

PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Method for Prevention of Corrosion in Carbon Dioxide Removal Systems

I, ALLEN GARLAND BICKMEYER, citizen of the United States of America, residing at 7204 Cherokee Drive, Prairie Village, Kansas, United States of America, do hereby declare the invention for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to corrosion prevention of ferrous metals in gas purification systems wherein carbon dioxide is removed by absorption in an aqueous alkaline solution of potassium carbonate, potassium borate, monoethanolamine, diethanolamine, diethanolamine borate or mixtures thereof.

In the removal of carbon dioxide from a gas mixture containing it, the crude gas mixture is contacted with the alkaline solution in an absorption tower, whereby the carbon dioxide selectively dissolves in the solution. The rich solution is transferred to another tower, wherein the solution is regenerated by steam stripping to carry off the dissolved carbon dioxide. The regenerated solution is continuously recycled to the absorption tower.

The towers and pipelines for such processing are generally constructed of carbon steel and a suitable corrosion inhibitor is necessary for a practical process. Potassium dichromate has been found to inhibit corrosion in hot potassium carbonate systems, but it has the serious disadvantage of forming solids which deposit in the towers and on heat exchanger tubes, which require cleaning of the equipment; therefore, it is not a satisfactory inhibitor.

In early laboratory corrosion tests in which a relatively small iron surface area was contacted by a relatively large volume of hot potassium carbonate solution, the addition of 0.1% to 0.3% sodium metavanadate was found to inhibit corrosion without formation of solids. Likewise, the equivalent amount of vanadium pentoxide (V_2O_5) dissolved in potassium carbonate to give potassium metavan-

adate was also effective. However, in a commercial hot carbonate system used for purifying hydrogen gas, it was found that the addition of 0.2 to 0.3% potassium metavanadate was not effective and rapid corrosion of steel equipment occurred. It was thus determined that the same inhibitor did not perform the same in plant operations as it did in the laboratory.

The present invention is designed to provide a method for inhibiting corrosion in CO_2 removal systems wherein the effective concentration of the inhibitor is maintained by the continuous or intermittent addition of an oxidising material during the operating cycle to prevent reduction of the inhibitor. In accordance with the invention, the corrosion of ferrous metals in a system for removing carbon dioxide from hydrogen-containing gases, wherein carbon dioxide is selectively dissolved in aqueous alkaline solutions of potassium carbonate, potassium borate, monoethanolamine, diethanolamine, diethanolamine borate or mixtures thereof and containing sodium, potassium or ammonium metavanadate or peroxyvanadate in small amounts relative to the alkaline solution is inhibited by a method which comprises during operation of the system either continuously or intermittently adding an oxidising material to maintain the vanadium-containing compounds in an oxidised condition.

In a later series of laboratory corrosion tests under uniform conditions, CO_2 was bubbled through hot solutions of potassium carbonate in contact with a relatively large iron surface area and the solution was then analyzed for iron content as a measure of the relative corrosion rate. In all cases, an aqueous solution was used containing 25% K_2CO_3 and 0.2% KVO_3 by weight. In some cases, as shown by Table 1, a small amount of an oxidising agent was added or air was bubbled through the solution. The results are summarised in Table 1.

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TABLE 1

Corrosion tests with 25% K_2CO_3 and 0.2% KVO_3 in water

Test No.	1	2	3	4	5	6
Oxidizing Agent (% by wt.)	None	.2% H_2O_2	.02% H_2O_2	.03% $K_2Cr_2O_7$	Air	Air
Air Bubbling Time	None	None	None	None	40 Min.	12 Hrs.
Iron Content mg/litre	563	1.7	8.7	10.8	140	20.7

In Test 1 of Table 1, it was found that the vanadate had disappeared, having become reduced to a lower state of oxidation, and rapid corrosion of the iron occurred as shown by the high concentration of iron in solution. Tests 2 and 3 of Table 1 showed that potassium peroxyvanadate, which was formed by reaction of the vanadate with hydrogen peroxide, provided excellent corrosion inhibition even when present in small amounts. In Test 3, Table 1, the amount of hydrogen peroxide was enough to give about 0.08% potassium peroxyvanadate. In Test 4, Table 1, a very small amount of another oxidizing agent, potassium dichromate, was used. The concentration of dichromate was only one tenth

of the usual concentration employed when dichromate alone is used as an inhibitor.

Tests 5 and 6, Table 1, show that where air, which contains 20.9% oxygen, is added in amounts sufficient to avoid the reduction of the metavanadate, good corrosion inhibition can be obtained.

Another series of laboratory corrosion tests were made under similar conditions and with similar compositions except that 10% diethanolamine borate was also present in the potassium carbonate solution. The results, given in Table 2, show a similar beneficial effect of the oxidizing agents on the metavanadate in preventing corrosion, even in the presence of an ethanolamine.

TABLE 2

Corrosion tests with 25% K_2CO_3 , 10% diethanolamine borate and 0.2% KVO_3 (by wt.) in water.

Test No.	7	8	9
Oxidizing Agent (% by wt.)	None	.04% H_2O_2	.03% $K_2Cr_2O_7$
Iron Content (mg/litre)	119	16.9	17.1

These laboratory tests indicated that slight oxidation of iron at the surface of steel equipment is essential to the formation and maintenance of a corrosion inhibiting film.

It is to be understood that smaller or larger amounts of the vanadium-containing compounds, i.e. inhibitors, may be used. Depending on the severity of the corrosive conditions, usually between 0.05% and 2% by wt. of the solution of sodium, potassium or ammonium metavanadate or peroxyvanadate is used. Also the metavanadate may be formed by dissolving the equivalent amount of vanadium pentoxide (V_2O_5) in the alkaline solution used in the process of the invention.

The oxidizing agent which may for example be air, oxygen, hydrogen peroxide or potassium dichromate, may be added separately, either continuously or intermittently, but when added intermittently a more careful check must be kept on corrosion and the rate of reduction of vanadate. Also, since the vanadate acts as a carrier for oxygen, the oxidizing agent may be added at any suitable point in the circulating system. For reasons of convenience and safety, I prefer to inject an oxygen-containing gas, such as air, into the pipeline carrying the rich solution to the top of the regenerator tower or into the line carrying the stripping steam entering the bottom of the

regenerator tower. However, air may be injected at some other point in the system or a portion of the circulating solution may be contacted with air and returned to the system.

5 When used as an oxidizing agent, hydrogen peroxide is preferably added with mixing to form a solution with the reflux condensate being returned to the system.

air or other oxidizing material is added to maintain the vanadium-containing compound at an effective concentration. The amount of air necessary will vary with plant conditions, including temperature of solution, amount of steel surface contacted by the solution, and the point of air injection which will determine the time and pressure of contact.

EXAMPLE

10 During the initial operation of a hot potassium carbonate system in an actual commercial ammonia plant, the iron content of the solution was determined frequently as an indication of any corrosion. At the start, the solution contained about 22% K_2CO_3 and 0.2—0.3% KVO_3 (potassium metavanadate) by wt. During the first five days in operation, without the addition of air, the iron content increased rapidly to 200 milligrams per litre.

15 Also, it was found that 53% of the original metavanadate had become reduced to a lower state of oxidation. The plant was shut down and repairs were made at points of corrosion in the pipelines. During this time the solution was filtered to remove the iron compound which had precipitated when the solution had cooled. Upon resuming operations, air at the rate of eight cubic feet per minute was injected near ground level into the rich solution line going to the top of the regenerator tower.

20 During the next ten days, the iron content of the solution remained essentially constant at between 50 and 60 milligrams per litre, thus indicating that the corrosion had been arrested.

25 Also, only 11% of the original metavanadate was reduced and 89% was present as metavanadate. At this time 48,000 cubic feet per minute of hydrogen plus nitrogen was being purified. On the basis of the purified gas, the oxygen contained in the injected air amounted to 35 parts per million by volume.

30 In order to keep the solution in an optimum condition wherein the vanadium-containing compound is properly oxidized rather than deteriorated to a reduced condition, sufficient

WHAT I CLAIM IS:—

1. A method for inhibiting the corrosion of ferrous metals in a system for removing carbon dioxide from hydrogen - containing gases, wherein carbon dioxide is selectively dissolved in aqueous alkaline solutions of potassium carbonate, potassium borate, monoethanolamine, diethanolamine, diethanolamine borate, or mixtures thereof, and containing sodium, potassium or ammonium metavanadate or peroxyvanadate in small amounts relative to the alkaline solution, which comprises during operation of the system either continuously or intermittently adding an oxidizing material to maintain the vanadium-containing compounds in an oxidised condition.
2. A method as claimed in claim 1, wherein the oxidizing material is air.
3. A method as claimed in claim 1, wherein the oxidizing material is oxygen.
4. A method as claimed in claim 1, wherein the oxidizing material is hydrogen peroxide.
5. A method as claimed in claim 1, wherein the oxidizing material is potassium dichromate.
6. A method as claimed in any one of the preceding claims wherein the alkaline solution contains 0.05 to 2% by weight of metavanadate or peroxyvanadate.
7. A method as claimed in claim 1 substantially as hereinbefore described with reference to the Example.

K. J. VERYARD,
15, Suffolk Street, S.W.1,
Agent for the Applicant.

regenerator tower. However, air may be injected at some other point in the system or a portion of the circulating solution may be contacted with air and returned to the system. When used as an oxidizing agent, hydrogen peroxide is preferably added with mixing to form a solution with the reflux condensate being returned to the system.

EXAMPLE

During the initial operation of a hot potassium carbonate system in an actual commercial ammonia plant, the iron content of the solution was determined frequently as an indication of any corrosion. At the start, the solution contained about 22% K_2CO_3 and 0.2–0.3% KVO_3 (potassium metavanadate) by wt. During the first five days in operation, without the addition of air, the iron content increased rapidly to 200 milligrams per litre. Also, it was found that 53% of the original metavanadate had become reduced to a lower state of oxidation. The plant was shut down and repairs were made at points of corrosion in the pipelines. During this time the solution was filtered to remove the iron compound which had precipitated when the solution had cooled. Upon resuming operations, air at the rate of eight cubic feet per minute was injected near ground level into the rich solution line going to the top of the regenerator tower. During the next ten days, the iron content of the solution remained essentially constant at between 50 and 60 milligrams per litre, thus indicating that the corrosion had been arrested. Also, only 11% of the original metavanadate was reduced and 89% was present as metavanadate. At this time 48,000 cubic feet per minute of hydrogen plus nitrogen was being purified. On the basis of the purified gas, the oxygen contained in the injected air amounted to 35 parts per million by volume.

In order to keep the solution in an optimum condition wherein the vanadium-containing compound is properly oxidized, rather than deteriorated to a reduced condition, sufficient

air or other oxidizing material is added to maintain the vanadium-containing compound at an effective concentration. The amount of air necessary will vary with plant conditions, including temperature of solution, amount of steel surface contacted by the solution, and the point of air injection which will determine the time and pressure of contact.

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2. A method as claimed in claim 1, wherein the oxidizing material is air.

3. A method as claimed in claim 1, wherein the oxidizing material is oxygen.

4. A method as claimed in claim 1, wherein the oxidizing material is hydrogen peroxide.

5. A method as claimed in claim 1, wherein the oxidizing material is potassium dichromate.

6. A method as claimed in any one of the preceding claims wherein the alkaline solution contains 0.05 to 2% by weight of metavanadate or peroxyvanadate.

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