13th International Conference on Fracture
June 16–21, 2013, Beijing, China

Developing New Innovative Descaling and Corrosion Inhibiting Solutions to Protect Steel Equipment in the Oil and Gas Industry

Abdulghani A. Jaralla[1], Muhannad M. Al-Darbi[2,*]

[1] GLS Limited, 31 Malabar Crescent, Broomfield, Christchurch, New Zealand

[2] Department of Chemical and Biological Engineering, University of British Columbia
2360 East Mall, Vancouver, B.C. V6T 1Z3, Canada

* Corresponding author: aldarbi@interchange.ubc.ca

Abstract

Previous studies have shown that corrosion is very costly and has a major impact on the economies of industrial nations. It is estimated that the annual cost of corrosion worldwide is over 3% of the world's GDP. In the oil and gas industry alone, corrosion costs billions of dollars a year. For that, corrosion control and mitigation technologies are of great importance. It is also our duty to protect the environment, preserve resources, and protect our fellow human beings. Descaling and corrosion inhibiting methods are widely used in many industries, like in the oil and gas industry. It is very important for any industry to clean the fire tube boilers, heat exchangers, and before commissioning to clean the pipes. For the oil and gas industry, in particular, it is extremely important to acidize the wells while keeping the downhole pipe safe. In this study, a new highly effective industrial cleaning solution which is effective in descaling without causing corrosion was found which comprises a mixture of hydrochloric acid, hydrofluoric acid, one or more chelating agents, a surfactant, a copper complexing agent, and a nontoxic acridine orange inhibitor, which serves to block the anodic and cathodic sites on the steel surfaces of the process equipment.

Keywords Corrosion, Descaling Solution, Oil and Gas Industry**,** Inhibiting Solution, Steel

---

1. Background

Corrosion has a huge economic and environmental impact on virtually all facets of the world's infrastructure, from highways, bridges, and buildings to oil and gas, chemical processing, and water and wastewater systems [1].

Equipment used in power plants, chemical and petrochemical plants, paper mills, sugar mills, pipelines, air conditioners in large buildings, and many other industrial environments are subject to the formation of scale, either by circulating water or by process compounds. This includes all types of heat exchangers, boilers, vessels, piping and other equipment [2].

Precipitated solids reduce the heat transfer efficiency and oftentimes cause tube failure due to overheating which may result in plugging or fouling of the equipment [3]. To prevent interference with industrial processes, cleaning of the metal surfaces of the equipment employed therein is required. The water-formed precipitates are generally inorganic in nature, especially precipitates formed in hot closed systems, for example, in steam generators or heat exchangers [4]. Common deposits which are found include iron oxides (magnetite and hematite), sulfides, alkaline earth carbonates, sulfates, and silicates [5].

Hydrochloric acid is widely used for the chemical cleaning of structural steel from which heat transfer and piping systems are fabricated. Hydrochloric acid forms soluble products which serve to dissolve calcium or magnesium carbonates [6]. Hydrochloric acid, does not, however, dissolve sulfates or silicates. Therefore, other chemicals must be mixed or incorporated with the hydrochloric acid. It is also well known that hydrochloric acid is highly corrosive [7]. In addition, if copper salts are present in the scale, they will dissolve and reprecipitate on iron surfaces causing severe localized corrosion [8].

It is an object of the present invention to provide a nontoxic, industrial descaling and cleaning composition which is effective in removing scales and oxides from the surfaces of the process equipment used in various industries while avoiding corrosion to the equipment.

2. Detailed description of the descaling and corrosion inhibiting Solution

The composition of the present invention includes as the non-toxic inhibitor from 40 to 200 parts per million, preferably from 60 to 100 parts per million (and most preferably 80 parts per million) of acridine orange. The chemical formula for acridine orange is: N,N,N'N'-tetramethyl-3,6 acridinediamine monohydrochloride. The use of this compound has been found to inhibit or block the anodic and cathodic sites in structural steel of the type that is commonly used in the fabrication of a variety of pieces of process equipment [9].

The benefits of using acridine orange (AO) are multifaceted and are as follows [10]:

1. AO has fast and direct protonation when added to acidic solutions. The protonation process is a charge transfer process, viz., flow independent.
2. The AO inhibitor molecules bind strongly to metal surfaces.
3. The free flat aromatic rings having a surface area of 38 A°, are bound in a plane which is parallel to the metal surface, such that the position of the positively charged hydrogen ring in AO is close to the predominant negatively charged electric layer on the metal surface.

The composition includes from about 5% to about 15%, by weight, hydrochloric acid, preferably from 5% to 10%, and most preferably 8% acid, which serves to remove most calcium, magnesium and iron oxides.

The composition also preferably includes 1% to 5%, by weight, preferably 1.5% of hydrofluoric acid, which aids in the removal of silicate containing scales [11]. The conjoint use of hydrochloric acid and hydrofluoric acid serves to accelerate the dissolution of many very hard and complex scale formations.

While various chelating agents can be employed in the composition and process of the present invention, such as EDTA, citric acid, HEDTA, etc., it has been found that a mixture of 2% citric acid and 2% EDTA is preferred since it is extremely effective in dissolving iron oxide deposits and also deposits containing copper oxides [12]. In point of fact, even sulfate-containing deposits will be dissolved when this mixture of chelating agents is employed.

The inclusion of from about 50 to about 200 parts per million (ppm), preferably 100 ppm of thiourea, will insure the maintenance of any dissolved copper in a soluble state. In the absence of such a copper complexing agent, copper oxides which are present in any scale, will dissolve and then plate out as metallic copper causing severe pitting of the industrial process equipment and the piping systems [13].

In addition, while it is optional, it has been found to be beneficial if the descaling composition includes about 0.1 grams/liter of a neutral emulsifying agent, such as alkyl benzene sulfonate to make it easier to penetrate in small cracks [14].

It has also been found that the benefits of the process of the present invention can best be achieved by employing a temperature of about 300 K or above for a period of about one (1) to about ten (10) hours, with eight (8) hours being preferred.

3. Procedure and Results

For a fuller understanding of the nature and objects of this invention, the following specific examples are given. These examples, however, are not to be construed as limiting the invention in any manner.

Example 1

A series of 5.0 cm x 2.5 cm mild steel specimens were prepared by cutting them from a single sheet of cold-rolled 1020 steel. The specimens were then polished under running tap water using a series of silicon carbide emery paper of 100, 400 and 600 grit, respectively, and then washed with distilled water and thereafter degreased with benzene and weighed on a Mettler AJ 100 electronic balance. One group of prepared steel specimens were fully immersed in 500 cc of a cleaning and descaling solution containing 8% hydrochloric acid, 1.5% hydrofluoric acid, 80 ppm of acridine orange, 2% citric acid, 2% EDTA, 0.1 g/1 of alkyl benzene sulfonate, and 100 ppm thiourea. This is referred to herein as the "inhibited solution".

Another group of steel specimens were also immersed in the foregoing cleaning and descaling solution except for the fact that the composition did not contain any acridine orange. This is referred to herein as the "uninhibited solution".

Potentiostatic polarization studies were carried out for both inhibited and uninhibited solutions under isothermal conditions at 303, 313, and 323 K and under controlled conditions of flow at 600, 1000, and 1400 rpm employing a potentiostat (Model 553-AMEL-Italy). The iron electrode was polarized from -900 mV to -100 mV (vs. saturated calomel electrode) at a sweep rate of 20 mV/min [15].

Another series of potentiostatic polarization studies were conducted for the heat transfer set of conditions, with a potential of -1000 mV being applied until a steady state heat flux was attained as indicated by the constant temperature reading from the thermocouples. Then the full polarization was carried out under isothermal conditions.

The duration of each of the weight loss experiments was eight (8) hours. At the conclusion of the test, the specimens were withdrawn, rinsed with water, then dried and reweighed. The percentage inhibitor efficiency (I%) was calculated by the following equation [16]:

$$I\% = W_u - \frac{W_I}{W_u} x100$$

Where: W_I is the weight of the inhibited sample, and W_u is the weight of the uninhibited sample.

Example 2

Performance of the Inhibitor (AO) under Controlled Conditions of Heat and Mass Transfer (Cathodic Region):

The effect of fluid flow, bulk temperature and heat transfer on the cathodic current density at a given cathodic potential of 0.1V below the corrosion potential are shown in Tables 1, 2, and 3 (Appendix I).

It can be seen from Tables 1, 2 and 3 that the cathodic current density values are independent of the flow rate, while the increase in temperature (bulk or interfacial) has a significant effect in stimulating the cathodic process [17]. This confirms the activation energy control of the cathodic reaction of hydrogen as the predominant reaction, as well as the lack of mass transfer effect on the adsorption processes of the inhibitor [18].

The increase in temperature (bulk or interfacial) has no significant effect on the inhibition efficiency, viz. the increase in temperature has no effect on the orientation of the adsorbed molecules or their geometry [19].

The high efficiency values are attributed to the ability of the inhibitor, acridine orange, to block the cathodic areas on the metal surface, leading to a significant reduction in hydrogen evolution [18].

Example 3

Acridine orange (AO) also showed high performance in blocking the anodic sites, as shown in the data presented in Tables 4, 5 and 6 (Appendix I). for both isothermal and heat transfer conditions [20].

The inhibition of the anodic sites (Tables 4-6) and cathodic sites (Tables 1-3) confirm the mixed effect of the inhibitor [15, 20].

The invention is not limited to the embodiments described above. The details involved in the description of these embodiments are for illustrative purposes only. Reasonable variations and modifications of this invention will be apparent to those skilled in the art without departing from the spirit and scope thereof.

4. Conclusion

What is claimed is:

1. A process for cleaning and inhibiting scale formation on the surfaces of process equipment which contacts circulating water and/or chemicals, which consists of: contacting the process equipment surfaces for a period of about 8 hours and at a temperature of about 300 °C and higher, which is effective to effect cleaning and/or scale inhibition with a aqueous composition consisting of:

   a) About 8%, by weight, of hydrochloric acid.
   b) About 1.5%, by weight, of hydrofluoric acid.
   c) A chelating agent which is a mixture of about 2%, by weight, of EDTA and about 2%, by weight, of citric acid.
   d) About 100 ppm of thiourea as a copper complexing agent.
   e) About 40 to about 200 ppm of acridine orange.
   f) Optionally a neutral emulsifying agent.

2. The process of claim 1, wherein the neutral emulsifying agent is present in the composition in an amount of 0.1 g/l.

Summary of the Invention

A highly effective industrial cleaning composition which is effective in descaling without causing corrosion has now been found which comprises a mixture of hydrochloric acid, hydrofluoric acid, one or more chelating agents, a surfactant, a copper complexing agent, and a nontoxic inhibitor, which serves to block the anodic and cathodic sites on the steel surfaces of the process equipment.

5. References

[1] Schmitt G., *et al*. (2009). Global Needs for Knowledge Dissemination, Research, and Development in Materials Deterioration and Corrosion Control. *World Corrosion Organization*. (http://www.corrosion.org/images_index/whitepaper.pdf).

[2] Li H., *et al*. (2011). Control of mineral scale deposition in cooling systems using secondary treated municipal wastewater. *Water Research* 45(2): 748–760.

[3] Vessakosol P., Charoensuk J. (2010). Numerical analysis of heat transfer and flow field around cross-flow heat exchanger tube with fouling. *Applied Thermal Engineering* 30(10): 1170–1178.

[4] Waly T. (2012). The role of inorganic ions in the calcium carbonate scaling of seawater reverse osmosis systems. *Desalination* 284: 279–287.

[5] Swietlika J. (2012). Corrosion in drinking water pipes: The importance of green rusts. *Water Research* 46(1): 1–10.

[6] Dolez P. I., Love B. J. (2002). Acid cleaning solutions for barnacle-covered surfaces. *International Journal of Adhesion and Adhesives* 22(4): 297–301.

[7] Wexler P. and Anderson B. (2005). *Encyclopedia of Toxicology* (2nd Edition): Hydrochloric Acid: 538–540 (by: Holstege C. P.). Academic Press, USA.

[8] Saremi M. and Yeganeh M. (2010). Corrosion behavior of copper thin films deposited by EB-PVD technique on thermally grown silicon dioxide and glass in hydrochloric acid media. *Materials Chemistry and Physics* 123(2–3): 456–462.

[9] Fink J. K. (2012). *Petroleum Engineer's Guide to Oil Field Chemicals and Fluids*: Chapter 6 Corrosion Inhibitors: 217–252. Elsevier, US.

[10] Sun L. *et al*. (2012). Graphene oxide adsorption enhanced by in situ reduction with sodium hydrosulfite to remove acridine orange from aqueous solution. *Journal of Hazardous Materials* 203: 101–110.

[11] Genuino H. C., *et al*. (2012). A review of hydrofluoric acid and its use in the car wash industry. *Journal of Industrial and Engineering Chemistry* 18(5): 1529–1539.

[12] Palma L. D. and Mecozzi R. (2007). Heavy metals mobilization from harbour sediments using EDTA and citric acid as chelating agents. *Journal of Hazardous Materials* 147(3): 768–775.

[13] Argañaraz M. B. Q., *et al*. (2010). Copper electrodeposition onto hydrogenated Si(1 1 1) surfaces: Influence of thiourea. *Journal of Electroanalytical Chemistry* 639 (1–2): 95–101.

[14] Song X-W., *et al*. (2012). Surface dilational rheological and lamella properties of branched alkyl benzene sulfonate solutions. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 412: 64–71.

[15] Al-Darbi M. M., *et al*. (2002). Protection of Mild Steel against Corrosion using Mixed Inhibitor Combinations. *NACE CORROSION-2002 Conference*. Denver, CO, USA. Paper No. 02013.

[16] Hegazy M.A. (2012). Evaluating four synthesized Schiff bases as corrosion inhibitors on the carbon steel in 1 M hydrochloric acid. Corrosion Science 65: 67–76.

[17] Parshin A. G., *et al*. (1982). The Influence of Heat Transfer on the Kinetics of Cathode Processes with Limiting Diffusion Stages. *Corrosion Science* 22(9): 845-855.

[18] Rozenfield I. L. (1981). *Corrosion Inhibitors*. New York: McGraw-Hill.

[19] Moccari A. A. (1999). Corrosion Inhibitor Evaluation for Materials used in Closed Cooling Water Systems. *Materials Performance* 38(9): 54-59.

[20] Singh P., *et al*. (2008). Adsorption and kinetic studies of L-leucine as an inhibitor on mild steel in acidic media. Applied Surface Science 254(18): 5927–5935.

6. Appendix I – Tables

TABLE 1

The Cathodic Current Density (mA/cm^2) for Uninhibited Chemical Cleaning Solution $\mathbf{I}_{c,u}$ and Inhibited Solution $\mathbf{I}_{c,I}$ and the Inhibition Efficiency **I%** under Isothermal Conditions. (Inhibitor Concentration 60 PPM)

	Temperature (K)								
	303			313			323		
RPM	$I_{c,u}$	$I_{c,I}$	I%	$I_{c,u}$	$I_{c,I}$	I%	$I_{c,u}$	$I_{c,I}$	I%
0	15	1.6	89	39	5.5	86	57	8.8	85
600	4.6	0.5	89	14	1.6	88.6	36	3.3	90.8
1000	4.6	0.46	90	14	1.6	88.6	34	3.0	91
1400	4.8	0.51	89.4	15	1.7	88.7	34	3.5	89.7

TABLE 2

The Cathodic Current Density (mA/cm^2) for Uninhibited Chemical Cleaning Solution under 60 kW/m^2 Heat Transfer Rate.
(The Interfacial Temperatures are Bracketed).

	Bulk Temperature (K)		
RPM	303	313	323
600	8 (322.7)	19 (330.5)	40 (339.9)
1000	7.3 (315.9)	17 (324.3)	39 (333.7)
1400	6.5 (312.3)	16 (321.6)	37 (331.4)

TABLE 3

The Cathodic Current Density $I_{c,I}$ (mA/cm^2) for Inhibited Chemical Cleaning Solution, under Heat Flux of 60 kW/m^2. I% is the Inhibitor Efficiency. Interfacial Temperature values are the same as in Table 2.

	Bulk Temperature (K)					
	303		313		323	
RPM	$I_{c,I}$	I%	$I_{c,I}$	I%	$I_{c,I}$	I%
600	0.65	92	2.3	88	4.2	89.5
1000	0.60	92	1.9	89	3.2	91.8
1400	0.58	91.1	1.7	89.4	2.8	92.4

TABLE 4

The anodic Current Density (mA/cm^2) for uninhibited Chemical Cleaning Solution $I_{a,u}$, Inhibited Solution $I_{a,I}$, and the Inhibitor Efficiency I% Under Isothermal Conditions.

	Temperature (K)								
	303			313			323		
RPM	$I_{a,u}$	$I_{a,I}$	I%	$I_{a,u}$	$I_{a,I}$	I%	$I_{a,u}$	$I_{a,I}$	I%
0	29	1.8	94	46	2.5	97	97	16	83.5
600	7	1.3	81	14	2.3	93.6	40	5.7	86
1000	6.8	1.3	81	15	2.0	86.7	36	4.8	87
1400	7.1	1.3	81.7	15	2.7	82	38	3.5	91

TABLE 5

The Anodic Current Density (mA/cm^2) for Uninhibited Chemical Cleaning Solution under 60 kW/m^2 Heat Transfer Rate (The Interfacial Temperatures are Bracketed).

	Bulk Temperature (K)		
RPM	303	313	323
600	13 (322.7)	23 (330.5)	63 (339.9)
1000	12 (315.9)	23 (324.3)	58 (333.7)
1400	11 (312.3)	20 (321.6)	48 (331.4)

TABLE 6

The Anodic Current Density $I_{a,I}$ (mA/cm^2) and the Inhibitor Efficiency I% for Inhibited Chemical Cleaning Solution, under 60 kW/m^2 Heat Transfer Rate.
(The Interfacial Temperature Values are the same as in Table 2)

	Bulk Temperature (K)					
	303		313		323	
RPM	$I_{a,I}$	I%	$I_{a,I}$	I%	$I_{a,I}$	I%
600	1.8	86	4.1	82	12	81
1000	1.6	87	3.7	84	7.8	87
1400	1.4	87	3.3	83	6.0	87