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PERFORMANCE STUDY ON CEMENTS

ABSTRACT

Protection of concrete against physical, chemical and mechanical effects is directly associated with the properties of materials mixed into its compound and mixture. Among them, cement has a distinctive role. When cement is investigated both as a compound of the concrete and the paste, it is quite significant in terms of durability, service life and aesthetics. The greatest problem of cement usages is cracks negatively affecting both the subjective properties and the properties of aggregate used with it. The type and amount of cement used in a concrete, physical and chemical properties, hydration process, mixing method and technique, its relation with aggregate and water and additives depending on the time factor, have an effect both on functionality and visual performance. In this study, key words such as adherence, workability and cracking were taken into the center by dwelling on the cement subject, and the possible problems were offered a solution in terms of cause and effect relationship.

Keywords: Cement, Concrete, Physical and Chemical Properties, Performance

1. INTRODUCTION

"About 2000 years ago, Romans began to use a hydraulic binder similar to properties of today's cement by mixing burnt lime with volcanic ashes (and later with the fine-grained material obtained from the burnt clay). In 1824, a masonry master named Joseph Aspdin obtained a hydraulic product by baking and grinding the fine-grained limestone and clay mixture. In 1845, a British man named Isaac Johnson also obtained a product similar to today's Portland cement" (Erdoğan, 2004). The history of geopolymer cements and concretes dates back to 7000 B.C. It is known that the Ancient Greece and Roma implemented the lime and then lime+clay+volcanic ash on the castles. According to an article published at OMNI journal by D.Starr, Egyptian workers; transported fine-grained limestone to the construction site, mixed it with silts (aluminium silicate) which is the deposit of Nile river, using the salt found in the area as a catalyst to provide alkali transformation and dried the molded mixture in the hot desert sun (Starr, 1983). Dr. J. Davidovits supported this theory with similar studies (Davidovits, 1987). Cement that is suitable for designer's demand and that has proven abilities to gain durability and strength in accordance with the surrounding conditions must be employed for concrete manufacturing. The cement should be handled as prescribed in the standard and preserved in such a way as not to lose its properties. There are a lot of factors causing concrete to be

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deteriorated and damaged in the structures. Some of these are internal factors and others are external factors. The reaction of materials containing lime and gypsum in the compound of concrete can be considered as internal, water and moisture as well as sulfates and acids, atmospheric effects, freeze-thaw effects, salt crystallization, fire, corrosion, chlorine can be considered as external factors. Beyond mold and laying techniques, attention should also be paid to the properties of the material mixture and composition so that the concrete can have the desired properties in the outdoor environment. The type, properties, amount, correct usage in the right place of the cement being used in concrete manufacturing, significantly affects the properties of concrete. These are reflected in the final quality of the concrete.

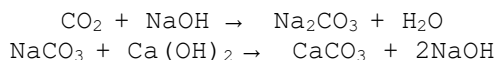
2. RESEARCH SIGNIFICANCE

The greatest problem of cement usages is cracks negatively affecting both the subjective properties and the properties of aggregate used with it. The type and amount of cement used in a concrete, physical and chemical properties, hydration process, mixing method and technique, its relation with aggregate and water and additives depending on the time factor, have an effect both on functionality and visual performance. In this study, key words such as adherence, workability and cracking were taken into the center by dwelling on the cement subject, and the possible problems were offered a solution in terms of cause and effect relationship.

3. FACTORS AFFECTING CEMENT PERFORMANCE

3.1. Mixture and Compound in Cement

The differences in the baking processes and raw materials in cements cause color differences. Solution is to use cements produced in same factories and that has same serial number on mass concrete applications. In the main raw material to be put in cement, type, amount and effectiveness of chemical or mineral additives are different for every cement type. For this reason, cement produced by a factory in any region is absolutely different from cement produced in a different factory and different region. Raw materials entering cement production CaCO_3 and Al_2O_3 and $\text{Ca}(\text{SO})_4 \cdot 2\text{H}_2\text{O}$ (gypsum) added in the grinding stage are heterogeneous materials extracted from nature. 0.03% carbon dioxide gas in the air reacts with hydroxides in the concrete to form carbonates. CO_2 does not react immediately with $\text{Ca}(\text{OH})_2$. If there is no alkali oxide in the cement (which of course is not possible), there will be no carbonation. First, Na_2CO_3 is formed, this salt reacts with $\text{Ca}(\text{OH})_2$ to form CaCO_3 , which is the salt causing carbonation, the NaOH comes out again and the event becomes continuous (Cilasun and Aksoy, 2000). Carbonation in cement causes corrosion on reinforced concrete steel. This event has two aspects. First, it creates proper electrolyte medium by filling cavities with water on concrete resulted from carbonation and volume expansion, separation of steel via electrolyzing, and the other is the transformation of the CaCO_3 environment itself to an aggressive corrosive chemical on metals.



There is a relationship between the corrosion and the structure of the cement in reinforced concrete bars. In the production process of cement, due to the improper raw material proportions, the types and amounts of oxides that formed are directly related to corrosion. Among



these oxides, MgO causes a certain unfavorable condition in terms of internal corrosion as the amount of $0.658 \text{ Na}_2\text{O} + \text{K}_2\text{O}$ (soda + potash) (alkali), which is called alkalis with SO_3 , is being above the limit values stated in TS EN 197-1. The excess of MgO causes capillary cracking due to volume expansion in the gel structure of the cement. The presence of SO_3 is caused by the excess of gypsum content in the production stage of the cement, which leads to the formation of the ettringite salt ($\text{C}_6\text{A}\text{S}_3\text{H}_{32}$). Ettringite is a white substance taking place during cement hydration that has a structure which can be dragged onto the concrete surface via decomposition with water. During this drag, it causes voids in the internal structure, causing white coloration on the concrete surface and accelerates (causing sulfate effect) the corrosion in the iron reinforcement. The instability of the amount of

CaO in the oxides formed in the cement will cause the formation of $\text{Ca}(\text{OH})_2$ in the cement, which will cause carbonation of the concrete by taking CO_2 from the air. In this formation, the carbonation products cause white spots on the concrete surface due to the dissolution by forming weak texture in the cement/concrete, reaching the iron reinforcement by volume expansion. There can be an occurrence in concretes called aggregate-alkali reaction. In this reaction, the capillary cracks occur in which factors affecting are aggregate and cement. The excess amount of alkali in the composition of the cement or the use of the inactive high alkali cement and being the kind of silica in the aggregate that can be deteriorated by the alkali effect is the main effect in the formation of the relevant cracks. Such negativity is usually seen in dam structures over 5 years old (Cilasun and Aksoy, 2000). "The sulphates and acids that can be found in the environments where the concrete is poured, will cause the cracking of the concrete with chemical effects" (Erdoğan, 2004). It is a common widespread view that salts such as sodium chloride, magnesium sulphate, and sodium sulphate decompose C_3S of the main compounds of cement during hydration of cement and concrete. Salts penetrating into hardened concrete could cause cracking in the cement by crystallization and volume expansion.

3.2. Cement-Aggregate Relation

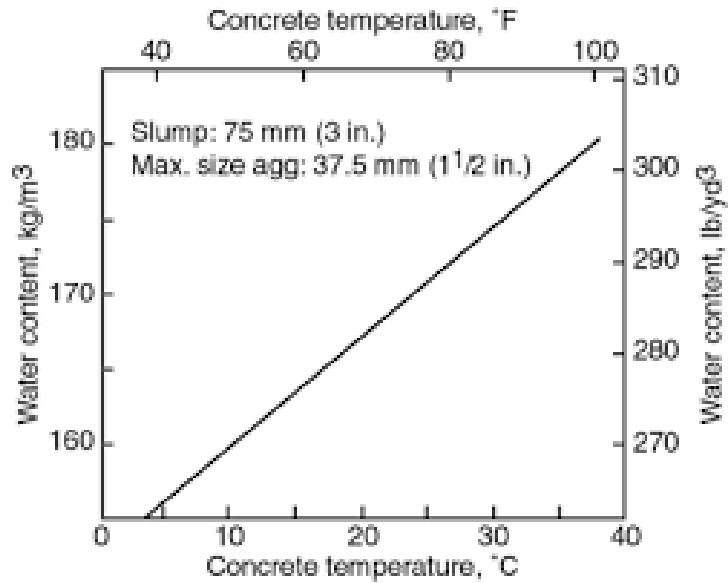
The aggregate to be used in concrete should comply with TS EN 706 12620 standards while taking the usage and environment of the structure into consideration. Due to its significant effect on concrete properties, the aggregate to be used should be determined by testing in advance whether it is appropriate or not. The amount of cement to be used in the granulometric (graded) aggregate structure will be optimum. The aggregate and cement interface connection (adherence) is directly related to aggregate surface roughness. Adhesion is maximum, provided that the surface is not dusty in angular aggregates. Adherence between cement paste and aggregate is related with the purity of aggregate. Clay on the aggregate surface, the presence of substances like silt resulted with crackings taking place on the intermediary surfaces. Especially, it is dangerous for cement with Al_2O_3 (aluminum oxide) structure to indicate a cracking character and to bring slippery when combined with water. Concrete strength is explained by the case of cement paste and aggregate bond strength and cement paste-aggregate bond strength (Uğurlu, 1999). There is a fact that the bond between the cement paste and the aggregate affects huge amountly the mechanical behavior of the concrete and it shows that this contact surface is a weak connection (Shah, et al., 1994).



3.3. Cement-Water Relation

Mixed water and curing water play an important role in achieving the targeted strength in concrete. The differences in water quantity, quality, and method of addition directly affect the quality of the concrete. While 30N/mm^2 of strength can be obtained by using 160kg/m^3 of water at an air temperature of 10°C with an aim of 7.5cm slump (Figure 1), the concrete with the same slump amount requires 175kg/m^3 of water at 32°C on hot weather. In short, for the concrete with the same velocity, approximately 15kg/m^3 more water will be needed in summer. In cases where the rate of outflow (bleeding) of the water inside the concrete is slower than the evaporation rate, factors such as air temperature and wind, relative humidity, cause drying shrinkage and cracks in the cement matrix. For this reason, the evaporation rate of the water in the future should not exceed $1.0\text{kg/m}^2/\text{hour}$ (Figure 2) (Erdoğan, 2004). If we look at the relationship between the different curing temperatures and the compressive strength, it has been found that the compressive strength of the cement/concrete cured at 4°C is stronger than those cured at higher temperatures (Mindess and Young, 1981). The concrete temperature illuminates the rate at which the hydration can take place. The length of elapsed time after the placement of a concrete illuminates the extent to which the hydration of the concrete will progress (maturation). Maturity is the function of the multiplication of the curing duration and the concrete temperature. The minimum curing time recommended by the American Concrete Institute (ACI 308-92) is 7 days and should be kept longer for concrete with a temperature below 4°C . The duration of curing in pozzolana cement is 2-3 weeks. "Concretes should be cured by steam. The maximum temperature of the steam is about $40\text{-}80^\circ\text{C}$. Since the elapsed time being momentary to increase the temperature of the concrete to ambience temperature and it will adversely affect the pressure strength. It is desirable that the temperature increase would be about $22\text{-}33^\circ\text{C}$ per hour and the time spend on steam curing should be maximum 18 hours since the time is too short for concrete temperature to increase to ambience temperature. Steam curing implemented concrete is a bit more permeable than those cured on standard conditions. However, decay and shrinkage rate is $1/3$ less (Neville and Brooks, 1987). Concrete can be cured at temperatures between 160 and 220°C under autoclave at $6\text{-}10$ atmospheric pressure. A concrete structure element placed in a pressure boiler called autoclave for steaming and cooling processes are subjected to a certain procedure. For instance, it should reach 50°C at the end of the first hour, 100°C at the end of the second hour and $160\text{-}185^\circ\text{C}$ temperatures at the end of the third hour. The time that spent at maximum temperature and curing temperature is about $7\text{-}10$ hours. This long-term application of maximum temperature results in the formation of crystalline calcium-silicate-hydrates and low strength in the structure. Emptying the autoclave should be done at a slow pace. The cooling time is about 2 hours. Otherwise, there will be strain differences and cracks in the inner structure. The 28-day compressive strength of a cured concrete under normal conditions can be obtained in 24 hours by autoclave curing method (Erdoğan, 2004). "Curing at high temperatures to normal concretes reduces compressive strength. However, in ultra-high strength concrete (due to internal structures) pressure strength will be positively affected and increases" (Şahin, et. al, 2015).

Figure 1. Effect of concrete temperature on mixing water requirement



in concrete content (Erdoğan, 2003)

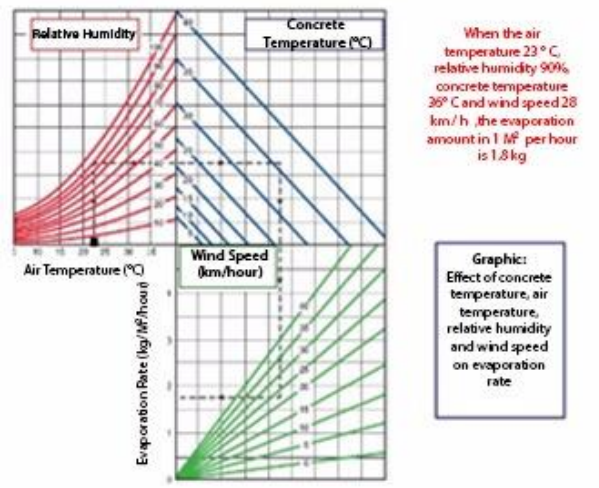


Figure 2. Relation of concrete temperature, air temperature, wind speed relative humidity, ambience temperature with evaporation rate of concrete (Erdoğan, 2003)

There is the possibility of water to be freeze, expand and create voids in the concrete poured in cold weather/climates. With the increase in the number of freeze-thaw cycles, cracks in the internal structure of the concrete may occur. This also applies to abnormal weather (rain, wind and hot sourcing). The water to be used in concrete must comply with the associated standards. Mixed water should not be acidic (pH should be below 7); it should not contain harmful amounts of carbonic acid, manganese compounds, ammonium salts, free chlorine, mineral oils, organic substances and industrial wastes. It can contain 15g of dissolved and 2g of mineral salts as a supernatant and 2g of SO₃ at the most per litre. There is a three-way disadvantage of the amount of water to increase in the fresh concrete by moving towards onto the upper part of the concrete surface. First, due to the weather conditions, water freezing on the surface and expanding its volume by up to 12%, causes concrete to increase planar capillary cracks and to have low strength in concrete. Second, due to increased



permeability, the penetration of acidic, sulphated water into concrete increases. And the third issue is the dragging of mineral-based thin materials that have not reacted with the upwardly moving water, negatively affecting the interface connection between the aggregate and the iron reinforcement. Since the water on the concrete surface will evaporate faster than the internal structure, it causes to form plastic shrinkage cracks on the concrete surface. The concrete temperature sheds light on at which speed the hydration can take place. The water that has entered the concrete composition must remain in the concrete as much as possible so that the hydration process can continue. The loss of water from the concrete through bleeding should be seen as a problem. Corrosion products formed in reinforced iron equipment cause the concrete to crack and break due to the increase in volume by expanding the concrete contacting with the steel (Erdoğan, 2004).

3.4. Cement-Time Relation

One of the important issues in the firing process of the cement is the relationship between the duration of the firing and the temperature and length, in a 3-4% inclined rotary kiln. A certain time passes depending on the rotational speed of the rotary kiln with a length/diameter ratio of 30 with 60-120m height. Firing times of the materials moving from the top down are subjected to changing temperatures. Since at the top point of rotary kilns have a temperature of 100-150°C and a bottom point temperature of 1500°C, a wider review can be made of how long the clay, limestone and mud should be cooked in the boiler, at what temperature it should be cooked. In the firing procedure before mixing, first, the mixture is loaded pre-heating systems and enters the rotary kiln after cooked there about 800-900°C temperatures. The prolonged waiting time of the produced cements and unfavorable storage conditions cause problems of strength. There is a loss of strength of about 4% per 28 days period after the first three months. It is extremely difficult to be sure of the quality control when cement is stored 6 months to 1 year in advance of construction and when the remaining cement is waited for another job for 6 months to 1 year after the end of construction. Overall pressure resistance of cement produced in Turkey is determined by 2, 7, 28 days and as CEM I 32.5, CEM I 42.5 and CEM I 52.5; added cement is only as CEM II 32.5; and the start and end times of the initial setting are determined to 1-10 hours as the volume expansion to be at most 10mm.

3.5. Cement-Additive Relation

The chemical additives which are used for lubrication between the aggregates in concrete are produced by many companies. The differences in the composition of the chemical additives affect its efficacy. For this reason, there is a relation between the amount of chemical additive and the mixing time of concrete. The mixing time of a concrete that has chemical admixture to be prolonged means that the slippery chemicals in the structure are absorbed more by the aggregates and the efficiency is reduced. Adding an excessive amount of chemicals, the presence of chemicals that are absorbed in the free environment or in the aggregate can have adverse effects on the main components of the cement and prevent the formation of healthy reaction between cement and water. In fresh concrete, hydration heat arises after the reaction of cement with water. This heats scarcity or abundance depends on the heat, amount and convenience to standards of the curing or mixing water, types, and amounts of chemicals with its



addition procedure and technique and cements refinement. For example, there is a relationship between air entraining chemicals and cement temperature. Providing that the same amount of air entrainment is used, less air is entrained in concretes with a higher temperature than those with lesser temperatures (Erdoğan, 2003).

The temperature of concrete can be caused by newly produced cement or by environmental conditions. Consequently, the temperature of fresh concrete mixes must be controlled by the formulas in the technical literature. Raising the cement fineness above the minimum 2800cm²/g required by the standards leads to an increase in hydration heat which is an indication of good chemical growth. The negativities in applications, mixes and compositions cause problems in the start and finish time of setting in concrete production, decrease in strength and increase in negativities such as shrinkage and creep. Air-entraining chemicals, which make air bubbles, are added (to increase workability) to allow the concrete to fill the mold with maximum compactness without wasting. On account of the bubbles acting as a kind of air cushion, the concrete can be filled with the mold by sliding over each other. With air entraining additives it is possible to add less water to the concrete and to give higher strength to the concrete. In addition, by decreasing the bleeding on fresh concrete with air bubbles the number of voids to be formed by aggregate grains or beneath bleeding equipment decreases and the concrete becomes impermeable. One of the main problems there is the possibility that the air bubbles formed in the concrete to be thrown out during the concrete vibration. Another issue is the ability to obtain close-grained concrete by throwing out the bubbles via vibration. Since the effect of air-entraining chemicals added in concrete is not consecutive and indefinite, the benefit lies in the initial placement of concrete. Pozzolans can be used by activating with alcalis in the production of concrete and mortars without using cement. For example using the zeolite and silica fume, which is a natural waste, can be possible by activating with sodium hydroxide on varying amounts of different molar values (which is cured at 60°C for 24 hours) while taking the shrinkage and durability of the samples into account (Koçkal and Oğuz, 2015). The majority of fly ashes has high lime content. Its features vary from plant to plant. Class C fly ash with high lime content does not cause a significant impairment in the volumetric stability of the concrete in the case of high usage. Superplasticizers with setting accelerating properties should be used in the operations with fly ash added cement because they increase the settling time.

3.6. Hydration Process on Cements

Cement is known as hollow dry disperse material. As it is cooked at very high temperatures, it is in a great tendency to merge with water. When combined with water, it becomes paste and the chemical reaction begins. In the reaction, with the effect of emerging heat, the proportion of the water between the cement particles evaporates and cohesion (internal attraction) is formed between the particles. Oxides like MgO and SO₃ occurring from the internal attraction on the one hand and chemical reaction on the other causes volume expansion by entering into cement particles and intricate structure through particles pushing each other. Meanwhile, the tobermorite gels resulting from the reaction of oxides with each other (C-S-H) causes to bond them together by filling the gap between grains. The reactions between cement and water are not abrupt due to 2-6% ratio gypsum added in the composition during the production of the cement. During the



hydration process, pozzolan can have an important function in terms of settlement period and chemically. For example, "Portland-pozzolana type cement-based concrete strengths to sulfates are greater than that is Portland cement-based" (Erdoğlan, 2004).

Pozzolans, natural or artificial, are silica or silica and alumina mineral based materials that are non-binding by themselves but become useful compounds when combined with the calcium hydroxide of the cement composition. In order for a mineral-based material to be used as a pozzolan, the material must be amorphous. When the clay is cooked, the crystal structure is distorted into an amorphous structure. In addition, SiO_2 , Al_2O_3 and Fe_2O_3 must be 70% or more in total and its activity index and test must be positive and it must be fine grained. According to ASTM C618, cements with pozzolana must have 7 and 28 day pressure strength of 75% more than cements that have no pozzolana. Clinkers have main chemical compounds and they have (%) values. [$2\text{CaO}.\text{SiO}_2=\text{C}_2\text{S}$), $3\text{CaO}.\text{SiO}_2=\text{C}_3\text{S}$), $3\text{CaO}.\text{Al}_2\text{O}_3=\text{C}_3\text{A}$) ve $4\text{CaO}.\text{Al}_2\text{O}_3.\text{Fe}_2\text{O}_3=\text{C}_4\text{AF}$]. All possible behaviors of the cement are determined by these compounds. Whichever the compound is high, the cement will carry the properties of that compound. The amount of salt (Cl^-) contained in the chemical composition of cements being higher than the limit given by the standards (0.1%) destroys the main compounds. This means that the mixed water of cement/concrete, both the raw material and the amount of Cl^- resulted from water should not be above the relevant standard data. Salt containing aggregates should be used in concrete. Five types of cement have been formed as their types and amounts of main compounds differentiate which can be found on market (Table 1). Their hydration temperatures are also different. The use of chemical additives beside mineral additives in concrete mortars improves their ability to be processed and ability to permeate. In the case of the use of mineral additives (pozzolanic), the expansion generally decreases (in crushed sandy mortars) rapidly after 900 °C, the thermal expansion coefficients decrease and changes to shrinkage state and the compressive strengths became zero by total deflection (Topçu et. al, 2015).

The Blaine fineness is one of the most important issues in cements. Increasing the fineness means shrinking cement grain size, expanding the subject surface area and increasing water requirement. As a matter of fact, the grains that has excessively increased fineness start to hydrate by taking moisture from the air which causes the cement to be deteriorated by hydration. "It is stated that the increase in cement fineness has a positive effect on the concrete strength to a certain level but not a significant change in the strength values after that level" (Delibaş et. al, 2015).

3.7. Cement as Architectural Aspect

White cement production should be seen as an advantage. Ability to give color by adding pigments, giving different surface finishes and textures creates visual richness in architectural concrete. The type of coloring chemicals and chemical bond that cement will make is important. As paint, basic soil dye or oxide dyes or modern nanotechnological dyes can be used. Basic soil dyes are not preferred because they are not a standard production and cannot provide color stability. "Pigments are mineral based oxides. If used together with other chemical additives (the process of protection of the pigments in a homogeneous and fine-grained dispersion state in the carrier medium), it is recommended to apply water reducer additives to increase the dispersion of the pigments and to prevent surface decomposition and to apply surface hardeners as a final step to



increase the wear resistance of the surface" (Mindess, 1981; Karagüler, 2002). Closing the stem holes in the gross concretes is another problem. When the holes are covered with normal cement mortars/pastes, two problems can be seen. The first is that cracks are formed around the hole due to the shrinkage of the cement, which sets the ground to the gas and water permeability and filling with dust that leads to vegetation. The second is the difference in color and texture of cement. The first problem can be solved by using expanding cement. The second problem is to make color experiments while considering the types and amounts of pozzolanic substances to be added into the cement.

Table 1. ASTM type portland cement pseudonyms and main components

Cement Type		Instruction	Main Components %			
			C ₃ S	C ₂ S	C ₃ A	C ₄ AF
Type I	CEM I	Normal Portland Cement (General Purpose)	49	25	12	8
Type II	CEM II	Modified Portland Cement (Portland composite cement) (hydration heat is lower, and more resistant to sulphates than Type I)	46	29	6	12
Type III	CEM III	Portland cement with high initial strength (Blast furnace slag cement)	56	15	12	8
Type IV	CEM IV	Low heat Portland Cement (Puzzolan Cement) (Used in dams and mass concretes, has low hydration temperature)	30	46	5	13
Type V	CEM V	Sulphate resistant Portland Cement (Composed cement)	43	36	4	12

Source: (Erdoğan, 2004)

4. RESULTS AND SUGGESTIONS

Cement is produced with primitive materials such as clay, limestone, gypsum and other additives as needed. Obtaining the cement in the desired properties is a process involving a variety of operations must be implemented carefully, which needs knowledge and experience. Both the reaction of cement with water and its chemical structure is extremely complicated. Cement and its composition with other materials must be known well in the concrete production that has high importance for loss of life and property. Cement, an industrial product can have different properties. Cement production and application method, technique and application environment, can change its properties. This stands as a problem in the appropriate selection and use of cements. In this study, information about the qualities of cement and its choices are given and the basic physical and chemical properties of aggregate, and where, when, how and where to use it with water and additives are examined.

NOTICE

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