THE ENGINEERING PROPERTIES OF HIGH STRENGTH HEAVYWEIGHT CONCRETE CONTAINING STEEL SLAG AGGREGATE AND STEEL FIBER WITH NANO MATERIAL ADDITIVES

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TABLE OF CONTENTS

APPENDICES

LIST OF PUBLICATIONS

LIST OF TABLES

Page

LIST OF FIGURES

Page

LIST OF ABBREVIATIONS

HSHWC	High Strength Heavyweight Concrete
SFSA	Steel Furnace Slag Aggregate
NSS	Nano-Silica Slurry
NCC	Nano-Calcium Carbonate
NZ	Nano-Zinc Oxide
SF	Steel Fiber
Z	Atomic Number
HWC	Heavyweight Concrete
VHRWRA	Very High Range Water Reducer Admixture
ITZ	Interfacial Transition Zone
NS	Nano-Silica
W/C	Water to Cement Ratio
W/b	Water/Binder
W/P	Water/Powder
ACI	American Concrete Institute
SP	Superplasticizer
HPHWC	High-Performance Heavyweight Concrete
GGBS	Ground Granulated Blast-Furnace Slag
XRF	X-Ray Fluorescence
ACV	Aggregate Crushing Value
BD	Bulk Density
WA	Water Absorption
ER	Expansion Rate
SG	Specific Gravity
LA	Los Angeles loss
AIV	Aggregate Impact Value
NA	Natural Aggregate
NCA	Natural Coarse Aggregate
OPC	Ordinary Portland Cement
GQD	Granite Quarry Dust
NGR	Natural Granite Rock

NRS	Natural River Sand
CT	Computed Tomography
SPECT	Single-Photon Emission Computed Tomography
PET	Positron Emission Tomography
ICRP	International Commission on Radiological Protection
NPGO	Nanoplatelets of Graphene Oxide
LOI	Loss of Ignition
SEM	Scanning Electron Microscopy
UPV	Ultrasonic Pulse Velocity

SIFAT KEJURUTERAAN KONKRIT BERAT BERKANDUNGAN TINGGI MENGANDUNGI AGGREGAT SANGGA KELULI DAN GENTIAN KELULI DENGAN BAHAN PENAMBAH NANO

ABSTRAK

Terdapat literatur yang terhad pada pengeluaran konkrit kelas berat berkekuatan tinggi (HSHWC) dengan pertimbangan holistik mengenai kandungan air, nisbah agregat, penggunaan bahan tambahan nano dan tetulang mekanikal dengan agregat berat kos rendah. Kerja ini bertujuan untuk mengatasi batasan dengan mewujudkan pendekatan baru untuk mengembangkan HSHWC yang mengandungi agregat slag gentian keluli (SFSA) dengan nisbah W/C yang sangat rendah, nisbah agregat volumetrik dioptimumkan, penggunaan bahan tambahan nano dan penambah serat. Selain itu, kesan penambahan aditif nano seperti buburan nano-silika (NSS), nano-kalsium karbonat (NCC), nano-zink oksida (NZ) telah dikaji. Gentian keluli (SF) digunakan untuk meningkatkan sifat mekanikal dan sifat penebat radiasi HSHWC. Program eksperimen dijalankan untuk menilai ujian mekanikal, ketahanan, struktur mikro, kestabilan dimensi dan pelindung sinaran. Nisbah W/C adalah 0.23 untuk mencapai sifat yang diperlukan. HSHWC menunjukkan bahawa peningkatan kekuatan mampatan dan ketumpatan tertinggi masing-masing sekitar 214.2% dan 7.3% dicapai dengan nisbah W/C 0.23. Selanjutnya, hasil untuk HSHWC yang dikembangkan dengan nisbah volumetrik disesuaikan dicapai dengan agregat kasar pecahan isipadu 0.428 dan nisbah agregat pengikat: halus: kasar 1: 2: 3. Parameter reka bentuk ini meningkatkan pelindung sinar-gamma (γ) dan sinar-X masing-masing sebanyak 900.3% dan 946.3%, dibandingkan dengan konkrit konvensional. Sementara itu, kekuatan mampatan HSHWC mencapai 106 MPa. Hasil HSHWC dengan NSS dan

NCC menunjukkan bahawa kenaikan tertinggi pada sifat yang disebutkan dicapai dengan tambahan 3.0% dan 2.0% NSS dan NCC, masing-masing, dengan berat simen. Tingkah laku redaman sinar-γ dan X masing-masing meningkat sebanyak 3.4% dan 5.3%. Peningkatan selanjutnya sifat HSHWC dicapai dengan penggunaan 3.0% NSS dan 1.5% NZ, dengan berat simen yang menunjukkan peningkatan prestasi redaman sinar γ dan sinar-X masing-masing sebanyak 16.3% dan 25.4%. Bagi hasil yang diperoleh dari pengembangan HSHWC menggunakan gentian keluli, pecahan terbaik mengikut isipadu adalah 1.0%. Ia meningkatkan spesifikasi konkrit, termasuk penebat radiasi. Kesimpulannya, HSHWC yang sesuai sebagai pelindung radiasi dan menawarkan perlindungan yang sangat baik dari pelepasan radioaktif tenaga tinggi, seperti sinar γ dan sinar-X dapat dihasilkan menggunakan SFSA sebagai agregat dan dengan kemasukan terkawal bahan nano dan gentian keluli.

THE ENGINEERING PROPERTIES OF HIGH STRENGTH HEAVYWEIGHT CONCRETE CONTAINING STEEL SLAG AGGREGATE AND STEEL FIBER WITH NANO MATERIAL ADDITIVES

ABSTRACT

There are limited literatures available on the production of high strength heavyweight concrete (HSHWC) with holistic considerations on the water content, aggregate ratios, use of nano additives and mechanical reinforcement with low cost heavy aggregate. The work is aimed to overcome the limitations by establishing a novel approach for developing HSHWC containing steel furnace slag aggregate (SFSA) with very low W/C ratio, optimized volumetric ratio of aggregates, use of nano additives and fiber reinforcements. Besides, the effect of the addition of nano additives such as nano-silica slurry (NSS), nano-calcium carbonate (NCC), nano-zinc oxide (NZ) was investigated. The steel fiber (SF) was used to enhance the mechanical properties and radiation insulation properties of the HSHWC. The experimental programme was carried out to evaluate the mechanical, durability, microstructure, dimensional stability and radiation shielding tests. The W/C ratio is 0.23 to achieve the required properties. HSHWC shows that the highest increase in compressive strength and density of approximately 214.2% and 7.3% respectively is achieved with a W/C ratio of 0.23. Furthermore, the results for the HSHWC developed by adjusted volumetric ratio were achieved with coarse aggregate a volume fraction of 0.428 and the binder: fine: coarse aggregate ratio of 1:2:3. These design parameters enhanced the gamma-ray (γ) and X-ray shielding by 900.3% and 946.3%, respectively, as compared to a conventional concrete. Meanwhile, the HSHWC compressive strength reached 106 MPa. HSHWC 's results with NSS and NCC show that the highest increase in mentioned properties was achieved by an additional 3.0% and 2.0% of NSS and NCC, respectively, by weight of cement. The γ and X-ray attenuation behaviour was improved by 3.4% and 5.3%, respectively. Further improvement of HSHWC properties was achieved by the use of 3.0% NSS and 1.5% NZ, by weight of cement which exhibited improved γ and X-ray attenuation performance by 16.3% and 25.4%, respectively. As for the results obtained from the development of HSHWC using steel fiber, the best fraction by volume is 1.0%. It improved concrete specifications, including radiation insulation. In conclusion, HSHWC which is suitable as a radiation shield and offers excellent protection from high energy radioactive emissions, such as γ and X-rays can be produced using SFSA as aggregate and with controlled inclusion of nano materials and steel fiber.

CHAPTER 1

INTRODUCTION

1.1 Overview

This section elaborates the introduction of the heavyweight concrete (HWC), its definition and historical development, as well as its functions and features, to establish the foundation upon which the whole review of the thesis is based.

1.1.1 Definition of Heavyweight Concrete and its Historical Development

Concrete can be defined as a building material invented by human beings to behave and perform as the stone does, with the additional superior feature upon the stone shaped under the human demand, according to their standards to fulfil their needs. ‘The term concrete” comes from the Latin word ‘concretus,’ meaning ‘to grow together.’ The concrete substance is a composition consisting of a coarse granular material called the aggregate embedded in a matrix of the hard binder material. The binder is the cement that glues the particles of the aggregate together by filling all the void spaces among them to give the overall shape and the final properties of the concrete.

Nevertheless, the term ‘filler’ is being used to refer to the aggregate, whereas the term ‘binder’ refers to the cement. Concrete is ‘a composite material consisting of a medium of binding in which fragments or particles of aggregates are embedded’ within the binder. Thus, the concrete’s definition can be interpreted as (Li, 2011).

$$\text{Concrete} = (\text{filler}) + (\text{binder}). \qquad \text{(Equation 1.1)}$$

In general, concrete is the main building material utilized worldwide. This fact is based on the tough basis of the cost-effectiveness of the concrete with the fascinating mechanical properties it exhibits, fulfilling the human being requirements and satisfying their goals and ambitions. The fact has produced various types of concrete, according to the elements consisting its composition to give the appropriate performance for the certain human usage. One of these types is heavyweight concrete (HWC). HWC is a very important type, most widely used as a material for reactor's shielding wall worldwide. It is commonly a mixture that consists of hydrogen and many other materials of light nuclei and high atomic number (Ikraiam et al., 2009). HWC has significantly higher bulk density compared with the ordinary concrete. By numerical values, the range of densities of HWC is 3360–3840 kg/m³, whereas the density of the normal-weight concrete is in the order of 2400 kg/m³. Such a high density qualifies this type of concrete to play a vital role in a special spectrum of purposes, and normal concrete cannot be utilized. The reason is that normal-weight concrete does not perform well and cannot fulfil the special requirements for such specialized applications. Concretes can be classified into four main categories, according to unit weight. Table 1.1 lists the main types of concretes according to the rang of unit weight (Li et al., 2003).

Table 1.1 Concrete's classification

Class	Unit Weight Kg/m³
The Ultra-Lightweight Concrete	Less than1200
The Lightweight Concretes	1200 < Unit Weight < 1800
The Normal-weight Concretes	Approximately 2400
The Heavyweight Concretes	More than 3200

Concretes with densities greater than 2900 kg/m³ is called HWC. Concrete's density can be increased using heavyweight aggregates (Topcu, 2003). The HWC's density is largely influenced by the aggregate's specific gravity and the concrete components' properties. Concrete with a density of more than 2600 kg/m³ is considered HWC. This difference in classifications for HWC densities is the result of the development of concrete performance over time as a result of the development of concrete additives. Therefore, aggregates of specific gravities of more than 3000 kg/m^3 are identified as the heavyweight aggregate, which has been set as a benchmark (EN, 2002). Historically, the progress of achieving or constructing a high compressive strength material was not rapid. Moreover, it was very idle before the 1960s when concretes of 30 MPa compressive strength were considered as high-strength concrete. After that period, the high-strength concrete's development made a huge progress due to two major factors. They are the invention of chemical admixtures for reducing the water content and the use of mineral admixtures, such as fly ash, silica fume and ground-granulated blast furnace slag in the binder phase of concrete (Caldarone, 2009).

1.1.2 HWC Functions and Features

HWC is utilized to prevent the harmful seepage from the radioactive structures, such as nuclear power plant and buildings equipped with X-ray facilities. The harmful impact of these rays on living organisms increases the risk to human safety. Protection from such rays is an obligatory requirement in a radioactive structure that may introduce exposure of human to radioactive rays, such as gamma-ray, X-ray and nuclear radiation. Given its main functions, HWC is mainly used in hospitals, such as in radiotherapy rooms, laboratories and buildings with activities that involve use of high energy nuclear radiation, nuclear reactors, nuclear power plants and storage facilities of the radioactive wastes (Li et al., 2003). Considering this overlapping state of the function and the features required, the HWC must have both high density and high strength property. In order to produce this type of concrete with such combination of features, a heavyweight aggregate need to be used as a constituent material in the concrete mix design. This aggregate must also contain a high content of material from the metallic phases with high atomic mass, such as ilmenite, hematite, barite or magnetite. These metallic phases of concrete are important to make it efficient in attenuating the high energy neutrons dissipated from radioactive sources (Akkurt et al., 2005; Akkurt et al., 2006; F. Demir et al., 2011; Mahdy et al., 2002; B Oto, 2013). These metallic phases are also widely applied since 1950s (Henrie, 1955). The aggregate containing a significant amount of heavy elements has an important impact on the improvement of the shielding properties of the resulting concrete.

Furthermore, the good shielding properties against the neutrons and photons in HWC are due to these types of aggregates (Abdo, 2002; Akkurt et al., 2012). As aforementioned, the radiation shielding properties are the main benefits of the HWC material (Gencel et al., 2011; Gencel et al., 2012). Nevertheless, the high strength of the HWC produces an additional advantage of reducing the thickness of the concrete structure element while maintaining the desired load-bearing capacity over the ordinary concrete. A prior study estimated that the use of HWC as structural material enables the reduction of wall thickness by approximately 40% when compared with the walls made from ordinary concrete(Akkurt et al., 2013). The primary objective of sustainable construction is to reduce the adverse environmental effects of the construction industry, which is the major consumer of natural resources. Waste management is a difficult and complex global issue that affects the environment. The rapid advancement of industrialization has resulted in the production of many waste by-products that harm the environment and lead to disposal concerns. Construction is one of the industries that consume these waste products in sizable amounts (Nadeem et al., 2012a). Numerous researchers have computed the number of materials created annually from iron. Every year, India generates 72.2 million metric tons of steel and produces approximately 18,000,000 metric tons of waste, but barely 25% of the material is utilized in cement manufacturing. Meanwhile, production in the European Union (EU) is at 10 million per year, of which 1.5 million per year is attributed to Spain (Beshr et al., 2003; Manso et al., 2004; Maslehuddin et al., 2003; Nadeem et al., 2012a). Steel slag is being widely disposed and utilized as a dump material; thus, it has slowly evolved into an environmental concern in recent decades (Chaurand et al., 2007). To address this issue, the EU has executed an environmental policy. EU members have recognized SFSA as a useful by-product (Liapis et al., 2015).

1.2 Problem Statement

Human safety is an urgent necessity that has led researchers to consider and find appropriate solutions that protect it from imminent radiation-related risks. One of these risks is the risk of high dose γ and X-rays exposure; so, it has been found that one of the best solutions is the use of HWC as this type of concrete can prevent and absorb these harmful radiations. The conventional HWC requires special types of aggregate which made them expensive and uneconomical to produce.

Generally, industrial waste is one of the main problems that directly affect the environment and human health in general. The disposal of the wastes from steel manufacturing industries has caused various environmental and human health-related problems. The conventional approach of landfilling of the material is unfavourable from both economic and long-term perspectives to the environment and the manufacturers.

Several challenges exist which must be addressed in the attempt to fabricate a high-strength HWC using coarse and fine steel furnace slag aggregate (SFSA). The specific problems are stated as follows.

1. There are several reports available on the production of concrete using SFSA as a partial or total aggregates replacement. Therefore, the possibility of using SFSA fine and coarse aggregates in the production of high strength heavyweight concrete (HSHWC) with low W/C ratio. However, these has been limited body of literature which was established in this aspect. In reviewing the previous studies, it became clear that there was no study of the effect of the volumetric ratio design approach of aggregates on the amount of cement and the extent of their influence on the mechanical properties and radiation insulation properties of the resulting concrete.
2. A review of the previous studies showed that there is a serious gap on the use of nano-admixtures in the production of HWC. The study on the effect of the addition of nano-silica slurry (NSS), and nano-calcium carbonate (NCC) are greatly important in determining their ability to increase mechanical and radiation isolation properties by enhancing the interfacial transition zone and an atomic number of HWC binder phase. As well as, the analysis of the previous studies showed a significant gap in the use of nano-mixtures in HWC development. Analysis of the effect of the addition of nano-silica slurry and nano-zinc oxide (NZ) is of great importance in assessing their ability to enhance the mechanical and radiation insulation properties of the HWC developed.
3. A thorough search of the existing literature showed that there is no research on the impact of using steel fiber (SF) in combination with nano additives

on the properties of HWC. Therefore, a future investigation on isolation of harmful radiation by enhancing the mechanical and durability properties of HWC via steel fiber and nano admixtures are necessary.

1.3 Research Objectives

This study focused on the physio-mechanical characterization of high-strength HWC containing steel slag aggregate. Aggregate is the major concrete component that contributes to its unit weight difference. HWC is a special form of concrete for building specialized structures like nuclear laboratories, nuclear power plants, and radiotherapy rooms where there is a need to protect people from the effects of radioactive elements.

The main aim of this research is to develop HWC that contains SFSA as fine and coarse aggregates with a high density from local by-product. It is also the aim of the study to enhance the shielding capacity of the concrete. It is done by increasing the bond of the “interfacial transition zone (ITZ) between cement paste and aggregate” using special types of admixtures like nano-silica slurry, nano-calcium carbonate, and nano-zinc oxide with very high range water reducer admixture (VHRWRA). Such approaches also increase the density of the resulting concrete. This study also aims to incorporate steel fiber to the concrete to increase its durability and to eliminate the cracks. Although the steel fiber is used in a small volume ratio, it plays an additional role by increasing the concretes’ density owing to its high specific gravity.

The detailed objectives of this research are as follows:

1. To study the optimum W/C ratio and their effect on the HWC properties and to select the optimum volumetric ratio of aggregate and cement content that enhance the physio-mechanical properties of HSHWC.

2. To establish the optimum percentage of incorporating nano-silica slurry and nano-calcium carbonate as additive by cement weight to enhance the HWC properties and shielding ability. As well as to select the optimum percentage of incorporating nano-silica slurry and nano-zinc oxide as additive by cement weight to enhance the HWC properties and shielding ability as well.

3. To investigate the possibility of improving the mechanical, durability and radiation shielding capability of HSHWC by select the optimum volume fraction of steel fiber.

1.4 Significance of Research

This research was conceived with two major concerns, i.e., saving cost and protecting human from radiation effects. Achievement of the aims and objectives of this research will usher in several benefits. However, the most significant and immediate benefit of this research is the large volume of the waste material SFSA used which will contribute to the management of this industry-related waste.

Waste materials have become a serious environmental problem which threatens human existence and concurrently influences the environmental aesthetic. Scientist nowadays still could not estimate the negative impact of the disposal of the waste as mentioned above to that particular area in future development. With the outcome of this study, SFSA will cease from being considered an industrial waste but will be considered valuable materials for the production of HSHWC through recycling processes. Hence, the possibility of such a recycling approach will encourage a wide-scale utilization of SFSA as a sustainable source in HWC production in the long term.

This research provides the insight towards the production of HWC using local aggregates, as well as the possibility of using ultra soft materials such as nano-silica slurry, nano-calcium carbonate and nano-zinc oxide with high range water reducer admixture, and steel fiber as well with the necessary tests to meet all the requirements for durability and for use in such projects.

In this research, the proposed testing parameters of HSHWC mix designs do not only focus on the ability to produce density concrete, but also on some testing parameter for the shielding properties.

Another aim of this research is to use the density concrete product in any structure that requires the attenuation of dangerous radiations in order to protect human from carcinogenic radiations, especially in nuclear power stations and used in retaining wall as well.

1.5 Scope of Work

The scope of this study is given as follows:

1. Evaluation of the physicochemical properties of the HWC materials.
2. Assessment of the properties of the HWC.
3. Utilization of the ACI Absolute volume design method to optimize the important HWC production parameters, such as the concentration of the

superplasticizer used to reduce the w/c ratio drastically and to get optimum mix proportions.

4. Examination on the effect of the employed nano admixtures on the durability, shielding, mechanical and physical properties of the produced HWC.
5. Study on the ability of steel fiber to improve the properties of HSHWC.
6. Investigation of the microstructure development of the HSHWC mixtures.

The chemical properties assessment of HWC includes studies on the chemical constituents and mineralogical phases, while studies on the particle morphology, particle size distribution, specific gravity, and specific surface area of the HWC made up the physical properties' assessment.

Concrete is usually evaluated based on mechanical properties, such as compressive strength, splitting tensile strength, and others. After evaluating the results of these tests, the optimal ratios for the materials used can then be determined. It is achieved in this research by studying the overall characteristics of the ratios that achieved the best density and evaluating the ratios of the optimal additives and the extent to achieve the required specifications. It also involves studying the properties of concrete under the effects of radiation harmful to human health.

The evaluation of HWC will be done by examining the microstructure (interfacial transition zone) and the efficiency of the ultra-fine materials (nano-silica slurry, nano-calcium carbonate and nano-zinc oxide) in achieving optimal bonding, thus achieving high density and optimal interconnection to reduce and prevent radiation penetration, and improve the durability of the concrete. Meanwhile, the same tests and the applications of the final HSHWC steps, reinforced with steel fiber were evaluate.

1.6 Limitations of The Study

This work was carried out to study the use of steel furnace slag as the main aggregate to produce high-strength heavyweight concrete. However, there are some limitations of the study than can be highlighted. Firstly, the incorporating of nano materials to enhance the heavyweight concrete properties. Other types of nano materials have not been used in the study. Secondly, the percentages of the nano materials were incorporated with a raise step of 1.0% for NSS and 0.50% for NCC and NZ. However, this raise step can be adjusted and more percentages of different nano materials can be used. Thirdly, the use of steel fiber in heavyweight concrete to increase general specification. There are other steel fiber type and size can also be used for the evaluation of the produced HWC. Lastly, the use of other than aggregate such as other types of by-product aggregate or any natural heavyweight aggregate can be tested in the heavyweight concrete to evaluate their performance as shielding concrete and compare them with the steel slag heavyweight concrete used in this study.

1.7 The Layout of the Thesis

The thesis consists of seven chapters. Chapter (1) presents the introduction of heavyweight concrete as a general research introduction. Meanwhile, the problem statement, research objectives, the research significance and the scope of the work are also discussed in depth. Chapter (2) covered a literature review concerning the constituents, properties and application of HWC. The physical properties, chemical composition of SFSA and the properties of concrete containing SFSA is provided. The modern HWC shielding principles, industrial applications and future challenges are discussed as well. Chapter (3) presented the experimental program parts, properties of the materials used, the mix design and procedure of testing. The results and discussion of the HSHWC by reduced the W/C ratio are discussed in chapter (4). Also, this chapter includes the presentation of the test results and discussion on the HSHWC with different aggregate volumetric ration. Whereas, chapter (5) presents the test results and discussion of HSHWC enhanced by nano materials. In chapter (6), the HSHWC results and discussion reinforced by steel fiber are discussed as well. The conclusions of the thesis and the recommendations for further research works are summarized in chapter (7).

CHAPTER 2

LITERATURE REVIEW

2.1 Overview

This part of the research is concerned with presenting previous studies and the latest research findings regarding HWC. The topic will focus to highlight three main goals cover the old findings and the latest HWC development as well. The first district is concerned with the constituents, properties and application of HWC. The second stage is concerned with listing the physical properties, chemical composition of steel furnace slag aggregate and the properties of concrete containing SFSA. The third stage is the modern HWC shielding principles, industrial applications and future challenges. This part of the research is not limited to presenting previous studies only, but is concerned with presenting the final outcome and shedding light on the most important findings of the researchers, as well as what are the scientific gaps that must be addressed in the present and future studies.

2.2 Introduction

The metallurgical waste from iron and steel manufacturing is the main interest area related to the management of industrial waste. Such waste is often processed then returned to production (reuse), and a certain amount of the waste can be used as a secondary raw material by other industries (recycling). However, substantial quantities of such waste have to be disposed and landfilled in factory grounds. The dumping of metallurgical waste in landfills adversely affects the environment (Sofilić, 2010). Thus, reducing the amount of steel and iron waste has become a core objective in the manufacturing of sustainable steel. The utilization of slag from steel and iron manufacturing as a raw material in other industries provides considerable environmental advantages because of the benefits of recovering or reusing this slag. SFSA is a typical waste generated during extraction of metals in steel and iron manufacturing. It is a by-product of pig iron and scrap metal smelting in electric arc furnaces (Yüksel, 2017). Previous research has shown that SFSA can be used to replace natural aggregates entirely or partially (Coppola et al., 2016; Faleschini et al., 2016; Faleschini et al., 2015; Lim et al., 2019; Rondi et al., 2016). The use of SFSA as aggregate enhances the durability and mechanical strength of concrete. However, the addition of SFSA degrades concrete’s workability (P. Awoyera et al., 2015; P. O. Awoyera et al., 2016b; Etxeberria et al., 2010) and dimensional stability (Arribas et al., 2015; Maslehuddin et al., 2003; Santamaría et al., 2018). Moreover, the chemical composition, physical properties and mineralogical properties of raw SFSA differ substantially depending on the source.

Nano concrete is ideally classified as a concrete with nanomaterials of less than 500 nm in particle size. Nano concrete shows significantly higher mechanical properties compared to traditional concrete. The reasons for improving the properties can be clearly described as nanomaterials manipulate the structure of the cement matrix at the nano-level. Nanoparticles act as a superb filler and enhance the packaging model structure, as well as refining the intersection zone in cement and creating a more tightly packed microstructure (Jindal et al., 2020; Chao Liu et al., 2018; Norhasri et al., 2017; Singh et al., 2018). Nanotechnology is the study of phenomena and the fine-tuning of atomic, molecular and macromolecular scales of materials, where properties vary considerably from those at a larger scale. It is also considered to be the most recent development in the field of material science & technology. With nanotechnology’s excellent economic impact and consumer potential, efforts have been geared towards exploring and developing the field in recent decades. (Drexler et al., 1991; Said et al., 2012). Evidences from recent studies (Damtoft et al., 2008; Ismaeel, 2013; Ismaeel et al., 2013; Said et al., 2012) suggest the possibility of using novel technologies to achieve significant industrial breakthroughs, especially in the production of supplementary cementitious materials. Nanotechnology has been approved as a promising field of research that has the potential of significantly improving mix designs, production, and performance of cement-based materials.

Nano-silica is one of the nanotechnology material with a great potential for concrete application. There two basic forms of nano-silica (NS) are densified dry grains and colloidal suspension. For dry nano-silica, a particular preparation technique is required before mixing to achieve even distribution of nanoparticles within the solvent. Colloidal nano-silica, on the other hand, is produced as a suspension that has been stabilized with a dispersive agent. It is available in a ready-to-use suspension form (Campillo et al., 2004). A study reported by (Said et al., 2012) suggested that the addition of colloidal nano-silica to mortar mixtures improved the behaviour of the mix by a greater extend when compared to that of dry grained nano-silica. The improvement in behaviour upon the addition of colloidal nano-silica was attributed to the low agglomeration rate of the colloidal nano-silica in the mixture, which improved their dispersion as compared to the dry nano-silica.

Since the introduction of nanomaterials, it has received much research attention and has been seriously explored in terms of the effects of nanosized materials on the properties of concrete and their potential applications. It has also been reported that numerous nano-additives achieved better performances as compared to their micro counterparts. For instance, the incorporation of nano-silicon dioxide (SiO_2) (particle size = 40 nm) into a concrete mixture has been reported to improve the early-age compressive strength of the resulting concrete by about 2 folds as compared to a concrete mix containing silica fume (0.1 µm) (Jo et al., 2007). Despite a large number of studies on the effects of ultrafine $CaCO_3$ particles, only a few studies have focused on the effects of introducing nano-calcium carbonate (NCC) into concrete mixtures, as well as their potential benefits & applications, especially in UHPC (J. Camiletti et al., 2013). Limestone powder is another common supplementary material that is mainly used as a micro filler material to improve the rheological property of concrete. Although the capability of limestone powder to influence cement hydration has been proven, numerous studies (Bentz et al., 2012; Ghrici et al., 2007; W. Li et al., 2015) have shown that its presence in concrete mixtures can facilitate early-age hydration. Notably, most of the existing studies have focused on micro-sized limestone powders, with less focus on the nanosized $CaCO_3$. Studies by (P. Balaguru, 2005; Kawashima et al., 2013; W. Li et al., 2015) suggested that silica fume & limestone powders can be co-applied as an additive for the strengthening of cement-based materials. The flexural and compressive strength capacities were enhanced with nano-SiO_2 and nano-$CaCO_3$. The mechanical strength was improved as the content of NS and NCC increased towards the threshold content. The strength decreased with the increase in NS and NCC contents when the threshold was exceeded. However, the possible effects of such co-application on the performance of high-performance HWC are yet to be investigated. As the nanomaterials work to encapsulate the cement particles and work by filling in the nano voids to strengthen the transition zone of the interface, this has led to an increase in the matrix density for the resulting concrete. ZnO nanomaterials are applicable in many areas, such as in drug deliveries, electronics, optics, cosmetics, photocatalytic-based organic pollutants degradation, radiation insulating dyes, steel bars protection from corrosion, etc. (Abdullah et al., 2020; Andrade et al., 2017; Mohamed et al., 2019; Saraswathy et al., 2007; Takai et al., 2019; Wozniak et al., 2017). The research interest in ZnO nanomaterials can be attributed to their unique physico-chemical characteristics, such as high photosensitivity, electron mobility, & chemical stability. They are also abundant, robust, non-toxic, and low cost materials(Umar et al., 2011).

Studies have recently been conducted on the use of nanomaterials in improving the performance of HWC in terms of increasing high energy radiation isolation, strength and physical properties. Researchers have used nano-TiO_2 (Nikbin et al., 2019b), nano-ferrite (Tobbala, 2019b), and nano SiO_2 with barite aggregate (Janković et al., 2016). The results demonstrated the positive effects of nanomaterials in improving all the properties related to HWC. Therefore, the employment of nanomaterials in HWC is desirable to improve the degree of impermeability of the material.

2.3 Materials for Making HWC and Factors Influencing its Properties

A careful selection of components and the proportioning of the mix is a more critical process in HWC fabrication than the conventional concrete mixes. Each constituent material of the HWC (cement, coarse aggregate, sand, admixtures and pozzolans) should be evaluated and considered according to type, amount, density, strength characteristics, fineness, gradation and the interaction of the elements with each other in the combination (Li, 2011). The constituent materials and design considerations of the HWC are discussed as follows.

2.3.1 Water Content and Water/Cement Ratio

An important property of the concrete is water to cement (W/C) ratio. In contemporaneous concrete, this ratio is usually replaced by the water/binder (W/b) or the water/powder (W/P), because the binding material is not the Portland cement only. The W/b or W/P ratio is the predominant factor influencing the concrete's properties, such as the compressive strength, the permeability and the diffusivity. Low W/C ratio increases the strength and durability of concrete. The influence of the W/C ratio on the compressive strength of concrete is known since the early 1900s (Abrams, 1927).

Meanwhile, the weight of the aggregate is the major important variable in the total unit weight of the concrete, and the W/C ratio is also one of the most important factors in preparing high strength HWC (Rashid et al., 2009). Previous studies showed that the preferred W/C ratio for the HWC is 40% by binder content, in which the water specified to the concrete is of potable quality (Li et al., 2003). A thorough review of contemporary literature related to HWC reveals a scarcity of research in decreasing the W/C ratio of HWC for density improvement to a degree where it can be considered as a gap of knowledge in this field of study.

Nevertheless, the ratios used for the W/C are ranging in the limited range between 35% and 50% of the total binder’s weight (Facure et al., 2007). Topcu (2003) used barite aggregate in his work instead of the traditional aggregate of silico-calcareous origins as a means to increase the unit weight of the concrete. Then, he prepared various compositions of concrete at different W/C ratios to identify the most favourable W/C ratio for the high-density concrete prepared using the barite. The conclusion was the most optimum W/C ratio for fabrication of heavyweight barite concrete is 0.40.

2.3.2 Cement Content

The cement paste is formed when water is added to a mix of concrete. The cement paste accomplishes three main functions, namely, binding, coating and lubricating. It binds reinforcing bars, individual aggregates and fibers to produce a unique composite material. It also covers the concrete’s surface by immersing the aggregates and fibers, forming the outer shape of the concrete during the fresh stage of concrete. The high levels of paste can make the aggregates, or the fibers move easily as if it is a lubrication agent. Cement content affects the workability of the concrete in the fresh state, the rate of heat release at the hydration stage and the volume stability in the hardened stage. Cement content in the mass concrete ranges between 160 and 200 kg/m³, whereas it is lower than 400 kg/m³ for the normal strength concrete and ranges between 400 and 600 kg/m³ in the high strength concrete (Li, 2011). The most important point of the cement content in the HWC is that it must be high enough to prevent the radioactive seepage and low enough to overcome the shrinkage effect which may cause an unwanted split in the concrete structure under restrained condition. As such, the recommended cement content should be above 350 kg/m³ for HWC. Studying the composition and the fineness of the cement and its compatibility with the chemical admixtures used for producing high strength and maintaining good workability of HWC at the same time are essential (Celik et al., 2015). Technically, HWC can be produced with any Portland cement, but the cement derived from coarsely ground clinker are unsuitable for making HWC (Horszczaruk et al., 2015; Ikraiam et al., 2009). The most suitable cement type used with the HWC is the ordinary Portland cement 'ASTM TYPE I.' The cement content is an important consideration in HWC, with minimum cement content requirement of 300 kg/m³ (Papachristoforou et al., 2018), whereas another radiation shielding concretes produced with barite, magnetite, or the bismuth oxide (Bi_2O_3) need high cement contents of 400 kg/m³ to 490 kg/m³ to reach such a level of strength (Gencel et al., 2011; Ouda, 2015; Y. Yao et al., 2016). The barite aggregate was used to prepare several high-density concretes produced with different W/C ratios. Thus, the cement dosage should be higher than 350 kg/m³ (Topcu, 2003).

2.3.3 Aggregate

Aggregate is the most important factor which influences the concrete performance and density significantly in both the fresh and the hardened states. The selection of an appropriate aggregate is important for all concrete structures because the aggregate possesses the largest amount of any other constituents in the concrete (Li, 2011). Several aggregate properties, such as specific gravity, chemical composition, mineral composition, hardness and strength, depending on the parent rock's properties (A. M. Neville, 2011). Each of those properties plays a significant role in forming the final HWC quality. Gradation of the corresponding particle size distribution and packing density of the combined aggregates in use represent the most important parameters among the parameters which influence the HWC performance. A good gradation of aggregate improves the important properties, such as modulus of elasticity, strength, shrinkage and creep. The particle shape and the surface texture are among the other important parameters influencing the packing efficiency. Great considerations are required for HWC at selecting coarse and fine aggregates with the suitable particle geometry. The consideration in the selection of the aggregates for the HWC includes balancing the water content demand and the potential of the paste to bind the aggregate (Li, 2011; Nadeem et al., 2012b). The concrete components including aggregates are based on the exact calculations of the HWC compositions by volume. Some natural minerals, such as barite, limonite, magnetite, hematite and borate colemanite, are used as HWC aggregates. Besides, some other artificial aggregates which include materials, such as the iron shot, steel punching, hydrous iron ore and bauxite, are employed as HWC aggregate (Gencel et al., 2011; Gencel et al., 2012; Lotti et al., 2019). The HWC properties, such as density and strength are influenced significantly by the coarse aggregate's characteristics. The physical and chemical aggregate phase features become a more important consideration for the HWC than the normal concrete. The reason is that the strength of the coarse aggregate, the adhesion or bond between the paste and the coarse aggregates and the coarse aggregate absorption characteristics significantly influence the properties of the resulting HWC. Therefore, each of these properties can be a limiting factor for ultimate strength which can be achieved (Ouda, 2015). Fine aggregate's particle shape and grading are the significant factors in producing HWC. For fine aggregate, particle shape and surface texture may have the same or great effect as the coarse aggregate on the water requirements and the compressive strength of HWC (T.-C. Ling et al., 2012b; Ouda, 2015).

2.3.4 Admixtures

Admixtures for concrete, mortar or paste are inorganic (including minerals) or organic materials in solid or liquid state, added to the normal components of the mix, in most cases up to a maximum of 5% by mass of the cement or cementitious materials. The admixtures interact with the hydrating cementitious system by physical, chemical or physio-chemical action, modifying one or more properties of concrete, mortar or paste, in the fresh, setting, hardening or hardened state. These materials are produced via chemical processes to accomplish its role in the concrete as an important component. The American Concrete Institute (ACI) committee 212.2R reported that the admixtures function as a modifier to the concrete's properties, either for improving the workability or for the economy or for other purposes, to improve the strength of concrete (Lewis, 1981). The major admixture types are two, namely, mineral and chemical.

2.3.4(a) Chemical Admixture

The superplasticizer (SP) or the 'High Range Water Reducer' is one chemical admixture widely used in concrete. Its utilization gives positive effects on the HWC properties, both in the fresh state and in the hardened state. In fresh state, superplasticizer normally reduces the tendency of bleeding as a result of reducing the W/C ratio, i.e. reducing the water content in concrete. However, if the W/C ratio is fixed, the superplasticizer prolongs the time consumed to set as abundant free water is made available for lubricating the mix. In hardened state, superplasticizer utilisation increases the compressive strength via the enhancement of the compaction effect to produce a dense concrete microstructure (Nadeem et al., 2012b; Yamakawa et al., 1990). Superplasticiser is utilised in the concrete for three purposes: increasing the workability for a constant W/C ratio, i.e. increasing slump for making a flowing concrete, reducing the W/C ratio for a constant workability, i.e. increasing the strength for making a high strength concrete, and reducing the cement content while maintaining both the W/C ratio and the workability (Kazjonovs et al., 2010; Song et al., 2004). The utilization of superplasticizers can improve the concrete's flowability through their actions of liquefying and dispersing the cement particles. As such, superplasticizers deflocculated the cement particles and freed the trapped water through dispersion, thus improving the 'high-performance heavyweight concrete' (HPHWC) flowability. The dispersing action reduces interparticle friction, decreasing the flow resistance and enhancing the concrete flowability. The admixtures adsorb on the cement surfaces, breaking up flocs to leave individual cement as individual grain, thus increasing the mix fluidity, as shown in Figure 2.1 (Dransfield, 2003; Ouda, 2015). Given this regular distribution, a well-bonded HWC, which is free from excessive pores and is, therefore, a very good barrier for harmful radiation, is produced.

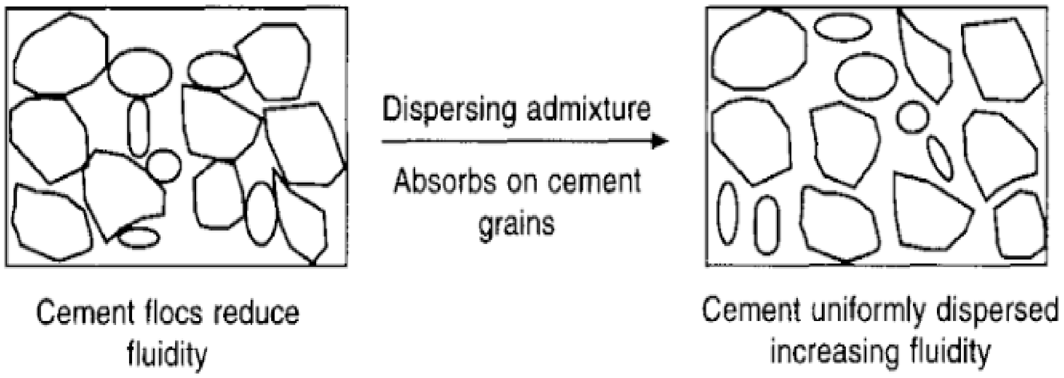

Figure 2.1 Dispersing admixtures impact on breaking up cement flocs, Adapted from (Dransfield, 2003)

2.3.4(b) Mineral Admixtures

Basically, concrete is the mixture consisting of the Portland cement, the coarse aggregates, the sand and water. Portland cement is the principal cementitious material in concrete. Nevertheless, most cementitious mixtures comprise of additional cementitious materials in the form of the supplementary cementitious component in the concrete. The supplementary materials of cement may be referred to as the mineral additives. These materials have to meet the established standard requirements, in which they are being used to improve the concrete performance in the fresh and the hardened states. Supplementary materials, such as the silica fume, the fly ash and the ground granulated blast-furnace slag (GGBS) enable the concrete industry to utilize hundred million tons of the industrial by-product materials which may otherwise be disposed in landfill.

Moreover, the supplementary materials minimize the consumption of Portland cement per unit volume of concrete. The high quantities of energy and carbon dioxide emissions of Portland cement resulting from manufacturing decreased due to the reduction of the amount of cement used in the concrete (Yılmaz et al., 2011). Another subclass for supplementary cementitious material is pozzolana, which is a material of silica or of aluminium and silica, which reacts chemically with $Ca(OH)_2$ in moisture presence to produce a strong material of cementing property, i.e. C-S-H gel. Therefore, pozzolans minimize the concrete's weak bonds, consequently consolidating the concrete, increasing the durability against the chemical attack and decreasing the permeability as a result. These materials are the silica fume, the fly ash and the GGBS (Nassif et al., 2003; Shah et al., 1994).

2.3.1(b)(i) Silica Fume

Silica fume also called the condensed silica fume, or the micro silica is used widely as an addition to the concrete for producing a high-performance and high-strength concrete. It is a by-product from reducing the high purity of quartz by wood chips and coke or coal in the electric arc furnace within the process of producing the ferrosilicon alloys or the silicon metal (Celik et al., 2015). Silica fume consists of very small spherical particles 'smaller than 0.1 μm' of amorphous silicon dioxide. The fine silica fume particle is beneficial for the concrete because they can fill the voids among the large cement particles and primary C–S–H gel network of Portland cement, producing a dense cement paste matrix. The use of any very small particles improves the concrete properties. Silica fume maximizes the concrete's strength significantly because it maximizes the bond strength between the aggregate particles and the cement paste. Even the small additions of the silica fume (2%–5%) affect the interfacial transition zone by producing a dense structure, with an increase in the fracture toughness and the microhardness (Nawy, 2000). The ACI committee 234R (1996) estimated that for every 15% of silica fume in cement, approximately 2,000,000 of silica fume particles exist for each Portland cement grain, as shown in Figures 2.2 and 2.3 (Holland et al., 2000).