, fuels etc...), complementary tests have been performed to test the possibility to reduce the amount of organics, and possibly the soluble metals salts present at trace level, that have an influence on the final color (such as iron, cobalt, copper, manganese, and so on) of the crystallized sodium sulfate.

Different tests on discoloring have been tested on a representative sodium sulfate residue from SO_x mitigation with sodium bicarbonate.

- Activated carbon

- Ozone (O₃) treatment

- H₂O₂ treatment at acidic pH

- Alkalization treatment.

Tests 3.1 with Active Carbons

Two qualities of active carbon were tested on 'a second aqueous solution' (after step (b) of the process of present invention) (pH = 10) obtained after dissolving sodium sulfate residue from a coke plant flue gas mitigation. Said active carbon were from Calgon Carbon Corporation: Filtrasorb F300D and IPGX. They were tested at 5 different concentrations reported to the weight of the aqueous solution at 0.01%, 0.05%, 0.10%, 1.0%, 2.0%.

Only a slight discoloration was observed when using active carbon: in the better case from strong yellow to middle yellow color, after filtration, enabling to reduce the COD from a. 20% of the total COD value: from 115 mg/ L to 95 mg / L when using active carbon at high concentration (2%). Results were similar for both active carbon tested.

Tests 3.2 with Ozone

Starting from a second aqueous solution (after step (b) of the process of present invention), similar as in the test 3.1, O₃ generated by an ozone generator, providing 30 mg O₃ per min and introduced in 50 mL of the same aqueous solution, it was observed that the strong yellow color (APHA value of 213) the value with O₃ injection raised to 451 APHA, with a precipitate. After filtration on a 0.2 µm membrane, the APHA value went down to a value of 12, and COD content decreases from 100 ppm to 50 ppm, but with a strong efficacy on the

color reduction (factor 18), even if the COD content was reduced by only a factor 2.

Therefore ozone is effective when used in combination with a filtration on said aqueous solution.

- 5 The APHA value was measured with platinum/cobalt scale according ASTM standard, expanded to compare the intensity of yellow-tinted samples, using an HACH DR3900 at a wavelength of 465nm.

Tests 3.3 with H₂O₂

- 10 Starting from same second aqueous solution obtained after step (b), at a pH of 9.3, acidified with H₂SO₄ down to pH 3.8, with air bubble injection for 30 minutes so that to remove sensitively all sodium carbonate and bicarbonate from the solution and transform them in sodium sulfate (corresponding therefore to step (c2), 100 and 500 ppm H₂O₂ were added to the solution stirred during 10 minutes, and then the acidic solution was neutralized with sodium hydroxide up to pH 7-8. A precipitate appeared and was filtered: the COD content of the solution did not change so much with 100 ppm of H₂O₂: 99 ppm COD in initial solution, and a close value of 104 ppm in the final solution. Using 500 ppm enabled to decrease COD from 99 ppm to 39 ppm.

- 20 Though the color decrease of the 100 ppm H₂O₂ treated solution was as effective as the 500 ppm H₂O₂ treated solution: the APHA color index went down from 139 in initial solution to less than 10 for both 100 ppm and 500 ppm H₂O₂ treated solutions. Therefore even at low concentration (100 ppm) H₂O₂ action at acidic pH, with then a filtration step is effective to discolor the sodium sulfate solution with impurities.

25 Tests 3.4 alkalizing the aqueous solution with an hydroxide

Second aqueous solution obtained after step (b), at a pH of 9.3 was treated in 2 different ways:

- method 1: acidifying with H₂SO₄ down to pH 3.8 (step (c3) with air injection to strip CO₂ for 30 minutes) and then pH was adjusted to pH 12-13 with NaOH and then filtrated and
 - method 2: directly alkalized up to pH 12-13 with sodium hydroxide, then filtrate, and then acidifying down to pH 3.8 with air bubbling during 30 minutes, and then neutralized to pH 7-8 with NaOH without filtration after neutralizing step.
- 35 Both methods 1 and 2 were efficient to discolor the aqueous solution before evaporation and crystallization (respective APHA values of 52 and 33 from a

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starting point of initial aqueous solution at 139), even though the COD content remains at same value or range (97-110 ppm).

Though method 1, acidifying first with H_2SO_4 to remove CO_2 and then alkalizing back to neutral value, is more interesting as the amounts of acid and alkaline are

5 decreased sensitively (-30% and -80%) compared to performing the steps reversely:

needing respectively 8.5 g H_2SO_4 / 0.68 g NaOH (100%) per 130 g of solution for method 1.

and 11.9 g H_2SO_4 / 3.30g NaOH (100%) per 130 g of solution for method 2.

10

CLAIMS

1. A process for purifying a sodium sulfate residue comprising: sodium sulfate, sodium carbonate and/or sodium bicarbonate, and sodium chloride, and optionally insoluble matter, said process comprising:
- 5 (a) dissolving the residue with a first aqueous solution to obtain a first aqueous suspension, comprising at least 5 wt% and at most 32 wt% sodium sulfate;
- (b) optionally separating insoluble matter by filtration, decantation, or centrifugation from the first aqueous suspension to obtain:
- 10 - a separated insoluble matter, and
- a second aqueous solution;
- (c1) acidifying the second aqueous solution with sulfuric acid to a pH less than 6 so that to transform at least part, or all, dissolved sodium carbonate and/or sodium bicarbonate to sodium sulfate;
- (c2) optionally aerating the second aqueous solution with oxygen or air to
- 15 convert sulfites to sulfates;
- (c3) alkalizing the acidified second aqueous solution obtained at step (c1) to a pH of about 7 or more, using an alkali or an alkaline solution such as sodium hydroxide or part of the second aqueous solution obtained at step (b);
- (d) removing at least part of the water from the second aqueous solution from
- 20 any step (c1) to (c3) to obtain a mother liquor and to crystallize sodium sulfate particles within said mother liquor,
- (e) separating sodium sulfate particles from the mother liquor
- (f) purging at least part of the mother liquor and recycling at least part of the non-purged mother liquor in at least one of the steps (a) to (d),
- 25 characterized in that the weight ratio of the purged separated mother liquor to the non-purged separated mother liquor is at most 0.20, preferably at most 0.10, more preferably at most 0.05 t/t, or at most 0.005 t/t.
2. The process of claim 1 wherein the sodium sulfate residue comprises:
- 30 - at least 70 wt% sodium sulfate,
- from 0.01 to 30 wt% insoluble matter,
- from 0.01 to 30 wt% sodium carbonate and/or sodium bicarbonate,
- from 0.01 to 30 wt% sodium chloride,
- expressed on the total weight of the residue, and wherein the sum of sodium

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sulfate, insoluble matter, sodium carbonate and/or sodium bicarbonate, and sodium chloride is at most 100 wt%.

3. The process of any one of the preceding claims wherein steps (c1) and (c2) are both operated in a same device.

5 4. The process of any one of the preceding claims, wherein the sodium sulfate residue comprises a residual salt from flue gas SO_x mitigation, said flue gas being selected from: a coke plant, a sinter plant, a steel plant, a cement plant, a glass plant, an oil refinery, a petro-chemical plant, a power plant, a lime kiln, a waste incinerator.

10 5. The process of the preceding claim, wherein the flue gas being from: a coke, or a steel plant or a sintering plant.

 6. The process of any one of the preceding claims, wherein the sodium sulfate residue comprises from 0.05 to 10wt.% sodium sulfite and/or sodium nitrite, and wherein step (c2) is performed so that to oxidize at least part of
15 sodium sulfite into sodium sulfate and/ or sodium nitrite into sodium nitrate.

 7. The process of any one of the preceding claims, wherein after acidifying step (c1) or during aerating step with oxygen or air (c2) or after step (c2), an oxidant selected among: hydrogen peroxide, ozone and sodium hypochlorite, or mixture thereof, is (are) added to the acidified second aqueous
20 solution, and then after alkalization step (c3) of pH about 7 or more, the alkalized aqueous solution is filtered to decrease the aqueous solution coloration measured with ASTM D1209 standard.

 8. The process of the preceding claim, wherein the acidified second aqueous solution after step (c1) has an APHA color measured with ASTM
25 D1209 standard of at least 100, and wherein after filtration the aqueous solution comprising sodium sulfate has an APHA value of less than 50, preferably less than 20.

 9. The process of any one of the preceding claims, wherein the non-purged separated mother liquor, before being recycled to any one of steps (a) to
30 (d) is treated with at least one of the following treatments:

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- adsorption of at least a part of dissolved organic matter on an adsorbent such as active carbon;
 - addition of an oxidant selected among: hydrogen peroxide, ozone, sodium hypochlorite, or mixture thereof, is (are) added to mother liquor at acidic pH of less than 6, preferably at pH about 3 to 4 and then the obtained mother liquor is alkalized to pH about 7 or more with an alkaline solution, such as of sodium hydroxide or of calcium hydroxide, to obtain an alkalized mother liquor, and the alkalized mother liquor is filtered to decrease the aqueous solution coloration measured with ASTM D1209 standard of the aqueous solution, and/or decrease total organic carbon (TOC) content or decrease chemical oxygen demand(COD).
10. The process of any one of the preceding claims, wherein the first aqueous suspension on step (a), or the second aqueous solution from any steps (b) to (c3), or the mother liquor from any step (d) to (f), or the non-purged separated mother liquor before or when being recycled to any one of steps (a) to (d), is treated with at least one of the following chemical agent in solid form or in solution:
- an hydroxide salt such as: hydrated lime ($\text{Ca}(\text{OH})_2$), or caustic soda (NaOH);
 - a silicate such as sodium silicate or sodium metasilicate;
 - a calcium salt such as lime (CaO), calcium hydroxide ($\text{Ca}(\text{OH})_2$), calcium sulfate (CaSO_4) anhydrous or hydrated (such as: calcium sulfate hemihydrate or calcium sulfate dihydrate ie.:gypsum), calcium chloride (CaCl_2), calcium nitrate ($\text{Ca}(\text{NO}_3)_2$);
 - a sulfide salt such as sodium sulfide (Na_2S) or an organic sulfide compound such as: trimercapto-s-triazine, trisodium salt (such as TMT15 from Evonik®);
 - a ferrous salt such as ferrous sulfate (FeSO_4), or a ferric salt such as: ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3$) or iron chloride (FeCl_3);
 - a phosphate salt such an alkaline metal phosphate salt or an alkaline earth metal phosphate salt, preferably in presence of calcium salt listed above;

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- a calcium phosphate solid chosen among: hydroxyapatite, apatite, tricalciumphosphate, whitlockite, phosphate octacalcium, brushite, monetite, preferably: apatite;
 - a lead salt, such as lead carbonate (PbCO_3);
- 5 or mixtures thereof,
for precipitating at least part of heavy metals or chemical residue elements
such as: aluminum (Al), arsenic (As), boron (B), barium (Ba), cadmium
(Cd), chromium (Cr), cobalt (Co), iron (Fe), manganese (Mn), mercury (Hg),
molybdenum (Mo), nickel (Ni), lead (Pb), antimony (Sb), selenium (Se),
10 titanium (Ti), vanadium (V), or zinc (Zn), or mixtures thereof, from the non-
purged separated mother liquor.

11. The process of the preceding claims, wherein the treatment with at least one of the chemical agent selected from: the hydrated lime (Ca(OH)_2), or caustic soda (NaOH); the calcium sulfate (CaSO_4); the silicate salt, the calcium salt, the
15 sulfide salt, the ferrous salt, the phosphate salt, the calcium phosphate solid, and mixtures thereof is operated at a pH of 7 to 13, or more preferably at a pH 8 to 10.5.

12. The process of claims 10 or 11, wherein the treatment of the first aqueous suspension on step (a), or of the second aqueous from any steps (b) to
20 (c3), or the mother liquor from any step (d) to (f), or the non-purged separated mother liquor is done with an hydroxide salt and is operated at a pH of at least 12, and is followed by a separation step of insoluble matter so that to discolor (decrease the aqueous solution coloration measured with ASTM D1209 standard) corresponding solution after said separation step.

25 13. The process of the preceding claim, wherein the treatment of the first aqueous suspension on step (a), or of the mother liquor from any step (d) to (f), or of the non-purged separated mother liquor with the hydroxide salt operated at a pH of at least 12 is done at step (a) so that to discolor the second aqueous solution from step (b).

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14. The process of any claims 12 or 13, wherein the pH is at most 13.

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15. The process of any one of the preceding claims, wherein the purged mother liquor has a sodium sulfate concentration of at most 15 wt% or at most 8 wt%.

5 16. The process of any one of the preceding claims, wherein the purged mother liquor has a sodium chloride concentration of at least 5 wt% or at least 15 wt%.

17. The process of any one of the preceding claims, wherein the purged mother liquor is then sprayed-dried.

18. The process of any one of the preceding claims, comprising further:

10 (f) drying the sodium sulfate particles separated from mother liquor at step (e).

19. Use of the sodium sulfate particles obtained from steps (e) or (f) of any one of the preceding claims, in detergent powder or detergent tablet.

20. Use of the sodium sulfate particles obtained from steps (e) or (f) of any one of the preceding claims, in glass furnace.

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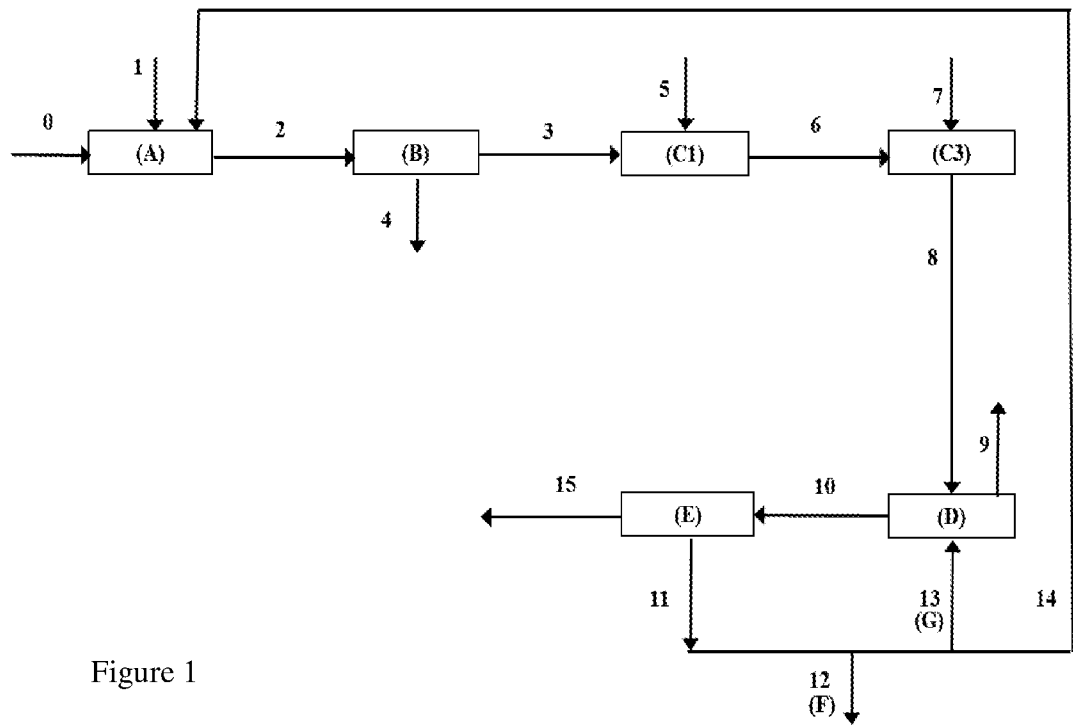


Figure 1

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2020/090982

A. CLASSIFICATION OF SUBJECT MATTER

C01D 5/16(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C01D 5/-

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CNABS, VEN, CNKI, ISI WEB OF SCIENCE: sodium sulfate, sodium sulphate, Na₂SO₄, purify, purge, recycle, mother liquor**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 6180074 B1 (NOVACARB) 30 January 2001 (2001-01-30) claims 1, 11 and 13	1-20
Y	CN 1738787 A (MITSUBISHI CHEM CO LTD) 22 February 2006 (2006-02-22) claim 1	1-20
Y	CN 108658353 A (SHJIAZHUANG GONGDA TECH DEVELOPMENT CO LTD) 16 October 2018 (2018-10-16) claim 1	1-20
Y	CN 104356007 A (LIAONING SHIXING PHARM & CHEM CO LTD) 18 February 2015 (2015-02-18) claim 1	1-20
Y	CN 105906126 A (SHUANGLIANG ECO-ENERGY SYSTEMS CO LTD) 31 August 2016 (2016-08-31) claim 1	1-20
Y	CN 103450287 A (SHANDONG HUAYI CORN SCI & TECHNOLOGY CO) 18 December 2013 (2013-12-18) claim 1	1-20



Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

“A” document defining the general state of the art which is not considered to be of particular relevance

“E” earlier application or patent but published on or after the international filing date

“L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

“O” document referring to an oral disclosure, use, exhibition or other means

“P” document published prior to the international filing date but later than the priority date claimed

“T” later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

“X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

“Y” document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

“&” document member of the same patent family

Date of the actual completion of the international search

21 July 2020

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2020/090982

Patent document cited in search report			Publication date (day/month/year)	Patent family member(s)		Publication date (day/month/year)
US	6180074	B1	30 January 2001	None		
CN	1738787	A	22 February 2006	JP	4140171	B2 27 August 2008
				AU	5261401	A 12 November 2001
				KR	20020092463	A 11 December 2002
				JP	2001316313	A 13 November 2001
				KR	100786042	B1 17 December 2007
				WO	0183416	A1 08 November 2001
CN	108658353	A	16 October 2018	None		
CN	104356007	A	18 February 2015	None		
CN	105906126	A	31 August 2016	None		
CN	103450287	A	18 December 2013	CN	103450287	B 23 September 2015