HIGH-STRENGTH CONCRETE INCORPORATING COPPER SLAG AND GROUND PUMICE

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Certificate of Original Authorship

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PUBLICATIONS

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ABSTRACT

Nowadays, concrete is the most widely used construction material which mainly consists of Portland cement, aggregate and water. For more than 200 years, concrete has been known as a durable and high strength construction material while its formability during its fresh stage results in building different shapes which are otherwise not possible. Due to widespread construction of high-rise buildings, bridges and other concrete structures, there is a growing demand from clients as well as technical requirements for using high-strength concretes in certain applications such as towers.

However, common belief is that more Portland cement should be used for obtaining a higher strength grade. In other words, producing high-strength concrete is synonymous with higher consumption of Portland cement. But, cement production is a high energy-consuming and polluting process to the extent that Portland cement production, on its own, contributes to over 7% of worldwide greenhouse gases (GHG) which is equal to 1.6 billion tonnes of GHGs. On average, production of each tonne of Portland cement results in releasing one tonne of CO_2. Current average consumption of concrete is about one tonne per year per every living human being. Because of large consumption of concrete and Portland cement as well as its energy-consuming and polluting production process, even small reductions in greenhouse gas emissions per tonne of manufactured concrete can make a significant and positive global impact.

Recent research shows that Portland cement and coarse aggregates have the highest environmental impacts and greenhouse gas emissions. Therefore, any attempt to make concrete more sustainable should firstly focus on these two materials.

On the other hand, using traditional materials such as natural limestone aggregate for producing concrete causes many environmental problems and such procedures are critically under scrutiny in terms of sustainability because it is not possible to renew these natural sources. Therefore, new procedures must be developed to use alternative raw materials for producing concrete.

Pumice is a volcanic rock which is made of highly vesicular rough textured volcanic glass. According to US Geological Survey Report, global production of pumice and pumicite was approximately 18 and 17 million tonnes in 2011 and 2012, respectively. Traditionally, pumice as aggregate has been used for producing light weight building blocks, concrete and assorted building products in construction industry. However, technical performance and properties of concretes with pumice aggregate conveys important concerns because of high water absorption of pumice aggregate. On the other hand, main chemical ingredient of pumice is SiO_2 and many researchers have reported that pozzolanic characteristics for pumice powder and its positive effects on mechanical and long-term properties of concrete. Therefore, it can be a good alternative cementitious material which can be used instead of Portland cement.

Copper slag is a by-product obtained during the matte smelting and refining of copper. Production of one tonne of copper produces around 2.2-3 tonne of copper slag. In the United States, the amount of copper slag manufactured is approximately four million tonnes, and in Japan is around two million tonnes per year. Although some researchers have attempted to use copper slag powder as a cement additive, a significant part of deposited copper slag is air-cooled slag which results in crystallised structure instead of

required amorphous structure for a cement additive. Furthermore, many researchers have reported promising results by using copper slag as coarse aggregates in concrete. This research aims to develop a novel type of green high-strength concrete by using copper slag coarse aggregate and pumice powder with less environmental impacts and carbon footprint with at least similar performance to common high-strength concrete. To achieve this purpose, a comprehensive assessment of results of an extensive experimental program on fresh and hardened concrete specimens including slump, unit weight, air content, compressive and splitting tensile strength measurements was undertaken.

16 different mixture proportions based on different levels of cement replacement with pumice and using copper slag instead of limestone coarse aggregate at two water to binder ratios of 0.3 and 0.4 were investigated. In addition, silica fume was used at level of 10% of cement weight in some mixtures. Compressive strength of concrete specimens were measured at different ages of 7, 28, 56 and 91 days while splitting tensile strength was measured at 7, 28 and 91 days to evaluate effects of pumice, copper slag and their combinations.

In general, it can be concluded that the presence of copper slag can increase compressive strength of concrete at different ages. This can be attributed to higher level of strength properties displayed by copper slag aggregate. In addition, the surface texture of coarse aggregate is partly responsible for the bond between the cement paste and aggregate because of the mechanical interlocking between cement paste and copper slag. At age of 91 days, all of concrete mixtures, except those containing finely ground

pumice as 20% of Portland cement replacement, showed approximately similar or even better performance in comparison with control mixtures.

In general, it can be concluded that using copper slag coarse aggregate increased the splitting tensile strength of concrete by around 12% in comparison with control mixtures with limestone coarse aggregate. In addition, adding finely ground pumice resulted in rapid reduction of the splitting tensile strength at all ages. However, satisfying results were obtained by combined use of pumice powder and copper slag coarse aggregate.

With regard to numerous test results of fresh and hardened high-strength concrete with and without copper slag coarse aggregate and finely ground pumice, it can be recommended that the most efficient and optimized value of finely ground pumice when copper slag coarse aggregate is used in concrete is 10% at water to binder ratio of 0.4 and 20% at water to binder ratio of 0.3 with the presence of 10% silica fume in concrete mixture. The 28-day compressive and splitting tensile strength were similar to control normal concrete with limestone coarse aggregate while at later ages they displayed superior performance in comparison with the control normal mixture in terms of compressive and splitting tensile strength. The recommended values of pumice and copper slag showed promising and excellent results at the age of 56 days which is the common age of measuring concrete properties including high level of supplementary cementitious materials. In this study, 30% of Portland cement was successfully replaced by silica fume and finely ground pumice while copper slag coarse aggregate as an industrial waste material was simultaneously used instead of whole of natural limestone coarse aggregate for producing sustainable high-strength concrete. With regard to the

Green Building Council of Australia’s Green Star Mat-4, this novel type of high-strength concrete can achieve concrete credits as green concrete.

Chapter 1

1. INTRODUCTION

Nowadays, concrete is the most widely used construction material which mainly consists of Portland cement, aggregate and water. For more than 200 years, concrete has been known as a durable and high strength construction material while its formability during its fresh stage allows building different and at times complex shapes. However, its production is a high energy-consuming and polluting process to the extent that Portland cement production, on its own, contributes to over 7% of worldwide greenhouse gases (GHG) which is equal to 1.6 billion tonnes of GHGs (Flower and Sanjayan, 2007). Many researchers have reported their findings when using supplementary cementitious materials (SCMs) and recycled aggregates as reliable and technically sound replacements for Portland cement and natural aggregates. However, there is a need for developing new types of concrete according to current requirements which consist of not only up-to-date technical specifications (for example, higher strength), but also less environmental impacts and negative effects on sustainable development in concrete and construction industry. Therefore, this study was carried out to develop a novel type of high-strength concrete containing both pumice powder and copper slag aggregates as replacements for the Portland cement and natural limestone aggregates, respectively.

1.1. RESEARCH BACKGROUND AND SIGNIFICANCE

With regard to high importance of sustainable development based on using green construction materials, many attempts have been made to adopt different strategies to implement sustainability in concrete industry. According to the World Commission on Environment and Development of the United Nations, sustainability is “meeting the needs of the present without compromising the ability of the future generations to meet their own needs”. To encourage concrete industry to implement sustainability aspects in its products and services, different organizations have published guidelines and specifications.

In Australia, the Green Building Council of Australia (GBCA) has introduced Green Star Mat-4 which describes credits for concrete materials. In the meantime, Cement Concrete and Aggregates Australia (CCAA) published an industry guide for the use of this document. According to GBCA and CCAA, a maximum value of three points can be gained in the Green Star rating system credit which has been developed in order to encourage and recognise attempts towards reduction in greenhouse gas emissions, resource use and waste associated with the use of concrete. According to GBCA, it is possible to achieve up to two points where the Portland cement content in all concrete used in the project has been reduced by replacing it with supplementary cementitious materials. Furthermore, there is another aspect which is related to use of alternative coarse or fine aggregates as well as captured or reclaimed water.

According to Flower and Sanjayan (2007), Portland cement is the major source of CO_2 emissions generated by typical commercially produced concrete mixes, so that it is responsible for approximately 74- 81% of total CO_2 emissions of concrete production. On the other hand, coarse aggregates are the next main source of CO_2 emissions in concrete and they are responsible for 13% to 20% of total CO_2 emissions. Consequently, it is crucial to find reliable and technically proven alternatives for Portland cement and natural coarse aggregate as two main ingredients of concrete with the highest environmental impact. Therefore, this study was carried out to evaluate the effects of using copper slag coarse aggregate as a waste industrial material and finely ground pumice as a natural pozzolanic material on properties of high-strength concrete.

Pumice is a volcanic rock which is made of highly vesicular rough textured volcanic glass (Jackson et al., 2005 and McPhie et al., 1993). According to US Geological Survey Report, global production of pumice and pumicite was approximately 18 and 17 million tonnes in 2011 and 2012, respectively. Traditionally, pumice as aggregate, has been used for producing light weight building blocks, concrete and assorted building products in construction industry. However, technical performance and properties of concretes with pumice aggregate have caused concerns because of high water absorption of pumice aggregate according to current literature review which is presented in this study. On the other hand, main chemical ingredient of pumice is SiO_2 which is approximately 61% to 76% and many researchers have reported pozzolanic characteristics for pumice powder and its positive effects on mechanical and long-term properties of concrete.

On the other hand, copper slag is a by-product obtained during the matte smelting and refining of copper (Biswas and Davenport, 2002). Production of one tonne of copper produces, around 2.2-3 tonnes of copper slag. In the United States, the amount of copper slag manufactured is approximately four million tonnes, and in Japan is around two million tonnes per year (Collins and Ciesielski, 1994; Ayano et al., 2000).

Although some researchers used copper slag powder as a cement replacement (Malhotra, 1993; Tixier et al., 1997; Arino and Mobasher, 1999; Douglas et al., 1986; Deja and Malolepszy, 1989), it should be noted that a significant part of deposited copper slag is air-cooled slag which results in crystallised structure instead of required amorphous structure for a cement additive. Furthermore, many researchers have reported suitability of copper slag for use as aggregates in concrete (Caliscan and Behnood, 2004; Shoya et al., 1997; Ayano and Sakata, 2000; Hwang and Laiw, 1989). To sum up, this research was initiated by considering all the environmental and technical aspects which are summarized below:

- Portland cement and coarse aggregates have the highest environmental impacts and significant greenhouse gas emissions, respectively. Therefore, any attempt for making concrete more sustainable should firstly focus on these two constituent materials.
- Due to widespread construction of high-rise buildings, bridges and other concrete structures, there is a growing demand from clients as well as technical requirements for using high-strength concretes in some applications.
- Technical performance and properties of concrete with pumice aggregate conveys important concerns because of high water absorption of pumice aggregate. On the other hand, main chemical ingredient of pumice is SiO_2 and

many researchers have reported pozzolanic characteristics for pumice powder and its positive effects on mechanical and long-term properties of concrete.

- Significant part of deposited copper slag is air-cooled slag which results in crystallised structure instead of required amorphous structure for a cement additive. Furthermore, many researcher have reported promising results by using copper slag as coarse aggregates in concrete.

1.2. AIM AND OBJECTIVES

The overall aim of this research is to develop a novel type of green high-strength concrete by using copper slag coarse aggregate and pumice powder with less environmental impacts and carbon footprint while it possesses at least similar performance to common high-strength concrete. To accomplish this, a combination of desktop studies and experimental programmes is required. It is hoped that the findings presented here will assist in reducing the environmental impacts of concrete by introducing a novel type of green high-strength concrete which has at least similar performance to control high-strength concrete.

The specific objectives of this study are:

- A comprehensive review of previous studies using pumice as Portland cement replacement and aggregate in concrete
- An in-depth review of utilisation of copper slag as a cement additive, fine and coarse aggregates in concrete
- Determination of fresh and hardened mechanical properties of high-strength concrete incorporating different levels of finely ground pumice
- Evaluation of effects of copper slag coarse aggregate on fresh and hardened mechanical properties of high-strength concrete

- Investigation of influences of using a combination of copper slag coarse aggregate and finely ground pumice on fresh and hardened mechanical properties of high-strength concrete
- Production of a novel sustainable high-strength concrete which can receive concrete credits according to Green Star Mat-4 rating system of Green Building Council of Australia (details are presented in Annex 1).

In order to achieve these objectives, an extensive experimental programme was undertaken and the results were carefully analysed to recommend an optimised mix design and relevant properties of a green high-strength concrete.

1.3. OUTLINE OF THESIS

This thesis is a chronological progression of introduction, literature review, materials and experimental methods, results and discussions, conclusions and recommendations.

Chapter 1 presents a brief introduction, research background and significance, aim and objectives and outline of the thesis.

Chapter 2 critically reviews published literature on different environmental and technical aspects of this research. The most up-to-date technical information on using pumice as cement replacement as well as fine and coarse aggregate in concrete is presented in this chapter. Furthermore, effects of pumice as aggregate and cement additive on different properties of concrete including mechanical characteristics and long-term properties are given in this chapter. In addition, different features of copper slag such as physical and chemical properties and effects on concrete properties as aggregate and cement replacement are provided by referring to available information.

Chapter 3 sets out the experimental programmes performed in this research. Materials, mix proportions, concrete specimens preparation procedure and experimental tests and variables considered are explained in detail in this chapter. In general, fresh and hardened properties of high-strength concrete are evaluated at different ages. Furthermore, 16 different mix proportions were designed to investigate all variations in detail.

Chapter 4 reports results obtained through experimental programmes, highlighting key observations and exploring a theoretical basis for explaining observed results. In this chapter, fresh properties of high-strength concretes, including slump, air content and unit weight are presented and discussed thoroughly. After that, results of mechanical properties of hardened concrete including compressive and splitting tensile strengths are given and discussed in detail.

Finally, Chapter 5 draws conclusions from the presented work, highlighting a number of promising results, contradictory findings and setting out a number of recommendations for further studies and experimental programmes.

Chapter 2

2. LITERATURE REVIEW

2.1. INTRODUCTION

Concrete is, undoubtedly, the most widely used construction material which mainly consists of Portland cement, aggregate and water. For more than 200 years, concrete has been known as a durable and high strength construction material while its formability during its fresh stage results in building different and even complex shapes. Current average consumption of concrete is about 1 tonne per year per every living human being. However, its production is a high energy-consuming and polluting process, and as mentioned earlier in Chapter 1, Portland cement production contributes to over 7% of worldwide greenhouse gases (GHG) which equates to about 1.6 billion tonnes of GHGs. On average, production of each tonne of Portland cement results in releasing one tonne of CO_2. Because of large consumption of concrete and Portland cement as well as its energy-consuming and polluting production process, even small reductions of greenhouse gas emissions per tonne of manufactured concrete can make a significant and positive global impact.

With regard to high importance of sustainable development based on using green construction materials, many attempts have been made to adopt different strategies to implement sustainability in concrete industry. Referring back to Chapter 1, and according to the World Commission on Environment and Development of the United Nations, sustainability is "meeting the needs of the present without compromising the ability of the future generations to meet their own needs". To encourage concrete industry for implementing sustainability aspects in its products and services, different organizations have published guidelines and specifications. In Australia, the Green Building Council of Australia (GBCA) has introduced Green Star Mat-4 which describes credits of concrete materials as mentioned earlier. In the meantime, Cement Concrete and Aggregates Australia (CCAA) published an industry guide for this document as referred to earlier. According to GBCA and CCAA, a maximum value of three points is available in the Green Star rating system credit which have been developed for encouraging and recognising positive steps in the reduction of greenhouse gas emissions, resource use and waste associated with the use of concrete. This credit system considers all types of concrete used in a project including structural and non-structural concrete elements. According to GBCA, it is possible to achieve up to two points where Portland cement content in all concrete used in a project has been reduced by replacing supplementary cementitious materials. Furthermore, there is another point which is related to use of alternative coarse or fine aggregates as well as captured or reclaimed water.

Flower and Sanjayan (2007) reported that Portland cement is the major source of CO_2 emissions generated by typical commercially produced concrete mixes, and that it is responsible for approximately 74- 81% of total CO_2 emissions.

On the other hand, coarse aggregates are the next main source of CO_2 emissions in concrete so that they are responsible for 13% to 20% of total CO_2 emissions. It should be noted that they reported concrete batching, transport and placement operations all found to contribute small amounts of CO_2 to total concrete emissions. Table 2.1 shows final CO_2 emission factors related to different concrete materials. As can be seen, emission factor for Portland cement is 30 and 6 times more than fly ash and blast furnace slag, respectively. Consequently, it is crucial to find reliable and technically sound alternatives for Portland cement and natural coarse aggregate as two main ingredients of concrete with the highest environmental impact. Therefore, this study is carried out to evaluate effects of using copper slag coarse aggregate as a waste industrial material and finely ground pumice as a natural pozzolanic material on properties of high-strength concrete. In this chapter, a comprehensive review of published literature on different aspects of this research is presented.

Table 2.1: Final CO_2 emission factors for different concrete materials (Flower and Sanjayan, 2007)

Activity	Emission factor	Unit
Coarse aggregates – Granite/Hornfels	0.0459	t CO_2-e/tonne
Coarse aggregates – Basalt	0.0357	t CO_2-e/tonne
Fine aggregates	0.0139	t CO_2-e/tonne
Cement	0.8200	t CO_2-e/tonne
Fly ash (F-type)	0.0270	t CO_2-e/tonne
GGBFS	0.1430	t CO_2-e/tonne
Concrete batching	0.0033	t CO_2-e/m^3
Concrete transport	0.0094	t CO_2-e/m^3
On aite placement activities	0.0090	t CO_2-e/m^3

2.2 PUMICE

2.2.1. Definition, production mechanism and specifications

According to Jackson et al. (2005) and McPhie et al. (1993), pumice is a volcanic rock which is made of highly vesicular rough textured volcanic glass. Despite similarities in chemical composition, it should be noted that pumice is different from scoria which is another vesicular volcanic rock as it has larger and thicker vesicles. In addition, colour of scoria is darker in comparison with colour of pumice which is normally light coloured. These vesicles are pore spaces created as a result of evacuation and exit of dissolved gas of magma after reaching the earth surface. According to King (2014), rush of gas from the vent shreds the magma and blows it out as a molten froth. Therefore, the froth rapidly solidifies as it flies through the air and falls back to earth as pieces of pumice. Figure below shows how volcanic eruptions can eject many cubic kilometres of materials with different sizes, from very small dust particles to large blocks of pumice. For example, five cubic kilometres of materials mainly pumice were ejected during explosive eruption of Mount Pinatubo in Philippines in 1991 (Fig. 2.1).

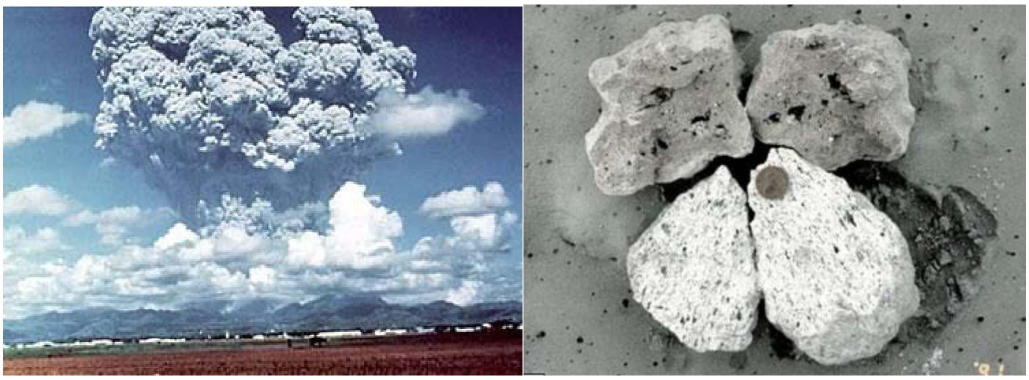


Fig. 2.1: Explosive eruption of Mount Pinatubo in Philippines in 1991 (King, 2014)

There are two kinds of pumice: acidic pumice (white or oyster white colour) and basic pumice (brown or black). However, acidic pumice is the most common pumice type in the world (Gunduz et al., 1998). According to US Geological Survey Report, global production of pumice and pumicite was approximately 18 and 17 million tonnes in 2011 and 2012, respectively (Table 2.2). Turkey and Italy are main producers of this material in the world followed by Iran, Greece, Saudi Arabia and Chile. Table 2.2 shows world mine production of pumice and pumicite in different countries in 2011 and 2012.

Table 2.2: World mine production of pumice (US Geological Survey, 2013)

Country	**Annual production (thousand tonnes)**	
	Year	
	2011	**2012**
Turkey	4500	4500
Italy	3020	3000
Iran	1500	1500
United States	489	515
Greece	1230	400
Ecuador	800	800
Chile	850	850
Syria	900	700
Saudi Arabia	950	1000
Cameroon	600	600
Other countries	2600	2700
World total(rounded)	**18000**	**17000**

However, identified but undiscovered resources of pumice and pumicite are much higher than these values. For example, the identified US resources which are located in the western states are more than 25 million tonnes while overall amount of identified and discovered resources in the western and great plains states are at least 250 million tonnes and perhaps as high as one billion tonnes.

In the US, more than 50% of total production of pumice is used for producing construction building blocks. Another half of pumice production is used in horticulture (33%), concrete admixture and aggregate (8%), abrasives (5%) and absorbent, filtration, laundry stone washing and other applications (4%).

In Iran, pumice resources are located in volcanic areas such as Ardebil, East Azarbaijan (particularly in Bostan Abad) and Kermanshah (Ghorveh). Pumice which is extracted in Bostan Abad is one of the whitest and lightest pumice types in Iran and usually used for producing construction blocks.

2.2.2. Characterization of pumice

Table 2.3 presents chemical composition of pumice reported by different researchers from different countries in the world. As can be seen, main chemical ingredient of pumice is SiO_2 which is approximately 61% to 76% of the total composition. Second chemical compound is Al_2O_3 which is around 10% to 17% of pumice chemical composition. Furthermore, Loss on Ignition (LOI) of pumice is between 2.56% and 4.27%.

Asgari et al. (2012) evaluated pumice particles by using scanning electron microscope (SEM). Fig. 2.2 indicates that the pumice has a porous surface. In addition, Ersoy et al.

(2010) investigated pumice samples collected from the Tatvan region of Turkey. The sizes of the sample as received were between 0.5 and 4 cm while testing sample was made by pulverizing 500 g of sample in a ball mill to reduce its size to 125 µm.

Table 2.3: Typical chemical composition of pumice

Chemical composition	Typical range* (%)
SiO_2	60.82 - 75.51
Al_2O_3	9.94 - 17.24
CaO	0.25 - 4.44
Fe_2O_3	1.05 - 3.39
K2O	2.5 - 5.12
MgO	0.34 - 0.99
Na_2O	2.04 - 5.20
SO_3	0.08 - 0.33
LOI (%)	2.56 - 4.27

* (Özodabaş and Yılmaz, 2013, Rashiddadash et al., 2014, Hossain, 2006, Hossain, 2005b, Hossain, 2008, Saridemir, 2013, Aydin and Gul, 2007, Aydin, 2008, Sepehr et al., 2014)

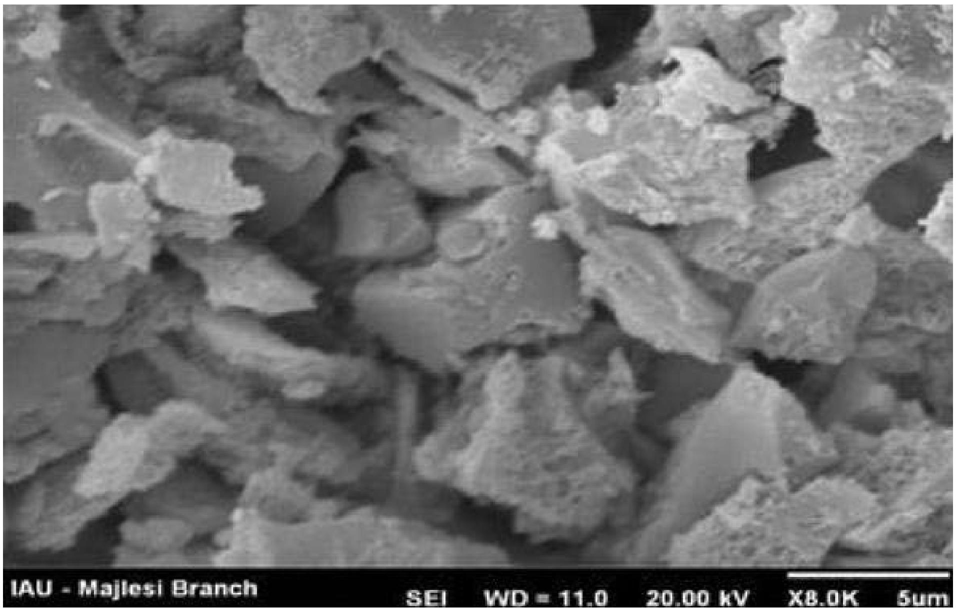


Fig. 2.2: Scanning electron microscope (SEM) image of pumice (Asgari et al., 2012)

They tested pumice sample by Scanning Electron Microscope (SEM), X-ray diffraction (XRD) and Thermal Analysis (DTA–TG). As can be seen in Fig. 2.3, SEM studies were conducted with two different magnifications, (a) enlarged by ×1000 times, (b) enlarged by ×250 times.

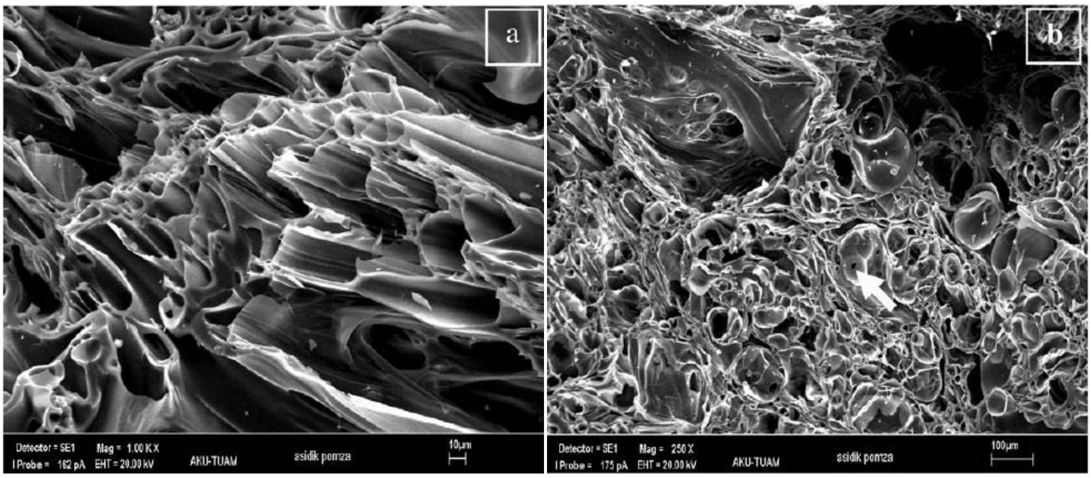


Fig. 2.3: SEM images of pumice (a) enlarged by ×1000, (b) ×250 times (Ersoy et al., 2010)

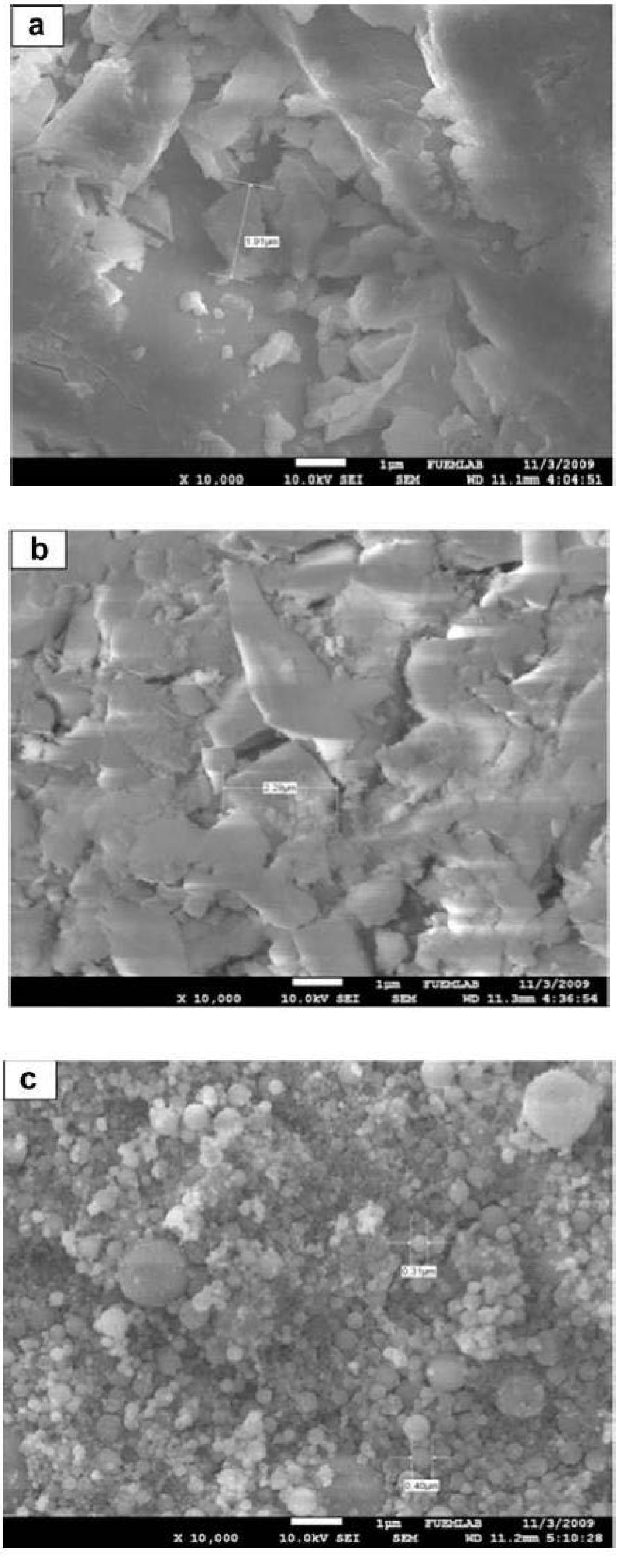


Fig. 2.4: SEM morphologies of (a) cement, (b) pumice powder and (c) silica fume (Kelestemur and Demirel, 2010)

To compare morphologies of pumice particles with Portland cement and silica fume, Kelestemur and Demirel (2010) carried out a microstructural study on them (Fig. 2.4). As can be seen in this figure, finely ground pumice powder mainly consists of very irregularly shaped particles with a porous cellular surface while silica fume mainly consists of very small spherical particles. It should be noted that pumice particles only passed through 75 µm sieve for use in concrete. In general, unit weight of pumice is less than 1.0 g/cm^3 (usually 500-900 kg/m^3) and its hardness is around 6 in Mohs scale (Bideci et al., 2013). According to Ersoy et al. (2010), true density and bulk density of pumice sample were 2.2 and 0.39 g/cm^3, respectively. It should be noted that liquid pycnometer was used to measure the true density of the sample while the surface of the pumice in aggregate size was coated with paraffin before measuring its bulk density. Fig. 2.5 shows XRD analysis of the pumice (Ersoy et al., 2010). As can be seen, there were two peaks. The first one was at 23° and another one was at 28°. These peaks are related to the mineral dachiardite [(Ca, Na, K, Mg)4, (Si, Al)24O48,13H2O)], which is a kind of natural zeolite.

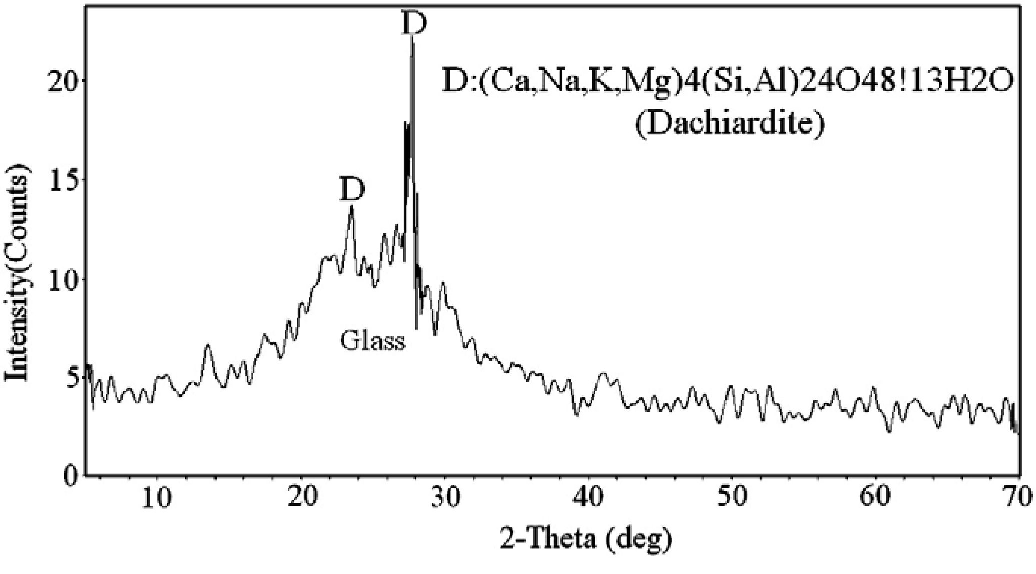


Fig. 2.5: XRD analysis of the pumice (Ersoy et al., 2010)

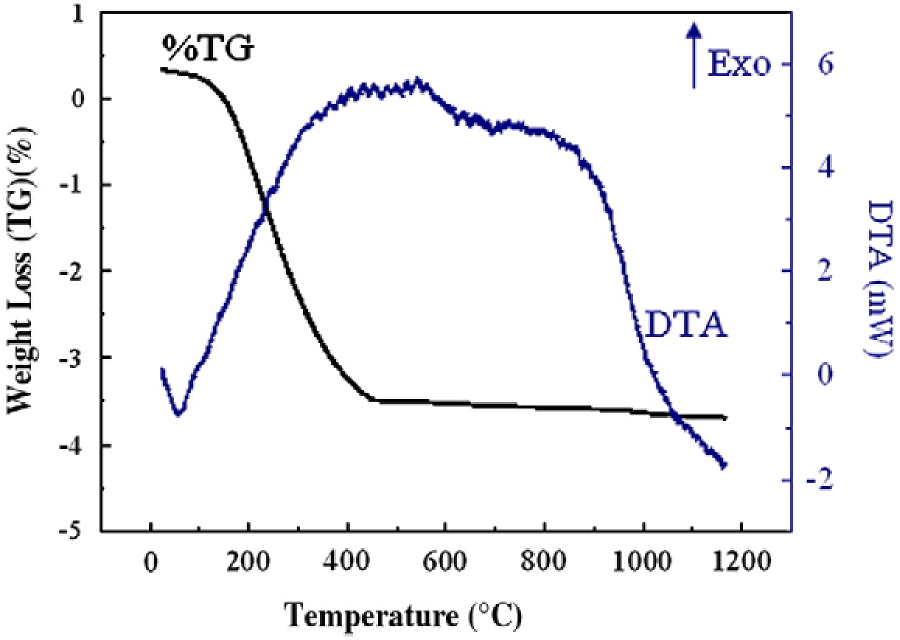


Fig. 2.6. DTA–TG curves of the pumice (Ersoy et al., 2010)

Thermogravimetric (TG) and Digital Thermal Analysis (DTA) curves derived from the thermal analysis under nitrogen atmosphere are shown in Fig. 2.6 (Ersoy et al., 2010). Close examination of these curves indicates that pumice loses about 3.5% of its mass between 100 and 400°C because of removal of moisture within powder pumice and volatile organic impurities. Loss of Ignition and mass loss was measured by chemical analysis and TG curve, respectively.

With regard to importance of porosity including pore volume, size and distribution, which are important in different industries and products such as building materials, Ersoy et al. (2010) evaluated the cumulative pore size distribution by measuring it with mercury intrusion porosimetry instrument (MIP) for all pumice samples (Fig. 2.7).

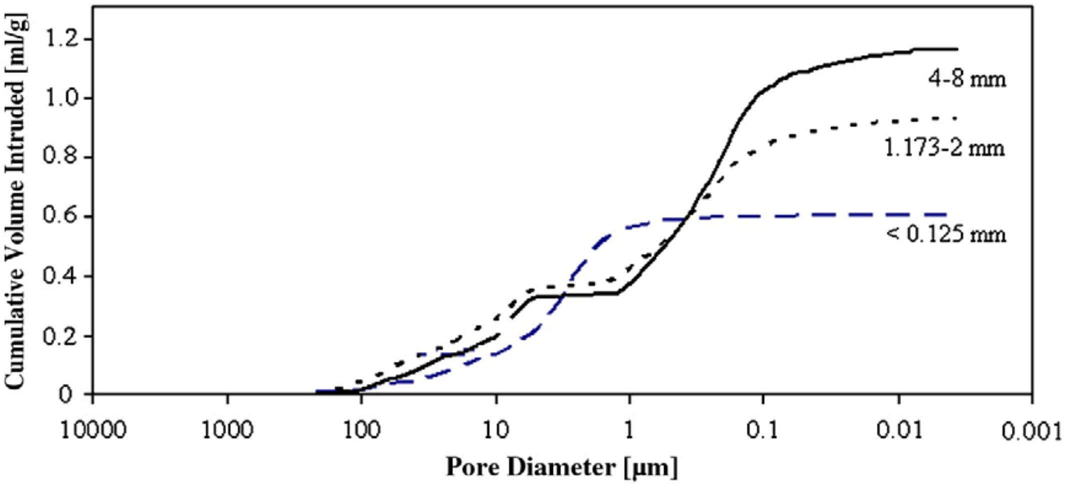


Fig. 2.7: Pore size distribution of pumice sample by MIP (Ersoy et al., 2010)

2.2.3. Pumice in concrete

Pumice rocks are porous and amorphous materials which consist mainly of SiO_2 and Al_2O_3 (Karimaian et al., 2013). Traditionally, pumice as aggregate has been used for producing light weight building blocks, concrete and assorted building products in construction industry (Seltan and Fndik, 2008; Crangle, 2010; Grasser and Minke, 1990; Rivera and Cabrera, 19999; Litvan, 1985; Yeginobali et al., 1998). For example, several investigations have been carried out to study performance of prefabricated concrete panels and frames with pumice. For example, Humay and Durrani (2001) investigated performance of prefabricated light weight pumice concrete infill panels under quasi-static loading. In addition, Carmichael (1986) reported satisfactory performance of precast light weight pumice concrete panels utilised in Oregon, USA. Furthermore, Cavaleri et al. (2003) made three different kinds of reinforced wall panels using lightweight pumice stone concrete, light weight expanded clay concrete and normal concrete to compare their structural responses under horizontal cyclic and constant vertical loading.

They recommended that pumice light weight concrete is a good alternative for use in construction, particularly in areas where pumice is locally available and for types of structural systems which consist of bearing elements that do not require high resistance against horizontal loads and ductility/energy dissipation.

In recent years, some researchers have evaluated the possibility of using pumice in geopolymer concrete. The industrial manufacturing process of cements based on the alkaline activation of blast furnace slag (AAS) commenced in Ukraine in 1960s (Glukhovski, 1980). This type of binder can save large amounts of energy and fuel as its production does not require traditional procedure of Portland cement production based on decarbonation of limestone. Yang et al. (2010) used pumice aggregate in geopolymer concrete but its strength was decreased. Ozodabas and Yilmaz (2013) studied strength and durability of alkali activated blast furnace slag concretes with very finely ground pumice at 5% and 10% replacement of slag. They reported that samples with and without pumice powder had close values of compressive, flexural and drying shrinkage while durability of samples with pumice powder were better than those without it.

Although concrete and construction industries are the main customers of pumice, it has other applications as well. For example, it is also used as an abrasive particularly in polishes, pencil erasers and cosmetic exfoliants. Furthermore, pumice has been used in the field of water and wastewater treatment both in natural and modified forms for the removal of fluoride (Noori Sepehr et al., 2013), azo dyes (Samarghandi et al., 2012), phenol and 4-chlorophenol (Akbal, 2005), heavy metals (Panuccio et al., 2009),SO_2 (Ozturk and Yildirim, 2008) and water hardness (Noori Sepehr et al., 2013).

Fig. 2.8: The Pantheon building which was constructed by the Romans in 126 AD (King, 2014)

However, pumice is still mainly used in construction industry and recently, many researchers have worked on using pumice in concrete as cement replacement and aggregate for developing a green sustainable construction material. According to Grasser and Minke (1990), pumice was used as a construction material in ancient Rome over 2000 years ago and several important buildings such as Pantheon building (Fig. 2.8) constructed in 126 AD are still standing (King, 2014).

2.2.3.1. Pumice as aggregate in concrete

There are several reasons for using aggregates in concrete which are technical, economic and environmental. In fact, aggregate makes up approximately 75% of concrete volume which acts as a strong skeleton for cement matrix and provides reasonable stability.

Pure cement paste without aggregates has high level of shrinkage and heat of hydration which can be reasonably controlled by using fine and coarse aggregates. In the meantime, cement is much more expensive than aggregate and using aggregate can save huge sums of money needed for supplying cement for large scale construction projects. Furthermore, Portland cement production is a high energy-consuming and pollutant process and it is possible to use lower amount of cement by using aggregate in concrete. Therefore, technical utilisation of different natural and recycled materials as aggregates in concrete can be useful not only for concrete and construction industry but also for our environment and the planet.

Because of huge amount of pumice available in different locations all over the world, it is reasonable to study technical feasibility of using pumice as aggregate in concrete. As mentioned earlier, for example, the identified US resources located in the western states are more than 25 million tonnes while the overall amount of identified and discovered resources in the western and great plains states are at least 250 million tonnes and perhaps up to one billion tonnes (US Geological Survey, 2013) as mentioned earlier.

One of the main advantages of using pumice aggregate in concrete is its low specific gravity in comparison with common aggregates which are used in concrete production. Therefore, it is possible to produce both structural and none-structural light weight concrete by using pumice aggregate. Another benefit of such concrete, incorporating pumice aggregate, is lower thermal and noise conductivity which is important particularly for concrete blocks which are used even in non-structural elements and walls.

However, there is no general agreement on the definition of structural light weight concrete so it is defined as a concrete with an air dry density of less than 1810 kg/m^3 in US while Japanese concrete industry prefers to focus on concrete properties instead of only concrete density (ACI 318, 2008; Newman, 2003). According to EN 206 (2000), density and compressive strength are the two main parameters for classification of light weight concrete in Europe. In general, concrete with oven-dry density of less than 2000 kg/m^3 is normally considered as light weight concrete. However, ACI 213 (2003) defines structural light weight concrete as a concrete with a minimum 28 day compressive strength of 17 MPa and an equilibrium density between 1120 and 1920 kg/m^3.

On the other hand, some researchers reported that compressive strength of concrete is decreased by reducing its density (Kabay, 2009; Gul et al., 1997; Faust, 2000; Lydon, 1982; Clarke, 1993; Ramamurty and Narayanan, 2000). Because compressive strength is one of the main properties of concrete which is often considered first, it is important to know the effects of light weight pumice on compressive strength. Sahin et al. (2003) evaluated the influences of different levels of pumice aggregate replacement on compressive strength and density of concrete with different slumps. They used pumice aggregate at levels of 25, 50, 75 and 100% of normal aggregate to make concrete with slumps of 3, 5 and 7 cm.

Fig. 2.9 shows stress-strain curves for different pumice aggregate ratio. It is clear that slope of stress-strain curve is significantly decreased by increasing the amount of pumice which translates to lower stiffness of concrete due to porous structure of pumice aggregate.

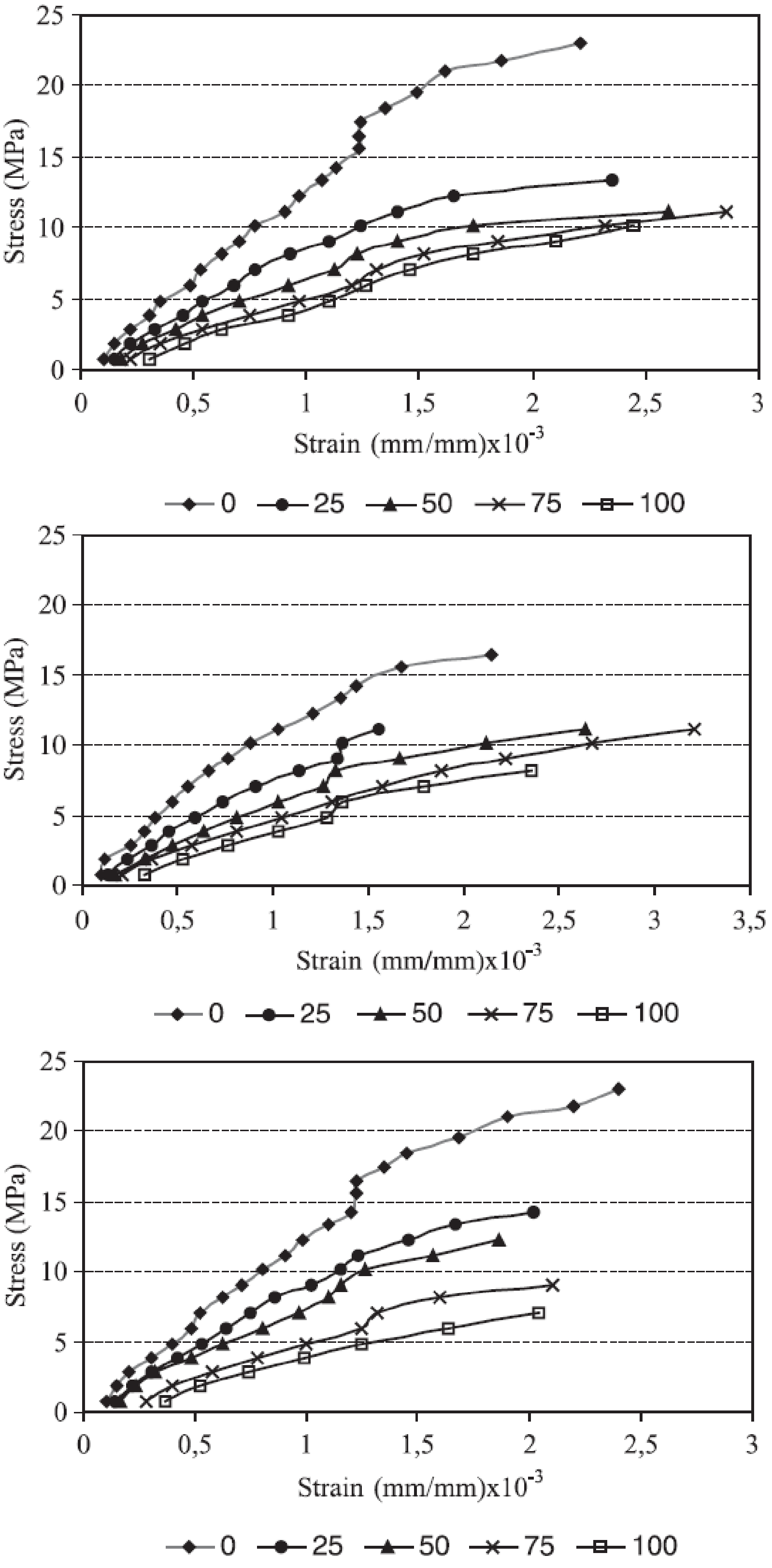


Fig. 2.9: Stress-strain curves for different concretes with different slumps (top: 5, middle: 7, bottom: 3 cm) and ratios of pumice replacement (Sahin et al., 2003)

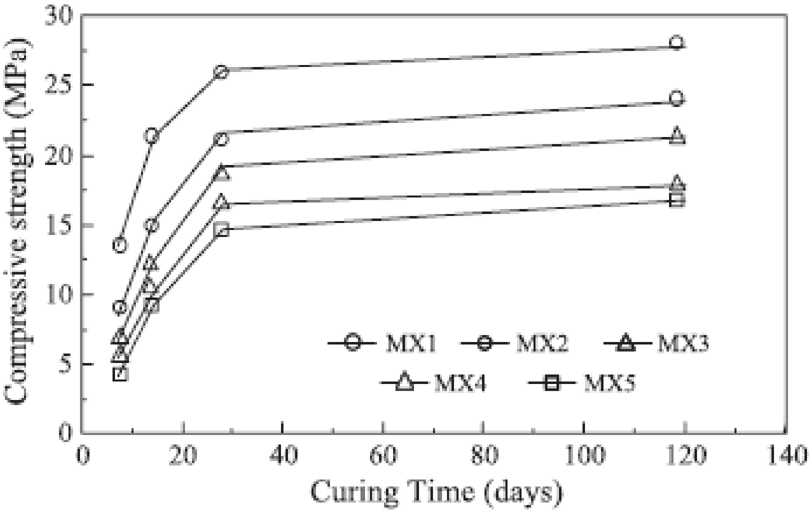


Fig. 2.10: Compressive strength of concretes with different aggregate/cement ratios of 2:1, 2.5:1, 3:1, 3.5:1 and 4:1 for MX1 to 5, respectively. (Gunduz and Ugur, 2005)

This is consistent with the results of another work which was carried out by Gunduz and Ugur (2005) as shown in Fig. 2.10. To compare effects of different ratios of pumice aggregate to cement on compressive strength of pumice concrete, they used fine and coarse pumice with different aggregate to cement ratios of 2:1, 2.5:1, 3:1, 3.5:1 and 4:1 for MX1 to 5, respectively. As seen, compressive strength reduction had a higher rate up to 28 days while different concretes almost showed similar trends between 28 and 120 days of curing.

Hossain et al. (2011) carried out a comprehensive investigation on variation of compressive and tensile strength of concrete with different levels of replacement of coarse aggregate (0, 50, 75 and 100%) by pumice (Fig. 2.11). It should be noted that general mix designs of Type A and B were the same which included Portland cement, coarse pumice, coarse gravel and sand with water to cement ratio of 0.45.

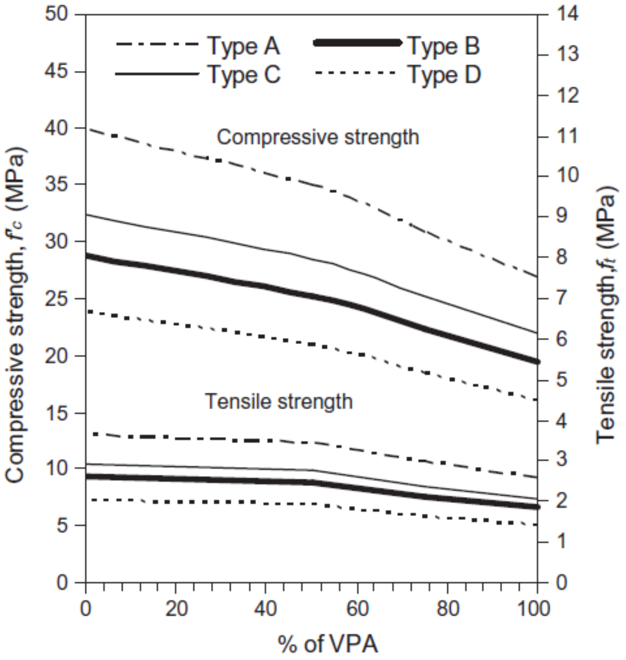


Fig. 2.11: Compressive and tensile strengths of pumice concrete versus level of pumice coarse aggregate replacement (Hossain et al., 2011)

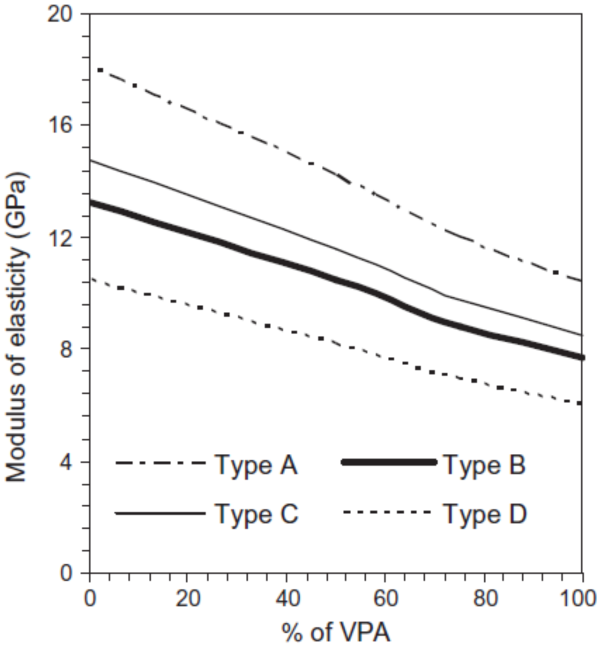


Fig. 2.12: Modulus of elasticity of pumice concrete versus level of pumice coarse aggregate replacement (Hossain et al., 2011)

The only difference was incorporation of fine pumice in Type B. As can be seen from this figure, compressive and tensile strengths of Type A were much higher than Type B. However, compressive and tensile strengths of both types of pumice concrete were decreased by increasing the level of replacement of pumice coarse aggregate which was more sever for compressive strength than tensile strength. Similar trends were reported by Hossain et al. (2011) for variation of modulus of elasticity as shown in Fig. 2.12.

It has been well-known that morphologic properties (compactness, width and physical adherence) of interfacial transition zone (ITZ) between aggregate and cement paste has a prominent effect on compressive strength and modulus of elasticity of concrete. Therefore, Ayhan et al. (2011) studied effects of pumice aggregate on morphologic properties of ITZ in load-bearing lightweight/semi light weight concretes. They concluded that pumice has a potential to make significant contribution to the morphologic properties of ITZ. Fig. 2.13 shows interlocking between cement paste and pumice due to the connected cavities of pumice.

In terms of density, a similar decreasing trend was reported by increasing the amount of pumice as shown in Fig. 2.14 (Sahin et al., 2003). This is consistent with results of other research works which were published in literature (Hossain et al., 2011; Gunduz and Ugur, 2005; Kabay and Akoz, 2012; Yasar et al., 2003; Gunduz, 2008; Libre et al., 2011).

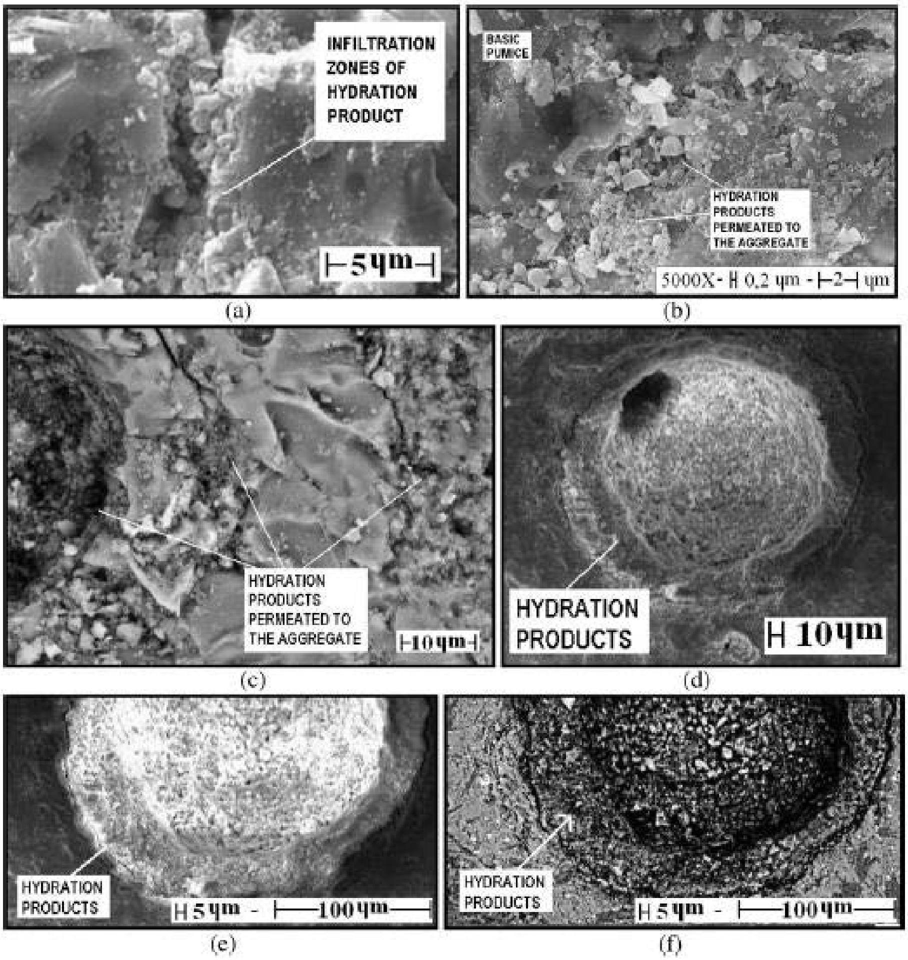


Fig. 2.13: The infiltration zones in pumice and hydration products developed in these zones (Ayhan et al., 2011)

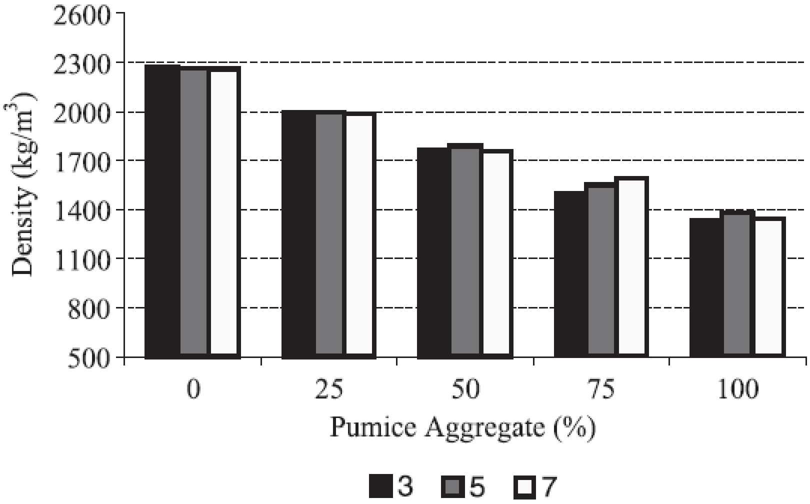


Fig. 2.14: Density versus level of pumice replacement (Sahin et al., 2003)

According to Sahin et al. (2003), concrete incorporating pumice had higher water absorption and the maximum was a 16.7% increase at 100% pumice aggregate. Similar results were reported by Gunduz and Ugur (2005).

Fig. 2.15 indicates fluctuations of water absorption of different concretes with fine and coarse pumice with different aggregate to cement ratio (2:1, 2.5:1, 3:1, 3.5:1 and 4:1 for MX1 to 5, respectively). It can be seen from this figure that concrete mixtures with pumice aggregates showed higher weight gain rapidly because of capillary absorptivity and after that, this rate was lower. Kostmatka et al. (2002) reported different water absorption values for light weight aggregates in the range of 5% -20% and Hossain et al. (2011) concluded that water absorption of pumice aggregate is generally higher than other light weight aggregates.

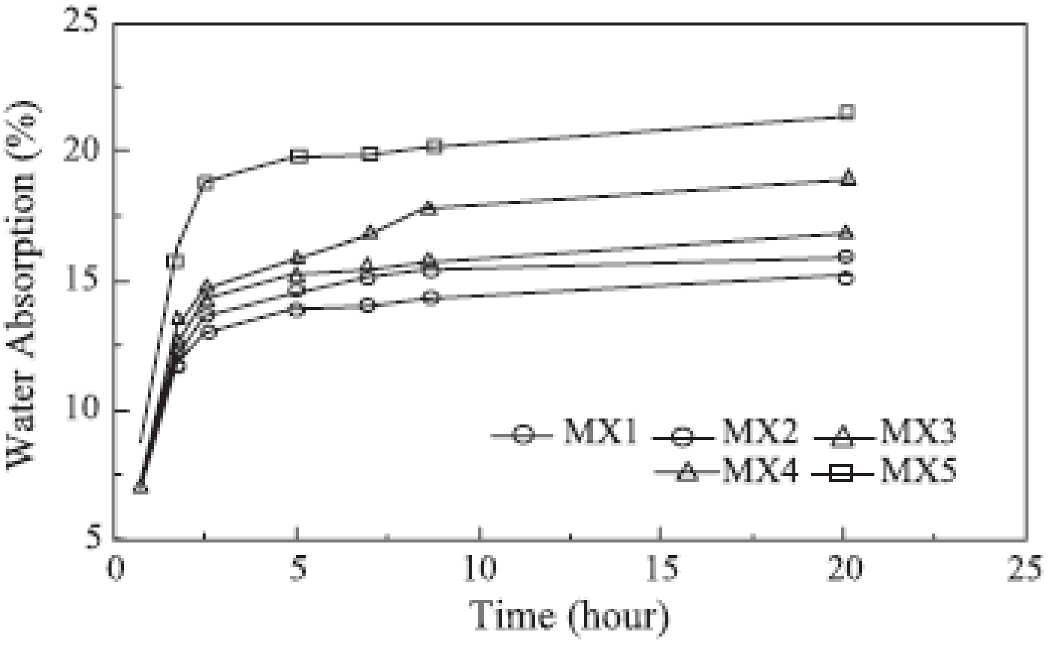


Fig. 2.15: Fluctuations of water absorption of different concretes with pumice after Kostmatka et al. (2002)

To eliminate disadvantages of pumice aggregate in concrete including higher water absorption, Bideci et al. (2013) used polymer-coated pumice aggregate in concrete. They reported that water absorption of polymer-coated pumice aggregate was significantly lower than uncoated aggregates. Although they reported some positive results, such works need more promising achievements. In general, drying shrinkage of concrete incorporating aggregate with high water absorption is expected to be higher than normal concrete. Hossain et al. (2001) showed that this is true for concrete with pumice aggregates as well. As it can be seen from Fig. 2.16, the 12-week drying shrinkage of concrete were increased by increasing of level of pumice coarse aggregate replacement.

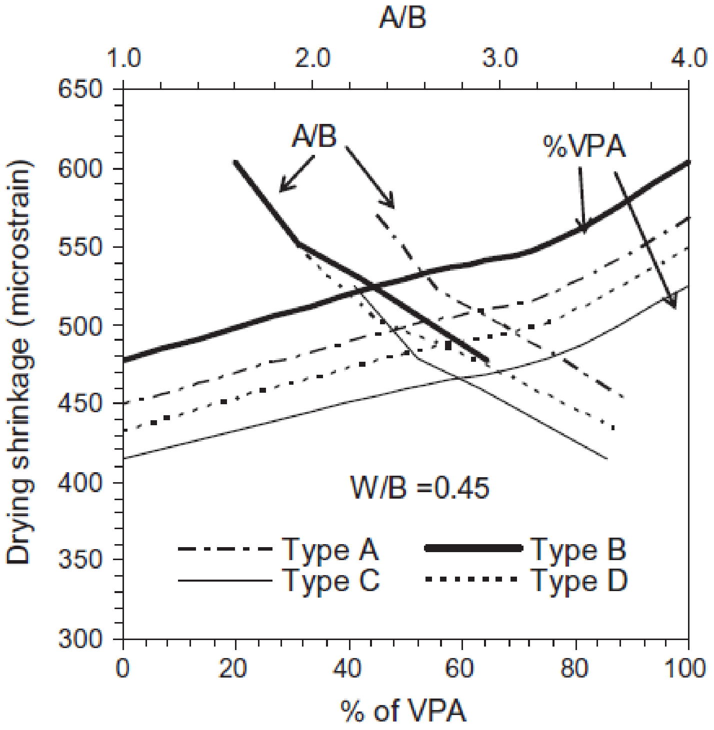


Fig. 2.16: 12-week drying shrinkage of pumice concrete versus level of pumice coarse aggregate replacement (Hossain et al., 2011)

The maximum increase in 12-week drying shrinkage was observed in concrete with 100% pumice coarse aggregate between 17% and 34% (with maximum in Type B) compared to normal concrete. The 12-week drying shrinkage also increased with the replacement of sand by fine pumice aggregate. In general, the drying shrinkage of light weight concrete can be higher up to 50% than normal concrete so that it increases by increasing of water to binder ratio and decreasing of aggregate to binder ratio.

Thermal insulating and high fire resistance are known as another benefits of using pumice in concrete (Gunduz, 2008). Some researchers reported results of their works for developing a high-temperature resistant concrete by using pumice. According to Neville (1995), fire resistance of concrete can be improved by decreasing of its thermal conductivity. On the other hand, pumice aggregates have in themselves high fire resistance and thermal conductivity of concrete incorporating pumice is lower than normal concrete (Shoaib et al., 2001; Turker et al., 2001). Therefore, different studies were carried out to evaluate high temperature performance of concrete with pumice aggregates incorporating fly ash or blast furnace slag (Aydin, 2008; aydin and Baradan, 2007).

Fig. 2.17 shows Scanning Electron Microscope image of concrete with pumice aggregate and slag after exposure to elevated temperature at 900 °C. As it can be seen from this figure, space ratio in cement paste was increased but matrix phase was damaged less than that of control sample. In addition, residual compressive and tensile strengths of these concretes were superior in comparison with control samples after subjecting to this temperature.

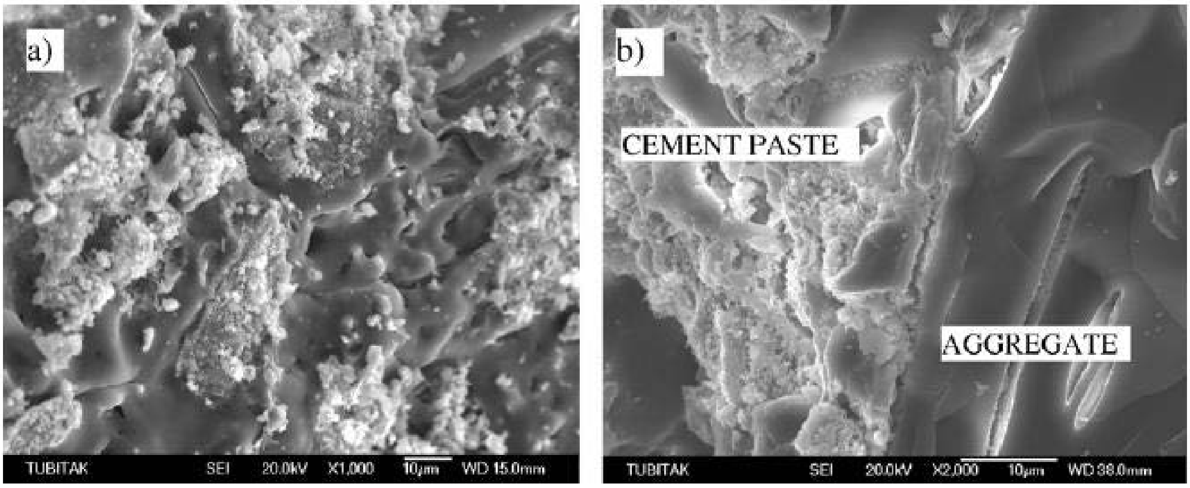


Fig. 2.17: Scanning Electron Microscope image of concrete with pumice aggregate and slag after exposure to elevated temperature at 900 °C a) cement paste, b) ITZ

In terms of durability of concrete, water permeability is one of the main characteristics of concrete which can affect long-term properties of concrete. For example, aggressive ions such as chloride can easily penetrate into concrete with high water permeability and consequently, risk of corrosion is increased and service life of concrete element and structure is decreased significantly. Therefore, Hossain et al. (2011) carried out a comprehensive study on changes of 12-week water permeability of concrete with different levels of replacement of pumice coarse aggregate (0, 50, 75 and 100%) and pumice fine aggregate as shown in Fig. 2.18. They reported that the 12-week water permeability of concrete was reduced from 3.7×10^{-10} cm/s to 2.5×10^{-10} cm/s when gravel was full replaced by coarse pumice aggregate which means a maximum decrease of approximately 32%. Furthermore, the 12-week water permeability of concrete was reduced by increasing of pumice coarse aggregate and replacement of sand by pumice fine aggregate.

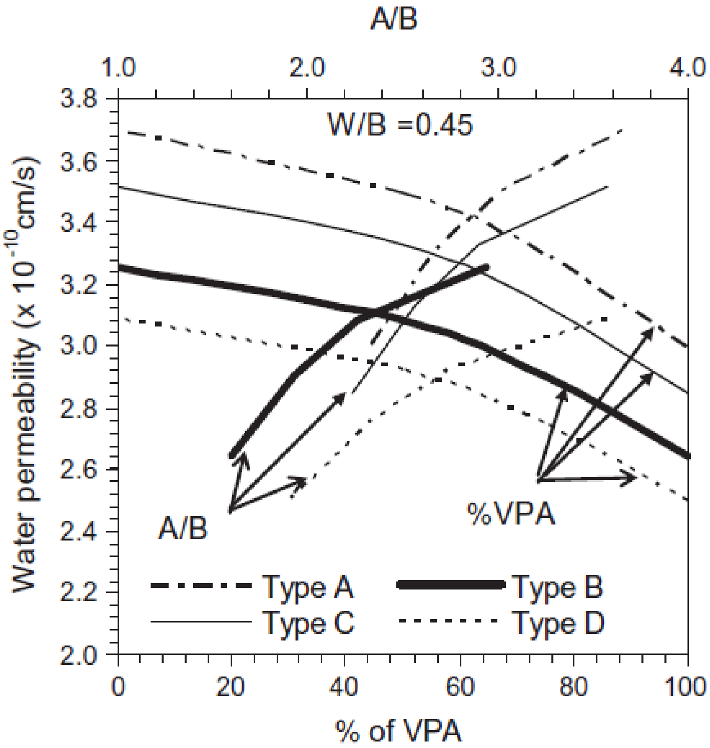


Fig. 2.18: 12-week water permeability of pumice concrete versus level of pumice coarse aggregate replacement (Hossain et al., 2011)

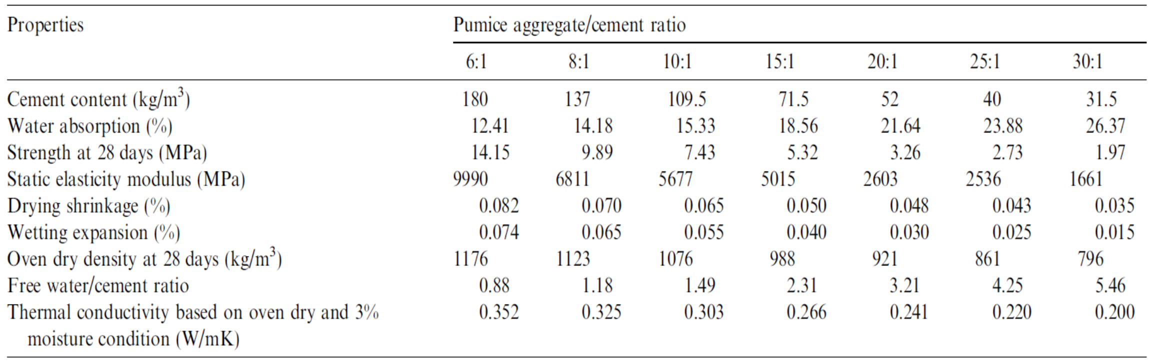
According to Hossain et al. (2011), earlier studies also reported that lightweight concrete had equal or lower permeability in comparison with same concrete with normal aggregate despite wide variations in concrete strengths, testing media, and testing methods (ACI, 2003; Bremner et al., 1992). It is maybe because of higher micro hardness of transition zone at the at the surface of the lightweight aggregate producing superior contact zone that enhances bond between the aggregate and the continuous matrix phase (Bremner et al., 1992). Two porous materials including the light weight aggregate and the cement paste provides the contact zone in lightweight concrete which allows for hygrol equilibrium to be obtained between two phases. Therefore, this can eliminate weak zones which are caused by water concentration (ACI, 2003; Bremner et al., 1992; Sugiyama et al., 1996).

However, another important aspect is related to possibility of internal curing in concrete with pumice aggregate. In other word, the lightweight aggregate can absorb some water during mixing and this water can wick out from their pores into the finer capillary pores in the cement paste and extends the period of moist curing which is known as internal curing. Consequently, it can remarkably promotes the paste-aggregate transition zone in the long term. Such high quality paste-aggregate transition zone derived from interface characteristics and internal curing reduces the permeability of pumice concrete compared to normal concrete.

To provide better understanding of effects of hybrid fiber reinforcement system (steel and propylene fibers) on performance of concrete with pumice aggregate, Libre et al. (2011) studied such concrete under compression and tension loading. They reported that the blocking influence of polypropylene and steel fibers decreased risk of segregation of aggregates and improved uniformity of concrete mixture. Furthermore, steel fibers remarkably affected flexural and compressive properties while PP fibers did not have significant effect on mechanical properties of hardened concrete. Finally, they concluded that presence of a hybrid system of PP and steel fibers improved thee splitting tensile strength. Batis et al. (2005) studied corrosion behavior of light weight concrete with pumice. One of their main motivations for doing this research was high porosity of such concretes. They used three different organic coatings for pumice aggregate and samples were partially immersed in 3.5% NaCl or exposed outdoors. They reported that applying protective coatings remarkably decreased corrosion of rebars in all samples while the best results were obtained by applying the aqueous acrylic dispersion including titanium oxide.

Furthermore, Binici et al. (2012) investigated durability properties of concrete pipes with blast furnace slag and pumice as fine aggregates. With regard to satisfactory performance and reasonable durability of such concrete, they claimed that this concrete can be used for producing concrete pipes for wastewater and sewage systems where different aggressive acids and salts can exist. According to Stepanova (1991), reinforced concrete with light weight aggregates such as pumice and slag had acceptable resistance against salt attack. Meantime, its corrosion resistance was satisfactory. He also evaluated suitability of using such concretes in load-bearing and enclosure structures. While structural concrete is usually needed to have higher mechanical and long-term properties such as compressive strength, there are many other concrete applications which do not need such a high compressive strength. Gunduz (2008) evaluated effects of pumice aggregate/cement ration on properties of low-strength concrete. Table 2.4 presents results of his work and related mix design of concretes which were used in this study. As it can be seen, quality properties of concrete including compressive strength, modulus of elasticity and density were increased by decreasing of aggregate to cement ratio (Gunduz, 2008).

Table 2.4: Mix design and properties of low-strength concrete with pumice aggregate (Gunduz, 2008)



Properties	Pumice aggregate/cement ratio						
	6:1	8:1	10:1	15:1	20:1	25:1	30:1
Cement content (kg/m^3)	180	137	109.5	71.5	52	40	31.5
Water absorption (%)	12.41	14.18	15.33	18.56	21.64	23.88	26.37
Strength at 28 days (MPa)	14.15	9.89	7.43	5.32	3.26	2.73	1.97
Static elasticity modulus (MPa)	9990	6811	5677	5015	2603	2536	1661
Drying shrinkage (%)	0.082	0.070	0.065	0.050	0.048	0.043	0.035
Wetting expansion (%)	0.074	0.065	0.055	0.040	0.030	0.025	0.015
Oven dry density at 28 days (kg/m^3)	1176	1123	1076	988	921	861	796
Free water/cement ratio	0.88	1.18	1.49	2.31	3.21	4.25	5.46
Thermal conductivity based on oven dry and 3% moisture condition (W/mK)	0.352	0.325	0.303	0.266	0.241	0.220	0.200

2.2.3.2. Pumice as cement replacement in concrete

Although using of pumice as aggregate seems an environment-friendly and cost-effective method for developing green concrete, technical performance of such concretes conveys important concerns because of high water absorption of pumice aggregate. Another option for utilizing pumice in concrete industry is developing usage of finely-ground pumice powder as a cement additive. Many researchers have studied effects of pumice as a pozzolanic material on properties of concrete which is reviewed in this section.

Hossain et al. (2011) investigated changes of compressive, tensile strengths and modulus of elasticity of concrete incorporating 20% of pumice as cement additives and different levels of pumice coarse aggregate replacement (Figs. 2.11 and 12). It should be noted that general mix designs of Type A and C were same which included Portland cement, coarse pumice, coarse gravel and sand with water to cement ratio of 0.45. The only difference was replacing of 20% of Portland cement by finely ground pumice in Type C. As it can be seen from this figure, compressive, tensile strengths and modulus of elasticity of Type C incorporating 20% pumice as cement additive were lower than Type A without finely ground pumice.

However, pumice has pozzolanic characteristics and can react with calcium hydroxide as one of hydration products of Portland cement to form more hydrate-silicate-calcium so that long term strength and durability can be improved (Hossain, 2006).

Rashiddadash et al. (2014) studied flexural toughness of hybrid fiber reinforced concrete containing pumice as replacement of Portland cement at two levels of 10 and 15%. They reported that compressive strength and modulus of rupture were decreased in comparison with the normal concrete, depending mainly on replacement level of pumice.

Hossain et al. (2011) studied fluctuations of drying shrinkage and water permeability of concrete incorporating 20% of pumice as cement additives and different levels of pumice coarse aggregate replacement (Figs. 2.16 and 2.18). They reported that presence of 20% pumice as cement additive can reduce 12-week drying shrinkage which can be attributed to the introduction of finely ground pumice.

In terms of water permeability, Hossain et al. (2011) reported that the replacement of Portland cement by 20% finely ground pumice resulted in decreasing of the 12-week water permeability of concrete. The pozzolanic reaction between finely ground pumice and calcium hydroxide produces a denser concrete as the age of concrete increases. Consequently, permeability should be lower. On the hand, the decreasing of permeability with age may have beneficial effect of improving the long-term corrosion resistance of such concretes.

Several researchers have evaluated effects of using finely ground pumice as a cement additive on corrosion behaviour of concrete (Kelestemur and Demirel, 2010; Hossain, 2003 and 2005; Binici et al, 2008).

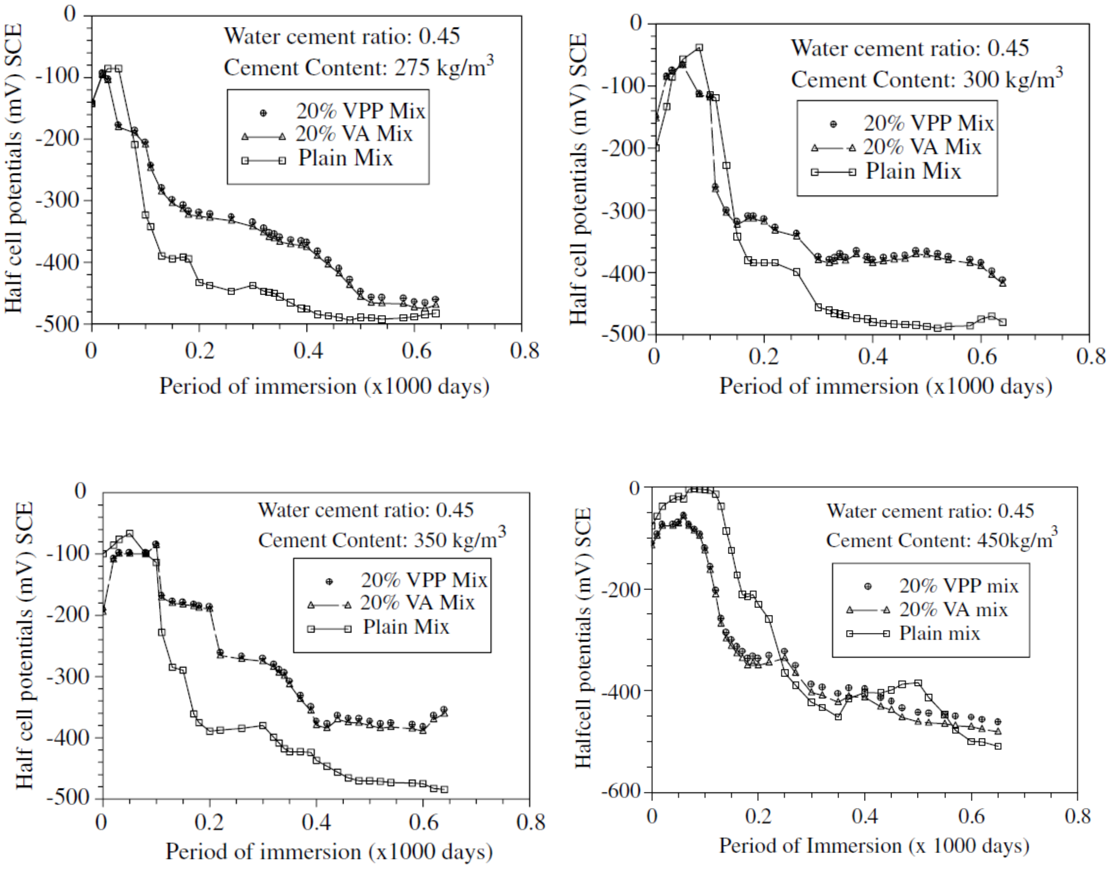


Fig. 2.19: Results of half-cell potentials of reinforcing bars in plain and pumice concrete (Hossain, 2005a)

Hossain (2005a) carried out a comprehensive study on corrosion behaviour of concrete containing 20% of finely ground pumice as cement replacement. Fig. 2.19 shows results of half-cell potentials of reinforcing bars in plain and pumice concrete mixes with different cement content. According to Hossain (2005a), additions of pumice is effective in preventing corrosion of reinforcing bars and this superior performance in inhibiting corrosion can be attributed to the densification of the cement paste because of pozzolanic reactions of pumice in concrete mixture.

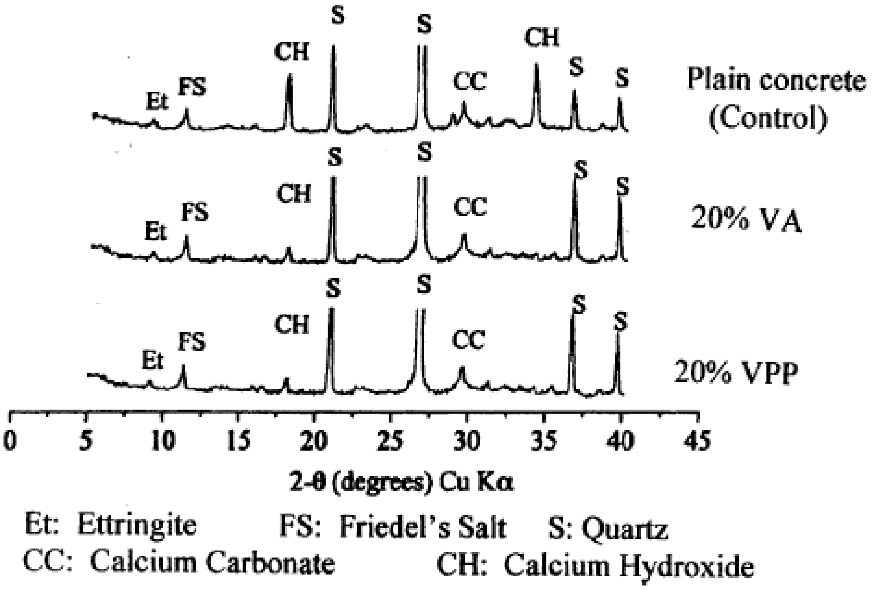


Fig. 2.20: Results of XRD analysis of plain and pumice concretes

This conclusion was confirmed by results of XRD analysis (Fig. 2.20) which showed lower amount of calcium hydroxide and formation of comparatively higher Friedel's salt which means lower availability of free chloride in pumice concrete. Furthermore, Hossain (2005a) reported lower corrosion rate in concrete with pumice in comparison with control samples which can be interpreted as reduction of chloride diffusion and consequently, lower chance of localized corrosion of steel in concrete.

Kelestemur and Demirel (2010) studied corrosion resistance of concrete mixtures incorporating 0, 5, 10, 15 and 20% by weight of pumice (P) and 10% of silica fume (S) as cement replacements. Fig. 2.21 shows results of changes of corrosion potential of different mixtures which were measured every day for a period of 160 days according to ASTM C 876.

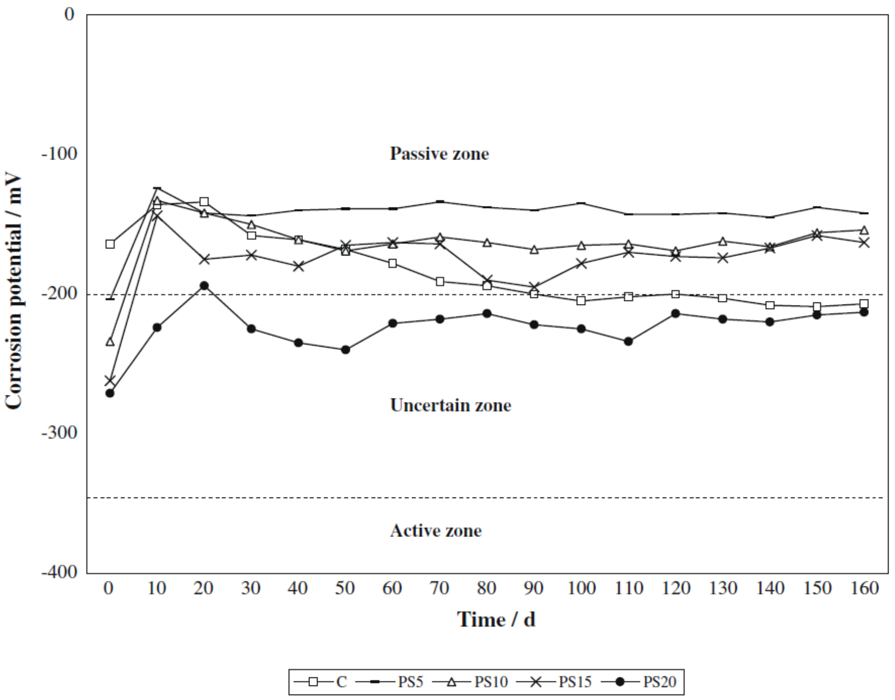


Fig. 2.21: Results of corrosion potential of concrete containing pumice and silica fume as cement replacements (Kelestemur and Demirel, 2010)

As it can be seen, overall corrosion performance of concrete mixtures with pumice and silica fume were better than control mixture and they almost remained in the passive zone during period of measurements.

To compare results of Kelestemur and Demirel (2010) and Hossain (2005a), it should be noted that they used pumice powder with different fineness. While Kelestemur and Demirel (2010) used pumice which was passed through 75 μm sieve, Hossain (2005a) used pumice powder with Blaine fineness of 295 m2/kg. It is well-known that fineness of a pozzolan is one of prominent factors in terms of its pozzolanic activity as well as its efficiency in terms of filler effect.

Hossain and Lachemi (2006) investigate performance of finely ground pumice based blended cement concrete in mixed magnesium-sodium sulphate environment with different immersion period up to 48 months. They evaluated deterioration of concrete due to mixed sulphate attack and corrosion of reinforcing bars by measuring weight loss, corrosion potentials and polarization resistance while 20% of Portland cement was replaced by pumice powder. They reported that overall performance of pumice samples were worse than plain concrete in terms of corrosion and sulphate resistance which can be attributed to the consumption of hydroxide calcium by pozzolanic reaction in blended cements containing pumice which causes magnesium ions react directly with C–S–H gel and converting it to cohesion-less, porous, reticulated M–S–H gel. However, using of Type V cements reduced the deterioration of pumice based blended concrete specimens compared with those of Type I.

Hossain (2008) investigated performance of concrete incorporating different percentages of finely ground pumice up to 30% as cement replacement subjected to marine environment for a period of one year. Hossain (2008) concluded that bending of Type I and Type II cements with pumice (between 10% and 20%) resulted in better resistance against seawater attack in comparison with Type V cement with low C_3A. The performance of pumice based concrete mixtures. Therefore, he recommended that Type I cement with pumice content between 10% and 20% would be a better choice in marine environment.

Litvan (1985) reported that using of pumice and perlite as additives improved freezing-thawing resistance of mortar and concrete significantly. Demirel and Kelestemur (2010) studied behaviour of concretes incorporating 0, 5, 10, 15 and 20% by weight of pumice (P) and 10% of silica fume (S) as cement replacements after exposure to high temperatures up to 800 °C. Fig. shows results of changes of relative compressive strength of different mixtures which were measured after subjecting to 20, 400, 600 and 800 °C. The relative strength was calculated as the percentage of strength retained by concrete with respect to the strength of the unheated specimen at room temperature which was 20 °C. According to Demirel and Kelestemur (2010), the relative compressive strength increased slightly up to heating at 400 °C (with the exception of the control specimen) and then marginally decreased between 400 and 600 °C. Finally, a rapid decrease in relative strength occurred above that point because of loss of crystal water, leading to the reduction of the $Ca(OH)_2$ content and changing the morphology and formation of microcracks. For example, the relative concrete strengths were about 80% and 30% when the concrete was exposed to 600 and 800 °C, respectively.

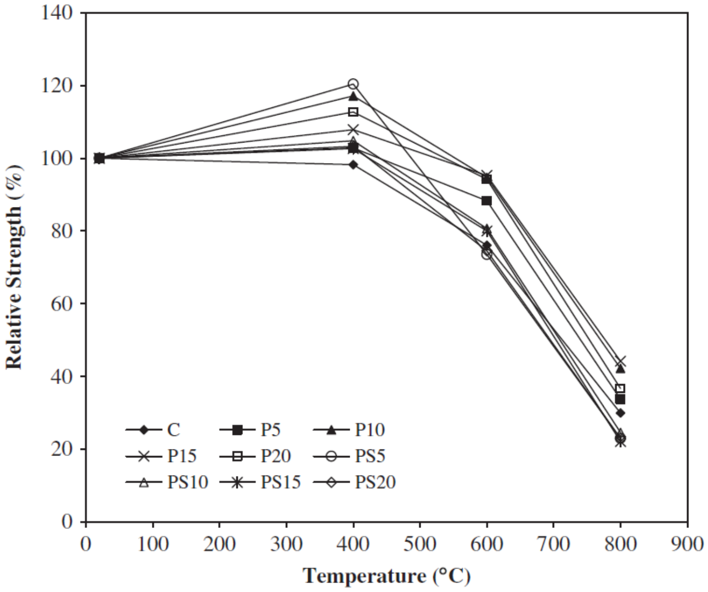


Fig. 2.22: Relative compressive strength of different mixtures after exposure to high temperatures (Demirel and Kelestemur, 2010)

Beside research works for evaluating effects of pumice powder as a cement additive on concrete properties, some researchers have attempted to develop new concrete elements including pumice powder. For example, Sahin et al. (2008) produced prefabricated building materials such as hollow concrete blocks, clinker bricks, gas concrete and lightweight concrete with pumice powder by using a pressure forming process and steam curing.

2.3. COPPER SLAG

The manufacturing of industrial slags refers to the starting of the extracting the metals from ores through the metallurgical methods. But, many of these industrial slags such as copper slag have not been used too much and remained useless as waste materials for many years. Copper slag is a by-product obtained during the matte smelting and refining of copper (Biswas and Davenport, 2002). Production of one ton of copper produces, around 2.2-3 tons copper slag. In the United States, the amount of copper slag manufactured is approximately four million tons, and in Japan, it is around two million tons per year (Collins and Ciesielski, 1994; Ayano et al., 2000). Furthermore, Iran and Brazil produces approximately 360,000 and 244,000 tons of copper slag, respectively (Behnood, 2005; Khanzadi and Behnood, 2009; Moura et al., 1999).

Available options for management of copper slag are recycling, recovering of metal, production of value added products and disposal in slag dumps or stockpiles. Copper slag has been widely used for abrasive tools, roofing granules, cutting tools, abrasive, tiles, glass, road-base construction, railroad ballast, asphalt pavements, cement and concrete industries.

Several researchers have evaluated the use of copper slag in cement clinker production, and the influence of copper slag on the characteristics of Portland cement mortar and concrete in the form of cement additive, coarse and fine aggregate. The use of copper slag in cement and concrete brings additional environmental as well as economic benefits for all related industries, mainly in regions where a substantial amount of copper slag is produced.

2.3.1. Production of copper slag

As mentioned above, copper slag is a by-product obtained during the matte smelting and refining of copper (Biswas and Davenport, 1994). Fig. 23 shows some pictures of a copper manufacturing complex in Iran. Major elements of a smelting charge are sulphides and oxides of iron and copper. The charge also consists of oxides such as SiO_2, Al_2O_3, CaO and MgO, which are either available in the original concentrate or added as flux. It is the iron, copper, sulphur, oxygen and their oxides which largely control the chemistry and physical constitution of the smelting system.

Fig. 2.23: Sarcheshmeh copper manufacturing complex in Iran (Courtesy of National Iranian Copper Industries Company)

A further main factor is the oxidation/reduction potential of the gases which are used to heat and melt the charge (Gorai et al., 2002). As a result of this process, copper-rich matte (sulphides) and copper slag (oxides) are formed as two distinct liquid phases. The addition of silica during smelting process forms strongly bonded silicate anions by combination with the oxides. This reaction forms copper slag phase, whereas sulphides form matte phase because of low tendency to make the anion complexes. Silica is added directly for the most complete isolation of copper in the matte which occurs at near saturation concentration with SiO_2 (Shi and Qian, 2000). The slag structure is stabilized by the addition of lime and alumina. The molten slag is discharged from the furnace at 1000-1300 °C. When liquid slag is cooled slowly, it forms a dense, hard crystalline product, while as fast solidification by pouring molten slag into water gives granulated amorphous slag (Gorai et al., 2002).

2.3.2. Chemical composition of copper slag

The chemical composition of copper slag relies on the types of furnace and production process. In general, the percentages of the main oxides of copper slag can be changed in the ranges as follows. Fe_2O_3: 35-60 %, SiO_2: 25-40 %, CaO: 2-10 %, Al_2O_3: 3-15 %, CuO: 0.3-2.1 %, MgO: 0.7-3.5 %. The chemical compositions of copper slag obtained from different areas are presented in Table 2.5. As it can be seen, Fe_2O_3 is the main chemical compound in copper slag. This is the main reason for high specific gravity of cooper slag aggregate which is discussed later. Furthermore, there is considerable amount of SiO_2which its crystallisation (amorphous or well-crystallised) depends on methods of slag melt cooling (air-cooled or water jet).

Table 2.5. Chemical Composition of Copper Slag from Different Sources (%)

No	Fe_2O_3	SiO_2	CaO	MgO	Al_2O_3	SO_3	CuO	Reference
1	52.50	27.80	4.60	1.20	7.80	0.98	1.20	(Behnood, 2005])
2	44.78	40.97	5.24	1.16	3.78	1.06	-	(Marghussian and Maghsoodipoor, 1999)
3	44.80	24.7	10.9	1.7	15.6	0.28	2.1	(Mobasher et al., 1996)
4	34.62	27.16	17.42	3.51	14.7	0.33	1.64	(Mobasher et al., 1996)
5	49.50	34.51	2.20	1.48	6.55	1.20	0.43	(Douglas et al., 1986)
6	50.00	36.78	1.93	1.49	7.16	1.13	0.41	(Douglas et al., 1986)
7	45.3	36.0	9.30	3.24	3.45	0.49	0.33	(Roper et al., 1983)
8	62	26	2.5	3.7	-	-	1.4	(Moura et al., 1999)
9	52.0	35.5	2.11	1.06	5.90	0.14	0.88	(Ayano and Sakata, 2000)
10	60.00	30.07	0.6	0.75	3.97	0.32	0.79	(Sanchez de Rojas et al., 2004)
11	53.72	34.3	7.91	0.94	3.83	3.02	-	(Hwang and Laiw, 1989)
12	36	31	4	-	6	-	0.33-0.80	(Zain et al., 2004)
13	41.53	37.13	-	-	-	0.11	0.79	(Imris et al., 2000)
14	39.65	31.94	3.95	2.82	2.4	-	1.01	(Kiyak et al., 1999)

2.3.3. Physical properties of copper slag

The physical properties of copper slag are presented in Table 2.6. As seen, the density of copper slag changes between 3.16-3.87 g/cm³ based on the amount of iron content. The average specific gravity of copper slag is about 3.5g/cm³ which means copper slag is heavier than ordinary natural aggregates. In general, water absorption of copper slag is very low. As mentioned earlier, when liquid slag is cooled slowly, it forms a dense, hard crystalline product whereas fast solidification by pouring molten slag into water results in granulated amorphous slag.

Table 2.6. Physical properties of copper slag[*]

Appearance	Black, glassy, more vesicular when granulated
Particle shape	Irregular
Density, g/cm³	3.16-3.87
Water absorption, %	0.15-0.55
Hardness, mohs	6-7
Water soluble chloride, ppm	< 50
Soundness, %	0.8-0.9
Aggregate crushing value, %	10-21
Aggregate impact value, %	8.2-16
Abrasion loss, %	24.1
Conductivity, µs/cm	500

[*] (Ayano and Sakata, 2000; Behnood, 2007; Gorai et al., 2003; Hwang and Laiw, 1989; Moura et al., 1999; Shoya et al., 2003; Shoya et al., 1997).

Therefore, granulated copper slag has a higher water absorption and less unit weight compared with air-cooled copper slag due to its more porous texture.

2.3.4. Use of Copper Slag in Cement

As it can be seen in Table 2.7, copper slag has a high Fe content and has been used as an iron adjustment material during the cement clinker production (Huang, 2001). Since the main composition of copper slag is vitreous $FeSiO_3$, it has low melting point and could decrease the calcinations temperature for cement clinker. Thus, the use of copper slag to replace iron powder as iron adjusting materials facilitated the cement production, decreases or removes the necessity of mineralizer. However, the use of iron powder does not indicate this benefit. The performance testing results showed that cement produced by using copper slag performed even better than using iron powder.

Guo (2003) reported that copper slag was effectively used as an iron adjustment material in cement clinker production. In another study, researchers used the tailings from Mo ores and copper slag to produce cement clinker. In addition, CaF was used as a mineralizer. The performance of the cement was even better than that produced using traditional clay, limestone and mill scale (Liu et al, 2007). Furthermore, the use of copper causes lower required calcinations temperature and facilitated grindability of the clinker although the raw materials cost may or may not be decreased depending on the local availability of copper slag (Tan et al, 2000; Huang, 2001).

The use of copper slag as a pozzolanic material for a partial replacement for ordinary Portland cement and its influences on the hydration reactions have been reported in the literature (Malhotra, 1993; Tixier et al., 1997; Arino and Mobasher, 1999; Douglas et al., 1986; Deja and Malolepszy, 1989). Roper et al. (1983) reported that copper slag does not require to be fully glassy for substantial hydration to occur.

One potential problem for such materials is their heavy metal content and the leaching characteristics. The leachability of copper, nickel, lead, and zinc ions from copper slag were lower than the regulatory limits. Zain et al. (2004) reported the mortar containing waste copper slag up to 10% replacement is safe with respect to leachability of the above heavy metal. Presence of the copper slag in the cement mortar does not result in increasing of the leached elements (Sanchez de Rojas et al., 2004).

Moura et al. (1999) evaluated the compressive and flexural strength of concretes containing copper slag as 10% of the cement by weight. The results showed that concretes with copper slag had lower compressive strength than concretes without copper slag admixture up to 91 days. The flexural strengths of concretes with and without copper slag were similar for water to cement ratio of 0.4 to 0.5.

Arino and Mobasher (1999) made mortar samples incorporating up to 15% copper slag as a cement replacement with constant water to cementitious solids ratio of 0.4. The compression-test results showed that copper slag concrete was remarkably stronger but more brittle than ordinary Portland cement concrete.

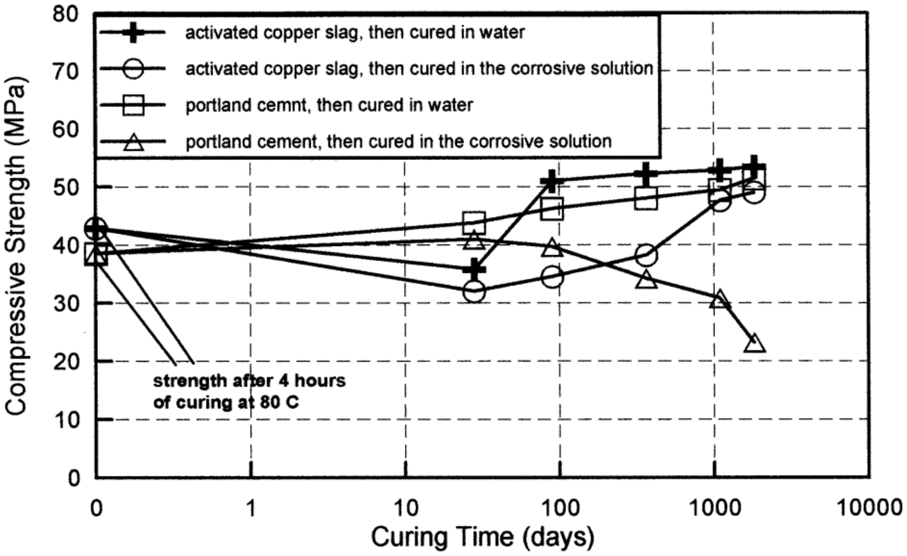


Fig. 2.24: Compressive strength of NaOH-activated copper slag and Portland cement mortars (Shi and Qian, 2000)

Fracture test results confirmed the increased brittleness of concrete because of the use of copper slag in the mentioned study. Fig. 2.24 shows that copper slag incorporating around 19% CaO had good cementitious property under the activation of NaOH.

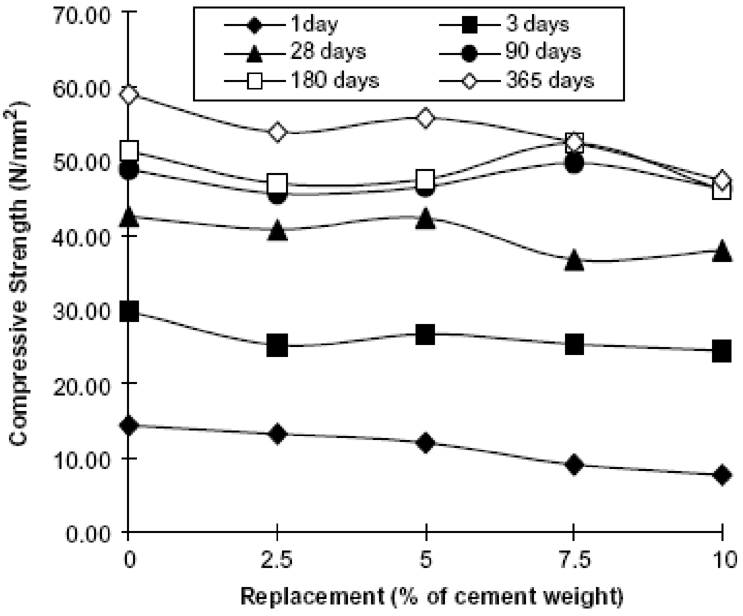


Fig. 2.25: Compressive strength of copper slag mortars as a function of replacement level (Zein et al., 2004)

The NaOH-activated copper slag mortars had higher strength in comparison with Portland cement mortars even after 4 hours of curing at 80°C (Deja and Malolepszy, 1989, 1994). Furthermore, they reported higher corrosion resistance of copper slag mortars in comparison with plain Portland cement mortars.

Fig. 2.25 shows the compressive strength of copper slag mortars as a function of replacement level (Zain et al., 2004). According to Zain et al. (2004), the strength of copper slag mortar is normally lower than that of the control mortar. They reported an optimum strength performance in the range of 5-7.5% for the copper slag mortar. In another study, it was reported that the replacement of 10 to 15% cement clinker does not have a remarkable influence on compressive strength, but considerably increase the abrasion resistance of the cement mortar (Dai et al., 1998).

2.3.5. Use of copper slag in concrete

Several researchers have evaluated the potential use of copper slag as fine and coarse aggregates in concrete and its effects on the different mechanical and long-term properties of mortar and concrete. With some advantages of using copper slag as fine and coarse aggregates, also some negative influences have been reported, such as delaying of the setting time, especially when only copper slag has been used as fine aggregate. Ayano and Sakata (2000) reported that the slag component was an insoluble residue of 0.15 mm size that could be readily removed by washing. They concluded that the influence of copper slag on the setting time was different with the particle size of copper slag (that is, the smaller size of copper slag results in the longer delay in the setting time).

However, the influence of copper slag on the setting time was reduced by increasing the washing times. Shoya et al. (1997) reported that the amount and rate of bleeding are increased by utilizing copper slag fine aggregate depending on the water to cement ratio, the volume fraction of slag and air content. They suggested that using less than 40% of copper slag can have positive effect for controlling the amount of bleeding to less than 5 l/m^2. Hwang and Laiw (1989) reported that the amount of bleeding of mortar containing copper slag relatively is less than that using natural sand. However, the heavy specific gravity and the glass-like smooth surface properties of irregular grain shape of copper slag aggregates are effective on specifications of bleeding. Hwang and Laiw (1989) and Ayano and Sakata (2000) reported that the shrinkage of specimens containing copper slag fine aggregate is similar or even less than that of specimens without copper slag (Fig. 2.26).

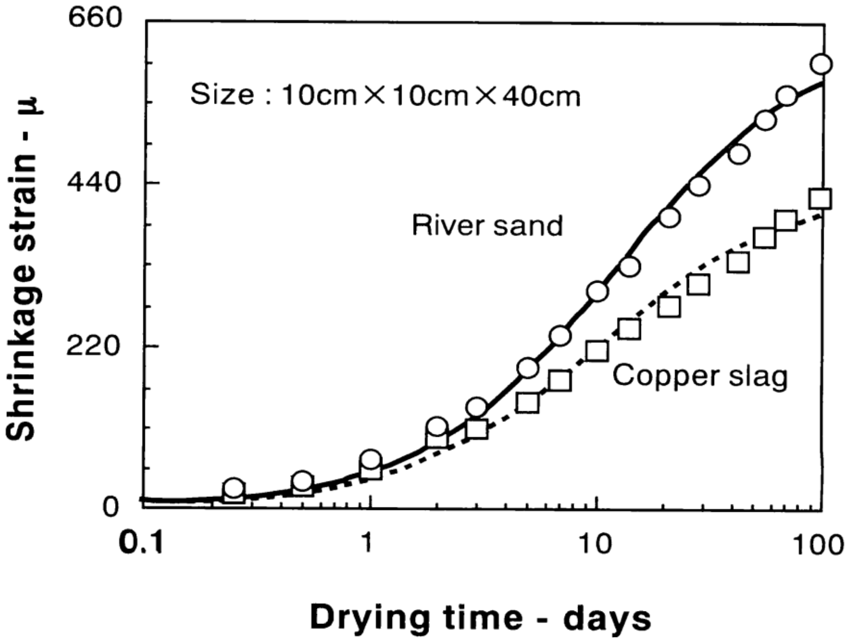


Fig. 2.26: Drying shrinkage strain using copper slag and river sand (Ayano and Sakata, 2000)

Several works reported that the compressive and tensile strengths of concrete specimens made with copper slag fine and coarse aggregates are almost the same as that of normal concrete or even significantly more than control mixtures (Caliscan and Behnood, 2004; Shoya et al., 1997; Ayano and Sakata, 2000; Hwang and Laiw, 1989).

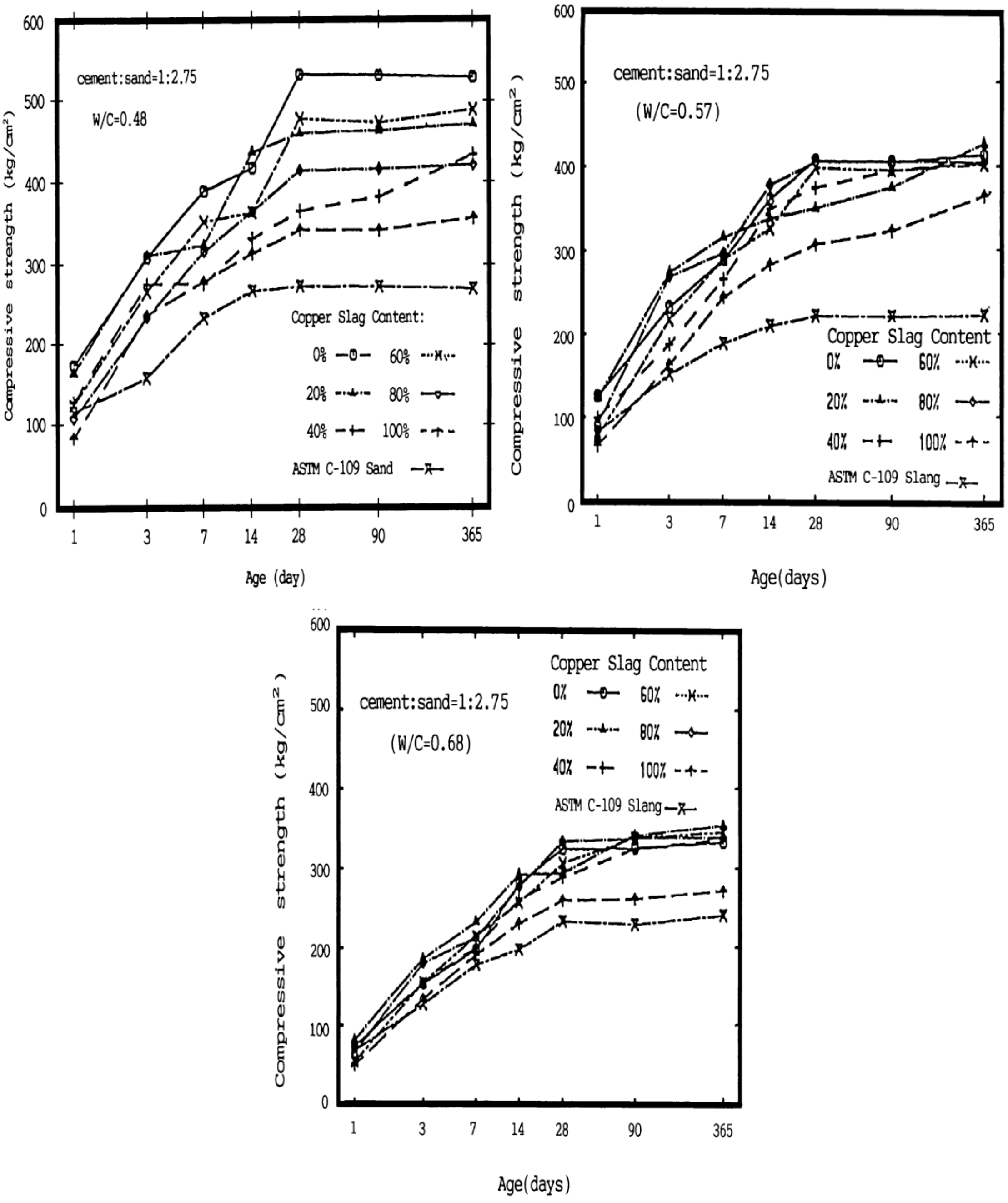


Fig. 2.27: Compressive strength development of mortars containing copper slag sand with different water to cement ratios (Hwang and Laiw, 1989)

It was noticed that the use of copper slag as fine aggregate could greatly increase the abrasion resistance of the cement mortar (Tang et al, 2000). Hwang and Laiw (1989) evaluated the compressive strength development of mortars and concretes containing fine copper slag aggregate with different water to cement ratios (Figs. 27 and 28). Fig. 27 shows the mortars containing the larger amounts of copper slag sand had lower early strengths at w/c of 0.48.

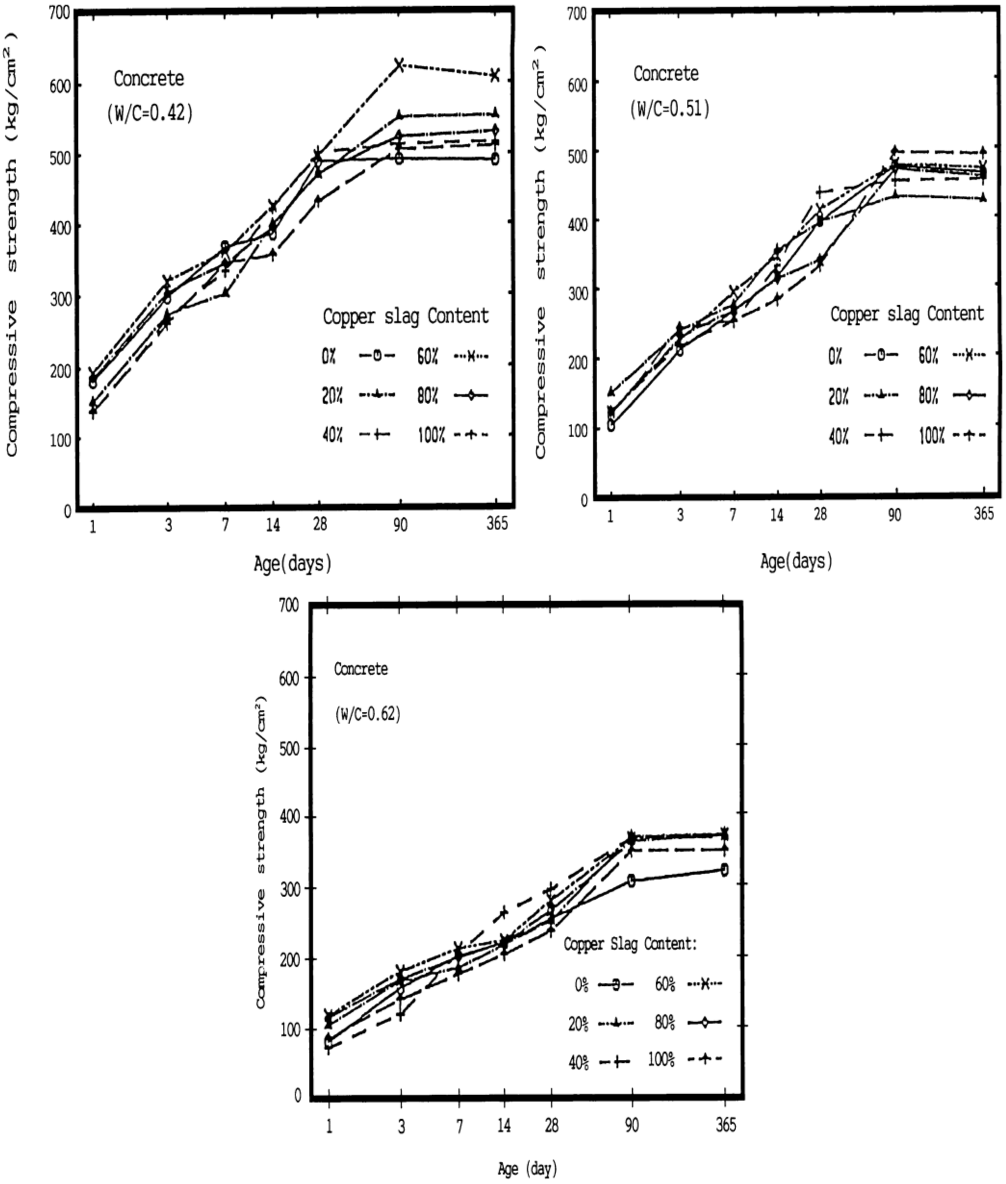
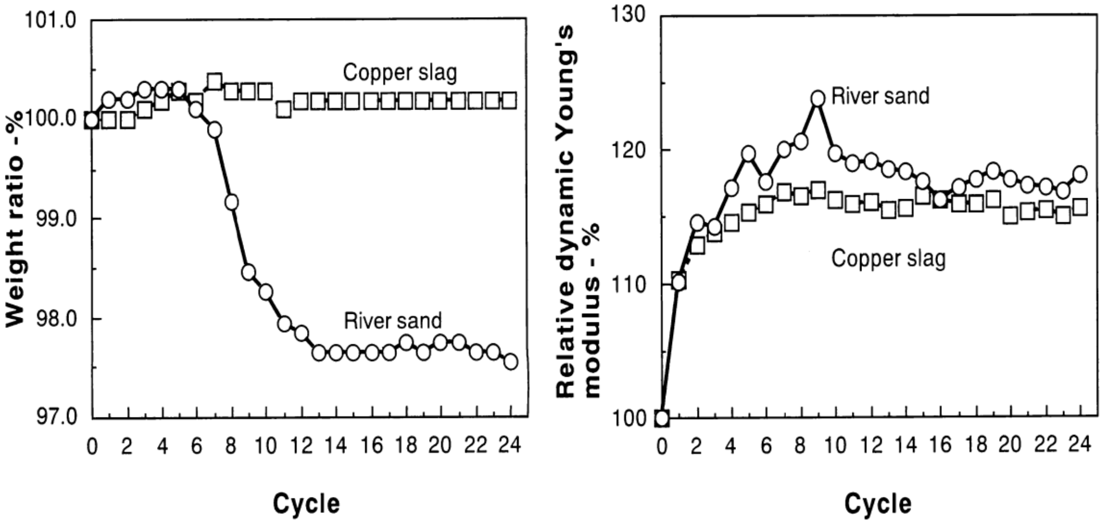


Fig. 2.28: Compressive strength development of concretes containing copper slag sand with different water to cement ratios (Hwang and Laiw, 1989)

The strengths of mixtures with 20-80% substitution of copper slag were higher than that of the control specimens. Fig. 28 indicates the similar trends of compressive strength development of concretes containing copper slag fine aggregate to those of mortars. Li (1999) and Zong (2003) also reported that concrete containing copper slag as fine aggregate exhibited the similar mechanical properties as that containing conventional sand and coarse aggregates. The evaluation of the effects of copper slag aggregate on the sulphate attack resistance (Fig. 2.29) and the depth of carbonation (Fig. 2.30) showed no significant attack and slower rate of carbonation by using copper slag (Hwang and Laiw, 1989; Ayano and Sakata, 2000).). Some researchers reported the freezing-thawing resistance of concrete containing copper slag aggregate is lower than control samples (Shoya et al., 1997; Shoya et al., 2003), whereas others reported similar or higher resistance for specimens made with copper slag fine aggregate (Li, 1999, Ayano and Sakata, 2000).



(a) (b)

Fig. 2.29: Resistance of sulphate attack of concrete using copper slag judged by (a) weight change, (b) relative dynamic young's modulus(Ayano and Sakata, 2000)

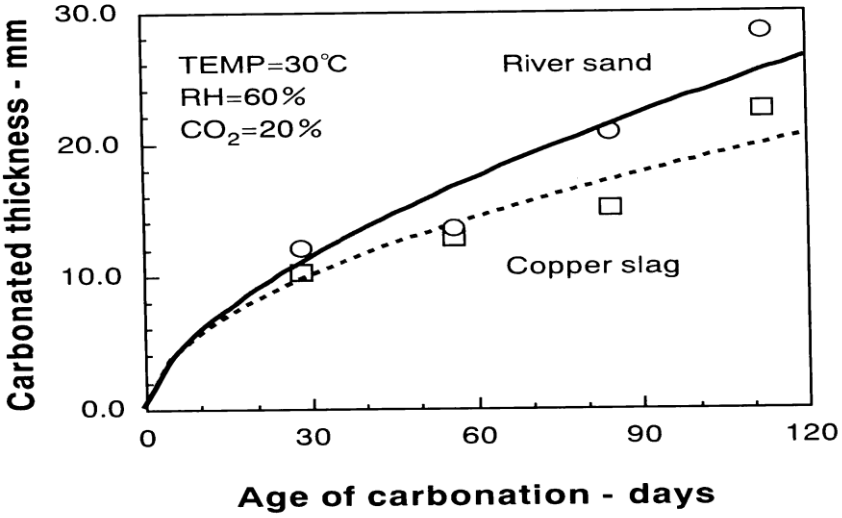


Fig. 2.30: Carbonated thickness of concrete using copper slag and river sand (Ayano and Sakata, 2000)

Caliscan and Behnood (2004) investigated the compressive strength of normal-strength concretes containing copper slag coarse aggregate (Fig. 2.31). As seen, the compressive strength of copper slag coarse aggregate concrete was marginally higher than that of limestone aggregate concrete.

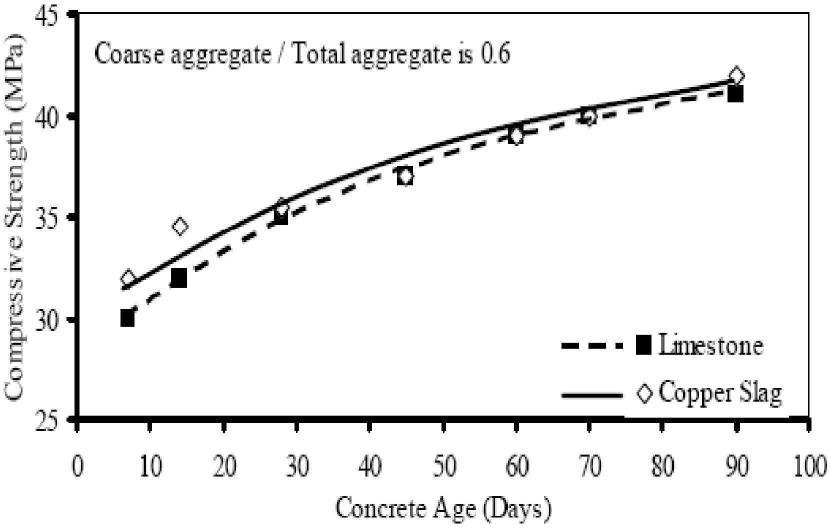


Fig. 2.31: Compressive strength development of concretes containing copper slag and limestone coarse aggregates (Caliskan and Behnood, 2004)

Good performance of copper slag as fine and coarse aggregates in normal concretes is the basis for researchers to evaluate its possible use in producing special concretes such as self-consolidating concrete (Shoya et al., 2003) and high-strength concrete (Khanzadi and Behnood, 2009).

Summary

This chapter critically reviewed all aspects which are related to environmental considerations of concrete production as well as production of copper slag and pumice for using in cementitious materials. It was shown that there a great potential for using pumice and copper slag as replacement for Portland cement and coarse aggregate in concrete.

Chapter 3

3. EXPERIMENTAL DETAILS AND PROGRAMME

Introduction

This chapter sets out the experimental programmes performed in this research. Materials, mix proportions, concrete specimens preparation procedure and experimental tests are explained in detail in this chapter. In general, fresh and hardened properties of high-strength concrete are evaluated at different ages. Furthermore, 16 different mix proportions were designed to investigate all variations in detail.

3.1. MATERIALS

Type I ordinary Portland cement meeting the requirements of ASTM C 150 was used in making of concrete mixtures. This cement was supplied by Tehran Cement Company. According to manufacturer's specifications, its specific gravity is 3.15 g/cm^3 and the autoclave expansion and loss on ignition (LOI) of this cement is less than 0.8 and 3, respectively. Also, its specific surface which was measured by Blaine method is more than 2800 cm^2/g. Furthermore, its initial and final setting are more than 45minutes and less than 6 hours, respectively. Furthermore, a high quality commercial silica fume (SF) with SiO_2 content of around 92% which was in accordance with ASTM C 1240 was used. Silica fume is a "very fine non-crystalline silica produced in electric arc furnaces as a by-product of production of elemental silicon or alloys containing silicon (Fig. 3.1).

This silica fume is produced by Ferro Alloy Company in Azna, Lorestan, Iran. According to manufacturer's specifications, its specific gravity is around 2.2 g/cm^3.

Fig. 3.1 : Sample of silica fume (left) and pumice (right)

Pumice was delivered from Bostan Abad, East Azarbaijan and ground in ball mill to provide required powder which can pass through ASTM standard sieve. Fig. 3.1 shows a sample of pumice. Chemical composition of Portland cement, silica fume and pumice are presented in Table 3.1. The main chemical compound of pumice and silica fume is SiO_2 which its percentage is approximately 64 and 92% while it is 22% in Portland cement. This is why pumice and silica fume are mainly known as pozzolanic materials. However, The CaO content of this cement was around 64% which is significantly higher than related values of silica fume and pumice. Furthermore, pumice has the highest content of Al_2O_3 between these materials. Percentages of other chemical compounds are not remarkable and they are within common ranges of chemical compositions.

Table 3.1: Chemical composition of Portland cement (OPC), silica fume (SF), copper slag (CS) and pumice (P)

Compound	OPC	SF	P	CS
SiO_2, %	21.46	91.70	63.45	27.80
CaO, %	63.95	1.68	3.22	4.60
Al_2O_3, %	5.55	1.00	17.24	7.80
Fe_2O_3, %	3.46	0.90	2.86	52.50
MgO, %	1.86	1.80	1.03	1.20
CuO, %	-	-	-	1.20
SO_3, %	1.42	0.87	0.16	0.98
K_2O, %	0.54	-	2.16	1.60
TiO_2, %	-	-	0.37	0.49
ZnO, %	-	-	-	0.84

Fig. 3.2: Samples of copper slag aggregate

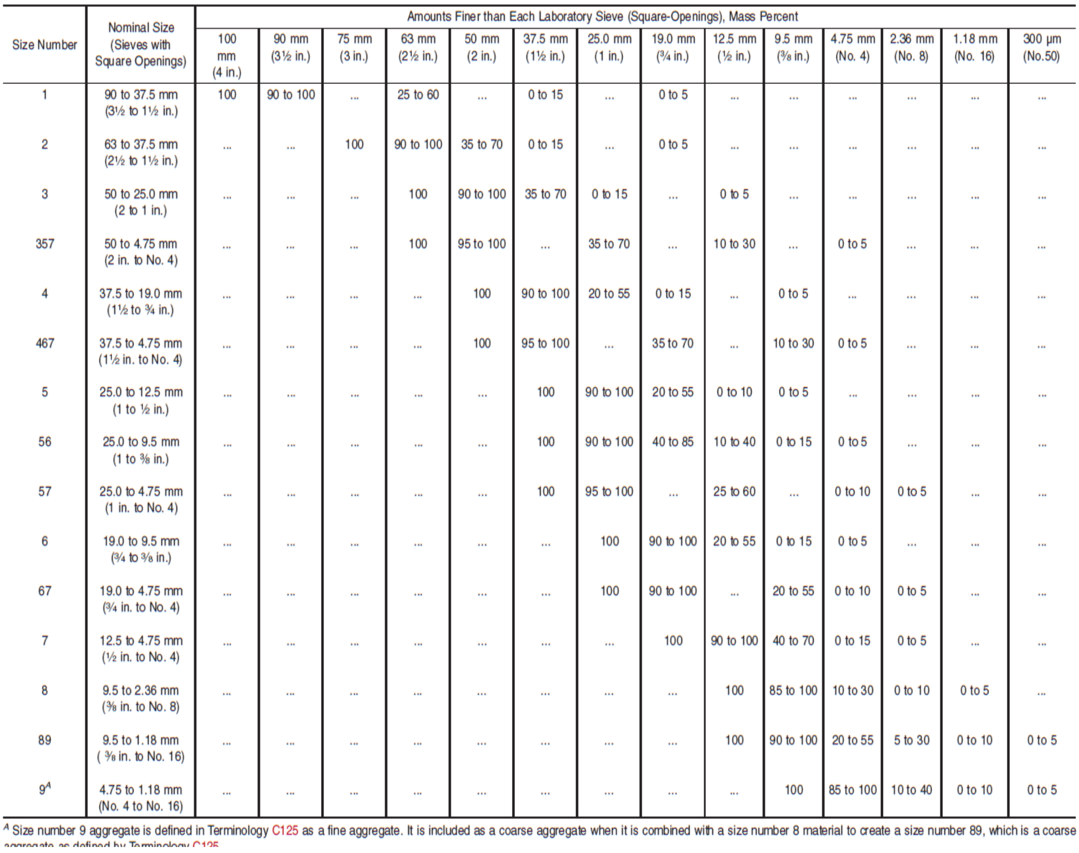
Two types of coarse aggregates with a nominal maximum size of 12.5 mm were used in this research. The first type was a limestone aggregate from areas around city of Shahriar and the other was a copper slag from the Sarcheshmeh Copper Manufacturing Complex which is located in Kerman, Iran. Fig. 3.2 shows photo of a sample of copper slag aggregate. Table 3.2 provides physical properties of limestone and copper slag aggregates.

Table 3.2: Physical properties of coarse aggregates

Properties	Copper slag aggregate	Limestone aggregate
Specific gravity, gr/cm³	3.59	2.65
Aggregate crushing value, %	10-21	23
Aggregate impact value, %	8.2-16	11
Water absorption, %	0.4	0.6
Particle size, mm	4.75-12.5	4.75-12.5

Both types of coarse aggregates met the grading requirements of size number 7 of ASTM C 33 which is presented in Table 3.3. It means that maximum size of aggregate (MSA) is 12.5 and coarse aggregates are in the range of 12.5 to 4.75 mm. The fine aggregate was river sand with a water absorption of 0.8% and specific gravity of 2.70 g/cm^3. With regard to required workability of high-strength concrete, a commercially available modified polycarboxylic-ether superplactizer with 44% solid particles was used to prepare the concrete mixtures. According to the manufacturer’s specifications, this superplasticizer is in accordance with ASTM C 494 “Standard specifications for chemical admixtures for concrete”.

Table 3.3: Grading requirements for aggregate according to ASTM C 33-2011



Size Number	Nominal Size (Sieves with Square Openings)	Amounts Finer than Each Laboratory Sieve (Square-Openings), Mass Percent													
		100 mm (4 in.)	90 mm (3½ in.)	75 mm (3 in.)	63 mm (2½ in.)	50 mm (2 in.)	37.5 mm (1½ in.)	25.0 mm (1 in.)	19.0 mm (¾ in.)	12.5 mm (½ in.)	9.5 mm (⅜ in.)	4.75 mm (No. 4)	2.36 mm (No. 8)	1.18 mm (No. 16)	300 µm (No.50)
1	90 to 37.5 mm (3½ to 1½ in.)	100	90 to 100	...	25 to 60	...	0 to 15	...	0 to 5	...	...	...	...	...	...
2	63 to 37.5 mm (2½ to 1½ in.)	...	...	100	90 to 100	35 to 70	0 to 15	...	0 to 5	...	...	...	...	...	...
3	50 to 25.0 mm (2 to 1 in.)	...	...	...	100	90 to 100	35 to 70	0 to 15	...	0 to 5	...	...	...	...	...
357	50 to 4.75 mm (2 in. to No. 4)	...	...	...	100	95 to 100	...	35 to 70	...	10 to 30	...	0 to 5	...	...	...
4	37.5 to 19.0 mm (1½ to ¾ in.)	...	...	...	...	100	90 to 100	20 to 55	0 to 15	...	0 to 5	...	...	...	...
467	37.5 to 4.75 mm (1½ in. to No. 4)	...	...	...	...	100	95 to 100	...	35 to 70	...	10 to 30	0 to 5	...	...	...
5	25.0 to 12.5 mm (1 to ½ in.)	...	...	...	...	...	100	90 to 100	20 to 55	0 to 10	0 to 5	...	...	...	...
56	25.0 to 9.5 mm (1 to ⅜ in.)	...	...	...	...	...	100	90 to 100	40 to 85	10 to 40	0 to 15	0 to 5	...	...	...
57	25.0 to 4.75 mm (1 in. to No. 4)	...	...	...	...	...	100	95 to 100	...	25 to 60	...	0 to 10	0 to 5	...	...
6	19.0 to 9.5 mm (¾ to ⅜ in.)	...	...	...	...	...	...	100	90 to 100	20 to 55	0 to 15	0 to 5	...	...	...
67	19.0 to 4.75 mm (¾ in. to No. 4)	...	...	...	...	...	...	100	90 to 100	...	20 to 55	0 to 10	0 to 5	...	...
7	12.5 to 4.75 mm (½ in. to No. 4)	...	...	...	...	...	...	...	100	90 to 100	40 to 70	0 to 15	0 to 5	...	...
8	9.5 to 2.36 mm (⅜ in. to No. 8)	...	...	...	...	...	...	...	...	100	85 to 100	10 to 30	0 to 10	0 to 5	...
89	9.5 to 1.18 mm (⅜ in. to No. 16)	...	...	...	...	...	...	...	...	100	90 to 100	20 to 55	5 to 30	0 to 10	0 to 5
9[A]	4.75 to 1.18 mm (No. 4 to No. 16)	...	...	...	...	...	...	...	...	...	100	85 to 100	10 to 40	0 to 10	0 to 5

[A] Size number 9 aggregate is defined in Terminology C125 as a fine aggregate. It is included as a coarse aggregate when it is combined with a size number 8 material to create a size number 89, which is a coarse aggregate as defined by Terminology C125

3.2. MIX PROPORTIONS

Sixteen different mix proportions were developed for evaluating effects of pumice as a cement additive and copper slag as coarse aggregate on fresh and hardened properties of high-strength concrete. Two water to binder ratios of 0.40 (F series) and 0.30 (S series) were selected. Furthermore, 10 % of weight of cement was replaced by silica fume (SF) in S series. In each series of F and S, there were two sub-categories including (1) fully replacement of limestone coarse aggregate (LS) with copper slag coarse aggregate (CS) and (2) partially replacement of Portland cement by 5, 10 and 20% of finely ground pumice (P5, P10 and P20). Each mixture was named based on its three parameters including water to cement ratio, coarse aggregate type and pumice replacement. For example. SLSP10 means that this mixture has 1) water to cement ratio of 0.3 (S), 2) coarse aggregate is limestone (LS) and 3) Pumice (P) replacement level is 10%.

This matrix of sample preparation was based on provided literature review regarding promising results of fully replacement of coarse aggregate by copper slag and satisfactory results of partially replacement up to 20% of Portland cement by pumice powder. Therefore, these mix proportions can provide reliable and enough data to carry out a comparative study on single effects of pumice and copper slag as well as combo influences of pumice and copper slag on properties of fresh and hardened high-strength concrete. Mixture proportions are presented in Table 3.4. Two basic cement contents of 430 and 450 kg/m^3 were considered for F and S series, respectively. It should be noted that different amounts of high-range-water-reducing admixture (superplasticizer) was used during mixing of concrete materials to achieve a final slump of 110±10 mm for different concrete mixtures.

Table 3.4: Concrete mixture proportions

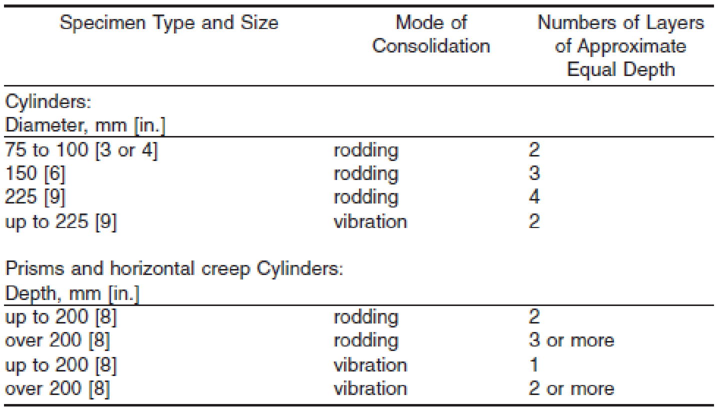
Mixture	FLS	FLSP5	FLSP10	FLSP20	SLS	SLSP5	SLSP10	SLSP20	FCS	FCSP5	FCSP10	FCSP20	SCS	SCSP5	SCSP10	SCSP20
Cement, kg/m^3	430	408.5	387	344	450	427.5	405	360	430	408.5	387	344	450	427.5	405	360
Silica fume, kg/m^3	-	-	-	-	45	45	45	45	-	-	-	-	45	45	45	45
Pumice, kg/m^3	-	21.5	43	86	-	22.5	45	90	-	21.5	43	86	-	22.5	45	90
Water, kg/m^3	172	172	172	172	149	149	149	149	172	172	172	172	149	149	149	149
Sand, kg/m^3	687	687	687	687	615	615	615	615	687	687	687	687	615	615	615	615
Limestone, kg/m^3	1030	1030	1030	1030	1168	1168	1168	1168	-	-	-	-	-	-	-	-
Copper slag, kg/m^3	-	-	-	-	-	-	-	-	1395	1395	1395	1395	1582	1582	1582	1582
w/cm	0.40	0.40	0.40	0.40	0.30	0.30	0.30	0.30	0.40	0.40	0.40	0.40	0.30	0.30	0.30	0.30
Superplasticizer, L/m^3	2.1	2.6	3.1	3.7	4.1	4.6	4.4	4.8	3.4	3.5	4.0	4.2	4.1	4.4	4.2	4.6

3.3. CONCRETE SPECIMEN PREPARATION METHOD

Before mixing the concrete, the concrete materials were brought to room temperature. Mixing of concrete ingredients including water, cement, pumice, silica fume, fine and coarse aggregates and superplactizer were done in accordance with ASTM C 192 which recommends required aspects for making concrete. The coarse aggregate, some of the mixing water, and the solution of admixture were added prior to starting rotation of the mixer. Main part of superplasticizer was added and dispersed into the mixing water before addition. After starting the mixer, the fine aggregate, cement, and water with the mixer running were added. After all ingredients were added in the mixer, the concrete was mixed for three minutes followed by a 3-min rest, followed by a 2-min final mixing. Special care should be done to cover the mixer to prevent evaporation during the rest period. Fig. 3.3 shows the time of adding water to mixture in a rotating pan mixer.

Fig. 3.3 : The time of adding water to mixture in a rotating pan mixer

Table 3.5: Number of layers required for samples according to ASTM C 192-2011



Specimen Type and Size	Mode of Consolidation	Numbers of Layers of Approximate Equal Depth
Cylinders: Diameter, mm [in.]		
75 to 100 [3 or 4]	rodding	2
150 [6]	rodding	3
225 [9]	rodding	4
up to 225 [9]	vibration	2
Prisms and horizontal creep Cylinders: Depth, mm [in.]		
up to 200 [8]	rodding	2
over 200 [8]	rodding	3 or more
up to 200 [8]	vibration	1
over 200 [8]	vibration	2 or more

The specimens were cast in two layers in cylindrical moulds of 102 mm diameter and 204 mm height, each layer being consolidated using a vibrating table. Casting in two layers and using vibration were selected in accordance with ASTM C 192 as shown in Table 3.5. After compaction by vibration, the surface of the concrete was struck off and floating was done with the minimum manipulation necessary to form a flat even surface that is level with the rim or edge of the mould and which has no depressions or projections larger than 3 mm. Then, the specimens immediately after finishing were covered by wet burlap and polyethylene sheet to prevent evaporation of water (Fig. 3.4).

Fig. 3.4: Covering concrete specimens after casting with wet burlap (left) and polyethylene sheet on top of the burlap (right)

Special care was done to keep the burlap away from surface of fresh concrete. Molded specimens under were kept under wet burlap and plastic sheets in the laboratory at room temperature for 24 hours. After demolding, concrete specimens were placed in a saturated limewater bath until the time of testing. The requirements of ASTM C 511 were fully considered for curing of concrete samples. Furthermore, special care was taken not to dry out specimens prior to testing. It should be noted that that standard method of concrete curing was selected for comparing results according to ASTM method. However, using other methods of curing can also be used for different applications particularly steam curing for pre-cast concrete.

3.4. TEST METHODS

In this research, different tests were carried out to measure fresh and hardened properties of different concrete mixtures. In general, unit weight, air content and slump of fresh concrete mixtures were measured in accordance with related standards. Furthermore, compressive and splitting tensile strength of hardened concretes were measured by applying loads by hydraulic pressure machine. A brief description of each test is presented in this section.

3.4.1. Workability (Slump test)

The most common test for measuring workability of fresh concrete is the slump test. Therefore, workability of fresh concrete samples of this study is measured by using slump test according to ASTM C 143.Test apparatus is mainly a metal mould which must be in the form of the lateral surface of the frustum of a cone with the base 200 mm in diameter, the top 100 mm in diameter, and the height 300 mm. Test steps are shown in Fig. 3.5. According to ASTM C 143, “a sample of freshly mixed concrete is placed and compacted by rodding in a mould shaped as the frustum of a cone. The mould is raised, and the concrete allowed to subside. The vertical distance between the original and displaced position of the centre of the top surface of the concrete is measured and reported as the slump of the concrete."

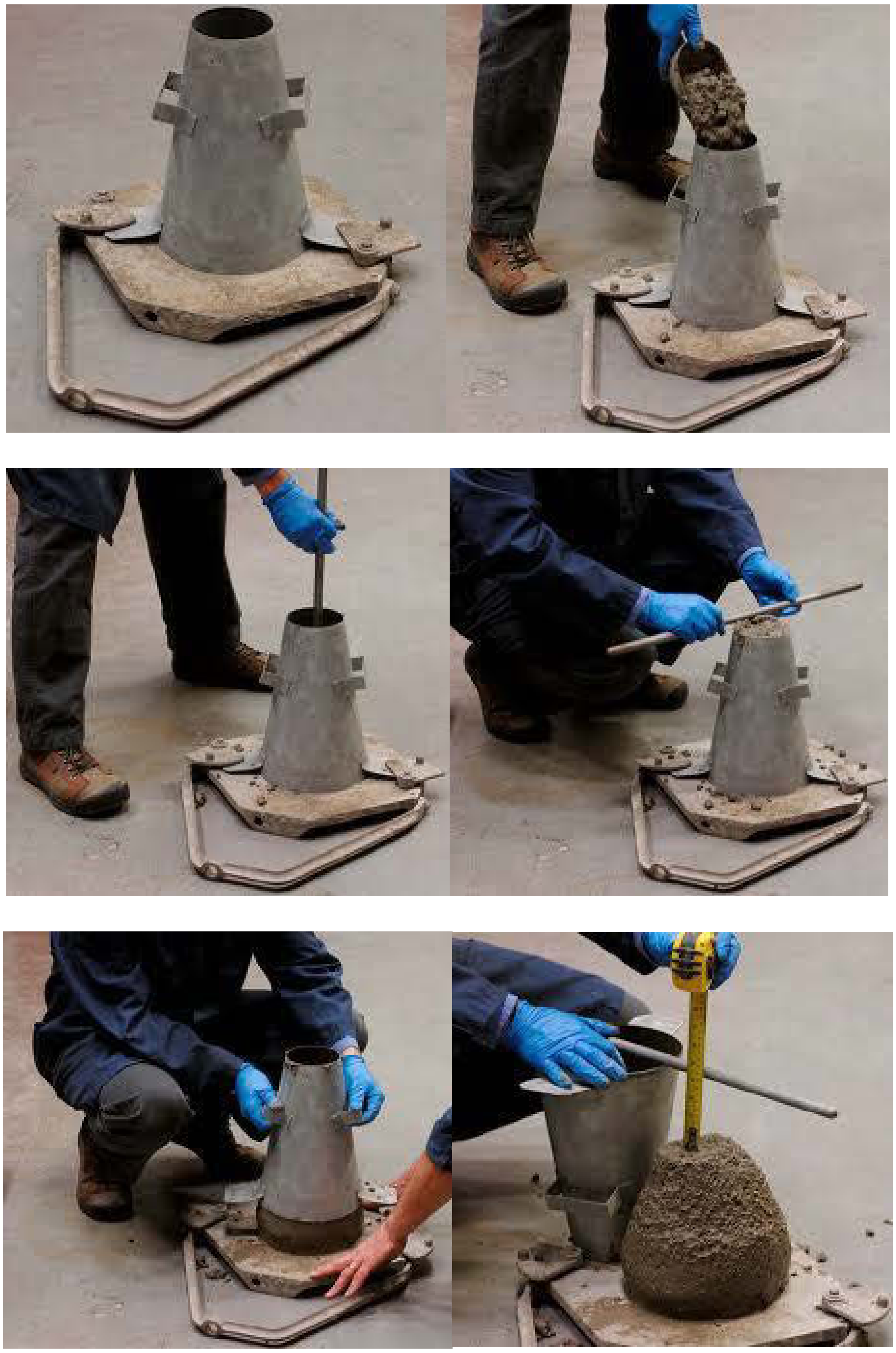


Fig. 3.5: Different steps of performing slump test

3.4.2. Air content

Air contents of fresh concrete were measured according to ASTM C 231 “Standard Test Method for Air Content of Freshly Mixed Concrete by the Pressure Method”. In general, the air content of fresh concrete is measured by three methods including gravimetric (which is similar to the mortar method), volumetric, and pressure. The pressure method which is the most commonly one is based on Boyles Law. There are two types of air content meters which work based on pressure method including "Type A" and "Type B" meter. According to ASTM C 231, “*Meter Type A* is an air meter consisting of a measuring bowl and cover assembly. The operational principle of this meter consists of introducing water to a predetermined height above a sample of concrete of known volume, and the application of a predetermined air pressure over the water. The determination consists of the reduction in volume of the air in the concrete sample by observing the amount the water level is lowered under the applied pressure, the latter amount being calibrated in terms of percent of air in the concrete sample. Also, *Meter Type B* is an air meter consisting of a measuring bowl and cover assembly. The operational principle of this meter consists of equalizing a known volume of air at a known pressure in a sealed air chamber with the unknown volume of air in the concrete sample, the dial on the pressure gauge being calibrated in terms of percent air for the observed pressure at which equalization takes place. Working pressures of 50 to 205 kPa [7.5 to 30.0 psi] have been used satisfactorily.” However, the Type B meter is the most common one which is used in this study. In this section, different steps for performing this test is explained (Fig. 3.6). First, fresh concrete is placed and compacted into a metal bucket. During mixing and casting , air bubbles are introduced into the concrete. There are generally two types of entrapped and entrained bubbles in concrete. Entrapped air bubbles are usually larger and have a small surface area while entrained air bubbles are small (less than 1 mm) and distributed throughout the cement paste. Consequently, the entrained air has more effective protection against freeze-thaw deterioration than the larger, poorly dispersed entrapped air voids. Large entrapped air voids are removed from the fresh concrete in the bucket using compaction with a steel rod. Rest of them are removed by striking the bucket frequently with a rubber mallet. After filling the bucket, the top of the concrete is made level with the top of the bucket by striking-off with a metal bar. The lid of the instrument is secured to the bucket and water is introduced to eliminate air voids above the concrete. Air is then pumped into a cylinder of known volume until a specified pressure is obtained. The pressurized air is then released into the vessel; the resultant pressure drop is related to the entrained air content in the concrete and the gauge has been designed such that the air content of the concrete can be read directly from the gauge.

Fig. 3.6: Measuring air content of fresh concrete

3.4.3. Unit weight

Unit weight of fresh concrete were measured in accordance with ASTM C 138. Different steps of measurement method based on this standard are as below:

First, dampen the interior of the measure and removing any standing water from the bottom. Placing the measure on a flat, level, firm surface. Then, place the concrete in the measure and filling the measure in in three layers of approximately equal volume and rod each layer with the rounded end of the rod. On completion of compaction, the measure must not contain a substantial excess or deficiency of concrete. After compaction, strike-off the top surface of the concrete and finish it smoothly using the flat strike-off plate so that the measure is level full.

Strike-off the measure by pressing the strike-off plate on the top surface of the measure to cover about two thirds of the surface and withdraw the plate with a sawing motion to finish only the area originally covered. Then place the plate on the top of the measure to cover the original two thirds of the surface and advance it with a vertical pressure and a sawing motion to cover the whole surface of the measure and continue to advance it until it slides completely off the measure. After strike-off, clean all excess concrete from the exterior of the measure and determine the mass of the concrete and measure to an accuracy consistent. Finally, calculate the net mass of the concrete in kilograms by subtracting the mass of the measure, from the mass of the measure filled with concrete and calculate the density in kg/m^3 by dividing the net mass of concrete by the volume of the measure.

3.4.4. Compressive strength

Cylindrical specimens with diameter of 102 and height of 204 mm were used for measuring compressive strength in accordance with ASTM C 39. Fig. 3.7 shows set up of compression test using a hydraulic pressure machine. Compressive strength was measured at different ages of 7, 28, 56 and 91 days. These ages were selected with regard to experimental conditions of this study. All test specimens for a given test age were loaded within permissible time tolerances in accordance with ASTM C 39. For test age of 7, 28 and 90 days is 6 hours (or 3.6%), 20 hours (3.0%) and 2 days (or 2.2%), respectively. For each age of each concrete mixture, three concrete specimens were tested and average value was reported. According to ASTM C 39, acceptable range of individual cylinder strengths for 100 by 200 mm cylinders made from a well-mixed sample of concrete under laboratory conditions is 10.6% when three cylinders are used. The load was applied continuously and without shock at a constant rate according to ASTM C 39. The compressive strength of the concrete specimen was calculated by dividing the maximum load carried by the specimens during the test by the average cross-sectional area of the concrete specimen and reported to the nearest 0.1 MPa.

Fig. 3.7: Set up of compression test using a hydraulic pressure machine

3.4.5. Splitting tensile strength

All measurements of splitting tensile strength of concrete specimens were done in accordance with ASTM C 496. Fig. 3.8 shows set up of splitting tensile strength test using a hydraulic pressure machine. It should be noted that cylindrical specimens with diameter of 102 and height of 204 mm were used. As shown in Fig. 3.9, two plywood strips (3.0 mmm thick, 25 mm wide and length equal to or slightly longer than that of the specimen) were used Splitting tensile strength was measured at different ages of 7, 28 and 91 days. For each age of each concrete mixture, three concrete specimens were tested and average value was reported.

Fig. 3.8: Set up of splitting tensile test using a hydraulic pressure machine

The load was applied continuously and without shock at a constant rate within range 0.7 to 1.4 MPa/min until failure of the concrete specimens according to ASTM C 496. Finally, the splitting tensile strength of the specimen was calculated as follows:

$$T = 2\ P/(\pi/d)$$

T = splitting tensile strength (MPa), D = diameter (mm), L = length (mm)

P = Maximum applied load indicated by testing machine, N

Fig. 3.9 : Specimen is located between two plywood strips for splitting tensile test

Summary

This chapter discussed the experimental programmes performed in this research. Materials, mix proportions, concrete specimens preparation procedure and experimental tests and variables considered are explained in detail. In general, fresh and hardened properties of high-strength concrete are evaluated at different ages. Furthermore, 16 different mix proportions were designed to investigate all variations in detail.

Chapter 4

4. RESULTS AND DISCUSSIONS

4.1. INTRODUCTION

This chapter provides comprehensive assessment of results of extensive experimental tests on fresh and hardened concrete specimens including slump, unit weight, air content, compressive and splitting tensile strength measurements. 16 different mixture proportions based on different levels of cement replacement with pumice and using copper slag instead of limestone coarse aggregate at two water to binder ratios of 0.3 and 0.4 were investigated. In addition, silica fume was used at level of 10% of cement weight in some mixtures. Compressive strength of concrete specimens were measured at different ages of 7, 28, 56 and 91 days while splitting tensile strength was measured at 7, 28 and 91 days to evaluate effects of pumice, copper slag and their combinations.

4.2. FRESH PROPERTIES

4.21. Slump measurements

Results of measurements of fresh properties of different concrete mixtures are given in Table 4.1. Workability of fresh concrete samples of this study was measured by using slump test method according to ASTM C 143. As it can be seen, slump values varied in the range of 105 to 131 mm while the minimum and maximum value was observed for mixture SLS (w/b: 0.3, SF:10% and limestone coarse aggregate) and FCSP5 (w/b: 0.4 and copper slag coarse aggregate), respectively (Fig. 4.1). The average slump value of different concrete mixtures was 117mm which is a well-accepted value of slump of concrete so that it can be transported, casted and compacted with common methods. In the meantime, it was within the designed range of slump variation for this research study which was 110±10mm. This value of slump is common due to importance of enough workability of high-strength concrete which is usually used in high-rise buildings and needs superior performance in terms of pumpability ti high elevations. In other word, using high-strength concrete with very low workability can result in many practical problems during pumping and casting of concrete. It should be noted that different levels of a commercially available modified polycarboxylic-ether high-range water reducing admixture (superplactizer in accordance with ASTM C) with 44% solid particles was used to prepare concrete batches.

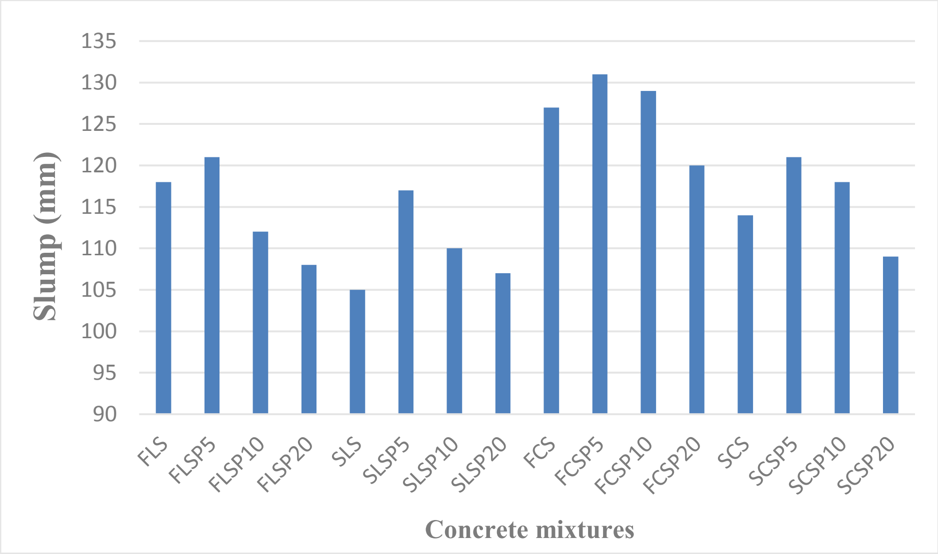


Fig. 4.1: Slump values of different concrete mixtures

Table 4.1: Slump, air content and unit weight of fresh concrete mixtures

	FLS	FLSP5	FLSP10	FLSP20	SLS	SLSP5	SLSP10	SLSP20	FCS	FCSP5	FCSP10	FCSP20	SCS	SCSP5	SCSP10	SCSP20
Slump, mm	118	121	112	108	105	117	110	107	127	131	129	120	114	121	118	109
Air content , %	3.2	2.9	2.7	2.4	2.4	2.2	2.2	2.0	3.0	3.0	2.9	2.6	2.1	2.0	2.4	2.1
Unit weight, kg/m^3	2317	2313	2307	2298	2415	2411	2408	2401	2672	2668	2665	2659	2783	2776	2773	2767

4.2.2. Air content

Air contents of fresh concrete were measured by using the pressure method according to ASTM C 231. Fig. 4.2 shows measured air contents of different concrete mixtures. As it can be seen, air content was generally decreased by increasing of amount of pumice. For example, air content of FLS which did not have pumice was 3.2% while air content of FLSP5, FLSP10 and FLSP20 (same concrete mixtures but with pumice) was decreased to 2.9, 2.7 and 2.4, respectively. In other word, air content of FLS was decreased approximately 9.4, 15.6 and 25% by adding 5, 10 and 20% of pumice to mixture. Similar trends can be seen for other mixtures including SLS series (SLSP5, SLSP10 and SLSP20), FCS series (FCSP5, FCSP10 and FCSP20) and SCS series (SCSP5, SCSP10 and SCSP20). In the meantime, series incorporating silica fume and lower water to binder ratio (S) had lower air contents in comparison with series without silica fume and higher water to bonder ratio (F) so that the air content of SLS and SCS was 25% and 30% lower than the air content of FLS and FCS, respectively.

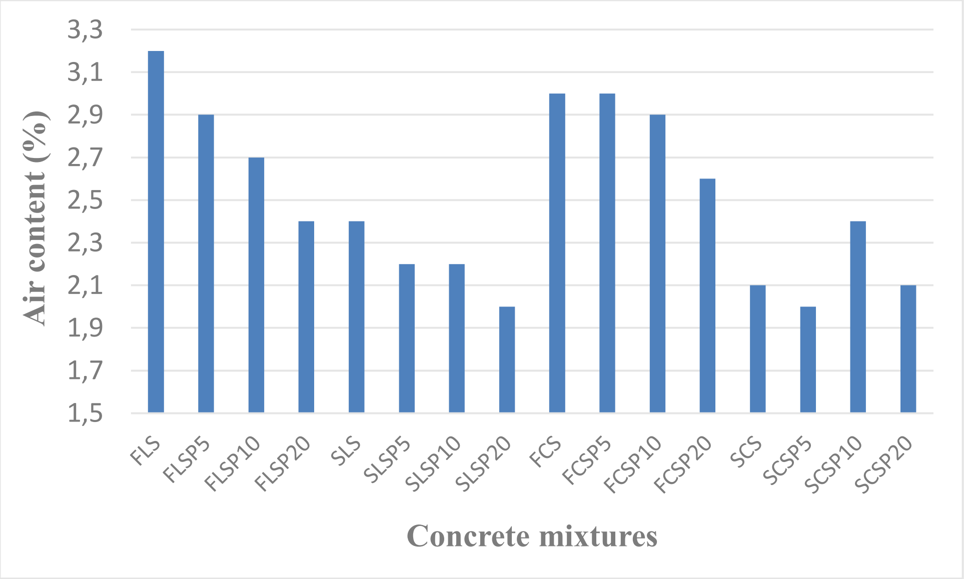


Fig. 4.2: Air contents of different concrete mixtures

Furthermore, air contents of each series of concrete mixtures were decreased by increasing of total amount of fine particles including silica fume and pumice powder. For the first series of concrete mixtures with limestone (LS), the average of air content value was 2.8% while this value was 2.2% for the second series of concrete with limestone. Similar reduction was observed for series of concrete with copper slag so that the average of air content value was 2.88% for the first series of concrete mixtures with copper slag while this value was 2.15% for the second series of concrete mixture with copper slag. It should be noted that presence of air inside concrete can have negative or positive effects depends of type of air voids. Entrapped air voids which are the biggest voids in concrete results in decreasing performance of concrete. In general, compressive strength of concrete can be reduced up to 5% for 1% of air content. Another type of air voids is entrained air bubbles which are created by using air-entraining admixture. These are spherical air bubbles with more and less same size which are required for improving frost and freezing0thawing resistance of concrete. In general, such reduction of air content of concrete mixture can be attributed to higher specific surface of ingredients of concrete with silica fume and pumice as well as appropriate consistency and cohesion of concrete mixture with good level of slump. However, it should be noted that special care was taken to perform measurements according to ASTM C 231 to minimize operational and instrumental errors.

4.2.3. Unit weight

As mentioned in previous chapter, unit weight of fresh concrete were measured in accordance with ASTM C 138. Fig. 4.3 shows changes of unit weight of different concrete mixtures which vary between 2298 and 2783 kg/m^3. With regard to higher value of specific gravity of copper slag (3.59 g/cm^3) in comparison to lime stone, higher unit weight of concretes incorporating copper slag coarse aggregate are expected as results also confirmed.

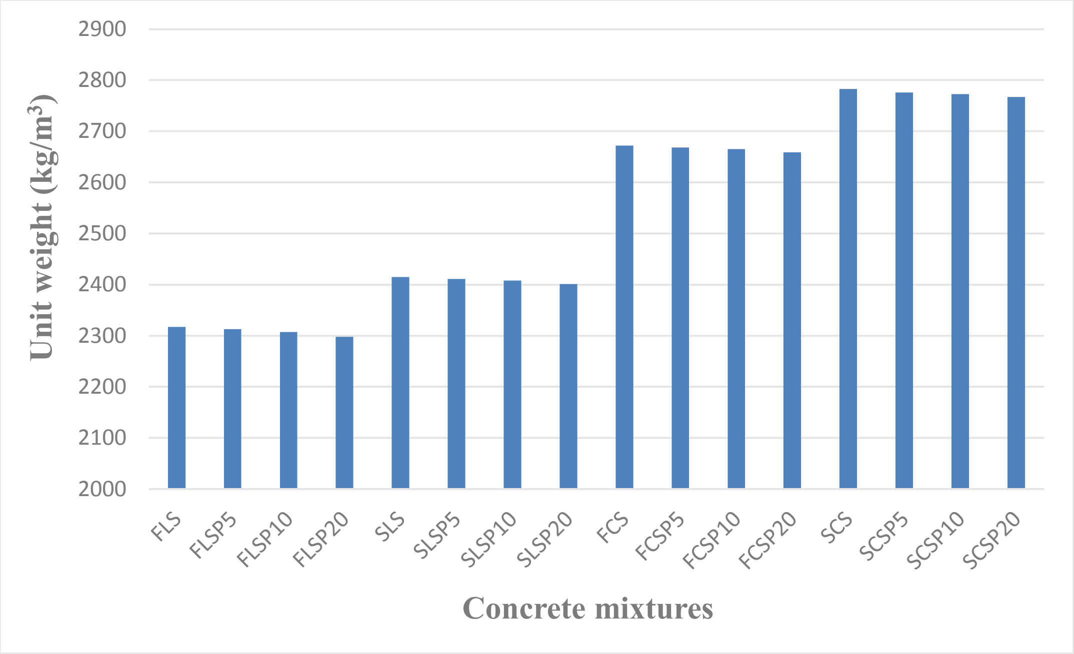


Fig. 4.3: Changes of unit weight of different concrete mixtures

The average value of unit weight of concretes with copper slag is 2720 kg/m^3 while this value for concretes with limestone coarse aggregate is 2359 kg/m^3. In other word, copper slag increased the average unit weight of concrete approximately 15.3%. Other researchers reported similar results (Caliskan and Behnood, 2005; Shoya et al., 1997; Ayano and Sakata, 2000; Khanzadi and Behnood, 2009). Furthermore, replacing cement by pumice and silica fume can slightly decrease unit weight of concrete with the same concrete mix proportions. This is attributed to lower specific gravity of silica fume and pumice in comparison to the specific gravity of Portland cement which is 3.15 g/cm^3. The maximum reduction in unit weight was occurred when 20% of cement was replaced by pumice. These changes are consistent with published literature (Kelestemur and Demirel, 2010; Hossain et al., 2011; Binici et al, 2008).

4.3. HARDENED CONCRETE

4.3.1. Compressive strength

Compressive strength was measured at different ages of 7, 28, 56 and 91 days. For each age of each concrete mixture, three concrete specimens were tested and average value was reported. According to ASTM C 39, acceptable range of individual cylinder strengths for 100 by 200 mm cylinders made from a well-mixed sample of concrete under laboratory conditions is 10.6% when three cylinders are used. Results of compressive strength measurements of different concrete mixtures at different ages are presented in Table 4.2. In this section, effects of copper slag, pumice and their combination on variation of compressive strength are presented and discussed.

4.3.1.1. Effects of copper slag

Compressive strength development for concretes with limestone and copper slag coarse aggregate with water to cement ratio of 0.4 (series FLS and FCS) are shown in Fig. 4.4. As it can be seen, the compressive strength at 7, 28, 56 and 91 days were increased approximately 9.5, 10.8, 11.0 and 8%, respectively by replacing limestone coarse aggregate with copper slag coarse aggregate. In other word, using copper slag instead of limestone increased the compressive strength on average around 9.8%. Similar trends are observed for another series of concrete mixtures (SLS and SCS). Fig. 4.5 shows compressive strength development for concretes incorporating silica fume as 10% of cement replacement with limestone and copper slag coarse aggregate and water to cement ratio of 0.3.

Table 4.2 : Compressive strength of different concrete mixtures at different ages

Mixtures with limestone containing 0, 5, 10 and 20% of pumice

Age	FLS	FLSP5	FLSP10	FLSP20
7-day	47.6	43.3	37.8	31.4
28-day	60.4	56.6	52.7	43.5
56-day	63.1	61.9	61.8	51.1
91-day	66.2	64.8	65.2	53.9

Age	SLS	SLSP5	SLSP10	SLSP20
7-day	71.8	68.0	63.6	57.7
28-day	82.6	80.1	77.2	71.4
56-day	90.4	93.5	91.2	86.0
91-day	95.1	98.5	96.9	91.6

Mixtures with copper slag containing 0, 5, 10 and 20% of pumice

Age	FCS	FCSP5	FCSP10	FCSP20
7-day	52.1	48.5	42.1	34.9
28-day	65.2	64.3	59.3	49.8
56-day	69.4	70.9	70.5	59.3
91-day	71.5	74.1	74.2	62.3

Age	SCS	SCSP5	SCSP10	SCSP20
7-day	76.1	73.3	69.5	65.0
28-day	92.1	91.6	88.8	83.8
56-day	106.7	111.2	110.4	107.4
91-day	111.3	117.8	116.5	112.6

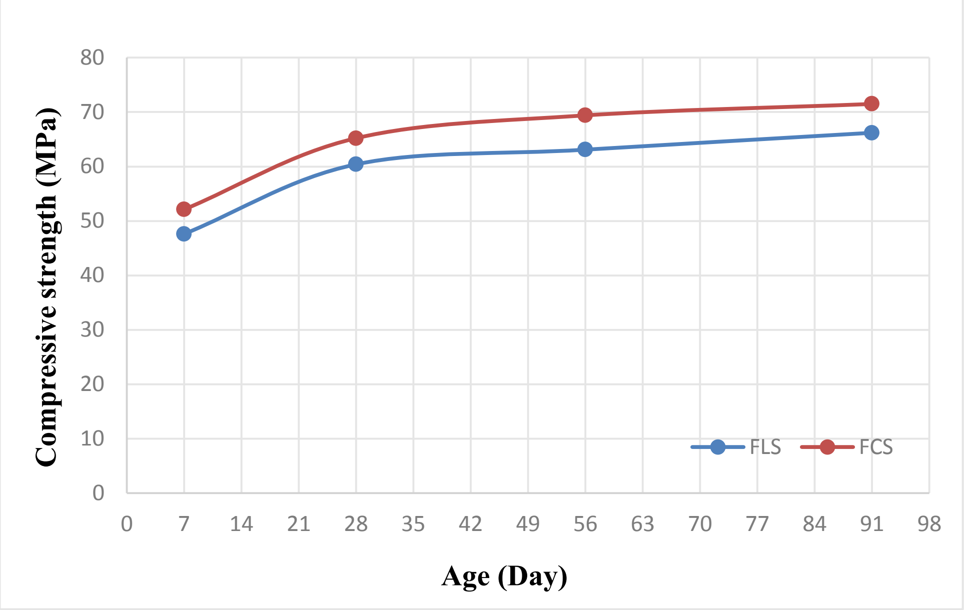


Fig. 4.4: Compressive strength development of concrete with limestone (FLS) and copper slag (FCS) coarse aggregate at different ages (w/b: 0.4)

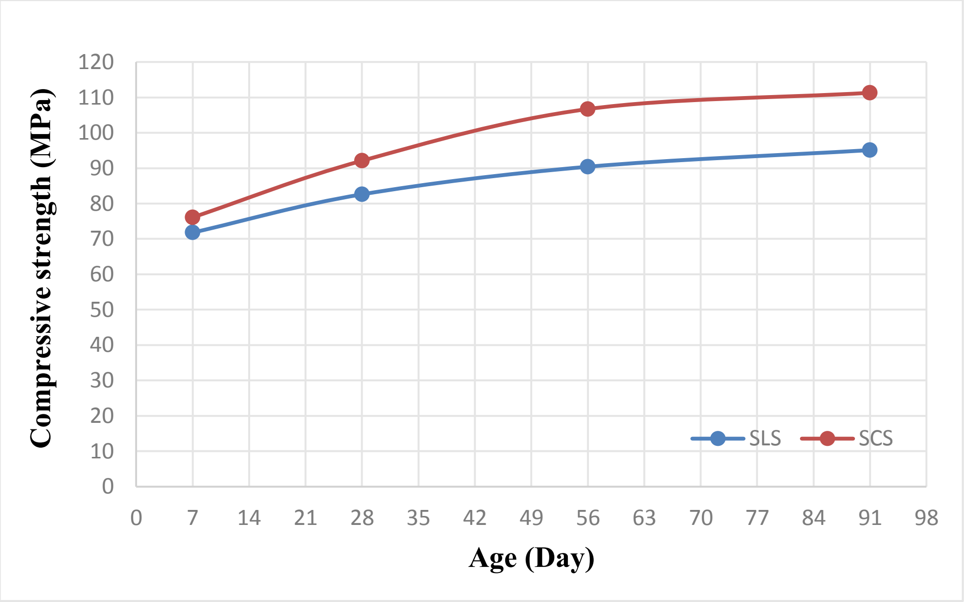


Fig. 4.5: Compressive strength development of concrete with limestone (SLS) and copper slag (SCS) coarse aggregate at different ages (w/b: 0.3 and SF: 10%)

In general, it can be concluded that presence of copper slag can increase compressive strength of concrete at different ages. This conclusion is consistent with what other researchers reported (Shoya et al., 2003; Al-Jabri, 2006; Khanzadi and Behnood, 2009; Caliskan and Behnood, 2004; Behnood, 2005). This can be attributed to higher level of the strength properties of copper slag aggregate.

In addition, the surface texture of coarse aggregate is partly responsible for the bond between the cement paste and aggregate because of the mechanical interlocking between cement paste and copper slag. It has been well established that the mechanical properties of concrete are significantly affected by the bonding between the cement paste and aggregate. Fig. 4.6 compares the failure surfaces of two representative specimens after completion of compressive strength test (Khanzadi and Behnood, 2009).

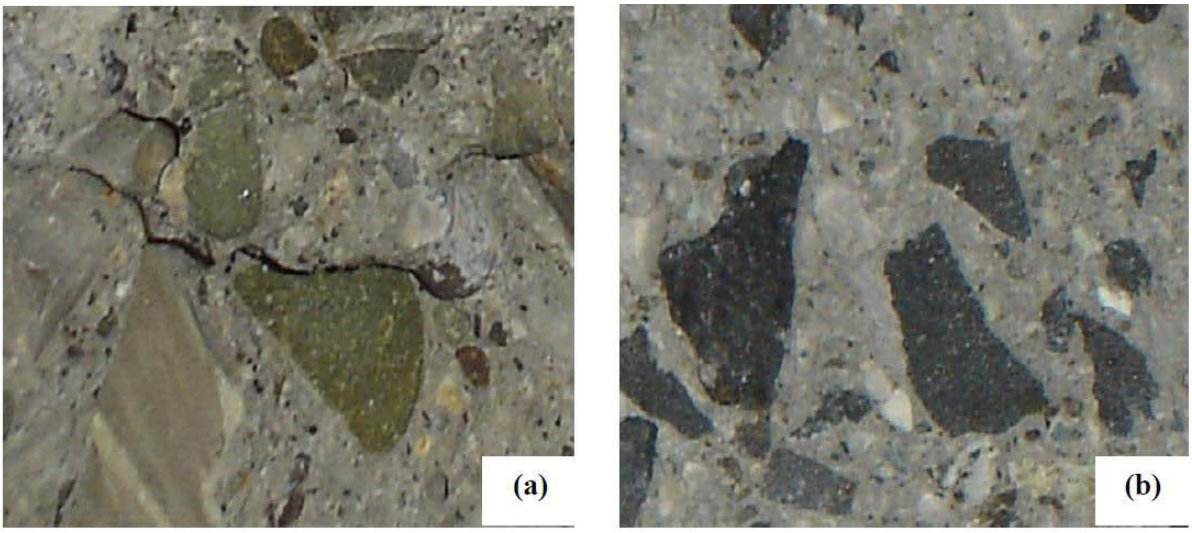


Fig.4.6: Comparison different failure surfaces of concrete specimens containing: a) limestone; b) copper slag

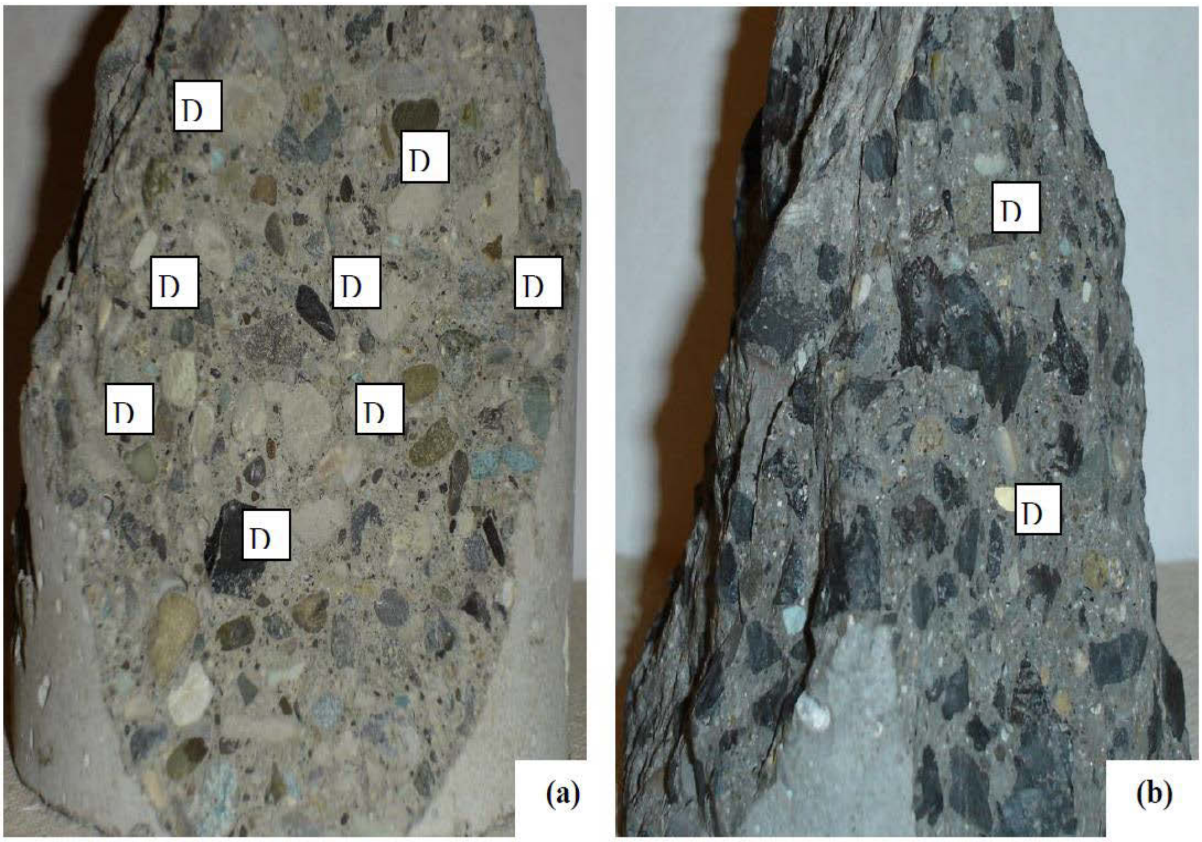


Fig. 4.7: Debonding of aggregates from cement matrix (D) of concrete specimens containing: a) limestone; b) copper slag

It can be seen that an extended crack propagated along the interface between cement paste and limestone aggregate, but not along the copper slag aggregate. Fig. 4.7 shows a more careful examination of the failure surfaces which demonstrates more occurrence of debonding in specimens with limestone coarse aggregate in comparison with copper slag coarse aggregate. Therefore, it can be concluded that copper slag coarse aggregates provided a superior bond and interfacial transition zone in comparison with the limestone coarse aggregate because of their porous and rough surface texture. However, more microstructural studies are needed to verify this explanation.

To quantify influences of copper slag coarse aggregate on compressive strength of concretes, "Strength Coefficient Index" is defined in this study as below:

Strength Coefficient Index: SCI (%) = (A/B) × 100

where:

A = average compressive strength of test concrete mixtures containing copper slag coarse aggregate, MPa

B = average compressive strength of control mixtures (limestone aggregate), MPa

Fig. 4.8 shows SCI values of two different series of F and S at different ages. As it can be expected, minimum SCI was at age of 7 days so that SCI value of F and S series was 109.5 and 106%, respectively. However, SCI was increased by increasing age of concrete specimens so that the SCI value of F and S series at age of 28 days was 110.8 and 111.5%, respectively. While the SCI values for series F at 56 and 91 days were 110 and 108%, respectively, the S series showed significantly higher values of the SCI (118 and 117%). Therefore, it can be concluded that comparative strength improving effect of copper slag aggregate is higher for a mixture with silica fume. As explained before, it can be attributed to denser microstructure of cement paste as well as better quality of interfacial transition zone including silica fume and stronger bonding between cement paste and copper slag aggregate. However, further microstructural studies should be done to investigate quality and properties of ITZ between rough surface of copper slag coarse aggregate and dense cement paste with silica fume and low water to binder ratio.

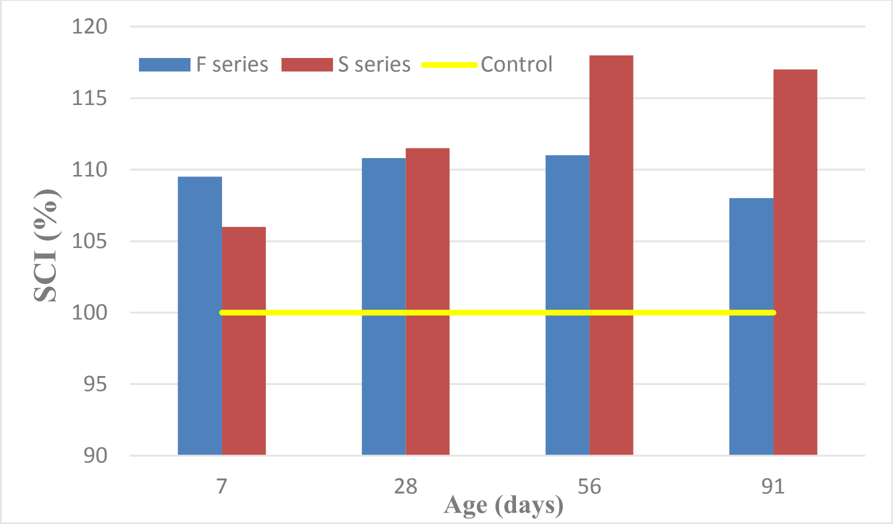


Fig. 4.8: Comparison of SCI of two different series F and S with copper slag

4.3.1.2. Effects of pumice

As mentioned in Chapter 3, Portland cement was replaced by pumice powder at different levels of 0, 5, 10 and 20% of cement weight. Figs. 4.9-12 show fluctuations of compressive strength of FLS, FCS, SLS and SCS, respectively.

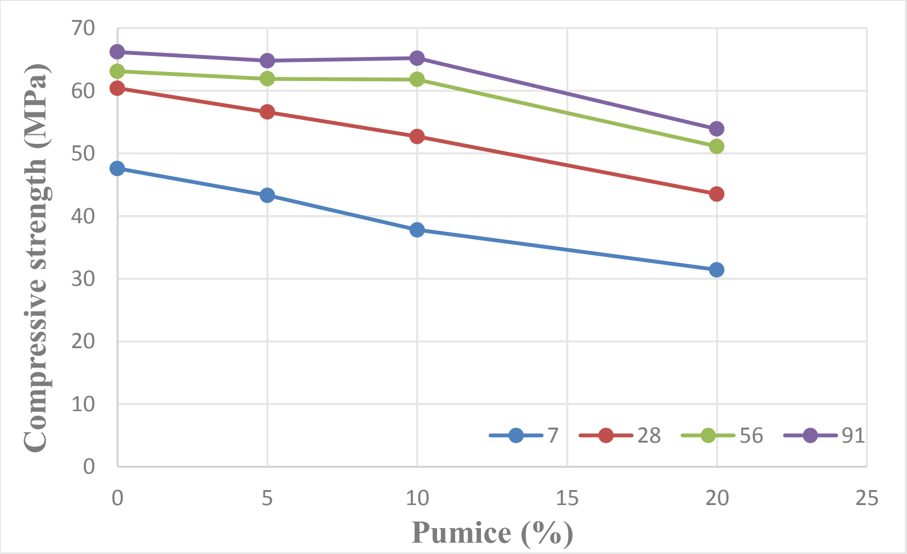


Fig. 4.9: Variation of compressive strength of FLS concretes versus pumice replacement at different ages

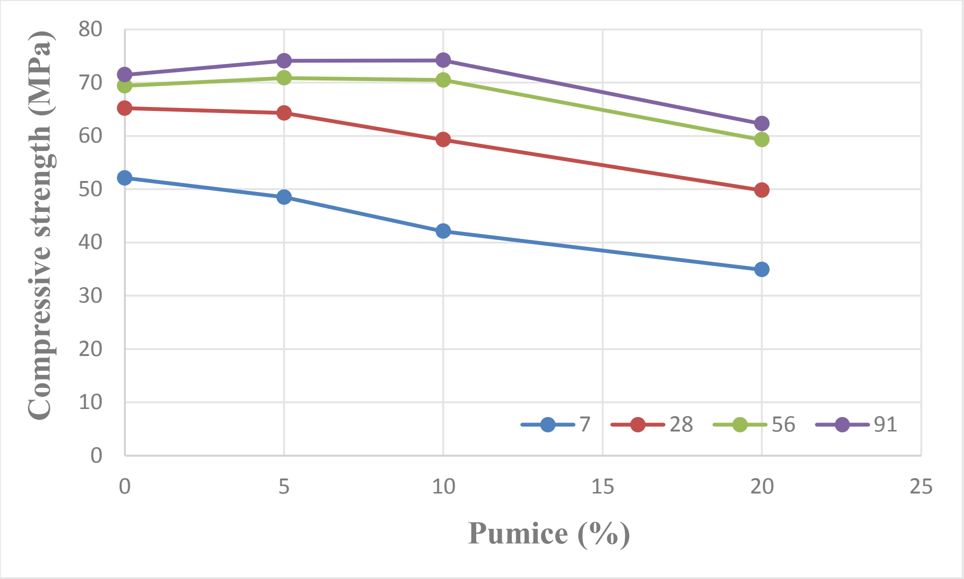


Fig. 4.10: Variation of compressive strength of FCS concretes versus pumice replacement at different ages

As it can be seen in these figures, presence of pumice can have positive or negative effects on compressive strength which depends on pumice replacement and test age.

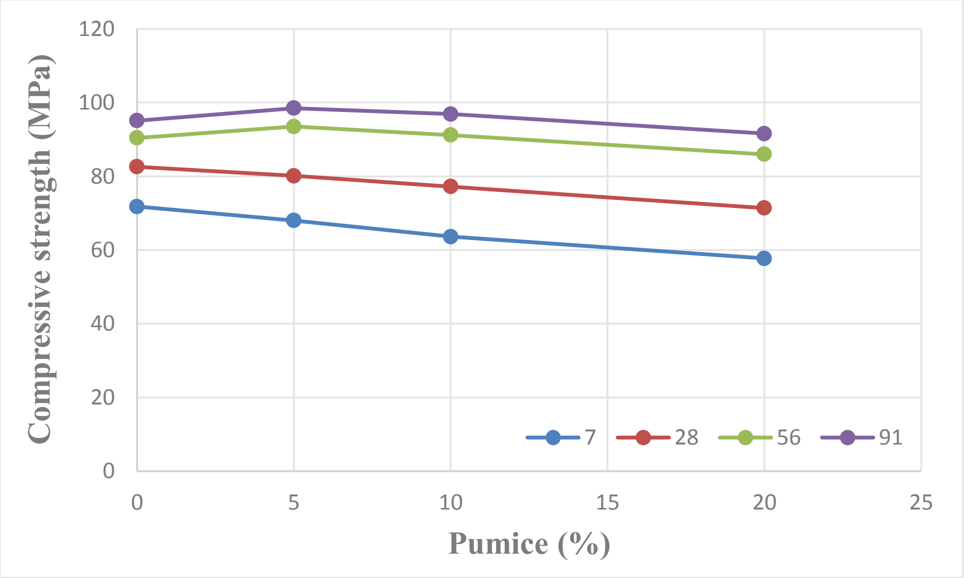


Fig. 4.11: Variation of compressive strength of SLS concretes versus pumice replacement at different ages

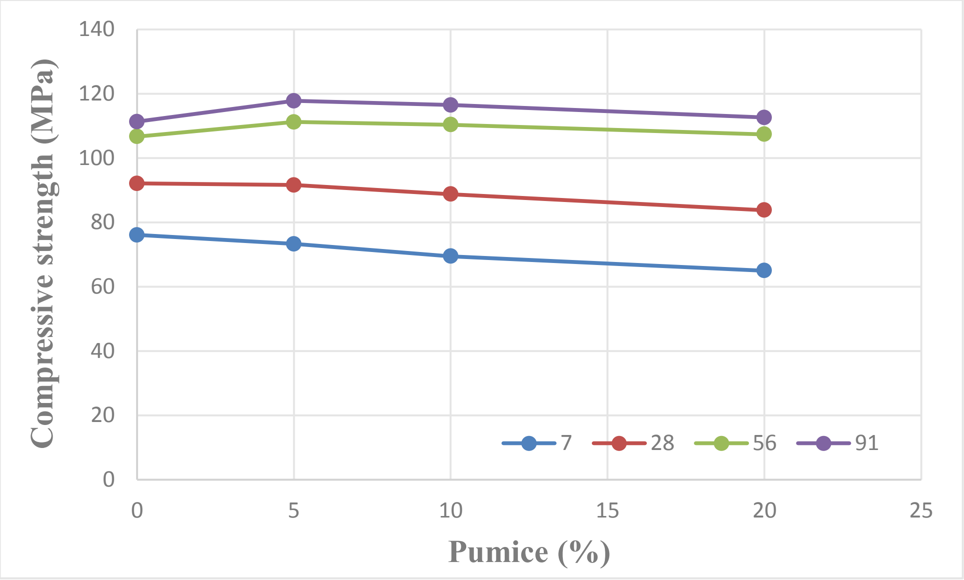


Fig. 4.12: Variation of compressive strength of SCS concretes versus pumice replacement at different ages

To quantify influences of pumice as a pozzolanic material on compressive strength of concretes, "Strength Coefficient Index" is defined in this study as below:

Strength Coefficient Index: SCI (%) = (A/B) × 100

where:

A = average compressive strength of test concrete mixtures containing pumice, MPa

B = average compressive strength of control mixtures (without pumice), MPa

Table 4.3 presents SCI values for different concrete series with different levels of cement replacement by pumice.

Table 4.3: SCI values for concrete mixtures containing different levels of pumice (P)

Mixtures with limestone containing 0, 5, 10 and 20% of pumice

SCI (%)	FLSP5	FLSP10	FLSP20
7-day	91.0	79.4	66.0
28-day	93.7	87.2	72.0
56-day	98.1	97.9	81.0
91-day	97.9	98.5	81.4

SCI (%)	SLSP5	SLSP10	SLSP20
7-day	94.7	88.6	80.3
28-day	97.0	93.5	86.4
56-day	103.4	100.9	95.1
91-day	103.5	101.9	96.3

Mixtures with copper slag containing 0, 5, 10 and 20% of pumice

SCI (%)	FCSP5	FCSP10	FCSP20
7-day	93.0	80.8	67.0
28-day	98.6	91.0	76.4
56-day	102.2	101.6	85.4
91-day	103.6	103.8	87.2

SCI (%)	SCSP5	SCSP10	SCSP20
7-day	96.3	91.3	85.6
28-day	99.5	96.4	91.0
56-day	104.2	103.5	100.7
91-day	105.9	104.7	101.1

Regardless of pumice dosage, 7-day compressive strength of all concretes were decreased significantly. The highest and lowest reduction was for FLSP20 and SCSP5 which was 34 and 3.7%, respectively. This is mainly because of the fact that Portland cement particles were replaced with less reactive pumice particles, i.e. more replacement resulted in more reductions at early age of 7 days. This is consistent with reported results by other researchers (Hossain and Lachemi, 2006; Ozodabas and Yilmaz, 2013; Hossain, 2008; Demirel and Kelestemur, 2010). In general, it has been well known that concrete mixture containing pozzolanic materials such fly ash and slag which are more common than pumice, have slower strength gain in comparison with the control concrete mixtures. With regard to the dominant C-S-H forming reaction, it is appropriate to compare hydration reactions of Portland cement and pozzolanic material and Portland cement. The main reactions in these two situations are as below:

Portland cement:

$$\mathrm{C_3S} + \mathrm{H} \xrightarrow{\text{fast}} \mathrm{C\text{-}S\text{-}H} + \mathrm{CH}$$

Portland-pozzolanic cement:

$$\mathrm{Pozzolan} + \mathrm{CH} + \mathrm{H} \xrightarrow{\text{slow}} \mathrm{C\text{-}S\text{-}H}$$

In general, the reaction between a pozzolan and calcium hydroxide is known as the pozzolanic reaction. There are three main technical benefits of using pozzolanic materials which are explained below.

1. The reaction is slow; therefore, the rates of heat liberation and strength development will be accordingly slow.

2. Second, the reaction is lime-consuming instead of lime producing, which has an important bearing on the durability of the hydrated paste in acidic environments.
3. Third, pore size distribution studies of hydrated

According to Table 4.3, there was no positive Strength Coefficient Index (SCI) at 28 days. The lowest and highest strength reduction at 28 days belongs to SCSP5 and FLSP20, respectively. However, strength reductions were significantly improved so that concrete mixtures except FLS series had more and less similar performance to the control mixture. By careful analysis of experimental results, it can be seen that some concrete mixtures incorporating finely ground pumice showed higher compressive strength gain and consequently, higher Strength Coefficient Index at the age of 56 days. This increase in compressive strength was approximately 4.2% and 3.4% for SCSP5 and SLSP5, respectively. Concrete mixtures without silica fume which containing 20% pumice showed poor performance in strength gaining so that strength reduction as a result of 20% pumice replacement was as low as 19 and 14.6% for FLSP20 and FCSP20, respectively.

At age of 91 days, all of concrete mixtures except those containing finely ground pumice as 20% of Portland cement replacement showed approximately similar or even better performance in comparison with control mixtures. For 20% pumice replacement, the worst result was observed for F series with limestone coarse aggregate so that compressive strength was decreased from 66.2 MPa (control mixture) to 53.9 MPa. It means that the Strength Coefficient Index (SCI) of this mixture was approximately 81.4% according to Table 4.3.

However, there is a significant gap between this mixture and same mixture with 10% pumice replacement so that SCI index of FLSP10 was 98.5% which was 17.1% higher than FLSP20. On the other hand, the difference between SCI values of SLSP10 and SLSP20 was 5.6%. It should be noted that similar performance was observed for concrete mixtures containing copper slag and pumice with and without silica fume and lower water to binder ratio. According to Table 4.3, SCI value of FCSP20 and FCSP10 was 87.2 and 103.8%, respectively which means that the difference between these SCI values was 16.6%. However, SCI value of SCSP 20 and SCSP10 was 101.1 and 104.7%, respectively which shows approximately 3.6% of difference between these two SCI values. As it can be seen, compressive strength reductions were significantly modified while silica fume was in the concrete mixtures (SLS and SCS series). This can be attributed to physical effects of micro silica particles as fillers in cement paste as well as their chemical influences as a pozzolanic material which resulted in stronger, denser and more homogeneous cement matrix and interfacial transition zone. Therefore, chance of better and stronger bonding was increased by using silica fume in the concrete mixtures.

In general, performance of concrete mixture with limestone coarse aggregate in series F was acceptable after 56 days at pumice replacement up to 10% of cement weight. In series S with limestone coarse aggregate, not only performance of mixes with 5 and 10% pumice replacement was better than control mix after 56 days, acceptable performance was observed when 5% of cement weight was replaced by finely ground pumice. In fact, it is not always necessary to achieve a specific 28-day compressive strength as a compulsory requirement in some projects. This is more likely for members or classes of concrete that will not have expected construction or service loads applied at 28 days.

In such situations, the concept of later-age strength requirement is relevant and applicable. Based on this concept, it is possible to make sustainable concrete with 20% replacement of Portland cement with supplementary cementitious materials including finely ground pumice and silica fume. Furthermore, it is feasible to make high-strength concrete with 15% replacement of cement by pumice and silica fume to achieve acceptable 28-day compressive strength in comparison with control mixture without finely ground pumice.

4.3.1.3. Effects of concurrent utilization of pumice and copper slag

With regard to lower environmental impact and lower usage of Portland cement, t is more beneficial for developing sustainable high-strength concrete that copper slag coarse aggregate as an industrial waste material and finely ground pumice as a natural pozzolanic material are used simultaneously in concrete production.

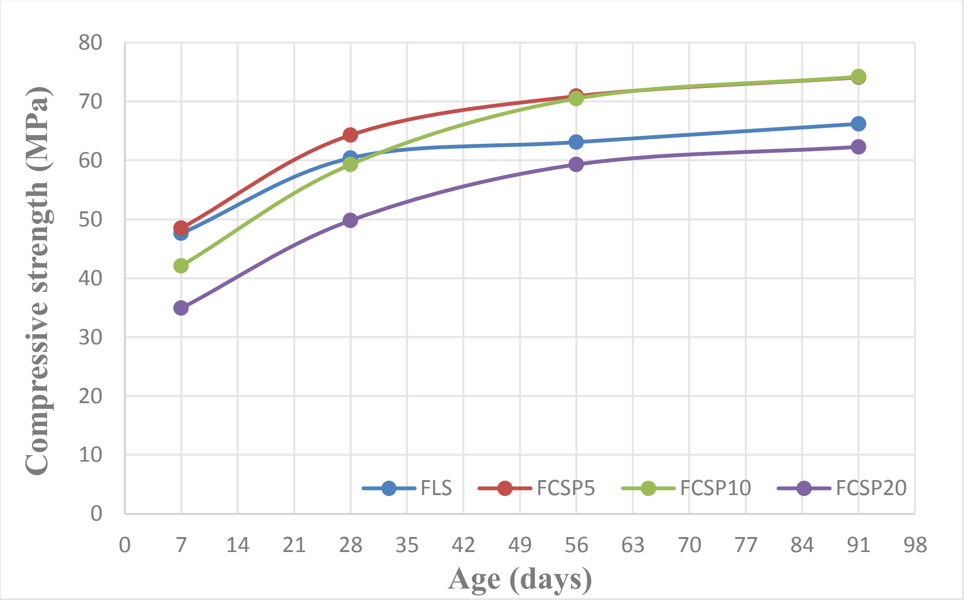


Fig. 4.13: Combined effects of copper slag coarse aggregate and pumice powder on compressive strength of F series

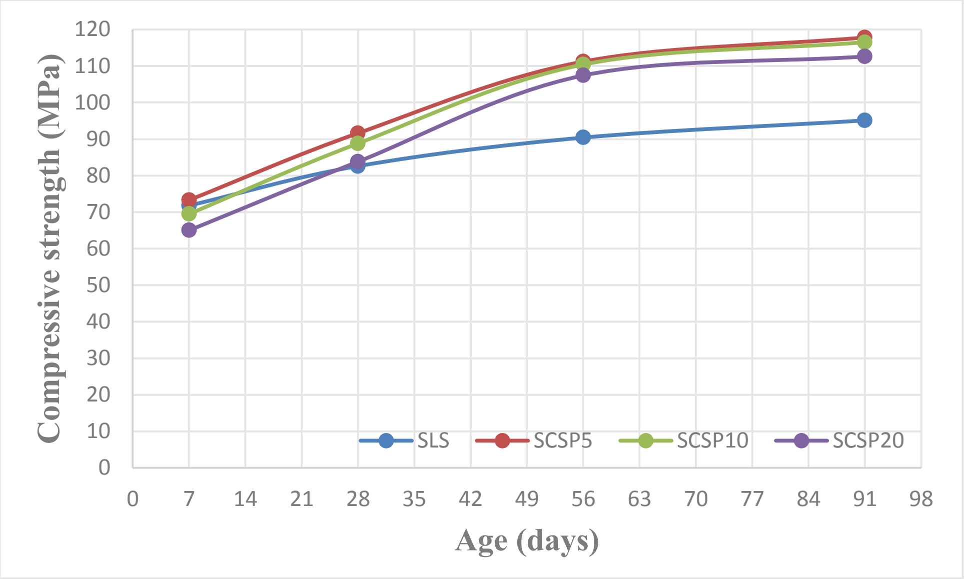


Fig. 4.14: Combined effects of copper slag coarse aggregate and pumice powder on compressive strength of S series

Therefore, it is important to study properties of high-strength concrete containing both of copper slag coarse aggregate and pumice powder. Fig 4.13 and 14 show combined effects of copper slag coarse aggregate and pumice powder on the compressive strength of F series (w/c=0.4) and S series (w/b=0.3 and SF=10%), respectively. To quantify influences of combined utilization of pumice and copper slag on compressive strength, "Strength Coefficient Index" is defined in this study as below:

Strength Coefficient Index: SCI (%) = (A/B) × 100

A = average compressive strength of test concrete mixtures containing pumice and copper slag, MPa

B = average compressive strength of control mixtures (without pumice and copper slag), MPa

Table 4.4 presents SCI values for different concrete series of S and F containing copper slag coarse aggregate and finely ground pumice at different levels.

Table 4.4: SCI values for concrete mixtures containing copper slag (CS) and different levels of pumice (P)

SCI (%)	FCSP5	FCSP10	FCSP20	SCSP5	SCSP10	SCSP20
7-day	101.9	88.5	73.3	102.1	96.8	90.5
28-day	106.5	98.2	82.5	110.9	107.5	101.5
56-day	112.4	111.7	94.0	123.0	122.1	118.8
91-day	111.9	112.1	94.1	123.9	122.5	118.4

As it can be seen in Fig. 4.13, 7-day compressive strength of control concrete mixture was increased from 47.6 MPa to 48.5 MPa after replacing limestone coarse aggregate by copper slag coarse aggregate and Portland cement by 5% pumice powder. However, using copper slag and pumice at the replacement level of 10% and 20% decreased compressive strength in comparison with control specimens at age of 7 days. Although 28-day compressive strength of concrete with copper slag and 20% pumice was still lower than control mix (7.5%), concrete with copper slag and 10% pumice had negligible difference in compressive strength compared to control mixture which was around 1.8%. Furthermore, FCSP5 showed significantly higher compressive strength at 28 days so that the compressive strength of control concrete was increased to 64.3 MPa.

At age of 56 days, effect of concurrent using of copper slag and pumice increased remarkably so that SCI value (Table 4.4) was 112.4 and 117.7% for FCSP5 and FCSP10, respectively. A similar trend was observed in changes of compressive strength of concrete mixtures at age of 91 days. While two mixes of FCSCP5 and FCSP10 had higher compressive strength values, FCSP20 showed lower performance comparing to control mixture.

In terms of series S, promising results were observed after using copper slag coarse aggregate and finely ground pumice. Fig. 4.14 shows compressive strength development of control mixture (SLS) as well as concrete mixtures with copper slag coarse aggregate and different levels of pumice powder. In general, concrete mixtures with copper slag and pumice had superior performance in comparison with the control mixture in series S (w/bb=0.3 and SF=10%). At age of 28 days, there was no lower compressive strength after using copper slag and pumice even up to 20% of Portland cement weight. According to Table 4.4, SCI values for SCSP5, 10 and 20 were 110.9, 107.5 and 101.5%, respectively. It means that it is possible to use 20% pumice with copper slag coarse aggregate when water to binder ration is 0.3 and 10% of Portland cement weight is replaced by highly reactive silica fume. Therefore, 30% of Portland cement was replaced by pumice and silica fume as supplementary cementitious materials while natural limestone coarse aggregate was also replaced by copper slag coarse aggregate. At age of 56 days, compressive strength of SCSP20 was approximately 18.8% higher than control mixture while this value was even higher for two other mixtures containing copper slag and 5 and 10% pumice powder. A similar trends were observed for these mixtures in comparison with control mixture at age of 91 days and SCI values were significantly higher than control specimens (18.4%-23.9%).

As mentioned earlier, presence of copper slag can increase compressive strength of concrete at different ages. This can be attributed to higher level of the strength properties of copper slag aggregate. In addition, the surface texture of coarse aggregate is partly responsible for the bond between the cement paste and aggregate because of the mechanical interlocking between cement paste and copper slag. It has been well established that the mechanical properties of concrete are significantly affected by the bonding between the cement paste and aggregate (Figs. 4.6 and 7). In the meantime, finely ground pumice is a pozzolanic material which has more than 70% of SiO_2. However, it has been well-known that pozzolanic reactions are slower than hydration reaction of Portland cement and when significant part of Portland cement is replaced with supplementary cementitious materials, there is always a possibility of observing a lower rate of strength gain while final strength is same or even higher due to chemical and physical effects of supplementary cementitious materials including silica fume and pumice. As it can be seen in Table 4.4, SCI values were significantly improved when silica fume was in the concrete mixtures regardless of type of coarse aggregate (limestone or copper slag). This can be attributed to physical effects of micro silica particles as fillers in cement paste as well as their chemical influences as a pozzolanic material which resulted in stronger, denser and more homogeneous cement matrix and interfacial transition zone. Therefore, chance of better and stronger bonding was increased by using silica fume in the concrete mixtures. As mentioned earlier in section 4.3.1.1, this effect of silica fume in improving bonding was more efficient in forming stronger interfacial transition zone between cement paste and rough surface of copper slag coarse aggregate.

To sum up, the most efficient and optimum value of finely ground pumice when copper slag coarse aggregate is used in concrete is 10% at water to cement ratio of 0.4 and 20% at water to binder ratio of 0.3 and presence of 10% silica fume in concrete mixture. First showed 28-day compressive strength similar to control normal concrete with limestone coarse aggregate while later showed superior performance in comparison with the control normal mixture in terms of compressive strength. However, these recommended values of pumice and copper slag showed promising excellent results at age of 56 days which is the common age of measuring concrete properties including high level of supplementary cementitious materials. In this study, 30% of Portland cement was successfully replaced by silica fume and finely ground pumice while copper slag coarse aggregate as an industrial waste material was simultaneously used instead of natural limestone coarse aggregate for producing sustainable high-strength concrete. With regard to the Green Building Council of Australia’s Green Star Mat-4, this novel type of high-strength concrete can achieve concrete credits for considering as green concrete.

4.3.2. Splitting tensile strength

All measurements of splitting tensile strength of concrete specimens were done in accordance with ASTM C 496. 4.3.1. Splitting tensile strength was measured at different ages of 7, 28 and 91 days. For each age of each concrete mixture, three concrete specimens were tested and average value was reported. Results of the splitting tensile strength measurements of high-strength concretes with and without copper slag coarse aggregate incorporating highly ground pumice as replacement of Portland cement at different levels of 0,5,10 and 20% (by weight). In this section, effects of copper slag, pumice and their combination on variation of splitting tensile strength are presented and discussed.

4.3.2.1. Effects of copper slag

Figs. 4.15 and 16. compare effect of copper slag coarse aggregate on the splitting tensile strength developments of series F (water to cement ratio of 0.4, with limestone coarse aggregate: FLS and with copper slag coarse aggregate: FCS) and S (water to binder ratio of 0.3, silica fume replacement at 10% of Portland cement weight, with limestone coarse aggregate: SLS and with copper slag coarse aggregate: SCS), respectively. By comparing two series of FLS and FCS which have same mix proportions and materials except copper slag coarse aggregate, it can be concluded that presence of copper slag coarse aggregate generally increased the splitting tensile strength approximately 11% on average. The maximum splitting tensile strength value was measured for FCS at 91 days which was 5.14 MPa while it was 4.53 MPa for same mixture without copper slag.

Table 4.5 : Splitting tensile strength of different concrete mixtures at different ages

Mixtures with limestone containing 0, 5, 10 and 20% of pumice

Age	FLS	FLSP5	FLSP10	FLSP20
7-day	2.97	2.57	2.26	1.93
28-day	4.24	3.85	3.57	2.98
91-day	4.53	4.35	4.32	3.65

Age	SLS	SLSP5	SLSP10	SLSP20
7-day	4.98	4.56	4.35	3.91
28-day	5.84	5.47	5.31	4.98
91-day	6.77	6.87	6.51	6.40

Mixtures with copper slag containing 0, 5, 10 and 20% of pumice

Age	FCS	FCSP5	FCSP10	FCSP20
7-day	3.29	2.92	2.56	2.19
28-day	4.72	4.56	4.22	3.55
91-day	5.14	5.18	5.19	4.44

Age	SCS	SCSP5	SCSP10	SCSP20
7-day	5.37	5.00	4.82	4.47
28-day	6.73	6.59	6.34	5.94
91-day	7.94	8.15	8.08	7.65

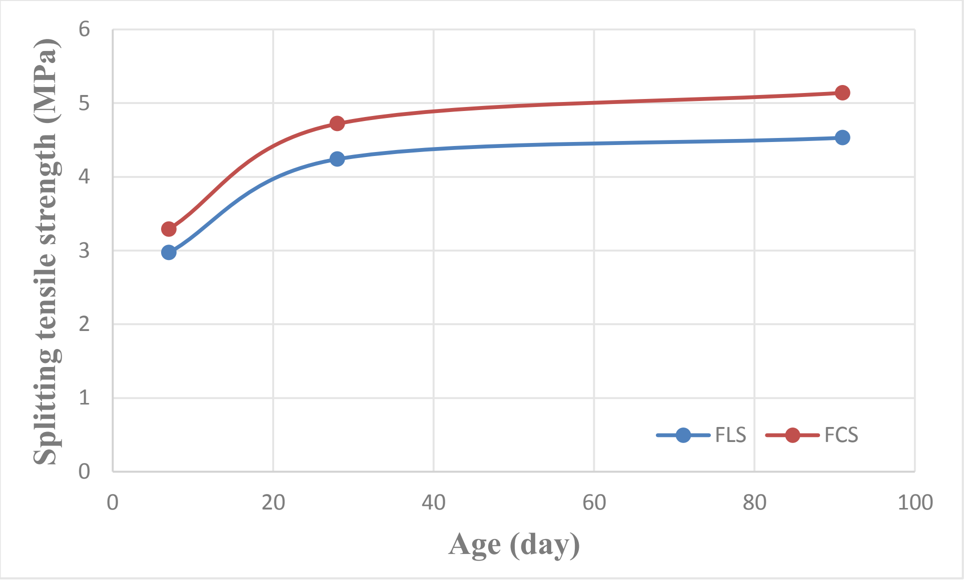


Fig. 4.15: Splitting tensile strength development of concrete with limestone (FLS) and copper slag (FCS) coarse aggregate at different ages (w/b: 0.4)

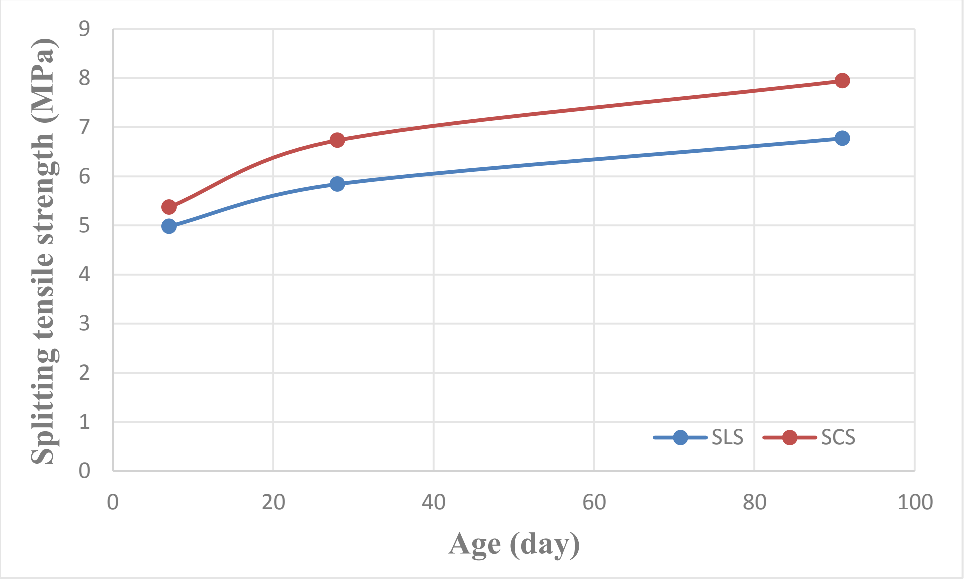


Fig. 4.16: Splitting tensile strength development of concrete with limestone (SLS) and copper slag (SCS) coarse aggregate at different ages (w/b: 0.3 and SF: 10%)

In other word, the splitting tensile strength was increased by using copper slag coarse aggregate approximately 13.5% at 91 days. Similar improvements were observed in series S by comparing the splitting tensile strength values of SLS and SCS (Fig. 4.16). As it can be seen, 28-day splitting tensile strength was increased from 5.84 MPa to 6.73 MPa and this improvement was even higher at 91 days so that the splitting tensile strength was 7.94 MPa which means 17.3% improvement in the splitting tensile strength by using copper slag coarse aggregate at age of 91 days.

In general, it can be concluded that using copper slag coarse aggregate increased the splitting tensile strength of concrete around 12% in comparison with control mixtures with limestone coarse aggregate. This conclusion is consistent with results which have been reported by other researchers (Shoya et al., 2003; Al-Jabri, 2006; Khanzadi and Behnood, 2009; Caliskan and Behnood, 2004; Behnood, 2005). This can be attributed to higher level of the strength properties of copper slag aggregate. In addition, the surface texture of coarse aggregate is partly responsible for the bond between the cement paste and aggregate because of the mechanical interlocking between cement paste and copper slag. It has been well established that the mechanical properties of concrete are significantly affected by the bonding between the cement paste and aggregate. Furthermore, the splitting tensile strength improvements were higher for the SCS mixture comparing to FCS mixture. This can be attributed to physical effects of micro silica particles as fillers in cement paste as well as their chemical influences as a pozzolanic material which resulted in stronger, denser and more homogeneous cement matrix and interfacial transition zone. Therefore, chance of better and stronger bonding was increased by using silica fume in the concrete mixtures.

4.3.2.2. Effects of pumice

As mentioned in Chapter 3, Portland cement was replaced by pumice powder at different levels of 0, 5, 10 and 20% of cement weight. Figs. 4.17-20 show development of splitting tensile strength of FLS, FCS, SLS and SCS, respectively. To quantify influences of pumice as a pozzolanic material on splitting tensile strength of concretes, "Strength Coefficient Index" is defined in this study as below:

Strength Coefficient Index: SCI (%) = (A/B) × 100

where:

A = average splitting tensile strength of test concrete mixtures containing pumice, MPa

B = average splitting tensile strength of control mixtures (without pumice), MPa

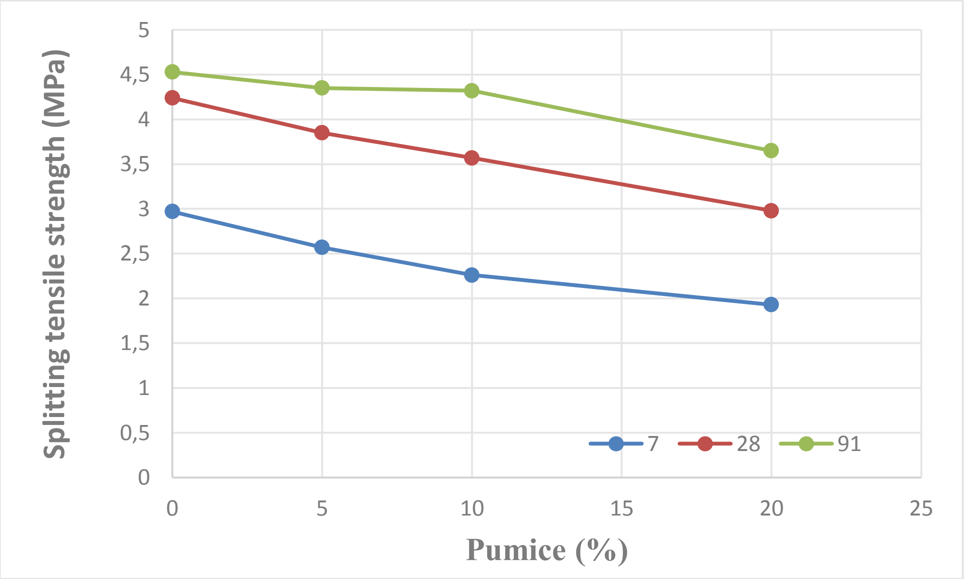


Fig. 4.17: Variation of splitting tensile strength of FLS concretes versus pumice replacement at different ages

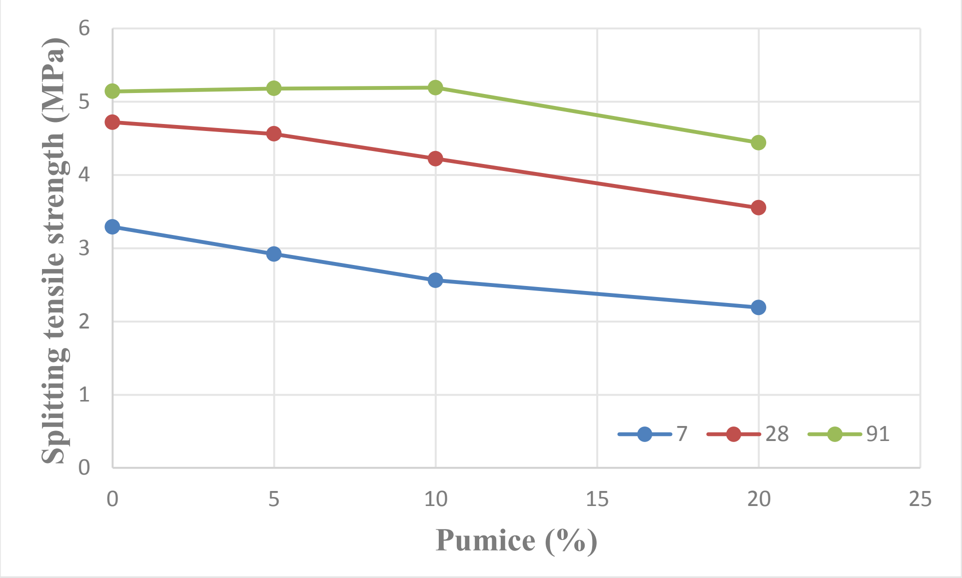


Fig. 4.18: Variation of splitting tensile strength of FCS concretes versus pumice replacement at different ages

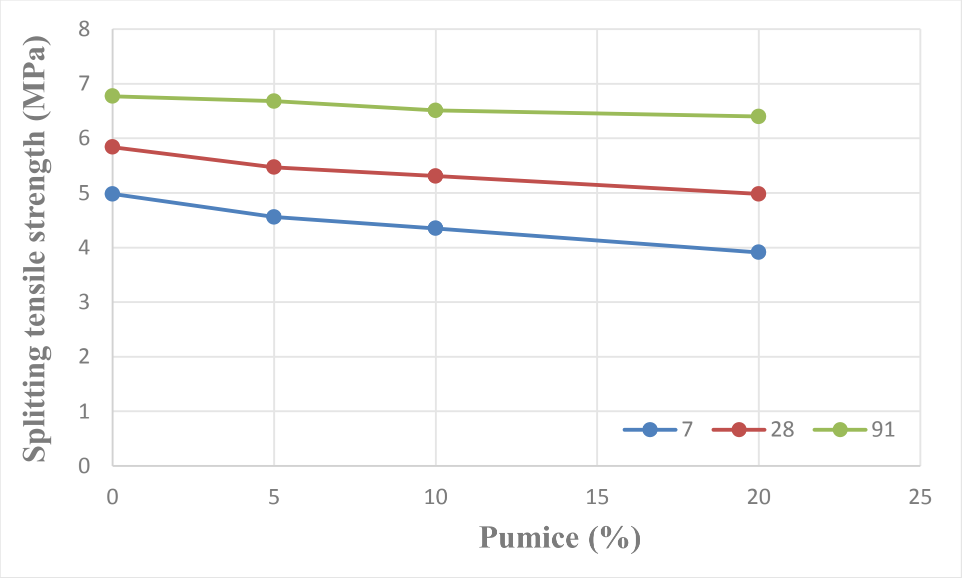


Fig. 4.19: Variation of splitting tensile strength of SLS concretes versus pumice replacement at different ages

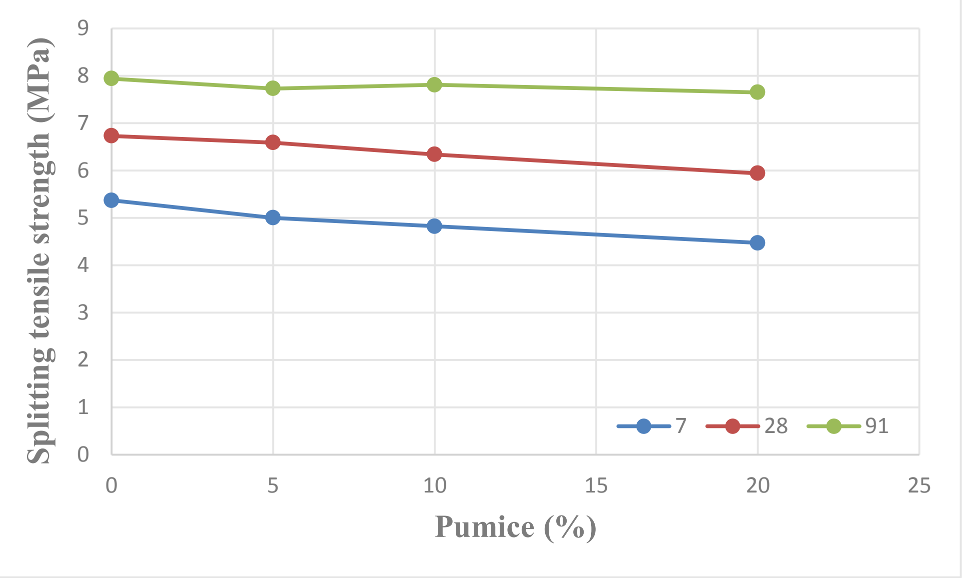


Fig. 4.20: Variation of splitting tensile strength of SCS concretes versus pumice replacement at different ages

As it can be seen from Fig. 4.17, adding finely ground pumice resulted in rapid reduction of the splitting tensile strength at all ages. The 28-day splitting tensile strength of the control mixture (FLS) was 4.24 MPa while it was decreased to 2.98 MPa by adding 20% pumice. Similar trends of strength variations were observed for other mixtures in comparison with the control mixtures in each series as shown in Figs. 18-20. For FCS series, the 28-day splitting tensile strength was decreased from 4.72 MPa to 4.56, 4.22 and 3.555 MPa by adding 5, 10 and 20% pumice, respectively. However, this reduction was lower for the S series so that the 28-day splitting tensile strength of the control mixtures of SLS and SCS were decreased by adding 5% pumice powder from 5.84 and 6.73 MPa to 5.47 and 6.59 MPa, respectively. In general, this strength reductions were significantly lower at the age of 91 days. Variations of the splitting tensile strength by adding different levels of pumice powder are discussed in details by considering the SCI values (Table 4.6).

Table 4.6: SCI values for concrete mixtures containing different levels of pumice (P)

Mixtures with limestone containing 0, 5, 10 and 20% of pumice

SCI (%)	FLSP5	FLSP10	FLSP20
7-day	86.4	76.2	64.9
28-day	90.9	84.1	70.3
91-day	96.1	95.3	80.6

SCI (%)	SLSP5	SLSP10	SLSP20
7-day	91.6	87.3	78.6
28-day	93.7	90.9	85.3
91-day	101.4	96.1	94.5

Mixtures with copper slag containing 0, 5, 10 and 20% of pumice

SCI (%)	FCSP5	FCSP10	FCSP20
7-day	88.8	77.9	66.6
28-day	96.6	89.3	75.2
91-day	100.8	100.9	86.3

SCI (%)	SCSP5	SCSP10	SCSP20
7-day	93.1	89.7	83.2
28-day	97.9	94.2	88.2
91-day	102.7	101.7	96.3

As it can be seen, 7-day splitting tensile strength of all concrete mixtures were reduced remarkably. The maximum and minimum reduction was for FLSP20 and SCSP5 which was 35.1 and 6.9%, respectively. This is mainly because of the fact that Portland cement particles were replaced with less reactive pumice particles, i.e. more replacement resulted in more reductions at early age of 7 days. This is consistent with reported results by other researchers (Hossain and Lachemi, 2006; Ozodabas and Yilmaz, 2013; Hossain, 2008; Demirel and Kelestemur, 2010). In general, it has been well known that concrete mixture containing pozzolanic materials such fly ash and slag which are more common than pumice, have slower strength gain in comparison with the conventional concrete mixtures at early ages which can be compensated over time.

According to Table 4.6, there was no positive Strength Coefficient Index (SCI) at 28 days. This is consistent with results which were plotted in Figs. 4.17-20. The lowest strength reduction at 28 days belongs to SCSP5 which was 2.1% and the highest 28-day strength reduction was observed in the FLSP20 which was 29.1%. However, strength reductions were significantly improved at age of 28 days in comparison with related values at age of 7 days in terms of pumice replacement. This improvement was more remarkable in the S series when 10% silica fume was used in making concrete mixtures which resulted in denser micro-structure of the cement matrix and stronger interfacial transition zone (ITZ). In this series (S), it seems that replacing of Portland cement by 5% finely ground pumice can generally satisfy 28-day strength requirements because resulted strength reductions were not significant. After careful assessment of SCI values at age of 91 days which are presented in Table 4.6, it can be seen that main strength recovery of the concrete mixtures incorporating pumice powder was occurred after age of 28 days and was recorded as the 91-day splitting tensile strength values.

At this age (91 days), several concrete mixtures showed similar or even better performance in comparison with the control concrete mixture. In general, promising results were observed for the SLSP5, FCSP5, FCSP10, SCSP5 and SCSP10 at 91 days. In other word, these concrete mixtures successfully not only satisfied the 91-day strength requirement but also had higher splitting tensile strength than required values. The highest splitting tensile strength was for the SCSP5 which its SCI index was 102.7%. This is more important when it is not necessary to achieve a specific 28-day compressive strength as a compulsory requirement in some projects. This is more likely for members or classes of concrete that will not have expected construction or service loads applied at 28 days. In such situations, the concept of later-age strength requirement is relevant and applicable. Based on this concept, it is possible to make sustainable concrete with 20% replacement of Portland cement with supplementary cementitious materials including finely ground pumice and silica fume. Furthermore, it is feasible to make high-strength concrete with 15% replacement of cement by pumice and silica fume to achieve acceptable 28-day splitting tensile strength in comparison with control mixture without finely ground pumice.

4.3.2.3. Effects of concurrent utilization of pumice and copper slag

In previous sections effects of copper slag coarse aggregate and finely ground pumice on the splitting tensile strength were discussed separately. However, it is more advantageous for developing sustainable high-strength concrete that copper slag coarse aggregate as an industrial waste material and finely ground pumice as a natural pozzolanic material are used in concrete production together.

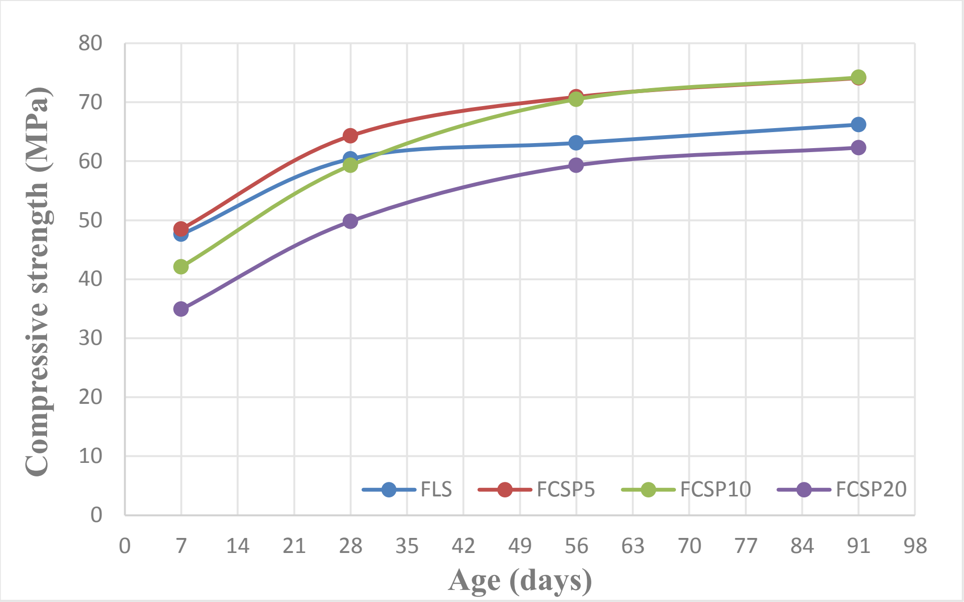


Fig. 4.21: Combined effects of copper slag coarse aggregate and pumice powder on splitting tensile strength of F series

Therefore, it is important to investigate variations of the splitting tensile strength of high-strength concrete containing both of copper slag coarse aggregate and finely ground pumice. Fig 4.21 and 22 demonstrate combined effects of copper slag coarse aggregate and pumice powder on the splitting tensile strength of F series (w/c=0.4) and S series (w/b=0.3 and SF=10%), respectively. To quantify influences of combined utilization of finely ground pumice and copper slag on the splitting tensile strength, "Strength Coefficient Index" is defined in this study as below:

Strength Coefficient Index: SCI (%) = (A/B) × 100

A = average splitting tensile strength of test concrete mixtures containing pumice and copper slag, MPa

B = average splitting tensile strength of control mixtures (without pumice and copper slag), MPa

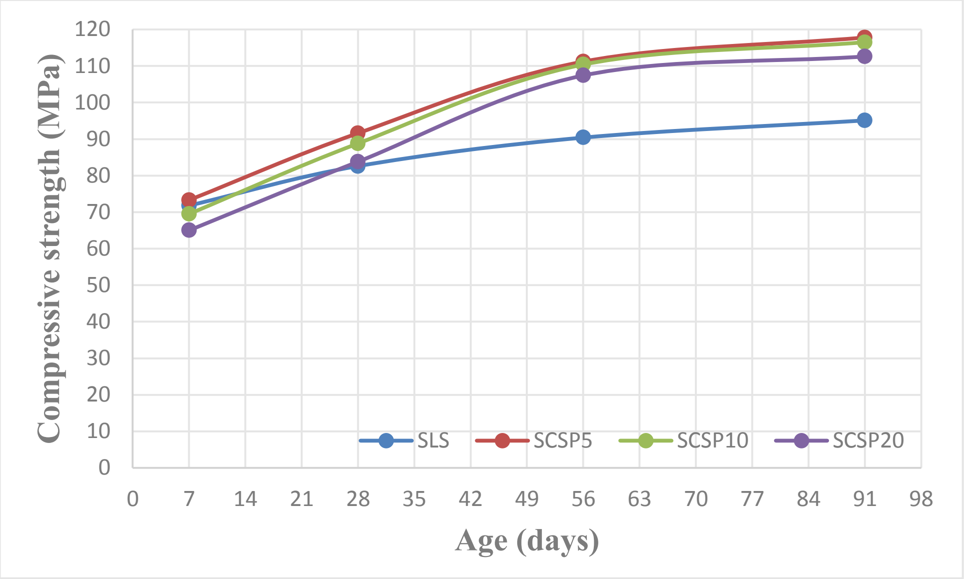


Fig. 4.22: Combined effects of copper slag coarse aggregate and pumice powder on splitting tensile strength of S series

The SCI values of series of S and F containing copper slag aggregate and finely ground pumice are presented in Table 4.7. It should be noted each column was compared to the control mixture of that series without copper slag and pumice powder, i.e. FCSP5, 10 and 20 were compared with FLS and SCSP5, SCSP10 and SCSP20 were compared with SLS. As mentioned earlier, main aim of this comparison is assessing effects of concurrent using of copper slag and pumice on the splitting tensile strength of concrete.

Table 4.7: SCI values for mixtures containing copper slag (CS) and pumice (P)

SCI (%)	FCSP5	FCSP10	FCSP20	SCSP5	SCSP10	SCSP20
7-day	98.3	86.2	73.7	100.4	96.8	89.8
28-day	107.6	99.5	83.7	112.8	108.6	101.7
91-day	114.4	114.6	98.0	120.4	119.6	113.0

In terms of F series (Fig. 4.21), the splitting tensile strength was decreased for all levels of pumice replacement at age of 7 days. The highest strength reduction was observed in FCSP20 which was 26.3% comparing to the control mixture. Although the 28-day splitting tensile strength of this mixture (FCSP20) was still lower than the control mixture, FCSP10 and FCSP20 showed similar and superior performance, respectively at age of 28 days. According to Table 4.7, the SCI value of the FCSP5 and 10 was 107.6 and 99.5%, respectively. It means that it is possible to use 100% finely ground pumice with copper slag coarse aggregate for producing high-strength concrete with acceptable 28-day splitting tensile strength when water to binder ratio is 0.4. However, the FCSP20 showed a significant strength gain in the period of 28 to 91 days so that its 91-day splitting tensile strength was 4.44 MPa, i.e. only 2% lower than the control mixture. But, other mixtures with copper slag and pumice had remarkably better splitting tensile strength value on average which was approximately 14% higher than the control mixture. This can be attributed to efficiency of pozzolanic reaction of finely ground pumice during this period which resulted in strength gain. Therefore, it can be concluded that optimum value of replacing Portland cement by finely ground pumice was 10% when natural limestone coarse aggregate was also replaced by copper slag coarse aggregate.

In terms of series S, promising results were observed after using copper slag coarse aggregate and finely ground pumice. Fig. 4.22 shows the splitting tensile strength development of control mixture (SLS) as well as concrete mixtures with copper slag coarse aggregate and different levels of pumice powder. At age of 7 days, despite lower splitting tensile strength of the SCSP10 and 20 (4.82 and 4.47 MPa, respectively), the SCSP5 showed similar performance in terms of the splitting tensile strength.

At age of 28 days, there was no lower splitting tensile strength after using copper slag and pumice powder even up to 20% of Portland cement weight. According to Table 4.7, SCI values for SCSP5, 10 and 20 were 112.8, 108.6 and 101.7%, respectively. The maximum splitting tensile strength was recorded for the SCSP5 which was 6.59 MPa. However, the SPSP20 showed a significant strength gain versus age so that its SGA value was 101.7% at age of 28 days while it was 89.8% at 7 days. This can be attributed to efficiency of pozzolanic reaction of finely ground pumice during this period which resulted in strength gain.

With regard to strength and SCI values, it can be concluded that it is possible to use 20% finely ground pumice with copper slag coarse aggregate for producing high-strength concrete with acceptable 28-day splitting tensile strength when water to binder ratio is 0.3 and 10% of Portland cement weight is replaced by highly reactive silica fume. Therefore, 30% of Portland cement was replaced by pumice and silica fume as supplementary cementitious materials while natural limestone coarse aggregate was also replaced by copper slag coarse aggregate. As mentioned earlier, presence of copper slag can increase the splitting tensile strength of concrete at different ages. This can be attributed to higher level of the strength properties of copper slag aggregate. In addition, the surface texture of coarse aggregate is partly responsible for the bond between the cement paste and aggregate because of the mechanical interlocking between cement paste and copper slag. It has been well established that the mechanical properties of concrete are significantly affected by the bonding between the cement paste and aggregate (Figs. 4.6 and 7).

In the meantime, finely ground pumice is a pozzolanic material which has more than 70% of SiO_2. However, it has been well-known that pozzolanic reactions are slower than hydration reaction of Portland cement and when significant part of Portland cement is replaced with supplementary cementitious materials, there is always a possibility of observing a lower rate of strength gain while final strength is same or even higher due to chemical and physical effects of supplementary cementitious materials including silica fume and pumice.

In general, this trend of strength gaining was significantly observed in all of concrete mixtures containing pumice in the S series at age of 91 days. The splitting tensile strength of the SCSP5, 10 and 20 were 8.15, 8.08 and 7.65 MPa, respectively which were remarkably higher than the splitting tensile strength of the control mixture which was 6.77 MPa. In other word, using 5, 10 and 20 % pumice powder increased the splitting tensile strength of concrete approximately 20.4, 19.6 and 13%, respectively.

Furthermore, it can be seen in Table 4.7 that SCI values were significantly improved when silica fume was in the concrete mixtures regardless of type of coarse aggregate (limestone or copper slag). This can be attributed to physical effects of micro silica particles as fillers in cement paste as well as their chemical influences as a pozzolanic material which resulted in stronger, denser and more homogeneous cement matrix and interfacial transition zone. Therefore, chance of better and stronger bonding was increased by using silica fume in the concrete mixtures.

As mentioned earlier in section 4.3.1.1, this effect of silica fume in improving bonding was more efficient in forming stronger interfacial transition zone between cement paste and rough surface of copper slag coarse aggregate. To sum up, the most efficient and optimum value of finely ground pumice when copper slag coarse aggregate is used in concrete is 10% at water to cement ratio of 0.4 and 20% at water to binder ratio of 0.3 and presence of 10% silica fume in concrete mixture. First showed 28-day splitting tensile strength similar to control normal concrete with limestone coarse aggregate while later showed even higher performance in comparison with the control normal mixture in terms of splitting tensile strength. However, these recommended values of pumice and copper slag showed promising excellent results at age of 91 days as well. In this study, 30% of Portland cement was successfully replaced by silica fume and finely ground pumice while copper slag coarse aggregate as an industrial waste material was simultaneously used instead of natural limestone coarse aggregate for producing sustainable high-strength concrete. With regard to the Green Building Council of Australia's Green Star Mat-4, this novel type of high-strength concrete can achieve concrete credits for considering as green concrete. This guideline was presented as Annex 1.

Summary

This chapter reported results obtained through experimental programmes, highlighting key observations and exploring a theoretical basis for explaining observed results. In this chapter, fresh properties of high-strength concretes, including slump, air content and unit weight are presented and discussed thoroughly. After that, results of mechanical properties of hardened concrete including compressive and splitting tensile strengths are given and discussed in detail.

Chapter 5

5. CONCLUSIONS AND RECCOMENDATIONS

5.1. Conclusions

This study provides comprehensive investigation of results of extensive experimental tests on fresh and hardened high-strength concrete specimens including slump, unit weight, air content, compressive and splitting tensile strength measurements. Overall, 16 different mix designs were investigated to understand effects of pumice and copper slag on different properties of high-strength concrete. Based on comprehensive results of this study, some conclusions can be drawn as below:

- Slump values varied in the range of 105 to 131 mm while the minimum and maximum value was observed for mixture SLS (w/(C+SF): 0.3, SF: 10% and limestone coarse aggregate) and FCSP5 (w/b: 0.4 and copper slag coarse aggregate), respectively. The average slump value of different concrete mixtures was 117mm which is a well-accepted value of slump of concrete so that it can be transported, casted and compacted with common methods. In the meantime, it was within the designed range of slump variation for this research study which was 110±10mm.

- Air content was generally decreased by increasing of amount of pumice. For example, air content of FLS which did not have pumice was 3.2% while air content of FLSP5, FLSP10 and FLSP20 (same concrete mixtures but with pumice) was decreased to 2.9, 2.7 and 2.4, respectively. In other word, air content of FLS was decreased approximately 9.4, 15.6 and 25% by adding 5, 10 and 20% of pumice to mixture. Similar trends can be seen for other mixtures including SLS series (SLSP5, SLSP10 and SLSP20), FCS series (FCSP5, FCSP10 and FCSP20) and SCS series (SCSP5, SCSP10 and SCSP20). In the meantime, series incorporating silica fume and lower water to binder ratio (S) had lower air contents in comparison with series without silica fume and higher water to bonder ratio (F) so that the air content of SLS and SCS was 25% and 30% lower than the air content of FLS and FCS, respectively.

- Air contents of each series of concrete mixtures were decreased by increasing of total amount of fine particles including silica fume and pumice powder. For the first series of concrete mixtures with limestone (LS), the average of air content value was 2.8% while this value was 2.2% for the second series of concrete with limestone. Similar reduction was observed for series of concrete with copper slag so that the average of air content value was 2.88% for the first series of concrete mixtures with copper slag while this value was 2.15% for the second series of concrete mixture with copper slag.

- With regard to higher value of specific gravity of cooper slag (3.59 g/cm^3) in comparison to lime stone, higher unit weight of concretes incorporating copper slag coarse aggregate are expected as results also confirmed. The average value of unit weight of concretes with copper slag was 2720 kg/m^3 while this value for concretes with limestone coarse aggregate was 2359 kg/m^3. In other word, copper slag increased the average unit weight of concrete approximately 15.3%.

- Compressive strength at 7, 28, 56 and 91 days were increased approximately 9.5, 10.8, 11.0 and 8%, respectively by replacing limestone coarse aggregate with copper slag coarse aggregate. In other word, using copper slag instead of limestone increased the compressive strength on average around 9.8%. Similar trends are observed for another series of concrete mixtures (SLS and SCS).

- In general, it can be concluded that presence of copper slag can increase compressive strength of concrete at different ages. This can be attributed to higher level of the strength properties of copper slag aggregate. In addition, the surface texture of coarse aggregate is partly responsible for the bond between the cement paste and aggregate because of the mechanical interlocking between cement paste and copper slag. It has been well established that the mechanical properties of concrete are significantly affected by the bonding between the cement paste and aggregate.

- Minimum SCI was at age of 7 days so that SCI value of F and S series was 109.5 and 106%, respectively. However, SCI was increased by increasing age of concrete specimens so that the SCI value of F and S series at age of 28 days was

110.8 and 111.5%, respectively. While the SCI values for series F at 56 and 91 days were 110 and 108%, respectively, the S series showed significantly higher values of the SCI (118 and 117%). Therefore, it can be concluded that comparative strength improving effect of copper slag aggregate is higher for a mixture with silica fume due to denser microstructure of cement paste as well as better quality of interfacial transition zone including silica fume and stronger bonding between cement paste and copper slag aggregate.

- Regardless of pumice dosage, 7-day compressive strength of all concretes were decreased significantly. The highest and lowest reduction was for FLSP20 (20% pumice, w/c: 0.4, limestone) and SCSP5 (5% pumice, w/b: 0.3, copper slag) which was 34 and 3.7%, respectively. This is mainly because of the fact that Portland cement particles were replaced with less reactive pumice particles, i.e. more replacement resulted in more reductions at early age of 7 days.

- At age of 91 days, all of concrete mixtures except those containing finely ground pumice as 20% of Portland cement replacement showed approximately similar or even better performance in comparison with control mixtures. For 20% pumice replacement, the worst result was observed for F series with limestone coarse aggregate so that compressive strength was decreased from 66.2 MPa (control mixture) to 53.9 MPa. It means that the Strength Coefficient Index (SCI) of this mixture was approximately 81.4%.

- Compressive strength reductions were significantly modified while silica fume was in the concrete mixtures (SLS and SCS series). This can be attributed to physical effects of micro silica particles as fillers in cement paste as well as their chemical influences as a pozzolanic material which resulted in stronger, denser and more homogeneous cement matrix and interfacial transition zone. Therefore, chance of better and stronger bonding was increased by using silica fume in the concrete mixtures.

- In general, performance of concrete mixture with limestone coarse aggregate in series F was acceptable after 56 days at pumice replacement up to 10% of cement weight. In series S with limestone coarse aggregate, not only performance of mixes with 5 and 10% pumice replacement was better than control mix after 56 days, acceptable performance was observed when 5% of cement weight was replaced by finely ground pumice.

- Based on comparison between results of compressive strength of limestone coarse aggregate concrete with and without pumice, it can be concluded that it is possible to make sustainable concrete with 20% replacement of Portland cement with supplementary cementitious materials including finely ground pumice and silica fume if 56-day compressive strength is considered as a requirement. Furthermore, it is feasible to make high-strength concrete with 15% replacement of cement by pumice and silica fume to achieve acceptable 28-day compressive strength in comparison with control mixture without finely ground pumice.

- In terms of concurrent using of copper slag and pumice, although 28-day compressive strength of concrete with copper slag and 20% pumice was still lower than control mix (7.5%), concrete with copper slag and 10% pumice had negligible difference in compressive strength comparing to control mixture which was around 1.8%. Furthermore, FCSP5 showed significantly higher compressive strength at 28 days so that the compressive strength of control concrete was increased to 64.3 MPa.

- At age of 56 days, concurrent using of copper slag and pumice increased remarkably so that SCI value (Table 4.4) was 112.4 and 117.7% for FCSP5 and FCSP10, respectively. A similar trend was observed in changes of compressive strength of concrete mixtures at age of 91 days. While two mixes of FCSCP5 and FCSP10 had higher compressive strength values, FCSP20 showed lower performance comparing to control mixture.

- By comparing two series of FLS and FCS which have same mix proportions and materials except copper slag coarse aggregate, it can be concluded that presence of copper slag coarse aggregate generally increased the splitting tensile strength approximately 11% on average. The maximum splitting tensile strength value was measured for FCS at 91 days which was 5.14 MPa while it was 4.53 MPa for same mixture without copper slag.

- In general, it can be concluded that using copper slag coarse aggregate increased the splitting tensile strength of concrete around 12% in comparison with control mixtures with limestone coarse aggregate. For example, the splitting tensile strength was increased by using copper slag coarse aggregate approximately 13.5% at 91 days. Similar improvements were observed in series S by comparing the splitting tensile strength values of SLS and SCS. As another example, the 28-day splitting tensile strength was increased from 5.84 MPa to 6.73 MPa and this improvement was even higher at 91 days so that the splitting tensile strength was 7.94 MPa which means 17.3% improvement in the splitting tensile strength by using copper slag coarse aggregate at age of 91 days.

- Adding finely ground pumice resulted in rapid reduction of the splitting tensile strength at all ages. The 28-day splitting tensile strength of the control mixture (FLS) was 4.24 MPa while it was decreased to 2.98 MPa by adding 20% pumice. Similar trends of strength variations were observed for other mixtures in comparison with the control mixtures in each series.

- 7-day splitting tensile strength of all concrete mixtures were reduced remarkably. The maximum and minimum reduction was for FLSP20 and SCSP5 which was 35.1 and 6.9%, respectively. This is mainly because of the fact that Portland cement particles were replaced with less reactive pumice particles, i.e. more replacement resulted in more reductions at early age of 7 days.

- Based on comparison between results of splitting tensile strength of limestone coarse aggregate concrete with and without pumice, it can be concluded that it is possible to make sustainable concrete with 20% replacement of Portland cement with supplementary cementitious materials including finely ground pumice and silica fume if 56-day compressive strength is considered as a requirement. Furthermore, it is feasible to make high-strength concrete with 15% replacement of cement by pumice and silica fume to achieve acceptable 28-day splitting tensile strength in comparison with control mixture without finely ground pumice.

- In terms of the splitting tensile strength, SCI values were significantly improved when silica fume was in the concrete mixtures regardless of type of coarse aggregate (limestone or copper slag). This can be attributed to physical effects of micro silica particles as fillers in cement paste as well as their chemical influences as a pozzolanic material which resulted in stronger, denser and more homogeneous cement matrix and interfacial transition zone.

5.2. Recommendations

5.2.1. Recommended optimized content of pumice and coarse aggregate

With regard to numerous test results of fresh and hardened high-strength concrete with and without copper slag coarse aggregate and finely ground pumice, it can be recommended that the most efficient and optimized value of finely ground pumice when copper slag coarse aggregate is used in concrete is 10% at water to cement ratio of 0.4 and 20% at water to cementitious materials ratio of 0.3 and presence of 10% silica fume in concrete mixture. First showed 28-day compressive and splitting tensile strength similar to control normal concrete with limestone coarse aggregate while later showed superior performance in comparison with the control normal mixture in terms of compressive and splitting tensile strength. However, these recommended values of pumice and copper slag showed promising excellent results at age of 56 days which is the common age of measuring concrete properties including high level of supplementary cementitious materials. In this study, 30% of Portland cement was successfully replaced by silica fume and finely ground pumice while copper slag coarse aggregate as an industrial waste material was simultaneously used instead of natural limestone coarse aggregate for producing sustainable high-strength concrete. With regard to the Green Building Council of Australia’s Green Star Mat-4, this novel type of high-strength concrete can achieve concrete credits for considering as green concrete.

5.2.2. Research limitations

Although efforts were done to carry out a comprehensive study on effects of copper slag and pumice on high-strength concrete, some instrumental, cost and time limitations resulted in not doing all required experiments for investigating influences of these two materials for producing a new green high-strength concrete. For instance, while shrinkage of normal concrete containing copper slag or pumice has been already studied and acceptable results have been reported, but effects of concurrent utilisation of these two material on high-strength concrete has not assessed yet. Therefore, these aspects of the work are presented as possible fields for further research in next section.

5.2.3. Recommended further research

With regard to provided literature review, it has been well known that pumice powder as a pozzolanic material and copper slag as coarse aggregate can be used in normal-strength concrete. However, this is the first time that both of copper slag coarse aggregate and pumice powder were used for producing high-strength concrete with lower environmental impact and carbon foot print. However, more micro-structural studies should be carried out to investigate micro changes in different phases of concrete and their influences on C-S-H as the main reason of strength of concrete. Therefore, it is recommended to perform such studies by using scanning electron microscope (SEM). In the meantime, porosity of concrete specimens should be evaluated by Mercury Intrusion Porosimetry (MIP) method to determine pore size distribution within high-strength concrete containing pumice powder. Although durability of concrete with pumice or copper slag have been thoroughly investigated before, it seems further evaluations are needed to study carbonation and carbonation accelerated chloride-induced corrosion behaviors of high-strength concrete with both of pumice and copper slag. Also, investigating shrinkage of high-strength concrete incorporating different levels of copper slag and pumice is very important which should be done as further research. In terms of mechanical properties, because this is the first time that combination of pumice and copper slag were used for producing high-strength concrete, it is recommended that other properties such as ductility, modulus of rupture and elasticity are studied in future works. In the meantime, effects of single or hybrid system of fibers on characteristics of this novel type of green concrete should be investigated. Finally, it is recommended that life-cycle assessment (LCA) and whole-life cost studies are organized to assess environmental and financial impacts of high-strength concrete with pumice powder and copper slag coarse aggregate.

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Appendix A*

GREEN STAR AND AUSTRALIAN BUILDING GREENHOUSE RATING

SCHEME (ABGR)

- **Green Building Council of Australia (GBCA) and Cement Concrete Aggregate Australia (CCAA)**

A.1. GREEN STAR

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A2. Mat-4 Concrete

Green Star / Concrete --1

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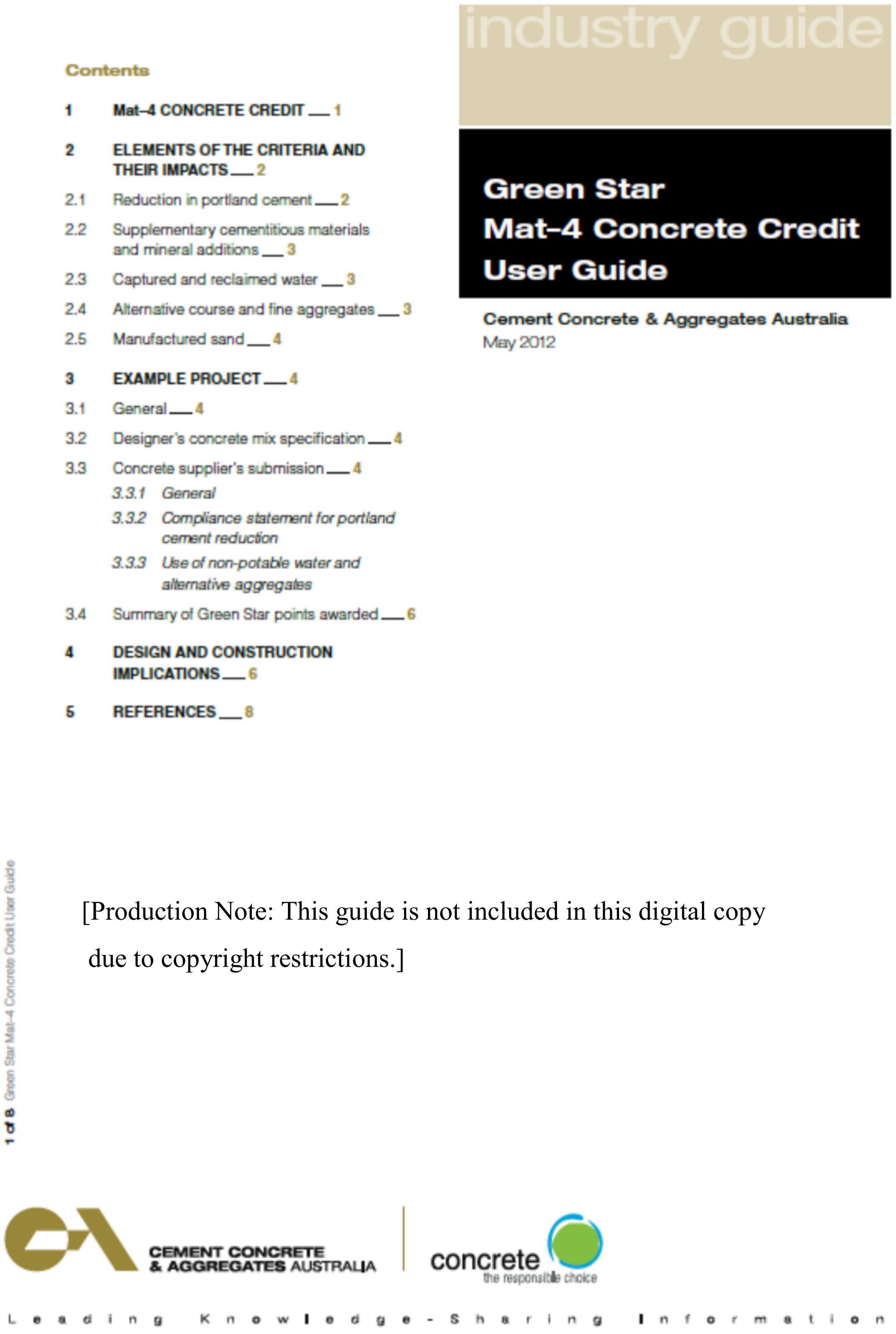
A.3.Industry Guide on Green Star Mat-4 Concrete



industry guide

Green Star
Mat-4 Concrete Credit
User Guide

Cement Concrete & Aggregates Australia
May 2012

Contents

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CEMENT CONCRETE & AGGREGATES AUSTRALIA

concrete
the responsible choice

Leading Knowledge-Sharing Information

Appendix B

COST ANALYSIS

Cost analysis

It is clear that it is not possible to perform a reliable and comprehensive whole life cost analysis only based on initial construction cost without considering other costs which are caused by environmental impacts (for example, carbon tax), long-term operation and maintenance, etc. Nowadays, service life of concrete structures can be increased even more than 100 years and with regard to such a long time of serviceability, these extra costs are important. However, this section considers only costs which are related to concrete from its initial materials to its casting and curing. Also, it should be noted that it is not possible to perform a general cost analysis which can be applicable for different countries and regions so that it must be calculated for each particular area based on its specific characteristics. In other word, cost of a specific material in a region which produces that material is cheaper than cost of the same material which is imported in another region. Also, it is possible that for example cost of coarse aggregate is lower while cost of Portland cement is high in the same area due to level of availability. However, this section discusses qualitatively about

In general, final direct cost of each concrete work can be divided into different sub-costs including costs of materials, production, transportation, placing (casting, vibrating and curing). Costs of materials includes costs which are derived from different ingredients of materials which are mainly Portland cement, water, fine and coarse aggregates. In other word, costs of materials are different between different concretes with different mix designs. In context of present study, costs of water and fine aggregate are same for conventional high-strength concrete (reference concrete) and new green high-strength concrete which was introduced in this work. In terms of Portland cement, up to 30% of total amount of Portland cement could be replaced by pumice and silica fume for developing this new high-strength concrete. Regarding coarse aggregate, there is one initial cost which is related to ownership of the query. This cost is not applicable for copper slag while it should be calculated in cost of natural coarse aggregate. In other word, copper slag is a freely available coarse aggregate so that copper manufactures even are ready for paying to remove them from manufacturing site while using natural coarse aggregate results in environmental costs and taxes.

However, other costs including production, transportation and placing (casting and curing) are same for these two types of conventional and green high-strength concrete. It should be noted that same distance was assumed for comparing cost of transportation of coarse aggregate in a region which pumice is also available with a same distance of a Portland cement factory. Also, it should be noted that 10% replacement level of silica fume is applicable for regions that this material is available or its cost is not much higher than similar amount of Portland cement. However, silica fume is a material which is obtained based on recycling processes and it can help too decrease environmental impacts of production of high-strength concrete. Therefore, it is reasonable to use it instead of Portland cement at this level to keep other environmental costs (such as carbon tax) lower even its initial cost could be a little bit higher than Portland cement.

In terms of coarse aggregate, it should be noted that although copper slag is relatively free material, its grinding process for obtaining same particle size of limestone coarse aggregate results in higher cost due to higher hardness of copper slag in comparison with limestone. However, this cost is inly some percent of the cost of buying limestone aggregate. In the meantime, extracting limestone from natural query results in more environmental and overhead costs.

In general, it can be concluded that the final cost of new green high-strength concrete is of course, cheaper than conventional high-strength concrete for close distances to sources of copper slag and pumice. However, this can be increased by increasing of distance which depends on transportation costs (fuel price, road taxes, etc.). It should be note that in the region which this research was carried out, there is a railway to national railway system and these materials can be transported by trains which are cheaper for longer distances and higher amounts of loads.