Soundness and Compressive Strength of Portland Cement Blended with Ground Granulated Ferronickel Slag

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Highlights:

1. Soundness and compressive strength of ferronickel slag (FNS) as SCM were studied.
2. Effects of FNS on water demand and setting times were similar to those of other SCMs.
3. The high Mg of FNS present in the form of forsterite ferroan did not increase expansion.
4. Effect of FNS on strength development is comparable to that of low-calcium fly ash.

Abstract: This paper evaluates the fresh and hardened properties of cement pastes and mortars blended with a ground granulated high-magnesium ferronickel slag (FNS). The main elements of the slag are Silicon (Si), Magnesium (Mg) and Iron (Fe). Test results show that water demand and setting times were not significantly changed by use of the FNS as cement replacement up to 50%. Le-Chatelier soundness test, autoclave expansion test and accelerated curing at 80 ^{o}C for 120 days showed no increase of expansion by up to 65% FNS despite its high magnesium content. This is because the Mg was found to be in the form of stable forsterite ferroan that did not take part in the

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hydration and expansive $Mg(OH)_2$ (Brucite) was not found in the scanning electron microscope (SEM) images of the microstructure and powder X-ray diffraction (XRD). The 28-day strength activity index of the FNS was 84%. The 90-day mortar compressive strengths were 93% and 68% of the control specimen for 20% and 50% FNS respectively. Thus the soundness and strength development of the ground FNS were found comparable to those of other commonly used supplementary cementitious materials such as class F fly ash.

Keywords: Blended cement, compressive strength, mortar, ferronickel slag, soundness.

1. Introduction

Cement is known as an energy intensive material, which is the conventional binder used for concrete. Concrete is the most widely used construction material because of its versatile properties, availabilities of raw materials, high strength and good durability. However, approximately one tonne of carbon dioxide is emitted to the environment in the production of one tonne of cement [1]. Globally, about 5% to 7% of the carbon footprint is estimated to be related to the production of cement [2]. Thus the reduction of greenhouse gas emission associated with concrete production has become an important consideration in mix design of concrete in the recent years. Besides, the increasing demand of energy, housing and infrastructure development will continue to increase the demand of concrete. Therefore, it is important to increase the use of industrial by-products as supplementary cementing materials (SCMs) in order to reduce the greenhouse gas emission of concrete production.

At present time, extensive research is focusing on the improvements of concrete properties by using SCMs [3]. The SCMs can be used individually with Portland or blended cement or in different combinations of them which can improve sustainability, economy and various fresh and

hardened properties of concrete through hydraulic and pozzolanic actions [4]. The high silica and alumina contents of SCMs can help reduce permeability and improve durability through pozzolanic reactions [5]. Typical examples of SCMs are fly ash, ground granulated blast furnace slag (GGBFS), silica fume, rice husk ash, palm oil fuel ash and natural pozzolans such as calcined clay and calcined shale which are incorporated in concrete as an additive or partial replacement of cement [6-9]. Over the last few decades, the uses of SCMs in concrete have been increased significantly in all over the world. Currently, more than 90% of concrete contains at least one SCM.

The suitability of using a proprietary ferronickel slag (FNS) as a supplementary cementitious material has been investigated in this study. Ferronickel slag is a by-product of the production of nickel. Some common types of ores used as the source of nickel are pentlandite, pyrrhotite, garnierite, millerite and niccolite. The specific FNS used in this study was produced from garnierite ore found in New Caledonia. The smelter produces about 2.0 Million tonnes of granulated slag every year [10]. The slag is a by-product of the pyro-metallurgical process of the ore in an electric arc furnace at temperatures between 1500 ^{o}C and 1600 ^{o}C [11]. The molten slag is granulated by rapid cooling using sea-water. It is currently deposited in the plant's premises and there has been a substantial quantity of the slag accumulated over many years despite its use in the local construction works for decades. Raw FNS was ground to fine powder using high energy ball milling for 5.5 hours. The chemical compositions of the FNS are given in Table 1. The sum of SiO_2, Fe_2O_3 and Al_2O_3 for the FNS is about 65%, which meets the requirement of class C natural pozzolans according to the ASTM C618 -12a Standard [12].

Sintering of the main elements of FNS namely silicon, magnesium and iron form a stable mineral called forsterite [13-15]. It was shown that periclase (MgO) and amorphous silica combine

70 together at temperatures above 900 ^{o}C to form forsterite [14]. Forsterite is a highly stable mineral
71 with melting point of 1890 ^{o}C [14-15]. The chemical compositions and characteristics of the
72 crystalline and non-crystalline minerals of FNS vary with the type of the ore, smelting temperature
73 and the cooling condition such as slow cooling by air or rapid cooling by water. Rapid water
74 cooling produces higher amount of bluish green non crystalline minerals. Chemical compositions
75 of the nickel slags used by other researchers are also collected in Table 1 for comparison with the
76 FNS used in this study. A wide variation of the chemical compositions, especially in terms of the
77 contents of magnesium and iron can be seen in the slags used by different researchers. The FNS
78 used in this study has the highest magnesium content among all these slags.
79

80 **Table 1. Chemical compositions of FNS used in this study and used by other researchers**

Oxides	Current Study	Lemonis et al. [16], Katsiotis et al. [17]	Yang et al. [18]	Zhang et al. [19]	Maragkos I. et al. [20]	Komnitas K. et al. [21]	Choi et al. [22]	Dourdounis et al. [23]
SiO_2	53.29	41.18	52.27	52.3	40.29	32.74	62.8	34.31
Al_2O_3	2.67	5.98	6.19	6.2	10.11	8.32	1.95	5.73
Fe_2O_3	11.9	40.02	4.2	4.2	37.69	43.83	7.13	10.33
FeO	-	-	-	-	-	-	-	37.55
MgO	**31.6**	**7.79**	**26.93**	**26.9**	**5.43**	**2.76**	**24.7**	**1.97**
SO_3	-	0.64	-	-	-	-	0.03	
CaO	**0.42**	**4.12**	**8.77**	**8.8**	**3.65**	**3.73**	**2.07**	**14.12**
Na_2O	0.11	0.09	0.11	0.1	-	-	0.13	-
K_2O	-	0.37	0.16	0.2	-	-	0.02	
Cr_2O_3	1.08	2.75	0.37	0.4	2.58	3.07	-	3.5
TiO_2	-	0.12	0.1	0.1	-	-	-	-
ZnO	-	-	0.02	<0.1	-	-	-	-
MnO	-	0.52	-	-	-	-	-	-
NiO	0.1	-	0.03	<0.1	0.09	0.1	-	0.26
Co_3O_4	0.01	-	-	-	-	0.02	-	-
CoO	-	-	-	-	-	-	-	-
P_2O_5	-	-	-	-	-	-	-	-
S	-	-	-	-	-	0.18	-	-

C	-	-	-	-	-	0.11	-	-
LOI	- 0.83	-3.44	-	0.5	-	-	0.94	0.00

Very limited number of studies are available in literature on the use of FNS in concrete. Hydration and leaching study of a low-magnesium FNS up to 20% of the binder showed slightly lower water demand and prolonged setting times [16-17]. Lower compressive strengths at the early ages and about 90% compressive strength at 90 days as compared to the control specimens were reported in these studies. Investigations on geopolymer technology [18-19] showed that the use of 20% high-magnesium nickel slag yielded higher compressive strength and lower drying shrinkage. Improved mechanical properties were attributed to the presence of glassy and more silicate phases of the FNS. It was also stated that the slag was much less reactive because of the pyro-metallurgical process at high temperature. Margakos et al. [20] and Komnitas et al. [21] used low-magnesium FNS for synthesis of inorganic polymers. Choi et al [22] studied the effect of a high-magnesium FNS fine aggregate on the alkali-silica reaction of concrete. Dourdounis et al. [23] studied the use of a low-magnesium FNS for the production of high alumina cement. Therefore, it can be seen from the reviews that studies on the use of high-magnesium FNS as a cement replacement are scarce in literature.

As the slag used in this study has relatively high magnesium content, it is necessary to investigate the effects of this slag on the soundness and strength development of the binder. Therefore, paste and mortar specimens were cast and tested using different proportions of the ground ferronickel slag as a partial replacement of cement. This study has focused on some important properties of the fresh and hardened paste and mortar samples. The fresh properties included the normal consistency and setting times, and the hardened properties included expansions by different test methods, strength activity index and the development of mortar compressive

strength with age. X ray diffraction (XRD), scanning electron microscopy (SEM) and energy dispersive X-ray spectra (EDS) tests were conducted on hardened paste samples to have an insight of the reaction products and understand the expansion behaviour shown by the specimens containing the FNS.

2. Experimental work

2.1 Materials

The maximum particle size of the granulated slag was about 5mm. It was ground using a laboratory ball mill to a fineness of 500 m^2/kg. The specific surface area of the ground slag was determined using the Blaine's air permeability method according to the ASTM C204-11 Standard [24]. The photographs of the raw slag and the ground slag are shown in Fig. 1. The specific gravity of the ferronickel slag was 2.95, which is similar to that of Portland cement (about 3.15) or other supplementary cementitious materials such as GGBFS (2.90).

Raw ferronickel slag Ground ferronickel slag

Figure 1. Raw and ground ferronickel slag

The chemical compositions of the FNS were determined by X-ray fluorescence (XRF) and the elements in terms of their oxides are given in Table 1. Though the XRF results show the Mg content in terms of MgO, an X-ray diffraction (XRD) phase analysis of the FNS showed the presence of magnesium mainly in the form of crystalline forsterite ferroan. The chemical compositions of the cement, fly ash and GGBFS used in the study are given in the Table 2. The Blaine's fineness of the ground FNS, cement, fly ash and GGBFS were 500 m^2/kg, 370 m^2/kg, 330 m^2/kg and 450 m^2/kg respectively.

Table 2. Chemical compositions of the cement, fly ash and GGBFS

Oxides	**OPC**	**Fly ash**	**GGBFS**
SiO_2	20.29	76.34	32.45
Al_2O_3	5.48	14.72	13.56
Fe_2O_3	2.85	3.69	0.82
MgO	1.24	0.54	5.10
SO_3	2.49	0.11	3.20
CaO	63.11	0.60	41.22
Na_2O	0.29	0.19	0.27
K_2O	0.45	0.96	0.35
Cr_2O_3	0.02	-	-
P_2O_5	0.17	0.10	0.03
SrO	0.05	-	-
TiO_2	0.27	0.61	0.49
Mn_2O_3	0.08	0.07	0.25
ZnO	0.04	-	-
LOI	3.39	0.53	1.11

The fine aggregate was natural river sand with fineness modulus of 1.95. The specific gravity (SSD) and apparent density of the sand was 2.15 and 2.30 t/m^3 respectively. Normal potable tap water was used in mixing of the pastes and mortar mixtures.

3. Methodology

A series of tests were conducted to assess the fresh properties of cement paste blended with the FNS. The test results were compared with those of the control mixtures without the slag. Comparison was also made with the results of cement paste mixtures blended with fly ash (FA) and ground granulated blast furnace slag (GGBFS) as two other commonly used supplementary cementitious materials. The properties include normal consistency, initial and final setting times, strength activity index and soundness by different methods. Compressive strength development of mortar specimens containing ferronickel slag was also determined. Powder X-Ray diffraction (XRD) phase analysis and investigation of the microstructure by scanning electron microscopy (SEM) image and energy dispersive spectra (EDS) were carried out to have an insight into the reaction product of the ferronickel slag in cement paste. The test methods, mixture proportions and specimens for each test are described in the following sections.

3.1 Normal consistency and setting time

The knowledge of the setting time of a cementitious mixture is required in order to determine the available time for mixing, transporting, placing and compacting the concrete effectively. Setting time tests are used to characterize how a particular cementitious paste sets. It is affected by a number of factors such as the fineness and chemical compositions of the cementitious materials, water-binder ratio, and the admixtures if used. Setting time and soundness properties are determined at a specified consistency rather than certain water-binder ratio [25].

Therefore, the water content for normal consistency is determined as a pre-requisite for the setting time and soundness tests.

Commercial GGBFS can be used up to 65% cement replacement and 20% is considered as the lower range of SCM dosage. Hence, the ferronickel slag was used from 20% to 65% by weight as partial replacement of cement. The normal consistencies and setting times of the mixtures were determined in accordance with the Australian Standards AS 2350.3 and AS 2350.4 respectively. The tests were conducted on freshly mixed pastes in the laboratory at a relative humidity of 70 ± 10% and temperature of 23 ± 2 ^{o}C.

3.2 Strength activity index

Strength activity index is defined as the ratio of the strength of 20% ferronickel slag-blended cement mortar to the strength of the reference cement mortar at a specific age. The control cement mortar mixture consisted of 500g of cement, 1375g of sand and 242g of water as specified in the ASTM C311M Standard [26]. The ferronickel slag blended cement mortar mixture contained 400g cement, 100g ferronickel slag, 1375g sand and 242g of water. Since the water demand for normal consistency of the 20% ferronickel slag blended paste was same as that of the control cement paste, the same water contents were used in both the mortar mixtures. Cube specimens of 50mm sides were prepared and tested in accordance with the ASTM C311M Standard [26]. After casting, the specimens were placed in a moist room at 23±2 ^{o}C for 24 h. The specimens were then demoulded and cured in lime saturated water until tested for compressive strengths at the ages of 7 and 28 days.

3.3 Soundness

As shown in Table 1, the magnesium content of the FNS obtained by XRF analysis expressed in terms of its oxide is about 32%. According to AS 3582.2 [27-28], the value of MgO in SCMs should be less than 15%. However, the reactivity of MgO depends on its calcination temperature. MgO can be classified in three temperature categories of calcination: a) lightly burnt MgO (850-1200 ^{o}C), hydration takes place within 180 days b) heavily burnt MgO (1500-1800 ^{o}C), hydration can be up to 1000 days and c) dead burnt MgO, Periclase (>1800 ^{o}C), hydration can proceed up to 6-8 years [29]. The higher the burning temperature, the smaller is the magnitude of early-age expansion and the longer the MgO hydration process lasts. When MgO hydrates, it produces $Mg(OH)_2$ (Brucite), which increases the volume by 17% [30]. The unsoundness caused by the excessive volume changes is usually accompanied by cracking and strength loss.

However, it should be noted that magnesium may not always be harmful for concrete depending on how it is chemically bound in the slag. XRD results of the FNS showed that the magnesium is present in the form of crystalline forsterite ferroan rather than in the form of MgO. Therefore, the actual effect of the high magnesium content of the slag on expansion needs to be determined by expansion tests. Thus, the soundness of the ferronickel slag blended cement pastes has been evaluated using the well-known Le-Chatelier soundness test, autoclave expansion test and an accelerated heat curing test.

The Le-Chatelier soundness test was carried out in accordance with the Australian Standard AS2350.5 [31]. Three samples were prepared for each type of mixture and an average value of the measured expansions is reported. The paste samples were prepared at normal consistency by replacing 0% to 65% of cement by the FNS.

The autoclave expansion was determined in accordance with the Australian Standard AS 3583.4 [32]. The paste specimens used for this experiment were prisms of 25 mm square by 285 mm length, having a 250 mm effective gauge length. A paste of normal consistency was prepared, moulded and cured for 24 hours in a moist cupboard. After curing, the specimens were demoulded and the initial lengths were measured. The specimens were then placed in the autoclave, containing water, to maintain an atmosphere of saturated steam. The temperature of the autoclave was raised at a rate that brought the steam pressure to 2000 kPa in 45 min to 75 min. A pressure of 2000 ± 70 kPa was maintained within the autoclave for 3 hours. Afterwards, the specimens were cooled down to room temperature and the changes of lengths were measured.

It was reported that curing at elevated temperature such as 80 ^{o}C could accelerate the hydration of lightly burnt (1000-1250 ^{o}C) MgO and complete hydration would be achieved within 30 days [29]. Therefore, accelerated heat curing tests were conducted to further investigate the expansion characteristics of the control and the FNS blended cement pastes. The specimens were of the same size as those used for the autoclave expansion test and were cast with 30% and 50% FNS as cement replacement. Another batch of samples was cast with the inclusion of 5% and 10% MgO (minimum 95% Magnesia) with cement in order to compare the expansions of the specimens containing the FNS and those with reactive MgO. One set of the specimens were cured at 80 ^{o}C in water for 120 days and another set was cured in water at ambient temperature to compare the expansions under normal and accelerated conditions. Three identical specimens were tested for each condition and the average value of the expansions is reported.

3.4 Compressive Strength of Mortar

The mortar mixtures consisted of one part of binder and three parts of sand by mass with a water-binder ratio of 0.50. Ferronickel slag was used to replace 20, 30, 40 and 50% of cement in the mixtures. Since the calcium content of the FNS was very low (0.42%), the cement replacement was limited to 50% considering that higher percentages of FNS would result in very low strength. The specimens were cured in water at 23 ± 2 ^{o}C and compression tests were conducted following the ASTM C109 Standard [33]. Three samples were tested for each mix at 3, 14 and 28 days of age and the average compressive strength is reported.

4. Results and discussion

4.1 Normal consistency and setting time

The normal consistency results of the pastes containing up to 65% ferronickel slag are shown in Fig. 2. The water contents required to achieve the normal consistency of the pastes are plotted against the percentage of ferronickel slag in this figure.

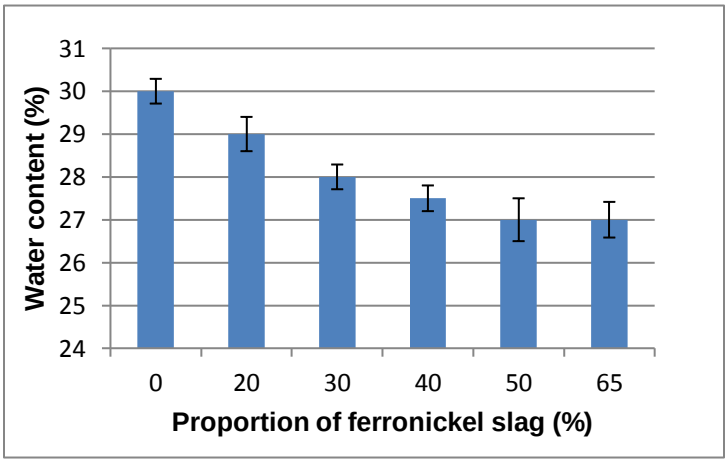

Figure 2. Water contents for normal consistency of paste containing different percentages of ferronickel slag

The results in Fig. 2 shows that the amount of water required for normal consistency of the paste slightly decreased with the inclusion of ferronickel slag. The water content required for normal consistency of the control mixture was 30% and that of the mixtures with ferronickel slag varied from 29% to 27%. Therefore, the required water content decreased from 30% to 27% with the inclusion of 65% ferronickel slag in the paste. The ratios of the water requirement of the control mix to those of the mixes containing 30% and 65% ferronickel slag are 1.07 and 1.11, respectively. ASTM Standard C618.12a [12] recommends the maximum ratios of 1.05 and 1.15 for fly ash and natural pozzolans respectively. Thus, the water requirements of ferronickel slag are comparable to those of other supplementary cementitious materials. The observed decrease in water requirement of the ferronickel slag is attributed to its low water absorption characteristics and the inert behaviour at the initial stage of mixing.

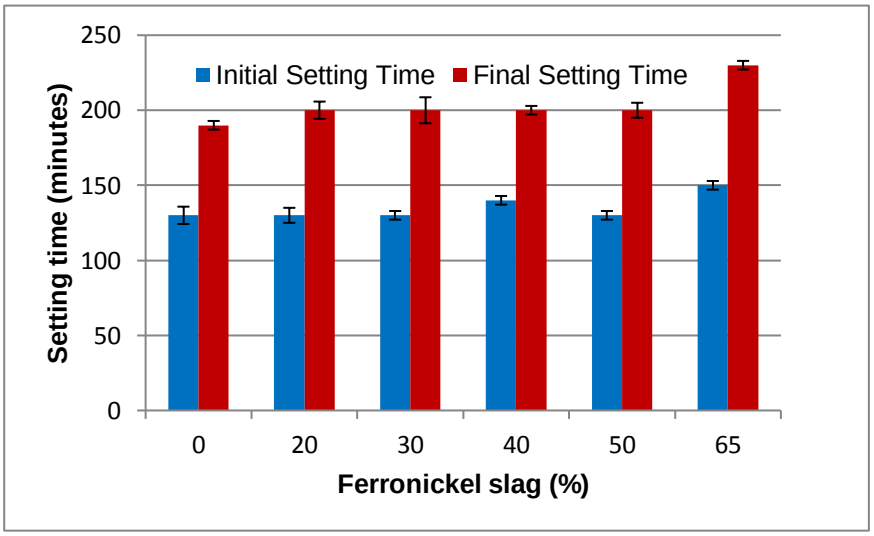

Figure 3. Variation of setting times with the percentage of ferronickel slag

The initial and final setting time results of the control cement paste and the mixtures with up to 65% ferronickel slag are shown in Fig. 3. It can be seen that the initial setting times of the

281 mixtures varied from 130 minutes to 150 minutes and the final setting time varied from 190 minutes
282 to 230 minutes. According to ASTM C150 [34] specification, the initial setting time shall not be
283 less than 45 minutes. However, an initial setting time of at least 90 minutes is usually preferred in
284 practice. A very long final setting time is not usually preferred because this may cause large
285 expenditures on the formwork. Therefore, the initial and final setting times of the mixtures
286 containing up to 65% ferronickel slag are considered suitable for usual applications of concrete.

287

288 No significant difference in the setting times was observed due to incorporation of the
289 ground ferronickel slag as a cement replacement up to 50%. At the cement replacement level of
290 65%, the ferronickel slag was found to retard the initial setting time by 20 minutes and final setting
291 time by 40 minutes. It is usually observed that increasing the amount of supplementary
292 cementitious materials such as silica fume, fly ash and GGBFS retards the setting time of concrete
293 [35]. Cement replacement by GGBFS at a rate more than 40% was shown to significantly increase
294 the setting time [36].

295

296 The normal setting time of Portland cement is related to the hydration of C_3S and C_3A, and
297 the formations of CSH gel and ettringite [37]. High level of cement replacement causes reduction
298 of the hydrated products from C_3S and C_3A. Also, the increased percentage of cement replacement
299 by SCMs causes the separation distance between hydrated cement particles to increase, which
300 eventually delays the formation of interlocking network between the particles. It should also be
301 noted that the ferronickel slag has a very low (0.42%) calcium content. Thus, the setting time is
302 increased at a high percentage of cement replacement such as 65% by the low calcium ferronickel
303 slag.

304

4.2 Strength activity index

The pozzolanicity of the ferronickel slag was quantified by its strength activity index. The strength activity index of any material depends on the surface area, particle size distribution and silica content. The strength activity index can be increased by reducing the particle size thus increasing the fineness. The average compressive strengths obtained from three specimens were used to determine the strength activity index. The results are given in Table 3.

Table 3. Strength activity index of ferronickel slag

SI No	Composition	Mean 7 days strength (MPa)	Mean 28 days strength (MPa)	Strength activity index	
				7 days	28 days
1	Control	31	37	74%	84%
2	20% FNS	23	31		

Table 3 shows that the strength activity indices for 7 days and 28 days were found 74% and 84% respectively. ASTM C618-08a [38] recommends a minimum strength activity index of 75% for fly ash and natural pozzolans at 7 or 28 days. Since the value for the ferronickel slag at 28 days is above 75% and that at 7 days is very close to 75%, the effect of the ferronickel slag on strength development may be considered comparable to those of other supplementary cementitious materials.

4.3 Le-Chatelier soundness

The Le-Chatelier expansion results are plotted against the percentage of ferronickel slag in Fig. 4. Expansions of two additional mixtures containing 40% fly ash and 40% GGBFS were also tested for comparison with the expansion of the mixture of 40% ferronickel slag. Besides, two other types of samples were prepared using 5% MgO and 10% MgO with the FNS and cement to investigate the effect of reactive MgO on the expansion.

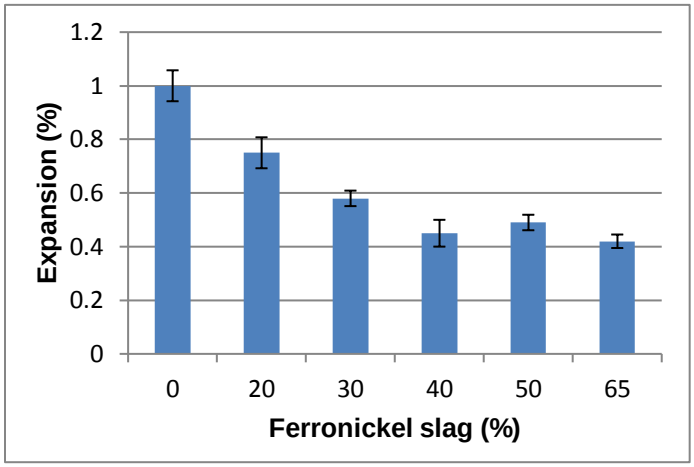

Figure 4. Variation of expansion with the percentages of ferronickel slag

It is observed from the results that the Le-Chatelier expansion of the mixtures containing 0% to 65% ferronickel slag varied between 0.42% and 1%. These values are well below 5%, which is specified as the limiting value of Le-Chatelier expansion in the Australian Standard [39]. It can be seen from Fig. 4 that the values generally decreased with the increase of cement replacement by the slag. The value decreased from 0.75% to 0.42% when the cement replacement increased from 20% to 65%.

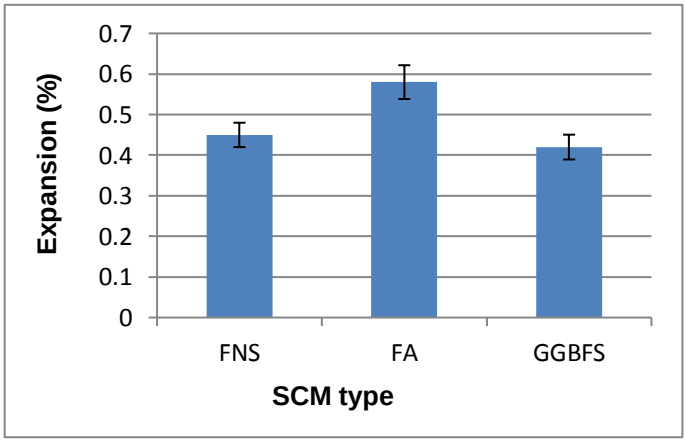

Figure 5. Le-Chatelier expansions of pastes containing 40% FNS, 40% fly ash and 40% GGBFS

Fig. 5 shows the Le-Chatelier expansions of the mixtures with 40% cement replacements by the ferronickel slag, class F fly ash and GGBFS. The mean expansions of the specimens with 40% GGBFS, 40% ferronickel slag and 40% fly ash were 0.42%, 0.45% and 0.58% respectively. These values are well below the 5% expansion limit of the Australian Standard [39]. Though the ground FNS had the highest fineness (500 m^2/kg) as compared to the fly ash (330 m^2/kg) and GGBFS (450 m^2/kg), the reaction of the FNS did not cause excessive expansion of the specimens. Thus the Le-Chatelier expansion of the mixture containing 40% ferronickel slag is similar to those of the mixtures containing the same percentage of other common supplementary cementitious materials such as fly ash and GGBFS.

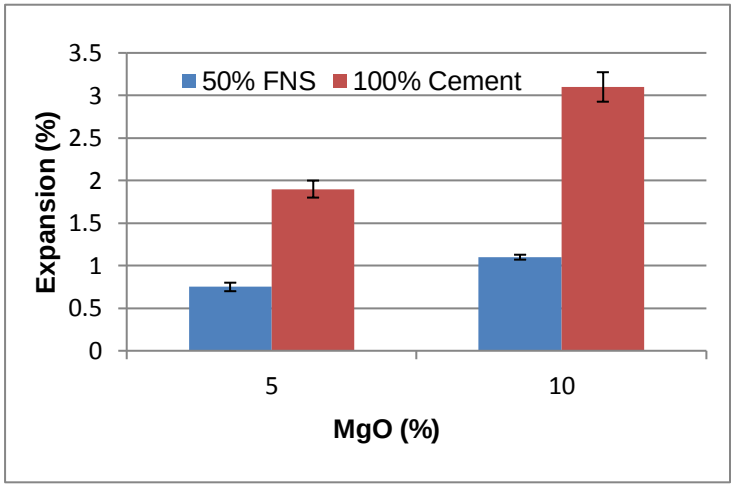

Figure 6. Le-Chatelier expansions of pastes containing 5% MgO and 10% MgO with and without ferronickel slag

Expansions of four other mixtures containing 5% or 10% reactive MgO was also measured in order to evaluate the sensitivity of the Le-Chatelier test to the expansions caused by the reaction product of reactive MgO. The MgO powder was added to the mixtures of 100% cement or 50%

cement and 50% ferronickel slag. The expansions of these four mixtures are shown in Fig. 6. When reactive MgO was added to the FNS blended cement mixtures, the expansion was increased with the increase of MgO. This is expected because of the expansion caused by formation of $Mg(OH)_2$ by hydration of MgO. As shown in the figure, expansion of the mixture with 10% MgO and without any FNS was 3.1%. The expansions of the mixtures with 50% ferronickel slag were less than those of the corresponding mixtures without ferronickel slag. This is because of the less lime available in the mixtures with 50% ferronickel slag as cement replacements. This indicates that the ferronickel slag did not produce expansive reaction product similar to that produced by reactive MgO.

Thus, the Le-Chatelier expansions of the pastes containing ferronickel slag up to 65% were found well below the 5% limit of the Australian Standard and were less than that of the control mixture. Expansion of the mixtures containing 40% FNS is comparable with expansions of the mixtures containing same percentage of other common supplementary cementitious materials such as fly ash and GGBFS.

4.4 Autoclave expansion

The autoclave expansion tests were conducted on specimens containing 0%, 20%, 30%, 40% and 50% ferronickel slag as cement replacement. The expansion results are given in Table 4. No cracks, disintegration or warping were observed in the specimens after completion of the tests.

Table 4. Autoclave expansion of ferronickel slag blended mixtures

FNS content (%)	Autoclave expansion (%)
0	0.08
20	0.01
30	0.06

40	0.03
50	0.08

The results show that the autoclave expansion values were scattered between 0.01% and 0.08% with no definite trend for the increase of the ferronickel slag up to 50%. ASTM Standards C150 [40] and C618-98 [41] limit the autoclave expansion of a cement or blended mix by 0.8%. Therefore, the expansions of these mixtures are very small as compared to the limit set by the ASTM Standards. The expansion in cement or any blended mixture occurs due to the presence of free lime or magnesia (Periclase). The autoclave test is especially designed for measuring the expansion due to periclase. The results do not show any increase in the expansion by the increase of the ferronickel slag in the mixture. This is because the magnesium present in the ferronickel slag is in the form of forsterite rather than periclase. Thus, the autoclave expansion is not increased by the ferronickel slag.

4.5 Expansion by accelerated heat curing

The changes in length of the specimens were measured weekly for 120 days. The expansion test results of the specimens after 120 days of curing in ambient condition and in accelerated heat curing at 80 ^{o}C are shown in Fig. 7. It can be seen that 120-day expansion of the ambient-cured control specimen was 0.33% and that of the specimens with either 30% or 50% ferronickel slag was 0.32%. Similarly, the expansion of the heat-cured control specimen was 0.37% and that of the specimens containing ferronickel slag was 0.35%. Thus, the 120-day expansions of the specimens containing ferronickel slag were similar to that of the control specimen. Generally, the heat curing at 80 ^{o}C increased expansion of the specimens with or without ferronickel slag. The results show

424 that the specimens containing MgO have higher expansions as compared with the control
425 specimens and the specimens containing ferronickel slag. The expansions of the ambient-cured
426 specimens with 5% MgO and 10% MgO were 0.46% and 0.62% respectively. Thus, the expansion
427 increased by about 39% and 94% by the use of 5% and 10% reactive MgO. Similarly, 38% and
428 86% increases in expansions of the specimens were also observed by the use of 5% and 10% MgO
429 for heat curing condition. Therefore, while the use of reactive MgO increased the expansion, the
430 use of ground ferronickel slag up to 50% did not increase expansion as compared to that of the
431 control specimens. This shows the difference between the reactivity of the Mg in MgO and that in
432 the FNS. Thus the effect of ferronickel slag on expansion in these tests is similar to those shown
433 by the Le-Chattelier test. Generally, the use of ferronickel slag as a cement replacement did not
434 increase expansion as observed by the results of Le-Chattelier soundness test, autoclave expansion
435 test and the accelerated heat curing test.
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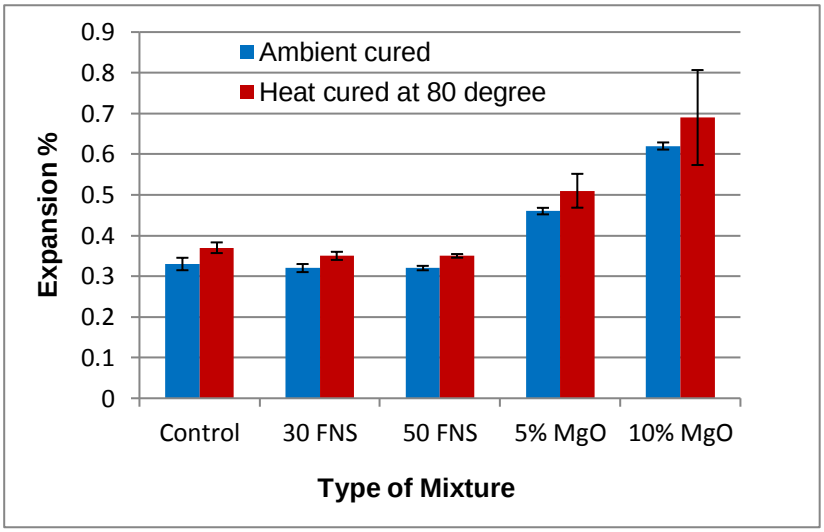

445 **Figure 7. Ambient and heat cured expansion test results**

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447 ***4.6 Compressive strength of mortar specimens***

The strength developments of mortar specimens containing 0% to 50% ferronickel slag as cement replacement are shown in Fig. 8.

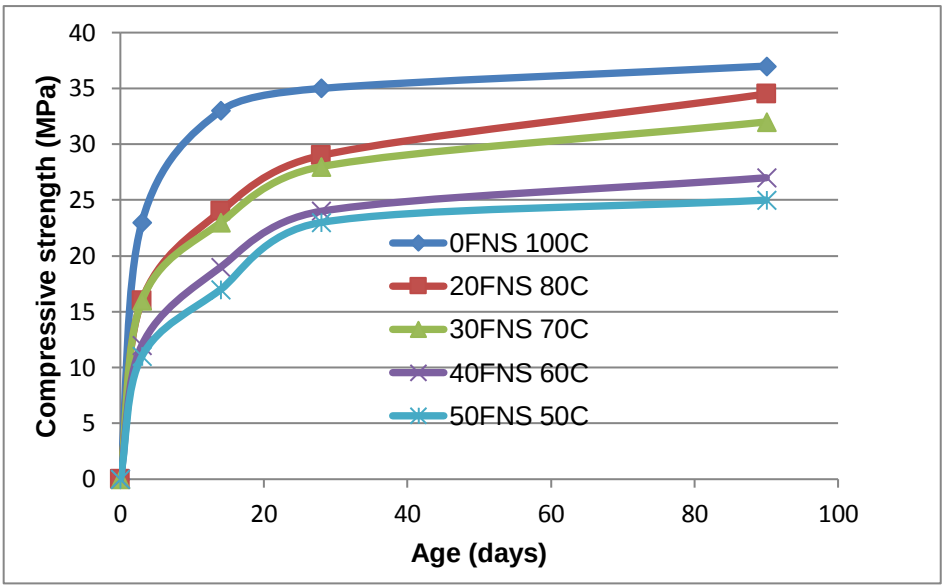


Figure 8. Compressive strength of mortars containing different percentages of ferronickel slag as cement replacement

It can be seen from the figure that strengths of the mixtures were decreased at the early ages by use of the ferronickel slag as cement replacement. The rates of strength development of the ferronickel slag blended mixes were higher during 14 to 28 days as compared to that of the control mix. The strength development of the ferronickel slag blended mortar mixtures showed increasing trend up to the age of 90 days. The control mortars of 100% cement developed to 35 MPa and 37 MPa strengths at 28 and 90 days respectively. The specimens with 20% and 50% ferronickel slag gained compressive strengths of 93% and 67% as compared with the control specimens at 90 days. Higher cement replacement by the slag resulted in lower strengths, as expected. Thus, the strength development behaviours of ferronickel slag blended mixtures are similar to the general behaviour of concrete containing pozzolanic materials such as class F fly ash.

4.7 Phase identification by XRD

The formation of different phases by the hydration process was identified using quantitative XRD analysis. The XRD results of the raw ferronickel slag and the specimens with 20% ferronickel slag and 50% ferronickel slag are shown in Fig.9. It is evident from the figure that the major crystalline components in raw ferronickel slag were forsterite ferroan with very small amount of quartz and enstatite. The quantitative analysis showed that raw ferronickel slag contained about 48 wt% forsterite ferroan, 2.2 wt% enstatite and 0.4 wt% quartz. The amorphous contents of the FNS are about 50%. Most of the silica is present in amorphous phase rather than in crystalline form. This amorphous silica has participated in the pozzolanic reactions and contributed to the late-age strength development of the mixtures containing ferronickel slag, as shown in Figure 8. In Fig.9, cement mineral hatrurite and the FNS mineral forsterite can be observed in both the paste samples containing ferronickel slag. It can be seen that the intensity of the peaks from the forsterite ferroan, which is contributed by the ferronickel slag, is higher in the sample with 50% ferronickel slag as compared to that of the sample with 20% ferronickel slag. This means that the magnesium containing crystalline phase of ferronickel slag is stable in the hydration process. Since no Brucite was identified in the XRD, the magnesium of the FNS did not take part in the reaction process and it did not contribute to the expansion of the specimens. For this reason, the expansions determined by the Le-Chatelier test, autoclave test and extended heat curing test of the specimens containing ferronickel slag were not higher than those of the control specimens despite the high magnesium content of the slag. The other hydration products found were melanterite and small amounts of ettringite and gypsum.

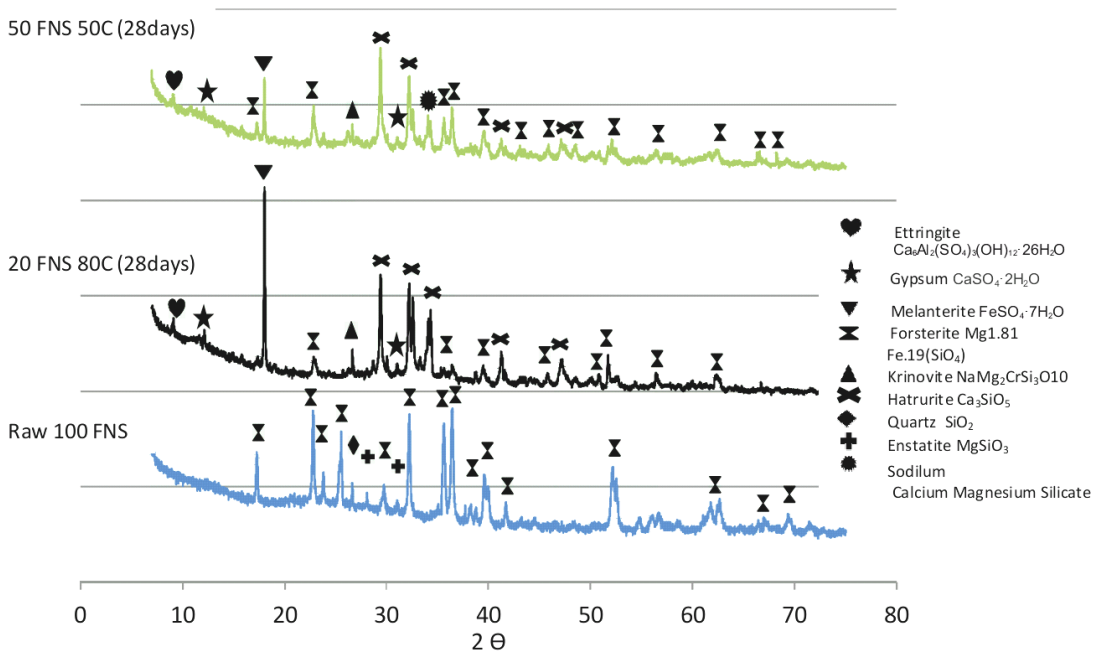
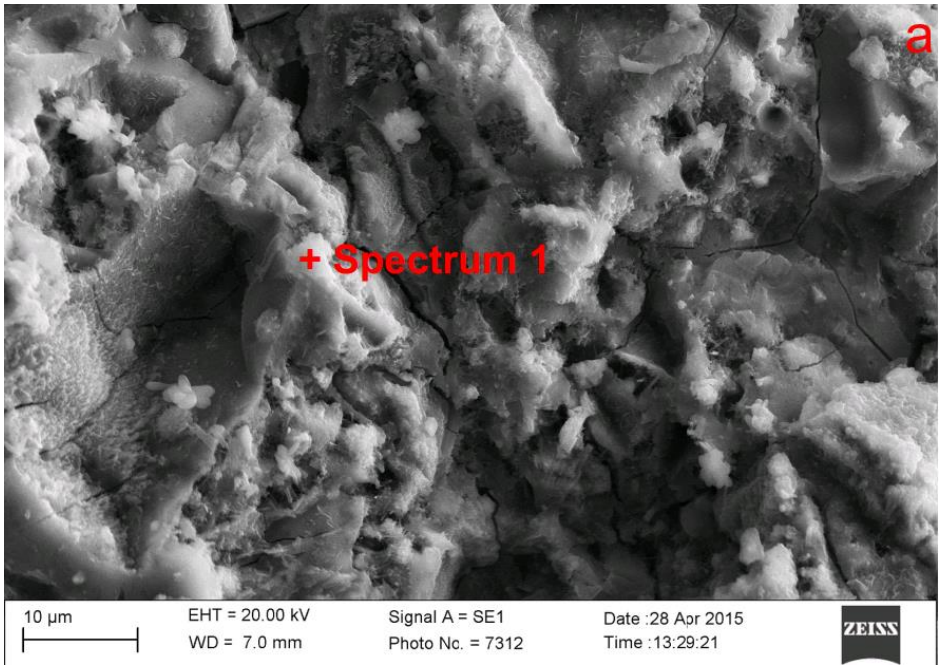


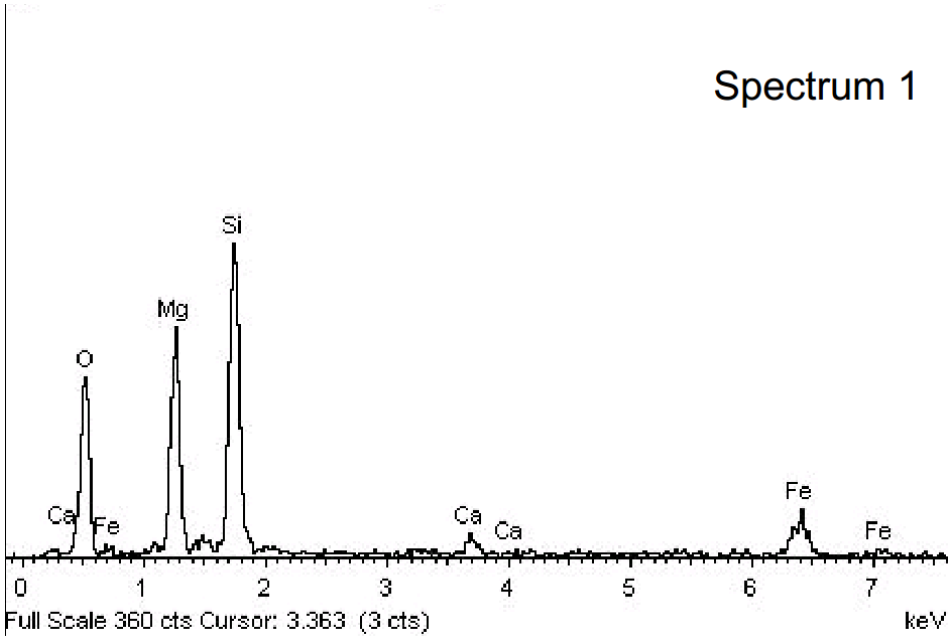
Figure 9. Phase analysis of raw FNS and FNS blended cement pastes by XRD

4.8 Microstructure observation by SEM and EDS

Further to the XRD, the microstructures of hardened paste specimens were investigated by SEM images and EDS in order to identify if there was any expansive Brucite present in the specimens containing 20% and 50% ferronickel slag. Figure 10(a) shows the SEM image and corresponding EDS of the specimen with 20% FNS and Fig. 10(b) shows the SEM image and corresponding EDS of the specimen containing 50% FNS. Generally, a compact microstructure could be observed in both the specimens. It was shown by several researchers [42-45] that the formation of Brucite or $Mg(OH)_2$ is identified as hexagonal plate shaped crystals that may be often found agglomerated in spherical shaped morphology when observed by SEM. This type of morphological shapes were not found in the SEM images as shown in Figs. 10(a) and 10(b). Thus no $Mg(OH)_2$ was visible in SEM images of the specimens containing 20% and 50% FNS. This observation is consistent with the XRD results shown in Fig.9 that no $Mg(OH)_2$ was found in the powder samples. As shown in Figs. 10(a) and 10(b), the EDS identified the presence of mainly Mg,

Si, O, Fe and Ca in both cases. These elements refer to the formation of calcium silicate hydrate (C-S-H) and the stable forsterite ferroan phase of the FNS. The ratio of Mg : Si for 20% and 50% FNS were found as 0.70 and 0.75 respectively. The amorphous silica of the FNS participated in pozzolanic reaction to continue the strength gain as shown in Fig.8.





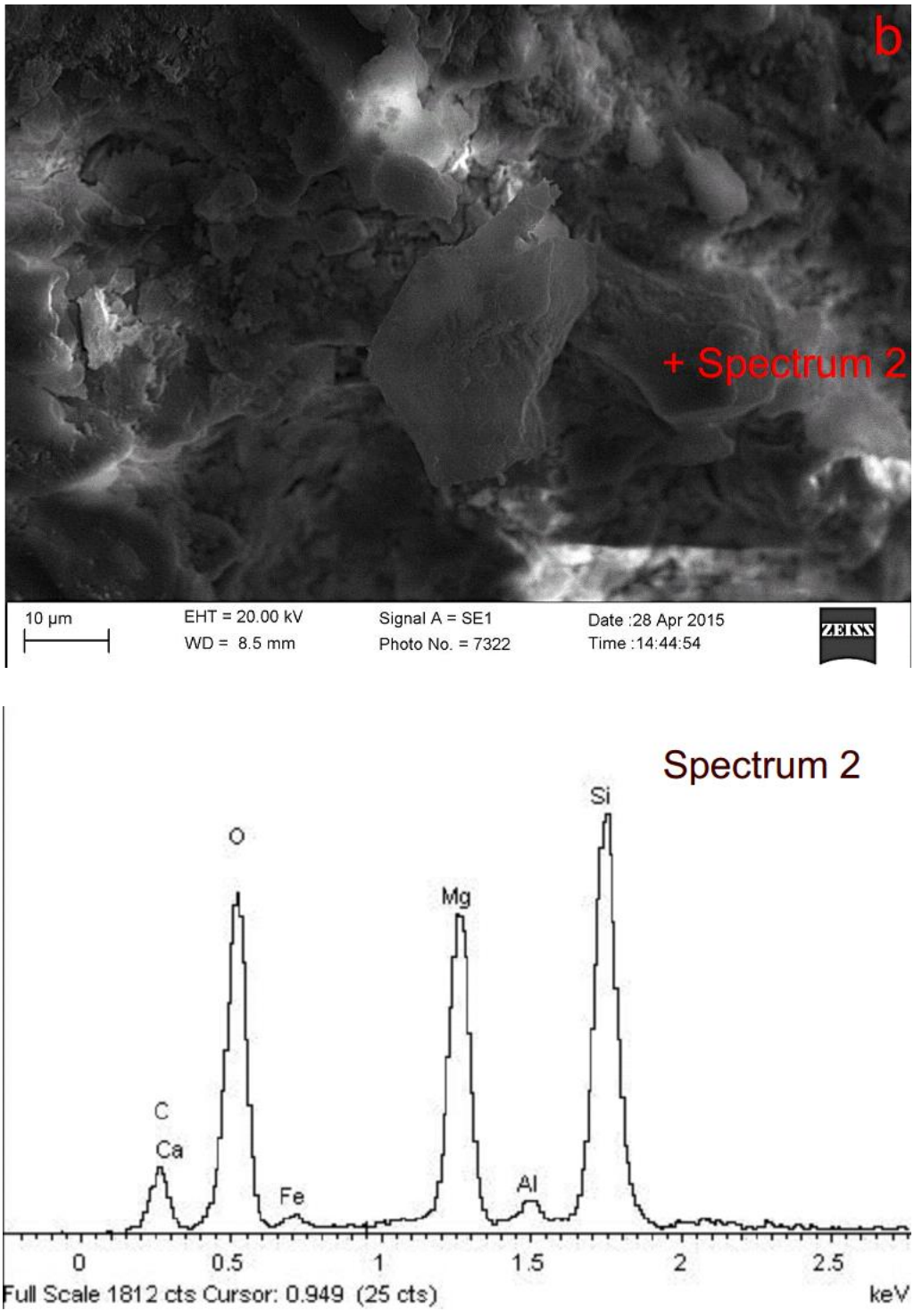


Figure 10. SEM and EDS of hardened paste samples containing 20% (a) and 50% (b) ferronickel slag.

5. Conclusions

This paper presents the fresh and hardened properties of cement paste and mortar specimens containing a high-magnesium ferronickel slag (FNS) as a partial replacement of cement. Water demand and setting times were not significantly affected by the FNS when used up to 50% in the binder. The strength activity indices of the slag at 7 and 28 days were 74% and 84% respectively. No negative effect on the expansion was shown by the slag in the Le-Chatelier, autoclave and extended heat curing tests. The expansions of the specimens with the FNS were less than those for pure cement paste specimens and specimens containing 5% or 10% reactive MgO. This is because of less free lime available in the mixes containing FNS as cement replacement. The expansions were well below the 5% and 0.8% limits set by Standards for the Le-Chatelier and autoclave tests respectively. The 90-day mortar compressive strength was reduced from 37 MPa to 35 MPa by 20% FNS and to 25 MPa by 50% FNS. The XRD, SEM and EDS analysis showed no trace of $Mg(OH)_2$ in the hydration product though the FNS had a high magnesium content. This is because the magnesium was present in the form of stable forsterite ferroan as shown by the XRD results. The amorphous silica present in the slag contributed to the late-age strength development of the specimens. Thus, the soundness and compressive strength development of the ground ferronickel slag was found comparable to those of other commonly used supplementary cementitious materials such as class F fly ash.

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