Stainless steel: Two case studies of corrosion. Importance of choosing the components with which they are in contact and cleanliness of manufacturing on the behaviour of installations

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Résumé :

L'emploi des aciers inoxydables dans les installations de distribution reste marginal car des corrosions entraînant des percements ou des fuites intempestives sont malheureusement souvent constatées. Ces dégradations rapides résultent généralement de la qualité de l'environnement de fabrication des éléments en acier inoxydable et notamment de la contamination des parois de l'acier par des particules ferreuses ou de traces d'oxydes formés lors des opérations de soudage. Elles peuvent aussi résulter du choix inadéquat de la nature d'éléments avec lesquels l'acier inoxydable est en contact.

Les deux exemples de corrosions présentés sont les suivants :

1- Cas de vannes de 900 mm de diamètre en acier austéno-ferritique 1.4460, dont les deux demi-corps sont assemblés avec des joints en graphite. Ces joints créent une pile galvanique qui conduit à l'attaque rapide de l'acier. Cette attaque a entraîné l'apparition de fuites après quelques semaines de fonctionnement. D'autre part, ces vannes présentaient de très nombreux points d'attaques tant sur les parties externes qu'internes qui résultaient de contaminations ferreuses survenue pendant l'usinage en atelier.
2- Cas de ballons de production d'eau chaude sanitaire en acier inoxydable austéno-ferritique 1.4362 ou en acier ferritique 1.4521 dont la tenue en eau relativement riche en chlorures (200 à 250 mg/l) n'excède pas quelques mois. Les principales causes de corrosion sont l'attaque par piqûre sur les zones affectées thermiquement au voisinage de cordons de soudure, et la présence de pollutions ferreuses sur l'ensemble des parois. La mise en place d'un banc d'essais permettant de simuler les conditions de fonctionnement dans ce type d'eau a permis de mettre en évidence notamment l'influence de la température de l'eau , des conditions d'inertage durant l'opération de soudage ainsi que la présence de pollutions ferreuses sur la vitesse de piquration des zones affectées thermiquement.

Ces exemples confirment la nécessité de choisir des composants constitués de matériaux compatibles avec les aciers inoxydables, de choisir des conditions de soudage adaptées à chaque nuance d'acier et d'aménager les ateliers de fabrication de manière à éviter les pollutions ferreuses. Si le recours à la décontamination-passivation est généralement conseillé, il ne doit pas être considéré comme la solution permettant de compenser les mauvaises conditions environnementales et technologiques de fabrication.

Abstract:

The use of stainless steels in distribution facilities is marginal because of corrosion causing openings or leakages are unfortunately often occurring. This rapid deterioration typically caused by environmental quality of the stainless steel manufacturing and especially the contamination of the walls of steel by ferrous particles projected during grinding or traces of oxides formed during welding operations. They may also result from improper choice of the nature of elements with which the stainless steel is in contact.

The two examples of corrosions presented are:

1. The case of valves ∅ 900 mm made of duplex stainless steel (1.4460), whose the two half-bodies are assembled with graphite seals. These seals create a galvanic cell which leads to the rapid attack of the steel. This attack resulted in the appearance of leaks after a few weeks of operation. Moreover, these valves had very many attacks both the external and internal portions which due to the contamination by ferrous particle occurring during machining in the workshop.
2. Case of hot water tanks made of duplex (1.4362) or ferritic (1.4521) stainless steel which held does not exceed a few months when they are fed by water containing chlorides in the range of 200-250 mg/l. The main causes of corrosion pitting are attack on the heat affected zones near the weld line, and the presence of ferrous pollution on all walls. The setting up of a test bench to simulate the operating conditions in this type of water allowed to highlight, in particular, the influences of the water temperature, of the conditions of welding operation and of the contamination of heat affected zones by ferrous particles on the pitting rate.

These examples confirm the need:

- to choose components made of compatible materials with stainless steel,
- to select welding conditions appropriate to each grade of steel,
- to arrange the fabrication shops to avoid ferrous contamination.

If the use of decontamination and passivation is generally recommended, it should not be seen as the solution to compensate for poor environmental and technological manufacturing conditions.

Zusammenfassung:

Die Verwendung von Edelstählen für Versorgungsleitungen ist marginal, da unglücklicherweise häufig Korrosion auftritt und dann Öffnungen und Lecks verursacht. Diese schnelle Zerstörung wird typischerweise von der Qualität des Umfelds bei der Edelstahlproduktion verursacht, insbesondere von der Kontamination der Stahlwandungen durch eisenhaltige Partikel, die beim Schleifen auftreffen, oder durch Spuren von Oxiden, die sich beim Schweißen bilden. Sie kann

aber auch auf der falschen Wahl der Art der Komponenten beruhen, mit denen der Edelstahl in Kontakt ist.

Es werden zwei Beispiele für Korrosion vorgestellt:

1. Im ersten Fall geht es um Ventile (∅ 900 mm) aus Duplex-Edelstahl (1.4460), deren zwei Gehäusehälften mit Graphitdichtungen montiert werden. Diese Dichtungen bilden eine galvanische Zelle, die dazu führt, dass der Stahl schnell angegriffen wird. Dieser Angriff führt zum Auftreten von Lecks nach wenigen Betriebswochen. Darüber hinaus waren diese Ventile sowohl außen als auch innen an vielen Stellen angegriffen. Das lag an der Kontamination mit eisenhaltigen Partikeln während der Bearbeitung in der Werkstatt.
2. Im zweiten Fall geht es um Warmwassertanks aus Duplex-Edelstahl (1.4362) oder ferritischem Edelstahl (1.4521), deren Haltbarkeit nicht über ein paar Monate hinausgeht, wenn sie mit Wasser gefüllt werden, das Chloride in einer Größenordnung von 200 - 250 mg/l enthält. Die Hauptursachen für Lochfraß sind ein Angreifen der erwärmten Bereiche in der Nähe der Schweißnaht und das Vorhandensein von eisenhaltigen Verschmutzungen auf allen Wänden. Die Einrichtung einer Prüfanlage zur Simulation der Betriebsbedingungen dieser Art von Wassertanks gestattete insbesondere, die Einflüsse der Wassertemperatur, der Bedingungen beim Schweißen und der Kontamination der erwärmten Bereiche durch eisenhaltige Partikel auf die Geschwindigkeit des Lochfraßes herauszuarbeiten.

Diese Beispiele bestätigen die Notwendigkeit,

- Komponenten aus mit Edelstahl kompatiblen Materialien zu wählen,
- für jede Stahlqualität geeignete Schweißbedingungen zu schaffen,
- die Fertigungsabteilung so einzurichten, dass eine Kontamination mit eisenhaltigen Partikeln vermieden wird.

Auch wenn im Allgemeinen der Einsatz von Dekontamination und Passivierung empfohlen wird, sollte darin keine Lösung gesehen werden, um schlechte Fertigungsbedingungen hinsichtlich Arbeitsumfeld und Technologie zu kompensieren.

INTRODUCTION

The use of stainless steels in distribution facilities stays marginal because of corrosion causing openings and leaks are unfortunately often occur. These rapid deteriorations typically caused by environmental quality manufacturing of stainless steel components including the contamination of the walls of steel with ferrous particles or traces of oxides formed during welding operations. They may also result of an improper choice of the nature of elements with which the stainless steel is in contact. The various causes of corrosion are illustrated by the two next examples.

1. CASE OF GALVANIC CORROSION ON DUPLEX STEEL 1.4460

1.1.- Background

In the framework of the development of a transportation facility and distribution of water in Libya, two pumping stations were built between 2004 and 2008. The pumping stations are supplied by ∅ 2800 mm steel mains. Feeding and outlet ∅ 600 mm pipes of each pump are also made of steel. All these pipes are protected by a cement mortar lining.

Each station is fitted with ∅ 900 mm flow control valves. The valves are maid of duplex stainless steel AISI 329 (1.4460) for the valve bodies and for the ball. The Q-trim is made of 316L austenite steel (1.4404) (Fig. 1.1). The balls are coated with hard chrome to reduce friction when changing position.

The choice of these materials has been guided by the concentration of chlorides in the water carried, which by its origin can reach 350 mg/l.

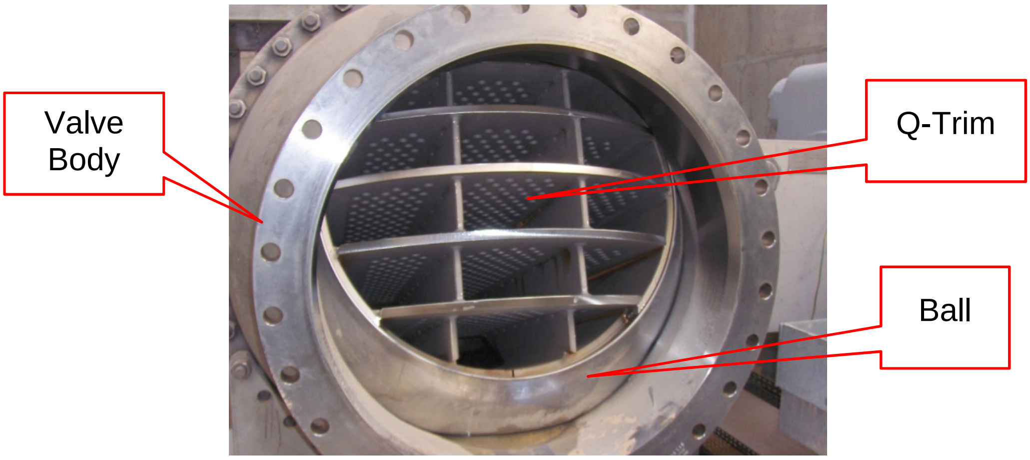


Fig. 1.1

Although the choice of a noble material, three main defects of manufacturing and design have led to significant corrosion of the valve elements.

1.2.- First defect

A few weeks after water filling of the pumping stations, the corrosions appeared on the welds of Q-trim plates (fig.1.2). Despite a local pickling followed by passivation, these traces of attacks appeared again immediately after filling.

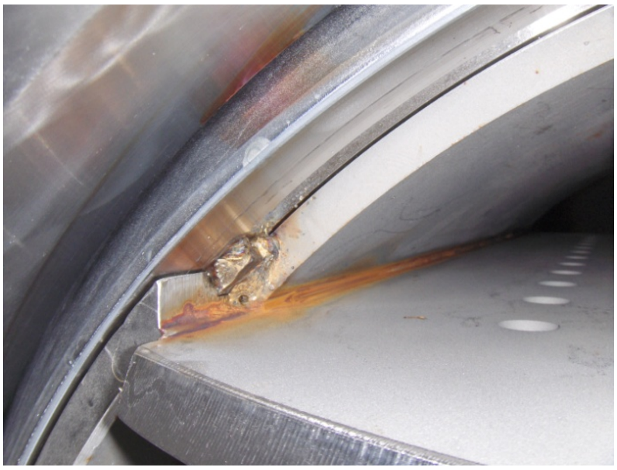


Fig. 1.2

After careful inspection of the valves, the Finnish manufacturer has diagnosed the presence of mild steel shims used for mounting plates and were not removed during welding. These shims are corroded very quickly as a result of galvanic couple formed by stainless steel and mild steel.

Although this corrosion does not substantially affect mechanical characteristics of the Q-Trim, it was decided to remove the valves for repairing them in the Finnish workshop.

1.3.- Second defect

When dismantling the valves it was found that the hard chromium coating of the ball corroded particularly under the sealing joint made of super duplex stainless steel (fig. 1.3).

Fig. 1.3

The coating deposited by electroplating directly on the duplex steel without nickel sublayer had a high porosity. The presence of pores in the coating allowed to maintain contact between the duplex and the water promotes the formation of galvanic cells that the support metal is the anode. The valve being not in use, the ball remains in the same position over several weeks. Thus the attacks are particularly located in the areas where the medium is confined that is to say under the sealing joint. Fig. 1.3 shows that the corrosion also appeared on the flow bore edges of the ball.

Considering the porosity of the chromium coating and the extent of corrosions, the manufacturer proposed to substitute a coating consisting of tungsten carbides and chromium. According to the manufacturer, this type of coating is best suited for contact with corrosive environments. Indeed, it also contains nickel and which constitutes a sealed reagent which screens the duplex steel.

1.4.- Third defect

When reassembling the valves after repairing, the manufacturer has replaced without notifying the customer, PTFE gasket sealing the two halves of valve body with graphite gaskets. According to the manufacturer, this type of joint harder than PTFE has a greater longevity under a pressure of 20 bars that can be reached downstream of the two pumping stations.

But after two months of operation, during an inspection of works reception there was very large craters of corrosion on the sealing surfaces (Fig. 1.4). On fig. 1.5 we can see the graphite gasket still in place in the female part and traces of attacks in the immediate vicinity of the gasket.

Fig. 1.4

Fig. 1.5 : Female body with the graphite gasket ;
Corrosion craters are visible near the gasket

The manufacturer explained that corrosion by the excessive chloride content of the water. But he finally admitted that the corrosion results from galvanic corrosion due to the couple created by the presence of the graphite gasket whose potential is very high and similar to that of gold or platinum.

On the other hand, the implementation of this graphite gasket requires special precautions because of the high friability of the material. It was noted that other points of corrosion had been initiated by graphite dust deposited during assembly (Fig. 1.6).

Fig. 1.6

1.5.- Ferrous contaminations

Finally, very many points of attack were found on the walls of the valve body both inside (Fig. 1.7) than outside.

Fig.1.7

This corrosion results from the presence of iron particles or iron oxide on the walls. These particles come from grinding operation of carbon steel or even duplex. Indeed, the workshop of the valves has no dedicated area for stainless steels work and flying particles during grinding castings can reach the walls of adjacent valves during machining.

During transport by sea between Finland and Libya, the iron particles on the surface of the valves were oxidized in contact with the salty air. Thus, when opening containers arriving on site, the valves appeared already corroded.

This corrosion results from the presence of iron particles or iron oxide on the walls. These particles come from grinding of carbon steel or even duplex. Indeed, the workshop of the valves has no area dedicated to the work of stainless steels. The projections of the ferrous particles generated by grinding of cast pieces can reach the walls of neighboring valves during their machining.

During transport by sea between Finland and Libya, the iron particles on the surface of the valves were oxidized in contact with the sea air. Thus, when opening containers arriving on site, the valves appeared already corroded.

While taking into account the thickness of the walls, these points of attack have no effect on durability of valves, we asked to conduct a pickling followed by passivation mainly to preserve the aesthetics of the stainless steel.

2. CASE OF PITTING CORROSION IN HOT WATER TANKS

2.1.- Background

The company ELM Leblanc sells for many years gas boilers fitted with hot water tanks. These tanks are made of stainless steel assembled by welding. Until 2008, the only grade used was austenitic steel 316L (1.4404). These tanks were mainly sold in France. The very low number of cases of corrosion of these tanks was not such as to call into question the reliability of that production.

With the rising cost of this grade, due to the increase in nickel prices, ELM Leblanc had to be oriented towards the use of grades less rich or not containing nickel (austenitic-ferritic steel, 1.4362 and ferritic steel 1.4521). The choice of these grades was particularly guided by their resistance to corrosion which is equivalent in terms of PREN that stays around 25 as the 316L grade. These new grades have also not led to significant disturbances in the French market for ferritic steel and on the UK market for duplex steel. But many cases of pitting of the ferritic steel were recorded when the boilers were fed with hard water (Total Hardness near 300 ppm of $CaCO_3$) with high chloride levels of about 150 to 200 mg/l.

2.2.- Design and realization of hot water tanks

The tanks are made from stainless steel sheet of variable thickness depending on the model and around 1 mm (Fig. 2.1). They are composed of three main parts, the two bottoms and the cylindrical body.

Fig. 2.1

The body is shaped by rolling and the two bottoms are stamped using a hydraulic press. Ferritic steel being less malleable than other grades, the discs surface for forming the bottoms is greased in order to preserve the quality of the metal surface. The bottoms are then degreased by passing through a spray-washing chamber with a solution containing surfactants and phosphates.

It should be noted that this processing line is not only dedicated for degreasing stainless steel bottoms but is also intended to prepare painting to mild steel elements.

Other elements such as inlet or outlet tubes for water heating coil are made out of 1.4404 stainless steel tubes that are cut to length and possibly bent in the workshop.

The two edges of the sheet constituting the body are assembled by welding (longitudinal weld). Both bottoms are then welded to the body. These circular welds as well as the longitudinal weld are carried out by the TIG method (Tungsten Inert Gas) with solder and under argon. The grade of stainless steel used for soldering is 316L (1.4404) regardless of the grade of the sheets to be joined.

Leak tests are then carried out to verify the quality of the assembly. When small leaks are detected, they can be repaired by spot welding performed manually.

2.3.- Localisation and possible origin of the corrosions

The openings observed on the tanks walls are linked to the pitting corrosion of metal mainly localized close to the weld in the heat affected zones (HAZ) (Fig. 2.2). Some other attacks are also observed on the solid sheet walls, but they rarely lead to perforations (fig. 2.3).

Fig. 2.2

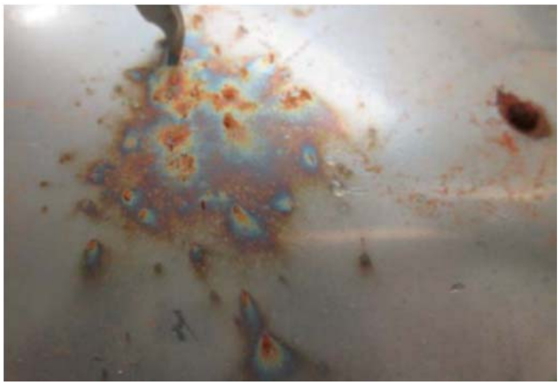


Fig. 2.3

These pitting of the solid sheet are related to ferrous pollution that result from:

- The grinding of welds presenting irregularities,
- The deposit of dust od mild steel, machining of the two types of materials being carried out in the same room,
- From iron deposits coming from the degreasing bath that is common to both types of materials.

The openings appear after a few months of service and are usually located in the HAZ adjacent to the upper circular weld where the water is the warmest.

One might conclude that these pitting result from a lack of passivation of the weld zone. The pitting potential of the metal samples taken from the HAZ of welds on stainless steel tanks of various grades are lower than those measured on the base metal. However, the values measured in HAZ of the various grades are very close one to the other and do not explain the differences in behaviour observed in the field (Table 2.1).

It is therefore necessary to investigate the possible causes of corrosion in the manufacturing process. To study the effect of changes in manufacturing operations, we developed a test rig to simulate the use of tanks in water of known composition.

Table 2.1: Pitting potential of the different stainless steel grades

Grade	E_{pit} outside of HAZ (mV/SCE)	E_{pit} in HAZ (mV/SCE)
1.4521	470	170
1.4404	540	125
1.4362	1105	205

2.4.- Test rig

The test rig aims to compare the corrosion resistance of water tanks made of different stainless steel grades or of the same grade but for which the manufacturing process has changed. It allows to perform the tests with various compositions of water. This water is prepared from the tap water to which are added specific quantities of salts in order to obtain the desired mineral composition. This test rig was built according to the scheme given in Figure 2.4 and can test up to 8 tanks simultaneously.

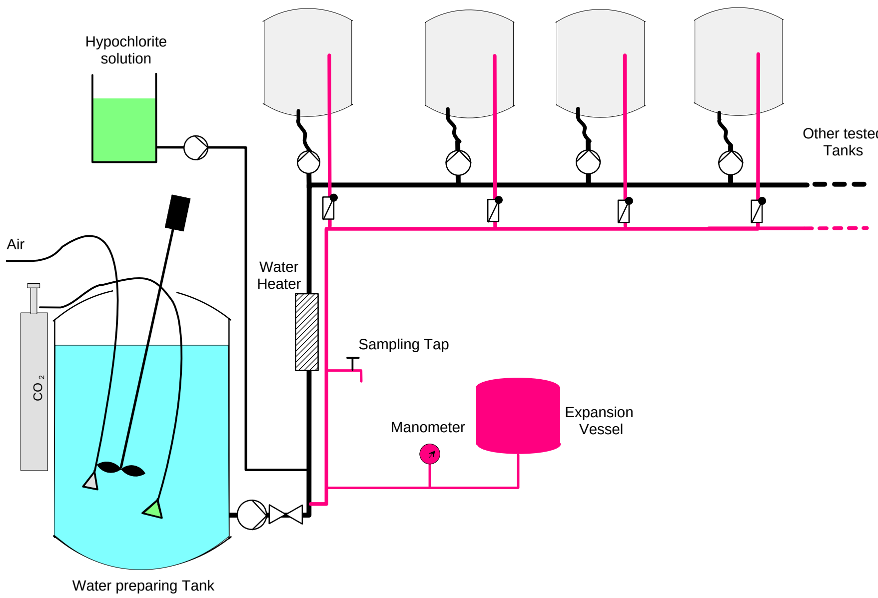


Fig. 2.4: Schema of the test rig

Each tank undergoes periods of water circulation and periods of stagnation that can simulate as closely as home use. The water used is the one distributed in the town to which were added chloride and sulphate ions as sodium salts and calcium and bicarbonate to reach the values given in the table 2.2.

Table 2.2 : Characteristics of the water used for the tests

Parameter	Chloride	Sulphate	Total Hardness	Total Alkalinity
Value	250 mg/l	150 mg/l	30 °f	30°f

The water temperature was set at 60 ± 5 °C for the first test and at 70 ± 5 °C for the following tests. Indeed, during the first test, only one pitting appeared after two months of operation. Thus, the temperature was increased in order to accelerate the corrosion rate.

Finally, the pH of the water was reduced to 6.2 for the preparation of the test water by the addition of CO_2 and was then adjusted to 6.8 at 20 °C by injection of air. Thus, it remains aggressive to calcium carbonate. Raised to 70 ° C, the water becomes slightly calcifying (Saturatio = $[Ca^{2+}]\ [CO_3^{2-}]$ / K's ≈ 2) and can deposit up to 50 mg/l of $CaCO_3$ with a very slow kinetics.

2.5.- First results

The main objective of the first test was to verify that the behaviour of the tested tanks is similar to that observed in the field and to validate the reproducibility of results.

For this purpose, in each test, two tanks made in each grade were tested at a temperature of 70 °C. The duration of these runs was set at 2 months.

Both tests showed:

- That the tanks made of ferritic steel 1.4521 systematically perforated by pitting corrosion in the HAZ after 7 days trial,
- That the tanks made in austenitic steel or ferritic-austenitic steel have not shown any pitting in the HAZ after 2 months trial.

These results confirm the very clear difference in the behaviour of ferritic steel tanks with respect to the other two grades. They also show that the repeatability of the tests is very satisfactory since the four tanks pierced after contact with hot water for a period of 7 days, varying only a few hours from one tank to the other.

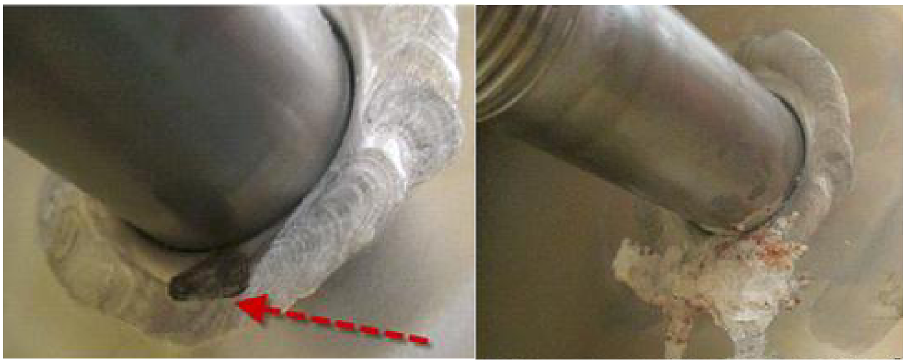
On the other hand, two tanks made of ferritic steel 1.4521 previously pickled and passivated were tested in the same trial. No pitting has been observed after two months of testing. This result confirms the need for the pickling/passivation of the tanks before they are marketed.

However intergranular corrosion appeared after 9 weeks of testing on one of the two tested tanks. This corrosion led to the perforation of the wall two weeks after (fig. 2.5).

This intergranular corrosion is due to the presence of unremoved grease on the walls of the elements in steel 1.4521 that is carbonized during welding. The carbon formed during welding leads to the formation of titanium, chromium or silicon carbides which precipitate in the grain boundaries.

Additional tests will be necessary to confirm the origin of this corrosion.

It therefore appears necessary to improve the degreasing process currently applied and to extend it to the all elements before welding.



A: Black deposits appearing after 9 weeks

B: Pitting appearing two week after

Fig. 2.5

3. CONCLUSIONS

The conclusions and lessons that it can be learned from these two cases of corrosion of stainless steels are:

- For the case of flow control valves made of steel austenitic-ferritic several errors of achievement (mild steel shims left during welding of plates, hard chrome coating laid without nickel underlayer) or design (use of graphite gaskets) have resulted in significant corrosion that required to return them in the factory for proceeding to heavy repairs. Pickling of the walls has only an aesthetic interest.
- For the case of hot water ferritic steel tanks, pickling/passivation is certainly a good thing. But this treatment often presented as the solution to corrosion problems, here appears totally inadequate. It is clear from this example that the comprehensive study of the manufacturing process remains essential in the research of the origins of corrosion. Here it is particularly suitable to conduct an effective degreasing of all of the components before welding to avoid the risk of appearance of intergranular corrosion. It should also be necessary to separate areas for machining of carbon steel from those dedicated to the work of stainless steel in order to reduce ferrous pollution. Similarly, grinding should be limited to the worst welds having an important defect. In this case pickling followed by passivation must be applied.

These two examples show the importance of ensuring that the elements of stainless steel are designed and assembled with care. The rules of basic good practice or specific to certain steel grades must be strictly observed.

Pickling/passivation can in no way compensate for errors in implementation or design. This operation only allows improving the aesthetics and the corrosion resistance of properly designed and built elements.

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