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Title: FLUE GAS DESULPHURISATION

Abstract: A process for desulphurisation of a gas containing sulphur oxides (SOx) in a wet scrubbing unit is described. The process comprises the step of: contacting said gas with an aqueous tricalcium aluminate hexahydrate (TCA6) scrubbing slurry to remove SOx from the gas by reaction with TCA6 to form a spent scrubbing solution comprising a calcium compound containing sulphur and oxygen, and an aluminium compound containing oxygen and hydrogen.

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FLUE GAS DESULPHURISATION

FIELD OF THE INVENTION
The present invention relates to a process and apparatus for flue gas desulphurisation in which sulphur oxides (SO\textsubscript{x} - usually SO\textsubscript{2} or SO\textsubscript{3}) contained in a flue gas are removed in a wet scrubbing unit through reaction with tricalcium aluminate hexahydrate (TCA6).

BACKGROUND TO THE INVENTION
Aluminium is the world’s second most used metal requiring annual global alumina production of >70 MT, with Australia currently accounting for >20 MT/yr. The extraction of alumina via the Bayer process is energy intensive, requiring both electrical power and steam, such that most alumina refineries produce their own power. Consequently, the alumina industry is a major emitter of greenhouse gases and, where the fuel is coal or heavy fuel oil, can also be a significant emitter of SO\textsubscript{x}, SO\textsubscript{x} emission control measures can be achieved before, during or after combustion. One example of a SO\textsubscript{x} emission control measure which is implemented after combustion is termed "flue gas desulphurisation" (FGD). Using current prior art processes, FGD is facilitated via any economically viable and readily available alkaline medium, with current systems dominated by the use of lime or limestone slurry.

With continuing global demand for aluminium and more stringent environmental legislation, the aluminium industry is increasingly focussed on environmental stewardship and the development of sustainable options for managing its waste and emissions. Utilisation of the highly alkaline red mud waste stream from the alumina refinery for emissions control is a viable option which has been successfully implemented for both SO\textsubscript{2} and CO\textsubscript{2}. However, utilising red mud for SO\textsubscript{2} removal is inefficient and can be costly to implement due to the large quantities of non-reactive species being unnecessarily cycled through the system. This approach can also result in the undesirable recycle of sulphite and sulphate anions back to the refinery's liquor streams.

Wet scrubbing methods for the removal of sulphur dioxide from powerhouse flue gases, using lime or magnesium as the scrubbing component, are known. For example, European Patent Publication Number 0162536, European Patent Publication Number 0697234 and US Patent 5,648,048 describe apparatus for wet type flue gas desulphurisation using limestone, quicklime or slaked lime, with gypsum produced as a by-product. US Patents 3,914,378; 3,919,393; 3,919,394;
4,487,784; 4,976,936; 4,996,032; 5,047,221; and 5,645,807 describe various methods in which an aqueous magnesium-enhanced lime scrubbing slurry is contacted with the sulphur dioxide-containing gas in a wet scrubbing unit to form calcium sulphite that is either disposed of or oxidised and converted to gypsum. Alternatively, an aqueous solution of magnesium scrubbing components can be used for the same purpose, with regeneration of the spent solution using lime or a magnesium-enhanced lime as described in US Patent 5,039,499 and 5,084,255. While these methods are technically viable and some have found commercial application, improvements to scrubbing efficiency, raw material use, capital cost and fate of the spent absorption medium are constantly sought.

SUMMARY OF THE INVENTION

According to a first aspect of the present invention there is provided a process for desulphurisation of a gas containing sulphur oxides (SOx) in a wet scrubbing unit, the process comprising the step of:

contacting said gas with an aqueous tricalcium aluminate hexahydrate (TCA6) scrubbing slurry to remove SOx from the gas by reaction with TCA6 to form a spent scrubbing solution comprising a calcium compound containing sulphur and oxygen, and a aluminium compound containing oxygen and hydrogen.

In one form, the calcium compound containing sulphur and oxygen is soluble calcium sulphite and the process further comprises the step of adding a source of oxygen to the spent scrubbing solution in an amount sufficient to encourage oxidation of soluble calcium sulphite to solid calcium sulphate. The amount sufficient to encourage oxidation of calcium soluble calcium sulphite to solid calcium sulphate may be at least one mole of oxygen for every two moles of sulphur dioxide to be removed from the gas. In one form, the aluminium compound containing oxygen and hydrogen is aluminium hydroxide which is present as a solid in the spent scrubbing solution.

The process may further comprise the step of removing the solid calcium sulphate and solid aluminium hydroxide from the spent scrubbing solution.
Advantageously, the TCA6 present in the aqueous TCA6 scrubbing slurry may be filter aid or spent filter aid from an alumina refinery. Alternatively or additionally, the TCA6 present in the aqueous TCA6 scrubbing slurry may be present with calcium carbonate in a causticizer underflow sludge.

In one form, the wet scrubbing unit includes an absorption tower and a dust scrubbing unit and the gas to be scrubbed is partially desulphurised and cooled in the dust scrubbing unit by contacting the gas with a stream of the spent scrubbing solution.

In one form, the step of contacting the gas with the aqueous TCA6 scrubbing slurry comprises spraying the aqueous TCA6 slurry into an absorption tower to achieve an even distribution of the aqueous TCA6 slurry across the cross-section of the absorption tower.

In one form, the spent scrubbing solution is collected in a recirculation tank arranged towards a lowermost section of the absorption tower for recirculation. Optimally, the step of recirculating the aqueous TCA6 scrubbing slurry continues until the pH of the spent scrubbing solution falls below 5.5 or 5.0. Alternatively or additionally, the step of recirculating the aqueous TCA6 scrubbing slurry may continue until the level of reduction of emissions in a desulphurised gas stream being discharged to atmosphere from the wet scrubbing unit exceeds a predetermined maximum discharge limit.

In one form, the desulphurised gas stream being discharged to atmosphere from the wet scrubbing unit has a sulphur dioxide content that has been reduced by between 90 and 100% compared with a gas containing sulphur oxides (SOx) which was fed to the wet scrubbing unit. Alternatively or additionally, the desulphurised gas stream is discharged to atmosphere from a wet scrubbing unit at a temperature in the range of 70 to 90°C.

In one form, the aqueous TCA6 scrubbing slurry is prepared by mixing a source of TCA6 with a source of makeup water together with a clarified recycled spent scrubbing solution.

In one form, a portion of the spent scrubbing solution is drawn off continuously from the wet scrubbing unit so as to control the residence time of the aqueous TCA6 scrubbing slurry within an absorption tower located within the wet scrubbing unit.
In one form, the TCA6 scrubbing slurry is recirculated through an absorption tower such that the residence time of the aqueous TCA6 scrubbing slurry in the wet scrubbing unit is in the range of about 15 to 90 minutes.

In one form, a portion of the spent scrubbing slurry from the wet scrubbing unit is directed to a reaction tank where residual unreacted TCA6 is decomposed by the addition of a stream of sulphuric acid to form a neutralised slurry. The neutralised slurry may be reacted with a source of oxygen to convert any remaining soluble calcium sulphite present in the neutralised slurry to solid calcium sulphate.

In one form, the aqueous TCA6 scrubbing slurry comprises at least one mole of tricalcium aluminate hexahydrate for every three moles of sulphur dioxide to be removed from the gas.

According to a second aspect of the present invention there is provided a process for desulphurisation of a gas containing sulphur oxides (SOx) in a wet scrubbing unit substantially as herein described with reference to and as illustrated in the accompanying illustrations and examples.

**BRIEF DESCRIPTION OF THE DRAWINGS**

In order to facilitate a more detailed understanding of the nature of the invention embodiments of the present invention will now be described in detail, by way of example only, with reference to the accompanying drawings, in which:

Figure 1 is a schematic flowchart of one embodiment of the present invention.

**DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS**

Particular embodiments of the process and system of the present invention are now described, with particular reference to the use of TCA6 filter aid for desulphurisation of a flue gas in an alumina refinery, by way of example only. The present invention is equally applicable to the removal of sulphur oxides from other types of gas, including exhaust gases and powerhouse stack gases or the flue gases from any stationary fossil-fuel combustion facility in an alumina refinery. The terminology used herein is for the purpose of describing particular embodiments only, and is not intended to limit the scope of the present invention. Unless defined otherwise, all technical and
scientific terms used herein have the same meanings as commonly understood by one of ordinary skill in the art to which this invention belongs. In the drawings, it should be understood that like reference numbers refer to like members.

The term "SO\textsubscript{x}" refers to sulphur oxides, usually sulphur dioxide (SO\textsubscript{2}) or sulphur trioxide (SO\textsubscript{3}).

The term "TCA" refers to pure anhydrous tricalcium aluminate having the general formula of Ca\textsubscript{3}Al\textsubscript{2}O\textsubscript{6}, also commonly represented as 3CaCaI\textsubscript{2}O\textsubscript{3}.

The term "TCA6" refers to tricalcium aluminate hexahydrate which has the general formula of Ca\textsubscript{3}[Al(OH)\textsubscript{6}]\textsubscript{2}, but it is also commonly represented as 3CaCaI\textsubscript{2}O\textsubscript{3}.6H\textsubscript{2}O.

The term "gypsum" refers to calcium sulphate dihydrate which has the general formula of CaSO\textsubscript{4}.2H\textsubscript{2}O.

The term "gibbsite" refers to the most commonly encountered form of aluminium hydroxide having the general formula of Al(OH)\textsubscript{3}. Where gibbsite is referred to in the text it should be noted that other forms of aluminium hydroxide, both crystalline and amorphous, are equally applicable.

A process (10) for desulphurisation of a gas (12) containing sulphur oxides (SO\textsubscript{x}) in a wet scrubbing unit (14) is now described with reference to the schematic flow sheet illustrated in Figure 1. In this example, the gas (12) is a flue gas. The process (10) comprises the step of contacting the flue gas (12) with an aqueous tricalcium aluminate hexahydrate (TCA6) scrubbing slurry (16) to remove SO\textsubscript{x} contained in the gas by reaction with the TCA6 to form a spent scrubbing solution (18) comprising a solid calcium compound containing sulphur and oxygen, and a solid aluminium compound containing oxygen and hydrogen. The aqueous TCA6 scrubbing slurry (16) is prepared in a slurry tank (20) before being fed to the wet scrubbing unit (14) using a slurry pump (22) via a slurry feed line (24).

Using the process of the present invention, when the aqueous TCA6 scrubbing slurry (16) is brought into contact with sulphur dioxide present in the flue gas (12), CaSO\textsubscript{3} is formed as an insoluble calcium salt by the following two general formulae:
SO₂ + 2H₂O → HSO₃⁻ + H₃O⁺  

Ca₃[Al(OH)]₆²⁺ + 3HSO₃⁻ + 3H₃O⁺ → 3CaSO₄·½H₂O + 2Al(OH)₃ + 7½H₂O  

At the same time, sulphur trioxide that may also be present in the flue gas will react via the following two general formulae:

SO₃ + 2H₂O → HSO₄⁻ + H₃O⁺  

Ca₃[Al(OH)]₆²⁺ + 3HSO₄⁻ + 3H₃O⁺ → 3CaSO₄·2H₂O + 2Al(OH)₃ + 3H₂O  

The conversion of the calcium sulphite to precipitated calcium sulphate is encouraged by adding a source of oxygen. This occurs through oxidation of the calcium sulphite with oxygen according to the following equation:

CaSO₃·½H₂O + ½O₂ + ½H₂O → CaSO₄·2H₂O  

Thus, in the preferred form of the present invention, the TCA6 present in the aqueous slurry (16) reacts with the sulphur dioxide present in the flue gas (12) and with the addition of a source of oxygen to precipitate solid calcium sulphate by the following general formulae:

Ca₃[Al(OH)]₆²⁺ + 3SO₂ + ½O₂ → 3CaSO₄·2H₂O + 2Al(OH)₃(s) + 3H₂O  

As can be seen from the formula (6) above, the two products of the reaction are both solids, specifically, a solid calcium compound containing sulphur and oxygen in the form of gypsum and a solid aluminium compound containing oxygen and hydrogen in the form of aluminium hydroxide. The solids are able to be separated from the spent scrubbing solution (18) using solid/liquid separation techniques well established in the art. Advantageously, both gypsum and aluminium hydroxide are valuable recyclable products.
TCA6 in the form of spent filter aid is a waste product of an alumina refinery. In most alumina refineries, bauxite is digested in a caustic solution under conditions of elevated temperature and pressure. This yields a slurry of mud in a concentrated sodium aluminate solution which must then be clarified to produce a solids-free liquor and a thickened mud that is subsequently washed and discarded. The prevalent technique for slurry clarification involves allowing the solids to settle in gravity thickeners (or mud settlers), and decantation of the clarified liquor. The separation of the mud from the concentrated liquor is assisted with flocculants, whilst the "green" (or pregnant) liquor, which is free of all but the finest suspended solids, overflows from the mud settlers. It is normal for the decanted liquor to then be further clarified by filtration, typically using pressure filters. This so-called "polishing" filtration step is critical in ensuring that the pregnant liquor is free of suspended mud particles that would otherwise result in contamination of the product alumina. Unaided, the cloths employed in these filters blind very quickly. This occurs because the fine suspended solids in the green liquor become entrapped within the weave of the cloth, and then proceed to form a dense, highly resistive bed at the filter's surface. To prevent this, it is common practice in an alumina refinery to supplement the feed to the polishing filter with a so-called "filter aid", which acts to prevent cloth blinding by the continuous formation of a bed of solids which trap the mud particles whilst still allowing the free flow of liquor through the interstices of the bed. Filter aid production is carefully managed to control particle size and morphology whilst limiting the extent of alumina and free caustic lost from the system.

In most alumina refineries, the filter aid role is performed using "new" tricalcium aluminate hexahydrate (TCA6) which is formed through the reaction of lime (having the general formula Ca(OH)$_2$) with caustic aluminate solutions (having the general formula of NaAl(OH)$_4$). TCA6 has an extremely low solubility and has low chemical reactivity in Bayer liquors, is reasonably cheap, and of such a size that the channels that form between the filter aid particles are just small enough to trap the mud particles, but not so small that they restrict the flow of liquid, or contribute to blinding of the filter cloth themselves. The resulting TCA6 filter aid possesses a relatively uniform particle size and individual refineries can produce many thousands of tonnes of TCA6 as filter aid per year. After use, the filter aid becomes "spent" and the spent TCA6 filter aid is discarded as a waste product. Although containing sodalite and lesser amounts of other silicates, oxides and organics in the solid phase (typically <1wt%), spent TCA6 filter aid is a relatively clean and easily isolated waste stream of the Bayer process. From a simplified stoichiometric perspective, formula (3) above demonstrates that each mole of TCA6 is capable of absorbing
approximately three moles of \( \text{SO}_2 \). Thus, for an alumina refinery emitting approximately 10,000 tonnes per year of \( \text{SO}_2 \), approximately 20,000 tonnes per year of TCA6 can be used for this duty. The theoretical amount of oxygen required to be fed to the aqueous slurry can be calculated from formula (6) above. Thus when the process of the present invention is used for the desulphurisation of a gas within an alumina refinery (or for the treatment of exhaust gases from its associate power station), the spent TCA filter aid is transformed from a waste product to an extremely effective desulphurisation medium.

Another source of TCA6 amongst the waste products produced in most alumina refineries is the underflow sludge from the causticizers. This waste product comprises TCA6 in combination with calcium carbonate.

Returning to Figure 1, the wet scrubbing unit (14) includes an absorption tower (26) and a dust scrubbing unit (28). The gas (12) to be scrubbed is fed into the dust scrubbing unit (28) via a gas inlet (30). A cover or awning (not shown) may be provided over the gas inlet (30) to help to initially deflect the incoming flue gas (12) in a downward direction to encourage more even flow of the gas through the wet scrubbing unit (14). When the flue gas (12) enters the dust scrubbing unit (28), it is subjected to cooling and removal of fine particulates or "dust" by contacting the flue gas (12) with a stream of recirculated spent scrubbing solution (33) using a spray nozzle (32). The temperature of the flue gas (12) at the inlet (30) to the dust scrubbing unit (28) is in the range of 60 to 200\(^\circ\)C, preferably 70 to 130\(^\circ\)C, most preferably 90\(^\circ\)C.

Any residual or unreacted TCA6 present in the recirculated spent scrubbing solution (33) can react with the sulphur oxides present in the gas (12) according to the reactions (1), (2), (3) and (4) above, with the result that the gas (12) is partially desulphurised as it passes through the dust scrubbing unit (28).

After coming into contact with the gas (12) in the dust scrubbing unit (28), the recirculated spent slurry (33) is collected in a dust scrubbing unit slurry collection tank (34) for re-use. The partially desulphurised gas (12) is then directed to flow into the absorption tower (26) where it is contacted again with the aqueous TCA6 scrubbing slurry (16) using a spraying means (38), in this example, a plurality of spray nozzles (36) arranged to achieve an even distribution of the aqueous TCA6 slurry (16) across the full cross-section of the absorption tower (26). The spraying means (38) is
further arranged to direct the aqueous TCA6 slurry downwardly through the absorption tower (26) so as to flow in a direction which is counter-current to the upward flowing partially desulphurised flue gas stream (12). A desulphurised gas stream (40) is discharged to atmosphere after passing through one or more mist breakers (42). The desulphurised gas (40) which exits the absorption tower (26) has a residual sulphur dioxide content that has been reduced by between 90 and 100% compared with the sulphur dioxide content of the gas (12) fed to the wet scrubbing unit (14). The temperature of the desulphurised gas stream (40) as it exits the absorption tower (26) is in the range of 70 to 90°C.

The aqueous TCA6 scrubbing slurry (16) is prepared in an agitated slurry tank (20), by mixing a source of TCA6 (44), either as a solid or in the form of a thickened slurry with a source of makeup water (46), for example, process water from the alumina refinery, together with clarified recycled spent scrubbing solution (48).

Using a slurry pump (22), the aqueous TCA6 scrubbing solution (16) is pumped from the slurry tank (20) to a recirculation tank (50), the recirculation tank (50) being arranged towards a lower portion (52) of the absorption tower (26). Aqueous TCA6 scrubbing solution (16) is then pumped from the recirculation tank (50) to the spray nozzles (36) of the spraying means (38) using a recirculation pump (54). As the aqueous TCA6 slurry is recirculated through the absorption tower (26), the reactions identified in equations (1) and (2), or (3) and (4) occur. In this manner sulphur oxides are removed from the gas (12) by reaction with TCA6. Within the recirculation tank (50) and absorption tower (26), the residence time of the aqueous TCA6 scrubbing slurry (16) is in the range of about 15 to 90 minutes, preferably about 25 minutes.

A portion (56) of the TCA6 scrubbing solution is drawn off continuously using a bleed pump (58) so as to control the residence time of the aqueous TCA6 scrubbing slurry (16) within the absorption tower (26). The portion (56) of the TCA6 scrubbing solution drawn off using the bleed pump (58) is directed to the dust scrubbing unit slurry collection tank (34). A stream (33) of the spent scrubbing slurry is recirculated using a pump (62) to the spray nozzle (32) to cool the gas (12) as it enters the dust scrubbing unit (28), in the manner described above. The remaining portion of the spent slurry (61) from dust scrubbing unit slurry collection tank (34) is directed to a reaction tank (60) where residual unreacted TCA6 is decomposed by the addition of a stream of sulphuric acid (64). Sufficient sulphuric acid (64) is added to satisfy equation (4) above as a
function of the amount of residual unreacted TCA6 present in the spent slurry (61).

The neutralised slurry (66) is then pumped via a pump (68) to an oxidation tower (70) where it is reacted with a source of oxygen, for example, air, using an air blower (72). The source of oxygen is added to convert any remaining soluble calcium sulphite present in the neutralised slurry (66) to solid gypsum according to equation (5) above. The resultant slurry of gypsum and aluminium hydroxide is then pumped via a slurry pump (74) to a suitable solid/liquid separation device (76) to produce a solid product (73) and a clarified spent scrubbing solution (48). As described above, the solid product (78) includes a solid calcium compound containing sulphur and oxygen in the form of gypsum and a solid aluminium compound containing oxygen and hydrogen in the form of aluminium hydroxide. The gypsum and aluminium hydroxide can be separately recovered for re-use or discarded. The clarified spent scrubbing solution (48) can be recycled to the slurry tank (20) in the manner described above or discarded.

Recirculation of the scrubbing slurry (16) continues until the level of reduction of emissions in the desulphurised flue gas (40) exceeds a predetermined maximum discharge limit or until the pH of the spent scrubbing solution as measured in the slurry collection tank (34) falls below a pH of either 5.5 or 5.0. Alternatively, recirculation of the scrubbing slurry (16) continues until the pH of the spent scrubbing solution as measured in the recirculation tank (50) falls below a pH of either 5.5 or 5.0.

Now that the preferred embodiments of the present invention have been described in detail, the present invention has a number of advantages over the prior art, including the following:

a) TCA6 reacts with sulphur oxide compounds over a wide range of pHs which provides it with greater absorption capacity than prior art processes which rely on the use of lime or magnesium;

b) Spent TCA6 filter aid is able to be recycled in a manner which reduces SOx emissions from the flue gases from any stationary fossil-fuel burning facility. Where the flue gas derives from an alumina refinery, this solves two environmental problems in one;

c) The by-products of the process (which are ultimately gypsum and gibbsite) are both benign and potentially able to be reused;

d) The higher reactivity of TCA6 relative to CaCO₃ permits a smaller, cheaper facility
to be built;
e) The process has potential to benefit the alumina industry via providing a mode of reclaiming alumina values which would otherwise be lost if spent TCA filter aid is discarded; and,
f) When applied at an alumina refinery, no new raw material is required.

Now that several embodiments of the invention have been described in detail, it will be apparent to persons skilled in the relevant art that numerous variations and modifications can be made without departing from the basic inventive concepts. For example, the particle size of gypsum produced is influenced by the rate of oxidation, with the particle size being lower for higher oxidation rates. Thus, if a fine grade gypsum by-product is desired, air can be introduced in an amount in the range of 1.5 to 3 times the theoretical amount required for formula (6) above. All such modifications and variations are considered to be within the scope of the present invention, the nature of which is to be determined from the foregoing description and the appended claims.

All of the patents cited in this specification, are herein incorporated by reference. It will be clearly understood that, although a number of prior art publications are referred to herein, this reference does not constitute an admission that any of these documents forms part of the common general knowledge in the art, in Australia or in any other country. In the summary of the invention, the description and claims which follow, except where the context requires otherwise due to express language or necessary implication, the word "comprise" or variations such as "comprises" or "comprising" is used in an inclusive sense, i.e. to specify the presence of the stated features but not to preclude the presence or addition of further features in various embodiments of the invention.
Claims defining the invention:

1. A process for desulphurisation of a gas containing sulphur oxides (SO\textsubscript{x}) in a wet scrubbing unit, the process comprising the step of:
   contacting said gas with an aqueous tricalcium aluminate hexahydrate (TCA6) scrubbing slurry to remove SO\textsubscript{x} from the gas by reaction with TCA6 to form a spent scrubbing solution comprising a calcium compound containing sulphur and oxygen, and a aluminium compound containing oxygen and hydrogen.

2. The process of claim 1 wherein the calcium compound containing sulphur and oxygen is soluble calcium sulphite and the process further comprises the step of adding a source of oxygen to the spent scrubbing solution in an amount sufficient to encourage oxidation of soluble calcium sulphite to solid calcium sulphate.

3. The process of claim 2 wherein the amount sufficient to encourage oxidation of calcium soluble calcium sulphite to solid calcium sulphate is at least one mole of oxygen for every two moles of sulphur dioxide to be removed from the gas.

4. The process of any one of the preceding claims wherein the aluminium compound containing oxygen and hydrogen is aluminium hydroxide which is present as a solid in the spent scrubbing solution.

5. The process of any one of the preceding claims further comprising the step of removing the solid calcium sulphate and solid aluminium hydroxide from the spent scrubbing solution.

6. The process of any one of the preceding claims wherein the TCA6 is filter aid or spent filter aid from an alumina refinery.

7. The process of any one of the preceding claims wherein the TCA6 is present with calcium carbonate in a causticizer underflow sludge.
8. The process of any one of the preceding claims wherein the wet scrubbing unit includes an absorption tower and a dust scrubbing unit and the gas to be scrubbed is partially desulphurised and cooled in the dust scrubbing unit by contacting the gas with a stream of the spent scrubbing solution.

9. The process of any one of the preceding claims wherein the step of contacting the gas with the aqueous TCA6 scrubbing slurry comprises spraying the TCA6 slurry into an absorption tower to achieve an even distribution of the aqueous TCA6 slurry across the cross-section of the absorption tower.

10. The process of claim 8 or 9 wherein the spent scrubbing solution is collected in a recirculation tank arranged towards a lowermost section of the absorption tower for recirculation.

11. The process of any one of the preceding claims comprising the step of recirculating the aqueous TCA6 scrubbing slurry until the pH of the TCA6 scrubbing slurry falls below 5.5 or 5.0.

12. The process of any one of claims 1 to 10 comprising the step of recirculating the aqueous TCA6 scrubbing slurry until the level of reduction of emissions in a desulphurised gas stream being discharged to atmosphere from the wet scrubbing unit exceeds a predetermined maximum discharge limit.

13. The process of any one of the preceding claims wherein the desulphurised gas stream being discharged to atmosphere from the wet scrubbing unit has a sulphur dioxide content that has been reduced by between 90 and 100% compared with a gas containing sulphur oxides (SO\text{x}) which was fed to the wet scrubbing unit.

14. The process of any one of the preceding claims wherein a desulphurised gas stream is discharged to atmosphere from a wet scrubbing unit at a temperature in the range of 70 to 90°C.
15. The process of any one of the preceding claims wherein the aqueous TCA6 scrubbing slurry is prepared by mixing a source of TCA6 with a source of makeup water together with a clarified recycled spent scrubbing solution.

16. The process of any one of the preceding claims wherein a portion of the spent scrubbing solution is drawn off continuously from the wet scrubbing unit so as to control the residence time of the aqueous TCA6 scrubbing slurry within an absorption tower located within the wet scrubbing unit.

17. The process of claim 15 wherein the TCA6 scrubbing slurry is recirculated through an absorption tower such that the residence time of the aqueous TCA6 scrubbing slurry in the wet scrubbing unit is in the range of about 15 to 90 minutes.

18. The process of any one of the preceding claims wherein a portion of the spent scrubbing slurry from the wet scrubbing unit is directed to a reaction tank where residual unreacted TCA6 is decomposed by the addition of a stream of sulphuric acid to form a neutralised slurry.

19. The process of claim 18 wherein the neutralised slurry is reacted with a source of oxygen to convert any remaining soluble calcium sulphite present in the neutralised slurry to solid calcium sulphate.

20. The process of any one of the preceding claims wherein the aqueous TCA6 scrubbing slurry comprises at least one mole of tricalcium aluminate hexahydrate for every three moles of sulphur dioxide to be removed from the gas.

21. A process for desulphurisation of a gas containing sulphur oxides (SO\textsubscript{x}) in a wet scrubbing unit substantially as herein described with reference to and as illustrated in the accompanying illustrations.
INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU20 10/000758

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.
BOID 53/50(2006.01)

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)

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)

EPODOC, WPI, BOID 53/-, COIB 17/48, C01B17/69, F23J and/or keywords: sulphur oxide, SO, SO2, SO3, absorb+, scrub+, de_sulphur+, TCA+, tricalcium aluminate, C3A, hydrogarnet, katoite, wet+, slurrying+, liquid+, etc. Google Patent and ISI Web of Science NPL searches with like keywords

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>US 7247601 B1 (HILLS ET AL.) 24 July 2007 See whole document</td>
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<td>US 5047222 A (ROCHELLE ET AL.) 10 September 1991 See whole document</td>
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<td>US 5270015 A (ROCHELLE ET AL.) 14 December 1993 See whole document</td>
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[ X 1 ] Further documents are, listed in the continuation of Box C  [ X ] See patent family annex

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  - "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

- 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
- 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
- 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
11 August 2010

Date of mailing of the international search report
17 AUB 2010

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Form PCT/ISA/210 (second sheet) (July 2009)
### DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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<tr>
<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No</th>
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<tbody>
<tr>
<td>A</td>
<td>JP 52-1 17297 A (MITSUI MINING &amp; SMELTING CO) 01 October 1977 English Abstract retrieved from EPODOC database See whole Abstract</td>
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**INTERNATIONAL SEARCH REPORT**

**Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)**

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. □ Claims Nos.:
   - because they relate to subject matter not required to be searched by this Authority, namely:

2. [XJ □ Claims Nos.:
   - because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
   - The claim does not comply with Rule 6.2(a) because they rely on references to the description and/or drawings

3. □ Claims Nos.:
   - because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a)

**Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:

1. □ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. □ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. □ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. □ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

**Remark on Protest**

□ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

□ I The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

□ No protest accompanied the payment of additional search fees.

Form PCT/ISA/210 (continuation of first sheet (2)) (July 2009)
This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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</table>

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.