STUDY ON SODIUM NITRATE AS ALTERNATIVE ADMIXTURE FOR OPC BASED BINDER

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ABSTRACT

Ordinary concrete refers to the ordinary Portland cement as a cementing material with water and admixtures which sometimes is added to a certain proportions according to the strength required and the function to be fulfilled. Nevertheless, the presence of high sodium Nitrate content in the source material can reduce the performance of cement paste binder, particularly in terms of its workability performance. This research studied the effect of sodium nitrate as the alternative admixture in Ordinary Portland Cement (OPC) based binder. Based on vicat setting time result, and these materials behave oppositely in cement paste and has an accelerating effect. Furthermore 90 samples a size 50mm x 50mm x 50mm, will be tested during the study where the test that carried out to measure the workability test, compressive strength test and porosity test at 1 day, 7 days and 28 days. In addition admixture Sodium Nitrate is 0.1%, 0.2%, 0.3%, 0.4% and 0.5% in cement paste. However, these results have presented an encouraging prospect for material to be developed as the admixture for cement paste.

ABSTRAK

Konkrit biasanya merujuk kepada simen Portland biasa sebagai bahan penyimen dengan air dan bahan tambah yang kadang-kadang ditambah dengan kadar tertentu mengikut kekuatan yang diperlukan dan fungsi yang perlu dipenuhi. Walau bagaimanapun kehadiran Natrium Nitrat yang tinggi dalam bahan sumber yang boleh mengurangkan prestasi pes simen pengikat, terutama dari segi prestasi kebolehkerjaan . Kajian ini mengkaji kesan natrium nitrat sebagai bahan tambah alternatif didalam Ordinary Portland Cement (OPC) pengikat. Berdasarkan vicat untuk menetapkan hasil masa, dan bahan-bahan ini bertindak berlawanan dalam adunan simen dan mempunyai kesan memperlambatkan proses pengerasan simen . Tambahan pula 90 kiub yang bersaiz 50mm x 50mm x 50mm akan diuji semasa kajian. Di mana ujian yang dilakukan adalah untuk mengukur ujian kebolehkerjaan, ujian kekuatan mampatan dan ujian keliangan pada 1 hari, 7 hari dan 28 hari. Selain campuran Natrium Nitrat adalah 0.1%, 0.2%, 0.3%, 0.4% dan 0.5% dalam adunan simen. Walau bagaimanapun, keputusan ini telah memberikan satu prospek yang menggalakkan bagi bahan untuk dibangunkan sebagai bahan tambah untuk tampalan simen.

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LIST OF ABBREVIATIONS

OPS	Ordinary Portland cement
ASTM	American Society for Testing and Materials
$NaNO_3$	Sodium Nitrate
C_3A	Tricalcium Aluminate
SO_2	Sulphur Dioxide
CSH	Calcium Silicate Hydrate
$CaCl_2$	Calcium Chloride
$CaNO_3$	Calcium Nitrate
$C_6H_8O_7$	Citric Acid
Al	Aluminium
W/C	Water Cement Ratio
Kg/m3	Kilogram per meter
Mm	Milimeter

CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

Cement paste is the most widely used construction material through the world and has gained a unique place in the construction industry. Workability, setting time, porosity and compressive strength of strength development, ultimate strength, durability and impermeability are among the most important characteristics of fresh and hardened concrete. The desired properties of fresh and hardened concrete can often be conventionally and economically achieved through intelligent selection of the basic concrete making materials.

The freshly-mixed and hardened properties of concrete may be changed by adding liquid (chemical) or mineral admixtures to the concrete, during batching. Admixtures are commonly used to (1) intentionally entrain air, (2) reduce water demand, (3) increase workability, (4) adjust setting time or hardening, and (5) adjust other concrete properties, such as strength. Common chemical admixtures include water reducers, set retarders and accelerators, air entraining, and super-plasticizers. Common finely-divided mineral admixtures are usually classified as either cementations materials (i.e. ground-granulated blast furnace slag and lime), or pozzolans (i.e. fly ash and silica fume).

In this project, it is a study of the on sodium nitrate as alternative for based binder. Sodium nitrate to be use in cement paste for particular attention has been given to the formulation of chloride-free set accelerating admixtures to replace the widely used sodium nitrate accelerator. As the alternative for the high cost of current admixture. The admixture Sodium nitrate were choose to be used as an alternative admixture for OPC based binder. Sodium nitrate ($NaNO_3$) was proposed as a basic component of a set accelerating admixture.

1.2 PROBLEM STATEMENT

As know, the chemical composition of which can easily be used as an additive. At the current price of commercial supplements are higher than other concrete component. Among the types of additives at this time should be reviewed to identify the factors that contribute to the strength of concrete with previous studies. At the present time the price of commercial supplements is higher than other concrete component. Among the types of additives at this time should be reviewed to identify the factors that contribute to the strength of concrete with previous studies. We want to know the details and how long and easy to do when really important for strength, simple really important to the 1, 7, 28 days concrete and simple really important to discuss the relationship between porosity and strength properties of the concrete.

1.3 OBJECTIVE

The objectives of this research are:

1. To determine the effect of Sodium Nitrate on the workability of fresh concrete.
2. To determine the effect of Sodium Nitrate on the compressive strength and porosity of hardened cement paste.
3. To determine the optimum amount of Sodium Nitrate that contributes to the Ordinary Portland Cement (OPC) binder performance.

1.4 SCOPE OF STUDY

This study is basically, related to the experimental investigation to observe the performance we will strengthen our sodium nitrate to test the strength of 1, 7, and 28 days. Additionally this study was to identify the level of hydration will be conducted at 1 and 7 days. Otherwise the porosity test will be conducted at 1 and 28 days. This study was performed to observe the effect and characteristic in sucrose and citric acid. Besides, it was also to test the performance of this additive will be based on Compressive Strength & Porosity Tests and Testing Workability.

This research will examine the concrete elements will be added, namely the study of Sodium Nitrate ($NaNO_3$). Compressive strength significantly more than most of the aggregate contained therein.

CHAPTER 2

LITERATURE RIVIEW

2.1 INTRODUCTION

That cement differing in chemical composition and physical characteristics may exhibit different properties when hydrated. It should thus be possible to select mixtures of raw materials for the production of cements with various desired properties. The hardened concrete could be considered as a three-phase composite material consisting of cement paste, aggregate and interface between cement paste and aggregate.

The load transfer mechanism between these phases depends on the type of cement paste, surface characteristics of aggregate. The bond between cement paste and aggregate depends largely on the interface zone characteristics. The cement-aggregate bond results from some combination of mechanical interlocking of cement hydration products with the aggregate surface and chemical reaction between aggregate and cement .strength of concrete is commonly considered its most valuable property, although, in many practical cases, other characteristics, such as durability and permeability, may in fact be more important.

2.2 Ordinary Portland cement (OPC)

Ordinary concrete refers to the ordinary Portland cement as a cementing material with sand, gravel, water and admixtures which sometimes is added to a certain proportions according to the strength required and the function to be fulfilled. During concrete mixing, the Portland cement paste and water will coats the surface of the fine and coarse aggregates.

The ordinary concrete is also adaptable to varying structural needs and is available practically anywhere as it is fire resistant and can be used by semiskilled workers. Choo (2003) has stated that there are many advantages of concrete such as built-in-fire resistance, high compressive strength and low maintenance. It has been widely used because of its rich resources of raw materials, simple production process, good performance, low price, high strength and durability and also can be combined with the reinforcement to produce a strong reinforced concrete structure.

However, since global warning has emerged as the most serious environmental and sustainability issue, the next development in the concrete industry will not be the new type of concrete manufactured with expensive materials and special methods but low cost and highly durable concrete mixtures containing largest possible amounts of industrial and urban by-product that are suitable for partial replacement of Portland cement, virgin aggregate and drinking water (Mehta, 2004).

ASTM C-150 describes five major types of Portland cement. They are: Normal Type I (when special properties specified for any other type are not required), Moderate Sulfate Resistant or Moderate Heat of Hydration-Type 11, High Early Strength-Type 111, Low Heat-Type N, and Sulfate Resisting-Type V. Ramachandran (1995).

The reactivity of CAF can be influenced by the amount of SO_2 ions consumed by C_3A. Some SO_2 ions may be depleted by being absorbed by the C-S-H phase. Gypsum is also known to affect the rate of hydration of calcium silicates. Significant amounts of Al and Fe are incorporated into C-S-H structure. The presence of alkalis in Portland cement also has an influence on the hydration of the individual phases. As a general rule, the rate of hydration in the first few days of cement compounds in cements proceeds in the order C3A > C3S > C,AF > C2S. The rate of hydration of the compounds depends on the crystal size, imperfections, particle size, particle size distribution, the rate of cooling, surface area, the presence of admixtures, the temperature, etc. Ramachandran (1995).

The minimum water-cement ratio for attaining completion hydration of ament has been variously give from 0.35 to 0.40, although completion hydration has been reported to have been achieved at water-cement ratio of 0.22.. Ramachandran (1995).

2.3 SODIUM NITRATE

Sodium nitrate (NaNO3) or "Chilean saltpeter", consists of white, hydroscopic crystals. It has a vapor pressure at 20 °C; melting point at 307 °C and boiling point at 380 °C (Young, 2002). Sodium nitrate is a strong oxidizing agent. It reacts violently with flammables, combustibles, many organic compounds and other reducing agents such as granulated or powered aluminum, magnesium, and other metals (Young, 2002).

Sodium nitrate application has been suggested in aquaculture ponds with several environmental and economic benefits such as its suitability as nitrogen source, and that it does not produce acidity by nitrification as an ammonium fertilizer (Boyd, 1997, 1995b). Conversely, adding nitrate to seawater may increase pH because of its dissolution process in seawater (Burford and Pearson, 1998). It is not toxic to fish and shrimp when used at moderate levels. The 96 h, LC 50 of nitrate on channel catfish fingerings is between 1,355-1,423 mg NO3- -N/L depending on temperature (Colt and Tchobanoglous, 1976). The main toxic action of nitrate is the result of the conversion of oxygen-carrying pigment to forms that are incapable of carrying oxygen (Camargo et al., 2005). It does not exert an oxygen demand. Sodium nitrate is a natural product manufactured by extracting it from deposits of the mineral caliche; thus, its production is not a fuel – intensive synthetic process such as used to produce ammonia by the reduction of atmospheric nitrogen or to synthesize urea from ammonia (Boyd, 1997, 1995b).

Since sodium nitrate is highly soluble and quickly dissolves in water; it would not be expected to accumulate at the soil surface if broadcast over ponds (Boyd, 1997). Nitrate generated by nitrification or added to ponds as an amendment will enter one of several biological pathways. Plants and microbes may absorb nitrate and reduce it to ammonia for amino acid synthesis in cells.

When dissolved oxygen concentration is low, nitrate may function as a terminal electron acceptor by denitrifying bacteria during the oxidation of organic matter. The nitrification results in the reduction of nitrate to NO, N_2O and N_2 or NH_3 and diffuse to the atmosphere (Hargreaves, 1998, Boyd and Tucker, 1998). Nitrate may penetrate deeper into the sediment than oxygen and create a larger pool of ferric iron than could be obtained by oxygen (Hansen et al., 2003). As a result, many theoretical advantages of sodium nitrate application, Seo and Boyd (2001) compared three different bottom soil management approaches; (1) dry-till treatment; (2) dry-till with sodium nitrate to maintain a high level of redox potential at the soil-water interface; (3) control (no drying, tilling or sodium nitrate application) on water quality in channel catfish Ictalurus punctatus ponds.

The results revealed that treatment ponds, dry, tilled bottom soil and dry, tilled bottom soil with sodium nitrate, had lower concentration of soluble reactive phosphorus, nitrate-nitrogen, total ammonia-nitrogen, total suspended and turbidity, and higher values of pH, Secchi disk visibility, total alkalinity, total hardness and calcium hardness ($P<0.01$) as compared to control ponds. Ponds of the dry-till treatment had lower concentration of total nitrogen and total phosphorus than control ponds. Concentration of dissolved oxygen and chemical oxygen demand did not differ among treatments. Organic carbon, total phosphorus and soil pH also did not differ among treatments.

These findings suggest that water quality improvement can be achieved by drying and tilling between crops. Applying sodium nitrate to dry, tilled pond bottom neither increased the extent of water quality improvement nor enhanced the ability of bottom soil to remove phosphorus from the water (Seo and Boyd, 2001). However, Yosoff et al. (2003) and Boyd et al. (1994) suggested that sodium nitrate is an oxidizing agent and may contribute to control the release of phosphorus and ammonia from pond sediment by maintaining oxidizing conditions at soil-water interface. Pavek (1998) reported that nitrate nitrogen, dissolved oxygen, pH, total ammonia- nitrogen and chlorophyll a were significantly higher in catfish ponds treated with sodium nitrate at dose of 5 to 10 mg/L NO3--N than in control ponds. Whereas, redox potential at the soil-water interface, temperature and soluble reactive phosphorus were unaffected.

2.4 ACCELERATION MIXTURE

A concrete accelerator was synonymous with an admixture increasing the 1 day compressive strength. It is only in the later years, with the implementation of the European standards that the industry distinguishes between setting and hardening accelerators, realizing practical utilizations of both admixture effects independently.

According to the European admixture standard EN 934-2 of 2001, a setting accelerator must give at least 30 min initial setting time at 20°C, and maximum 60% of the initial setting time of the reference at 5°C measured on mortar with equal flow. A hardening accelerator should give minimum 120% compressive strength compared to the reference after 1 day at 20°C, and minimum 130% compressive strength compared to the reference after 2 days at 5°C, as measured on concrete of equal flow. Requirements are set to long term strength and air also.

Calcium chloride, $CaCl_2$, was an ideal accelerator being a combined setting and hardening accelerator, in addition to being an industrial bulk product. However, in 1960's awareness on corrosiveness of chlorides on embedded reinforcement arose and today chloride containing admixtures is prohibited for steel reinforced concrete (limits are set to < 0.4% Cl- of cement mass, or < 0.1% for structures serving in chloride containing environment). In the search for a relatively cheap chloride-free accelerator, calcium nitrate, $Ca(NO_3)^2$, has arisen as an alternative setting accelerator, but it must be combined with other components to function as a hardening accelerator. Unless otherwise stated the calcium nitrate (abbreviated CN) referred to here is of granulated, technical quality with formula $xNH_4NO_3 \cdot yCa(NO_3)^2 \cdot zH_2O$ where x = 0.092, y = 0.500 and z = 0.826, or in other words composed of 19.00 % Ca_2+, 1.57 % NH_4+, 64.68 % NO_3- and 14.10 % H_2O. When testing accelerators, it is important to know that outcome may strongly depend on the composition of the Portland cement used. Justnes and Nygaard [1] published the set accelerating efficiency of calcium nitrate (CN) at 5-7°C on pastes (w/c = 0.40) based on 5 different Portland cements with a C_3A content ranging from 7.4 to 1.0 %.

The accelerating efficiency ranged from very strong to slight and there was no correlation between set accelerating efficiency and C_3A as initially assumed, but rather surprisingly with the belite, C_2S, content as plotted in Fig. 1. The correlation between belite content and set accelerating efficiency of CN was confirmed by Justnes and Nygaard [2] in a study of five other cement pastes at 5°C. Justnes and Nygaard [3] discussed the reason for acceleration efficiency differences among Portland cements by analyses of the liquid of cement pastes prior to setting. They found a linear correlation between the alkali content of the fluid of 9 cement pastes in the fresh state with the reduction in initial setting time when 1.55 % calcium nitrate was added, as reproduced in Fig. 2. In order to find out whether setting acceleration is dominated by the calcium cat ion or nitrate anion in $Ca(NO_3)^2$, Justnes [4] tested the efficiency of both calcium nitrate (65% NO_3- due to some crystal water) and sodium nitrate (73 % NO_3-) as set accelerators for 4 different Portland cements pastes at 5 °C by Vicat needle. The dosages were 0.00, 0.25, 0.50, 0.75 and 1.00 % calcium nitrate of cement mass, while sodium nitrate was dosed to give correspondingly equimolar nitrate content.

The influence on setting time is listed in Table 1. From this limited study, calcium nitrate seems in general to be a substantially better set accelerator than sodium nitrate for Portland cements. Specifically, Ca(NO3)2 gave shorter setting time relative to reference than NaNO3 in 10 out of 12 comparative tests and about twice or more reduction in setting time in 6 of the 12 cases. It seems like Ca2+ dominates setting, while NO3- may have an effect as well, depending on cement type. Temperature evolution profiles in insulated concrete (i.e. semi-adiabatic) and early compressive strengths for concrete cubes cured at 20°C have been measured for different additions of Ca(NO3)2 [5]. The concrete composition corresponded to w/(c+s) = 0.45 and 4 % silica fume replacement of cement for both CEMI 52,5R-LA and CEM I 42,5R.

The accelerating effect of Ca(NO3)2 was also compared to additions of calcium acetate, $Ca(CH_3COO)^2$, and format, $Ca(HCOO)^2$, at equimolar concentrations of Ca2+ for 3.5 % $Ca(NO_3)^2$ added to the CEM I 42,5R concrete. Calcium acetate and format gave about the same acceleration according to the temperature profiles in Figure 2.1, while $Ca(NO_3)^2$

showed greater accelerating effect in spite of soluble calcium ions dominating the set accelerating effect. The reason for the lesser efficiency of calcium salts of organic acids (i.e. format, acetate etc.) may be due to partial complex formation with one of the anions (e.g. $CaOOCCH_3+$), meaning that the overall chemical equilibrium of the paste fluid does not experience the same effective concentration of Ca_2+ ions as for $Ca(NO_3)^2$.

The temperature profiles in Figure 2.2 reveal that setting time is accelerated (criterion is 2°C above base line) and not the early strength development rate (i.e. temperature increase slope not steeper than reference) which is of importance avoiding thermal cracks in massive structures. Increased 8 h strength for HSC (CEMI 52,5R-LA) and OPC (CEM I 42,5R) concretes with increasing CN dosage is due to increased maturity at this early age due to the set acceleration. Another important parameter to control when testing accelerators is the temperature. Justnes et al [6] measured reductions in initial and final set at 5°C, 13°C and 23°C for cement pastes with 1.55% calcium nitrate and equimolar Ca dosage of calcium chloride hex hydrate, and compared them with neat cement pastes (two different Portland cements). The results revealed that the efficiency of calcium nitrate as set accelerator is higher at lower temperatures.

Table 2.1: Initial setting time for different cement pastes.

CEMENT TYPE	CEM I 42,5R	CEM II A-V 42,5R	CEM I 52,5R-LA	-
$Ca(NO_3)^2$ (%)	8.10 (100)	6.75 (100)	7.40 (100)	12.25 (100)
0.00	5.50 (67.9)	5.41 (80.1)	5.80 (78.4)	4.7 (38.4)
0.25	5.25 (64.8)	4.41(65.3)	3.00 (40.5)	7.5 (61.2)
0.50	5.33 (65.8)	5.83 (86.4)	4.60 (62.2)	3.8 (31.0)
0.75	4.30 (53.1)	5.70 (84.4)	1.80 (24.3)	4.0 (32.7)
$NaNO_3$ (%)	5.60 (69.1)	5.15 (76.3)	6.10 (82.4)	8.33 (68.0)
0.25	5.55 (68.5)	6.55 (97.0)	5.40 (73.0)	6.33 (51.7)
0.50	6.00 (74.1)	7.52 (111.4)	4.80 (64.9)	5.00 (40.8)

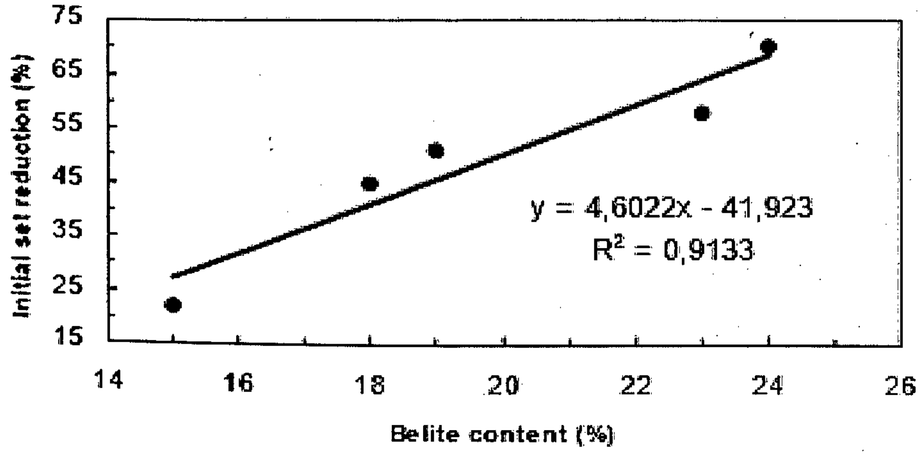

Figure 2.1: The linear correlation between accelerating efficiency of 1.55 % CN additions of different cements and their belite content.

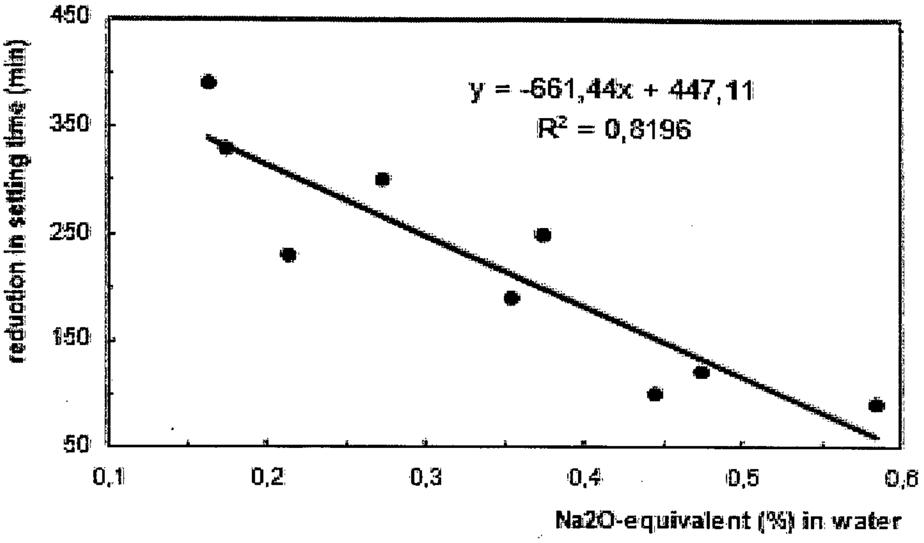

Figure 2.2: The reduction in setting time for Portland cement pastes when 1.55 % calcium nitrate is added vs. the alkali content of the liquid phase 20 min after mixing.

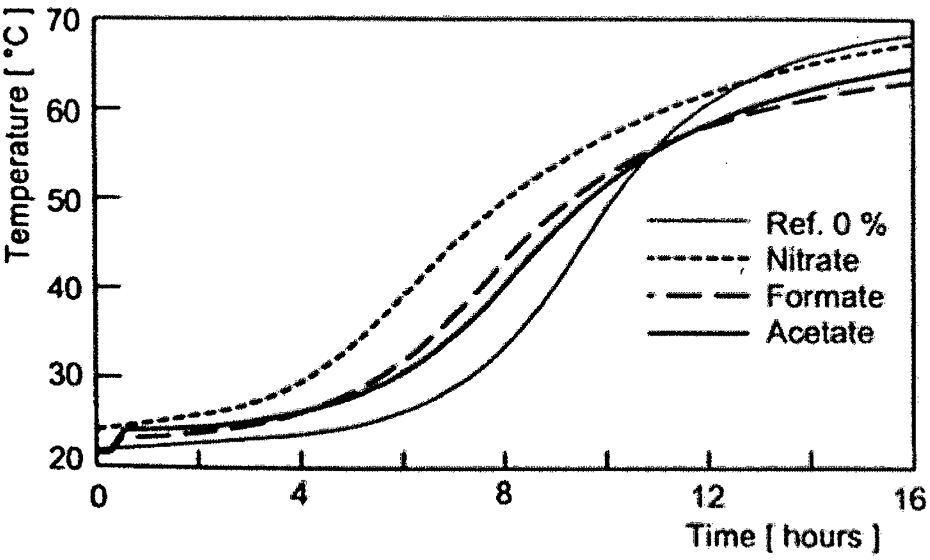

Figure 2.3: Temperature vs. hardening time curves for OPC concrete with equivalent dosages of soluble calcium from nitrate, acetate and formatted compared with reference concrete.

2.5 CITRIC ACID

Citric acid can be used to retard the hydration of cement. Experiments were carried out to investigate the influence of citric acid on the composition of solid and liquid phases during cement hydration. Analyses of the solid phases showed that dissolution of a lite and aluminate slowed down while analyses of the pore solution showed that citric acid was removed almost completely from the pore solution within the first hours of hydration.

Citric acid ($C_6H_8O_7$) is added to concrete formulations to retard the set rate and reduce the amount of water required. In the retarding the set rate, the Citrate interferes with the hydration of Portland cement. In its role as a water reducer, citrate acts as a dispersants, reducing the viscosity of the cement slurry so less water is needed to make a workable mixture. The complexion of the ions by citrate was weak, which could also be confirmed by thermodynamic calculations. Only 2% of the dissolved Ca and 0.001% of the dissolved K formed complexes with citrate during the first hours. Barbara Lothenbach et.al (2009).

Thus, citric acid retards cement hydration not by complex formation, but by slowing down the dissolution of the clinker grains. Thermodynamic calculations did not indicate precipitation of a crystalline citrate species. Thus, it is suggested that citrate sobbed onto the clinker surface and formed a protective layer around the clinker grains retarding their dissolution. Barbara Lothenbach et.al (2009).

2.6 SUCROSE

The performance of sucrose in cement hydration, including both the early structure formation and further development of cement paste under different curing temperatures, was studied by measures of setting time, heat evolution, resistivity evolution, compressive strength, and porosity. The results showed that there was a critical dosage of sucrose. When the dosage was less than, the retarding effect was enhanced by increasing the dosage. Greater than T0, sucrose became less retarding and even became accelerating. Increasing the curing temperature decreased the critical dosage. When the dosage was less than 0.08%, sucrose showed less retarding effect at 40°C than at 20°C, but better retarding effect at the dosage of