تقيم الاثار السلبية لمياه البحار المالحة على المبانى الخرسانية بموانى البحر المتوسط وطرق الصيانة والمعالجة

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تعتبر وحدات التسليح المعدنية هى الاكثر معاناه نتيجة وجود االاملاح ذات الاثر السلبى على الخواص المختلفة للمبنى الخرسانى. وهذا التاثير له بالغ الاثر على عملية ترميم وصيانة الموانى. تتناول الدراسة تاثير مياه البحر المتوسط على كل من المبانى الخرسانية للميناء وكذلك الاجزاء المعدنية المتعلقة بالعملية الانشائية للمبانى الخرسانية للموانى. وتضمنت الدراسة التأثيرات السلبية على الخواص الفيزيائية والميكانيكة وكذلك الخواص الكيميائية لمبانى الميناء وتم الاستعانة بتقنية طيف المعاوقة الكهربية وكذلك نظم الاستقطاب الكهربى لدراسة هذا الاثر وتم تاكيد النتائج باستخدام االميكروسكوب الاليكترونى. وتضمنت الدراسة سبل تحليل نتائج هذه التاثيرات وما يتبع ذلك من توصيات لصيانة المبانى وكذلك نموذج للمبانى بعد عملية المعالجة والصيانة حسب متطلبات نتائج الدراسة. وقد اشارت الدراسة الى الاثر البالغ على منشأت المبانى الخاصة بالموانى وانخفاض اعمار هذه الموانى نتيجة هذه الاثار السلبية مما يساعد الأنظمة على تحديد الازمنه الخاصة بعمليات الصيانة والمتابعه لاعمال الترميمات والمعالجات الدورية للموانى. . وقد اشارت النتائج فى هذه الجزء الى امكانية الاستبدال الجزئىى للمكونات الخرسانية للموانى ليقل بذلك تاثير مياه البحر على هذه المبانى.

The negative effects of Mediterranean see on the concrete buildings and methods of maintenance and treatment

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Reinforcing steel are the most suffering as a result of the salts negative impact on the various attributes of the concrete building. This impact has greatly affected the process of restoration and maintenance of ports. Study addresses the impact of the Mediterranean waters to all my concrete buildings of the port as well as Reinforcing parts for the process of construction of concrete buildings for harbors. The study included negative impacts on the physical, mechanical and chemical properties of the port buildings were using impedance spectroscopy technology and electric polarization to study this effect was confirmed using the results SEM. The study included analysis of the results of these influences and the consequent recommendations for building maintenance as well as a model of the buildings after the treatment process and maintenance requirements according to the results of the study. The study pointed to the impact of plants on private buildings in ports and lower age of these ports result of these negative effects of the regulations help to identify times for operations and maintenance follow-up work and repairs to patrol ports treatments. . The results indicated in this segment to the possibility of partial replacement of the concrete components of the ports for less so the impact of sea water to these buildings.

1. Introduction:

The corrosion of concrete reinforcement is a very expensive problem, amounting in billions of dollars of damage worldwide. Corrosion repair costs due to the use of deicing salts have been estimated at $325 million to $1 billion per year in the United States [1, 2]. When steel is embedded in concrete a passive film develops and covers the steel surface. Cement paste is alkaline (pH between 12 and 14) and enables the formation of this thin passive film coating on steel that protects the steel from corroding. After passing through the hardened concrete the chloride ions present in deicing salts destroy this protective layer.
Several solutions to this problem have been proposed and tested, though to date no ideal solution has been found. Some of these methods involve increasing the concrete cover over the rebar, reducing water/cement ratios, using denser concrete, using latex or polymer modified concrete overlays, adding waterproofing membrane with asphalt overlay, coating the rebar with epoxy or zinc, protecting the rebar cathodically, and using corrosion inhibiting admixtures. Initially, the use of epoxy coatings was

thought to be the "ideal" solution for the prevention of rebars corrosion, but the long-term effectiveness of this method is being questioned [3]. Ideally, a concrete corrosion prevention system would protect the reinforcing steel from the initiation of corrosion for the duration of the structure's service life. Some of the many compounds and chemicals that have been tried as corrosion inhibiting admixtures [4, 5, and 6] produced favorable results as an inhibitor. However, some of these chemicals had adverse effects on some of the concrete properties, and some were also too expensive. Presently there is few corrosion inhibiting admixtures in use that do not have detrimental effects on other aspects of the concrete properties. Furthermore, these existing inhibitors only delay the onset of corrosion in laboratory tests [7, 8].

2. Experimental

Materials used in this investigation were Egyptian granulated slag produced from Iron and Steel Company (Local granulated slag cement), Both Ordinary Portland cement and Sulphate resistance cement (SRC) produce from Egypt Cement Company. The chemical analysis of the starting material is shown in Table (1).

Table 1
Chemical composition of starting material.

Chemical composition(%)	OPC	SRC	Local slag
CaO	64.80	63.50	35.43
SiO_2	21.40	21.70	34.13
Al_2O_3	6.36	3.97	11.83
Fe_2O_3	3.35	4.95	0.85
MgO	1.85	2.10	2.21
SO_3	1.77	1.94	0.69
K_2O	0.54	0.11	0.32
Na_2O	0.28	0.13	1.25
TiO_2	0.02	0.01	0.51
L.O.I	0.81	0.94	1.47
BaO			11.02

2.1 Determination of physico-mechanical properties.

A weight amount of cement was placed on a smooth, non absorbent surface, and a crater was formed in the center. The required amount of mixing water was poured into crater by aid of trowel. The

paste cement was placed in the mould until homogeneous specimen was obtained after the top layer was compacted; the surface of the paste was made smooth and even with the top surface of the mould by the aid of thin edged trowel. Immediately after molding specimens were cured in a humidifier (100%R. H.) at room temperature for 24 hours. At the end the moist curing period. During the effect of aggressive medium, the cube were demolded and curied under water about 30 days, then the cube is immersed in sea water up to one year.

2.2 Determination of electrochemical behaviors.

The reinforcing steel used in the presented investigation was mild steel bars, 6mm in diameter. The rods were mechanically polished and degreased with acetone then coated with epoxy and wax at all point without certain area (1 cm^2). The coating by cement pastes was applied to steel reinforcement in moldier have certain volume and high. Then the cement cylinder is immersed in sea water up to 3 menthes.

3. Results and discussion

The influence of seawater was studied on the granulated slag cement pastes, as well as SRC and OPC pastes up 270 days. The results in this part mainly divided into two parts, the first part concerned with the variation in the cement structure during to the determination of chemical, physical and mechanical properties. While the second part mainly related to the corrosion behavior or reinforcing steel which presented in different type of cement. The designs of the mix of granulated slag cement and plain cement are given in Table (2).

Table 2: Mix design of plain and slag blended cement

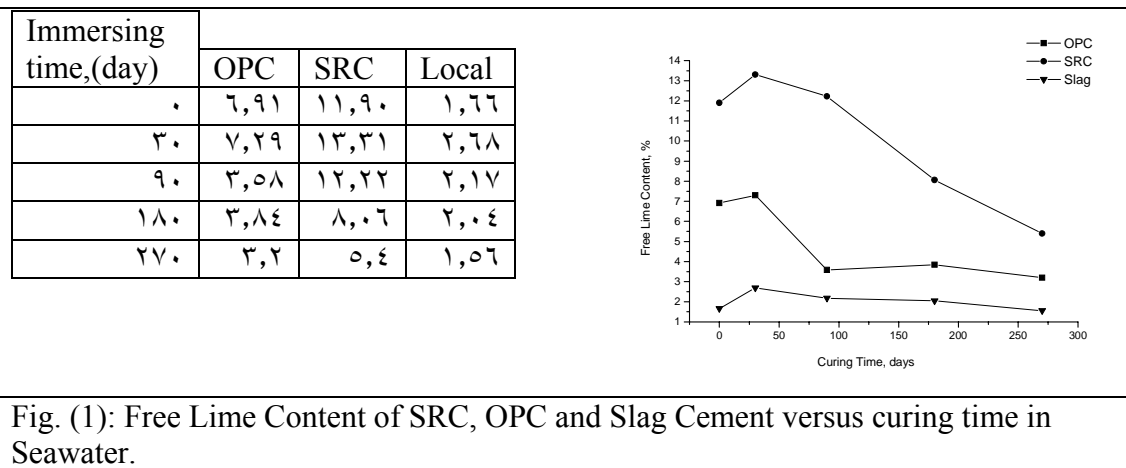| S1	Slag cement (20% OPC+ 80%GGBS local)
OPC	100% OPC
SRC	100% SRC

3.1.Chemical properties.
3.1.1Determination of Free lime

The results in Fig.(1) indicates that the free lime content in plain and blended cement types increase with time up 30 days. This is attributed to continuous hydration of the main cement phases such as C$_3$S
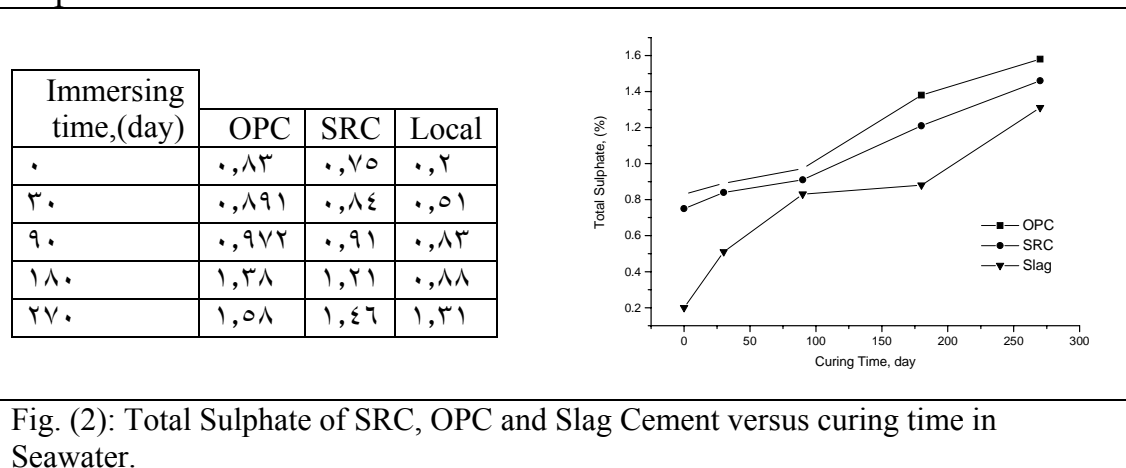
and β-C$_2$S producing free lime. The free lime decreases with time up to the end of hydration times.

The low value of free lime in case of blended slag cement is attributed to the pozzolanic reaction of slag which consumes a part of free lime (Ca(OH)$_2$) librated during the hydration of Portland cement phases to form of calcium aluminates hydrate and Calcium silicate hydrate (CSH). Furthermore, mix designing content low amount of OPC in Mix design. The reduction in OPC shapely decreases with time compared to other types of cement.

Immersing time,(day)	OPC	SRC	Local
٠	٦,٩١	١١,٩٠	١,٦٦
٣٠	٧,٢٩	١٣,٣١	٢,٦٨
٩٠	٣,٥٨	١٢,٢٢	٢,١٧
١٨٠	٣,٨٤	٨,٠٦	٢,٠٤
٢٧٠	٣,٢	٥,٤	١,٥٦

Fig. (1): Free Lime Content of SRC, OPC and Slag Cement versus curing time in Seawater.

3.1.2 Determination of Total sulphate

Total sulphate contents of the different cement pastes after had being immersed in sea water for various ages shown in Fig (2). The total sulphate increases with curing time increasing for all hardened cement pastes. This is due to the migration of sulphate ions from aggressive medium to cement pastes which reacts with aluminates and ferrite or Ca(OH)$_2$ forming hydrated calcium sulpho aluminates as ettringite and/ or monosulphate hydrate. The total sulphate decreases in presence of blended slag cement due to lower content of C$_3$A which can react with sulphate ions.

Immersing time,(day)	OPC	SRC	Local
٠	٠,٨٣	٠,٧٥	٠,٢
٣٠	٠,٨٩١	٠,٨٤	٠,٥١
٩٠	٠,٩٧٢	٠,٩١	٠,٨٣
١٨٠	١,٣٨	١,٢١	٠,٨٨
٢٧٠	١,٥٨	١,٤٦	١,٣١

Fig. (2): Total Sulphate of SRC, OPC and Slag Cement versus curing time in Seawater.

3.2.Physical properties.
3.2.1. Determination of bulk density.

The values of bulk density of the hardened blended slag cement and plain cement pastes are given in Fig (3) at several of curing times.
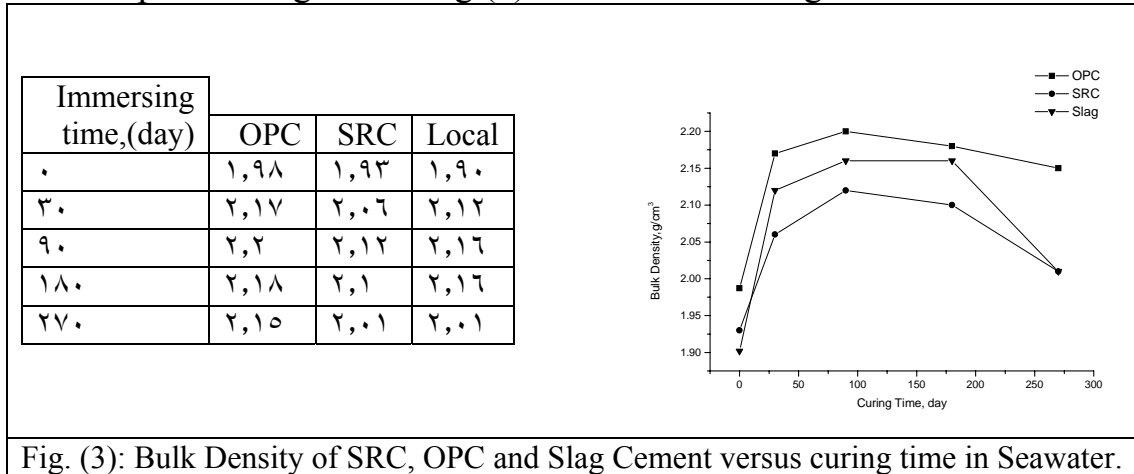
Immersing time,(day)	OPC	SRC	Local
٠	١,٩٨	١,٩٣	١,٩٠
٣٠	٢,١٧	٢,٠٦	٢,١٢
٩٠	٢,٢	٢,١٢	٢,١٦
١٨٠	٢,١٨	٢,١	٢,١٦
٢٧٠	٢,١٥	٢,٠١	٢,٠١

Fig. (3): Bulk Density of SRC, OPC and Slag Cement versus curing time in Seawater.

The results of Fig.(3) indicates that, the bulk density of the plain cement increases up to 3- months, then decreases gradually with time up to 270 days. The increase in bulk density is mainly due to increasing in the amount products which were formed and precipitated in the pores originally filled with water leading to an increase in the bulk density up to 3 months. After that, the hydration products react with the salt solution sodium sulphate to form gypsum and ettringite.

In case of SRC the decreases in bulk density were limited compared with OPC due to the variation in amount of C_3A in each cement types. The increase in content of C3A leads to a decrease in bulk density, which is the effect in the formation of calcium sulpho aluminate, calcium sulpho aluminate precipitated in pore system and had given a lower value in bulk density.

In blended slag cement gets the lower variation in bulk density due to the formation of ettringite according to the amount of C_3A.

3.2.2.Determination of Total porosity

Fig.(4) represent the variation in total porosity in both blended and plain cement. The results of total porosity for the hardened specimen are typically correlated with the results of bulk density in the above section.
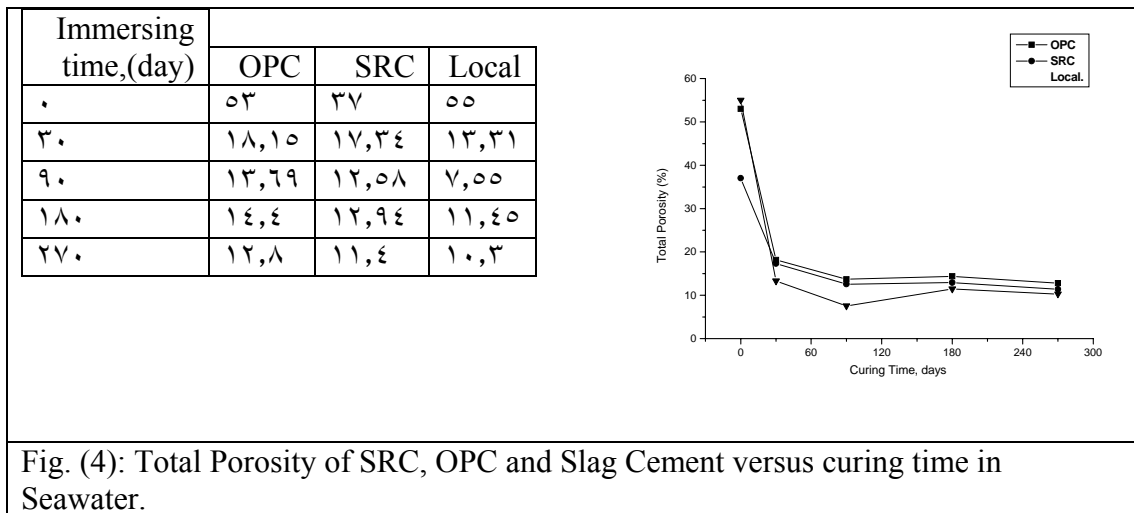
Immersing time,(day)	OPC	SRC	Local
٠	٥٣	٣٧	٥٥
٣٠	١٨٫١٥	١٧٫٣٤	١٣٫٣١
٩٠	١٣٫٦٩	١٢٫٥٨	٧٫٥٥
١٨٠	١٤٫٤	١٢٫٩٤	١١٫٤٥
٢٧٠	١٢٫٨	١١٫٤	١٠٫٣

Fig. (4): Total Porosity of SRC, OPC and Slag Cement versus curing time in Seawater.

3.3.Mechanical properties.
3.3.1.Determination of strength

Change in compressive strength values of the different cement pastes immersed in seawater and the results are graphically represented in Fig. (5).
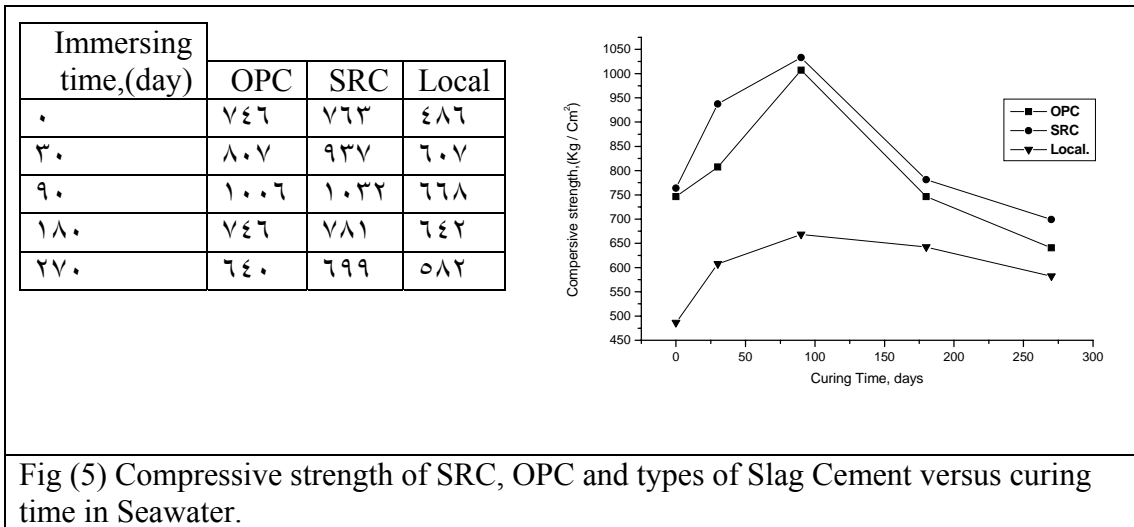
The results can be summarized as following:

The gain in the strength for the samples having OPC mainly attributed to the hydration of aluminate, ferroaluminate and C_3A in addition to calcium silicate phase. The hydration product fills the pores and at the same time having binder characteristic .

The kinetic of hydration and the nature of hydration product of SRC are similar to OPC, the only difference in C_3A content at SRC is lower than OPC while the C_4AF is higher in SRC. Also the content of C_3S and C_2S for SRC are higher than that of OPC. Based on the above, the strength growth of hardened specimens.

The change in compressive strength value of cements increase up to 3- months of immersed in sea water then decreases linearly up to 270 days. Increasing of compressive strength mainly due to the continuous hydration of unhydrated cement components to form more hydration products in addition to production of $Ca(OH)_2$, the second reaction related to the Reaction between sulfate ions and hydrated cement components to form gypsum and calcium monosulfoaluminate hydrate.

In case of slag cement,(S1), increasing in compressive strength occurred attributed to continuous hydration of unhydrated cement (20% OPC) in addition to production of $Ca(OH)_2$, After 3-months, the decrees in compressive strength may be attributed to the reaction between sulfate ions with hydrated cement components to form gypsum and calcium monosulfoaluminate hydrate and this reaction continuous as shown in

OPC. In addition, effects of sulfur species, such as S, SO_2, S_2O_3, etc., derived from slag. In case of SRC, the compressive strength increases up to 3 months, then the compressive strength decrease by different rate.

Immersing time,(day)	OPC	SRC	Local
٠	٧٤٦	٧٦٣	٤٨٦
٣٠	٨٠٧	٩٣٧	٦٠٧
٩٠	١٠٠٦	١٠٣٢	٦٦٨
١٨٠	٧٤٦	٧٨١	٦٤٢
٢٧٠	٦٤٠	٦٩٩	٥٨٢

Fig (5) Compressive strength of SRC, OPC and types of Slag Cement versus curing time in Seawater.

3.4.Electrochemical properties of reinforcing steel.

The electrochemical impedance spectroscopy (EIS) have been studied the microstructure of reinforcing steel embedded in cement pastes. Bode diagrams of reinforcing steels are shown in Fig from (6-9). These Figures represent the relation between the frequency against both of variation in Impedance and phase angle.

At high frequency, the bode diagrams reported the electrochemical parameters which includes R_H and C_H. The resistance (R_H) values recorded in other types of cement at early days due to the activation of slag in high alkaline medium NaOH. Generally, (R_H) increase in all types of cements with time due to the formation physical protection of cement phases,

The resistance at high frequency follow the order

OPC<SRC<Local slag

The (R_H) values with both OPC and SRC record low resistance value and this is due to the porosity of cement, which produce during the movement of $Ca(OH)_2$ and the formation of holes. While in presence of blended slag cement, the (R_H) values record high value than other types of cement due to the reduction of porosity during the hydration of slag cement and cutting of the conductive path between the bulk solution and steel surface. The Portlandite $Ca(OH)_2$ not extracted in presence of slag because it is consuming in the hydration of slag cement and producing of C-S-H.

The Second parameter at high frequency is the capacitance of the double layer in pores (C_H). Generally, the (C_H) decrease with time due to

the reduction of the surface area, which contact directly with bulk solution. The (C_H) values get high value at early days of hydration due to exist of free water in sample, which consider as a carrier of ions.

At 90 days the capacitance at high frequency (C_H) follows the order.

Local slag >OPC > SRC

At low frequency, an electric resistance in series with (R-C) network can describe the spectra. The series resistance represents the solution resistance (R_s), the solution resistance increasing with time due to the formation of protected layers (passive layer and cement phases). The solution resistance at the end of determination followed the order

OPC < SRC < Local slag

The solution resistance in presence of SRC and OPC get values lower than other type of cement due to the degree of permeability in OPC and SRC cements, which decrease in presence of slag cement. The solution resistances with Reference slag cement decreases sharply in presence of Chloride ions due to the penetration of Chloride ions. The solution resistance decreases in presence of mobile ions and the blended slag cement can decrease the mobile ions by adsorption of free cation and anion.

The polarization resistance (R_P) increases in all types of cement up to 28 days then the polarization resistance decrease with time, the increase in resistance is due to the growth of passive layer on surface of steel, which produced in alkaline pH during the formation of Portlandite. The decrease in resistance is due to the penetration of chloride ion and the chloride attacks on the passive surface.
. The polarization resistance at 90 days followed the order

OPC < Local slag < SRC.

The double layer capacitance of reinforcing steel imbedded in sea water (C_{dl}) decreases with time due the formations of passive layer and the physical protection by the cement layers.
The double layer capacitance followed the order.

Local slag < OPC < SRC.

Local slag gets a high values due to presence of active sulphide in internal solution., while SRC cement record very low values due to its chemical composition and low amount of C_3A.
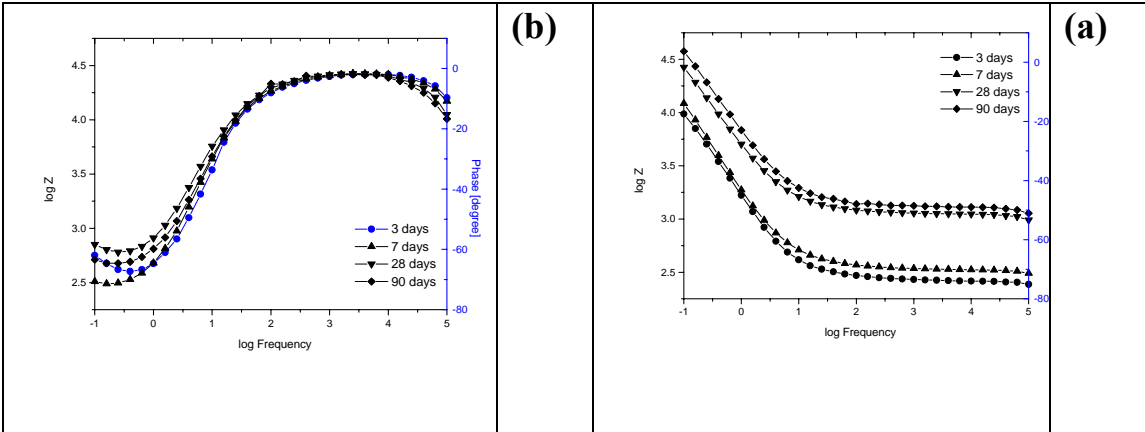
Fig. 6. Bode plot of reinforced steel for the OPC cement pastes at different immersion times in seawater.

    a-   The variation of logZ against log Frequency.

    b-The variation of Phase (degree) against log Frequency.
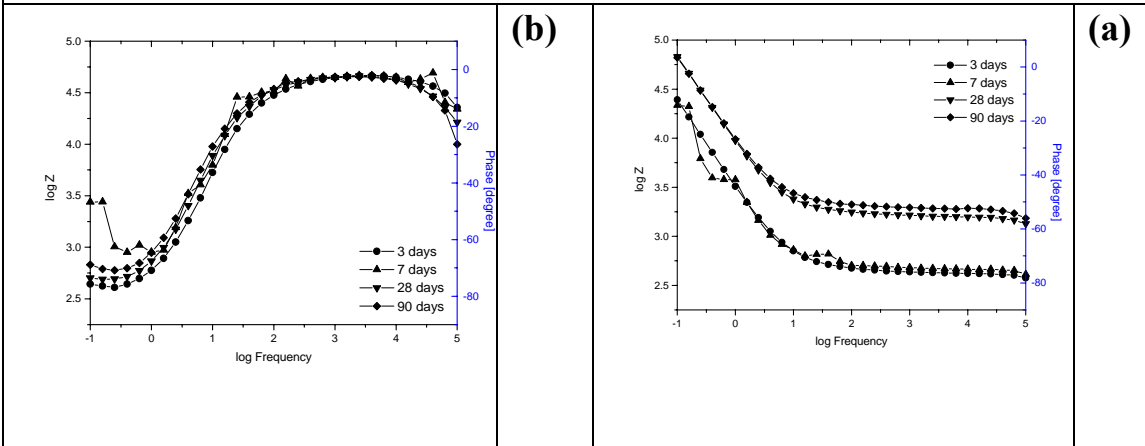

Fig. 7. Bode plot of reinforced steel for the SRC cement pastes at different immersion times in seawater.

    a-The variation of logZ against log Frequency.

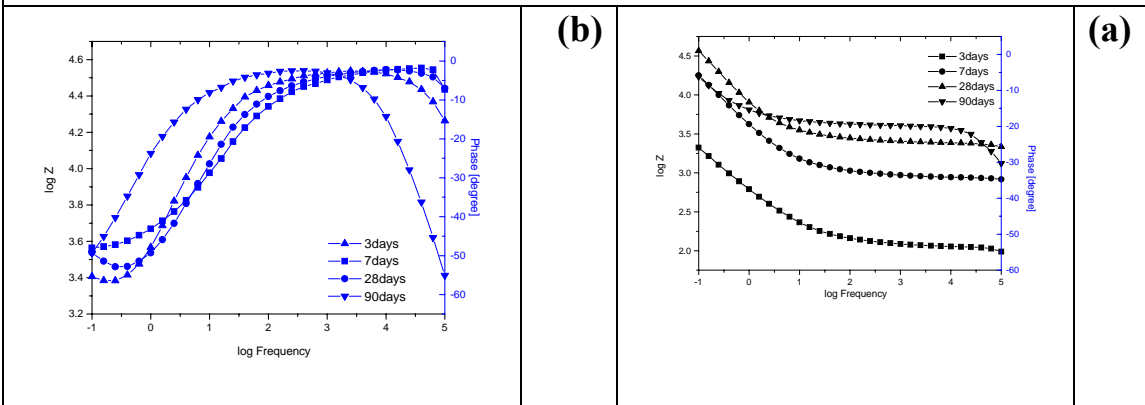   b-The variation of Phase(degree) against log Frequency.

Fig. 8. Bode plot of reinforced steel for the Slag Cement pastes at different immersion times in seawater.

    a-   The variation of logZ against log Frequency.

    b-   The variation of Phase (degree) against log Frequency.

3.5. SEM determination

Fig (9)represent the SEM micrographs of cement pastes immersed in sea water after 9 -months.

Figure 9-a) represented the variation in cement microstructure which produces the formation of microcrakes also the effect of aggressive medium are presented in the formation of ettrengite.

Figure 9-b) represented the variation in cement microstructure which produces the formation of pores and low amount of free lime also the effect of aggressive medium are presented in the formation of ettrengite and gypsum.

Figure 9-C) represented the variation in slag cement microstructure which represented the formation of dense CSH and low amount of free lime also the effect of aggressive medium are presented in the formation of microcrakes.
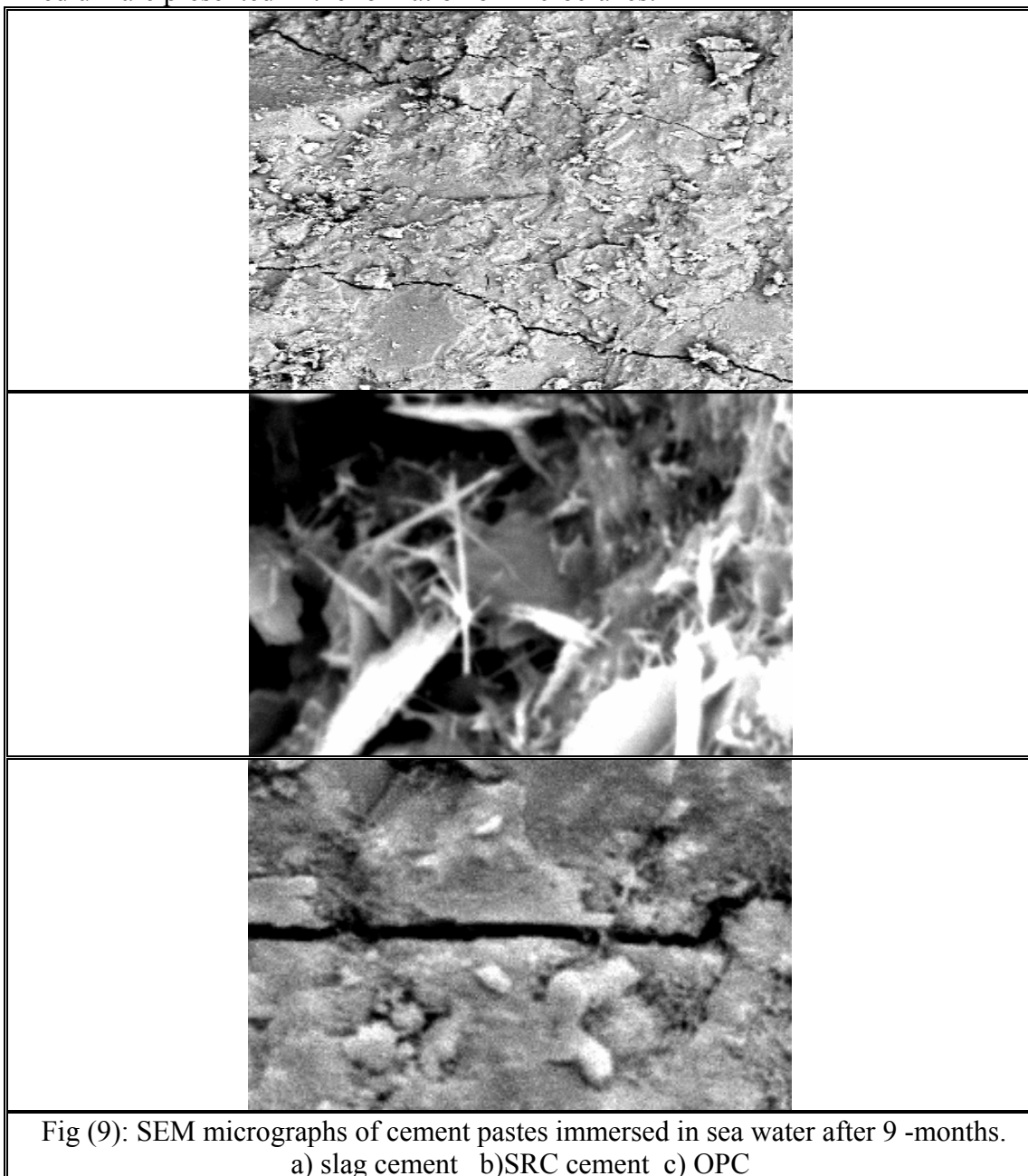

Fig (9): SEM micrographs of cement pastes immersed in sea water after 9 -months.
a) slag cement   b)SRC cement c) OPC

4. Comments

1- Maintenance and treatment must be measured according to the electrochemical methods.
2- Blended cement must be used in maintenance and treatment.
3- OPC not used in the building of ports
4- The reinforcing steel in ports suffer from the aggressive ions
5- Slag cement used in presence of highly aggressive medium

5. Reference

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