

GAZIANTEP UNIVERSITY
GRADUATE SCHOOL OF
NATURAL & APPLIED SCIENCES

MECHANICAL PROPERTIES OF
BORON BLENDED CEMENT
CONCRETES

M. Sc. THESIS IN
CIVIL ENGINEERING

BY

ALİ ŞEREF CENGİZ

April 2011

**Mechanical Properties of Boron Blended Cement
Concretes**

**M.Sc. Thesis
in
Civil Engineering
University of Gaziantep**

**Supervisor
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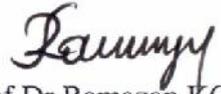
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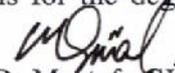
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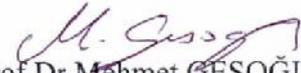
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To my family
Mehri, Mustafa Kaan and Berra

ABSTRACT

MECHANICAL PROPERTIES OF BORON BLENDED CEMENT CONCRETES

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Tez Yöneticisi: Doç. Dr. Mehmet GESOĞLU
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Cement manufacturing process requires high energy consumption. On the other hand, one of the major environmental problems that are faced in this process is the emission of greenhouse gases to the atmosphere. Therefore, the researchers have been investigating the ways to mitigate these problems. During the production of Boron Modified Active Belite (BAB) cement a considerable energy savings and reduced CO₂ emission is known to be possible. However the properties of this type of cement have not widely been known, yet. In this, study some mechanical and permeability properties of BAB cement concretes exposed to different initial curing conditions were investigated and compared to those of ordinary Portland cement concretes. Mechanical properties were evaluated through compressive and splitting tensile strength development, while the durability of the concretes was measured by means of rapid chloride penetration and water sorptivity tests. The results showed that mechanical properties of BAB cement concrete, at especially later ages, were slightly better than Portland cement concretes. According to the durability test results, the BAB cement concretes had superior permeability characteristics than the Portland cement concretes.

Keyword: Boron modified active belite cement; Curing regimes; Mechanical properties; Permeability

ÖZET

BOR KATKILI ÇİMENTOLARLA ÜRETİLEN BETONLARIN MEKANİK ÖZELLİKLERİ

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Çimento üretiminde yüksek enerji kullanımı gerektirmektedir. Bu enerjinin yanısıra, çimento üretim sürecinde atmosfere yayılan sera gazlarının çevreye olan etkileri ciddi sorunlar oluşturmaktadır. Bundan dolayı araştırmacılar, bu problemleri ortadan kaldırmak için çeşitli yollar araştırmışlardır. Borlu aktif belit (BAB) çimento üretiminde ciddi miktarda enerji tasarrufu ve CO₂ yayılımında azalma sağlanabilmektedir. Ancak bu çimentonun özellikleri henüz detaylı bir şekilde bilinmemektedir. Bu çalışmada BAB çimentosu ile üretilen ve farklı başlangıç kürlere tabii tutulan betonların bazı mekanik ve geçirimsizlik özellikleri incelenerek, portland çimentosu ile üretilen betonlarıkiyle karşılaştırılmıştır. Mekanik özellikler basınç ve yarma dayanım gelişimleri açısından değerlendirilirken, dayanıklılık özellikleri hızlı klorür geçirimsizliği ve kılcal su geçirimsizliği açısından ele alınmıştır. Elde edilen mekanik deney sonuçlarına göre BAB çimentolu betonların özellikle ileri yaşlarda, portland çimentolu betonlara göre daha iyi sonuçlar verdiği gözlemlenmiştir. Durabilite test sonuçları BAB çimentolu betonların geçirimsizlik özelliklerinin, portland çimentolu betonlarıkine nazaran daha üstün olduğunu göstermiştir.

Keyword: Borlu aktif belit çimentosu; Kür Koşulları; Mekanik özellikler; Geçirimsizlik.

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LIST OF SYMBOLS/ABBREVIATIONS

AASHTO	American Association of State Highway and Transportation Officials
ACI	American Concrete Institute
ASTM	American Society for Testing and Materials
B	Boron
BAB	Boron Modified Active Belite
FA	Fly ash
GGBFS	Ground granulated blast furnace slag
IB	Initial Burlap Curing
IH	Initial High Temperature Water Curing
IW	Initial Water Curing
MK	Metakaolin
OPC	Ordinary Portland cement
PW	Permanent Water Curing
RCPT	Rapid Chloride Permeability Test
RHA	Rice Husk Ash
SEM	Scanning electron microscope
SF	Silica fume
SP	Superplasticizer
TS EN	Turkish Standard European Norm
TS	Turkish Standard Institution

1. INTRODUCTION

1.1. General

Regarding the developments for providing a sustainable technology, energy savings and protection of natural resources are the most important concerns in environmental issues. Cement manufacturing industry is responsible for 8% of total CO₂ emissions to atmosphere (Mehta, 2002; Malhotra and Mehta, 2002). Through production of Boron Modified Active Belite (BAB) cement, energy saving and reduction in CO₂ emissions would be possible. Because manufacturing BAB cement requires clinkering temperature of around 1325°C which is relatively less than that is required for conventional cement. Due to the fact that C₃S is not formed in the production of BAB cement, approximately 10% energy saving can be achieved, thus leading to decrease in CO₂ emissions up to 25% (Sağlık et. al., 2008).

Turkey is known to have about 75% of the total earth boron deposits. Boron is used in a variety of products including glass and glass products, cleaning products, agrochemicals, insecticides, flameproofing compounds and corrosion inhibitors (Çöl and Çöl, 2003). However, utilization of Boron in cement industry has not yet been wide enough. Limited studies regarding this issue have been conducted by some researchers (Türk et. al., 2006; Sağlık et. al., 2008).

Boron contains some important minerals such as Borax, Kernit, Ulexit, Colemanite, Pandermite and Hydroboraxide. Colemanite mineral is available in Turkey, USA, Argentina, Kazakhstan and China, however USA and Turkey are the main producers of this mineral (Baysal O., 1972; Helvacı and Alonso, 2000; Anthony et al., 2003). The compounds (CaO, B₂O₃ and SiO₂) existing in the chemical structure of Colemanite ore can be used as raw materials for the production of cement. Colemanite does not contain alkaline minerals so that Boron cement can be utilized

for the environments where there is a severe alkali-silica reaction. Since the properties of the BAB cement has not yet been well known, BAB cement was standardized by Turkish Standard Institution as a type of Portland cement called “boron modified active belite cement” (TS 13353, 2008).

In this study, two series of concrete mixtures including either Portland or BAB cement were designed, and cast at w/c ratios of 0.35 and 0.55. To evaluate the effect of initial curing condition, four different curing regimes were adopted. The properties of the concretes were assessed by mechanical and permeability tests. The mechanical properties were tested in terms of compressive and splitting tensile strengths while permeability characteristics of the concretes were observed by rapid chloride penetration and water sorptivity test. The compressive strength developments of the concretes were measured at 7, 14, 28, 56, and 90 days. However, splitting tensile strength and the permeability tests were carried out at 28 and 90 days.

1.2 Outline of the Thesis

Chapter 1- Introduction: Aim and objectives of the thesis are introduced.

Chapter 2-Literature review and background:A literature survey was carried out on Boron Modified Active Belite (BAB) cement. The previous researches on the utilization of this material have been summarized.

Chapter 3-Experimental study:Materials, mixtures, casting, initial curing conditions, and test methods are described.

Chapter 4-Test results and discussions: Indication, evaluation, and discussion of test results are presented.

Chapter 5- Statistical evaluation of test results: General linear model analysis of variances of the experimental test result was carried out.

Chapter 6-Conclusions: Conclusion of the thesis and recommendation for future works are given.

2. LITERATURE REVIEW AND BACKGROUND

2. 1. Boron

Boron is the chemical element with atomic number of five and the chemical symbol B. Boron is a trivalent metalloid element which occurs plentifully in the evaporite ores borax and ulexite.

Several allotropes of boron exist: amorphous boron is a brown powder and crystalline boron is black, extremely hard (about 9.5 on Mohs' scale), and a poor conductor at room temperature. Elemental boron is used as a dopant in the semiconductor industry, while boron compounds play important roles as light structural materials, insecticides and preservatives, and reagents for chemical synthesis.

Boron is an essential plant nutrient. Whereas lack of boron results in boron deficiency disorder. High soil concentrations of boron may also be toxic to plants. As an ultratrace element, boron is necessary for the optimal health of rats and presumably other mammals, though its physiological role in animals is not yet fully understood.

The name boron originates from the Arabic word *buraq* or the Persian word *burah* (Shipley and Joseph, 2001) for the mineral borax.

Boron compounds were known thousands of years ago. Borax was known from the deserts of western Tibet, where it received the name of *tincal*, derived from the Sanskrit. Borax glazes were used in China and some *tincal* even reached the west, where the Arabic alchemist *Jābir ibn Hayyān* seems to mention it in 700. Marco Polo brought some glazes back to Italy in the 13th century. Boric acid was recognized in the hot springs (*soffioni*) near Florence, Italy, and became known as *sal sedativum*, with mainly medical uses in 1777.

The rare mineral is called sassolite, found at Sasso at Italy. This was the main source of European borax from 1827 to 1872, at which date American sources replaced it (Garrett and Donald, 1998; Garrett, 1998).

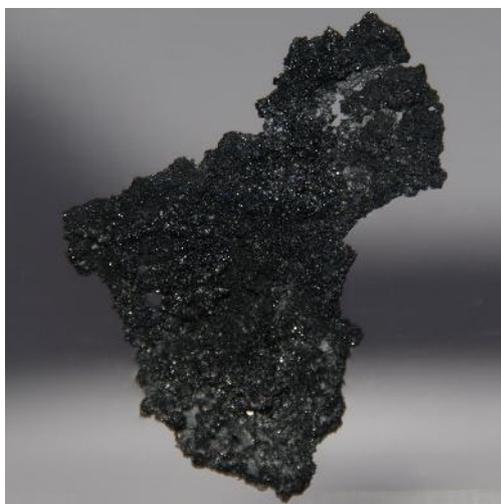


Figure 2.1 Picture of Crystalline Boron
(<http://images-of-elements.com/boron.php>, 2011)

Boron was not recognized as an element until it was isolated by Sir Humphry Davy, Joseph Louis Gay-Lussac, and Louis Jacques Thénard in 1808 through the reaction of boric acid and potassium. Davy called the element *boracium* (Weeks and Elvira, 1933). Jöns Jakob Berzelius identified boron as an element in 1824. The first pure boron was produced by the American chemist W. Weintraub in 1909 (Laubengayer et al., 1943; Borchert et al., 1970).

2.1.2. Physical and Chemical Properties

Boron is the first element of group III A, with atomic number of 5. The boron atom contains five electrons, two in the inner shell (the K electrons) and three in the outer shell (the L electrons). The ground state electron configuration of boron is $1s^2 2s^2 2p^1$. Boron is similar to carbon in its capability to form table covalently bonded molecular networks. Even nominally disordered (amorphous) boron contains regular boron icosahedra which are, however, bonded randomly to each other without long-range order (Delaplane et al., 1988a; Delaplane et al., 1988b). Crystalline boron is a very hard, black material with a high melting point of above 2000 °C. It exists in four major polymorphs: α , β , γ and T. Whereas α , β and T

phases are based on B₁₂ icosahedra, the γ -phase can be described as a rocksalt-type arrangement of the icosahedra and B₂ atomic pair (Oganov et al., 2009). It can be produced by compressing other boron phases to 12-20 GPa and heating to 1500-1800 °C; it remains stable after releasing the temperature and pressure. The T phase is produced at similar pressures, but higher temperatures of 1800-2200 °C. As to the α and β phases, they might both coexist at ambient conditions with the β phase being more stable (Oganov et al., 2009; Van Setten et al., 2007). Compressing boron above 160 GPa produces a boron phase with an as yet unknown structure, and this phase is a superconductor at temperatures 6-12 K (Eremets, 2001).

Chemically, boron is closer to silicon than to aluminium. Crystalline boron is chemically inert and resistant to attack by boiling hydrofluoric or hydrochloric acid. When finely divided, it is attacked slowly by hot concentrated hydrogen peroxide, hot concentrated nitric acid, hot sulfuric acid or hot mixture of sulfuric and chromic acids (Laubengayer et al., 1943).

Oxidation of boron depends upon the crystallinity, particle size, purity, and temperature. Boron does not react with air at room temperature, but at higher temperatures it burns to form boron trioxide:



Boron reacts with sulfur to similarly to give boron sulfide, B₂S₃.

Boron undergoes halogenation to give trihalides, e.g.:



These compounds are however usually made from the oxides.

Boron forms a full range of compounds where boron has the formal oxidation state III. These include oxides, sulfides, nitrides, and halides. A large number of organoboron compounds have also been described e.g. triphenylboron. In its halides, boron can form compounds whose formal oxidation state is less than three, such as in the highly unstable boron fluorides BF and B₂F₄ (Greenwood et al., 1997).

The most distinctive chemical compounds of boron are its hydrides, which adopt structures not commonly seen with other elements. Included in this series are diborane (B_2H_6), decaborane ($B_{10}H_{14}$), and the carboranes (e.g., $C_2B_{10}H_{12}$). Like many elements that form highly covalent bonds, oxidation states are often have little meaning in the hydrides of boron, e.g. the polyhedral boranes.

Boron has two naturally occurring and stable isotopes, ^{11}B (80.1%) and ^{10}B (19.9%). The mass difference results in a wide range of $\delta^{11}B$ values, which are defined as a fractional difference between the ^{11}B and ^{10}B and traditionally expressed in parts per thousand, in natural waters ranging from -16 to +59. There are 13 known isotopes of boron; the shortest-lived isotope is 7B which decays through proton emission and alpha decay. It has a half-life of 3.5×10^{-22} s. Isotopic fractionation of boron is controlled by the exchange reactions of the boron species $B(OH)_3$ and $B(OH)_4$. Boron isotopes are also fractionated during mineral crystallization, during H_2O phase changes in hydrothermal systems, and during hydrothermal alteration of rock. The latter effect results in preferential removal of the ^{10}B $(OH)_4$ ion onto clays. It results in solutions enriched in ^{11}B $(OH)_3$ and therefore may be responsible for the large ^{11}B enrichment in seawater relative to both oceanic crust and continental crust; this difference may act as an isotopic signature (Barth, 1997). The exotic ^{17}B exhibits a nuclear halo, i.e. its radius is appreciably larger than that predicted by the liquid drop model (Liu, 2003).

2.1.2. Boron Compositions

2.1.1.1. Borax (Tincal)

Borax is a colorless, crystalline solid sparingly soluble in cold water but dissolves readily in hot water. It forms two important hydrates: octahedral borax $Na_2B_4O_7 \cdot 5H_2O$ and monoclinic borax $Na_2B_4O_7 \cdot 10H_2O$. Borax has a wide variety of uses. It is a component of many detergents, cosmetics, and enamel glazes. It is also used to make buffer solutions in biochemistry, as a fire retardant, as an anti-fungal compound for fiberglass, as an insecticide, as a flux in metallurgy, a texturing agent in cooking, and as a precursor for other boron compounds.

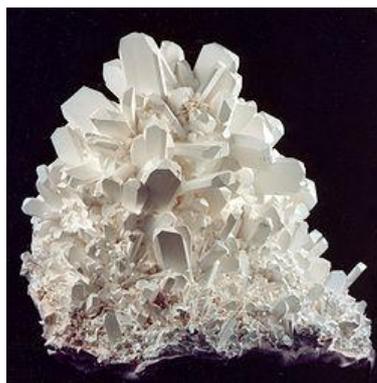


Figure 2.2-Picture of Borax (Tincal) (<http://nl.wikipedia.org/wiki/Tincalconiet>, 2011)

Table 2.1. Physical Properties Of Boron
 (<http://www.lenntech.com/periodic/elements/b.htm>, 2011)

Property	Value
Atomic weight	10.81 ± 0.005
Melting point	2190 ± 20°C
Boiling point	3660 °C
Density of boron (Crystalline, 25 - 27 °C)	2.33 ± 0.02 g/cm ³
Density of boron (Amorphous, 25 - 27 °C)	2.3 g/cm ³
Hardness, mineralogical scale	9.3
Heat capacity (25 - 927 °C)	1.54 ± 0.0044 · T kcal/g-atom · deg
Heat of combustion	306 ± 1 kcal/g-atom
Heat of transition, B am → B cryst	0.4 kcal/g-atom
Heat of vaporization	128 kcal/g-atom
Heat of fusion	5.3 kcal/g-atom
Mohs hardness	11
Knoop hardness	2100 -2580 HK
Vickers hardness	5000 HV
Oxidation number	3
Electronegativity	2
Atomic radius	1.78 Å
Ionic radius of B ³⁺	0.23 Å

2.1.1.2. Kernite (Rasorite)

Kernite, like other borates, is a structurally complex mineral. It is a colorless to white mineral crystallizing in the monoclinic crystal system typically occurring as prismatic to acicular crystals or granular masses. The basic structure of kernite contains chains of interlocking $\text{BO}_3(\text{OH})$ tetrahedrons. The chains' basic unit has a formula of $\text{B}_4\text{O}_6(\text{OH})_2$ and a charge of negative two (-2). Connected to the chains are triangular BO_3 groups with the sodiums and water molecules interspersed between the chains.



Figure 2.3-Picture of Kernite (Rasorite)

(<http://www.mineral-forum.com/message-board/viewtopic.php?t=819>, 2011)

2.1.1.3. Ulexite

The basic structure of ulexite contains chains of sodium, water, and hydroxide octahedrons linked in endless chains. The chains are linked together by calcium, water, hydroxide and oxygen polyhedra and massive boron units. The basic boron unit has a formula of $\text{B}_5\text{O}_6(\text{OH})_6$ and a charge of negative three (-3). It is composed of three borate tetrahedrons and two borate triangular groups. It is a white or gray to colorless. Ulexite is found with the mineral borax and is directly deposited in arid regions from the evaporation of water in intermittent playa lakes. The precipitated ulexite commonly forms a "cotton ball" tuft of acicular crystals. Ulexite is also found in a vein-like bedding habit composed of closely-packed fibrous crystals. Ulexite decomposes in hot water.



Figure 2.4-Picture of Ulexite

(<http://www.cs.cmu.edu/~adg/images/minerals/b/ulexite2.jpg>, 2011)

2.1.1.4. Colemanite

Colemanite is a complex mineral that is found in playa lakes and other evaporite deposits. The basic structure of colemanite contains endless chains of interlocking $\text{BO}_2(\text{OH})$ triangles and $\text{BO}_3(\text{OH})$ tetrahedrons with the calciums, water molecules and extra hydroxides interspersed between the chains. Colemanite is a secondary mineral that forms by alteration of borax and ulexite. Color is white to clear. Colemanite forms small but richly faceted crystals.



Figure 2.5-Picture of Colemanite

(http://realgems.org/edelsteine_liste/pic/big%20colemanite%2005.jpg, 2011)

2.1.3. Environmental Occurrences of Boron Deposits

The element boron (B) is widely distributed in nature. Because of its high affinity for oxygen, boron always occurs in nature bound to oxygen in the form of inorganic borates. Apart from their occurrence in a few commercially exploitable deposits (mainly as sodium or calcium borate minerals), the borates are present everywhere at low concentrations in rocks (15—300 mgB/kg), soils (<10—20

mgB/kg), fresh waters (<1 mgB/L) and sea water (5 mgB/L). The content of boron in the lithosphere by mass is about 1.10^{-3} %. Table 2.2 gives data on the distribution of boron in various components of the earth's crust.

The world's oceans have by far the greatest content of borate, with an average concentration of 5 mgB/L. Lakes and rivers in most parts of the world, except in areas of volcanic activity with more elevated concentrations, contain an environmental background content of <1 mgB/L, generally between 0.01 to 0.3 mgB/L. No typical concentration of borate can be cited for groundwater, which includes flowing springs (both hot and cold), geysers, aquifers (both flowing and confined), oilfield brines, etc. The recent review of the borate content of European ground waters shows that values can vary from <0.1 to >1 mgB/L and are dependent upon geological circumstances, especially in areas of volcanic activity. Mineral waters contain a range of from < 0.02—4.3 mgB/L (ECETOC, 1997).

Boron is a relatively rare element in the Earth's crust, representing only 0.001%. The worldwide commercial borate deposits are estimated as 10 million tons (Argust, 1998; Woods and William, 1994). Turkey and the United States are the world's largest producers of boron (Kostick and Dennis, 2006).

Table 2.2. Distribution of boron (Walker, 1975)

Source	Weight (%)	Source	Weight (%)
Earth's Crust	$1 \cdot 10^{-3}$	Meteorites	$3 \cdot 10^{-4}$
Inside rocks	$1 \cdot 10^{-4}$	Sea water (dry residue)	$1.5 \cdot 10^{-2}$
Acid rocks (granites, etc.)	$1.5 \cdot 10^{-3}$	Salt springs (dry residue)	$(3-20) \cdot 10^{-3}$
Sedimentary rocks	$1.2 \cdot 10^{-2}$	Salt lakes (dry residue)	$(1-60) \cdot 10^{-2}$
Soils	$1 \cdot 10^{-3}$	Water of mud volcanoes (dry residue)	$(6-400) \cdot 10^{-2}$
Granite pegmatites	$(1-10) \cdot 10^{-2}$	Petroleum brine	$(1-60) \cdot 10^{-2}$
Marine clays	$5 \cdot 10^{-2}$	Marine plants (ash)	$1.5 \cdot 10^{-1}$
Iron ores (maritime)	$5 \cdot 10^{-2}$	Marine animals (ash)	$(3-100) \cdot 10^{-4}$
Iron ores (nonmaritime)	$5 \cdot 10^{-4}$	Rye, wheat, oats and other grains (dry matter)	$(0.6-36) \cdot 10^{-4}$
Lime stones	$5 \cdot 10^{-4}$	Clover, alfalfa (dry matter)	$(7-57) \cdot 10^{-4}$

Table 2.3. Boron reserves in the world (million tons, as B₂O₃)
(<http://www.etimaden.gov.tr>, 2010)

Country	Proven Economic	Probable & Possible	Total Reserve	(%) in Total Reserve	Reserve Life-span
Turkey	224,000	339,000	563,000	64	389
USA	40,000	40,000	80,000	9	55
Russia	40,000	60,000	100,000	11	69
China	27,000	9,000	36,000	4	25
Chile	8,000	33,000	41,000	5	28
Bolivia	4,000	15,000	19,000	2	13
Peru	4,000	18,000	22,000	2	15
Argentina	2,000	7,000	9,000	1	6
Kazakhstan	14,000	1,000	15,000	2	10
TOTAL	363,000	522,00	885,000	100	610

Table 2.4. Boron reserves in the Turkey (thousand tons, as B₂O₃)
(<http://www.etimaden.gov.tr>, 2010)

Mine Areas	Natural Borate	Total Reserve (thousand tons)	% B ₂ O ₃
Bigadiç, Balıkesir	Colemanite, ulexite	623.459	29-31
Emet, Kütahya	Colemanite	1.682.562	28-30
Kestelek, Bursa	Colemanite	6.995	29
Kırka, Eskişehir	Tincal	750.620	26

2.1.4. Industrial Processing of Boron

The earliest methods involved reduction of boric oxide with metals such as magnesium or aluminum. However, the product is almost always contaminated with metal borides. Pure boron can be prepared by reducing volatile boron halides with hydrogen at high temperatures. Ultrapure boron, for the use in semiconductor

industry, is produced by the decomposition of diborane at high temperatures and then further purified with the zone melting or Czochralski processes (Berger, 1996).

2.1.5. Applications and Usage Areas of Boron

Boron compounds are used for many different purposes in industry. Boron is used to make glass, ceramics, and enamels, including fiberglass for insulation. Boron compounds are used to make water softeners, soaps, and detergents. Other uses are in agricultural chemicals, pest controls, fire retardants, fireworks, medicine, and various minor applications.

The most important boron compound is sodium borate pentahydrate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 5\text{H}_2\text{O}$). Large amounts of this compound are used in the manufacture of fiberglass insulation and sodium perborate bleach. The second most important compound is boric acid (H_3BO_3), which is used to manufacture textile fiberglass and is used in cellulose insulation as a flame retardant. Sodium borate decahydrate ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$), better known as borax, is the third most important boron compound. Borax is used in laundry products and as a mild antiseptic.

Boron compounds are widely employed in many branches of the national economy, for example in medicine for the preparation of disinfectants and drugs, in the glass industry for the production of optic and chemically stable glass (glass products use 53.6% of the boron consumption in the United States, and 32.7% in Western Europe (Butterwick et al., 1989), as components of enamels to increase hardness, for the protection of metals against oxidation during soldering, as additives to electrolytes in nickel plating, in the production of heat resistant polymers and also as catalysts. Boron compounds are also used in cosmetic, leather, textile, rubber, and paint industries. They also find application in the wood-processing industry as a protection against molds (ECETOC, 1997).

Boron is used in pyrotechnics and flares to produce a green color. Boron has also been used in some rockets as an ignition source. Boron-10, one of the naturally occurring isotopes of boron, is a good absorber of neutrons and is used in the control rods of nuclear reactors, as a radiation shield and as a neutron detector. Boron filaments are used in the aerospace industry because of their high-strength and

lightweight.

Cleaning and washing products also use boron compounds. In North America, boron is mostly used as a washing aid and softener where ten percent of boron consumption is used in the cleaning industry. In Western Europe, sodium perborate is used as a bleaching agent in soap and detergent. Over 41% of their boron consumption is in cleaning products (Butterwick et al. 1989).

Boron, an essential trace element for plant growth, is often added to crops in a fertilizer. In higher concentrations, it can also be used as a non-selective herbicide for weed control, insecticide, and algacide in water treatment and as a timber preservative.

Moreover, there is a boron-containing natural antibiotic, boromycin, isolated from streptomyces. Boron is an essential plant nutrient, required primarily for maintaining the integrity of cell walls. Conversely, high soil concentrations of greater than 1.0 ppm can cause marginal and tip necrosis in leaves as well as poor overall growth performance. Levels as low as 0.8 ppm can cause these same symptoms to appear in plants particularly sensitive to boron in the soil. Nearly all plants, even those somewhat tolerant of boron in the soil, will show at least some symptoms of boron toxicity when boron content in the soil is greater than 1.8 ppm. When this content exceeds 2.0 ppm, few plants will perform well and some may not survive. When boron levels in plant tissue exceed 200 ppm symptoms of boron toxicity are likely to appear (Mahler, 2009; Blevins and Lukaszewski, 1998).

As an ultra trace element, boron is necessary for the optimal health of rats, although it is necessary in such small amounts that ultra purified foods and dust filtration of air is necessary to show the effects of boron deficiency, which manifest as poor coat/hair quality. Presumably, boron is necessary to other mammals. No deficiency syndrome in humans has been described. Small amounts of boron occur widely in the diet, and the amounts needed in the diet would, by analogy with rodent studies, be very small. The exact physiological role of boron in the animal kingdom is poorly understood (Nielsen, 1998).

Boron occurs in all foods produced from plants. Since 1989, its nutritional value has been argued. It is thought that boron plays several biochemical roles in animals,

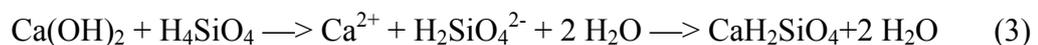
including humans. The U.S. Department of agriculture conducted an experiment in which postmenopausal women took 3 mg of boron a day. The results showed that supplemental boron reduced excretion of calcium by 44%, and activated estrogen and vitamin D. However, whether these effects were conventionally nutritional, or medicinal, could not be determined. The US National Institutes of Health quotes this source. Total daily boron intake in normal human diets ranges from 2.1–4.3 mg boron/day

2.2. Mineral admixtures

2.2.1. Pozzolanic Reaction

Pozzolans are inorganic materials, either natural or artificial, which have no Cementitious value when contact with water, but harden in water when mixed with calcium hydroxide or with materials that can release calcium hydroxide (portland cement clinker).

The term “pozzolanic activity” addresses all the reactions occurring in a lime-pozzolan-water system. In spite of the fact that this definition for pozzolanic activity seems to be cursory, it is acceptable from a technical and practical point of view. Since it is very difficult to observe the evolution of pozzolanic activity in terms of hydration products, the progress of pozzolanic reaction is commonly evaluated by depletion of the free calcium hydroxide in the system (Massaza, 1998) . At the basis of the Pozzolanic reaction stands a simple acid- base reaction between calcium hydroxide, also known as Portlandite, or $(Ca(OH)_2)$, and silicic acid (H_4SiO_4 , or $Si(OH)_4$). For simplifying, this reaction can be schematically represented as following:



or summarized in abbreviated notation of cement chemists:



The product of general formula $(CaH_2SiO_4 - 2 H_2O)$ formed is a calcium silicate hydrate, also abbreviated as CSH in cement chemist notation. The ratio Ca/Si, or C/S

and the number of water molecules can vary and the here above mentioned stoichiometry may differ (Mertens et al., 2009).

The term 'pozzolanic activity' covers all reactions occurring among the active constituents of pozzolanas, lime, and water. The definition, although approximate, is however acceptable from a technical and practical viewpoint. Notwithstanding the difficulty in following the evolution of pozzolana's active phases throughout the hydration process, the progress of pozzolanic reaction is commonly evaluated in terms of diminution of the free lime in the system or increase in the silica + alumina soluble in acid Bonavetti and Irassar (1994) by using the Florentin attack method. There is a general agreement that the overall amount of combined lime essentially depends on the following;

1. The nature of the active phases
2. Content in pozzolana
3. SiO₂ content
4. The lime/pozzolana ratio of the mix
5. Curing time
6. The specific surface area (BET) of pozzolana
7. water/solid mix ratio
8. Temperature

Some natural pozzolana displays an initial reaction rate higher than that of some low-lime fly ashes. Afterwards, the rate in natural materials slows down whereas that in fly ashes accelerates. This different behaviour can be attributed to many factors, one being certainly the higher BET specific surface area of natural pozzolanas, which favours a higher initial rate of lime combination (Shergold, 1953).

2.2.2. Types of Mineral Admixture

Admixtures vary widely in chemical composition, and many perform more than one function. Two basic types of admixtures are available: chemical and mineral. All admixtures to be used in concrete construction should meet specifications; tests should be made to evaluate how the admixture will affect the properties of the

concrete to be made with the specified job materials, under the anticipated ambient conditions, and by the anticipated construction procedures.

According to a survey by the Portland Cement Association published (Portland Cement Association, 2000), at least 60 percent of ready mixed concrete contains other cementitious materials, often referred to as mineral admixtures or supplementary cementitious materials.

According to ASTM, (American Society of Testing and Materials) mineral admixtures (fly ash, silica fume [SF], and slags) are usually added to concrete in larger amounts to enhance the workability of fresh concrete; to improve resistance of concrete to thermal cracking, alkali-aggregate expansion, and sulfate attack; and to enable a reduction in cement content.

2.2.2.1. Fly ash (FA)

Fly ash, a by-product from the combustion of pulverized coal, is widely used as a cementitious and pozzolanic component in hydraulic cement concrete. The pozzolanic activity of fly ash depends on the presence of SiO_2 and Al_2O_3 in the amorphous form (Baker, 1984; Gesoglu, 2004; Naik and Singh, 1997). The use of fly ash in concrete technology dates back 1930's (Şengül, 2006).

The worldwide production of fly ash at present is estimated to be about 500 million tons per year. According to coal ash production and utilization in the world survey in 1989, (Manz, 1993; Michalsh, 1991) approximately 562 million tons of coal ash was produced in 1989, of which approximately 90 million tons or 16.1% was utilized.

Fly ash is generally finer than Portland cement and consists mostly of spherical, glassy particles varying from less than 1 μm to over 100 μm in diameter. The chemical composition of the glass in the particles varies significantly. But the main constituents include silica, alumina, and oxides of calcium and iron. The chemical composition of fly ashes generally varies with the source of coal. ASTM specification C618 defines two broad types of fly ash, Class F and Class C, related to the type of coal burned. The fly ash produced from burning anthracite or bituminous coal is classified as Class F as per ASTM C618, whereas Class C fly ashes normally result from the burning of subbituminous coal and lignite.

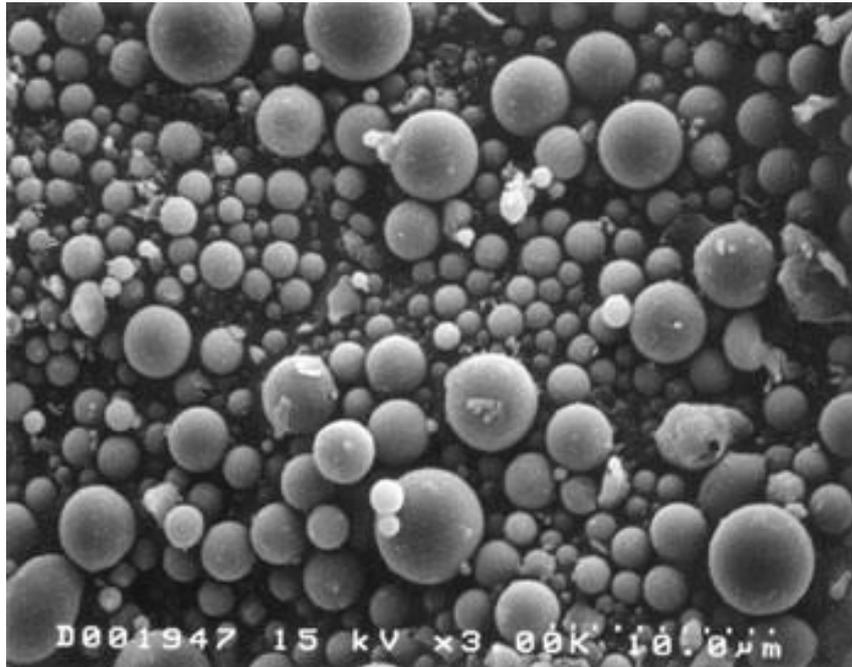


Figure 2.6-Electron Microscope Images of Fly Ash Particles - 2,000 X Magnifications (AASHTO M 295, 2007)

2.2.2.2. Silica fume (SF)

The use of silica fume, also called microsilica, has significantly increased as a supplementary cementing material in concrete construction. Silica Fume is also collected as a byproduct in the production of other silicon alloys such as ferrochromium, ferromanganese, ferromagnesium, and calcium silicon (ACI 234R-96, 1996). During the last 10 to 15 years, many structures all over the world have been constructed using Silica Fume in concrete. It is a very fine powder with glassy spherical particles having diameters 100 times finer than Portland cement. The particle size ranges from 0.1 μm to 0.2 μm literature. The extremely small size and spherical shape of glassy Silica fume particles makes it highly reactive pozzolan which considerably improves the properties of concrete both in fresh and hardened state. Silica Fume consists of very fine vitreous particles with a surface area ranging from 13,000 to 30,000 m^2/kg . When measured by nitrogen absorption techniques, with particles approximately 100 times smaller than the average cement particle. Because of its extreme fineness and high silica content, Silica Fume is a highly effective pozzolanic material (ACI 234R-96, 1996; Luther, 1990).

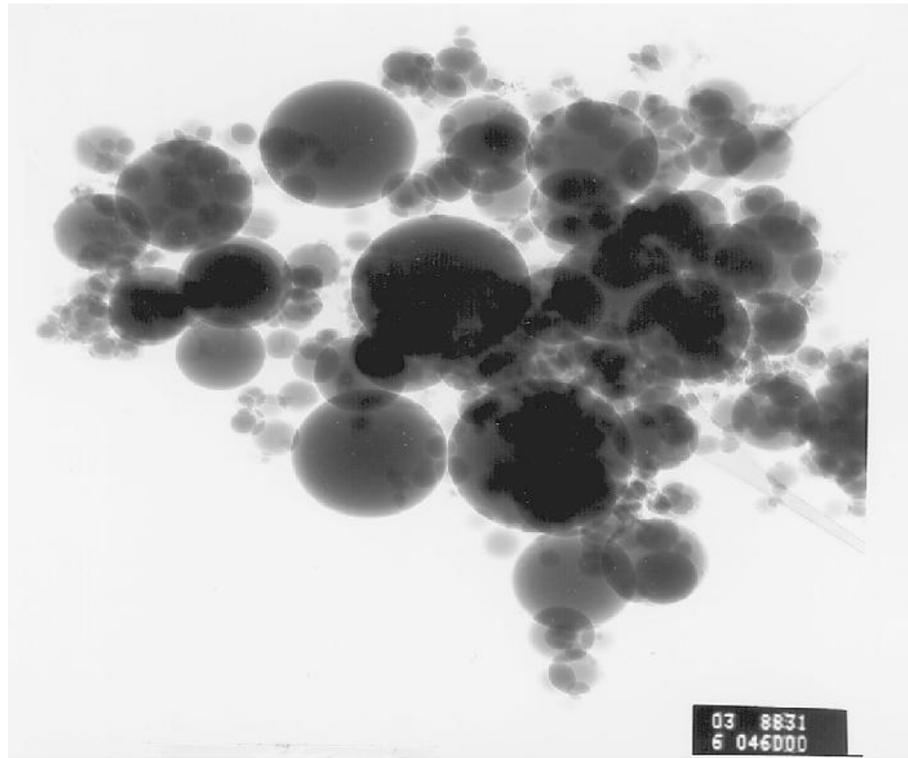


Figure 2.7- TEM micrograph of silica fume (ACI 234 R-96, 1996)

2.2.2.3. Ground granulated blast furnace slag (GGBFS)

Granulated slag, obtained as waste product from both ferrous and non ferrous metal industries in finely ground form, has been used as mineral admixture, mostly as component of blended cements, called slag cements. The use of separately ground slag combined with Portland cement at the mixer as a mineral admixture did not start until the late 1970s (Lewis, 1981). It is a granular product with very limited crystal formation, is highly cementitious in nature and, ground to cement fineness, and hydrates like Portland cement (Transportation Research Board, 1990; Lewis, 1981; ACI 233R-95, 1995). The generation of slags from the metallurgical industry is estimated around 40 million tons per year. More than 85% of the slags produced is used as a construction material for roads, raw material for cement, fertilizer, and pottery and as a soil stabilizer. Blast furnace slag is produced as a byproduct in iron and steel industries.

Ground granulated blast furnace slag (GGBFS) is, however, an accepted mineral admixture for use in concrete due to its glassy nature and chemical composition

which make it pozzolanic and a cementitious material. The hydraulic reactivity of the quenched or rapidly chilled glassy GGBFS depends upon processing conditions, chemical composition, and particle characteristics.

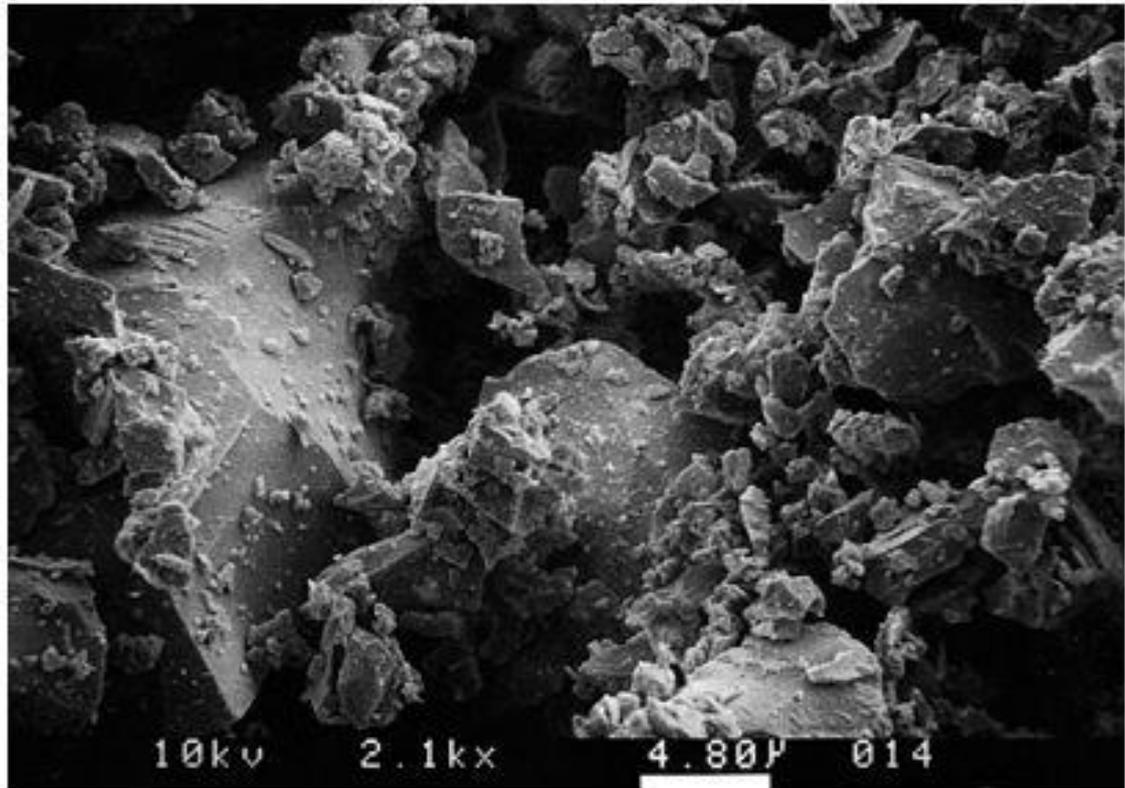


Figure 2.8- Scanning electron microscope image of ground granulated blast furnace slag particles (Lee, 1974)

2.2.2.4. Metakaolin (MK)

Metakaolin is a dehydroxylated form of the clay mineral kaolinite. Kaolin is a fine, white, clay mineral that has been traditionally used in the manufacture of porcelain. It is thought that the term kaolin is derived from the Chinese Kaoling, which translates loosely to white hill and has been related to the name of a mountain in China. Kaolin is a mineral typical of continental weathering where solutions percolate and are purified over time. Kaolinite cannot develop in sedimentary basins where solutions accumulate and are enriched. Kaolin is one of the more highly prized of the industrial mineral clays. Kaolin's traditional markets in ceramics over the past centuries have yielded to the now dominant consumption by the paper industry

where it is extensively used as a filler, opacifier, and as an important input to high-end coatings. In addition, smaller markets for kaolin are in the refractory, rubber, paint, plastic, chemical, pharmaceutical, and ceramic industries. (www.metakaolin.com/metakaolin/, 2007).

At about 100-200°C, clay minerals lose most of their adsorbed water. The temperature at which kaolinite loses water by dehydroxilation is in the range of 500-800 degrees °C. This thermal activation of a mineral is also referred to as calcining. Beyond the temperature of dehydroxylyzation, kaolinite retains two-dimensional order in the crystal structure and the product is termed metakaolin.

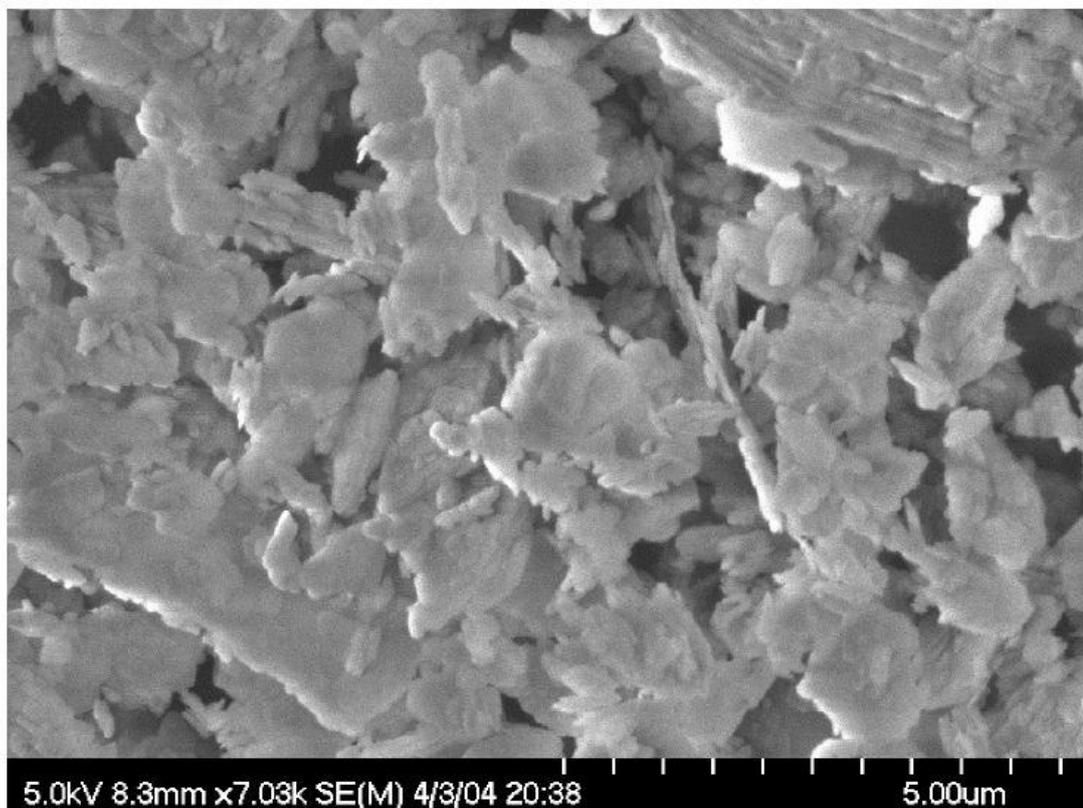


Figure 2.9 SEM micrograph of natural Metakaolin at higher magnification
(Kriven at al, 1994)

2.2.2.5. Rice Husk Ash (RHA)

The presence of silica in rice husk ash has been known since 1938 (Martin, 1938). Rice husk is an agro-waste material which is produced in about 100 million of tons. Approximately, 20 kg of rice husk are obtained for 100 kg of rice. Rice husks contain

organic substances and 20% of inorganic material. Rice husk ash (RHA) is obtained by the combustion of rice husk. At 550° – 800°C amorphous ash is formed and at higher temperatures, crystallization occurred. The most important property of RHA that determines pozzolanic activity is the amorphous phase content. RHA contains around 85 % - 90 % amorphous silica. RHA is a highly reactive pozzolanic material suitable for use in lime-pozzolana mixes and for Portland cement replacement. RHA contains a high amount of silicon dioxide and its reactivity related to lime depends on a combination of two factors, namely the non-crystalline silica content and its specific surface.

Investigated the effect of pyroprocessing on the pozzolanic reactivity of RHA.(Mehta, 1992).

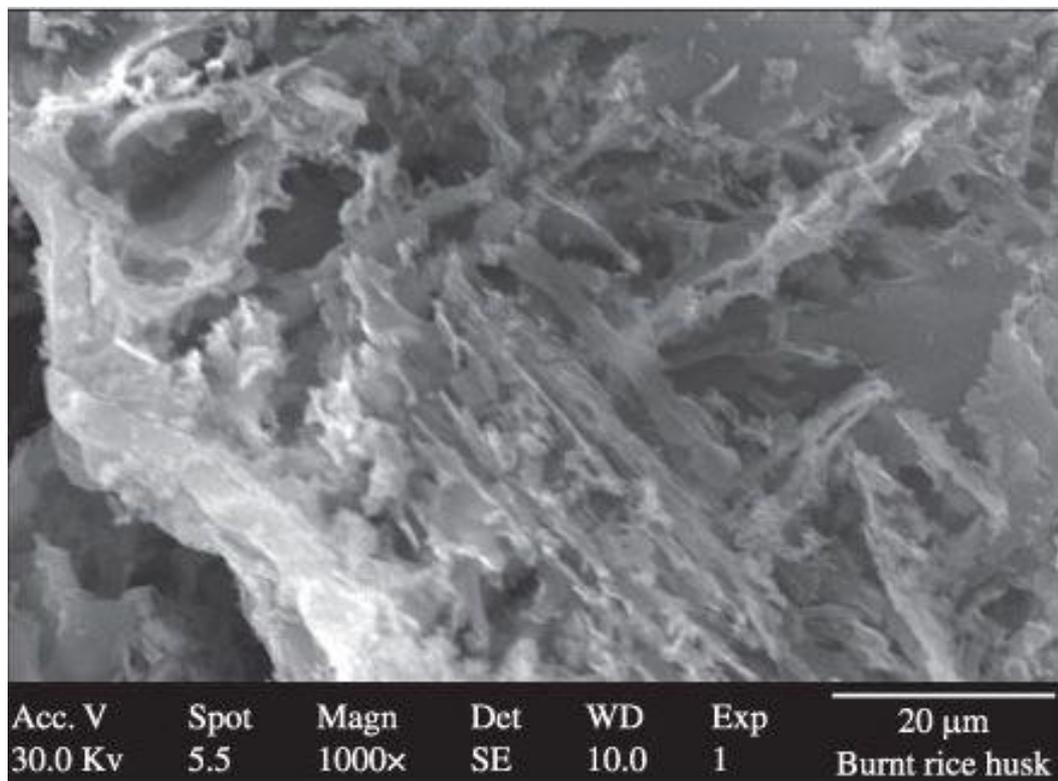


Figure 2.10 SEM for RHA particles. (Habeeb et al., 2010)

2.2.3. Effect of curing conditions on concretes containing mineral admixtures

It is generally agreed that ingress of aggressive substances into concrete causes, in many structures, severe deterioration. The concrete performance is mainly depended on the environmental conditions, the microstructures, and the chemical

characteristics of concrete. The continuation of hydration reactions in Portland cement is essential to improve the potential strength and durability of concrete. This continuation depends on the type (chemical and mineralogical composition) and fineness of cement, the type, and the amount of supplementary material present, the w/cm ratio, and the curing condition, especially at early ages (Khatri et al., 1997). It is obvious that those factors are essential to obtain the durable concrete structures. Curing is necessary for concrete to fully gain its potential properties (Güneyisi et al., 2005; Ramezani pour et al., 1995). Therefore, the curing becomes more important for concretes those including pozzolans, especially in hot and dry environments (Chindaprasirt et al., 2004)

2.3. Use of Boron Minerals in the production of Cement

2.3.1. Boron Modified Active Belite (BAB) Cement

Boron modified active belite (BAB) cement, a hydraulic binder, is finely ground and an inorganic material and forms cement paste hardening with hydration reactions when mixed with water. This cement paste maintains its strength and stability by the means of stable hydrate phases formed after hydration. This definition is completely compatible with Portland cement definition in TS EN 197-1 standard (Sağlık et al., 2008). Main component of BAB cement clinker is di-calcium silicate (α and/or α' -C₂S modifications), which is in active belite phase. Other mineralogical components are tri-calcium aluminates (C₃A) and tetra-calcium alumina ferrite (C₄AF) phases. Difference of BAB cement clinker from Portland cement clinker is that the main component is hydraulically high active belite phase instead of the alite phase. Hydraulically hardening of BAB cement rely on hydration of active belite phase, but other cement phases can also play some roles in the hardening process.

Boron contain some important minerals are Borax, Kernit, Ulexit, Colemanite, Pandermite and hydroboraxide (Kistler and Helvaci, 1994). Some of the raw materials needed for cement production abundantly exist in Colemanite. Colemanite mineral is just a raw material of cement because it mainly contains CaO, SiO₂, and B₂O₃. The results of chemical and physical analysis of the BAB cement are given Table 2.5:

Table 2.5. Results of Chemical Analysis of Göлтаş BAB Cement (BOREN, 2010)

Results of Chemical Analysis of BAB Cement	(%)
Silicon Dioxide (SiO ₂)	19.10
Aluminum Dioxide (Al ₂ O ₃)	4.68
Ferric oxide (Fe ₂ O ₃)	3.42
Calcium oxide (CaO)	57.10
Magnesium oxide (MgO)	1.32
Chloride (Cl ⁻) (%)	0.001
Sulphur trioxide (SO ₃)	2.68
Loss on Ignition	3.82
Insoluble Residue	0.70
Equivalent Alkalies (Na ₂ O+0,658.K ₂ O) (Na ₂ O=0,34)(K ₂ O=0,78)	0.86
Boric oxide (B ₂ O ₃)	3.00
Clinker	86.10
Gypsum	4.85

Table 2.6. Results of physical test of Göлтаş BAB cement with different Blaine values (BOREN, 2010).

Test and Standard	Göлтаş BAB Cement
Density, TS EN 196-6, g/cm ³	3.09
Specific Surface (Blaine), TS EN 196-6, cm ² /g	3562
Setting Times, TS EN 196-3,(Initial and Final), Min.	145 – 180
Soundness, TS EN 196-3, mm (<10,0 mm)	1.00
Standard Consistency Water, TS EN 196-3 (Normal Portland CEM I 42,5R Water = 28 g)	22.00

Boron modified active belite (BAB) cement has been developed by using these main characteristics of Colemanite mineral. Usage of boric oxide (B₂O₃) in the cement production is not a new phenomenon. Some researchers in the world determined that there have been improvements in the properties of the cement which are produced by using pure boric oxide. The composition of BAB cement contains about 3.0% (wt.) of B₂O₃ (boric oxide) (TS, 2008).

It has been determined that colemanite is the most suitable boron mineral in the production of cement. This new type of cement called as Boron Modified Active Belite (BAB) cement has very low heat of hydration, good ultimate strength and produces very durable concrete against most serious environmental conditions. During the production of industrial pilot scale, it is observed that this cement has decreased the CO₂ emission by up to about 25 %. In addition to this, because the alite (C₃S) phase which is the most important phase of Portland cement, cannot be formed due to B₂O₃, clinker sintering temperature decreased to 1325 °C and energy saving of about 10 % has been obtained (Sağlık et al., 2008).

The chemical composition of boron modified active belite cement has no C₃S, there is active and stable structured α and/or α' - C₂S crystal phase in extremely high amounts and the rate of hydration is significantly higher than cement containing the β -C₂S phase; as a result in the formation of a more compact and more dense concrete microstructure. In normal situation the hydration of the β - C₂S phase of cement is very slow as compared to that of C₃S and gaining strength values is lately. However, the final strength is the same or greater than that for C₃S. Reaction of the β -C₂S and the reaction of the C₃S phase with water can be sum up as follows: (Sağlık et al., 2008)



The hydration reaction of C₃S with water forms three times more Ca(OH)₂ than that of C₂S. Calcium hydroxide constitutes about 20% or 25% by volume of Portland cement paste.

Hydration of BAB cement has two fundamental properties. First, it has low hydration heat. For mass concrete applications total hydration heat after 7 days must be less than 60 cal/g. BAB cement has the hydration heat of 50 cal/g (<60 cal/g). This value is also less than 52.5 cal/g which is the upper limit of very low heat cement classification (BOREN, 2010).

Otherwise Concrete made with BAB cement has lower porosity ratio, which results

in more compact and less permeable structure. Lower permeability leads to a longer service life and better durability of concrete for various applications. Therefore strength and durability of concrete will be higher with a more dense structure (DSİ, 2009).

The fineness of BAB cement is a critical parameter because the strength development depends on the degree of fineness. All the research, the degree of fineness of BAB cement and normal Portland cement were chosen to be almost the same. The degree of fineness of both cements was around $3300 \text{ cm}^2/\text{g}$. For mass concrete structures the fineness of BAB cement is considered acceptable at around $3500 \text{ cm}^2/\text{g}$. However, when high early strength values are needed in structures such as concrete bridges, concrete roads and residence buildings and the like, it is possible to attain early strength development when using BAB cement as compared to normal Portland cement by increasing the fineness value of the BAB cement to $4000 \pm 50 \text{ g/cm}^2$. Moreover, without increasing the fineness of the cement, high early strength values can easily be accomplished by using concrete chemical admixtures (Sağlık et al., 2008).

BAB cement low heat of hydration makes it ideal for mass construction and also, low permeability of BAB cement concrete increases its durability.

Sağlık et al. performed strength development test on the concrete samples. In pre-tests phase, a few chemical admixtures such as set-accelerator and high range water reducer were tried in concrete castings in order to investigate the early strength development of BAB cement concrete at 1, 3, 7 and 28 days. Compressive strength of concretes with a set-accelerator chemical admixture reached about 5,0 MPa, 18,0 MPa and 29,0 MPa, while the concretes and with a high range water reducer chemical admixture had 8,8 MPa, 31,2 MPa and 54,2 MPa strengths at 1, 3 and 7 days respectively (Sağlık et al., 2008).

2.3.2. Utilization of boron waste on the properties of mortar and concrete

2.3.2.1. Mechanical Properties

Colemanite ore wastes of particle size less than 25 mm and sludge from concentrator were dried by hot air flow and then were mixed with Portland and trass cements (Erdoğan et al., 1998). The effects on the setting and mechanical properties of the colemanite ore wastes mixed with Portland and trass cements were investigated who found that some colemanite wastes can be used as cement additives and suggested that colemanite wastes can be used as cement additives up to 5% by weight of cement.

The physical and chemical properties of colemanite ore waste from concentrator, coal bottom ash, fly ash, cement - ash mixtures, cement - colemanite ore waste, and their effects on the mechanical properties of concrete were investigated (Kula et. al., 2001). Materials with various proportions were substituted with Portland cement. Physical properties such as setting time, volume expansion, and compressive strength were obtained and compared to the reference mixture and Turkish standards (TS). Consequently cement replacement materials had clear effects on the mechanical properties. The use of fly ash and bottom ash even at the concentration of 25% showed either comparable or better result compared to reference mixture. Despite the fact that replacement of Portland cement by 9 % of colemanite ore waste cause's reduction in the compressive strength, the values obtained are within the limit of TS. Therefore, colemanite ore waste, fly ash, and bottom ash can be used as cementitious materials (Kula et. al., 2001).

Boncukoğlu et. al., studied to stabilize borogypsum, and produce cements by adding borogypsum instead of natural gypsum to clinker. Concrete using cement produced with borogypsum was tested to find the mechanical properties. The test values also were compared with those of concrete from cement with natural gypsum. Compressive strength of concrete from cement produced with borogypsum was found to be higher than that of natural gypsum. In addition that the setting time of cement with borogypsum was longer than that of the Portland cement (Boncukoğlu et. al., 2002)

2.3.2.2. Durability Properties

Durability is one of the critical problems in the development of concrete technologies and construction of reinforced concrete structures with long service lives (i.e. 250 years or more) due to some economical and environmental reasons (Mehta 1997, 1999, 2002). Concrete technologies must be developed by using three criteria such as cost of materials and construction, durability and environmental friendliness for the future of the world (Mehta 1999).

3. EXPERIMENTAL STUDY

3.1 Materials

3.1.1. Cement

3.1.1.1. Portland Cement

The cement used in this study is Portland cement (CEM I 42.5R) conforming to the Turkish Standard TS EN 197-1 (which mainly based on the European EN 197-1). It has a specific gravity of 3.14 and a surface area (Blaine) of 327 m²/kg. The physical and chemical properties of the cement used are given in Table 3.1. It was supplied by Adana Cement Factory.

3.1.1.2. Boron Modified Active Belite (BAB) Cement

BAB cement conforming TS 13353- Draft Turkish Standard was used in this study. Major characteristic of the BAB cement is shown in Table 3.1

3.1.2. Aggregate

Both fine and coarse aggregates were used to produce the plain and Boron Modified Active Belite (BAB) cement concretes. The fine aggregate was a mix of river sand and crushed sand whereas the coarse aggregate was river gravel with a maximum particle size of 24 mm. Both aggregates were obtained from local sources. Properties of the aggregates are presented in Table 3.2. and grading of the them is shown in Figure 3.1.

Table 3.1. Chemical compositions and physical properties of Portland cement and BAB cement

Item	Portland Cement	BAB Cement
SiO ₂ (%)	19.73	19.10
Al ₂ O ₃ (%)	5.09	4.68
Fe ₂ O ₃ (%)	3.99	3.42
CaO (%)	62.86	57.1
MgO (%)	1.61	1.32
SO ₃ (%)	2.62	2.68
Equivalent Alkalies (Na ₂ O+0,658.K ₂ O) (Na ₂ O=0,34 K ₂ O=0,78)	0.18	0.86
Cl ⁻ (%)	0.01	0.001
Insoluble residue (%)	0.24	0.70
Loss on ignition (%)	1.90	3.82
Free lime (%)	0.57	--
Specific gravity (g/cm ³)	3.14	3.09
Setting time, Vicat needle Initial/Final (h-min)	2-46/3-44	2-25/3-00
Le chatelier (mm)	1	0.5
Specific surface area (m ² /kg)	327	356
Boric Oxide (B ₂ O ₃)	--	3.00
Gypsum	--	4.85
Clinker	--	86.1

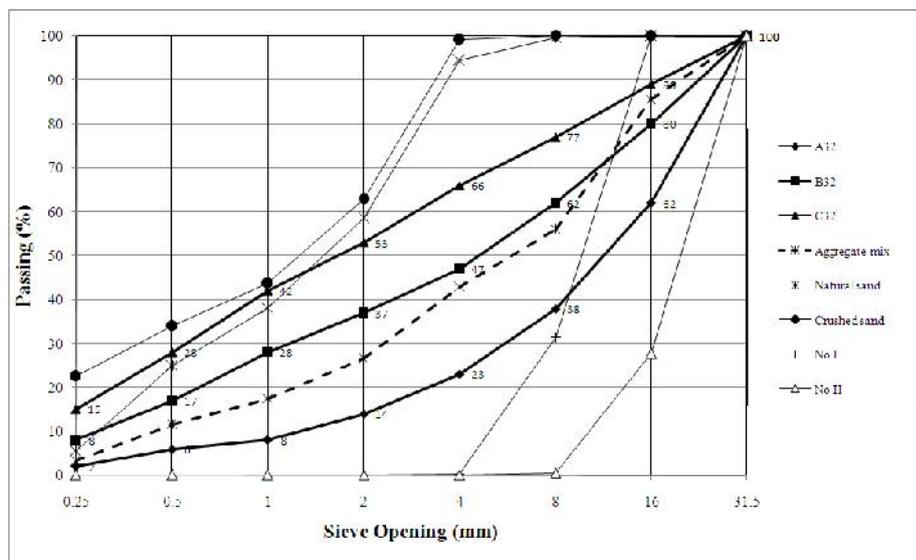


Figure 3.1 Aggregate grading curves zones

Table 3.2 Physical properties of aggregates

Sieve size (mm)	Fine aggregate		Coarse aggregate	
	Natural Sand	Crushed Sand	No I	No II
Fineness modulus	2.79	2.38	5.68	6.72
Specific gravity	2.66	2.45	2.72	2.73
Absorption, %	0.55	0.92	0.45	0.42

3.1.3. Superplasticizer

A commercially available sulphonated naphthalene formaldehyde-based superplasticizer was used to give a consistent workability. The properties of the superplasticizer are given in Table 3.3. It was supplied by Grace Chemical Corp.

Table 3.3 Properties of the superplasticizer

Color	Dark brown
State	Liquid
Specific gravity (g/cm ³)	1.22
Freezing point	-4 °C
Chloride content	None
Nitrate content	None

3.2. Details of Concrete Mixtures

Two series of control mixtures with w/c ratios of 0.35 (Series 1) and 0.55 (Series 2) were designed. BAB concrete mixtures were designed for both series. Therefore, totally four different mixtures were prepared in this study. Details of the mixtures are given in Table 3.4. Grading of the aggregate mixture was kept constant for all concretes. The superplasticizer was added at the time of mixing to obtain the specified workability at each w/cm ratio.

Table 3.4 Mixture proportions of the concrete in kg/m³

Materials		Concrete series			
		Series 1 (w/cm=0.35)		Series 2 (w/cm=0.55)	
		Portland Cement Concretes	BAB Cement Concretes	Portland Cement Concretes	BAB Cement Concretes
Cement		450.0	450.0	350.0	350.0
Water		157.5	157.5	192.5	192.5
Fine Aggregate	Natural Sand	741.0	741.0	727.8	727.8
	Crushed Sand	92.6	92.6	91.0	91.0
Coarse Aggregate	No I	648.4	648.4	636.8	636.8
	No II	370.5	370.5	363.9	363.9
Superplasticizer		4.50	4.50	3.50	3.50

3.3. Casting and Curing Conditions of Test Specimens

All of the concretes were mixed in conformity with ASTM C192 standard in a power driven revolving pan mixer. Specimens cast from each mixture consisted of fifteen 150x150x150 mm cubes for compressive strength testing, four 100x200 mm cylinders for sorptivity and six 150x300 mm cylinders for splitting tensile strength tests, four 100x200 mm cylinders for chloride ion permeability measurements. All mixtures were placed into the steel moulds in two layers, each of which being vibrated for a couple of seconds. All of the moulded specimens were covered with a plastic sheet and left in the casting room for 24 hours. After mould removal, the specimens were divided into four groups for different curing regimes. The details of the curing regimes are as follows.

3.3.1. Initial Water Curing (IW)

Specimens were kept in the water for 6 days then they were take out of water and left in air to cure continuously in the laboratory under ambient condition until the test age. The temperature was moderately controlled at 20 °C, but humidity was uncontrolled and generally ranged between 50 to 80%. Specimens were designated as IW and were called initially water cured concretes.

3.3.2. Permanent Water Curing (PW)

Specimens were left to cure continuously in water at 20 ± 2 °C until the test age. Specimens were designated as PW and were called permanent water cured concretes.

3.3.3. Initial High Temperature Water Curing (IH)

Specimens were cured 6 days in the water having temperature of 35 ± 2 °C then the specimens were kept in air to cure continuously in the laboratory under ambient condition until the test age. Specimens were designated as IH and were called initial high temperature water cured concrete.

3.3.4. Initial Burlap Curing (IB)

Specimens were cured 6 days under wet burlap then the specimens were kept in air as IW and IH concretes until test age. Specimens were designated as IB and are called initial burlap cured at ambient temperature.

In this study, the concrete were marked according to cement type and initial curing condition. For instance, BABC-IB represents the concrete produced with BAB cement and initially cured under wet burlap.

Thereafter, the specimens were tested in conformity with the specified test methods.

3.4. Test Procedures

3.4.1. Compressive Strength

For compressive strength measurement of concretes, 150x150 mm cubes were tested according to ASTM C 39 by means of a 3000 kN capacity testing machine. On

150x150x150 mm cubes for each mixture at the ages of 7, 14, 28, 56 and 90 days in order to evaluate early and late compressive strength gain. The compressive strength was computed from average of three specimens at each testing age.

3.4.2. Splitting Tensile Strength

Splitting tensile strength of the concretes will be measured on 150x300 mm cylinder specimens at 28 and 90 days as recommended by ASTM C 496. The splitting tensile strength reported herein is the average of three cylinders.

3.4.3. Water Sorptivity

The sorptivity test measures the rate at which water is drawn into the pores of concrete. For this, three test specimens having a dimension of Ø100x50 mm are employed. The specimens are dried in an oven at about 50 °C until constant mass and then allowed to cool to the ambient temperature in a sealed container. Afterwards, the sides of the specimens are coated by paraffin and as shown in Figure 3.2, the sorptivity test is carried out by placing the specimens on glass rods in a tray such that their bottom surface up to a height of 5 mm is in contact with water. This procedure is considered to allow free water movement through the bottom surface. The total surface area of water within the tray should not be less than 10 times that of the specimen cross-sectional area. The specimens are removed from the tray and weighed at different time intervals up to 1 hour to evaluate mass gain. The volume of water absorbed is calculated by dividing the mass gained by the nominal surface area of the specimen and by the density of water. These values are plotted against the square root of time. The slope of the line of the best fit is defined as the sorptivity coefficient of concrete. For each test, the measurements are obtained from three specimens and the average values are reported. The test will be conducted at the ages of 28 and 90 days.

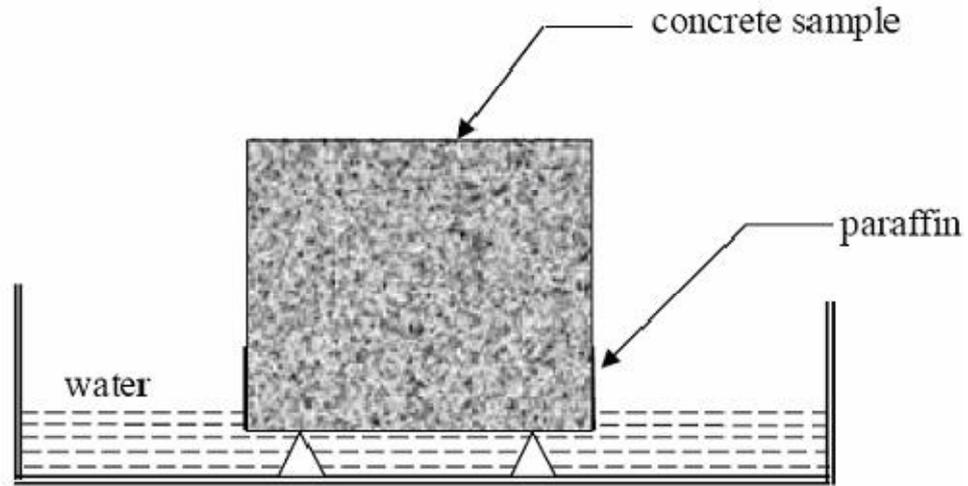


Figure 3.2 Sorptivity test set up (ASTM C1585)

3.4.4. Rapid Chloride Permeability Test (RCPT)

The rapid chloride permeability test (RCPT) will be conducted in order to determine the resistance of the concretes to the penetration of chloride ions according to “Standard Method of Test for Rapid Determination of the Chloride Permeability of Concrete” (AASHTO T277). Three specimens for each mortar mixture will be tested simultaneously at each testing age (28, 90 days). After curing, a 50 mm thick disc sample is cut from the middle of each Ø100x200 mm cylinder and moisture conditioned as mentioned in AASHTO T277. Then, the disc specimens are transferred to the test cell in which one face of the specimen is in contact with 0.30 N NaOH solutions and the other face is with 3% NaCl solution (Figure 3.3 – Figure 3.4). A direct voltage of 60.0 ± 0.1 V is applied across the faces. A data logger registered the current passing through the concrete specimen over a period of 6 hours. Terminating the test after 6 hours, current (in amperes) versus time (in seconds) are plotted for each concrete and the area underneath the curve is integrated to obtain the charge passed (in coulombs). AASHTO T277 classifies the chloride permeability into five classes from ‘High’ to ‘Negligible’ on the basis of the coulombs calculated (Table 3.5).

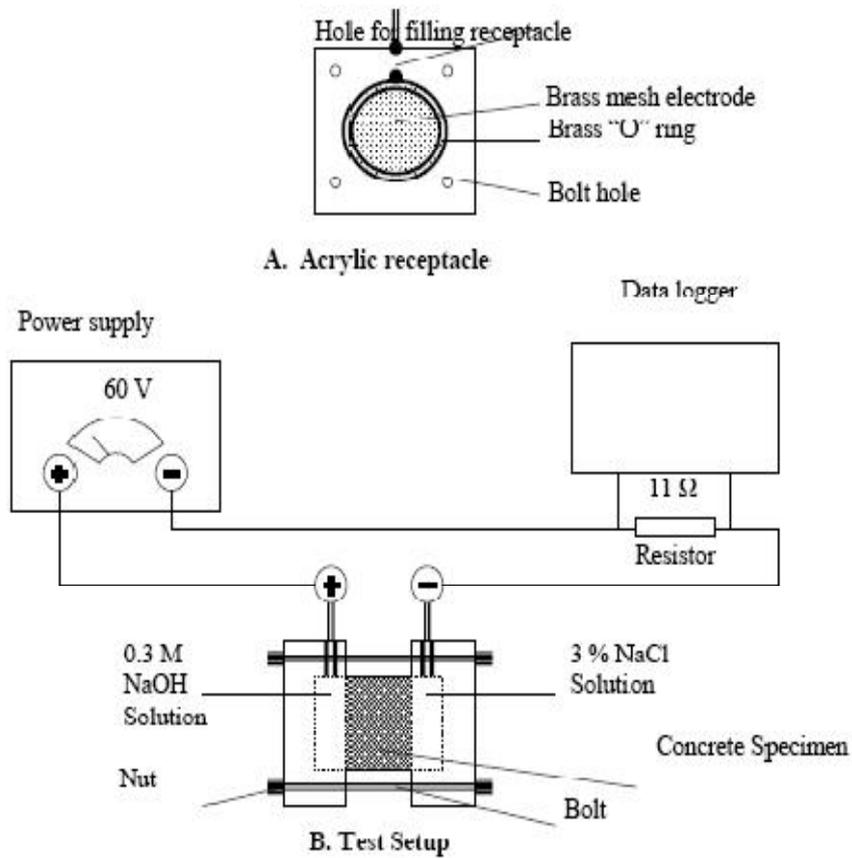


Figure 3.3 Schematic presentation of the test set up for RCPT (AASHTO T277; ASTM C1202-94)



Figure 3.4 Photographic view of the RCPT test set up

Table 3.5 Interpretation of the test results obtained using RCPT test (ASTM C1202-94)

Charge Passed [Coulombs]	Chloride Permeability	Typical of -
>4.000	High	High w/c ratio (< 0.6) conventional Portland cement concrete
2.000 – 4.000	Moderate	Moderate w/c ratio (0.4 - 0.5) conventional Portland cement concrete
1.000 – 2.000	Low	Low w/c ratio (< 0.4) conventional Portland cement concrete
100 – 1.000	Very Low	Latex-modified concrete, Internally sealed concrete
<100	Negligible	Polymer-impregnated concrete, Polymer concrete

4. TEST RESULTS AND DISCUSSIONS

4.1. Compressive Strength

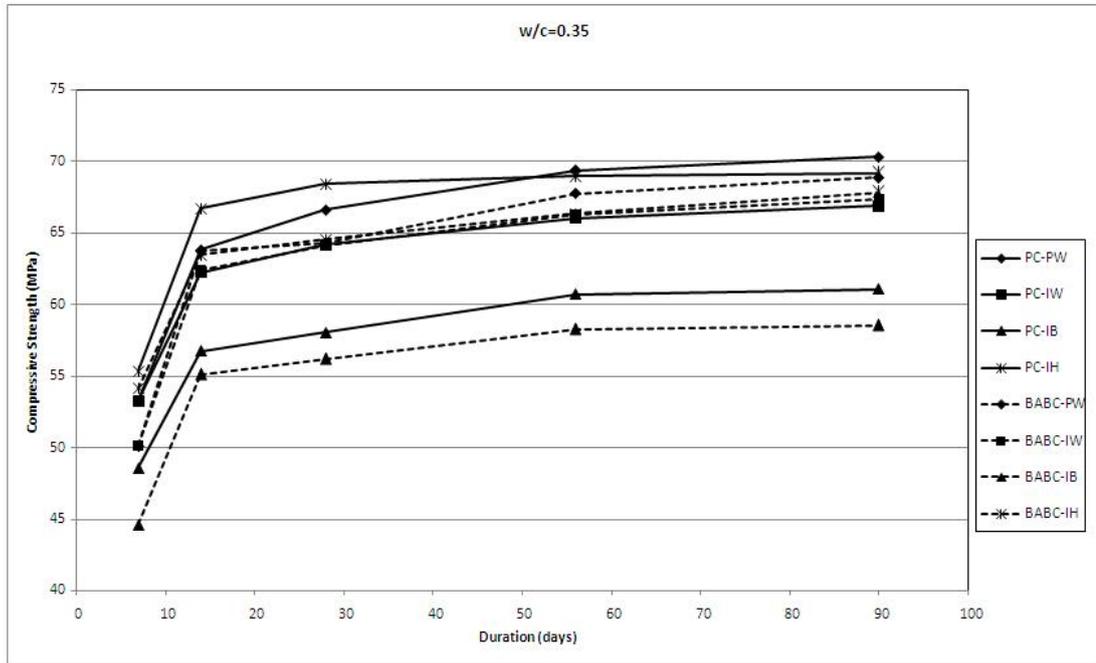
The compressive strength developments of the concretes are shown in Figure 4.1. The compressive strength values are also given in Table 4.1. It was observed that the effect of cement type and initial curing conditions and w/c ratios had of major importance. Regardless the initial curing condition and the type of cement, compressive strength of the concretes having w/c ratio of 0.35 ranged from 44 to 55 MPa and from 58 to 71 MPa for 7 and 90 days in between respectively. However, for the concretes with w/c ratio of 0.55 these ranges were 23 and 29 MPa and 35 and 52 MPa.

For all of the concrete type, permanent water curing provided the highest compressive strength development independent of w/c ratio and cement type. The lowest compressive strength values were observed at concretes exposed to IB. The concretes produced with BAB cement were observed to be more susceptible to IB curing especially at w/c ratio 0.35. The compressive strength development of the BABC-IB is lower than PC-IB at w/c ratio of 0.35, while at w/c ratio of 0.55 this situation was reversed. For example, 90-day compressive strengths of the PC and BAB cement concretes with w/c ratio of 0.35 were measured as 61 and 58.5 MPa, whereas the concretes with 0.55 w/c ratio had 90-day compressive strength values of 35 and 41 MPa, respectively. The concretes exposed to IH curing, had the highest early age strength values without depending on w/c ratio and cement type. Nevertheless, the compressive strength values of the concretes under PW curing condition reached to that of IH cured concretes at 28 days. At later ages (56 and 90 days) the highest compressive strength values were observed at PW cured concretes. This situation was more pronounced for the concretes produced with BAB cement. For instance, BABC-PW and BABC-IH concretes with w/c ratio of 0.55, had

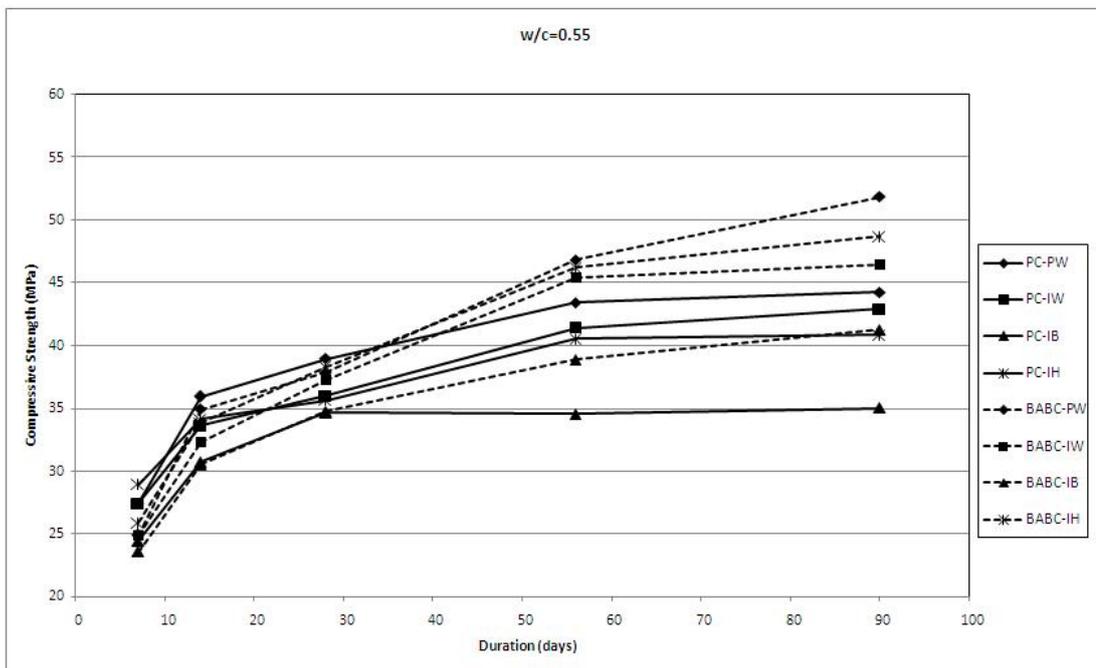
approximately similar compressive strength values at 28 days of curing, however, there was a noticeable divergence at later ages. BAB cement concretes were observed to be more vulnerable to the curing condition especially at w/c ratio of 0.55. The compressive strength developments of the BAB cement concretes exposed to IW curing were less than that of IH and PW curing. However at w/c ratio of 0.35, BABC-IW concretes demonstrated similar trend of compressive strength development at all ages.

For the concrete group having w/c ratio of 0.35, the concretes containing PC demonstrated better compressive strength development than that of BAB cement concretes under the same initial curing conditions. However, the compressive strength development of PC and BAB cement concretes demonstrated a close trend until 90 days. On the other hand, the concretes with 0.55 w/c ratio showed a different trend. While at early ages the ranges of compressive strength values of BAB cement and PC concretes were close to each other, but at later ages there was a noticeable distinction. Moreover, the range of compressive strengths at each age showed the effect of w/c ratio on the compressive strength development. For example, irrespective of the cement type and curing conditions, the differences between the maximum and the minimum compressive strengths were 10.73 MPa and 11.81 MPa for concretes having 0.35 w/c ratios at 7 and 90 days respectively, while the concretes produced with 0.55 w/c ratios had 5.4 MPa and 16.83 MPa compressive strength ages. BAB cement concrete with w/c ratio of 0.55 showed better performances than PC concretes in terms of compressive strength development for all initial curing regimes. The highest 90-day compressive strengths were measured as 52 and 44 MPa for BABC-PW and PC-PW concretes with 0.55 w/c ratio, respectively.

The author has not yet found further studies in the literature regarding the compressive strength developments of the BAB cement concretes or mortars. Sağlık et al. (2008) studied the characteristics of BAB cement concrete. They reported that the compressive strength development of the BAB and Portland cement concretes beginning from 2 days to 365 days. The ranges of the compressive strengths of PC and BAB cement were 26-58 MPa and 17-74 MPa, respectively.



a)



b)

Figure 4.1 Compressive strength development of concretes produced with w/c ratios of a) 0.35 and b) 0.55

Table 4.1. Compressive strength values of PC and BAB cement concrete

Cement Type	w/c ratio	Initial Curing	Days				
			7	14	28	56	90
PC	0.35	PW	53.26	63.82	66.62	69.35	70.32
		IH	55.32	66.7	68.42	68.95	69.15
		IW	53.26	62.22	64.15	66.02	66.85
		IB	48.54	56.73	58.02	60.71	61.05
	0.55	PW	27.42	35.93	38.95	43.46	44.29
		IH	28.95	34.13	35.65	40.55	40.88
		IW	27.42	33.65	36.02	41.42	42.92
		IB	24.42	30.72	34.65	34.56	35.04
BABC	0.35	PW	50.09	63.71	64.26	67.72	68.85
		IH	54.11	63.46	64.52	66.34	67.8
		IW	50.09	62.42	64.11	66.28	67.35
		IB	44.59	55.08	56.16	58.24	58.51
	0.55	PW	24.88	34.94	37.87	46.85	51.87
		IH	25.87	33.82	38.35	46.21	48.73
		IW	24.88	32.35	37.25	45.46	46.44
		IB	23.55	30.55	34.75	38.88	41.28

4.2. Splitting Tensile Strength

Splitting tensile strength values of the concretes produced by PC and BAB cements were presented in Figure 4.2. Splitting tensile strength values are also given in Table 4.2. Unlike compressive strength development, the 90-day splitting tensile strengths of the PC concretes were generally lower than those of BAB cement concretes at w/c ratio of 0.35. On the other hand, the PC concretes with 0.55 w/c ratio had higher splitting tensile strength than BAB cement concretes, irrespective of the initial curing regimes. For example, while IH cured concretes produced with 0.35 w/c ratio and including PC and BAB cement had 90-day splitting tensile strength values of 3.47 MPa and 3.55 MPa, respectively, the concretes with 0.55 w/c ratio at the same curing condition possessed 3.39 and 2.80 MPa for PC and BAB cement concretes.

There is a remarkable difference between 28 and 90 days splitting tensile strengths of the concretes especially for those produced with BAB cement. The variations of 28

and 90 days splitting tensile strength values for PC and BAB cement concretes with w/c ratio of 0.35 were observed as 1 to 26% and 20 to 50% respectively, independent of curing condition. However, these changes were observed as 37%-58% and 51%-83% for PC and BAB cement concretes with w/c ratio of 0.55.

In the study of Sui et. al. (2004), compressive, splitting, and flexural tensile strengths of the high belite cement (HBC) concretes was studied. They reported that the development trend of the flexural strength and splitting tensile strength of HBC concrete with age is similar to that of compressive strength, namely, lower early strength, equivalent 28 day strength and higher late strength compared with OPC concretes.

When considering the splitting tensile strength developments, the curing regimes can be put in order from the best to the poor curing regime as PW, IH, IW, and IB irrespective of w/c ratio and cement type, as it was observed in compressive strength development.

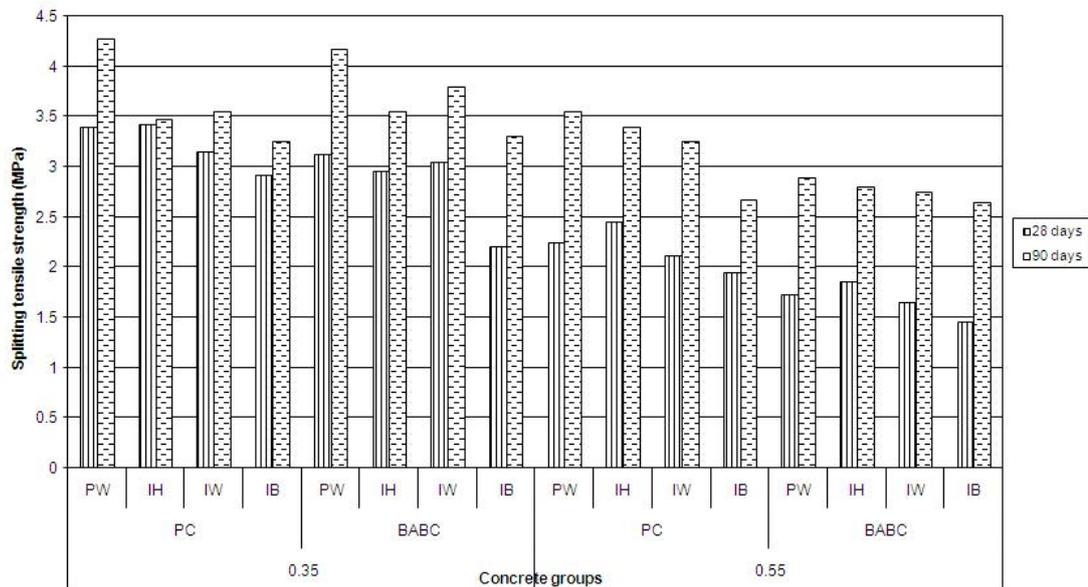


Figure 4.2 Splitting tensile strength development of concretes according to cement type, w/c ratio, and curing regimes

Table 4.2. Splitting tensile strength values of PC and BAB cement concrete

Cement Type	w/c ratio	Initial Curing	Days	
			28	90
PC	0.35	PW	3.39	4.27
		IH	3.42	3.47
		IW	3.15	3.55
		IB	2.92	3.25
	0.55	PW	2.25	3.55
		IH	2.45	3.39
		IW	2.11	3.25
		IB	1.95	2.67
BABC	0.35	PW	3.12	4.17
		IH	2.96	3.55
		IW	3.05	3.8
		IB	2.2	3.31
	0.55	PW	1.72	2.89
		IH	1.85	2.8
		IW	1.65	2.75
		IB	1.45	2.65

4.3. Water Sorptivity

The variation in sorptivity index of the concretes produced with PC and BAB cement is shown in Figure 4.3. The corresponding sorptivity values are also presented in Table 4.3. It was observed that there is a systematic decrease in the sorptivity values as curing period increases from 28 to 90 days. While sorptivity coefficients for the concretes produced with w/c ratio of 0.35 varied between 0.063 and 0.122 mm/min^{1/2}, the concretes with 0.55 w/c ratio had sorptivity of 0.171-0.306 mm/min^{1/2}, irrespective of the cement type, age, and curing type. As a matter of the fact that the BAB cement has lower hydration kinetics than Portland cement (Sui et. al., 2004; Sağlık et. al., 2008), thus, the change in 28 and 90-day sorptivity values of BAB cement concretes were observed to be more pronounced than PC concretes, especially at w/ c ratio of 0.55. For instance PC-IB concrete showed 2.5% change in sorptivity coefficient, while at BABC-IB concrete, 17.3% change was observed.

For both w/c ratios BAB cement concretes illustrated better performance at 28 and 90 days of curing in terms of sorptivity compared to Portland cement concretes. For example, when considering 90 days sorptivity coefficients of IW cured concretes at w/c ratio of 0.35, PC and BAB cement concretes had sorptivity of 0.101 mm/min^{1/2} and 0.072 mm/min^{1/2}, respectively. This situation can be attributed to that BAB cement has better pore refinement property than that of Portland cement. Because, the lower the permeability of concrete, the better the pore structure of the concrete (Guerrero et al., 2005; Poon et al., 2006; Güneysi and Mermerdas, 2007; Güneysi et al., 2008). Moreover there is a direct relationship with the pore refinement and improved strength; strength enhancement can be linked to the sorptivity of concretes.

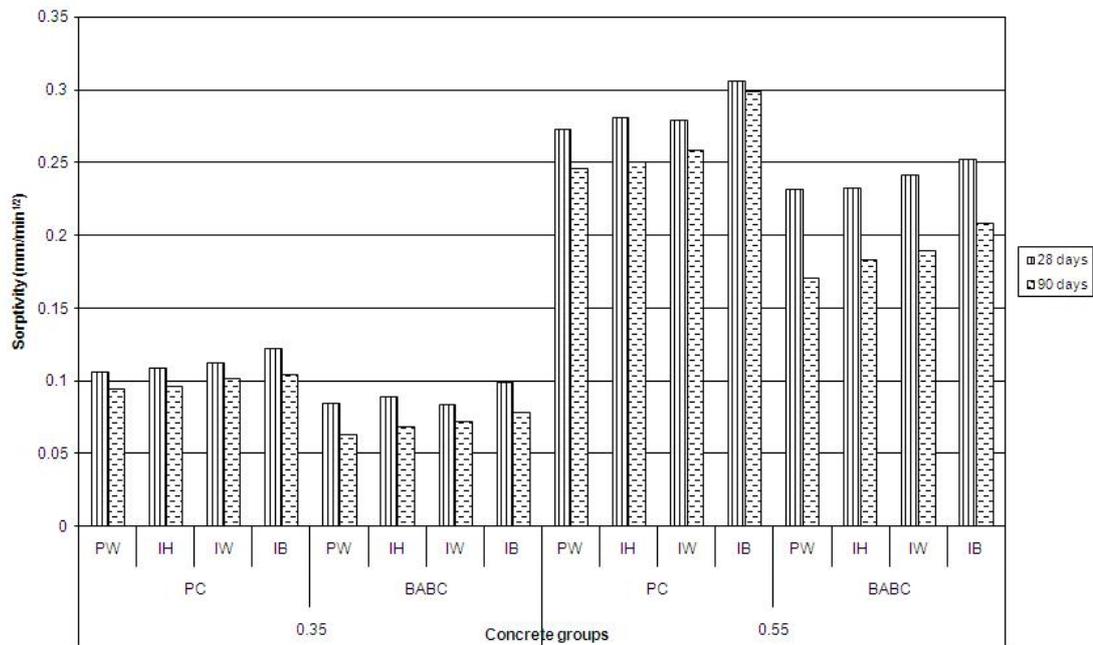


Figure 4.3 Variation of sorptivity coefficients of concretes according to cement type, w/c ratio, and curing regimes

Table 4.3. Sorptivity coefficients of PC and BAB cement concrete

Cement Type	w/c ratio	Initial Curing	Days	
			28	90
PC	0.35	PW	0.10599	0.09429
		IH	0.10818	0.09615
		IW	0.1125	0.1011
		IB	0.12216	0.1044
	0.55	PW	0.27211	0.24585
		IH	0.28075	0.25008
		IW	0.2785	0.25854
		IB	0.30565	0.29814
BABC	0.35	PW	0.08435	0.06275
		IH	0.08855	0.06856
		IW	0.08345	0.07156
		IB	0.09875	0.07774
	0.55	PW	0.23125	0.17046
		IH	0.23239	0.18284
		IW	0.24074	0.18935
		IB	0.25184	0.20838

4.4. Rapid Chloride Permeability

Test results related to the resistance of PC and BAB cement concretes against chloride ion penetration are presented in Figure 4.4. RCPT values are also given in Table 4.4. The reduction of the w/c ratio from 0.55 to 0.35 reduced the rapid chloride ion permeability in both concrete groups. As in the water sorptivity, chloride ion permeability of the concretes demonstrated a systematic reduction with an increase in curing period from 28 to 90 days, especially in the case of concretes included BAB cement. The change between 28 and 90 day-RCPT values were much clear in BAB cement concretes as in water sorptivity variation. BABC-PW concretes had the lowest chloride ion permeability at both w/c ratios while the PC-IB concretes had the highest values.

The concretes with w/c ratio of 0.35 were generally classified as low chloride permeability concretes. However, the concretes exposed to IB curing illustrated

moderate chloride permeability. The range of the charge passed were measured as 1125 to 2125 C and 1643 to 2472 C for BAB cement and PC concretes, respectively. For both w/c ratios BAB cement concretes possessed lower chloride permeability than PC concretes, mainly depending on the curing condition and age. Whilst the lowest charges passed were measured at the PW cured concretes, the highest values were observed at IB cured concretes, independent of cement type and w/c ratios.

When 28 day RCPT values were taken into account, the concretes with 0.55 w/c ratio were rated as high chloride permeability concretes (>4000 C) according to ASSHTO T277-89. Nevertheless, according to 90 day RCPT values, only BABC-PW and BABC-IH concretes had moderate chloride permeability. This situation depicts that even at high w/c ratios, harmful effect of chloride ions may be mitigated to some extents by using BAB cement.

Although there are limited studies in the literature regarding the durability properties of active belite cement concretes, some supporting results with the finding of the current study have been reported. For example, Sui et al. (2004) studied some durability properties of high belite cement (HBC) concretes. They concluded that HBC concretes show better freeze-thaw resistance, higher chloride permeability resistance and carbonation resistance and less shrinkage compared with PC concretes. In the study of Sağlık et. al. (2008) some durability tests like water permeability and chloride penetration resistance tests were applied to the concretes produced with BAB cement. They reported that, the concrete specimens made with BAB cement indicated more resistance as comparing to the specimens made with normal Portland cement even at lower cement contents.

Aforementioned outcomes indicate that BAB cement can be utilized in concrete production incorporated with a proper curing for such an environments where there is a severe chloride attack. For instance, when considering 90 day-RCPT results, concretes produced with w/c ratio of 0.35, 1643 C (low) and 1125 C (low) were measured for PC-PW and BABC-PW concretes, respectively. In the same manner, for the concretes with 0.55 w/c ratio the charges passed were measured as 4271 C (high) and 3586 C (moderate) for these concretes, respectively

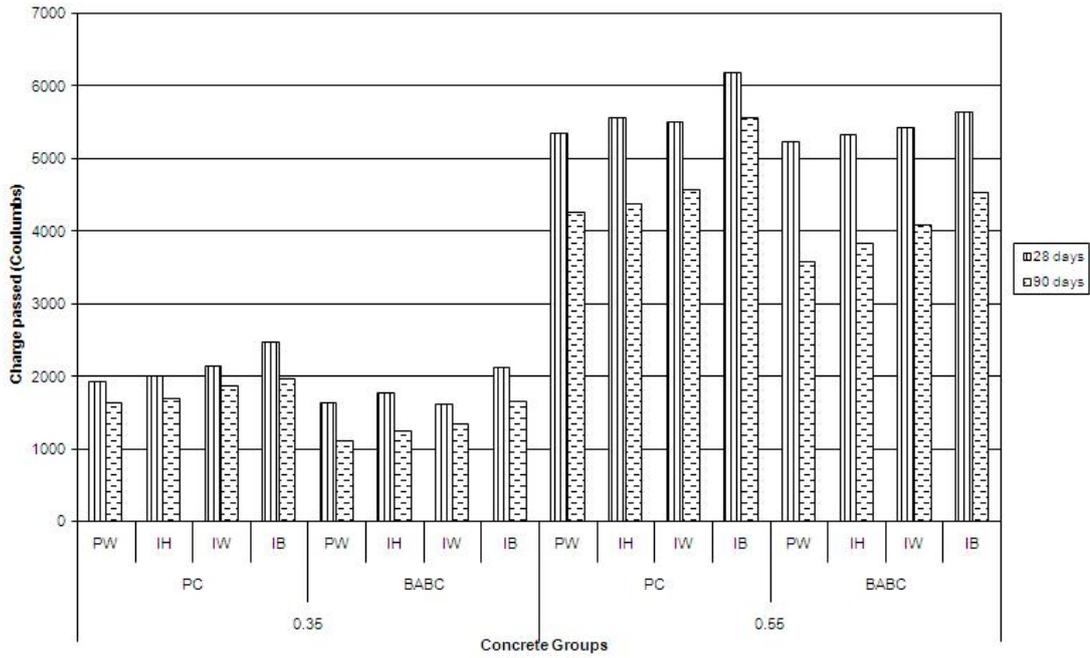


Figure 4.4 Variation of chloride ion permeability of concretes according to cement type, w/c ratio, and curing regimes

Table 4.4 RCPT values of PC and BAB cement concrete

Cement Type	w/c ratio	Initial Curing	Days	
			28	90
PC	0.35	PW	1933	1643
		IH	2006	1705
		IW	2150	1870
		IB	2472	1980
	0.55	PW	5353	4271
		IH	5569	4377
		IW	5513	4589
		IB	6191	5579
BABC	0.35	PW	1645	1125
		IH	1785	1252
		IW	1615	1352
		IB	2125	1658
	0.55	PW	5231	3587
		IH	5335	3846
		IW	5444	4084
		IB	5646	4535

5. STATISTICAL EVALUATION OF THE TEST RESULTS

5.1. An overview of the Analysis of Variance (ANOVA)

In statistics, analysis of variance (ANOVA) is a collection of statistical models, and their associated procedures, in which the observed variance in a particular variable is partitioned into components attributable to different sources of variation. In its simplest form ANOVA provides a statistical test of whether or not the means of several groups are all equal, and therefore generalizes t-test to more than two groups. ANOVAs are helpful because they possess an advantage over a two-sample t-test. Doing multiple two-sample t-tests would result in an increased chance of committing a type I error. For this reason, ANOVA are useful in comparing three or more means (Weiss, 2006).

ANOVA is similar to regression in that it is used to investigate and model the relationship between a response variable and one or more predictor variables. However, analysis of variance differs from regression in two ways: the predictor variables are qualitative (categorical), and no assumption is made about the nature of the relationship (that is, the model does not include coefficients for variables). In effect, analysis of variance extends the two-sample t-test for testing the equality of two population means to a more general null hypothesis of comparing the equality of more than two means, versus them not all being equal.

5.2. Statistical evaluation of test results

In order to assess the statistical significance of the experimental test parameters, namely, cement type, w/c ratio, initial curing condition, and age of the concrete on the mechanical and permeability properties of concretes, a general linear model analysis of variance (GLM-ANOVA) was performed at a 0.05 level of significance (Weiss, 2006; Lindman, 1992). GLM-ANOVA is an important statistical analysis and diagnostic tool which helps in reducing the error variance and quantifies the

dominance of a control factor. In the analysis, compressive strength, splitting tensile strength, sorptivity and RCPT values were assigned as the dependent variables while the experimental test parameters (cement type, w/c ratio, initial curing, age) were selected as the independent factors. The general linear model analysis of variance was performed and the effective test parameter and/or parameters and their percent contributions on the above mentioned properties of concretes were determined. The statistical parameters were presented in Table 5.1.

The p-values in Table 5.1 show the significance of the given test parameters on the test results. If a system has a p-value of less than 0.05, it is accepted as a significant factor on the test result. As it can be seen in Table 5.1, the p-value of all parameters on the splitting tensile strength, water sorptivity, and chloride ion penetration test results were less than 0.05, indicating that the variability of experimental test results can be explained in terms of test parameters. However, if the test results GLM-ANOVA of compressive strength values are taken into consideration, it was observed that there is not sufficient evidence for equality of the means of the compressive strengths of the concretes produced with different cement types.

The estimated contributions of the parameters on the measured test results are also presented in Table 5.1. The column under the percentage contribution provides an estimate of the degree of effectiveness of the independent parameters on the measured response. The higher the contribution ratio is determined, the higher the effectiveness of the parameters to that particular result. Likewise, if the percentage contribution is low, the contribution of the factors to that particular response is low. According to the contribution column in Table 5.1, w/c ratio is observed to be the most effective parameter on the mechanical properties, however when considering permeability characteristics, cement type was proved to be dominantly effective on sorptivity and chloride ion penetration. Since cement type was statistically determined as insignificant on the compressive strength values, contribution ratio was not calculated.

Table 5.1 Summary of the general linear model analysis of variance (GLM-ANOVA) analysis of the experimental test result

Dependent variable (properties of SCM)	Source of variation	Statistical parameters					Significant	Contributon %
		Degree of freedom	Sum of square	Mean square	F	<i>p</i> -value		
Compressive Strength	Cement Type	1	0.10	0.10	0.01	0.0926	NO	-
	w/c Ratio	1	12684.20	12684.20	2183.92	0.000	YES	79
	Curing	3	617.80	205.90	35.46	0.000	YES	3.8
	Age	4	2763.80	691.00	118.97	0.000	YES	17.2
	Error	70	406.60	5.80				
Splitting Tensile Strength	Cement Type	1	0.8192	0.8192	13.21	0.001	YES	5.6
	w/c Ratio	1	6.3013	6.3013	101.64	0.000	YES	43.2
	Curing	3	1.6234	0.5411	8.73	0.000	YES	11.1
	Age	1	5.8482	5.8482	94.33	0.000	YES	40.1
	Error	25	1.5499					
Water absorption	Cement Type	1	0.182467	0.182467	883.89	0.000	YES	88.7
	w/c Ratio	1	0.01494	0.01494	72.37	0.000	YES	7.3
	Curing	3	0.002808	0.000936	4.53	0.011	YES	1.4
	Age	1	0.005433	0.005433	26.32	0.000	YES	2.6
	Error	25	0.005161	0.000206				
Chloride ion penetration	Cement Type	1	80742661	80742661	998.04	0.000	YES	90.5
	w/c Ratio	1	1503486	1503486	18.58	0.000	YES	1.7
	Curing	3	2047811	682604	8.44	0.000	YES	2.3
	Age	1	4930389	4930389	60.94	0.000	YES	5.5
	Error	25	2022537	80901				

5. CONCLUSIONS

The following conclusions can be drawn according to the experimental results obtained in the current study.

1. Although compressive strength development at low w/c ratio were observed to be higher at PC concretes, the BAB cement concretes at high w/c ratio exhibited relatively better performance.
2. Splitting tensile strength development of BAB cement concretes have similar tendency as PC concretes. However there were slight differences between splitting tensile strength values.
3. All of the sorptivity coefficient values of concretes produced with BAB cement were considerably less than those of the PC cement concretes. Due to higher amount of C2S content in BAB cement compared to PC, there is a further hydration reaction at later ages to form additional tobermorite gel. This situation leads in better matrix structure resulting in lower capillary water transport.
4. At both w/c ratios the concretes produced with BAB cement had lower chloride permeability than PC concretes, depending on the curing type and age. Utilization of BAB cement in concrete production was proved to be effective when durability aspects in terms of chloride resistance are taken into consideration.
5. Both mechanical and durability properties of the concretes were fluctuated due to the curing condition. Yet, BAB cement concretes were observed to be more susceptible to the curing regime adopted.
6. GLM-ANOVA results have shown that all of the experimental parameters were effective on water sorptivity and chloride ion permeability, however, when considering the compressive and splitting tensile strength developments, there is not sufficient evidence that the type of cement effective on the mechanical properties.

6. REFERENCES

American Association of State Highway and Transportation Officials. (2007). *Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for Use in Concrete*. AASHTO M 295

American Association of States Highway and Transportation Officials. (1990). *Rapid determination of the chloride permeability of concrete, Standard specifications-part, II*. Washington DC. ASSHTO T277-89

American Concrete Institute. (1995). *Ground Granulated Blast-Furnace Slag as a Cementitious Constituent in Concrete*. ACI 233R-95.

American Concrete Institute. (1996). *Guide for the Use of Silica Fume in Concrete*. ACI 234R-96.

American Society for Testing and Materials. (2010). ASTM C 1202-10 Standard Test Method for Electrical Indication of Chloride's Ability to Resist Chloride. *Annual Book of ASTM Standards*. V.04.02, West Conshohocken, PA.

American Society for Testing And Materials. (2010). Standard test method for splitting tensile strength of cylindrical concrete specimens designation. *Annual Book of ASTM Standards*. V.04.02, West Conshohocken, PA. ASTM C496-90

American Society for Testing And Materials.(2010). Standard Specification for Coal Fly Ash and Raw or Calcined Natural Pozzolan for use as a Mineral Admixture in Concrete *Annual Book of ASTM Standards*. V.04.02, West Conshohocken, PA. ASTM C 618-08A

American Society for Testing And Materials.(2010). Standard Specification for Ground Granulated Blast-Furnace Slag for Use in Concrete and Mortars. *Annual Book of ASTM Standards*. V.04.02, West Conshohocken, PA. ASTM C 989

American Society for Testing And Materials.(2010). ASTM Standards C1585 Standard Test Method for Measurement of Rate of Absorption of Water by Hydraulic-Cement Concretes. *Annual Book of ASTM Standards*. V.04.02, West Conshohocken, PA.

Anthony, J.W., Bideaux, R.A., Bladh, K.W., Nichols, M.C. (2003). Handbook of Mineralogy, Borates, Carbonates, Sulfates. *Mineral Data Publishing, Volume V*. pp.158, Tucson, Arizona.

Argust, Peter (1998). Distribution of boron in the environment. *Biological Trace Element Research*, 66, 131–143.

Baker, M. (1984). Evaluation on the utilization options, combustion by products utilization manual. *EPRI report* No. CS-3122.

Barth, S. (1997). Boron isotopic analysis of natural fresh and saline waters by negative thermal ionization mass spectrometry. *Chemical Geology*, 143: 255–261.

Baysal O. (1972). A mineralogical study and genesis of Sarıkaya (Kırka) borate deposits. Hacettepe University, Ankara

Berger, L. I. (1996). *Semiconductor materials*. CRC Press. pp.37–43. ISBN:0849389127.

Blevins, D.G., Lukaszewski, K.M. (1998). Functions of Boron in Plant Nutrition. *Annual Review of Plant Physiology and Plant Molecular Biology* 49: 481–500

Bonavetti V.L., Irassar E.F. (1994). The effect of stone dust content in sand. *Cement and Concrete Research*, 24(3): 580-90.

Boncukçuoğlu , R., Yılmaz, M.T., Kocakerim, M.M and Tosunoğlu, V. (2002). Utilization of trommel sieve waste as an additive in Portland cement production. *Cem. Concr. Res.* 32, pp. 35–39.

Borchert D.W., Kolker, H.W. (1970). Crystal Growth of Beta–Rhombohedral Boron. *Zeitschrift für Angewandte Physik* 29: 277.

BOREN.(National Boron Research Institute) (2008). Klinker üretiminde Kolemanit Kullanımının Araştırılması ve Çimento Endüstrisinde Uygulanabilirliği. Ankara, Turkey.

Chindaprasirt , P., Homwuttiwong, S., and Sirivivatnanon, V. (2004). Influence of fly ash fineness on strength, drying shrinkage and sulfate resistance of blended cement mortar. *Cement and Concrete Research*, **34**, 1087-1092

Çöl M, Çöl C. (2003). Environmental boron contamination in waters of Hisarcik area in the Kutahya Province of Turkey., *Food Chem. Toxicology*, **41**, No. 10, pp.1417-20.

Delaplane R.G., Dahlborg, U., Howells, W., Lundstrom, T. (1988b). A neutron diffraction study of amorphous boron using a pulsed source. *Journal of Non-Crystalline Solids*, 106: 66.

Delaplane, R.G., Dahlborg, U., Graneli, B., Fischer, P., Lundstrom, T. (1988a). A neutron diffraction study of amorphous boron. *Journal of Non-Crystalline Solids* 104: 249.

DSİ (TAKK). (2009). Technical Research and Quality Control Department, Concrete Materials Laboratory, *Technical journal*,**105**

ECETOC.(1997). *European Centre for Ecotoxicology and Toxicology of Chemicals*,

Erdoğan, Y., Zeybek, M.S., Demirbaş, A. (1998). Cement mixes Containing Colemanite Wastes From Concentrator. *Cement and Concrete Research*, **28** No: 4 605- 609.

Eremets, M. I. (2001). Superconductivity in Boron. *Science* 293: 272.

Garrett D. E. (1998). Borates. *A recent survey of the industry.:* Academic Press, San Diego, CA.

Garrett, Donald E. (1998). *Borates: handbook of deposits, processing, properties, and use*. Academic Press. pp. 102;385–386. ISBN:0122760603.

Gesoglu, M. (2004). Effects of lightweight aggregate properties on the mechanical, fracture, and physical behavior of lightweight concrete. *PhD thesis*, Bogazici University, Istanbul.

Greenwood N., Earnshaw, A. (1997). Chemistry of the Elements (2nd ed.), *Oxford: Butterworth-Heinemann*, ISBN:0080379419

Guerrero A., Goni S., Moragues A., Dolado J. S. (2005). Microstructure and Mechanical Performance of Belite Cements from High Calcium Coal Fly Ash, *Journal of American Ceramic Society*, V.**88** No.7 pp.1845–1853

Güneyisi, E., Gesoğlu, M., Mermerdaş, K. (2008). Improving strength, drying shrinkage, and pore structure of concrete using metakaolin. *Materials and Structures*, V.**41**, pp. 937–949

Güneyisi, E., Mermerdaş, K.(2007). Comparative study on strength, sorptivity, and chloride ingress characteristics of air-cured and water-cured concretes modified with metakaolin. *Materials and Structures*, V. **40**, pp.1161–1171

Güneyisi, E., Özturan, T., and Gesoğlu, M. (2005). A study on reinforcement corrosion and related properties of plain and blended cement concretes under different curing conditions. *Cement and Concrete Composites*, **27**, 449-461

HABEEB, G. A., MAHMUD, H. B. (2010). Study on properties of rice husk ash and its use as cement replacement material. *Materials Research*, V.**13**, N.2, pp. 185-190.

Helvaci C., Alonso R.N. (2000). Borate Deposits of Turkey and Argentina; A Summary and Geological Comparison. *Turkish Journal of Earth Sciences*, V. **9**, No.1, pp. 1-27

<http://images-of-elements.com/boron.php>

<http://metakaolin.com/metakaolin/>

<http://nl.wikipedia.org/wiki/Tincalconiet>,

http://realgems.org/edelsteine_liste/pic/big%20colemanite%2005.jpg

<http://www.cs.cmu.edu/~adg/images/minerals/b/u/ulexite2.jpg>

<http://www.etimaden.gov.tr>

<http://www.lenntech.com/periodic/elements/b.htm>

<http://www.mineral-forum.com/message-board/viewtopic.php?t=819>

Khatri, R.P., Sirivivatnanon, V., Yu, and L.K. (1997). Effect of curing on water permeability of concretes prepared with normal Portland cement and with slag and silica fume. *Magazine of Concrete Research*, **49**, 162-172

Kistler, R.B., Helvacı, C. (1994) Boron and Borates. in: *Industrial Minerals and Rocks (Donald D. Carr editor) 6 th Edition. Society of Mining, Metallurgy and Exploration, Inc.*, 171-186.

Kostick, Dennis S. (2006). Boron. *Mineral Yearbook*

Kriven, W.M., Bell, J.L. and Gordon, M. (1994). Advances in Ceramic Matrix Composites. In N.P. Bansal, J.P.Singh, W.M. Kriven, and H. Schneider (Eds.), *Microstructure and Microchemistry of Fully-Reacted Geopolymers and Geopolymer Matrix Composites*.

Kula I., Olgun A., Erdoğan Y. and Sevinç, V. (2001). Effect of colemanite waste, cool bottom ash, and fly ash on the properties of cement. *Cem. Concr. Res.* **31** pp. 491–494.

Laubengayer, A. W., Hurd, D. T., Newkirk, A. E., Hoard, J. L. (1943). Boron. I. Preparation and Properties of Pure Crystalline Boron. *Journal of the American Chemical Society* **65**: 1924–1931.

Lee, A.R. (1974). Blast furnace and steel slag: Production, properties and uses. *London: Edward Arnold Ltd.*

Lewis, D. W. (1981). History of slag cements. *Paper presented at University of Alabama Slag Cement Seminar, American Slag Association MF 186-6.*

Lindman HR (1992) Analysis of variance in experimental design. Springer-Verlag Publishing, NY, 531 pp

- Liu, Z. (2003). Two-body and three-body halo nuclei. *Science in China G: Physics Mechanics and Astronomy*, 46: 441.
- Luther, M. D. (1990). High-performance silica fume (microsilica) modified cementitious repair materials. 69th annual meeting of the Transportation Research Board, paper no. 890448
- Mahler, R. L. (2009). Essential Plant Micronutrients. Boron in Idaho. *University of Idaho. Retrieved*
- Malhotra, V.M., Mehta, P.K. (2002). High-Performance, High-Volume Fly Ash Concrete: Materials, Mixture Proportioning, Properties, Construction Practice, and Case Histories. *Supplementary Cementing Materials for Sustainable Development*, Ottawa, Canada, pp.101.
- Manz, O. E. (1993). Worldwide Production of Coal Ash and Utilization in Concrete and Other Products. *Proc. Tenth Int'l. Ash Use Symp. V. 2*, EPRI-TR-101774, V. 2, Project 3276, pp 64-1 to 64-7
- Martin, J. L. (1938). The Densification of Rice Hulls and a Study of the Products Obtained. *MS Thesis, Louisiana State University, Eunice, LA.*
- Massaza, F. (1998). Pozzolana and Pozzolanic Cements, Lea's Chemistry of Cement and Concrete. (Editor: P. C. Hewlett), Elsevier,
- Mehta, P.K. (1992). Rice Husk Ash-A Unique Supplementary Cementing Material. *in Proceedings of the International Symposium on Advances in Concrete Technology*. Athens, Greece.
- Mehta, P.K. (1997). Durability critical issues for the future. *Concrete International*, **19**, 69–76.
- Mehta, P.K. (1999). Advancements in concrete technology. *Concrete International*, **21**(6), 27–33.
- Mehta, P.K. (2002). Greening of the concrete industry for sustainable development. *Concrete International*, **24**(7), 23–27

Mehta, P.K. (2002). Greening of the concrete industry for sustainable development. *Concr. International*, V.24, No.7, pp. 23– 28.

Mertens, G., Snellings, R., Balen, K. V., Bicer-Simsir, B., Verlooy, P., and Elsen, J. (2009). Pozzolanic reactions of common natural zeolites with lime and parameters affecting their reactivity. *Cement and Concrete Research* **39** (3): 233–240.

Michalsh, B. (1991). International Energy Annual 1987. Dept. of Energy Information Administration, *DOEEIA-20 19*, Washington, D. C. Table 4

Naik, T.R. and Singh, S.S. (1997). Influence of fly ash on the setting and hardening characteristics of concrete systems. *ACI Material Journal*, **94**, 355-360

Nielsen, Forrest H. (1998). Ultratrace elements in nutrition: Current knowledge and speculation. *The Journal of Trace Elements in Experimental Medicine* **11** (2–3): 251–274.

Oganov A.R., Chen J., Gatti C., Ma Y.-M., Yu T., Liu Z., Glass C.W., Ma Y.-Z., Kurakevych O.O., Solozhenko V.L. (2009). Ionic high-pressure form of elemental boron. *Nature* 457: 863–867.

Poon, C.S, Kou, S.C., and Lam L. (2006). Compressive strength, chloride diffusivity, and pore structure of high performance metakaolin and silica fume concrete. *Construction and Building Materials* **20**:858–865

Portland Cement Association. (2000), Survey of Mineral Admixtures and Blended Cement in Ready Mix Concrete, PCA, 16 pp.

Ramezaniapour, A.A., and Malhotra V.M. (1995). Effect of curing on the compressive strength, resistance to chloride ion penetration and porosity of concretes incorporating slag, fly ash, or silica fume. *Cement Concrete Composites*, **17**, 125–33

Sağlık, A., Sümer, O., Tunç, E., Kocabeyler, M.F., Çelik, R.S. (2008). Borlu Aktif belit (BAB) Çimentosunun Özellikleri ve Kütle Betonu ile Klasik Betonda Kullanılabilirliği. 2. *Ulusal Bor Çalıştayı Bildirileri Kitabı*, Ankara, Turkey.

Sağlık, A., Sümer, O., Tunç, E., Kocabeyler, M.F., Çelik, R.S. (2008). The Characteristics Of Boron Modified Active Belite (BAB) Cement And Its Utilization

In Mass And Conventional Concrete, *11.DBMC International Conference on Durability of Building Materials and Components*, ISTANBUL, Turkey

Şengül, Ö. (2006). Effects of pozzolanic materials on the mechanical properties and chloride diffusivity of concrete. *PhD thesis, Istanbul Technical University*, Istanbul.

Shergold, F.A. (1953). The percentage voids in compacted gravel as a measure of its angularity. *Magazine of Concrete Research*; **5**(13): 3-10.

Shipley, J.T. (2001). *The Origins of English Words: A Discursive Dictionary of Indo-European Roots*. JHU Press. ISBN: 9780801867842.

Sui, T., Fan, L., Wen, Z., Wang, J., and Zhang, Z. (2004). Study on the properties of high strength concrete using high belite cement. *Journal of Advanced Concrete Technology*, V.2, No.2, pp. 201-206

Transportation research. (1990). Admixtures and ground slag for concrete. *Transportation research circular, no. 365 Washington: Transportation Research Board, National Research Council*.

TS 13353 (Turkish Standard Institution). (2008). Boron modified active belite cement – Definitions, composition, specifications and conformity criteria, Ankara, TURKEY

Türk, S., Gürbüz, G., Ertün, T., and Yeginobali, A. (2006). Heat of hydration and shrinkage properties of Boron containing active belite cements, *ConcreteLife'06 - International RILEM-JCI Seminar on Concrete Durability and Service Life Planning: Curing, Crack Control, Performance in Harsh Environments*, RILEM Publications SARL, pp.397 – 404

United States Geological Survey. (2008). *Mineral Commodity Summaries. Boron*. Retrieved 2008-09-20.

United States. Environmental Protection Agency. (1993). Office of Water, U. S. Environmental Protection Agency Staff Health advisories for drinking water contaminants: *United States Environmental Protection Agency Office of Water health advisories*. CRC Press. p. 84. ISBN 087371931X.

Van Setten M.J., Uijtewaal M.A., de Wijs G.A., de Groot R.A. (2007). Thermodynamic stability of boron: The role of defects and zero point motion.. *J. Am. Chem. Soc.* **129** (9): 2458–2465.

Walker, C.T. (1975). *Geochemistry of Boron*. Dowden, Hutchinson&Ross, New York, pp. 47-63

Weeks, M. E. (1933). XII. Other Elements Isolated with the Aid of Potassium and Sodium: Beryllium, Boron, Silicon and Aluminum. *The Discovery of the Elements*. Easton, PA: Journal of Chemical Education. ISBN 0-7661-3872-0.

Weiss DJ (2006) *Analysis of variance and functional measurement*, 1st edn. Oxford University Press, NY, 271 pp

Woods, William G. (1994). An Introduction to Boron: History, Sources, Uses, and Chemistry. *Environmental Health Perspectives* **102**, Supplement 7.

Zook, E. G. (1965). Total boron. *J. Assoc. Off Agric. Chem* **48**: 850.