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Research Article

Utilisation of alkali-activated blast furnace slag in paste backfill of high-sulphide mill tailings: Effect of activator type and addition time

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ABSTRACT

This study investigates the mechanical, microstructural, and acoustic performance of cemented paste backfill (CPB) incorporating alkali-activated blast furnace slag (AAS) prepared using solid sodium metasilicate (SMS), liquid sodium silicate (LSS), and sodium hydroxide (NaOH). Each was formulated as a pre-prepared binder gel at an equivalent design dosage. Unconfined compressive strength (UCS) assessments at 360-day revealed that SMS-activated specimens outperformed LSS-, NaOH-, and OPC-based specimens by 16%, 1.94 times and 4.82 times, respectively. LSS-activated specimens yielded UCS values 1.82 and 4.38 times higher than NaOH- and OPC samples, while NaOH-activated specimens surpassed OPC by 2.41 times in strength. Pre-mixing the activator with slag before its addition to the paste backfill material mixture medium reduced UCS by 3.6–9.01% in LSS and NaOH-based systems, demonstrating the sensitivity of mechanical performance to the binder preparation method. Mercury intrusion porosimetry (MIP) revealed that SMS-, LSS-, and NaOH-activated specimens reduced total porosity by 14.25%, 15.79%, and 10.68% relative to OPC, respectively, with Mixture-1 and Mixture-6 recording the most refined pore microstructures. Ultrasonic P-wave velocity (UPV) measurements confirmed the mechanical findings. Samples activated with SMS, LSS, and NaOH had UPV values that were 25.14%, 21.87%, and 20.84% higher than OPC, respectively, with the ranking being SMS > LSS > NaOH > OPC. Although there were consistent ranking trends between UCS and UPV results, AAS systems provided a 2.23–4.82-fold improvement in UCS compared to OPC. However, UPV improvements remained modest at 1.22–1.25%, suggesting that UPV alone may not fully reflect the degree of microstructural advancement achieved through alkaline activation.

1. Introduction

Materials produced with binders resistant to acid and sulfate effects are of great importance in the underground paste backfill operations in the mining industry. Although Portland cement is the most commonly used hydraulic binder in the construction and building materials, it is a vulnerable binder against acid and sulfate effects due to its high CaO, C_3S and C_3A content [1]. In addition, since cement is produced in very large volumes worldwide, Portland cement production brings problems with it related to economy, energy and environment. 1 ton Portland cement production causes approximately 1 ton CO_2 emission release to the atmosphere, which makes 10% of total fossil fuel-based CO_2 emissions in the world; corresponds to 6% CO_2 equivalent of all greenhouse gas emissions [2].

Due to industrial activities, millions of tons of pozzolanic waste materials are produced every year. These materials can cause environmentally hazardous effects when not stored under suitable conditions. Therefore, depending on their mineralogical and chemical composition, the use of these materials as secondary raw material products is very important in terms of both environmental and natural resources protection. For this reason, it is very important to conduct new studies and researches on both better performing and environmentally sensitive binding systems.

In connection with cement production, one of the ways to solve problems related to energy, economy and environment is to develop alternative binders with properties similar to Portland cement.

In recent years, alkali-activated binders or geopolymer binders have been produced by activating wastes (by-products) such as natural raw materials and industrial by-products (blast furnace slag, fly ash, etc.) containing silicoaluminate with alkaline chemicals.

Alkali-activated binders or geopolymers are inorganic binders obtained by the activation of pozzolanic minerals using alkaline chemicals. It is known that the designs prepared in this method reduce the energy costs, binder preparation costs and CO_2 emissions while increasing the durability by preventing the loss of strength. If the

pozzolanic by-products are used as an additive to cement or as an alternative, CO_2 emissions can be reduced by up to 30% to 50% [2], [3]. The binders produced by alkali activation provide many important advantages such as higher early strength values, lower hydration temperatures, more resistant materials to corrosive environments and freeze-thaw effects, and stronger bond strengths than normal Portland cements. Consequently, this has led to a significant increase in research on these binding agents in recent decades.

While prior researches have made significant contributions to understanding the role of activator chemistry, concentration, silicate modulus, and slag composition in alkali-activated blast furnace slag (AAS)+paste backfill systems, those studies consistently employed activators in pre-dissolved liquid form added directly into the paste mixture during preparation. The present study departs from this conventional approach in two ways. First, three chemically distinct activator systems are compared with respect to their physical form: solid sodium metasilicate (SMS), liquid sodium silicate (LSS), and sodium hydroxide (NaOH). The inclusion of a solid activator (SMS) introduces unique in-situ dissolution dynamics, differential heat evolution, and early-age reaction kinetics that are absent when pre-dissolved solutions are used. Second, and critically, in this study the alkali activator is not introduced directly into the paste backfill mixture. Instead, each activator is pre-reacted with the blast furnace slag to form a binder gel, which is subsequently incorporated into the paste backfill mixture medium at a constant design. This pre-gelation allows the degree of slag activation to be partially controlled prior to contact with tailings, potentially decoupling the binder formation process from the complex chemical environment of the paste. To the best of the authors' knowledge, this combination of solid versus liquid activator form and pre-formed gel addition methodology has not been previously investigated in the paste backfill studies, representing the primary novelty of this work.

2. Experimental Program

2.1. Characterization of Tailings and Binder Materials

Sulfidic tailings (ST) sourced from a copper-zinc sulfide ore flotation plant located in the northeastern region of Türkiye (Fig. 1) were employed as the primary material for CPB specimen production. Particle size distribution of the tailings was characterized using a Malvern Mastersizer Hydro 2000 MU laser diffraction particle size analyzer (Fig. 2). Based on the fine material content, the ST may be classified as a medium-grade tailings (proportion of particles finer than 20 µm ≈ 53.7%) in accordance with the classification framework by Landriault (2001). Grading assessment based on the coefficients of uniformity (C_u) and curvature (Cc) confirmed that the tailings exhibits a well-graded particle size distribution (Fig. 2; Table 1). The elemental and chemical composition of the ST were determined at ACME Analytical Laboratories (Canada) by Inductively Coupled Plasma–Atomic Emission Spectroscopy (ICP-AES). Notably, the tailings contained approximately 30.09% sulfidic sulfur (S^{2-}) by mass (Table 1).

Figure 1. Sulphidic mill [2].

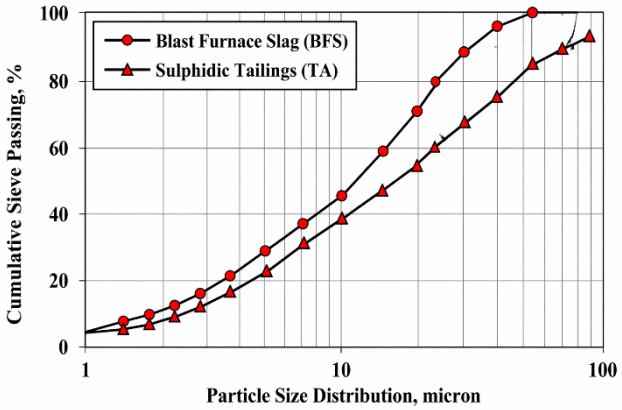

Figure 2. Particle size distribution, micron (BFS: Blast Furnace Slag, TA: Sulfidic Tailings).

Table 1. Chemical and physical properties of the tailings [2].

Chemical composition	Tailings (%)	Physical charact.	Tailings
SiO_2	12.8	Spesific gravity	3.93
Al_2O_3	4.33	Spesific surface (cm^2/g)	3000
Fe_2O_3	46.32	D_{10}	1.757
CaO	2.55	D_{30}	6.464
MgO	2.37	D_{50}	17.16
TiO_2	0.09	D_{60}	25.48
CrO_3	0.016	D_{90}	73.84
Na_2O	0.17	Cu	14.5
K_2O	0.25	Cc	2.88
MnO	0.11		
Heat loss	26.2		
Sulfide Sulfur	30.09		
Total Sulfur	34.22		
Initial pH	9.17		
Initial SO_4^{-2} (ppm)	2500		

Three alkaline activator systems - solid sodium metasilicate (SMS), liquid sodium silicate (LSS), and sodium hydroxide (NaOH) were evaluated as activators for AAS preparation using BFS. Ordinary Portland cement (CEM I 42.5R; OPC) was used as reference binder. Ground granulated blast furnace slag (GGBFS: BFS) was obtained from an iron and steel manufacturing facility located in northwestern of Türkiye, while OPC was taken from a regional cement producer. The chemical compositions of

all solid binder materials were determined at ACME Analytical Laboratories (Canada) and the Turkish Cement Manufacturers Association (TCMA) laboratories through X-ray fluorescence (XRF) spectrometry and, wet chemical analysis, respectively. Based on its chemical composition, the GGBFS used in this study is classified as acidic slag [15]. Physical and chemical properties of all binder materials are summarized in Table 2.

Table 2. Physical and chemical properties of binders [2].

Physical charact.	**CEM I 42.5 R (OPC)**	**BFS**
Specific gravity	3.16	2.92
Specific surface (cm^2/g)	4170	4270
90 µm screen res. (%)	-	-
45 µm screen res. (%)	2.33	3.78
32 µm screen res. (%)	7.65	9.17
Chemical composition	**CEM I 42.5 R (%)**	**BFS (%)**
SiO_2	19.93	39.62
Al_2O_3	5.12	11.38
Fe_2O_3	3.13	0.68
CaO	69.72	36.15
MgO	2.59	5.87
TiO_2	0.26	0.98
CrO_3	0.04	0.01
Na_2O	0.28	0.29
K_2O	0.69	1.19
MnO	0.07	2.00
P_2O_5	0.11	<0.01
Free lime	2.96	-
Heat loss	3.90	0.20
SO_3	2.95	1.62

2.2. Alkaline Activators

Liquid sodium silicate at Ms ≈ 2.0 (Ms: mass ratio of SiO_2 to Na_2O), granule sodium hydroxide (99.5%) and sodium metasilicate at Ms ≈ 1.0 ($Na_2O{\cdot}SiO_2{\cdot}5H_2O$) were used as activators.

SMS was used in two different forms. The first is in the solid form (sSMS) and, the second is in the solution form obtained after dissolution in water (dSMS).

In the activation processes, the modulus of sodium silicate (Ms) was adjusted with NaOH. NaOH was added to the mixture after dissolving in water according to the pre-prepared mixture designs.

2.3. Preparation of CPB Samples

For this study, 9 different CPB designs (8 AASs and 1 OPCs) with 2 different mixing forms (pre-mixed, instant-mixing) were prepared using 3 different activators (SMS, LSS and NaOH). Detailed explanations of CPB designs are given in Table 3.

We can define pre-mixed designs where the binder gel formed by the mixture of BFS and alkaline activator is prepared separately from other components in advance. In instant-mixing designs, all components that make up the CPB mixture (binder, tailings, water and activator) are added to the mixer at the same time. The purpose of this process is to see the effects of addition type and timing of binder gel formation in the mixing medium and hence the structure of the fresh CPB. CPB specimens were fabricated by thoroughly mixing of tailings, alkaline binders, and water until a consistent slump at 7.5 ± 0.2 inches was achieved, providing adequate workability for all mixtures.

Table 3. Experimental conditions of CPB samples (CPBs)

CPB Designs	**Binding Agent Type**	**Activator Type**	**Activator Mixing Type**
Mix-1	BFS	Solid SMS (sSMS)	Pre-mix
Mix-2	BFS	Solid SMS (sSMS)	Instant-mixing
Mix-3	BFS	Dissolved SMS (dSMS)	Pre-mix
Mix-4	BFS	Dissolved SMS (dSMS)	Instant-mixing
Mix-5	BFS	LSS	Pre-mix
Mix-6	BFS	LSS	Instant-mixing
Mix-7	BFS	Dissolved NaOH	Pre-mix
Mix-8	BFS	Dissolved NaOH	Instant-mixing
Mix-9	CEM I 42.5 R	-	Instant-mixing

	Binder ratio (%)	**Na_2O dosage (%)**	**Solid content (%)**	**Water (%)**	**Tailings (%)**	**Binder (%)**	**Water/Binder ratio**	**Slump (inch)**
Mix-1	7	8	79.19	20.81	73.65	5.54	3.76	7.7
Mix-2	7	8	79.43	20.57	73.87	5.56	3.7	7.7
Mix-3	7	8	79.43	20.57	73.87	5.56	3.7	7.5
Mix-4	7	8	79.43	20.57	73.87	5.56	3.7	7.6
Mix-5	7	8	79.45	20.55	73.89	5.56	3.7	7.5
Mix-6	7	8	79.38	20.62	73.82	5.56	3.71	7.5
Mix-7	7	8	77.67	22.33	72.23	5.44	4.1	7.5
Mix-8	7	8	77.67	22.33	72.23	5.44	4.1	7.5
Mix-9	7		76.82	23.18	71.44	5.38	4.31	7.6

*The binder ratio is the percentage by weight of the total solid amount (binder / (tailings + binder)).

The binder proportion for both alkali-activated slag (AAS) systems and ordinary Portland cement (OPC) was set at 7 wt.% of total dry solids (tailings+binder), a dosage selected on the basis of strength optimization criteria established in the relevant literature [1,5,9,10,11,12,13,26]. The sodium oxide (Na_2O) concentration was maintained at 8 wt.% relative to the dry mass of ground granulated blast furnace slag (GGBFS), as determined from previously published experimental datasets [5]. The silicate modulus (Ms) was set to 1.0 through controlled addition of sodium hydroxide. Prior to use, NaOH granules were pre-dissolved in water at a mass ratio of 1:2 to yield the target alkaline activating solutions.

CPB specimens (CPBs) (100^{mm} diameter×200^{mm} height) were cast in plastic moulds with perforated bottom allowing the drainage of excess water. Following casting, all specimens were individually sealed in polyethylene bags and placed in a controlled curing environment maintained at 20 ± 1°C and 85 ± 1% relative humidity for the duration of the curing period. For each mixture design and curing age, triplicate specimens were prepared and tested. A total of 162 CPBs were prepared for UPV and UCS tests.

2.4. Ultrasonic P-Wave Velocity and Unconfined Compressive Strength Tests

CPBs (100 mm diameter × 200 mm height) were subjected to ultrasonic P-wave velocity (UPV) and unconfined compressive strength (UCS) tests. UPV and UCS tests were conducted at curing ages of 14-, 28-, 56-, 112-, 224-, and 360-day using a Pundit Plus ultrasonic device operating at a transducer frequency of 54 kHz and a computer-controlled hydraulic loading frame at a constant displacement rate of 0.5 mm/min, respectively (Fig. 3). Average of the three measurements is reported in the results. UCS value of 1.0 MPa was adopted as the threshold strength criterion for both early-age stability (≤ 28-day) and long-term durability (≥ 90-day), consistent with the guidelines proposed by Landriault [4].

Figure 3. UPV and UCS tests, respectively [2].

2.5. Monitoring of pH and Water-Extractable Sulphate Content

The pH and water-extractable sulphate contents of pore solution of CPBs were monitored throughout a 360-day curing period to evaluate the susceptibility of CPBs to acid-generating and sulphate-bearing environments and, to evaluate their consequent effects on mechanical integrity, microstructural stability, and long-term durability. Specimens were prepared at a water-to-solid ratio of 1:1 (by mass) after grinding the solid CPBs with a kitchen grater (<2.36mm). Then, grated materials were mixed with deionized water, sealed and agitated for 1 hours at ambient temperature. Thereafter the suspension was filtered through a 11 µm membrane filter. The pH of the filtrate was measured using a calibrated digital pH meter, and sulphate concentrations were determined by the turbidimetric method in accordance with standard procedures (Palintest Photometer). The monitoring protocol adopted in this study followed the procedure proposed by Cihangir et al. [1], as illustrated in Fig. 4. Initial pH and sulphate content of the tailings pore water are presented in Table 1 as reference.

Figure 4. Steps of pH-sulphate analysis [2].

2.6. Microstructural Characterization - Mercury Intrusion Porosimetry Test

Mercury intrusion porosimetry (MIP) analysis was performed on CPBs at a curing age of 56-day using a Micromeritics AutoPore IV 9510 automated porosimeter (Fig. 5) to elucidate the relationship between pore structure characteristics and the mechanical performance of CPBs. A total of 18 additional CPBs were cast exclusively for microstructural testing purposes.

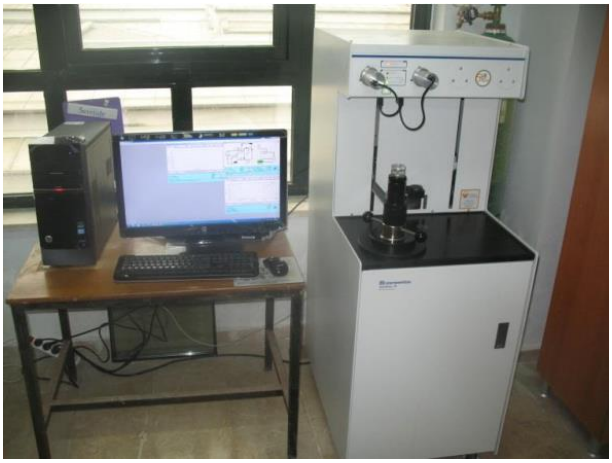

Figure 5. Mercury intrusion porosimeter (MIP) [2].

All specimen preparation procedures for MIP testing were carried out in accordance with the methodology described in [9] and, in conformity with ASTM D4404-10. Pore size evaluation of MIP results were conducted following the the International Union of Pure and Applied Chemistry (IUPAC) instructions, where pores are categorized as micro-pores (<2 nm), meso-pores (2–50 nm), and macro-pores (>50 nm).

3. Results and Discussions

3.1. Effect of Activator Type on Strength Development of CPB

The short- and long-term UCS development profiles of all CPBs are presented in Fig. 6. All CPB designs satisfied the minimum threshold strength criterion of 1.0 MPa at both early- and long-term curing ages, confirming their suitability for underground paste backfill applications.

Among all CPBs, OPC-based specimens consistently recorded the lowest UCS values (UCSs) across all curing ages relative to AAS-containing samples (AASs). During the early ages, OPC specimens exhibited a progressive mean strength gain of approximately 50% between successive curing intervals up to 56-day. Beyond this age, UCS values remained relatively stable up to 224-day. However, a 13.82% strength loss was subsequently recorded at 360-day. This long-term strength loss is attributed to the inherent susceptibility of OPC hydration products - particularly calcium silicate hydrate (C-S-H) and portlandite ($Ca(OH)_2$) to sulphate and acid attack. Sulphate and acid products were generated through the oxidation of sulfidic tailings constituents causing adverse physicochemical interactions within CPB body [8,9,11].

SMS samples (SMSs) have the highest strength values in all curing times compared to other CPBs (Fig.6). SMSs showed an increasing trend in strength during the curing. However, this increase was negligible (~ 1%) after 224 days of curing. CPBs prepared with solid mix SMS (Mix-1 and Mix-2) produced an average of 1.9 times higher strength values in the short term (14-day) and 4.82 times higher strength in the long term (360-das) compared to OPCs. The strength difference between Mix-1 and Mix-2 was 3.98% on average. This is thought to be due to the complete homogeneous mixing of the slag and the activator in advance. CPBs prepared by SMS dissolved in water (dSMSs) (Mix-3 and Mix-4) produced relatively low strength results (9.01%) compared to solid mixing SMSs (Mix-1 and Mix-2) recipes. In addition, dSMSs produced an average of 1.54 times higher strength in the short term (14-day) and 4.52 times higher strength in the long term (360-day) compared to OPCs. It is considered that the reason for the early slightly higher strength in sSMSs than dSMSs is the faster and higher dissolution of slag particles due to the rise of the temperature of the mixture medium as a result of the heat dissipation caused by the sudden dissolution of SMS particles [2,6]. Ravikumar and Neithalath [7] stated that the setting time in case of solid sodium silicate use was faster than liquid sodium silicate.

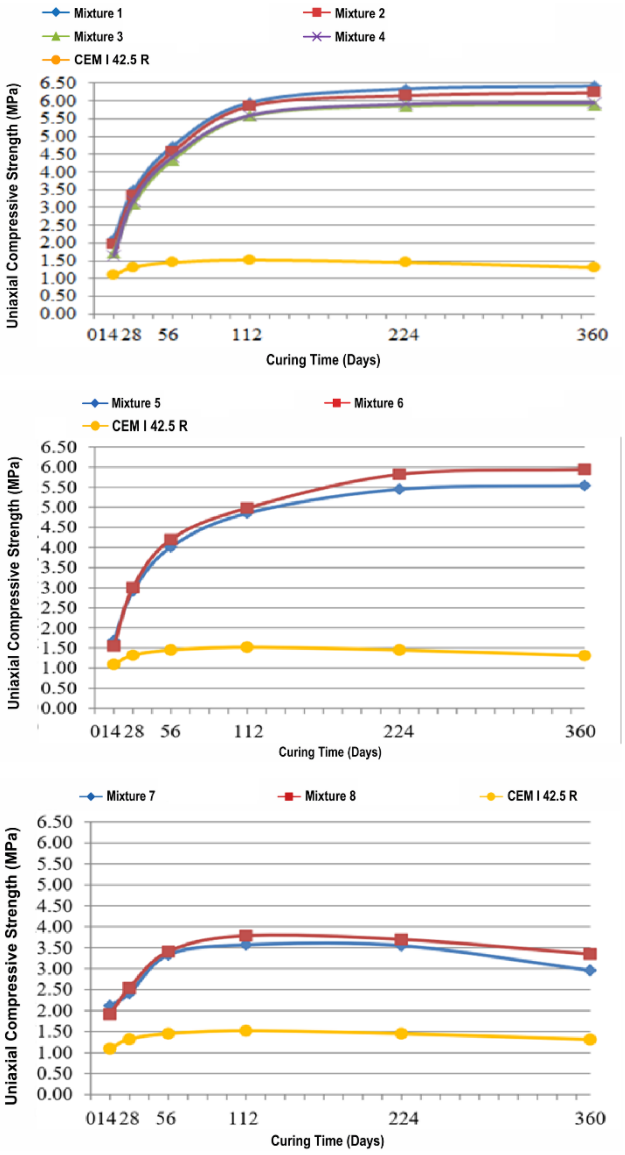

Figure 6. Strength and durability performance of CBPs for each activator in the short and long term (A: SMS, B: LSS, C: NaOH) [2].

Strength development tendencies of LSSs and SMSs in the short term (28-day) were very similar. CPBs prepared with LSS (Mix-5 and Mix-6) produced an average of 3.01 times higher strength values compared to OPCs. In addition, CPBs produced with sSMS (Mix-1 and Mix-2) and dSMS (Mix-3 and Mix-4) had an average strength of 16% and 6.49% higher than LSSs (Mix-5 and Mix-6), respectively. Therefore, it is seen that the use of sSMS is more advantageous in terms of strength gain compared to dSMS and LSS activators. During the 14 days of curing period, Mix-5 CPBs (pre-mixed) produced 9% higher strength than Mix-6 (instant-mixed) samples. However, starting from this curing time, Mix-6 CPBs resulted in 4.9% higher strength than Mix-5 at all curing times.

CPBs prepared with NaOH produced an average of 2.23 times higher strength values compared to OPCs. NaOHs (Mix-7 and Mix-8) showed a loss of strength approximately 14.35% in the long term (360-day) compared to other AASs. Strength loss in long term can be attributed to the i) high concentration of Na^+ ions that cannot penetrate the internal structure of C-S-H, ii) form complexes on the outer surface of C-S-H [2] and, iii) the brittleness of the samples due to the high Na^+ concentration in the binding gel medium [5,6]. In addition, NaOHs have an average higher strength of 30% than LSSs at 14-days curing. This diversity can be attributed to a higher charge density in the mixing medium and a higher concentration of OH^- which breaks the solid slag bonds. It is also believed that the pH value is too high in NaOH samples during early curing times and may result from more slag dissolution and more dense binder gel formation [6,17,18]. During all curing times, Mix-8 (instant-mixed) samples produced 3.6% higher strength than Mix-7 (pre-mixed) CPBs.

3.2. Influence of Activator Type on UPV Evolution of CPBs

According to Fig.6 and Fig.7 it is seen that strength development tendencies and UPV values of CPBs were very similar. It was observed that the strength loss of OPC exhibited a trend parallel to UPV, and the results were found to be consistent with previous studies [14,16]. UPV values of SMSs, LSSs and NaOHs produced high values of 25.14%, 21.87% and 20.84% on average compared to OPC samples, respectively.

In addition, SMSs produced 2.68% and 3.56% higher UPV values than LSSs and NAOHs, respectively. Although AASs produced an average strength of 2.23-4.82 times higher than OPCs, the difference between UPV values was 1.22-1.25%. The higher UPV velocities of SMSs and LSSs compared to other samples especially OPCs can be explained by the faster curing process due to silicate polymerization and stronger bonds in these binders [14,17]. It is also believed to be related to low water / binder ratios and high solid / liquid ratios in these samples [19,20]. The decrease in UPV after 224 days of curing in OPCs is thought to be due to the high porosity contents and the heterogeneous structure due to the long-term acid and sulfate effects of these samples.

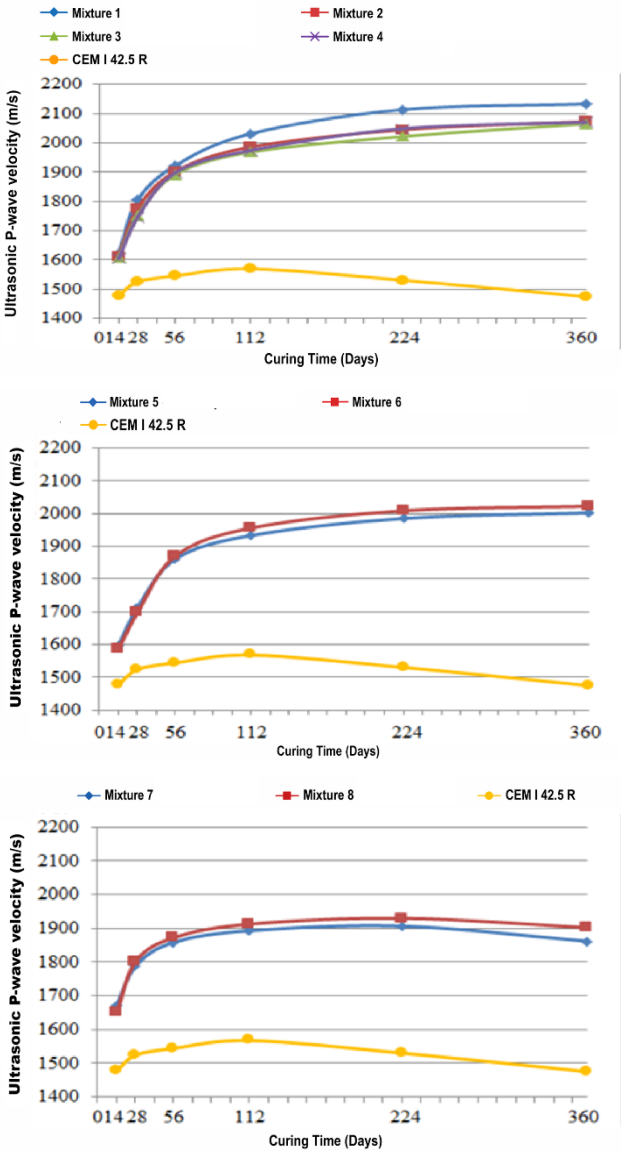

Figure 7. UPV values of CBPs for each activator in the short and long term (A: SMS, B: LSS, C: NaOH) [2].

3.3. Influence of Activator Type on the Microporosity Evolution of CPB

Porosity characteristics and technical parameters of CPBs are given in Table 4. Effect of activator and mixing type on porosity of CPBs are given in Fig.8. According to Table 4 and Fig.8, porous structure characteristics (total porosity, threshold porosity diameter, dimensional proportions of porosities...) of CPBs are very similar for CPBs produced from SMS and LSS, for CPBs of NaOH, among themselves.

SMSs had an average total porosity of 36.79% and the lowest porosity was of Mix-1 (Fig.8). In general, meso- and macro-porosity amounts were close to each other and differences were observed below 1%. The threshold and critical pore diameters are also very close to each other, as shown in Table 4.

Table 4. Porosity content and technical parameters of CPBs [2].

Binder Recipe	Critical pore diameter, dk:(µm)	Threshold pore diameter, de:(µm)	Meso-pore n_{meso} (%)	Macro-pore n_{macro} (%)	Total porosity n_{tot} (%)
Mix-1	4.73	0.88	9.38	26.81	36.19
Mix-2	4.21	0.84	9.29	27.70	36.99
Mix-3	4.57	0.93	9.40	27.63	37.03
Mix-4	5.03	0.92	8.94	27.99	36.93
Mix-5	3.97	0.75	9.42	27.29	36.71
Mix-6	4.73	0.71	8.03	27.51	35.54
Mix-7	5.62	25.89	5.96	32.45	38.41
Mix-8	4.68	32.94	5.56	32.66	38.22
Mix-9	5.92	0.98	4.06	38.83	42.90

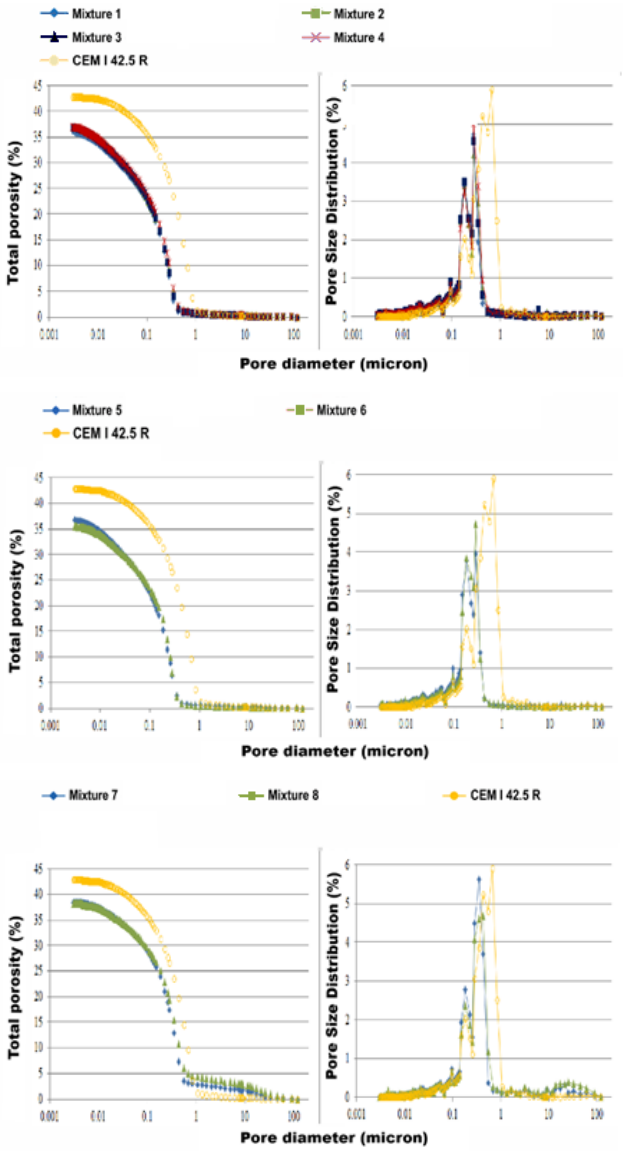

Figure 8. Effect of SMS, LSS and NaOH on porosity of CPB, respectively [2].

Total and macro-sized porosity contents of SMSs were 14.25% and 29.1% less than OPCs, respectively. The meso-size pore amount is 2.28 times higher than OPCs. Critical pore diameters of SMSs are smaller than OPCs. Additionally, total porosity and macro-porosity of SMSs were 3.99% and, 15.43% lower than those of NaOHs, respectively, while SMSs exhibited 1.61 times higher meso-porosity content.

Total porosity, macro- and meso-porosity amounts of LSSs were 5.72%, 15.85% less and, 1.52 times higher than NaOHs, respectively. According to the results, LSS (Mix-5 and Mix-6) was found to be the most effective binder to improve the porosity of CPB. In addition, total porosity, macro- and meso-porosity amounts of LSSs were 15.79%, 29.44% less and 2.15 times higher than OPCs, respectively.

The total porosity of NaOHs is 38.32% on average. Total porosity, macro- and meso-porosity amounts of NaOHs were 10.68%, 16.15% less and 41.87% higher than OPCs, respectively.

In general, AAS-containing binders significantly improved the porosity of CPB compared to OPC. LSS and SMS are the most effective activators where Mix-1 and Mix-6 were found to be the most effective binders.

Strength and durability characteristics of cementitious materials depend on the binder composition, gel structure formed as a result of hydration, amount of porosity and characteristics of porous structure. Therefore, cements with different composition will have different strength and durability properties. However, samples with a lower porosity are expected to have higher strengths [9,21] depending on the bond strength of the binding gel [22]. Furthermore, the high strength and durability values in the SMSs and LSSs can be attributed to the better quality of the porous microstructure owing to the lower total porosity and the higher amount of meso-porosity [9,23,24,25].

3.4. Influence of Activator Type on pH and Sulphate Ion Content of CPB

The pH values (pHs) of CPBs prepared with SMS, LSS, and NaOH depending on the curing time are presented in Fig.9. In all CPBs, the higher pH levels at early curing ages are attributed to the hydration products formations during the initial hydration reaction process [1].

The pH levels of SMS and LSS specimens remained nearly identical throughout all curing periods. NaOH-activated specimens consistently produced the highest pH

values over the 360-day curing period, while CEM I 42.5R specimens generally exhibited the lowest pH values with the exception of the 14- and 28-days of curing periods.

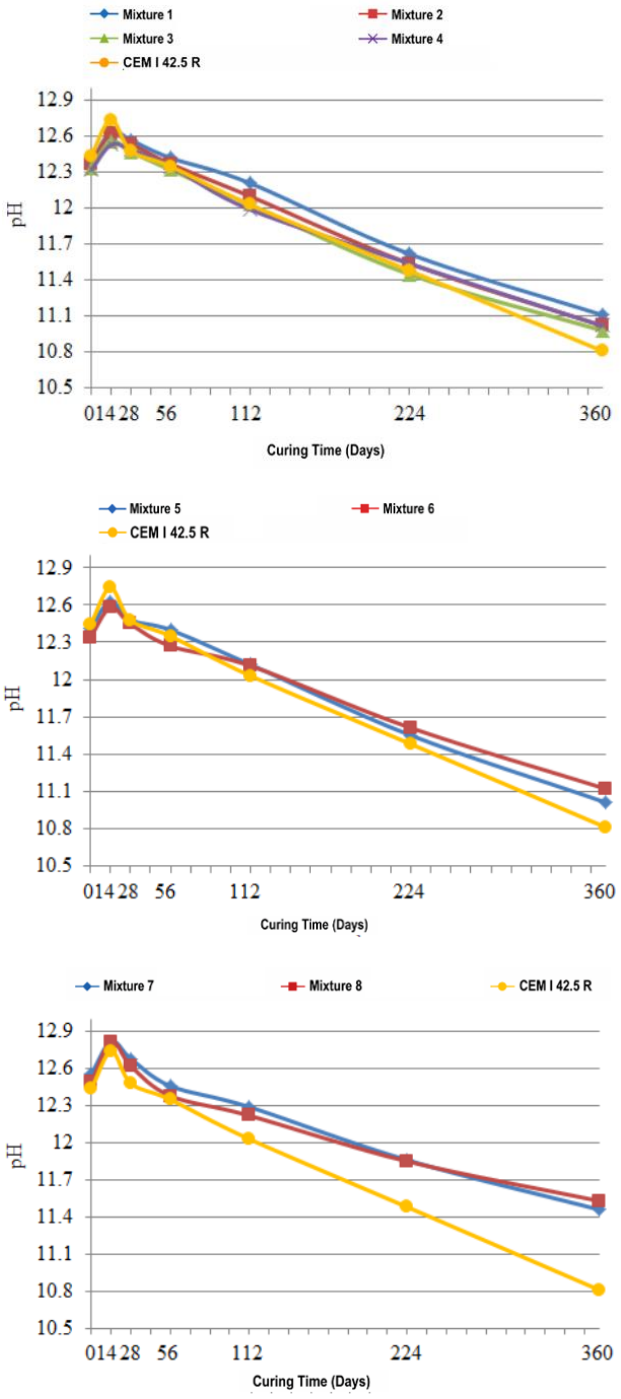

Figure 9. Effect of SMS, LSS and NaOH on pH of CPBs, respectively [2].

When solid SMS was used as the activator, slightly higher pH values were obtained compared to LSS specimens. At the 14-day curing age, the pH of all specimens reached its peak, exhibiting an increasing trend attributable to the formation of hydration products. As the curing period progressed, a gradual decline in pH was observed across all specimens. The pH values of solid SMSs were generally higher than those of liquid LSSs, albeit within narrow margins. This behavior is believed to stem primarily from $Ca(OH)_2$ (portlandite) ions generated as a product of cement hydration.

In the long term, the lowest pHs were recorded for CEM I 42.5R specimens, whose pH dropped below 12.00 after 112 days of curing. It has been reported that $Ca(OH)_2$ dissolves completely when the pH falls below 12 [17], leaving a porous microstructure behind within the CPBs. Consequently, in CEM I 42.5R specimens, the acid products generated under these conditions progressively deteriorate the binder gel structure, ultimately leading to strength losses [1]

Fig.10 shows the sulphate ion concentrations of CPBs at all curing times. At the end of the 360-days curing period, the highest sulphate ion concentrations were obtained in CPBs prepared with SMS, LSS and NaOH, respectively.

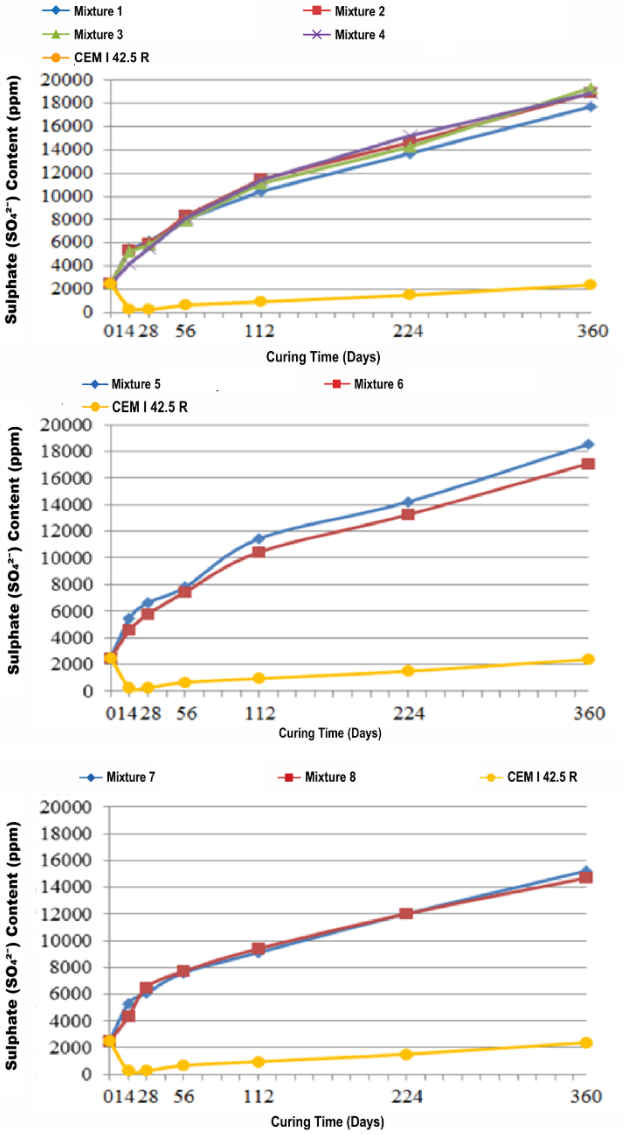

Figure 10. Effect of SMS, LSS and NaOH on sulphate ion content of CPBs, respectively [2].

All AASs showed an increasing trend in sulfate ion concentrations over the entire curing time. Although the sulphate content of OPCs was very low during the early age, it increased in the long term and reached the initial sulphate concentration level. This shows that all of the sulfate ions present in the tailings from the moment of mixing are consumed by reacting with portlandite ($Ca(OH)_2$;(CH)) ions and considering the pHs, sulphate consumption continues in the long term. Fall and Pokharel [24] stated that secondary sulphate-containing compounds (secondary gypsum and ettringite etc.) formed during the hydration process could positively contribute to the strength by filling the pores in CPB. But the formation of excess sulphate products negatively affects the strength and durability of CPBs. In addition, it was observed that secondary minerals containing excessive amounts of sulphated products with expansion properties caused heterogeneous structure formation in CPB, penetration of sulfated products into the binding CSH gel structure and, decreased the gel quality and caused micro cracks in CPB as a result of expansion [9,11,24,27].

4. Conclusions

In this study, the effect of AASs prepared in different forms and ways on the strength, geochemical, microstructural and ultrasonic P-wave velocity properties of CPB was investigated. SMS, LSS and NaOH were used as activators while blast furnace slag was used as pozzolan.

CPBs prepared with SMS (Mix-1 and Mix-2) have the highest strength values. SMSs produced an average of 4.82, 16%-, and 1.94-fold high strength values in the long term (360-day) compared to OPCs, LSSs and NaOHs, respectively.

LSSs produced 1.82- and 4.38-times higher strengths than NaOHs and OPCs at 360 days of curing time, respectively. NaOHs have 2.41 times higher strength than OPCs. OPCs and NaOHs showed strength losses after 112 days of curing time.

The long-term strength of pre-mix samples produced 3.6% to 9.01% lower strengths compared to instant-mixed samples due to the relatively reduced binding gel quality due to the extra mixing time.

The pH and sulfate levels of the SMSs and LSSs followed a similar trend. In the long term, the lowest pH and sulphate values were obtained from OPCs. The highest pH and lowest sulphate levels in AASs belong to NaOHs.

According to the type of activator (SMS, LSS and NaOH), the pore structure characteristics are almost the same in the samples containing same activator. The total porosity and porous structure characteristics are very similar.

SMS, LSS and NaOH samples reduced the total porosity by 14.24%, 15.78% and 10.68% compared to OPCs, respectively.

Binders containing AAS considerably improve the porous structure of CPB compared to OPC.

LSS and SMS have been the most effective activators. In addition, mix-1 and mix-6 are the best binder designs that improve the porous structure of CPB.

UPV rates of SMSs, LSSs and NaOHs were 25.14%, 21.87% and 20.84% higher compared to OPCs, respectively. The average UPV values are SMS> LSS> NaOH> OPC from highest to lowest. Therefore, similar trends were observed between UPV and strength values.

Although AASs produced an average of 2.23 - 4.82 times higher strength results than OPCs, the difference between UPV values was about 1.22 - 1.25%.

Ethics Committee Approval and Conflict of Interest Statement

There is no need to obtain permission from the ethics committee for the article prepared. There is no conflict of interest with any person / institution in the article prepared.

Authors' Contributions

- Study conception and design: [Cihangir]
- Acquisition of data: [Sahin, Koc]
- Analysis and interpretation of data: [Cihangir, Koc]
- Drafting of manuscript: [All]
- Critical revision: [Koc]

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