# EDS Microanalysis of Blast Furnace Slag Grains in Aged Concrete

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by

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### மாற்றங்கள் வினா, மாற்றங்களே விடை!

Change is the question, You adapting to it is the answer.

In loving memory of my Grandmother, Thank you for being the strongest person I know. I miss you.

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Kural, 108

#### நன்றி மறப்பது நன்றன்று நன்றல்லது அன்றே மறப்பது நன்று

(Tis never good to let the thought of good things done thee pass away Of things not good, tis good to rid thy memory that very day) - Thiruvalluvar

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### Abstract

The chemistry of ground granulated blast furnace slag (GGBFS) is one of the main factors affecting its reactivity. Knowing the composition of GGBFS used in aged concrete may help understand its past performance and estimate remaining service life. It is well known that GGBFS generally react slower than cement clinker. This thesis proposes that partially hydrated GGBFS grains found in aged concrete could be used to determine its chemical composition. The feasibility of using standard-based energy dispersive X-ray spectroscopy (EDS) microanalysis, along with electron imaging, as a tool for quantitative measurement of the chemical composition of GGBFS grains in cement/concrete is explored in this research. X-ray spectra collected from minerals or glasses of known composition are known as standards for quantitative EDS microanalysis. This study initially examined the performance of mineral and slag standards to quantify X-ray spectra obtained from GGBFS-cement paste specimens of known composition. Parameters such as GGBFS properties, experimental conditions, and microanalysis methodologies that affect the EDS quantitative total and accuracy were elaborated. Then, the same standards were used to quantify the unknown composition of GGBFS used in seven concrete specimens collected in the Netherlands representing different service life, which revealed the variation in GGBFS chemistry over the years. Finally, as a supplementary study, the variation in significant hydration products formed due to variation in GGBFS composition in a cement-GGBFS system was predicted using thermodynamic modelling with GEMS. Altogether, it was concluded that standard-based EDS is a solid tool to characterize the chemical composition of GGBFS used in aged concrete.

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### Introduction

In the last century, blast furnace slag (BFS) cement in concrete has become an increasingly popular alternative to ordinary portland cement (OPC) due to its durability, sustainability, and cost-effectiveness. It is made by partially substituting ground granulated blast furnace slag (GGBFS), a by-product from the iron industry, into the cement mixture. Depending on the type of cement, the ratio of GGBFS used can vary between 6% and 95% [1]. With a market share of 70% for CEM III type cement (35% to 95% GGBFS substitution) and more than a century of experience, the Netherlands has been the forerunner in using GGBFS substituted cement [2]. Due to its resistance against chloride-initiated corrosion, sulfate resistance and alkali-silica reaction, structures built with GGBFS cement are proven durable even in the harshest marine conditions, especially in the Netherlands.

The chemical composition of GGBFS has varied notably over the years, according to several industrial reports depending on the raw materials and metallurgical technology used to process iron [3], [4]. Industrial experts in the Netherlands have recently observed several new structures built with GGBFS cement showing performance issues. They have come to a consensus that contemporary GGBFS composition is likely to be the source of this issue [5]. Moreover, there are claims that surface durability issues are partly brought on by the recent changes in GGBFS chemistry and quality [6]. Since these claims and observations are purely based on experience, scientific evidence is needed for validation.

Knowing the chemical composition of GGBFS in well-performing aged concrete could be useful for estimating its service life and designing modern GGBFS-rich concrete. But, obtaining the composition of materials used in older concrete structures is often futile since material quality control reports are generally discarded after a few years. Available bulk material composition characterization techniques such as X-ray fluorescence spectrometry (XRF) and inductively coupled plasma-mass spectrometry (ICP-MS) cannot be used to quantify partially reacted GGBFS due to high interference from other phases in concrete. To address this challenge, energy-dispersive X-ray spectroscopy (EDS) microanalysis using a scanning electron microscope (SEM) was proposed as a favourable technique to quantify the composition of the partially hydrated GGBFS in cement-GGBFS concrete.

Scanning electron microscope-energy dispersive X-ray spectroscopy (SEM-EDS) microanalysis is a versatile and non-destructive technique that allows for high-resolution imaging and semi-quantitative (standardless) and quantitative (standard-based) elemental analysis. The SEM generates an electron beam that is focused onto a sample surface, producing a variety of signals, such as secondary electrons and backscattered electrons, that can be used to generate high-resolution images of the sample surface and characteristic X-rays. The EDS detector integrated with the SEM detects these X-rays rapidly. It allows for the accurate analysis of the elemental composition of the sample under study using quantitative microanalysis [7]. It is carried out by comparing the intensity of the spectrum of the unknown sample with that from standards of known composition measured under identical conditions. In the past, SEM-EDS microanalysis in cementitious material research has been successfully used in durability-related characterization [8]–[10].

#### 1.1. Aim and objectives

The main aim of this study is to explore the feasibility and establish a protocol to apply SEM-EDS microanalysis methodology for quantitative measurement of the chemical composition of GGBFS using partially hydrated GGBFS grains in cement/concrete. To reach this goal, the following sub-objectives were identified.

The SEM-EDS methodology was proposed considering two sets of standards, namely, mineral standards and slag standards. Using cement-GGBFS paste samples of known concentration, the first sub-objective is to evaluate the performance of available mineral standards to quantify all the elements in an X-ray spectrum obtained from partially hydrated GGBFS. Besides this, the next sub-objective is to study the potential to use raw GGBFS as a standard to quantify elements in partially hydrated GGBFS. Based on the performance of these two sets of standards, the subsequent sub-objective is to use these standards to quantify the chemical composition of GGBFS used in aged concrete obtained from the field with different service life. The last sub-objective was to study the variation in hydration products formed due to the variation in chemical composition using thermodynamic modelling.

#### 1.2. Scope and significance

In this thesis, CEM 42.5 N (manufactured by ENCI B.V.), commercial GGBFS (provided by Ecocem Benelux B.V.) and synthetic GGBFS covering the broad composition range of GGBFS used in the field were produced in the laboratory were used for the cement-GGBFS paste samples. This research considered the characterization of raw and partially hydrated GGBFS through EDS microanalysis methodology, which is highly sensitive to various experimental parameters. So, the research findings should only be considered in relation to the materials, equipment, and methods used in this study.

The findings of this research might help to understand the relation between GGBFS composition and the long-term durable performance of cement-GGBFS concrete by determining the composition of GGBFS in aged concrete using the proposed SEM-EDS methodology. The research used several cement-GGBFS concrete samples of different service life obtained from random locations in the Netherlands. Quantifying the composition of GGBFS used in these samples would reveal the variation of GGBFS chemistry over time in the Netherlands. Overall, this work could pave a standardised methodology for using quantitative SEM-EDS to study cementitious materials.

#### **1.3. Thesis outline**

The report is divided into six chapters, and the contents of each chapter are summarized as follows.

The current chapter (Chapter 1) introduces the research background, objective, and scope of the work. In Chapter 2, a systematic literature review of the history of slag, the production process, its properties and reactivity is given. Followed by this, a brief description of SEM, its principle, and the basis for microanalysis is discussed with a summary of past applications in concrete technology.

Chapter 3 explores the feasibility of using EDS microanalysis as a tool to characterize partially hydrated GGBFS in the cement matrix. This chapter elaborates on the SEM-EDS microanalysis protocol. It explains in detail the performance of characterization methods and the mineral standards and slag standards used to quantify the samples of known composition.

In Chapter 4, the methodology formulated in the previous chapter is applied to concrete specimens. The variation in the chemical composition of GGBFS used in the industry is studied, and The potential pitfalls of using SEM-EDS microanalysis are elaborated.

Chapter 5 elaborates on the hydration phase assemblages predicted using thermodynamic modelling for variation in the composition of the four principal oxides in GGBFS. The important hydration products that affect the performance of GGBFS used in cement-BFS binders are studied.

Finally, Chapter 6 presents the conclusions from this research followed by the recommendations for future work. The list of references used to compare and analyze the data gathered for this study is provided at the end of the report,

 $\sum$ 

### **Literature Review**

This chapter describes the characteristics of GGBFS. First, the history of the usage of BFS cement is presented, followed by a brief explanation of the production process of GGBFS. Next, a comprehensive review of the various properties of GGBFS and its reactivity is discussed. Then, the essential concepts of scanning electron microscopy and microanalysis are summarized. Finally, the current state-of-the-art regarding the use of SEM-EDS microanalysis in concrete technology is presented.

#### 2.1. Ground-granulated blast furnace slag

#### 2.1.1. History of BFS cement in The Netherlands

BFS cement has been used for over a century in Europe and mainly in the Netherlands [11]. Emil Langen first discovered the latent hydraulic property of GBFS in 1862 [4]. The first recorded production of BFS cement was in Germany in 1892 [12], and it had acquired treatment equal to that of OPC in 1917. However, the acceptance and use of BFS cement in the Netherlands took longer. Initially, the use of GGBFS in cement was mistrusted, and according to the Dutch Reinforced Concrete Regulations (Gewapend Beton Voorschriften(GBV)) of 1918, it was explicitly forbidden in the Netherlands. Nevertheless, in the 1920s, GGBFS cement imported from Germany was partly used to construct North Sea canal locks at Ijmuiden, where it showed better performance in marine conditions. Subsequently, the attitude of GBV towards BFS cement changed considerably over the years. The GBV of 1930 allowed the use of BFS cement, only if the client and contractor agreed to it in advance. In 1931, Dutch portland cement(PC) producer ENCI and Dutch iron and steel producer Hoogovens established CEMIJ to produce BFS cement has increased rapidly. Eventually, in GBV of 1962, the contractor was allowed to freely choose the type of cement for use without any obligations [11], [13], [14]. Currently, about 10 million cubic metres of cement-GGBFS concrete is produced in the Netherlands annually [15].

#### 2.1.2. Production of ground-granulated blast furnace slag

BFS is a by-product of the ironmaking industry. The raw materials used in the ironmaking process are iron ore, coke and fluxing stone. The use of flux here makes the impurities in the raw materials fusible and provides a substance where more impurities may combine in preference to the metal. Limestone and dolomite are used as basic fluxes that supply lime (CaO) and magnesia (MgO), which at around 1400 -1500 °C during smelting, react and combine with the acidic impurities silica (SiO<sub>2</sub>) and alumina (Al<sub>2</sub>O<sub>3</sub>) in the iron ore to form molten BFS. Depending on the cooling regimes, four distinct types of BFS products can be formed: air-cooled slag, granulated slag, expanded or foamed slag and pelletized slag. To obtain GGBFS, the molten BFS is solidified by quick water quenching to prevent crystallization and to form a granulated vitreous material that is ground to a similar fineness as cement. This material presents latent hydraulic properties and reacts similarly to PC in a highly alkaline environment [16].

#### 2.1.3. Properties of GGBFS

GGBFS is off-white in colour, rough, angular in shape, has a specific gravity value between 2.85-2.95 and bulk density varying between 1050-1375 kg/m<sup>3</sup> [16]. According to BS EN 15167-1 [17], the minimum specific surface area (fineness) of GGBFS determined by Blaine's air permeability method should be  $275 \text{ m}^2/\text{kg}$  when added as a supplementary cementitious material. In practice, this value varies between  $350-550 \text{ m}^2/\text{kg}$ ; consequently, the average particle size varies between 9  $\mu$ m to 16  $\mu$ m [18], [19] which is limited by economic and performance considerations. The reactivity of GGBFS increases with an increase in specific surface area [20].

According to BS EN 15167-1 [17], GGBFS must contain at least two-thirds by mass of glassy phases for its use in cement. For the high performance of GGBFS in blended cement, more than 90% of reactive amorphous glassy phases is preferred [11]. The structure of glassy phases is a supercooled liquid silicate in which a few network-forming Si-O-Si covalent bonds are broken and neutralized by metal cations called network modifiers. Dron and Brivots model suggests that the network-forming atoms are in straight or branched chains of various lengths [21]. Four-coordinated network formers, such as  $SiO_4^{4-}$ ,  $AlO_4^{5-}$ , are isolated or polymerised with bridging oxygen atoms. The negative charges of these anionic groups are neutralized by six coordinated network modifiers, such as  $Ca^{2+}$ ,  $Al^{3+} Mg^{2+}$ ,  $Mn^{2+}$ ,  $Na^+$ ,  $K^+$  [22], [23]. The remaining crystalline fraction in GGBFS commonly consists of mellite, a solid solution of gehlenite and akermanite and some traces of pseudo-wollastonite (SC), rankinite (C<sub>3</sub>3S<sub>2</sub>), merwinite (C<sub>3</sub>MS<sub>2</sub>) monticellite (CMS) and oldhamite (CaS) [23], [24]. Despite being inert, the presence of crystalline phases like merwinite up to 5% has been observed to improve the reactivity of GGBFS as they provide mechanical stress in the glass and nucleation sites for hydration products [21], [25], [26].

The composition of GGBFS varies over region and time, depending on the metallurgical technology, and the type and quality of ores, fluxing stone, and coke used in the metallurgical process [4], [23]. Table 2.1 and table 2.2 show the range of GGBFS composition from different periods and different regions, respectively. According to BS EN 15167-1 [17], GGBFS must contain at least two-thirds by mass of the sum of CaO, SiO<sub>2</sub> and MgO and the mass of MgO should not exceed 18%. Typically, more than 95% of GGBFS is made up of CaO, SiO<sub>2</sub>, MgO, and Al<sub>2</sub>O<sub>3</sub> compounds with minor quantities of TiO<sub>2</sub>, MnO, FeO, S<sup>2-</sup>, Na<sub>2</sub>O, and K<sub>2</sub>O. Figure 2.1 illustrates the position of GGBFS between cement and fly ash in the CaO-SiO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> ternary diagram with other common supplementary cementitious materials [27]. The chemical composition of highly amorphous GGBFS is microscopically homogeneous whereas highly crystalline GGBFS is heterogeneous [28], [29].



Figure 2.1: CaO-Al<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> ternary diagram of cementitious material [27]

Table 2.1: Typical composition range of BFS over the years [3]

	1949	1957	1968	1985
CaO	34-48	31-47	32-44	34-43
$\mathrm{SiO}_2$	31 - 45	31-44	32-40	27-38
$Al_2O_3$	10-17	8-18	8-20	7-12
MgO	1 - 15	2-16	2-19	7-15
FeO or $Fe_2O_3$	0.1-1.0	0.2-0.9	0.2-0.9	0.2 - 1.6
MnO	0.1-1.4	0.2-2.3	0.2-2.0	0.15 - 0.76
$\mathbf{S}$	0.9 - 2.3	0.7-2.3	0.6-2.3	1.0-1.9

1949 (22 sources); 1957 (29 sources); 1968 (30 sources) and 1985 (18 sources).

Table 2.2: Typical composition range of BFS in different regions [4]

	North	Central	Western	Eastern	India, Japan,
	America	America	Бшоре	Europe	RSA RSA
CaO	34.6-39.9	33.5 - 34.8	32.0-39.4	33.5-41.5	32.6-36.9
$SiO_2$	35.3 - 42.8	39.1 - 43.8	34.9-44.3	36.9-47.5	33.0-43.0
$Al_2O_3$	6.6 - 11.5	10.0-13.0	9.5 - 12.5	5.5 - 12.4	10.2-19.3
MgO	7.0-13.1	5.9 - 9.9	5.0 - 13.4	2.5-11.2	4.9-13.8
$\mathrm{TiO}_2$	0.3-0.8	0.5 - 0.6	0.4-1.3	0.2-1.3	0.6-2.1
$Na_2Oeq$	0.3-0.8	0.4-0.8	0.3-1.2	0.6-1.1	0.4-0.8
$SO_3$	2.0-3.0	1.1 - 3.7	2.0-4.5	1.6-3.8	1.7-4.0

#### 2.1.4. Reactivity of GGBFS

Several attempts have been made to employ ratios of the metal oxides in GGBFS to assess its reactivity. Hydraulic activity or hydraulicity of GGBFS is broadly favored by more basic composition with the existence of alkaline activators [21]. A simple basicity index of GGBFS is defined as the ratio of the mass of CaO to SiO<sub>2</sub>. Generally higher the basicity, the more soluble the GGBFS and thus more reactivity [23]. According to BS EN 15167-1 [17], it is required that the ratio of the mass of CaO plus MgO to the mass of SiO<sub>2</sub> should exceed 1. In general, CaO and MgO contents have a positive effect while SiO<sub>2</sub> content has a negative effect on the reactivity of GGBFS [24], [30]. The effect of Al<sub>2</sub>O<sub>3</sub> is complex and contradictory. At early age Al<sub>2</sub>O<sub>3</sub> positively affects the reactivity, but at a later age, Al<sub>2</sub>O<sub>3</sub> content greater than 13% has a negative effect. Trace elements such as TiO<sub>2</sub> and MnO, with content above 1% have a negative effect on the reactivity of GGBFS [30], [31].

Owing to the latent hydraulic property of GGBFS, it starts to react rapidly under the alkaline environment provided by the hydration of cement. However, the GGBFS hydration rate is far slower as shown in Figure 2.2a, than cement which is evident from the late-age strength observed with GGBFS blended cement [32]. Partially hydrated GGBFS grain can be seen in a 15-year-old concrete sample as shown in Figure 2.2b. Frbort et al., [33] reported that within 15 years, only 5-30 vol% of slag particles smaller than  $100\mu$ m hydrated completely.



Figure 2.2: (a) Hydration degree of different proportions of GGBFS blended with cement paste [34]; (b) BSE image of a 15-year-old concrete sample showing partially reacted GGBFS grains [33]

#### 2.2. Microstructural characterization of cementitious material

Microstructural characterization is crucial in understanding the performance of a material. In recent times, there has been substantial progress in developing techniques to measure the microstructure of cementitious materials, with a focus on increasing the accuracy of these methods. Microstructural quantification is crucial since the composition of most cementitious materials are relatively comparable. Many of the methods for evaluating microstructure in cementitious materials are related to the field of materials science, and therefore should also be explored by concrete technologists [35].

#### 2.3. Scanning electron microscope

SEM is one of the most powerful imaging tools with a great depth of field and resolution for microstructural characterization of materials [36]. There has been a substantial increase in the use of SEM to study cement-based materials since the first known publication of its application to image the fractured surface of cement paste to view the three-dimensional arrangement of hydration products [37]. Since then, significant advances have been made in applying SEM for microstructural imaging, and qualitative and quantitative phase identification of cement-based materials, as well as their hydration and degradation reactions. During analysis, a finely focused beam of electrons is made to interact on a bulk specimen surface and it emits back-scattered electrons (BSE), secondary electrons (SE), X-rays, etc., that are useful for microstructural analysis [35]. Figure 2.3 shows a schematic view of the main components of SEM [38].

#### 2.3.1. Electron beam - solid interactions

The interaction of beam electrons with solid atoms leads to various physical processes, referred to as scattering events. The elastic scattering will change the trajectory of the beam electrons, and inelastic scattering will transfer energy to the solid atoms from the beam electrons, thus limiting their travel



Figure 2.3: Schematic form of SEM [38]

within the solid. The volume of the region within a bulk solid up to where the beam electrons will travel is referred to as 'electron interaction volume' [7]. The size of this interaction volume is a few microns for cement-based materials since they are made up of elements with low atomic number [35].

Depending on whether the collision between the beam electrons and solid atoms is elastic or inelastic, signals will be emitted, as shown in Figure 2.4. One or multiple elastic scatterings may result in a few beam electrons completely reversing their initial trajectory and exiting the bulk solid with energies similar to that of the incident electrons. They are called BSEs and their intensity depends on the topography and average atomic number of the solid. Processing this signal to an image for a flat well polished solid would show clear compositional contrast.

In inelastic scattering, numerous signals will be emitted as the beam electrons steadily lose their energy while interacting with the orbital electrons of the solid atoms. The ejection of outer shell electrons of the solid atoms called SE can be collected and processed to image the topographical contrast of the solid. They have much lower energy than incident electrons, and their intensity depends on the inclination of the surface to the incoming beam. When a beam electron ejects an inner shell electron, an outer shell electron jumps to the inner shell of the solid atom. The energy released by this transition which is equal to the energy difference between the two shells, either knocks another outer shell electron referred to as the Auger electron or emits an X-ray photon characteristic of the atom species. These characteristic X-rays can be used to qualitatively determine the elements and quantitatively assess the composition of the interaction volume. X-rays will also be emitted continuously, called bremsstrahlung X-rays when the beam electron undergoes deceleration and loses kinetic energy in the negative charge cloud of atomic electrons. The energy lost can be any value between a few electron volts to the total incident electron energy [7].



Figure 2.4: Interaction of electrons with a solid and the signals generated [39]

#### 2.3.2. Monte Carlo simulations of electron interaction and characteristic X-rays

Monte Carlo simulations are commonly used to model the complex behaviour of scattering of electrons within the specimen by a step-wise simulation of electron trajectory incorporating elastic and inelastic scatterings from its entry point until its energy is small enough or escapes the specimen. This simulation is used to investigate the shape and size of interaction volume, the spatial and energy distribution of BSE and X-rays in a bulk specimen with complex geometric shapes, boundaries, and distinct compositions [7], [40].

The distribution of characteristic X-rays as a function of depth, known as  $\phi(\rho z)$  curves, can be modelled with Monte Carlo electron trajectory simulations. The interaction volume in the specimen is divided into layers of constant thickness parallel to the surface to count the X-rays produced in each layer. It is then normalized by the intensity produced in a single unsupported thin layer with no significant elastic scattering. Then, the intensity of X-rays in each layer is plotted as a histogram to obtain  $\phi(\rho z)$  curves. Karduck and Rehbach [41] used Monte Carlo simulations to determine  $\phi(\rho z)$  curves with excellent agreement from tracer experiments. There are various Monte Carlo simulation programs specifically for EDS like CASINO [42], DTSA-II [43], etc. CASINO is used to quickly calculate and display electron solid interactions in bulk samples for various beam conditions and sample geometries. Along with these functions, DTSA-II can also simulate the X-ray spectrum for arbitrary complex samples. Wong and Buenfeld [40] used CASINO to simulate electron-solid interactions in cement-based materials. They found the shape of interaction volume to be hemispherical with the maximum penetration depth ranging from 0.75 to 1.5 $\mu$ m at 10keV and 2.5 to 5.0 $\mu$ m at 20keV. Further, they observed that the sampling volume of the characteristic X-rays depended on the beam energy and critical excitation energy of the respective element.

The fraction of ionizations that results in X-ray emission is known as fluorescence yield  $\omega$ . It increases rapidly with atomic number as shown in Figure 2.5 for K-shell, L-shell and M-shell. The energy states of each sub-shell in an atom are unique to a specific element. Therefore, energy lost in the transition of an outer shell electron to a vacant inner shell is characteristic of the atomic number, thus emitting characteristic X-ray photons [45]. X-ray transition energies for different elements are given by Vaughan, [46] and many authors. These emitted X-rays may be absorbed by the solid atoms as they escape from the solid [7].



Figure 2.5: Fluorescence yield as a function of atomic number for electron ionization within the K,L and M electron shells [44]

#### 2.3.3. X-ray absorption and X-ray fluorescence

When the energy of the X-ray photon exceeds the binding energy of an atomic shell, it may transfer its energy and eject the bound electron from the solid atom, which again initiates the same process of Auger electron and X-ray emission, as mentioned in section 2.3.1. This process is called photoelectric absorption. It reduces the X-ray intensity emitted from the solid at all energies; hence, absorption loss occurs in each layer of the  $\phi(\rho z)$  distribution. This loss is quantified using the "mass absorption coefficient", which determines the fraction of X-rays that pass and get absorbed through a given material thickness. This coefficient usually decreases with an increase in X-ray photon energy. Due to the electron ejected by photoelectric absorption, the solid atom emits lower energy characteristic secondary X-rays, referred to as secondary X-ray fluorescence [7].

#### 2.4. Quantitative X-ray microanalysis

Detecting the characteristic emitted X-ray photon and analysing it based on energy or wavelength using an EDS or wavelength-dispersive spectrometer (WDS), respectively, is the underlying principle behind X-ray microanalysis. It was initially developed based on an electron probe microanalyser (EPMA)/WDS system for composition analysis. WDS counts the X-rays according to the wavelength that is diffracted following Bragg's law, whereas EDS counts X-rays according to energies using a semiconductor [47]. Although EDS has inferior quantitative analytical accuracy compared to WDS due to its poor energy resolution, recent advances after the introduction of the silicon drift detector show that EDS measurement can produce results that are as accurate and precise as WDS measurements for both major (greater than 10wt%) and minor (1wt% to 10wt%) elements. EDS also has the advantage of detecting all elements within the energy range in one measurement, and it is relatively less expensive [48].

Quantitative elemental X-ray microanalysis is carried out by comparing the intensity of the characteristic X-ray photon lines of elements in the sample spectrum with that from standards of known composition measured using the same equipment and analytical conditions. The intensity is also corrected for the differences in matrix effects from the sample and standard [47]. The ground rule for this protocol was first proposed by Castaing, referred to as the "k-ratio method" given by equation 2.1,

$$k = C_{i,unk} / C_{i,std} = I_{i,unk} / I_{i,std}$$

$$\tag{2.1}$$

where  $C_{i,unk}$  and  $C_{i,std}$  are the concentrations of the element i in the specimen and standard, respectively and  $I_{i,unk}$  and  $I_{i,std}$  are the intensities of the element i in the specimen and standard, respectively. The k-ratio eliminates the need to know the efficiency of the detector and the physics of the X-ray generation process. In this first approximation, Castaing assumed that the standard and the unknown have similar chemical constituents and that the absorption and fluorescence effects are small, which is far from reality and calls for the need for matrix correction procedures. He proposed two methods for this procedure, of which a theoretical physics-based quantitative method to account for absorption (A) and fluorescence (F) effects and later developed to account for atomic number (Z) effects by depth distribution of characteristic X-rays or  $\phi(\rho z)$  function is now prevalently used [7], [47].

#### 2.4.1. Matrix correction procedures

Matrix effects cause deviations from the simple linear behaviour given in equation 2.1 due to differences in composition, electron backscatter (R) and energy loss (S), X-ray absorption and X-ray fluorescence for the electrons travelling through the standard and unknown material to reach the detector [7]. Thus, to incorporate these effects by matrix correction procedures, equation 2.1 becomes:

$$C_{i,unk}/C_{i,std} = [ZAF]_i * I_{i,unk}/I_{i,std} = [ZAF]_i * k$$

$$(2.2)$$

where ZAF is the matrix correction factor contributed by three factors Z,A, and F. There are two approaches to calculating these factors. The first approach uses direct fundamental equations that describe the physical processes to calculate Z,A, and F. The second approach uses the  $\phi(\rho z)$  curves to determine the X-ray generation in depth, as a function of atomic number and electron beam energy to calculate Z, sums the effect of absorption of X-rays by elements in each layer of the  $\phi(\rho z)$  distribution using the "mass absorption coefficient" to calculate A and an analytical equation to calculate F [44]. There is an overall trend to incorporate the  $\phi(\rho z)$  corrections as they perform better than fundamental equations.

#### 2.4.2. Standardless microanalysis

Standardless microanalysis is a semi-quantitative procedure that only uses the unknown spectrum for the quantification of required elements. Almost 95% of EDS results are based on standardless microanalysis. It only requires accurate values of beam energy, X-ray take-off angle, and spectrometer efficiency while eliminating the need for standards and control over many other instrumental parameters, thus simplifying the overall analysis procedure. The approach to standardless microanalysis can be classified based on fundamental equations, peak-to-background ratio, monte carlo simulations, virtual standards and remote standards [44], [49], [50]. At present, remote standards standardless analysis is prevalently used. It consists of pure elements and stoichiometric binary compounds, measured at several beam energies with consistent probe dose using a well-characterized EDS and then adjusted to local measurement conditions [51]. Standardless quantification can overcome the difficulties related to the availability, maintainability and consistency of standards, and reduce analysis time but at the cost of less accuracy than standards-based microanalysis [47]. In the microanalysis of cementitious material hydrates, the analytical totals can never reach 100% because hydrogen is not detected in EDS and normalizing this total can lead to incorrect conclusions in standardless analysis [35].

#### 2.4.3. Important parameters for SEM-EDS X-ray microanalysis

During microanalysis, the constituents are assigned according to mass concentration ranges as major (greater than 10wt%), minor (1wt% to 10wt%) and trace (below 1wt%). Achieving reliable measurements for constituents in all these ranges requires careful attention to SEM-EDS parameters which should be chosen to provide appropriate counting statistics and minimise beam damage. Higher elec-

tron beam voltage might damage the sample but also increase the interaction volume, and peaks of higher atomic number elements can be observed. If the beam damage is excessive, it can change the chemical structure and composition of the cementitious material. Overvoltage, defined as the ratio of SEM beam energy in keV to the critical ionization energy of an element's atomic shell, should be about 1.5-2 to properly measure the element with the highest energy X-ray [7], [52]. Cementitious materials typically contain elements with a low atomic number such as Na, Mg, Al, Si, S, Ca, Fe, etc. Here Fe is the element with the highest energy X-ray of 6.405keV, so 10-15kV is the recommended beam voltage for obtaining EDS spectra [29], [35]. Figure 2.6 shows the periodic table illustrating X-ray shell choices for elemental measurement at a beam energy of 10 keV. For elements up to Fe, it can be seen the K-shell can be comfortably used for analysis.



Figure 2.6: Periodic table illustrating X-ray shell choices for beam energy 10 keV [7]

The probe dose is the product of collection time and probe current that consists of those electrons which could produce measurable X-rays and determines the relative intensity of the spectrum. Probe current/beam current (measure of the number of electrons that impact the specimen) and detector time constant (time taken to process each incoming X-ray photon), should be chosen optimally to ensure deadtime (% of incoming X-ray photons that are not processed by the detector) of less than 10% to obtain acceptable X-ray counts with good peak resolution. The solid angle of collection for the detector affects the number of photons detected per unit dose. By fixing the solid angle, the rate of production of X-rays will be controlled by the beam current. Adequate X-ray counts must be accumulated to distinguish a peak from the continuum background X-ray. For standard-based quantitative analysis, all these parameters are recommended to be kept consistent for all measurements [7].

Depending on the nature of the analysis, there are three modes in SEM-EDS for combining spatial and spectral information: Point mode, line scan and X-ray mapping. Point mode collects the X-ray spectrum from a chosen position on the sample. Line scan shows the variation in elemental composition by obtaining spectrum for a fixed number of points on a line across the sample. X-ray mapping shows the variation in elemental composition in two-dimension across the sample by obtaining the spectrum for each pixel in the image.

#### 2.4.4. SEM-EDS microanalysis in concrete technology

One of the earliest applications of SEM-EDS microanalysis to study cementitious material was by Diamond [53], who used spot analysis on a fractured surface to determine the approximate compositions by ratios of major elements present in the local regions of interest in the hydrated cement. They assembled a suite of pure well-characterized samples of synthetic cementitious materials, cement hydration compounds and pure minerals to be used as standards for quantification without any background correction using calibration curves. With this method, they investigated the molar ratios of C-S-H gel, CH, residual  $C_3S$ , and  $C_2S$ . Initially, the use of SEM-EDS to determine the chemical composition was limited to anhydrous phases since they gave analytical totals greater than 95 [35]. Crumbie et al. [54] performed microanalysis with standards on clinker phases, specifically for ferrite phases. Besides, they suggested the use of SEM-EDS along with XRD-Rietveld analysis to achieve reliable information about the phase composition of cement clinkers, their complex chemistry, and crystallography. Kocaba [55] quantified the atomic ratios of anhydrous cement clinker phases including alite, belite, aluminate and ferrite using EDS point analysis and compared them against the results of Bogue calculations. Ma et al. [56] used microanalysis on Alite-ye'elimite cement to identify the composition of clinker phases before and after heat treatment. They used mineral standards to quantify the chemical compositions of alite and belite. Kutchko and Kim [57] prepared polished epoxy-impregnated fly ash samples for qualitative elemental analysis. With the EDS spectra, they categorized the components into major, minor, and trace constituents. However, one should note that details regarding the standards employed in these researches were not given clearly.

Winter [29] was the first to lay out a thorough description of procedures and favourable experimental conditions for SEM-EDS application in concrete technology. He compiled the EDS spectra for common cementitious materials and cement hydration products. Based on this experience, they suggested suitable minerals to be used for SEM-EDX microanalysis in concrete technology, namely, Albite for Na, Dolomite for Mg, Corundum or pure C<sub>3</sub>A for Al, Quartz for Si, Gypsum for S, Arcanite for K, Calcite for Ca, Rutile for Ti, etc. With this, several researchers started exploring standard-based SEM-EDS microanalysis in concrete technology. Mendonça Filho et al. [9] performed semi-and full quantitative microanalysis of chlorine in reinforced mortars subjected to chloride ingress and carbonation. They used scapolite mineral for the quantification of chlorine and mineral standards from a commercial mineral standard mount for the quantification of other elements in the EDS spectrum obtained from the sample. The results confirmed the inaccurate interpretations in standardless EDS microanalysis and the necessity to use a standard-based EDS microanalysis. Pacheco and Copuroglu [8] extensively analysed the performance of six different minerals used as standards for chlorine quantification in the C-S-H gel phase with quantitative SEM-EDS. They found that scapolite showed the best performance for the quantification of chlorine. It was one of the first research to quantify all the elements in the C-S-H gel phase describing in detail the experimental parameters and standards used. One of the major recommendations was the use of spot scanning mode over window scanning mode for collecting spectra of heterogeneous matrices.

Generally, hydrated products from cementitious materials have analytical totals ranging from 65 to 85 [35]. Harrisson et al. [58] analyzed the cause of low EDS analytical totals in a microporous material like C-S-H gel phase using brucite, quantified with mineral MgO as standard. They found that low analytical totals might be obtained when the material has a high porosity on a scale smaller than the interaction volume. Most research with SEM-EDS microanalysis in concrete technology often used atomic ratio scatter plots to interpret their results and minimize errors in quantification. Chabrelie

et al. [10] used SEM-EDS microanalysis for the identification and semi-quantification of hydration products and sulphate attack phases. The used atomic ratio plots of S/Ca versus Al/Ca to identify C-S-H gel, CH along with typical sulphate attack involved phases such gypsum, thaumasite, ettringite, monosulfoaluminate, monocarboaluminate and plots of Mg/Ca versus Al/Ca and Cl/Ca versus Al/Ca to identify brucite and Friedel's salt, respectively at different depths in field concrete made of PC and silica fume exposed to seawater for 25years. Mejdi et al. [59] used SEM-EDS microanalysis to quantify the hydrated phases in the cementitious matrix of glass powder-cement blend pastes. They used the following standards for quantification: pure synthetic  $C_2S$  for Ca and Si, pure synthetic  $C_3A$  for Al, olivine for Mg and Fe, anhydrite for S, orthoclase for K, tugtupite for Na and Cl, and sphene for Ti. They investigated the C-(N)-S-H phase composition using Si/Ca, Si/Na atomic ratios and the sum of oxides was around 58 - 66.

#### 2.5. Summary

Based on the investigations in this chapter it can be seen that GGBFS chemistry varies with time and geography due to several factors. This variation in composition can affect the performance of GGBFS. As GGBFS has a slower rate of hydration compared to PC, partially hydrated GGBFS grain can be observed in a cement-GGBFS binder matrix in concrete even after several years. It is speculated that if needed this grain can be used to quantify the original composition of GGBFS with standard-based SEM-EDS microanalysis. However, extensive details regarding the experimental parameters for EDS analysis are scarce and there seems to be less published data relative to the use of standard-based microanalysis on cementitious materials. Studies based on large EDS sets of data are typically based on ratios and not absolute analytical totals. This work intends to bridge this research gap and establish a detailed protocol to use standard-based SEM-EDS microanalysis for quantifying the composition of GGBFS.

3

# Quantitative Energy-Dispersive X-ray microanalysis protocol for partially hydrated GGBFS

In this chapter, the author establishes the protocol for using SEM-EDS microanalysis to determine the chemical composition of GGBFS in a cement-GGBFS matrix. To explore the feasibility of using this protocol to field concrete samples, partially hydrated GGBFS grains of known composition in cement-GGBFS paste samples were analysed with standard-based SEM-EDS microanalysis. The performance of two sets of standards, from minerals and glassy GGBFS, is examined. A flowchart of the workflow in this chapter is shown in Figure 3.1.

#### 3.1. Materials and methodology

#### 3.1.1. Materials information

Five reference GGBFS powders, S1-S5, with varying compositions were obtained from Mr. Yu Zhang [60] to cover the broad composition range of GGBFS used in the field. Among them, S1 is commercial slag (provided by Ecocem Benelux B.V.,). S2-S5 was synthesized in the laboratory by Mr. Yu Zhang [60] using analytical reagents (provided by Honeywell Research Chemical, Germany) CaO, SiO<sub>2</sub>, MgO, and Al<sub>2</sub>O<sub>3</sub> according to different composition targets. The raw materials were melted using an Al<sub>2</sub>O<sub>3</sub> crucible in an oven at 1550 °C for 3h (heated from room temperature to 1550 °C at 10°C/min and maintained at 1550 °C for 3hrs). Then, the molten liquid was quenched to obtain glassy slag which was ground using a ball mill to the required fineness. Bulk compositions of these GGBFS, as given in Table 3.1, were determined by X-ray Fluorescence (XRF) with a Panalytical Axios Max wavelength dispersive XRF (WD-XRF) spectrometer. These reference GGBFS were blended with CEM I 42.5 N (manufactured by ENCI B.V.,) with a slag-to-cement ratio of 7:3 by mass.



Figure 3.1: Flowchart of the workflow in this chapter

#### 3.1.2. Specimen preparation

Using the cement and reference GGBFS, five paste specimens with water to binder ratio of 0.4 were cast into small cylindrical containers (20 mL), sealed, and cured in the laboratory at 20  $\pm$  3°C for 3 months. At this age, these specimens were cut using a sample cutting machine cooled with 100% ethanol to approximately 6 mm in height across the cross-section and immersed for 1 week in an isopropanol solution to stop hydration. Then, the cut samples were dried at 40°C oven for 1 h to evaporate any excess isopropanol.

#### 3.1.3. Sample preparation for EDS microanalysis

The five cut samples were impregnated with low-viscosity epoxy resin in a vacuum chamber and allowed to harden for 48h. To remove any excess epoxy on the sample surfaces and make the sample flat, they were ground in order with #320, #800, #1200, and #2000 silicon carbide (SiC) grinding papers, cooled with 100% ethanol. Following this, the samples were polished by 9 µm, 3 µm, 1 µm and 0.25 µm diamond paste on a rotary table. Between each grinding and polishing step, the sample surface was

		S1	S2		S3	
	Std.based	Normalized	Std.based	Normalized	Std.based	Normalized
CaO	41.00	41.67	41.60	41.90	32.32	34.09
$\mathrm{SiO}_2$	37.07	37.68	40.79	41.08	31.27	32.99
$Al_2O_3$	10.48	10.65	16.32	16.44	14.27	15.05
MgO	6.91	7.02	0.41	0.41	15.23	16.07
${\rm TiO}_2$	0.62	0.63	-	-	0.69	0.73
${\rm MnO}/{\rm Mn_2O_3}$	0.12	0.12	-	-	0.15	0.16
$Na_2O$	0.23	0.23	-	-	0.21	0.22
$K_2O$	0.32	0.33	-	-	0.20	0.21
$SO_3$	1.21	1.23	0.01	0.01	0.01	0.01
Others	0.44	0.44	0.17	0.17	0.45	0.47
Total	98.40	100.00	99.30	99.30	94.80	100.00

Table 3.1: Bulk Compositions (wt%) of reference GGBFS as determined by XRF

	S4			S5		
	Std.based	Normalized	Std.based	Normalized		
CaO	43.42	42.07	35.23	35.23		
$SiO_2$	44.68	43.30	33.74	33.74		
$Al_2O_3$	3.81	3.69	19.17	19.17		
MgO	11.18	10.83	8.97	8.97		
${\rm TiO}_2$	-	-	0.99	0.99		
${\rm MnO/Mn_2O_3}$	-	-	0.25	0.25		
$Na_2O$	-	-	0.61	0.61		
$K_2O$	-	-	0.40	0.40		
$SO_3$	0.01	0.01	0.02	0.02		
Others	0.10	0.10	0.62	0.62		
Total	103.20	100.00	100.10	100.00		

cleaned by immersing it in an ultrasonic bath with pure ethanol for 60sec. Once again, the polished samples were dried at 40°C oven for 1 h to evaporate any excess ethanol that might have seeped into the pores during grinding and polishing. Finally, the well-polished flat samples were carbon coated in a Leica EM CED 030 carbon evaporator to a thickness of about 10 nm.

#### 3.1.4. Electron-slag interaction volume

Monte Carlo simulation using CASINO software version 2.51 was used to estimate the interaction volume of electrons in a GGBFS particle. Figure 3.2 illustrates the simulation of penetration of electron trajectories of 500 electrons accelerated at 10 kV in a beam of radius 10 nm into a slag particle of density 2.95 g/cm<sup>3</sup>. Here, accelerating voltage was chosen based on the study in [29]. The red trajectories are BSEs' from elastic scattering events. Yellow trajectories represent high-energy electrons, and blue trajectories represent low-energy electrons, from inelastic scattering events, causing a reduction of the energy of electrons as they penetrate far into the specimen bulk. The maximum penetration depth of electron trajectories was around 1.2  $\mu$ m, and the interaction volume was estimated to be around 1.5  $\mu$ m<sup>3</sup>. Considering the typical diameter of the analyzed GGBFS grains was around 5-30  $\mu$ m, choosing analysis spots sufficiently far from the grain perimeter ensured the collection of X-rays that were representative of GGBFS composition alone within the interaction volume and free from interferences from the surrounding matrix. The final oxide composition results from microanalysis was reported in wt% of interaction volume, i.e., the portion of material from which X-rays were generated and analyzed by the detector.



Figure 3.2: Monte Carlo simulation of electron interaction at 10kv in a hypothetical slag particle

#### 3.1.5. Instrumental parameters

For the microanalysis, an FEI Quanta FEG 650 ESEM equipped with a Thermo Fischer energy dispersive spectrometer (EDS) was used in high vacuum chamber condition. The EDS detector used was a silicon drift detector (SDD) equipped with a light element NORVAR window type and a calibrated resolution of 126.7 eV for the Mn-K $\alpha$  line at 10 kV accelerating voltage. All EDS analyses were performed at a working distance of 10 mm, accelerating voltage of 10 kV and take-off angle of 35.3°. The X-ray collection time was set to 60 live-seconds per analysis with 71400 counts per second in order to obtain acceptable statistics without causing excessive thermal damage to the sample. During the analysis, a stable beam current of approximately 1.2 nA was measured periodically using a Faraday cup and a picoammeter. X-ray spectra of the microanalysis standards were collected under stable beam conditions, defined as less than 5% variation in beam current over 60 live-seconds at 10% deadtime. Each spot analysis was performed exclusively on a partially hydrated GGBFS particle. Around 30 - 50 randomly chosen points per sample were investigated in order to increase the representativeness and reliability of the data. For semi-quantitative EDS microanalysis (standardless), the results were generated using the remote standard standardless routine by the Pathfinder<sup>TM</sup> X-ray microanalysis software.

#### 3.1.6. Microanalysis standards

Two sets of standards were employed for quantitative microanalysis. The first set consisted of minerals chosen from a commercial mineral standard mount (ASTIMEX MINM25-53). Since the current study attempts to quantify the major elements, i.e., Ca and Si, minor elements, i.e., Al, and Mg, and trace elements S, Mn, K, Na, and T, eight minerals with similar matrix to GGBFS were chosen accordingly as shown in Table 3.2.

The second set consisted of standards were prepared in the lab by embedding raw GGBFS in epoxy. First, epoxy was poured into small cylindrical containers (D35mm X H60mm) and allowed to harden for 72h. It was then cut into 5 small cube moulds of size approximately L10mm x B10mm x H12mm. An extra height of 2mm greater than the sample size was given to accommodate the height reduction while grinding and polishing. A drill was used to make holes in the centre of the cubes, which would act as a mould to hold the slurry mixture of raw GGBFS and epoxy. The prepared moulds were then washed
Element	Mineral	Composition
Ca	Calcite	CaCO <sub>3</sub>
Si	Quartz	$SiO_2$
Al	Albite	$NaAlSi_3O_8$
Mg	Dolomite	$MgCa(CO_3)_2$
Ti	Rutile	${\rm TiO}_2$
Mn	Rhodonite	$MnSiO_3$
Na	Albite	$NaAlSi_3O_8$
Κ	Sanidine	$KAlSi_3O_8$
S	Anhydrite	$CaSO_4$

Table 3.2: Minerals employed as standards for Quantitative EDS Microanalysis

and dried in the 40°C oven for an hour. Slurries of epoxy and GGBFS S1-S5 were mixed individually and poured into these moulds in vacuum conditions to avoid any voids and allowed to harden for 48h. Finally, these moulds with GGBFS were grounded and polished the same way as given in section 3.1.3. Additional care was taken while grinding the epoxy since it was soft. These slag standards (ES1-ES5) were prepared assuming it would minimize the matrix effects between the GGBFS particle investigated and mineral standards.

#### 3.1.7. EDS data acquisition

Figure 3.3 shows a motorized stage in the SEM chamber consisting of a Faraday cup, composite Cu-Al target, ASTIMEX MINM 25-53 mount and a sample to be analysed. Pathfinder<sup>TM</sup> X-ray microanalysis software provided by the vendor was used to collect all the EDS spectra in point ID mode (spot analysis). Stable beam conditions was checked using the Faraday cup before collecting any spectra. The position of the Faraday cup in the stage was saved in the software for periodic monitoring of beam current.



Figure 3.3: Motorized stage in the SEM chamber holding a) Faraday cup, b) composite Cu-Al target c) Astimex MINM25-53, d) a sample to be analysed

Firstly, Cu spectrum was collected to calibrate the detector in NIST DTSA-II software from the composite Cu-Al target. Next, multiple spectra (3-5) of each mineral standard given in Table 3.2 and slag standards were acquired at different locations to compare and identify any potential pitfalls in the spectra. A few additional spectra of pure and binary compounds were also collected to be used as reference spectra in NIST DTSA-II software (For detailed calibration process, please refer to section A.3). Then, in each sample 3-5 cross sections were chosen with enough number of large GGBFS particles. A typical BSE micrograph is shown in Figure 3.4a. Points for EDS spectrum acquisition were selected manually, as shown in Figure 3.4b, making sure to spot and point the grain centre of relatively large GGBFS particles to avoid surrounding matrix interferences.



Figure 3.4: (a) A typical BSE micrograph with chosen (b) EDS points chosen at partially hydrated GGBFS grains

#### 3.1.8. EDS spectrum processing

All the spectra were processed and quantified with NIST DTSA-II Microscopium software [61] using MLLSQ peak fitting routine and matrix correction calculations based on XPP - Pochou and Pichoir simplified [62]  $\phi(\rho z)$  model with the mass absorption coefficients from Chantler et al., [63] and Sabbatucci and Salvat [64] compilations. Table 3.3 shows the family of characteristic X-rays of elements used to quantify the spectra and their regions within which the family of lines can be located in the spectra. Figure 3.5a shows a typical EDS spectrum from a partially hydrated GGBFS grain, with X-ray peaks labelled for the elements C, O, Na, Mg, Al, Si, S, Ca and Ti. The carbon (C) peak is mainly due to the carbon coating. Here the used-defined threshold for low energy cut-off was set to 200eV in order to include the oxygen (O) peak. The thin window present in the EDS instrument used here allows the detector to detect the oxygen peak and carbon peak. Multiple spectra from the same standard were compared for any pitfalls and then bundled into a single spectrum before using it to quantify the EDS spectrum collected from the investigated samples. All the unknown EDS spectra were quantified using mineral standards and slag standards, respectively. The detailed procedure for quantifying the spectra is given in appendix A.

Figure 3.5b shows a typical residual spectrum after standard-based quantification. This residual spectrum was checked for any unidentified peaks. It was accepted that the analysis was completed with acceptable accuracy, as no unassigned peak was left, and the residual count was sufficiently low with only a continuum background X-ray. A standard result output from NIST-DTSA II spectrum quantification is listed in table 3.4 showing the elemental composition in mass fraction, ZAF correction factors, the estimated uncertainties in these factors and the uncertainties due to the counting statistics associated with the measurements of the unknown and the standard for all the elements quantified. The error due to these uncertainties was negligible for all the spectra analysed here. The oxide composition of each element is calculated stoichiometrically using the assumed oxidation states given in Table 3.5. Analytical totals within the range of 90% to 110% [29] were used for the final analysis and totals outside this range were considered an error. The chemical compositions of reference GGBFS S1-S5 determined using quantitative standard-based and semi-quantitative standardless EDS microanalysis

were compared with the bulk GGBFS compositions that were detected by XRF.



Figure 3.5: (a) EDS spectra of a partially hydrated GGBFS grain (b) A typical residual spectra after standard-based quantification

Table 3.3: Characteristic X-rays of elements in concrete

Element	Family of X-rays [Region of Interest]
Calcium	K-family $[3.459, 4.222 \text{ keV}]$
Silicon	K-family $[1.546, 1.992 \text{ keV}]$
Aluminium	K-family $[1.298, 1.706 \text{ keV}]$
Magnesium	K-family [1.071, 1.436 keV]
Titanium	K-family $[4.264, 5.154 \text{ keV}]$
Manganese	K-family $[5.630, 6.729 \text{ keV}]$
Sodium	K-family $[0.865, 1.217 \text{ keV}]$
Potassium	K-family [3.088, 3.792 keV]
Sulphur	K-family [2.101, 2.643 keV]

	N	Ja	Mg			Al		Si	S
C (mass fraction)	0.0	018	0.0393		0.0	0.0574		714	0.0139
Z-correction	1.0	025	1.(	042	1.0	025	1.0	032	1.003
A-correction	0.9	906	1.(	004	0.9	971	0.9	937	0.941
F-correction	0.9	999	1.(	004	0.9	995	1.0	003	0.999
Counting error, std	9.10	E-06	1.00	E-03	2.00	E-04	3.00	E-04	5.30E-05
Counting error, unk	2.00	E-04	3.00	E-03	3.00	E-04	5.00	E-05	3.00E-04
A-factor error	3.20	E-05	2.00	E-03	5.00	E-04	1.10	E-03	7.10E-05
Z-factor error	3.90	E-07	6.40	E-06	6.60	E-06	1.40	E-05	6.40E-07
Combined errors	0.0	002	0.0	0004	0.0006		0.0012		0.0003
		K	2	C	a	Т	i	Mn	
C (mass fractio	on)	0.0031		0.3029		0.0060		0.0015	
Z-correction		1.013		1.024		0.930		0.952	
A-correction	L	1.0	11	0.943		0.967		0.991	
F-correction		1.0	44	1.0	00	1.0	00	0.999	)
Counting error,	$\operatorname{std}$	2.001	E-05	9.001	E-04	2.201	E-05	1.50I	E-05
Counting error,	ting error, unk 3.00		E-04	1.101	E-03	6.001	E-04	1.20I	E-03
A-factor erro	or 5.40H		E-06	4.001	E-04	1.901	E-05	1.70I	E-06
Z-factor erro	r	6.10I	E-08	4.301	E-06 4.5		E-08	4.00I	E-09
Combined erro	ors	0.00	)03	0.00	)15	0.00	006	0.001	12

Table 3.4: Standard result output from NIST DTSA-II with concentration and uncertainties expressed in mass fraction

Table 3.5: Assumed oxidation states of elements in GGBFS

Element	Oxidation state
Ca	CaO
Si	$SiO_2$
Al	$Al_2O_3$
Mg	MgO
Ti	${ m TiO}_2$
Mn	MnO
Na	$Na_2O$
Κ	$K_2O$
S	$SO_3$

# 3.2. Results

# 3.2.1. Heterogeneity in a slag particle



Figure 3.6: Three large GGBFS particles chosen from reference samples from GGBFS (a) S1 (b) S3 (c) S5, respectively

Five reference GGBFS S1 to S5 were almost entirely amorphous based on X-ray diffraction characterization with low amounts of heavy metal oxides. Although several works of literature state that GGBFS particle was homogeneous [28], the homogeneity of slag grains was evaluated with EDS for confirmation in the current study. Three relatively large particles were selected from S1, S3 and S5 reference paste samples, respectively, on which around ten spots were picked as shown in Figure 3.6. A statistical summary of the chemical compositions regarding the four main metal oxide (CaO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, MgO contents is shown in table 3.6. The extremely low coefficient of variation and small standard deviation shows that these GGBFS grains were highly homogeneous and there was negligible heterogeneity.

Table 3.6: Chemical composition of reference GGBFS determined by quantitative EDS microanalysis on a single large slag grain

	$\mathbf{S1}$	% CV	$\mathbf{S3}$	%CV	S5	% CV
CaO	$38.38 \pm 0.22^{a}$	0.57	$34.12 \pm 0.25$	0.73	$36.39 \pm 0.28$	0.77
$\mathrm{SiO}_2$	$38.53 \pm 0.20$	0.53	$34.79 \pm 0.24$	0.69	$33.23 \pm 0.20$	0.6
$Al_2O_3$	$10.19\ {\pm}0.22$	2.18	$13.82\ {\pm}0.45$	3.26	$17.40 \pm 0.25$	1.44
MgO	$7.51 \pm 0.16$	2.15	$15.88\ {\pm}0.17$	1.07	$8.01 \pm 0.08$	1.00

<sup>*a*</sup>Values given in Mean ±Standard deviation.

#### 3.2.2. Mineral standard-based EDS microanalysis of reference GGBFS

Table 3.7 and Table 3.8 show the mean analytical total, the mean value of each metal oxide composition in wt% of interaction volume and the standard deviation of the corresponding data set of the results. They were obtained by quantifying the EDS spectra of reference cement-GGBFS paste samples S1-S5 using semi-quantitative standardless EDS microanalysis and mineral standard-based quantitative EDS microanalysis, respectively, for all the peaks observed. The analytical total values for all the samples lay within the accepted range of 98% to 102% [7] except for S5 in mineral standard-based microanalysis. The standard deviation of the four main metal oxides CaO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and MgO in S1-S5 were far less for mineral standard-based EDS microanalysis than standardless EDS microanalysis. With mineral standard-based microanalysis, trace elements such as Ti, Mn, Na, K, and S were also quantified for samples S2, S3, S4 and S5 however standardless microanalysis was not able to detect a few of them.

Table 3.7: Chemical Compositions (wt%) of reference GGBFS S1-S5 in paste samples determined by semi-quantitative standardless EDS microanalysis

Standardless	S1	S2	S3	S4	S5
CaO	$41.52 \pm 0.88^{a}$	$43.54 \pm 3.48$	$35.24 \pm 4.67$	$42.00 \pm 1.84$	$36.26 \pm 0.69$
$SiO_2$	$38.06 \pm 0.89$	$41.27 \pm 6.33$	$34.95 \pm 2.96$	$44.03 \pm 1.61$	$35.12 \pm 0.65$
$Al_2O_3$	$10.09 \pm 0.41$	$12.58 \pm 2.83$	$13.31 \pm 2.30$	$3.84 \pm 3.68$	$19.06 \pm 1.37$
MgO	$7.03 \pm 0.61$	$1.49 \pm 3.32$	$15.22 \pm 3.52$	$10.11 \pm 0.72$	$7.42 \pm 0.29$
${\rm TiO}_2$	$0.85 \pm 0.49$	$0.11 \pm 0.35$	$0.72 \pm 0.31$	-	$1.33 \pm 0.16$
MnO	$0.03 \pm 0.09$	-	-	-	-
$Na_2O$	$0.44 \pm 0.10$	$0.06 \pm 0.15$	-	-	$0.38 \pm 0.11$
$K_2O$	$0.34 \pm 0.08$	$0.08 \pm 0.19$	$0.19 \pm 0.23$	-	$0.43 \pm 0.06$
$SO_3$	$1.64 \pm 0.57$	$0.87 \pm 2.31$	-	-	-
Total	100.00	100.00	100.00	100.00	100.00

<sup>*a*</sup>Values given in Mean  $\pm$ Standard deviation

Mineral Standard	S1	S2	S3	S4	S5
CaO	$42.64 \pm 0.99^{a}$	$42.30 \pm 1.19$	$34.17 \pm 1.07$	$42.43 \pm 1.39$	$34.50 \pm 1.12$
$SiO_2$	$37.74 \pm 0.95$	$42.69 \pm 1.29$	$34.65 \pm 0.85$	$44.83 \pm 1.64$	$34.28 \pm 0.62$
$Al_2O_3$	$10.83 \pm 0.42$	$12.67 \pm 2.19$	$13.55 \pm 1.20$	$2.84 \pm 2.12$	$18.25 \pm 0.71$
MgO	$6.74 \pm 0.59$	$0.24 \pm 0.04$	$15.57 \pm 0.52$	$10.63 \pm 0.75$	$7.26 \pm 0.17$
${ m TiO}_2$	$1.12 \pm 0.26$	$0.07 \pm 0.10$	$0.87 \pm 0.61$	$0.07 \ {\pm} 0.06$	$1.17 \pm 0.12$
MnO	$0.14 \pm 0.20$	$0.03 \pm 0.08$	$0.06 \pm 0.14$	-	$0.06 \pm 0.14$
$Na_2O$	$0.27 \pm 0.05$	$0.09 \pm 0.04$	$0.25 \pm 0.04$	$0.05 \ {\pm} 0.02$	$0.37 \pm 0.03$
$K_2O$	$0.41 \pm 0.11$	$0.01 \pm 0.02$	$0.27 \pm 0.05$	-	$0.47 \pm 0.04$
$\mathrm{SO}_3$	$0.86 \pm 0.23$	$0.14 \pm 0.09$	$0.10 \pm 0.08$	$0.14 \pm 0.13$	$0.11 \pm 0.06$
Total	$100.76 \pm 1.63$	$98.23 \pm 0.95$	$99.49 \pm 2.07$	$101.01 \pm 2.82$	$96.46 \pm 2.19$

Table 3.8: Chemical Compositions (wt%) of reference GGBFS S1-S5 in paste samples determined by quantitative mineral standard-based EDS microanalysis

<sup>*a*</sup>Values given in Mean  $\pm$ Standard deviation



Figure 3.7: Box plots of four main metal oxide contents of reference GGBFS S1-S5 in paste samples based on standard-based EDS microanalysis. (a) CaO, (b) SiO<sub>2</sub>, (c) Al<sub>2</sub>O<sub>3</sub>, (d) MgO

Figure 3.7 shows a comparative box plot on the results obtained for mineral standard-based quantitative EDS microanalysis for the four main metal oxide contents in the reference GGBFS samples S1-S5. Each plot corresponds to a single metal oxide mass percentage. The middle line indicates the median value



Figure 3.8: Deviation plots of four main metal oxide contents of reference GGBFS paste samples based on standard-based EDS microanalysis with XRF oxide contents. (a) CaO, (b) SiO<sub>2</sub>, (c) Al<sub>2</sub>O<sub>3</sub>, (d) MgO

(at 50% of all values). The top edge and bottom edge of the box indicate the third (upper) quartile and first (lower) quartile, respectively. The difference between the upper quartile and lower quartile is called the interquartile range (IQR). Values outside 1.5 times IQR from the upper and lower quartile are called outliers and are indicated here by ( $\circ$ ). The upper and lower whiskers are located 5% below and above the 1.5 times IQR region, respectively. The mean of the data set is indicated by ( $\times$ ). The boxplot of MgO, seems to have a small IQR where as the boxplot of CaO has a relatively larger IQR for all compositional ranges under study. The boxplot of Al<sub>2</sub>O<sub>3</sub> has several outliers and a large whisker range. The presence of a few outliers indicates sporadic compositional imperfections. On the other hand, an overall slender IQR implies a relatively homogeneous composition.

Figure 3.8 shows the deviation of the four main metal oxide compositions between the mineral standardbased EDS microanalysis and XRF analysis. It should be noted that these plots do not attempt to correlate XRF oxide composition as equal to the EDS microanalysis wt% of interaction volume. Within the measured concentration range of the reference samples, it can be seen that CaO and SiO<sub>2</sub> tended to be overestimated, and  $Al_2O_3$  and MgO tended to be underestimated in standard-based EDS microanalysis compared to XRF. The deviation from the XRF values was consistent and small within the given concentration range for MgO and SiO<sub>2</sub>, while it increased slightly for  $Al_2O_3$  and CaO. Overall, it is confirmed that the performance of mineral standard-based EDS microanalysis was acceptable for

	S	1	S2		S3		S4		$\mathbf{S5}$	
	RD1 <sup>a</sup>	RD2 <sup>b</sup>	RD1	RD2	RD1	RD2	RD1	RD2	RD1	RD2
CaO	4.00	2.63	1.68	2.93	5.72	3.13	2.28	1.01	2.07	5.10
$\mathrm{SiO}_2$	1.81	0.85	4.66	3.33	10.81	0.87	0.34	1.78	1.60	2.45
$Al_2O_3$	3.34	6.83	22.37	0.71	5.05	1.77	25.46	35.21	4.80	4.44
MgO	2.46	4.30	41.46	520.83	2.23	2.25	4.92	4.89	19.06	2.20
${\rm TiO}_2$	80.65	24.11	-	57.14	26.09	17.24	-	-	18.18	13.68
MnO	16.67	78.57	-	-	-	-	-	-	-	-
$Na_2O$	17.39	62.96	-	33.33	-	-	-	-	39.34	2.70
$K_2O$	28.13	17.07	-	700.00	35.00	29.63	-	-	17.50	8.51
$SO_3$	28.93	90.70	-	521.43	-	-	-	-	-	-

the major and minor metal oxides in GGBFS.

Table 3.9: Relative deviation between the values of Quantitative EDS microanalysis and XRF Analysis, as well as Quantitative EDS microanalysis and semi-quantitative EDS Microanalysis for reference GGBFS S1-S5 used in paste samples

 $^{a}$ RD1 = (|EDS-XRF|/XRF)\*100

 ${}^{b}\text{RD2} = (|\text{standard based - standard less}|/\text{standard based})*100$ 

The relative deviation between the values of Quantitative EDS microanalysis and XRF Analysis (RD1), as well as Quantitative EDS microanalysis and semi-quantitative EDS Microanalysis (RD2) for reference GGBFS S1-S5 used in paste samples, is given in Table 3.9. It can be seen that there is an acceptable deviation and quantification accuracy between the values obtained for the four main metal oxides CaO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and MgO in S1-S5, considering that majority of RD1 was less than 5% when oxides were present in the major and minor concentration range. It indicated that standard-based EDS microanalysis and XRF results were in close agreement for elements Ca, Si, Al and Mg for the concentration range observed here. Mg in reference GGBFS S2 and Al in reference GGBFS S4 were present in trace concentration according to XRF analysis and hence this can explain the high RD1 observed. For other elements present in the trace concentration range, like Ti, Mn, S, Na and K, high RD1 was observed. For the mass percentage of the four main metal oxides present in the major concentration range, the quantification results of RD2 less than 5% is similar to the trend observed by Newbury and Ritchie [51]. Considerable deviation (over 5%) is observed for a few results, especially for the elements present in the minor and trace concentration ranges, which stresses the need to choose a particular quantification method based on the requirement with proper awareness of the uncertainties involved.

#### 3.2.3. Slag standard-based EDS microanalysis of reference GGBFS

Table 3.10 shows the mean chemical composition in wt% of interaction volume of the four major metal oxides in reference GGBFS S1-S5 used in paste samples determined by standard-based EDS microanalysis using slag standards ES1-ES5 and the standard deviation of the corresponding data set. A lesser standard deviation for all the quantified metal oxides was observed here when compared to mineral standard-based EDS microanalysis in Table 3.8.

The RD between the oxide composition values determined by slag standard-based EDS microanalysis and XRF analysis is given under RD3 and RD between the oxide composition values determined by mineral standard-based EDS microanalysis and slag standard-based EDS microanalysis is given under RD4 in Table 3.11. Generally, it was found that when a particular slag standard was used to quantify

		$\mathbf{S1}$	S2	$\mathbf{S3}$	$\mathbf{S4}$	S5
	CaO	$41.87 \pm 0.72^{a}$	$42.39 \pm 0.65$	$33.91 \pm 0.57$	$41.60 \pm 0.99$	$34.83 \pm 0.99$
$\mathbf{ES1}$	$SiO_2$	$36.72 \pm 0.60$	$41.59 \pm 1.01$	$33.17 \pm 0.36$	$42.54 \pm 0.87$	$33.35 \pm 0.53$
	$Al_2O_3$	$10.57 \pm 0.39$	$12.54 \pm 1.12$	$14.64 \pm 1.22$	$2.96 \pm 2.38$	$19.85 \pm 0.67$
	MgO	$6.81 \pm 0.23$	$0.28 \pm 0.03$	$14.37 \pm 0.35$	$9.79 \pm 0.43$	$6.90 \pm 0.15$
	CaO	$40.44 \pm 0.70$	$40.90 \pm 0.63$	$32.76 \pm 0.55$	$40.18 \pm 0.96$	$33.64 \pm 0.96$
ES2	$SiO_2$	$35.79 \pm 0.59$	$40.39 \pm 0.97$	$32.44 \pm 0.36$	$41.45 \pm 0.84$	$32.55 \pm 0.51$
	$Al_2O_3$	$11.85 \pm 0.44$	$13.96 \pm 1.25$	$16.50 \pm 1.37$	$3.33 \pm 2.67$	$22.23 \pm 0.75$
	MgO	$9.00 \pm 0.30$	$0.37 \pm 0.04$	$18.96 \pm 0.45$	$12.93 \pm 0.57$	$9.12 \pm 0.20$
	CaO	$40.59 \pm 0.70$	$41.09 \pm 0.63$	$32.88 \pm 0.55$	$40.33 \pm 0.96$	$33.77 \pm 0.96$
ES3	$SiO_2$	$32.97 \pm 0.54$	$37.33 \pm 0.90$	$29.80 \pm 0.33$	$38.17 \pm 0.78$	$29.96 \pm 0.47$
	$Al_2O_3$	$10.31 \pm 0.38$	$12.22 \pm 1.10$	$14.28 \pm 1.18$	$2.89 \pm 2.32$	$19.34 \pm 0.66$
	MgO	$6.56 \pm 0.22$	$0.27 \pm 0.03$	$13.84 \pm 0.33$	$9.43 \pm 0.42$	$6.64 \pm 0.14$
	CaO	$45.25 \pm 0.78$	$45.79 \pm 0.70$	$36.66 \pm 0.62$	$44.98 \pm 1.07$	$37.64 \pm 1.07$
$\mathbf{ES4}$	$SiO_2$	$37.77 \pm 0.62$	$42.68 \pm 1.04$	$34.16 \pm 0.38$	$43.84 \pm 0.92$	$34.26 \pm 0.55$
	$Al_2O_3$	$10.22 \pm 0.38$	$12.09 \pm 1.08$	$14.21 \pm 1.18$	$2.87 \pm 2.30$	$19.21 \pm 0.65$
	MgO	$8.27 \pm 0.28$	$0.34 \pm 0.04$	$17.43 \pm 0.42$	$11.87 \pm 0.52$	$8.38 \pm 0.18$
	CaO	$42.26 \pm 0.73$	$42.77 \pm 0.66$	$34.23 \pm 0.58$	$42.01 \pm 1.00$	$35.14 \pm 1.00$
ES5	$SiO_2$	$38.75 \pm 0.63$	$43.80 \pm 1.06$	$35.04 \pm 0.39$	$44.96\ {\pm}0.94$	$35.16 \pm 0.56$
	Al <sub>2</sub> O <sub>3</sub>	$10.26 \pm 0.38$	$12.14 \pm 1.09$	$14.26 \pm 1.18$	$2.88 \pm 2.31$	$19.28 \pm 0.65$
	MgO	$8.05 \pm 0.27$	$0.33 \pm 0.03$	$16.97 \pm 0.41$	$11.55 \pm 0.51$	$8.16 \pm 0.18$

Table 3.10: Chemical composition of major metal oxides in reference GGBFS S1-S5 used in paste samples determined by quantitative standard-based EDS microanalysis using slag standards ES1-ES5

<sup>*a*</sup>Values given in Mean  $\pm$ Standard deviation.

itself in the respective reference sample, RD3 was lower in most cases. RD3 was mostly under 5% for constituents in the major concentration range. ES1 and ES5 showed acceptable RD3 values (under 5%) when the constituents were present in the major and minor concentration ranges. ES2 and ES4 showed relatively high RD3 values since their MgO and  $Al_2O_3$  concentrations, respectively, were in the trace constituent range. ES3 was not considered for further evaluation since its total analytical total by standard-based WD-XRF was less than 95 and due to large RD3 values showing heavy uncertainty. Most of the metal oxides quantified with ES2, ES3 and ES4 presented larger RD4 (greater than 5%) irrespective of the concentration range. However, ES1 and ES5 showed small RD4 (less than 5%) values for almost all the four main metal oxides. Thus, ES1 and ES5 will be considered for further quantification.

Figures 3.9 and 3.10 display the deviation of the four main metal oxide compositions determined by standard-based EDS microanalysis using slag standards ES1 and ES5 with mineral standard-based EDS microanalysis. All graphs exhibited a good correlation between these two methods. ES1 tended to underestimate the concentration of CaO, SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> and overestimate MgO. The deviation from the mineral standard-based result was small but increased with an increase in concentration for all metal oxides, within the concentration range of the reference samples. Likewise, ES5 tended to overestimate SiO<sub>2</sub> and MgO concentrations. In general, the deviation from the mineral standard-based result was small and consistent for SiO<sub>2</sub> and MgO concentrations. However, CaO tended to be overestimated initially and underestimated towards the end of the range whereas Al<sub>2</sub>O<sub>3</sub> tended to be underestimated

		S	1	S S	2	s	3	s	4	S	5
		RD3 <sup>a</sup>	RD4 <sup>b</sup>	RD3	RD4	RD3	RD4	RD3	RD4	RD3	RD4
	CaO	2.13	1.80	1.90	0.21	4.91	0.77	4.18	1.94	1.14	0.95
$\mathbf{ES1}$	$SiO_2$	0.93	2.69	1.96	2.58	6.28	4.27	4.80	5.12	1.15	2.71
	$Al_2O_3$	0.89	2.37	23.15	1.01	2.61	8.06	22.25	4.31	3.55	8.77
	MgO	1.40	1.08	32.25	15.73	5.64	7.70	12.45	7.92	23.04	4.91
	CaO	1.37	5.16	1.67	3.30	1.36	4.13	7.47	5.31	4.52	2.50
ES2	$SiO_2$	3.46	5.17	0.98	5.39	3.95	6.37	7.23	7.54	3.54	5.06
	$Al_2O_3$	13.08	9.43	14.45	10.19	15.66	21.80	12.54	17.34	15.99	21.84
	MgO	30.32	33.60	10.35	53.16	24.51	21.79	15.68	21.66	1.64	25.58
	CaO	0.99	4.80	1.23	2.87	1.73	3.78	7.12	4.95	4.15	2.12
ES3	$SiO_2$	11.05	12.63	8.48	12.55	4.53	14.01	14.56	14.85	11.20	12.60
	$Al_2O_3$	1.66	4.84	25.11	3.53	0.04	5.36	24.10	1.83	0.91	6.00
	MgO	5.02	2.63	35.12	10.84	9.16	11.14	15.66	11.29	25.92	8.48
	CaO	10.37	6.12	10.06	8.24	13.42	7.28	3.58	6.00	6.83	9.09
ES4	$SiO_2$	1.89	0.08	4.63	0.03	9.45	1.42	1.87	2.20	1.54	0.06
	$Al_2O_3$	2.44	5.60	25.90	4.56	0.42	4.87	24.65	1.09	0.18	5.23
	MgO	19.67	22.69	18.10	39.92	14.43	11.94	6.16	11.65	6.58	15.43
	CaO	3.08	0.88	2.81	1.11	5.90	0.16	3.25	0.99	0.25	1.87
ES5	$SiO_2$	4.54	2.69	7.37	2.59	12.28	1.14	0.63	0.29	4.21	2.56
	$Al_2O_3$	2.08	5.25	25.63	4.21	0.06	5.25	24.41	1.41	0.55	5.62
	MgO	16.49	19.43	19.95	36.75	11.41	8.98	3.35	8.70	9.04	12.39

Table 3.11: Relative deviations of reference GGBFS determined by quantitative slag standard-based EDS microanalysis

 $^{a}$ RD3 = (|Slag EDS-XRF|/XRF)\*100

 $^{b}$ RD4 = (|Slag standard - mineral standard|/mineral standard)\*100

initially and overestimated towards the end of the range.

# 3.3. Discussion

#### 3.3.1. Analytical totals of different quantification methodologies

For XRF and EDS microanalysis used in the present research, the analytical totals are computed stoichiometrically based on the assumed oxidation states of the elements. The standard-based WD-XRF analytical totals for reference GGBFS S1-S5 given in table 3.1 vary between 94.8-103.2. The deviation of analytical totals here can be due to many aspects, e.g., the assumption of associating all elements to oxygen, the stoichiometric assumption of oxidation states of the respective elements, signal attenuation due to matrix effects, mismatch of the matrix of the sample with that of the standards and non-uniform grain size and voids in the pressed pellets used, etc. Fused beads can be an alternative sample preparation method for WD-XRF to achieve high-quality results. The mineral standard-based EDS microanalysis totals for S1-S5 given in table 3.8 vary between 96.46 - 100.76. In standard-based SEM-EDS, analytical totals less than 100 can be due to a missed element in the spectrum, reduced excitation volume due to an unstable electron beam, unanticipated inclusion in the interaction volume, or deviation from the measurement conditions between the unknown and standard. Analytical totals greater than 100 likely arise from the measurement condition deviation like probe dose or sample geometry issues [7].



Figure 3.9: Deviation plots of four main metal oxide contents of reference GGBFS paste samples based on standard-based EDS microanalysis using slag standard ES1 with mineral standard-based EDS microanalysis. (a) CaO, (b) SiO<sub>2</sub>, (c) Al<sub>2</sub>O<sub>3</sub>, (d) MgO

The normalized mass fractions should always be reported with the analytical total for both methods. Normalization of analytical totals can cover the measurement errors mentioned and lead to inaccurate conclusions. The analyst must be aware of what normalization scheme is applied to the results. A crucial step in the unknown material quantification procedure is carefully examining the raw analytical total. If all constituents present are measured with a standards-based/matrix correction procedure, the analytical total can be expected to fall within the range of 98 to 102 [7]. The general experience for microanalysis of cementitious materials is that raw analytical total ranging from 90 to 110 can be considered to minimize the impact of geometric factors and to reduce time in the data collection process [29]. Several iterations of qualitative and quantitative analysis of the X-ray spectra may be needed to discover all of the constituents of a complex unknown material. In this situation, the analytical total and the residual spectrum after quantification serve as useful guides for achieving valuable results.

#### 3.3.2. Remarks on EDS microanalysis methodologies

There is always a debate over the widespread use of standardless quantitative analysis that undermines the potential of standard-based EDS microanalysis. It can be understood that the remote standards standardless protocol used in this project is not a true standardless procedure. It uses a suite of



Figure 3.10: Deviation plots of four main metal oxide contents of reference GGBFS paste samples based on standard-based EDS microanalysis using slag standard ES5 with mineral standard-based EDS microanalysis. (a) CaO, (b) SiO<sub>2</sub>, (c) Al<sub>2</sub>O<sub>3</sub>, (d) MgO

vendor-measured standard intensities of pure elements and stoichiometric binary compounds under set conditions to quantify the unknown spectra. Since the probe dose is not taken into account in this method, the analytical total has to be normalized to unity [51]. If the unknown spectrum is measured with a different beam energy or a different EDS photon efficiency, or if any of the element present in the unknown spectra is not represented in the standard database, several assumptions and calculations will be made by the software to adjust the available data to quantify the unknown. Since the user is not provided with detailed documentation about the software implementations, several uncertainties might arise in these analytical values. The potential pitfalls of standardless routines, as observed in the results of this study, included normalisation of the analytical totals to 100%, which proved to be highly erroneous in certain cases, where the analytical totals from standard-based analyses for a few partially hydrated GGBFS grains were as low as 60%. Even for the 3months old cement-GGBFS paste samples used as references here, certain large and angular GGBFS grains could be partially hydrated with thick hydration rims surrounding them, which may not be visible through the 2-dimensional view of the SEM-BSE image. If such grains are chosen for quantification, the interaction volume of the electron beam might include the hydration products, thus giving a lower analytical total. Normalising these results might give a higher standard deviation observed for standardless quantitative analysis. (Images)

#### 3.3.3. Matrix effects

The available mineral standards show poor resemblance in structure and composition to any cementitious material. Therefore, choosing mineral standards for the microanalysis of cementitious materials is not a straightforward process. Likewise, GGBFS is not structurally or chemically similar to commonly available rock-forming minerals. This could lead to variation and errors in quantification totals since significant differences in the matrix between the standard mineral and the unknown spectra could lead to errors in the ZAF corrections. If selecting appropriate standards suitable for every element and assemblage is not attainable, the best practice is minimising the differences in ZAF corrections between the standard mineral spectra and unknown spectra. The relatively small variation in deviation plots between the EDS microanalysis and XRF results shows that mineral standards used in the present research show minimal matrix effects. In general, matrix correction methods used for quantification apply to a homogeneous interaction volume and effectively but incorrectly assume that any inclusion/heterogeneity, if present, is distributed evenly within the interaction volume [65]. Therefore, sufficient EDS points must be selected for quantification to verify and ensure the homogeneity of the sample. The standard deviation of the mass fractions quantified for an element and analytical totals are true indicators of any such heterogeneity.

#### 3.3.4. Influence of properties of GGBFS

Although GGBFS is highly homogeneous, certain intrinsic grain defects and variations might have affected the analytical totals observed here. Uchikawa et al. [28] showed that within the same GGBFS grain, the crystalline phases tend to have less Al<sub>2</sub>O<sub>3</sub> and a higher MgO than the amorphous phase. Meng and Schneider [66] reported that within a GBFS grain, amorphous phases in-between the merwinite crystals were enriched in Al and significantly depleted in Mg compared to the majority of the amorphous phase. Müller et al. [67] observed that crystalline inclusions in GBFS grains were concentrated in a few single grains rather than uniformly distributed across all the grains. They found that these inclusions often appeared at the bubble or grain boundary, and eventually, grains containing a large number of crystals were also rich in gas bubbles. The porosity of wet GBFS grain reported by Ehrenberg [31] is around 11% by volume. With the distribution of these pores unknown, it was speculated that a certain fraction of these pores might exist in GGBFS after grounding. Harrisson et al., [58] and Kjellsen and Atlassi [68] found that when the interaction volume included the local pores, it may result in lower analytical totals. This was due to the energy loss that resulted in a deficit in X-ray generation at these pores, which affected the  $\phi(\rho z)$  distribution curves and subsequently the Z and A corrections used for microanalysis [69].

#### 3.3.5. Trace elements significance/quantification

The influence of trace additions in GGBFS is determined by their stabilizing or destabilizing role in the glass network formation. The dissolution rate of GGBFS is likely to be increased by network modifiers and will be stabilized and reduced by network forming elements [70]. There is no specific requirement regarding the amount of trace elements in GGBFS in BS EN-15167-1. Trace elements like Ti and Mn in their oxide form with a concentration of less than 1% have little to no effect on GGBFS reactivity [31]. Most elements in the trace concentration range that might be present in GGBFS are heavy metals with high atomic numbers. These metals are directly dissolved in the glass matrix [71]. So the acceleration voltage of 10kV used here to study the GGBFS glass may not be sufficient to excite these heavy metal atoms due to the small overvoltage ratio. If detecting the elements in trace concentration

is of importance, assuming that they are evenly distributed in the GGBFS matrix, EDS analysis with sufficient accelerating voltage and high count EDS spectra can be performed to detect concentrations of elements up to 100ppm in the absence of interference and 500ppm with interference provided that the specimen can withstand the chosen conditions [7]. Due to its higher spectral resolution, WDS can also be a viable alternative.

#### 3.3.6. Influence of experimental parameters

Existing research has extensively discussed the influence of experimental parameters in quantitative EDS analysis such as accelerating voltage, beam current, collection time, number of points, etc., [8], [29], [52]. Although 10kV is sufficient for the major and minor elements considered here for analysis, if traces of iron are expected or found in the initial qualitative analysis, then 15kV or higher would be the ideal accelerating voltage, with special attention should be given to the larger interaction volume associated. Minor variation in probe dose during spectrum collection greatly affects the standard-based microanalysis results. Since it represents spectral intensity, any small variation or misreading will significantly impact the analytical total. Also, care must be taken to monitor the probe dose decreases the analytical total, and a probe dose reading lesser than the actual probe dose increases the analytical total. For peak fitting techniques like MLLSQ used here, which fits a constant shape model of each elemental peak to the spectrum of the unknown and standards, the stability of the resolution and calibration of the SDD-EDS spectra with input count rate is also essential [72].

### 3.4. Summary

This chapter explored the potential to use standards-based EDS microanalysis to quantitatively measure the chemical composition of partially hydrated GGBFS grains in a cement-GGBFS matrix. The results showed that mineral standard-based EDS microanalysis proved to be a viable method to quantify the metal oxide contents of GGBFS. A small deviation in standard-based EDS microanalysis with respect to XRF analysis was observed for oxide contents of elements present in the major and minor concentration ranges. Amongst the available slag standard, two were chosen for further quantification of elements present in major and minor concentration ranges based on the deviation. The reasons behind the variation in analytical totals and deviation of results between different methodologies were discussed. Based on the results and discussion, it can be seen that standard-based EDS microanalysis can be used to quantify the composition of partially hydrated GGBFS in field concrete samples.

# 4

# Quantitative Energy-Dispersive X-ray Microanalysis of partially hydrated GGBFS in field samples

In this chapter, the author presents a detailed report on the applicability of the protocol examined in the previous chapter to determine the chemical composition of GGBFS used in cement-GGBFS concrete specimens obtained from the field. The variation in the composition of GGBFS in concrete specimens from different time periods in the Netherlands is studied. A flowchart of the workflow in this chapter is shown in Figure 4.1.



Figure 4.1: Flowchart of the workflow in this chapter

# 4.1. Materials and Methodology

## 4.1.1. Sample information

Courtesy of Mr.Yu Zhang, seven concrete specimens from different locations in the Netherlands were sourced, to be analysed with SEM-EDS. A brief description of the samples is given in Table 4.1. The samples are labelled according to their age with A being the oldest and G being the youngest. These samples with different service life were investigated to see whether there are compositional changes in GGBFS over different periods in the past. It was assumed that the Portland cement clinkers that were blended together with this GGBFS also showed variations in chemical composition and fineness.

Table 4.1: Descriptive information	of the concrete samples studied
------------------------------------	---------------------------------

Sample	Details
А	The sample was taken from a stairwell dating back to around 1940. Exact
	location was unknown.
В	The sample was collected from a wind deflection screen near Calandbrug, Europoort Rotterdam (Port of Rotterdam), which was built in 1985. The cement type was reported as CEM III/B.
С	The sample was sourced from a parking garage built around 1980. It was located in Jupiterstraat, Hoofddorp.
D	The sample came from second Benelux tunnel in Vlaardingen, Rotterdam. It was built in 2000, and made of CEM III/B.
Ε	The sample was drilled from the beams above a tunnel in Delft, which was built in 2002. The binder used was mainly CEM III/B.
F	The sample was cast in Microlab, Delft University of Technology, Delft, in 2006. CEM III/B was employed as the binder.
G	The sample was from the underpass Neherkade in Hague built in 2015. In the concrete mixture, CEM III/C was used.

# 4.1.2. Specimen preparation

Most specimens were received as large cylindrical cores and had to be cut into smaller samples. Prior to that, the entire core was impregnated with low-viscosity epoxy resin in a vacuum chamber and allowed to harden for 48 h to preserve the integrity of the structure and protect the micro-structure from damage caused by mechanical sawing. Then, these cores were initially cut into discs of a height of around 10 mm and split into smaller pieces with length and width of around 10-12 mm using a concrete cutting machine cooled with water. These cut samples were immediately immersed in an isopropanol solution for 1 week to stop any hydration that might have started in the cross-section while cutting the sample using water. Then, the cut samples were dried in a 40  $^{\circ}$ C oven for 1 h to evaporate the isopropanol and impregnated again with low-viscosity epoxy resin in a vacuum chamber and allowed to harden for 48 h.

### 4.1.3. Sample preparation for EDS microanalysis

To remove any excess epoxy on the sample surfaces and make the surface flat, these samples were ground in order of #180, #320, #800, #1200, and #2000 silicon carbide (SiC) grinding papers, cooled with 100% ethanol. Subsequently, the surfaces were polished by 9  $\mu$ m, 3  $\mu$ m, 1  $\mu$ m and 0.25  $\mu$ m diamond paste on a rotary table. Between each grinding and polishing step sample surface was cleaned by immersing it in an ultrasonic bath with pure ethanol for 60 sec. Once again, the polished samples were dried in a 40 °C oven for 1 h to evaporate any excess ethanol that might have seeped into the matrix



Figure 4.2: Typical BSE images of field samples

during grinding and polishing. Finally, the well-polished flat samples were carbon coated in a Leica EM CED 030 carbon evaporator to a thickness of about 10 nm.

#### 4.1.4. Instrumental parameters and microanalysis standards

The same instrument and instrumental parameters used in Chapter 4 for the reference samples were also adapted in this Chapter. Around 50 randomly chosen points were investigated per field sample in order to increase the representativeness and reliability of the data. The spectra collected for the mineral standards used in Chapter 4 were also employed here for mineral standard-based quantitative EDS microanalysis. Only slag standards ES1 and ES5 were used for slag standard-based quantitative EDS microanalysis.

### 4.2. Results

Figure 4.2 shows the typical BSE images of samples A-G. It can be seen that old samples like A-D present relatively large GGBFS particles and thick rim around the partially hydrated GGBFS particle when compared to new samples like E-G. Samples A, B, E, and G have traces of Fly Ash, which may have been used as an additive in the mixture.

#### 4.2.1. Mineral standard-based EDS microanalysis

Standardless	A	В	С	D
CaO	$36.33 \pm 5.68^{a}$	$35.32 \pm 3.53$	$35.01 \pm 5.99$	$35.47 \pm 1.07$
$\rm SiO_2$	$38.44 \pm 7.70$	$31.50 \pm 0.73$	$31.70 \pm 5.31$	$32.04 \pm 0.74$
$Al_2O_3$	$9.47 \pm 3.29$	$16.14{\pm}1.78$	$15.19 \pm 1.88$	$16.07 \pm 0.38$
MgO	$11.00 \pm 5.00$	$12.21 \pm 1.51$	$12.86 \pm 3.92$	$11.18 \pm 0.66$
$\mathrm{TiO}_2$	$0.75 \pm 0.35$	$1.09 \pm 0.23$	$1.24 \pm 0.53$	$1.73 \pm 0.49$
MnO	$0.25 \pm 0.49$	$0.29 \pm 0.50$	$0.10 \pm 0.38$	$0.08 \pm 0.26$
$Na_2O$	$0.26 \pm 0.22$	$0.53 \pm 0.08$	$0.52 \pm 0.19$	$0.44 \pm 0.10$
$K_2O$	$0.38 \pm 0.22$	$0.55 \pm 0.15$	$0.73 \pm 0.21$	$0.37 \pm 0.10$
$SO_3$	$3.12 \pm 0.64$	$2.37 \pm 0.33$	$2.65 \pm 0.74$	$2.62 \pm 0.44$
Total	100.00	100.00	100.00	100.00

Table 4.2: Chemical composition of concrete samples determined by standardless EDS microanalysis

<sup>*a*</sup>Values given in Mean  $\pm$ Standard deviation.

Standardless	Ε	$\mathbf{F}$	G		
CaO	$31.17 \pm 8.63^{a}$	$35.77 \pm 1.07$	$40.15 \pm 7.99$		
$SiO_2$	$35.05 \pm 5.29$	$32.08 \pm 0.80$	$36.30 \pm 3.41$		
$Al_2O_3$	$16.52 \pm 5.41$	$16.26 \pm 0.39$	$11.28 \pm 7.35$		
MgO	$10.49 \pm 4.98$	$11.16 \pm 0.63$	$9.42 \pm 2.28$		
${\rm TiO}_2$	$1.74 \pm 1.01$	$1.20 \pm 0.51$	$0.63 \pm 0.42$		
MnO	$0.08 \pm 0.30$	$0.05 \pm 0.20$	-		
$Na_2O$	$0.43 \pm 0.18$	$0.46 \pm 0.09$	$0.35 \pm 0.16$		
$K_2O$	$0.37 \pm 0.19$	$0.34 \pm 0.09$	$0.37 \pm 0.14$		
$SO_3$	$4.15 \pm 3.12$	$2.68 \pm 0.50$	$1.50 \pm 0.67$		
Total	100.00	100.00	100.00		

 $^a\mathrm{Values}$  given in Mean ±Standard deviation.

Table 4.2 and 4.3 exhibit the mean analytical total, the mean value of each metal oxide composition in wt% of interaction volume, and the standard deviation of the corresponding data set. They were obtained by quantifying the EDS spectra of field samples using semi-quantitative standardless EDS analysis and mineral standard-based quantitative EDS microanalysis, respectively, for all the peaks observed. The analytical total values for all the samples exceed 100%, and for samples B, C, and G, it is slightly greater than 102%. Similar to the results found for reference GGBFS in Chapter 3, the standard deviations of the four main metal oxides, i.e., CaO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, and MgO in GGBFS, are comparatively less for mineral standard-based EDS microanalysis than standardless EDS microanalysis. In addition to the four main metal oxides, sulfur tends to be the next important element in terms of mass percentage. Except for sample G and D, all other samples has a sulphur content of 3-4%.

Mineral standard	А	В	С	D
CaO	$39.71 \pm 2.59^{a}$	$36.10 \pm 1.81$	$35.14 \pm 0.75$	$36.51 \pm 1.33$
$SiO_2$	$35.80 \pm 1.54$	$31.45 \pm 1.24$	$32.37 \pm 0.73$	$33.02 \pm 1.13$
$Al_2O_3$	$10.85 \pm 0.55$	$16.70 \pm 0.80$	$16.52 \pm 0.39$	$16.83 \pm 0.61$
MgO	$10.29 \pm 2.15$	$12.14 \pm 0.84$	$12.55 \pm 0.45$	$11.71 \pm 0.64$
${ m TiO}_2$	$0.66 \pm 0.16$	$1.10 \pm 0.29$	$0.98 \pm 0.16$	$1.17 \pm 0.33$
MnO	$0.24 \pm 0.29$	$0.41 \pm 0.22$	$0.53 \pm 0.32$	$0.30 \pm 0.25$
$Na_2O$	$0.31 \pm 0.08$	$0.44 \pm 0.12$	$0.53 \pm 0.07$	$0.41 \pm 0.05$
$K_2O$	$0.37 \pm 0.11$	$0.49 \pm 0.20$	$0.68 \pm 0.20$	$0.38 \pm 0.06$
$\mathrm{SO}_3$	$3.77 \pm 0.32$	$3.65 \pm 0.35$	$3.38 \pm 0.36$	$0.78 \pm 0.12$
Total	$102.00 \pm 0.87$	$102.48 \pm 2.61$	$102.69 \pm 0.70$	$101.10 \pm 3.17$

Table 4.3: Chemical composition of concrete samples determined by standard-based quantitative EDS microanalysis

<sup>*a*</sup>Values given in Mean  $\pm$ Standard deviation.

Mineral Standard	E	$\mathbf{F}$	G
CaO	$34.83 \pm 1.31^{a}$	$34.86 \pm 0.76$	$41.74 \pm 1.90$
$\mathrm{SiO}_2$	$32.94 \pm 0.99$	$32.42 \pm 0.97$	$36.41 \pm 1.02$
$Al_2O_3$	$16.17 \ \pm 0.53$	$16.11 \pm 0.41$	$11.25 \pm 0.89$
MgO	$11.20\ {\pm}0.83$	$11.27 \pm 0.71$	$9.86 \pm 0.93$
${\rm TiO}_2$	$1.65 \pm 0.64$	$1.70 \pm 0.38$	$0.85 \pm 0.29$
MnO	$0.40 \pm 0.21$	$0.18 \pm 0.23$	$0.22 \pm 0.24$
$Na_2O$	$0.42 \pm 0.06$	$0.40 \pm 0.04$	$0.36 \pm 0.08$
$K_2O$	$0.44 \pm 0.08$	$0.42 \pm 0.09$	$0.48 \pm 0.11$
$\mathrm{SO}_3$	$3.57 \pm 0.42$	$3.88 \pm 0.58$	$1.00 \pm 0.23$
Total	$101.62 \pm 1.89$	$101.25 \pm 0.92$	$102.18 \pm 2.61$

<sup>*a*</sup>Values given in Mean  $\pm$ Standard deviation.

Figure 4.3 shows a comparative box plot for the four main metal oxide contents in the field samples A-G obtained by mineral standard-based quantitative EDS microanalysis. The IQR of sample A, which was dated back to the 1940s, shows a comparably large scatter for all the main metal oxides. The change in GGBFS chemistry is insignificant for samples B to F. Sample G presents a higher quantity of CaO and SiO<sub>2</sub> and a lower quantity of Al<sub>2</sub>O<sub>3</sub> and MgO.

#### 4.2.2. Slag standard-based EDS microanalysis

Table 4.4 and 4.5 exhibit the mean chemical composition in wt% of interaction volume regarding the four major metal oxides in field sample A-G, determined by standard-based EDS microanalysis using slag standards ES1 and ES5, respectively, as well as the standard deviation of the corresponding data set. The RD between the values determined by slag standard-based EDS microanalysis and mineral



Figure 4.3: Box plots of four main metal oxide contents of GGBFS in concrete samples based on standard-based EDS microanalysis. (a) CaO, (b) SiO<sub>2</sub>, (c) Al<sub>2</sub>O<sub>3</sub>, (d) MgO

standard-based EDS microanalysis is given under RD5. Using slag standard ES1, the RD5 values of CaO and SiO<sub>2</sub> is less than 5% while the RD5 values of  $Al_2O_3$  and MgO are less than 10%. Likewise, using standard ES5, the RD5 values regarding CaO, SiO<sub>2</sub>, and  $Al_2O_3$  are less than 5% and it is around 10% for MgO.

# 4.3. Discussion

#### 4.3.1. Chemical composition of GGBFS used in the industry

GGBFS compositions generally vary over different regions, as seen in Table 2.2, due to the differences in metallurgical technology used to extract iron, geographical variation in raw material compositions and GGBFS utilization requirements [4], [16]. The composition of GGBFS also varies over time in a single location as reported by [31]. Only the GGBFS produced from the same blast furnace plant is expected to exhibit a constant composition [4]. This variation in GGBFS chemistry ultimately leads to a variation in basicity and, thus, differences in the latent hydraulic property of GGBFS. The only observable compositional trend in the samples studied here is the sharp increase in CaO and SiO<sub>2</sub> contents of GGBFS in sample G. Recent publications also indicate a trend for producing Ca-rich/Mgpoor GGBFS, which appears to be especially distinct across Europe ([73]–[75], North America [76], and Australia[77].  $\mathrm{SiO}_2$ 

 $Al_2O_3$ 

MgO

ES1	А	RD5	В	RD5		С	RD5		D		RD5
CaO	$37.95 \pm 4.$	01 4.43	$35.90 \pm 1$	.40 0.54	35.	$.17 \pm 0.$	0.08	35	$.13 \pm 1.28$	;	3.78
$\mathrm{SiO}_2$	$34.67 \pm 2.5$	47 3.16	$30.25 \pm 1$	.02 3.82	31.	.44 ±0.	71 2.88	30	$.82 \pm 1.06$	;	6.66
$Al_2O_3$	$11.78 \pm 0.$	80 8.60	$17.91 \pm 0$	.76 7.21	17.	.83 ±0.	42 7.92	17	$.48 \pm 0.64$	Į	3.82
MgO	$11.26 \pm 3.$	33 9.44	$11.40 \pm 0$	.71 6.15	11.	$.85 \pm 0.$	42 5.55	10	$.63 \pm 0.57$	,	9.21
		·									
	ES1	Е	RD5	F		RD5	G		RD5		
	CaO	$34.69 \pm 1.3$	37 0.39	$34.90 \pm 0.5$	76	0.11	$40.21 \pm 1.$	52	3.65		

 $31.50 \pm 0.94$ 

 $17.40 \pm 0.44$ 

 $10.64 \pm 0.67$ 

2.85

7.98

5.61

 $33.93 \pm 0.82$ 

 $11.65\ {\pm}0.92$ 

 $8.93 \pm 0.83$ 

6.81

3.57

9.44

Table 4.4: Chemical composition of concrete samples determined by quantitative slag standard-based (ES1) EDS micro-analysis

<sup>*a*</sup>Values given in Mean  $\pm$ Standard deviation.

 $31.78 \pm 1.07$ 

 $17.34 \pm 0.62$ 

 $10.49\ {\pm}0.78$ 

 $^{b}$ RD5 = (|Slag standard EDS-Mineral EDS|/Mineral EDS)\*100

3.51

7.19

6.38

Table 4.5: Chemical composition of concrete samples determined by quantitative slag standard-based (ES5) EDS microanalysis

$\mathbf{ES5}$	A	RD5	В	RD5	С	RD5	D	RD5
CaO	$40.00 \pm 2.59$	0.72	$36.17 \pm 1.41$	0.20	$35.43 \pm 0.75$	0.82	$35.39 \pm 1.29$	3.07
$SiO_2$	$36.66 \pm 1.59$	2.40	$31.93 \pm 1.07$	1.53	$33.19 \pm 0.75$	2.52	$32.53 \pm 1.11$	1.49
$Al_2O_3$	$11.39 \pm 0.57$	4.97	$17.43 \pm 0.74$	4.32	$17.35 \pm 0.41$	5.03	$17.00 \pm 0.61$	1.01
MgO	$11.47 \pm 2.37$	11.48	$13.46 \pm 0.83$	10.84	$14.00 \pm 0.50$	11.52	$12.56 \pm 0.68$	7.21

$\mathbf{ES5}$	Е	RD5	F	RD5	G	RD5
CaO	$34.95 \pm 1.38$	0.35	$35.16 \pm 0.77$	0.85	$40.52 \pm 1.53$	2.93
$SiO_2$	$33.54 \pm 1.13$	1.83	$33.24 \pm 0.99$	2.53	$35.83 \pm 0.86$	1.60
$Al_2O_3$	$16.87 \pm 0.60$	4.28	$16.93 \pm 0.43$	5.05	$11.32 \pm 0.89$	0.64
MgO	$12.39 \pm 0.92$	10.58	$12.56 \pm 0.79$	11.47	$10.55 \pm 0.98$	6.92

 $^a \textsc{Values}$  given in Mean ±Standard deviation.

 $^{b}$ RD5 = (|Slag standard EDS-Mineral EDS|/Mineral EDS)\*100

#### 4.3.2. Outliers and omitted data vs Standardless data

GGBFS grains in old concrete samples tend to have a thicker hydration rim due to a higher degree of hydration. Out of the 50 EDS points chosen from each sample, on average, only around 30 points had analytical totals of 90% to 105% after standard-based EDS microanalysis. In Figure 4.4, the BSE image of sample B with points chosen to collect EDS spectra is shown. It can be seen few GGBFS grains have been hydrated completely. For reference, Point 10 is chosen at a fully hydrated GGBFS grain, point 6 gave an analytical total of 53.00. Within the available partially hydrated GGBFS grains, point 6 gave an analytical total of 82.09 and point 9 gave an analytical total of 75.13, although a large fraction of this grain seems unhydrated. As mentioned in the previous chapter, this can be ascribed to the restricted view of a 2-dimensional BSE image, which cannot exhibit the complete state of a partially hydrated GGBFS grain. The interaction volume of EDS points in these grains might include some hydration products, leading to a lower analytical total. Point 8 gave an analytical total of 108.18. This can be



Figure 4.4: EDS points Sample B

due to surface blemishes. Such variations cannot be easily identified using standardless analysis, which normalizes the analytical total to 100.

#### 4.3.3. Sulphur content in GGBFS

Sulphur in BFS comes from the iron ore and coke used as raw materials. A certain amount of sulphur will be released as  $H_2S$  with water vapour while the residual sulphur remains in BFS. For EDS microanalysis, sulphur trioxide (SO<sub>3</sub>) is assumed to be the oxide form existing in GGBFS. It is observed that the mass percentage of SO<sub>3</sub> in these field samples is commonly less than 4 wt%. However, most sulphur exists as sulfide (S<sup>2-</sup>) in GGBFS. Arai et al., [78] and Roy [79] found that reduced forms of sulfur are present as sulfide (S<sup>2-</sup>) and sulfate (SO<sub>4</sub><sup>2-</sup>) with the majority of sulfide mostly in glassy GGBFS. BS EN 15167-1 [17] requires that the sulfide and sulfate contents in GGBFS should be less than 2.0 and 2.5%, respectively. However, the standard did not specify how to measure sulfide and sulfate contents in GGBFS and neither can they be differentiated using EDS or XRF analysis. Thus, analytical totals greater than 100 could have originated from this uncertainty in the oxidation state of sulphur. Based on stoichiometry, it is inferred that the amount of sulphate is 2.5 times the amount of sulfide. So quantifying the sulfur content in GGBFS assuming one oxidation state should not be considered accurate. Bowden [80] and Schramm [81] used WD-XRF to determine the composition of sulphur species in anhydrous cement. Thus, the same technique could be explored to determine the concentration and forms of sulphur in anhydrous GGBFS.

#### 4.3.4. Feasibility of using slag standard to quantify unknown slag composition

Ideally, the employed standards should resemble the unknown material as closely as possible in microanalysis. For analysing GGBFS with EDS microanalysis, mineral standards that resembled the structure or composition of GGBFS were non-existent. The use of slag standards was expected to reduce the matrix effects between the unknown spectra and standard spectra. Z corrections can be reduced due to similar mean atomic number values, while A and F corrections were expected to decrease since the differential absorption of X-rays and emission of secondary X-rays, respectively, between the partially hydrated GGBFS in a cement matrix and raw GGBFS used as standard, could be similar. Since the raw GGBFS used in this study was almost entirely amorphous, it was speculated to perform better when used as a standard for EDS microanalysis. A major drawback in using raw GGBFS as a standard to quantify partially hydrated GGBFS grains in cement matrix is to know its exact composition. In this study, apart from the reasons mentioned in Section 3.2.3 for using ES1 and ES5 as standard,

# 4.4. Summary

This chapter explored the applicability of standard-based EDS microanalysis to quantify the chemical composition of GGBFS used in field concrete. Using the quantification results, the variation in GGBFS composition used in the Netherlands over the years was reviewed. The analytical totals of mineral standard-based EDS microanalysis proved that it is a viable tool that can be used to quantify the metal oxide composition in partially hydrated GGBFS grain in field concrete. Slag standards were seen as a viable alternative only to detect elements in the major concentration range. Finally, potential problems that might affect the analytical totals of EDS microanalysis were discussed briefly.

# 5

# Thermodynamic modelling of GGBFS hydration products with varying composition

This chapter gives an insight into the GGBFS-cement hydration phase assemblages predicted using thermodynamic modelling for variation in the composition of the four principal oxides; CaO, SiO<sub>2</sub>, MgO, and Al<sub>2</sub>O<sub>3</sub> in GGBFS. The important hydration products that affect the performance of GGBFS used in cement-GGBFS binders are studied. A flowchart of the workflow in this chapter is shown in Figure 5.1.



Figure 5.1: Flowchart of the workflow in this chapter

# 5.1. Thermodynamic modelling for cementitious system

Thermodynamic modelling predicts the stable phase assemblage of cementitious material hydrates and aqueous phase composition from the total bulk elemental composition of the components under study at a given temperature and pressure. The flexibility and comprehensiveness of these theoretical calculations allow them to consider the intrinsic complexity of cementitious systems fully and can be used to supplement experimental results to evaluate and conclude the performance of novel cement-based systems. The success and accuracy of these predictions depend directly on a reliable, accurate, and complete thermodynamic database consisting of standard state properties of the aqueous species and the cement hydrates [82]. There are many thermodynamic modelling software packages available such as PHREEQC [83], The Geochemist's Workbench [84] and Gibbs Energy Minimization Software for geochemical modelling (GEMS) [85]. In this study, opensource GEMS v.3 together with thermodynamic data from Nagra-PSI [86] and SUPCRCT92 [87] thermodynamic database supplemented by cementspecific data from Cemdata18 [88] is used. GEMS, as its name suggests, primarily uses the Gibbs energy minimization technique that provides information on the minimum amount of energy required for the systems to react and attain equilibrium at the given temperature and pressure to determine every combination of phases that might be formed using stoichiometric mass balance. Chemical interactions involving solids, solid solutions, aqueous electrolytes and gas phases are simultaneously considered to calculate the speciation, the kind, and the amount of solids precipitated. [89].

# 5.2. Hydrate assemblage

To carry out the thermodynamic calculations, the bulk composition of GGBFS S1 determined by XRF given in table 3.1 and the default composition of the portland cement (PC) provided in the software was chosen as the primary input. For this study, the slag-to-cement ratio was 7:3 by mass and the water-to-binder ratio was 0.4. The C-S-H phase was modelled using the calcium-alkali aluminosilicate hydrate ideal solid solution model (CNASH ss) from Myers et al. which accounts for the uptake of elements other than Ca, Si, H and O in the structure of C-S-H gel. MA-OH-LDH ss containing three end-members with Mg/Al ratios of 2, 3 and 4 reformulated into an ideal solid solution was employed to perform the modelling of hydrotalcite-like solid solution series. The modelling was carried out at a temperature of 20°C and a pressure of 1 bar. All other settings and input parameters for the software were based on the tutorials provided by Lothenbach and Winnefeld [90]. The crystalline phases in GGBFS were considered to be inert and only the amorphous phases were assumed to react. The hydration assemblages were calculated for a reaction time of 1 year. At this age, the degree of hydration for PC estimated using the empirical kinetic approach of Parrot and Killoh [91] was 0.87. For GGBFS, the degree of hydration for the given slag-to-cement ratio and the water-to-binder ratio was kept at 0.40 based on the findings of Lumley et al. [92]. The main objective of this study is to observe the changes in the hydration phase assemblage of the cement-GGBFS system for variation in the composition of four principal oxides; CaO, SiO<sub>2</sub>, MgO, and Al<sub>2</sub>O<sub>3</sub> in GGBFS. The ranges of these oxides were taken from Table 2.1, Table 2.2 and Table 4.3. To simplify the calculations, the ratios between the oxides that were not varied were kept constant and their composition was varied proportionately with the oxide under study. Also, the variation in hydration of GGBFS due to varying oxide composition was neglected, and the degree of hydration was assumed to be constant over the given range of oxide composition under study.

### 5.3. Results and discussion

For this study, the simulated hydrated phases are C-(N)A-S-H, portlandite, Al-Fe siliceous hydrogarnet, Aft-phases, Afm-phases, and hydrotalcite. Figure 5.2 illustrates the influence of CaO content in GGBFS on the hydrates assemblage in a cement-GGBFS system. As the CaO content was increased (Ca/Si ratio increased), the amount of C-(N-)A-S-H and hydrotalcite gradually decreased. Beyond CaO content of



Figure 5.2: Phase assemblages of cement-GGBFS system as predicted by thermodynamic modelling as a function of CaO content

34% remains of portlandite can be observed, which can be used by the GGBFS for further hydration. This portlandite increases as the CaO is increased. Traces of Aft-phases remain throughout the range of CaO. The amount of Al-Fe siliceous hydrogarnet seems to be unaffected by the variation of CaO content.

Figure 5.3 illustrates the influence of  $SiO_2$  content in GGBFS on the hydrates assemblage in a cement-GGBFS system. Here, as the  $SiO_2$  content was increased (Ca/Si ratio decreased), the amount of C-(N-)A-S-H increased. Although  $SiO_2$  content in GGBFS is expected to negatively affect its reactivity since the degree of hydration was kept constant throughout the oxide range in this study the increase in  $SiO_2$  content could be used for the formation of C-(N-)A-S-H phase. A significant amount of portlandite is observed at lower concentrations of  $SiO_2$  which GGBFS could use up to hydrate further. Afm-phases and hydrotalcite gradually decreased as  $SiO_2$  content increased. Initially, constant traces of Aft-phases was observed which at higher concentration of  $SiO_2$  increased slightly. The amount of Al-Fe siliceous hydrogarnet seems to be unaffected by the variation of  $SiO_2$  content.

Figure 5.4 illustrates the influence of  $Al_2O_3$  content in GGBFS on the hydrates assemblage in a cement-GGBFS system. As the  $Al_2O_3$  content was increased, the amount of C-(N-)A-S-H starts to decrease as observed by Haha et al. [93]. Aft-phases observed at lower content of  $Al_2O_3$  get converted to Afmphases with the increase in  $Al_2O_3$  content as observed by Zhang et al. [60]. Afm-phases forms at  $Al_2O_3$ content of 6.5% and gradually increases along with  $Al_2O_3$  content. Portlandite content decreased with the increase in  $Al_2O_3$  content which was correlated to the formation of Afm-phases by Zhang et al. [60]. Here, hydrotalcite seems unaffected by the variation of  $Al_2O_3$  content.

Figure 5.5 illustrates the influence of MgO content in GGBFS on the hydrates assemblage in a cement-GGBFS system. As the MgO content was increased, the amount of C-(N-)A-S-H and Afm-phases



Figure 5.3: Phase assemblages of cement-GGBFS system as predicted by thermodynamic modelling as a function of  $SiO_2$  content



Figure 5.4: Phase assemblages of cement-GGBFS system as predicted by thermodynamic modelling as a function of  $Al_2O_3$  content

decreased. In contrast, hydrotalcite gradually increased since at high MgO content, a higher fraction of available Mg is bound by hydrotalcite [60], [94]. Traces of ettringite is observed at lower MgO



Figure 5.5: Phase assemblages of cement-GGBFS system as predicted by thermodynamic modelling as a function of MgO content

content which increases marginally at higher MgO content. The amount of portlandite increases with an increase in MgO content.

Table 2.1, 2.2, 4.3 shows the wide variation in GGBFS composition observed across locations. As seen in the thermodynamic modelling phase assemblages, variation in GGBFS composition leads to changes in hydration products formed, affecting the performance of the cement-GGBFS system. Compared to a pure cement paste, GGBFS has more SiO<sub>2</sub> and less CaO that leads to a lower Ca/Si ratio in C-(N-)A-S-H gel phase. This reduces the total porosity by filling up the capillary pores and thus increases durability. Hydrotalcite phase and Ca-Al Afm phases reduce the effect of carbonation on the cement-GGBFS system by absorbing the CO<sub>2</sub> [95]. Ideal composition favouring the formation of these phases could lead to a longer service life of a structure using a cement-GGBFS binder.

# 5.4. Summary

The differences in hydration phase assemblages due to the variation in the chemical composition of GGBFS used in cement-GGBFS system is discussed in this chapter. Primary hydration products such as C-(N)-A-S-H, Aft phases and hydrotalcite that affect the cement-GGBFS system's performance varied significantly due to the variation in the chemical composition of GGBFS.

# 6

# **Conclusion and Recommendation**

The research's primary focus is to explore the feasibility of using EDS microanalysis for quantifying the chemical composition of GGBFS used in existing field concretes. The potential to use mineral standards and slag standards to quantify an EDS spectrum from a partially hydrated GGBFS grain was examined and applied to cement-GGBFS concrete of different service life. Also, the variation in the hydration products formed due to the variation in the chemical composition of GGBFS used in a cement-GGBFS system was studied. Through these investigations, the following conclusions can be drawn:

- Quantitative mineral standard-based EDS microanalysis can be used to characterize partially hydrated GGBFS grains in existing field concrete to know the composition of GGBFS used. Reliable quantification data can be obtained for the four main metal oxides (CaO, SiO<sub>2</sub>, MgO, and Al<sub>2</sub>O<sub>3</sub> content in GGBFS. When present in the major and minor concentration range, oxide contents from mineral standard-based EDS microanalysis showed less deviation (<5%) with respect to XRF analysis.
- Quantitative slag standard-based EDS microanalysis analysis can be used to quantify the composition of elements in the major concentration range only when the composition of the raw GGBFS is known accurately. When used to quantify the oxide contents of the four main metal oxides (CaO, SiO<sub>2</sub>, MgO, and Al<sub>2</sub>O<sub>3</sub> content in field concrete, it showed less deviation (<5%) with respect to mineral standard-based EDS microanalysis.
- The selection of standards for quantitative microanalysis is crucial. Due to the lack of minerals resembling anhydrous GGBFS grain, minerals similar to the composition of the material under study should be chosen to reduce the matrix effects between the standard and the unknown.
- Quantitative standard-based EDS microanalysis should be used over semi-quantitative standardless EDS analysis in all SEM-EDS-based microanalysis of cementitious materials due to the variation in analytical totals that would be normalized to 100 in standardless analysis.
- When approaching an unknown material to quantify using EDS, the following protocol is suggested.
  - Obtain multiple EDS spectra of the unknown material.

- Identify the peak and estimate matrix constituents.
- Choose suitable mineral standards for all the constituents considering matrix effects.
- Obtain mineral spectrums and multiple unknown spectra at different spots.
- Check for homogeneity of the material with standard-based EDS data.
- Quantify unknown spectra using mineral standard spectra.
- If more accuracy is needed, obtain/synthesize a glass using the composition data from mineral standard-based quantification.
- Obtain EDS spectra from this glass and use them to quantify the unknown material.
- The quantified GGBFS composition of field concrete showed considerable variation with no evident trend for the four main metal oxides (CaO, SiO<sub>2</sub>, MgO, and Al<sub>2</sub>O<sub>3</sub> content. A large relative deviation in oxide contents between different methodologies was observed for the elements in the minor-trace range, especially Sulphur and Titanium.
- To enhance/sustain the performance of cement-BFS concrete, GGBFS composition favouring hydration products such as C-(N)-A-S-H, hydrotalcite-like phase and Aft phases is recommended.

Based on the findings of this research, certain limitations were encountered that led to many recommendations for future research. They are suggested as follows:

- Accurate methods to quantify anhydrous GGBFS should be studied. Existing bulk material analysis techniques like XRF and ICP-MS have their own disadvantages. The potential to use SEM-EDS to quantify the composition of raw materials can be explored.
- The repository of potential minerals that could be used as standards for the microanalysis of cementitious materials should be explored further. A standard protocol to synthesize standards for ease of use should be established.
- For more accuracy, the prospect of using calibration curves to calculate the limit of detection and the limit of quantitation for an element in a cementitious matrix quantified using a particular standard can be investigated.
- The potential to use WDS microanalysis to quantify raw and partially hydrated GGBFS accurately should be studied, and a suitable protocol can be established. Although time-consuming, WDS is speculated to quantify elements in trace concentration range accurately.
- As sulphur was found to exist as multiple species in GGBFS, WDS could potentially be used to study and quantify the different sulphur species.
- The potential to use SEM-EDS to quantify other cementitious materials and their hydration products can be explored.

# A

# Exploring NIST DTSA-II for quantitative microanalysis

DeskTop Spectrum Analyzer-II (DTSA-II) is a multi-platform free software tool developed at the National Institute of Standards and Technology (NIST) for quantifying and simulating energy dispersive X-ray spectra [96]. The EDS instrument vendor's software has been simplified over the years by removing advanced spectrum manipulation and interrogation tools, which are retained by DTSA-II to give a deeper understanding of how spectrum analysis works. It is designed to perform high-quality X-ray microanalysis by connecting three integral tools: simulation, which allows users to understand the measurement process; quantification, which allows users to estimate composition from the spectra; and experiment design, which allows users to develop a measurement protocol [7]. In this chapter, the author gives detailed instructions about this software based on several articles [96]–[99], books [7] and the author's personal experience while using the software.

### A.1. Setting up the detector

DTSA-II uses the concept of detectors to connect simulation and quantification. The user needs to create a detector model to represent the physical X-ray detector used in the instrument. They are configured in the "Preferences" dialog as shown in Figure A.1 under "File" main menu item and allows the user to declare properties of their instruments and X-ray detectors. This information is critical for accurate quantification as it is used to determine the position and width of measured characteristic X-ray lines [96]. It can be obtained from the vendor, product manual, or can also be imported directly to the software from the simulated spectrum file (should be cross verified by opening the same spectrum file using notepad and with information from Zaluzec et al. [100]).

The critical values that are needed to model the detector are window type, elevation angle, optimal working distance, sample-to-detector distance, detector area, crystal thickness, number of channels, nominal energy scale, nominal zero offset, resolution at Mn-K $\alpha$  and azimuthal angle. Unfortunately, some of them can only be approximated or are difficult to obtain. In that case, it is advised to choose the default values [7]. Nominal energy scale, nominal zero offset, and full width at half-maximum(FWHM)



Figure A.1: The preferences dialog showing (a) the type of detector to be added and (b) properties of a detector to be entered

resolution at Mn-K $\alpha$  values can be calibrated later using the "Calibration alien" tool in DTSA-II.

# A.2. Calibrating the detector

Before attempting to identify/quantify spectra, it is important to properly calibrate the EDS system to guarantee that accurate energy values are measured for characteristic X-ray peaks. The user needs to obtain spectrum from a known material such as copper or manganese that provides characteristic X-ray peaks at low photon energy (e.g., Cu-L $\alpha$  at 0.930 keV, Mn-L $\alpha$  at 0.637 keV) and at high photon energy (e.g., Cu-K $\alpha$  at 8.048 keV, Mn-L $\alpha$  at 5.900 keV [46]). Then, the "Calibration alien" dialog under "Tools" main menu item is opened to start the calibration process. As shown in Figure A.2a, the first step is to choose the detector to be calibrated, which was set up as given in section A.1. Next, the calibration method is chosen as shown in Figure A.2b which in this case it is to "Calibrate using an elemental reference". Here, Cu/Mn spectra is used as reference spectra to calibrate the detector (Figure A.2c). Finally, a linear fit type is selected to obtain the calibration results as shown in Figure A.2d. Note that the detector should be calibrated periodically to ensure quality assurance of results.

# A.3. Quantification of spectra

Prior to starting the quantification process, the user needs to collect three types of spectra: standards, references and unknowns. Standard spectra are those taken from materials with well-known chemical compositions. DTSA-II compares the unknown spectrum to spectra obtained from established standard materials for quantification. This spectrum provides characteristic X-ray intensity information i.e., the element peaks in the spectrum which are used to obtain the k-ratio.

In certain cases the characteristic lines present in a standard spectrum for two or more elements may overlap, causing interference which makes it difficult to determine the peak intensities on an elementto-element basis. This can be resolved by using reference spectra with clear well-resolved peaks for those specific elements which are typically collected from pure elements or simple compounds. Using standard spectra and reference spectra the unknown spectra will be quantified. Table A.1 shows the properties that should be considered for these three types of spectra.

Before quantification, the user should load the unknown spectrum and manually identify the peaks using NIST DTSA-II and also use the automatic peak identification provided by EDS vendor to confirm the manual peak identification at all levels of the constituent composition range. Following this, the user

brate an EDS detector	X Calibrate an EDS detector	
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Figure A.2: The calibration alien dialog showing (a) detector to be calibrated and (b) calibration method chosen (c) reference spectra to be selected for calibration (d) calibration results

Table A.1: Common parameters required for different spectra types [98]

Spectrum type	Beam energy	Probe current	Live time	Peak elements	Clear X-ray lines
Standard	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	
Reference				$\checkmark$	$\checkmark$
Unknown	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$	

Spectrum type	Detector type	Detector				
Spectrum type	Detector type	Position	Resolution	Calibration		
Standard	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$		
Reference	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$		
Unknown	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$		

can start the quantification process, using the "quantification alien" dialog under "Tools" main menu item. The user will be guided through the quantification procedure in steps as shown in Figure A.3. For the first step, the user needs to choose the type of quantification they would like to perform. In this case, the user can select the option "Determine the composition of an 'unknown' spectrum by MLLSQ fitting to standards" as shown in Figure A.3a. Next, the user should specify the beam energy and verify the instrument details for the spectra to be quantified. Depending on the elements to be quantified identified with manual peak selection, the required standards should be chosen as shown in Figure A.3c. The software asks the user to provide any missing critical information associated with the



Quantification Allen X
Previous: Select a quantification mode
Previous: Select a quantification mode
Next: Specify the instrument
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with callender RWH4[4m Ka]=136.7 eV - 2021;04-21 12:00
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at a beam energy of 10 keV.
Message:
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Resc, Next Proh

(b)

Specify unmeasured elements

(d)

ne Family a Al [0.665, 1.217 keV] g Al [1.027, 1.416 keV] J Al [1.298, 1.706 keV] J K-L3 + 2 others [1.546, 1.992 keV] J K-L3 + 2 others [1.546, 1.992 keV] Ca K-family [0.86, 7.972 keV] ~~(4.244, 5.154 keV] ~~(4.244, 5.154 keV]

O No extra element

C Element by differe

Oxygen by stoichiometry

Specify lines to quantify.

ly used to quantify each element

(f)

×

Details...

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(c)







Figure A.3: The quantification alien dialog showing (a) the methods for quantification and (b) instrument specifications to be entered (c) specifying the standard spectra used (d) specify method to quantify unmeasured elements, if any (e) specifying the reference spectra used (f) specifying element lines used (g) specifying unknown spectra to quantify (h) quantification results
standard spectrum loaded in this dialog. It is also advisable to manually verify the "properties" of the standards used. The composition of each standard in mass fraction (%) has to be entered manually by the user. It is recommended to enter all the elements in the standard spectra in the material editor. Further, the method to quantify any unmeasured elements in the spectra without standards is chosen as shown in Figure A.3d. In this case, the oxygen is calculated by stoichiometry and the user should check the oxidation states of all the elements to be quantified.

In the next dialog, the reference spectra for all the elements that are needed to be quantified are chosen by the user as shown in Figure A.3e. It is important to note here that the software asks a reference spectrum for all the elements in the standards chosen for quantification. The user needs to make sure a good signal-to-noise ratio is reflected for the family of lines of the elements under consideration. Figure A.3f shows the characteristic family of X-ray lines chosen for quantification. The default family of lines provided by the software gives optimal results, but if necessary the user may choose the desired family of lines to be used for quantification. The final step is to select all the unknown spectra to be quantified and verify their properties as shown in Figure A.3g. Probe current recorded for each spectrum during collection and the type of coating on the specimen should be entered here. After choosing and verifying all the spectra to be quantified, the next step produces the quantification results as shown in A.3h. The results are tabulated on a spectrum-by-spectrum basis showing the elemental concentration and associated uncertainty in the quantification process for each element chosen to quantify in the spectra. These results can be imported to Excel in either mass fraction, normalized mass fraction or atomic percent. A report will also be saved by the software that summarizes the standards, references, parameters chosen for quantification and the quantification results.



## NIST DTSA-II output report

The detailed NIST DTSA-II result output report file for all the X-ray spectra quantified in this thesis is attached through links in this chapter. Select the standard with which the X-ray spectra were quantified to view the corresponding software result output.

- Chapter 3 Results of reference samples quantified using mineral standards.
- Chapter 3 Results of reference samples quantified using slag standards ES1, ES2, ES3, ES4 and ES5.
- Chapter 4 Results of field samples quantified using mineral standards.
- Chapter 4 Results of field samples quantified using slag standards ES1 and ES5.

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