

## **CORROSION OF 316L STAINLESS STEEL TUBES OF HIGH PRESSURE HEAT EXCHANGER**

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The study aims to estimate causes for 316L stainless steel tubes failure in chloride contaminated environment.

All the conditions were established and studied like temperature difference, thermal stresses, oxygen content and chloride concentration.

All the observations on the performed tests suggest that chloride does not affect 316L stainless steel cracking deeply, but there was a conjugate effect appeared when thermal stresses exists. Uniform corrosion was observed in the case of oxygen film absences.

Visual and microscopic inspections have been used to observe the effect of chloride and oxygen concentration on corrosion form.

### **KEY WORDS**

Stress corrosion, stainless steel, thermal cracking, chlorides.

## INTRODUCTION

Stress certainly plays a role in the stress corrosion cracking SCC process, but it should be pointed out that not all types of stresses facilitate stress corrosion. Compressive stresses may even be deliberately introduced to the surfaces by shot peening to combat SCC. The stresses imposed upon the structures during service seldom cause SCC because the applied loads are usually limited by a generous factor of safety and are well below the yield points. In fact, SCC is often caused by residual stresses generated during forging, assembly, or welding <sup>[1]</sup>.

Chloride stress corrosion cracking (CSCC) is certainly not a new problem nor is it specifically related to tubing bundles. In fact, controlling or eliminating this type of failure is much more attainable in a remanufactured tubing bundle than with field construction. 316SS and 304SS are particularly susceptible to this type of stress corrosion and 316SS is the most commonly used grade of SS tubing. A combination of factors must be present before CSCC is created. Generally these factors are agreed to be:

- Residual or applied stress in the tube.
- Temperatures above 95°C (200°F).
- The presence of free chlorides.
- Crevices or surface scratches.
- Wet/dry or damp locations.<sup>[2]</sup>

There are many purposes for corrosion monitoring in industrial systems. These purposes generally include one or more of the following:

- Diagnoses of corrosion problems.
- Monitoring of corrosion control methods (e.g. inhibition, pH control, etc.).
- Advanced warning of system upsets leading to corrosion damage.
- Invoke process controls.
- Determination of inspection and/or maintenance schedules.
- Estimation of use service life of equipment<sup>[3]</sup>.

However, there are several basic aspects of corrosion monitoring that are often over looked. First, corrosion assessment can be complex since industrial process operations provide a wide variety of dynamic environments and service conditions. Secondly, no single method will necessarily work or provide optimum results in all applications. In some cases, multiple technologies may be needed in combination to provide accurate and reliable corrosion monitoring information that can be used with confidence to make engineering decisions<sup>[4]</sup>.

The purpose of this paper is to introduce several of the more common techniques utilized for monitoring corrosion in industrial process operations and to define their advantages and

limitations. Additionally, examples will be presented on how these techniques are employed for in-plant corrosion monitoring.

Availability of free chlorides, elevated temperatures and residual/applied stress will always be present. While wet/dry locations and surface defects are particularly likely spots where chloride stress corrosion will occur <sup>[5]</sup>.

Many modifications were developed to improve 316L stainless steels resistance towards chlorides like adding molybdenum (2%min.) to 316L alloy <sup>[2]</sup>, releasing all residual stress <sup>[2]</sup>, or by laser shock waves <sup>[6]</sup>, also by vacuum induction melting (VIM) practice which provides high purity 316L stainless steel alloy having higher hardness <sup>[7]</sup>.

On coming, investigation will tend to characterize causes for tubes failure and the possible ways to increase the lifetime of tubes by performing multiple tests to verify the cause of tube failure.

## **EXPERIMENTAL WORK**

Weight loss technique was used to perform the experimental, also visual and microscopic inspections were performed.

### **Materials**

The material used was AISI 316L stainless steel having the composition:

C: 0.03, Mn: 1.5, Si: 1.5, Cr: 25, Ni: 22, Mo: 2.5

### **Metal Specimens**

Specimens 3.5cm long, 2cm inside diameter and 2.3 outside diameters were cut and grounded, they were degreased with annular benzene and acetone, then annealed in vacuum oven at 1000°C for 1hr and furnace cooled to room temperature. This was carried out in order to remove mechanical stresses, after annealing, the specimens were stored in a desiccator over silica gel until use. Half of the specimens were cut manually (cold work specimens by manual saw) and grounded (with out thermal treatment), they were degreased as mentioned above and also stored in a desiccator over silica gel.

### **Solutions**

Analar magnesium and calcium chloride and hydrochloric acid were used. Solutions were made up with double distilled water.

Throughout the experiments multiple concentrations of chloride were tested as a corrosive solution (10, 15, 20, 25 & 30 ppm Cl<sup>-</sup>).

### **Procedure**

The tests were carried out in 500-ml conical flask; its neck was fitted with water condenser, it was filled with test solution to a level such that the specimens were completely covered with the solution. Temperature was held constant in a constant temperature heating mantel at  $115 \pm 0.5^{\circ}\text{C}$ . A stream of air was

introduced (10cc/min) to the conical flask to test the effect of oxygen content on annealed and cold worked specimens. The test flask was allowed to come to thermal equilibrium before immersing the specimens. Each test was made in duplicate as each test was repeated. Every test was lasted for 12 days at boiling temperature. After each test, the specimens were washed with running tap water, scrubbed with a piece of wet cotton to remove adherent corrosion products, then washed with running tap water followed by distilled water and dried on a clean tissue, rinsed with analar benzen, and left in a desecator over silica-gel for two hours before weighing them accurately to the fourth decimal.

## **RESULTS AND INTERPRETATIONS**

### **A-Annealed Specimens**

#### **A-1.Influnce of Chloride Concentration**

The results are presented in table (1) show the influence of chloride concentrations on corrosion rate of 316L stainless steel in presence and absence of oxygen. Hydrochloric acid evolution is a measure of the acid that will be formed during steam distillation under prescribed conditions. It is formed by hydrolysis of magnesium and calcium chlorides, collected in the condensed steam from water (or any aqueous reacted mixture) forming a solution that is corrosive to the material of a reactor or condenser (specially the upper part),so the results show that

corrosion rates increase as chloride concentration increase. Visual inspection shows dark points of the specimens surfaces, when these points were checked microscopically ( $1\times 1200$  power) it was realized that these points are shallow pits (localized type corrosion).

### **A-2.Influnce of Oxygen Concentration**

The results are presented in table (1) show that the absence of oxygen accelerates corrosion rate at all chloride concentrations, because the presence of oxygen accelerates corrosion at the range of 25-88°C, above this range (beyond boiling temperature and higher than boiling temperature) oxygen acts as a protecting film for metal surface<sup>[8]</sup>. It was realized under microscopic inspection that pit is the same as in absence of oxygen (didn't become deeper) so there is no doubt that corrosion rate increases due to thinning of metal surface (uniform corrosion) as shown in figure (1), visually a darken-red color layer of corrosion product was realized before cleaning, this layer didn't exist in the presence of oxygen.

## **B-Cold Work Specimens**

### **B-1.Influnce of Chloride Concentration**

The results are presented in table (2) show the marked increase of corrosion rate of 316L stainless steel in presence and absence of oxygen at the same chloride concentrations, visually the dark points becomes larger than those of case (A), and microscopic inspection shows that pits become deeper, referring

to figure (2) the difference in corrosion behavior in the presence microscopic inspection shows that pits become deeper, referring to figure (2) the difference in corrosion behavior in the presence and absence of thermal stresses (cold and annealed specimens) can be clearly seen.

### **B-2.Influence Of Oxygen Concentration**

The results are presented in table (2) show that the absence of oxygen accelerates corrosion rate at all chloride concentrations, also it was realized under microscopic inspection that pit is the same as that in absence of oxygen (didn't become deeper) .Thinning of metal surface didn't accelerate by thermal stress so the darken-red color layer of corrosion product wasn't become thicker.

## **DISSCUSION**

Chloride ions may cause stainless steel to corrode depending on temperature and concentration <sup>[9]</sup>. In the case of high pressure operation heat exchanger there is no marked effect of pressure on corrosion rate(uniform or localized type)<sup>[10]</sup>, but when stresses exist –thermal or mechanical- localized corrosion (observed pits) may be an initiation of stress corrosion cracking (SSC) which appears clearly after a period of time as shown in figure (3) and (4). The only way to completely eliminate this would be to fully anneal the tubing after it is installed which is not a practical solution. The next best solution is to minimize the amount of unrelieved stress in the tubing. The stress comes from

two sources, bundle manufacturing and installation. There is no inherent advantage with different assembly or construction methods. The temperature will be determined by the process fluid and the application. The only consideration is that more is not better; keep temperatures as low as possible.

### **CONCLUSIONS**

- 1) It is shown that the form of stress cracking was resulted from the conjugate effect of temperature drop and the presence of chloride ions.
- 2) The pitting corrosion by chloride ions was the initiation point of stress corrosion cracking.
- 3) Injection of neutralizing agent affects the corrosion inhibition slightly.
- 4) The absence of protecting film of oxygen causes a uniform corrosion and does not affect the initiation of pits.

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**Table (1) Corrosion Rates of 316L stainless steel (annealed specimens) at 115°C in various concentrations of chloride solution.**

<b>NO.</b>	<b>Chloride Concentration (ppm)</b>	<b>Corrosion Rate (mdd) (with out O<sub>2</sub>)</b>	<b>Corrosion Rate (mdd) (with O<sub>2</sub>)</b>
1	10	68.143	57.521
2	15	74.435	62.425
3	20	81.689	73.641
4	25	97.206	80.547
5	30	113.708	95.412

**Table (2) Corrosion Rates of 316L stainless steel (cold worked specimens) at 115°C in various concentrations of chloride solution.**

<b>NO.</b>	<b>Chloride Concentration (ppm)</b>	<b>Corrosion Rate (mdd) (with out O<sub>2</sub>)</b>	<b>Corrosion Rate (mdd) (with O<sub>2</sub>)</b>
1	10	112.254	82.543
2	15	125.653	88.414
3	20	138.512	102.764
4	25	152.420	111.947
5	30	182.624	115.513

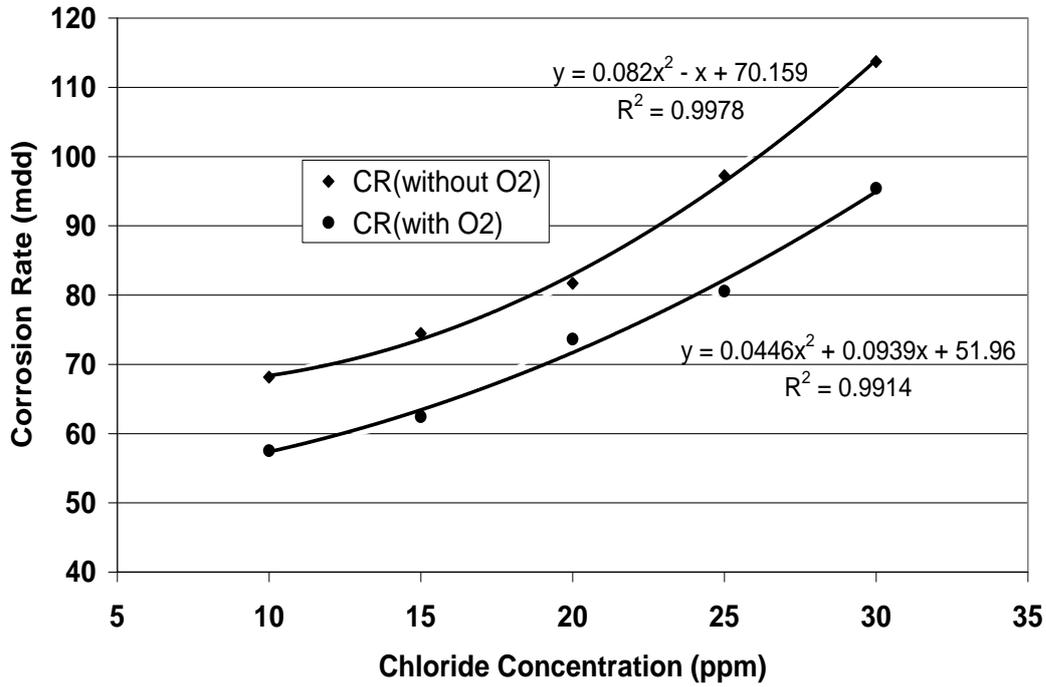


Figure (1) Effect of Chloride Concentration on Corrosion Rate of 316L-Stainless Steel (annealed specimens) at 115°C.

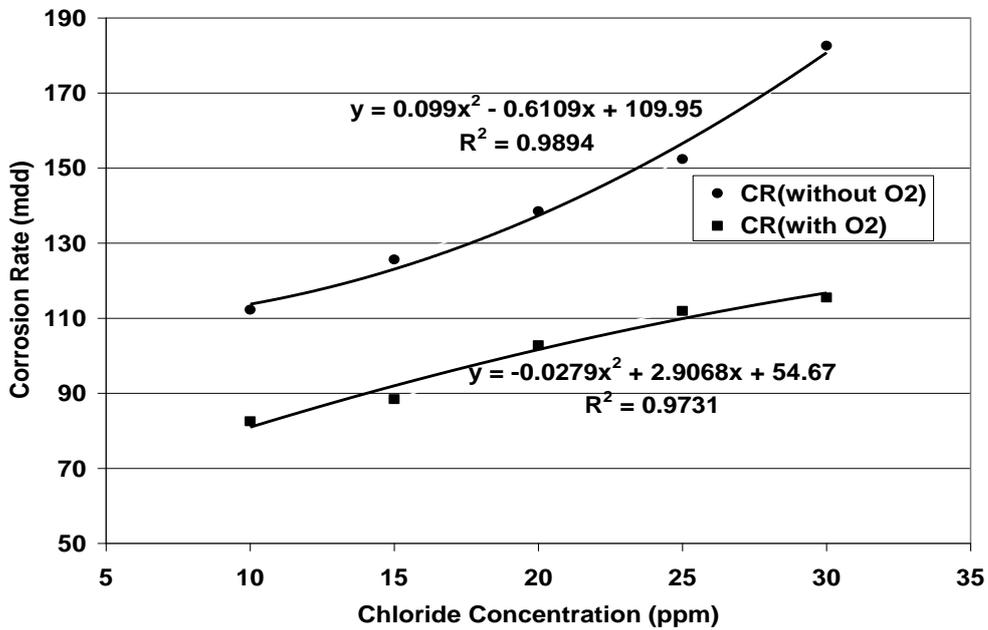
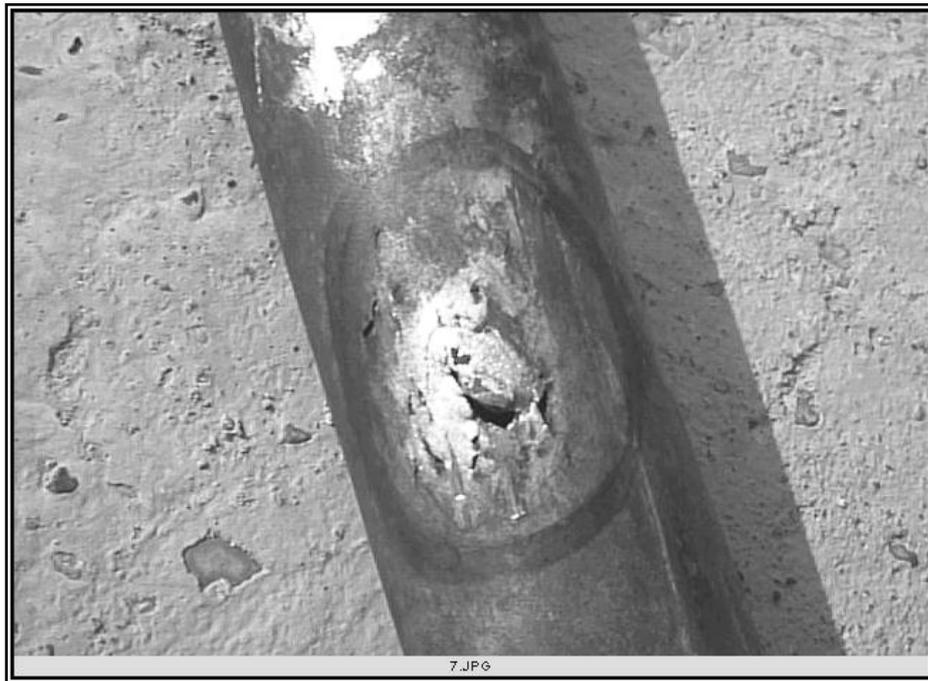
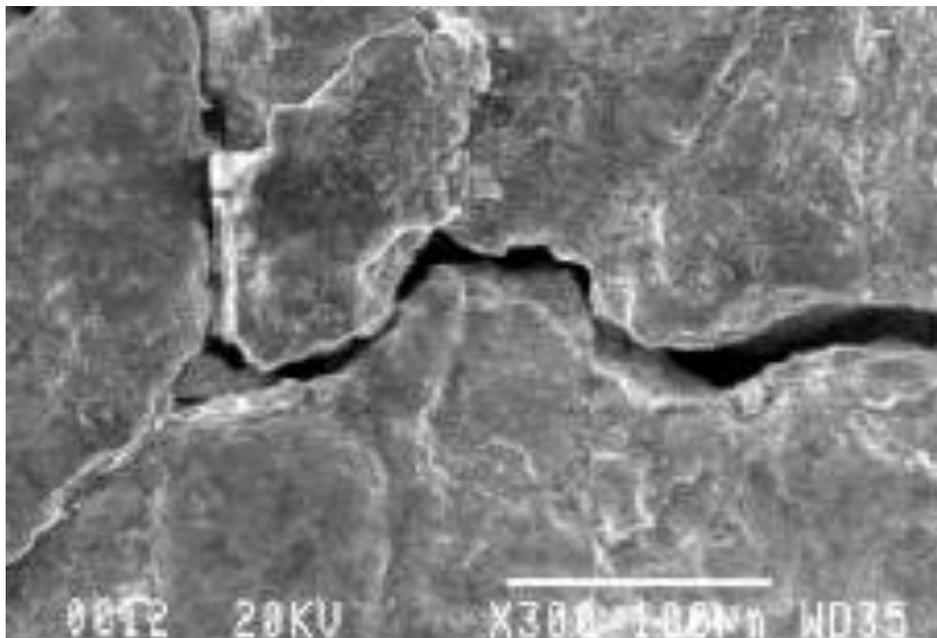


Figure (2) Effect of Chloride Concentration on Corrosion Rate of 316L-Stainless Steel (cold worked specimens) at 115°C.



**Figure(3) Stress Corrosion Cracking of 316 L Exposed to Chloride Solution at 115° C**



**Figure(3) Micro-photograph of chloride induced stress corrosion cracking of 316SS in 30 ppm chloride solution in 115°C water.**

## التآكل بسبب الإجهاد في أنابيب نوع 314 الحديد المقاوم للصدأ

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### الخلاصة

تهدف هذه الدراسة لمعرفة أسباب تآكل الحديد المقوم للصدأ 316 في المحاليل التي تحوي على أيونات الكلورايد. تم دراسة كافة التأثيرات و الظروف العملية مثل فرق درجات الحرارة و الاجهاد الحراري و محتوى الاوكسجين و الكلورايد. كل الملاحظات تم تثبيتها بخصوص التجارب التي اجريت و تم ملاحظة أن وجود تراكيز من أيون الكلورايد لا يؤثر بقدر ملموس على الاجهادت الحرارية. لوحظ وجود تآكل منتظم في حالة غياب غشاء الاوكسجين الواقى. تم اجراء فحص بصري و مايكروسكوبي لبيان تأثير الاوكسجين و الكلورايد.

### الكلمات الدالة

تآكل إجهادي، حديد مقاوم للصدأ، إجهاد حراري، أيونات الكلورايد.