STATE OF THE ART OF ACIDIC CORROSION

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Abstract

The Thesis Project is based on a thorough research regarding Acidic Corrosion Mechanism with metallic materials using cutting edge technology available, and discussions about some approach that may be considered in application for the best possible result against corrosive environment.

Metallic materials discussed are Carbon Steel, Stainless Steel, Copper and Nickel with their different compositional alloys. Because they are very essential in our daily lives and for their strategic and economic impact, in terms of quantity, availability, cost and usefulness in Construction of Infrastructure, Transportation, Chemical storage, Oil/Gas industries and many other important parts of facilities and structures.

For Carbon steel in aggressive environment, the corrosion morphology is mainly that of generalized corrosion, which affects the entire surface of a metal or a large part of it as a result of the substantial coincidence of the anodic and cathodic areas, affecting metal-environment systems in an active state. In the first instance the loss of thickness could be uniform over the whole surface, or in other case it takes a more or less regular form,

The corrosion morphology as in the case of Stainless steel in acidic environment, like chemical storage plants, and Oil & Gas internal pipelines, is usually that of localized corrosion. It affects only a limited part of the surface compared to the exposed area to the environment as a result of the anodic and cathodic reactions which take place on different surfaces like Galvanic Corrosion, Pitting Corrosion, Crevice Corrosion, Stress Corrosion Cracking, Hydrogen Embrittlement (Sulfide Stress Cracking), Microbial Induced Corrosion and Stray Current Corrosion.

The circulation of electrons in the metal from the anodic to the cathodic area and the circulation of ions in the solution with positive ions migrating from the anodic to the cathodic area and negative ones in the opposite direction. This causes the establishment of a galvanic current, due to the differing nobility of the metals or alloys in electrical contact, causing galvanic contact corrosion for example when the cathodic area >> anodic area. The different oxygen availability leads to the separation of the anodic and cathodic areas, in active-passive materials like stainless steel.
The corrosion morphology as in the case of Copper and Nickel with their different alloys in acidic environment, like chemical storage plants, and Oil/Gas internal pipelines, are usually that of an intermediate as they can suffer both generalized and localized corrosion.

The prevention of this type of corrosion, is less insidious for generalized corrosion than localized corrosion, because its initiation and the mean velocity of thickness loss can be predicted. Generally by adding an extra thickness of metal, sized by multiplying the uniform corrosion rate by the project life and using traditional methods such as cathodic protection, coatings (organic, inorganic and metallic), paints and corrosion inhibitors. But for localized corrosion, its initiation and the mean velocity of thickness loss cannot be easily predicted.

Cathodic protection is effective during both the initiation and propagation phases as well as using **large anodic areas and small cathodic areas**, avoiding coupling materials with different nobility, painting, avoiding electrolytes with low resistivity, use of uniform solution heat treatment after welding, use of insulating joints on pipelines and correct positioning of structures in the ground.
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1. INTRODUCTION

General Aspect of Corrosion

We are reliant on metallic structures to support our everyday activities, be it getting to work, transporting goods around the world, or storing and preserving food. Metals are everywhere. However, from the moment most metals come into contact with aggressive environment, they are subject to sustained and continuous attack which can lead to the metal corroding and failing to do its job. It is therefore important to understand when corrosion will occur, how fast it will proceed and what can be done to slow down or stop it. Corrosion involves two separate processes or half-reactions, oxidation and reduction. **Oxidation is the reaction that consumes metal atoms when they corrode, releasing electrons. These electrons are used up in the reduction reaction.**

In general, when a metallic material undergoes a form of physical and chemical decay as a result of contact with an aggressive environments is called Corrosion. Corrosion can be defined as the destruction or deterioration of a metallic material by reaction with the environment or as the tendency of a metallic material to return to its original state, as it is found in nature (Fig. 1; Fontana, 1986); as a consequence, it is also known as metallurgy in reverse. Due to corrosion processes, metallic materials are spontaneously brought back to their most stable thermodynamic state, in which they combine with other elements, especially Oxygen and Sulphur.

The morphology of *corrosion* processes mainly occur at the surface of metallic materials in a generalized or localized way (Pedeferrri, 2007). Generalized corrosion occurs when the attack affects the entire surface of the material exposed to the environment, which could be uniform or non-uniform corrosion. Localized corrosion, by contrast, occurs when the attack affects only some parts of the surface of the material exposed to the environment, with a specific morphology, for example in the form of cracks, cavities and pitting. We speak of selective corrosion when specific constituents of the material are attacked, such as some phases present as grains or around the grains. Corrosion is a complicated issue, and depends on the metallic materials used, the fluids acidic concentration, pH, the fluid temperatures and the surrounding environment, could result in different corrosion mechanism.
Fig. 1: The corrosion process as metallurgy in reverse (Fontana, 1986).
2. CORROSION BY ORGANIC ACID

Organic acids belong to the group of the most important chemicals used in several industries such as textile, leather, chemical and food, pulp and paper, drugs and pharmaceuticals, plastics and fibers, refineries and petrochemicals. These acids are used as reagents for the manufacture of various chemicals for production. Most of these acids are produced more as precursors for the other chemicals than for end use as acids themselves.

This paper concentrates on corrosion by acetic, citric and formic acids as they are generally used as chemical intermediates (e.g. vinyl acetate monomer, cellulose acetate, acetic anhydride, and terephthalic acid).

The corrosion of metallic materials by organic acid is often confounded by trace impurities such as oxygen and metallic salts. Formic acid is used more as an environmentally benign storage and transportation medium for hydrogen, the clean energy of the future. Acetic and formic acids are usually used as reactants or solvents in many industrial processes.

2.1 ACETIC ACID

Acetic acid is recognized as an important factor in corrosion of metallic materials. Like carbonic acid, acetic acid is a weak organic acid which partially dissociates as a function of pH and the solution temperature. Stronger than carbonic acid, acetic acid is the main source of hydrogen ions when the concentration of each acid is the same.

According to many studies, acetic acid enhances the corrosion rate of metallic materials by accelerating the cathodic reaction. The mechanism of acetic acid reduction at the metal surface is still being debated.

Typical concentrations of organic acid reported in the field are of the order of 100 ppm, while in some cases, up to 3000 ppm of organic acids was reported. Among organic acids, acetic acid (CH₃COOH, or shortly HAc) is known as the dominant low molecular weight acid found in produced fluids (usually about 50-90 % of the total).
Carbon Steel

In the present study, electrochemical techniques using potentiodynamic sweeps was used in order to investigate the effect of acetic acid on the cathodic reaction. It was found that acetic acid affects only the limiting cathodic current, but had no effect on the charge transfer current. The charge transfer current is found to respond to a change of pH.

Potentiodynamic sweeps were performed at the same pH in order to investigate the effect of acetic acid on the charge transfer current. At pH 4, an increase of acetic acid concentration only affects the limiting current, arising from mass transfer, but has no influence on the charge transfer current (Fig. 2).

The same result was obtained in a laminar and turbulent flow regime (using the RCE and RDE): the charge transfer current does not change with the acetic acid concentration. This indicates that, besides the reduction of hydrogen ion, there are no additional electrochemical reactions at the metal surface, such as the hypothesized reduction of acetic acid.

In other words, under all these conditions, acetic acid acts primarily as a source of hydrogen ions which only causes an increase in the mass transfer controlled limiting current for hydrogen evolution.

Fig. 2: Comparison of potentiodynamic sweeps obtained for different acetic acid concentration at 25 °C, pH 4, 3% NaCl, aqueous solution saturated with N₂, RCE rotating speed 1000 rpm.
Since hydrogen ions appear to be the only cathodic reactants, the change of hydrogen ion concentration should affect the charge transfer current.

(Fig. 3) clearly show a change of charge transfer current when pH changes, in the presence of acetic acid. In this cases, a higher charge transfer current is expected when pH decreases (i.e. the hydrogen ion concentration increases). This result confirms that hydrogen ions are the main cathodic reactant in the systems studied in this work.

![Potentiodynamic sweeps](image)

**Fig. 3**: Comparison of potentiodynamic sweeps obtained for different pH at 25 °C, 0 ppm with 3% NaCl, aqueous solution saturated with N₂, RCE rotating speed 1000 rpm.

When the reduction of the adsorbed acetic acid molecule occurs at the metal surface, the mechanism is called “direct reduction”.

If the role of acetic acid is to dissociate near the metal surface to provide additional hydrogen ions and the only cathodic reduction is reduction of hydrogen ions, this mechanism is referred to as a “buffering effect”. As a result, the dominant cathodic reaction mechanism related to reduction of acetic acid on steel is the buffering effect.
Stainless Steel

Stainless steel with 13 % Chromium is resistant to acetic acid at moderate temperature, but is attacked by boiling acetic acid of any concentration. The annealing temperature affects the corrosion behavior. The start of the steep increase of the corrosion rates and the position of the corrosion maximum of the steels which contain 13 % chromium are shifted to longer tempering times with decreasing tempering temperature from 600 to 550 to 500 °C, for example X20 Cr 13 in 5 %, X 22 Cr-Ni 17, X 15 Cr-Mo 13, X 35 Cr-Mo 17 in 20 % boiling acetic acid. The addition of molybdenum has a favorable effect on the behavior in all cases and it also described that in the case of 12 % Chromium as little as 3 % molybdenum are sufficient for stabilization. Titanium and nickel do not have a specific effect, and manganese and niobium are even impairing.

A chromium-molybdenum stainless steel ((% 2.25 Cr, 1 Mo) became embrittled by hydrogen in 0.5 % acetic acid saturated with hydrogen sulfide. The effect of temper embrittlement on hydrogen embrittlement was investigated on the same steel in the same medium in; it was found that temper embrittlement enhances the susceptibility to hydrogen embrittlement on grain boundaries. The threshold stress intensity factor decreases with fracture surface transition temperature, grain size, hydrogen content, and has a good correlation with the hydrogen embrittlement susceptibility factor. The relation between these two factors was used to determine the maximum of residual hydrogen content in a pressure wall. Hardened martensitic stainless steels are also susceptible to hydrogen embrittlement and can be subject to stress corrosion cracking in acetic acid + hydrogen sulfide. Cathodic protection by means of magnesium, zinc, aluminum or unalloyed steel is possible; likewise, chromium layers are suitable.

The ferritic-austenitic stainless steels OKh21N5tT and OKh21N6M2T (Soviet steel) have good corrosion resistance in 6 % acetic acid and other organic acids at room temperature and at 60 °C. As expected, the addition of chloride ions increases the weight loss. In acid solutions which have a high chloride content, ferritic-austenitic steels, in particular OKh21N5tT, corrode faster than the austenitic steels.

Technical media for the production of acetic acid by the synthesis from methanol and carbon monoxide often contain 0.01 to 1 % hydrogen iodide. This iodide content was found to cause pitting corrosion in 70 % acetic acid solutions at 90 °C on steel OKh21N6M2T, and was promoted in the presence of oxidants. For the production of 2-methyl-5methoxybenzotriazole by reduction of 4.4’-dimethoxy-2.2dinitrophenyl sulfide by zinc powder in acetic acid, the steel O8Kh21N6M2T (X 8CrNiMoTi 21 6 2) exhibits sufficient corrosion resistance in the medium.
High tensile stress in combination with exposure to chloride ions causes stress corrosion cracking. Severe inter-crystalline corrosion was observed at the heat-affected zones in the region of welding’s in stainless austenitic steels on exposure to acetic acid. The contamination of the acetic acid with sodium chloride, involves subsequent formation of hydrochloric acid. Corrosion of stainless steel equipment by the hydrochloric acid, for example, produces ferric chloride (along with chromium and nickel chlorides) which, because of its volatility and strong oxidizing nature, is particularly pernicious.

The volatility of ferric chloride allows it to move freely through a processing system, and, because it is a strong oxidant, it promotes stress-corrosion cracking (SCC). Besides SCC, a condition of accelerated corrosion and pitting results from chloride contamination. Reportedly, slightly less than 20 ppm of chloride in the acetic acid stream can be tolerated, but higher concentrations are likely to cause rapid equipment failure.

The service life of austenitic stainless steel in glacial acetic acid is longer than in acetic acid/formic acid mixtures. For hot (above 120 °C) mixtures of acetic acid with more than 2 % formic acid, stainless steel is not as suitable as copper alloys or Monel; however, for dilute acetic acid/formic acid solutions, Mo-containing Cr-Ni stainless steels are preferred to copper or nickel alloys.

According to electrochemical measurements, 18/10 stainless steel has very good resistance to acetic acid even in high concentrations in the presence of dissolved oxygen; the reduced resistance at low concentrations is attributed in particular to the higher dissociation rate of acetic acid. However, the requirement for the favorable effect of molybdenum is a sufficiently low carbon content, since otherwise local chromium depletion is caused due to precipitation of chromium carbide, which leads to risk of intergranular corrosion at these points.

The austenitic Cr-Ni-Mo stainless steel AISI 316 and 317 are suitable for acetic acid of all concentrations up to the boiling point; as a rule, the steel AISI 317 has the best resistance to concentrated acetic acid at or near the boiling point.
Copper

The acetic acid production from calcium carbide, copper is used for acetaldehyde condensers and for distillation vessels, fractionating columns etc. Copper equipment is used for the catalytic purification of crude acetic acid between 201 °C and 300 °C and equally used for benzene distillation.

In an investigative field test, it was observed that in a rectifying columns and heat exchangers in plants for wood chemicals remained resistant for 27 years if made of copper produced in America and only 5-7 years if the copper is produced in Russia. The reason for this result, is the difference in oxygen content of the copper. The Russian made copper with low oxygen content had a higher corrosion rate (test duration 30 hours in 65 % acetic acid) than the American made copper with high oxygen content.

Furthermore investigation on the corrosion behavior of Cu in acetic acid with addition of methanol, ethanol or water were made. The corrosion rate are higher in alcoholic medium than in aqueous solutions, especially in methanolic solutions. Corrosion rate in time indicate a remarkable increase in the corrosion of copper in methanolic acid solutions. Copper is also not considered in the food industry due to the high corrosion rate in acetic acid media.

Copper alloys with nickel (Monel) have higher service lives in acetic/formic acid mixtures than in glacial acetic acid, while for the austenitic stainless steels the opposite is the case. For hot (100 °C) mixtures of acetic acid with more than 2 % of formic acid, stainless steels are not as suitable as Cu-alloys or Monel. However, for dilute acetic-formic acid solutions, Cr-Ni-Mo-steels are preferable to Cu-alloys and Ni-alloys.

In contrast to the high-alloy steels, Cu-alloys are resistant to acetic acid if it contains reducing components like oxygen, chromic acid, ferric chloride and potassium permanganate, and they are most frequently used materials for handling acetic acid of all concentrations and temperatures. The exceptions are completely anhydrous acetic acid at the boiling point and Cu-alloys with more than 30 % zinc and systems containing peroxide.

The corrosion rate depends directly on the oxygen content of the copper and increases with increasing acetic acid concentration and temperature, if the oxygen content remains the same.
Nickel

Boilers made of nickel or Ni-Cu alloys have proved to be suitable for hydrogenations (even under pressure) of substances dissolved in glacial acetic acid.

The corrosion behavior of nickel in acetic acid depends greatly on the presence of air oxygen and other oxidizing agents.

Table 1: Corrosion behavior of nickel in acetic acid of various concentration and temperatures.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Acetic acid %</th>
<th>Temperature °C</th>
<th>Corrosion Rate mm/y</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>NICKEL</td>
<td>50</td>
<td>20</td>
<td>&lt; 0.1</td>
<td>Air</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>100</td>
<td>&lt; 3.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Concentrated</td>
<td>20</td>
<td>&lt; 0.1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Concentrated</td>
<td>100</td>
<td>&lt; 10.0</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1 - 100</td>
<td>20</td>
<td>0.04 – 0.202</td>
<td>Air free</td>
</tr>
</tbody>
</table>

In contrast to the stainless steel, nickel and Monel are more resistant to acetic/formic acid mixtures than to glacial acetic acid, in particular in the presence of more than 2 % formic acid at temperatures of more than 120 °C.
Nickel coatings with some elements in addition like 14 % of phosphorus are attacked by glacial acetic acid, 5 % acetic acid when deposited at zero current even at room temperature. Although heat treatments of high temperature can slightly improve the corrosion resistance.

Equally nickel coating (about 0.076 mm thick) produced at zero current by the Kanigen process have a good corrosion resistant in acetic acid after heat treatment at 760 °C. The self-fluxing Ni-hard alloy deposited on steel improved the wear and friction resistance in acetic acid.

Ni-Cr-Fe alloys like Incoloy 825 are resistant to acetic acid over very long periods of time and have proved to be suitable for plants in which acetic acid and acetic anhydride are prepared, in which stainless steel have a tendency for pitting corrosion, stress corrosion cracking and severe uniform corrosion. The alloy Incoloy 825 ((%) Ni-21.5Cr-30Fe-3.0Mo-2.2Cu-1Ti-0.04C) is used instead of conventional stainless steel for heat exchangers, in boilers and condensers, for false bottoms and the like. Ni-Cr-Fe alloy of the type Inconel 375 are also resistant to dilute acetic acid and are better than Monel in the case of vigorously aerated acetic acid solutions.

Ni-Cr-Mo-alloys, such as Hastelloy C, Hastelloy N ((%) Ni-7Cr-16Mo-5 Fe), Hastelloy F ((%) Ni-22Cr, 6 Mo, 22 Fe, 2 Nb/Ta), are among the most resistant materials to acetic acid of all concentrations and at all temperatures. Due to their high cost, they are mainly used for pumps, valves, nozzles and the likes, and for stems of gate valves. Hastelloy C and F have the best corrosion resistance to acetic acid. Hastelloy F has also good resistance to mixtures of acetic/formic acid. However, in halide-containing acid, Hastelloy C is subject to inter-crystalline corrosion; in particular ferric chloride must be excluded under all circumstances.

Nickel-copper alloys such as Monel 400 ((%) 65.7Ni-31.59Cu-1.27Fe-0.87Mn-0.14Si-0.13C) are resistant at room temperature to air-free acetic acid solutions of all concentrations. However, the corrosion rate increases rapidly in hot aerated acetic acid solutions, thus the materials cannot be recommended under these conditions.

Monel is more resistant to acetic acid/formic acid mixtures than to glacial acetic acid and is better than Cr-Ni-Mo-steel in hot mixtures of acetic acid of higher concentration in the presence of more than 2 % formic acid (> 121 °C), whereas the latter is preferred for dilute acetic acid/formic acid solutions. Monel valves are suitable for handling acetic acid at higher temperatures, and inter-alia, in the food industry. Monel is extensively used for reactors, heating coils, pipelines, stirrers and pumps for air-free acetic acid solutions even in the presence of sulfuric acid. However, it must be kept in mind that under heat transfer conditions Monel 400, annealed at 927 °C for 1 h and quenched with water, loses 0.36 mm/y in 56 % acetic acid + 1 % sulfuric acid.
2.2 CITRIC ACID

Citric acid is mostly used in industrial process as reactant, acidifier, flavoring and chelating agent. It can be in the form of anhydrous or monohydrate state appearing as a white powder. Although it occurs in nature, it is only available in trace amounts in citrus containing fruits and vegetables such as lemons and limes in the range of 0.30 mol/L.

Citric acid is a weak organic acid and has better prospects as an industrial chemical due to its environmentally friendly nature. Its industrial-scale production first began in 1890 based on the Italian citrus fruit industry, where the juice was treated with hydrated lime (\(\text{Ca(OH)}_2\)) to precipitate calcium citrate, which was isolated and converted back to the acid using diluted sulfuric acid.

The corrosiveness of citric acid is slightly lower as compared to other organic acid, but it has also been found to play a major role in the corrosion of metallic materials. It can be used for cleaning & passivating conventional steels, stainless steels etc. as an alternative to nitric acid. Solution strengths of 5-10 % citric acid are used for passivation treatments.

Carbon steel

Carbon steel is well known as one of the best preferred industry material due to its availability, desirable mechanical properties and low cost. Carbon steel in contact with citric acid solution is severely attacked at all concentration and temperature. Bare carbon steel is not suitable for services in direct contact with citric acid. But in coating carbon steel, it will be suitable to work in contact with citric acid.

An investigation on the corrosion mechanism of carbon steel in citric acid has shown that light has an accelerating effect on the behavior. The experiment was carried out using photo-potential analysis was carried out to observe the effect of visible light on carbon steel in a citric acid solution. The photo-potential show that the steady state potential and current after illumination of one of the electrodes is negative with respect to the electrode in darkness, indicating an increase in the corrosion rate of the illuminated electrode.

(Fig. 4) shows a photo-potential-time curves constructed for carbon steel in a citric acid solution. It shows the effect of switching the 60 W light on for 3 h and illuminating one electrode.
This figure shows a rapid change in potential of approximately 10 mV in the negative direction as soon as the light was switched on. Thereafter the potential remains approximately constant, followed by a slow increase in the potential in the positive direction while the light source remained on. When the light is switched off, the potential moves in the positive direction, falling back after 1 h to the potential recorded before the light was switched on. An examination of the electrodes after removal from the solution at the end of this test did not show the presence of any solid corrosion products, but the surface of both electrodes had become slightly etched. But on coating the carbon steel with a vinyl lacquer, the effect of illumination was eliminated.

![Photo-potential/time curve](image)

**Fig. 4**: Photo-potential/time curve for carbon steel in 0.01 M citric acid after 15 hour pre-immersion test.

In another experiment using both the impedance and harmonic analysis techniques show a corresponding increase in the corrosion rates of the illuminated electrode (approximately 65 %). Pre-polished carbon steel electrodes covered with a vinyl lacquer (VMCH) 65/mm thick were studied. No difference of behavior after 25 days pre-immersion and 40 h after switching the light on in the different solutions was found. No corrosion of the carbon steel was observed.

At this state of the test, a flaw was introduced in the lacquer film, and after a further 15 h period in solution, the response on switching the light on was similar to the one observed for bare metal.

Thus, the presence of the vinyl lacquer suppresses the effect of illumination.
Stainless steel

Either of the AISI 304 or 316 stainless steel types can be considered for most storage and handling applications in contact with citric acid. Citric acid is used for cleaning and passivating stainless steels, thus stainless steel which is rarely attacked by citric acid is generally suitable for service in the environment.

The Iso-corrosion diagram 0.1 mm/y lines in (Fig. 5) show that either the 304 (Blue) or 316 (Red) types can be selected for normal storage & handling applications. (The chain line represents the solubility and the broken line the boiling point).

![Iso-corrosion diagram with 0.1 mm/y of stainless steel AISI 304 (Blue) & 316 (Red).](image)

The AISI 304 types should be adequate for most applications. The low carbon types (304L or 316L) may be needed for temperatures above around 60 °C to avoid any risk of intergranular attack in weld heat affected zones. At temperatures above 80 °C the 316, or preferably the 316L types, should be considered.

In common with most acid handling applications, chloride contamination may be a cause of pitting corrosion and so in these cases more pitting resistant grades may need to be considered. Passivation treatments are sometimes specified, but it is important to consider whether this is strictly necessary or not. Stainless steels cannot be passivated unless the steel surface is clean and free from contamination and scale from welding operations.
Conventional uses of citric acid with stainless steels can be for cleaning and passivating stainless steels, as an alternative to nitric acid as both provide the oxidizing conditions necessary for passivation. Solution strengths of 5-10% citric acid are used for passivation treatments. Citric acid is a less hazardous method and has environmental benefits in terms of 'NOx' fume emission and waste acid disposal. Solution strengths of 4-10% citric acid are specified for passivation treatments for ASTM A967 (Table 2).

ASTM A967 citric acid passivation treatments standard also allows any combination of citric acid concentration, temperature and time, provided that the passivation test criteria can be met.

**Table 2:** Standard strength range of citric acid solution for stainless steel passivation ASTM A967.

<table>
<thead>
<tr>
<th>COMPOSITION (Wt %)</th>
<th>TREATMENTS</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CODE</td>
</tr>
<tr>
<td>4-10% CITRIC ACID</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>3</td>
</tr>
</tbody>
</table>

Copper and Nickel

Citric acid (hydroxyl-propane tricarboxylic acid) is a more aggressive compound to Copper and Nickel materials. This tart-tasting constituent of citrus products can be handled well by the austenitic stainless steels. It will be noted that Alloy 400 is a candidate for use in many of the food product services. Others have described the use of Monel 400 and other nickel-base alloys for such use as with citric acids,

The presence of air will determine the rate of corrosion on Copper and Nickel materials in citric acid solutions. Alloy 600 and other alloys of nickel with chromium have good resistance to citric acid and can be used when desired. Chloride is a commonly encountered contaminant in citric acid solutions, thus copper alloys and nickel alloys at room temperature to 100 °C, 1-5% citric acid has a corrosion rate of 0.5mm/y. Presence of oxygen increases the corrosion rate.
2.3 FORMIC ACID

Formic acid has proven to be highly corrosive at concentrations over 50 % and being the most corrosive of the common organic acids because it is highly ionized especially if contaminated by acidic oxidizing chlorides. Because of its corrosive nature at high concentrations material selection can be a challenge. Formic acid is somewhat unstable and decomposes to carbon monoxide and water, especially when heated above 35 °C.

Formic acid is corrosive to many alloys, and as a reducing agent attacks stainless steels unless an oxidizing agent is added. Ni-alloys perform better than SS 316, but are attacked if an oxidizing agent is present.

Carbon steel

Carbon steel which is commercially available for the fabrication of reaction vessels, storage tanks, etc. by industries which either manufacture formic acid or use it as one of the reactants, is attacked by formic acid at all concentrations and temperatures and is normally not considered suitable for formic service.

The corrosion rate of carbon steel in 5, 10, 20, 40, 60 and 80 % (vol.) formic acid solution was determined by the weight loss method for different immersion periods (6, 12, 24, 48 and 72 h) at 25, 35 and 45 °C. It was observed that at each concentration of formic acid solution the corrosion rate of the carbon steel at first increases as the immersion period is increased from 6 to 24 h. On further increasing the period of immersion from 24 to 72 h, the corrosion rate at all concentrations of formic acid is found to decrease. For an immersion period of 24 h the maximum corrosion rate is observed, irrespective of the concentration of the electrolyte and temperature.

Equally, it was also noted that with increase in concentration of the formic acid the corrosion rate initially increases rapidly, attains a maximum value at the concentration of 20 % and then, on further increase in the concentration, slowly decreases. The nature of the effect of temperatures is almost identical. However, as the temperature of the system is increased a sharp increase in corrosion rate at each concentration is observed. The increase is more rapid between 25-35 °C than the corresponding increase in corrosion rate when the temperature is raised from 35 to 45 °C. The above observations show that the corrosion rate of carbon steel in formic acid depends markedly on the acid concentration and the temperature.
Stainless steel

The various conventional stainless steel grades in the 300 series and the 400 series are usually not resistant to formic acid, even at room temperature the corrosion is visible as the temperature increases.

The corrosion resistant of some stainless steel are strongly influenced by the addition of impurities in higher percentages especially molybdenum which have favorable effect on the corrosion behavior. However a molybdenum content in the range of 2 % has proved not to be adequate without the addition of other alloying elements.

Electrochemical investigations to determine the influence of increasing molybdenum contents, of nil, 2 %, 3 %, 4 % Mo, on the corrosion behavior of 17 % of ferritic stainless steel in contact with 20 % formic acid at 70 °C were carried out in an aerated and non-aerated medium. The tests were performed by recording polarization vs. time curves in combination with determinations of weight loss by analytical determination of the metal ions transferred into the medium.

A 17 % Cr Stainless steel without molybdenum and a 17 % Cr Stainless steel with a molybdenum content of 2 % (Fe-17Cr-2Mo) proved not to be resistant; the materials corrosion rate was at 33048 mdd for the 17 % Cr Stainless steel and 7500 mdd for the Cr Stainless steel containing 2 % Mo in the deaerated medium (0.1 ppm residual O2) and 32640 mdd/10800 mdd when saturated with oxygen (20 ppm O2).

For a 17 % Cr Stainless steel containing higher than 2 % molybdenum, the 3 % and 4 % content of molybdenum exhibited better resistance with regards to the corrosion in these investigations. The materials corrosion rate with a molybdenum content of 3 % were at 65 mdd and the one with a molybdenum content of 4 % was at 57 mdd in the non-aerated medium and 0.8 mdd in the oxygen saturated formic acid.

Furthermore, Super-ferrites with improved ferritic Cr stainless steel are significantly superior with improved corrosion resistance against formic acid to the conventional Cr Stainless steel. They were developed by increasing the chromium content to more than 25 %, (Fe-26Cr-1Mo) also offering good weldability and toughness.
Copper

Copper and copper alloy are severely attacked by formic acid in the presence of oxygen. The corrosion rate depends on the influence of oxygen partial pressure and on the rate at which oxygen is transferred to the surface of the metal in the media. Since oxygen was identified as the cause of the increased corrosion rate of copper in a media containing formic acid, the most recommended remedy to control the corrosion was ‘de-aeration’ of the environment.

The corrosion rate of copper in operational and laboratory tests describes the influence of oxygen on corrosion of copper in formic acid. At operational test in 90 % of formic acid, the corrosion rate of 0.97 mm/y in the liquid and 0.15 mm/y in the vapor space were determined respectively for copper at 100 °C in a distillation column. The corrosion rate of the same copper in the vapor space of a storage vessel at a room temperature of 25 °C, were of the same order of magnitude at 25 °C. While on the contrary they were lower at 0.33 mm/y in the liquid.

At the laboratory test, there are cases where oxygen was excluded and the resulting corrosion rate of the copper where significantly low at 0.0022 mm/y with exposure to 50 % boiling formic acid with air excluded by continuous gassing with ultra-purity nitrogen (99 % N2). The other case was of copper with formic acid present both in aerated and non-aerated in liquid and vapor space media. The resulting corrosion rate at different formic acid concentration of (10, 50 and 90 %) equally shows that in the non-aerated medium the corrosion rate was very low at 0.10 mm/y and 0.08 mm/y respectively. Whereas at the corrosion rate at aerated medium was 5.59 mm/y and 0.38 mm/y.

The behavior in contact with formic acid of copper alloys such as Cu-Al, Cu-Ni, Cu-Sn (Bronze), Cu-Zn (Brass) and silicon bronze, largely corresponds to that of copper. Grades of brass with high zinc content are susceptible to dezincification in organic acid. Therefore the use of copper and copper alloys with formic acid presupposes that oxygen is excluded at the point of use.
Nickel

The corrosion mechanism of nickel in formic acid in different percentages of concentrations differ very widely, with regards to the working medium from laboratory tests and operational tests and the influence of some important alloying elements.

In a laboratory test of a 48 hour, the result on exposure to a deaerated 10% boiling formic acid showed no difference between the corrosion rates of nickel and copper, both being 0.15 mm/y. But at a deaerated 90% boiling formic acid, there was a marked effect on the corrosion of nickel than on copper. Whereas in the presence of air, nickel is attacked substantially less than copper at the same concentration of 90%. However, at the same time, the corrosion rate of 0.38 to 0.99 mm/y for nickel in the liquid phase and 0.30 to 0.53 mm/y in the vapor phase are quite high as such as to exclude their use.

According to the results of an operational test, also in this case the material loss of nickel on exposure for several days is about 4-7% compared to that of copper, although with the corrosion rate of 0.46 mm/y equally means that nickel cannot be used.

Other laboratory test were carried out on the corrosion behavior of various nickel alloys in boiling formic acid. The resulting corrosion rates from the test, determined the influence of alloying elements in increasing the corrosion resistance. For example the corrosion behavior of the nickel based alloys Hastelloy C 276 and Hastelloy B 2 on exposure to boiling 40% and 88% formic acid, relatively showed high increase in the corrosion resistance. According to the results, the maximum corrosion rate for Hastelloy C 276 in formic acid is < 0.05 mm/y and it is a very significant reduction.
3. CORROSION BY STRONG ACID

Strong acids belong to those acids that are completely or nearly 100% ionized in their solutions. Thus the strength of an acid is defined by its ionization constant, which is a constant and does not change. Strong acids have a variety of usefulness in the industries and are often pumped into wells to stimulate production by increasing formation permeability. The most common types are the Sulfuric acid, Nitric acid and Hydrochloric acid. Its Corrosion depends also on variables such as what it is reacting with and its concentration and temperature. All the strong acids are highly corrosive under the right circumstances.

While strong acids are generally assumed to be the most corrosive, this is not always true. The carborane super-acid H(CHB11Cl11), which is thousand times stronger than the strength of sulfuric acid, is entirely non-corrosive, whereas the weak acid hydrofluoric acid (HF) is corrosive and can dissolve, among other things, glass and most metals.

In chemical uses, high chemical reactivity is often desirable, as the rates of chemical reactions depend on the activity (effective concentration) of the reactive species. For instance, catalytic sulfuric acid is used in the alkylation process in an oil refinery: the activity of carbo-cations, the reactive intermediate, is higher with stronger acidity, and thus the reaction proceeds faster. Once used, corrosives are most often recycled or neutralized. However, there have been environmental problems with untreated corrosive effluents or accidental discharges.

3.1 Sulfuric Acid

Sulfuric acid (H₂SO₄) is one of the most commonly used chemicals in the industries and, at concentrations greater than 90%, it is also very corrosive and very oxidizing. It is important that there is a thorough knowledge of exposure conditions, including not only the temperature and concentration of the acid but also the presence or absence of oxidizing agents and other impurities, acid velocity and heat transfer effects before selecting a material of construction for a sulfuric acid environment.

Sulfuric acid is a chemical that is used in numerous industrial processes as well as in the leaching of many metals from their ores. It’s a product of sulfur dioxide, which may be generated by burning sulfur, it may be a by-product of a metallurgical smelting process, or it may be produced by thermal decomposition (regeneration) of spent acid.
Carbon Steel

When carbon steel contacts dilute sulfuric acid, an immediate attack on the metal takes place, with the formation of ferrous ions and hydrogen gas, as shown in reactions (1) and (2).

(a) Anodic reaction

$$\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^- \quad (1)$$

(b) Cathodic reaction

$$2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \quad (2)$$

Accordingly, the rate of corrosion of carbon steels in dilute acids depends strongly on steel chemical compositions, especially the carbon content. The oxidation reaction of iron ($\text{Fe} \rightarrow \text{Fe}^{2+} + 2e^-$) occurs on the ferrite phase, and the cathodic reduction reaction of hydrogen ($2\text{H}^+ + 2e^- \rightarrow \text{H}_2$) occurs on the cementite phase. These reactions explain the important role of the carbon content on the steel corrosion rates and are shown in (Fig. 6).

![Graph showing corrosion rate of carbon steel as a function of carbon content](image)

**Fig. 6**: Corrosion rate of carbon steel as a function of carbon content in 6.5 mol/L, at 25 °C, test duration of 24 hours.
The figure shows the corrosion rate of carbon steels in 6.5 mol/L (corresponding to almost 50 %) H$_2$SO$_4$ as a function of the carbon content. The carbon steel with 0.19 % carbon exhibited the lowest corrosion rate.

(Fig. 7) shows the dependence of the corrosion rate on the concentration of H$_2$SO$_4$. Up to concentrations within the range of (5-6) mol/L (corresponding to 40-46.5 %), the corrosion rate of carbon steels tends to increase with different intensities depending on their carbon content.

![Corrosion rate vs. H$_2$SO$_4$ concentration](image)

**Fig. 7:** Corrosion rate as a function of H$_2$SO$_4$ concentration for carbon steel with different amount of Carbon at 25 °C in test duration of 24 hours.

(Fig. 7) also shows that, at concentrations greater than (5-6) mol/L H$_2$SO$_4$, the corrosion rate decreases in the same way for all steels, and above a concentration of approximately 9 mol/L (which corresponds to 63 %) H$_2$SO$_4$, the corrosion rate becomes low and assumes almost the same value for all tested steels. These results suggest that, in high acid concentrations, the rate of corrosion no longer depends on the carbon content, which means that another corrosion mechanism is occurring.
When carbon steel contacts concentrated sulfuric acid, the former is in fact reduced to form $\text{H}_2$ and the iron oxidizes with the formation of ferrous sulfate ($\text{FeSO}_4$), as shown in reaction (3),

$$\text{H}_2\text{SO}_4 + \text{Fe} \rightarrow \text{FeSO}_4 + \text{H}_2 \quad (3)$$

The $\text{FeSO}_4$ adheres to the steel surface and forms a protective layer. This layer prevents the metal against further attack by concentrated sulfuric acid. Therefore, the durability of tanks made of carbon steel depends on the preservation of the $\text{FeSO}_4$ layer.

According, the mass transfer of $\text{FeSO}_4$ is the controlling step in the corrosion mechanism for acid concentration between 50 % and 99 % for carbon steel at ambient temperature. At concentrations less than 50 %, corrosion rates are lower and are influenced by the carbon content of the carbon steel.

In the other case, the ‘hydrogen iron reduction’ process is the rate-limiting factor rather than the dissolution of $\text{FeSO}_4$. Carbon steel ring in concentrated 96 % $\text{H}_2\text{SO}_4$ at 25 °C at various immersion times, shows immediately after the immersion, the formation of a large amount of $\text{H}_2$ can be observed. After 24 h of immersion, a strong decrease of the metal attack is observed because of the presence of a dark protective layer of $\text{FeSO}_4$ on the metallic surface.

Stainless steel

Sulfuric acid is oxidizing when concentrated but is reducing at low and 'intermediate' concentrations. The response of most stainless steel types is that in general they are resistant at either low or high concentrations, but are attacked at intermediate concentrations. Commercially concentrated acid is around 96 % (specific gravity (sg) = 1.84).

Care is needed with very concentrated (98-100 %) acid at higher temperatures as slight changes to the conditions that help resistance i.e. the high concentration falling by dilution, increases in velocity or reductions in oxidizing conditions, can affect the corrosion resistance anticipated.

In the (Fig. 8) of iso-corrosion diagrams, each line shows the 0.1 mm/year corrosion rate. This is usually regarded as the boundary between acceptable and unacceptable performance. (The broken line represents the boiling point).
Fig. 8: Iso-corrosion diagram, 0.1 mm/y, for austenitic stainless steel in naturally aerated sulfuric acid of chemical purity. Broken line represents the boiling point.

Grade 904L stainless steel was specifically developed for sulfuric acid use and can be used across the whole concentration range up to 35 °C. The presence of chlorides in sulfuric acids can be an additional hazard.

The improvement in corrosion resistance moving from 304 to 316 is due to the addition of molybdenum. Further additions of molybdenum and copper in the (904L) grade extend the corrosion resistance in these reducing acid conditions. The molybdenum in types 316 and grade also helps improve resistance to chloride attack, when present as impurities in the acid. The alloying addition of copper is most beneficial to extending the resistance of stainless steels in intermediate concentrations of sulfuric acid. Silicon stainless steel grades should be considered for hot, very concentrated acid applications.

Aeration or the presence of oxidizing 'agents' in sulfuric acid contributes to the corrosion resistance of stainless steels. Stainless Steels have lower resistance to de-aerated sulfuric acid. Reducible ions such as Fe³⁺, Cu²⁺ and Sn⁴⁺ are effectively oxidizing agents and can reduce corrosion if present in the acid. Similarly oxidizing agents like chromic or nitric acid reduce corrosion rates, if present in the sulfuric acid. Chromium content is important to the resistance of the stainless steel and so type 310 can be considered when oxidizing agents are present.

important to be careful with corrosion data, as small variations in impurities or conditions can affect service corrosion rates and hence potential durability of stainless steels in sulfuric acid.

Stainless steels are more suitable than carbon steels for handling high flow rates of concentrated acid (90-98 %). The passive layer on stainless steels is more stable than the ferrous sulfate layer formed on carbon steel in turbulent flow conditions.
Copper

Copper does not normally displace hydrogen, even from acid solutions, and it is therefore virtually not attacked in non-oxidizing conditions. For strongly reducing conditions in the temperature range 300-400 °C, corrosion resistance is comparable, if not better, than stainless steel.

The corrosion resistance of copper alloys has been attributed to the formation of a protective film of cuprous oxide (Cu2O), and to doping of Cu2O layers with ions such as iron. This doping reduces the ionic or electronic conductivity of the film improving the corrosion resistance.

However, when copper alloys come into contact with most solutions, which invariably contain dissolved air, cathodic depolarization can occur which increases the chances that corrosion will take place. Therefore, it is difficult to lay down any general recommendations for the use of copper in acid solutions, since the rate of attack significantly depends on the particular circumstances.

In an investigation, the corrosion behavior of Cu-Fe and Cu-Al-Fe was studied in H2SO4 solutions in the absence and presence of different concentrations of some inorganic additives, Na2MoO4, K2Cr2O7, KIO3, and Na2B4O7. The technique of measurements used was open-circuit potential with potentiodynamic polarization. The polarization measurements indicated that the corrosion current of Cu-Fe is less than that of Cu-Al-Fe. The investigated additives in H2SO4 shifted Ecorr to more positive values and increases Icorr.

Under fairly mild conditions copper alloys are successfully used for handling sulfuric acids solutions. Corrosion rate, in general, increase with concentration of acid, temperature, amount of aeration, and speed of flow. All copper-based alloys are attacked rapidly by oxidizing acids such as, strong sulfuric acid, nitric acid or chromic acid (including di-chromates) and hydrocyanic acid.

Tin–bronzes, aluminum–bronzes, silicon–bronzes, and cupronickels are among the copper alloys most resistant to H2SO4 acids. For instance, aluminum-bronze will withstand 50% sulfuric acid at 120 °C and 60% sulfuric acid at 30 °C. Brasses should not normally be used in acids.

The dissolution of copper and brasses in acid solutions has been studied by several authors. In sulfuric acid, pitting attack has been found to occur in 95% sulfuric acid at 50 °C, in 80% sulfuric acid at 70 °C, and in 60% sulfuric acid at 100 °C. Various substances like Mn have been found to have an inhibiting effect on the rate of attack of copper or brasses in sulfuric acid.
Nickel

Sulfuric acid is the most widely used acid in all industry. It is less corrosive than hydrochloric acid, and its aggressiveness is highly dependent on acid concentration, temperature, and the presence of impurities. (Fig. 9) shows the corrosion rate of several alloys in boiling pure sulfuric acid.

![Fig. 9: Corrosion rate in boiling sulfuric acid.](image-url)

It shows that the nickel B-3 alloy has the lowest corrosion rate in boiling sulfuric acid. Only at the highest acid concentration (>70 %) does the corrosion rate of B-3 start to increase. However, these boiling points increase dramatically at the medium and high concentrations. For instance, at 20 % sulfuric acid, the boiling point is 104 °C, at 50 % is 123 °C, and at 80 % is 202 °C. Titanium Grade 2 and stainless steel 316L are not adequate for sulfuric acid service.

As in the case of HCL solutions, the temperature has a strong influence on the corrosion rate of Ni-alloys such as C-2000 and G-30; whereas, the corrosion rate of a Ni-Mo alloy (B-3) is almost unaffected by the temperature ‘low activation energy’.

(Table 3) show types of nickel alloy that should be considered for service in pure sulfuric acid, depending on the acid concentration and temperature. The selections are based on evidence that these alloys from the chosen groups exhibit rates of 0.5 mm/y or less over significant concentration and temperature ranges. The important revelations of this chart are the excellent corrosion resistance of the Ni-Mo alloys in pure sulfuric acid, the good resistance of the Ni-Cr-Mo alloys, and the usefulness of several groups at lower concentrations and temperatures.
Table 3: Nickel alloys for pure sulfuric acid.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>0 to 30% H$_2$SO$_4$</th>
<th>30% to 70% H$_2$SO$_4$</th>
<th>70% to 96% H$_2$SO$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>79°C to B. P.</td>
<td>Ni-Mo (B-3)</td>
<td>Ni-Mo (B-3)</td>
<td>Ni-Mo (B-3)</td>
</tr>
<tr>
<td>(175°F to B.P.)</td>
<td>Ni-Cr-Mo (C-2000)</td>
<td>Ni-Cr-Mo (C-2000)</td>
<td>Ni-Cr-Mo (C-2000)</td>
</tr>
<tr>
<td></td>
<td>Ni-Fe-Cr (G-30)</td>
<td>Ni-Fe-Cr (G-30)</td>
<td>Ni-Fe-Cr (G-30)</td>
</tr>
<tr>
<td></td>
<td>Ni-Cr-Si (D-205)</td>
<td>Ni-Cr-Si (D-205)</td>
<td>Ni-Cr-Si (D-205)</td>
</tr>
<tr>
<td></td>
<td>Ni-Cu (400)</td>
<td>Ni-Cu (400)</td>
<td>Ni-Cu (400)</td>
</tr>
<tr>
<td>52°C to 79°C</td>
<td>Ni-Mo (B-3)</td>
<td>Ni-Mo (B-3)</td>
<td>Ni-Mo (B-3)</td>
</tr>
<tr>
<td>(125°F to 175°F)</td>
<td>Ni-Cr-Mo (C-2000)</td>
<td>Ni-Cr-Mo (C-2000)</td>
<td>Ni-Cr-Mo (C-2000)</td>
</tr>
<tr>
<td></td>
<td>Ni-Fe-Cr (G-30)</td>
<td>Ni-Fe-Cr (G-30)</td>
<td>Ni-Fe-Cr (G-30)</td>
</tr>
<tr>
<td></td>
<td>Ni-Cr-Si (D-205)</td>
<td>Ni-Cr-Si (D-205)</td>
<td>Ni-Cr-Si (D-205)</td>
</tr>
<tr>
<td></td>
<td>Ni-Cu (400)</td>
<td>Ni-Cu (400)</td>
<td>Ni-Cu (400)</td>
</tr>
<tr>
<td>RT to 52°C</td>
<td>Ni-Mo (B-3)</td>
<td>Ni-Mo (B-3)</td>
<td>Ni-Mo (B-3)</td>
</tr>
<tr>
<td>(RT to 125°F)</td>
<td>Ni-Cr-Mo (C-2000)</td>
<td>Ni-Cr-Mo (C-2000)</td>
<td>Ni-Cr-Mo (C-2000)</td>
</tr>
<tr>
<td></td>
<td>Ni-Fe-Cr (G-30)</td>
<td>Ni-Fe-Cr (G-30)</td>
<td>Ni-Fe-Cr (G-30)</td>
</tr>
<tr>
<td></td>
<td>Ni-Cr-Si (D-205)</td>
<td>Ni-Cr-Si (D-205)</td>
<td>Ni-Cr-Si (D-205)</td>
</tr>
<tr>
<td></td>
<td>Ni-Cu (400)</td>
<td>Ni-Cu (400)</td>
<td>Ni-Cu (400)</td>
</tr>
</tbody>
</table>

However the presence of contaminants in sulfuric acid could change the corrosion rate of the nickel alloys. (Fig. 10) shows the corrosion rate of alloys B-3 and C-2000 in pure sulfuric acid and in sulfuric acid contaminated with 200 ppm chloride ions (as NaCl). The corrosion rate of both alloys increases if the solution is contaminated; however, the effect seems more pronounced for the Ni-Cr-Mo alloy.

Fig. 10: The effect of contamination by chloride in sulfuric acid on alloy B-3 and C-2000.
3.2 Nitric acid

Nitric acid (HNO₃) is one of the most widely used acids in the chemical processing industry. It is a strongly oxidizing acid that is aggressively corrosive to many metals. The acid temperature and concentration affect corrosion rate as does the composition of the alloy exposed to it. Nitric acid is normally considered to be a strong acid at ambient temperatures. There is some disagreement over the value of the acid dissociation constant, though the pKa value is usually reported as less than −1. This means that the nitric acid in diluted solution is fully dissociated except in extremely acidic solutions. The pKa value rises to 1 at a temperature of 250 °C.

Nitric acid can act as a base with respect to an acid such as sulfuric acid. General attack, crevice attack, and intergranular attack are common in HNO₃. Velocity, aeration, and the presence of impurities such as chlorine and fluorine in the acid all affect corrosion rate. Stainless steels, chromium-containing alloys, and to a lesser degree-titanium alloys are useful in HNO₃. Carbon steel and copper alloys are not generally advisable.

Carbon Steel

The corrosion behavior of carbon steel in various concentrations of nitric acid (HNO₃), has been studied. Specimens were exposed in the acidic media for a week and corrosion rates evaluated, using the weight loss method. It was observed that nitric acid environment was very corrosive to carbon steel because of its oxidizing nature.

The acidic concentration and exposure time affected the corrosion of the steel. Corrosion rates of carbon steel in the nitric acidic media studied were found to be quite high. This could be attributed to the fact that the carbon content in itself has little if any effect on general corrosion resistance of steels.

Carbon steel was found to corrode in different concentrations of HNO₃ solutions. This was evidenced by the decrease in the original weight of the metal coupons. The corrosion of carbon steels in HNO₃ is attributed to the presence of water, air, and H⁺ which accelerated the corrosion process. (Fig. 11) shows that the weight loss of carbon steel increased with time and concentration. This observation is attributable to the fact that the rate of a chemical reaction increases with increasing concentration.
It can also be clear from (Fig. 11) that the corrosion of carbon steel is not a simple homogeneous process, but a heterogeneous one. It consists of intermediate steps as revealed by the non-uniformity of the plots.

![Graph: Weight loss as a function of Time for carbon steel in different HNO₃ concentrations.]

**Fig. 11**: Weight loss as a function of Time for carbon steel in different HNO₃ concentrations.

The corrosion of carbon steel in nitric acid is very significant because nitric acid is known to be a strong oxidizing agent. An autocatalytic mechanism has generally been proposed to explain the high rate of corrosion in this medium. The primary displacement of H⁺ ions from the solutions is followed by HNO₃ reduction rather than hydrogen evolution since the acid reduction leads to a marked decrease in free energy. The reaction (4) can be summarized as follows:

\[
\text{Fe} + 4\text{HNO}_3 \rightarrow \text{Fe (NO}_3)_2 + 2\text{H}_2\text{O} + 2\text{NO}_2
\]  

(4)

This reaction leads to the evolution of nitrogen (II) oxide and production of Fe (NO₃)₂ which led to further coloration of the medium.

Furthermore, the corrosion rates of the coupons after the 3rd and 7th days reveal that dissolution of carbon steel is faster within the first three days, and then gradually slows down as a result of the formation of passivating corrosion complexes that normally shield the metal surface from the media. The observed trend in the corrosion behavior of the carbon steel is significant in that the more the material is exposed to the environment, the lower the corrosion rate. This behavior could be explained from the concept of passivity and the decrease in the strength of the acid as corrosion complexes get formed in the media.
Stainless Steel

Selection of stainless steels for service in nitric acid requires consideration of all forms of corrosion, along with impurity levels and degree of aeration. When an alloy with sufficient general corrosion resistance has been selected, care must be taken to ensure that the material will not fail by pitting or SCC due to chloride contamination. Alloy selection also depends on fabrication and operation.

Nitric acid is strongly oxidizing and promotes the resistance of stainless steel to corrosion. Generally stainless steels are resistant to corrosion in nitric acid. Nitric acid is used in the chemical 'passivation' of stainless steels. Commercially concentrated acid is around 65%.

An investigation has been carried out, and it was reported that the resistance of stainless steel to nitric acids depends on the hydrogen ion (H\(^+\)) concentration and the oxidizing capacity of the acid, with variables as chromium, nickel and carbon content; and heat treatment. For example, annealed stainless steel resists strong HNO\(_3\) in spite of the low pH, because HNO\(_3\) is highly oxidizing and forms a passive film due to the chromium content of the alloy.

Fig. 12: Corrosion rates of various stainless steel in boiling HNO\(_3\).
As noted above, stainless steels have broad applicability in HNO₃ primarily because of their chromium content. Most AISI 300-series stainless steels exhibit good or excellent resistance in the annealed condition in concentrations from 0 to 65 % up to the boiling point.

(Fig. 12) illustrates the good resistance of type 304 stainless steel, particularly when compared with the lower-chromium type 410 stainless steel. More severe environments at elevated temperatures, require alloys with higher chromium. In HNO₃ cooler-condensers, such stainless alloys as 7-Mo PLUS (UNS S32950) and 2RE10 (UNS S31008), are candidates for service.

This also shows that the 304 types can be used over a wide range of concentration and temperature, up to 95 %, for storage applications. The 304 types are preferable to 316 types for nitric acid applications. However, this is an exception to the ‘general rule’ for stainless steels where the 316 types are normally found to be more corrosion resistant than 304 types. Over 95 % concentration, aluminum alloys should be considered OR 4 % silicon stainless steels.

Any additional chlorides or fluorides in nitric acid may increase corrosion rates by pitting. Localized attack at grain boundaries (IC) can occur in hot concentrated nitric acid. This can occur in the heat-affected-zone (HAZ) of welds. Prolonged heating in a range of around 600-800 °C, followed by exposure to concentrated nitric acid, can also result in localized attack, due to the precipitation of the brittle “intermetallic” (iron-chromium) compounds (sigma phase).

To avoid the risk of localized corrosion, especially where post weld heat treatment is impractical, the low carbon 304L stainless steel types should be considered. Solution heat treatment (1050 - 1100 °C followed by fast cooling) on the standard carbon 304 type can be considered as an alternative. These treatments should also re-dissolve any sigma formed. Compositions of 304L type have been used with silicon, phosphorous & Sulphur limited to very low residual levels to improve the resistance in hot concentrated nitric acid.
Copper

Copper is not resistant in nitric acid. It is attacked by 15 mg/l HNO₃ at 15 °C with a material consumption rate of 20 g/m²h after 1 h and 160 g/m²h after 5 h. This rate could be reduced to about 27 g/m²h after 4 h by 2 mg/l maize extract (PH inhibitor, Russian grade of (40 – 50) % protein + (22 – 27) % soluble hydrocarbons + (1 – 3) % fat + < 0.5 % starch + (0.7 – 1.1) % lactic acid), which corresponds to an inhibition efficiency of 74 %. At a concentration of 10 mg/L nitric acid, the inhibition efficiency at 2 g/m²h was 82 %.

The severe corrosion on copper in nitric acid can also be seen from current density measurements. At a polarization voltage of + 0.23 V (SHE), the current density at room temperature could be reduced to < 0.001 mA/cm², which corresponds to a corrosion rate of 0.01 mm/y, if the current density was stationary.

Also to clarify the influence of the crystal structure of copper on its corrosion in nitric acid, dissolution tests were carried out on copper mono-crystal beads in nitric acid (0.037 to 0.21 mol/mol) between 25 °C and the boiling point. The corrosion rate on the (100), (111), (311) planes was between 1 and 10 µm/min.

The wear resistance and corrosion resistance of copper and bronze in nitric acid were improved by diffusion layers of aluminum at 947 and chromium at 900 – 930 °C. Addition of polyvinyl alcohol, which improves chemical polishing of copper in dilute nitric acid and dilute mixtures of nitric and phosphoric acids, reduces the solubility of copper and increases the uniformity of material removal as a result of an increase in the solution viscosity.

The corrosion rate of copper alloys of different combinations are generally high in varying concentrations of nitric acid. The inhibition efficiency of most alloys are not sufficient to reduce the corrosion rates, in particular in more highly concentrated nitric acid, to values of industrial interest.

Although in some cases, the high corrosion rate of some copper alloys are reduced. For instance, copper-tin alloys BrKh08 and SP19 in concentrated nitric acid at room temperature is drastically reduced by ‘aluchromizing’ of the alloys at 980 °C for 6 and 9 h respectively. Also with the use of some mechanical heat treatments, considerable resistance to corrosion can be achieved.
Nickel

Nickel have little resistance to oxidizing acids such as nitric acid. The material consumption rate and the corrosion potential of nickel as a function of the concentration of nitric acid at room temperature; has shown that at the concentration of about 8 mol/L, a sharp decrease in the material consumption rate from about 500 to 15 g/m²h occurred, coupled with a rise in the corrosion potential from about 0.2 to 0.85 V (SHE).

The behavior of nickel in nitric acid solutions depends ‘greatly’ on the acid concentration. At concentrations below 40 %, Ni dissolves rapidly, while it is passivated in a stable form above 50 %. If chlorides are simultaneously present, pitting corrosion can be expected. Passivity is also achieved in dilute acid by oxidizing agents, such as potassium dichromate.

31 and 103 min respectively are needed to remove a 12 or 52 µm thick nickel layer on steel using the following pickling solution (100 mL/L HNO₃ + 200 mL/L ethylene-diamine + 50 g/L sodium m-nitro-benzenesulfonate; pH = 10) at 65 °C. The steel is not attacked during this experiment.

Ni-Cr alloy heated at 1100 °C is severely attacked by nitric acid. The main advantage of Ni-Cr alloys in comparison with steels, such as, for example, 12Kh18N10T, is their resistance in nitric acid solutions containing fluoride ions.

Ni-Cr-Fe (Inconel 690) alloy is more resistant than (Inconel 600) by a factor of 100, and it is resistant to inter-crystalline (IC) corrosion. The corrosion behavior of various hard Ni-based alloys in hot 30 % nitric acid at 50 °C, has shown that the corrosion resistance of the alloys increases with increasing chromium content, decreasing molybdenum content and the addition of tungsten.

Ni-Cr-Mo alloys (Hastelloy C4) alloy has a corrosion rate 0.2 mm/y in 10 % nitric acid at 100 °C while Hastelloy C 276 has a corrosion rate of 0.43 mm/y at the same conditions. Hastelloy C 276 can be used for processing the spent fuel elements from pressurized water reactors in solutions of HNO₃ + HF + dissolved substances. However, the welding joints of the alloys are preferentially attacked. The Ni-Cr-Mo-Nb alloy (JS-625) shows not only high strength but also a good corrosion resistance, also in contaminated nitric acid.

Nickel-copper alloys are not recommended as materials in the presence of oxidizing acids, such as nitric acid, because their corrosion rates are too high. For rapid and reliable differentiation using Monel series, the U.S. Navy utilizes rapid dissolution in 50 % nitric acid at room temperature.

Ni-Mo alloys (Hastelloy) are not resistant in nitric acid. Hastelloy B2 corrodes in boiling 10 % nitric acid with a corrosion rate of 483 mm/y, while Hastelloy B suffers catastrophic corrosion in nitric acid even at room temperature.
3.3 Hydrochloric acid

Hydrochloric acid (HCl) is second to sulfuric acid in the numerous and diverse applications of the manufacturing and chemical industry. It is an extremely corrosive and aggressive acid depending on its concentration, temperature, and oxidizing impurities. Hydrochloric acid is a reducing solutions and generally induce hydrogen evolution at cathodic sites.

Chlorides can originate from both the ovens in the petroleum-refining unit and the decomposition of organic chlorides that are initially added to hydrogenase the petroleum. It should be neutralized afterwards, so to avoid corrosion in the following stages. In modern refineries, petroleum first goes to chloride removal units that reduce the chloride content between 2.85 g/m$^3$ and 28.5 g/m$^3$ (1 to 10 lb. in 1000 barrels), but even at such concentrations, HCl corrosion still remains an issue. Over pH 5, however, this corrosion is considered negligible.

In other words, neutral environments that have pH in the range of 5-8 seem to be the most appropriate conditions for corrosion events not to occur. Corrosion due to aluminum chloride (AlCl$_3$) is negligible in the absence of water, but with water it hydrolyzes, forming HCl which is very corrosive and leads to pitting corrosion even in austenitic steels.

Carbon Steel

Carbon steel is one of the major construction materials, which is extensively used in chemical and allied industries for the handling of acid, alkali and salt solutions. Hydrochloric acid is the most difficult of the common acids to handle from the standpoints of corrosion and materials of constructions. Extreme care is required in the selection of materials to handle the acid by itself, even in relatively dilute concentrations or in process solutions containing appreciable amount of hydrochloric acid. HCl is very corrosive to most of the common metals and alloys.

HCl has the following corrosion reactions (5) & (6) with iron in presence of H$_2$S, which is commonly found in petroleum:

Fe + 2HCl → FeCl$_2$ + H$_2$  \hspace{1cm} (5)

FeCl$_2$ + H$_2$S → 2HCl + FeS  \hspace{1cm} (6)
An experiment was used to investigate the corrosion mechanism of carbon steel in solutions of HCl (0.25-2.5 mol/dm³) at 25 °C by using chemical (hydrogen evolution, HE and Mass loss, ML) methods. The morphology of carbon steel surface before and after immersion in HCl solutions was examined at different concentrations of the acid.

The morphology of the carbon steel surface was studied by making photomicrograph of the surface before and after immersion in HCl solutions of different concentrations, in aerated, stagnant solutions at 25 °C.

![Graph](image)

**Fig. 13**: Hydrogen volume vs Time for carbon steel in different HCl concentration at 25 °C.

Data are plotted for volume of H₂ gas evolved against time in minutes for 0.25 to 2.50 mol/dm³ of HCl concentrations and presented in (Fig. 13). Slopes of such lines are estimated and taken as the rates of corrosion reaction. The good linearity in the relations indicates the absence of insoluble film on the metal surface during corrosion.

**Table 4**: Corrosion rate for carbon steel sample at different HCl concentration at 25 °C.

<table>
<thead>
<tr>
<th>$c_{\text{HCl}}$ (mol dec⁻³)</th>
<th>0.25</th>
<th>0.5</th>
<th>1.0</th>
<th>1.5</th>
<th>2.0</th>
<th>2.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho_{\text{H₂}} \times 10^2$ ml cm⁻² min⁻¹</td>
<td>2.083</td>
<td>3.308</td>
<td>5.157</td>
<td>5.658</td>
<td>7.645</td>
<td>9.106</td>
</tr>
<tr>
<td>$\rho_{\text{MH}} \times 10^8$ g cm⁻² min⁻¹</td>
<td>5.841</td>
<td>8.143</td>
<td>12.214</td>
<td>13.060</td>
<td>17.756</td>
<td>20.986</td>
</tr>
</tbody>
</table>
The calculated corrosion rates obtained from (HE and ML) measurement, respectively, against concentrations are tabulated in (Table 4). As observed, both HE and ML increase with increasing of acid concentration, indicating acceleration behavior for the metal dissolution. This result is expected because with increasing acid concentration, both acidity and Cl⁻ ion concentration are increased too. Accordingly, iron dissolution in HCl solutions depends principally upon the chloride ion activity over the pH range 0.0 to –0.6. While at more negative pH values and at high chloride ion activity, the corrosion rate is more dependent upon pH. On the other hand the iron dissolution in HCl solutions depends on H⁺ ion more than the Cl⁻ ion.

(Fig. 14) shows that there is discrepancy between (HE and ML) only at the lowest HCl concentrations. The straight line in this figure correlates all points (even that showed discrepancy between HE and ML) with good correlation coefficient of 0.969.

Microstructural studies for the carbon steel surface were performed before and after immersing the studied specimen in the tested solution for 90 min. at 25°C and illustrated in (Fig. 15). Before exposure to the corrosive solution, parallel features on the clean polished steel surface which are associated with polishing scratches were observed, (Fig. 15a).

Examination of (Fig. 15b) revealed that the corrosion attack (general and pitting corrosion) becomes more pronounced as HCl concentration increases. At acid concentrations 1.00 M, (Fig. 15b (1-2)), the pits were partly closed, deep and did not contain visible deposit, while at acid concentrations > 1.00 M, (Fig. 15b (3-4)), the pits were open and their diameter was very large.
These pits were full of black corrosion products. These observations can be explained on the basis of Cl\(^-\) ion activity and the extent of its contribution in acceleration metal dissolution.

**Fig. 15 (a/b):** Micrographs for carbon steel surface in (a) before and (b) after immersion for 90 mins at 25 °C in HCl solutions. (1) 0.25, (2) 1.00, (3) 1.50 and (4) 2.50 mol/dm\(^3\).
Stainless steel

The most commonly used austenitic stainless steel, such as types 304 and 316, are not resistant to hydrochloric acid at any concentration and temperature. At ambient temperatures and above, corrosion rates are high. Nickel, molybdenum, and to a lesser extent copper impart some resistance to dilute hydrochloric acid, but pitting, local attack, and stress corrosion cracking may result. Sub-ambient temperatures will slow the corrosion rate, but will invite stress corrosion cracking. Type 316 stainless steel has been known to crack in 5 % hydrochloric acid at 0 °C.

At high corrosion rate (> 0.25 mm/y), stress corrosion cracking is unlikely to occur. However, the corrosion products, particularly FeCl₂, will cause cracking. Chlorides can penetrate and destroy the passivity (oxide film) that is responsible for the corrosion resistance of stainless steel, and the corrosion engineer should resist every attempt to use stainless steels in environment containing chlorides.

The standard ferritic stainless steels, such as the type 410 and 430, should not be considered, because their corrosion resistance to hydrochloric acid is lower than that of carbon steel. An exemption is 29-4-2 stainless steel, which reportedly resists up to 1.5 % hydrochloric acid to the boiling point and remains passive. However, it is not suitable at higher concentrations, and the alloy is susceptible to stress corrosion cracking, although its resistance is reported to be high.

Some stainless steels – such as 20 Cb-3, with its high nickel content (32 to 38 %), 2 to 3 % Mo, and 3 to 4 % Cu; resist dilute hydrochloric acid at ambient temperatures. However, 20 Cb-3 is susceptible to pitting and crevice attack in acid chlorides and should be used with caution.

The low-carbon grades will be more satisfactory if welding is involved. Furthermore, corrosion studies of sintered austenitic stainless steels have shown that the corrosion resistance improves significantly with increasing density in acidic environments such as dilute hydrochloric acid.
Copper

Copper are among the earliest metals known to man, as they have been used from prehistoric times, and their present-day importance is greater than ever before. Their widespread use depends on a combination of good corrosion resistance in a variety of environments, excellent workability, high thermal and electrical conductivity, and attractive mechanical properties at low, normal, and moderately elevated temperatures. Copper and its alloys have a very diverse range of properties and their application exposes them to many types of environment.

Copper does not normally displace hydrogen, even from hydrochloric acid solutions, and it is therefore virtually not attacked in non-oxidizing conditions. For strongly reducing conditions in the temperature range 300-400 °C, corrosion resistance is comparable, if not better, than stainless steel. However, when copper alloys come into contact with most solutions, which invariably contain dissolved air, again cathodic depolarization can occur which increases the chances that corrosion will take place.

Therefore, it is difficult to lay down any general recommendations for the use of copper in HCl solutions, since the rate of attack significantly depends on the particular circumstances. Under fairly mild conditions copper are successfully used for handling solutions of hydrofluoric, hydrochloric, sulfuric, phosphoric, acetic, and other fatty acids. Rates of corrosion, in general, increase with concentration of acid, temperature, amount of aeration, and speed of flow.

Tin-bronzes, aluminum-bronzes, silicon-bronzes, and cupronickels are among the copper alloys most resistant to hydrochloric acids. For instance, the alloys containing 6 to 10 % aluminum and up to 3 % iron have a good to moderate resistance to 5 to 30 % hydrochloric acid at room temperature. Aluminum-bronzes are distinctly superior to unalloyed copper; they are not even attacked locally. Comparative investigations showed that Al-bronze (Cu-6.8Al 3.2Fe 0.8Mn) is more resistant to 5, 10, 15 % HCl than alpha brass Cu-21Zn 2Al. However, 1 % ferric chloride in 15 % hydrochloric acid increases the corrosion of Al-bronzes by a factor of 6 to 8. Silicon bronze is resistant to hydrochloric acid over the range 10 % HCl at 70 °C, 20 % HCl at 50 °C, 35 % HCl at 15 °C. They show a corrosion rate of less than 0.125 mm/y at room temperature, they are quite suitable for use in 20 % hydrochloric acid.

Brasses should not normally be used in hydrochloric acids. In brass, the zinc content of which is less than 15 % has moderate resistance in hydrochloric acid and loses up to 1.55 mm/y at room temperature. Alloys which contain 30 or 39 to 40 % zinc are severely attacked not only by cold but also warm hydrochloric acid and are therefore completely unsuitable.
The attack leads to dezincification, and the resulting copper (II) chloride accelerates the corrosion. Brass is dissolved with the evolution of hydrogen at higher temperatures. All copper-based materials are attacked rapidly by oxidizing acids such, nitric acid, strong sulfuric acid, or chromic acid.

The maximum temperature of operation of copper in dry HCl is 93 °C and in dry chlorine is 200 °C. The dissolution of copper and brasses in hydrochloric acid solutions has been studied by several authors. Various substances have been found to have an inhibiting effect on the rate of attack of copper and copper alloys in hydrochloric acid such as; 0.05-2.0 % Mercaptobenzothiazole, 2-benzimidazolethiol (inhibition efficiency about 99 %), benzothiazole and benzotriazole (each with the addition of a small amount of ammonium chloride, inhibition efficiency about 95 %), 10-2 mol/L 2 mercapropylimidine (2-MP) in 0.1 mol/L HCl (inhibition efficiency about 55 %), 0.8mL/L Rodine No.213 for removing deposits from copper pipes.

Ions of trivalent iron and divalent copper reduce the inhibition efficiency of the inhibitors. Aqueous extracts of substances occurring in nature showed less effective inhibition for copper in HCl solutions. The corrosion rate and behavior of copper in hydrochloric acid is highly dependent on temperature, concentration and aeration.

Nickel

The corrosion behavior of nickel was studied in different concentrations of HCl using conventional known techniques. It was found that, HCl accelerate the corrosion of nickel and its alloys. The corrosion rate decreases in the following the order of nickel alloys > nickel. This was attributed to the presence of alloying content in the chemical composition of nickel.

Hydrochloric acid is used in applications in the chemical process industry, where carbon steel, stainless steel and copper alloys cannot generally tolerate exposure to HCl; therefore, the use of nickel alloys is essential. These alloys possess the ability to passivate in the presence of HCl, yet in many cases high concentrations and temperatures can disrupt the alloy’s passive state.

Alloying with copper, molybdenum, and tungsten all increase the inherent corrosion resistance of nickel. In addition, molybdenum and tungsten are significant in highly aggressive environments,
strengthening agents, due to their large atomic sizes. The role of chromium is the same as that in the stainless steels; it enhances the formation of passive surface films, in the presence of oxygen. These passive films impede the corrosion process. Iron, if added to the nickel alloys, also affects passivation. Silicon is beneficial at high corrosion potentials, where chromium-rich passive films cannot be maintained. It offers extended protection through the formation of protective (silicon-rich) oxides.

The nickel alloys that should be considered for service in pure HCl acid are shown in (Table 5), a nine-segment chart organized by concentration and temperature. The selections are based on evidence that alloys from the chosen groups exhibit rates of 0.5 mm/y or less over ranges, within those segments. (Table 5) covers only concentrations up to 20 %, the maximum that can be sustained in a boiling solution. It indicates that, of the nickel alloys, only those from the nickel-molybdenum group are suitable at high concentrations and temperatures.

In fact, molybdenum is the most important alloying element for good performance of nickel base alloys in pure hydrochloric acid (reducing conditions). The corrosion rate in boiling HCl decreases as the content of molybdenum in the alloy increases.

Table 5: Nickel alloy selection for pure HCl.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>0 to 5% HCl</th>
<th>5% to 10% HCl</th>
<th>10% to 20% HCl</th>
</tr>
</thead>
<tbody>
<tr>
<td>79°C to B.P.</td>
<td>Ni-Mo (B-3)</td>
<td>Ni-Mo (B-3)</td>
<td>Ni-Mo (B-3)</td>
</tr>
<tr>
<td>(175°F to B.P.)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>52°C to 79°C</td>
<td>Ni-Mo (B-3)</td>
<td>Ni-Mo (B-3)</td>
<td>Ni-Mo (B-3)</td>
</tr>
<tr>
<td>(125°F to 175°F)</td>
<td>Ni-Cr-Mo (C-2000)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ni-Cu (400)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RT to 52°C</td>
<td>Ni-Mo (B-3)</td>
<td>Ni-Mo (B-3)</td>
<td>Ni-Mo (B-3)</td>
</tr>
<tr>
<td>(RT to 125°F)</td>
<td>Ni-Cr-Mo (C-2000)</td>
<td>Ni-Cr-Mo (C-2000)</td>
<td>Ni-Cr-Mo (C-2000)</td>
</tr>
<tr>
<td></td>
<td>Ni-Fe-Cr (G-30)</td>
<td>Ni-Cu (400)</td>
<td></td>
</tr>
</tbody>
</table>

*For each alloy group, one example is given. B.P. = boiling point, RT = room temperature.

Monel is in general resistant to up to 20 % cold hydrochloric acid but is vigorously attacked at 50 °C to 60 °C even by 2 % acid. Monel is very sensitive to the presence of air: in aerated hydrochloric acid the corrosion rate increases by a factor of 5 to 10. However, Monel is not sensitive to stress corrosion cracking in hydrochloric acid.
Since Monel has good resistance to dilute 0.5 % boiling acid, distillation columns and rectification equipment for the distillation and steam distillation of chlorinated hydro-carbons are manufactured from this material. The corrosion rate at the boiling point of the solvents is 0.007 mm/y in the absence of water and 0.025 to 0.25 mm/y in the presence of water.

Monel is often used in the pickling of objects made of iron by means of cold hydrochloric acid of a concentration below 10 %. Thus, chains, hooks, bars, baskets, stands, bolts, nuts, and hoods made of Monel have proved to be suitable in the pickling operation and have attained a service life of 10 to 15 years. It should be noted that hydrogen always creates a reducing atmosphere in the pickling bath. Thus, Monel is protected cathodically by contact with the steel parts.

However, Monel pickling vessels must not be used under any circumstances in contact with hydrochloric acid; for this purpose, Hastelloy B is more suitable. Inhibitors which are added to the pickling bath render the pickling material passive, so that only the scale is attacked by hydrochloric acid.

Oxidizing impurities in hydrochloric acid, such as ferric ions (Fe$^{3+}$), are detrimental to the performance of the nickel-molybdenum and nickel-Copper alloys. Under such conditions, the nickel-chromium-molybdenum alloys constitute the best choice, because they are tolerant of residuals, although they are temperature-limited at the higher acid concentrations.

![Graph](image)

**Fig. 16:** Corrosion rate of commercial alloys in a solution of HCl contaminated with ferric ions.
(Fig. 16) shows the corrosion rate of several alloys in boiling 2.5 % HCl solution as a function of the concentration of Fe$^{3+}$ in the solution. The corrosion rates of 316L SS and alloy 825 are high, and are not affected significantly by the presence of ferric ions.

The corrosion rate of the B-3 alloy in the pure boiling acid is low, but it gradually increases as the content of Fe$^{3+}$ in the solution increases. The corrosion rate of C-2000 in pure acid is higher than that of the B-3 alloy; however, a content of only 3 ppm Fe$^{3+}$ produces a decline in its corrosion rate by almost two orders of magnitude. The oxidizing Fe$^{3+}$ promote the passivation of C-2000 by the formation of a chromium-rich oxide film that reduces the uniform dissolution rate.

It shows that the nickel-chromium-molybdenum alloys such as C-2000 are resistant to HCl in a moderately broad range of concentrations and temperatures whereas 316L stainless steel is generally unsuitable for hydrochloric acid services. Alloy 400 and 825 may be adequate at room temperature.
4. CORROSION BY WEAK ACID

The weak acidic gases are CO₂ Corrosion (Sweet Corrosion) and H₂S Corrosion (Sour Corrosion). Their corrosion behavior has been one of the major problems in the Oil/Gas industry since 1940. The presence of carbon dioxide, hydrogen sulfide (H₂S) and free water can cause severe corrosion problems in oil and gas pipelines. Internal corrosion in wells and pipelines is influenced by temperature, CO₂ and H₂S content, water chemistry, flow velocity, oil or water wetting and composition and surface condition of the steel. A small change in one of these parameters can change the corrosion rate considerably. The corrosion product of CO₂ and H₂S are those of Iron Carbonate (FeCO₃) at high T and Iron Sulfide (FeS) respectively at Low T. Localized corrosion with very high corrosion rates can occur when the corrosion product film does not give sufficient protection, and this is the most feared type of corrosion attack in oil and gas pipelines.

4.1 CO₂ corrosion

Carbon dioxide (CO₂) corrosion has been recognized as the major problem in internal pipeline corrosion, and is one the most studied form of corrosion in Oil/Gas industry. This is generally due to the fact that the crude oil and natural gas from the oil reservoir / gas well usually contains some level of CO₂. The major concern with CO₂ corrosion in oil and gas industry is that CO₂ corrosion can cause failure on the equipment especially the main downhole tubing and transmission pipelines and thus can disrupt the oil/gas production. The basic CO₂ corrosion reaction mechanisms occurs when water wetting takes place and dissolves in water phase to give carbonic acid which is weak acid, bicarbonates and carbonates as a function of pH and the solution temperature. It is of general type (mesa corrosion) or localized one (pitting type).

The major chemical reactions that forms carbonic acid as shown in equations (7), (8) and (9),

CO₂ dissolution to carbonic acid

\[
H₂O + CO₂ = H₂CO₃ \quad (7)
\]

Carbonic acid (weak acid) dissociates to bicarbonates and carbonates

\[
H₂CO₃ = H+ + HCO₃^- \quad (8)
\]
\[
HCO₃^- = H+ + CO₃²^- \quad (9) \quad \text{at PH is slightly acid (> 3)}
\]
Carbon steel

The presence of CO\(_2\) and therefore, carbonic acid enhances the corrosion rate of carbon steel by accelerating the cathodic reaction. When the reduction of the adsorbed carbonic acid molecule occurs at the metal surface, the mechanism is called direct reduction known as ‘De Waard Williams approach for CO\(_2\) (Sweet) Oil & Gas’ in 1975. An alternative explanation has carbonic acid providing additional hydrogen ions via its dissociation while the dominant cathodic reaction is ‘reduction of hydrogen ions’; in a mechanism called buffering effect.

In a recent investigation using electrochemical technique, it was found out that the exact mechanism of carbonic acid, affects only the ‘cathodic limiting current’. The charge transfer current is found to respond only to a change in pH, indicating ‘reduction of hydrogen ion’ as the main cathodic reaction. The ‘buffering effect’ is therefore considered to be dominant. The ‘direct reduction’ of carbonic acid appears to be insignificant in comparison.

The presence of carbonic acid only affects the ‘cathodic limiting current’ due to the ability of carbonic acid to provide hydrogen ions by dissociation, when the latter are rapidly consumed by reduction at the metal surface. Hydrogen ions are the dominant cathodic reactants reduced at the metal surface, irrespective of whether carbonic acid is present.

The complexity of the CO\(_2\) mechanism also investigated noted the effect of chlorides in increasing the corrosion of carbon steel in CO\(_2\). For instance (Fig. 17) shows the variation in corrosion rate of N80 carbon steel with different Cl- contents (0–150 g/L), at a CO\(_2\) partial pressure of 20 bar and temperature of 100 °C. The curve appears as a reversal ‘V’ shape, showing a peak.

![Fig. 17: Corrosion rate of N80 carbon steel in solution with different Cl- content at 100 °C and at a CO\(_2\) partial pressure of 20 bars after 72 hours.](image-url)
The corrosion rate increases sharply with increasing Cl- content and reaches the maximum value at 25 g/L. The corrosion rate sharply decreases as the Cl- content increasing from 25 to 100 g/L and then gradually decreases between 100 and 150 g/L.

Increasing chloride content can reduce CO₂ solubility and CO₂ corrosion process is mix-controlled by both activation and mass-transfer steps with increasing Cl- content. Cl- has no effect on the composition of the corrosion product. Moreover, Cl- can destroy the corrosion product films and change the morphology of corrosion product films. Inhibiting of the carbon steel can be achieved by improving the Cr content in the carbon steel matrix.

Stainless steel

The ferritic stainless steel X 10 Cr 13, X 20 Cr 13, X 22 Cr-Ni 17 and X Cr-Ti 17 with 13 to 18 % chromium and the austenitic Cr-Ni steels X 5 Cr-Ni 18 9, X 10 Cr-Ni-Ti 18 9 and X 10 Cr-Ni=Nb 18 9 are used in aqueous solutions of carbon dioxide. A stainless steel containing 12 % chromium loses only 0.02 mm/y in aqueous solution containing carbonic acid.

Under the conditions of natural gas extraction, in which unalloyed and low-alloyed steels suffer corrosion rates of 5 to 6 mm/y, due to gas condensates, the 13 % Cr stainless steel X 10 Cr 13 is successfully used for the Christmas tree (of ascending pipeline). Although the chlorine content of the natural gas indicates pitting corrosion of Cr stainless steel, resulting in the greater loss of material.

The corrosion rate of the 13 % Cr stainless steel are 0.022 mm/y in the aerated and 0.003 mm/y in the gas-rich condensate. The Stainless steel X 10 Cr 13 (Type 410) is not resistant in salt solutions of 18 % NaCl and 9 % CaCl₂ saturated with CO₂ and H₂S such as occur in deep wells. The corrosion rate after 240 hours at 20 °C was about 0.2 mm/y in salt solution saturated with CO₂. But stainless steel containing 9 % Cr and 1 % Mo can be used in NaCl solution containing CO₂ when temperature are below 100 °C and the chloride content does not exceed 10 g/L.

The erosion-corrosion resistance of stainless steel X 20 Cr 13 in aqueous solution containing carbon dioxide is incomparably better than that of an unalloyed steel, as is exhibited by C 15 with a corrosion rate of about 40 mm/y under identical conditions with increase in temperature from 60 to 80 °C resulting in an increase of 25 % in the corrosion loss. Thus material loss can be further reduced by 50 % by using the stainless steel X 2 Cr-Ni-Mo-N 22 5 instead of X 20 Cr 13.
Copper

The corrosion of copper decreases with decreasing corrosive carbonic acid content. After formation of a protective layer, the solubility of the copper falls to 0.3 mg/L. The corrosion loss of copper, including the loss in water containing carbonic acid, is of great significance in pipe installation; and using the general rule of thumb for copper pipes carrying water should never be installed preceding, for example galvanized steel pipes in other to avoid pitting corrosion.

Cu-Al alloys are recommended for handling flue gases containing moist CO$_2$. Also pumps, piping and valves made of this alloy is good for handling mineral waters containing carbonic acid. Cu-Ni alloys are very suitable as material for hot water systems, like boilers, vessels and piping. They are resistant under all conditions in aqueous solutions containing carbonic acid.

Cu-Zn alloys with higher copper content should be used in water containing carbonic acid, since they exhibit better chemical corrosion properties than the alloys with low copper content.

Nickel

In water containing CO$_2$, nickel is corrosion resistant up to 464 °C. Nickel is especially resistant to water which contains sulfur dioxide or free CO$_2$. In mains water saturated with CO$_2$ and O$_2$, the corrosion rate of nickel after a test duration of 20 hours was 0.11 mm/y, after 80 hours 0.16 mm/y and after 120 hours 0.38 mm/y. In distilled water saturated with CO$_2$ and O$_2$ the corrosion rates after 20 hours were 0.08 mm/y, after 60 hours 0.01 mm/y and fell after 120 hours to approximately zero.

An alloy containing (%) 70 Ni, 14 to 16 Cr, 2.25 to 2.75 Ti, 0.7 to 1.2 Nb, 0.4 to 1.0 Al, 5 to 9 Fe, 0.3 to 1.0 Mn, < 0.5 Si, < 0.2 Cu, < 0.08 C and < 0.01 S (Inconel X is resistant to fresh and distilled water as well as to most natural waters containing free carbonic acid, iron compounds, chlorides or dissolved air.) The corrosion rate of these alloys is stated to be 0.005 mm/y when it is exposed at 70 °C and 3.53 MPa to an aqueous solution saturated with 30 or 70 % CO$_2$, with the balance air.

Ni-Cr alloys containing 15 % Cr are not attacked in gas condensates from geothermal steam. The exhibit no susceptibility to pitting corrosion and stress corrosion cracking. Ni-Cu alloys behave rather like nickel in aqueous solutions containing carbonic acid, while CO$_2$ do not attack Ni-Mo alloys even in the presence of air.
4.2 $\text{H}_2\text{S}$ corrosion

The presence of $\text{H}_2\text{S}$ leads to various forms of corrosion; the generalized corrosion of carbon steels; the formation of blisters and cracks, also known as HIC (Hydrogen Induced Cracking); SSCC (Sulfide Stress Corrosion Cracking) of materials susceptible to hydrogen embrittlement. $\text{H}_2\text{S}$ is a weak acid, but causes severe corrosion attacks because the formation of iron sulfide FeS, with an extremely low solubility product and at elevated temperatures, leading to a decrease in the anodic potential of iron and the consequent availability of a driving force even in neutral solutions.

Resistance of metallic materials to hydrogen damage depends on many parameters like cleanliness, fine grain size, homogeneity, stability and it should be evaluated specifically for any different kind of damage; it isn’t even possible to simply state that a material is ‘resistant to hydrogen damage’, but it is better to say that it is resistant to HIC or SSC or SOHIC. In many cases even if the fluid is “sweet” at the beginning of the production life of a field, materials suited for sour service are adopted in order to take into account that field production often tends to turn into sour conditions during service.

Carbon steel

Carbon steels are used in the area of slightly to moderate sour service and their possible use can be extended by using suitable inhibitors. In the presence of chlorides, carbon steel are severely attacked in sour service as observed in a weight loss test; where the corrosion rate of carbon steel in 5 % NaCl solution saturated with $\text{H}_2\text{S}$ at different temperatures is shown in (Fig. 18).

![Fig. 18: Corrosion rate as a function of temperature in 5 % NaCl solution saturated with $\text{H}_2\text{S}$](image-url)
It can be seen that the corrosion rate of the carbon steel increased significantly as temperature increased from 20 to 40 °C. With further increase of temperature, the corrosion rate decreased obviously. The corrosion rate could reach the maximum value of 0.905 mm/y at 40 °C, which was approximately 4-fold greater than that of the carbon steel at 90 °C with 0.224 mm/y corrosion rate.

In industrial practice the maximum value yield strength for carbon steel pipes to be used in sour service is 450 Mpa (=65 ksi). If a higher yield strength value is needed then low alloy steels are used (steels with a total content of alloy elements <10 % mainly Cr-Mo steels in quenched and tempered conditions with a nickel content below 1%).

When the fluid corrosiveness increases, carbon steel and low alloy steels are no more suitable for the service and Corrosion Resistant Alloys (CRA) must be used, although higher alloy of CRA are also insensitive to embrittlement phenomena due to the austenitic (fcc) microstructure.

Stainless steel

Stainless steel are mainly used due to their excellent resistance to aqueous corrosion and are also used at high temperature environments when carbon steel do not provide adequate corrosion resistance and/or strength. Equally, Stainless steel can find practical applications in H₂S environment considering the alloying composition. Its corrosion resistance is superior when compared to carbon steel and thus, should be suitable for use in H₂S environment.

Martensitic stainless steels have been used in oilfield production for many years, providing very good serviceability within their limiting conditions of pH and H₂S partial pressure. These materials have been nominally 12 % Cr (0.1 5% C). New grades of martensitic stainless steel recently introduced contain 4 to 6 % Ni and 1.5 to 2 % Mo to improve corrosion resistance. In Q&T conditions these materials have a yield strength up to 760 Mpa (110 ksi).

Although conventional austenitic stainless steel, i.e. AISI 304 and 316, have a corrosion resistance a little better than martensitic stainless steel, they have rather poor mechanical strength that can be improved only by cold working.
Fig. 19: Microstructure of stainless steels (Schaeffler’s Diagram)

(Fig. 19) shows duplex stainless steel as a mixture of, ferrite and austenite, with yield strengths of 350-620 MPa in cast or 400-900 MPa in wrought conditions. Its microstructure and mechanical properties are from a balanced chemical composition which contains alloying additions of Cr, Ni, Mo and N. Unlike martensitic stainless steel, duplex stainless can be strengthened by cold working.

Duplex stainless steel have a corrosion resistance generally superior to those of the martensitic stainless steel in H₂S, CO₂ and brine environments together with a material strength greater than conventional austenitic stainless steel.

Copper

Copper and copper base alloys have not been fully established in sour services due to their environmental limitations. This means copper and its alloys could only be used in sour services on the basic requirement of NACE MR0175/ISO 15156.

However, copper and copper based alloys should not be used because severe corrosion attack will likely occur. Copper are seldom used in direct contact with H₂S.
Nickel base alloys have very good resistance to cracking in sour service and chloride containing environments. There are 2 different categories of nickel base alloys certified by standard in NACE MR0175/ISO 15156, due to their alloy composition and with iron content between 5 and 20 % are considered highly resistant, and they are;

The solid-solution Ni-based alloys are Hastelloy C, Incoloy 825 and Inconel 625, with chemical composition of (19Cr-29.5Ni-2.5-Mo; 14.5Cr-52Ni-12Mo; 22Cr-9Mo-2Fe). The precipitation harden-able Ni-based alloys used in valves and specialized equipment which often require more complex shapes or welding are the Incoloy 925, Inconel 718 and X750 type alloys.

The corrosion resistance of Inconel 625 (22Cr-9Mo-2Fe) in H$_2$S/CO$_2$ environments in the absence of elemental sulfur, is remarkably high with a Corrosion rates of ≤ 0.05 mm/y and no SSC or SCC.

Ni-base alloys may exhibit environmental cracking in H$_2$S environments at temperatures ranging from 25 to higher than 220 °C. However the material condition where HIC is observed is limited to hardness in excess of HRC 40 produced by cold working or heat treatment and may vary with alloy composition and microstructure. (Fig. 20) shows Ni-alloys with SS at different Cl- concentration and temperature.

![Diagram](image.png)

**Fig. 20:** Diagram of Corrosion Resistant Alloys (CRA) practical application at different H$_2$S concentration and at increasing Cl- concentration/temperature.
CONCLUSION

From the experiments conducted and researched on this thesis for carbon steel, stainless steel, copper and nickel, it is easy to ascertain their ideal usefulness for ultimate application as durable materials in different acidic environments. The following conclusions can be made:

- In general, most of the corrosion mechanism initially has a high corrosion rate as acid concentration, temperature and oxygen increases, but at a certain threshold in time and concentration the corrosion rate starts to decrease or become stable as a result of corrosion products on the metal surface.
- For Organic acids, the most suitable and corrosion resistant metallic materials are those of stainless steels and nickels alloys. Copper is also resistant except in formic acid, while carbon steel is not suitable.
- For Strong acids, it is important to take into account the presence of impurities and pH as they can affect the corrosion rate. Thus the most corrosion resistant materials suitable for the environment is stainless steels. Only in nitric acid that copper and nickel alloys are not resistant and carbon steel is definitely not suitable.
- For Weak acids, occurring mainly in the Oil/Gas facilities, proper nature of the environment has to be analyzed because pH, flow rate, presence of chlorides and sulfates can affect the corrosion mechanism. Generally, stainless steels, copper and nickel alloys are the most suitable, while carbon steel have low corrosion resistance.
- And for the records, basic corrosion prevention principles has to be considered when using metallic materials for constructions. Thus it outlines the understanding of the corrosion phenomena, selecting ideal proper material, use of corrosion resistant coatings, chemicals, electrochemical techniques for optimum performance.
FUTURE WORKS

The topic of this thesis project is a very broad scientific research in relation to the understanding of their specific phenomenon, so thorough effort was taking in extracting and picking just the main mechanism at which acidic corrosion occurs. Considering the time limitation, some of areas related to the topic, that are still under research had to be overlooked. Also it should be remembered that corrosion is a surface phenomenon and that if the surface can be rendered resistant the nature of the bulk of the metal is of little consequence; this is, of course, the idea behind the use of metallic coatings. The following could be some of the recommendations for future work:

- Since the development of nanoscience can have a great impact in the field of corrosion engineering, further study is needed for corrosion resistant materials which could be completely explored and improved with nanotechnology. For example, better understanding and engineering of complex structure at nanoscale will definitely result in a new generation alloys, stronger, more resistant and more durable, with self-healing, self-cleaning, self-limiting behavior and possibly with the whole range of new smart alloys.
- Further study is needed on CO$_2$ and H$_2$S corrosion for higher temperature and pressure, as the temperature and pressure are usually higher in oil and gas pipelines.
- All the experiments were done for a very limited period of time. Thus, further studies and key technologies can be incorporated for longer term effect of the mechanisms investigated in order to develop materials to improve corrosion resistance.
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