ACIDIZING FOR WELL STIMULATION WITH A CHROME SRP BARREL DOWNHOLE – HOW WORRIED SHOULD YOU BE?

Pinar Karpuz-Pickell, Ph.D., Levins Thompson

Lufkin Industries

Abstract: Surface coatings are often needed for sucker rod pump components to protect them from the harsh downhole environments of corrosives, formation solids, and even treatment chemicals. Most coatings have both positive and negative characteristics in protecting from each of the downhole aggressors, therefore further precautions must be taken to ensure the survival rate of components, given the economics of wellbore interventions.

A common dilemma when using chrome plating on barrels is although the high hardness is capable to protect against solids abrasion, the very method to effectively stimulate a well is proved to be detrimental to chrome. Hydrochloric Acid (HCl), a commonly used ingredient in stimulate solutions, will dissolve away the chrome when in contact. Once the chrome is compromised the life expectancy of the pump is greatly reduced.

Therefore, better understanding the deteriorating effects that acidizing has on chrome will better inform users on how to protect downhole equipment. Is the acid concentration and soak times being implemented too risky? Are they too conservative and sacrificing possible extra wellbore stimulation?

This study focuses on discovering the degradation rates of chrome coatings when placed in various concentrations of HCl solutions to observe the survivability of one of the industry's most useful coatings.

INTRODUCTION

Acidizing using hydrochloric acid is a common technique used to stimulate oil wellbores by removing formation damage and increasing permeability. The process involves injecting a solution of hydrochloric acid into the wellbore to dissolve minerals and open up pore spaces in the reservoir rock, which allows for increased flow of oil and gas to the wellbore. The acid solution is pumped down the wellbore at high pressure and left to react with the formation for a period of time, typically ranging from a few hours to a few days, depending on the specific formation and treatment design. After the acid has been allowed to react, it is removed from the wellbore, and the well is flushed with a neutralizing solution to prevent further acid corrosion. Acidizing using hydrochloric acid can be an effective way to increase oil production from wells that have low permeability or have become blocked or damaged over time.

Functional or hard Chrome electrodeposits are excellent coatings due to their unique combination of corrosion and wear resistance. Engineers use chrome, a barrier-type coating, in a multitude of corrosive environments. Accordingly, they find a wide range of applications in oil and gas industries, including rotors, ESP tooling, polished rods, and surface valves, to name a few. Sucker rod pump barrels are also Chrome plated, and their usage is so common that the plating properties are standardized by API 11AX. Despite being a great candidate for utilization in even the harshest downhole conditions, it is an industry-wide known fact that the operators need to use caution if a pump with a Chrome plated barrel will be used in an acid-treated well. Nevertheless, a question frequently raised by the operators to pump manufacturers is the extent of the damage of the acid treatment to Chrome plated barrels, since the concentrated acid that is poured behind the tubing gets spent during the well stimulation process, and the amount that enters the pump, if any, is expected to be incremental.

To examine this premise, this study focuses on exploring the degradation rates and behavior of different chrome coatings when placed in various concentrations of HCl solutions. Three chrome plated barrels obtained from different sucker rod pump vendors are studied, to observe the survivability of Chrome plated barrels in mild HCl exposure.

CORROSION RESISTANCE OF CHROME COATINGS

In literature, the corrosion resistance of hard Chrome is mostly studied quantitatively by salt spray testing [1]. A quantitative study on the effect of HCl on the corrosion resistance of a Chrome protected steel was carried out by Ajeel et.al [2] to report an almost linear increase in the corrosion rate (determined by weight loss method at a constant exposure time) with increasing HCL and H2SO4 concentrations. The coating's exposure to various chemicals is widely presented qualitatively in many sources [3], including ASM Handbook [4]. For immersion in HCl, the document does not even state a corrosion rate at any temperature or HCl concentration, and only reports "rapid attack".

The corrosion performance of hard chrome coatings is dependent up the pretreatment, plating, and post treatment processes [4]. For a finished coating, there are 2 main factors that contribute to the performance during service:

Protective Oxide Layer

The corrosion resistance of the chromium is mainly due to the chromium oxide on the surface. Chromium metal rapidly reacts with air or oxidizers to form a thin chromium oxide film, which is very passive. The level of protectiveness of the oxide layers on coatings is defined by Pilling-Bedworth (PB) ratio; the ratio of the metal oxide volume divided by the metal volume. A PB ratio of much less than or much greater than 1 denote a detrimental oxide formation. With PBR << 1, the oxide coating does not consume enough of the parent material compared to the volume of oxide and is too porous to be protective. In the case of a PBR >> 1, the oxide consumes too much of the base metal resulting in coating frequently falling off and exposing more base metal. The protective chromium oxide has a desirable Pilling-Bedworth (PB) ratio of 1.99 [5].

Hard Chrome coatings can be employed in some rather corrosive wellbore conditions; and the presence of harmful salts, sulfates, chlorides, and other corrosive compounds can be blocked out by the oxide protection layer.

Inhomogeneous Coating Structure

Chromium electrodeposits are not homogenous, since they contain microcracks that form during plating by stress relief in the chromium. The microcracks are filled by plating with material that contains more oxide and less metallic chromium than the bulk. Microcracks are not voids but are a three-dimensional network of areas that are more electrochemically active than the bulk of the chrome. These microcracks are not detrimental to corrosion resistance as one might expect, and there are two main reasons for this. First, as stated, the microcracks are not voids, but are areas with a structure and composition that are different from those of the bulk. Microcracks contain more chromium oxide which increases the deposits microhardness. According to Cymboliste [6], as deposit hardness increases or crystal size decreases, the rate of attack by sulfuric acid (H2SO4), and hydrochloric acid (HCl) decreases. Second, the microcracks spread out the corrosion over a larger surface area decreasing the corrosions penetration of the coating.

Regardless of their focus, any scientific paper written on Chrome coatings and their properties discuss the crack numbers and structures and relate those to the important service properties like corrosion and wear resistance. However, oil and gas industry standards do not cover or standardize the crack number or characteristics. Accordingly, a wide range of properties in the Chrome plated barrels are observed in the industry. These differences and their effects on corrosion resistance will be experimentally demonstrated in the further chapters.

TEST SETUP

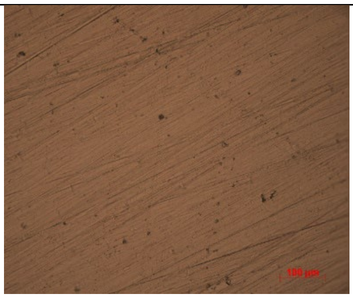
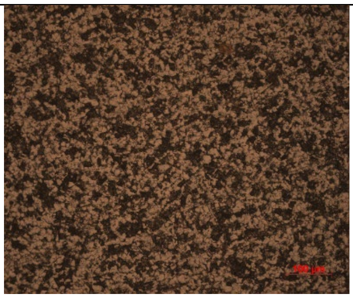
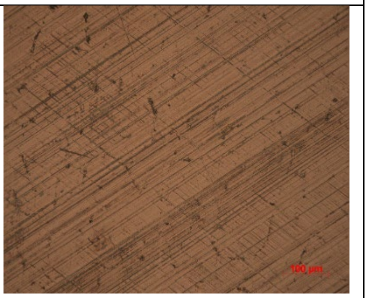
Three Chrome coated barrels; Chrome A, Chrome B and Chrome C, are used in this study. Test specimens are sectioned at around the central region of the barrels. Cross sections are prepared according to ASTM E-3 Standard. Crack structures are revealed by reverse electro-etching. Zen Core software is used for quantitative measurements methods.

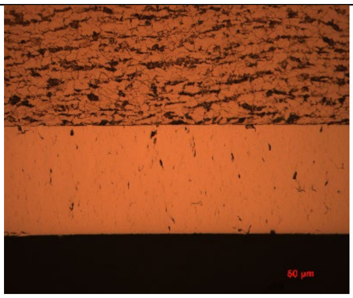
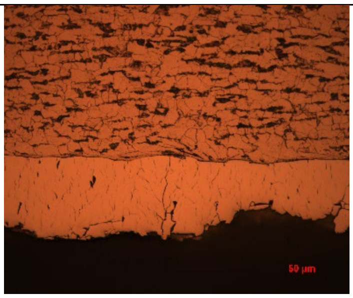
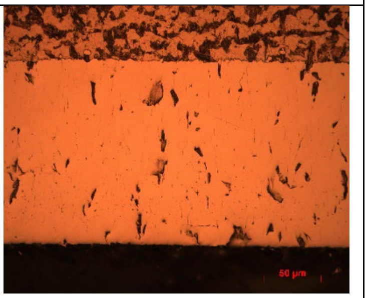
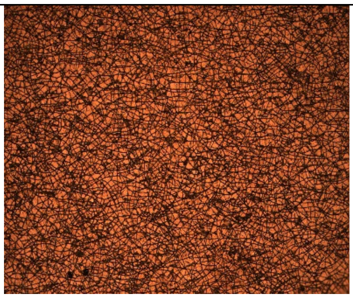
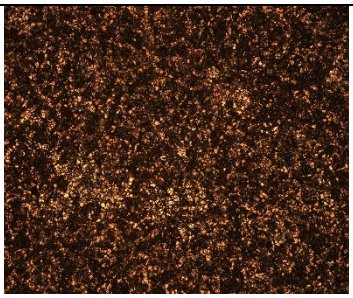
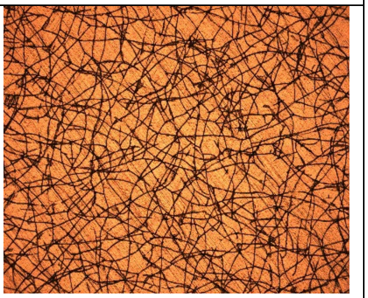
Chrome A has a bright appearance, does not have macrocracks and has very high hardness. Microcrack density is measured to be 4400 cracks per inch (cpi). Chrome B has a dark and dull appearance, with the magnified structure revealing surface defects. The structure has macrocracks and has a relatively lower hardness. Microcrack number could not be determined due to possible excessive nodulation and other defects on the surface. These defects are most likely caused by ineffective pre-treatment, plating, or post-treatment processes. Chrome C has a shiny appearance and the macrocracks were not observed throughout the cross section. It has a lower microcrack density of 1700 cpi.

The properties and characteristics of Chrome coatings A, B and C are summarized in Table 1.

Once the specimens are prepared and characterized, they are masked such that there is one square inch of the coated region exposed on the ID. 0.1%, 0.5%, 1%, 2%, 3%, 4% and 5% HCl solutions are prepared for immersion testing of Chrome A, Chrome B and Chrome C samples. The test specimens are immersed in the solutions and the degradation of the Chrome coating is observed visually. Once Chrome start dissolving, the aqueous chromium (II) ions turn the solution blue. In addition, gas bubbles start forming on the specimen surface, especially in relatively higher HCl concentrations. The time elapsed for the initiation of degradation is recorded based on the observation of the initial bubble formation and color change of the solution. Each experiment is performed three times, to ensure the repeatability of the results.

Table 1. Characteristics of Chrome coatings A, B and C

	Chrome A	Chrome B	Chrome C
			
Coating on ID			
Coating Thickness	101.4 microns	64.4 microns	169.0 microns (Double Chrome)

Coating Hardness (HV100)	1046.7	926.0	971.1
Coating Cross Section			
Coating Microcrack Structure			
Coating Microcrack Density	4400 cpi	N/A	1700 cpi

RESULTS and DISCUSSION

The average reaction times are plotted against HCl concentration for all 3 Chrome coating samples, as given in Figure 1. The results are also presented separately in Figure 1 (a), (b), and (c), as the details of the data points could be missed for Chrome B and C due to the large reaction time scale for Chrome A.

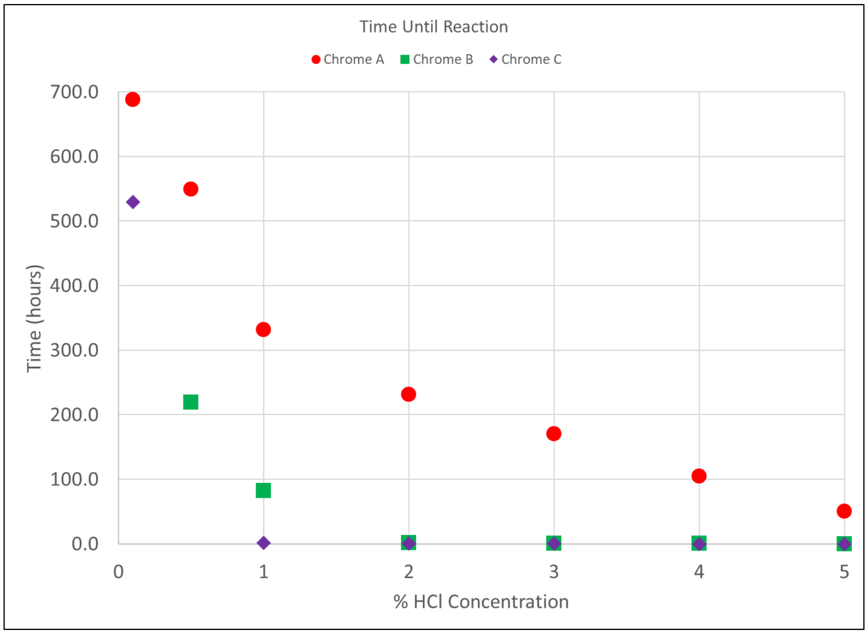


Figure 1. Average reaction time (days) vs HCl concentration (%)
(Note: Some datapoints are overlaid due to scale)

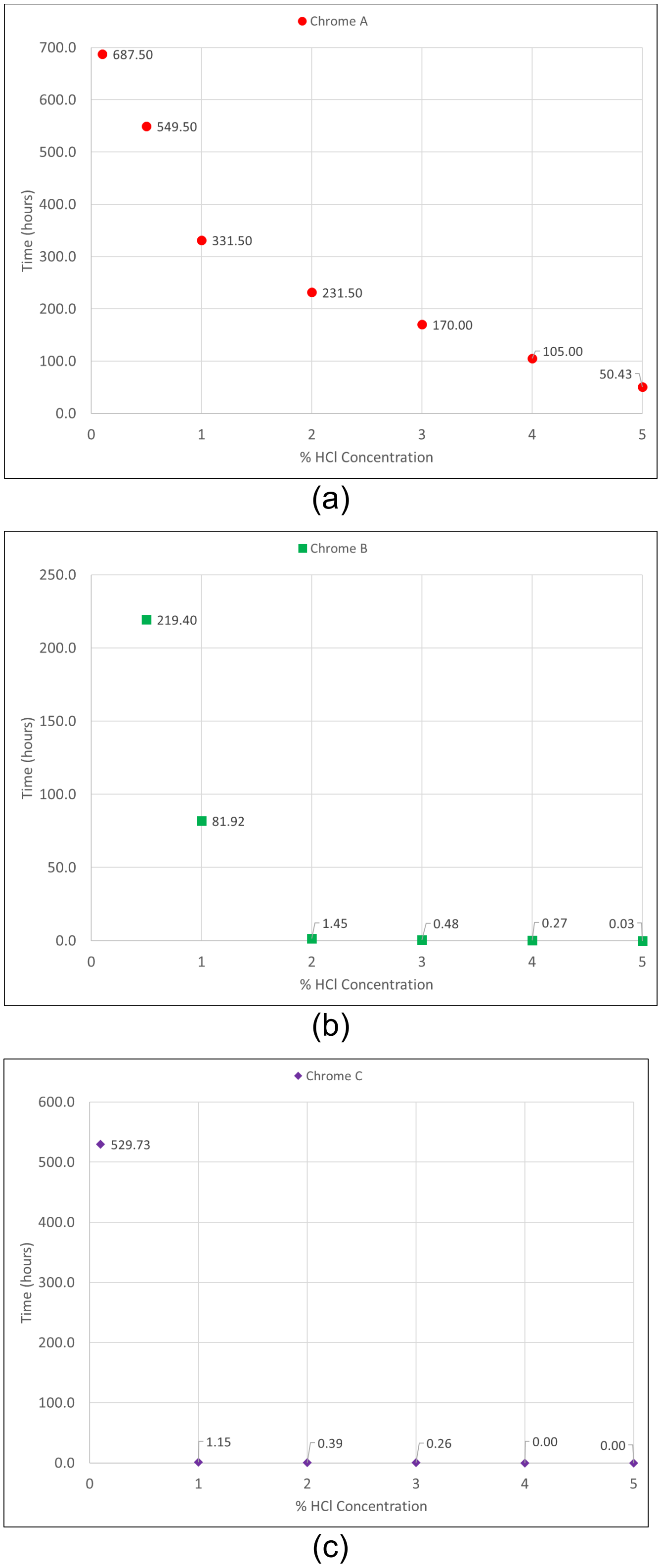


Figure 2. Average reaction time (hours) vs HCl concentration (%) for (a) Chrome coating A, (b) Chrome coating B and (c) Chrome coating C

Studying the experimental data and plots, it is observed that the time elapsed before the first signs of deterioration increases exponentially with decreasing HCl concentration. This time can also be associated with the destruction of the protective oxide layer, as Chrome would start to react with HCl immediately on contact once the protective barrier layer is gone. This effect is clearly observed in Chrome A, whereas for Chrome B and Chrome C, exposure of the Chrome coating to HCl occurs very fast for all test concentrations above 1%. Regarding all the data, 1%HCl can be considered a threshold value for oxide layer deterioration, when there are no macrocracks or other visible coating defects are present in the coating. HCl concentrations below this value require longer exposure times for the dissolution of the Chrome coating at room temperature, regardless of their behavior at the concentrations above 1% HCl.

The significant superiority of Chrome A over Chrome B and Chrome C in resistance to HCl attack can be attributed to its high hardness and high microcrack density. Chrome B clearly has macrocracks and other plating defects, which led to almost instantaneous HCl attack in concentrations higher than 0.1%. Chrome C did not have the macrocracks or visible plating defects, and performed slightly better than Chrome B despite not performing as good as Chrome A with the highest hardness and microcrack density.

CONCLUSION

This study focuses on the degradation rates of Chrome coatings in various concentrations of HCl solutions. Three commercial Chrome coated barrels with different physical and microstructural properties were utilized. Studying the results, it was observed that lower HCl concentrations led to higher recorded times required for degradation to start, regardless of the Chrome coating characteristics, as expected. In addition, Chrome coating characteristics are shown to play an important role in the HCl corrosion resistance of the structure. Higher crack counts, and absence of macrocracks and other plating defects led to longer reaction times.

REFERENCES

[1] Santos, B. A. F.; Serenário, M. E. D.; Pinto, D. L. M. F.; Simões, T. A.; Malafaia, A. M. S.; Bueno, A. H. S., Evaluation of Micro-Crack Incidence and their Influence on the Corrosion Resistance of Steel Coated with Different Chromium Thicknesses, Rev. Virtual Quim., 1984

[2] Ajeel, S. A., Waadulah, H. M., Sultan, D. A., Effects of H2SO4 and HCL Concentration on the Corrosion Resistance of Protected Low Carbon Steel:, technical report, 2012

[3] ASM Handbook, Volume 13: Corrosion

[4] Jones, A.R., Corrosion of Functional Chromium Electrodeposits, Technical Report

[5] Eriksson, M. Sliding wear performance of electroplated hard chromium and autocatalytic nickel-phosphorus coatings at elevated temperatures Master Thesis, 2014

[6] M. Cymboliste, T. Electrochem. Soc., Vol 73, 1938, p 353–363