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Researches Regarding Marine Environment Corrosion on Coastal Structures

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Abstract

The impact of the marine environment on the coastal structures was reported since the middle of the XIX century. In order to test the aggressiveness potential of the Black Sea water on the coastal constructions, between the years 2009-2010, a seawater sampling program was carried out in the Navodari - Vama Veche sector of the Romanian coastline. Therefore, seawater samples were collected from 15 locations situated along the Black Sea coastline in order to determine their action on coastal constructions. For all the samples the pH, electrical conductivity, salinity were determined in-situ and presented normal values. The aggressiveness of the seawater samples was determined in laboratory, through a parallel analysis of the SO_4^{2-} and Mg^{2+} ions concentrations in seawater compositions. The results showed the presence of $MgSO_4$ in the analyzed samples, which affected the mortars used in determinations even after 3 months of storage. It was also observed that the only materials resistant to the water aggressiveness were the mortars with 20% dolomitic limestone. Additionally, the investigation determined that the seawater aggressiveness affects not only the concrete structure but also has a great impact on the metallic parts found in these structures by highly corroding them, as seen for the Mamaia Bridge, build in 1935, the hydrotechnics nodes and other coastal structures.

Keywords: Coastal constructions, seawater aggressiveness, corrosion potential.

Introduction

The concretes are the most important and widely used materials in construction works due to the good mechanical properties that they develop. Generally, these materials were exploited after reinforcement with steel bars, making them more resistant to flexural and compression stresses. The sustainability of the concretes for different environmental conditions, used in exploitation, is the key requirement for the concrete composition development. The degradation causes of concrete were in relation with the chemical reactions that occur in cement stone, with alkali-aggregate interactions and/or water permeability (Buenfeld and Newman, 1986).

The aggressive environments are generally the external environments, which may exercise their aggressive potential on concrete structures, in different ways (Teoreanu *et al.*, 1982): through chemical processes – carbonate aggressiveness, SO_2 and H_2S aggressiveness, alkaline, sulphate, magnesium, biochemical aggressiveness etc.; through physical processes – dissolving and leaching, erosion, abrasion, freeze-thaw etc. The actions of seawater on the concrete represent the most complex form of physico-chemical corrosion, due to its complex composition and also, due to the wave movements. The seawater can affect the concrete structure through different types of aggressiveness: sulphate, magnesium, carbonation (in areas with biological activity), alkaline, by dissolution and leaching, erosion or abrasion.

The corrosion concrete problem due to seawater actions was discussed by J. Smeaton and L.J. Vicat since 1840. Other papers, with similar topic, were published later, in 1917, by R.J Wig and L.R. Ferguson (Tibbetts, 1968; Kuhail and Shihada, 2001). In our country, the researches regarding the Black Sea water aggressiveness have started since the early 60s of last century.

The corrosion concrete process due to seawater actions begins with diffusion, transport and ion exchange. The corrosive ions (Cl^-, SO_4^{2-}, CO_3^{2-}, Mg^{2+}), once inside the intergranular solution of concrete, react with $Ca(OH)_2$ or with calcium aluminate hydrates and calcium silicates hydrates and the compounds without binding properties which result are $Mg(OH)_2$, $CaS0_4•2H_20$, $Al(OH)_3$, $Ca_2Al(OH)_6(Cl, OH)•2H_2O$. At the surface of steel bars, the presence of Cl^- ions in a certain concentration, can determine the corrosion processes (Mather, 1964; Costa and Appleton, 1999; Montemor, 2003; Sosa *et al.,* 2011). In the case of the concrete totally immersed in the seawater, the corrosion processes are delayed due to the formation of an aragonite and brucite layer at surface, phenomenon that is called the passivation of the concrete (Mather, 1964; Costa and Appleton, 1999; Montemor, 2003; Buenfeld and Newman, 1984; Wegen, 1993; Georgescu and Puri, 2004).

In this paper, data regarding the corrosive potential of the Black Sea on coastal constructions were presented. Water samples, from the section between Navodari and Vama Veche, along the Romanian coastline, were analyzed in order to identify the aggressiveness types which are being exercised over coastal structures and also the mechanisms by which the seawater affects the coastal structure durability were presented.

Materials and Methods

In order to determine the corrosive potential of the Black Sea on concrete structures and coastal constructions, near the marine constructions and the confluence of the Danube-Black Sea (Agigea sluice), the seawater was sampled. The sampling points cover the coastline section between Navodari and Vama Veche:

P1. the Black Sea - Navodari close to the sluice;
P2. the Black Sea – Navodari;
P3. the Navodari sluice - Midia-Navodari Channel (at the exit to the Black Sea);
P4. the Black Sea - Mamaia Casino Pontoon;
P5. the Black Sea – Mamaia (in right of the protection dam);
P6. the Channel to the Agigea sluice exit (100 m);
P7. the Agigea sluice - the Danube-Black Sea Channel (at the sea confluence)
P8. the Black Sea – Constanta (in right of Tabacarie Lake);
P9. the Black Sea - North Eforie beach;
P10. the Black Sea - Costinesti beach;
P11. the Black Sea – Neptun (at the tetrapod dock);
P12. the Black Sea - Saturn-Venus;
P13. the Sulphur Spring - on the beach between Saturn and Venus;
P14. the Black Sea - near the tourist port Mangalia dam;
P15. the Black Sea - Vama Veche beach.

The water samples were subjected to the following physico-chemical analysis:

- in-situ determination: “m” alkalinity, “p” alkalinity, pH, electrical conductivity and salinity;
- ex-situ determination, represented by chemical analysis performed in order to identify the aggressiveness type which may affect the concretes, the reinforced concretes and the metallic reinforcements. The determined parameters were the concentration of ion types of bicarbonates, carbonate, calcium, magnesium, sulphate, chlorine and hydroxyl.

In order to identify the water aggressiveness against the metallic reinforcements two methods were used: the *Langelier method* implies the determination of the saturation index, Is, for a water pH between 7.00 and 10.00 and the *Hoover method* uses the monogram Hoover pattern. The relation used for Is determination was:

$$Is = pH - pHs \quad (1)$$

where pHs is the saturated pH and its determined by using the Langelier diagram.

The durability at sulphate water aggressiveness was determined in laboratory, according to the standard method (STAS 2633-76), using two different sulphate solutions with 3,000 and 6,000 mg SO_4^{2-}/dm^3 concentration.

Results

The results of the in-situ and ex-situ analysis were shown in Table 1. The laboratory tests demonstrated that the water shows sulphate, magnesium and chlorine aggression type. Based on this data, in Figure 1, the concentration of magnesium and sulphate ions and also the salinity were graphical represented. In the case of SO_4^{2-} and Mg^{2+} ions, it can be seen an almost parallel evolution of the concentrations; the SO_4^{2-} concentration does not exceed the value of 1,500 mg/dm^3, and the value of 750 mg/dm^3 in the case of Mg^{2+} concentration. This evolution can be explained with the presence of the SO_4^{2-} anion bounded as $MgSO_4$ rather than as $CaSO_4$ or Na_2SO_4 (Mather, 1964; Moncea and Georgescu, 2013).

The concentration values of SO_4^{2-} and Mg^{2+} *ions* enface to the water a corrosive character against the concrete due to the complex effects of the chemical reactions that occur between these ions and cement hydrates. The aggressive attacks of ions lead to the increase of the concrete permeability and susceptibility to the future corrosion processes of the same type of ions; ultimately, it may result in the concrete destruction (Moncea and Georgescu, 2012; Poteraş, 1993).

According to several researchers (Mather, 1964; Biczok, 1965; Moncea and Georgescu, 2012), the magnesium sulfate attack against the cement stone is developed by interactions with different types of hydrates: calcium aluminate, calcium silicate and calcium hydroxide (eq. 2-4). According to the eq. 2, the magnesium sulphate reacts with tricalcium aluminate hydrate and results ettringite and magnesium hydroxide.

$$2\,(3CaO\cdot Al_2O_3\cdot 12H_2O) + 3(MgSO_4\cdot 7H_2O) \rightarrow 3CaO\cdot Al_2O_3\cdot 3CaSO_4\cdot 31H_2O + 2Al(OH)_3 + 3Mg(OH)_2 + 8H_2O \quad (2)$$

Table 1. Chemical analyses of the seawater sampled of the 15 points situated along the Romanian coast of the Black Sea

Determination / Sampled place	Aspect	pH	Electrical Conductivity	M alkalinity at $100cm^3$ of water	P alkalinity at $100cm^3$ of water	Calcium (Ca^{2+})	Magnesium (Mg^{2+})	Sulfates (SO_4^{2-})	Hydroxyl (HO^-)	Carbonates (CO_3^{2-})	Chlorine (Cl^-)	Salinity
Measuring units	-	pH	µS/cm	cm^3 HCl 0.1N		mg/dm³						g/dm³
Black Sea at Năvodari sluice	Clear	8.29	22,400	3.6	0.6	160.32	486.40	1,057.55	0	36	8,165	13.2
Năvodari sluice, Midia – Năvodari Channel at the exit of the sea	Clear	8.81	22,300	3.4	0.4	200.40	437.76	1,018.87	0	24	8,094	13.3
Black Sea, Năvodari	Clear	8.25	26,800	4.0	0.4	320.64	462.08	1,202.40	0	24	10,011	16.3
Black Sea, beside of Tăbăcărie lake - Mamaia	Clear	8.39	20,200	3.6	1.0	240.48	243.20	849.33	0	60	7,597	12.1
Black Sea at pontoon bridge at Mamaia Casino	Clear	8.54	22,000	7.6	1.8	10.02	437.76	1,065.78	0	108	8,165	13.2
Black Sea, on the right of the protection dam	Clear	8.23	26,200	3.6	0.6	240.48	656.64	1,207.34	0	36	9,798	15.8
Agigea sluice, the Danube-Black Sea Channel, at the sea confluence	Clear	8.25	19,530	3.6	0.6	160.32	312.00	840.28	0	36	7,526	11.7
Channel to the Agigea sluice exit (100 m)	Clear	8.53	13,480	3.8	1.2	80.16	48.64	592.56	0	72	4,899	7.8
Black Sea, North Eforie beach	Clear	8.07	28,300	3.6	0.2	1,202.40	72.96	1,389.22	0	12	11,076	17.3
Black Sea, Costinesti beach	Clear	8.03	27,400	3.8	0.2	240.48	705.28	1,260.83	0	12	10,579	16.8
Black Sea, Neptun, to the tetrapod dock	Clear	8.06	27,800	4.0	0.4	400.00	364.80	1,218.86	0	24	11,005	17.1
Black Sea, Saturn-Venus	Clear	8.20	25,800	3.8	0.8	320.64	559.36	1,209.81	0	48	9,372	15.8
Sulphur Spring, on the beach between Saturn and Venus	Clear	7.80	1,630	6.4	0.4	40.08	121.60	40.32	0	24	355	0.6
Black Sea, near to the tourist port Mangalia dam	Clear	8.20	26,100	4.2	0.4	280.56	411.01	1,240.26	0	24	9,514	16.0
Black Sea, Vama Veche beach	Clear	8.06	27,600	3.8	0.4	360.72	535.04	1,334.90	0	24	9,230	16.9

According to the Equation 3, the magnesium sulphate reacts with calcium hydroxide resulting calcium sulphate, which in turn reacts with calcium aluminate hydrate, forming new quantities of ettringite (see eq. 4).

$$Ca(OH)_2 + MgSO_4{\cdot}7H_2O \rightarrow CaSO_4{\cdot}2H_2O + Mg(OH)_2 + 5H_2O \quad (3)$$

$$3CaO{\cdot}Al_2O_3{\cdot}12H_2O + 3(CaSO_4{\cdot}2H_2O) + 13H_2O \rightarrow 3CaO{\cdot}Al_2O_3{\cdot}3CaSO_4{\cdot}31H_2O \quad (4)$$

The magnesium sulphate could also react with calcium silicate hydrates forming calcium sulphate, magnesium hydroxide and silica gel (see eq. 5); the new quantities of calcium sulphate resulted are available to react with calcium aluminate hydrates forming ettringite. Ultimately, the magnesium hydroxide formed in eq. 2 and eq. 5, react with the silica gel resulting the magnesium silicate hydrate, $4MgO{\cdot}SiO_2{\cdot}8.5H_2O$, a compound without binding properties, identified by other researchers in the composition of damaged concrete due to the corrosion processes (Cole and Hueber, 1957).

$$3CaO{\cdot}SiO_2{\cdot}nH_2O+MgSO_4{\cdot}7H_2O \rightarrow CaSO_4{\cdot}2H_2O+Mg(OH)_2 + SiO_2{\cdot}nH_2O \quad (5)$$

In order to explain the significance of sulphate compound, the stability of four different types of cement to sulphate water aggressiveness was determined in laboratory conditions (Table 2) (STAS 2633-76). It can be shown that the exposure of CEM II at sulphate attack leads to the destruction of the samples; the $MgSO_4$ salt, in both high and lower concentration (6,000 and 3,000 mg SO_4^{2-}/dm^3), acts destructively even after 3 months and also after 6 months of curring. A certain strength reduction of the ordinary Portland cement at the magnesium sulphate solution was also reported (Prasad *et al.*, 2006). The researchers noted that using ground granulated blast furnace slag, fly ash, silica fume or other additions can improve the cement resistance in aggressive medium. Unlike the magnesium sulphate solution, a better stability to the corrosive action of SO_4^{2-} ion was encountered for the concretes made of cement with dolomitic limestone additions which, in most cases, had the stability coefficient ≥0.9.

The salinity of the seawater sampled along the Black Sea coastline recorded normal values for Romanian coastline (7.8–17.3 g/L). The minimum value of 0.6 g/L (Figure 1) was recorded for P13, because the water was sampled from Sulphur Spring. The lower values were also recorded for the water

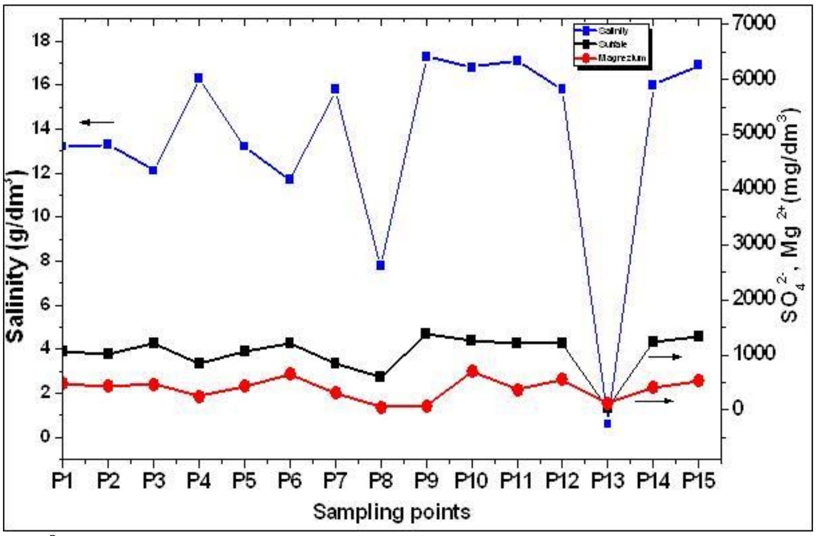

Figure 1. The SO_4^{2-}, Mg^{2+} concentrations and the salinity along the Romanian coast of the Black Sea.

Table 2. The stability of some concretes to the sulphate water aggressiveness

Cement type	Curring time (month)	Sol. conc. ($mgSO_4^{2-}/dm^3$)	Stability coefficient, K_n*					
			$CuSO_4$	$Na_2SO_4+MgSO_4$	$MgSO_4$	K_2SO_4	Na_2SO_4	$(NH_4)SO_4$
CEM II	3	6,000	0.71	0.63	-	0.30	-	0.19
	6	3,000	-	-	-	-	-	-
CEM II**	3	6,000	1.23	1.33	1.10	1.14	0.88	0.42
	6	3,000	1.45	1.21	0.96	0.98	0.91	0.45
Hz 35	3	6,000	1.10	1.13	1.06	0.84	0.81	0.49
	6	3,000	1.09	0.91	0.94	0.88	0.90	0.34
Hz 40	3	6,000	1.10	0.95	1.03	0.78	0.72	0.25
	6	3,000	1.14	0.92	0.73	0.80	0.88	0.19

*The sulphate solution is considered non-aggressive against the concrete made of cements having the stability coefficient ≥0.9.
** Ordinary Portland cement with maximum addition of 20% dolomitic limestone.

sampled at Navodari sluice (P3) and Agigea sluice (P6) due to the high freshwater contribution brought by the Danube in these points.

The chlorine corrosion is one of the main corrosion processes, which affects the hardened structure and the performances of concretes and also the metal reinforcements for long periods of time. The concrete layer gives to the metallic reinforcement physical and chemical protection against the penetration of Cl^- ions which once inside of the concrete, at steel bar/concrete interface, leads to the depassivation of steel and the increase of the corrosion risk (Teoreanu, 1982; Neville, 1995). So, the resistance of the metallic reinforcement at chlorine action depends mainly by the permeability and the thickness of the concrete layer. Based on the chemical analysis results of the water sampled along Black Sea coastline (Table 1) and by using the two calculation methods of saturation indexes (Langelier and Hoover), it was determined that the water shows aggression towards the metal reinforcements and therefore on the concrete. The results obtained by applying Langelier and Hoover methods were not presented in this paper because of the extensive calculation and representation modes.

Visual Appearances of the Concrete, Degraded under the Aggressive Actions of the Black Sea. Recommendations Regarding the Protection against Corrosive Effects of the Seawater

The effect of the seawater impact towards the concrete structures and on steel reinforcement was visually analyzed in different areas of the Black Sea coastline. Therefore in the northern part of the Romanian coastline (Navodari), at the Hydrotechnics Node, the aggressiveness of the marine environment (both water and air) can be observed by the high level of degradation encountered in the structure, which was produced by corrosion (Figure 2). Further down the coastline, at Mamaia, an affected reinforced concrete bridge was observed, as it can be seen in Figure 3. The bridge presented serious corrosion of its metallic parts, both the ones exposed to seawater and the ones found in the bridge's structure, showing the seawater aggressiveness. A similar behavior was encountered in the south of the Black Sea coastline (2 Mai, Neptun and Costinesti), as it is presented in Figure 4.

The coastal structure protection to the seawater aggressiveness assumes two aspects: the preventive protection by choosing the cement type resistant to aggressive environment and by adoption of adequate constructive measures before the execution of construction, followed by a protection after the construction was finalized or exploited for a period of time. The election of the cement type, resistant to an aggressive environment where the concrete structure will be exploited, is done after a study on the different environment aggression types. In general, the degradation of the concrete begins with the diffusion and transport processes. So, it can be considered the use of cement with pozzolanic additives, with the ability to bind in hydrates the calcium hydroxide, formed by hydration of the calcium silicates. It was demonstrated the better resistance of the cements with additives (dolomitic limestone or slag) at the double corrosive attack of the magnesium sulphate, the main compound of the seawater (see Table 2).

The steel bars, used as reinforcements of the concretes, are coated with epoxy resins in order to isolate and create a barrier against the corrosive action of Cl^- ions. The following must be considered at the beginning of a construction subjected to the marine corrosion: the smallest water/cement ratio, the additives with filler effect (i.e. silica fume) and the use of aggregates with low reactivity.

The exploited concrete structures periodically require maintenance and/or rehabilitation operations which may be done by applying a polymer concrete layer at the surface of the structure. The polymer concrete consists of a mixture of Portland cement, polymers and fine aggregates, but also coarser aggregates can be used in the case of reconstruction. The outside surfaces of concrete reinforced elements may be covered with waterproof membranes (i.e. rubberized asphalt), in order to protect the concrete and the reinforcements from corrosion processes.

Conclusions

In order to establish the corrosive character of the seawater on the concrete structures and the coastal constructions, the seawater was sampled near the constructions located along the Black Sea coast, between Navodari and Vama Veche and at the confluence of the Danube-Black Sea (Agigea sluice). The water samples were subjected to *in-situ* determinations (pH, electrical conductivity, salinity) and to laboratory analysis, in order to determine their chemical compositions. The results showed that the seawater present aggressiveness on the concretes and on the coastal structures. The parallel evolutions of the SO_4^{2-} and Mg^{2+} ions concentrations suggest the presence of $MgSO_4$ in seawater compositions rather than other sulphates. The salinity recorded values between 7.8–17.3 g/L, the lowest of them are the result of the high freshwater contribution brought by the Danube in those sampling points (Navodari sluice and Agigea sluice).

The stability of the mortars without additions (CEM II) at the sulphate water aggressiveness (the $MgSO_4$ and Na_2SO_4 solutions with 3,000 and 6,000 mg SO_4^{2-}/dm^3 were used) was seriously affected even after 3 months of storage. It was determined that the stability coefficient, K, for these samples was less than 0.9. The mortars with 20% dolomitic limestone (CEM II**) resisted better in the corrosive environments (K being higher than 0.9).

The results regarding the water aggressiveness

Figure 2. The corrosion appearances of the metallic elements caused by marine environment, the Hydrotechnics Node Năvodari.

Figure 3. Reinforced concrete bridge, carried out in 1935, Mamaia. Different affected sections by the seawater corrosion were present.

a b c

Figure 4. The marine environment corrosion on the reinforced concrete of the dams located along the beaches on 2 Mai (a), Neptun (b), Costineşti (c).

on the metallic reinforcements obtained by the Langelier and Hoover methods showed an aggressive character of the water on the metals and therefore on the concrete.

The visual aspects of the concrete structures in contact with Black Sea water were presented and the effects of corrosion processes can be observed. The protective methods of coastal structures against the seawater aggressiveness were also mentioned.

References

Biczok, I. 1965. The concrete corrosion and protection, Tehnica Edition, Bucharest.

Buenfeld, N.R. and Newman, J.B. 1984. The permeability of concrete in a marine environment, Magazine of Concrete Research, 36(127): 67-80. doi: 10.1680/ macr.1984.36.127.67

Buenfeld, N.R. and Newman, J.B. 1986. The development and stability of surface layers on concrete exposed to sea-water, Cement and Concrete Research, 16(5): 721–732, doi: 10.1016/0008-8846(86)90046-3.

Cole, W.F. and Hueber, H.V. 1957. Hydrated magnesium silicates and aluminates formed synthetically and by the action of seawater on concrete, Silicates Industriels, 22(2): 75-85.

Costa, A. and Appleton, J. 1999. Chloride penetration into concrete in marine environment- Part I: Main parameters affecting chloride penetration, Materials and Structures/Matériaux et Constructions, 32(4): 252-259. doi: 10.1007/BF02479594

Georgescu, M. and Puri, A. 2004. Inorganic binders chemistry, Politehnica Press Edition, Bucharest.

Kuhail, Z. and Shihada, S. 2001. Permeability and chloride penetration of concrete subjected to Gaza seawater exposures, Journal of the Islamic University of Gaza, 9(2): 67–84.

Mather, B. 1964. Effects of sea water on concrete, U.S. Army Engineer Waterways Experiment Station, Vicksburg, Miscellaneous Paper no: 6, Misissippi, 690 pp.

Moncea, A., Georgescu, M. and Voicu, G. 2012. Sulfate and acid corrosion of some ternary binders consisting of Portland cement-calcium aluminate cement-calcium sulfate. In: F.A. Finger (Ed.), IBAUSIL, Institut für Baustoffkunde, Weimar: 18(1): 540–547.

Moncea, A. and Georgescu, M. 2013. The influence of the calcium sulfate nature on the hydration and hardening processes of some ternary binders silicate-aluminate-sulfate, U.P.B. Scientific Bulletin, 75(3): 119-128.

Montemor, M.F., Simoes, A.M.P. and Ferreira, M.G.S. 2003. Chloride-induced corrosion on reinforcing steel: from the fundamentals to the monitoring techniques, Cement and Concrete Composites, 25(4-5): 491-502. doi: 10.1016/S0958-9465(02)00089-6.

Neville, A. 1995. Chloride attack of reinforced concrete: an overview, Materials and Structures, 28(2): 63-70. doi: 10.1007/BF02473172.

Poteraş, G. 1993. Research on the behavior of a new range of cement with additives for granulated blast furnace slag replacement, in various aggressive sulphating environments, Project, INCDPM 802/1993

Prasad, J., Jain, D.K. and Ahuja, A.K. 2006. Factors influencing the sulphate resistance of Cement concrete and mortar, Asian Journal of Civil Engineering (Building and Housing), 7(3): 259-268.

Sosa, M., Perez-Lopez, T., Reyes, J., Corvo, F., Camacho-Chab, R., Quintana, P. and Aguilar, D. 2011. Influence of the marine environment on reinforced concrete degradation depending on exposure conditions, International Journal of Electrochemical Science, 6(12): 6300–6318.

STAS 2633-76 Cements. Stability determination at the sulphate water aggressiveness.

Teoreanu, I., Moldovan, V. and Nicolescu, L. 1982. The concretes sustainability, Tehnica Edition, Bucharest

Tibbetts, D.C. 1968. Performance of concrete in seawater: some examples from Halifax. In: T. Thorvaldson and E.G. Swenson (Eds.), Performance of Concrete resistance of Concrete to Sulphate and other Environmental Conditions. A Symposium in Honour of Thorbergur Thorvaldson, Series No. 2, University of Toronto Press, Toronto: 159-180.

Wegen, G.V., Bijen, J. and Selst, R.1993. Behavior of concrete affected by sea water under high pressure, Materials and Structures/Matériaux et Constructions, 26(9): 549-556, doi: 10.1007/BF02472865