



KATKILARIN ÇİMENTO HAMURU HİDRATASYON İSİSİNE ETKİLERİ

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ÖZET

Bu çalışmada, Trisodyum sitrat ($C_6H_5Na_3O_7$ – Ret. 1), sitrik asit ($C_6H_8O_7$ – Ret.2) ve tartarik asit ($C_4H_6O_6$ – Ret.3) çimento harçlarının hidratasyon süreçlerini geciktirmek amacıyla kullanılmıştır. Katkılar Portland çimentosunun hidratasyon ısısı üzerine etkileri ele alınarak incelenmiştir. Hidratasyon süreçleri boyunca karışımların ısı çıkışı grafikleri izotermal kalorimetre kullanılarak çizilmiştir. Karışımların ısı çıkışları katkıların hızlı çözünme özelliklerine bağlı olarak değişirler. Katkısız çimento hamuru bütün karışımlar arasında en erken priz süresine sahiptir. Kalorimetre grafikleri katkı oranı arttıkça priz süresinin uzadığını işaret eder. 0.2 % oranında, tartarik asit geciktirme üzerinden güçlü etkiye sahiptir.

Anahtar Kelimeler: Hidratasyon ısısı, Organik katkılar, İzotermal kalorimetre

EFFECTS OF ADMIXTURES ON HYDRATION HEAT OF CEMENT PASTE

ABSTRACT

In this study, Trisodium citrate ($C_6H_5Na_3O_7$ – Ret. 1), citric acid ($C_6H_8O_7$ – Ret.2) and tartaric acid ($C_4H_6O_6$ – Ret.3) were used to retard the hydration process of cement paste. Admixtures were investigated with respect to their effects on the hydration heat of ordinary Portland cement. Heat liberation graphs of mixes during hydration process were plotted by using isothermal calorimetry. Heat liberation of mixes varies due to their different rapid dissolution properties. Cement paste without a retarder has an early setting time between all mixes. The calorimetric graphs indicate that the setting time increases as the ratio of retarder increases. At the ratio of 0.2 %, tartaric acid has the strongest effect on retardation.

Keywords: *Hydration heat, Organic admixtures, Isothermal calorimetry*

1. INTRODUCTION

Hydration of Portland cement affects the mechanical and physical properties of concrete in fresh or hardened state. Hydration is an exothermic reaction affected by the temperature and the fineness of cement grains. The rate of hydration is temperature dependent and increases with increasing temperature. At the same time, however, the structure of the hydrated material may also be altered [1]. The hydration rate increases with increasing specific surface of cement and with particle size distribution, indeed.

Concrete is subjected to different environmental conditions in its production and hydration process. Hot weather leads to thermal shrinkage and also rapid hydration of concrete. Especially, thermal shrinkage leads to shrinkage cracking on the surface of concrete. These cracks may cause some durability problems. Rapid hydration may cause a decrease in setting time. Decrease of setting time causes a shorter period for workability. Also, concretes subjected to rapid hydration process may have more porous and irregular microstructure.

One of the ways to improve the properties of a concrete mix in fresh and hardened states is to add small doses of chemical admixtures into the mix. The number of admixtures is so great that they must be classified according to their types of action. Many such classifications have been proposed, but it is important that each includes two types of admixtures in which one slows down and another one speeds up the setting rate of cement.

Such admixtures are called set-controlling admixtures. Set-controlling admixtures are added to retard or accelerate the hydration reaction processes of cement.

Also, the rapid generation of hydration heat may lead to degradation in long-term strength. The addition of a set-retarder can alleviate the situation. Retarders extend the induction period of hydration process and lengthen the setting time. These may cause more regular and less porous microstructure. Regarding to this, microstructure-property relationship has an important effect on physical and mechanical properties such as permeability and strength.

Both inorganic and organic chemical substances can serve as retarders. The organic retarders include wastes from pulp production (sulfite waste liquor- SWL, sulfite-yeast waste liquor), hydroxycarboxylic acids (adipic, citric, malic, tartaric, etc.) and their salts, and also starch, proteins and sugars [2].

Some studies have been performed to investigate the effects of retarders on cement properties. Effects of sugar and calcium saccharates on the setting time and the heat liberation of concrete were investigated. It is found that syrup is a sufficiently reliable agent for retarding the time of setting. Also, the addition of syrup markedly decreases the rate of heat liberation of concrete, which can simplify considerably the technology of concreting and sealing the joints of massive structures. The observations are noted in the presence of organic retarder; the induction period lengthens and an increase in the level of calcium hydroxide before crystallization begins and a higher rate of heat liberation [2].

Properties of fresh cement paste such as fluidity and setting time were measured and heat evolution rate by hydration were estimated using cement pastes with different organic admixtures such as polycarboxylic acid, aminosulfonic acid, β -naphthalenesulfonic acid and lignin sulfonic acid. The retardation and the difference between the initial setting time and final setting time of cement paste prepared by later addition of admixture are larger than those by simultaneous addition [3].

Malic acid was added to ordinary Portland cement, indeed. The results show that malic acid is a strong retarder for the hydration of cement. Spectroscopic studies show that some sort of interaction occurs between malic acid and some mineral phases of ordinary Portland cement (silicate phase) leading to the formation of some new compound. The new compound formed may be responsible for the retardation of hydration of the cement [4].

Combinations of citrate, pyrophosphate and sulfate ions were used to modify the physico-chemical properties of calcium phosphate cement (CPC). This study indicates that not all admixtures are suitable for practical applications. Sulfate leads an increase in tensile strength. However, sulfate has a minor effect on setting time. Therefore, citrate and pyrophosphate should also be used. Because of their competitive interaction, mixtures of sulfate and citrate are inappropriate. Thus, mixtures of sulfate and pyrophosphate appear to be most interesting in controlling the physico-chemical properties of this cement type [5]. Therefore, several organic admixtures are used for retardation of hydration [6-11].

Hydration heats of cementitious materials have been studied in last decades. Therefore additions of chemical admixtures, finding their usage limits in concrete industry have been become more important. In this study, to define utilization and usage limits of some chemical admixtures have been investigated. Morphologies of these retarders were obtained by using SEM analysis. Also, the effects of retarders on the heat of hydration were obtained by calorimetry test.

2. EXPERIMENTAL

Cement pastes were prepared by adding organic admixtures with different ratios. The properties of organic admixtures are given in Table 1. Organic retarders were added in the mix with the ratios 0.2, 0.3 and 0.4 % of cement weight. Also, the morphologies of retarders were obtained by using SEM. The results show that citric acid has the smallest size between all admixtures. Tartaric acid has also an angular shape; however the particle size is smaller than tri-sodium citrate.

Table 1 Properties of retarders

Retarder	Molecular weight	Melting point(C°)	Density	Water solubility
Citric acid	192.125	153	1.542	10 g / 100 ml
Trisodium citrate	258.07	150	1.7	72 g / 100 ml
Tartaric acid	150.0878	170	1.7598	139 g / 100 ml

Ordinary Portland cement was obtained from Jura cement factory. The mineralogical, oxide compositions are given in Table 2 and Table 3, respectively.

Table 2 Mineralogical composition of cement

Phase	Composition (wt.%)
C ₃ S	51.17
C ₂ S	17.06
C ₄ AF	5.58
C ₃ A	13.0
CaO	0.26
MgO	3.3
Gypsum	1.6

Table 3 Chemical composition of cement

Oxide	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	K ₂ O	Na ₂ O	P ₂ O ₅	ZnO	Cl
Composition (%)	19.22	5.24	2.91	62.01	2.09	3.35	1.10	0.15	0.22	0.04	0.031

2.1. SEM and X-RD analysis

Morphology is one of the dominant characteristics of an admixture which provide the reactivity properties. SEM analysis was performed for each retarder and cement to obtain its morphology. The fracture specimen of each retarder and cement were prepared. Carbon evaporator was used to cover specimens by carbon.

Each specimen was investigated under SEM. Also, mineralogical composition of cement was obtained using Rietveld method by X-RD.

2.2 The heat of hydration

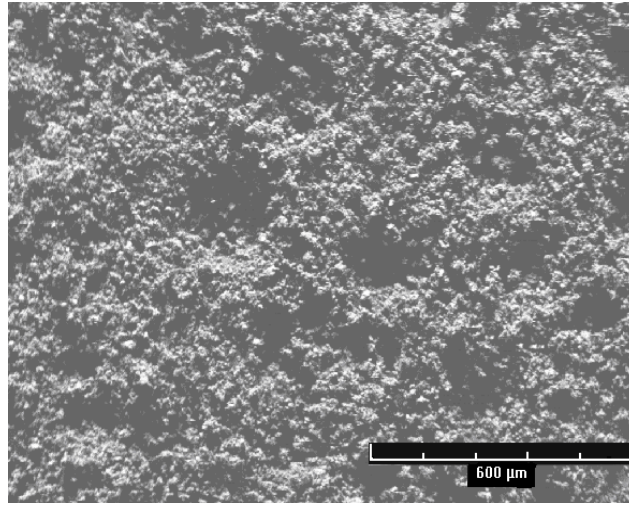
The isothermal calorimetry was used to obtain the heat of hydration of each mix. The mixes were examined in the isothermal calorimeter. The mixes were prepared by using the retarders with different ratios. The admixtures and cement were mixed before adding mixing water. The ratios are shown in Table 4.

Table 4 Retarder additions

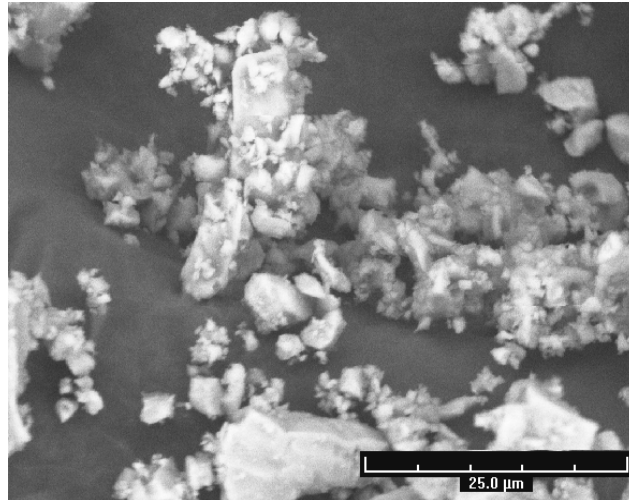
Retarder	Admixture content (%) by the weight of Cement
Tartaric acid	0.20, 0.30, 0.40
Citric acid	0.20, 0.30, 0.40
Trisodium Citrate	0.20, 0.30, 0.40

3. RESULTS

The fracture specimen of each retarder and cement was prepared. The SEM analyses were performed. The morphologies are shown below. The figures indicate that trisodium citrate has a smooth face and more angular shape. It is obvious that citric acid has the smallest size between all retarders. Tartaric acid has also an angular shape; however the particle size is smaller than tri-sodium citrate.

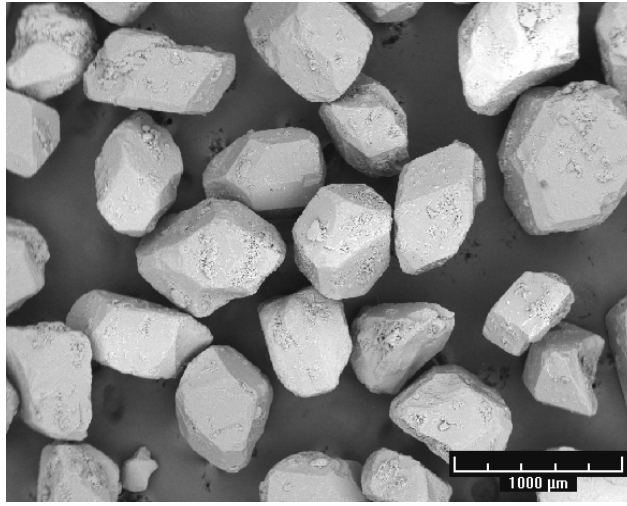


(a)

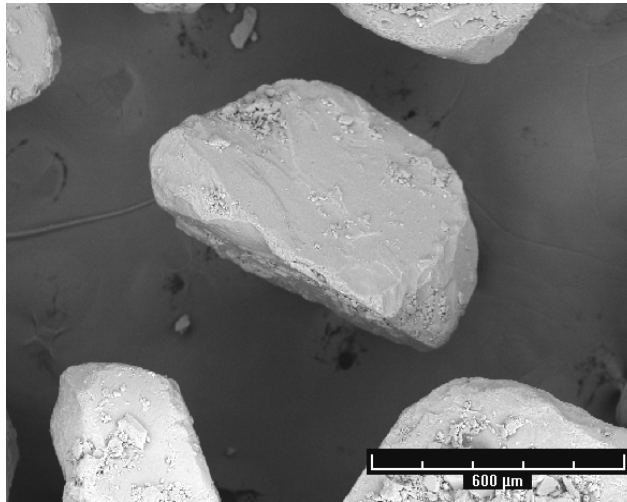


(b)

Fig. 1. Micrographs of cement for (a) magnification 160X (b) magnification 5000X

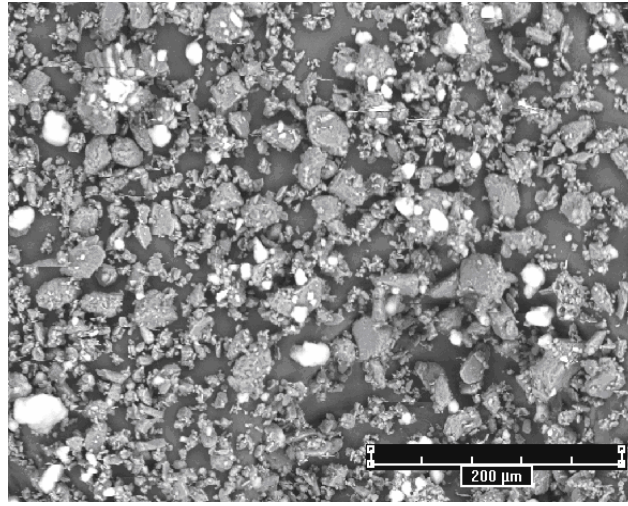


(a)

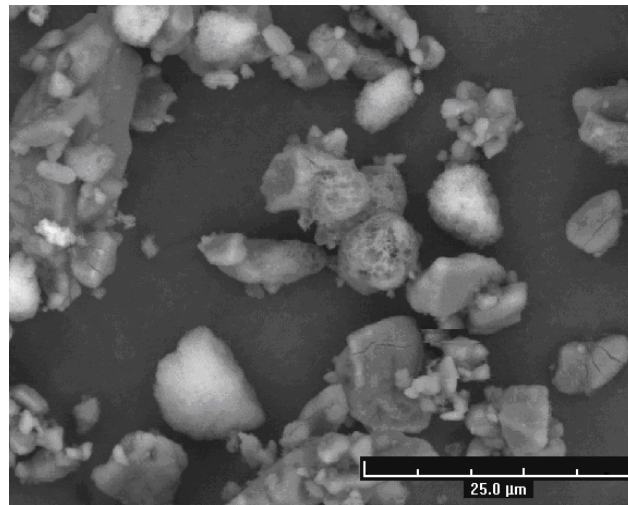


(b)

Fig. 2. Micrographs of Tri-Sodium citrate for (a) magnification 80X (b) magnification 200X

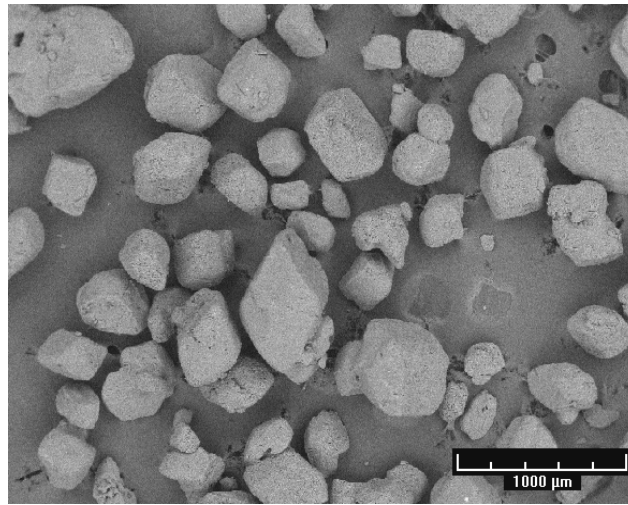


(a)

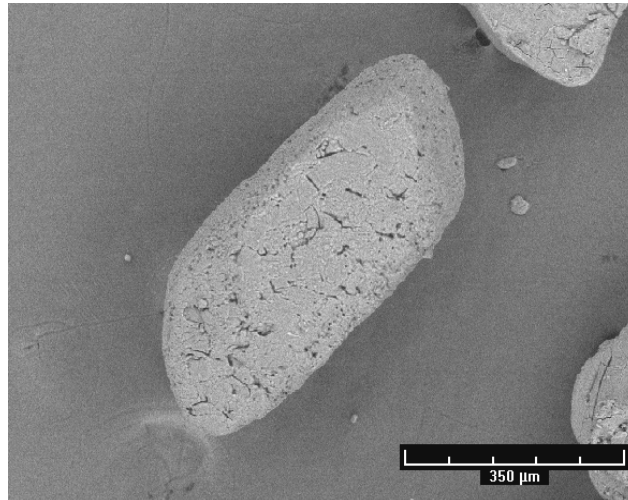


(b)

Fig. 3. Micrographs of Citric acid for (a) magnification 600X (b) magnification 3000X



(a)



(b)

Fig. 4. Micrographs of Tartaric acid for (a) magnification 80X (b) magnification 300X

The heat of hydration curves were obtained for each mix by isothermal calorimeter. The heat liberation graphs are given below. All retarders have a longer induction period than ordinary Portland cement does. The effect on retardation increases as the ratio of retarder in the mix increases. Calorimetric curves indicate that the higher the ratio of retarder in the mix, the lower the heat liberated at the beginning. Also, the ratio of retarder has the same effect on the peak of curves.

All retarders have a retardation effect, and decrease heat liberated during hydration. Tartaric acid has the strongest effect on the heat of hydration and hydration process. Trisodium citrate is shown more effective than citric acid. All retarders have different solution properties. Tartaric acid is the most soluble one in others. The solution property of each retarder has affected its retardation effect on cement paste. Also, size effect has a role on the retardation effect of a retarder. The liberated heat during hydration increases as the size of retarder decreases.

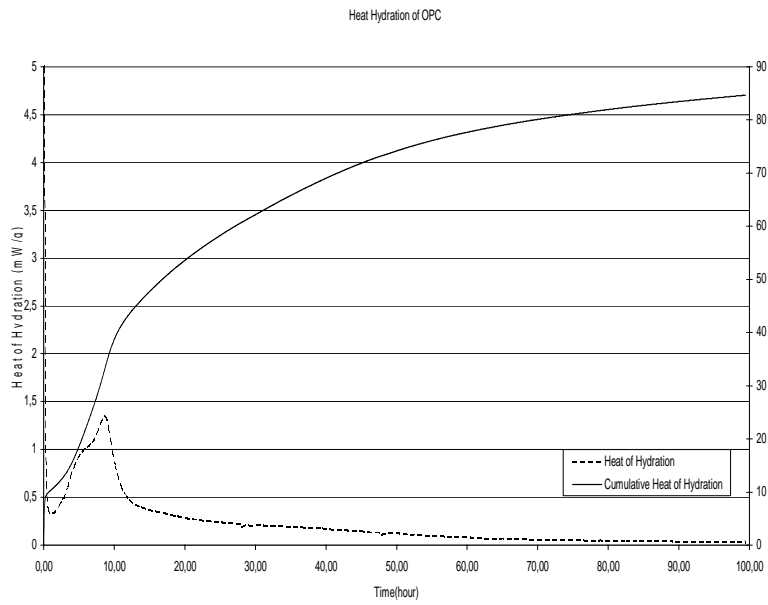


Fig. 5. Heat of Hydration of OPC

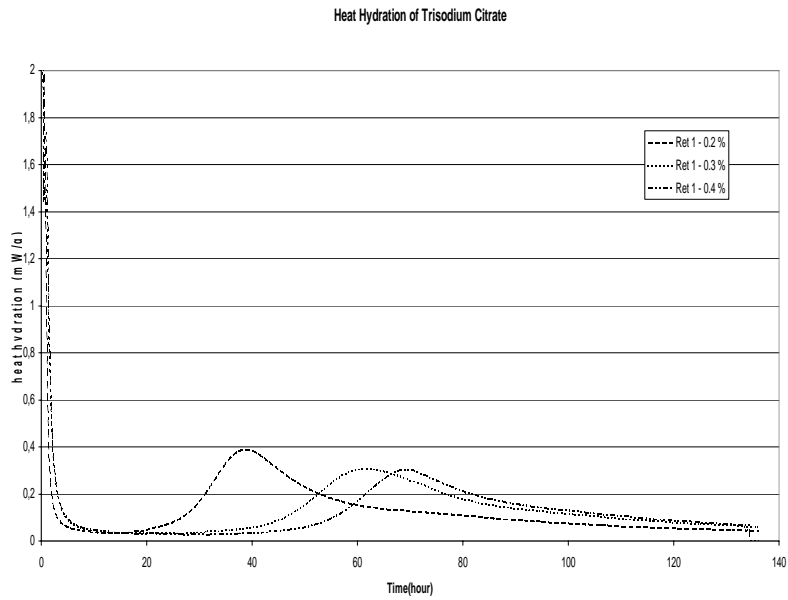


Fig.6. Heat of Hydration of Trisodium Citrate

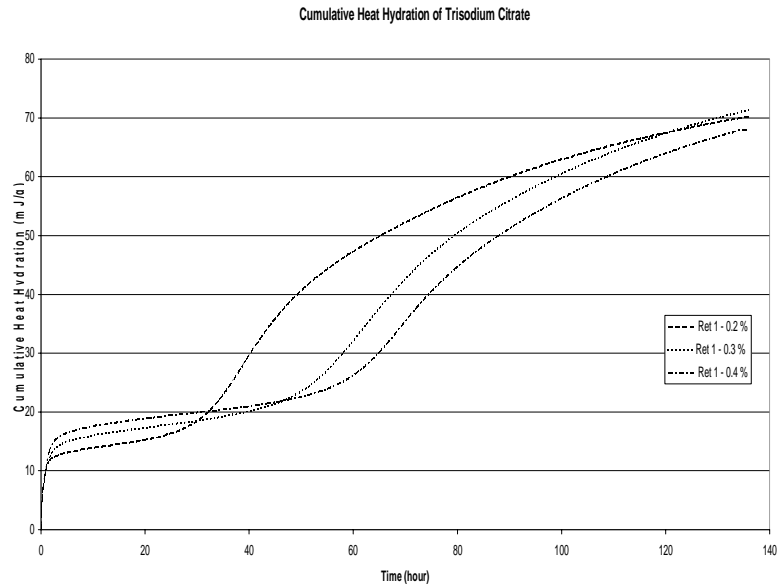


Fig. 7. Cumulative Heat of Hydration of Trisodium Citrate

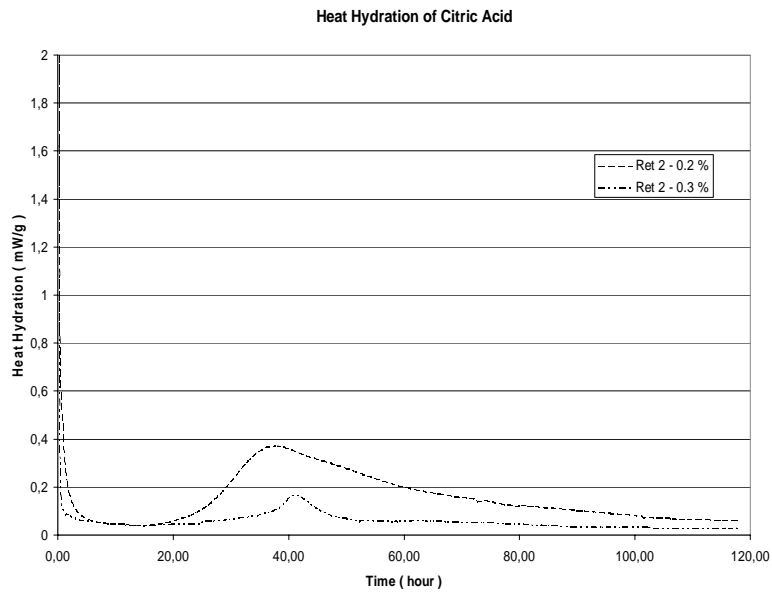


Fig. 8. Heat of Hydration of Citric Acid

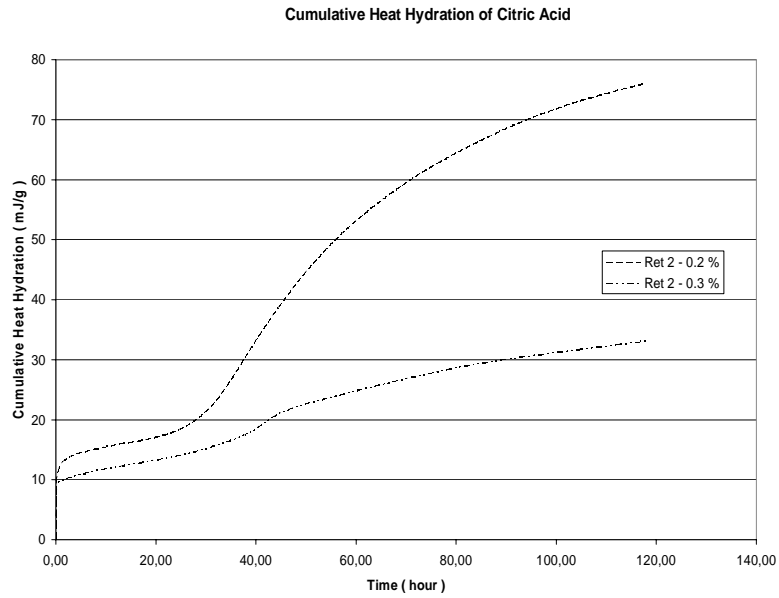


Fig. 9. Cumulative Heat of Hydration of Citric Acid

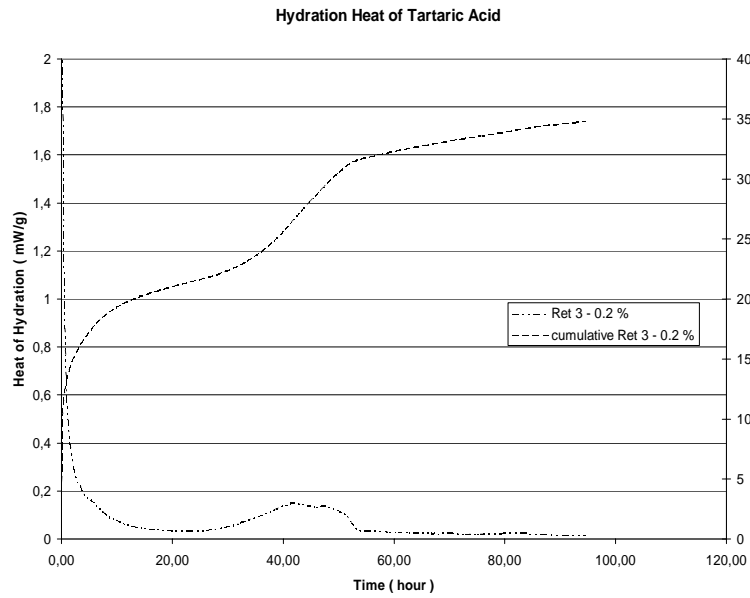


Fig. 10. Heat of Hydration of Tartaric Acid

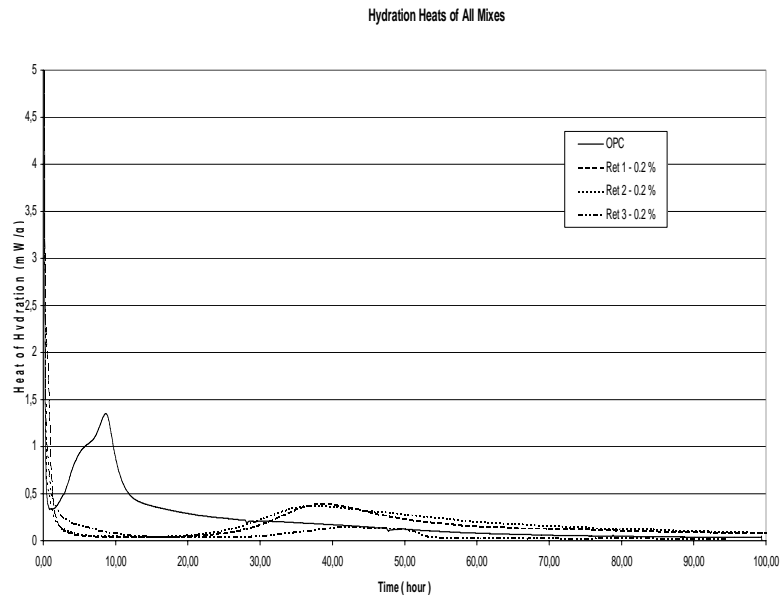


Fig. 11. Heat of Hydration of All Mixes

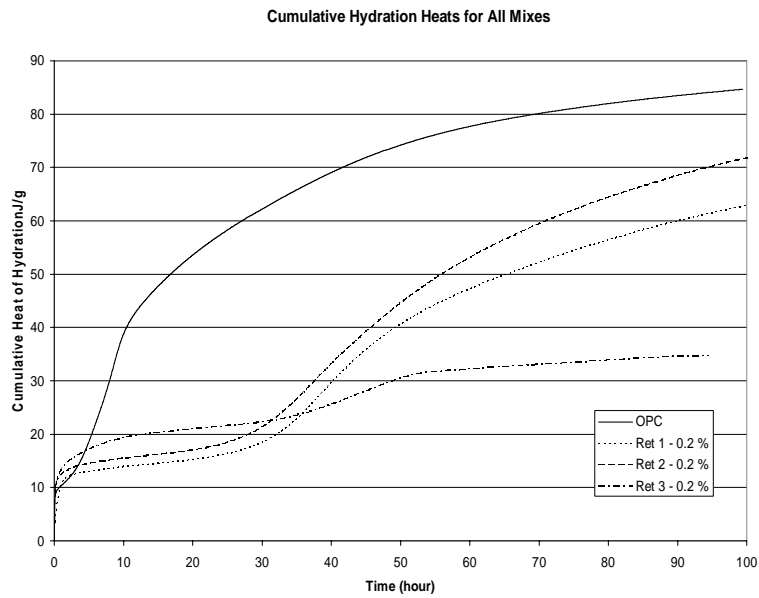


Fig. 12. Cumulative Heat of Hydration of All Mixes

4. CONCLUSIONS

Observation of utilization of new kinds of admixtures using in cement and concrete industry is one of the most required concepts in the new concrete production process. Admixtures such as retarders are needed for different conditions like hot weather concreting and concreting for large scale systems. Engineers should produce and define new admixtures. Chemical substances should be used in production new admixtures to get benefits against such conditions written above.

1. The morphologies are determined by using SEM techniques. The micrographs indicate that trisodium citrate has a smooth face and more angular shape and citric acid has the smallest size between all retarders.
2. All retarders have a longer induction period than ordinary Portland cement does. Calorimetric curves indicate that the higher the ratio of retarder in the mix, the lower the heat liberated at the beginning.
3. Tartaric acid is the most soluble one in others, it has the strongest effect. The solution property of each retarder has affected its retardation effect on cement paste.
4. Indeed, size effect has a role on the retardation effect of a retarder and, liberated heat during hydration process of cement increases as the size of retarder decreases.

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