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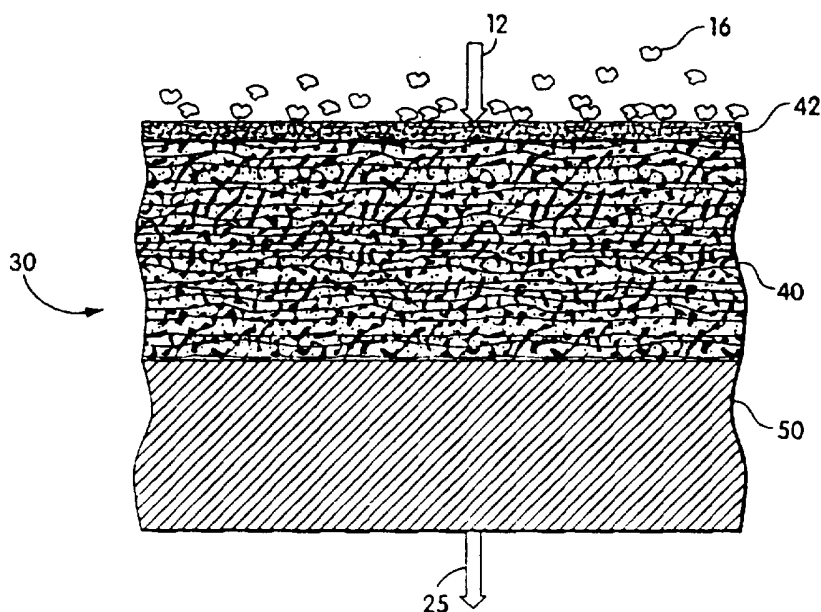
(57) Abstract

A filter for multiphase cleanup of gas streams, in particular flue gas streams, includes filter wall composites comprising a bulk macroporous support (40) having a microporous membrane (42) on one side and a chemically-active deposit (50) on the opposite side. The bulk macroporous support has a surface area of less than 5.0 m²/g, a compressive crush strength of between about 1.0 lb/mm to about 10.0 lb/mm, and a thickness of between about 1.0 mm to about 3.0 mm. The microporous membrane and the chemically active deposit have thicknesses of less than about 100.0 microns and less than about 10.0 mm, respectively. The process of multiphase cleanup of gas streams includes passing a gas stream, comprising particulate pollutants (16) and gaseous pollutants, through a filter having composite walls formed of a bulk macroporous support having a microporous membrane on one side, and a chemically-active deposit on the opposite side.

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ACTIVE FILTERS FOR INTEGRATED CLEANUP
OF GAS STREAMS

BACKGROUND OF THE INVENTION

1.   Field of the Invention
      This invention relates to filters in general, and more
specifically to using chemically-active and regenerable
filter wall composites for the simultaneous removal of
entrained particulate matter and gaseous pollutants from flue
gases, fuel gases and other industrial gas streams.

2.   Description of Prior Art
      Continually changing environmental laws and regulations
throughout the world have imposed new, more stringent
performance standards for the removal of pollutants from
effluent gas streams. Better, more efficient control of air
emissions from power plants, waste incinerators and various
industrial processes, require creative application of new
technologies to achieve the required control levels without
excessive cost penalties. For example, in coal-fired power
plants flue gases containing pollutants such as nitrogen
oxides (NO_x), sulfur oxides (SO_x), and particulate
pollutants such as fly ash are produced. Costly equipment
must be used to remove the particulate matter, and gaseous
sulfur and nitrogen oxides. Similarly, in integrated coal
gasification combined-cycle power generation, removal of
particulate matter, alkali metals, hydrogen sulfide, and
ammonia must be performed before the fuel gas is combusted in
the gas turbine.
      FIG. 1 shows an example of a prior art power-plant, with
boiler 10, and economizer 11, producing flue gas 12 which is
treated in seriatim to achieve removal of NO_x,
particulates, and SO_2 using, respectively, selective
catalytic reduction of NO_x in vessel 13 with injected

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ammonia gas 14 to produce nitrogen and water vapor, a filter
house 15 to remove particulate matter (fly ash) 16 and wet
(or dry) scrubbers 17 for SO_2 removal. The SO_2 is
typically in the form of a waste 18, e.g. calcium sulfate,
and needs further disposal. Typically, scrubber off-gas is
reheated and sent to stack 19 from which treated gases 20 are
released. Removal efficiencies are typically about 80% of
NO_x, 98% of particulates, and 90% of SO_2. Each of these
units is operated at different temperature for peak
efficiency, which fixes their respective installation at
different locations along the flue gas ductwork.

The prior art also teaches partially integrated
emissions control devices that combine particle filtration
with at least one gaseous pollutant removal. For example,
U.S. Patent 4,220,633 to Pirsh teaches baghouses for fly ash
removal with simultaneous catalytic reduction of nitric
oxides with injected ammonia gas on a catalyst phase coated
on or lodged within the fiber structure of the baghouse. The
SO_2 in the flue gas is removed downstream of the baghouse
by scrubbing to produce a waste as explained above.

U.S. Patent 4,728,503 to Iida describes a filter medium
for treating exhaust gases, especially those emitted by
municipal waste incinerators. The filter described consists
of several layers of different materials performing several
functions in a prescribed direction, and is limited to a
filter having a free outer surface. More specifically, this
filter consists of a porous ceramic filter medium to capture
fly ash. On one side (inner) of this filter medium a
denitration catalyst is applied as a coating to remove nitric
oxides by selective catalytic reduction with ammonia, while
on the other side (outer) of the filter medium a composite
layer is applied to remove hydrogen chloride by slaked lime
(as $CaCl_2$ waste). Because the outer layer is
non-regenerable, it has to be scraped off periodically and a
fresh powder layer is reapplied. Thus, the outer side of the
filter must be free to permit this mechanical cleaning.

Filter configurations such as those disclosed in U.S. Patent
4,632,683 to Fukutani et al. for an exhaust gas purifying
filter having a honeycomb structure, or EP 0,057,251 to
Westinghouse for a filtration system configuration useful for
cleaning high temperature raw gas containing fine
particulates, therefore, cannot be used in combination with
the Iida disclosure. The SO_2 in the exhaust gas can be
removed by the slaked lime, or easier by alkaline substances
included in the outer surface coating, but the solid sulfates
produced will also need to be removed by mechanical
scraping. This method leads to large volumes of waste
by-product to be disposed.

Therefore, an integrated emissions control device that
also avoids waste by-product formation would be highly
desirable to reduce costs associated with waste handling and
disposal. If the initially dilute pollutant is recovered in
concentrated form and further processed into a salable
product, additional credits will result. The regenerative
removal of SO_2 by metal oxides that form sulfates which can
be easily reduced back to the oxide form during regeneration
is an attractive method that has been considered, especially
in conjunction with NO_x removal to eliminate the need for,
and the costs of operating, two separate units. In the
latter case the metal oxide chosen has to show both high
reactivity with SO_2 and be active for denitration, e.g. by
selective catalytic reduction with ammonia, shown generally
by the formulae:

$$MO + SO_2 + 1/2O_2 \rightarrow MSO_4 \tag{1}$$

$$NO + 2NH_3 + O_2 \xrightarrow[MSO_4]{MO} 3/2\ N_2 + 3H_2O \tag{2}$$
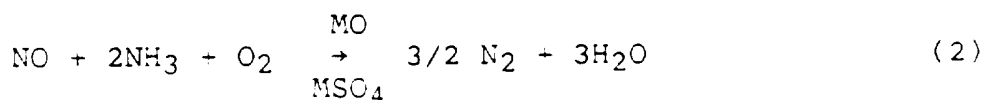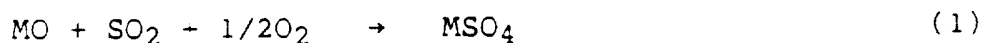
where M, shown here to be of valence 2, can be of any valence
and is a transition metal, rare earth element, alkali or
alkaline earth or other element or oxide which is not
poisoned by SO_2 for catalyzing reaction (2), or the sulfate

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of which is also a catalyst for reaction (2), as shown above. Additionally, the sulfate should be regenerable by thermal or chemical treatment. There are several metal oxides that meet these criteria, for example, CuO, Fe_2O_3, NiO, CeO_2. Also, mixed metal oxides each possessing a different activity for reactions (1) and (2) may be used.

However, the development of these processes is hindered by sorbent attrition problems in moving bed, or fluidized-bed reactors which allow operation in the presence of fly-ash. Conventional fixed-bed designs employing pellets, tablets, rings, etc., which provide the least attrition to solid sorbent/catalysts, cannot be used under high-dust loading because of excessive pressure drop due to plugging of the bed. On the other hand, in advanced fixed-bed designs employing honeycomb monoliths with gas flowing in an array of parallel channels, very large reactor volumes would be required to process the flue gas, because the sorbent would exist only as a thin coating on the channel walls along which the gas flows. In either of these fixed-bed designs, undesirable (often detrimental) interaction of fly ash particles with the active catalyst-sorbent surface can take place since impaction of fly ash on the sorbent cannot be avoided.

For the fixed-bed to become viable, a combination of a filter/sorbent-catalyst medium is required, first presenting the filtering function, followed by the sorbent-catalyst function. PCT International Application Serial No. PCT/US88/03726, by the present applicant, now abandoned, described such a filter medium. The application described methods and devices for gas cleaning consisting of walls with a first, fine-pore ceramic filter layer for fly-ash removal, followed by an active layer of coarser pore-structure to perform reactions (1) and (2). Backflushing with air would be applied periodically to clean the filter surface from collected particulates. Further, the sulfate formed via reaction (1) would be regenerated with a reducing gas, back

to the oxide form. Although this filter device overcomes
prior art deficiencies, it did not provide preparation and
performance characteristics of the proposed device to
effectively remove all three pollutants without operating
difficulties. Significant among these operating problems are
pressure drop increase, and structural problems such as
non-uniformity of coating, spalling, fly-ash penetration and
lodging within the active wall, and the strength of the
large-pore active wall.

U.S. Patent, 4,977,123 to Flytzani-Stephanopoulos et al.
teaches a method for preparation of extrusions of bulk mixed
oxide compounds with both high macroporosity and mechanical
strength. Several compositions are described as regenerable
absorbents of hydrogen sulfide for application to
desulfurization of gasifier exit fuel gas streams at high
temperatures. A similar extrusion process could be used for
extruding compositions for various applications, such as for
combined SO_x/NO_x removal from flue gases, waste
incinerator exhausts, or other industrial gases. Further,
the reference generally discloses the possibility of
combining the active phase functions with particulate
filtration. It is noted however, that based on the porosity
requirements of the active phase such a filter would be, in
large-part, a depth-filter allowing fly-ash particles to
lodge permanently within the porous active phase, increasing
the pressure drop and, potentially, decreasing the efficiency
of conversion of the active phase.

Ceramic filters including layered or gradiated porosity
have been described. For example, U.S. Patent 4,629,483 to
Stanton describes a method for forming a monolithic, layered,
tubular ceramic filter structure with clearly defined layers
of different porosities and permeabilities. Alternatively,
U.S. Patent 4,810,273 to Komoda describes how to make a
ceramic filtering layer of gradually increasing porosity on a
planar ceramic support of larger porosity. Neither reference
discloses "active" filters, i.e. filter bodies comprising

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chemically-active phases useful for combined pollutant
removal in the absence of interaction from fly ash which is
effectively retained on the surface of the barrier filter.
These references utilize refractory ceramic materials to form
the filter body, including: alumina, silica, zirconia,
cordierite, mullite, or silicon carbide.

In place of refractory ceramics, one can use an active
phase composition, e.g. of single or mixed metal oxides, to
form the filter body. This would require firing the filter
body at high temperatures to increase the strength of the
filter walls. It is noted however, that certain active phase
compositions are limited to low-temperature preparations, so
that they retain certain phases in uncombined form or high
dispersion. With lower firing temperatures the strength of
the filters described by the above references would be
greatly compromised.

It is therefore an object of the present invention to
provide an improved multifunctional active filter and method
for combined pollutant removal, unlimited by the choice of
the specific active phase.

SUMMARY OF THE INVENTION

Accordingly, improved compositions and methods are
disclosed for active filter/sorbent/catalyst media aimed at
simultaneous fly ash/gaseous pollutant removal applications,
not limited by the choice of the specific active phase
composition.

A filter for multiphase cleanup of gas streams, in
particular flue gas streams, includes filter wall composites
comprising a bulk macroporous support having a microporous
membrane on one side and a chemically-active deposit on the
opposite side. The bulk macroporous support has a surface
area typically less than 15.0 m^2/g, a compressive crush
strength of between about 1.0 lb/mm to about 10.0 lbs/mm, and
a thickness of between about 1.0 millimeter to about 3.0
millimeter. The microporous membrane on the bulk macroporous

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support has a thickness of less than about 100.0 microns.
Lastly, the chemically-active deposit has a thickness of
between about 0.0 millimeter to about 10.0 millimeter. By
"zero" thickness, we imply that the macroporous support
itself possesses adequate chemical reactivity and
regenerability in pollutant removal to render the application
of the chemically-active deposit unnecessary. When a deposit
is needed, however, it is applied in a separate step as a
coating on or as a macroporous solid foam integrated with the
support wall.

The process of multiphase clean-up of gas streams
comprises passing a gas stream, comprising particulate and
gaseous pollutants (such as nitrogen oxides, sulfur oxides,
volatile organic compounds (VOC's), hydrogen sulfide,
organosulfur compounds, etc.) through a filter having walls
formed of a microporous membrane, a bulk macroporous support,
and a chemically-active deposit. The gas is forced to pass
through the microporous membrane, which acts as a barrier
filter, blocking passage of the particulates entrained in the
gas. The non-particulate pollutants in the flue gas are then
passed through the bulk macroporous support and the
chemically-active deposit, where they react so that a clean
effluent gas is discharged from the filter. The
chemically-active deposit may be a denitration catalyst, an
ammonia decomposition catalyst, a VOC oxidation catalyst, a
regenerable sulfur dioxide or hydrogen sulfide absorbent, or
possess a compatible combination of such functions.
Alternatively, as may be desirable for certain gas clean-up
applications, the bulk macroporous support may be coated with
a high-activity catalyst, e.g. a denitration catalyst,
followed by a chemically-active deposit that functions
primarily as a regenerable SO_2-sorbent. Still, in other
applications, a certain catalyst may be poisoned by SO_2,
whereupon the SO_2-sorbent may be deposited upstream of a
layer of the sensitive catalyst. Regeneration of the
saturated sorbent would be accomplished thermally or

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chemically to recover the sulfur value in concentrated form and the solid in the original active form. Backflushing with air, jet pulsing or other similar method can be used periodically to remove the particulates collected on the membrane side of the filter.

BRIEF DESCRIPTION OF THE DRAWINGS

The foregoing and other objects and advantages will be more fully appreciated from the following drawings in which:

FIG. 1 illustrates a prior art process flow diagram for removing particulate pollutants, sulfur oxides and nitrogen oxides from a flue gas stream;

FIGS. 2A, 2B, and 2C are schematic, sectional views of various embodiments of the filter wall composite of the present invention;

FIGS. 3A and 3B are schematic views of a candle filter utilizing various embodiments of the filter wall composite of the present invention;

FIG. 4 is a schematic sectional view of an alternately plugged-cell, honeycomb-monolith active filter geometry;

FIGS. 5A and 5B are detailed views of various embodiments of the filter shown in FIG. 4;

FIG. 6 illustrates the process flow diagram of FIG. 1 utilizing active filters incorporating the filter wall composites of the present invention;

FIG. 6A is a special case of FIG. 6 wherein sulfur recovery is performed in a single stage with the regeneration of the active filters;

FIG. 7 is a graph of combined SO_2/NO removal by sorbent/catalyst composition C (Table 1) at 500°C, wherein conversion of sorbent is based on $CuSO_4$ and $Ce_2(SO_4)_3$ formation;

FIG. 8 is a graph of cyclic sulfation performance of composition A (Table 1) at 400°C, having an inlet gas composition (mol%) 0.15 SO_2, 3 O_2, balance N_2, wherein conversion is based on $CuSO_4$ formation;

FIG. 9 is a graph of cyclic sulfation performance of composition F (Table 1) at 500°C and regeneration at 600°C; conversion of sorbent is based on $CuSO_4$ and $Ce_2(SO_4)_3$ formation;

FIG. 10 is a graph of sulfur products distribution in regeneration of sorbent composition C (Table 1) with 10%CO, 10%CO_2, balance N_2;

FIG. 11 is a graph of a comparison of SO_2 removal by sorbent composition E (Table 1) and foamed monolith J (Example II) at 400°C from a gas containing 1500 ppm SO_2, 3%O_2, balance N_2; conversion is based on $CuSO_4$ formation, S.V. = 25,000h^{-1} for powder composition E; S.V. = 2,500h^{-1} for monolith J; and

FIG. 12 is a graph of NO conversion over powder composition E and foamed monolith J as a function of temperature; inlet gas composition (mol%):0.06 NO, 0.06 NH_3, 3O_2, bal. N_2; powder: 0.5g, 0.5L/M (SA= 310m^2/g), SV=25,000 h^{-1}, foamed monolith: 1.0g, 1.0L/M (SA 310m^2/g), S.V. = 2500h^{-1}.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides active, multifunctional filter media composition and methods for multiphase clean up of gas streams.

Referring to FIG. 2A, a filter wall composite 30 for multiphase clean up of gas streams includes a bulk macroporous support 40 having a microporous membrane 42 on one side, and a chemically-active deposit 50 on the opposite side.

Bulk macroporous support 40 may be made from a wide variety of materials, depending on the operating conditions of a particular application. Preferred materials are those which are able to withstand high temperatures and long-term exposure to pollutants, such as sulfur and nitrogen oxides, alkali metals, etc. For example, these materials include ceramics, metal alloys, cermet composites, and certain

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polymers. More preferably, bulk macroporous support 40 is
constructed of refractory ceramic materials having good
mechanical strength, thermal shock resistance, chemical
resistance, etc. required for a long service of the filter.
Such materials include oxides of aluminum, silicon,
magnesium, zirconium, titanium, nitrides and carbides of
silicon, binary and ternary oxide compounds, such as mullite
and cordierite, and several others. When the above
requirements can be relaxed, the macroporous support 40 may
be constructed from a mixture of compounds, at least one of
which is chemically-active, while another serves as a
dispersant or structural or textural promoter. Active
compounds include elements and oxides of the groups of the
transition metals, alkali, alkaline earths, copper, zinc,
rare earths, either single or combined in mixed oxide form,
alloy form, oxide compound or oxide solid solution form,
etc. The structural promoter can be alumina, chromia,
titania, silica, magnesia and other such oxides added to
improve dispersion or structural stability, resistance to
chemical attack, mechanical strength, etc. of the active
phase.

Similar compositions in extruded form, used as single
and mixed oxide absorbents and catalysts, having high
macroporosity and mechanical strength are described in U.S.
Patent No. 4,977,123 to Flytzani-Stephanopoulos et al., which
is incorporated herein by reference. The reference teaches
preparation of the extrusion by a complexation technique
which includes pyrolysis-calcination of amorphous citrate
precursors between about 550°C to about 850°C, sizing the
resultant powder to a broad particle size distribution,
extruding a paste formed by adding a binder and water, and
drying and heat treating the processed extrusion.

The bulk, macroporous support 40 may be extruded in
planar, tubular or other form as a single element or a
multi-element filter body. The filter may, thus, be of
cross-flow configuration, such as the one described by

Westinghouse in EP 0,057,251; or a through-flow honeycomb
monolith with alternatively plugged inlet and exit passages,
such as that described by Fukutani in U.S. Patent 4,632,683;
or it may be in the form of ceramic candles, hollow tubes,
etc. prepared by techniques well-known in the art.

The bulk, macroporous support 40 typically has a surface
area less than about 20.0 m^2/g, and a compressive crush
strength of between about 1.0 lb/mm to about 15.0 lbs/mm of
extrusion length. Preferably, macroporous support 40 has a
surface area between about 1.0 m^2/g to about 15.0 m^2/g,
and a compressive crush strength between about 2.0 lbs/mm to
about 10.0 lbs/mm. Typically, the macroporous support 40 is
between about 1.0 millimeter to about 3.0 millimeters thick
possessing sufficient mechanical strength to withstand
stresses that occur in the filter during operation and
regeneration. Macroporous support 40 has at least 60% of its
porosity in large pores with diameters of between about 2.0
microns to about 50.0 microns, which allows for low pressure
drop as gas streams are passed through the macroporous
support 40.

Although macroporous support 40, prepared as above, may
possess adequate activity for certain reactions with gaseous
pollutants, often its reactivity is limited due to the
high-temperature heat-treatment used to strengthen the filter
body during preparation. High temperature firing decreases
the surface area and enhances solid oxide compound formation
which may not be the desired chemically-active phases. Also,
often, the support 40 may contain a large fraction of inert
phases to improve the structural stability and/or mechanical
strength of the active phase. In such situations, it will be
necessary to incorporate a higher-activity phase in the
filter wall. Several methods may be used for this step,
depending on the specific application of the active filter
For example, a thin coating of the active composition may be
deposited on the discharge side of the macroporous support by
wet or dry application techniques, such as washcoating from

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slurries followed by impregnation, slip casting, spraying, physical or chemical vapor deposition, etc., all well-known in the fields of ceramics and catalyst processing.

The chemically-active deposit 50 may be made of the same chemically-active compositions described above. The deposit 50 provides more efficient removal and conversion of the non-particulate pollutants, such as sulfur and nitrogen oxides, when used in combination with macroporous support 40. This is because deposit 50 is prepared at a lower temperature than support 40, preserving desirable active phases and high dispersion (high surface area). If utilized, the active compositions can be applied to the macroporous support 40 in quantities ranging from about 5.0 to about 50.0 percent by weight.

Chemically active deposit 50 may be in the form of a film or a foam, which is coated onto macroporous support 40 on the gas-discharge side (opposite microporous membrane 42). The chemically-active film deposit typically has a thickness less than 2.0 millimeters; a foam deposit is typically between about 2.0 millimeters and about 10.0 millimeters thick. It is noted, however, that variously sized deposits may be utilized, depending upon the chemical composition of deposit 50, pressure drop through the filter wall, and system design.

The chemically-active film deposit 50 is prepared as described above and is applied to macroporous support 40 prior to construction of a filter monolith, or slip-coated within an existing monolith's channels. A macroporous solid foam, chemically-active deposit is typically prepared from a slurry, consisting of the metal oxide composition, water, a foaming agent, and a binder. Any suitable binder material can be used, including inorganic binders, such as aluminum phosphate, or organic binders, such as methyl cellulose, ethyl cellulose, polyvinyl alcohol, or a mixture, thereof. The slurry is charged into a monolith's channels where it is dried and foamed, thereby expanding within the passage. A

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similar foam preparation is described in U.S. Patent No. 4,363,644 to Sato et al., which is incorporated herein by reference.

As shown in FIGS. 2B and 2C, deposit 50 may occasionally consist of two zones, 50' and 50", of distinct chemical composition, either of which is disposed next to support 40, depending, on the application. For example, in SO_2/NO_x removal, zone 50' may be an active SCR catalyst that precedes the sorbent zone 50" (lower activity) to improve the NO_x removal efficiency. Conversely, zone 50' may be a denitration catalyst sensitive to SO_2 which should, therefore, be disposed downstream of the SO_2-sorbent zone 50" to preserve its activity.

Microporous membrane 42 may be made from the same variety of materials used to form macroporous support 40. Similar to macroporous support 40, microporous membrane 42 may be an inert, ceramic phase or a mixture of inert- and active-phase compositions. Extruded microporous membrane 42 compositions are fused with macroporous supports 40 by techniques known in the art. It is noted that at least one component material of the microporous membrane is desirable to be present in the macroporous support 40 to prevent spalling, or delamination.

Typically, microporous membrane 42 is less than about 100.0 microns thick and has an average pore diameter less than about 2.0 micron. Preferably, the average pore diameter of microporous membrane 42 is less than about 0.5 micron. Microporous membrane 42 serves as a barrier filter of particulate pollutants, such as fly ash, typically present in fuel gas or combustion gas streams, thereby reducing filter contamination.

In a preferred embodiment, microporous membrane 42 is unitary with macroporous support 40. For example, they may be produced together from the 'green state' according to a technique described in U.S. Patent 4,629,483 to Stanton, which is incorporated herein by reference. Alternatively, a

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technique described in U.S. Patent 4,810,273 to Komoda, which
teaches how to make a ceramic filtering layer of gradually
increasing porosity on a planar ceramic support of larger
porosity may be used, and is incorporated herein by reference.

In operation, filter wall 30 is part of a candle filter
or a multi-element, cross-flow or through-flow monolith (not
shown), which is disposed in the flow path of a multiphase
pollutant gas stream 12. Gas stream 12 is typically a flue
gas, fuel gas, or other industrial gas stream comprising
particulate pollutants 16, and gaseous pollutants, such as
sulfur and nitrogen oxides, hydrogen sulfide, organosulfur
compounds, ammonia, VOC'S, etc. While passing through filter
wall 30, the particulate pollutants 16, such as fly ash, are
blocked by and collected on the microporous membrane 42. The
non-particulate pollutants, such as sulfur and nitrogen
oxides and the like, are reacted with chemically-active
composition(s) disposed in the macroporous support 40 and/or
chemically-active deposit 50. The non-particulate pollutants
are absorbed or converted into innocuous species by the
sorbent or catalyst phases of the deposit, respectively. For
example, for SO_2/NO_x removal, such processes occur
according to reactions (1) and (2). Upon traversing
chemically-active deposit 50, clean gas stream 25 exits
filter wall 30. Filter bodies are constructed from filter
wall composites 30 (FIGS. 2A, 2B and 2C), by techniques known
in the art, to form overall structures of various
configurations. For example, cross-flow filters with
orthogonally displaced inlet and discharge channels can be
formed as described in EP 0,057,251 to Westinghouse.
Chemically-active deposit 50, in either film or foam
composition, can be deposited into discharge channels as
described above. Similarly, cylindrical candle filters may
be used. Schematic, sectional views of such filters are
shown in FIGS. 3A and 3B. These can be extruded in various
sizes and wall thicknesses to meet required ranges of
mechanical strength and pressure drop.

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Referring now to FIG. 4, a schematic, sectional view of
a through-flow filter 70 is shown. In this embodiment gas
flows in and out of filter 70 along the same axis. The
through-flow filter 70 can be extruded in a variety of
configurations, sizes and cell densities, such as a honeycomb
monolith design. The filter 70 is modified by plugging the
entrance of every other channel 71 with a ceramic plug 72 on
each end of the monolith. The alternate channel plugging
limits the entrance of flue gases into every other channel
71, and subsequently blocks the exit of the flue gases though
the channel 71 it entered. The flue gas 12 is then forced to
cross through the wall composites 30, and exits through a
parallel channel 71. Particulate pollutants 16 are blocked
by microporous membrane 42 (FIGS. 2A, 2B and 2C), while the
non-particulate pollutants are removed in macroporous support
40 and/or chemically-active deposit 50, which is deposited
into alternate (clean side) channels 71 where clean exhaust
gas 25 is discharged.

FIGS. 5A and 5B are detailed views of the elements of
through-flow filter 70 shown in FIG. 4. FIG. 5A shows flue
gas 12 entering channel 71 of filter 70. The gas 12 is
forced to cross through filter wall composite 30.
Particulate pollutants 16 are filtered by the microporous
membrane 42, while non-particulate pollutants are removed in
the macroporous support 40 and/or chemically-active deposit
50. A film 51 deposit is coated onto clean side channel 71
where clean exhaust gas 25 is discharged.

FIG. 5B is similar to FIG. 5A, except chemically-active
deposit 50 is a foam 52 deposited in clean-side channel 71.

Referring now to FIG. 6, active filters of the present
invention are included in the process flow diagram shown in
FIG. 1. It can be seen that the active filters 21 replace
traditional in seriatim units, including a filter house to
remove particulate matter, a separate vessel for NO_x
reduction, and wet (or dry) scrubbers for SO_2 removal. In
the process, boiler 10 and economizer 11 produce flue gas 12,

which is passed through filters 21. The filters 21 remove
particulate pollutants, and react with SO_2 to form sulfated
metal oxides which, together with the original oxides,
catalyze the conversion of NO_x to molecular nitrogen by
reaction with ammonia, fed by ammonia stream 14. Clean gas
28 is taken to stack 19, from which treated gas stream 20' is
discharged into the atmosphere without reheating.

Periodically, one active filter 21 is cleaned by
backflushing, while a second filter 21 is utilized as
described above. Fly ash, or other particles 16, blocked by
the microporous membrane, are removed and collected for
disposal. Further, the chemically-active compositions can be
regenerated with a reducing gas, such as natural gas, carbon
monoxide, hydrogen, or mixtures thereof, produced from a
gasifier 22 or another source. The reducing gas is typically
diluted with nitrogen, steam, or other suitable diluent gas.
During reaction of the sulfated metal oxide compositions with
the reducing gases, an off-gas is produced, containing
primarily SO_2 in variable concentration, depending on the
conditions of regeneration. This stream is then taken to a
catalytic sulfur recovery unit 23, where SO_2 is reacted
with a reducing gas stream 24 over a catalyst to produce
elemental sulfur 25, which is separated out by condensation.
Any unconverted SO_2 and reduced sulfur compound products
(e.g. COS, H_2S) are then recycled through line 26 to active
filters 21 or to the boiler 10 (not shown in FIG. 6).
Alternatively, the concentrated SO_2-containing off-gas
stream may be taken to a catalytic oxidation unit to produce
oleum, SO_3, or to produce sulfuric acid, H_2SO_4. In all
these cases, the sulfur value of the flue gas is recovered in
the form of salable products, and no waste by-product is
generated.

There are situations where the sulfur recovery catalyst
material is compatible with the sorbents and conditions used
in active filters 21. In such cases, the catalyst can be
mixed with the active composition in filters 21. In a

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limiting case, the catalyst is also an active composition for SO_2/NO_x removal. When sulfur recovery is performed in active filters 21, sulfur recovery reactor 23 is not needed. In this case, provision is taken to recycle stream 27 to the active filters 21. Figure 6A shows a schematic of such a single-stage, regeneration-sulfur recovery process, where the sulfur value is recovered in the form of elemental sulfur. Accordingly, the regeneration off-gas is recycled (stream 27) to the regenerator vessel of active filters 21 to increase conversion of SO_2 to elemental sulfur, which is separated out by condensation 25. Any unconverted SO_2 and reduced sulfur compounds in the tail gas 26 are recycled to boiler 10 or to absorption vessel of active filters 21.

According to the present process therefore, no solid or sludge waste is generated. The sulfur value of the SO_2 pollutant in the flue gases is recovered as elemental sulfur, a saleable product.

Removal efficiencies, utilizing the active filters of the present invention, are about 99.9% particulates, and greater than 98% and 80% for SO_2 and NO_x, respectively.

The active compositions used in this invention for combined removal of SO_2/NO_x were bulk mixed oxides of copper and aluminum, copper and cerium, or copper, cerium, and aluminum. Various compositions of the mixed oxides can be used, depending on the flue gas type and clean-up temperature. Occasionally, it may be advantageous to include small amounts of transition metal oxides, such as iron, nickel, etc.; other rare earth or alkaline earth oxides as catalyst/sorbent promoters; or it may be beneficial to replace aluminum oxide by other oxides typically used as dispersants, or structural or textural promoters of the active composition, as discussed above. Such cases are considered to fall within the scope of the present invention.

It is well known that when molecular expansion takes place during reaction, such as from a solid oxide to a solid sulfate as in the present case, diffusion of the gas through

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the typically non-porous, solid product layer is hindered, so
that only partial utilization of the active phase occurs. In
such situations, it is beneficial to keep the active phase
dispersed in small particle size. A common approach is to
support the active phase on high-surface area carriers, such
as γ-alumina, silica, titania, and the like. This,
however, limits the amount of sorbent on the support to less
than 10 percent by weight. If higher amounts are used, the
bulk phase properties dominate and grain growth, sintering,
etc. are not avoided. When the active phase is a sorbent to
be used in a fixed-bed design in conjunction with a filter,
as in the present invention, the low loading of the carrier
necessitates large, i.e. uneconomical, reactor volumes.

An alternative is to disperse the active phase, in an
inert or low-activity phase, such as oxides of aluminum,
chromium, titanium in bulk. In other words, use a bulk,
mixed oxide approach to retain the active phase in dispersed
form and at higher weight fraction than what is possible when
a support (carrier) is used.

The present invention will be further illustrated by the
following examples which are intended to be illustrative in
nature and are not to be construed as limiting the scope of
the invention.

EXAMPLE I

Active metal oxide compositions were prepared according
to a slightly modified complexation technique, namely, the
amorphous-citrate technique. Marcilly, C., Courty, P.,
Delmon, B., "Preparation of Highly Dispersed Mixed Oxides and
Oxide Solid Solutions by Pyrolysis of Amorphous Organic
Precursors", J. Amer. Ceram. Soc., Vol. 53(1), 56-57 (1970).
The technique involves rapid denydration (under vacuum at
70°C) of an aqueous solution containing metal salts (e.g.
nitrates, chlorides, sulfates, etc.) and citric acid in
desired proportions, followed by pyrolysis and further
calcination of the resulting, amorphous solid foam in air at

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relatively low temperatures (500-650°C). Citric acid is
added in a 1:1 mole ratio to the total metal salts in
solution. A higher ratio is used when a higher surface area
and porosity are desired in the final oxide composition.
Compositions A-E were prepared by the amorphous citrate
technique. In some cases, a coprecipitation technique is
employed to prepare binary or ternary oxides. Active
composition F, comprising copper, cerium, and aluminum
oxides, was prepared by coprecipitating the carbonates, or
hydroxycarbonates, of the metals from an aqueous solution of
the respective nitrate salts by addition of sodium
carbonate. The precipitate was filtered, washed of sodium
several times, dried at 110°C overnight, and then calcined in
air at 550°C for 3 hours. Active metal oxide compositions
A-F are presented in Table 1.

Table 1

Designation	Composition (wt%)	Preparation[1] Conditions (°C,h)	Citric Acid Metals (mol:mol)	BET,SA (m^2/g)
A: Cu-7Al	18CuO-82Al$_2$O$_3$	500,3	2:1	373
B: Ce	100CeO$_2$	550,3	1:1	25
C: Cu-Ce	32CuO:68CeO$_2$	500,3	1:1	24
D: Ce/Cu-7Al	100CeO$_2$/18CuO-82Al$_2$O$_3$	B/A[3]	B/A[3]	25/373
E: Cu-7Al(H)	18CuO-82Al$_2$O$_3$	550,3	2:1	310
F: Cu-Ce-Al	33CuO-33CeO$_2$-34Al$_2$O$_3$	550,3	-[2]	110

1.   Bulk oxide preparation by amorphous citrate complexing
     of nitrate salts; pyrolysis in air at 450°C for 1/2h
     preceded the calcination step.
2.   Prepared by coprecipitation.
3.   Two-zone system with gas flowing first through
     composition B, then composition A.

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The bulk oxide compositions (in 20-35 mesh particle size) were tested in a fixed-bed, quartz reactor assembly under isothermal conditions. Simplified, simulated flue cases were used in these tests with composition (mol%): $3O_2$, $0.15SO_2$, $0.06NO$, balance N_2. For the denitration tests, gaseous NH_3, in 1:1 molar ratio with NO, was added in the inlet gas stream after it was preheated. After some time on stream, different for each sorbent type, SO_2 would break through. The time at which 150 ppm SO_2 would be measured into the exit gas streams was recorded as the breakthrough-time-at-90%-SO_2 removal efficiency. Regeneration of the sulfated sorbent would then follow, using, carbon monoxide diluted in nitrogen, or in nitrogen and CO_2 gas mixtures, at temperatures of 400-600°C. Gases were analyzed by on-line NO/NO_x gas analyzers and gas chromatographs equipped with sulfur compound detectors. Gas flowrates were set to give corresponding gas hourly space velocities (G.H.S.V.) of 2,000-25,000 h^{-1} (STP).

Table 2 shows the combined SO_2/NO removal performance of various active compositions. Clearly, cerium oxide alone is an excellent SCR catalyst, better than CuO-containing compositions, at temperatures exceeding 400°C. On the other hand, copper oxide has a higher sulfation activity, so that it can be fully sulfated (100%) at 400°C, either when it is combined with aluminum oxide, as in composition A, or when it is combined with cerium oxide, as in composition C. Note that 26% sulfation conversion of composition C at 400°C is equivalent to fully sulfating, the CuO-component of that material. A new finding in this work was the promotion of the cerium oxide sulfation by copper. In fact, at 500°C, where CeO_2 alone is only 7% sulfated prior to 150 ppm SO_2-breakthrough, the equimolar $CuO-CeO_2$ composition C is completely sulfated (100%). Since both materials, B and C, have the same moderately high surface area of about 25 m^2/g, this is not a mere dispersion effect, but a promotion/mixing effect that, to date, has not been reported in the literature.

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Table 2[4]

Composition	Sorbent Sulfation (%)[5]			NOx Conversion(%)	
	400°C	500°C	600°C	400°C	500°C
A: Cu-7Al	100	100	--	90	56
B: Ce	4	7	100	100	98
C: Cu-Ce	26	100	--	98	70

4.   Gas composition (mol%): $3O_2$, $0.15SO_2$, $0.06NO$, $0.06NH_3$, balance N_2 at S.V. = 2000 h^{-1} (STP).
5.   At 150 ppm SO_2-breakthrough (SO_2 removal efficiency is 100% prior to breakthrough).

To improve the SCR catalyst activity of compositions A or C at 500°C, a two-zone approach can be followed. Thus, composition D, which was not an admixture of B and A, but a two-layered B/A bed with B first in the gas stream flow and A following, achieved 98% NO_x removal at 500°C, identical to the performance of composition B, while its sulfation conversion was similar to that of composition A.

The NO_x conversion shown in Table 2 is attained after partial sulfation of the oxide compositions. The initial activity (for fresh or regenerated composition) is typically lower. In other words, at 400 and 500°C, the sulfates are better SCR catalysts than the corresponding oxides. FIG. 7 shows an example of the combined SO_2/NO_x removal performance of composition C at 500°C.

The regenerability of performance in multiple sulfation/regeneration cycles is shown for composition A in FIG. 8. There is a small loss of sulfation conversion after the first cycle, which corresponds to loss of surface area. From then on, however, no further loss of performance is observed. The inclusion of NO_x in the simulated flue gas does not affect the sulfation performance of the sorbent. The regeneration off-gas consisted of SO_2, CO_2, and N_2, i.e. in regenerating composition A with diluted CO gas, the only sulfur product was SO_2.

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The multi-cycle sulfation performance of composition C
was inferior to that of composition A. While the latter
could be regenerated at 400°C, the former had to be
regenerated at 600°C. Apparently grain growth during this
higher regeneration temperature reduces the extent of
subsequent sulfation.

Composition F is an example of a ternary oxide mixture
of copper, cerium, and aluminum, prepared by coprecipitation,
containing 33 percent by weight of each oxide, i.e. 66
percent by weight active phase. FIG. 9 shows the sulfation
performance of composition F (sulfation at 500°C,
regeneration at 600°C). After initial loss of conversion,
the second and third cycle performances were identical, a
definite improvement over composition C. Thus, the use of an
inert alumina framework suppressed the structural degradation
of the active phases caused by volume expansion, or grain
growth, and the like. Large porosity also helps to moderate
similar structural problems in mixed metal oxides. Such
guidelines will help to optimize the compositional structure
of these and similar sorbent/catalyst materials which have to
show performance regenerability over multi-cycle operation at
high temperatures.

Sulfated cerium oxide, supported on alumina, has been
reported to produce a mixture of SO_2 and reduced sulfur
compounds (H_2S) during regeneration with hydrogen. In
addition, it is known that when CO is used in regeneration of
sulfated ceria, a mixture of SO_2, COS, and elemental sulfur
is produced. This is also true when mixed oxides of copper
and cerium are used. For example, FIG. 10 shows the sulfur
products distribution during regeneration of composition C at
various temperatures. Elemental sulfur produced was
collected in an ice bath and is not indicated in the figure.

The selectivity of cerium oxide for the production of
elemental sulfur during regeneration offers the possibility
of recycling the off-gas back to the regenerator to continue
reduction of SO_2 with CO over the now-regenerated cerium

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oxide catalyzing the formation of elemental sulfur. In such
a process, the need for downstream processing of regenerator
off-gases is eliminated. The only product is elemental
sulfur condensed out of the off-gas and a tail gas carrying
any unconverted SO_2 and product COS back to the boiler or
the oxidative absorption unit.

EXAMPLE II

The sulfation, deNO$_x$, and regeneration properties of
the active compositions were compared in powder form and as a
solid-foam integrated within the channels of a monolith
filter,
such as that shown in FIGS. 4 and 5B. In one such
comparison, we used composition E (Table 1). To prepare the
foam, we ground the material into a fine powder
($<10\mu m$-sized particles). A slurry of the powder was made
by mixing, under continuous stirring, 3.77 grams of
composition E with 11 milliliters of de-ionized water and
0.26 grams methyl cellulose (as binder). To this, 0.02 gram
aluminum and 0.03 gram hydrochloric acid were added to form a
foam. The foam was poured into the discharge channels of a
monolith piece (3/4" dia., 100 cells/in^2), supplied by
CeraMem Corporation, with a filtering membrane slip-coated on
the walls (as in FIG. 4). The loaded monolith (designated J)
was dried in an oven at 175°C overnight and then transferred
to a muffle furnace, where it was heated in air at 500°C for
3 hours. The weight change of monolith J, after cooling,
corresponded to 12 percent by weight loading with the active
phase E.

Active filter J exhibited overall performance
characteristics similar to powder composition E used to make
the foam. Also, the pressure drop through the foamed filter,
while higher than that of the bare one, was below 4" H_2O
for a gas flowrate of 1 SLM. All of the powder and active
filter tests were conducted at the same ratio of sorbent mass
to gas flowrate (0.5 gram sorbent per liter/min of gas).

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Because of the different geometry of the two systems (packed powder in a tube versus a honeycomb filter with foam-containing channels), the two systems had different space velocities: 25,000 h^{-1} for the powder and 2,500 h^{-1} for the active filter.

FIG. 11 shows the stabilized sulfur dioxide removal performance of the active filter, compared to the sorbent powder composition E at 400°C. Both systems achieved 100% SO_2-removal efficiency prior to breakthrough. Similarly high (80-90%) sorbent conversion at breakthrough was measured for the powder and the active filter. Since these similarities were obtained at very different space velocities, design flexibility is indicated for the active filters, namely, that they can be operated at relatively high space velocities (>20,000 h^{-1}). FIG. 12 shows the catalytic activity of the two systems in fresh (unsulfated) form for NO reduction by NH_3 as a function of reaction temperature. Both tests were conducted with a gas mixture containing (mol%): 0.06NO, 0.06NH_3, 3O_2, and N_2 balance. The results show that the SCR characteristics of active filter J are very similar to those of powder composition E.

Although particular embodiments of the invention have been described in detail for purposes of illustration, various modifications may be made without departing from the spirit and scope of the present invention. Design considerations may alter the configuration of the active filters, the number of elements carrying active phase compositions with or without a microporous membrane, to optimize the efficiency of certain applications and minimize the cost associated with gas cleanup operation. Accordingly, the invention is not to be limited except by the appended claims.

What is claimed is:

CLAIMS

1.   A filter wall composite for multiphase cleanup of gas
streams comprising particulate and gaseous pollutants,
comprising:

      a bulk macroporous support having a microporous membrane
on one side thereof for blocking passage of particulate
pollutants, and a chemically-active deposit on the opposite
side thereof for reacting with gaseous pollutants;

      said bulk macroporous support having a surface area of
less than 35.0 m^2/g, a compressive crush strength of
between about 1.0 lb/mm and about 10.0 lbs/mm, and a
thickness of between about 1.0 millimeter to about 3.0
millimeters;

      wherein said microporous membrane has a thickness of
less than about 100.0 microns; and

      said chemically-active deposit has a thickness of less
than about 10.0 millimeters.

2.   The filter wall of claim 1 wherein said gas stream is a
flue gas comprising particulate pollutants, and gaseous
pollutants from the group consisting of sulfur oxides,
nitrogen oxides, volatile organic compounds, and mixtures
thereof.

3.   The filter wall of claim 1 wherein said gas stream is a
fuel gasifier exit gas comprising particulate pollutants,
and gaseous pollutants from the group consisting of hydrogen

sulfide, carbonyl sulfide, organosulfur compounds, ammonia and mixtures thereof.

4.   The filter wall of claim 2 wherein said chemically-active deposit reacts with said sulfur oxides to form sulfated metal oxides.

5.   The filter wall of claim 4 wherein said sulfated metal oxides and said chemically-active deposit are selective catalytic reduction catalysts for said nitrogen oxides.

6.   The filter wall of claim 5 wherein said nitrogen oxides are reacted with ammonia in the presence of said selective catalytic reduction catalysts to produce molecular nitrogen.

7.   The filter wall of claim 4 wherein said sulfated metal oxides are regenerated with a reducing gas producing a sulfur dioxide-containing gas stream which is converted to elemental sulfur.

8.   The filter wall of claim 3 wherein said chemically-active deposit reacts with said hydrogen sulfide, carbonyl sulfide and other organosulfur compounds to form sulfided metal oxides, and catalyzes decomposition of said ammonia.

9.   The filter wall of claim 1 wherein said bulk macroporous support is made of refractory ceramic materials having high mechanical strength, thermal shock resistance, and chemical resistance.

10. The filter wall of claim 9 wherein said refractory ceramic materials are selected from the group consisting of mullite, cordierite, oxides of aluminum, silicon, magnesium, zirconium, titanium, and nitrides and carbides of silicon.

11. The filter wall of claim 1 wherein said bulk macroporous support comprises:

a chemically-active component selected from the group consisting of elements and oxides of transition metals, alkali metals, alkaline earth metals, rare earth elements, and mixtures thereof; and

a structural promoter component selected from the group consisting of alumina, chromia, titania, silica, magnesia, zirconia, and mixtures thereof.

12. The filter wall of claim 11 wherein said gas stream is a flue gas comprising particulate pollutants, and gaseous pollutants from the group consisting of sulfur oxides, nitrogen oxides, volatile organic compounds, and mixtures thereof.

13. The filter wall of claim 12 wherein said chemically-active deposit reacts with said sulfur oxides to form sulfated metal oxides.

14. The filter wall of claim 13 wherein said sulfated metal oxides and said chemically-active deposit are selective catalytic reduction catalysts for said nitrogen oxides.

15. The filter wall of claim 14 wherein said nitrogen oxides are reacted with ammonia in the presence of said selective catalytic reduction catalysts to produce molecular nitrogen.

16. The filter wall of claim 1 wherein said bulk macroporous support has at least 40% of its porosity in large pores with an average pore diameter of between about 2.0 micron to about 50.0 microns.

17. The filter wall of claim 1 wherein said chemically-active deposit is selected from the group consisting of elements and oxides of transition metals, alkali metals, alkaline earth metals, rare earth elements, and mixtures thereof.

18. The filter wall of claim 1 wherein said microporous membrane has an average pore diameter of less than about 2.0 microns.

19. The filter wall of claim 1 wherein said macroporous support and said microporous membrane have a unitary construction.

20. The filter wall of claim 1 wherein said microporous membrane and said bulk macroporous support have at least one common component.

21. The filter wall of claim 1 wherein said chemically-active deposit is a film, having a thickness of

less th?? about 2.0 millimeters, deposited on said bulk macroporous support.

22. The filter wall of claim 1 wherein said chemically-active deposit is a macroporous solid foam, having a thickness of between about 2.0 millimeters to about 10.0 millimeters, deposited on said bulk macroporous support.

23. The filter wall of claim 1 wherein said chemically-active deposit comprises two zones, and said two-zone chemically-active deposit achieves about 98% nitrogen oxide removal in a first zone, and about 100% sulfur oxide conversion in a second zone.

24. The filter wall of claim 23 wherein said zones are layered, and said first zone comprises CeO_2 and said second zone comprises CuO and Al_2O_3.

25. The filter wall of claim 17 wherein said chemically-active deposit comprises a ternary oxide of copper, cerium, and aluminum.

26. The filter wall of claim 25 wherein said ternary oxide comprises equal parts of CuO, CeO_2, and Al_2O_3.

27. A filter for integrated clean up of gas streams comprising particulate and gaseous pollutants, comprising:
   filter walls comprising bulk macroporous supports having microporous membranes on one side thereof for blocking passage of particulate pollutants, and chemically-active

deposits on the opposite side thereof for reacting with gaseous pollutants;

wherein said bulk macroporous supports have a surface area of less than 35.0 m^2/g, a compressive crush strength of between about 1.0 lb/mm to about 10.0 lbs/mm, and a thickness of between about 1.0 millimeter to about 3.0 millimeters,

said microporous membranes have a thickness of less than about 100.0 microns, and

said chemically-active deposits have a thickness of less than 10.0 millimeters.

28. The filter of claim 27 wherein said filter is a cross-flow device.

29. The filter of claim 27 wherein said filter is a through-flow device.

30. The filter of claim 27 wherein said filter is periodically backflushed with a gas stream to remove particulate pollutants deposited on said microporous membrane.

31. The filter of claim 27 wherein said gas stream is a flue gas comprising particulate pollutants, and gaseous pollutants from the group consisting of sulfur oxides, nitrogen oxides, volatile organic compounds, and mixtures thereof.

32. The filter of claim 27 wherein said gas stream is a fuel gasifier exit gas comprising particulate pollutants, and

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gaseous pollutants from the group consisting of hydrogen
sulfide, carbonyl sulfide, organosulfur compounds, ammonia
and mixtures thereof.

33. The filter of claim 31 wherein said chemically-active
deposit reacts with said sulfur oxides to form sulfated
metal oxides.

34. The filter of claim 33 wherein said sulfated metal
oxides and said chemically-active deposit are selective
catalytic reduction catalysts for said nitrogen oxides.

35. The filter of claim 34 wherein said nitrogen oxides are
reacted with ammonia in the presence of said selective
catalytic reduction catalysts to produce molecular nitrogen.

36. The filter of claim 33 wherein said sulfated metal
oxides are regenerated with a reducing gas producing a
sulfur dioxide-containing gas stream which is converted to
elemental sulfur.
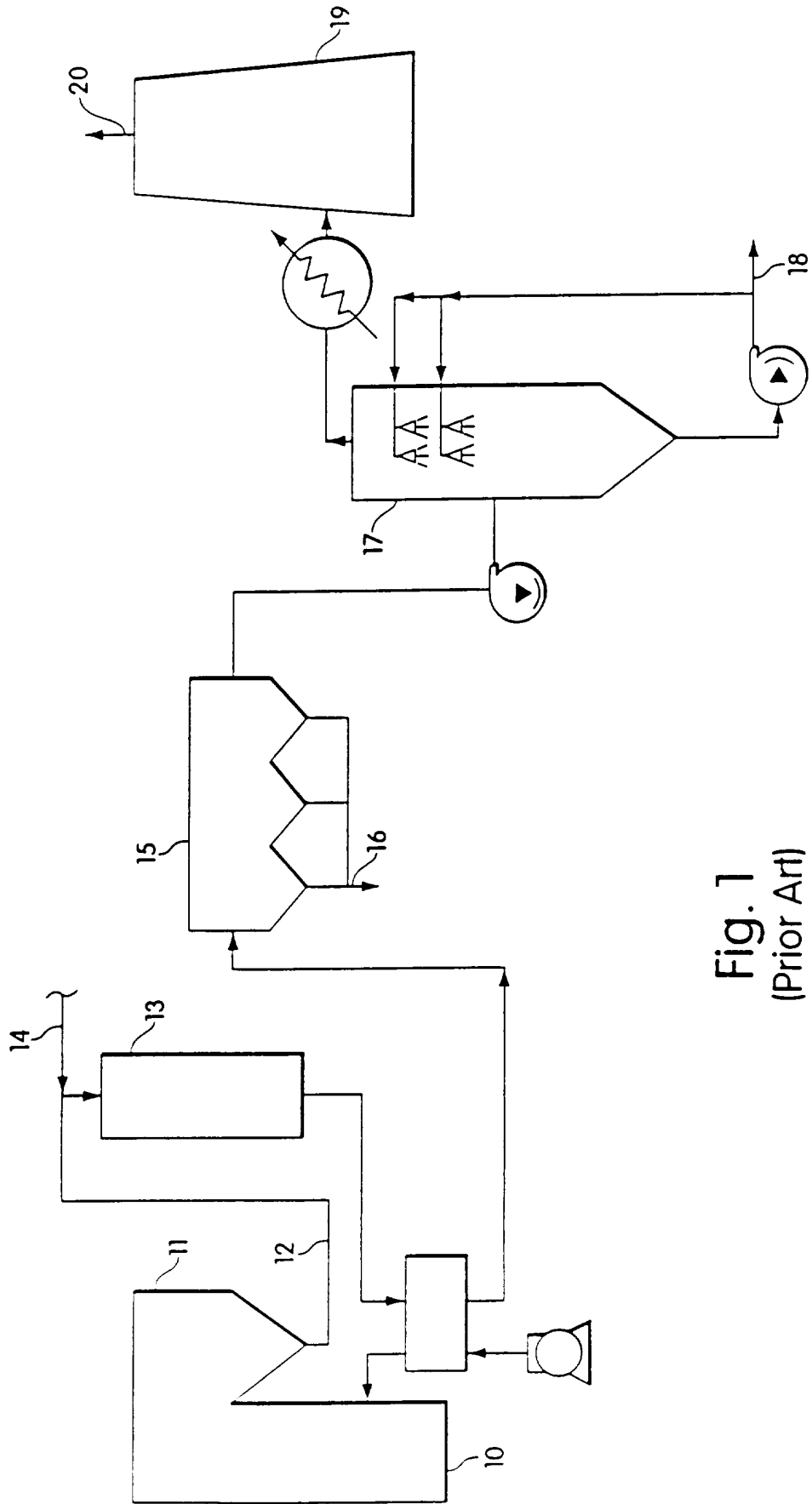
Fig. 1
(Prior Art)
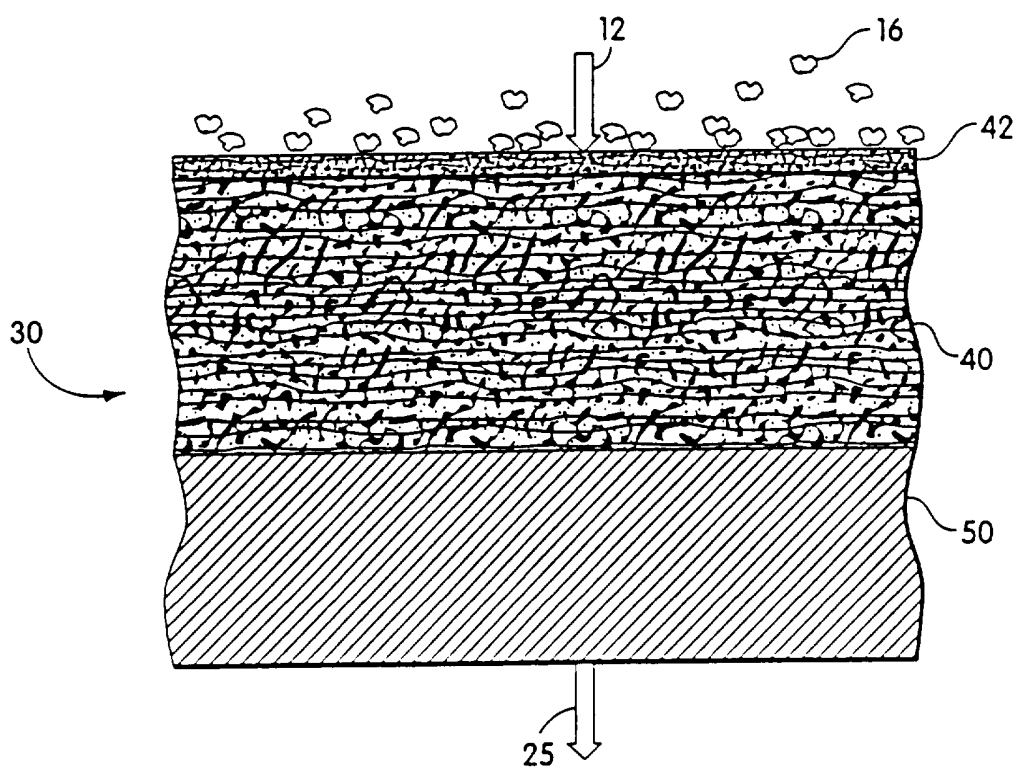
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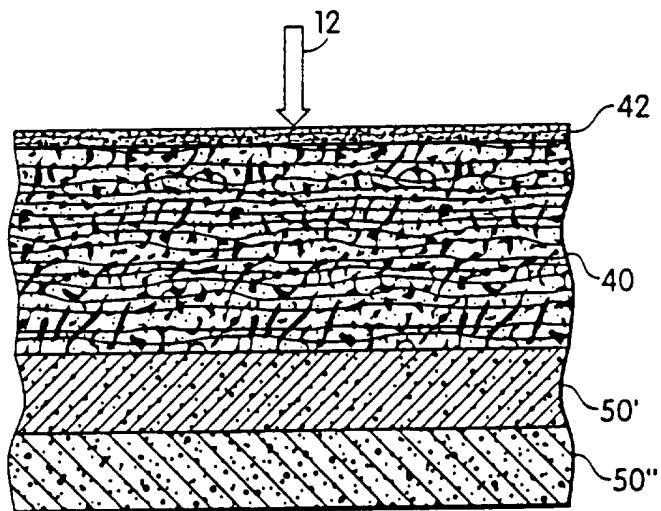
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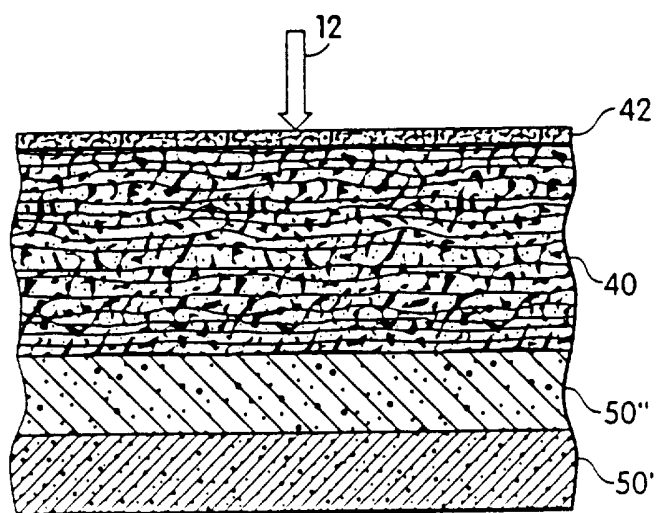
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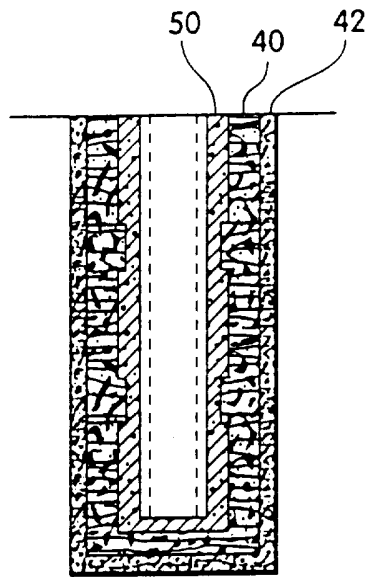
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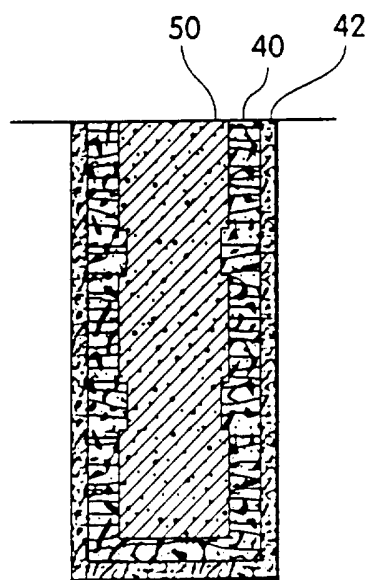
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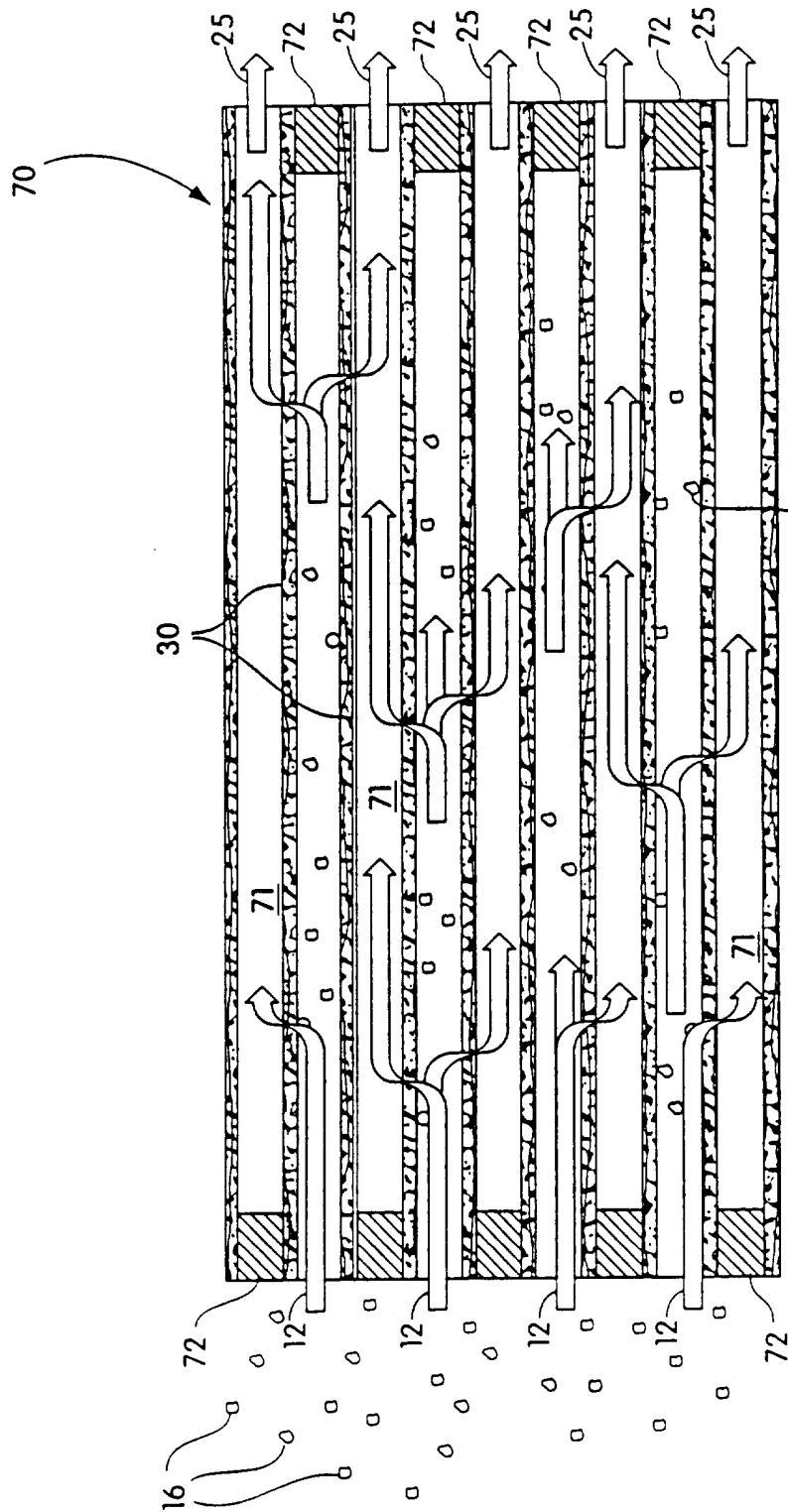
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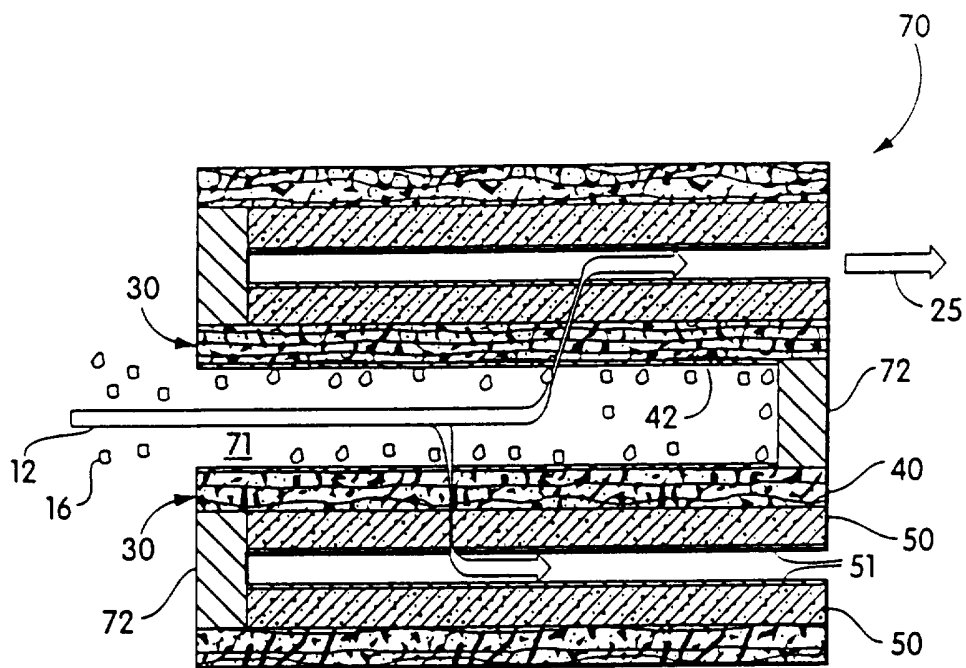
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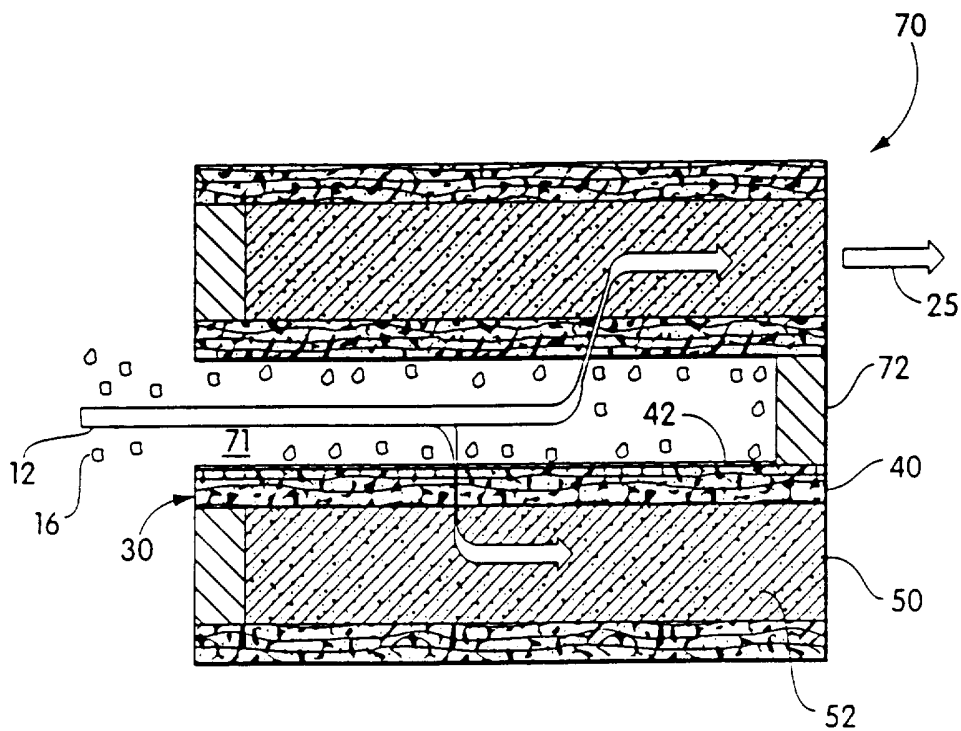
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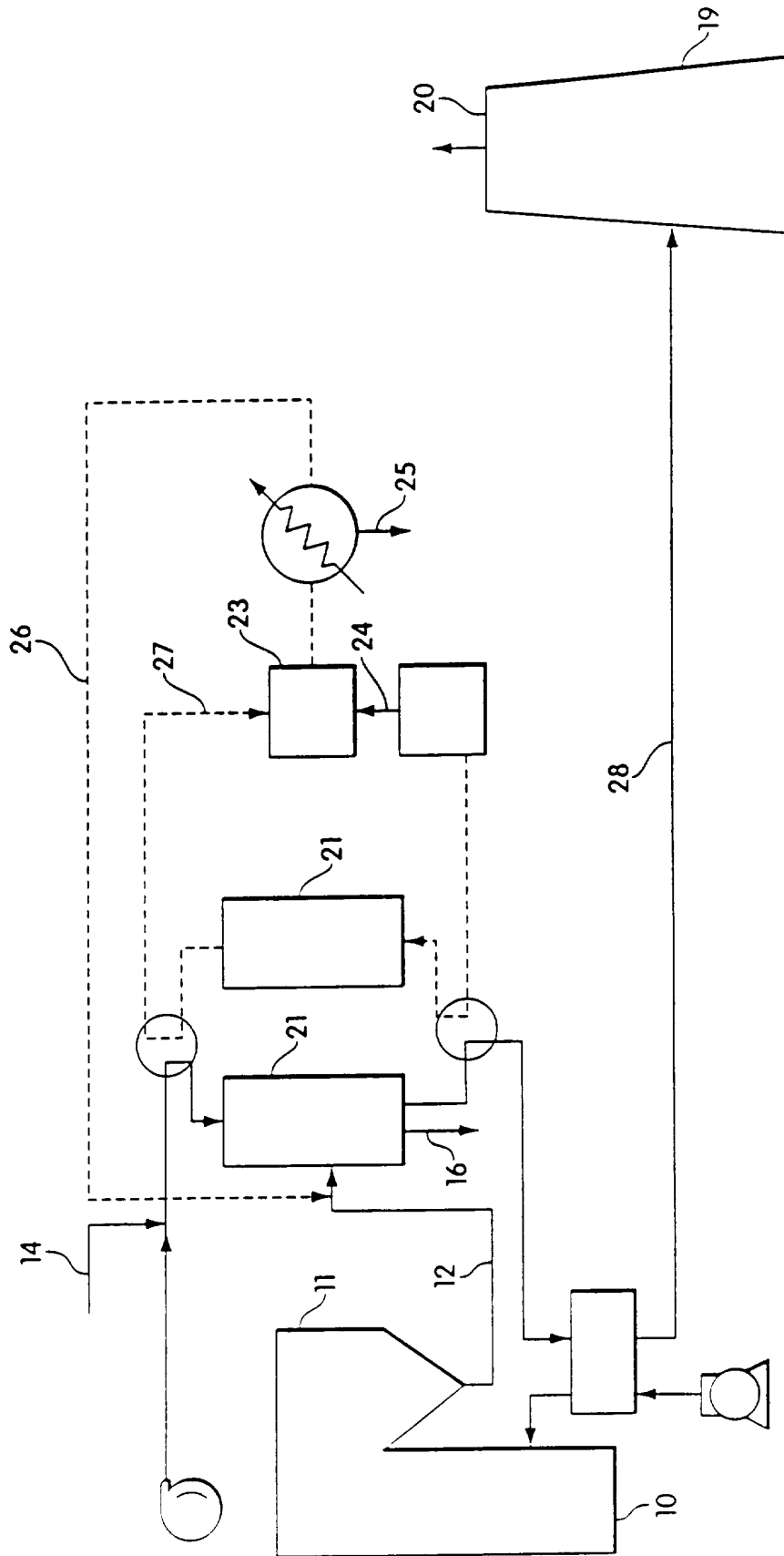
Fig. 6A
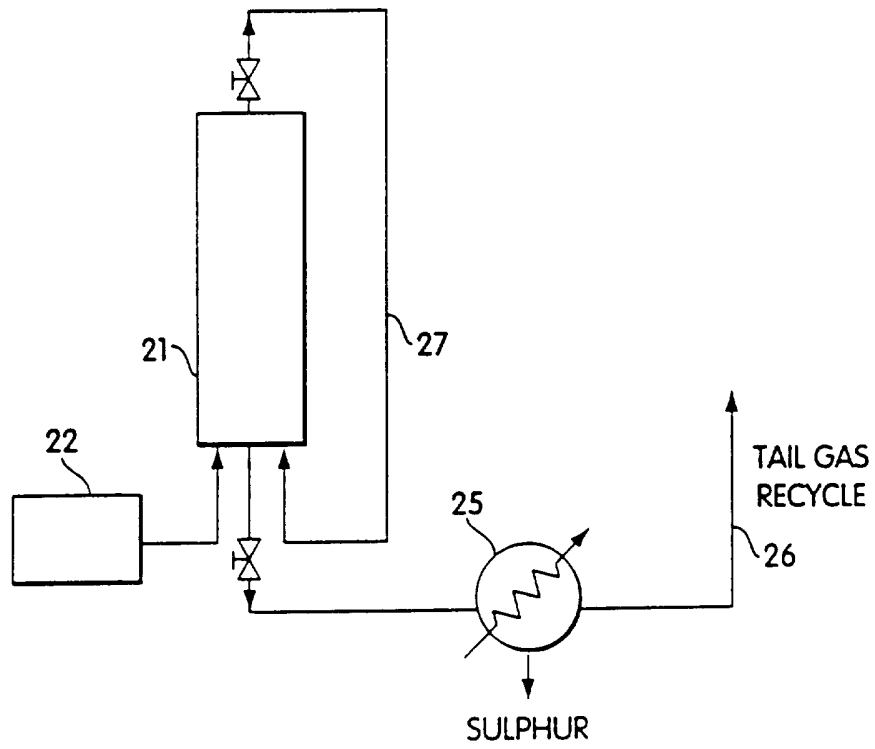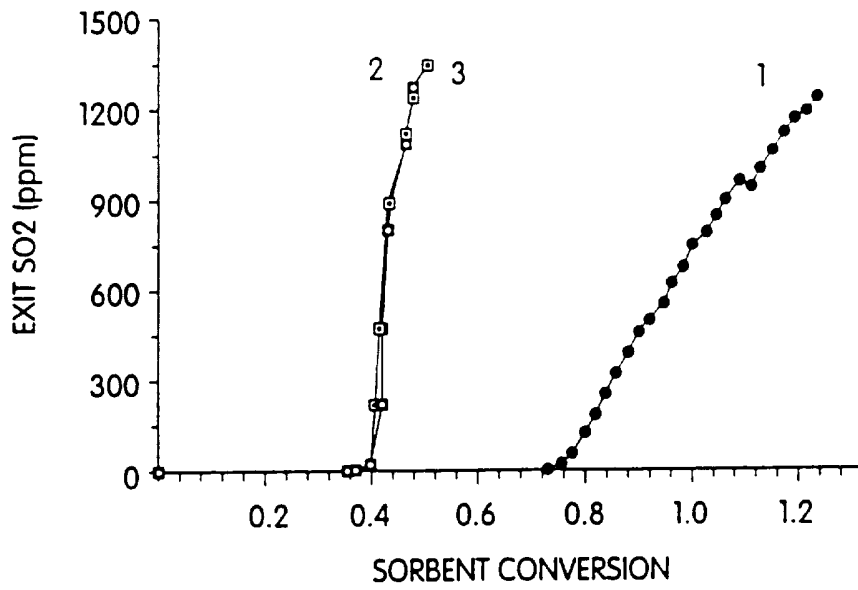
Fig. 6B
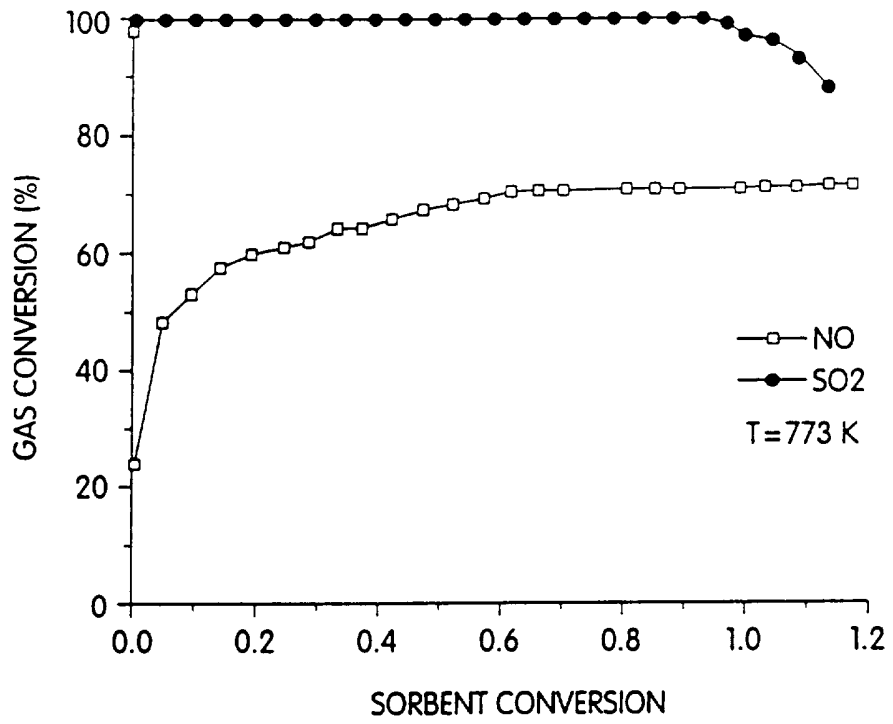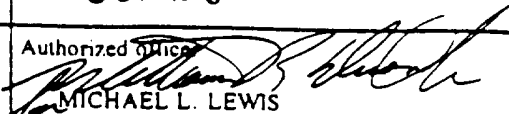
Fig. 7
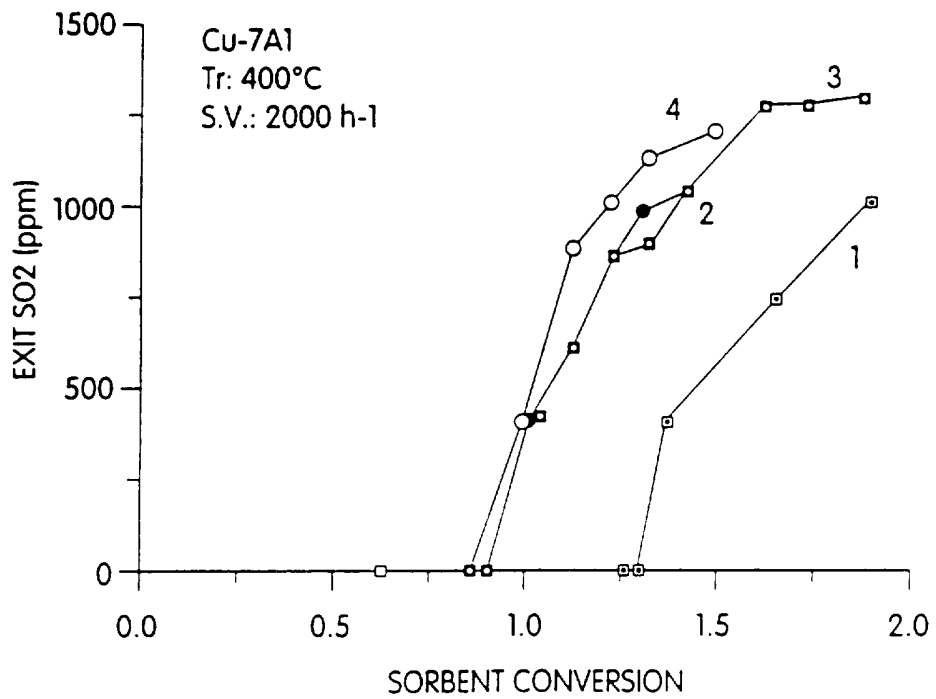
Fig. 8

Fig. 9
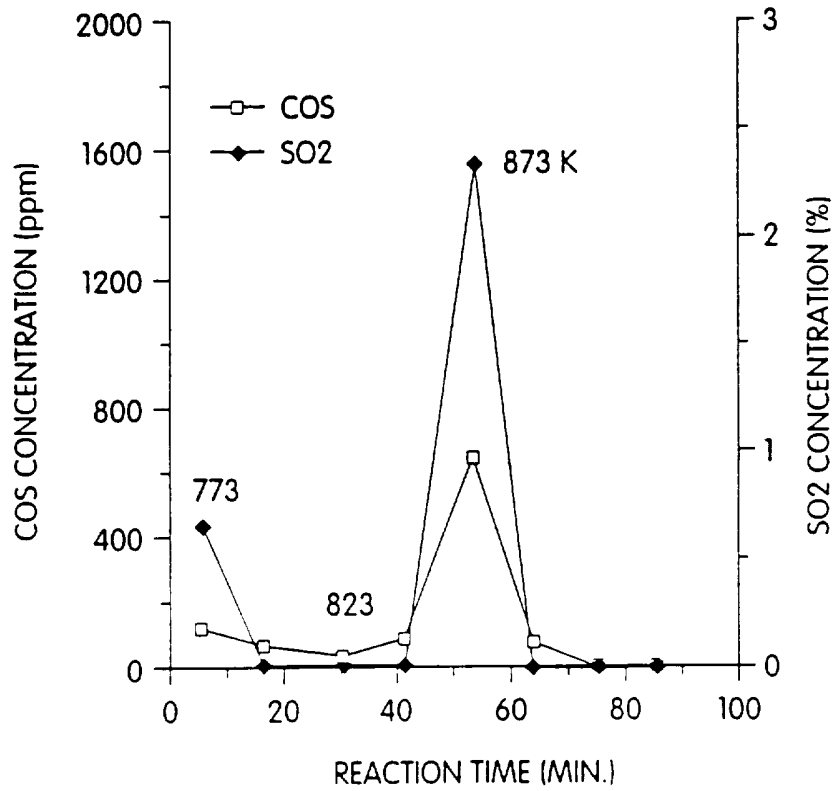
Fig. 10
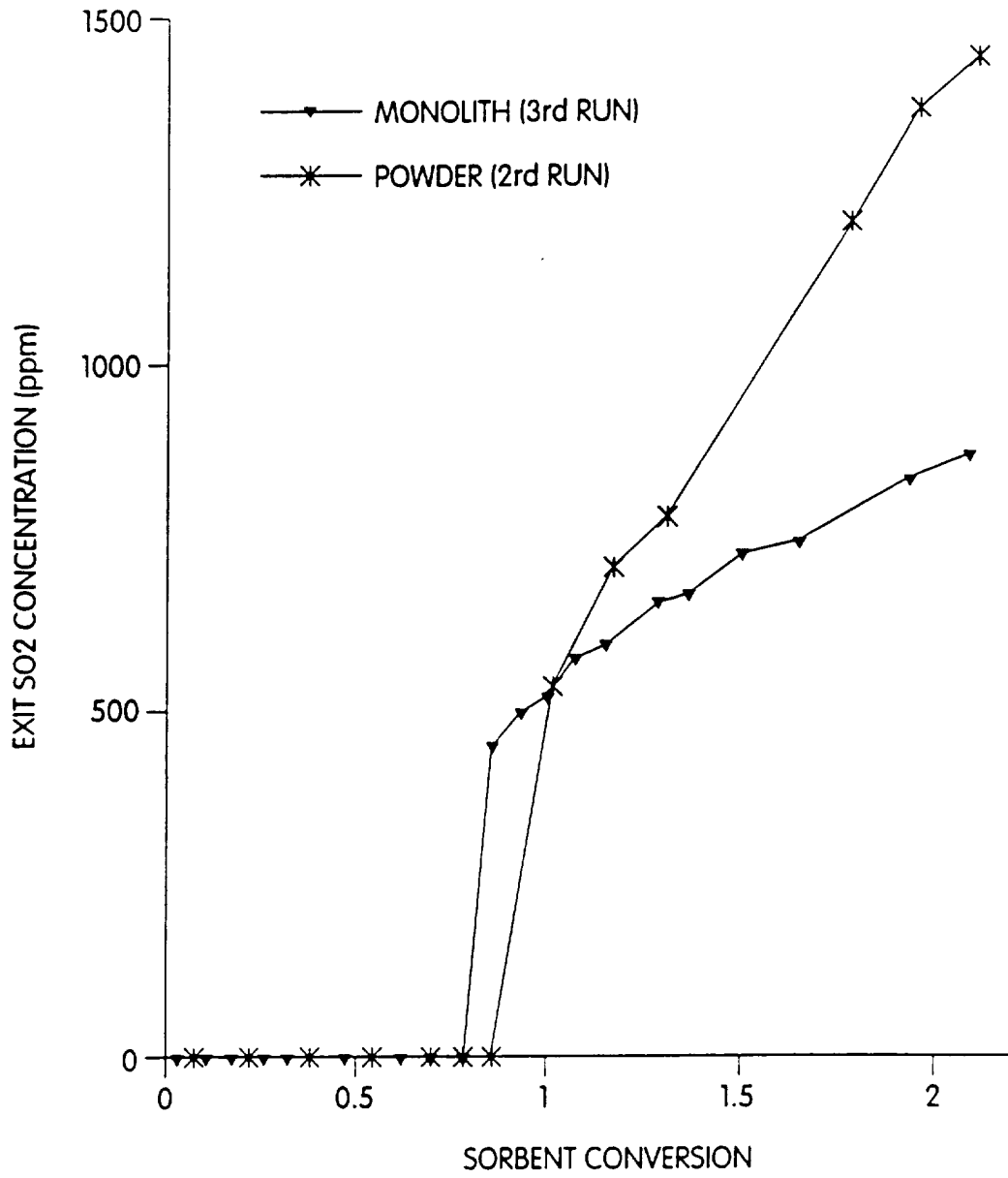
Fig. 11

Fig. 12

INTERNATIONAL SEARCH REPORT

A.	CLASSIFICATION OF SUBJECT MATTER

IPC(5) :B01D 35/01, 39/20

US CL :55/523, 524; 502/100; 423/230,239.1,244.02

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

B.	FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S : 423/230,239.1,244.02,244.06;55/523,524;502/100

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO,A, 89/03720 (Flytzani-Stephanopoulos) 05 May 1989, see page 1, line 8-page 2, line 17 and page 3, line 15-page 4, line 13 and page 10, line 9-page 11, line 34 and page 15, lines 15-34.	1-36
Y	M. Satriana, ed; "New Developments in Flue Gas Desulfurization Technology", published 1981, Noyes Data Corporation (New Jersey) pages 267-268 and 270-272	1-36
A	US,A, 4,728,502 (IIDA) 01 March 1988, see entire document.	1-36
A	US,A, 4,973,459 (LIPPERT) 27 November 1990, see entire document.	1-36

[X]	Further documents are listed in the continuation of Box C.	[ ]	See patent family annex.

*	Special categories of cited documents:
"A"	document defining the general state of the art which is not considered to be of particular relevance
"E"	earlier document published on or after the international filing date
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O"	document referring to an oral disclosure, use, exhibition or other means
"P"	document published prior to the international filing date but later than the priority date claimed

"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
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Date of the actual completion of the international search	Date of mailing of the international search report
10 JUNE 1994	JUN 2 0 1994

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4,729,889 (FLYTZANI-STEPHANOPOULOS ET AL) 08 MARCH 1988, see entire document.	1-36
A	US,A, 4,810,273 (Komoda) 07 March 1989, see entire document.	1-36
A	US,A, 4,977,123 (Flytzani-Stephanopoulos) 11 December 1990, see entire document.	1-36