

THE CORROSION PROBLEMS IN HOUSEHOLD WATER HEATERS OF SABRATHA CITY

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Abstract

The corrosion destructive action can reach the home of millions of people, thus costing a tremendous amount of money and causing a great inconvenience. With the up rise of brackish water in Sabratha city, corrosion can damage water heaters, pipe network, refrigerators and many more items found at homes. In addition, in the absence of adequate specifications, major failures of water heaters have been reported in the recent years creating a great deal of concern. This study investigated the reasons of water heaters failure, and the methods needed to overcome or limit such a problem.

Three main components, which have a direct relationship with the corrosion phenomena of heaters, were studied namely water, heater storage tank and heating element cover. To achieve that a chemical analysis of water samples and an examination of the microstructure and the chemical composition of heater storage tank and the heating element cover were carried out. The results revealed that the likelihood of forming a scale of Ca CO_3 increases with increasing temperature, salt concentrations and the PH value.

The metallographic examination showed the presence of a ferrite-pearlite structure. The microstructural studies revealed the presence of un-equivalent distribution of carbon content responsible for galvanic corrosion. They also revealed that grain growth in Heat Affective Zone (H. A. Z.) was responsible for pitting type corrosion. The weld showed typical WIDMANSTAATEN structure. Chemical composition of the sample indicated that the structure belongs to the low carbon steel which is identical to ASM 1020, and that the cover of heating element is made of pure copper.

Keywords: Electrical household water heater; Corrosion; Microstructure and Water analysis.

Introduction

The corrosion of water heaters fed by potable water is one of the problems noted in Sabratha city. This phenomenon is characterized by an increasing consumption of heaters and excess costs for maintenance or replacement. Through field trips to Sabratha city and by running visual inspection for not working samples of water heaters, it was noticed that most failures

were at the bottom of the heater storage tank (near the cold and hot water pipe holes, heating unit hole). These failures result from damage of the interior coating layer after welding process, this damage can let the water to contact the metal surface directly and form an anodic site, and the other coated points of metal surface will act as a cathodic site and hence pitting corrosion will take place. Scale formation due to the saturation of water by salts, solid particles “in suspension” and its solubility will decrease with increasing of operating temperature of the heater. These scales will precipitate on the interior surface of the heater body, especially on the heating unit “cover of heating element”, causing a hot spot in which the temperature of the metal “usually made of pure copper” will exceed the safe operating temperature and cause equipment failure. Uneven deposited scale deposition may cause pitting corrosion. If the deposited scale is particularly impermeable and the system contains dissolved oxygen, it is possible that an oxygen concentration cell may form between the covered iron and the uncovered iron resulting into pitting corrosion beneath the scale, Ostroff, A. (1981), Widder S. (2013).

Electric Household Water Heater

Household electric water heater consists of a water storage tank, which is thermally insulated, covered with an outer shell, operated by one heating element or more and fed from an electric supply. It mainly contains an automatic thermostat to control the water temperature and an automatic safety valve. The main parts are shown in figure (1) below.

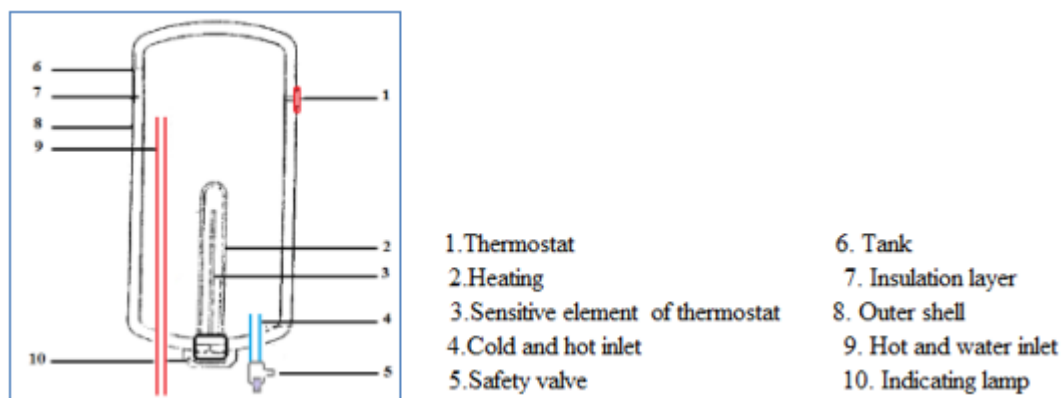
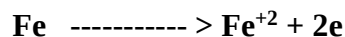


Figure (1): Diagrammatic Sketch for Household Electric Water Heater.

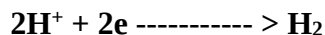
Corrosion

Corrosion can be defined as the destructive attack of a metal by a chemical or electrochemical reaction within its environment. In order to have an electrochemical corrosion, it is necessary to have:

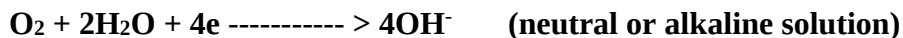
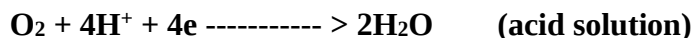
- I. Anode. e.g. typical reaction:



II. Cathode. e.g. typical reaction:



Or if oxygen is present two other reactions are possible:



III. Electrolyte: The electrolyte used household water heater is water.

Removing any of these factors ceases corrosion. The combination of anode, cathode and external connection (electrolyte) is called Electrochemical Corrosion Cell, Ostroff, A. (1979), Widder S. (2013).

Forms of Corrosion Damage

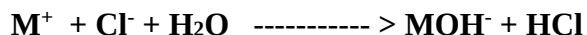
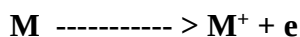
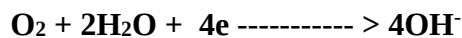
Crevice Corrosion

Intensive localized corrosion frequently occurs within crevices and other shielded areas on metal surfaces exposed to corrosives. This type of attack is usually associated with small volumes of stagnant solution caused by holes, gasket surfaces, lap joints, surfaces deposits and crevices under bolt and rivet heads. As a result, this form of corrosion is called crevice corrosion or, sometimes, deposit or gasket corrosion, Fontana, M. (2005), Popoola, L. (2013).

The mechanism of crevice corrosion is divided into two stages:

Initial stage: general corrosion or uniform attack of corrosion within and without crevice, remains the same or equal.

Later stage: after oxygen is depleted no further oxygen reduction occur and the dissolution of metal continuous and tends to produce an excess of positive charges in solution (M^+), which need balance by migration of chloride ions (Cl^-) into crevice.



Because of increase in concentration, the corrosion within the crevice increases and the rate of oxygen on the adjacent surface decreases. Thus, the cathode protected the external surface, Fontana, M. (2005), as shown in figure (2).

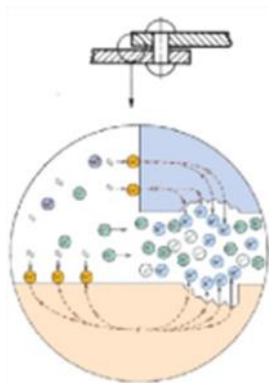


Figure (2): Crevice Corrosion – Later Stage.

Pitting Corrosion

This is the most common type of attack that occurs with heterogeneous metals such as steels and other alloys. It is caused by differences in potential between the different points on the metal surface. Pitting usually requires an extended initiation period before visible pits appear, Fontana, M. (2005). A corrosion pit is a unique type of anodic reaction; it is an auto catalytic process. This is illustrated schematically in figure (3). A metal M is being pitted by an aerated sodium chloride solution. Rapid dissolution occurs within the pit, while oxygen reduction takes place on the adjacent surfaces. The rapid dissolution of metal within the pit tends to produce an excess of a positive charge in this area, resulting in the migration of chloride ions to maintain electro-neutrality. Thus, in the pit there is a high concentration of MCl because of hydrolysis.

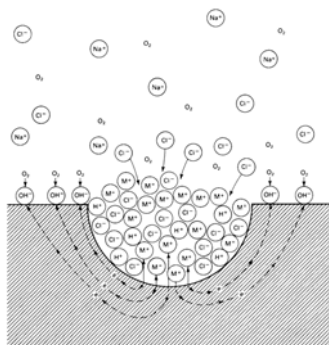
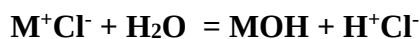


Figure (3): Autocatalytic Processes Occurring in a Corrosion Pit.

Galvanic Corrosion

This type mostly results from the difference in potential between two dissimilar metals when they are immersed in a corrosive or conductive solution. The less resistance metal becomes anodic and the other becomes cathodic which corrodes very little or not at all in this type of couple due to the electric currents and dissimilar metals involved.

Apparently, the corrosion products on the zinc in this case make it act as a surface noble to steel, Fontana, M. (2005), Herbert, H. (2008). The experiment of Whitman and Russell proved that weight loss of iron coupled to copper is the same as if the entire surface had been iron. In addition, it showed that the actual penetration of iron increases when it is coupled to a more noble metal. The general relation between penetration P of a metal having an area A_a coupled to a more noble metal of area A_c , where P_o is the normal penetration of the metal uncoupled, is given by:

$$P = P_o * (1 + A_c / A_a)$$

If the ratio of areas (A_c / A_a) is large, the increased corrosion caused by coupling can be great. Figure (4) shows polarization curves for an anode which polarizes little in concentration to a cathode at which hydrogen is evolved. Slope 1 represents polarization of a noble metal area having high hydrogen overvoltage. slopes 2 and 3 represent metals with lower hydrogen overvoltage, Herbert, H. (2008).

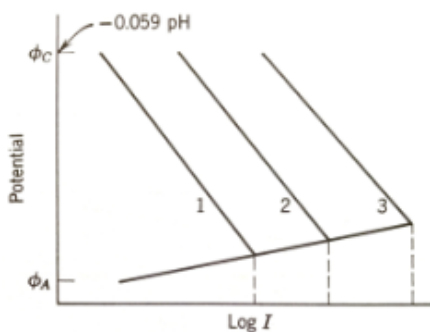


Figure (4): Effect of Hydrogen Overvoltage of Cathode on Galvanic Corrosion in De-Aerated Non-Oxidizing Acids.

In figure (5), the galvanic current density at the anode produced by coupling can be shown as following:

$$\text{Log } i_{\text{galv.}} = ((-E_{\text{coros}} - 0.059 \text{ PH}) / B) + (\text{log}(A_c/A_a) * i_o)$$

Where:

E_{coros} = corrosion potential.

B & i_o = Tafel constants for hydrogen ion discharge on the noble metal.

The increased penetration at the anode is given by: $P - P_o = i_{galv.} / k$

By assuming that, the anode is polarized very little as a result of coupling, we can set $(-E_{coros} - 0.059 \text{ PH}) / B = \log K$ and then approximately, $P - P_o = (KA_c / kA_a) i_o$

From this equation it appears that the corrosion rate of the less noble anode of a couple increases with increase in exchange current density (i_o) for the more noble metal and with decrease in B (corresponding to low hydrogen over voltage), Herbert, H. (2008), Robert E. (2008).

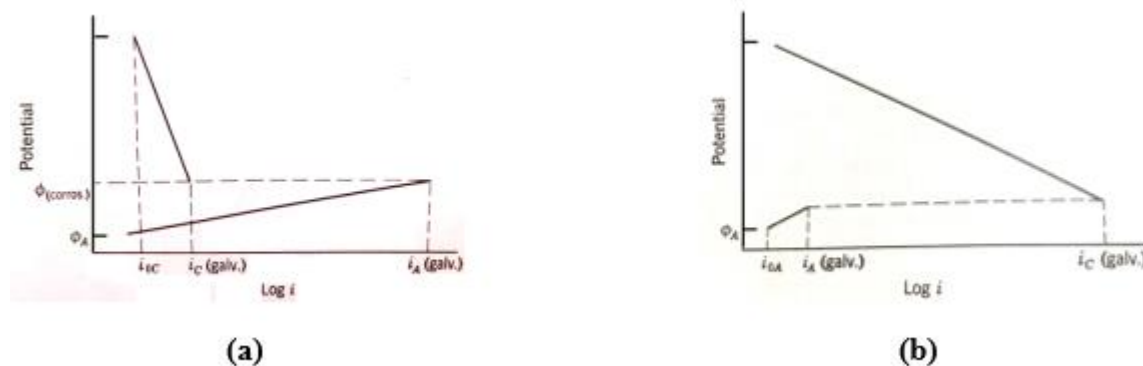


Figure (5): The Effect of Anode-Cathode Area Ratio on Corrosion of Galvanic Couples in Deaerated Non-Oxidizing Acids. (a): Large Cathode Coupled to Small Anode, (b): Large Anode Coupled to Small Cathode.

Corrosivity of Water

Water containing impurities or dissolved substances can be corrosive or non-corrosive, depending on the nature of the dissolved substances. There are many factors affecting corrosivity of water such as dissolved oxygen, carbon dioxide, PH scale, water temperature, and dissolved salts, M. Farland M. (2008).

Scaling

The direct cause of scaling problems is frequently due to pressure drop, temperature change, mixing two incompatible waters, or exceeding the solubility product. The heat transfer property of scale is generally less than metals; a build up of scale on a metal surface of the heater can cause hot spots in which the temperature of the metal exceeds the safe operating temperature causing efficiency decrease and equipment failure, Ostroff, A. (1979), Widder S. (3013).

There are many methods which are used to predict scale formation “calcium carbonate solubility calculation” such as Langelier Saturation Index, and Stiff and Davis Extension of Langelier Method. In the case of calcium, calcium precipitates as CaCO_3 , as shown in the following equation: $\text{Ca}^{+} + \text{CO}_3^{-} = \text{CaCO}_3(\text{s})$, Ostroff, A. (1981), Widder S. (2013). Accumulation of scale and corrosion can decrease the lifetime and influence the performance of water heating equipment, Widder S. (2013).

Both, chloride and sulfate, are known to promote abiotic and biotic corrosion. If chloride concentrations are low, usage of untreated tap water is possible. Otherwise, tap water can be blended with demineralized water until an appropriate water quality is attained, Oliver O. (2018).

D.R. Turriff and M.N. Bailey found that the hole location coincided with the stepped overlap weld area on the interior of the tank, which is referred to as a gap or crevice region. A significant amount of rust and corrosion deposit had accumulated in this area. The interior surface also contained corrosion pits that indicated corrosion of the steel surface. It is clear that the tapered corrosion hole penetrated through the lower tank wall very close to the weld, thus explaining the water leak. A significant corrosion deposit is observed near the crevice opening, this failure is consistent with the gradual under-deposit pitting corrosion of the tank wall. Manufacturing product defects product or manufacturing defects can also can contribute to tank failure, Turriff D. (2010).

Microstructure Effect

Another important factor which has great influence on the corrosion of heaters is the microstructure of the heater body which is exposed to different manufacturing processes such as welding. Therefore, it is necessary to study the changes in the microstructure of water heater body, especially at (H.A.Z.).

Metallography

Metallography or microscopy consists of the microscopic study of the structural characteristic of a metal or an alloy by a microscope to determine grain size, shape, size and distribution of the various phases and inclusions. The steps required to prepare a metallographic specimen properly are sampling, mounting, grinding, polishing and etching, Avner H. (1987).

Experimental Work

The experimental work included the chemical analysis of water samples, microstructure examination of heater storage tank, by using OP, and examining tank's chemical composition. The selected samples used in this study were taken from different zones in Sabratha city. The prepared samples were ground, polished and examined under optical microscope after application of NITAL etching solution (2% Nitric acid and 98% Methanol). Each sample was micro graphically examined at “500” magnifications. In this investigation, the study was concerned with on the ARISTON type of heaters.

Results and Discosion

Results of chemical analysis of water samples are tabulated in Table (1) as following:

Table (1):

Component Sample	HCO ₃ ⁻		SO ₄ ⁼		Cl ⁻		Ca ⁺⁺		Mg ⁺⁺		Na ⁺	
	PPM	mol/l	PPM	mol/l	PPM	mol/l	PPM	mol/l	PPM	mol/l	PPM	mol/l
A	307.5	0.005	373.4	0.0039	887.5	0.025	133.06	0.003	113.7	0.005	38	0.002
B	201.8	0.003	261.3	0.0027	2414	0.068	157.11	0.004	191.5	0.008	28	0.001
C	383	0.006	224.6	0.0023	2911	0.082	198.79	0.005	289.7	0.012	32	0.001
D	321	0.005	264.5	0.0027	994	0.028	102.6	0.025	104.5	0.004	26	0.001

Results obtained from “stability” index calculation by using Stiff & Davis method steps are tabulated in Table (2).

Table (2):

Scale Sample	PH	μ	K		P _{Ca}	P _{alk}	SI	
			50 °C	80 °C			50 °C	80 °C
A	7.18	0.0395	1.76	1.18	2.5	2.3	0.62	1.2
B	7.38	0.065	1.84	1.22	2.4	2.5	0.64	1.26
C	7.55	0.0829	1.88	1.24	2.3	2.2	1.17	1.81
D	7.37	0.036	1.72	1.16	2.6	2.3	0.75	1.31

Results indicate that all samples of water show positive SI, which means that the water is very saturated with respect to CaCO₃ and scale formation is likely. SI values showed a great effect by the values of the constant “K” which depends on the values of ionic strength “μ”. SI increases as “K” increases; when the concentration of ions in the water increases, the value of “μ” increases, which leads to increasing of “K”. As a result, SI became more positive especially with sample C as shown in the Table (2). The value of SI shows a great effect by the temperature. Due to decreasing of solubilities of salts by raising water temperature, the “K” values decreased, as shown in Table (2). As the temperature of water increased, the “SI”

values became more positive, as a result, a large amount of scaling was formed. “PH” had an obvious effect on the “SI” value as shown in the sample “C”. Finally, these results revealed that, Sabratha city is suffering from scaling problems due to the high percentage of salts in the potable waters, which leads to decreasing the service life of the household water heater. The obtained results of metal microstructure investigation indicated the presence of ferrite-pearlite mixture with uniform grain size as shown in figure (6). The pearlite was distributed evenly with no signs of banding. The microstructure was typical of well-annealed low carbon steel. However, some porosity was occasionally observed. Figure (7) shows another area of the same sheet where the pearlite content is obviously lower than those in figure (6), which indicates lower carbon content. In H.A.Z, abnormal grain growth is occasionally observed, as illustrated in figure (8), which indicates a tendency to secondary recrystallization. The H.A.Z. was characterized by unique granularity of ferrite as shown in figure (9); this fact added to the higher corrosion susceptibility of this zone, as illustrated in figure (10). The H.A.Z. shows two distinct areas, one with coarse grains (adjacent to the weld metal), while the other with finer grains (adjacent to the base metal), as shown in figure (11). The grain size in the H.A.Z. sudden changes indicate that the temperature gradient in welding was sharp, while the metal is of inherent fine-grained structure. The weld metal shows a typical “WIDMANSTAATEN” structure, as illustrated in figure (12), and (13) which indicate that the cooling rate on solidification was relatively high. Ferrite ejecting from austenite dendrites grew along certain crystallographic planes giving rise to the characteristic **widmanstaaten** structure.

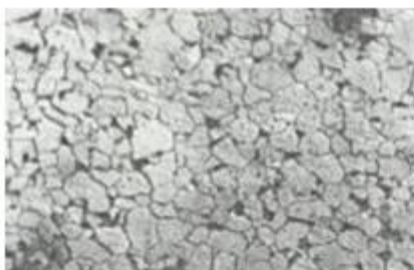


Figure (6): Ferrite-Pearlite Structure with Some Porosity, X500 “Normal Section of Heater Body”.

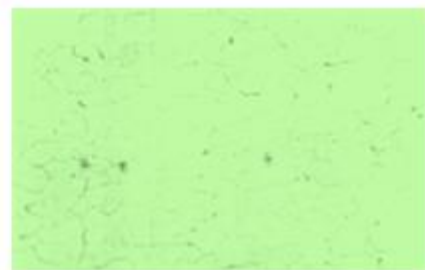


Figure (7): Ferrite with Small Amount of Pearlite, X500 “Other Side of Heater”

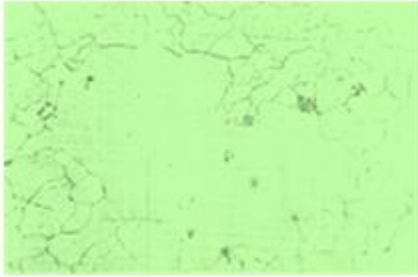


Figure (8): Abnormal Grain Growth in H.A.Z. “Recrystallization” X500.

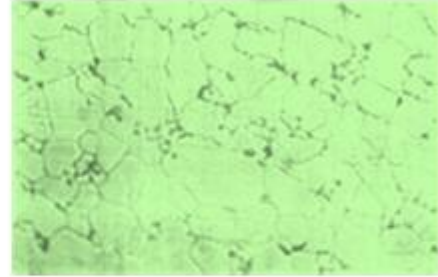


Figure (9): Unequigranularity in H.A.Z.

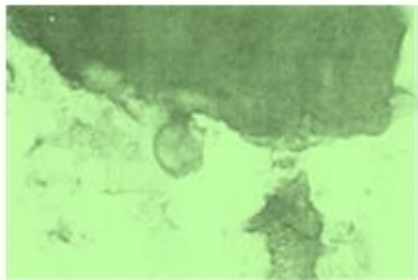


Figure (10): Place of Pitting [Shows Removing of Some Grains Together], X500.

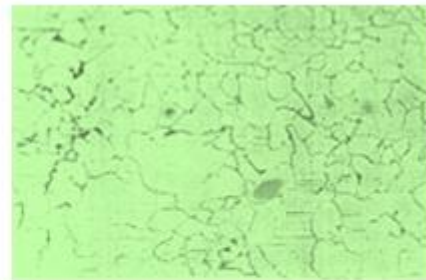


Figure (11): Heat Affective Zone (H.A.Z.) X500.

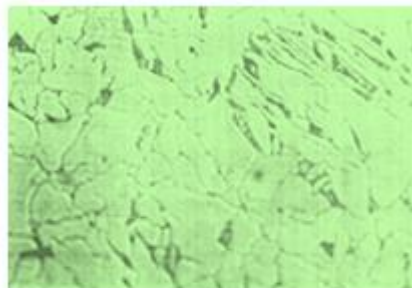


Figure (12): Interface Between Weld Metal and H.A.Z, X500.

Results of Chemical Composition Test

Results show that the storage tank is made of a mild steel with thickness of 1.5 mm, and a protective layer made of phenolic paint. The result of chemical analysis of the mild steel as following (%):

Fe	98.27	C	0.18	Cr	0.15	Cu	0.17	Mn	0.73	Si	0.34
V	0.03	Mo	0.00	S	0.01	P	0.018	Ni	0.04	Al	0.01

Steel grade: 1020

Cover of heating element was made of pure copper approximately with chemical composition as following (%):

Cu	97.79	Si	0.09	Fe	0.85	Mn	0.14
P	0.006	Ni	0.33	Pb	0.047	Zn	0.03

Conclusion

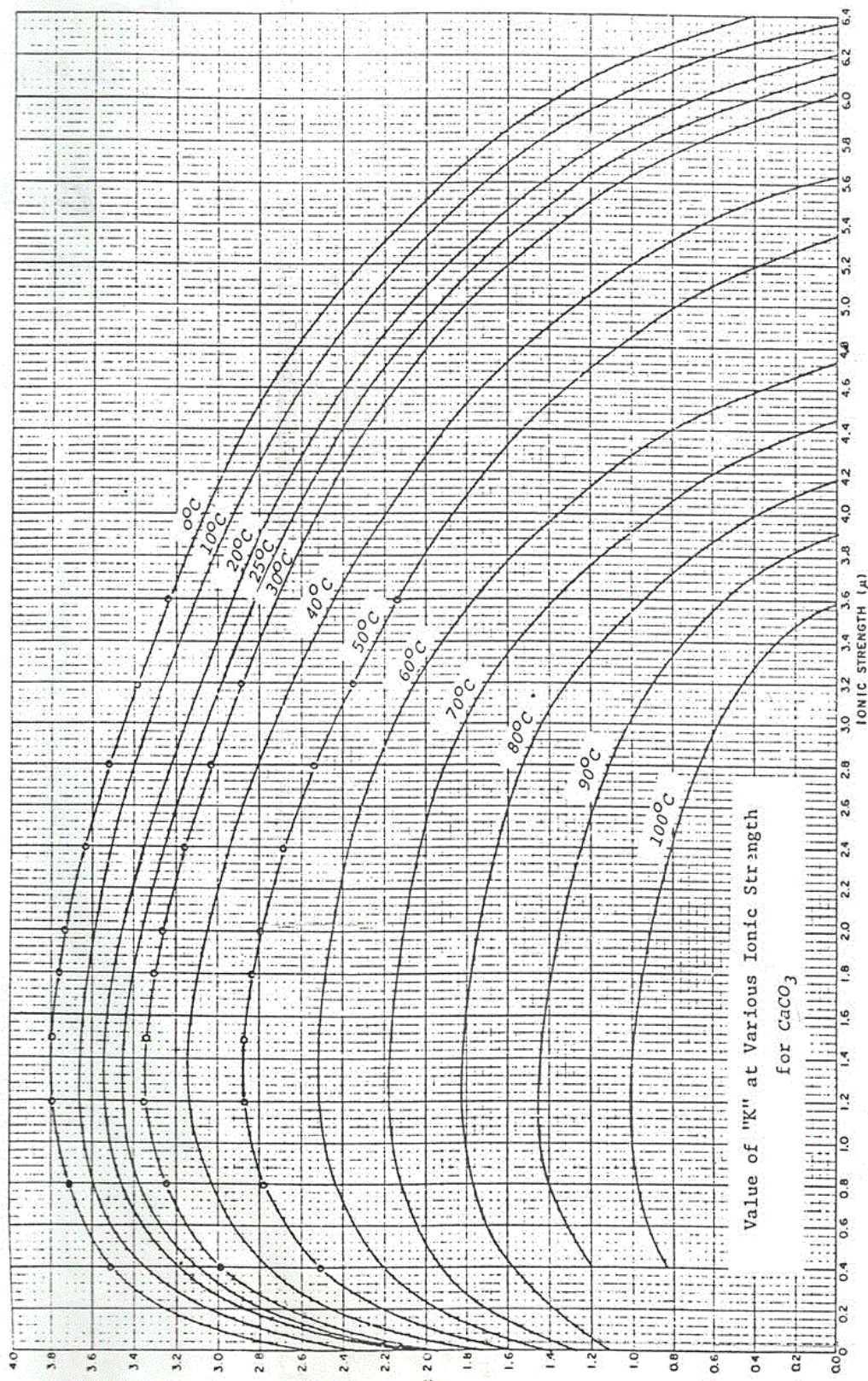
The likelihood of forming scales e.g. CaCO_3 increases as temperature, salt concentrations, and the PH increase. Metallographic examination showed the presence of ferrite-pearlite structure. Microstructural studies revealed the presence of unequivalent distribution of carbon content, which was responsible for galvanic corrosion and they reveal grain growth in H.A.Z., which was responsible for pitting type corrosion. The weld showed a typical WIDMANSTAATEN structure. The chemical composition of steel sample indicated that the structure belonged to the low carbon steel, which was identical to ASM 1020.

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Appendix (A):



Appendix (B):

