Modern experiment methods to verify the efficiency of using mineral admixtures in cementitious material of hardened cement applied for concrete of marine structures

Nguyen Thi Thu Huong[1]

Abstract: An experimental study using modern experiment methods for the cement specimens incorporating 0% fly ash+0% silica fume-F_0S_0, 30% fly ash+0% silica fume-$F_{30}S_0$, 25% fly ash+5% silica fume-$F_{25}S_5$, 20% ash fly+10% silica fume-$F_{20}S_{10}$, 15% fly ash+15% silica fume-$F_{15}S_{15}$ was reported. Results confirmed that the specimens with the replacement fly ash and silica fume showed the helpful transformation of hydration products and a good improvement of microstructure on hardened cement. This is due to the reduction of calcium hydroxide and the increase of secondary CSH in the cement matrix from the pozzolanic reaction of a mineral admixture. The result of the study with modern experiment methods confirmed the improvement of strength and durability for hardened cement using mineral admixture, thereby ensuring the good applicability of the additional admixtures used in concrete of marine structures.

Keywords: Modern experiment method, cementitious material, admixture, hardened cement, hydration products, $CaO.SiO_2.H_2O$-CSH, concrete of marine structures.

1. Introduction

For coastal engineering, one of the most important problems is the deterioration of the concrete structures caused by serious corrosion (P.Kumar Mehta, 1991). For that reason, marine concrete structures normally show lower durability and lifetime than similar structures in the river. One of the effective solutions to improve the quality of concrete, and ensure the maintenance of workability and long service life is to use composite mineral admixtures in concrete. Today, cementitious materials contained in this type of concrete employ blended cement that includes silica fume, fly ash, and blast furnace slag. These cementitious materials were studied because of their high pozzolanic properties (V.M. Malhotra and P.K. Mehta, 1996). The effects of fly ash, silica fume, and slag on the durability and mechanical properties of concrete have been widely reported (J.M.R. Dotto et al., 2004, V.M. Malhotra, P.K. Mehta, 2008, JS.W. M. Supit, F.U.A Shaikh, 2014, A.M. Rashad et al., 2014). To have clear evidence of the effectiveness of using mineral admixture, it is necessary to conduct experiments using different types of admixture with different rates, make samples, and then consider the transformation of products and microstructures on the hardened products. The modern experiment methods can clearly show the transformation of hydration products and the improvement of microstructure on hardened cement using admixture, leading to the improvement of strength and durability for hardened cement.

Recent works have shown that the use of mineral admixtures has the effect of increasing the corrosion resistance of concrete through the effect of altering the products of hydration, converting highly soluble and chemically active hydration products into new

[1]Division of Construction Materials, Faculty of Civil Engineering, Thuyloi University
Received 29th Aug. 2022
Accepted 13rd Dec. 2022
Available online 31st Dec. 2022

less soluble products, and at the same time improving the microstructure of hardened cement thanks to spherical and super fine size particle of mineral admixtures (Hisham M. Khater, 2010, Yoshihiko Okada, 1994, Li Fangxian et al., 2009).

The present article reports my findings on the application of the modern experiment methods to verify the effects of fly ash and silica fume on the durability of concrete as indicated from phase formation and microstructural properties when fly ash and silica fume are introduced as cement replacements in cement mortar specimens.

2. Introduction to modern experiment methods

According to the theoretical bases that have been analyzed (V.S.Ramachandran, Ralpha M.Paroli, Jame J.Beaudoin, Ana H.Delgado, 2002, N.M. Phat, 2007), the modern experimental methods used in this study are as follows:

2.1. X-Ray analysis

X-ray fluorescence scattering analysis was carried out for qualitative analysis and to check the discrimination of the constituent elements of the sample. X-Ray analysis experiments that can analyze, without sample loss, fixed samples in the form of pads, liquids, and powders, are widely used in research, development, and quality control in various aspects.

2.2. Thermal Gravimetric Analysis or Thermogravimetric Analysis - TGA

Thermogravimetric analysis of TGA is applied to quantitatively analyze the mineral composition or the composition of thermally active substances in the research sample based on the characteristic thermal effects of the solid. This method is based on determining the mass of a sample of matter lost or gained during the phase transition as a function of temperature. TGA spectra characterize a compound or system because the order of chemical reactions occurring at a specified temperature range is a function of the molecular structure. The information received helps determine the mass composition of substances present in the sample.

2.3. Scanning Electron Microscope–SEM

A scanning electron microscope is a type of electron microscope that can produce high-resolution images of the surface of a solid specimen by using a narrow electron beam (cluster of electrons) scanning the surface of the sample. The images taken from the experiment allow us to evaluate the process of changing components in hardened cement when there are mixing substances such as admixture. Each type of crystal has a different geometry, so looking at the image from the scanning electron microscope with the image of the crystals will help to see which new components have formed.

Thus, modern analytical experiments are evidence that has a scientific basis to evaluate the effectiveness of using admixture compared to the case of no admixture, from which correct conclusions can be drawn about the role of admixtures used in concrete components with high strength and durability requirements for coastal protection works.

3. Researched results and discussion

3.1. Materials and proportion of the cementitious material mixture

3.1.1. Materials

Among the solutions to improve the durability of concrete for marine structures, the solution using commercially available admixture to form a binder combination will be the most effective in improving the quality of concrete such as resisting corrosion and increasing concrete strength (N.T.T.Huong, 2016).

Because the effect of using admixtures in concrete affects the cement composition, in order to clarify this effect, the article only focuses on the experiment with cement hardening from the mixture of the cementitious material compound with additional admixture, to have a basis to verify the accuracy of the effectiveness of improving the durability for concrete when using the admixture combination in this study. The cementitious material mixture will consist of cement, fly ash, and silica fume.

The materials used in this research contain Butson cement PC40 (TCVN 2682), Phalai fly ash (TCVN 10302), silica fume of Castech (TCVN 8827), high water reducer HWR100 of Castech; Water (TCVN 4506).

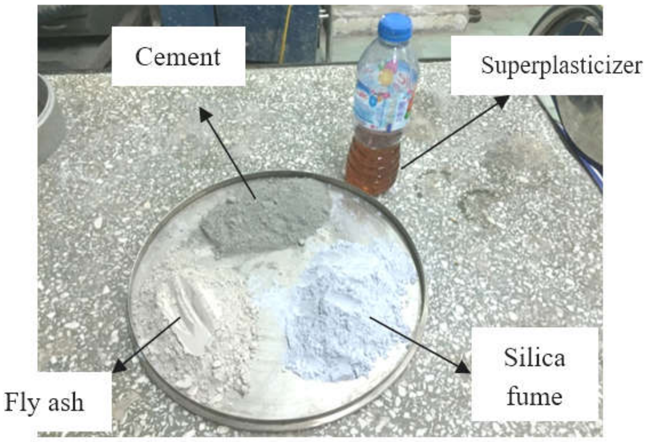

Figure 1. Components of cementitious materials and superplasticizer used in the study

Figure 2. Samples of hardened cement used in the study

3.1.2. Proportion of cementitious material mixture and specimen of hardened cement

Based on the theoretical basis and recommended rates in previous studies (N.V. Trung et al., 2010, Pham Duy Huu et al., 2008), this study proposes to use four grades with mineral admixture to replace cement so that the total amount of admixture is 30% and one grade without admixture to have a basis for comparing the effectiveness of the selected solution. Specifically, four ratios of using mineral admixture to replace cement and symbols used in the study are: 30% fly ash+0% silica fume-$F_{30}S_0$, 25% fly ash+5% silica fume-$F_{25}S_5$, 20% ash fly+10% silica fume-$F_{20}S_{10}$, 15% fly ash+15% silica fume-$F_{15}S_{15}$.

Based on the manufacturer's recommendation, the superplasticizer used is 0.3-:-0.5% of the total amount of binder, in this study, the rate of superplasticizer was chosen at 0.4%- P0.4.

Combining the symbols for the proportions of mineral admixture and superplasticizers, the samples tested in the study were finally denoted as follows: $F_0S_0P_0$, $F_{30}S_0P_{0.4}$, $F_{25}S_5P_{0.4}$, $F_{20}S_{10}P_{0.4}$, $F_{15}S_{15}P_{0.4}$.

After testing to determine the water for standard consistency of cement paste, carry out mixing and casting 5 samples of cement, including 4 samples with admixture and 1 sample without admixture. Cement samples are cubes cast in a 2x2x2cm mold, after 24 hours, the mold is removed and soaked in water for curing. These samples were used as X-Ray, TGA, and SEM modern analytical experiments at 28 days and 60 days to determine the efficiency of conversion of hydration products due to the presence of fly ash and silica fume. Pictures of the test samples are shown in Figure 2.

3.2. Results and discussions

Due to the restriction on the number of pages of the article, within the scope of this paper, only the experimental results of some typical samples are presented for analysis. Full experimental results can be found in the documents of N.T.T.Huong, 2016.

3.2.1. X-Ray analysis

The results of X-Ray analysis of 2 grades of hardened cement, control sample without using admixture $F_0S_0P_0$, and sample using admixture $F_{20}S_{10}P_{0.4}$ at 28 days are shown in Figure 3. The analysis results show that: Compared with the control sample without admixture, in the samples with fly ash and silica fume, minerals SiO_2 have been added, proving that the active ingredient in puzzolan has appeared in the hardened cement and will perform the role of changing the hydration products of cement according to its action mechanism.

In addition, the results also show the formation of hydration products in hardened cement such as $Ca(OH)_2$, CSH, and Ettringite in samples of both types with and without additives.

In order to estimate the amount of substances formed in the hardened cement, X-Ray samples were also used for the TGA thermogravimetric analysis which is presented in the next part.

a)

b)

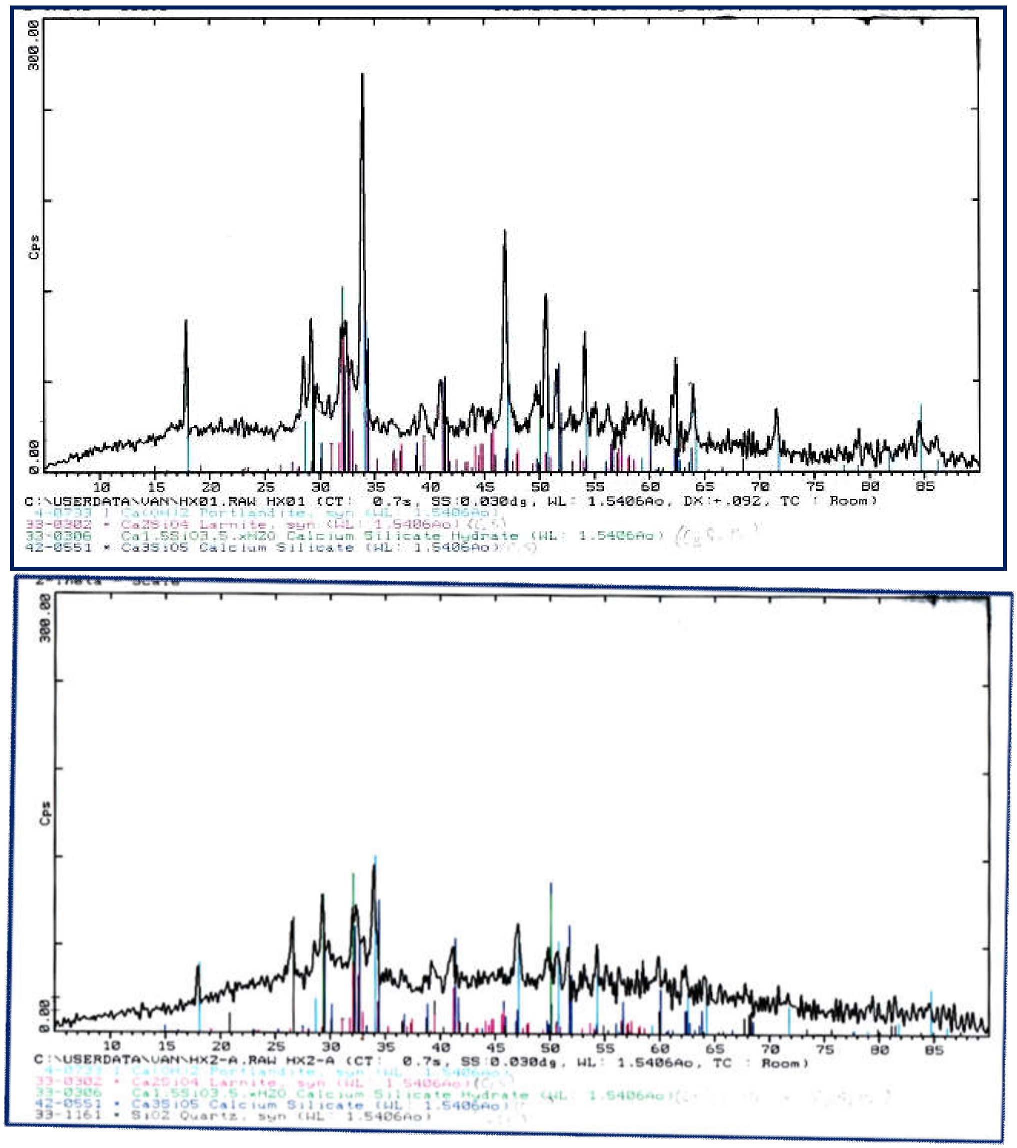

Figure 3. X-Ray of sample a)$F_0S_0P_0$-28 days; b) $F_{20}S_{10}P_{0.4}$-28 days

3.2.2. TGA analysis

Theoretically, when conducting thermal analysis with hardened cement samples, there will be a mass change corresponding to the following thermal effects (V.S. Ramachandran and et al (2002), Yoshihiko Okada (1994):

50-:-100^oC: Free water evaporates;

90-:-150^oC: Water in the CSH Gel structure evaporates;

150-:-200^oC: Separation of water of crystallization in Ettringite $C_3A.3CaSO_4.31H_2O$;

400-:-470^oC: Dissolution $Ca(OH)_2 \rightarrow CaO+H_2O$;

650-:-700^oC: Water of crystallization in CSH separates.

Based on the above effects, it can be seen that the first 3 temperature ranges have overlapping regions, which means that simultaneous effects can occur due to the same reaction temperature. Since the experimental study was only carried out up to a maximum temperature of 850^oC, to facilitate the analysis of results from thermal effects, they can be classified into 3 main groups of effects as follows:

- Effect 1(0^oC-:-200^oC): Combination of 3 processes, loss of free water, loss of adsorbed water in CSH, and separation of chemically bound water in $C_3A.3CaSO_4.31H_2O$.

- Effect 2(400^oC-600^oC): $Ca(OH)_2$ decomposition, so from the analytical results it is possible to estimate the lime composition in the hardened cement created from the hydrolysis reactions of mineral composition in cement and also after the pozzolanic reaction.

- Effect 3(600^oC-:-800^oC): Separation of crystalline water in CSH, so the analysis results can help to estimate the composition of crystalline CSH formed in hardened cement.

The experimental results of TGA analysis of 2 grades of hardened cement, control sample without using admixture $F_0S_0P_0$, and sample using admixture $F_{20}S_{10}P_{0.4}$ at 28 days are shown in Figure 4.

Based on the results of the TGA thermal analysis, it is possible to estimate two main components related to the durability of hardened cement in the two temperature ranges of effect 2 (400-:-600^oC) and effect 3 (600-:-800^oC) as shown in table 1.

Table 1. Estimation results of components in hardened cement from TGA experiment

Mix	Effect 2 $Ca(OH)_2$ (%)		Effect 3 crystalline CSH (%)	
	28 days	**60 days**	**28 days**	**60 days**
$F_0S_0P_0$	4.09	3.56	2.55	2.56
$F_{30}S_0P_{0.4}$	2.42	2.26	3.34	3.39
$F_{25}S_5P_{0.4}$	2.36	1.76	3.70	3.78
$F_{20}S_{10}P_{0.4}$	2.03	1.46	3.62	3.85
$F_{15}S_{15}P_{0.4}$	2.56	1.98	3.55	3.73

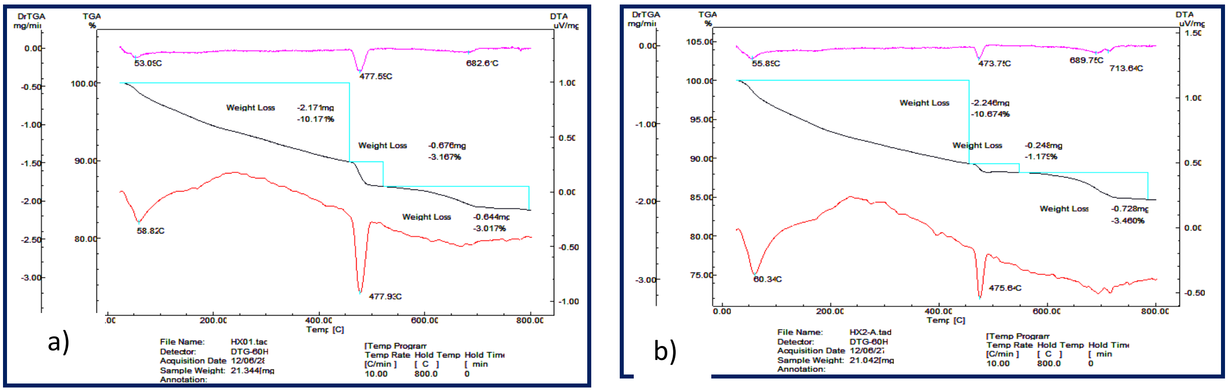

Figure 4. TGA of sample a)$F_0S_0P_0$-28 days; b) $F_{20}S_{10}P_{0.4}$-28 days

The results of the analysis showed:

For effect 2 to estimate the amount of $Ca(OH)_2$: At 28 days of age, the samples with admixture had significantly reduced lime content compared to the control sample without admixture. Specifically, in the control sample, the estimated amount of $Ca(OH)_2$ was 4.09%, which decreased in the samples with the additional admixture to 2.42% ($F_{30}S_0P_{0.4}$); 2.36% ($F_{25}S_5P_{0.4}$); 2.03% ($F_{20}S_{10}P_{0.4}$) and 2.56% ($F_{15}S_{15}P_{0.4}$). Up to 60 days, the amount of $Ca(OH)_2$ of the samples decreased but still followed the same change as at 28 days. The explanation for the decrease in the mass of $Ca(OH)_2$ from 28 days to 60 days is that the amount of lime produced by the hydrolysis reaction of C_3S and C_2S has not fully reacted with SiO_2 in the pozzolanic effect, then when the amount of $Ca(OH)_2$ reacts with SiO_2 is more, the remain $Ca(OH)_2$ is less.

For effect 3 to estimate the amount of crystalline CSH: At 28 days, the fraction of crystalline CSH in the control sample was the smallest with an estimated amount of 2.55%, while in the samples with additional admixture this amount was more, detail is 3.34% ($F_{30}S_0$P0.4), 3.7% ($F_{25}S_5P_{0.4}$), 3.62% ($F_{20}S_{10}P_{0.4}$) and 3.55% ($F_{15}S_{15}P_{0.4}$). At 60 days, the amount of crystalline CSH in the samples increased slightly but still followed the same rule of mass difference as at 28 days.

Theoretically, there is a part of CSH that is formed in the form of a gel that will gradually turn to a crystalline form over time. This mass is quantified at effect 1 together with the amount of free water evaporating and the amount of Ettringite formed making it difficult to separate for precise estimation.

To evaluate the effectiveness of using mineral admixture at different mixing ratios based on the amount of CSH formed, it is necessary to quantify the total of both crystalline CSH and gel CSH. However, this result is practically difficult to determine precisely because the amount of gel CSH from effect 1 cannot be estimated due to the overlapping reactions at the same temperature range. If based on the analysis results of the amount of crystalline CSH, it can be seen that it is effective to use mineral admixture in cement compared to the case of no admixture because of the amount of crystalline CSH in the samples with the additional admixture is higher compared with samples without admixture.

Thus, the results of TGA analysis to estimate the compounds formed in hardened cement are completely consistent with the theoretical bases that have been analyzed and help to prove the role of active mineral admixture, fly ash, and silica fume in limiting corrosion.

3.2.3. Scanning Electron Microscope–SEM

The SEM scanning electron micrograph

results of 2 typical hardened cement samples are the control sample without admixture $F_0S_0P_0$ and the sample using admixture $F_{20}S_{10}P_{0.4}$ at 28 and 60 days with the same magnification 30000 as shown in Figures 5, 6.

The analytical results showed that: At 28 days, in the structure of hardened cement without admixture $F_0S_0P_0$, there were many interconnected voids and the cohesion between the molecules of the compound was formed more discretely than that of the hardened cement samples with additional admixture. Up to 60 days, it can be seen that the non-additive sample cracks in the structure, while the sample with additional admixture does not see this phenomenon. Images taken on samples with additional admixture samples at the age of 60 days show that the structure is somewhat denser, more evenly distributed, and more continuous than that of samples without additives. These factors will help to improve the mechanical properties of hardened cement and concrete especially strength and durability.

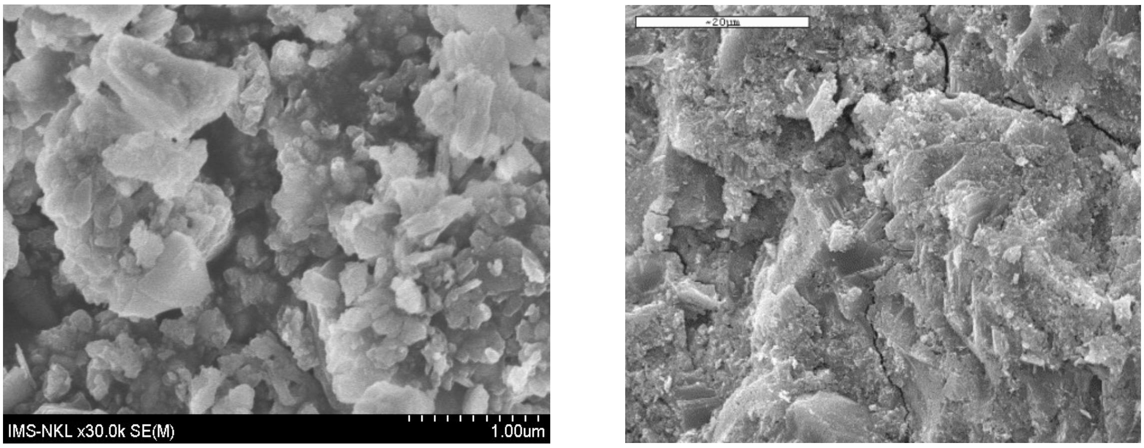

Figure 5. SEM of sample a) $F_0S_0P_0$-28 days, b) $F_0S_0P_0$-60 days

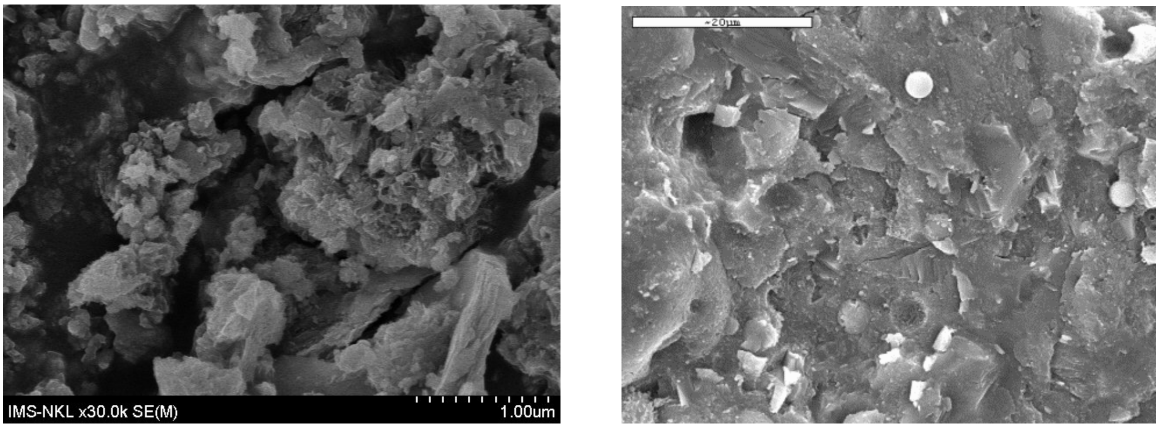

Figure 6. SEM of sample a) $F_{20}S1_0P_{0.4}$-28 days, b) $F_{20}S_{10}P_{0.4}$-60 days

Experimental results on hardened cement samples have partly shown the effectiveness of using combinations of admixtures to increase consistency, change hydration products and limit harmful components to concrete and reinforced concrete, which is the basis to ensure the applicability of the combination of mineral admixtures in the composition of concrete of coastal protection works.

4. Conclusion

The results of X-Ray, TGA analysis, and SEM images for the cement specimens incorporating fly ash and silica fume - F_0S_0, $F_{30}S_0$, $F_{25}S_5$, $F_{20}S_{10}$, $F_{15}S_{15}$ showed that the $Ca(OH)_2$ component appeared very clearly in the control sample and the estimated concentration was higher than that of the samples with additional admixture. For samples with additive admixture, the amount of $Ca(OH)_2$ was reduced, and the amount of CSH product was increased instead. Sample $F_{20}S_{10}P_{0.4}$ has the lowest amount of $Ca(OH)_2$ and the highest amount of CSH, but the difference is not much compared to samples of the same additional admixture samples.

The results of modern analytical experiments (TGA; X-Ray; SEM) for cement with additional admixture are the scientific basis to demonstrate the effect of using admixture to improve strength, durability for concrete, ensuring the applicability of admixtures including fly ash and silica fume along with superplasticizer for concrete of marine structures.

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