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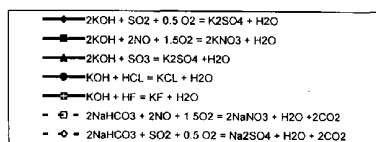
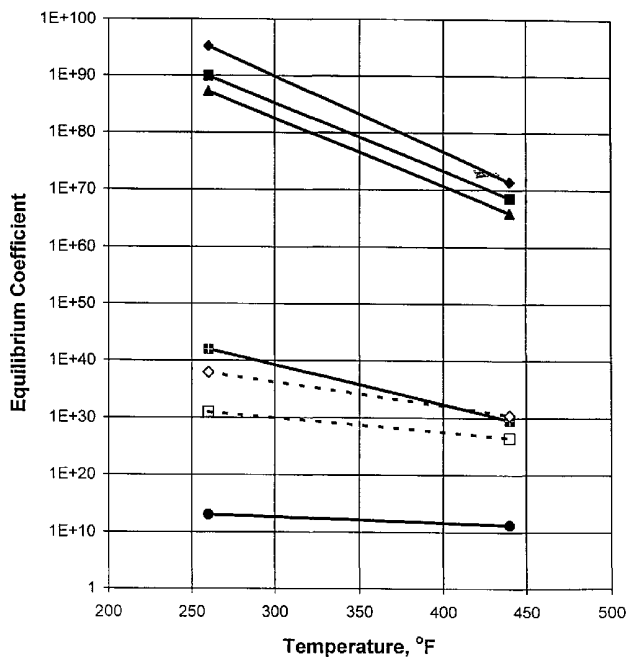
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(54) Title: POTASSIUM HYDROXIDE FLUE GAS INJECTION TECHNIQUE TO REDUCE ACID GAS EMISSIONS AND IMPROVE ELECTROSTATIC PRECIPITATOR PERFORMANCE



(57) Abstract: A method for reducing acid gas emissions from a carbonaceous fuel burning power plant. An aqueous potassium hydroxide dry scrubber method is used to reduce the formation of nitrogen oxides, sulfur oxides, hydrogen chlorides and hydrogen fluoride from plant flue gases. For those plants utilizing an electrostatic precipitator to remove particulate matter from the flue gas, the performance of this component is also enhanced by the injection of potassium hydroxide upstream of the component. As an added advantage, the final product has beneficial commercial utility as a fertilizer product, rather than having to be disposed in a landfill.



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— *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

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TITLE**POTASSIUM HYDROXIDE FLUE GAS INJECTION TECHNIQUE TO REDUCE ACID GAS EMISSIONS AND IMPROVE ELECTROSTATIC PRECIPITATOR PERFORMANCE****BACKGROUND OF THE INVENTION****Related Application**

This application is a continuation in part of application Serial No. 09/243,501 filed February 3, 1999, and now U.S. Patent No. 6,085,674; and is related to Provisional Patent Application Serial No.60/140,174 filed June 21, 1999.

1. Field of The Invention

This invention relates to an aqueous potassium hydroxide dry scrubber method that provides for reduction of acid gases, nitrogen oxides, sulfur oxides, hydrogen chloride and hydrogen fluoride from carbonaceous fuel combustion flue gases. In addition, if an electrostatic precipitator (ESP) is used to remove particulate from the combustion flue gases, its performance will also improve.

2. Description of The Prior Art

U.S. Patent Nos. 4,246,245; 5,814,288 describe the use of calcium/magnesium hydroxide/oxides in a dry scrubber mode wherein the flue gas is brought near to its dew point to enhance the alkali-sulfur dioxide reactions. The alkalis, either in slurry or dry form are introduced into the flue gas upstream of normally a baghouse to capture the sulfur dioxide as alkali sulfites/sulfates that are collected on the bags and removed from the flue gas stream. While these methods accomplish their intended purposes, they provide only SO₂ removal from the flue

gas; however, sulfur trioxide (SO_3), a fly ash conditioning agent, is also removed. With these technologies, if a downstream ESP is used to collect particulate, the efficiency suffers due to increased fly ash resistivity.

Sodium based compounds have also been used in a dry scrubber mode (e.g. U.S. Patent Nos. 4,960,445 and 5,002,741). These alkalis are also introduced into the flue gas upstream of an ESP or baghouse. They have proved effective for reducing both sulfur and nitrogen oxide emissions. In addition, ESP performance is improved. Whereas the sodium based compounds are effective in reducing sulfur and nitrogen oxide emissions and improving ESP performance, they have no commercial value. Further, sodium based compounds are not desirable in landfills for they are soluble and can enter underground aquifers to increase water salinity. Although sodium sorbents are very effective at reducing air pollutants, the potential ground water pollution with the use of these sorbents can offset their air pollutant reduction benefits.

There are many types of devices to reduce sulfur dioxide emissions to the levels prescribed by the U.S. EPA, but the same cannot be said about nitrogen oxides. In the Year 2003, the U.S. EPA will regulate nitrogen oxides emissions for all types of coal-fired boilers to $0.15 \text{ lb NO}_x/10^6 \text{ Btu}$ in the Eastern and Midwestern States during the ozone season (May through September).

Most commercial NO_x reduction technologies cannot meet this limit. Although technologies are in the developmental stage, the only technology available today that will guarantee such a low level of NO_x emissions is the Selective Catalytic Reduction (SCR) technology. The SCR method uses ammonia addition and a downstream catalyst placed in the flue gas stream to destroy the NO_x produced in the coal combustion process. This approach is expensive both from capital and operating cost perspectives. Further, arsenic in the coal ($< 10 \text{ ppmw}$) can poison the catalyst, shortening its life. Still further, ammonium sulfites/sulfates and calcium sulfates from the

combustion process can blind the catalyst, reducing its effectiveness. The U. S. EPA also regulates particulate matter at sizes less than 2.5 microns ($PM_{2.5}$). SCR technology requires ammonia addition and there is always some ammonia slip present to react with sulfur dioxide (SO_2) and nitrogen dioxide (NO_2) to increase fine particulate [$(NH_4)_2SO_4$ and NH_4NO_3] concentrations in the atmosphere ($PM_{2.5}$).

The method of the present invention provides the benefits seen with the use of sodium sorbents but rather than creating landfill ground pollution problems, provides a potassium sulfate/nitrate/fly ash mix that has considerable fertilizer value (the K_2SO_4/KNO_3 value estimated at \$150/ton by agricultural engineers). The potassium hydroxide spray-dry scrubbing technique can be used as a NO_x trim in combination with low NO_x burners and Reburning technology to bring coal-fired power plants into NO_x emission compliance, thus providing an option to the SCR technology.

It is also the low cost method, when used in combination with a baghouse to bring small-scale coal-fired stokers (stokers up to 50 million Btu/hr) into SO_2 , NO_x and particulate compliance without the need for any additional SO_2/NO_x control techniques. Today, small-scale coal-fired stokers are facing elimination due to the more stringent state environmental regulations. The only solution currently available today is to replace coal-fired stokers with relatively expensive fluidized bed coal combustion systems wherein sulfur dioxide and nitrogen oxides may be controlled and baghouses are included for particulate control. Thus, many small-scale stoker users are switching to lower capital cost natural gas fired boilers/hot water heaters. Although low in capital cost, the switch to natural gas drives production/manufacturing costs up due to the higher price of natural gas compared to coal that increases annual operating costs. What is needed for these coal-fired stokers is a low capital and operating cost retrofit technology

that reduces nitrogen and sulfur oxides and particulate from small coal fired stoker units and that is what the potassium hydroxide dry scrubber provides.

SUMMARY OF THE INVENTION

I have discovered a process using an aqueous solution of potassium hydroxide to reduce acid gases; nitrogen oxides, sulfur oxides, hydrogen chloride and hydrogen fluoride from carbonaceous fuel combustion flue gas. In addition, if an electrostatic precipitator (ESP) is used to remove particulate from the combustion flue gases, its performance will also improve. The application of the technology preferably comprises adding a co-current flue gas-spray tower upstream of an ESP or baghouse. Aqueous potassium hydroxide (KOH) is spray dried into the flue gas upstream of the particulate control device. The KOH reacts with SO_2 and SO_3 to form K_2SO_4 , NO and NO_2 to form KNO_3 , HCL to form KCl and HF to form KF. These salts are captured as particulate and removed with the carbonaceous-fuel fly ash from an ESP or baghouse.

BRIEF DESCRIPTION OF THE DRAWINGS

Various other objects, features and advantage of the invention will become more apparent by reading the following detailed description in conjunction with the drawings, which are shown by example only, wherein:

Fig. 1 shows reaction equilibria for KOH and NaHCO_3 reactions with SO_2 and NO, and KOH with HCL and HF; and

Fig. 2 is a pictorial description of the potassium hydroxide spray-dry scrubbing system.

DETAILED DESCRIPTION OF THE INVENTION

I have discovered a process that can be used to remove sulfur oxides and nitrogen oxides from carbonaceous fuel combustion flue gas by spray drying potassium hydroxide into the gas, the potassium hydroxide reacting with the sulfur and nitrogen oxides to form potassium sulfates/sulfites and nitrates/nitrites. Further, the presence of these potassium salts on electrostatic precipitator (ESP) rods and plates facilitates added current flow to the passing flue gas thus increasing the "spark over" voltage from the rods to the plates. The increased voltage improves the ESP performance.

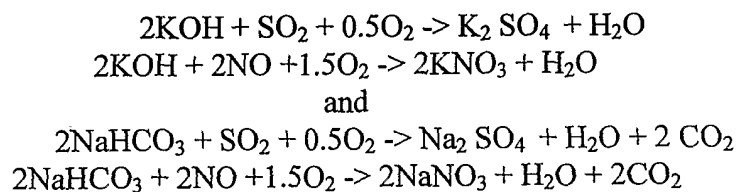
NaTec Resources Inc. (U.S. Patent No. 5002741) uses a naturally occurring sodium bicarbonate (Nahcolite) that is injected as a particulate into the carbonaceous fuel combustion flue gas, upstream of an ESP or baghouse. The technique was applied to a 575 MWe lignite-fired Texas electric utility boiler and showed a 70% sulfur oxides (SO_2 and SO_3) emissions reduction with a simultaneous 40% reduction in nitrogen oxide (NO_x) emissions. Further, even though SO_3 , a fly ash conditioner, is removed the sodium salts increase the "spark over" voltage to increase ESP performance.

It was also shown that the smaller the Nahcolite particle size, the higher the acid gas removal and sorbent utilization efficiencies. With a particle size of 9 micron, about 100% of the SO_2 was removed with a normalized stoichiometric ratio (NSR) of 1.0. With a particle size of about 44 microns, SO_2 removal dropped to a range of 65 to 70% with an NSR of 1.0.

Nahcolite has been shown to work well in a dry scrubber to remove sulfur and nitrogen oxides from coal combustion flue gases and to also improve ESP performance. However, the sodium sulfate and nitrate produced have no immediate commercial use and sodium is not an

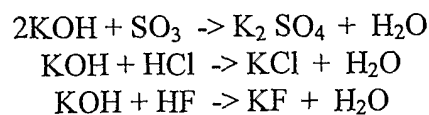
element that is desired to be in a solid waste disposal stream. The sodium salts produced from the flue gas dry scrubber are highly soluble and have to be placed in expensive clay-lined landfills to prohibit potential contamination of underground aquifers.

Potassium sulfate and potassium nitrate, although similar chemically to the corresponding sodium salts, are desirable salts that have a market potential in the fertilizer industry. Although kinetic rates are not readily available to compare sodium and potassium compound reactions with SO₂ and NO; the equilibrium coefficients of sodium bicarbonate NaHCO₃ and KOH reactions with SO₂ and NO were calculated using the Janaf Thermochemical Tables for the flue gas temperature range of interest:



The compared equilibrium coefficients for these reactions are shown in Figure 1. As shown, the equilibrium coefficients for the KOH reactions are much higher than that for NaHCO₃.

Therefore, one could expect that KOH would be more effective than NaHCO₃ in removing sulfur and nitrogen oxides from flue gases. In addition, the following reaction equilibria were calculated for potassium hydroxide reactions with other flue gas acid components:



As seen in Figure 1, the sulfur trioxide reaction with KOH is more favored than the halogen gases (HCl and HF), but all three of these acid gases will be removed to a degree. SO₃ can cause a bluish white opacity problem with flue gas concentrations of 25 ppmv and greater.

SO₃ opacity is often seen with oil-fired power plants which operate at high combustion temperatures and have vanadium pentoxide in the fly ash that promotes SO₃ formation.

It is also well known that the smaller the particle size of a sorbent, the larger its surface area per unit weight, and the higher its reactivity. Therefore, KOH injected as a solution (particles at the molecular level) will have an infinite surface area for reaction and 100% KOH utilization will be quickly achieved in the spray-dry scrubber.

The potassium hydroxide-water solution used for the spray-dry scrubber can be of any pumpable concentration from less than 1% up to nominally 50% by weight. The rate of potassium hydroxide addition into the flue gas is determined for each application, depending on flue gas rate and flue gas concentrations of SO₂, SO₃, NO, HCL and HF. The rate of KOH is set for a specific application, depending on the reduction of acid gases desired. The rate of KOH for any application will be set to yield the desired (accounting for molar concentrations of all acid gases) stoichiometric ratio (NSR). With an NSR of one, there would be exactly enough KOH to react with all of the acid gases. If the technique is used for SO₃ opacity control only, the rate will be set to reduce SO₃ (other acid gases will also be reduced) down to a level where the flue gas loses its bluish white haze, normally there is no haze at levels of 10 to 20 ppmv. If the KOH is used to improve ESP performance only, the rate will be set to create a concentration of KOH reactant, injected into the flue gas, that creates the desired ESP performance.

A typical example of the process of the present invention is shown schematically in FIG. 2. It will be understood by those skilled in the art that certain variations from this schematic could be made with such variations still being within the context of the present invention. In the embodiment shown in Figure 2, a spray-dry tower 2 is added upstream of the flue gas particulate control device 8. The flue gas temperature upstream of particulate control devices on

carbonaceous-fuel fired boilers is normally in the range of 250 to 500 °F. A KOH solution (e.g. 25% KOH) is pumped to the spray-dry tower where it is atomized into the flue gas stream 1.

The spray can be injected in a counter-current or cross-flow direction relative to the flow of the flue gas; preferably, it is injected in a co-current direction as shown in Figure 2. Either a mechanical or dual fluid nozzle 5 can be used to atomize the KOH solution. Air, steam or inert gases may be used as the atomizing fluid. As the KOH solution comes into intimate contact with the hot flue gas, the water component of the atomized solution evaporates and the KOH, at the molecular level, reacts with the acid gas components in the flue gas stream. The produced potassium salts, in suspension, leave the tower 7 to enter into the particulate control device. The particulate control device 8 can be an electrostatic precipitator, a baghouse, or other type of particulate control device. Particulate, including the potassium salts, are removed from the gas stream in a dry form 9. The flue gas exits 10 the particulate control device and enters the atmosphere through a stack.

The fly ash mixed with the potassium salts may be sold as a fertilizer. Alternatively, if a wet electrostatic precipitator is used, the soluble potassium salts may be separated (salts are in solution) from the fly ash and then be precipitated in an applicable crystallizer, filtered and dried to make a more concentrated K_2SO_4/KNO_3 fertilizer product.

While specific embodiments of practicing the invention have been described in detail, it will be appreciated by those skilled in the art that various modifications and alternatives to those details could be developed in light of the overall teachings of the disclosure. Accordingly, the particular arrangements disclosed are meant to be illustrative only and not limiting to the scope of the invention which is to be given the full breadth of the following claims, and any and all embodiments thereof.

CLAIMS:

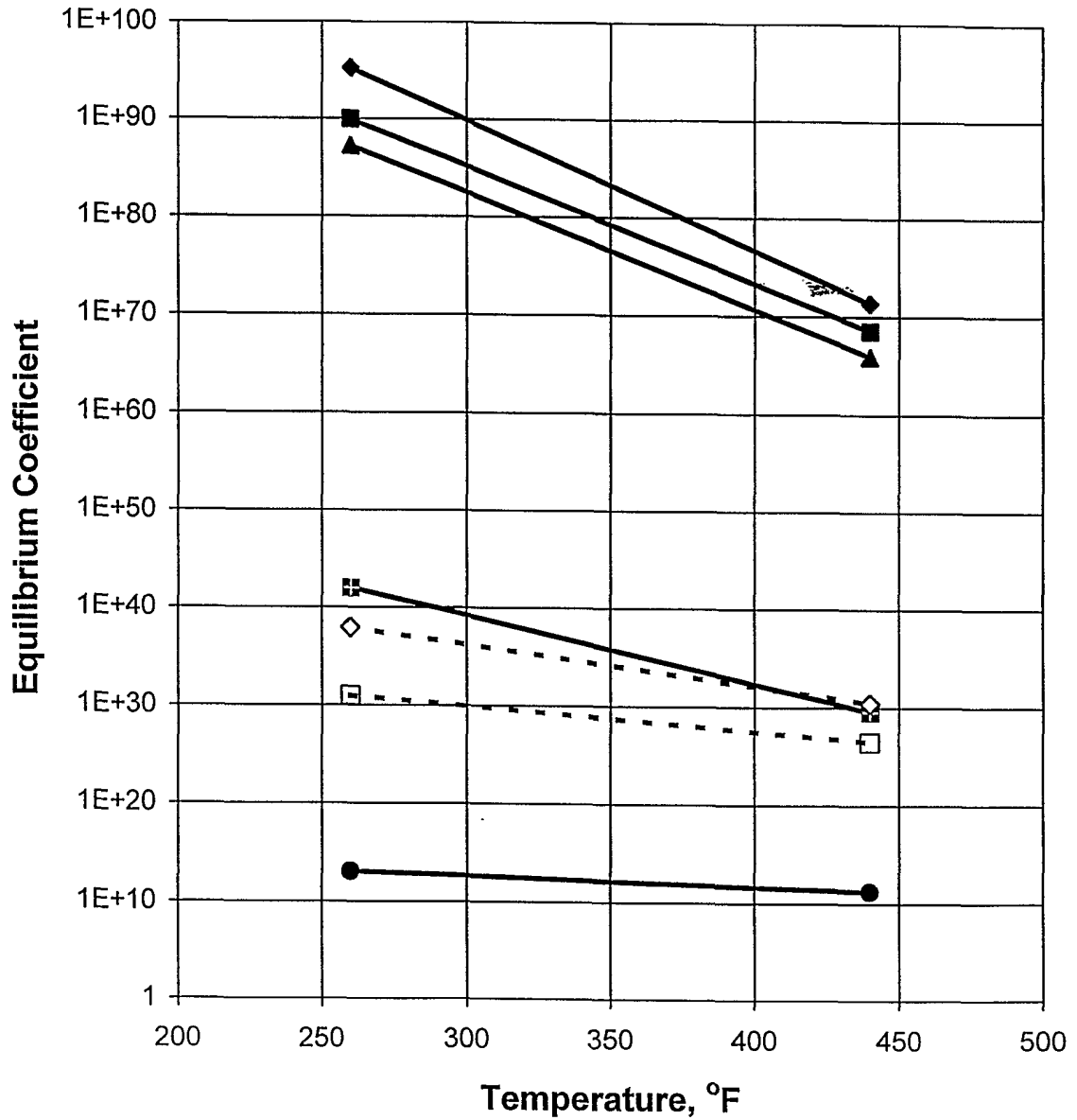
1. A method for reducing nitrogen oxides (NO_x) and/or sulfur oxides (SO_2 and SO_3) emissions from carbonaceous fuel combustion flue gases, said method comprising the steps of:
 - a) introducing an aqueous potassium hydroxide solution into a flue gas contacting device upstream of a particulate control device wherein the said aqueous potassium hydroxide solution is atomized into the flue gas;
 - b) providing a residence time in the flue gas contacting device that is sufficient to provide for said aqueous potassium hydroxide solution water evaporation and for reaction of said potassium hydroxide with acid gases contained in said flue gas to form potassium salts;
 - c) removing said particulate that includes said potassium salts co-mingled with carbonaceous fuel fly ash from the flue gas by a particulate control device; and
 - d) preparing said removed particulate for use as a soil fertilizer.
2. The method according to claim 1 wherein said carbonaceous fuel comprises one or more of the class consisting of anthracite, bituminous, sub-bituminous and lignitic coals, tar and emulsions thereof, bitumen and emulsions thereof, natural gas, propane, butane, petroleum coke, petroleum oils and emulsions thereof, and water and/or oil slurries of coal, paper mill sludge solids, sewage sludge solids, and combinations and mixtures thereof of all the fuels within this class.
3. The method according to claim 1 wherein the aqueous potassium hydroxide solution contains from less than one weight percent potassium hydroxide to nominally fifty weight percent potassium hydroxide.

4. The method according to claim 3 wherein the aqueous potassium hydroxide solution contain between about 20 to 50 weight percent potassium hydroxide.
5. The method according to claim 1 wherein the flue gas contacting device comprises one or more of the class consisting of in-duct injection, spray tower injection or other type of suitable flue gas-potassium hydroxide solution contacting devices.
6. The method according to claim 1 wherein said aqueous potassium hydroxide solution is sprayed into said carbonaceous flue gas stream in a co-current, cross-flow or counter-current direction relative to the direction of said flue gas stream; most preferably the said solution being sprayed in a co-current orientation to said flue gas stream.
7. The method according to claim 1 wherein the aqueous potassium hydroxide solution is atomized with a mechanical or dual fluid nozzle.
8. The method according to claim 7 wherein the atomizing fluid for the dual fluid nozzle comprises one or more of the class consisting of air, steam, nitrogen or inert gas generator gas.
9. The method according to claim 1 wherein the particulate control device comprises one or more of the class consisting of dry electrostatic precipitators, wet electrostatic precipitators, baghouses, wet scrubbers or other high efficiency particulate removal devices.

10. The method as in claim 9 wherein the precipitation, filtering and drying equipment comprises one or more of the class consisting of crystallizers, filters, centrifuges, rotary kiln dryers, fluid bed dryers, spray dryers, screw dryers and other applicable separation/drying devices.
11. The method according to claim 1 wherein the said fly ash and said potassium salts comprising primarily potassium nitrate and potassium sulfate are collected in a dry state as a co-mingled product for use as a fertilizer or a fertilizer component.
12. The method according to claim 1 wherein the said potassium salts comprising primarily potassium nitrate and potassium sulfate are collected in a solution, separated from the fly ash particulate and then are precipitated from solution, filtered and dried for use as a fertilizer or a fertilizer component.
13. The method as in claim 1 wherein the potassium hydroxide is added precipitation, filtering and drying equipment comprises one or more of the class consisting of crystallizers, filters, centrifuges, rotary kiln dryers, fluid bed dryers, spray dryers, screw dryers and other applicable separation/drying devices
14. The method as in claim 1 wherein a potassium hydroxide spray is injected into a flue gas stream to reduce flue gas stack opacity created by sulfur trioxide in the flue gas, the rate of potassium hydroxide added being such to reduce the sulfur trioxide in the flue gas to a level of 25 ppmv or less.
15. The method as in claim 1 wherein a potassium hydroxide spray is injected into a flue gas stream to improve electrostatic precipitator performance by increasing the precipitator "spark over" voltage to

improve electrostatic precipitator performance, the rate of potassium hydroxide added being such to provide the degree of performance desired.

Fig. 1



- ◆— 2KOH + SO2 + 0.5 O2 = K2SO4 + H2O
- 2KOH + 2NO + 1.5O2 = 2KNO3 + H2O
- ▲— 2KOH + SO3 = K2SO4 + H2O
- KOH + HCL = KCL + H2O
- ⊠— KOH + HF = KF + H2O
- ⊠ - 2NaHCO3 + 2NO + 1.5O2 = 2NaNO3 + H2O + 2CO2
- ◆ - 2NaHCO3 + SO2 + 0.5 O2 = Na2SO4 + H2O + 2CO2

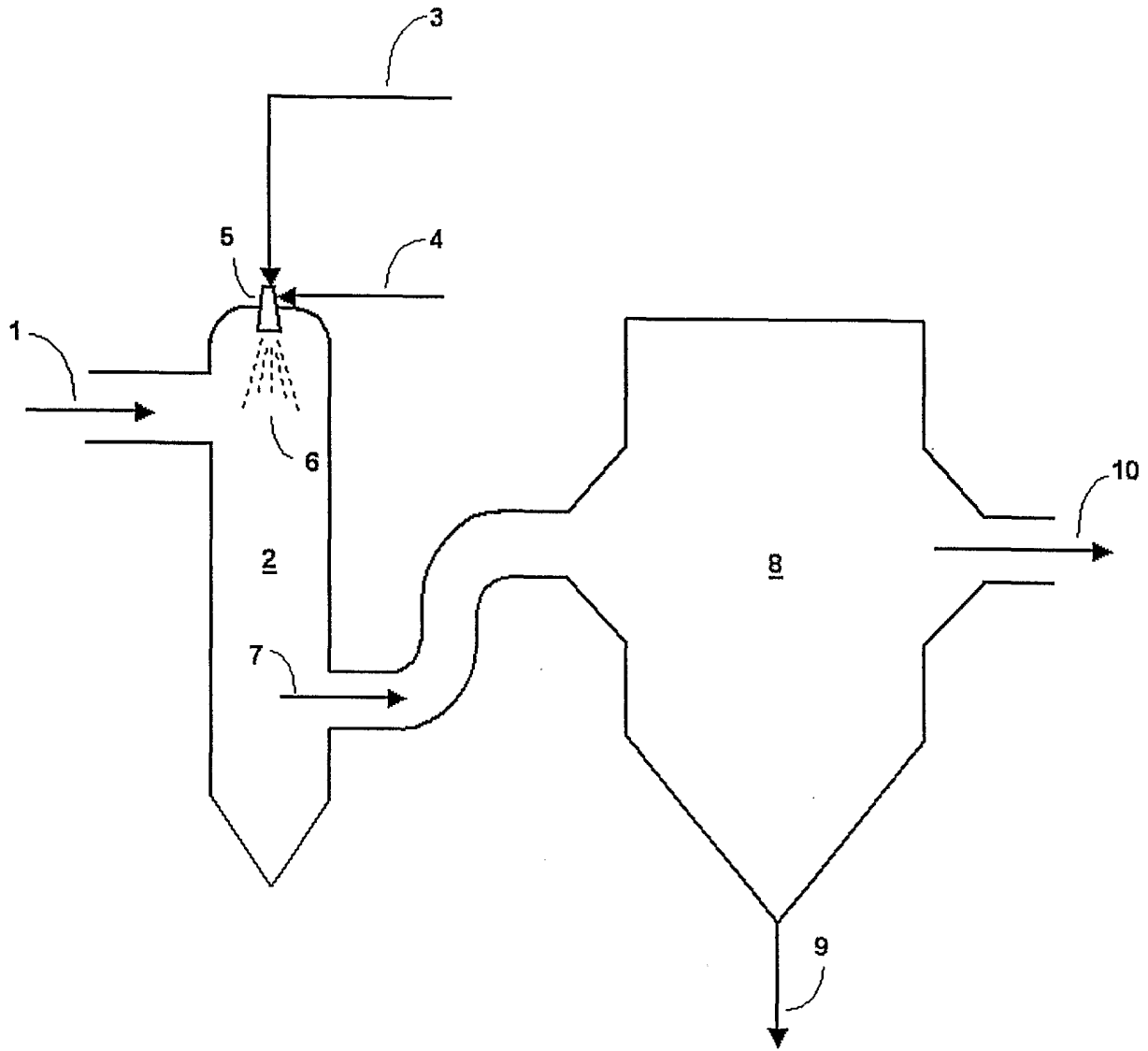


Fig. 2

INTERNATIONAL SEARCH REPORT

International Application No
PCT/US 01/17908

<p>A. CLASSIFICATION OF SUBJECT MATTER IPC 7 B01D53/50 B01D53/56 B01D53/60</p>		
<p>According to International Patent Classification (IPC) or to both national classification and IPC</p>		
<p>B. FIELDS SEARCHED</p>		
<p>Minimum documentation searched (classification system followed by classification symbols) IPC 7 B01D</p>		
<p>Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched</p>		
<p>Electronic data base consulted during the international search (name of data base and, where practical, search terms used) PAJ, EPO-Internal, WPI Data</p>		
<p>C. DOCUMENTS CONSIDERED TO BE RELEVANT</p>		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 884 092 A (VON ROLL UMWELTTECHNIK AG) 16 December 1998 (1998-12-16)	1
A	claims 1,8	2-15
A	----- PATENT ABSTRACTS OF JAPAN vol. 015, no. 113 (M-1094), 18 March 1991 (1991-03-18) & JP 03 005616 A (TAKUMA CO LTD;OTHERS: 08), 11 January 1991 (1991-01-11) abstract	1-15
A	----- US 4 201 753 A (DAYEN WILLIAM R) 6 May 1980 (1980-05-06) claims 1,2,7	1-15
A	----- US 4 540 554 A (DAYEN WILLIAM R) 10 September 1985 (1985-09-10) column 4, line 25 - line 47; claim 1 -----	1-15
<p><input type="checkbox"/> Further documents are listed in the continuation of box C. <input checked="" type="checkbox"/> Patent family members are listed in annex.</p>		
<p>* Special categories of cited documents :</p>		
<p>'A' document defining the general state of the art which is not considered to be of particular relevance</p>		<p>'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>'&' document member of the same patent family</p>
<p>'E' earlier document but published on or after the international filing date</p>		
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<p>'O' document referring to an oral disclosure, use, exhibition or other means</p>		
<p>'P' document published prior to the international filing date but later than the priority date claimed</p>		
<p>Date of the actual completion of the international search</p>		
<p>11 October 2001</p>		<p>Date of mailing of the international search report</p> <p>19/10/2001</p>
<p>Name and mailing address of the ISA European Patent Office, P.B. 5618 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016</p>		<p>Authorized officer</p> <p>Faria, C</p>

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0884092	A	16-12-1998	CA 2240765 A1	13-12-1998
			CZ 9801837 A3	17-03-1999
			EP 0884092 A1	16-12-1998
			HU 9801348 A2	28-06-1999
			JP 11070317 A	16-03-1999
			NO 982684 A	14-12-1998
			PL 326775 A1	21-12-1998
JP 03005616	A	11-01-1991	JP 2788997 B2	20-08-1998
US 4201753	A	06-05-1980	NONE	
US 4540554	A	10-09-1985	NONE	