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(54) Title: METHOD OF CORROSION INHIBITION IN ABSORPTION REFRIGERATION SYSTEMS

(57) Abstract

Process for preventing or limiting the corrosion of metals due to contact with solutions containing lithium bromide, comprising causing Sn** ions to be present in the solution.
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METHOD OF CORROSION INHIBITION IN ABSORPTION REFRIGERATION SYSTEMS

Field of the Invention
The present invention relates to a method for inhibiting corrosion in absorption refrigeration systems using lithium bromide or lithium bromide and chloride as the absorber.

Background of the Invention
Absorption refrigeration systems use heat energy directly through the medium of generator-absorber-pump circuit which replaces the complex mechanical compressor. Absorption refrigeration systems have been known in the art for a long time. They are described, e.g., in E.K. Tanzer, "Comparing Refrigeration Systems", in Chem. Eng. June 10 and June 24, 1963, and are now attracting renewed attention. Such systems using lithium bromide as the refrigerant are described e.g. in J. Katzel, "The Rediscovery of Absorption Chillers". Plant Eng., April 23, 1992, and M. J. Lane et al, "Lithium bromide absorption chiller passes gas conditioning field test", Oil and Gas Journal, July 31, 1995, p. 70-73.

In such absorption refrigeration systems, which use concentrated solutions of lithium bromide or containing lithium bromide, corrosion occurs since the solutions come in contact with metallic parts, such as pumps, pipes, valves, heat exchangers, condenser, and absorber, particularly when they are made or contain parts thereof are made of copper or copper alloys or carbon steel or of stainless steel. Although the corrosion occurs at all temperatures of the refrigeration cycle, it gets more severe as the temperature of the refrigerant liquid rises.
The art is aware of this corrosion problem. Thus JP 07174429 discloses an operational method of an absorbing type freezer which comprises stainless steel and copper components and has a lithium bromide solution as absorption liquid, in which method the absorption liquid solution contains lithium hydroxide by 0.3N or less, sub-sulfuric acid sodium or sub-sulfuric acid hydrogen sodium by 250 ppm or more, molybdenum acid lithium of 30 ppm or more and nitric acid lithium of 200 ppm or less. This is said to prevent local corrosion of stainless steel.

The stress corrosion of austenitic stainless steels in 55% lithium bromide environments has been discussed by D. Itzhak and O. Elias in *Corrosion* Vol. 50, No. 2. pp. 131,137 (1995).

The corrosion and stress corrosion cracking (SCC) behavior of type 316 stainless steel in a 55% lithium bromide environments was investigated by D. Itzhak, O. Elias and Y. Greenberg, using slow strain rate testing and potentiodynamic polarization measurements (*Corrosion*, Vol. 52, No. 1, pp. 72-78 (1996). Addition of 1 wt% KI to 55% LiBr brine of pH=4 was found to act as an inhibitor to SCC, while addition of 1wt% of K$_2$CrO$_4$ has an opposite effect.

The art, however, has not found a satisfactory solution to the problem of corrosion of copper, copper alloys, carbon steel and stainless steels in contact with lithium bromide solutions.

It is a purpose of this invention to provide a solution to said problem.

It is another purpose of this invention to provide such a solution that is simple and economical.
It is a further purpose of this invention to provide such a solution that involves no negative effects in the operation of an absorption refrigeration system.

Other purposes and advantages of the invention will appear as the description proceeds.

Summary of the Invention

According to the invention, corrosion of metals, in particular copper, copper alloys, carbon steel and stainless steels, in lithium bromide solution environments, is prevented, or at least substantially decreased, by causing Sn\textsuperscript{2+} ions to be present in the solutions containing lithium bromide. The solutions can also contain lithium chloride, the presence of which leads to lower vapor pressure and permits to increase the concentration, and therefore what is said hereinafter with respect to LiBr solution is equally applicable to LiBr+LiCl solutions.

The invention is particularly applicable to absorption refrigeration systems which comprise metallic components, particularly made of, or comprising parts made of, copper, copper alloys, carbon steel and stainless steels, and which further use solutions containing LiBr in their operation.

Sn\textsuperscript{2+} ions can be introduced and maintained in the solutions in various ways. They can be introduced directly, by adding to the LiBr solution a soluble tin salt, such as SnCl\textsubscript{2}. Preferably, however, metallic tin in any form - powder, granules, foil, plates, bars etc. is placed in contact with the solution, resulting in the formation of Sn\textsuperscript{2+} ions in situ. In any case, the concentration of said ions in the solution is preferably comprised between 200 and 500 ppm. The concentration of Sn\textsuperscript{2+} ions can be detected by means of atomic absorption spectroscopy. When metallic tin is placed in contact with the LiBr solution, the concentration of said ions is determined by a steady state that results.
When a tin salt is added to the LiBr solution, the concentration of said ions is determined by the amount of salt added, until saturation is reached.

The invention is preferably applied to LiBr solutions at a maximum concentration of 60%, for example 55%. When the solution contains LiCl in addition to LiBr, the concentration can be higher, e.g. up to 63%. A typical such solution may contain up to 53% of LiBr and up to 11% of LiCl. All the percentages in this specification and claims are by weight.

When Sn^{++} ions are present in the refrigerant solution, tin is deposited on the metal surfaces with which the solution is in contact. The deposition of tin creates, at least in part, a crystal layer which contains tin in its crystal lattice. Hereinafter, however, for simplicity's sake, the tin deposited on an underlying metal such as copper, copper alloy or stainless steel, will be referred to as a "tin coating".

**Brief Description of the Drawings**

Figs. 1 and 2 are graphs illustrating the deposition of tin on metal surfaces in contact with LiBr solutions containing tin ions; and Figs. 3 and 4 are x-ray diffraction (XRD) diagrams illustrating the results of the exposure of commercial copper to a 55% LiBr solution containing tin ions.

**Detailed Description of Preferred Embodiments**

Fig. 1 is a bar graph illustrating the deposition of tin over various metals in contact with a 55% LiBr solution in the presence of metallic tin which causes Sn^{++} ions to be present in the solution. Tin was provided in the form of powder in an amount of about 10 wt% with respect to the solution. However, it is only required that metallic tin be always present, even though in small amounts. The concentration of Sn^{++} ions in the solution is comprised, under these conditions, between 200 and 500 ppm. The deposition of tin on the metal surfaces is illustrated by an increase of weight of the said metals during 7
days of exposure to the said solution at 145°C and pH ~10.6. Said increase -
to which the ordinate in the bar graph of Figure 1 refers - is the average
increase over the whole time of exposure expressed in grams per square
centimeter per hour. The metals tested in the test of Fig. 1, indicated by
numerals 1, 1', 2, 2', 3, 3', 4 and 4' under the abcissa were (the aforesaid test
was carried out twice for each of the metals): 1 and 1' - a copper-zinc-lead
alloy containing Cu 60% - Zn 37.5% - Pb 2.5%, 2 and 2' - Tungum, which is an
alloy containing Cu 84% - Zn 15% - Ni 1%, 3 and 3' - commercial copper, and
4 and 4' - AMP, which is an alloy containing 84% Cu - Al 10% - Fe 4% - Zn
2%.

As shown in the figure, generally there were differences in the weight
increments found in the two tests, but since the weight increments are in the
order of tens of milligrams, said differences are in the order of experimental
errors. However, in no tests was a decrease in the weight of the sample
found, viz. no evidence for corrosion was found, and this is the decisive fact as
far as this invention is concerned.

Fig. 2 is a bar graph comparing the increase of weight of several copper alloys
exposed to a 55% LiBr solution at 140°C and pH~10.6 to the decrease in
weight of the metallic tin. Both increase of weight of the various copper
alloys (unshaded rectangles indicated by numerals 1, 2, 3 and 4 according to
the meanings referred to in Figure 1) and decrease in weight of the tin
(shaded rectangles) are given in grams per square centimeter per hour. The
tin was present in the form of plates. The samples were exposed for a week
(168 hours). The figure does not show a constant relationship between the
decrease of weight of the tin and the increase of weight of the copper samples,
but indicates in each case that the corrosion process has been inhibited.
Figs. 3 and 4 show the result of the exposure of commercial copper to a 55% LiBr solution at 140°C and pH~10.6. The concentration of the Sn^{++} ions was 200 ppm. Fig. 3 refers to an exposure for one day, and Fig. 4 to an exposure for seven days. Both figures show the XRD results (the abcissa being the glancing angle and the ordinate being the peak intensity), said results indicating the presence of a Cu_6Sn_5 phase with the corresponding decrease of the Cu peaks. This indicates that the copper-tin crystalline phase was formed at the expense both of the copper sample and of the tin ions.

EXAMPLE 1

Table I shows the results of exposing various samples of copper and metal alloys to 55% LiBr solution at 140°C and pH~10.6, with and without the introduction into the solution of SnCl_2 salt, which provides Sn^{++} ions. As indicated, the tested metals were commercial copper, Tungum, and various types of AISI. Specifically: AISI-316 is stainless steel containing 0.08% C, 2% Mn, 1% Si, 16-18% Cr, 10-14% Ni, 2% Mo; AISI-1040 is stainless steel containing 0.4% C; and AISI-430 is stainless steel containing 0.2% C, 1% Mn, 1% Si, 16-18% Cr.

**TABLE I**

<table>
<thead>
<tr>
<th>Weight Loss gr/[cm² x hour]</th>
<th>Solution of</th>
<th>Metal Tested</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 x 10^{-4}</td>
<td>LiBr + SnCl_2</td>
<td>commercial copper</td>
</tr>
<tr>
<td>1.5 x 10^{-4}</td>
<td>LiBr</td>
<td>commercial copper</td>
</tr>
<tr>
<td>3 x 10^{-4}</td>
<td>LiBr + SnCl_2</td>
<td>Tungum</td>
</tr>
<tr>
<td>&gt;1 x 10^{-3}</td>
<td>LiBr</td>
<td>Tungum</td>
</tr>
<tr>
<td>nil</td>
<td>LiBr + SnCl_2</td>
<td>AISI - 316</td>
</tr>
<tr>
<td>nil</td>
<td>LiBr</td>
<td>AISI - 316</td>
</tr>
<tr>
<td>1 x 10^{-4}</td>
<td>LiBr + SnCl_2</td>
<td>AISI - 1040</td>
</tr>
<tr>
<td>2.5 x 10^{-4}</td>
<td>LiBr</td>
<td>AISI - 1040</td>
</tr>
<tr>
<td>nil</td>
<td>LiBr + SnCl_2</td>
<td>AISI - 430</td>
</tr>
<tr>
<td>nil</td>
<td>LiBr</td>
<td>AISI - 430</td>
</tr>
</tbody>
</table>
It is seen that the presence of tin ions reduces the loss of weight of the tested metals, except when no corrosion occurs anyway. The inhibition of corrosion is most marked in the case of Tungom.

EXAMPLE II

Table II lists the change of weight, in grams per square centimeter per hour, of various metals exposed to a 55% LiBr solution at 140°C and pH~6.1, with or without the introduction of tin powder into the LiBr solution or, in some cases, to a solution of LiBr and LiCl of 63% concentration.

<table>
<thead>
<tr>
<th>Observations</th>
<th>Weight Change Per Unit Area [gr² x hour]</th>
<th>Solution of</th>
<th>Metal Tested</th>
</tr>
</thead>
<tbody>
<tr>
<td>The metal acquired a dark color, the solution a brown/red color</td>
<td>-340 x 10⁻⁷</td>
<td>LiBr</td>
<td>AISI 1040</td>
</tr>
<tr>
<td></td>
<td>-16 x 10⁻⁷</td>
<td>LiBr</td>
<td>Commercial Copper</td>
</tr>
<tr>
<td>The metal acquired in part a dark color</td>
<td>-18 x 10⁻⁷</td>
<td>Sn ions + LiBr</td>
<td>AISI 1040</td>
</tr>
<tr>
<td></td>
<td>+98 x 10⁻⁷</td>
<td>Sn ions + LiBr</td>
<td>Commercial Copper</td>
</tr>
<tr>
<td>The metal became slightly opaque</td>
<td>-13 x 10⁻⁷</td>
<td>Sn ions + LiBr + LiCl</td>
<td>AISI 1040</td>
</tr>
<tr>
<td></td>
<td>+59 x 10⁻⁷</td>
<td>Sn ions + LiBr + LiCl</td>
<td>Commercial Copper</td>
</tr>
</tbody>
</table>

The above examples illustrate the application of the invention to an LiBr solution at 140°C and pH~6.1. Similar results are obtained at temperatures up to 155°C and pH 6 to 11.

While some embodiments of the invention have been illustrated, it will be clear that the invention may be carried out by persons skilled in the art with
many modifications, variations and adaptations, without departing from its spirit or exceeding the scope of the claims. Thus, e.g., metals different from those exemplified may be protected by the addition of tin ions to the Li salt solution and different means of creating and maintaining the presence of tin ions in the solution may be used, and the invention may be applied to apparatus different from that herein mentioned.
CLAIMS

1. Process for preventing or limiting the corrosion of metals due to contact with solutions containing lithium bromide, comprising causing Sn\textsuperscript{++} ions to be present in the solution.

2. Process according to claim 1, wherein the metals are chosen from among copper, copper alloys, carbon steel and stainless steels.

3. Process according to claim 1, wherein the metals constitute at least parts of components of absorption refrigeration systems.

4. Process according to claim 1, wherein the concentration of the Sn\textsuperscript{++} ions in the solution is comprised between 200 and 500 ppm.

5. Process according to claim 1, wherein Sn\textsuperscript{++} ions are introduced and maintained in the solutions containing lithium bromide by placing metallic tin in contact with the solution.

6. Process according to claim 1, wherein Sn\textsuperscript{++} ions are introduced and maintained in the solutions containing lithium bromide by introducing soluble tin compounds into the solution.

7. Process according to claim 6, wherein Sn\textsuperscript{++} ions are introduced and maintained in the solutions containing lithium bromide by introducing SnCl\textsubscript{2}.

8. Process according to claim 1, wherein the solution containing lithium bromide is a LiBr solution of lithium bromide at a concentration up to 60%.

9. Process according to claim 1, wherein the solution containing lithium bromide is a solution of lithium bromide and lithium chloride.
10. Process according to claim 9, wherein the solution contains up to 53% of lithium bromide and up to 11% of lithium chloride.

11. Process according to claim 1, wherein the metals constitute metallic components of absorption refrigeration systems or are comprised in such components.

12. Process according to claim 11, wherein the metals are chosen from among copper, copper alloys, carbon steel and stainless steels.

13. Process for preventing or limiting the corrosion of metals due to contact with solutions containing lithium bromide or lithium bromide and lithium chloride, substantially as described and exemplified.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C23F11/18

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)
IPC 6 C23F C09K F25B

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 practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<th>Category</th>
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<td>PATENT ABSTRACTS OF JAPAN vol. 095, no. 010, 30 November 1995 &amp; JP 07 174429 A (OSAKA GAS CO LTD), 14 July 1995, cited in the application see abstract</td>
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<td>CORROSION, vol. 52, no. 1, 1 January 1996, HOUSTON US, pages 72-78, XP002032943 ITZHAK D.: &quot;Behavior of type 316 austenitic stainless steel under slow strain rate technique conditions in lithium bromide heavy brine environment&quot; cited in the application see abstract</td>
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Further documents are listed in the continuation of box C. Patent family members are listed in annex.

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Date of mailing of the international search report
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