

Aggressive Attack of Sea Water on Composites Containing High Amounts of Granulated Slag

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Abstract-the composite cement containing 6% silica fume (SF) can be obtained by partial replacement of Ordinary Portland Cement by granulated blast furnace slag on the aggressive attack of these pastes immersed in sea water up to 12 months was investigated. Most of the cement pastes produced with granulated slag should be better in sea water resistance than the control samples. The cement paste without granulated slag gives lower durability in sea water than other samples. The data show that as by increasing the substitution of OPC by granulated slag, the resistance of sea water of the cement pastes also increased at all immersing times. The X-ray results show that the peak of calcium hydroxide ettringite and gypsum exert higher intensity in cement without slag and completely disappear in other samples.

Key words: composite cement, silica fume, granulated slag, sea water

I. INTRODUCTION

Durability and deterioration of concrete structures exposed to chemicals and harmful ions are subjected of the major discussion; i.e. as regards service life high cost or key concrete structures. For over a century, the reinforced and unreinforced structures exposed to sea water will suffer from chemical reaction between sulfate and chloride ions and hardened cement composition in the structure of cementitious matrix.

The most common reactions often used to explain the defined sulfate attack are ettringite and gypsum formation [1]. It is generally indicated that sodium and magnesium sulfate attack of hydrated cement matrix occur as a results of the reaction of sulfate ions with calcium hydroxide and calcium aluminate phases, producing gypsum and ettringite. It was found that there is no correlation between the expansion of cement samples and the quality of crystalline calcium sulfo-aluminate formed. These other factors influence the expansion. Gypsum can be formed by decomposition of SCH phases or directly by the reaction of lime with sulfate solutions. By thermal investigation (DTA) it was found that, in addition to the crystalline phase there exists a gel phase which could not be detected by X-ray diffraction method.

Magnesium sulfate reaction is the degradation and disintegration of C-S-H gel to M-S-H gel, producing non-cementitious products leading to softening of the cement matrix [2-6]. This can mainly be attributed to the high severity sulfate attack condition. The damage of hardened cement paste structure resulted from the deterioration as a result of the reaction of MgSO₄ with the cement hydrates as follows:



The sequence of chemical reaction of magnesium sulfate with cement hydrates in the different hardened cement pastes may slightly vary from mix to another depending on the Ca(OH)₂ content. In order to prevent the C-S-H gel from softening, calcium hydroxide amount should be limited. As regards, in the concrete mixtures containing silica fume, calcium hydroxide percent is less than the ordinary mixes and the pore structures are finer [7].

Sea water attack on mortar specimens made with different types of cement was studied [8-10]. In addition, the effect of MgSO₄ in the presence of MgCl₂ on mortar samples was evaluated [7, 8]. Moreover, the evaluation of sulfate attack on blended cements, incorporating supplementary cementitious materials (SCM) have been carried out by many investigators [10-18].

It is noticed that, the use of (SCM) such as, (SF), meta-kaolin (MK), (GBFS) and fly ash (FA) are cheaper and sustainable than cements [19, 20]. The suited replacement levels of SCM can improved the economic, physico-chemical, mechanical, durability and sustainability properties of concrete [21-23].

The attack of sodium sulfate on concrete may be due to the reaction of Na₂SO₄ and Ca(OH)₂ forming gypsum then the reaction of the formed gypsum with calcium aluminate hydrates producing sulfoaluminate phase. It is noticed that, MgSO₄ react with cement compounds, including C-S-H thus decomposing cement and subsequently forming gypsum and ettringite [24-26].

Pozzolanic materials improve the sulfate and sea water resistance of concrete [21, 27-30]. Also, by increasing the GBFS mass %, the liberated Portlandite decreases. This is attributed to the following reasons: 1) The pozzolanic reaction of slag with free lime forming additional amounts of calcium silicate hydrate (C-S-H), calcium aluminate hydrate (CAH) and calcium aluminosilicate hydrate (CASH), 2) The reaction of the liberated Portlandite with MgSO₄ and NaCl to form gypsum and CaCl₂, producing sulphoaluminate as well as chloroaluminate hydrates and brucite, Mg(OH)₂. Also, MgCl₂ reacts with another part of Ca (OH)₂ to form Mg(OH)₂.

The strength of Ordinary Portland cement pastes decreased to various extends in sea water, while the strength of the granulated slag cement pastes maintain or even increased to different extend; especially the flexural strength increased considerably[29].

Luo et al. investigated pure Portland cement and granulated slag blended cement with respect to their pore structure, chloride diffusion coefficient, internal and external chloride binding capabilities by the expansion method and leaching method [31].

The aim of this investigation is to study the durability of composite cement pastes containing different amounts of granulated slag in sea water.

II. EXPERIMENTAL WORK

2.1. Materials

2.1.1. Ordinary Portland Cement

The Portland cement was obtained from National Cement Company, Helwan, Egypt. The chemical analysis of Ordinary Portland Cement (was carried out using the XRF technique) aided with normal wet chemical analysis technique (ASTM C114-1988) [32]. The results are given in Table 1. The chemical analysis of the sea water of Suez Canal region is shown in Table 2.

Table 1: Chemical analysis of the starting materials, (wt. %)

Materials	Oxide							
	SiO ₂	AL ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na ₂ O
Portland cement	21.3	5.41	3.77	63.14	1.21	2.35	0.09	0.4
Silica fume	96.89	1.03	0.56	0.21	0.15	0.16	0.62	0.17
Granulated Slag	39.89	13.72	2.56	26.38	3.47	1.22	1.06	1.0

2.1.2 Granulated blast furnace slag

It was obtained from the Egyptian Iron and Steel Company, Helwan. It is usually obtained by water quenching of the molten slag. It was ground in steel ball mill to obtain a Blain surface area (4.56 m²/kg). The results of chemical analysis of granulated slag were given in Table 1.

Table 2: The chemical analysis of sea water (Suez Canal region)

Constituent	(ppm)
Na	11600
K	386
Ca	460
Mg	1700
CL	22450
SO ₃	3170

2.1.3 Silica fume

It is a by-product of manufacture of ferro-silicon materials. It was obtained from Ferrosilicon Company, Edfo, Upper Egypt. The chemical analysis of the silica fume (SF) after drying at 105 oC for two hours is given in Table 1. Its surface area as measured by the BET method is 20m²/kg.

2.2. Preparation of composite cements

The dry constituents of OPC, silica fume and slag were mechanically mixed for 30 minutes in a porcelain ball mill to attain homogeneity of the cement samples. The samples were kept in airtight container until the time of paste preparation. The mix composition of different prepared cements is shown in Table 3.

Table 3: Mix composition of different prepared cement, wt, %

Mix no.	Granulated slag	Silica fume	OPC
M0	0	6	94
M1	40	6	54
M2	50	6	44
M3	60	6	34
M4	70	6	24

The specific surface area of the Portland cement was 3150 g/cm². The prepared cement was mixed with the water of consistency [33], molded in one inch cubic mould for 24 hours in saturated humidity chamber, de-molded then immersed in sea water for 1, 3, 6, 9 and 12 months. The aggressive solutions were renewed every month to keep the concentration of salt ions in sea water nearly constant. At the end of each period, three cubes representing each mix were tested for their physic-mechanical properties.

The kinetic of hydration was followed by the determination of free lime (ASTM 114) [32]. The bulk density and total porosity (ASTM C373) [34] as well as compressive strength (ASTM C109) [35] and (ASTM C191)[44] were also measured up to one year. The mixing, molding and stopping of hydration were described elsewhere [36]. Some selected samples were investigated by XRD phase analysis.

X-ray diffraction (XRD) analysis was performed using BRUKER D8 ADVANCE, Target: Cu K α . The phases were identified with the help of the Appendix 1, on Tabulated crystallographic Data of Taylor (1997)[37].

III. RESULTS AND DISCUSSION

The chemical reaction of sea water on cement paste or concrete is mainly due to the presence of magnesium sulfate [16]. Magnesium sulfate reacts with the free lime liberating during the hydration of Portland cement to form calcium sulfate and Mg (OH)₂. Both Ca (OH)₂ and calcium sulfate are considerably more soluble in sea water than in plain water, which must lead to an increased leaching action. Leaching actions remove lime while calcium sulfate formed leads to formation of sulfoaluminate hydrate which may cause expansion, rendering the concrete more open for further attack and leaching.

The compressive strength values of the hardened cement pastes cured for 1, 3, 6, 9 and 12 months in sea water are presented as a function of curing time in Fig. (1). At early immersing time (0-3 months), the compressive strength rapidly increases then enhanced slowly up to 12 months for all cement pastes except the sample (M0) which enhances up to 3 months then decreases up to one year [38, 39]. It seems that, by increasing the substitution of Portland cement by granulated slag, the durability of the pastes also enhanced at all immersing time. This was due to the lower Portland cement in these mixes and increasing the amount of granulated slag [31].

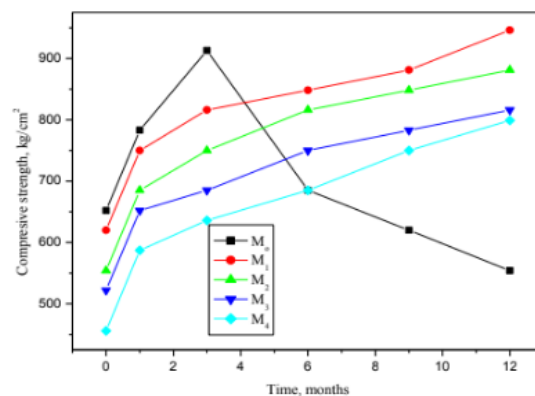


Figure (1): Compressive strength of composite cement pastes as a function of immersed time.

The values of apparent porosity of the composite cement pastes cured with time in Fig. (2). The total porosity of all cement pastes decreases at one month due to the precipitation of hydration product in a part of available pores volume then increases till one year. The results demonstrated that, the sample (M0) gives lower values of porosity

than other samples at one month immersion while the porosity values enhances up to one year due to sulfate attack and formation of gypsum and ettringite[24-26] . Also as the substitution of OPC by granulated slag content increases the porosity decreases at later ages (9-12 months). This is attributed to the pozzolanic reaction of slag with free lime forming (C-S-H), (CAH) and (CASH), leading to the improvement of the durability and sea water resistance of the cement pastes [21, 28-30, 40]. Chloride-ion permeability of GGBS concrete specimen is reduced as period of curing or amount of GGBS by binder weight was increased. On the other hand, an initial reduction of porosity is expected because calcium hydroxide is the first phase attacked by carbonation and the volume of the carbonate formed (calcite) is 11-12% greater than the volume of calcium hydroxide, leading to an increase in the weight of hydrated sample as well as lower porosity and higher compressive strength at early ages of hydration [41].

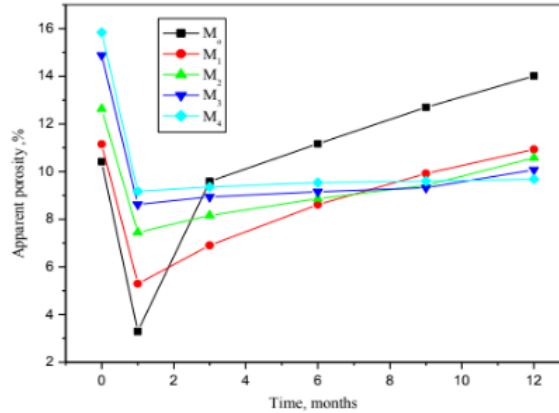


Figure (2): Total porosity of composite cement pastes as a function of immersed time.

The bulk density of the cement composite pastes is shown in Fig. (3). The data shows that the bulk density of the hardened cement pastes containing granulated slag are increased with immersed time. Also, the bulk density of the control sample increases up to 3-months then decreases with time till 12-months. This is attributed to the acceleration effect of the chloride and sulfate ions of sea water on the hydration of the silicate and aluminate phases of the composite cement. Therefore, the hydration products will precipitate into part of available pores volume of the pastes then the bulk density increases. On the other hand, the decrease of bulk density of the cement pastes without slag after 3-months is mainly due to the formation of gypsum as well as chloro- and sulfoaluminate hydrates which cause more softening and expansions.

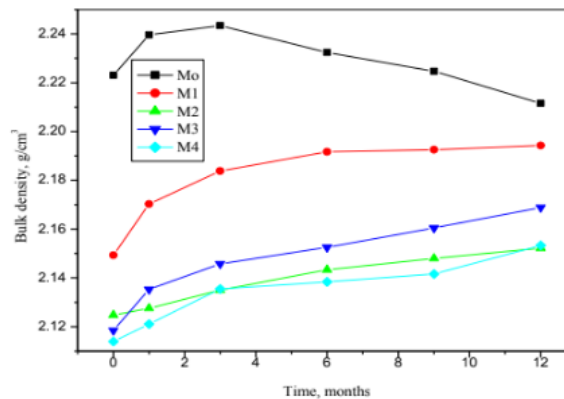


Figure (3): Bulk density of composite cement pastes as a function of immersed time.

The results of free lime contents for different cement pastes immersed in sea water for 1, 3, 6, 9 and 12 months are presented in Fig.(4). It is clear that the values of free lime decreases with increasing slag content as well as immersing time. The free lime contents of (MO) increase with immersed time up to 3-months due to the liberation of free lime during the hydration the silicates phases of Portland cement, then decreases up to 12-months. This is attributed to the acidic attack of MgSO₄ and MgCL₂ in sea water, in presence of Ca (OH)₂ liberating during the OPC hydration , leading to the formation of gypsum and sulfoaluminate phases . On the other side, by increasing the amount of granulated slag, the free lime contents decrease at all times due to the activation of the slag materials with lime forming hydrated products.

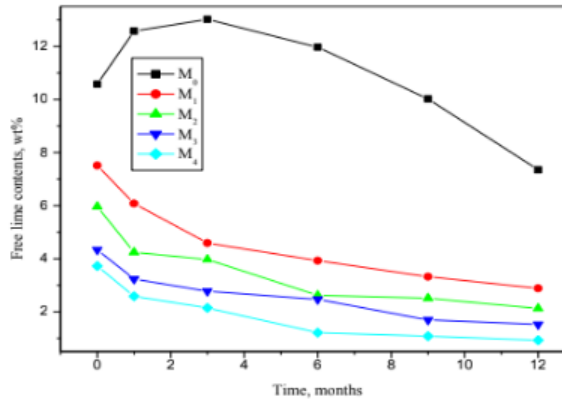


Figure (4): Free lime of composite cement pastes as a function of immersed time.

The XRD pattern of the sample (MO) cured at 1, 6 and 12 months in sea water are shown in Fig. (5). Results indicate that the free lime enhances with immersion time up to 6-months then decreases up to 12- months. This may be due to the chemical reaction between the free lime liberating during the cement hydration and the chloride and sulfate ions producing deleterious materials. The existence of gypsum as well as ettringite was detected with different intensity for all ages of immersing times. On the other hand, as the immersing time increases the deleterious materials such as gypsum, monosulfate and ettringite enhance in the cement pastes [42]. Taylor and Gollop [43] come to similar conclusions and considered that the formation of ettringite leads to expansion but the formation of gypsum leads to loss of cohesion and softening of the cement matrix.

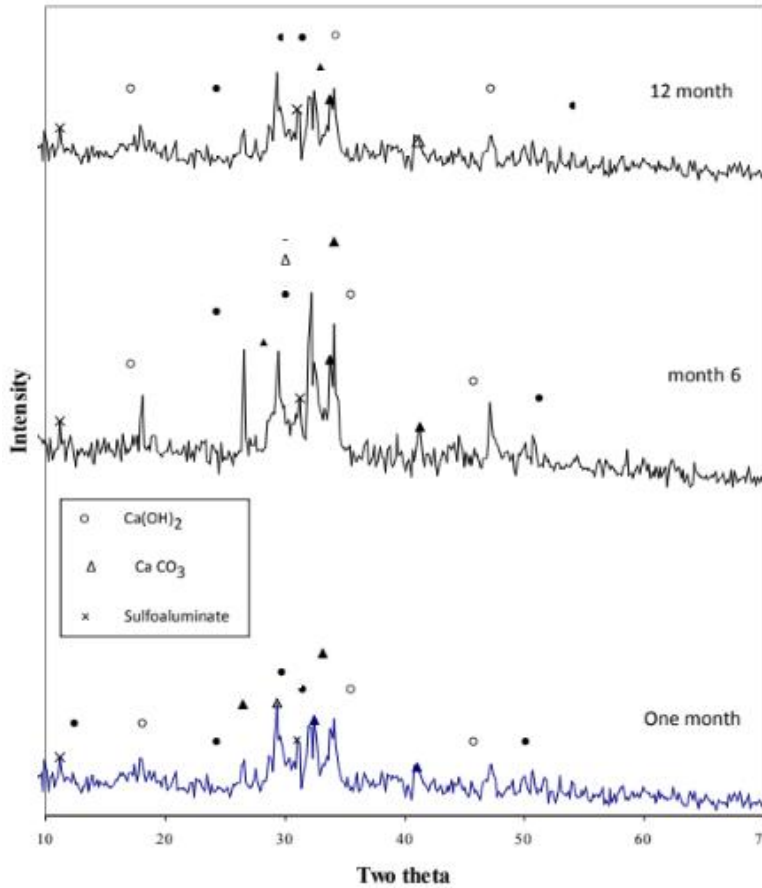


Figure (5) XRD patterns of (Mo) Samples of composite cement pastes immersed at different times in sea water.

The XRD pattern of composite cement pastes with 50% slag content (M2) cured at 1, 6 and 12 months in sea water are shown in Fig. (6). The results indicate that the $\text{Ca}(\text{OH})_2$ peak was completely disappeared at all immersion time. The intensity of CaCO_3 peak decreases at later ages of immersion. Quartz peaks and C_4AH_{13} were detected in composite cement pastes containing GGBS. The diffraction patterns present the high intensity of C-S-H peaks indicating more dense structure of additional C-S-H in (M2).

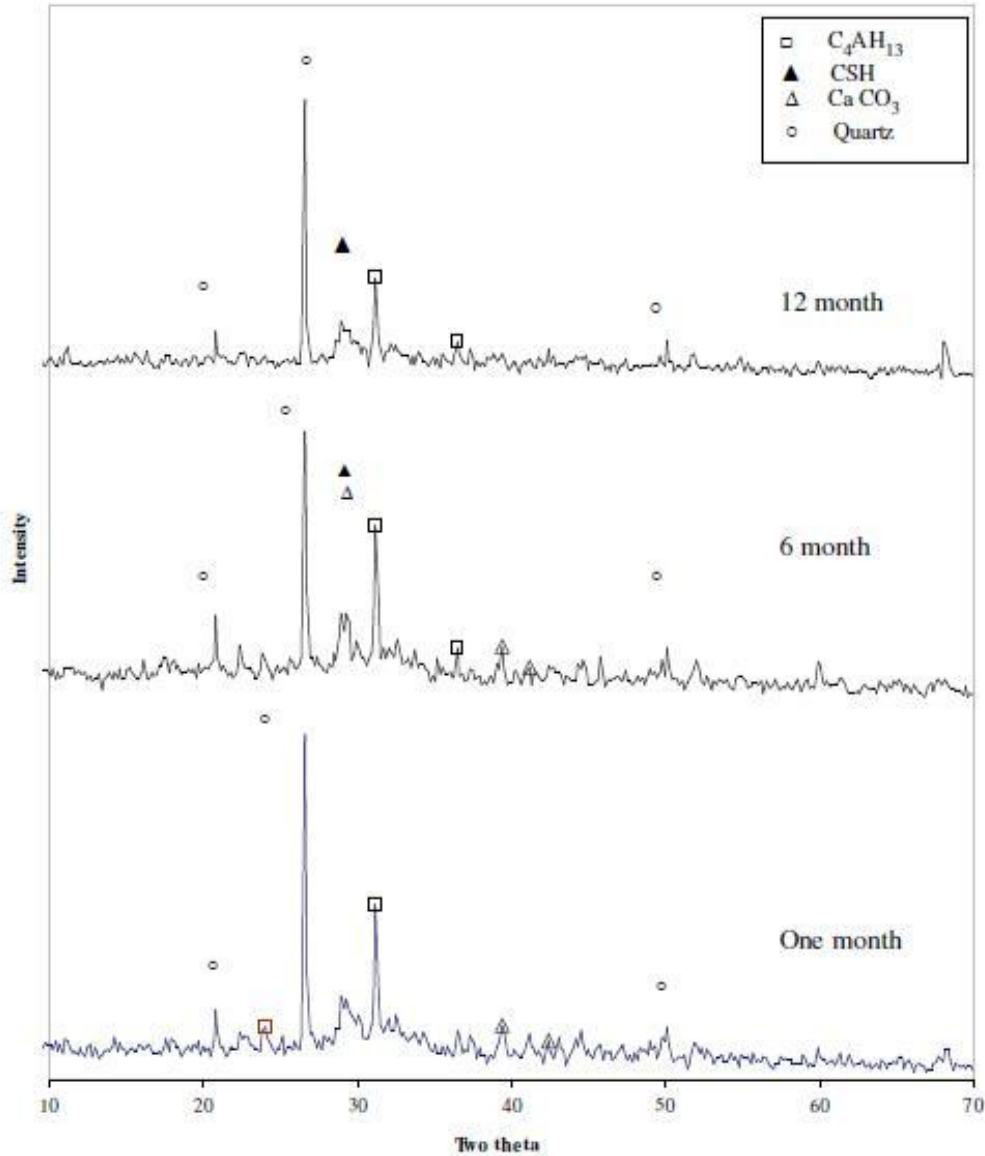


Figure (6) XRD patterns of (M2) Samples of composite cement immersed at different times in sea water.

The XRD pattern of composite cement pastes with 70% slag content (M4) cured at 1, 6 and 12 months in sea water are shown in Fig. (7). Results showed that relatively large intensity peak for quartz as well as C_4AH_{13} in the paste specimens with slag sample; ettringite, $\text{Ca}(\text{OH})_2$ and gypsum were not found in any examined pastes. The intensity of CaCO_3 and C-S-H peaks were detected.

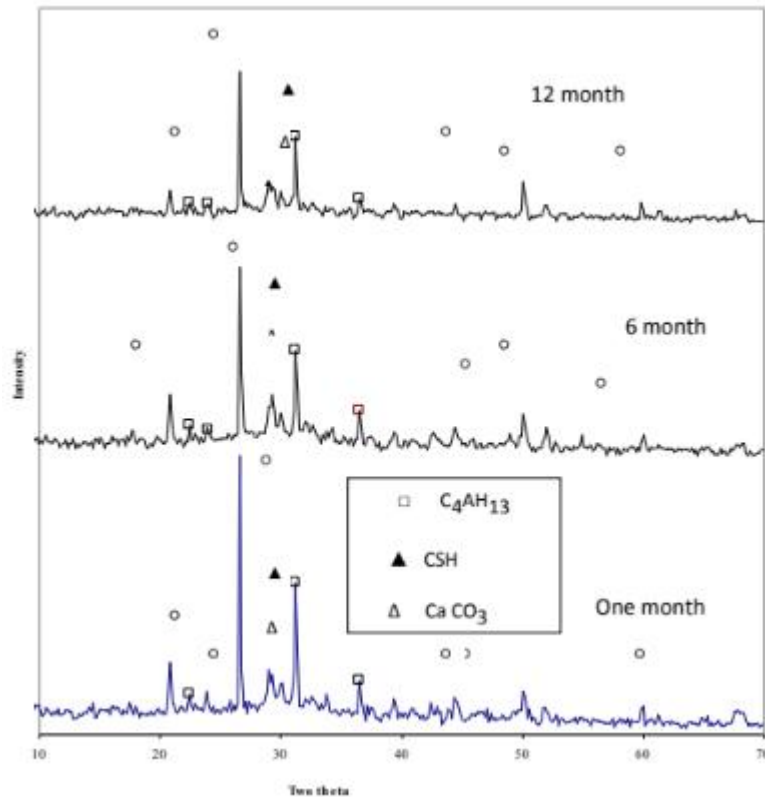


Figure (7) XRD patterns of (M4) Samples of composite cement pastes immersed at different times in sea water.

IV. CONCLUSION

The conclusions of this work are:

- ◆The replacement of Ordinary Portland cement by granulated slag in the composite cement containing 6 % (S) improves the physico-mechanical properties of cement pastes and resistance of cement stone against the corrosion agents.
- ◆Cement pastes with granulated slag had a relatively good sea water resistance performance when replaced OPC cement by 40-70% slag.
- ◆The X-ray data show that the peaks of calcium hydroxide, gypsum and sulfoaluminate phases have higher intensity in cement without slag and completely disappear in presence of granulated slag samples.

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