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PROCESS FOR THE RECOVERY
OF CO₂ FROM GASES

The supply of carbon dioxide from natural sources, by-product CO₂ from ammonia manufacture, and hydrogen purification, is not sufficient for present and future industrial requirements.

5 The potential supply of CO₂ from power plant flue gas could furnish the required amount, providing it could be economically recovered. Flue gas normally is at or near atmospheric pressure and contains about 6-10 percent CO₂ and about 2-5 percent
10 oxygen. Sulfur dioxide may be an additional contaminant if the fuel source is coal instead of "sweet" or commercial natural gas.

 Most known solvents that can recover CO₂ under these conditions will undergo severe solution
15 oxidative degradation and cause corrosion, thus rendering the process uneconomical.

 The removal of carbon dioxide from flue gas was practiced in the 1950's and early 1960's by extracting the carbon dioxide from the combustion
20 products resulting from burning a fuel. Inert

atmospheres for large annealing furnaces were produced in a like manner.

The principal solvent used in the removal of CO₂ from flue gas during this same period employed an aqueous monoethanolamine (MEA) solution in the concentration range of 5-12 percent. The system was operated until oxidative degradation products and corrosion became sufficiently severe as to warrant discarding the solution with plant cleanup and recharging with fresh solution.

Some processes were improved, vis-a-vis using only the dilute MEA solution until it went bad by operating a side stream reclamation still. Such still removed some of the oxidative degradation products as a bottom product while taking substantially the MEA and water as an overhead product for recycle. The side stream still operated on a 2-3 percent side stream. This approach was not particularly successful because the degradation products were removed only to a limited extent in the side stream reclaimer. In addition, degradation products continued to be produced at a higher rate due to the high temperatures necessary for operating the reclaimer still.

Another mode of operation of the dilute solution process was the utilization of a 5-8 percent aqueous MEA solution with a 4-8 percent concentration of sodium carbonate. Sodium carbonate neutralized degradation products that were acidic in nature (formic acid is the prime oxidation product in this environment). This mode of operation was somewhat

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successful but like the other two mentioned systems, was unpredictable in the length of time the system would operate before losing capacity to recover CO₂.

5 All the processes mentioned above were extremely energy intensive due to the extremely high circulation rates necessitated by the low concentration of MEA and the very low loadings of CO₂ that were permitted in order to minimize corrosion.

10 The recovery of CO₂ from a flue gas using a combustion zone to lower residual oxygen is described in U.S. Patent 4,364,915, dated 1982 December 21.

15 A mode of operation utilizing copper salts as an inhibitor is disclosed in U.S. Patent 2,377,966, dated 1945 June 12. This method was used in the above mentioned systems that did not include the use of a reclaimer in the operation. Copper was only moderately successful as a corrosion inhibitor even at the low CO₂ loadings and low concentrations of alkanolamine.

20 Precipitation of elemental copper was a serious limitation of this process and resulted in enhanced corrosion due to galvanic attack in the peripheral area of the deposited copper metal. This system was operated much the same way that the uninhibited aqueous MEA solution

25 first mentioned was utilized, in that when the system became sufficiently degraded the entire solution was dumped, the internals of the plant cleaned, fresh alkanolamine charged back to the system, and the system put back in service. The length of time the system

30 remained on stream was again unpredictable.

The use of activated carbon or ion exchange resin to remove contaminants from aqueous alkanolamine solutions is known from U.S. Patents 1,944,122; 2,797,188; 3,568,405; and 4,287,161. However, these
5 patents do not suggest the surprising results obtained herein using an effective amount of copper salts in the alkanolamine solution in conjunction with the use of activated carbon or ion exchange resin.

In accordance with the present invention, generally
10 stated, gas containing carbon dioxide and oxygen is contacted in the conventional manner in a suitable gas-liquid contactor with an alkanolamine solution. The above alkanolamine solution contains an amount of copper effective to inhibit corrosion. The actual
15 amount of copper used can be any amount of copper greater than about 5 parts of copper per million parts of solution wherein the carbon dioxide and, if present, sulfur containing acid gases (e.g. SO_2 with trace amounts of other sulfur compounds, H_2S , COS , and the like) are
20 absorbed.

More particularly, the present invention provides a process for the recovery of carbon dioxide from a feed gas containing carbon dioxide and oxygen, the process comprising contacting the gas with a circulating
25 alkanolamine solution and treating the resultant

solution rich in CO_2 with heat to release the CO_2 , thereby producing a lean solution and returning the so treated lean solution to the contacting step, wherein an amount of copper effective to inhibit corrosion and/or degradation of the solvent is maintained in the circulating solution, and the circulating solution is contacted with at least one of the following

- (1) a mechanical filter;
- (2) an activated carbon bed;
- 10 (3) an anion exchange resin; and/or
- (4) any combination thereof.

Included within the scope of the invention is carbon dioxide whenever recovered by the process of the invention and the use of such carbon dioxide in a carbon-dioxide consuming process. The process in which the carbon dioxide is consumed may be any of the processes now used which require carbon dioxide, such as conventional chemical or industrial process which require carbon dioxide.

Conventionally liquid effluent (rich solvent) is withdrawn from the bottom of the contactor and cross exchanged with solvent which has been heated to release the carbon dioxide and sulfur containing gases (lean solvent). The rich solvent after heat exchange with the lean solvent is delivered to a stripper wherein the rich solvent is contacted with rising vapours from the lower end of the stripper. The liquid in the lower end of the stripper is circulated through a reboiler wherein conventionally it is heated to about 240° to 260° F (115° to 126.5°C) and returned to the lower portion of

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the stripper or reboiler surge tank. A portion of the bottoms drawn off the stripper or reboiler surge tank is then returned to the absorption column.

5 The present invention involves treating all or a portion of the alkanolamine solution at any temperature, however it typically consists of passing a solution, cool rich or cool lean (conveniently the lean solution after heat exchange with the rich solution from the contactor), into and through a mechanical filter, into
10 and through activated carbon, and into and through a second mechanical filter. Following this treatment, the carbon/filtered treated solution can be passed through an ion exchange resin bed thence to the top of the contactor.

15 The above procedure surprisingly effectively removes ionic iron and solvent degradation products. This allows sufficient ionic copper in solution to abate corrosion, minimizes the formation of degradation products, and maintains substantially the efficiency of
20 the alkanolamine solution.

 It is to be understood that while the above preferred mode of operation includes the activated carbon treatment, mechanical filtration and ion exchange treatment; some improvement, e.g. lower corrosivity
25 and/or degradative quality of solvent, can be achieved if only one of the unit operations is employed in treating the solvent. Thus, under certain operating conditions, activated carbon treatment can remove certain of the degradation products both by adsorption
30 and/or absorption and its inherent filtering effects such as mechanical removal of particulate material to

obtain some improvement. It however has been found advantageous to couple mechanical filtration both before and after activated carbon treatment to extend the life of the carbon bed and collect the insoluble iron. Ion exchange treatment may also be employed to remove some of the degradation products, with or without either mechanical filtrations or activated carbon treatment, but the bed must be cleaned more often to avoid plugging with insoluble iron or other solid degradation products. Here again, mechanical filtration is preferred to keep at a low level the insoluble iron and/or solid degradation products from plugging the bed. Likewise, the use of one or both filtration mediums as the only treatment will improve the operation of the process but not to the same degree as operating on the three unit operations, i.e. mechanical filtration, activated carbon treatment, and ion exchange.

The present invention is illustrated by Figure 1 which is a schematic diagram of a typical commercial operation showing the association of the contactor 16 with the stripper 74, the activated carbon bed 48, mechanical filters 42 and 44, and ion exchange bed 34.

In Figure 1 of the drawings 10 represents an inlet line for the flue gas to be treated. A knock-out drum 12 with drain line 32 is provided to collect liquid condensates. From the drum 12, line 14 leads the flue gases into absorber 16 which has a plurality of trays 18 and a demister 20.

The effluent gases from the absorber 16 are led by line 22 optionally to a condensor 24 and to outlet line 26.

Recirculating alkanolamine solution is led by
5 line 36 into the absorber 16 and the rich amine solution i.e., amine containing absorbed CO_2 , leaves the absorber by exit line 30 and thence to the inlet of pump 68. From the pump outlet 66, the rich amine solution flows through the heatexchanger 58 and line 64 to the inlet
10 of the stripper 74 wherein the rich amine is heated and stripped of carbon dioxide. The CO_2 is removed by outlet 78 where it flows through a condensor 80 and then by line 82 to a condensate collector 86. The pure
15 CO_2 gas is removed by line 84 and the condensate is removed by line 88 for reuse by passing it through a pump 90 and line 94 back to the stripper 74.

At the bottom of the stipper 74, there is provided an outlet line 112 which leads the alkanol-
amine solution to the inlet of the reboiler 100. The
20 heated solution recirculates back to the stripper by line 98. Steam (here described but other sources of heat may be used) lines 102 and 104 provide an inlet and an outlet for the steam to heat the reboiler 100.

The heated lean alkanolamine solution leaves
25 the reboiler 100 by line 108 where the solution is recirculated by pump 70 and the associated lines 120 and 72 to the heat exchanger 58. A portion of the lean alkanolamine solution can be withdrawn by line 114 and
oxidized with an oxygen containing gas such as air in
30 the oxidizing unit 116. The portion is contacted, eg. blown, with the oxygen-containing gas. Line 118 is provided to return the oxidized solution back to the main line 120.

Oxidizing gases are provided by inlet 92 and the used gases are removed by an outlet (not shown).

From the heat exchanger 58, the alkanolamine solution flows by line 56 to an amine cooler 54 and
5 thence by line 40 to a cartridge filter 42 for removal of fine particulates. From the filter 42 the solution goes by line 46 to an activated carbon bed 48 and thence by line 50 to a second cartridge filter 44 for the removal of carbon fines.

10 Line 52 is provided to lead the solution back to the absorber by line 36. If desired, part or all of the solution can be passed by line 33 to an ion exchange bed 34 for further purification of the solution prior to reuse. It is to be understood that in the above
15 description the necessary valves and controls have not been illustrated in order to clearly point out the invention. It is also understood that some of the solution may by-pass the filtration/purification section through line 38.

20 With a brief description of the unit operations which constitute the present invention, the limits of operating parameters are now set forth.

Inhibitor -- The inhibitor of choice for this particular system is ionic copper introduced as any
25 salt soluble in the alkanolamine solution in a concentration greater than about 5 ppm by weight based on the total solution. The preferred soluble salt is copper carbonate. The preferred range is between about 50 ppm and about 750 ppm and the most preferred range is

between about 100 ppm and about 500 ppm copper, however it is not implied that greater concentrations of copper are not effective since concentrations in excess of 2000 ppm have been successfully used. It has been
5 shown by both laboratory data and pilot plant data that passivation of the corrosion process can be achieved and maintained even in concentrations less than 50 ppm. Likewise, it has been established that between about 5-80 percent concentration of MEA can be effectively
10 inhibited against corrosion by maintaining a proper level of copper in the treating solution.

Alkanolamine concentration -- from about 5 to about 80 percent solutions of alkanolamine would usually be employed with reduced corrosion and reduced solvent
15 degradation resulting in improved life of solvent, that is, longer periods between turnarounds or unscheduled down times to replace the solvent. Primary, secondary, and tertiary alkanolamines, or mixtures thereof, may be employed. The preferred alkanolamine being monoalkano-
20 lamine, particularly monoethanolamine, desirably in an amount of from about 25 to about 50 percent by weight. It has been found from pilot plant data that the incorporation of the present invention results in little or no downtime occasioned by corrosion and/or necessity to replace the solvent.

25 Temperature control -- It has been found that the reduction of active copper ion content, in for example, monoethanolamine, is greatly accelerated above 150°F (65.6°C) and that reboiler bulk temperatures of from 240°F (116°C) to 260°F (127°C) and above are
30 conducive to excessive reduction of copper particularly increased residence times. It is preferable to maintain the reboiler bulk temperature at or below

240°F (116°C) to 260°F (127°C). Also it is desirable to employ a maximum heat transfer flux of less than about 10,000 BTU per square foot hour (31.5 kW/m²) and preferably less than about 6,000 BTU per square foot hour (18.9 kW/m²). Higher heat flux and/or residence times will, of course, function but will contribute to a higher rate of copper depletion and thus loss of operability of the overall system.

10 Contact Pressure -- In accordance with the present invention flue gas will typically be contacted with the alkanolamine at about atmospheric pressure. However, the invention is applicable to higher pressures, limited only by the condensation pressure of the gas mixture being processed.

15 Mechanical Filter/Activated Carbon Treater --
The judicious use of activated carbon coupled with mechanical filtration will remove harmful contaminants resulting from thermal oxidation of alkanolamine, auto-oxidation of alkanolamine, and corrosion of the
20 plant equipment. The activated carbon treaters in conjunction with mechanical filters are utilized for the passage of alkanolamine solution through first a mechanical filter operating in for example the 10-75 micrometer range, preferably in about the 25-50 micro-
25 meter range for protection of the activated carbon treater which is located immediately downstream. The activated carbon treater will operate to some extent on any of a variety of activated carbons, however, it has been found that the most efficient removal for a
30 broad range of degradation products and capacity coupled with longevity of the activated carbon rests with the coal based activated carbons. Allowable bed

pressure drop usually determines carbon particle size. A preferred size is in the 12-40 mesh range (openings = 1.68 mm - 0.420 mm) such as Calgon F-400 or its equivalent. CALGON is a Registered Trade Mark.

5 The carbon treatment removes certain of the degradative products of the alkanolamine which are suspected to be strong iron chelators. Examples of these products are higher molecular weight organic acids. It is reported that these acids are produced
10 from formic acid, generated as a degradation product of the alkanolamines, and oxalic acid which is the further degradation product of formic acid and formates. The primary function of the mechanical filter down stream of the activated carbon bed is to recover insoluble
15 iron and other particulate material that may be released during the activated carbon function. The pore openings may range from 1 to 50 micrometers with the preferred range being between 5 to 25 micrometers. A secondary function is to collect
20 activated carbon fines thus protecting downstream equipment.

To illustrate the significance of adequate solution filtration a pilot plant was operated with and without filtration while measuring the amount of copper
25 and iron in solution. At temperatures sufficient to strip the solution of CO₂ and while the solution was being filtered, the concentration of soluble iron was maintained at low enough concentrations to prevent rapid redox with the copper in solution. When the
30 solution was not filtered or when the filter medium, activated carbon, was spent, the soluble iron concentration increased and the soluble copper concentration

rapidly decreased until no copper remained in the solution which was followed by the occurrence of corrosion. In the absence of mechanical filtration the carbon itself caught particulate matter and insoluble iron salts which diminished the number of active sites and reduced the overall efficiency of the filtration process. In addition, insoluble iron which was not removed from the system accelerated the rate of soluble iron buildup as the activated carbon began to loose efficiency or become spent. This experiment established the practical necessity, in an economically competitive operation, to carbon filter the solution in order to maintain low iron levels and to mechanical filter the solution in order to increase carbon life and minimize the potential for rapid copper redox as the carbon began to loose efficiency.

The solvent stream is activated carbon treated and filtered full flow or as a partial side stream utilizing 0.025 bed volume per minute to 1 bed volume per minute. The preferred rate is 0.1-0.2 bed volume per minute. The present invention likewise has been surprisingly improved by minimizing both activated carbon bed and solvent temperatures to a 150°F (65.6°C) maximum. Operation in this mode improves the capacity and improves the selectivity for particular degradation species. Due to the relatively low temperature requirements for most efficient operation, it is advantageous to place the activated carbon treater and mechanical filters downstream of the amine cooler just prior to introduction of the lean solution to the absorber.

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Ion Exchange -- Heat stable salts of a number of varieties and from a number of sources are continually produced and/or inadvertently added to alkanolamine systems, especially those processing oxygen containing gas streams. The majority of these salts such as, for example, sodium chloride, amine oxalate, and sodium nitrate are of a type which are not effectively removed by activated carbon and/or mechanical filtration. However, the fact that these salts promote both solvent degradation and inhibitor reduction makes it necessary to remove them from solution. There are two methods of doing this. The known method is solvent reclamation by distillation. This method is not recommended as it depletes the inhibitor level (Cu is not carried over in the distillation process) and unless controlled very carefully can cause increased solvent degradation. The present invention preferably utilizes ion exchange to remove the anionic portion of the heat stable salt. This is accomplished by passage of the contaminated solvent through an anion exchange resin, for instance any of the number of strong base anion exchange resins of the styrenedivinylbenzene type which have a quaternary amine as their functional group, e.g. DOWEX* 1, DOWEX* 2, DOWEX* MSA-1, DOWEX* MSA-2 (*Trademark of The Dow Chemical Company). The anions present in solution displace the hydroxide groups present on the resin and are removed from solution. After the resin is spent (its exchange capacity fully utilized) the resin may be discarded or regenerated with a sodium hydroxide solution of essentially any concentration. The preferred concentration being 2-5N. The regeneration effluent, containing the unwanted salts, is then discarded and the resin is ready for reuse.

Exemplary of such ion exchange treatment was the treatment of 100 ml. of a foul 30 percent MEA solution from the plant which had 300 ppm copper inhibitor and which was carbon treated. The solution was treated by passing it downflow through a 25 ml packed column of DOWEX*1 (OH⁻ form) (*Trademark of The Dow Chemical Company) at 5 cm³ and 78°F (25.6°C). After discarding the hold-up volume of water, the alkanolamine solution was collected and a sample of both the starting material and resin bed effluent were analyzed for heat stable salt content.

<u>Sample</u>	<u>% Heat Stable Salt</u>
Starting Solution	2.4
Resin Effluent	1.8

Net one pass removal 25%

There was substantially no loss of copper as a result of the ion exchange treatment.

Inhibitor Regeneration -- Regeneration of inhibitor is not normally required as long as the conditions taught by this invention are followed specifically. However, if by improper plant design or non-adherence to the conditions set forth herein, copper metal or copper compounds are formed by the reduction of the copper, this inhibitor exhibits the surprising capability of regenerability. There can be provided a sidestream withdrawal of a portion of the solution of the bottom of the reboiler, going through an external cooler to drop the temperature of the hot lean alkanolamine containing particulate matter (which contains the reduced inhibitor) down to a temperature less than 150°F (65.6°C), preferably 130°F (54.5°C) or less into a tank

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or suitable vessel as shown in Figure 1 in which the solution is aerated with an oxygen-containing gas by a variety of means common to those skilled in the art. The lean solution thus cooled and with the inhibitor
5 regenerated it may be returned back to the lean solution downstream of the heat exchanger or any other advantageous spot in the lean circuit.

CLAIMS:

1. A process for the recovery of carbon dioxide from a feed gas containing carbon dioxide and oxygen, the process comprising contacting the gas with a circulating alkanolamine solution and treating the resultant solution rich in CO₂ with heat to release the CO₂, thereby producing a lean solution and returning the so treated lean solution to the contacting step, wherein an amount of copper greater than about 5 parts per million parts of solution and effective to inhibit corrosion and/or degradation of the solvent is maintained in the circulating solution and the circulating solution is contacted with at least one of the following

- (1) a mechanical filter;
- (2) an activated carbon bed;
- (3) an anion exchange resin; and/or
- (4) any combination thereof.

2. A process as claimed in claim 1 wherein the alkanolamine is a monoalkanolamine.

3. A process as claimed in claim 2 wherein the alkanolamine is monoethanolamine and the maximum bulk temperature thereof is no greater than 260°F (126.7°C).





4. A process as claimed in any one of the preceding claims wherein a portion of the circulating solution is withdrawn and contacted with an oxygen-containing gas and the portion is returned to the alkanolamine circuit.

5. A process as claimed in Claim 4 wherein the portion is a portion of the lean solution.

10 6. A process as claimed in any one of the preceding claims wherein the maximum bulk temperature of the alkanolamine is no greater than 260°F (126.7°C) and is subjected to a heat flux of less than about $10,000 \text{ BTU/ft}^2 \text{ hr}$ (31.5 kW/m^2).

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7. A process as claimed in any one of the preceding claims wherein the copper ion is maintained at between 50 ppm and 750 ppm.

20 8. A process as claimed in any one of the preceding claims wherein the feed gas is a flue gas.

9. A process as claimed in any one of the preceding claims wherein the anion exchange resin is a strong base anion exchange resin.

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10. A process as claimed in any one of the preceding claims circulating solution is passed firstly through an activated carbon bed and secondly through an anion exchange resin.

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11. A process as claimed in Claim 10 wherein the circulating solution is additionally passed through a mechanical filter before being passed through the activated carbon bed.

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12. A process as claimed in Claim 10 or 11 wherein the circulating solution is additionally passed through a mechanical filter after being passed through the activated carbon bed and before being passed through the anion exchange resin.

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13. A process as claimed in any one of the preceding claims wherein the feed gas further contains one or more sulphur compounds.

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14. A process for the recovery of carbon dioxide from a feed gas containing carbon dioxide substantially as hereinbefore described, other than one of the prior art processes hereinbefore described.





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15. Carbon dioxide whenever recovered from a process as claimed in any one of the preceding claims.

16. The use of carbon dioxide as claimed in claim
5 15 in a carbon dioxide-consuming process.

