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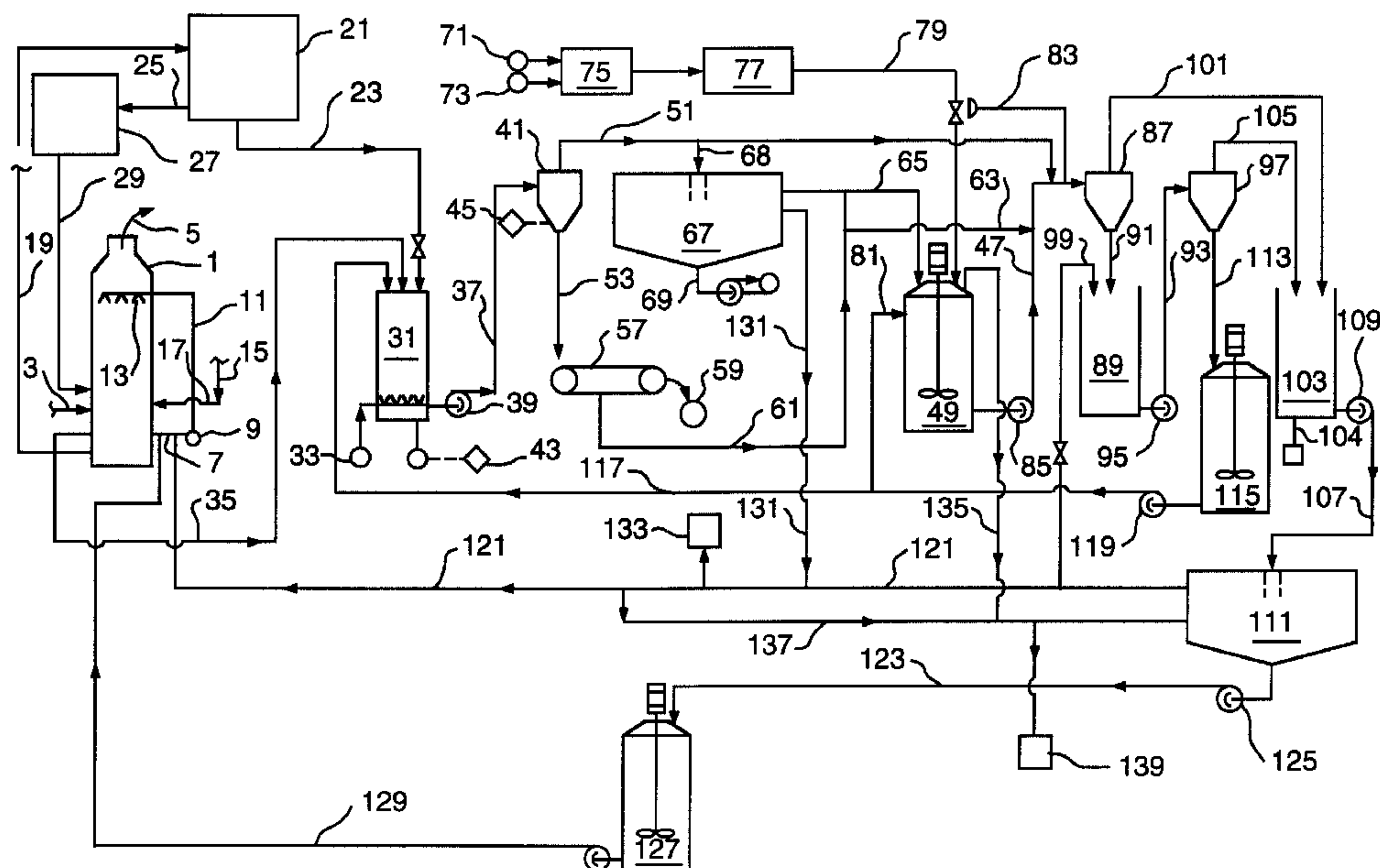
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(54) **REDUCTION DU CALCIUM ET DU CHLORURE DANS LE
PROCESSUS DE DESULFURATION DES GAZ DE
COMBUSTION**

(54) **REDUCTION OF CALCIUM AND CHLORIDE IN THE FLUE
GAS DESULFURIZATION PROCESS**



(57) The method of the present invention achieves a reduction in scale formation in process lines and collection tanks following a regeneration tank in the flue gas desulfurization (FGD) process system. The method achieves a reduction in scale formation by the removal of sulfates, primarily in the form of calcium sulfate or gypsum, as well as calcium chloride from the system. Removal occurs by one or more of the following which achieve a removal of sulfates from the system: 1) crystallizing gypsum in an overflow tank located after a regeneration tank by providing seed crystals; 2) producing and crystallizing gypsum from a post regeneration tank liquor line while at the same time producing $MgCl_2$; and 3) producing and crystallizing gypsum from the system return line while at the same time producing $MgCl_2$.

ABSTRACT OF THE DISCLOSURE

The method of the present invention achieves a reduction in scale formation in process lines and collection tanks following a regeneration tank in the flue gas desulfurization (FGD) process system. The method achieves a reduction in scale formation by the removal of sulfates, primarily in the form of calcium sulfate or gypsum, as well as calcium chloride from the system. Removal occurs by one or more of the following which achieve a removal of sulfates from the system: 1) crystallizing gypsum in an overflow tank located after a regeneration tank by providing seed crystals; 2) producing and crystallizing gypsum from a post regeneration tank liquor line while at the same time producing $MgCl_2$; and 3) producing and crystallizing gypsum from the system return line while at the same time producing $MgCl_2$.

REDUCTION OF CALCIUM AND CHLORIDE
IN THE FLUE GAS DESULFURIZATION PROCESSField of the Invention

The present invention relates to a process for substantially preventing gypsum scaling in a process for removing sulfur dioxide from a gaseous stream using magnesium components, wherein a purified magnesium hydroxide product is produced from the scrubbing effluent.

Background of the Invention

10 The need to remove sulfur dioxide from gaseous streams, such as flue gases from power plants using fossil fuels, in order to protect the environment has become increasingly important with the enactment of legislation limiting the amount of sulfur dioxide that can be discharged from facilities. In order to meet this need, various sulfur dioxide removal processes have been developed, including dry removal systems and wet scrubbing systems. In wet scrubbing systems, aqueous slurries of reactant products result which are normally dewatered and the dewatered slurry may be disposed of as a landfill material.

20 In order to recover various components of an aqueous sludge from a sulfur dioxide wet scrubbing system, attempts have been made to convert the sludge components to saleable byproducts. In systems where lime or limestone are used and calcium sulfites and/or sulfates are present in the sludge, for example, processes have been developed to produce gypsum in a form that would be saleable for use in wallboard or other products using gypsum.

Certain improved sulfur dioxide wet scrubbing systems are based on the use of magnesium hydroxide scrubbing liquor. US Pat. No. 5,039,499, issued to Donald Stowe, Jr., which is incorporated

by reference herein and which is assigned to the assignee of the present invention, describes a process where magnesium hydroxide is added to an aqueous scrubbing liquor to remove sulfur dioxide from a gaseous stream, with effluent from the scrubber oxidized and then treated with a magnesium-containing lime slurry to obtain regenerated magnesium hydroxide for recycle to the scrubbing unit.

In systems where magnesium components are present in a wet scrubbing slurry for sulfur dioxide removal, with magnesium sulfite produced that is then oxidized to magnesium sulfate, and the sulfate contacted with lime to produce calcium sulfate as gypsum and magnesium hydroxide, the resultant magnesium hydroxide produced is contaminated with gypsum. The resultant magnesium hydroxide can be partially purified by physical separation, such as froth floatation, elutriation or hydrocloning, but in such cases, the magnesium hydroxide will still retain an amount of gypsum as a contaminant that limits the uses to which such magnesium hydroxide may be put. Generally, it has been found that following such physical separation, the magnesium hydroxide separated portion can contain between about 20 - 45 percent contaminants, a major portion of which is calcium sulfate, or gypsum. In order to purify the magnesium hydroxide so separated, various purification processes may be used but such processes contain use of additional chemicals or expensive equipment and the production of various by-products or the like which must be discarded.

It is an object of the present invention to provide a flue gas desulfurization method using an aqueous scrubbing medium containing magnesium components which substantially prevents gypsum scaling in the system process lines and collection tanks and provides for the collection of magnesium hydroxide and gypsum as salable products.

Other objects, features and advantages of the present invention will become apparent from the following detailed description taken in conjunction with the accompanying drawing.

SUMMARY OF THE INVENTION

The method of the present invention achieves a reduction in scale formation in process lines and collection tanks following a regeneration tank in the flue gas desulfurization (FGD) process system. The method achieves a reduction in scale formation by the removal of sulfates, primarily in the form of calcium sulfate or gypsum, as well as calcium chloride from the system. Removal occurs by one or more of the following which achieve a removal of sulfates from the system: 1) crystallizing gypsum in an overflow tank located after a regeneration tank by providing seed crystals; 2) producing and crystallizing gypsum from a post regeneration tank liquor line while at the same time producing $MgCl_2$; and 3) producing and crystallizing gypsum from the system return line while at the same time producing $MgCl_2$.

As will be described, these embodiments can be utilized to solve the gypsum scaling problem by making modifications to the process flow scheme utilizing existing process streams.

BRIEF DESCRIPTION OF THE DRAWING

The present invention will become more readily apparent from the following description of a preferred embodiment thereof shown, by way of example only, in the accompanying drawing, wherein a flow diagram illustrates the preferred process of the present invention.

DETAILED DESCRIPTION OF THE INVENTION

The present process provides for the prevention of scaling in the removal of sulfur dioxide from flue gases using magnesium components in a wet scrubbing system. First, the method of the present invention will be described generally along with the description of the flue gas desulfurization system.

In the removal of sulfur dioxide from flue gas, the aqueous scrubbing medium is an aqueous suspension of magnesium hydroxide which forms magnesium sulfite by reaction with the sulfur dioxide in the gas, such as described in US Pat. No. 5,270,026, issued to John College and Lewis Benson, which is incorporated by reference herein and which is assigned to the assignee of the present invention, and US Pat. No. 5,039,499 also referred to hereinbefore.

Referring to the drawing, the preferred process is schematically illustrated, showing a wet scrubbing unit 1, with a gaseous stream containing sulfur dioxide fed thereto through a line 3 and clean gas discharged through a line 5. An aqueous scrubbing medium containing a magnesium component is charged to the wet scrubbing unit 1 and such aqueous medium recycled therethrough by means of a line 7, a pump 9, and a line 11 to the upper region of the wet scrubbing unit 1 and discharged through nozzles 13 so as to flow downwardly, countercurrent to the upward flow of the gas, in the wet scrubbing unit 1. A supply of aqueous magnesium hydroxide, for use as the aqueous scrubbing medium, is fed through a line 15 to a line 17 for charging to the wet scrubbing unit 1.

During operation of the wet scrubbing unit 1, a bleed stream containing magnesium sulfite is removed from the wet scrubbing unit 1 through a line 19 and fed to a separator, such as a thickener unit 21. In the thickener unit 21, an underflow, in

the form of a thickened aqueous sludge which contains solids, is separated and discharged through a line 23 as an underflow portion, while the clarified or overflow portion containing dissolved magnesium sulfite is fed through a line 25 to a thickener overflow surge tank 27, and thickener overflow, as desired, is returned to the wet scrubbing unit 1 through a recycle line 29. The species present in the scrubber liquor are MgSO_3 , MgCl_2 , MgSO_4 , trace amounts of CaSO_3 , CaCl_2 and trace amounts of CaSO_4 .

10 The thickener sludge or underflow from thickener unit 21 is passed through line 23 to an oxidizer 31 and an oxygen containing gas, such as air, from a line 33, may be charged thereto to oxidize magnesium sulfite to magnesium sulfate and form an aqueous solution. A bleed stream of spent desulfurization solution can also be removed from scrubbing unit 1 through a removal line 35 and fed directly to oxidizer 31. The aqueous solution formed in oxidizer 31 is passed through a line 37, by means of a pump 39, to a solids separator 41, typically a hydroclone separator. A hydroclone logic controller 43 may be used to control solids separator 41 indirectly by controlling parameters like flow rate and effluent density. Solids separator 41 may also have sensors and controllers associated with it like an oxidation level controller 45 which can detect, calculate, regulate and control oxygen levels in the solids separator 41.

20 The major products of the oxidizer 31 are aqueous MgSO_4 , H_2SO_4 , MgCl_2 , CaCl_2 and CaSO_4 from wet scrubbing unit 1 and an additional amount of CaSO_4 which is be added in purified form from a downstream surge tank, which will be described later.

30 The purpose of adding gypsum to oxidizer 31 from a downstream surge tank is two fold. First, oxidizer 31 contains calcium sulfate in solution in ionic form. It is undesirable to

have the calcium sulfate precipitate out of solution and form scale on the inside of the vessel of oxidizer 31. Therefore the gypsum added to oxidizer tank 31 acts as seed crystals causing the calcium sulfate to crystalize out of solution onto the face of the gypsum seed crystals. This helps reduce the possibility of gypsum scale in oxidizer 31.

Second, the gypsum added to oxidizer 31 ensures that there is gypsum in suspension in the aqueous solution formed in oxidizer 31 which passed through line 37, by means of pump 39, to solids separator 41. In the method of the present invention it is important to have gypsum in suspension in the process system following oxidizer 31 so that there exists a supply of seed crystals for removing dissolved calcium sulfate by precipitation.

The method of the present invention reduces calcium and chloride levels by precipitating CaSO_4 and CaCl_2 at the appropriate times in the process lines so the precipitated solids can be separated and removed and the remaining dissolved constituents can be recycled. In order to precipitate CaSO_4 and CaCl_2 downstream, for example from a liquor line 47 downstream from a regeneration tank 49, the appropriate streams of products from oxidizer 31, namely aqueous MgSO_4 , H_2SO_4 , MgCl_2 , CaCl_2 and suspended CaSO_4 , are prepared so they can be used later in the appropriate amounts. Thus locating solids separator 41 after the oxidizer 31 provides process flexibility and control over the subsequent treatment process by the creation of an overflow line 51 and an underflow line 53 from the solids separator 41, that have different solids content. The creation of an overflow stream and an underflow stream from the solution exiting oxidizer 31 allows an operator to have two lines with different amounts of gypsum in the form of suspended solids which can act as seed crystals and varying amounts

of sulfates in the form of dissolved MgSO_4 . As will be shown with data later, the suspended gypsum and dissolved MgSO_4 will be used by the method of the present invention to reduce calcium and chloride levels in downstream process lines.

Referring to the drawing, the underflow line 53 of solids separator 41 transports a thick sludge of aqueous MgSO_4 and crystallized gypsum, to a filter 57 which discharges the gypsum as a filter cake 59 and returns remaining aqueous MgSO_4 having some suspended gypsum to the process by a return line 61. The aqueous magnesium sulfate in return line 61 has a very low solids content because filter 57 collects substantially all the gypsum and discharges the mass as filter cake 59. Return line 61 connects to the liquor line 47 of regeneration tank 49 via a branch line 63. Return line 61 also connects to a charge line 65 of regeneration tank 49; the charge line 65 directly connecting an upstream fines thickener 67 to downstream regeneration tank 49.

The overflow line 51 from solids separator 41 takes aqueous MgSO_4 , H_2SO_4 , suspended gypsum, as well as small amounts of MgCl_2 , CaCl_2 to both fines thickener 67 and the downstream liquor line 47 that exits the regeneration tank 49. First, overflow line 51 goes to fines thickener 67 via a line 68. In fines thickener 67 solids, mostly gypsum and gypsum contaminated with other solids, settle at the bottom half of fines thickener 67. A heavier underflow in an underflow line 69 of fines thickener 67 goes to waste removing the gypsum and undesolvable solids from the system. A lighter overflow in the overflow line 65 containing some gypsum in suspension and trace amounts of CaCl_2 also in suspension is charged to regeneration tank 49.

The overflow line 51 of solids separator 41 also goes directly to downstream liquor line 47 exiting the regeneration tank

49. The purpose is to provide a magnesium sulfate stream to the regeneration tank 49 effluent stream in liquor line 47.

Lime or dolomite, through a line 71, and water, through a line 73, are mixed in a slaker 75 and a slurry tank 77 and the slaked lime produced is fed through a line 79 to the regeneration tank 49. In regeneration tank 49 the lime precipitates calcium sulfate from the magnesium sulfate solution, charged via charge line 65, while simultaneously forming an aqueous magnesium hydroxide suspension. Gypsum can also be charged to regeneration tank 49 in an effective amount via branch line 81 which is branched from a downstream recycle stream. Slaked lime fed through line 79 can also be bled by a line 83 and added to liquor line 47 for the purpose of regulating pH in the liquor line 47.

The aqueous media, in regeneration tank 49, now containing $Mg(OH)_2$, gypsum, dissolved $CaCl_2$ is passed through liquor line 47, by means of a pump 85, to a second solids separator 87, such as a hydroclone. According to the method of the present invention, as will be described later, $MgSO_4$ is added to liquor line 47 via overflow line 51 and branch line 63 to react the dissolved $CaCl_2$ to precipitate $MgCl_2$ and $CaSO_4$. Second solids separator 87 physically separates the $CaSO_4$ solids from the magnesium hydroxide aqueous overflow.

Gypsum is separated from the magnesium hydroxide suspension in second solids separator 87 and is collected in a tank 89, via an underflow line 91, from which the separated solids are charged through a line 93, having a pump 95, to a third solids separator 97, typically a hydroclone separator. A magnesium hydroxide solution containing other components from downstream can be added via a line 99 to tank 89 before the separation in the third solids separator 97.

The contents of the tank 89 are then fed through line 93 to the third solids separator 97. In the third solids separator 97, additional magnesium hydroxide solids are separated from gypsum and crystallized gypsum will form a lower layer, while a suspended gypsum and CaCl_2 solution will form an upper supernatant phase and separation is effected. The magnesium hydroxide and gypsum suspension is discharged from the third solids separator 97, into a tank which will be described later. The supernatant suspended gypsum and CaCl_2 can be subsequently be returned to the scrubbing system as make-up water.

An overflow line 101 from the second solids separator 87 is directed toward an overflow tank 103. Overflow line 101 contains mostly magnesium hydroxide with some gypsum in suspension. An overflow line 105 from the third solids separator 97 also reports to the overflow tank 103. The solution in overflow tank 103 is discharged via line 107 having a pump 109 to a magnesium hydroxide thickener 111, from which the solution is carried by recycle lines back to upstream locations in the process, including line 99 which discharges solution into tank 89.

An underflow line 113 of the third solids separator 97 reports directly to a gypsum surge tank 115 which recycles substantially purified gypsum back to oxidizer 31 and regeneration tank 49 via a gypsum recycle line 117 with a pump 119. Recycling gypsum post-oxidation in the present invention provides necessary seed crystals to crystallize solids from suspension causing less scaling.

Providing overflow line 105 from the third solids separator 97 provides seed crystals to the supersaturated solution in overflow tank 103, containing solids like gypsum and dissolved CaCl_2 . Actually, the overflow from the second solid separator 87

and the third solid separator 97 contain sufficient gypsum content to act as seeding sites and thus discourage gypsum scaling in the lengthy sections of lines following overflow tank 103. Gypsum is crystallized from solution in overflow tank 103 thereby preventing scale formation on vessel walls. The crystallized products are discharged through line 104.

10 Once the magnesium hydroxide solution, containing some suspended gypsum and $MgCl_2$, enters magnesium hydroxide thickener 111, the magnesium hydroxide travels by one of two routes back to wet scrubbing unit 1. Inside magnesium hydroxide thickener 111 the magnesium hydroxide solution will settle into an underflow of magnesium hydroxide solids, gypsum, aqueous calcium chloride and $MgCl_2$, and an overflow of a magnesium hydroxide solution containing dissolved calcium chloride. The magnesium hydroxide solution will exit via a purge line 121 and will report to the recycle stream, line 7, of wet scrubbing unit 1. The solids underflow will be taken by an underflow line 123 and a pump 125 to a magnesium hydroxide storage tank 127. Here the solid magnesium hydroxide is stored until it may be returned by a line 129 to the recycle stream, line 7, of wet scrubbing unit 1.

20 Before magnesium hydroxide from magnesium hydroxide storage tank 127 is returned by a line 129 it will typically be diluted in a recycle tank (not shown) connected to line 7. Similarly, the magnesium hydroxide returning by line 121 would also typically enter a recycle tank connected to line 7 which is part of the recycle stream.

30 Purge line 121, containing high dissolved magnesium like overflow line 51, can be utilized to reduce or prevent calcium buildup in the process system by the method of the present invention. Calcium buildup can be reduced by systematically

lowering calcium levels returning to the scrubbing loop by precipitation of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ and further providing for additional $\text{Mg}(\text{OH})_2$ production and removal of a magnesium-free CaCl_2 stream for commodity recovery.

Referring to the drawing, a bleed line 131 of fines thickener 67, containing suspended gypsum, calcium chloride and magnesium chloride, can be mixed with purge line 121 to produce and crystallize gypsum and produce aqueous magnesium chloride. The solid phase gypsum created can report to a filter 133 whereas the
 10 liquor phase MgCl_2 can report either to the recycle stream, line 7, or be recovered via conventional means as a commodity, or serve as a participant in a further reaction, where it will be mixed to react with lime slurry from an overflow line 135 from regeneration tank 49. Overflow line 135 will discharge into a line 137. The resultant solid phase $\text{Mg}(\text{OH})_2$ of the reaction can report to the magnesium hydroxide thickener 111, from line 137, while the liquor phase CaCl_2 can be concentrated and/or crystallized via conventional means and recovered at location 139 as a valuable by-product. Thus, calcium loadings to the scrubber loop are further reduced by
 20 the method of the present invention, and chloride levels are controlled to acceptable levels.

The general problem to be overcome by the present invention can be described as follows: The regeneration tank 49 shown in the drawing, serves as a crystallizer in which gypsum and magnesium hydroxide are produced from the reaction of lime slurry and oxidizer 31 effluent, shown in (R1):



The gypsum and magnesium hydroxide products are subsequently separated, typically via hydroclone separators. The potential for scaling arises from the regeneration tank 49 onward because the presence of chlorides, associated with magnesium before regeneration, associates now with calcium and raises the calcium level in the regenerated liquor to the point of gypsum saturation and beyond, as shown in (R2):

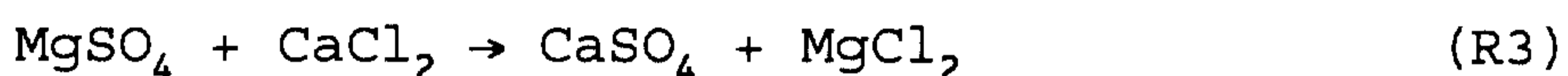


10 Where the solids separators are hydroclones, the hydroclone overflow and overflow tank 103, in the above process, is particularly susceptible to gypsum scaling since they are characterized by the magnesium hydroxide product and have both low percent solids and low gypsum content. In effect, overflow tank 103 has been depleted of seed crystals and the gypsum forms as a scale in the process lines and equipment rather than forming on a growing crystal face.

20 As described generally above, the method of the present invention achieves a reduction in scale formation by the removal of sulfates, primarily in the form of calcium sulfate or gypsum, as well as calcium chloride from the system. Removal occurs by one or more of the following which achieve a removal of sulfates from the system: 1) crystallizing gypsum in an overflow tank located after the regeneration tank by providing seed crystals; 2) producing and crystallizing gypsum from the post regeneration tank liquor line while at the same time producing MgCl_2 ; and 3) producing and crystallizing gypsum from the system return line while at the same time producing MgCl_2 .

Referring to the drawing, in the first embodiment, for example, gypsum seed crystals can be added to the overflow tank 103 to prevent gypsum scaling from that point onward by allowing the underflow of solids separator 97, which typically would go to the magnesium hydroxide thickener 111, to report to the overflow tank 103. The overflow from second solid separator 87 and third solid separator 97 contain sufficient gypsum content to act as seeding sites and thus discourage gypsum scaling in the lengthy sections of lines following this tank.

10 In the second embodiment, liquor phase magnesium chloride can be provided to the process lines downstream of the regeneration tank 49 by reacting oxidizer effluent in line 37, which is low in pH and high in dissolved magnesium, as magnesium sulfate, with the high dissolved calcium, as calcium chloride, gypsum supersaturated post-regeneration tank liquor. The reaction, (R3), below is utilized to lower the dissolved calcium content and provide liquor phase magnesium in the make-up return to the scrubber:



20 This reaction scheme thus provides both gypsum seed crystals and liquor phase magnesium chloride to the process circuits susceptible to gypsum scaling. In addition, as illustrated in the drawing, this technique can be utilized further upstream in the process. If a higher gypsum seed content is desired, then hydroclone overflow line 51 can be added to effluent liquor line 47 of regeneration tank 49. If a low solids stream is preferred, gypsum product filtrate from return line 61 can be added to the liquor line 47.

Both streams, overflow line 51 and return line 61, added in optimal ratios can also be utilized since they are both high in the necessary magnesium sulfate species. The first and second embodiments of the present invention can also be combined to reduce the possibility of scaling.

The advantages of the second embodiment are further realized by the substitution of liquor phase magnesium chloride in place of liquor phase calcium chloride in the scrubber return liquor in purge line 121. The exchange of magnesium for calcium in the scrubber loop translates to less calcium sulfite formation in the recycle lines and ultimately higher oxidation efficiency since liquor phase magnesium sulfite replaces solid phase calcium sulfite in the oxidizer.

EXAMPLE 1

Example 1 simulates the second embodiment of the present invention which is the reaction of the effluent of oxidizer 31 with gypsum supersaturated post-regeneration tank liquor. Example 1 simulates the reaction resulting from the mixing the oxidizer effluent and the regeneration tank effluent. Overflow line 51 is the overflow from the first hydroclone in this FGD system and a good approximation of the effluent of oxidizer 31 and therefore a first solution was prepared to simulate this composition. The overflow line 101 is the overflow from the second hydroclone 87 and a good approximation of the effluent from the regeneration tank 49 and therefore a second solution was prepared to simulate this composition.

Solutions were prepared as follows:

Solution 1: simulating the first hydroclone overflow (the solution in overflow line 51);

Solution 2: simulating the second hydroclone overflow liquors (liquor in overflow line 101); and Solution 3: a combination of Solution 1 and Solution 2; and the above solutions were based on field analyses of the process streams from pilot plant operations.

10 The solutions (1 and 2) were mixed at either 1:7 or 1:14 volume ratios of first hydroclone overflow (solution 1) to the second hydroclone overflow (solution 2). These mix ratios were chosen on the basis of practical pilot plant flow rates, but an optimal ratio would be 1:4 based on stoichiometry.

Two cases were tested: a relatively low magnesium level case and a relatively high magnesium level case. In both cases, solution 1 was mixed with solution 2 at one or both of the 1:7 and 1:14 ratios and the resultant product liquor was examined and analyzed. The analyses were used as inputs to a computer program which calculated the gypsum relative saturation (GRS) of the starting liquors and the resultant liquor.

Table 1 shows the tabulated results and the change in gypsum relative saturation values of the process streams.

20

TABLE 1: Low Magnesium Level

PROGRAM RESULTS [$\rho=1.02$ (g/cm³); T=45°C; P=1 atm]

Event	pH	[Ca ⁺⁺]	[Mg ⁺⁺]	[Cl ⁻]	[SO ₄ =]	GRS
IS-1	6.93	877	3201	6184	7401	1.00
IS-2	11.18	3884	2	5513	1131	1.05
R=1:7	9.93	3222	365	5820	1141	0.92

where, concentrations are given in parts per million (ppm); IS - 1 represents the high magnesium sulfate stream from the

oxidizer/gypsum product loop (overflow line 51); IS - 2 represents the low magnesium/ high calcium, magnesium hydroxide second hydroclone overflow loop that is susceptible to gypsum scaling (overflow line 101); R = ratio of mixing of one of solution 1 with solution 3; GRS = gypsum relative saturation; ρ = density; T = temperature; and P = pressure.

Table 1 shows that addition of the first hydroclone overflow (solution 1) to the second hydroclone overflow (solution 2) in a 1:7 ratio reduces gypsum relative saturation from 1.05 to 0.92 and raises the liquor magnesium level for return to the scrubber from 2 ppm to 365 ppm.

Table 2 is the tabulated results and the change in gypsum relative saturation (GRS) values of the process streams for the high magnesium level case.

TABLE 2: High Magnesium Level

PROGRAM RESULTS [$\rho=1.02$ (g/cm³); T=45°C; P=1 atm]

Event	pH	[Ca ⁺⁺]	[Mg ⁺⁺]	[Cl ⁻]	[SO ₄ ⁼]	GRS
IS-1	6.32	547	6600	4599	18,253	0.89
IS-2	8.69	2723	9	4002	1388	1.23
R=1:14	8.83	2253	413	4100	1578	1.11
R=1:7	8.69	1743	797	4187	1609	0.86

where the units and symbols are the same as in Table 1.

Table 2 reveals that addition of the first hydroclone overflow (solution 1) to the second hydroclone overflow (solution 2) in a 1:14 ratio reduces gypsum relative saturation from 1.23 to 1.11 and raises the liquor magnesium level for return to the scrubber from 9 ppm to 413 ppm. The addition of the first

hydroclone overflow to the second hydroclone overflow in a 1:7 ratio reduces gypsum relative saturation from 1.23 to 0.86 and raises the liquor magnesium level for return to the scrubber from 9 ppm to 797 ppm.

The above data show improved liquor characteristics with respect to both magnesium content and gypsum scaling potential. In addition, laboratory analysis of the precipitate from the mixing reaction verify the precipitated solids to be gypsum, which adds additional seed crystals to the circuit.

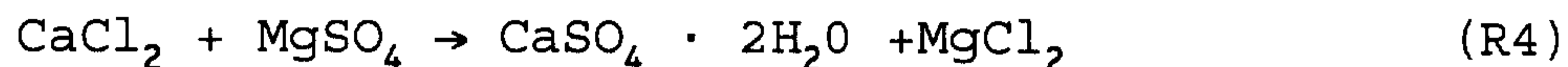
10 Addition of the oxidizer effluent in close proximity to the regeneration tank outlet would give time for gypsum formation and separation in the product hydroclone circuit, representing an improvement in magnesium hydroxide product quality over utilizing the addition of seed crystals to the overflow tank.

 This second embodiment of the present invention is also preferable from the standpoint of injecting liquor phase magnesium to the post-regeneration tank system, which is beneficial not only to the scrubber return but also reduces gypsum relative saturation on a chemical basis by allowing magnesium to associate with the sulfate in solution, making it unavailable for gypsum formation.

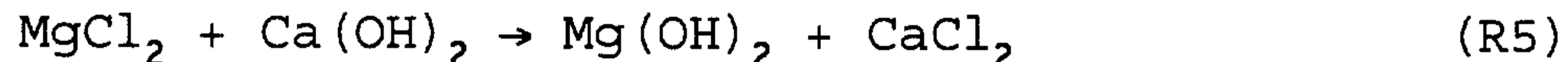
20 Reducing gypsum scaling in the system recycle lines also achieves the object of the present invention. Reacting bleed line 131 of fines thickener 67 and overflow line 135 of regeneration tank 49, overflow line 135 and line 137 containing high amounts of dissolved magnesium, is the third embodiment of the present invention for reducing scale in the FGD process. The improved dewatering of gypsum over CaSO_3 results in a tighter water balance than in the magnesium enhanced lime process and hence chloride levels in the scrubbing liquor tend-to-build up (+20,000ppm) which represents a containment to the gypsum and $\text{Mg}(\text{OH})_2$ by-products. In

addition, chloride association with calcium in the scrubber loop, causes detrimental performance by formation of CaSO_3 solids which decreases scrubbing liquor alkalinity, increases oxidizer power consumption, and further contaminates by-products.

The problem of calcium build up can be solved by systematically lowering calcium levels returning to the scrubbing loop by precipitation of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$, and further providing for additional $\text{Mg}(\text{OH})_2$ production and removal of a magnesium-free CaCl_2 stream for commodity recovery. The solution relies on two
 10 reactions, (R4) and (R5):



If desired, the reaction products can be separated and the MgCl_2 liquor returned to the scrubber or recovered as a commodity; otherwise a second reaction can be run:



The (R5) reaction products can be separated, the magnesium hydroxide solid phase as additional by-product and the magnesium-free CaCl_2 liquor sent for by-product recovery via conventional crystallization or concentration techniques. The following is an
 20 example of the effectiveness of the third embodiment of the present invention.

EXAMPLE 2

The two reactions, (R4) and (R5), envisioned to accomplish the goals of the invention can be utilized to suit the particular needs of any specific magnesium hydroxide sulfur dioxide

scrubbing process application. Synthetic mixtures of thickener overflow and oxidizer liquor were prepared and reacted. A first solution was prepared to simulate the composition of overflow line 131 which is the overflow from the fines thickener 67. A second solution was prepared based on the composition of the overflow line 135.

10 An advantage is that the method of the present invention will lower the pH of the magnesium thickener overflow stream, reducing alkalinity and allowing better primary pH control of the scrubbing loop with $Mg(OH)_2$ product.

First, solutions were prepared to simulate the relevant part of the FGD process. Table 3 shows S_1 as solution 1, the solution prepared to simulate overflow line 131 from fines thickener 67, and S_2 as solution 2, the solution prepared to simulate the overflow line 135 from the regeneration tank 49:

TABLE 3

Sol.	H ₂ O	Gypsum	MgSO ₄	MgCl ₂ 6H ₂ O	CaCl ₂	pH
S_1	0.5	3.3	14.8	4.3	-	5.3
S_2	3.0	10.0	-	-	14.1	10.8

20 Above reagents are shown as the weight in grams and reagents anhydrous unless otherwise noted. H₂O volume is in liters of deionized water. Lime is added in the experiment to create the further reaction (R5).

The mixing of S_1 and S_2 to obtain the solution S_3 results in the reaction (R4). S_3 is a simulation of the composition in purge line 121 which can be returned to scrubbing

unit 1. S_3P is designates the precipitated product of S_3 which, as given in reaction (R4), is gypsum.

The mixing of S_3 with lime creates the reaction (R5) and produces a solution S_4 with a solid precipitate S_4P_1 of gypsum and S_4P_2 of magnesium hydroxide and a filter product S_4F of calcium chloride which can be recycled or wasted. Table 4 shows the liquor chemical analysis of the reaction solutions:

TABLE 4: Liquor Chemical Analyses

10	Soln.	pH	ρ	Ca ⁺⁺	Mg ⁺⁺	Cl ⁻	SO ₄ ⁼ Calc (Mg/l)
	S_1	5.3	1.003	669	6882	2920	25,000
	S_2	10.7	1.008	2124	Ø	2815	1,250
	S_3	9.4	1,003	1125	928	2955	2,400
	S_4F_1	10.9	1,001	2514	Ø	2805	2,200
	S_4F_2	10.9	1,002	2118	Ø	2895	1,100

20 Table 5 shows the chemical analysis of the precipitated products above.

TABLE 5: Precipitate Analyses: Percent

Soln.	DRY Wet grams	% solids Filter Cake	CaO	MgO	S Total
S_3P	16.6	69.5	36.30	1.61	19.63
S_4P_1	3.2	28.3	7.62	24.38	2.89
S_4P_2	5.3	36.6	17.81	60.93	8.77

For S_4F_1 and S_4P_1 , lime was added at 65°F, while for S_4F_2 and S_4P_2 , lime was added at 108°F.

30 Table 6 compares the concentration of each of S_1 , S_2 and S_3 as well as pH for three different tests.

TABLE 6: Series 1: Thickener Overflow and Ox. Bleed Stream

TEST #	SOLUTN #	pH	[Ca] ppm	[Mg] ppm	[Cl] ppm	[SO ₄] ppm	
10	1	1	5.0	40	3182	3184	7874
		2	10.7	1930	0	2876	824
		3	9.3	1299	572	3048	2286
	2	1	5.5	24	2949	3085	7887
		2	10.8	2013	0	2893	844
		3	9.1	1360	722	2969	2190
	3	1	5.1	14	7672	3705	25412
		2	10.8	2085	0	2793	901
		3	8.9	948	1630	3015	4546

Table 7 shows the same data as Table 6 only arranged differently for ease of comparison.

TABLE 7: Series 2: Thickener Overflow and Ox. Bleed Stream

TEST #	SOLUTN #	pH	[Ca] ppm	[Mg] ppm	[Cl] ppm	[SO ₄] ppm		
20	1	1	5.0	40	3182	3184	7874	
	2	1	5.5	24	2949	3085	7887	
	3	1	5.1	14	7672	3705	25412	
	1	2	10.7	1930	0	2876	824	
	2	2	10.8	2013	0	2893	844	
	3	2	10.8	2085	0	2793	901	
	1	3	9.3	1299	572	3048		
	2286	2	3	9.1	1360	722	2969	2190
	4546	3	3	8.9	948	1630	3015	

30 The results of Table 6 and Table 7 show a magnesium ion concentration in solution S₃ in each test run T1=572ppm, T2=722ppm and T3=1630ppm, which is adequate to prevent scaling in the FGD system by the method of the present invention. Therefore the chemistry as proposed by the method of the present invention prevents scaling by the removal of sulfates primarily in the form of calcium sulfate or gypsum.

While there has been illustrated and described several embodiments of the present invention, it will be apparent that various changes and modifications thereof will occur to those skilled in the art. It is intended in the appended claims to cover all such changes and modifications that fall within the true spirit and scope of the present invention.

What is Claimed is:

1. A process for the desulfurization of sulfur dioxide-containing gases comprising:

contacting a sulfur dioxide-containing gas stream with an aqueous solution of magnesium hydroxide in a wet scrubbing unit to remove sulfur dioxide therefrom, and after said contact, said aqueous solution contains dissolved sulfites of magnesium;

passing said aqueous solution to an oxidizer, whereby an oxidized product is formed containing dissolved magnesium sulfates;

10 adding gypsum to said oxidizer;

discharging said oxidized product and said gypsum to a first separator which separates said oxidized product and gypsum into a liquid overflow (A) containing dissolved magnesium sulfates and gypsum in suspension and an underflow (B) containing mostly a salable gypsum product of high-solids content which can be dewatered by a belt filter or a rotary drum;

20 passing a first portion of said liquid overflow (A) to a first thickener whereby said solution in said first thickener separates into a liquid overflow (C) containing mostly dissolved magnesium sulfate with some gypsum in suspension and an underflow (D) containing mostly undissolved solids and solid impurities;

passing a second portion of said liquid overflow (A) to an effluent line from a regeneration tank;

passing said underflow (B) of said first separator to a filter to separate the solids in said underflow (B) from said magnesium sulfate solution;

introducing into said regeneration tank a lime slurry and said liquid overflow (C) from said first thickener whereby

30 said gypsum, said calcium chloride and aqueous magnesium hydroxide are produced;

adding gypsum to said regeneration tank;

discharging the regeneration tank solution to said effluent line whereby magnesium sulfate and gypsum are introduced to produce and crystalize gypsum remaining in the solution and to produce magnesium chloride;

separating said gypsum from the aqueous magnesium hydroxide; and

recycling said magnesium hydroxide back to said wet scrubbing unit.

2. The method of Claim 1, wherein said gypsum introduced into said regeneration tank effluent line is gypsum in suspension from said liquid overflow (A) of said first separator.

3. The method of Claim 1, wherein said gypsum introduced into said regeneration tank effluent line is gypsum in suspension from said liquid overflow (A) from said first separator and from said liquid overflow (C) from said first thickener.

4. The method of Claim 1, wherein said underflow (B) of said solids separator is passed to a filter to separate the solids in said underflow (B) from said magnesium sulfate solution leaving a clarified solution for recycling to said effluent line of said regeneration tank.

5. The method of Claim 4, wherein said gypsum introduced into said regeneration tank effluent line is gypsum in suspension from said clarified solution of said underflow (B) of said first separator.

6. The method of Claim 1, wherein said gypsum introduced into said regeneration tank effluent line is gypsum in suspension from said liquid overflow (A) from said first separator; said liquid overflow (C) from said first thickener; and said underflow (B) which is clarified and recycled to said effluent line.

7. The process for the desulfurization of sulfur dioxide-containing gases according to Claim 1, wherein prior to recycling said magnesium hydroxide, the following steps occur:

passing said regeneration tank discharge to a second separator which separates said regenerated products into a liquid overflow (E) containing magnesium hydroxide and an underflow (F) containing mostly suspended undissolved solids and gypsum;

passing said underflow (F) to a dilution tank where magnesium hydroxide is added;

10 passing the contents of said dilution tank to a third solids separator which creates a magnesium hydroxide overhead solution and suspended gypsum in the underflow which reports to a gypsum surge tank; and

passing said overflow (E) to said separator overflow tank.

8. The process for the desulfurization of sulfur dioxide-containing gases according to Claim 1, wherein prior to

recycling said magnesium hydroxide, the following steps occur:

passing said regeneration tank discharge to a second separator which separates said regenerated products into a liquid overflow (E) containing magnesium hydroxide and an underflow containing (F) mostly undissolved solids and gypsum;

passing said underflow (F) to a dilution tank where magnesium hydroxide is added;

10 passing the contents of said dilution tank to a third solids separator which creates a magnesium hydroxide solution with suspended gypsum which reports to a separator overflow tank;

passing the overflow (E) of second solids separator to said separator overflow tank;

passing the solution from the overflow tank to a thickener to be returned in a thickener purge (G) to said scrubbing unit;

20 introducing into said thickener purge (G), a bleed line from said first thickener forming solid phase magnesium hydroxide and calcium chloride.

9. The method of Claim 8, wherein the calcium chloride is removed from thickener purge (G) and purified.

10. The method of Claim 8, wherein the pH of said thickener purge (G) is lowered which reduces alkalinity and allows pH control in said thickener purge (G).

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