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(54) Virsraksts: **Paņēmiens sēra dioksīda atdalīšanai no gāzes plūsmas ar vienlaicīgu ģipša alfa-pushidrāta iegūšanu**

(57) Kopsavilkums: Paņēmiens paredzēts sēra dioksīda atdalīšanai no karstas gāzes plūsmas un ģipša alfa-pushidrāta vienlaicīgai iegūšanai no dubļu notekūdeņiem, kas rodas attīrot dūmgāzes termospēkstacijās vai citās iekārtās, ko kurina ar oglēm. Daļu šķīduma, kas iegūta gāzu attīrīšanas iekārtā skalošanas procesā ar ūdeni un kas satur kalcija un magnija sulfītu, izvada no attīrīšanas mezgla un ievada oksidēšanas reaktorā, kur sulfīti pie paaugstināta spiediena un paaugstinātas temperatūras reaģē ar oksidējošo gāzi, pārvēršot kalcija sulfītu ģipša alfa-pushidrātā un magnija sulfītu - magnija sulfātā. Ūdens šķīdumu, kas satur kalcija sulfāta alfa-pushidrāta nogulsnes un šķīstošo magnija sulfātu, nepārtraukti izvada no oksidēšanas reaktora. Tālāk kalcija sulfāta alfa-pushidrātu atdala no ūdens šķīduma.

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IZGUDROJUMA FORMULA

1. Sēra dioksīda izdalīšanas metode no karstas gāzes plūsmas, kas satur sēra dioksīdu, un kalcija sulfāta α-pushidrāta kā ejošas preces iegūšanas paņēmiens, kurā ietilpst sekojošas stadijas:

gāzes plūsmas, kas satur šo sēra dioksīdu, kontaktēšana ar mazgāšanas ūdens šķīdumu, kas satur kalcija un magnija komponentus, attīrīšanas mezglā, kurā iepriekš minētais sēra dioksīds ūdens šķīdumā pārvēršas kalcija un magnija sulfītos;

ūdens šķīduma porcijas, kas satur kalcija sulfītu un magnija sulfītu, nepārtraukta izvadīšana no attīrīšanas mezgla, nepārtraukti aizvadot vismaz daļu no iepriekš minētā atdalītā ūdens šķīduma, kas satur no 5 līdz 35 masas % kalcija sulfīta un magnija sulfīta ar magnija jonu saturu 250-8000 ppm robežās, uz atsevišķu hermētisku oksidēšanas reaktoru, kas darbojas paaugstinātās temperatūrās no 100°C līdz 145°C pie virsspiediena no 206,7 līdz 344,5 kPa (30-50 mārciņas uz kvadrātcollu);

ūdens šķīduma, kas satur kalcija sulfītu un magnija sulfītu, mijiedarbība oksidēšanas reaktorā ar oksidējošo gāzi, lai pārvērstu kalcija sulfītu par kalcija sulfāta α-pushidrātu, kas ūdens šķīdumā izkrīt nogulsnēs, un lai pārvērstu magnija sulfītu par magnija sulfātu, kas šķīst ūdens šķīdumā;

ūdens suspensijas pH uzturēšana starp 2,5 un 5,5 oksidēšanas reaktorā;

ūdens šķīduma, kas satur kalcija sulfāta α-pushidrāta nogulsnes un šķīstošo magnija sulfātu, nepārtraukta aizvadīšana no oksidēšanas reaktora; un

kalcija sulfāta α -pushidrāta atdalīšana no ūdens šķīduma.

2. Paņēmiens saskaņā ar 1. punktu, kas atšķiras ar to, ka ūdens šķīdumu, ko izvada no attīrīšanas mezgla, padot nostādinātājā; nostādinātājā veidojas sabiezināts (sakoncentrēts) produkts, kas satur no 20 līdz 25 masas % kalcija sulfīta un magnija sulfīta, un šis produkts tiek padots oksidēšanas reaktorā.

3. Paņēmiens saskaņā ar 1. punktu, kas atšķiras ar to, ka lai uzsāktu nepārtrauktu procesu, ūdens šķīduma, kas satur kalcija sulfītu un magnija sulfītu hermētiskā oksidēšanas reaktorā, sākumu daļu sasilda līdz 100°C, pie kam reakcijas siltumu, kas izdalās kalcija sulfīta pārvēršanas rezultātā par α-pushidrātu izmanto, lai uzturētu paaugstinātu temperatūru oksidēšanas reaktorā.

4. Paņēmiens saskaņā ar jebkuru no iepriekšējiem punktiem, kas atšķiras ar to, ka oksidējošā gāze ir skābeklis.

5. Paņēmiens saskaņā ar vienu no 1.-3. punktiem, kas atšķiras ar to, ka oksidējošā gāze ir gaiss.

6. Paņēmiens saskaņā ar jebkuru no iepriekšējiem punktiem, kas atšķiras ar to, ka ūdens suspensijas pH oksidēšanas reaktorā uztur starp 3 un 4.

7. Paņēmiens saskaņā ar jebkuru no iepriekšējiem punktiem, kas atšķiras ar to, ka ūdens šķīdumu oksidēšanas reaktorā samaisa.

8. Paņēmiens saskaņā ar jebkuru no iepriekšējiem punktiem, kas atšķiras ar to, ka magnija jona saturs šķīdumā, kas padots oksidēšanas reaktorā, ir 500-5000 ppm robežās.

Description

[0001] **THE PRESENT INVENTION** provides a method of removing sulfur dioxide from hot flue gas streams while directly producing α-hemihydrate calcium sulphate ("α-hemihydrate") as a by-product of the method.

[0002] The use of wet scrubbing processes for removing sulfur dioxide from hot flue gases has become a primary means for cleaning stack gases from power plants or other coal combusting units. Such processes usually use an aqueous lime or limestone slurry which is passed downwardly through a wet scrubbing unit to react with, and remove sulfur dioxide from, hot gases passing upwardly through the wet scrubbing unit. Especially favourable results have been commercially achieved by using aqueous lime slurries that are enriched with a magnesium component such as magnesium oxide or magnesium hydroxide, such as disclosed in US-A-3,919,393 and US-A-3,919,394.

[0003] In scrubbing of hot sulfur dioxide-containing gases by magnesium enhanced lime scrubbing processes, calcium sulfite is formed which must be removed from the scrubbing system through use of a bleed stream from the recycling aqueous scrubbing medium. This bleed stream will also contain minor amounts of magnesium sulfite and chlorides. The bleed stream is normally passed to a thickener or separator where a resultant thickened sludge, or underflow, is separated and removed from the system while clarified aqueous media, or overflow, is normally returned to the aqueous scrubbing slurry in the wet scrubbing unit. The sludge removed from the wet scrubbing system contains primarily calcium sulfites and magnesium sulfites, along with various chloride salts and other impurities. The calcium sulfite sludges are difficult to dewater due to their physical properties and, when deposited into settling ponds or collection areas, require a large area and a period of time before solidification occurs.

[0004] One procedure for reducing the amount of sludge produced and discarded has been to oxidise the calcium sulfite-containing sludge so as to convert the calcium sulfite to calcium sulfate which is more easily dewatered and thus provides less volume of sludge that must be handled and used a landfill.

[0005] US-A-4,046,856 relates to a procedure in which the calcium sulfite is converted to calcium sulfate. In the teaching of this Specification a stack gas containing sulfur dioxide is contacted with an aqueous scrubbing medium which contains calcium and magnesium scrubbing components. Following a double decomposition reaction, in which magnesium sulfate and calcium hydroxide react to form magnesium hydroxide and calcium sulfate, the slurry is passed to an oxidiser where sulfuric acid is added and air is supplied to effect an oxidising process to produce gypsum ($2H_2O.CaSO_4$). The gypsum precipitates from an aqueous medium whilst magnesium sulfite present is converted to be magnesium sulfate which dissolves in the aqueous medium. Following oxidation, the resulting slurry is discharged from the oxidiser into a thickener. The gypsum is sedimented and separated and is dewatered in a centrifuge. According to this document, the speed of sulfite solution and the speed of oxidation is increased due to the presence of $MgSO_3$.

[0006] When calcium sulfate is produced as gypsum, or calcium sulfate dihydrate ($CaSO_4$-$2H_20$), the gypsum can, at times, be used in various products such as industrial and building plasters such as gypsum wallboard. The demand for gypsum is not, however, sufficiently high to absorb all of the gypsum produced by various commercial processes as well as that which would be produced if all sulfur dioxide lime scrubbing sludges were converted to gypsum. In addition, magnesium present in gypsum can have an adverse affect on the gypsum performance in conventional usage.

[0007] An especially useful form of calcium sulphate, α-hemihydrate ($\alpha\ CaSO_4 \cdot \frac{1}{2}\ H_2O$), which is not normally formed in sulfur dioxide removal aqueous sludges, has specific uses which provide value over and above conventional gypsum or calcium sulfate dihydrate. The production of α-hemihydrate is generally effected by heating natural or by-product gypsum in an autoclave at elevated temperatures of above 100°C and superatmospheric pressure. The production of α-hemihydrate from gypsum obtained from power plant flue gas desulfurisation processes has been proposed, for example, in US-A-5,015,449 and US-A-5,015,450, where moist fine grained gypsum is moulded into a body and the moulded body fed to an autoclave where it is subjected to a temperature in the range of 110°C to 180°C under pressure.

[0008] When gypsum (calcium sulfate dihydrate) is converted to α-hemihydrate, energy is required to drive off the excess water and provision of such energy is costly to the process.

[0009] In US-A-4,069,300, a process is described for producing a-type hemihydrate calcium sulfate by oxidising calcium sulfite in a suspension that contains at least one anionic, nonionic or asymphoteric surface active agent. The Specification refers to oxidation at superatmospheric pressures and temperatures up to 130°C, but advises against the use of such high pressures and temperatures. That process suggests that the calcium sulfite suspension used could be one produced by absorbing a waste gas containing $S0_2$ with a slayed lime slurry. In that process temperatures as low as 90°C are used, and no autoclave is used meaning that the process is not carried out under superatmospheric pressure, which is said to result in coarser crystals. the suspension must contain seed crystals of α-type hemihydrate which are added in an amount of between about 10 to 150 times the weight of the surface active agent used. Addition of Mg is not mentioned.

[0010] DE-A-2659860 discloses a process for the manufacture of calcium sulphate in the α-hemihydrate form. In the described process, waste gas containing sulfur oxides convert a slurry of calcium carbonate or lime to obtain a calcium sulfite slurry. The pH of the slurry is adjusted and the slurry is oxidised with oxygen or air under super-atmospheric pressure and at an elevated temperature. α-hemihydrate is thus formed which is subsequently separated by a filtration step.

Addition of Mg is not mentioned.

[0011] It is an object of the present invention to provide a method for the removal of sulfur dioxide from a hot gas stream, using an aqueous scrubbing medium containing calcium and magnesium scrubbing components, and continuously produce α-hemihydrate from the scrubber effluent.

[0012] According to this invention there is provided a method of removing sulfur dioxide from a sulfur dioxide-containing hot gaseous stream and producing saleable α-hemihydrate calcium sulphate, said method comprising the steps of contacting said sulphur dioxide containing gaseous stream with an aqueous scrubbing medium containing calcium and magnesium scrubbing components in a scrubbing unit, wherein said sulfur dioxide is converted to calcium and magnesium sulfites in an aqueous medium; continuously removing a portion of said aqueous medium containing calcium sulfite and magnesium sulfite from said scrubbing unit, continuously with a passing of at least a portion of said removed aqueous medium containing 5 to 35 percent by weight calcium sulphite and magnesium sulphite, with magnesium ion content of between 250-8000 ppm to a single pressurised oxidation vessel, operated at an elevated temperature of between 100 and 145° and at superatmospheric pressure of between about 206.7 to 344.5 kPa (30-50 pounds per square inch), contacting said aqueous medium containing calcium sulfite and magnesium sulfite, in said oxidation vessel, with an oxidising gas, to convert said calcium sulfite to α-hemihydrate calcium sulphate which precipitates from said aqueous medium, and to convert said magnesium sulfite to magnesium sulfate, which dissolves in said aqueous medium; maintaining the pH of the aqueous slurry in the oxidation vessel at between 2.5 and 5.5; continuously removing aqueous medium containing precipitated α-hemihydrate calcium sulphate and dissolved magnesium sulfate from said oxidation vessel; and separating said α-hemihydrate calcium sulphate from said aqueous medium.

[0013] Preferred embodiments of the process of the invention are defined in the dependent claims.

[0014] Preferably the aqueous medium removed from the scrubbing unit is passed to a thickener, the thickener producing an under-flow containing 20 to 25 percent by weight calcium sulphite and magnesium sulphite.

[0015] In a preferred method of the invention sulfur dioxide is removed from a sulfur dioxide-containing gaseous stream such as a flue gas stream from a coal combustion power plant, by contacting the sulfur dioxide-containing gaseous stream with an aqueous scrubbing medium containing calcium components and magnesium components, such as lime and magnesium hydroxide, with the sulfur dioxide converted to calcium and magnesium sulfites in the aqueous medium. A portion of the aqueous medium containing calcium sulfite and magnesium sulfite is continuously removed from the scrubbing unit and passed to a single pressurised oxidation vessel with a solids content of 5 to 35 percent by weight. In a preferred process the aqueous medium removed from the scrubbing unit is passed to a thickener. The underflow of the thickener, which has a solids content of 20-25 percent by weight, is passed to the pressurised oxidation vessel. In the pressurised oxidation vessel, the aqueous medium containing calcium sulfite and magnesium sulfite, and preferably magnesium bisulfite, is contacted with an oxidising gas, such as air or oxygen, under super-atmospheric pressure and at elevated temperature of between 100-145°C. The pH of the aqueous medium in the oxidation vessel is maintained between 2.5 and 5.5, and the medium within the oxidation vessel is agitated. The calcium sulfite is directly converted to α-hemihydrate and the magnesium sulfite converted to magnesium sulfate. The α -hemihydrate precipitates from the aqueous medium while the magnesium sulfate dissolves in the aqueous medium. The aqueous medium, which now contains precipitated a-hemihydrate gypsum and dissolved magnesium sulfate is continuously removed from the pressurised oxidation vessel and the α-hemihydrate separated therefrom, such as by filtration. Crystal modifiers may be added to the aqueous medium to enhance certain properties of the α-hemihydrate product.

[0016] Magnesium sulfate contained in the aqueous medium removed from the pressurised oxidation vessel may be converted to magnesium hydroxide and either returned to the scrubbing unit as a magnesium scrubbing component or used elsewhere or sold as a by-product.

[0017] The present invention will become more readily apparent from the following description and the accompanying drawing which is a schematic illustration of a preferred embodiment of the method of sulfur dioxide removal from a hot gaseous stream with α-hemihydrate formation.

[0018] In the method according to the present method, sulfur dioxide gases are removed from a hot gaseous stream, while concomitantly producing α-hemihydrate as a saleable product.

[0019] In the process, a hot gaseous stream containing sulfur dioxide is contacted in a wet scrubber with an aqueous medium containing calcium and magnesium scrubbing components. A preferred aqueous medium containing calcium and magnesium components is one such as described in US-A-3,919,393 and US-A-3,919,394, referred to hereinbefore. In the processes described therein, the addition of a specified amount of magnesium components is made to a lime slurry which results in an increased removal of sulfur dioxide. As described therein, a calcium oxide aqueous slurry containing a specified amount, such as between 250 to 5000 parts per million (ppm), of magnesium ions is used as the aqueous scrubbing medium in a wet scrubbing unit.

[0020] A portion of the aqueous scrubbing medium is removed from the wet scrubber so as to prevent build-up of excess solids. The portion of aqueous medium removed is preferably taken from a location in the scrubbing unit, such as at a downcomer, prior to passage to a hold tank. This provides the portion of aqueous medium at a somewhat lower pH, such as about 5.5, rather than at a value of about 6.5 that results from passage of the aqueous scrubbing medium

to a hold tank and recycle back to the scrubbing unit. The removed portion of aqueous scrubbing medium, which contains primarily calcium sulfite, magnesium sulfite and preferably magnesium bisulfite, is passed to a thickener where a concentrated aqueous medium or thickener underflow is separated from a clarified aqueous medium or thickener overflow. The thickener overflow which has primarily dissolved components may be recycled to the wet scrubber.

[0021] The thickener underflow, is an aqueous medium containing between 5-35 percent, and usually about 20-25 percent by weight calcium sulfite and magnesium sulfite. The underflow is passed to a pressurised oxidation vessel and is contacted with an oxidising gas, such as air or oxygen, at elevated temperatures and under superatmospheric pressure to form α-hemihydrate and magnesium sulfate.

[0022] The oxidation is carried out at an elevated temperature of between 100-145°C (212-293°F). The use of temperatures below about 100°C will not provide a sufficient rate of oxidation, while the use of temperatures in excess of 145°C, while usable, will waste energy and provide an inefficient process.

[0023] During the oxidation, the pressure within the pressurized oxidation vessel should be maintained between 206.7 and 344.5 kPa (30-50 pounds per square inch). Pressures less than about 206.7 kPa (30 pounds per square inch) will provide poor oxidation and an unacceptable slow rate of oxidation, while pressures in excess of about 344.5 kPa (50 pounds per square inch) do not provide compensating benefits and would require more specialized equipment.

[0024] The pH of the aqueous medium in the pressurized oxidation vessel, during oxidation of the calcium sulfite to α-hemihydrate and the magnesium sulfite to magnesium sulfate, would be maintained between 2.5 to 5.5 and preferably in a range of 3-4. A pH of less than about 2.5 should be avoided since excess acid would be required over that necessary and could cause corrosion problems in the equipment, while a pH in excess of about 5.5 results in a slow rate of oxidation and poor conversion.

[0025] It has been found that the presence of magnesium ions, such as in the form of magnesium bisulfite and magnesium sulfite which are converted to magnesium sulfate during the oxidation of calcium sulfite to α-hemihydrate gypsum, has a beneficial affect on the conversion, The magnesium ion content of the portion of aqueous medium fed to the pressurized oxidation vessel is between about 250-8000 ppm, and preferably between about 500-5000 ppm. Also, the presence of magnesium bisulfite in the aqueous scrubbing medium removed from the downcomer of the scrubbing unit provides an acidic component to lower the pH during the oxidation. The magnesium bisulfite is oxidized to magnesium sulfate while producing sulfuric acid that aids in controlling the pH of the aqueous medium in the pressurized oxidation vessel within the desired acidic range.

[0026] An advantage provided by the present method is than the oxidation of calcium sulfite to α-hemihydrate is an exothermic reaction. Thus, once the oxidation reaction has been initiated, the elevated temperature required to produce α-hemihydrate is maintained by the exothermic reaction. This is a distinct advantage over processes that produce α-hemihydrate from calcium sulfate, since those processes require a continuous supply of heat energy to effect the conversion, which is not exothermic. In addition, the exotherm provided by the present method in a sealed oxidation vessel may also provide a portion of the pressure needed to maintain the conversion to α-hemihydrate.

[0027] Crystal modifiers, such as succinic acid or potassium sulfate, or mixtures thereof, may be added to the aqueous medium in the pressurized oxidation vessel to enhance the crystal structure of the α-hemihydrate produced.

[0028] An embodiment of the present invention will now be explained with reference to the drawing. In the drawing, a desulfurization facility for the removal fo sulfur-dioxide from a hot gaseous stream with concomitant production of α-hemihydrate is designated by the numeral 1. A hot gaseous stream containing sulfur dioxide is introduced into a wet scrubbing unit 3 through line 5, such as a flue gas stream from a coal combustion device of a power plant. The hot gaseous stream passes upwardly through the scrubbing unit 3 and is contacted therein by an aqueous scrubbing medium containing calcium scrubbing components and magnesium scrubbing components introduced through sprayers 7, the cleaned gas being discharged from the wet scrubbing unit 3 through outlet 9 to the atmosphere. The acqueous scrubbing medium, after contact with the sulfur dioxide contains calcium sulfite and magnesium and is normally passed to a hold tank 11. From the hold tank 11, aqueous scrubbing medium is recycled through line 13 back to the sprayers 7 for further contact with the sulfur dioxide-containing gaseous stream, while fresh aqueous scrubbing medium containing calcium scrubbing components and magnesium scrubbing components may be added from a source 15 through line 17 to the hold tank 11. In order to remove solids from the scrubbing system, a portion of the aqueous scrubbing medium, or bleed stream, which contains calcium sulfite and magnesium sulfite solids, is removed, preferably from a downcomer in the west scrubbing unit 3, through line 19 and fed to a thickener 21, in the nature of a clarifying unit, wherein concentrated solids will collect at the bottom while clarified liquor rises to the top. The clarified liquor or thickener overflow is removed from the thickener 21 through line 23 and may be returned for use in the wet scrubbing unit 3, while the thickened slurry, or underflow, containing calcium sulfite and magnesium sulfite is removed from the thickener 21 by means of line 25.

[0029] The thickener underflow, as aqueous medium containing calcium sulfite and magnesium sulfite, is passed through line 25, from the thickener 21 to a pressurized oxidation vessel 27 and continuously passed therethrough. In the pressurized oxidation vessel, the aqueous medium is agitated, such as by the use of an agitation device 29, such as a multi-bladed stirrer comprising a shaft 31 and blades 33, driven by a motor 35.

[0030] An oxidizing gas is introduced into the aqueous scrubbing medium containing calcium sulfite and magnesium sulfite, from a source 37, through line 39 and contacts the aqueous scrubbing medium being agitated by the agitation device 29, while under superatmospheric pressure, at an elevated temperature, such that the calcium sulfite contained in the aqueous medium is converted to α-hemihydrate and precipitates while the magnesium sulfite contained in the aqueous medium is converted to magnesium sulfate which is dissolved in the aqueous medium and forms an aqueous solution. Acid, as desired or required, to maintain the proper pH of the aqueous medium in the oxidation vessel 27 may be provided thereto through line 41. Because of the exothermic reaction caused by oxidation of the components in the aqueous medium, in order to maintain the proper temperature and pressure within the oxidation vessel 27, vapours, primarily steam, may be released through exhaust line 43 and, if desired, a portion of such vapours, after condensation, may be returned to oxidation vessel 27 through line 45.

[0031] After oxidation, the aqueous medium containing α-hemihydrate solids and dissolved magnesium sulfate is continuously removed from the oxidation vessel 27 through line 47 and passed to a separator 49, such as a filter, where the α-hemihydrate is separated from the aqueous medium containing dissolved magnesium sulfate. Water, through line 51, may be supplied to wash the α-hemihydrate which is then discharged through line 53 to a storage bin 55. The aqueous medium containing dissolved magnesium sulfate is passed from the separator 49 through line 57. The separated aqueous medium containing magnesium sulfate may be fed to a regenerator 59 where lime is added through line 61 to produce magnesium hydroxide that may be returned to the scrubbing system, such as to the source of scrubbing components 15 through line 63, while gypsum produced in the regenerator 59 is discharged through line 65.

[0032] As an experimental example, a simulated aqueous medium from a magnesium-enhanced lime scrubbing process was provided in a diluted state containing about 7.5 percent solids by weight. A conventional such aqueous medium would contain about 20-30 percent solids, primarily calcium sulfite. The aqueous medium contained about 75,000 mg/l calcium sulfite and 5000 mg/l magnesium sulfite. In a series of runs, aqueous medium was fed to a pressurized oxidation vessel and oxygen sparged through the aqueous medium, which was heated to the temperature listed in the following Table. The pressure used and pH (adjusted by addition of sulfuric acid) of the aqueous medium were varied as shown in the Table, as was the flow rate of the oxygen.

TABLE

Run No.	Pressure	pH	O_2 Flow Rate (l/min.)	Temp. (°C)	Sulfite Concentration in Product (Wt.% as SO_2)	Percent Conversion to α-hemihydrate
1	55	3.1	11	127	0.21	99.52
2	60	2.2	11	127	0.26	99.41
3	80	3.1	11	127	0.05	99.89
4	60	3.8	11	127	0.64	98.55
5	60	5.1	10	124	8.74	80.14
6(1)(*)	40	3.2	11	118	0.96	97.82
7(*)	40	4.1	10	118	0.46	98.96
8	60	4	11	127	0.33	99.25
9(*)	30	3	10	116	0.36	99.20
10(*)	30	4	10	116	6.02	86.32
11	20	3.1	11	110	17.64	59.91
12	20	4	10	117	14.47	67.12
13	17	3.1	13	117	16.8	61.82
14	16	4.1	11	104	21.2	52.05
15(2)	67	3	11	130	7.39	83.21
16(3)	60	3	20	127	5.65	87.16
17	60	4	11	110	0.23	99.48

(1) Solids content = 15 percent
(2) Air used instead of oxygen
(3) No magnesium ions present
(*) conditions of pressure according to the present invention

[0033] The present invention as defined in claim 1 provides a method for forming α-hemihydrate while removing sulfur dioxide from a sulfur dioxide-containing hot gaseous stream with the presence of magnesium components in a calcium component aqueous scrubbing medium enhancing such formation

[0034] The method of the present invention as defined in claim 1 comprises the removal of sulfur dioxide from a hot gas stream, using an aqueous scrubbing medium containing calcium and magnesium scrubbing components and continuously produces α-hemihydrate from the scrubber effluent at exceptionally high conversion rates while removing magnesium sulfate therefrom.

[0035] Also, the method of the present invention as defined in claim 1 comprises the removal of sulfur dioxide from a hot gas stream using an aqueous scrubbing medium containing calcium and magnesium scrubbing components and continuously producing α-hemihydrate from the scrubber effluent in an energy efficient manner.

[0036] Additionally, the method of the present invention as defined in claim 1 comprises the removal of sulfur dioxide from a hot gas stream using an aqueous scrubbing medium containing calcium and magnesium compounds and continuously producing α-hemihydrate while using the exothermic energy of calcium sulfite oxidation to produce heat and a portion of the pressure required to form α-hemihydrate.

Claims

1. A method of removing sulfur dioxide from a sulfur dioxide-containing hot gaseous stream and producing saleable α-hemihydrate calcium sulphate, said method comprising the steps of contacting said sulphur dioxide containing gaseous stream with an aqueous scrubbing medium containing calcium and magnesium scrubbing components in a scrubbing unit, wherein said sulfur dioxide is converted to calcium and magnesium sulfites in an aqueous medium; continuously removing a portion of said aqueous medium containing calcium sulfite and magnesium sulfite from said scrubbing unit, continuously passing at least a portion of said removed aqueous medium containing 5 to 35 percent by weight calcium sulphite and magnesium sulphite, with a magnesium ion content of between 250-8000 ppm, to a single pressurised oxidation vessel, operated at an elevated temperature of between 100 and 145°and at superatmospheric pressure of between about 206.7 to 344.5 kPa (30-50 pounds per square inch), contacting said aqueous medium containing calcium sulfite and magnesium sulfite, in said oxidation vessel, with an oxidising gas, to convert said calcium sulfite to α-hemihydrate calcium sulphate which precipitates from said aqueous medium, and to convert said magnesium sulfite to magnesium sulfate, which dissolves in said aqueous medium; maintaining the pH of the aqueous slurry in the oxidation vessel at between 2.5 and 5.5; continuously removing aqueous medium containing precipitated α-hemihydrate calcium sulphate and dissolved magnesium sulfate from sad oxidation vessel; and separating said α-hemihydrate calcium sulphate from said aqueous medium.

2. A method as defined in Claim 1 wherein the aqueous medium removed from the scrubbing unit is passed to a thickener, the thickener producing an under-flow containing 20 to 25 percent by weight calcium sulphite and magnesium sulphite which is fed to said oxidation vessel.

3. A method of as defined in Claim 1 wherein, in order to commence the continuous process an initial portion of said aqueous medium containing calcium sulfite and magnesium in said pressurised oxidation vessel is heated to about 100°, the heat of reaction resulting from said conversion of calcium sulphite to α-hemihydrate being used to maintain the elevated temperature of the oxidation vessel.

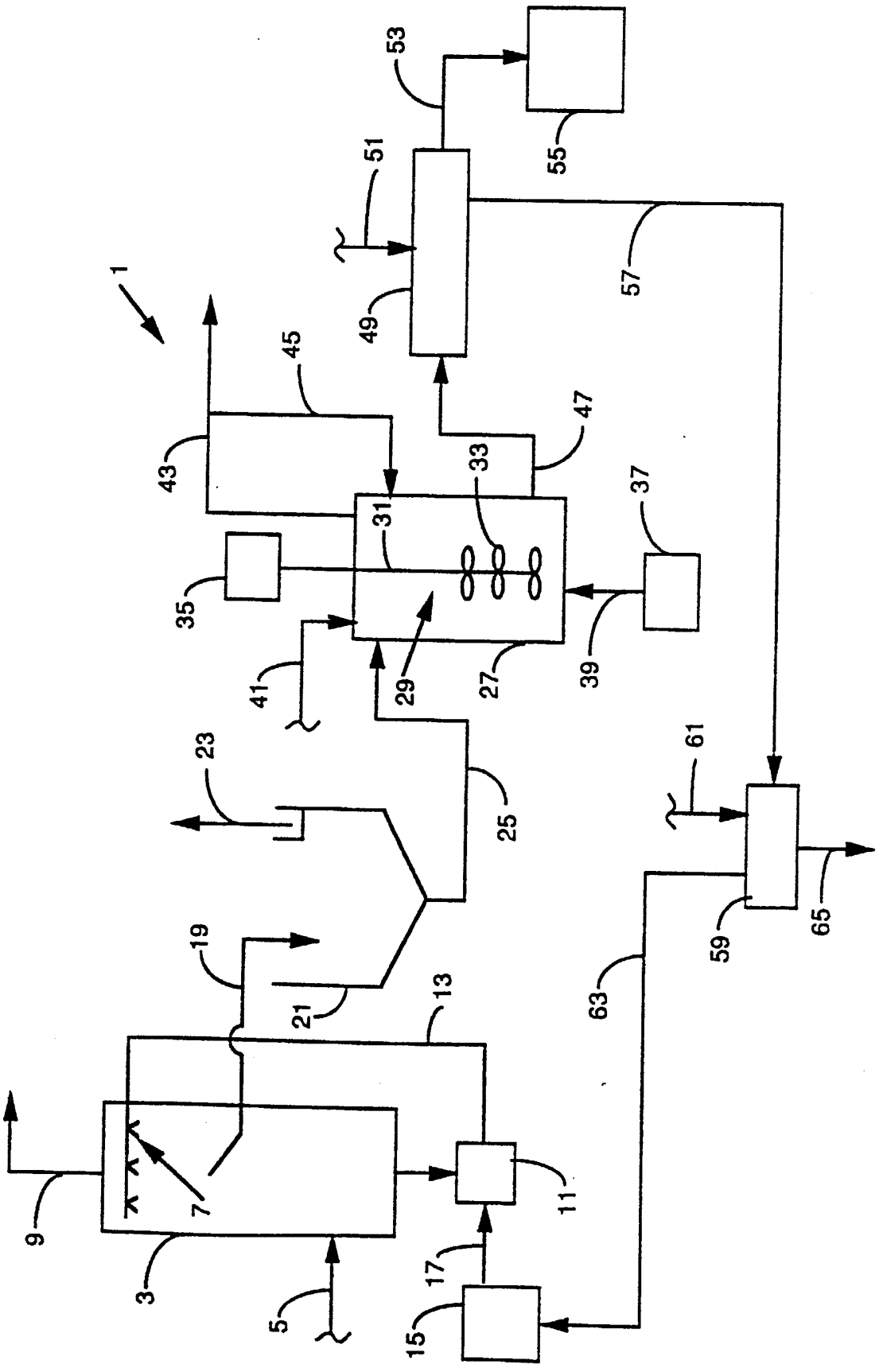
4. A method as defined in any one of the preceding Claims wherein said oxidising gas is oxygen.

5. A method as defined in any one of Claims 1 to 3 wherein said oxidising gas is air.

6. A method as defined in any one of the preceding Claims wherein the pH of the slurry in the oxidation vessel is maintained at between 3 and 4.

7. A method as defined in any one of the preceding Claims wherein the aqueous medium in the oxidation vessel is agitated.

8. A method as defined in any one of the preceding Claims wherein the magnesium ion content of the portion of the medium passed to the oxidation vessel is between 500-5000 ppm.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