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ИССЛЕДОВАНИЕ КОРРОЗИИ ТЕПЛООБМЕННИКОВ В НАГРЕВАТЕЛЬНЫХ ПЕЧАХ СТАЛЕПРОКАТНЫХ ПЕЧЕЙ

Аннотация: *Данное исследование включает исследование коррозии теплообменников в печах повторного нагрева в печах для прокатки чугуна. Исследование коррозии трубок теплообменника в железных печах, конструкции теплообменника и характеристик сирийского топлива, а также типов теплообменников. Я рассмотрел типы коррозии, вызванной H2S, различные факторы, влияющие на процесс коррозии, и способы прогнозирования степени этой коррозии. Затем многие образцы теплообменников были изучены в Международной компании по производству стали (ICSR) в промышленном городе Хасия для выявления причин и коррозии и поиска оптимального решения этой проблемы.*

Ключевые слова: *теплообменники, углеродистая сталь, коррозия расплавом солей.*

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STUDY OF CORROSION IN HEAT EXCHANGERS IN REHEATING FURNACES IN IRON ROLLING FURNACES

Abstract: *This research includes a study on the study of corrosion in heat exchangers in reheating furnaces in iron rolling furnaces. Examination of the corrosion in the tubes of the heat exchanger in iron ovens, the structure of the heat exchanger and the characteristics of the Syrian fuel, in addition to the types of heat exchangers. I reviewed types of corrosion caused by H2S, the different factors that influence corrosion process, and how to predict the severity of this corrosion. Then many samples of heat exchangers were reviewed to infer the causes and corrosion in the International Company Steel Rolling (ICSR) in the industrial city of Hasia and to find the optimal solution to this problem.*

Key words: *heat exchangers, carbon steel, corrosion by molten salts.*

1. Introduction:

Heat exchangers are considered one of the most important industrial and processing equipment used in all parts of the world, as it is one of the applications of thermal physics - thermodynamics and also it is considered one of the applications of heat transfer science.

Heat exchangers are a unit used to change the temperature of fluids (liquid and gaseous materials) by passing them into tubes permeating another medium. The other medium is high temperature if we want to raise the temperature of the liquid or gas that is desired to raise its temperature. The liquid or gas to be cooled can also be cooled by passing it in tubes passing in another medium with a low temperature. The process of transferring heat from one medium to another is called a heat exchange, and the device in which the process is performed is called a heat exchanger. And the swap tubes in the iron rolling furnaces are subject to severe corrosion, as these tubes are corroded by oxidation, sulfur and corrosion in molten salts. Upon undertaking a field visit to the International Company Steel Rolling (ICSR), I found many problems and a complete collapse in the heat exchanger in iron ovens, so I took a set of samples in the places that suffer from the collapses in order to determine the mechanical and chemical properties and make the comparison. [1]

2. Reference study:

Research was published in the year 2006 by the researcher Natesan [2] :

Discuss the Fe-C-Ni mixtures, such as the 800H alloy, the austenitic stainless steel alloy, and the nickel alloy, such as the 617 alloy, and made a plan for the best performing alloyes as shown in Figure (1):

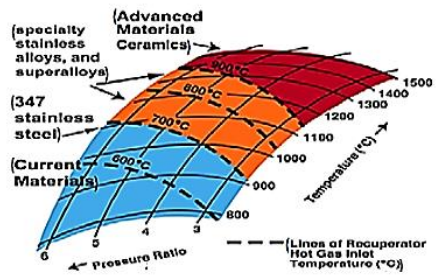


Figure (1) The use of alloys according to temperature

he notice that the choice of materials is done through the temperature and pressure in the workplace, such us stainless steel (347 alloy) is used at a temperature of 1100^0C and a pressure rate of 3 and the temperature decreases with increasing pressure, so that the temperature of stainless steel becomes 700^0C at a rate of pressure 6.

The researcher found, through the alloys he studied, that alloys of stainless steel can be used in various media with the presence of sufficient nickel and chromium ratio to withstand various pressures and temperatures.

2- A paper was published in 2007 by George Y. Lai, [3]:

George Y. Lai discussed in his book through a group of articles many topics related to corrosion at high temperatures and the materials used according to these applications where he mentioned that corrosion in fuel fired boilers is exposed similarly to what is exposed to the rolling mill furnace exchanger as by using the fuel it may form Vanadium, sulfur and sodium during its combustion contain low melting points compounds.

These compounds are a mixture of (Na_2So_4), (Na_2O), (V_2O_5). Which is deposited in front of the boiler tubes, the composition of these deposits fluctuates greatly according to the chemical composition of the fuel.

3. Reasons for research and its objective:

This research aims to study the corrosion processes in the pipes, and seek to find appropriate solutions (practical and theoretical), by studying the various corrosion problems that follow the working conditions, and to develop appropriate and appropriate proposals in order to avoid these problems.

In addition to collecting a set of samples taken from the heat exchanger tubes located in the International Iron Rolling Company in the industrial city of Hasia in order to perform many tests on these samples in corrosive media at different time periods, and to study the corrosion rate in these tubes.

4. Research method:

4-1- Determine the type of mixtures used:

To find out the type of mixtures used, several exchanger samples were taken and analyzed using a spectroscopy device. The samples were taken from an undamaged area of the tube, where they were smoothed and sanded with smoothness sheets of 60 *.

The test type was chosen for Ni-Cr steel alloys stainless steel alloys. This analysis is consistent with AISI 409 according to Figure (2) and Figure (3). The test was also performed on other samples of the exchanger, type S275JR.

Figure (2) AISI 409 alloy

Figure (3) Sample Test

4.2. Check the chemical composition:

The chemical composition was verified by a Spectrometer shown in Figure (4). After placing the sample in the test site, the device is controlled by computer so that the result is obtained directly.

Figure (4) Spectrometer

The results of the analysis for sample 409 are shown in table (1):

Table (1) chemical component for 409 steel

element	Test 1	Test 2	Test 3	average
Fe	86.2	86.2	86.3	**86.233**
C	0.0422	0.0314	0.0375	**0.037**
Si	0.594	0.534	0.527	**0.552**
Mn	0.312	0.311	0.310	**0.311**
P	0.0146	0.0225	0.0213	**0.019**
S	0.0065	0.0057	0.0057	**0.006**
Cr	12.2	12.3	12.2	**12.233**

Mo	0.0132	0.0092	0.0131	**0.012**
Ni	0.0826	0.0923	0.104	**0.093**
Al	0.0430	0.0194	0.0324	**0.032**
Co	0.0210	0.0213	0.0206	**0.021**
Cu	0.0036	0.0324	0.323	**0.120**
Nb	0.0020	0.0020	0.0020	**0.002**
Ti	0.276	0.233	0.244	**0.251**
V	0.0916	0.0850	0.0943	**0.090**
W	0.0200	0.0200	0.0200	**0.020**

Table (2) shows the results of the spectroscopy of the S275JR sample:

element	Test 1	Test 2	Test 3	average
Fe	98.5	98.6	98.6	**98.567**
C	0.147	0.137	0.136	**0.140**
Si	0.331	0.318	0.324	**0.324**
Mn	0.621	0.641	0.643	**0.635**
P	0.0276	0.0252	0.0283	**0.027**
S	0.0141	0.0137	0.0160	**0.015**
Cr	0.0752	0.0592	0.0473	**0.061**
Mo	0.0074	0.0089	0.0123	**0.010**
Ni	0.0283	0.0196	0.0146	**0.021**
Al	0.0275	0.0250	0.0289	**0.027**
Co	0.0036	0.0031	0.0032	**0.003**
Cu	0.0214	0.0198	0.0192	**0.020**
Nb	0.0082	0.0088	0.0109	**0.009**
Ti	0.0090	0.0091	0.0106	**0.010**
V	0.0020	0.0020	0.0020	**0.002**
W	0.0150	0.0150	0.0150	**0.015**
Pb	0.0250	0.0250	0.0250	**0.025**
Sn	0.0020	0.0020	0.0020	**0.002**
B	0.0012	0.0011	0.0011	**0.001**
Ca	0.0010	0.0010	0.0010	**0.001**
Zr	0.0129	0.0124	0.0166	**0.014**
As	0.0050	0.0050	0.0065	**0.006**
Bi	0.0615	0.0671	0.0551	**0.061**

4.3. Sample selection and weight examination:

Metal type AISI 409 (ferritic stainless steel). The sample was chosen from the first row (located in the far left corner of the exchanger)

Figure (5) Aisi 409

- Corrosion area in place of molten salts:

  The level of erosion in this area was measured by measuring the weight loss after surveying and cutting the affected area.

  By visual examination, this sample was subjected to severe erosion of molten salts that led to perforation of the tube and thus loss of its efficacy in the effective area thereof, as rust spread was found over the entire tube (demolishing resistance of chromium oxide and the spread of iron oxide over the entire sample). The percentage of weight loss in the lower part (molten salts region) of the tube: 26% , compared to the upper part of the tube that was exposed to rust (Weight loss test).

Figure (6) Aisi 409 and Balance has 0.0001 accuracy for weight loss test

The middle and upper region of the tube:

Corrosion in areas exposed only to the influence of heat and the impact of corrosion by sulfur compounds and moisture (the ratio of moisture measured in Syrian fuel is 15% (through experiences). We see a breakdown of the resistance of the chromium oxide layer to be replaced by a layer rich in iron oxide, as we note sulfur attack spots on these tubes without any apparent or effective corrosion.

Examining the erosion using a weight loss method, he found:

Central region: 4%

Upper region: 3%

This is due to the nominal weight of a similar tube with a wall thickness of 3 mm, identical to the samples used.

- S275JR EN 10025-2004 steel tubes.

It found some traces of sulfur in the upper areas and completely covered with rust. After examining several samples, it was found that the sulfur effects are macular effects that do not significantly affect the tubes. After mechanically removing the rust from the tubes and checking them by weight, it was found that there was a 5% weight decrease for these tubes.

4.4. Choose the perfect mixture for this application

Refer to ASM Publications:

High-Temperature Corrosion And Materials Applications George Y. Lai, editor, p1 [3]

Discussing mixtures subject to corrosion at elevated temperatures in which the most suitable mixtures (stainless steel mixtures - nickel mixtures) were nominated as a possible alternative to the mixture AISI 409

And according to the following tables:

Table (3) shows the corrosion rates of several mixtures of austenitic stainless steels within 10% water vapor for 1000 hours at different temperatures.

Table (3)

alloy	980°c (1008 °F)		1095°c (2000 °F)		1150°c (2100 °F)		1205°c (2200 °F)	
	Metal lose, mm	Metal lose average , mm	Metal lose, mm	Metal lose average , mm	Metal lose, mm	Metal lose average , mm	Metal lose, mm	Metal lose average, mm
214	0.0025	0.005	0.0025	0.0025	0.005	0.0075	0.005	0.018
601	0.013	0.033	0.03	0.067	0.061	0.135	0.11	0.19
600	0.0075	0.023	0.028	0.041	0.043	0.074	0.13	0.21
230	0.0075	0.018	0.013	0.033	0.058	0.086	0.11	0.2
S	0.005	0.013	0.01	0.033	0.025	0.043	>0.81	>0.81
617	0.0075	0.033	0.015	0.046	0.028	0.086	0.27	0.32
333	0.0075	0.025	0.025	0.058	0.05	0.1	0.18	0.45
X	0.0075	0.023	0.038	0.069	0.11	0.147	>0.9	>0.9
671	0.0229	0.043	0.038	0.061	0.066	0.099	0.086	0.42
625	0.0075	0.018	0.084	0.12	0.41	0.46	>1.2	>1.2
Waspa -loy	0.0152	0.079	0.036	0.14	0.079	0.33	>0.40	>0.40
R-41	0.0178	0.122	0.086	0.3	0.21	0.44	>0.73	>0.73
263	0.0178	0.145	0.089	0.36	0.18	0.41	>0.91	0.91
188	0.005	0.015	0.01	0.033	0.18	0.2	>0.55	>0.55
25	0.01	0.018	0.23	0.26	0.43	0.49	>0.96	>0.96
150	0.01	0.025	0.058	0.097	>0.68	>0.68	>1.17	>1.17
6B	0.01	0.025	0.35	0.39	>0.94	>0.94	>0.94	>0.94
556	0.01	0.028	0.025	0.067	0.24	0.29	>3.8	>3.8
Multi-met	0.01	0.033	0.226	0.29	>1.2	>1.2	>3.7	>3.7
800H	0.023	0.046	0.14	0.19	0.19	0.23	0.29	0.35
RA33 0	0.01	0.11	0.02	0.17	0.041	0.22	0.096	0.21
310	0.01	0.028	0.025	0.058	0.075	0.11	0.2	0.26
316	0.315	0.36	>1.7	>1.7	>2.7	>2.7	>3.57	>3.57
304	0.14	0.21	>0.69	>0.69	>0.6	>0.6	>1.7	>1.73
446	0.033	0.058	0.33	0.37	>0.55	>0.55	>0.59	>0.59

Table (4) shows the corrosion rates of several austenitic stainless steels in sulfur vapor at 571 ° C for 1295 hours.

Table (4)

mm/yr Corrosion aaverage	alloy
0.43	314
0.48	310
0.57	309
0.69	304
0.76	302B
0.79	316
1.39	321

Table (5) alloys and corrosion average

Corrosion aaverage **at 700 C° mm/yr**	Corrosion aaverage **at 600 C° mm/yr**	Corrosion aaverage **at 550 C° mm/yr**	Corrosion aaverage **at 500 C° mm/yr**	**alloy**
8.94	2.79	1.45	0.91	**310**
10.2	2.95	1.57	1.12	**304**
10.8	4.45	2.44	1.5	**316**

The mixtures described in this table are mixtures intended for all heat exchangers. These mixtures vary between nickel alloys and stainless steel mixtures.

The relative prices of the mixtures used in the heat exchangers according to the following table [6]:

table [6]

Compare the heat capacity of the mixture 304	alloy
0.67	A 387 Gr 22 (2-1/4Cr, 1Mo)
1.00	304L, 304H
0.77	409
1.67	316L
1.58	410, 410S
1.75	RA2205
1.75	RA321
2.25	RA309
2.42	317L
2.83	RA17-4 (3/8” plate)
2.83	RA310
2.42	RA 253 MA®
3.92	RA330®
6.08	RA600
12.33	RA333®
11.33	625
13.50	718
4.33	20Cb-3®
4.33	AL-6XN®
5.83	2507
6.42	400
9.08	C-276
9.83	200
6.17	K-500 (one inch bar)
11.17	686
11.75	C-22

After taking into consideration the locally available materials and the economic criteria, the experiment options were limited to the following mixtures:

Aisi 316 - Aisi 304 - Aisi 310 (It is not currently available on the market as tubes as required). At the same time, we will test the Aisi 409 base mixture (not available in the domestic market enough to manufacture a complete exchanger) to ensure that the examination is carried out in one conditions and compare the results within the available test period.

5.4. Characteristics of the selected mixtures [4]:

- The mixture Aisi304 :

chemical composition:

table (7) chemical composition alloy 304

C	MN	P	S	SI	CR	NI		elements	
					18.00	8.00	min	UNS S30400	AISI 304
0.08	2.0	0.045	.030	1.00	20.00	10.50	max		
					18.00	8.00	min	UNS S30403	AISI 304L
0.03	2.0	0.045	.030	1.00	20.00	12.00	max		

- Mechanic properties:

Table (8) Mechanical properties 304

Tensile sterngth Ksi [MPa]	Yield strength Ksi [MPa]	% Relative elongation 5d	% Decrease in cross section	hardness HB
85[585]	35[240]	40	50	150

Table (9) Recommended maximum temperature

304 Temoerature of	321 (°C) temperature	Conditions of operation
830	830	Continuous work
800	800	Intermittent work

Corrosion resistance:

304 / 304L SS has excellent corrosion resistance in a wide range of corrosive media, including food applications and sterile atmospheres, most chemicals, organic dyes and a wide variety of inorganic chemicals. During service, acid corrosion may be accelerated or slowed by the presence of chemicals or other pollutants. The reaction of this mixture to all the variables in working conditions cannot be fully evaluated in the laboratory. Consequently, laboratory tests can only be an indication of performance. And the real practical reality remains truer and more reliable than any laboratory tests.

The mixture Aisi316

chemical composition:

table (10) chemical components of 316 alloy

C	Mn	P	S	Si	Cr	Ni	Mo		elements	
					16.00	10.00	1.5	min	UNS	AISI
0.08	2.0	0.045	0.030	1.00	18.00	14.00	2	max	31600	316
					16.00	10.00	1.5	min	UNS	AISI
0.03	2.0	0.045	0.030	1.00	18.00	14.00	2	max	31603	316L

Chemical nominal characteristics (Solid case):

Table (11) Mechanical properties 316

Tensile sterngth Ksi [MPa]	Yield strength Ksi [MPa]	% Relative elongation 5d	% Decrease in cross section	hardness HB
80[550]	30[200]	45	55	140

Table (12) Recommended maximum temperature 316

(°C) temperature	Conditions of operation
920	Continuous work
870	Intermittent work

- Physical properties : Unless otherwise indicated, the values given are for 20 ° C

Table (13) The physical properties of the alloy 316

8000kg/m3	density
193GPa	Modulus of elasticity in tensile strength
70GPa	Tangential elastic modulus
0.25	Poisson factor
500J/kgK	Specific heat capacity
16.2W/mK 21.5W/mK	@ 100°C Thermal conduction @ 500°C
740 ηm	electrical resistance
Coefficient of thermal expansion	
15.9µm/mK 16.2µm/mK 17.5µm/mK 18.5µm/mK	0 - 100°C 0 - 315°C 0 - 540°C 0 - 700°C
1 390-1 430°C	Melting area
1.02	Relative permeability

316 type has superior corrosion resistance compared to 304 SS. 316SS has good resistance to most complex sulfur compounds such as those found in papermaking. It also has good corrosion resistance in phosphorous acids and has excellent corrosion resistance in marine environments.

6.4. Work Stages:

1- Confirm the type of metal. 2- Selection and weight of samples .3- Place the samples in the exchanger in the molten salt area .4- Sample removal and visual examination. 5- Weight test .6- Compare the results. 7- Conclusion

6.4.1. Confirmation of the type of metal:

It was confirmed that the samples were installed on the spectroscopy apparatus and the results were as follows:

Table (14) alloy Aisi 316

element	Test1	Test 2	Test3	average
Fe	70.4	70.6	70.6	**70.533**
C	0.0773	0.101	0.0619	**0.080**
Si	0.919	1.03	0.910	**0.953**
Mn	0.867	0.858	0.898	**0.874**
P	0.0410	0.0435	0.0436	**0.043**
S	0.0104	0.0137	0.0123	**0.012**
Cr	15.0	15.1	15.4	**15.167**
Mo	1.76	1.74	1.73	**1.743**
Ni	10.2	9.81	9.72	**9.910**
Al	0.0196	0.0266	0.0184	**0.022**
Co	0.123	0.119	0.126	**0.123**
Cu	0.179	0.195	0.218	**0.197**
Nb	0.0050	0.0050	0.0050	**0.005**
Ti	0.0116	0.0126	0.0122	**0.012**
V	0.0510	0.0539	0.0580	**0.054**
W	0.0985	0.1280	0.0825	**0.103**
Pb	0.0500	0.0500	0.0500	**0.050**

Table(15) alloy Aisi 304

element	Test1	Test 2	Test3	average
Fe	69.7	69.8	69.3	**69.600**
C	0.0647	0.0773	0.0649	**0.069**
Si	0.415	0.395	0.393	**0.401**
Mn	0.851	0.840	0.850	**0.847**
P	0.0312	0.0360	0.0317	**0.033**
S	0.0050	0.0050	0.0050	**0.005**
Cr	19.2	19.2	19.4	**19.267**
Mo	0.0215	0.0225	0.0233	**0.022**
Ni	9.21	9.15	9.45	**9.270**
Al	0.0087	0.0096	0.0098	**0.009**
Co	0.189	0.190	0.186	**0.188**
Cu	0.105	0.102	0.106	**0.104**
Nb	0.0020	0.0020	0.0020	**0.002**
Ti	0.0078	0.0074	0.0085	**0.008**
V	0.0896	0.0899	0.9030	**0.361**
W	0.0200	0.0200	0.0200	**0.020**

6.4.2. Weight of samples:

The samples were cut in 38 mm diameter with the following lengths, after removing the appendages resulting from the cutting process and flattening them on the lathe and weighed according to the attached table:

Table (16) length and weight of samples

Aisi 304	Aisi 316	Aisi 409	sample
313.3	327.8	292.6	(mm) length
1036	1084	955	(g) weight

6.4.3. Place the samples in the exchanger in the molten salt area:

The samples were placed in the molten salts area through the detection opening in front of the exchanger, according to Figure (4-8).

Figure (7) Slot detection in front of the exchanger

6.4.4. Sample removal and visual examination:

By visual examination, it was found that:

The sample aisi 316 remained preserved on the layer of chromium oxide covering it, while it was subjected to corrosive molten ash like the rest of the samples.

* The samples aisi 304 and aisi 409 showed corrosion in the molten salts area at the bottom, and a layer of sediments with a height of 30-50 mm appeared before it. Corrosion has appeared in this area quickly.

* There are no multiple levels of corrosion in all samples as found in the previous exchanger samples due to the relatively shorter period of time and the inability to maintain a large layer of sediment.

A complete destruction of the chromium oxide layer covering all samples was found, and a layer rich in iron oxide appeared in its place, and the corrosion area with molten salts appeared brightly, with an irregular decrease in the thickness of the samples.

We also notice the formation of an iron oxide-rich layer over the entire section of the tube in areas subject to exhaust run off.

Figure (8) sample of Aisi 304 **Figure (9) sample of Aisi 304**

Figure (10) sample of Aisi 409 **Figure (11) sample of Aisi 409**

Figure (12) sample of Aisi 316 **Figure (13) sample of Aisi 316**

6.4.5. weight test: The samples were cut and the cutting surfaces are normalized and weighed on the digital scale:

Table (17)

Aisi 304	Aisi 316	Aisi 409	alloy
1036	1056	955	(g) wright

6.4.6. Comparing results:

Table (18) Weight loss

Weight loss	Weight after (g) test	Weight before (g) test	alloy
6%	901	955	Aisi 409
5%	1029	1056	Aisi 304
2%	1016	1036	Aisi 316

Table (19) Corrosion

Mass corrosion (mg/cm^2) ratio	Alloy
122.45	Aisi 409
57.60	Aisi 304
42.35	Aisi 316

Mass erosion ratio=weight difference before and after the test/side area of the test tube.

As the test tube length is 30 Cm and the outer diameter is 48 mm. price comparison:

Table (20)

(S.P./Kg) price	Alloy
1300	Aisi 409
2000	Aisi 316
1600	Aisi 304

Microscopic examination of the structure of the tested samples:

The structure of the samples was examined microscopically before and after erosion to see the changes that occurred in the structure. The samples were sharpened with sharpened sheets of different roughness from B60 to B600, then the surface of the samples was polished and after that the acid treatment (etching) was performed as follows:

5 g $FeCl_3$ + 50 ml HCl + 100 ml distilled water (distilled water)

The results were as follows (200x zoom ratio):

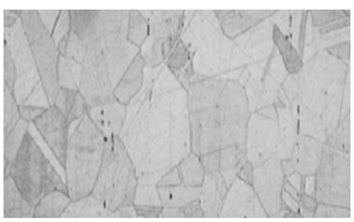
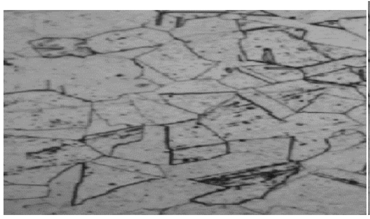


Figure (8) alloy 316 before test **Figure (9) alloy 316 after test**



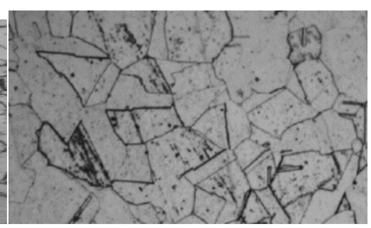


Figure (10) alloy 304 before test **Figure (11) 304 alloy after test**

The results of the microscopic examination indicated that the structure of the samples did not change and remained in preservation of their properties and therefore there was no change in the austenitic structure of 316 and 304

6.4.7 Conclusion and recommendations:

After comparing the results, it was found that the Aisi 316 mixture is the best in terms of resistance to corrosion among the mixtures available in the local market because its resistance to soluble salts is better than the resistance of the mixture 304 and that its resistance to rust is better, therefore we recommend using the Aisi 316 mixture in the new exchanger and for the better relative resistance shown by The mixture is within the tested environment.

Additional engineering solutions were proposed to the company's management as follows:

Proposal No. 1: Flip the exchanger position to horizontal as fol

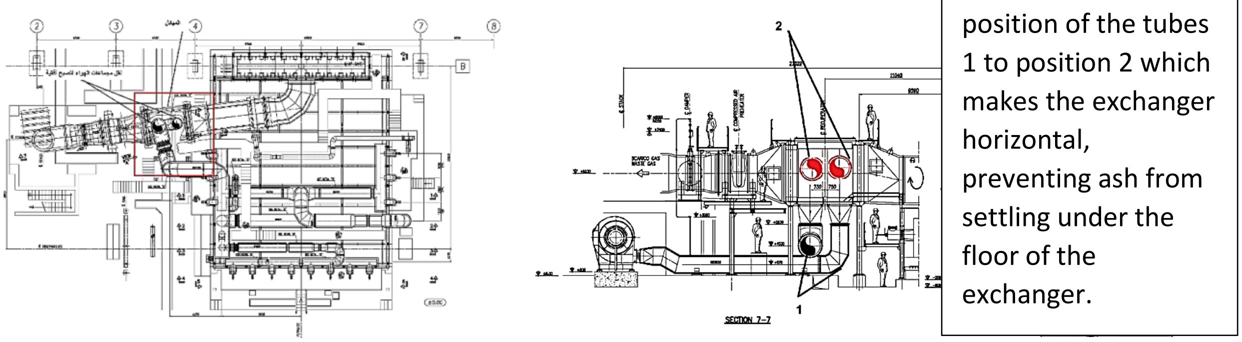


Figure (12) Flip the exchanger position to horizontal and Flip the exchanger position to horizontal

The proposal is now being studied by company officials.

1- The result of the practical study showed that the AISI 316 mixture is considered the best among the selected mixtures in terms of rust resistance and corrosion resistance with molten ash.

2- It is not recommended to use a tempering fan to reduce the heat exchanger temperature to reduce corrosion, because its cost is almost ten times higher than the operating cost of the exchanger.

Recommendations:

It is recommended that the exchanger be placed horizontally so that dissolved salts are deposited on the insulation block rather than on the exchanger tubes.

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