MODIFICĂRI COMPOZIȚIONALE ȘI MICROSTRUCTURALE ÎN ELEMENTE DE BETON SITUATE ÎN ZONA DE COASTĂ A ROMÂNIEI
COMPOSITIONAL AND MICROSTRUCTURAL MODIFCATIONS IN CONCRETE ELEMENTS FROM ROMANIAN COASTLINE

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Concrete corrosion represents a complex process, the mechanisms by which it occurs being particularized depending on the environment where it is exploited. Thus, for a concrete exploited in natural aggressive environments (alpine, marine), the corrosion processes will take place with lower speeds than for a concrete exploited in aggressive industrial environments.

In order to highlight the effects of marine environment on the concrete structure, at high periods of time, the ancient concrete constructions from the Romanian coastline, represented by casemates (built since 1942), in the present paper, these type of structures were visually assessed in situ. The effects of marine corrosion at microstructural level were also analyzed by sampling the concrete specimens, mainly from the concrete/reinforcement interface areas, from the body of casemates located in Tuzla, Costineşti, Olimp, Mangalia, 2 Mai and Vama Veche resorts. For this purpose, X-ray fluorescence (XRF) was used to determine the content of chemical species with corrosive potential from the concrete composition, and scanning electron microscopy analyses (SEM) coupled with energy dispersive X-ray spectroscopy (EDS) to identify the crystalline corrosion products formed at the concrete/reinforcement interface.

The visual assessment of the ancient concrete structures showed a precarious conservation state of these strategic military objectives, with significant historical value. The chemical analyses, performed through XRF on ground and sieved concrete specimens, highlighted the presence of high amounts of Fe_2O_3, extracted by metal corrosion from the reinforcement, as well as high amounts of Cl and alkali, originating from the natural marine environment. The SEM analyses revealed a porous microstructure with crystalline compounds belonging to the hardened cement structure - ettringite, calcium hydroxide and calcium silicates hydrates – and corrosion compounds such as magnetite (Fe_2O_3), akaganeite (β-FeOOH) and lepidocrocite (γ-FeOOH), formed by chemical interactions between the aggressive ions of the marine environment and iron from the reinforcement.

Coroziunea betonului reprezintă un proces complex, mecanismele prin care se desfăşoară fiind particularizate în funcție de mediul în care este exploatat betonul. Astfel, în cazul betonului exploatat în medii agresive naturale (alpin, marin), procesele de coroziune se vor desfăşura cu viteze mai mici decât în cazul betonului exploatat în mediu agresiv industrial.

Pentru a evidenția efectele mediului marin asupra structurii betonului, la perioade mari de timp, vechile construcții de beton din zona de coastă a României, reprezentate de cazemate (construite începând cu anul 1942), în cadrul lucrării prezente, au fost evaluate vizual în situ astfel de structuri. De asemenea, s-au analizat efectele coroziunii marine la nivel microstructural, fiind prelevate probe de beton, cu preponderență din zonele de interfață beton/armătură, din corpul cazematelor situate în stațiunile Tuzla, Costineşti, Olimp, Mangalia, 2 Mai și Vama Veche. S-au utilizat, în acest scop, fluorescența de raze X (XRF), în vederea stabilirii conținutului de specii chimice cu potențial coroziv din compoziția betonului și analize de microscopie electronică de baleiaj (SEM) cuplate cu spectroscopie de raze X cu energie dispersivă (EDS), în vederea identificării produșilor de coroziune cristalini, formați la interfața beton/armătură.

Evaluarea vizuală a vechilor structuri de beton a arătat starea precară de conservare a acestor obiective strategice militare cu valoare istorică semnificativă. Analizele chimice, prin XRF, realizate pe probe de beton măcinate și sitate, au evidențiat prezența în beton a unor proporții semnificative de Fe_2O_3, extras prin coroziune metalică din armătură, dar și proporții semnificative de Cl și alcalii, provenite din mediul natural marin. Analizele SEM au indicat o microstructură poroasă, în care sunt evidentiați compuși cristalini proprii pietrei de ciment - etringit, hidroxid de calciu și hidrosilicați de calciu - și compuși de coroziune de tipul magnetitei (Fe_2O_3), akaganeitului (β-FeOOH) sau lepidocrocitului (γ-FeOOH), formați prin interacții chimice între ionii agresivi ai mediului marin și fierul din armătură.

Keywords: *concrete corrosion, marine environment, SEM, EDS, XRF analyses*

1. Introduction

Most of the concrete constructions located in aggressive environments develop in time distinctly signs of degradation due to a plurality of factors acting on them: the aggressiveness of the environment to which the concrete structure is exposed, the quality of the used concrete, inadequate standards based on conventional measures, inappropriate design due to the lack of information regarding the factors that influence the concrete degradation processes. The degradation of the concrete structures exposed to marine environment appears due to various complex chemical, electro-chemical and physical processes, that determine the modification of structure in time as well as its functionality and aesthetic appearance [1 - 6].

In the coastal area, the marine atmosphere and sea water is rich in aggressive chemical species with corrosive effect on the concrete and metallic reinforcements: CO_2, Cl^-, SO_4^{2-} and Mg^{2+}.

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These chemical species, especially Cl^-, by absorption and diffusion mechanisms of water through the concrete pores and microcracks, reach the surface of the iron reinforcement, determining its depassivation. The corrosion process is fed by the presence of O_2 and H_2O which are both needed for transforming metallic iron into iron oxides (rust). In consequence the exposure of the concrete constructions with a certain permeability degree, for a long time to an aggressive wet environment causes their degradation by corrosion mechanisms which operate simultaneously [7 - 11]. It should also be noted that while for metals the effects of corrosion are evident from the early stages [12], in the case of concrete and reinforced concrete, the destructive effects of the marine environment are often visible at an advanced stage of corrosion.

The damage state of the concrete constructions with historical and cultural value (e.g. the military casemates built since 1942, the Constanta casino built since 1905), situated in the Romanian coastal area requires a significant budget for the rehabilitation works. The lack of involvement of the Romanian authorities in the casemates preservation as well as the absence of a monitoring program regarding its behavior in exploitation and minimum maintenance measures have brought these objectives in different degradation stages [13, 14]. Until now, there are little studies only at a laboratory level regarding the corrosion processes occurring in concrete and reinforcement [15, 16]. The available information regarding the evolution in time of the corrosion processes "in situ" (in the naturally marine environment), the resulted degradation products as well as detailed microstructural information on the state of concrete and reinforcement are insufficient [17 - 19].

The present paper, which includes some relevant scientific results, can contribute to the enrichment of the available information in the field of concrete corrosion in marine environment after long periods of exposure. For this purpose were identified and localized the ancient concrete structures represented by casemates situated along the Romanian coast line. Initially, in order to determine their preservation status, an in situ visual assessment was performed. Afterwards, concrete specimens were sampled from the analyzed casemates structure. On the sampled specimens chemical analyses were performed by using X-ray fluorescence (XRF) to identify the chemical species implied in corrosion processes (Fe_2O_3, MgO, Na_2O, K_2O and Cl^-). In order to identify the corrosion products, formed especially at the concrete/metal reinforcement interface, microstructure analyses using scanning electron microscopy (SEM) coupled with dispersive energy spectroscopy (EDS) were performed.

2. Materials and methods

In order to investigate the corrosion processes that affect the concrete structures was necessary a preliminary identification of the casemates, positioned along the Romanian seaside, for which a GPS station (Leica Viva GS 08 Plus) was used. To highlight the effects produced by the coastal marine environment on the concrete, after long periods of time (over 70 years), the ancient concrete structures were visually assessed in situ. For the chemical and microstructure analyses, concrete specimens were sampled from the casemates body. On the concrete fine fractions x-ray fluorescence (XRF) analyses were performed by using a Rigaku Supermini fluorescence spectrometer equipped with Pd target. For this purpose, fragments form the sampled concrete specimens were dried at T = 100°C for 2 hours, ground and sieved on a 90μm mesh in order to remove the rough sand granules and to obtain a good homogeneity of the material. On the compact samples, extracted from the concrete structure, scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS) analyses were performed, using the Hitachi SU-70 FE-SEM microscope equipped with EDS detector, X -Max N. The concrete specimens were preliminary dried at T = 55ºC for 3 hours (to avoid the ettringite decomposition) and subsequently coated with an AuPd conductive layer.

3. Results and interpretation

Although is difficult to determine the precise number of bunkers and casemates existing on the Romanian seashore and their location, however, some of these structures could be identified and localized, as shown in Table 1.

In-situ researches started from the most southern point of the Romanian seashore, Vama Veche beach, continuing to the north, up to Constanta. Considering that the number of casemates is relatively high, in Figure 1 only a few selected ones are presented.

Generally, the identified and in situ examined casemates are placed on the beach, excepting one in the Vama Veche resort, placed at a relatively long distance from the beach (Fig. 1a). As a result of continuous changing of the shoreline, many casemates are currently in the sea waves (the case of casemates located on the 2 May and Tuzla beaches) or even in the sea water (case of the Costinesti casemates) (Fig. 1c, g – j). The casemates stands are severely affected due to the action of the sea waves and loss of important parts of the land due to marine erosion process. The visual examination revealed the precarious preservation state of all casemates, the concrete being strongly damaged and the reinforcement being exposed to the corrosion. The

Table 1

Localisation of the casemates positioned along the Romanian seashore/*Localizarea cazematelor situate de-a lungul litoralului românesc*

Locality	GPS point
Vama Veche	N/E: 43.759636,28.573478
2 Mai	N/E: 43.783345,28.580758
Mangalia	N/E: 43.831466,28.590087 N/E: 43.837332,28.590287
Jupiter/Cap Aurora	N/E: 43.850796,28.608149 N/E: 43.850995,28.608095
Olimp	N/E: 43.895531,28.613591
Costinești	N/E: 43.958858,28.643707 N/E: 43.959368,28.644683 N/E: 43.960216,28.645941
Tuzla	N/E: 43.985634,28.666684 N/E: 43.994462,28.664189 N/E: 43.996889,28.663565 N/E: 43.997238,28.663444 N/E: 44.002847,28.662378 N/E: 44.004267,28.662459 N/E: 44.006449,28.663629 N/E: 44.007342,28.664346 N/E: 44.008089,28.664348 N/E: 44.009719,28.663721 N/E: 44.012816,28.661829
Eforie Sud	N/E: 44.027603,28.656537 N/E: 44.043271,28.647417
Eforie Nord	N/E: 44.054517,28.642134 N/E: 44.085845,28.653139
Constanța	N/E: 44.164496,28.658076 N/E: 44.170212,28.663427 N/E: 44.172028,28.665556 N/E: 44.172117,28.665586 N/E: 44.177505,28.658245 N/E: 44.196881,28.655297

most vulnerable parts of the casemates to the aggressiveness of marine environment are the firing holes (Fig.1d, f and k). These are areas where the metallic elements are directly exposed to marine environment (Fig. 1l), and by their corrosion the concrete layer deterioration is accelerated.

Figures 2 - 5 present the results of the XRF analyses performed on the obtained fine fraction from the concrete specimens. For the present work the oxides whose ions have corrosive action on concrete were considered (MgO, alkali), also the ones that could result by the corrosion process (Fe_2O_3) and the Cl^- ion. The maximum allowed values of oxides and chlorides in cements were considered as reference, these limits being imposed by the standards ASTM C150-07 and SR EN 197-1 / 2011 [20, 21]. In case of alkali, the values, expressed in percentages represent the equivalent alkalis (Na_2O + 0.658K_2O) [20, 22].

In the fine fraction of concrete sampled from Vama Veche casemate, the content of Fe_2O_3 has values below the limits imposed by the standard (Fig. 2a). This result can be explained by the fact that the corrosion of the metal reinforcement either did not begun or it is at an early stage considering its positioning at a longer distance from the beach. A similar situation can be observed for MgO, which highlights the absence of magnesium aggressiveness [3]. Due to the high content of saline ions in the atmosphere, the recorded concentrations of alkali and chlorine exceed the allowed limit values (Fig. 2b).

Fig. 1- Casemates situated on the Romanian seashore: a and b – casemate in Vama Veche; c and d – casemate in 2 Mai; e and f – casemate in Olimp; g and h – casemates in Costinesti; i – l casemates in Tuzla beach / *Cazemate amplasate pe litoralul romanesc: a și b - cazemata de pe plaja Vama Veche; c și d - cazemata de pe plaja 2 Mai; e și f - cazemata de pe plaja Olimp; g și h - cazemate de la Costinești; i – l - cazemate de pe plaja Tuzla.*

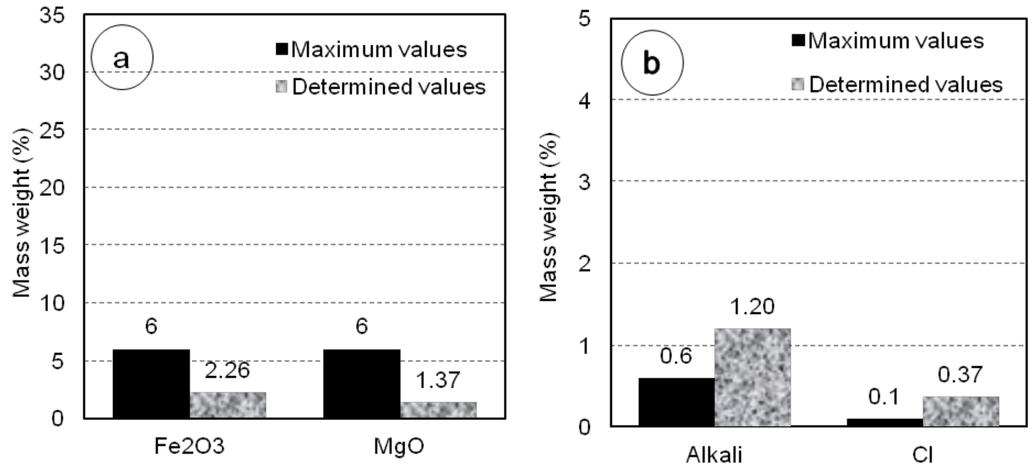

Fig. 2 - The content of compounds/elements involved in corrosive phenomena of the concrete specimen sempled from Vama Veche casemate: a) Fe_2O_3 and MgO oxides; b) alkali and Cl / *Conținutul de compuși/elemente implicate în fenomene corozive din proba de beton prelevată de la o cazemată din Vama Veche: a) oxizii Fe_2O_3 și MgO; b) alcalii și Cl.*

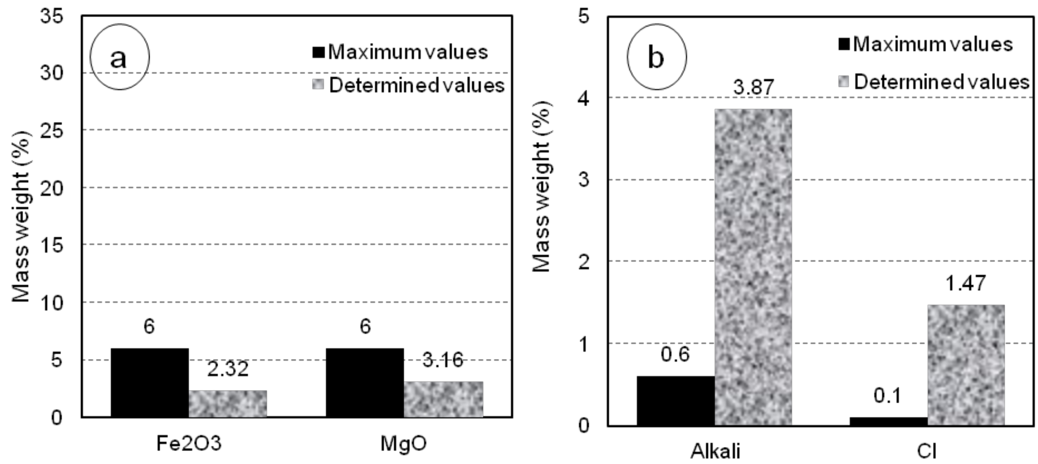

Fig. 3 - The content of compounds/elements involved in corrosive phenomena in the concrete specimen sempled from 2 Mai casemate: a) Fe_2O_3 and MgO oxides; b) alkali and Cl / *Conținutul de compuși/elemente implicate în fenomene corozive din proba prelevată de la o cazemată din 2 Mai: a) oxizii Fe_2O_3 și MgO; b) alcalii și Cl*

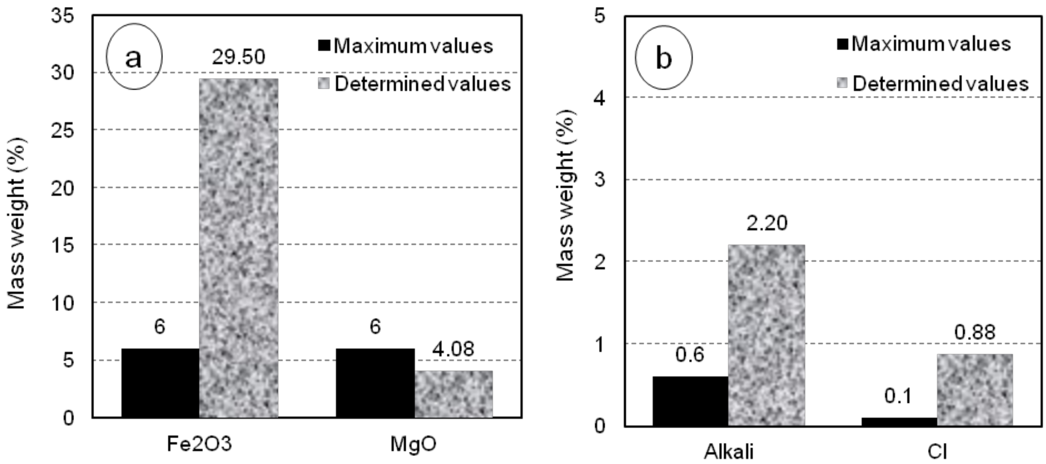

Fig. 4 - The content of compounds/elements involved in corrosive phenomena in the concrete specimen sempled from Mangalia casemate: a) Fe_2O_3 and MgO oxides; b) alkali and Cl / *Conținutul de compuși/elemente implicate în fenomene corozive din proba prelevată de la o cazemată din Mangalia: a) Fe_2O_3 și MgO; b) alcalii și Cl.*

A similar situation regarding the content of Fe_2O_3 and MgO oxides was observed for the fine fraction of concrete sampled from the body of 2 Mai casemate (Fig. 3a). In this case the corrosion process of steel reinforcement appeared predominantly in the contact area with the sea water and does not affect the entire concrete structure. However, its position on the seashore determines a great exceeding of the limit values established for alkali and chlorine (Fig. 3b).

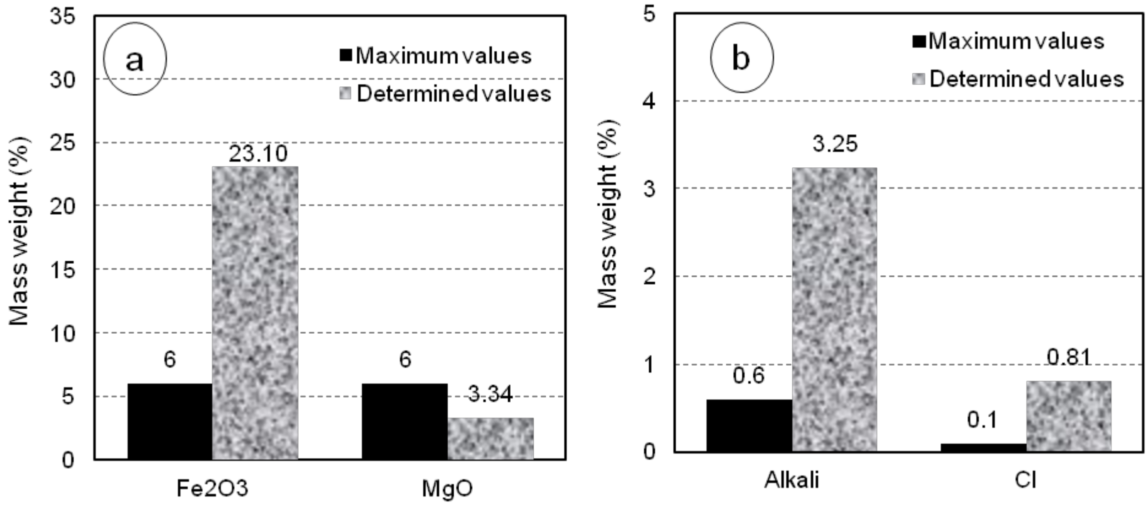

Fig.5 - The content of compounds/elements involved in corrosive phenomena fin the concrete specimen sempled from Tuzla casemate: a) Fe_2O_3 and MgO oxides; b) alkali and Cl / *Conținutul de compuși/elemente implicate în fenomene corozive din proba prelevată de la o cazemată din Tuzla: a) - Fe_2O_3 și MgO; b - alcalii și Cl*

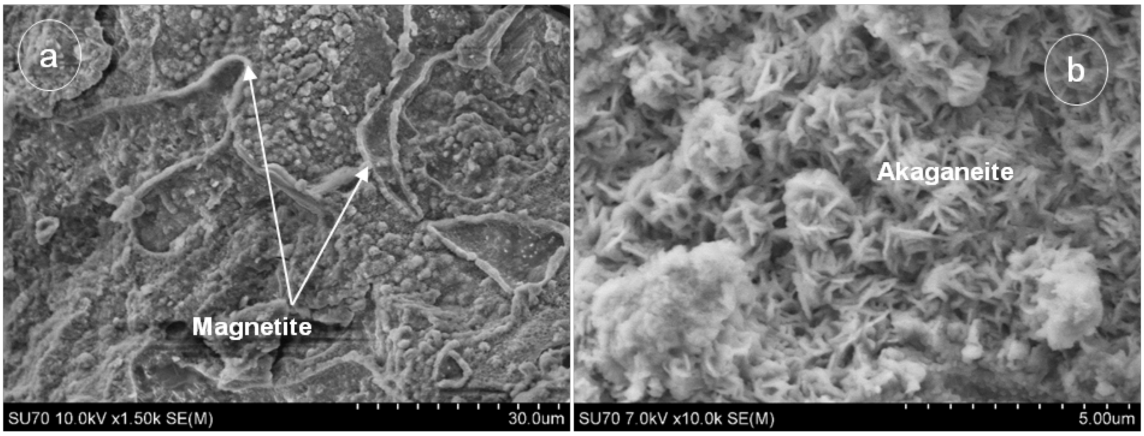

Fig.6 - SEM images performed on the concrete specimen sampled from the body of 2 Mai casemate, presented at different magnitudes: a-1,5K and b-10K / *Imagini SEM realizate pe probă de beton prelevată din cazemata de la 2 Mai, prezentate la măriri diferite: a-1,5K și b-10K.*

For the specimens proceeded from the body of the casemates situated in Mangalia and Tuzla (Fig. 4 and 5) the fluorescence analyses results are different comparing with those presented above.

Thus, in the fine fraction of concrete proceeded from Mangalia casemate, the concentration of Fe_2O_3 is very high – 30%, a value five times bigger than the maximum allowed limit in cement (Fig.4a). For the specimen proceeded from Tuzla casemate the Fe_2O_3 content is 23%, four times bigger than the maximum allowed limit, (Fig.5a). These results could be explained by the diffusion in the concrete matrix of supplementary Fe quantities from metallic reinforcement as a result of their excessive corrosion. In the case of MgO, the determined values did not exceed the maximum allowed limit.

For alkali (Na_2O and K_2O) and Cl content, the determined values were also above the allowed limit specified in the cement quality standard (Fig. 4b and 5b). Taking into account the position of the casemates from where concrete specimens were extracted (see Fig. 1i, j), it can be specified that these higher values appear due to the saline ions intrusion, from the marine environment, through the concrete matrix. The presence of alkaline ions modifies the chemical balance of the intergranular concrete solution by the diffusion of Ca^{2+} ions to the concrete surface and the gradual solubilisation of calcium silicate hydrates which are responsible for the mechanical strength and durability of concrete.

The scanning electron microscopy (SEM) was performed on selective concrete specimens which had a damaged appearance, with visible corrosion marks. SEM analyses were coupled with EDS in order to identify the chemical elements into some observed crystalline formations. The SEM images presented in Figure 6 were obtained on a concrete specimen sampled from the body of the 2 May casemate.

Taking also into account other works [19] the crystalline formations evidenced in Figure 6a, were attributed to magnetite (Fe_2O_3). This compound forms elliptic cordons around the dendritic formations, attributed to the akaganeite

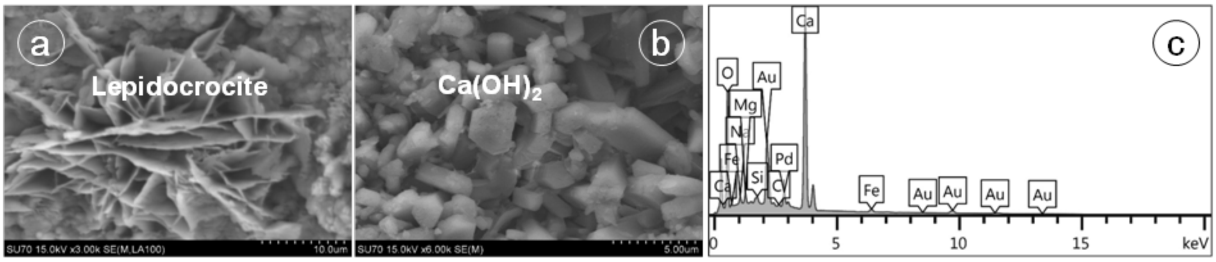

Fig.7 -SEM images performed on a concrete specimen sampled from the body of Mangalia casemate and its EDS spectrum / *Imagini SEM realizate pe probă de beton prelevată din cazemata de la Mangalia și spectrul EDS al acesteia.*

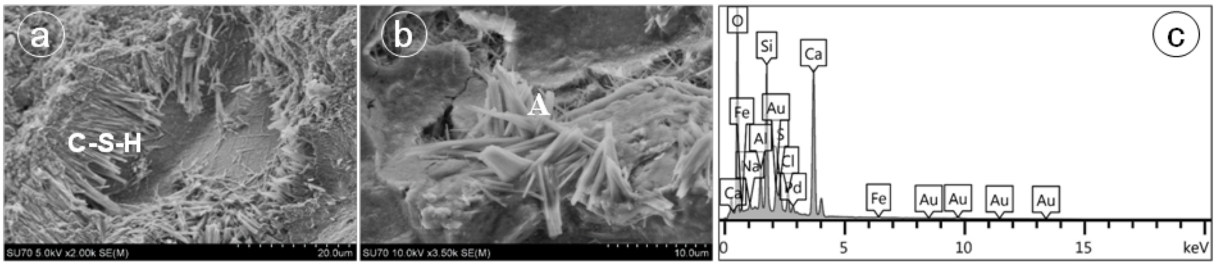

Fig.8 - SEM images performed on a concrete specimen sampled from the body of Olimp casemate presented at different magnitudes: a - 2k; b - 3,5K and its EDS spectrum (c) / *Imagini SEM realizate pe probă de beton prelevată din cazemata de la Olimp la diferite măriri: a - 2k; b - 3,5K și spectrul EDS al acesteia (c).*

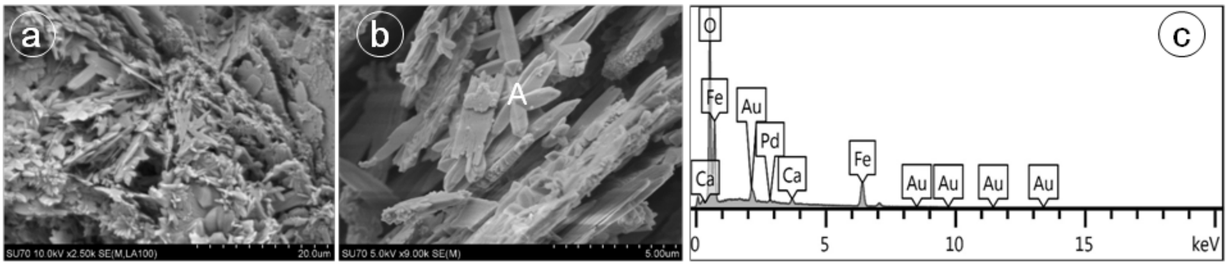

Fig.9 - SEM images performed on a concrete specimen sampled from the body of Olimp casemate (a and b) and the EDS spectrum of the A marked area (c) / *Imagini SEM realizate pe probă de beton din cazemata de la Olimp (a și b) și spectrul EDS al zonei notat cu A din poziția b a figurii (c).*

crystals (β - Fe(O,OH)) [23], highlighted in the extended image in Figure 6b. The akaganeite is a corrosion compound which is present at the concrete/metallic reinforcement interface [19, 24]. The SEM images presented in Figure 7 correspond to the microstructure of the concrete specimen sampled from the casemate in Mangalia.

The analyzed concrete specimen was sampled from an area severely affected by corrosion. The microstructure is characterized by a porous and irregularly surface, in whose concavities "floral" crystalline formations were developed. By similarity with microstructures presented in other researches [19, 24, 25] these floral formations were attributed to the lepidocrocite crystals – (γ-FeOOH) (Fig.7a). The lepidocrocite is a corrosion product, being a polymorphic form of the iron hydroxide, whose development mechanism and kinetics are currently uncertain. The image presented in Figure 7b shows a region rich in calcium hydroxide, crystallized as interpenetrated hexagonal prisms, or as hexagonal plaques, often overlapped. $Ca(OH)_2$ was also confirmed by the EDS analysis, whose spectrum is presented in Figure 7c.

The SEM analyses performed on the concrete specimens collected from casemate body located on Olimp beach evidenced different microstructures compared to those presented above (Fig.8).

Thus in the SEM image presented in Figure 8a, needle shape crystals developed unidirectional or intertwined can be observed. For the A marked area (Fig. 8b), the EDS spectrum was made and it is presented in Figure 8c. The spectrum shows the presence of Ca and Si as predominant elements, what allows the assignment of these acicular formations to calcium silicates hydrates, possibly formed as crystalline compounds after a very long period of time. It is not excluded the presence of ettringite crystals as the EDS spectrum also confirms the presence of Al and S. These types of compounds have been mentioned also in other scientific papers [4, 16]. Another analyzed area, belonging to the same sample, allowed the highlighting of iron oxide, crystallized in star shape (Figs. 9a and b), developed as a result of reinforcement's corrosion and confirmed by the EDS spectrum in Figure 9c.

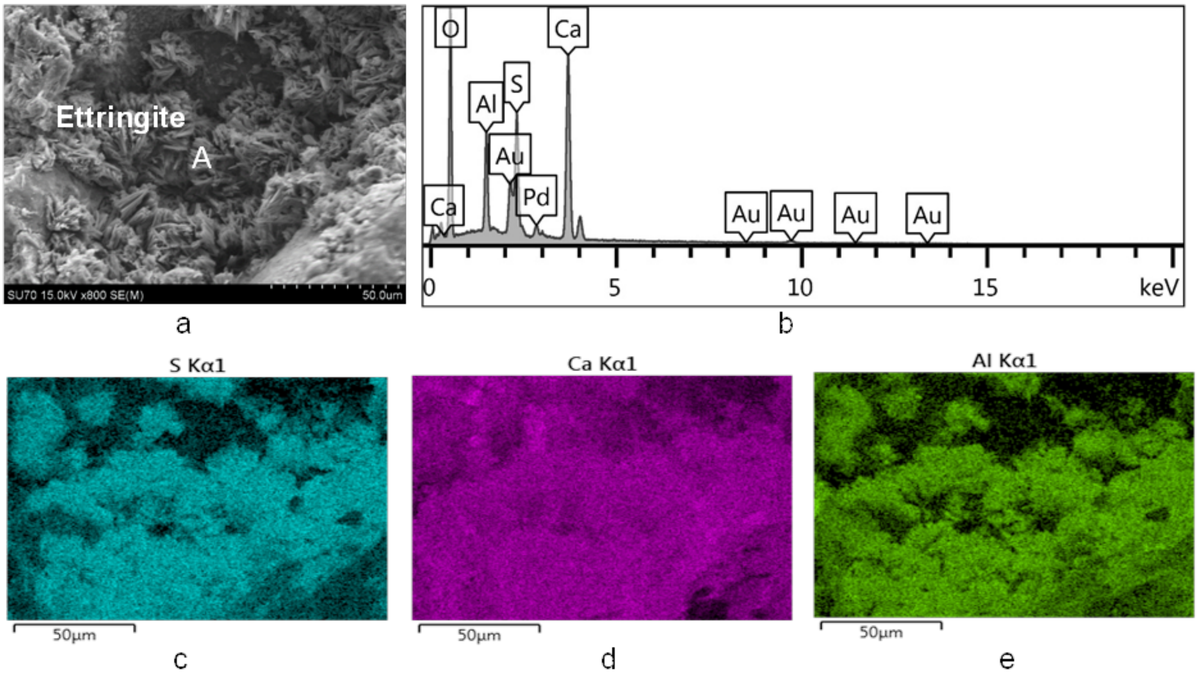

Fig.10 - SEM image (a) coupled with EDS (b) and the elemental maps (c, d and e) performed on a concrete specimen sempled from the body of Olimp casemate / *Imagine SEM (a) cuplată cu analize EDS (b) și hărțile elementale (c, d și e) realizate pe o probă de beton prelevată din cazemata de la Olimp.*

The microstructure presented in Figure 10a suggests another crystalline compound, namely ettringite ($C_3A\cdot 3C\bar{S}\cdot H_{32}$). This compound, crystallized in binder matrices as short needle shapes wisps, has an important role in the concrete strength, as observed in other investigations [26, 27]. Its presence was confirmed by both EDS spectra of the area marked with A (Fig. 10b) and elemental maps (c, d and e positions), which evidenced the predominance of Ca, Al and S elements.

4.Conclusions

In situ visual assessment of casemates located in the south of the Romanian seashore, highlighted the precarious preservation state of these military strategic structures, as a consequence of the lack of interest of the authorities involved in their management and conservation. In other countries such constructions are included in the tourist circuits.

The results of XRF analyses showed the existence in the fine fraction from the concrete specimens of high Cl^- (0.8-1.4%) and alkalis (up to 3.8%) proportions, proceeded both from sea water and marine environment. Due to the corrosion of both reinforcement and metalic elements from the firing holes, in the samples resulted from casemates bodies of Mangalia, Olimp and Tuzla, were determined high proportions of Fe_2O_3, (up to 30%). The MgO did not exceeded the allowed limit of 6% in any of the analyzed specimen, which confirms that this compound was not involved in the concrete corrosion process.

SEM analyses performed on concrete specimens displayed irregular surfaces and porous microstructures with crystalline compounds belonging to the hardened cement structure and others formed by chemical interactions between aggressive ions of marine environment and concrete. By correlation with other papers, the SEM analyses revealed the microstructures characteristic of the following compounds involved in corrosion process: magnetite (Fe_2O_3), akaganeite (β-FeOOH) and lepidocrocite (γ-FeOOH), predominantly formed at the concrete/reinforcement interface, by chemical interactions between aggressive ions, the iron from reinforcement and the concrete hydrates (mainly $Ca(OH)_2$). Crystalline compounds specific to the cement stone (ettringite, calcium hydroxide and calcium silicates hydrates) have been also identified and confirmed by EDS analyses.

The paper is valuable because presents the preservation state of some historical constructions, little or unstudied until now, namely the casemates built during the Second World War. In order to apply the most effective conservation methods it is important to know the effects of the aggressive marine environment on concrete.

Acknowledgements
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