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Experimental study and classification of natural zeolite pozzolan for cement in South Africa

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The present study investigated the performance of South African natural zeolite for potential use as a cement extender. To the best knowledge of the authors, the natural zeolite studied has not been employed before as pozzolan in the cement industry, and its proposed use would be new in concrete construction. In the investigation, mortar mixtures were prepared using ordinary Portland cement CEM I 52.5N blended with 0, 10, 20 and 30% natural zeolite. The effectiveness of natural zeolite was also compared with performance results of mixtures containing 30% fly ash. The tests conducted were workability, compressive strength, pozzolanic activity with lime, drying shrinkage, alkali-silica reaction, and sulphate resistance. Analytical studies were done using X-ray diffraction and scanning electron microscopy coupled with energy dispersive spectroscopy. It was found that, while incorporation of natural zeolite in cement reduces workability, its effects on mechanical properties and on durability characteristics were superior to those of fly ash, as the former effectively enhanced long-term strength and mitigated drying shrinkage, alkali-silica reaction and sulphate attack. Incorporation of 20% natural zeolite in cement gave an effective overall performance, meeting the ASTM C618 (2015) criteria for Class N pozzolan. Based on EN 197-1 (2000) / SANS 50197-1 (2013), the blend of natural zeolite and ordinary Portland cement met the criteria for its classification as CEM II/A-P 32.5N,R cement type.

INTRODUCTION

Over the past decades, the blending of cement extenders or pozzolans with ordinary Portland cement (OPC) has become conventional practice, following numerous early studies conducted to investigate their different effects on properties of cementitious systems (Neville 1981; Ding & Li 2002). Once blended with OPC, pozzolans react with the calcium hydroxide (CH) formed from cement hydration to generate secondary calcium silicate hydrate phases (CSH). Pozzolans or cement extenders are of two categories comprising, (i) natural pozzolans such as volcanic ash, natural zeolite (NZ), volcanic tuff, kaolin, etc, and (ii) artificial pozzolans which are industrial waste by-products including fly ash (FA), ground granulated blast-furnace slag (GGBS) and silica fume (SF), amongst others (Ekolu *et al* 2006; Naghizadeh & Ekolu 2017a; Tchadjie & Ekolu 2018; Tchadjie *et al* 2021).

Besides the environmental and economic benefits of blending pozzolans with

cement, extenders also generally improve the engineering properties and durability performance characteristics of cementitious systems (Mardani-Aghabaglou *et al* 2014). For example, it is well established that cement extenders significantly reduce permeability levels of, and mitigate various deterioration processes that occur in hardened cementitious systems (Valipour *et al* 2013). Some common extenders are typically blended with OPC at high proportions, such as 30 to 50% FA, GGBS, etc. Consequently, such extenders tend to reduce early-age strength and also reduce the hydration heat of cementitious systems (Addis 1998).

In South Africa, artificial pozzolans comprising FA, GGBS and SF are the most widely used cement extenders (Addis 1998), as underscored by their existing standard specifications comprising SANS 50450-1 (2014), SANS 55167-1 (2011) and SANS 53263-1 (2011), respectively. While no similar separate standard specifications

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exist for local natural cement extenders, SANS 50197-1 (2013) makes general provision including that for use of natural pozzolans. Meanwhile, there is presently little to no local research on the utilisation of natural pozzolans such as NZ in cement and concrete. Prior to the present study, only one material characterisation study on South African NZ could be found, which also was not focused on the use of zeolite as pozzolan in cement (Diale *et al* 2011).

Existing literature on the use of zeolites as pozzolans

Natural zeolites (NZs) form when volcanic rocks react with alkaline groundwater, leading to crystallisation in a post-depositional environment occurring in shallow basins over long periods of time (Colella *et al* 2001; Diale *et al* 2011). It may be noted that NZs have a high water demand. As such, a relatively higher water content is needed to achieve adequate workability of cementitious mixtures containing NZ (Colella *et al* 2001; Marantos *et al* 2020). The higher water demand of NZ/OPC blended mixtures is related to the presence of numerous small pores found within the pozzolan's vesicular structure. Blends containing higher than 10% NZ may require use of a plasticiser for the mixture to attain similar workability as that of the control (Marantos *et al* 2020).

Various literature sources have reported contradicting findings on the effect of NZ upon early-strength development. Sicakova *et al* (2017) reported that the early-age compressive strength of concrete increased upon replacement of OPC with 15% NZ. In contrast, Yilmaz *et al* (2007) found that concrete mixtures containing 5, 10, 20 and 40% NZ exhibited lower early-age strength values, relative to that of the control mixture. Subsequently, however, the 28-day compressive strength of the 10, 20 and 40% NZ/OPC concretes increased by 15.9, 22.3 and 4.1% respectively (Yilmaz *et al* 2007).

Jana (2007) observed that concrete mixtures containing 10 to 20% NZ gave drying shrinkage results that were similar to those of the control OPC mixture. However, the 30% NZ/OPC concrete mixture gave drying shrinkage that was 20% higher than that of the control. Interestingly, a study by Najimi *et al* (2012) showed that incorporation of NZ into OPC significantly improved the durability properties of mortars. In their study, the 15% NZ/OPC blend was found to effectively mitigate sulphate attack and alkali-silica reaction (ASR).

Table 1 Chemical compositions of the cementitious materials used

Oxides (%)	Ordinary Portland cement (CEM I 52,5N OPC)	Natural zeolite (NZ)	Fly ash (FA)
Al ₂ O ₃	4.49	12.9	30.27
CaO	64.47	1.4	4.59
Fe ₂ O ₃	3.07	2.4	3.58
MgO	1.11	1.6	1.06
P ₂ O ₅	0.08	–	0.38
K ₂ O	0.32	–	0.77
SiO ₂	20.57	61.3	56.45
Na ₂ O	0.05	2.1	0.14
TiO ₂	0.53	–	1.57
LOI*	4.04	15.8	0.42
Relative density	3.14	2.33	2.24
Percentage retained on 45 µm sieve (%)	4.03	0	2.46

* LOI–loss on ignition

Study objectives

Presently, hardly any past research exists on potential utilisation of South African NZ as pozzolan. As such, the objectives of the present study were to investigate performance characteristics of NZ, and to determine its classification along with suitable proportions for blending with OPC. Proposed use of NZ in cement and concrete would be a new development, since this cementitious material has not been employed before as cement extender.

In the present study, mortar mixtures were prepared in which CEM I 52,5N OPC cement, was partially replaced with 0 to 30% NZ. The mechanical properties measured were workability, compressive strength development and pozzolanic activity of NZ with lime (PAL). Also measured were durability properties comprising drying shrinkage, ASR and sulphate attack. Analytical studies were done using X-ray diffraction (XRD) and scanning electron microscopy (SEM) coupled with energy dispersive spectroscopy (EDS).

EXPERIMENTAL STUDY

Materials

CEM I 52,5N OPC cement obtained from Pretoria Portland Cement (PPC) (Pty) Ltd, was used in all the mortar mixtures. In South Africa, deposits of NZ are found in the provinces of the Western Cape and KwaZulu-Natal. The NZ supplied by Serina Trading for use in the present study, was

obtained from the Riversdale mine in the Western Cape. The extender was incorporated into OPC in proportions of 0, 10, 20 and 30% NZ, then used to prepare mortar mixtures. For performance comparison of the NZ with conventional pozzolans, mortar mixtures containing 30% FA were also prepared. The siliceous fly ash (SANS 50450-1 2014), which is a low calcium (Class F) fly ash (ASTM 618 2015) used in the present study, was obtained from Lethabo Power Station as supplied by Ash Resources (Pty) Ltd. Table 1 gives the chemical compositions of the different cementitious materials employed in the study. The PAL test was done for both calcined and non-calcined NZ. Calcination of NZ was done using a laboratory furnace set at a heating rate of 2°C/min, then maintained at 500°C peak temperature for an hour, before cooling back to room temperature.

Local silica sand was used as the non-reactive aggregate in mortar mixtures that were prepared for determination of compressive strength, for PAL test, sulphate resistance and drying shrinkage tests. The silica sand used was obtained from Sallies Silica (Pty) Ltd. Particle sizes of 0–0.6 mm, 0.4–0.85 mm and 0.8–1.8 mm were blended at proportions of 38, 12 and 50%, respectively, to obtain standard sand grading (Ekolu 2014).

Greywacke (GW) aggregate, obtained from Peninsula Quarry in the Western Cape Province, was used to prepare mortar samples for ASR testing. This aggregate type is known to be highly ASR-reactive

(Naghizadeh & Ekolu 2017b). The GW aggregate was received in 19 mm stone size, then crushed using a laboratory jaw crusher to obtain various fine particle sizes. The crushed GW fine aggregate particles were graded as per ASTM C1260 (2014) and SANS 6245 (2006). Prior to use in mixtures, the GW fine aggregate was washed to remove dust content, and then it was oven-dried at 50°C for 48 hours.

Sodium hydroxide (NaOH) of technical grade was supplied by Merck (Pty) Ltd for use to prepare the storage solution for the accelerated mortar bar test (AMBT), as per ASTM C1260 (2014) and SANS 6245 (2006). To prepare one litre of 1M NaOH solution, 40 g pellets of the chemical reagent were dissolved in 100 g of water, then more water was added to make up one litre of the solution. Anhydrous sodium sulphate (Na_2SO_4), also supplied by Merck (Pty) Ltd, was used to prepare the storage solution for the sulphate resistance test conducted as per ASTM C1012 (2017). In the experiment, 50 g of Na_2SO_4 were dissolved in distilled water to prepare one litre of solution.

Mortar samples

Samples for testing of mechanical properties

Mortar cubes of 50 mm size were prepared for compressive strength testing as per ASTM C109 (2019). The mortar mixtures containing 0, 10, 20, 30% NZ and 30% FA, were prepared at aggregate/cement ratio = 3, as given in Table 2a. Using a laboratory

mortar mixer, the dry materials were first mixed at slow speed for one minute. With the mixer running, water was added slowly over a duration of one minute, then mixing was continued for a further two minutes. Finally, mixing was done at high speed for one minute (ASTM C305 2016). Flow workability of the fresh mortar mixtures was tested as per ASTM C1437 (2015). Fresh mortar cubes of 50 mm in size were cast and covered with a plastic sheet, then kept for 24 hours at room temperature in the laboratory. Afterwards, the mortar samples were demoulded, and then cured in a water tank at room temperature until testing. Compressive strength testing of the cube samples was done at the ages of 3, 7, 28, 56, 90 and 180 days.

The PAL test is done to evaluate reactivity and to classify the quality of the pozzolan. In the present study, both NZ and calcined NZ (CNZ) were subjected to the test as per ASTM C311 (2013). Mixtures for the PAL test were prepared at pozzolan to lime ratio = 2, while the ratio of standard sand to lime was = 9. The amount of water added was adjusted for each mix, to obtain a flow of 110 ± 5 mm. Mixing of the mortars was done in accordance with ASTM C305 (2016), as already described above. After casting of the 50 mm mortar cubes for the PAL test, they were covered with a rigid glass and then kept at room temperature for 24 hours. Afterwards, the samples in their moulds were wrapped using plastic cling film and then stored at 55°C in an oven, until the age of compressive strength testing at seven days.

Prisms of $25 \times 25 \times 285$ mm were prepared for conducting the drying shrinkage test, in accordance with ASTM C596 (2018). Table 2a gives the mixtures used for the drying shrinkage test. The fresh mortar prisms were cast, and then wrapped using plastic cling film for 24 hours to prevent moisture loss. The prisms were demoulded and then cured in a water tank for six days. After removal of the samples from the water, the initial length readings were recorded, following which the prisms were air-dried. Subsequent length change measurements were done after 1, 7, 14, 28, 42, 56, 70, 84, 98, 112, 126 and 140 days of drying at room temperature in laboratory air.

Samples for measurement of durability properties

The AMBT for ASR was conducted using mortars containing 0, 10, 20 and 30% NZ or 30% FA. Table 2b gives the ASR mortar mixtures made with the GW reactive aggregate, then used to conduct the AMBT. The $25 \times 25 \times 285$ mm fresh mortar prisms for AMBT were cast and wrapped using a plastic cling film, and then kept at room temperature for 24 hours. On the following day, the prisms were demoulded, and then their initial length values were measured using a length comparator. Afterwards, the prisms were immersed in tap water inside an airtight sealed container, and then the assembly was stored inside an 80°C oven for 24 hours. Immediately after removal of samples from the oven, their surfaces were wiped off using a cloth, and then initial length values were again measured.

Table 2a Mortar mixtures used for the workability, compressive strength and drying shrinkage tests

Mix ID	Sample size (mm)	Mix ingredients					Tests
		*OPC (CEM I 52,5 N)	Natural zeolite (NZ)	Fly ash (FA)	Water	Silica sand	
		(g)	(g)	(g)	(g)	(g)	
OPC	50 × 50 × 50	586	–	–	360	1 758	Compressive strength
10NZ	50 × 50 × 50	527	59	–	360	1 758	Compressive strength
20NZ	50 × 50 × 50	469	117	–	360	1 758	Compressive strength
30NZ	50 × 50 × 50	411	176	–	360	1 758	Compressive strength
30FA	50 × 50 × 50	411	–	176	240	1 758	Compressive strength
CEMI-DS	25 × 25 × 285	391	–	–	215	1 172	Drying shrinkage
10NZ-DS	25 × 25 × 285	351	39	–	215	1 172	Drying shrinkage
20NZ-DS	25 × 25 × 285	313	78	–	215	1 172	Drying shrinkage
30NZ-DS	25 × 25 × 285	274	117	–	215	1 172	Drying shrinkage
30FA-DS	25 × 25 × 285	274	–	117	215	1 172	Drying shrinkage

* OPC – ordinary Portland cement CEM I 52,5N

Table 2b Mortar mixtures used for the alkali-silica reaction (ASR) and sulphate resistance tests

Mix ID	Mix ingredients							Tests
	Sample size (mm)	*OPC (CEM I 52,5N)	Natural zeolite (NZ)	Fly ash (FA)	Water	Silica sand	Greywacke aggregate (GW)	
		(g)	(g)	(g)	(g)	(g)	(g)	
OPC-ASR	25 × 25 × 285	400	–	–	200	–	900	ASR
10NZ-ASR	25 × 25 × 285	324	36	–	216	–	810	ASR
20NZ-ASR	25 × 25 × 285	288	72	–	216	–	810	ASR
30NZ-ASR	25 × 25 × 285	252	108	–	216	–	810	ASR
30FA-ASR	25 × 25 × 285	336	–	144	240	–	1 080	ASR
OPC-SR	25 × 25 × 285	391	–	–	215	1 172	–	Sulphate attack
10NZ-SR	25 × 25 × 285	351	39	–	215	1 172	–	Sulphate attack
20NZ-SR	25 × 25 × 285	313	78	–	215	1 172	–	Sulphate attack
30NZ-SR	25 × 25 × 285	274	117	–	215	1 172	–	Sulphate attack
30FA-SR	25 × 25 × 285	274	–	117	215	1 172	–	Sulphate attack

* OPC – ordinary Portland cement CEM I 52,5N.

Subsequently, the mortar prisms were immersed in 1M NaOH solution inside an airtight sealed plastic container, and then placed back in the 80°C oven for storage. Length change measurements were made every 14 days until the age of 160 days.

The sulphate resistance behaviour of mortars containing NZ was evaluated in accordance with ASTM C1012 (2017), using the mortar mixtures given in Table 2b. Samples for the sulphate resistance test comprised prisms of 25 × 25 × 285 mm. The prisms were cast and then cured in water at 35°C for 24 hours, along with some cubes of 50 mm size. On the following day the samples were demoulded and further cured in a water bath maintained at 23°C, until the compressive strength of the 50 mm cubes attained ≥ 20 MPa. At this point, the initial length values of the prisms were measured, and then the samples were immersed in 2.8M Na₂SO₄ solution inside an airtight sealed plastic container stored at room temperature. Subsequent length change measurements were done at the ages of 7, 14, 42, 56, 84, 112, 140 and 160 days.

RESULTS AND DISCUSSION

Workability results

Figure 1 gives workability results of the mortar mixtures (Table 2a) prepared at 0.5 and 0.6 water/cementitious (w/cm) ratios. The control mixture prepared using plain OPC gave flow values of 159 mm and

170 mm for the 0.5 and 0.6 w/cm mortars, respectively. All mixtures containing NZ gave lower workability values relative to those of the corresponding control mixtures. The 0.5 w/cm mixtures containing 10, 20 and 30% NZ gave workability reductions of 8, 13 and 17%, respectively. A similar trend was observed for the 0.6 w/cm mixtures. It can be seen in Figure 1 that the higher the NZ proportion incorporated, the lower the workability value obtained. These observations are in agreement with those reported by Ding and Li (2002). As

expected, the mixtures containing 30% FA exhibited higher workability results relative to those of the corresponding control mixtures. The observed workability-reducing effect of NZ is attributed to its high water demand, as already discussed above under the section titled *Existing literature on the use of zeolites as pozzolans* on page 3 (Marantos *et al* 2020).

Compressive strength results

Figure 2 and Table 3 show compressive strength results for the different mortar

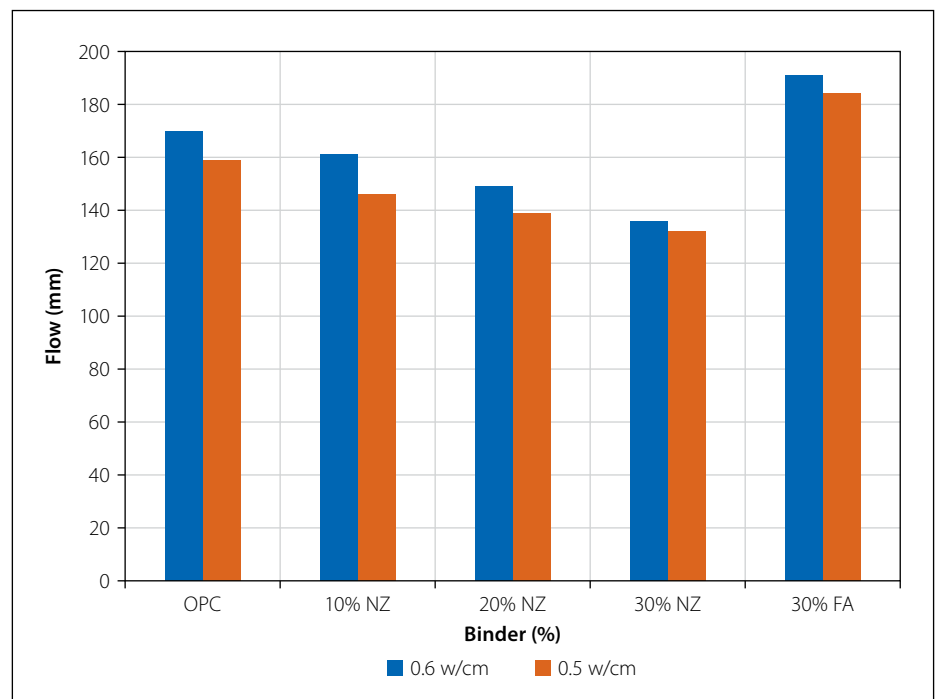


Figure 1 Flow workability results of mortar mixtures prepared at 0.5 and 0.6 water/cementitious (w/cm) ratios: OPC (ordinary Portland cement CEM I 52,5N), NZ (natural zeolite), FA (fly ash)

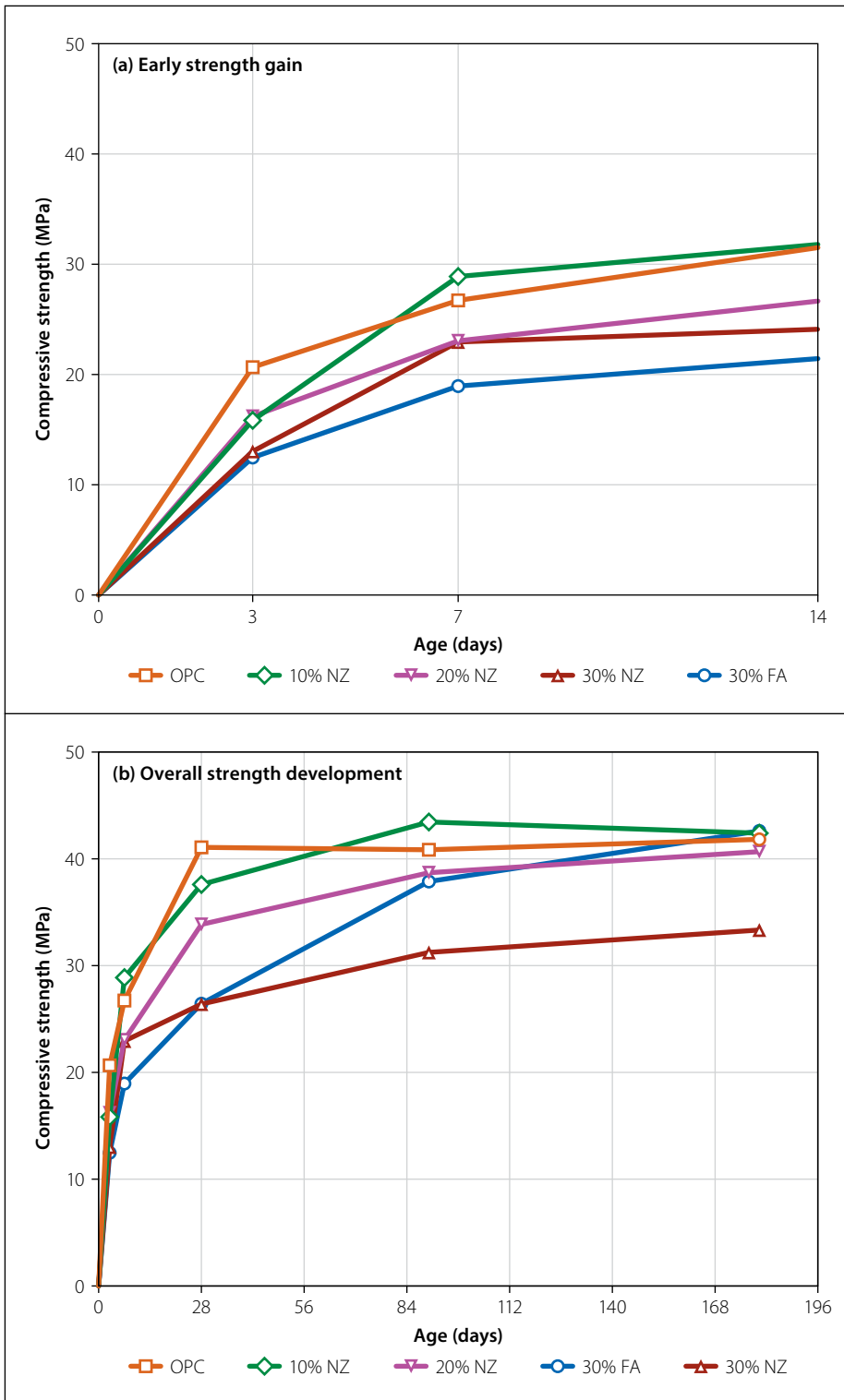


Figure 2 Compressive strength results of mortar mixtures containing varied proportions of natural zeolite (NZ) or fly ash (FA): (a) early strength gain, (b) overall strength development – OPC (ordinary Portland cement CEM I 52,5N)

Table 3 Compressive strength results of NZ/OPC mixtures: NZ (natural zeolite), FA (fly ash), OPC (ordinary Portland cement CEM I 52,5N)

Compressive strength (MPa) on varied ages					
Mix ID	3 days	7 days	28 days	90 days	180 days
OPC	20.7	26.7	41.1	40.8	41.8
10NZ	15.8	28.9	37.6	43.4	42.4
20NZ	16.2	23.0	33.9	38.7	40.7
30NZ	13.0	22.9	26.4	31.2	33.3
30FA	12.5	18.9	26.4	37.9	42.6

mixtures tested at various ages of up to 180 days. Early strength is typically evaluated for ages of up to seven days, while standard strength is determined at 28 days (SANS 50197-1 2013). Strength tendency at ages beyond 28 days is considered to be late or long-term strength behaviour. It can be seen in Figure 2a that, at the age of three days, the control mixture showed relatively rapid early strength gain. However, by the age of seven days, strength results of the 10% NZ mixture had caught up with corresponding values of the control mixture, beyond which both mixtures exhibited similar strength behaviour at all later or long-term ages of up to 180 days (Figure 2b).

Indeed, it is evident in Figure 2b that beyond 28 days there were significant gains in compressive strength values of mixtures containing the extenders, while the strength curve for the control OPC mixture plateaued. By the age of 180 days, the lagging strength curves of the 20% NZ and 30% FA mixtures had caught up with or exceeded that of the control mixture. For example, at 28 days, 20% NZ and 30% FA samples gave values of 33.9 and 26.4 MPa, both of which were lower than 41.1 MPa of OPC, but at 180 days all three mixtures gave similar values of 40 to 43 MPa (Table 3).

It was mentioned earlier (under *Materials* on page 3) that 30% FA is generally recognised and conventionally employed in structural concrete. It can be seen in Figure 2 that 20% NZ generally gave an overall strength performance closest to that of 30% FA, considering behaviour across all ages from early to late-age strength development. Meanwhile, the performance of 30% NZ was very weak or poor, and therefore not worth considering for structural concrete. Drawing from the foregoing, performance comparison between 20% NZ and 30% FA was considered to be meaningful and was thus adopted, particularly in the analytical studies given later in this paper (*Analytical studies* on page 9).

Drying shrinkage results

Figure 3 shows the drying shrinkage results determined at different ages of up to 140 days. The control OPC mixture (OPC-DS) gave the 28-day drying shrinkage of 0.04%. Partial replacement of OPC with 30% NZ (30NZ-DS) resulted in a significant reduction of the 28-day drying shrinkage to 0.02%. Also, the mixture containing

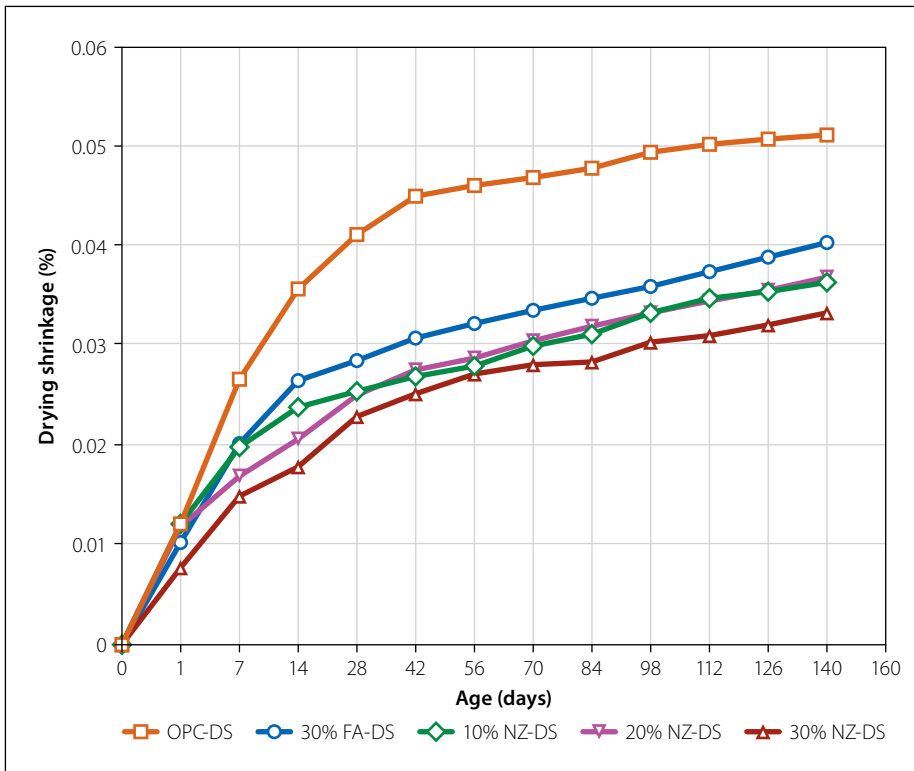


Figure 3 Drying shrinkage results of mortar mixtures containing varied proportions of natural zeolite (NZ) or fly ash (FA): OPC (ordinary Portland cement CEM I 52,5N)

Table 4 Alkali content levels in the extenders used

Material	Alkalis (%)		
	Na ₂ O	K ₂ O	*Na ₂ O _{eq}
OPC	0.05	0.32	0.26
NZ	2.1	2.5	3.75
FA	0.14	0.77	0.65

*Na₂O_{eq} = Na₂O + 0.658K₂O

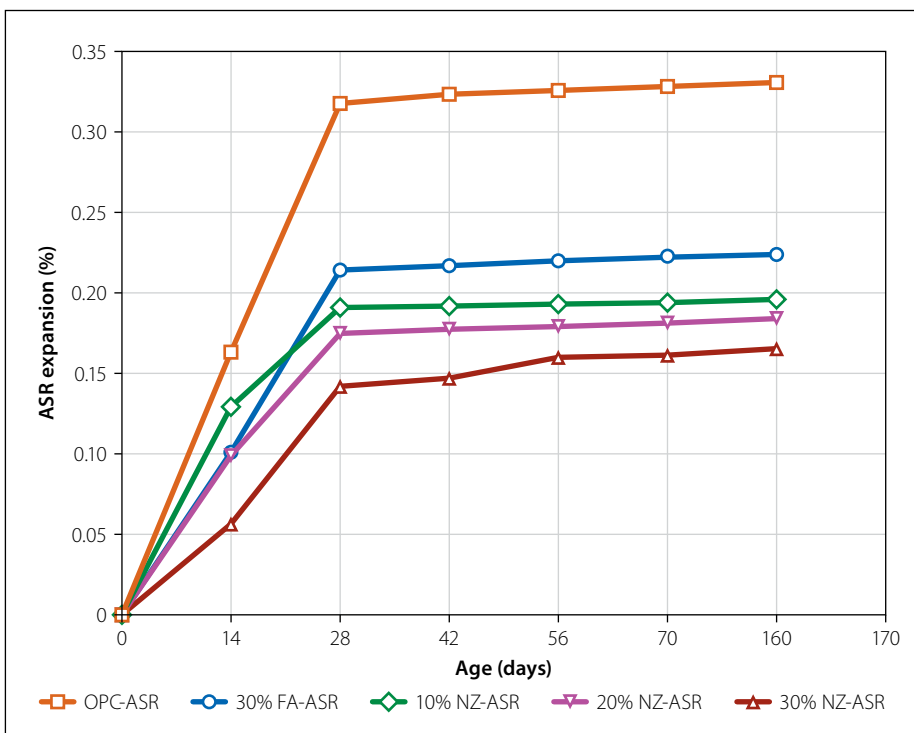


Figure 4 Expansion due to alkali-silica reaction (ASR) in mortar mixtures containing varied proportions of natural zeolite (NZ) or fly ash (FA): OPC (ordinary Portland cement)

30% FA (30FA-DS) gave a considerably low 28-day shrinkage value of 0.028%. Throughout the 140 days of the experimental study, all mixtures containing cement extenders showed lower drying shrinkage levels relative to that of the control. Mortars containing 10 to 20% NZ gave similar results, while the mixture containing the higher 30% NZ content (30NZ-DS) gave the lowest drying shrinkage of all the mixtures investigated. Generally, however, all mixtures gave shrinkage values that were lower than the maximum limit of 0.1% specified in ASTM C596 (2018).

ASR test results

Table 4 gives the alkali content levels in the extenders used. NZ had the highest alkali content equivalent of 3.75%, followed by FA which had an alkali level of 0.65%. Each of these values exceed the maximum allowable alkali content of 0.6% Na₂O_{eq} for OPC mixtures (Neville 1981). However, it is generally recognised that the alkalis in pozzolans do not typically contribute to or participate in ASR (Kalina *et al* 2021), except in some peculiar cases. For example, Ekolu *et al* (2006) found that volcanic tuff pozzolan promoted ASR expansion.

Given in Figure 4 are the ASR expansion results measured over a prolonged period of up to 160 days. The control OPC mixture (OPC-ASR) gave a high 14-day ASR expansion of 0.15%, which exceeds the recommended maximum level of 0.10%, thereby confirming the already established understanding that GW aggregate is highly reactive. Partial replacement of OPC with 10% NZ led to slight reduction of the 14-day ASR expansion to 0.13%. Incorporation of higher zeolite proportions of 20 and 30% NZ into OPC led to corresponding significant reductions in the 14-day ASR expansion, giving values of 0.10 and 0.056% respectively, which are incidentally better or similar to the 0.10% value obtained for the 30% FA mixture. Evidently NZ mitigated ASR, becoming more effective with increase in proportion of the pozzolan from 10 to 30% NZ. The observed effectiveness of NZ against ASR attack is partly attributed to the pozzolan's high SiO₂ content (Table 1) which reacts with calcium to reduce the potential for ASR gel formation (Naghizadeh & Ekolu 2017b). But perhaps the most significant ASR mitigating effect of pozzolans arises from the ability of the extenders to bind freely available alkalis in the mixture,

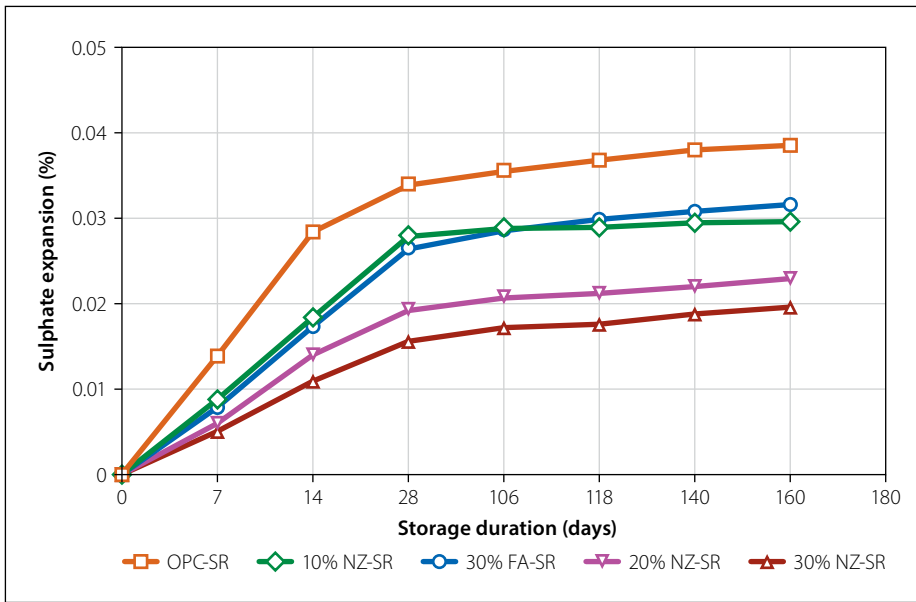


Figure 5 Sulphate expansion results of mortars containing varied proportions of natural zeolite (NZ) or fly ash (FA): OPC (ordinary Portland cement)

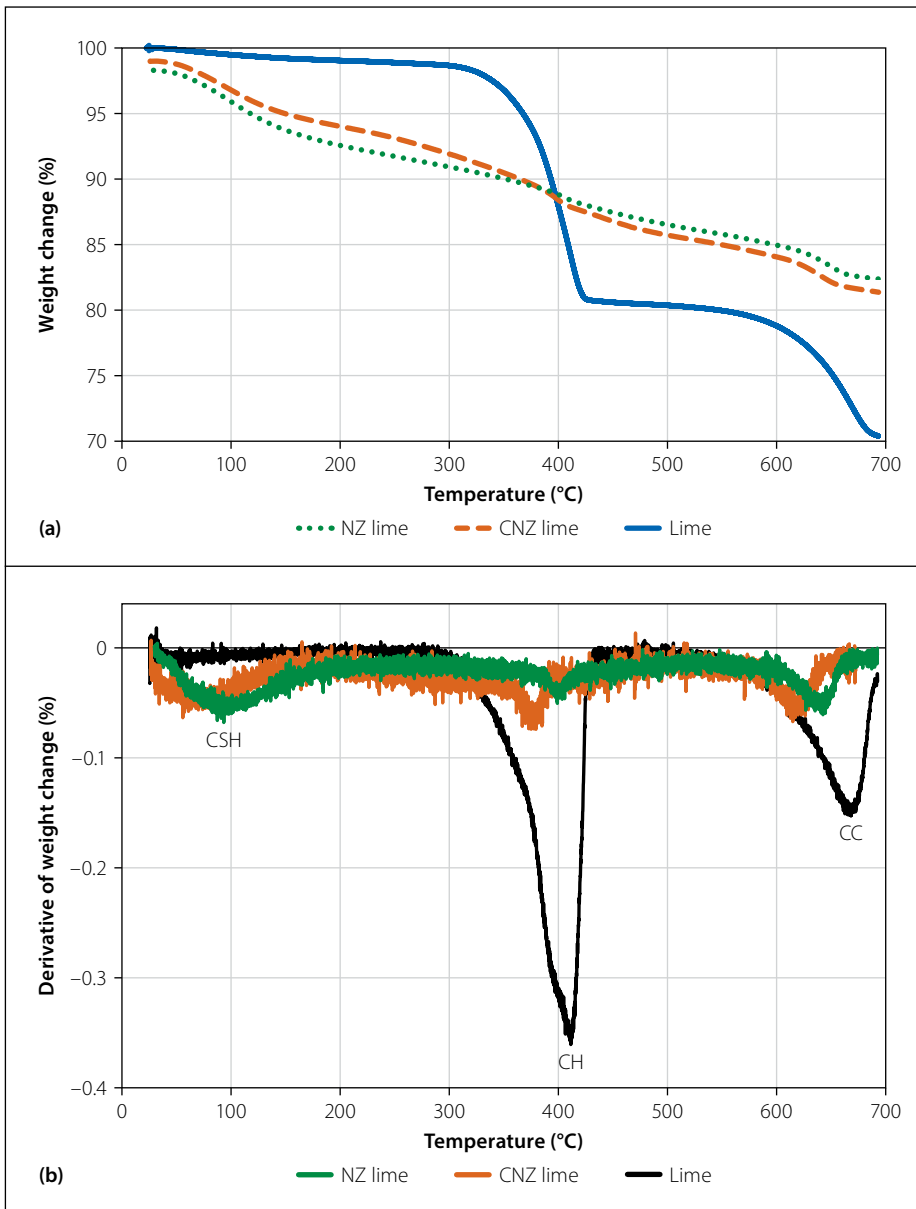


Figure 6 Thermogravimetric analysis of zeolite-lime mortar mixtures: (a) weight loss curves, (b) derivatives: NZ (natural zeolite), CNZ (calcined natural zeolite), CH (calcium hydroxide), CSH (calcium silicate hydrate), CC (calcite)

converting them into salts (Shafaatian *et al* 2013).

Sulphate attack

The long-term mortar expansion results due to sulphate attack are given in Figure 5. The control sample (OPC-SR) gave a 28-day expansion of 0.03%, which also was the highest value obtained among all the mixtures investigated. Interestingly, the 20 and 30% NZ mortar mixtures exhibited significantly lower 28-day expansion values, giving 0.019 and 0.015%, respectively. At the age of 160 days, the 20 and 30% NZ mortars gave long-term expansion values of 0.022 and 0.019% respectively, which are much lower than the corresponding 0.038% of OPC and 0.032% of the 30% FA mortars. As expected, the 30% FA mortar also reduced sulphate expansion.

Pozzolanic reactivity and thermogravimetry

It was found that CNZ gave the 7-day PAL test compressive strength of 18.09 MPa, which is much higher than the 5.67 MPa of the NZ sample. Evidently, calcination of NZ had a remarkably significant effect, leading to high enhancement of pozzolanic reactivity, as already recognised in the literature (Mielenz *et al* 1950; Marantos *et al* 2020). It is known that the crystalline structures of NZs, change to amorphous phases upon heat treatment of the zeolites at high temperatures, leading to enhancement in pozzolanic reactivity (Marantos *et al* 2020).

Figure 6a shows weight loss graphs of thermogravimetric analyses for the NZ-lime and CNZ-lime samples. Also shown in Figure 6b are the weight loss derivatives, distinctly identifying points of drastic weight loss, which indicate temperatures at which particular phases underwent decomposition. The peaks seen between 50 to 100°C in Figure 6b, show the formation of CSH in the NZ-lime and CNZ-lime samples, owing to pozzolanic reaction (Collier 2016). Evidently, no CSH peak formed in the lime sample due to the absence of pozzolanic reaction in this sample, as expected.

It can also be seen that the sample of lime showed rapid conversion at a temperature range of 340 to 439°C, as did both the CNZ-lime and NZ-lime samples. Close inspection shows that the CNZ-lime graph exhibited more substantial weight loss at around 355°C relative to that of the NZ-lime sample (Figure 6b). This

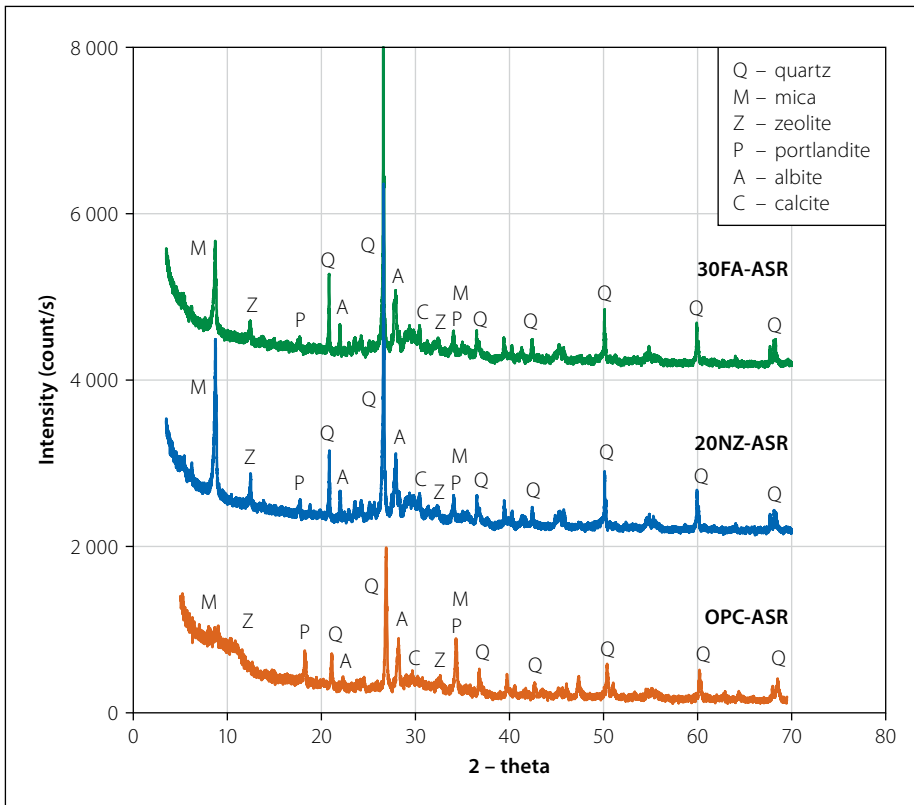


Figure 7 XRD patterns of ASR expansion mortars containing natural zeolite (NZ) or fly ash (FA): ASR (alkali-silica reaction), OPC (ordinary Portland cement)

observation indicates that more CH had been consumed by CNZ during the lime-pozzolan reaction, which explains this sample's higher compressive strength of 18.09 MPa relative to the lower 5.67 MPa of the NZ-lime mixture. All the samples

exhibited another peak at 600 to 700°C, which is attributed to calcite (CC) formation due to carbonation that occurred upon exposure of samples to atmospheric CO₂ during sample preparation (Collier 2016; Ekolu 2016, 2018).

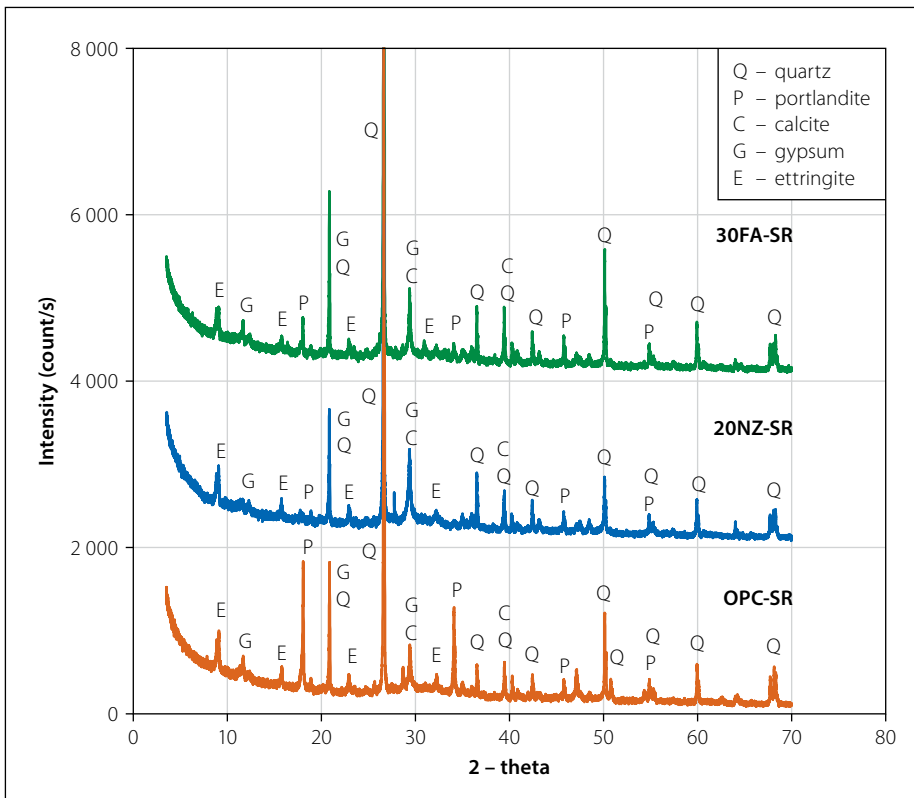


Figure 8 XRD patterns of sulphate attack in mortars containing natural zeolite (NZ) or fly ash (FA): OPC (ordinary Portland cement)

Analytical studies

Based on the results of physical tests as discussed above in the sections titled *Compressive strength results*, *Drying shrinkage results*, *ASR test results*, and *Sulphate attack* (pages 5–8), it was observed that 20% NZ gave the closest overall mechanical performance to that of 30% FA, but with the former exhibiting better durability properties. Accordingly, results showed that 20% NZ would perhaps be the maximum suitable dosage for conventional use of the natural pozzolan in cement. On this basis, the 20% NZ and 30% FA samples were selected for the microanalytical investigations provided in the subsequent sections.

X-ray diffraction

(a) Mortar samples subjected to alkali-silica reaction

Figure 7 shows XRD patterns of ASR mortar samples that had been immersed in 1M NaOH at 80°C for 140 days during the AMBT. The strong peaks of quartz, albite and mica minerals observed in all samples are crystalline phases of the GW aggregate.

Also seen are peaks of portlandite and calcite crystals, being the crystalline products resulting from cement hydration and carbonation, respectively. Interestingly, zeolite peaks occur in all samples, as observed at angles of 12.5° and 32.8° (2θ). Evidently, new zeolites formed during storage of the samples at the elevated temperature of 80°C. The relatively higher intensity of the zeolite peak seen at the 12.5° (2θ) angle for the 20% NZ sample may indicate the presence of some unreacted NZ particles in the mixture. By comparing the XRD patterns of samples in Figure 7, made with the GW aggregate versus those for the samples prepared using silica sand as given later in Figure 8, it is evident that the zeolite which formed in the former emanated from phases in the reactive GW aggregate. Clearly, no zeolite formed in samples made with silica sand (Figure 8).

In all the XRD patterns of Figure 7, a broad hump occurs within the range of a 26° to 35° (2θ) angle, which is a feature majorly attributed to the presence of an amorphous ASR gel phase (Shi *et al* 2019), along with other non-crystalline phases such as unreacted glassy phases of NZ.

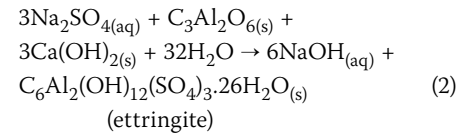
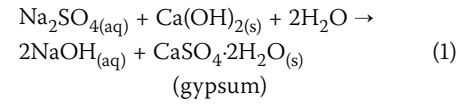
(b) Mortar samples subjected to sulphate attack

Figure 8 gives XRD patterns of mortar samples that had been subjected to

sulphate attack under storage in 2.8M Na₂SO₄ solution at 23°C for 160 days. The strong peaks of quartz seen in the XRD patterns of all the mortar samples, arose from the silica sand used as fine aggregate in mortar mixtures. Similarly, peaks of portlandite and calcite can be seen in the XRD patterns of all mortar mixtures, the former being a product of cement hydration while the latter is CaCO₃ formed due to carbonation of samples under exposure to the atmosphere during specimen preparation (Collier 2016; Ekolu 2016, 2018).

During pozzolanic reaction, the CH found within the hardened cement paste is consumed, leading to secondary formation of an amorphous CSH phase in the binder matrix. In turn, a relatively denser binder matrix develops which reduces permeability and improves the durability performance of the hardened cementitious system. It can be seen in Figure 8 that the mortar containing 20% NZ gave the lowest peaks of portlandite, as seen at 2θ angles 18°, 34° and 45.7°. This observation indicates that the 20% NZ mortar exhibited much greater pozzolanic reactivity than the other mixtures, including the 30% FA sample.

Also in Figure 8, peaks of gypsum and ettringite are seen in patterns of all the mortar mixtures. It can be seen at the 11.6° (2θ) angle that the 20% NZ sample had the lowest peak of gypsum, which confirms the NZ's effectiveness in mitigating sulphate attack, as discussed earlier (Figure 5). The formation of expansive gypsum and ettringite in the hardened binder system is the mechanism responsible for expansion due to sulphate attack, as given in Equations 1 and 2 (Clifton & Pommersheim 1994). However, the presence of ettringite peaks, as seen in XRD patterns, does not strictly indicate that the mortar mixtures were expansive, considering that the observed intensities include the early-age ettringite phase that formed during cement hydration. Typically, during sulphate attack, expansive ettringite forms in confined spaces within the hardened cement paste. Since gypsum and ettringite occupy more volume than their reactants, the formation of these mineral phases in confined spaces leads to expansion. Indeed, the reactions given in Equations 1 and 2 result in volume increase with volume expansion factors of 1.24 and 2.38, respectively (Clifton & Pommersheim 1994; Mather 1978).



Scanning electron microscopy

(a) Alkali-silica reaction features

Figure 9 shows SEM features of the control OPC mortar following 160 days of the AMBT. It can be seen in Figure 9a that intense internal cracking of the reactive aggregate particles occurred throughout the mortar matrix. The observed severe microcracking of reactive aggregate particles is a diagnostic feature typical of ASR attack. Figure 9b gives a close-up image of observed microcracking, showing the ASR gel infilling characterised by the gel's smooth surface texture. The predominant presence of Si/Al elements seen in the EDS patterns, is characteristic of ASR gel. The gel substance is a reaction product of NaOH and Si/Al elements found in the reactive GW aggregate. ASR gel has a high affinity for water, which it imbibes, leading

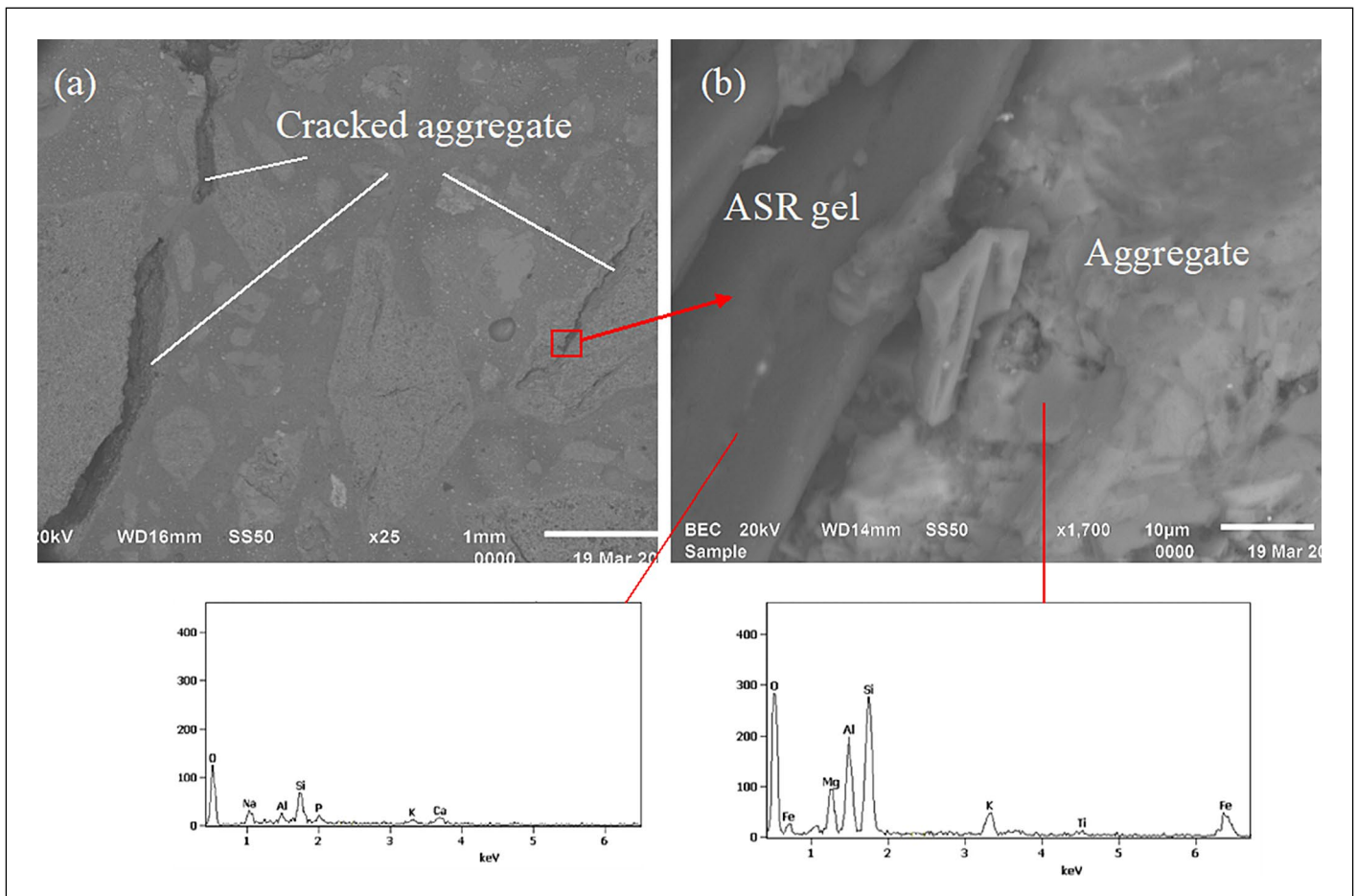


Figure 9 SEM features of alkali-silica reaction (ASR): (a) ordinary Portland cement (OPC) mortar, (b) close-up image of the cracked aggregate in (a)

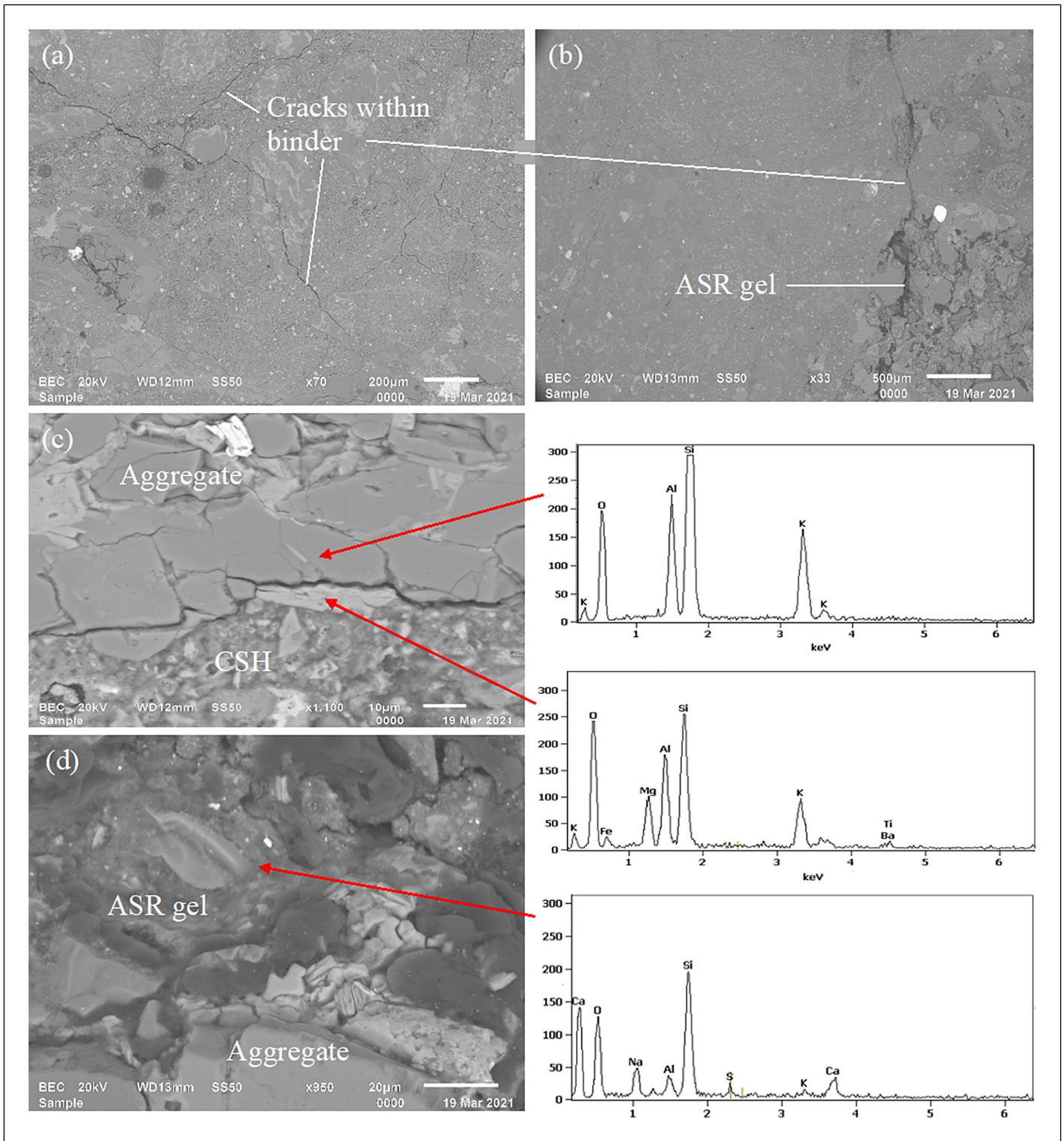


Figure 10 SEM features of alkali-silica reaction (ASR) in mortars: (a) 20% NZ microstructure, (b) 30% FA microstructure, (c) 20% NZ, EDS, (d) 30% FA, EDS: NZ (natural zeolite), FA (fly ash)

to expansion and disruptive cracking of the hardened cementitious system.

Figure 10 shows the SEM features of ASR in the mortars containing 20% NZ and 30% FA, following 160 days of AMBT at 80°C. Some cracks can be seen in the mortar samples of Figures 10a and 10b. The reactive aggregate particles can be seen containing a light-coloured mica mineral phase. Evidently, the overall ASR damage was significantly less in the mortars containing 20% NZ and 30% FA (Figures 10a and 10b),

relative to the severe damage exhibited by the control sample (Figures 9a and 9b).

Figures 10c and 10d give the EDS analyses of the different phases present in the 20% NZ and 30% FA mortar samples. Upon close inspection, it is evident in Figure 10c that the mica phase exhibited intense cracking, while the other phases in the aggregate remained relatively stable. It appears that mica is the reactive phase of the GW aggregate.

The elemental composition of the ASR gel product that was formed in the 30% FA

mortar sample (Figure 10d) is similar to that which occurred in the control mortar (Figures 9a and 9b). It may, however, be recalled that the mixtures containing 20% NZ and 30% FA both exhibited significantly lower ASR expansion levels relative to that of the control, as discussed earlier (see Figure 4).

(b) Sulphate attack features

Figure 11 shows SEM features of the control OPC mortar that had been subjected to

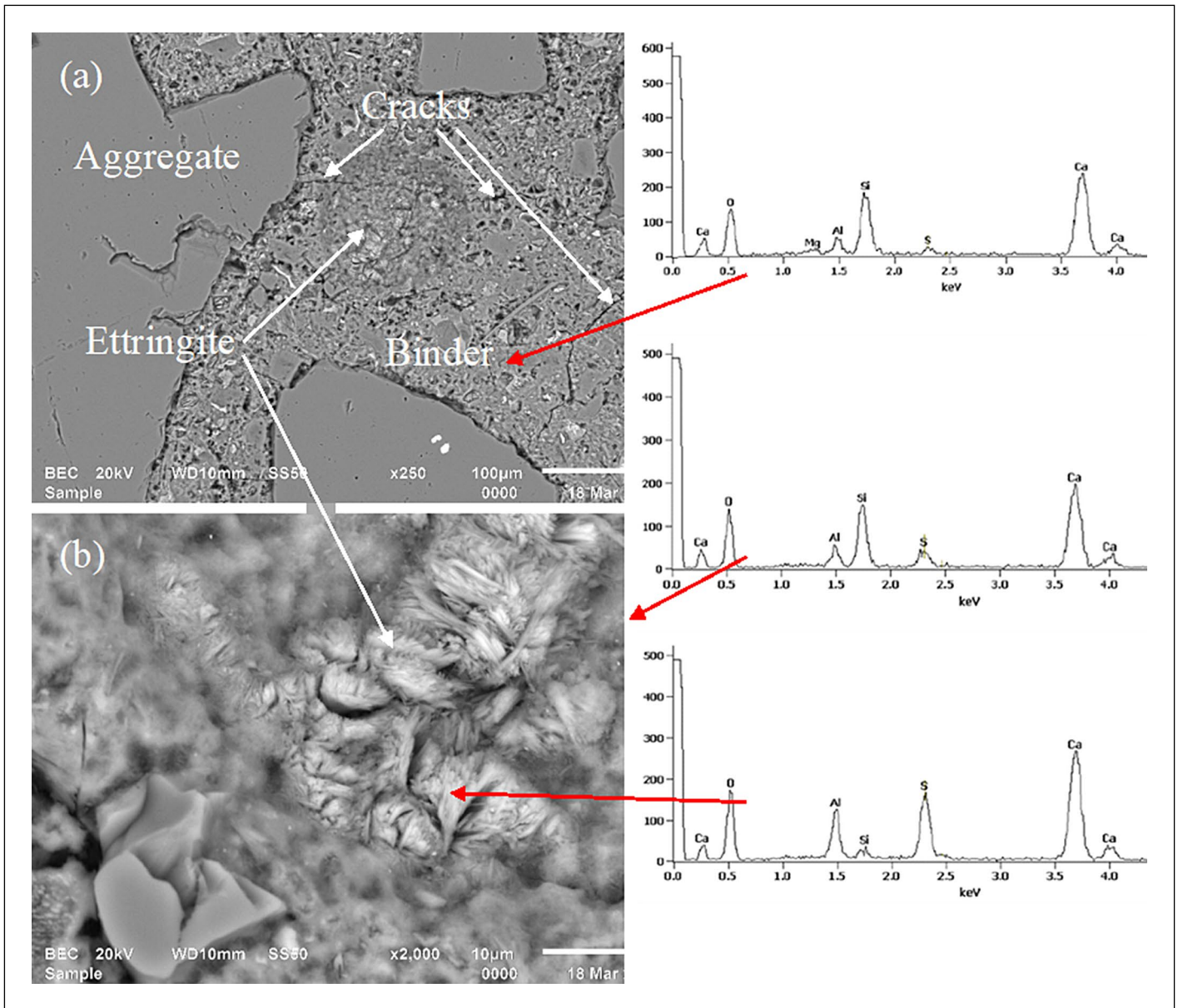


Figure 11 SEM features of sulphate attack in the control ordinary Portland cement (OPC) mortar: (a) ettringite infilling in an air pore, (b) close-up image of the ettringite in (a) showing needle-like crystals

sulphate attack for 140 days. It can be seen in Figure 11a that the originally empty air pore in cement paste was completely infilled by ettringite. The close-up image of Figure 11b shows needle-like crystals of the ettringite infilling, also confirmed by the associated EDS analysis. These observed SEM features are consistent with findings from XRD analysis (as discussed under *X-ray diffraction* on page 9) and with the high sulphate expansion results of the control OPC mortar (as discussed under *Sulphate attack* on page 8 (Figure 5)). The observed severe microcracking of mortars, as seen in Figure 11a, is attributed to expansive formation of gypsum and ettringite phases, which generated intense internal stresses within the matrix, in turn causing high physical expansion (Figure 5) as per the mechanism explained under *Mortar samples subjected to sulphate attack* on pages 9 and 10.

Figure 12 shows SEM features of sulphate attack in the mortars containing 20% NZ and 30% FA. It can be seen that the 20% NZ mortar had a relatively dense and uniform microstructure (Figure 12a) with limited microcracking, which is consistent with its higher sulphate resistance, as also indicated by its observed lower expansion level (Figure 5). In contrast, the 30% FA mortar seemed to have been majorly affected by sulphate attack, as the sample exhibited extensive microcracking (Figure 12b). However, it may be recalled that sulphate resistance of the 30% FA mixture was still higher than that of the control OPC mixture, as expected.

Figures 12c and 12d give elemental analyses of mortars containing 20% NZ and 30% FA, respectively. The EDS analyses results show that the 20% NZ mortar formed Na-rich ettringite within cracks, in

contrast with the 30% FA mortar in which normal ettringite occurred. The phase alteration of ettringite involving alkali (Na) enrichment may have significantly contributed to the observed higher sulphate resistance behaviour of the NZ mixture.

CLASSIFICATION OF THE NATURAL ZEOLITE POZZOLAN

ASTM C618 (2015) specifies the criteria that must be met for the purpose of classifying natural pozzolans as supplementary cementitious materials or cement extenders. In Table 5, experimental results of NZ are compared against the standard specification requirements. It can be seen that use of the zeolite at 20% NZ proportion meets the criteria for 'Class N' pozzolan, giving values that are well within acceptable prescribed limits. As seen in Table 5, the criteria

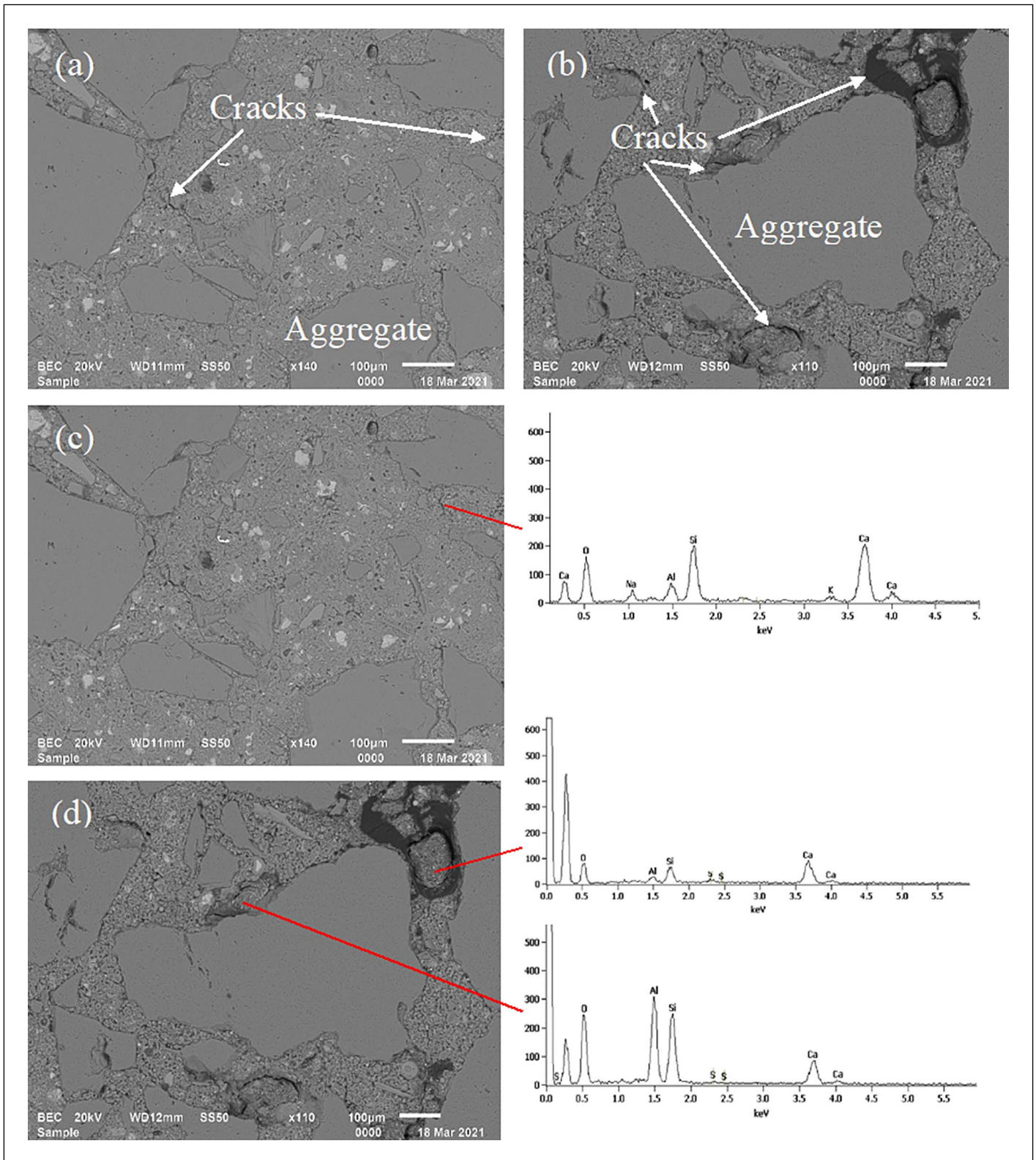


Figure 12 SEM features of sulphate attack in mortars: (a) 20% NZ microstructure, (b) 30% FA microstructure, (c) 20% NZ, EDS, (d) 30% FA, EDS: NZ (natural zeolite), FA (fly ash)

comprise chemical and physical requirements. Pozzolanic aluminosilicate materials of natural origin are required to contain $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$ content exceeding 70%, of which NZ had 76.6% content, mostly being SiO_2 (61.3%) and Al_2O_3 (12.9%) (Table 1). In clays and other materials, LOI typically indicates the content of carbonates and/or bound water, while carbon content is the key impurity indicated by LOI of FA

(Chen *et al* 2019). In the present study, NZ had somehow higher LOI of 15.8% > 10%, most likely due to the presence of bound water from hydroxyl-bearing minerals.

As expected, the effect of pozzolan on physical properties depends on its proportion in the mixture. From the various experiments conducted and discussed under the above two sections titled *Experimental study* and *Results and*

discussion (pages 3–12), it was found that 20% NZ content provided an optimum overall performance across all the crucial characteristics and properties investigated. Accordingly, the ASTM C618 (2015) criteria presented in Table 5 are compared against the performance of mixtures containing 20% NZ.

The main mechanical properties of importance in the evaluation of pozzolans

Table 5 Classification of natural zeolite (NZ) based on the criteria specified in ASTM C618 (2015)

	ASTM C618 Class N	Natural zeolite 20% NZ
SiO ₂ + Al ₂ O ₃ + Fe ₂ O ₃ , min (%)	70.0	76.6
SO ₃ , max	4.0	–
Moisture content, max (%)	3.0	0.32
Loss of ignition, max (%)	10.0	15.8
Fineness, amount retained on the 45 µm sieve, max (%)	34.0	0
Strength activity index: at 7 days, min (%)	75	86
: at 28 days, min (%)	75	83
Pozzolanic activity index with lime, min (MPa)	5.5	5.67
Increase of drying shrinkage of mortar bars at 28 days, max difference in % over control	0.03	-0.016
ASR expansion of test mixture as a percentage of low-alkali cement control at 14 days, max (%)	100	65.1
ASR mortar expansion at 14 days in alkali expansion test, max (%)	0.06	0.10
Sulphate expansion of test mixture as a % of control after 160 days exposure, max %	100	59.5

are compressive strength, PAL, and drying shrinkage. Strength gain effects of pozzolans are evaluated at the early age of seven days and at the standard age of 28 days. It can be seen that, at seven days and 28 days, the strength activity index values of 86% and 83% for the 20% NZ/OPC blended mixtures are well above the 75% minimum requirement. The foregoing is consistent with the PAL test result of 5.67 MPa which exceeds the 5.5 MPa minimum, showing that the NZ has sufficient pozzolanic reactivity. Based on ASTM C618 (2015), pozzolans may be expected to increase drying shrinkage up to a level of 0.03% over that of the control. Interestingly, NZ reduced the 28-day drying shrinkage with a significant difference of -0.016% below that of the control, which indicates the potential benefit of employing the pozzolan towards crack control.

ASR and sulphate resistance responses of mixtures are the main durability performance characteristics that are considered in the criteria. The high effectiveness of NZ in mitigating both ASR and sulphate attack, is indicated by the expansion reductions comprising 65.1% < 100% and 59.5% < 100% for mixtures containing the pozzolan.

The approach of EN 197-1 (2000) and SANS 50197-1 (2013) on quality evaluation of natural pozzolans is quite different from that of ASTM C618 (2015), with the former specifying reactive silica content < 25% along with strength class of cement type, as the main criteria. For employment of the zeolite as cement extender at 10 to 20% NZ, the blend falls under CEM II/A-P cement type. From Figure 2 and Table 3, the 20% NZ/OPC blend gave 3-day and

7-day strength values of 16.2 and 33.9 MPa, which meet the criteria for Strength Class 32,5 N, R. Accordingly, the 20% NZ/OPC blend investigated in the present study meets the main EN/SANS criteria for classification as CEM II /A-P 32.5N,R.

CONCLUSIONS

Natural zeolite (NZ) was investigated to determine its performance and classification for potential use as pozzolan or cement extender. Varying proportions of 0, 10, 20 and 30% NZ were blended with CEM I 52,5N ordinary Portland cement (OPC), then used to prepare mortar mixtures. Various mechanical and durability properties of NZ/OPC blended mortar mixtures were evaluated. Performance results of NZ/OPC blended mixtures were also compared with those of 30% fly ash (FA) mortar. Based on experimental observations from the study, the following conclusions are drawn:

1. Incorporation of 20% NZ in OPC met the ASTM C618 criteria for classification of the zeolite as 'Class N' pozzolan. The 20% NZ/OPC cement blend fulfilled the main requirements for its classification as CEM II / A-P 32.5N,R, based on EN 197-1 / SANS 50197-1.
2. Blending of NZ with OPC led to reduction in workability of mixtures. Workability reduces with corresponding increase in proportion of NZ in mixtures.
3. Consistent with the typical effects of common pozzolans, NZ gave lower early-age strength but higher late-age strength development. It was observed that the late-age compressive strength

of 20% NZ mortar was similar to that of the control OPC mortar.

4. The NZ pozzolan significantly reduced the drying shrinkage of mixtures – the higher the NZ proportion used in mixtures, the greater the observed reduction in drying shrinkage.
5. Mortars containing 20 to 30% NZ exhibited significant mitigation of expansion due to alkali-silica reaction (ASR) and were more effective in controlling ASR than the 30% FA mortar.
6. Mortars containing 20 to 30% NZ were more effective in controlling sulphate attack than the 30% FA mixture.

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