The Effect of Time on the Formation & Growth of Passive Layer on Carbon Steel A516 Gr.70 in Sour Water

E. H. Dehkordi[1] and A. R. Tavakoli[2*]

Pioneer Energy Industries Development Company

Abstract

A proposed method for protecting carbon steel and hence reducing iron release in an aqueous solution saturated with H_2S is presented in this paper. The method is based on forming a stable and resistant sulfide layer (pyrite, FeS_2, or pyrrhotite, $Fe_{(1-x)}S$, phase or a mixture of both) on the carbon steel surface. The study on the formation of the sulfide layer was carried out considering the effects of exposure time and surface status of the steel samples under conditions of static solution saturated with H_2S. The sample weight was measured and the chemical composition of the sulfide layer produced was analyzed using the XRD (X-ray diffraction). The crystalline structure was identified by SEM (Scanning Electron Microscope) and EDAX analysis. The results showed that after a 12-day exposure time at a pressure of 15.7 bars and temperature of 130 °C, a passive layer including the pyrite phase was formed on various samples. In addition, the acid citric washed samples enjoyed a more coherence and layer thickness as compared other samples that had a different surface condition.

Keywords: Corrosion, Passivation, Carbon Steel, Sulfide, Sour Water.

Introduction

In oil and gas industries, carbon steel is used as the main structural material in heat exchangers, towers, vessels, pipes and etc. The high solubility of iron content from the components of a plant, in an aqueous medium saturated with hydrogen sulfide, causes the formation of different layers of iron sulfide such as makinawite (Fe S_{1-x}), triolit (Fe S), pyrrhotite ($Fe_{1-x}S$, both momoclinic and hexagonal, marcasite (FeS_2), and pyrite (FeS_2)[1]. It is noted that the solubility of different layers of iron sulfide on carbon steel materials, in the presence of H_2S (25 °C and 1.8 MPa) varies in the range of 1:10:40:80:6000 for makinawite, triolite, monoclinic pyrrhotite, hexagonal pyrrhotite and pyrite, respectively [2,3]. In addition, for some of the iron sulfide layers, the solubility also depends on the pH such that in a pH range of 0.9 to 4, the solubility of triolite depends primarily on the $[H^+]$.

The high solubility of iron, iron sulfide and transfer of various corrosion products within an equipment or from one equipment to another within a system (usually due to temperature differences) causes precipitation and occurrence of numerous utility problems. These phenomena can be observed especially in the surfaces of cold towers trays and heat exchanger tubes. In order to deal with the aforementioned problem, primary preparation of carbon steel surface and formation of a protective sulfide layer can be very useful. This protective layer, besides suppressing corrosion, can prevent hydrogen embrittlement that can cause untimely cracks [4-6].

In the present paper, the ASTM-A516Gr.70 carbon steel was used as the material for the study. The corrosion rate of the carbon steel, in an aqueous solution saturated with H_2S under static conditions using autoclave was determined. The effects of time and surface preparation on the protective sulfide layer under operational conditions was also investigated and is presented in this study.

Experimental Method

In the present work, ASTM-A516Gr.70 carbon steel was used and the surface exposure was performed under static conditions. The chemical analysis of the carbon steel is presented in Table 1.

A high pressure and temperature autoclave with an internal volume of 1 liter was used. Various samples with dimensions of 35x16x5 mm were cut and a 2 mm diameter hole was drilled into their ends. The samples were then fixed within the autoclave and immersed in an aqueous solution saturated in H_2S gas. The required gas was injected into the autoclave via a pressurized cylinder. In addition, various surface conditions of the samples were also investigated to determine the optimum surface condition for the formation of the sulfide layer. The different surface conditions, used in this study, were:

* *Corresponding author:*
Tel:+98- 311-8586451 Fax:+98- 311-8583378
E-mail: t_shantiya@yahoo.com
Address: Pioneer Energy Industries Development Company, Isfahan, Iran

1. Associate Professor
2. M. Sc.

Table 1. Chemical analysis of the steel used weight percent

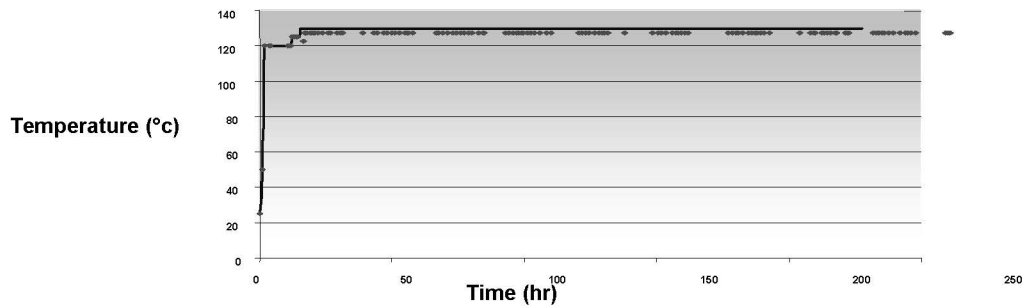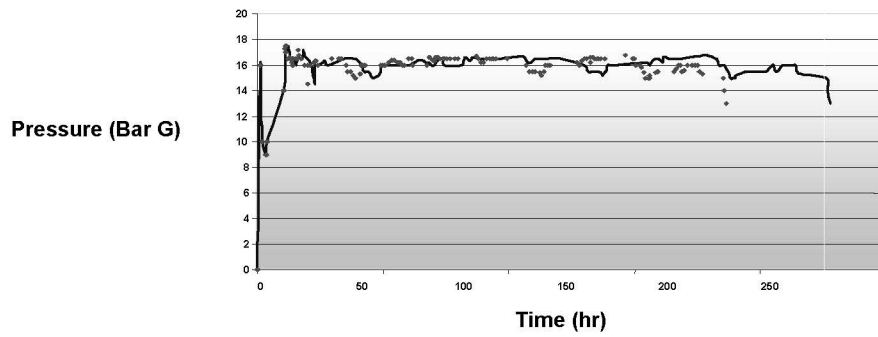| Fe	C	Si	S	P	Mn	Ni	Cr
98.07	0.242	0.338	<0.005	<0.008	1.27	0.0387	0.0331

Fig. 1.Temperature variation versus time in the 1st experiment for 9 days.

Fig. 2. Pressure variations versus time in the 1st experiment for 9 days.
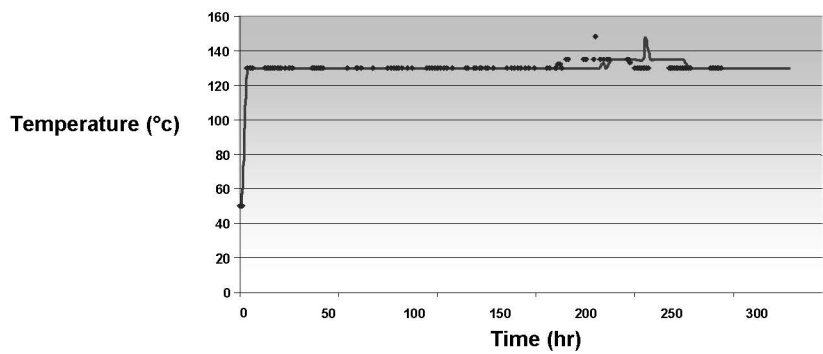

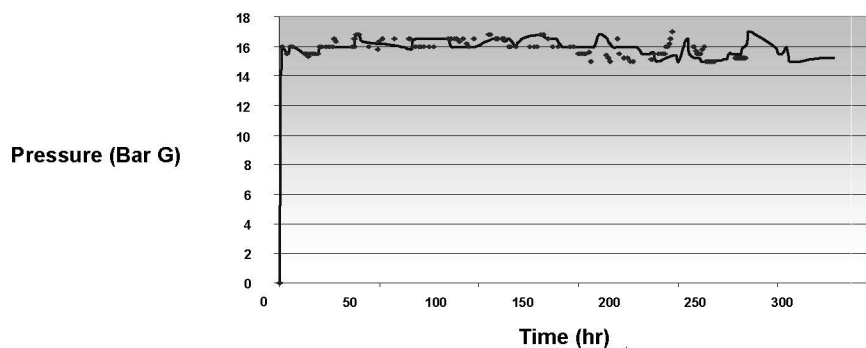*Fig. 3. Temperature variation versus time in the 1st experiment for 12 days.*

Fig. 4. Pressure variations versus time in the 1st experiment for 12 days.

- Samples that were dipped in a 5 % citric acid at 75°C + 5°C for 2 hours,
- Samples that were sand blasted,
- Samples that were rusted.

In order to study the effects of time on the coating surface, two experiments were performed at 15.7 bars and 130 °C. The first one was performed for nine days while the second one was carried out for twelve days. The experiment temperature and pressure were monitored through measurements at various times during the tests and the results are shown in Figures 1– 4.
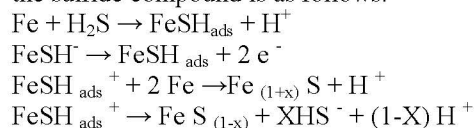
Distilled water was initially deaerated with nitrogen at a rate of 100 cc/min/lit for 1 hour in order to prepare one liter of the aqueous solution saturated in H_2S. The saturation conditions for the experiments were obtained by considering the experiment conditions (15.7 bars and 130 °C) and the solubility rate of H_2S in the solution.

Once the sulfide layers were formed on various samples, they were removed from the autoclave, washed with demineralized water and acetone and finally dried with hot air. The crystalline structure and phase of the sulfide layers on various samples were identified using X-ray diffraction, EDAX and SEM analytical methods.

Results and Discussion

The weight increase of various samples, due to the formation of sulfide layers, is shown in Tables 2 and 3. As observed, the weight increase of various samples indicates that this increase is more prominent for the acid washed samples. This can be explained by considering the reaction of S^{2-} (present in the H_2S gas soluble in water) with Fe^{2+} on the surface of the metal which produces more sulfide compound, and hence a higher weight of the

produced layer. In fact, the mechanism that produces the sulfide compound is as follows:

$$Fe + H_2S \rightarrow FeSH_{ads} + H^+$$
$$FeSH^- \rightarrow FeSH_{ads} + 2 e^-$$
$$FeSH_{ads}^+ + 2 Fe \rightarrow Fe_{(1+x)} S + H^+$$
$$FeSH_{ads}^+ \rightarrow Fe S_{(1-x)} + XHS^- + (1-X) H^+$$

As indicated above, the sulfide layers formed on the surfaces of the acid washed samples will enjoy more thickness, and hence a higher weight. In addition, an increase in the time of exposure will result in an increase in the rate of precipitation and thus a higher layer thickness [7,8].

Results of X-ray Diffraction Analysis:

The x ray diffraction (XRD) results of the sulfide layers formed on the acid washed samples are shown in Figures 5 and 6 for the exposure times of 9 and 12 days, respectively. As observed in Figure 5, the sulfide layer formed on the samples that were exposed for 9 days were pyrrhotite phase (Fe_7S_8 and/or $Fe_{1-x}S$) in which the peaks are primary phases such as makinawite & pyirhotite as shown in the XRD graph. Figure 6 shows the same samples exposed for 12 days and shows that the sulfide layer has a pyrite phase (FeS_2). Therefore, it can be concluded that the formation of sulfide layers, as a result of the reaction of the sulphur in the H_2S gas with the metal corrosion prouct Fe^{2+} requires enough time, in this case 12 days, and thus is an important factor.

The pyrite (FeS_2) layer

The sand blasted and rusted samples were much different from the acid washed samples (Figures 7–9). As observed, the sulfide layers formed

Table 2. Weight variation of the Samples 1st experiment for 9 days

sample type	Primary weight(gr)	Secondary weight(gr)	Weight variation(gr)
Exposed to acid	23.0106	23.0544	0.0438
Exposed to acid	22.5920	22.6333	0.0413
Sandblasted	20.8950	20.9223	0.0273
Sandblasted	16.4389	16.4554	0.0165
With oxide layer	23.1848	23.2076	0.0228
With oxide layer	22.9658	22.9896	0.0238

Table 3. Weight variation of the Samples second experiment for 12 days

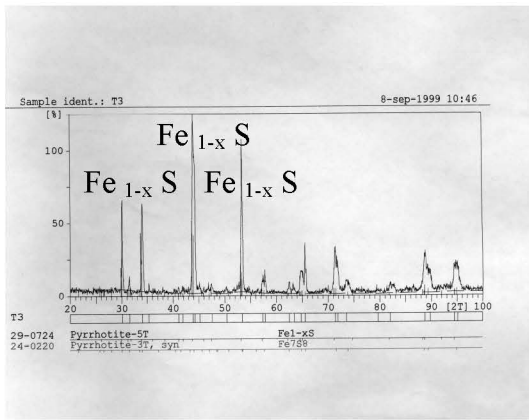| sample type	Primary weight(gr)	Secondary weight(gr)	Weight variation(gr)
Exposed to acid	22.7680	22.8202	0.0522
Exposed to acid	22.7871	23.0041	.217
Sandblasted	21.5298	21.5875	0.0577
Sandblasted	21.3035	21.3550	0.0515
With oxide layer	23.2824	23.3463	0.0639
With oxide layer	23.3631	23.4287	0.0656

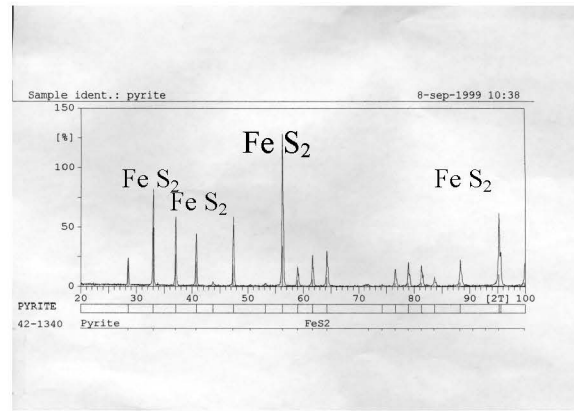*Fig. 5. XRD analysis results of the 1st experiment acid washed samples.*

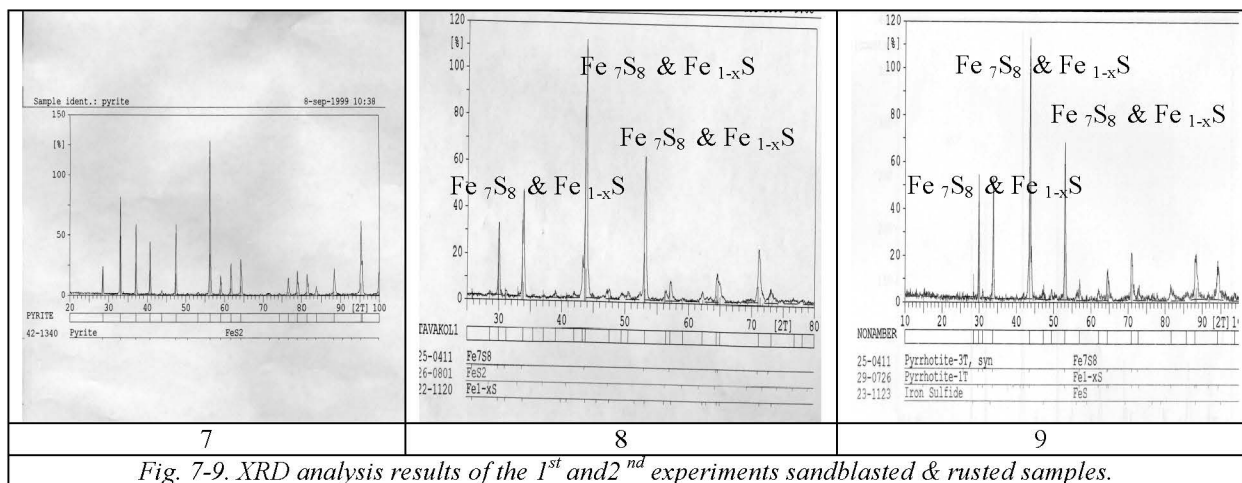*Fig. 6. XRD analysis results of the 2nd experiment acid washed samples.*

| 7 | 8 | 9 |

Fig. 7-9. XRD analysis results of the 1st and 2nd experiments sandblasted & rusted samples.
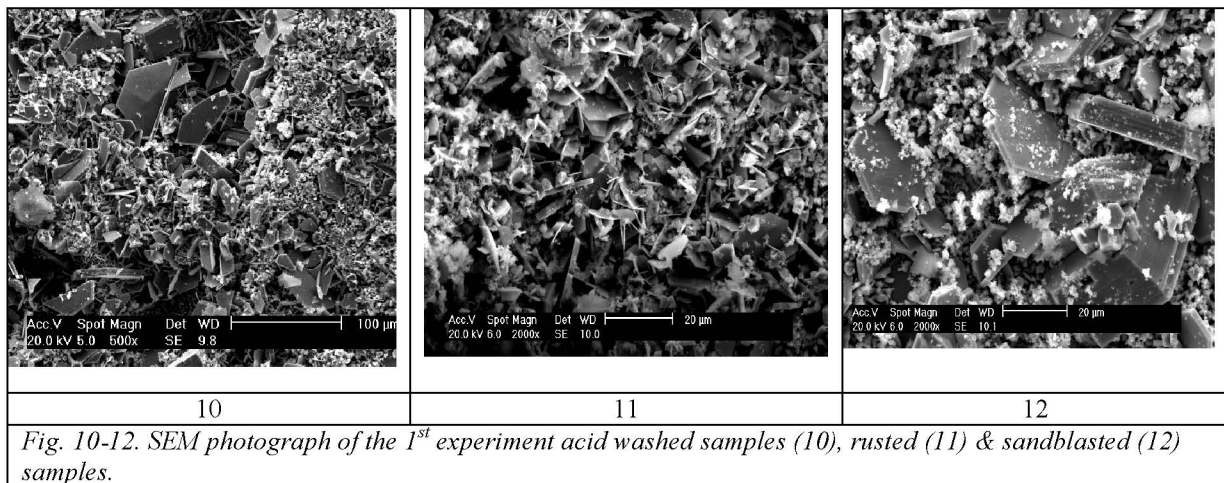

| 10 | 11 | 12 |

Fig. 10-12. SEM photograph of the 1st experiment acid washed samples (10), rusted (11) & sandblasted (12) samples.

on both samples were pyrite (FeS_2, fig. 7) for an exposure time of 12 days. Whereas, the sulfide layer was pyrrhotite ($Fe_{1-x}S$, Figs. 8-9) for an exposure time of 9 days.

SEM photomicrographs and EDAX Analysis:

The SEM photomicrographs and EDAX analysis results are shown in Figs. 10 – 18 for exposure times of 9 and 12 days. The 9-day exposed samples surface

microscopic images (Figures 10–12) show that the layers formed on the metal surface have a structure with circular and blade-like grains. The atomic percent of Fe & S in Figures 16–18 and chemical formula of iron sulfide compounds indicate that the sulfide layers are makinawite (FeS_{1-x}) and pyrrhotite ($Fe_{1-x}S$). The spot EDAX analysis on the hexagonal crystals shows the presence of pyrrhotite on these samples as well.

Regarding the 12-day exposure samples, the surface SEM photomicrigraphs are shown in Figures 13-15. It is observed that the crystalline structure of the formed layer is octahedral. In the acid washed samples, compacted grains were formed as shown in the SEM images, and hence they result in a thicker layer as compared to other samples. This result is confirmed further by samples weight increases. On the other hand, the grain sizes of the sulfide layer formed on the rusted samples are not homogeneous, and hence the grains are small in one region and oarse in another. Comparison of the sulfide layer formed on the sand blasted samples with other samples shows that the layers have a coarser grain size.

The EDAX analysis results are shown in Figures 19-21. As observed, the atomic percent of Fe and S in Figures 19-21 indicated the presence of the pyrite ($Fe\ S_2$) phase on the samples surfaces regarding the chemical formula and stochiometry coefficient of iron sulfides compounds.
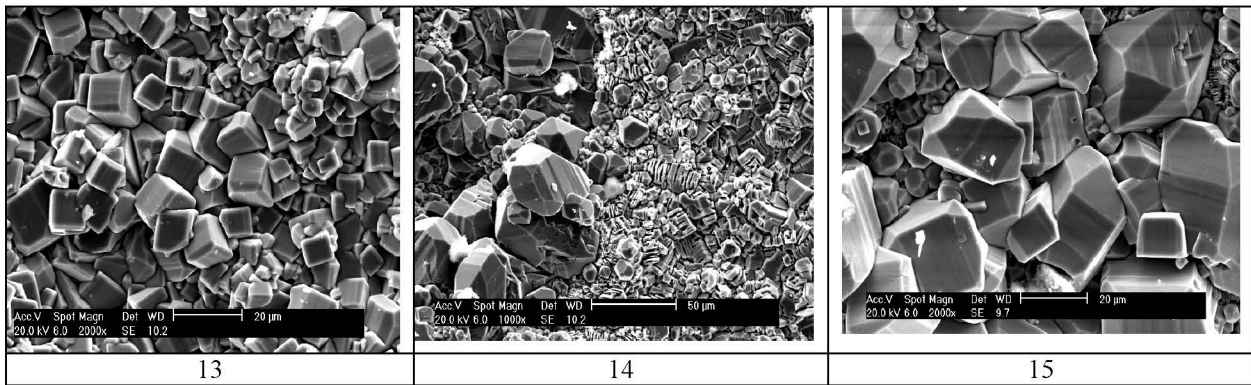

| 13 | 14 | 15 |

Fig. 13-14. SEM photograph of the 2nd experiment acid washed samples (13), rusted (14)& sandblasted (15) samples.

| 16 | 17 | 18 |
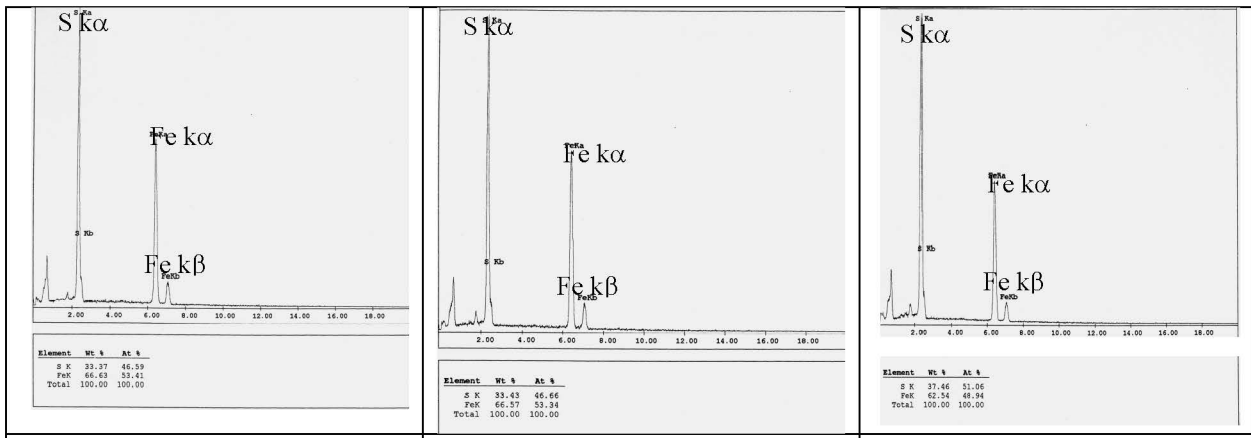
Fig. 16-18. EDAX analysis results of the 1st experiments acid washed samples, rusted & sandblasted samples.
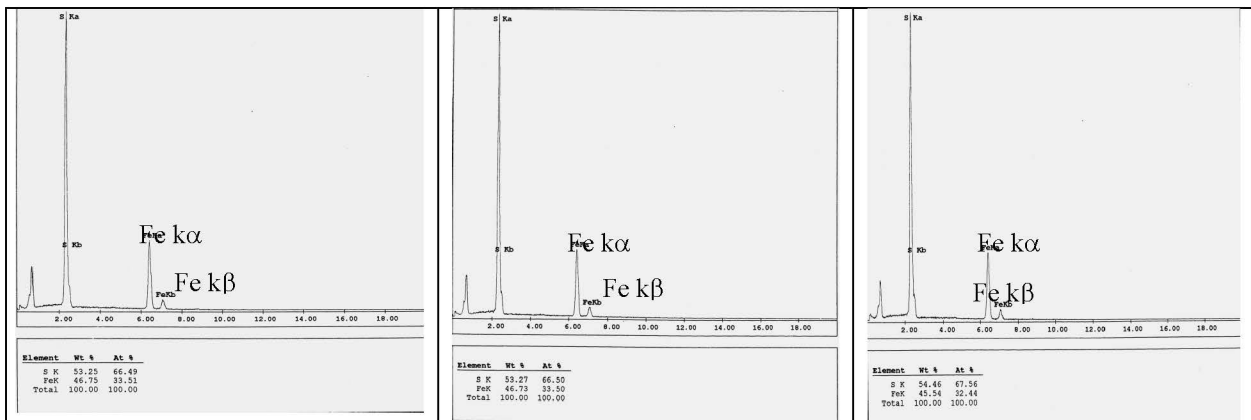

| 19 | 20 | 21 |

Fig. 19-21. EDAX analysis results of the 2nd experiments acid washed samples, rusted & sandblasted samples.

Conclusion

From results obtained in this study by the XRD analysis, microscopic investigations and EDAX analysis, it can be concluded that the exposure time is a determinant factor in the formation of the required pyrite (FeS_2) layer on the surface of the steel. The 9-day exposure layers are of the pyrrhotite ($Fe_{1-x}S$) type, and in the best state the pyrite was formed on only one of the samples surface.

The acid washed samples were also found to be better than the other samples prepared by sand blasting and rusted samples. The weight increase of various samples, due to the formation of the sulfide layers, was more prominent for the acid washed samples. In addition, it was observed that the sulfide layer in the 9-day exposure is not stable and is initially makinawite (FeS_{1-x}) phases that has no defined crystalline structure, and then is converted to triolite (FeS) phase having a cubic structure, and is further converted into pyrrhotite ($Fe_{1-x}S$) with a hexagonal crystalline structure, and at the end into pyrite (FeS_2) with an octahedral crystalline structure. Therefore, a longer exposure period with suitable conditions would result in these primitive phases to be converted and, results in the formation of pyrite (FeS_2) and pyrrhotite (Fe_{1-x} $_-$ S) layers i.e. at least 12 days of exposure time.

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