Corrosion Behaviour of Some Steels in Black Sea Water

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Corrosion of shipbuilding elements in seawater depends both by the marine salts action and by the microbiological components existent into the water. The paper contains a chemical and structural analysis for the oxides from the biological corrosion and the corrosion due to the chemical compounds from the Black Sea. The oxides layers analysis, in terms of shape, size thickness, consistency also porosity degree and chemical compounds, gives an indication for the corrosion severity and the need for protection. This study was made on two types of welding steels, used for shipbuilding, and the analysis was performed using the scanning electrons microscope and the EDX detector. The oxidation study is a first step to achieve efficient passivation or protection.

Keywords: corrosion, marine algae, sea water, oxides, electronic microscopy

The corrosion process represents the spontaneous chemical modification, for the metals or alloys composition, as a result of a chemical, electrochemical or biochemical reactions, in the course of their interaction with the external environment. Corrosion, by its action, leads to physical properties changes, converting a part of the metal mass in chemical compounds, [1-5].

Corrosion can be regarded as a series of anodic and cathodic reactions. Corrosion occurs if four elements are present: the anode, the cathode, the aggressive agent and the metal. When all these four elements are present they form a corrosion cell [6].

Văireanu D.I. [7] explains that in most corrosion processes, with the exception of controlled cathode processes, the metals are dissolved. An example of corrosion is taking place in seawater, solution of salts or alkaline solutions. Almost in all of these systems, corrosion occurs only if dissolved oxygen is present. Aqueous solutions rapidly dissolve the oxygen in the air and this is the source of oxygen necessary to carry out the corrosion process.

Algae are photosynthetic feeding organisms, with simple nutritional requirements: light, water, air and certain inorganic compounds. It can be found in waters with varying degrees of salinity, from seawater to distilled water and can survive in different depths. Corrosion reactions produced by these algae are stimulated by their metabolic oxygen production (according to photosynthetic principle, algae produce oxygen when exposed to light), as well by certain corrosive organic acids produced during metabolism of some species [8-17].

Experimental part

Materials and methods

For the experiment were used two types of weldable steel used to build ship hulls. Samples were immersed in seawater without biological compounds and in seawater with marine algae, ULVA and FUCUS, [13, 14]. The maintenance period in corrosive environment was 90 days, in both cases. After the experiment, the samples were analyzed with EDX detector in order to determine of the chemical structure of the oxides surface and photographed with scanning electrons microscope in order to highlight the shape of the corrosion products.

For the study were chosen two types of low alloy steel samples, used in ship building welded or riveted. Their chemical compositions are presented in table 1. The studied steels are:

-Normal-strength steel, S235JR (EN 10025-2);

-High-strength steel, S275JO (EN 10025-2).

They were developed at Mittal Steel Galati SA, used in ship building. The first steel has the symbol A, by the internal manufacturer specification and is denoted by A, and the second has the symbol E32 is denoted B.

It has been used as corrosion environment seawater from the Black Sea, because the metal sheets tested are used for achieve ship hulls construction or maintenance. This materials are used in the shipyards of Constanta.

Table 1

THE CHEMICAL COMPOSITIONS OF STEEL, [Weight %]

Alloy	C	Si	Mn	P	S	Al	As	Ti	Cu	Ni	Cr	Mo	Fe
A (A)	0.170	0.220	0.750	0.025	0.011	0.005	-	-	0.020	0.020	0.050	-	96.75
B (E32)	0.170	0.360	1.470	0.020	0.011	0.080	0.010	0.007	0.032	0.016	0.013	0,004	97.72

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Samples from the two samples were immersed, separately, in a limited volume of seawater, with green and brown seawater algae, closed for 90 days into airtight glass vessels. The corrosion environment is represented by the Black Sea water, having the ionic composition, expressed in gL^{-1}: : Cl^- - 8.26; HCO_3 - 0.183; CO_3^{2-} - 0.022; SO_4^{2-} - 1.137; Na^+ - 4.47; K^+ - 0.158; Ca^{2+} - 0.203; Mg^{2+} - 0.557, with the salinity 15.0 g L^{-1}.

Seaweed

Algae causes corrosion participating in two ways in the process of corrosion: direct and indirect. Directly they can cause corrosion of metal by autotrophic metabolism that alter the environment; the assimilation of algae chlorophyll increase the dissolved oxygen content and adjust the *p*H and water purity. Indirectly, algae occur through the formation of gelatinous precipitates or crusting, fixed to the walls of the reservoirs or water pipes, which develops bacteria and fungi that cause corrosion. Approximately 70% of seas and oceans biomass contains algae, forming the phytoplankton, which is the nutrition base of other marine organisms: crayfish, mollusks, fish, birds and aquatic mammals. Through photosynthesis, the algae form the biggest part of the oxygen in the water breathed by aquatic animals. (90% of the existing oxygen on the planet, is provided by seaweed).

Two types of algae were used:

a) Ulva - (fig.1 a) solid, tall and green seaweed. Green algae designate a group of algae whose main photosynthetic pigment are chlorophyll and xanthophylls and carotenes pigments. It multiplies by zoospores, lives in the Black Sea salt water and causes corrosion for ships and boats.

b) Brown algae (Pheophyceae) (fig.1 b) are superior in terms of morphology containing microscopic and macroscopic multicellular forms, which are autotrophic and saprophytic. The main characteristic is the presence of fucoxantină pigment and chlorophyll. They have a relatively large tall, can reach up to 60 m. The cell wall is formed of sulphate fucans and alginic acid. Can live in the seas and oceans, especially in the cold ones, down to a depth of 200 m, fixed on rocks or other seaweed. The used seaweed in this study was Fucus algae, macroscopic shape, dichotomy branched, with floating vesicles.

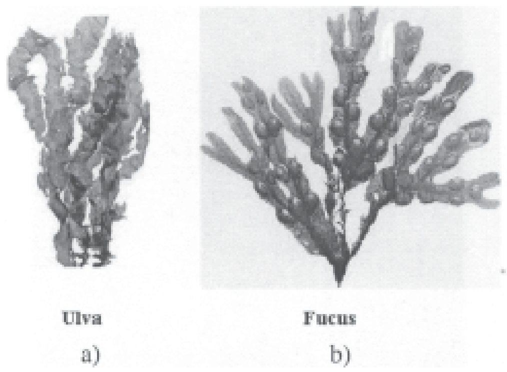
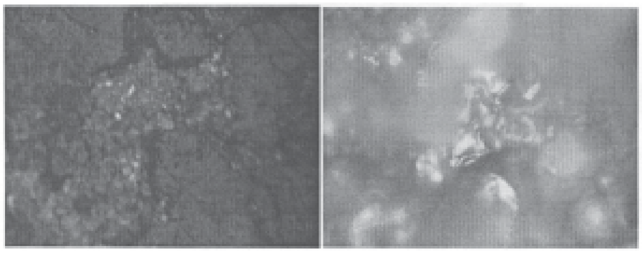


Fig.1. Used algae: a) Green marine algae; b) Brown algae

Results and discussions

Samples from the two samples were immersed, separately, in a limited volume of seawater, with green and brown seawater algae, closed for 90 days into airtight glass vessels. After one week interval, oxygenation was made by bubbling air through. After this period the samples were removed from the solution (seawater) and without



Sample A - 90 days in seawater Sample B - 90 days in seawater

Fig. 2. Optical images of the surface of the samples A and B, maintained in the Black Sea water: (x250)

being washed it were dried by blotting with filter paper and then dried in an oven at 45°C.

Optical Microscopy

The corroded surface was analyzed using the optical microscope. Solid corrosion product, the rust, is a red-brown crust with white spots, with a thickness of approx. 0.3 mm, easily to peel from the surface. The appearance of the surface of the two samples immersed for 90 days in the seawater without algae is illustrated in figure 2, where are presented optical images of the surface, obtained from a microscope XJP-6A (Wuzhou New Found Instrument Co., Ltd, China).

It may be noted that after 90 days of immersion, the sample surface is completely covered with a thick and heterogeneous products layer, where can be observed rust pustules, quasi-spherical, along with some saline deposits (calcium and magnesium carbonate, calcium chloride and sodium chloride, adsorbed in the rust porous layer).

A more complex analysis for surface structure of the immersed samples was done by electron microscopy (VEGA II LSH microscope, made by Tescan Co., Czech Republic, coupled by an EDX QUANTAX QX2 detector made by Bruker/Roentec Co., Germany). Also a microanalysis was made using the EDX detector.

SEM Analysis

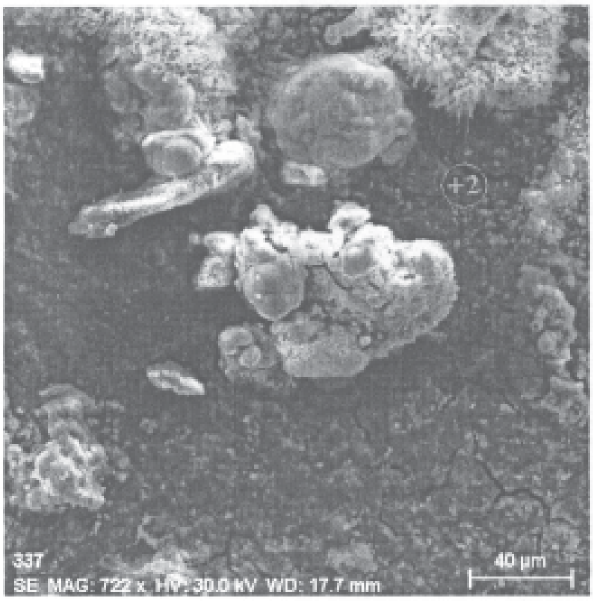
The appearance and composition of the surface in different areas of the sample A, maintained 90 days in water without algae is presented in figure 3.

Microanalysis data highlights the fact that the main corrosion products are iron oxides, sometimes accompanied by calcium and sodium chlorides or carbonates. May be distinguished three different areas depending the chemical composition of the products crust.

In area (1) the molar ratio Fe:O is 0.59, which leads us to consider that it is a mixture of FeOOH (where the ration Fe:O=0.5) and Fe_2O_3 (where ratio Fe:O = 0.67). Next to them are found in small amounts, chlorides and carbonates - or even carbon from the composition of the sample (probably adsorbed or precipitated during the drying process).

In the area (2), which represents the base of the products crust, the molar ration Fe:O = 0.81, which would correspond to the presence of Fe_3O_4 (with the ratio Fe:O = 0.75). In this case, on the surface there are absorbed or precipitated calcium and sodium compounds.

In the area (3) the molar ration Fe:O = 0.49, corresponding to the Fe oxy-hydroxide (FeOOH), but also, in this case the product is contaminated with chlorides and carbon. The product from this area is crystalline. This can be seen better at a higher magnification, in the same area, presented in figure 4. The crystalline structure from



Sample A – 90 days in seawater

Point 1

Element	AN	series	Net	[wt.%]	orm. wt.%]	orm. at.%]	r in %
Iron	26	K-series	54648	62,378759	64,269046	34,381104	1,624
Oxygen	8	K-series	11909	30,31467	31,233307	58,321956	4,168
Chlorine	17	K-series	3131	2,2958456	2,3654175	1,9933166	0,119
Carbon	6	K-series	926	2,0695167	2,1322301	5,3036237	0,664
			Sum:	97,058791	100	100	
			n(Fe)/n(O)=0,59				

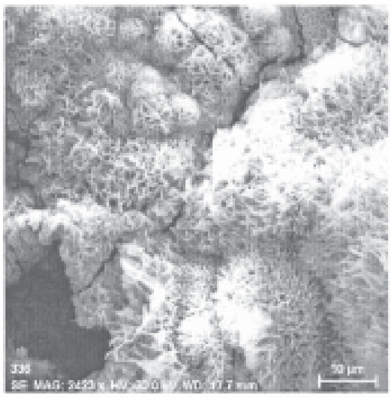
Point 2

Element	AN	series	Net	[wt.%]	orm. wt.%]	orm. at.%]	r in %
Iron	26	K-series	67958	60,984822	64,857468	36,127405	1,583
Oxygen	8	K-series	8990	21,580465	22,950864	44,524357	3,093
Sodium	11	K-series	1061	4,9643071	5,2795496	7,1435577	0,446
Carbon	6	K-series	1389	2,6972184	2,8684967	7,429367	0,76
Calcium	12	K-series	1015	2,6326363	2,7998124	3,6835208	0,222
Chlorine	17	K-series	1892	1,1695411	1,243809	1,0913926	0,077
			Sum:	94,028989	100	100	
			Fe:O = 0,81				

Point 3

Element	AN	series	Net	[wt.%]	orm. wt.%]	orm. at.%]	r in %
Iron	26	K-series	76917	53,270973	54,555478	26,379019	1,384
Oxygen	8	K-series	24503	37,481944	38,385734	53,786761	4,731
Calcium	20	K-series	1E+05	29,663373	23,895158	10,551742	0,9
Chlorine	17	K-series	10511	4,6213683	4,7320018	3,604866	0,194
Carbon	6	K-series	1696	2,2712209	2,3259861	6,2293542	0,61
			Sum:	97,645507	100	100	
			Fe:O = 0,490				

Fig.3. The image and the local chemical composition for the A sample, maintained 90 days in seawater, without algae.



Characteristic structure for FeOOH (detail from point 3)

Fig.4. Corrosion product structure from area 3; 2400X

the corrosion products, FOOH monocyclic crystals, can be distinguished very well.

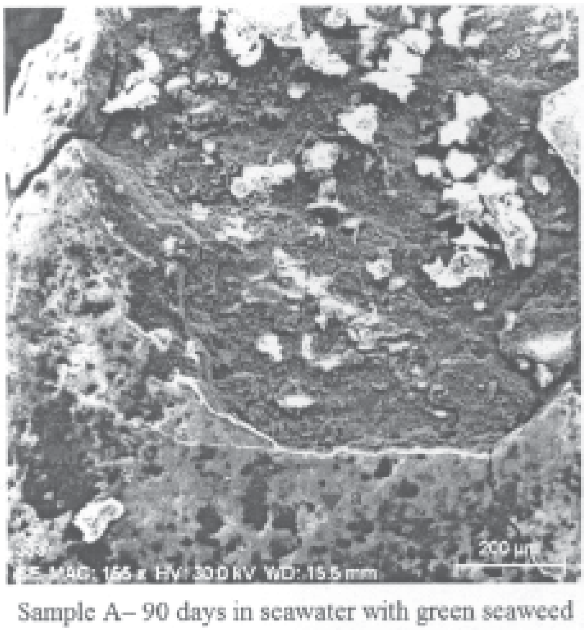
Maintaining sample A for 90 days in Black Sea water, together with seaweed Ulva, (green seaweed), leads to formation of the corrosion products crust more complex and different from that obtained in the absence of the algae. On the sample surface three study areas were chosen: I, II and III. The surface structure and chemical composition at various points are shown in figures 5, 6 and 7.

In area I, (fig.5), on large surfaces (where is point **a** contained) the iron compounds are essentially non-existent, instead are predominant other oxygenated products, with calcium, magnesium, sodium, and carbon. Higher level of oxygenation is due to the presence of green algae, generating oxygen through photosynthesis.

In other areas of the surface of the sample, for example, area II, (fig.6), the crust is made up exclusively of iron oxides like oxy-hydroxide (points 1 and 3), or Fe_2O_3 (points 2 and 4).

Should also note here the presence of chlorine, most likely due to crystallization during drying of the sodium chloride water absorbed in the porous oxide layer. In some points of the area III surface (fig.7), the molar ratio Fe:O appears unexpectedly high, placed around the unit value (1.01 and 1.21 – in the points 6 and 7) which would correspond to the FeO oxide, the hematite.

Next to, it is found the FeOOH. The lower the value found for the molar ratio Fe:O (0.41 instead of 0.5), it is due to the deterioration caused by the presence of other oxygenates in particular carbonates.



Sample A– 90 days in seawater with green seaweed

Point a

Element	AN	series	Net	[wt.%]	orm. wt.%]	orm. at.%]	r in %
Oxygen	8	K-series	10267	72,180684	65,06571	80,03004	10,090
Calcium	20	K-series	137105	32,649195	28,47604	14,47114	0,9873
Carbon	6	K-series	3303	2,5470053	2,299471	3,76072	0,4776
Iron	26	K-series	3575	1,8341955	1,655937	0,582813	0,0825
Sodium	11	K-series	964	0,9691178	0,874939	0,747787	0,1084
Magnesium	12	K-series	1076	0,5846281	0,527806	0,426696	0,0683
			Sum:	110,76482	100	100	

Point b

Element	AN	series	Net	[wt.%]	orm. wt.%]	orm. at.%]	r in %
Iron	26	K-series	121475	76,816727	77,19726	48,07189	1,9767
Oxygen	8	K-series	12665	19,447323	19,52858	42,4475	2,6794
Carbon	6	K-series	2676	3,2608506	3,274427	9,480886	0,6032
			Sum:	99,584781	100	100	
					Fe:O=1,13		

Point c

Element	AN	series	Net	[wt.%]	orm. wt.%]	orm. at.%]	r in %
Iron	26	K-series	148835	94,317859	82,96475	60,18548	2,436
Oxygen	8	K-series	13160	15,094089	13,27719	33,62021	2,3819
Chlorine	17	K-series	2845	1,9987562	1,758163	2,009139	0,1084
Calcium	20	K-series	1990	1,2323872	1,083978	1,095747	0,3735
Carbon	6	K-series	925	1,0412654	0,915925	3,089432	0,4085
			Sum:	113,68423	100	100	
					Fe:O=1,78		

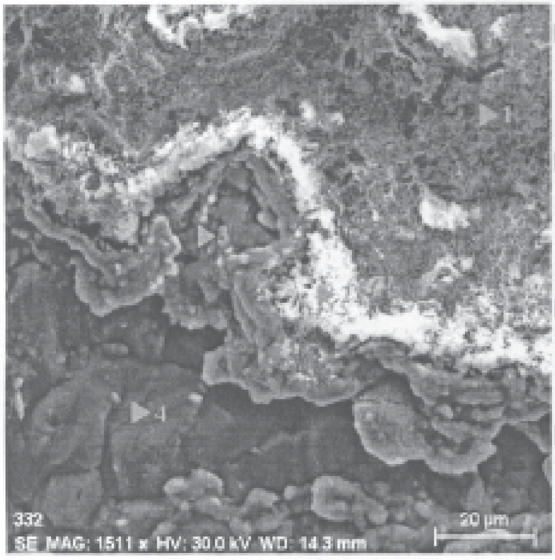
Point d

Element	AN	series	Net	[wt.%]	orm. wt.%]	orm. at.%]	r in %
Oxygen	8	K-series	10919	64,505116	58,75292	78,28461	9,0533
Calcium	20	K-series	111091	27,874688	23,47139	13,20703	0,8307
Iron	26	K-series	26913	12,810656	11,6648	4,340282	0,3595
Carbon	6	K-series	3822	3,233007	2,945525	5,096154	0,3416
Sodium	11	K-series	1220	1,3024071	1,185862	1,071911	0,1331
			Sum:	109,82787	100	100	

Fig.5. Area I, in detail, from the products crust after maintaining in the seawater with green seaweed

For the sample B, maintained 90 days in water without algae, the appearance and composition of the surface in different areas are presented in figure .8.

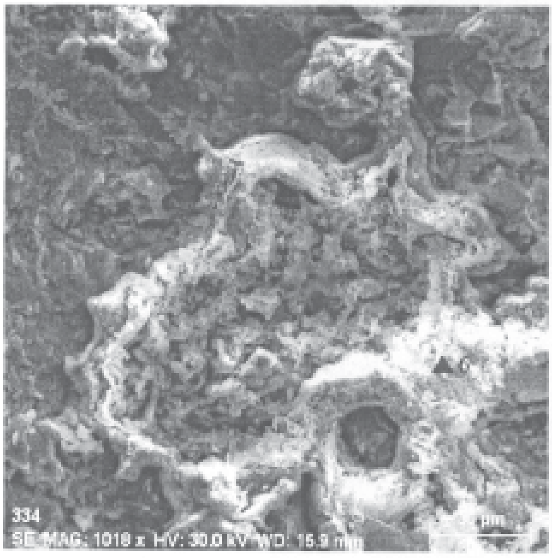
As in the case of the A sample, the predominant part of the crust (the interior deposit where it is placed point 2) is formed exclusively by FeOOH (ratio Fe:O=0,5), and the crust is cracked. For a different number of crystals the ratio Fe:O is equal with 0.7 (point 3) the corresponding oxide is Fe_2O_3 (ratio Fe:O = 0.67), Fe_3O_4 (ratio Fe:O = 0.75, but most likely a mixture of these two oxides). The ratio Fe: O



Sample A– 90 days, green seaweed (area II)

Element	AN	series	Net	[wt.%]	norm. wt.%]	rm. at.%]	or in %
Point 1							
Iron	26	K-series	104484	55,2397	60,842709	32,85616	1,456
Oxygen	8	K-series	24952	30,2372	32,711927	61,66099	3,814
Chlorine	17	K-series	17526	5,95775	6,4453643	5,482948	0,238
			Sum	92,4346	100	100	
		Fe:O=0.53		(FeOOH)			
Point 2							
Iron	26	K-series	111519	60,1741	62,329603	34,12257	1,554
Oxygen	8	K-series	21435	28,5861	29,60859	56,58269	3,655
Chlorine	17	K-series	17475	6,4442	6,6747215	5,756412	0,255
Carbon	6	K-series	1024	1,34198	1,3899854	3,538307	0,427
			Sum	96,5464	100	100	
			Fe:O=0,603		(probabil Fe2O3 (Fe:O=0,67))		
Point 3							
Iron	26	K-series	98212	55,5625	58,781868	30,65039	1,438
Oxygen	8	K-series	29479	33,6939	35,540332	64,68599	4,167
Chlorine	17	K-series	16025	5,36684	5,6777956	4,66362	0,217
			Sum	94,5232	100	100	
		Fe:O=0,474	(probabil FeOOH)				
Point 4							
Iron	26	K-series	111395	58,9062	64,009996	34,56469	1,522
Oxygen	8	K-series	24771	29,4991	32,054928	60,41915	3,725
Chlorine	17	K-series	8251	2,69613	2,929728	2,492077	0,125
Carbon	6	K-series	775	0,92519	1,0053474	2,524181	0,333
			Sum	92,0266	100	100	
			Fe:O=0,572				

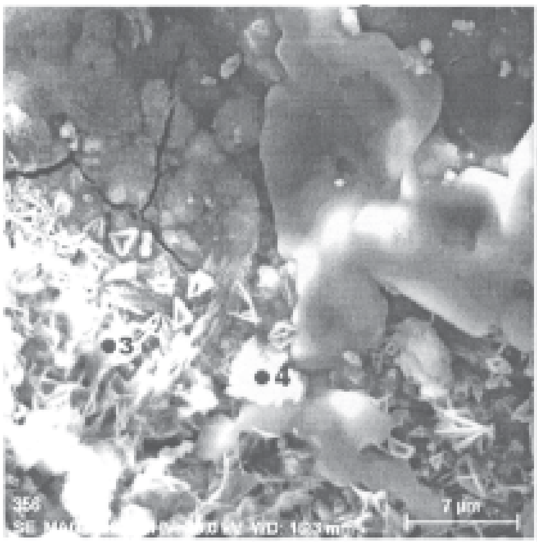
Fig.6. Area II, in detail, from the products crust after maintaining in the seawater with green seaweed



Sample A– 90 days, green seaweed (area III)

Element	AN	series	Net	[wt.%]	rm. wt.%]	orm. at.%]	ror in %
Point 5							
Oxygen	26	K-series	142470	91,0886	87,42103	65,27527	2,3348
Iron	8	K-series	7056	10,7713	10,33759	26,94314	1,6151
Carbon	6	K-series	1614	2,33541	2,241378	7,781592	0,4779
			Sum	104,196	100	100	
				Fe:O=0,41			
Point 6							
Iron	26	K-series	125126	69,1046	72,74055	45,80257	1,779
Oxygen	8	K-series	13067	19,5281	20,54885	45,15876	2,6524
Chlorine	17	K-series	9789	3,89689	4,091736	4,058221	0,1678
Magnesium	12	K-series	723	1,00475	1,057703	1,53019	0,1052
Carbon	6	K-series	688	0,96555	1,016431	2,975612	0,4347
Calcium	20	K-series	1441	0,51176	0,538728	0,472651	0,0467
			Sum	94,9936	100	100	
				Fe:O=1,014			
Point 7							
Iron	26	K-series	134402	73,2739	79,56484	53,82682	1,8838
Oxygen	8	K-series	13689	17,3391	18,82769	44,46013	2,3517
Chlorine	17	K-series	3013	1,48038	1,607472	1,713056	0,0863
			Sum	92,0934	100	100	
				Fe:O=1,21			

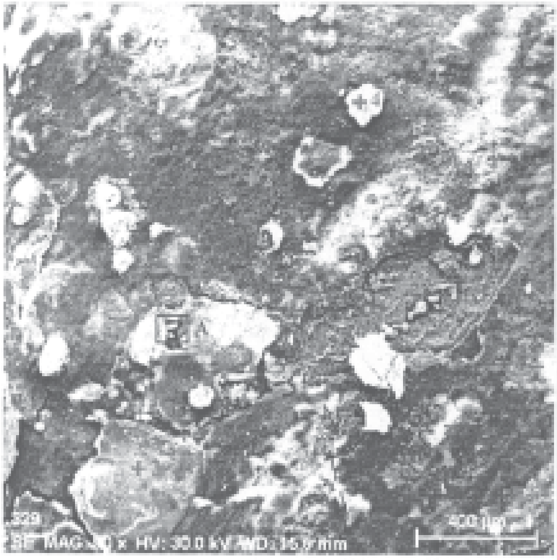
Fig.7. Area III, in detail, from the products crust after maintaining in the seawater with green seaweed



Surface structure for sample B, after 90 days in seawater

Element	AN	series	Net	[wt.%]	orm. wt.%]	orm. at.%]	or in %
Point 1							
Iron	26	K-series	99736	57,71936	61,82568	32,59884	1,493
Oxygen	8	K-series	27514	31,87669	34,14437	63,61289	3,98
Chlorine	17	K-series	11630	3,762291	4,029961	3,388285	0,162
			Sum	93,35824	100	100	
				Fe:O=0,52			
Point 2							
Iron	26	K-series	1E+06	53,66284	60,09241	31,82331	1,39
Oxygen	8	K-series	23880	30,87799	34,57812	63,51802	3,912
Chlorine	17	K-series	9190	2,847343	3,188542	2,669919	0,13
Calcium	20	K-series	2941	0,999884	1,119701	0,82627	0,051
Potassium	19	K-series	3030	0,911845	1,021226	0,772483	0,059
			Sum	89,2992	100	100	
				Fe:O=0,498			
Point 3							
Iron	26	K-series	1E+06	59,82045	65,99005	38,5906	1,545
Oxygen	8	K-series	16090	24,44829	26,96978	55,83817	3,241
Chlorine	17	K-series	9937	3,204635	3,535147	3,25573	0,143
Calcium	20	K-series	4321	1,468156	1,619617	1,319861	0,076
Sulfur	16	K-series	3387	1,14621	1,264424	1,287474	0,075
Potassium	19	K-series	1841	0,562521	0,620978	0,518572	0,048
			Sum	90,6587	100	100	
				Fe:O=0,781			
Point 4							
Iron	26	K-series	70370	47,63176	42,53363	23,25184	1,241
Oxygen	8	K-series	36761	36,06776	32,30727	53,53827	4,384
Sodium	11	K-series	12484	16,7829	14,99966	17,33405	1,2
Chlorine	17	K-series	22815	7,136072	6,374946	4,781455	0,278
Magnesium	12	K-series	4167	3,698657	3,233944	3,603631	0,257
Sulfur	16	K-series	2133	0,676234	0,603863	0,500749	0,056
			Sum	111,5864	100	100	
				Fe:O=0,378			

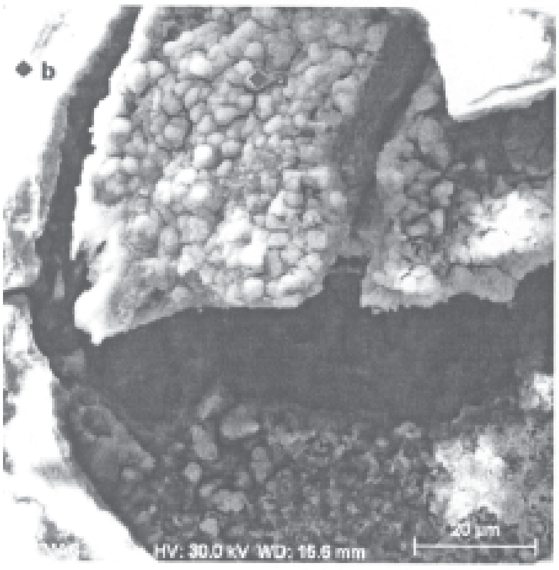
Fig.8. The image and the local chemical composition for the B sample, maintained 90 days in seawater



Surface of the sample B after maintaining 90 days in the seawater with brown seaweed

Point 1							
Element	AN	series	Net	[wt.%]	orm. wt.%]	orm. at.%]	or in %
Iron	26	K-series	132045	75,26587	77,10759	50,3908	1,935
Oxygen	8	K-series	12597	18,67814	19,13416	43,64754	2,558
Calcium	20	K-series	6765	2,503844	2,564978	2,335776	0,107
Carbon	6	K-series	1024	1,164833	1,193273	3,625885	0,313
			Sum:	97,61668	100	100	
				Fe:O=1,15			
Point 2							
Element	AN	series	Net	[wt.%]	orm. wt.%]	orm. at.%]	or in %
Oxygen	8	K-series	10754	71,66235	63,00966	79,32072	10,06
Calcium	20	K-series	138925	32,99426	29,01045	14,57913	0,998
Iron	26	K-series	6487	3,583428	3,150756	1,138313	0,129
Magnesium	12	K-series	4831	2,589255	2,276631	1,886601	0,166
Carbon	6	K-series	3642	1,858788	1,634354	2,740628	0,351
			Sum:	113,7323	100	100	
Point 3							
Element	AN	series	Net	[wt.%]	orm. wt.%]	orm. at.%]	or in %
Oxygen	8	K-series	18687	60,84218	60,93267	78,41203	9,569
Calcium	20	K-series	122639	31,21211	27,95886	14,35984	0,946
Iron	26	K-series	12229	6,313642	5,66386	2,084482	0,157
Magnesium	12	K-series	4349	2,815448	2,52127	2,135797	0,202
Carbon	6	K-series	2579	1,455397	1,303327	2,234141	0,351
Chlorine	17	K-series	4075	0,871304	0,780264	0,453136	0,06
			Sum:	111,6678	100	100	
Point 4							
Element	AN	series	Net	[wt.%]	orm. wt.%]	orm. at.%]	or in %
Oxygen	8	K-series	11962	71,79344	61,6832	78,80354	9,83
Calcium	20	K-series	117925	31,2127	26,8172	13,67697	0,946
Iron	26	K-series	12665	6,673826	5,73399	2,058648	0,206
Magnesium	12	K-series	4094	2,077506	1,784943	1,501186	0,156
Chlorine	17	K-series	7001	1,640244	1,409258	0,812581	0,087
Carbon	6	K-series	2745	1,590601	1,366636	2,325663	0,413
Sulfur	16	K-series	2917	0,699349	0,600864	0,383913	0,056
			Sum:	116,3906	100	100	

Fig.9. The image and the local chemical composition for the B sample, maintained 90 days in seawater with brown seaweed



Surface structure for the sample B after maintaining in seawater with brown seaweed

Point a							
Element	AN	series	Net	[wt.%]	orm. wt.%]	orm. at.%]	ror in %
Oxygen	8	K-series	23299	51,6777	44,18008	66,08882	6,5963
Iron	26	K-series	42012	27,051	23,12632	9,510876	0,7221
Calcium	20	K-series	49770	16,1949	13,84528	8,268009	0,5074
Magnesium	12	K-series	12037	9,75225	8,337363	0,2099	0,6061
Chlorine	17	K-series	18771	5,75258	4,917975	3,328032	0,2335
Carbon	14	K-series	6984	3,11884	2,66635	2,272167	0,1738
Phosphorus	15	K-series	2866	1,12248	0,959623	0,741561	0,0783
Aluminium	13	K-series	1245	0,70697	0,605692	0,581615	0,0746
Sulfur	16	K-series	2128	0,68772	0,587943	0,438829	0,057
			Sum:	116,971	100	100	
Point b							
Element	AN	series	Net	[wt.%]	orm. wt.%]	orm. at.%]	ror in %
Oxygen	8	K-series	19461	81,6008	65,73308	79,60198	10,625
Calcium	20	K-series	1E+05	29,6634	23,89616	11,65174	0,9002
Magnesium	12	K-series	10255	5,81695	4,685811	3,735363	0,3736
Carbon	6	K-series	5146	2,48767	2,003924	3,232564	0,5376
Iron	26	K-series	3181	1,78377	1,436902	0,498507	0,0819
Sulfur	16	K-series	3375	0,75904	0,611439	0,369447	0,0578
Chlorine	17	K-series	3208	0,6977	0,562025	0,30716	0,0636
Silicon	14	K-series	2086	0,63489	0,51143	0,352815	0,0593
			Sum:	124,14	100	100	
Point c							
Element	AN	series	Net	[wt.%]	orm. wt.%]	orm. at.%]	ror in %
Oxygen	8	K-series	14653	70,4285	61,71126	79,47919	9,3951
Calcium	20	K-series	1E+05	27,0016	23,65947	12,16443	0,8226
Iron	26	K-series	19150	10,3175	9,040489	3,335684	0,2973
Sulfur	16	K-series	11157	2,22696	1,951319	1,253038	0,1119
Magnesium	12	K-series	3810	1,62352	1,422567	1,206063	0,1278
Carbon	6	K-series	2037	1,28107	1,122509	1,925766	0,3027
Chlorine	17	K-series	5739	1,24671	1,092403	0,634531	0,0727
			Sum:	114,126	100	100	

Fig.10. Detail, from the sample B after maintaining 90 days in the seawater with brown seaweed (area A from fig.9).

for crystals in point 4 is equal to 0.4, this is probably due to the fact that the crystals are contaminated with NaCl and other compounds (magnesium, sulfur, etc.).

Sample B was maintained for 90 days in seawater brown algae. The formed crust structure in this case more complex.

From this surface we examined two areas, and the results of these analyzes are presented in figures 9 and 10. At a magnification of 100x superficial crust on this sample is very heterogeneous, presenting a series of irregular fragments and a series of cracks and caverns. In some parts of the surface, such as the area in which it is placed point (1), ferrous oxide is predominant (FeO where n(fe):n(O)=1) together with minor amounts of calcium carbonate. Otherwise, on the surface, in the areas (2), (3) and (4) are present the iron oxides. If they were formed on the surface of the sample they are covered with salts (carbonates, sulfates and chlorides), precipitated from the water or adsorbed. In contrast the sample B, immersed in water without the algae, the quantities of iron-containing corrosion products are very small.

The presence of brown seaweed apparently favors the complex crusts formation on the steel surface, containing carbonates, sulfates or chlorides and calcium, magnesium, silicon and iron. This can be seen better in detail presented in figure 10.

Conclusions

In order to overcome a technical drawback, detailed studies must be performed. In this context can be justified the interest to characterize the oxide layer resulted after marine corrosion.

From the present study we con conclude several aspects, as following:

- Speaking of the chemical compounds, in the corroded layer it can be mentioned the presence of the: FeOOH, Fe_3O_4, FeO, Fe_2O_3.
- Oxides and hydrogenated oxides are encountered into the layer as porous films, loose for corrosion with the marine algae, as coral deposits in the case of corrosion with just the seawater.

- In both cases the corrosion was achieved over the entire surface (generalized corrosion), without forming islands with uncorroded material.

- Due to the porosity and loosing of the oxides layer, the corrosion have continuous destructive effect, with the water entering through the pores, thus continuing destruction until the total destruction of the metal.

- At the sample A, corroded in the seawater, can be observed that the oxygen percent varies between 21.58 - 37.48%. In the presence of green algae can see an increase in the mass percentage for the physically and chemically absorbed oxygen by forming chemical combination of the oxides which generates rust, his value varies between 64.5 - 72.18%. Higher level of oxygenation is due to the presence of green algae, generating oxygen through photosynthesis.

- In the sample B case, corroded without algae, the mass percent in the oxides crust, adherent to the part surface is between 24.44 - 36.06%. The maintenance for 90 days in seawater with brown algae, increases the oxygen percent, in the crust, to a value between 68.06 – 71.79%.

- For the corrosion, the brown algae favor the formation of carbonates, sulphates and chlorides of calcium, magnesium, silicon and iron, being more aggressive than green algae.

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