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SCALE REMOVAL

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This invention deals with the cleaning of metal surfaces. More particularly, it concerns itself with a new and improved process for the removal of iron oxide and other metallic oxide scale from metals.

Operational scale deposited in steam-generating equipment such as high pressure boilers, superheater tubes, heat exchanger tubes, etc. usually consists of oxides of iron, often magnetite ($\text{Fe}_2\text{O}_3 \cdot \text{FeO}$) together with some red iron oxide (Fe_2O_3). Where the unit is fabricated in part from alloys of copper, e.g., for the condensers, the scale will be found to contain copper as well, in the form of the elemental metal and sometimes as cuprous and cupric oxides. Such scale is generally tightly adherent and low in porosity. Its gradual build-up on the surfaces of vessels is undesirable for a number of reasons, e.g., it hinders the flow of fluid therethrough, thermally insulates and hinders the conduction of heat through the walls of the vessel, increases the consumption of fuel, requires high pressures to force fluids therethrough and, in general, increases the cost of the operation. As a result, about every one to four years, the scale must be removed. Since the shutdown of a high capacity boiler can easily represent losses of thousands of dollars per day, it is obvious that the most rapid and effective cleaning is desirable.

In the past, hydrochloric acid and other mineral acids have been employed for this purpose. However, it has been found that where the scale contains copper or copper oxides, iron oxide scale removal is accompanied by redeposition or plating out of elemental copper throughout the system. This copper not only accelerates corrosion and interferes with heat exchange, but it may flake off during operation and be carried through the superheater, causing expensive damage to the turbine surfaces.

Furthermore, high pressure boilers containing austenitic parts, e.g., superheater tubes, and operating at pressures of 2500–3000 p.s.i. and higher are subject to chloride stress fatigue, and hence, hydrochloric acid is frequently unsuitable as a cleaning agent. Mineral acids in general have the added disadvantage of attacking steel, even where corrosion inhibitors are incorporated, and present a safety hazard to personnel. Because of these problems, the non-toxic acids such as citric have been tested. Citric acid offers advantages in cleaning new units of preoperational scale because of its safety to equipment and personnel, and because it readily dissolves rust and mill scale. However, dense operational scales containing magnetite are removed quite slowly by citric acid, and where copper is present the objectionable copper plating is encountered.

The use of citric acid solutions in descaling operations is known. For example, in pending U.S. patent application, Serial No. 89,116, filed February 14, 1961, now U.S. Patent No. 3,072,502, and having a common assignee, a method of descaling is disclosed employing a citric acid solution at a pH of 2.5 to 5. There are, however, certain disadvantages inherent in using such a solution. The corrosion rate of the metal and the hazards to personnel, for example, must be considered.

It has also been proposed to use a series of solutions to remove the various components of operational scale and to provide a relatively clean surface resistant to rapid re-corrosion. Such processes are only partially successful and, since they entail many time-consuming steps, may

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require 24 hours or more to complete. They therefore, involve high costs in lost operation, and also usually require appreciable quantities of expensive ingredients. Additionally, where such processes employ a hydrochloric acid step they retain many of the described disadvantages and are usually not applicable to the cleaning of high pressure boilers containing austenitic materials.

It is an important object of this invention to provide a process for the rapid and complete removal of copper-containing iron oxide scales from metal surfaces.

A further object of this invention is to provide a process which will remove both copper and iron oxide deposits using a single solution, without the necessity for intermediate drainage and rinsing.

Still a further object of this invention is to provide a process which will not only remove copper-containing iron oxide scales from metal surfaces, but which will provide passivation of the metal surfaces.

Another object is to provide a process which will passivate metals whose surfaces are scale-free.

Other objects of this invention will become apparent from the following detailed description and claims.

Up until now, the art has considered the use of acid solutions for the removal of copper-containing iron oxide scales from metal surfaces. It has now been found that a neutral solution will effectively remove the iron oxide scales from metal surfaces.

According to the present invention, copper-containing iron oxide scales are removed from metal surfaces by a new and improved process which comprises contacting said scaled metal surfaces with a neutral ammonium citrate solution at elevated temperatures to chemically dissolve magnetic iron oxide. During the course of the reaction, ammonia and/or ammonium hydroxide is produced in situ thus raising the pH of the solution. The ammoniacal solution thus produced dissolves the copper oxides. Through the use of this process, it is possible to achieve a rapid removal of copper-containing iron oxide scales from metal surfaces with no danger of attacking metal surfaces and with a minimum of expense and inconvenience. Surprisingly, it has been found that the process of the instant invention will passivate metal surfaces. Furthermore, this process lends itself conveniently to the removal of iron and copper oxide scales as a one-step process without the necessity of periodically analyzing the cleaning solution to determine when the iron oxide scale has been totally removed before proceeding with the removal of copper and copper oxides. Also, there are certain other advantages in starting with a substantially neutral ammonium citrate solution. The tendency for corrosion of metal surfaces to occur is much less with a neutral solution than it is with a solution of low pH; the ammonia becomes available almost immediately for use in the dissolution of copper and copper oxides; and a neutral ammonium citrate solution permits one to operate at higher temperature and pressures with less hazard to personnel and equipment. Furthermore, at higher temperatures and pressures the reaction rates are increased, thus decreasing the cleaning time. A further distinct advantage of the instant invention is that the scale removal and passivating steps may be carried out at elevated temperatures and pressures, thus enabling the units to be cleaned without completely removing them from service. Temperatures and pressures normally encountered in the operation of boilers may be as high as about 900 to 1100° C. and 2500 to 3000 p.s.i. respectively. The temperatures and pressures at which the process of the instant invention may be carried out effectively are within the scope of temperatures and pressures encountered in normal boiler operations. For example, the process may be carried out quite effectively at pressures up to about 500 p.s.i.

The invention is carried out by contacting the unit to be cleaned with a neutral ammonium citrate solution (pH 7.0), in concentrations of about 0.5 to 5%, by weight of citric acid although higher concentrations may also be effective. Concentrations below about 0.5% are not very effective in that the citrate is readily exhausted thereby making it difficult to maintain neutral pH. Temperatures in the range of about 150° to 200° F. or higher are found to be satisfactory. Agitation by nitrogen, or more preferably, by air, will speed the process, especially in helping to dissolve the metallic copper.

An alternative method in the use of the process of the instant invention is to contact the surface to be cleaned with a 1% solution of ammonium citrate, for example, and as the pH rises additional citric acid may be added to maintain neutral pH during the removal of the iron oxides; thereafter, allowing the pH to rise to effect removal of the copper and copper oxides.

In order to fully stabilize copper to effect its removal, the final pH of the system preferably should be 9 or above. If necessary, additional anhydrous ammonia may be added and contacted with the system for about one hour before draining.

In cleaning steam generating equipment, to insure adequate contact with all scaled surfaces, sufficient solution may be introduced to substantially fill the system, i.e., the boiler, the risers and the steam drum. The solution may then be slowly circulated with pumps to contact all surfaces including the downcomers. Furthermore, the process may be used to clean units without completely removing them from service. High pressure units may be cleaned at pressures up to about 500 p.s.i. by filling with dilute neutral ammonium citrate and blowing down constantly to remove spent solvent, while replenishing with fresh neutral ammonium citrate. On draining, clean passive metal remains. It is to be noted that the process of this invention is a safe one and that no corrosion inhibitor is required, even at the higher temperatures.

Neutral ammonium citrate as used herein has a pH of 7.0 and is considered to be the triammonium citrate. The cleaning operation may be regarded as substantially complete when the analysis of liquid samples shows that the copper content is substantially constant. The entire operation usually requires from about one to about eight hours depending on the size of the unit and temperature and pressure of operation. Cleaning under a positive steam pressure of about 100 to 300 p.s.i. would require temperatures of about 320–420° F. Since most units to be cleaned of such scale deposits, e.g., boilers, heat exchangers, drums, superheaters, reheaters, etc., are fully enclosed, with small vents at best, ammonia vapors will not tend to escape rapidly. Sufficient solution should be used to substantially fill the system.

In cases where the unit is small and heavily scaled, it is possible that the volume of cleaning solution which it can hold will become exhausted before all of the iron oxides have been removed. This situation is readily detected since one mole of iron is complexed by each mole of citrate, i.e., 56 parts by weight of iron to each 192 parts by weight of citric acid. Therefore, if the molar iron content of the solution levels off at a value corresponding to the original molar concentration of citric acid introduced, it is possible that the iron oxide has not been completely removed. If this is the case, it is safest to introduce additional neutral ammonium citrate and repeat the process. Past experience frequently dictates, in general, the amount of iron oxides to be removed, thus enabling one to employ a suitably high level of citrate where such will be required.

As disclosed hereinbefore, a novel feature of the process of this invention, using neutral ammonium citrate, lies in the fact that the system not only dissolves iron oxides, but also, as a direct result of the release of ammonia molecules, dissolves and stabilizes copper and copper oxides. Another novel feature of this process is the passivating ef-

fect the process has on metal surfaces. Scaled metal surfaces and unscaled metal surfaces when treated by this process are highly passivated and, therefore, not subjected to corrosion.

Oxidizing agents may be added in this process to increase the rate of the reaction; generally by helping to dissolve metallic copper. A wide range of oxidants are suitable. Air or oxygen are eminently suitable and are readily introduced by injection into the solution through a sparger or bubbler during the cleaning. Another gaseous oxidant which may be employed in the same manner is nitrogen tetroxide. Where it is inconvenient to provide a sparger, liquid or solid oxidants may be incorporated in the cleaning solution to the same advantage. These include potassium permanganate, nitrophenylsulfonic acid sodium salt, and the sodium, potassium and ammonium salts of persulfates, perchlorates, bromates or nitrites. Very small quantities of such oxidant are required for the desired beneficial effect, about one part by weight for each part by weight of copper to be removed.

During that phase of the process wherein ammonia molecules are released and copper and copper oxide dissolution occurs, it is preferred that the pH of the system be at least 9 or above. If necessary, additional anhydrous ammonia may be added to maintain the level of pH at 9 or above. When a standard analysis of liquid samples indicates that the copper content is substantially constant, the cleaning solution may be drained to waste and the unit rinsed with water. The treated surfaces are left silvery grey in color, scale- and copper-free, and ready for return to service. Furthermore, the surfaces thus cleaned have been passivated thus enhancing their ability to resist corrosion.

To further illustrate the invention, the following examples are given. The examples are not to be construed as limiting the invention, the scope of which is defined by the appended claims.

Example I

A two foot section of 3 inch O.D. boiler tube, taken from an 1800 p.s.i.g. steam generator is placed in a circulating loop, and water is circulated at 180° F. The inner surface has a thin, uniform deposit containing mostly magnetic iron oxide and a trace of copper oxide. When the temperature is stabilized at 180° F., a previously prepared concentrate of neutral ammonium citrate, 3% by weight, is added to the circulating water. Samples are withdrawn periodically.

Time, Hours	Temp., ° F	pH	Ferrous Ion, grams	Total Dissolved Iron, grams
0.0-----	180	6.97	0.0	0.0
1.0-----	180	6.97	0.28	1.5
1.5-----	180	7.08	0.55	1.8
2.0-----	180	7.30	0.83	2.5
3.0-----	200	7.94	3.5	5.8
3.5-----	200	8.07	4.7	6.9
4.0-----	200	8.17	6.3	10.1
4.5-----	200	8.21	7.5	11.0
5.0-----	180	8.30	9.1	14.0
6.0-----	180	8.31	9.1	14.1

After 6 hours, the system is treated with ammonia to pH 10, 0.25 weight percent sodium nitrite is added and the system is aerated while cooling. After aerating overnight, the solution is drained and the system is flushed well with water. On inspection, the tube is clean, free of deposits and shows a grey, passive surface. A total of 106 mg. copper is removed.

Example II

Five hundred ml. of 1.5% citric acid, neutralized to pH 7.0 are placed in a 600 ml. beaker and heated to 180° F. A panel of carbon steel (2" x 2" Q AISI 1010 steel panels) is inserted and the weight loss measured after 5

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hours. Data with citric acid (pH 2.0) and monoammonium citrate (pH 3.6) are presented.

Solution	Run No.	Weight Loss, mg.	Corrosion Rate, lbs./ft. ² /day
1.5% citric acid (pH 2.0)-----	A	650	0.124
	B	622	0.116
1.5% citric acid (as monoammonium salt) pH 3.6-----	A	450	0.087
	B	435	0.083
1.5% citric acid (neutralized to pH 7 with NH ₃)-----	A	97.0	0.0187
	B	102.0	0.0194
	C	96.4	0.0184
	D	94.1	0.0179

Example III

Three carbon steel panels, cut from the same piece of steel to 4" x 4" size, and having a uniform aged red rust coating on the surfaces, are placed in a beaker containing 500 ml. of 3% citric acid adjusted to pH 7.0 with ammonia, and previously heated to 180–190° F. After one hour, the panels are removed from the solution and are free of all rust and scale. The pH of the solution is 7.5. During the experiment there is no evidence of hydrogen gas evolution, thus supporting the lack of corrosion.

Example IV

A 1" x 6" carbon steel strip covered with red iron oxide, Fe₂O₃, is inserted in a stainless steel cylinder containing 100 ml. of 3% neutralized (pH 7) ammonium citrate. The cylinder is sealed and immersed in a constant temperature oil-bath at 300° F. After 40 minutes exposure at 300° F., the cylinder is removed from the bath, opened and the steel strip examined. All rust has dissolved, leaving clean passive steel. The solution in the cylinder is a clear green-brown color, pH 7.8, and contains only a trace of insoluble matter. The strip is free of pits and shows no evidence of localized attack.

Example V

Two carbon steel strips, each ½" x 6", are welded together. Each strip has a covering of mill scale, and after welding, a weld scale is also present. After placing in a stainless steel cylinder, containing the solution of Example IV, the strips are exposed to elevated temperatures as in Example IV. After 4 hours, the cylinder is opened and the welded steel specimen is found to be free of rust, mill scale and other iron oxides. Only a trace of weld scale remains. The solution is similar in appearance to that of Example IV.

Example VI

Rusted steel strips are cleaned in 5% inhibited hydrochloric acid at 150° F. When the strips are visually clean, they are removed and without rinsing, quickly placed in a solution (pH 9) of 1% ammonium citrate and 0.25% sodium nitrite, and maintained at 140° F. The solution is aerated by slowly sparging air through a sintered glass nozzle. After 30 minutes, the specimens are removed, rinsed with distilled water and air dried. No re-rusting is observed. The strips of steel are of uniform grey color. Standing in the air for several weeks does not produce re-rusting. Strips cleaned as above, but not passivated with the alkaline ammonium citrate solution re-rust readily.

Example VII

A 3 inch O.D. boiler tube, approximately 2 feet long is filled with water and heated to 180° F. This tube contains a thick, hard, encrusted deposit of 40–60% magnetite and 60–40% cuprous oxide. When the metal temperature is uniform at 180° F., 3% ammoniated citric acid, pH 10, is added and the solution aerated. Immediately the solution assumes a blue color indicating dissolution of copper oxide. Since the tube is open to the atmosphere, it is necessary to periodically add aqueous ammonia to maintain pH 9.5–10.0. After 6 hours the

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copper content is stabilized at a concentration of 0.18% (32 g. copper). The solution is then treated with citric acid, to bring pH to 7.0. Temperature is maintained at 180°–190° F. for 4 hours, during which time the iron content levels off at 0.28% (50 g. total iron). The solution is again treated with ammonia to pH 10, sufficient sodium nitrite added to give 0.5% concentration by weight and the solution aerated for 3 hours while cooling. After the temperature drops to 90° F., the solution is removed from the tube which is rinsed well with pH 8 distilled water (adjusted with ammonia). All traces of iron oxide and copper-containing deposits are absent, and the tube has a clean, grey appearance.

Example VIII

A natural circulation boiler capable of producing 1,500,000 lbs. of steam per hour is allowed to cool to 150 p.s.i. steam pressure. A concentrated solution of 4000 lbs. citric acid, previously neutralized to pH 7 with ammonia, is added through the lower headers. Samples are withdrawn over a 3 hour period, during which time the pressure decreases to 50 p.s.i.

Time, Hours	pH	Dissolved Iron, Percent	Dissolved Copper, Percent
0.25-----	7.1	0.083	trace
0.50-----	7.4	0.122	trace
1.0-----	7.7	0.35	0.008
1.5-----	7.9	0.42	0.016
2.0-----	8.2	0.66	0.031
3.0-----	8.3	0.67	0.031

The boiler is drained to waste and immediately flushed with hot boiler feed water. Inspection reveals no remaining deposits on drum internals, headers and generating tubes.

Example IX

A controlled circulation boiler (operating pressure 2200 p.s.i. producing 1,800,000 lbs. of steam per hour) is allowed to cool to 200 p.s.i. and sufficient neutral ammonium citrate metered in to give a concentration of 1% (as citric acid). The pH rises to 8.4 within 30 minutes and the dissolved iron content is 0.25%. Approximately 10% of the boiler volume is drained to waste through the blow-down drain system and replaced with water containing sufficient neutral ammonium citrate to give a citrate concentration of 2% (including the 1% originally added). Again, after 40–45 minutes the pH rises to 8.7 and the total dissolved iron content is 0.45%. About 10% of the boiler volume is removed through blowdown and replaced with neutralized ammonium citrate to give 3.0% total citrate. After 1 hour, the pH is 8.5 and the iron content is level at 0.62% and no longer tends to increase. Gaseous ammonia is then admitted to raise the pH to 10, and air is bubbled into the system. After 30 minutes, the solution contains 0.18% dissolved copper, which does not increase in concentration with time.

The boiler, which by this time has cooled to about 60 p.s.i., is drained and immediately flushed with hot boiler feed water through the steam drum, with all drain valves open. After 15 minutes of flushing, the boiler is opened at the steam drum and is free of all iron oxide and copper deposits. The total time for cleaning, from the first addition of citrate until clean boiler feed water is added preparatory to returning the boiler to service, is 7.5 hours.

Example X

A rusted 3 inch O.D. boiler tube, approximately 12 inches long, is cleaned in 5% inhibited hydrochloric acid at 150° F. When the tube is visually clean, it is removed from the acid and immediately placed in a solution (pH 10) of 1% ammonium citrate and 0.25% potassium bromate, and maintained at 150° F. The solution is aerated by slowly sparging air through a sintered glass

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nozzle. After 30 minutes, the boiler tube is removed from the solution, rinsed with distilled water and air dried. No re-rusting is observed. The tube has a uniform grey color. After standing in the air for several weeks, no re-rusting occurs. A second boiler tube, cleaned as above, but not passivated with the alkaline ammonium citrate solution, re-rusts readily.

Example XI

Rusted steel strips are cleaned in 5% inhibited hydrochloric acid at 150° F. When the strips are visually clean, they are removed from the acid and immediately placed in a solution (pH 10) of 1% ammonium citrate and 0.25% sodium perchlorate, and maintained at approximately 150° F. The solution is aerated by slowly sparging air through a sintered glass nozzle. After 30 minutes, the strips are removed from the solution, rinsed with distilled water and air dried. No re-rusting is observed. The strips of steel are of uniform grey color. After standing in the air for several weeks, no re-rusting occurs. Strips cleaned as above but not passivated with the alkaline ammonium citrate solution re-rust readily.

Example XII

Scale-free steel strips are placed in a solution (pH 11) of 1% ammonium citrate and 0.30% sodium nitrite and maintained at about 150° F. The solution is aerated by slowly sparging air through a sintered glass nozzle. After 30 minutes, the strips are removed, rinsed with distilled water and air dried. No re-rusting is observed. The strips of steel are of uniform grey color. After standing in air for several weeks, no re-rusting occurs.

What is claimed is:

1. The method of removing copper-containing iron oxide scale from metal surfaces consisting essentially of contacting said surfaces with a composition comprising a substantially neutral aqueous solution of ammonium citrate, continuing said contact until the iron content of said solution becomes substantially constant as the pH rises, then continuing said contact at a pH of at least 9 and maintaining said pH with ammonia until the copper content of said solution becomes substantially constant.

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2. The method of claim 1 wherein said contacting is carried out at elevated temperatures and pressures.

3. The method as set forth in claim 1 wherein said aqueous solution of ammonium citrate is heated to a temperature of between about 150° F. and the boiling point of said solution.

4. The method as set forth in claim 1 wherein an oxidizing agent is added to the aqueous ammonium citrate solution.

5. The method as set forth in claim 4 wherein said oxidizing agent is selected from the group consisting of potassium permanganate, nitrophenyl-sulfonic acid sodium salt and the sodium, potassium and ammonium salts of persulfates, perchlorates, bromates and nitrites.

6. The method as set forth in claim 4 wherein said oxidizing agent is air injected into the solution.

7. The method of passivating scale-free metal surfaces consisting essentially of contacting said surfaces with a composition comprising an aqueous solution of ammonium citrate adjusted to a pH of at least 9 with ammonia and an oxidizing agent; continuing said contact for a period of at least about thirty minutes, and, thereafter, rinsing said metal surfaces with water.

8. The method of claim 7 wherein the contacting step is carried out at elevated temperatures and pressures.

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