

RECYCLING PHOSPHORUS SLAG AS A PRECURSOR FOR ALKALI-ACTIVATED BINDER; IMPACT OF TYPE AND DOSAGE OF ACTIVATOR

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The objectives of this study were to investigate the suitability of phosphorus slag as a precursor for alkali-activated binder by studying the effects of type and dosage of alkaline activators on compressive strength and efflorescence formation of the material. Different alkaline activators including; potassium hydroxide, sodium hydroxide, sodium carbonate, calcium hydroxide, and their combinations with liquid sodium silicate were used. Different levels of total alkali content (1, 3, 5 and 7 % by weight of binder) at different silica moduli ($M_s = \text{SiO}_2/\text{Na}_2\text{O}$) of 0.5, 1 and 1.5 were considered. The results show that combined activators of higher reactivity and pH values containing a higher number of moles of alkali cations are more effective and 28-days compressive strengths up to 120 MPa can be achieved. Efflorescence, however, is an important issue and it is necessary to compromise between achieving the highest strength and controlling the efflorescence severity. The most suitable mix design exhibiting comparatively a high 28-day compressive strength along with a relatively low efflorescence formation was then characterized by laboratory techniques, including Fourier Transform Infrared Spectroscopy, X-ray diffractometry, and Scanning electron microscopy.

INTRODUCTION

Today, waste recycling has become an essential issue with continuous industry growth. Long term successful and beneficial recycling experiences on blast furnace slag have encouraged scientists to find suitable recycling ways for many different types of slags. Phosphorus slag (PHS), as a non-ferrous and non-metallic slag, is an example of such different slags. It is an industrial by-product of elemental phosphorus manufacturing industry, which is produced by smelting a phosphate rock in an electric-arc furnace. Usually, a large amount of PHS (approximately ten tons of slag per each ton of elemental phosphorus) is generated during the production of yellow phosphorus. The production statistics are therefore significant, for example China produced approximately 16 million tons of PHS in 2006 [1-2].

PHS is primarily a compound of calcium oxide and silica and therefore exhibits interesting hydraulic properties. However, recent investigations have confirmed that phosphorus slag cannot be used as a supplementary cementing material for inorganic binders based

on Portland cement and its derivatives. This is due to the strong retarding and inhibiting effects imposed by phosphorus oxide content of the slag on hydration reactions resulting in significantly reduced mechanical properties [2-4]. As a result, phosphorus slag is now mostly considered as a useless industrial waste that is mainly landfilled, except very few recycling applications for aggregate substitute in hot mix asphalt or lightweight masonry aggregate [5].

Shi *et al.* [3] have shown that PHS can be used as an alkali activated binder. They reported that when PHS was activated with liquid sodium silicate with silica modulus of 1.0, compressive strengths up to 120 MPa were achieved after 28 days of curing and the main hydration product was calcium silicate hydrate with low C/S ratio. They reported that this alkali-activated cement gave higher early compressive strengths and better mechanical properties than cements produced by alkali-activation of other source materials.

New research on alkali-activated or geopolymer cements shows that these materials due to their simple production process, suitable engineering properties, significant potential for energy and investment conserva-

tion in the manufacturing process and also their environmentally friendly factors (using by-products as raw material and low CO₂ emission) may provide significant potential to be considered as alternatives to Portland cement [6].

Until now, different materials consisting of fly ash [7-11], metakaolin [12-14], natural pozzolans [15-18] and different types of slags [19-21] have been used in development and production of alkali-activated or geopolymer cements. However, very few efforts have been devoted to the use of phosphorus slag (PHS) [3] as an alternative source material in the development and production of alkali-activated or geopolymer cements.

There are many parameters influencing alkali-activation process. Among which, the most important ones include the type and the properties of source material, the type, composition and dose of activator, and also curing conditions. For a given source material, the selection of the activator type and the optimization of its composition and dose are the key factors in developing a sound and cost effective binder. Different alkalis including caustic alkalis and alkaline salts have been used as activator. Glukhovskiy [2] classified these activators into six groups according to their chemical compositions. Many results have confirmed that different activators result in different strength development when applied to the same or different source materials. Shi *et al.* [2] have shown that even a given activator may result in different compressive strength development when applied to slags of different origins.

As mentioned, PHS has been studied very little and the effects of activator type and dosage engineering properties of alkali-activated PHS are not well investigated. In this work, the effects of different alkali-activators at different levels of alkali contents on 28-day compressive strength of activated PHS paste, as a measure of its mechanical properties, and also on its

potential for efflorescence formation, as a measure of soundness, were studied. Since formulations based on usual common alkali-activators, i.e. NaOH and KOH and their combinations with liquid sodium silicate, are relatively less viable for general practical applications due to cost concerns, attempts were made to consider some uncommon low cost alkali-activators in addition to the common ones.

EXPERIMENTAL

Raw Materials

The granulated PHS, used in this work, was obtained from an Iranian phosphoric acid plant. The slag was ground in a laboratory ball mill of 380 mm in length and 110 mm in radius to the specific surface area of 3030 cm²/g measured by a calibrated Blaine air-permeability apparatus. The ground PHS was also characterized for its chemical and mineralogical compositions. The results of chemical analysis performed in accordance with ASTM C311 are given in Table 1. Figure 1 represents the X-ray diffractogram of PHS. It indicates that PHS is almost completely amorphous and only a small amount of crystalline MgO exists in it. The density of PHS, determined in accordance with ASTM C188 (standard test method for density of hydraulic cement), was 2.94 g/cm³.

Different activators including sodium hydroxide (NaOH, 98% purity, MERCK), potassium hydroxide (KOH, 84% purity, MERCK), sodium carbonate (Na₂CO₃, 98% purity, MERCK), calcium hydroxide (Ca(OH)₂, 98% purity, Acros) and their combination with liquid sodium silicate (Na₂SiO₃, 99% purity, MERCK, SiO₂/Na₂O= 3.375) was used.

Specimen Preparation

Different alkali-activators were prepared in accordance with the compositions and dosages given in Table 2. To adjust the silica modulus ($M_s = \text{SiO}_2/\text{Na}_2\text{O}$) of the activators at 0.5, 1.0 and 1.5, enough sodium hydroxide was added to liquid sodium silicate solution. The total alkali content (Na₂O or K₂O) of the slag cements were adjusted at four different levels of 1, 3, 5 and 7% by weight of PHS. To achieve suitable workability in cement pastes, the amount of added water to each mix design was controlled at a spread diameter of approximately 177 mm in flow table test in accordance with ASTM C1437 (standard test method for flow of hydraulic cement mortar).

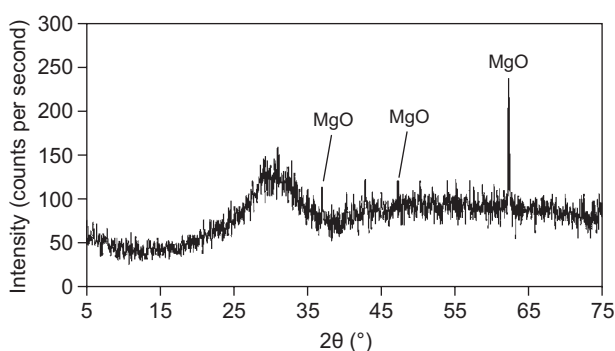


Figure 1. X-ray diffractogram of phosphorus slag.

Table 1. Chemical composition of phosphorus slag.

Oxide	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	P ₂ O ₅	K ₂ O	Na ₂ O	SO ₃	Cl	LOI
wt%	38.42	7.65	0.90	45.14	2.60	1.50	0.56	0.43	ND	ND	1.87

Table 2. Composition and dosage of alkali-activators.

Type of activator	Total alkali (Na ₂ O or K ₂ O) content of binder by wt.% of PHS	Silica Moduli
NaOH	1, 3, 5, 7	–
KOH	1, 3, 5, 7	–
Na ₂ CO ₃	1, 3, 5, 7	–
K ₃ PO ₄	1, 3, 5, 7	–
Ca(OH) ₂	1, 3, 5, 7	–
LSS* + NaOH	1, 3, 5, 7	Ms = 0.5, 1, 1.5
LSS + KOH	1, 3, 5, 7	Ms = 0.5, 1, 1.5
LSS + Na ₂ CO ₃	1, 3, 5, 7	Ms = 0.5, 1, 1.5
LSS + K ₃ PO ₄	1, 3, 5, 7	Ms = 0.5, 1, 1.5
LSS + Ca(OH) ₂	1, 3, 5, 7	Ms = 0.5, 1, 1.5

* Liquid Sodium Silicate or water glass

To prepare paste specimens, the activators were added to the ground PHS and mixed for 5 minutes. The fresh pastes were cast into molds of 20×20×20 mm in size, and cured at more than 95% relative humidity and ambient temperature (25±2 °C) for the first 24 hours until the specimens were enough hard. The specimens were then removed from molds and stored in the humid bath at 95% relative humidity and 25 °C until the time of testing.

Test Procedure

The 28-day compressive strength of the specimens was determined by using a Toni Technic instrument (Toni Technic, Germany). For each measurement, 3 specimens were used and the average of the three values was reported as the result. Mix designs exhibiting a 28-day compressive strength higher than 60 MPa were then selected for efflorescence formation test.

Efflorescence formation of the mixes was evaluated and compared qualitatively. For this reason, from each of the selected mix designs a 28-day cured paste spe-

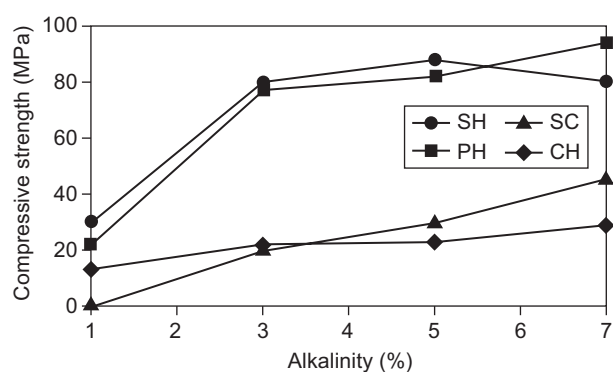


Figure 2. 28-day compressive strength of phosphorus slag activated with sodium hydroxide (SH), potassium hydroxide (PH), sodium carbonate (SC) and calcium hydroxide (CH).

cimen was placed in 40 mL of distilled water and kept in open-air atmosphere at the ambient temperature (25 °C) for two weeks until the free water was evaporated completely. The most suitable mix design exhibiting comparatively a high 28-day compressive strength along with a relatively low efflorescence formation was then characterized by laboratory techniques, including Fourier Transform Infrared Spectroscopy (FTIR; Nicolet 740), X-ray diffractometry (XRD; Philips Expert System, Cu Ka-radiation and Ni-filter), and Scanning electron microscopy (SEM; CamScan MV 2300, EDS; Oxford 7538).

RESULT AND DISCUSSION

Compressive strength

Activators without liquid sodium silicate

Figure 2 shows the 28-day compressive strength of the mix designs activated with sodium hydroxide (SH), potassium hydroxide (PH), sodium carbonate (SC) and calcium hydroxide (CH). Based on achieved 28-day compressive strengths, these activators can be classified into the following two groups:

1. Chemicals of relatively strong activating properties (SH and PH);
2. Chemicals of relatively weak activating properties (SC and CH).

For the first group, as seen, the 28-day compressive strength increases with increase of the total alkali content up to 7%, except for SH. Thus for SH, it can be deduced that a 5% total alkali content is closer to the stoichiometric value and a 7% total alkali content exceeds the stoichiometric value and yields a lower 28-day compressive strength.

It is clear that chemicals of relatively strong activating properties result in higher compressive strengths especially when used at higher amounts providing a higher number of cations close to the stoichiometric values. It is however reported that concentrations exceeding the stoichiometric values delay the formation of coagulated structures because excessive alkali can limit the cations mobility and increase ions stability [22]. Alonso and Palomo [22] indicated that polymerization is not favoured when dissolved components are in ion form. On the other hand, with increasing the activator concentration more stable ion species were produced. Also, ion mobility based on higher activator concentration provides more difficulty in the species diffusion in the aqueous phase and delaying the formation of coagulated structures. Based on Krivenko's [23] research, alkali activation process consists of a set of destruction–condensation reactions with coagulated structures being produced in the middle steps. The condensation of the coagulated structures then forms the hydrated products.

Additionally, Figure 2 indicates that the 28-day compressive strengths achieved by SH activator were slightly higher than values obtained by PH activator in total alkali contents between 1 to 5%. This behavior can be attributed to the higher number of cations present in SH activators than PH activators at the same value of total alkali content. It must be noted that the total alkali content (Na_2O or K_2O) of the mixtures were adjusted by weight of PHS. By converting the total alkali content to the number of moles per 100 g of slag, the levels of alkalinity were changed to 0.0161, 0.0484, 0.0807 and 0.1129 moles for Na_2O and 0.0002, 0.0005, 0.0009, 0.0012 moles for K_2O . As seen, at the same level of total alkali content (by weight); SH activators have much higher number of ions than PH activators. This can result in higher compressive strengths in total alkali contents between 1 to 5% and of course more severe efflorescence formation at higher concentrations.

The second group resulting in relatively lower 28-day compressive strengths consists of SC, CH. The pH of the second group solution is lower than the first group (Table 3). The pH value of the activator solution is an important factor controlling the compressive strength of the alkali activated materials. Some authors have reported that compressive strength at $\text{pH} = 12$ is 50 times smaller than its value at $\text{pH} = 14$. They were considered that it was due to a lot of smaller chain oligomers and silicate monomers available for reaction with dissolved alumina in the high pH values of activator solution [24-25]. However, as seen in Table 3, for chemicals of relatively weak activating properties, the pH value is not the only controlling factor. In case of SC, the pH of activator solution is lower and it slightly increases with increasing total alkali content, therefore, the compressive strength increases with increasing total alkali content. In case of CH, because of low solubility of CH in water, the pH of the activator is not changed with increasing total alkali content and the compressive strength was not increased greatly with increasing total alkali content. This observation confirms that in addition to pH value, the reactivity of the activator cation, i.e. the cation size and the charge density, is also an important controlling factor.

Table 3. pH value of $\text{Ca}(\text{OH})_2$ and Na_2CO_3 activator solutions.

Type of activator	Total alkali content (%)	pH	28-day compressive strength (MPa)
Na_2CO_3	1	11.00	0
Na_2CO_3	3	11.14	20
Na_2CO_3	5	11.34	30
Na_2CO_3	7	11.50	46
$\text{Ca}(\text{OH})_2$	1	12.45	13
$\text{Ca}(\text{OH})_2$	3	12.45	22
$\text{Ca}(\text{OH})_2$	5	12.45	23
$\text{Ca}(\text{OH})_2$	7	12.45	29

Activation with combination of LSS and SH

Figure 3 shows the effect of the total alkali content and the silica modulus of the compound activator based on LSS and SH on the 28-day compressive strength. Comparisons between Figure 2 and Figure 3 reveals that proportioned combinations of SH and LSS can result in higher 28-day compressive strengths. It confirms the positive impact of LSS in activation process. The presence of soluble silica in LSS provides good inter-particle bonding by synthesizing aluminosilicate gel and suitable condition for structure formation [21]. On the other hand, results show that the highest 28-day compressive strength is achievable at the silica modulus equal to 1. The silica modulus of the activator, therefore, plays an important role in compressive strength development as already confirmed by Wang [26] and Shi [3].

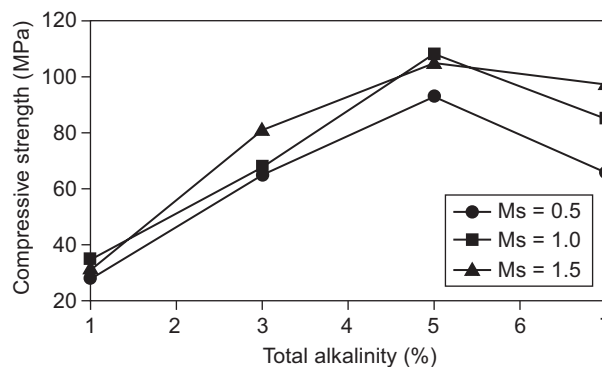


Figure 3. 28-day compressive strength of phosphorus slag activated with liquid sodium silicate and sodium hydroxide.

As seen, total alkali content of the material again shows a similar effect as before. At all the three values of silica modulus, the 28-day compressive strength increases with increasing total alkali content up to 5%. Additional increase in total alkali content, however, decreases the 28-day compressive strength. According to the previous discussion, the excessive alkali limits the ion's mobility and delays the formation of coagulated structures.

Therefore, the compound activator with silica modulus adjusted at 1 and total alkali content controlled at 5 wt.% of the PHS provides the most effective composition for obtaining the highest 28-day compressive strength that is 108 MPa.

Activation with combination of LSS and PH

As seen, compared to PH alone as an activator, a combination of PH and LSS is more effective in activating PHS and results in relatively higher 28-day compressive strengths (Figure 4). Also, Figure 4 shows silica modulus of 0.5 gives the lowest compressive strengths at most

of the total alkali contents. This is due to the fact that at silica modulus of 0.5, activator solutions contain relatively small amount of soluble silicate originating from water glass. Higher values of silica moduli (1.0 and 1.5), however, result in significantly higher compressive strengths. At these silica moduli, the total number of moles of alkali cations and the type of alkali cations play important roles, so that higher values of total alkali contents (5% and 7%) gives the maximum achievable 28-day compressive strengths that is identical for both silica moduli of 1 and 1.5. This is considered to be due to more reactivity of potassium than sodium and also the total number of moles of Na^+ and K^+ in the activator solution (Table 4). There were more K^+ ions in gel at total alkali content of 1 and 3% and silica modulus of 1 than gel with $M_s=1.5$. Therefore, these mixes indicate higher compressive strengths. When the total alkalinity increases and is adjusted at 5 and 7%, the numbers of K^+ ions increases in both $M_s=1$ and 1.5 providing positive effect on compressive strength.

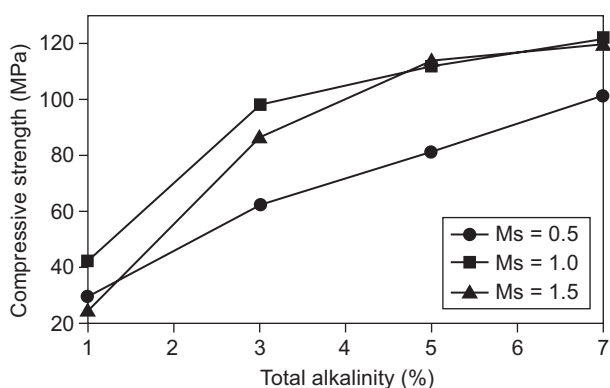
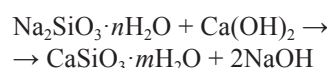


Figure 4. 28-day compressive strength of phosphorus slag activated with liquid sodium silicate and potassium hydroxide.

Activation with combination of LSS and CH

Activator made from combinations of LSS and CH resulted in a very different setting behavior in the mixes. All the tested mixes exhibited fast or very fast setting behaviors. At $M_s=1$ and 7% total alkali content and $M_s=1.5$ with 3, 5 and 7% total alkali contents, the setting was so fast that molding was not easy. As seen in Figure 5, the 28-day compressive strengths, however, are all relatively low ranging from 5 to 34 MPa. The maximum 28-day compressive strength (34 MPa) was achieved at $M_s=0.5$. These observations show that increasing silica modulus and total alkali content to higher values result in significantly shorter setting times and lower 28-day compressive strengths. Such different behaviors in setting and hardening can be attributed to the side reactions between CH and LSS [27-28]:



or

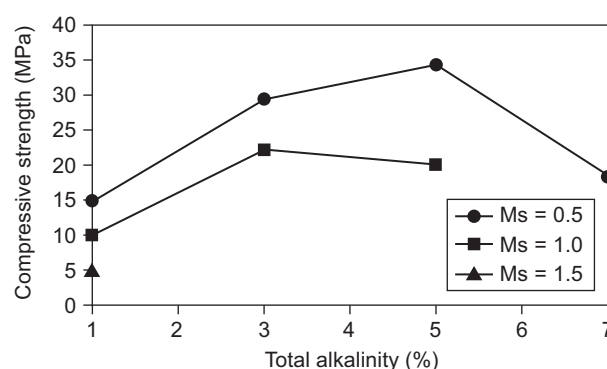
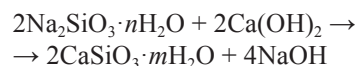


Figure 5. 28-day compressive strength of phosphorus slag activated with liquid sodium silicate and calcium hydroxide.

Table 4. Number of moles of Na^+ and K^+ in activator solution with combination of LSS and PH for 100 g slag.

Total alkali content (%)	M_s	No. of moles of Na^+	No. of moles of K^+	No. of moles of Na^+ and K^+	28-day compressive strength (MPa)
1	0.5	0.00478	0.01809	0.02286	30
3	0.5	0.00478	0.06055	0.06533	63
5	0.5	0.00478	0.10301	0.10779	81
7	0.5	0.00478	0.14548	0.15025	102
1	1	0.00955	0.01494	0.02450	43
3	1	0.00955	0.05741	0.06696	98
5	1	0.00955	0.09987	0.10942	112
7	1	0.00955	0.14233	0.15189	121
1	1.5	0.01433	0.01180	0.02613	25
3	1.5	0.01433	0.05426	0.06859	87
5	1.5	0.01433	0.09673	0.11106	113
7	1.5	0.01433	0.13919	0.15352	120

This reaction is relatively fast and it consumes most of the used LSS before alkali-activation reaction can proceed significantly. As seen, more NaOH is produced in this reaction, but because of fast setting time of these mixes and high water absorbent property of the produced calcium silicate [29], the produced NaOH goes into solid phase and becomes inactive.

Activation with combination of LSS and SC

Figure 6 shows the effect of the total alkali content and the silica modulus of the compound activator based on LSS and SC on the 28-day compressive strength. Comparisons between Figure 2 and Figure 6, shows that in all cases combinations of SC and LSS can result in higher 28-day compressive strengths again confirming the positive impact of LSS in activation process.

Comparing Figure 6 to Figure 3, it can be concluded that in terms of total alkali content activator made from combinations of LSS and SC results in similar trends in compressive strength behavior as observed for activator made from LSS and SH, but with lower 28-day compressive strengths. Combinations of LSS and SC are not as strong as combinations of LSS and SH in alkalinity and result in lower pH media in the reacting mixes. This lower activation ability affects the kinetics and the extent of the progress of chemical reactions and finally leads to lower 28-day compressive strength. On the other hand, achievement of 28-day compressive strengths up to about 85 MPa is an interesting result when considering the economy of the two compound activators. The effect of silica modulus on compressive strength behavior of the material, however, is different. As seen in Figure 6, 28-day compressive strength decreases with increasing the value of Ms from 0.5 to 1 and to 1.5. This can be simply attributed to the composition and pH of the activator. With increasing the silica modulus of the activator solution, the soluble silica content of which increases at the expense of its alkali content that determines the alkalinity and pH value. The activator, therefore, loses its ability to effectively start reactions

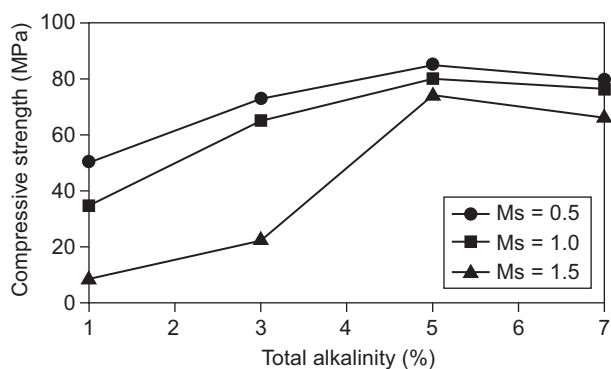


Figure 6. 28-day compressive strength of phosphorus slag activated with liquid sodium silicate and sodium carbonate.

due to its relatively low alkalinity and also excess SiO_2 in the gel preventing structure formation [21]. As Figure 6 shows, activator with relatively higher silica modulus of 1.5 cannot effectively activate PHS at relatively lower total alkali content of 1 and 3%.

As in the case of activators based on SH and combinations of SH with LSS, increasing total alkali content from 5 to 7% does not result in any strength development because excessive alkali limits the ions mobility delaying the formation of coagulated structures [22].

Efflorescence

In porous construction and building materials efflorescence is referred to as a deposit, usually white in color that develops on the surface of the material. In alkali-activated cements, it is caused by migration of excess or un-reacted alkalis to the surface followed by carbonation reaction with atmospheric CO_2 that results in deposition of alkali carbonate [30-31]. Alkali-activated cements are very susceptible to efflorescence formation and excessive efflorescence formation can cause expansion in regions close to surfaces that may finally disrupt the material surface. Therefore, when developing an alkali-activated binder, it is necessary to investigate the soundness of the material by evaluating its susceptibility to efflorescence formation.

To evaluate the soundness of the formulations studied in this work, qualitative efflorescence formation tests were performed on mix designs exhibiting relatively high compressive strengths (higher than 50MPa).

Based on visual observations, the severity of the efflorescence formation of the mix designs were classified by assigning letter grades. Mix designs exhibiting severe, medium, slight and no efflorescence formation were specified by letters A, B, C and D, respectively. Figure 7 shows images taken from typical paste specimens exhibiting relatively severe, medium and slight efflorescence formation.

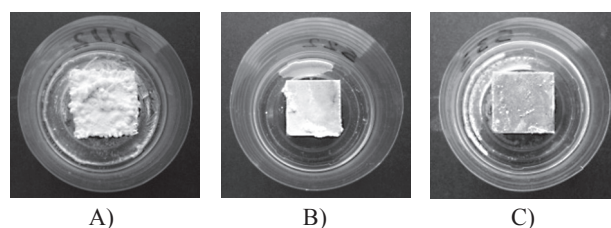


Figure 7. Qualitative comparison of efflorescence formation in three typical mix designs; A: LSS + SH with Ms=1.5 and 7% total alkali content, severe efflorescence, B: SH with 5% total alkali content, medium efflorescence, C: SH with 3% total alkali content, slight efflorescence.

Table 5 represents the results of qualitative efflorescence formation tests. The results show that mix designs with relatively higher free alkali contents (e.g. LSS+SH with Ms=1.5 and 7% total alkali content) and those containing higher amounts of SC as a less reactive soluble salt (e.g. LSS+SC with Ms=1.5 and 7% and total alkali content) exhibit more severe efflorescence formation.

According to Table 5, mix designs activated with sodium hydroxide show more susceptibility for efflorescence formation in contrast with those activated with potassium hydroxide. This behavior can be attributed to the differences between these two hydroxides. As mentioned before at the same level of total alkali content, activators based on potassium hydroxide contain significantly fewer amounts of K⁺ ions resulting in a lower content of un-reacted alkali in the material. On the other hand, potassium hydroxide is more reactive than sodium hydroxide and produces more and stronger bonds in the aluminosilicate gel framework [31]. These differences mean that mix designs based on potassium hydroxide

include less un-reacted alkali contents of lower mobility, which make the material less vulnerable to efflorescence formation compared to similar formulations based on sodium hydroxide. The same trend can be observed when SH and PH activators are used in combination with LSS. Presence of LSS in the activators, however, slightly increases the extent of efflorescence formation.

Now, the optimum mix designs for the type and dosage of activator can be simply selected by considering the results of 28-day compressive strength and efflorescence formation. Table 5 shows that activation with combinations of LSS and PH with Ms between 1 to 1.5 and total alkali content ranging between 5 to 7% gives the highest 28-day compressive strength (112 up to 120 MPa) and a relatively low susceptibility for efflorescence formation (class C).

One of these combinations (LSS+PH with Ms=1 and total alkali content of 5%) was, therefore selected for characterization studies with X-ray diffractometry, FTIR spectroscopy and scanning electron microscopy.

Table 5. Effect of total alkali content and silica modulus on efflorescence formation severity.

Mix design No.	Type of activator	Ms	Total alkali content (%)	Efflorescence severity	28-day compressive strength (MPa)
1	NaOH	–	3	C	80
2	NaOH	–	5	C	88
3	NaOH	–	7	A	81
4	KOH	–	3	D	77
5	KOH	–	5	D	82
6	KOH	–	7	D	99
7	LSS* + NaOH	0.5	3	C	68
8	LSS + NaOH	0.5	5	B	93
9	LSS + NaOH	0.5	7	B	66
10	LSS + NaOH	1	3	C	68
11	LSS + NaOH	1	5	A	108
12	LSS + NaOH	1	7	A	85
13	LSS + NaOH	1.5	3	B	81
14	LSS + NaOH	1.5	5	A	105
15	LSS + NaOH	1.5	7	A	97
16	LSS + Na ₂ CO ₃	0.5	3	C	73
17	LSS + Na ₂ CO ₃	0.5	5	A	85
18	LSS + Na ₂ CO ₃	0.5	7	A	80
19	LSS + Na ₂ CO ₃	1	3	C	65
20	LSS + Na ₂ CO ₃	1	5	B	80
21	LSS + Na ₂ CO ₃	1	7	A	76
22	LSS + Na ₂ CO ₃	1.5	5	B	74
23	LSS + Na ₂ CO ₃	1.5	7	A	66
24	LSS + KOH	0.5	3	C	63
25	LSS + KOH	0.5	5	C	81
26	LSS + KOH	0.5	7	C	102
27	LSS + KOH	1	3	B	98
28	LSS + KOH	1	5	C	112
29	LSS + KOH	1	7	B	121
30	LSS + KOH	1.5	3	C	87
31	LSS + KOH	1.5	5	B	113
32	LSS + KOH	1.5	7	B	120

* Liquid Sodium Silicate

XRD analysis

The X-ray diffractogram of the 28-day cured paste of PHS activated with LSS+PH at Ms=1 and 5% total alkali content is presented in Figure 8. The obtained diffraction pattern indicates that the activated PHS is mainly amorphous due to large diffuse diffraction peak centered at 30° (2θ) and there exist only few amounts of crystalline phases including periclase (MgO) and calcite (CaCO_3). A comparison of the diffraction patterns of slag and hardened paste, Figures 1 and 10, respectively, shows that periclase was originally present in the slag. The formation of calcite in the alkali-activated PHS is due to hydration of amorphous calcium silicates, which were originally present in the PHS. Calcite formation is a common observation when activating slags [32-34]. Amorphous and/or poorly crystalline structure of calcium-silicate-hydrates (C-S-H) and polymerization degree of the silicate units are still controversial issues in alkali-activated slag mineralogy. Some authors have mentioned that C-S-H gel phases are the major hydration products of alkali-activated slag [35-36].

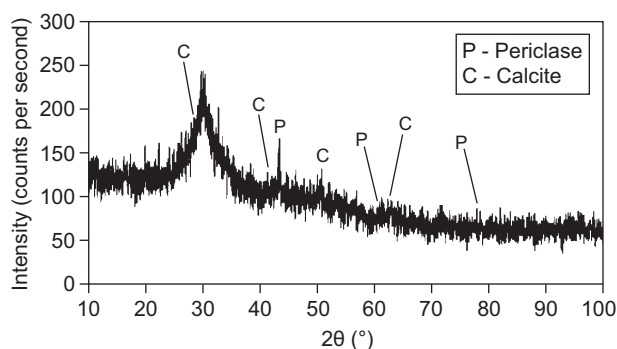


Figure 8. X-ray diffractogram of 28-day cured paste of phosphorus slag activated with LSS + PH at Ms = 1 and 5% total alkali content.

FTIR spectroscopy analysis

Figure 9 shows the FTIR spectra of raw PHS and 28-day cured paste of PHS activated with LSS+PH at Ms=1 and 5% total alkali content. The major peaks present in these spectra, as well as the origin of the peaks, are shown in Table 6.

Peaks between the wave numbers of 450 and 500 cm^{-1} are devoted to absorption bands due to Si-O-Al bending vibration [36]. As observed in Figure 9, the intensity of this peak is higher in alkali-activated PHS confirming the formation of more Si-O-Al bonds in the course of activation reactions. The infrared absorption bands observed around 1100, 1000, 970, 900 and 850 cm^{-1} for $n = 4, 3, 2, 1$ and 0 are associated with the Si-O stretching modes for the SiQ^n units, respectively [38]. Peaks centered at 1000 cm^{-1} in PHS are due to

the Si-O vibrations of silica tetrahedra of various coordination states. As seen in Figure 9, this peak has shifted to 968 cm^{-1} in the alkali-activated PHS and becomes stronger, therefore, alkali-activation reactions result in the polymerization and the C-S-H (SiQ^2) or C-A-S-H are formed in amorphous shape [37, 41]. The peaks around 1497, 1470, 1429 and 1421 cm^{-1} are due to the asymmetric stretching of C-O bond in CO_3^{2-} , indicating the presence of some kinds of carbonated minerals due to absorption of atmospheric CO_2 [39]. Figure 9 shows a strong peak at 3450 cm^{-1} in the spectrum of activated PHS. This peak is due to the stretching vibration of OH groups that can be found in water or other weakly-bonded OH-bearing molecules [40].

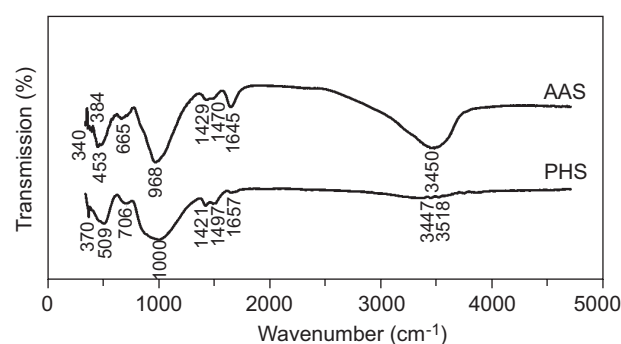


Figure 9. FTIR spectra of phosphorus slag and 28-cured phosphorus slag cured with LSS + PH at Ms = 1 and 5% total alkali content.

Table 6. Major peaks and their origins in phosphorus slag and its 28-day cured alkali-activated paste.

PHS	AAS	Origin	Refer.
460-509	453	Si-O-Al bending	[36]
706	665	Al-O bonds in AlO_4 groups	[37]
945-1000	968	bonds in C-S-H and C-A-S-H	[37-38]
1421-1497	1429-1470	C-O bond in CO_3^{2-}	[39]
1657	1645	O-H bond	[40]
-	3450	O-H bond	[40]

Scanning Electron Microscopy

Figure 10 shows the microstructure of hardened paste activated with LSS+PH at Ms=1 and 5% total alkali content. As seen the microstructure is relatively rough due to the presence of many partially-reacted slag particles with sharp edges, which are embedded in a relatively uniform glassy matrix. Ground PHS of higher fineness will probably react more effectively with alkali-activated and this could result in some improvement in the microstructure of the material and its mechanical properties. No crystalline structure was detected in the observations by SEM.

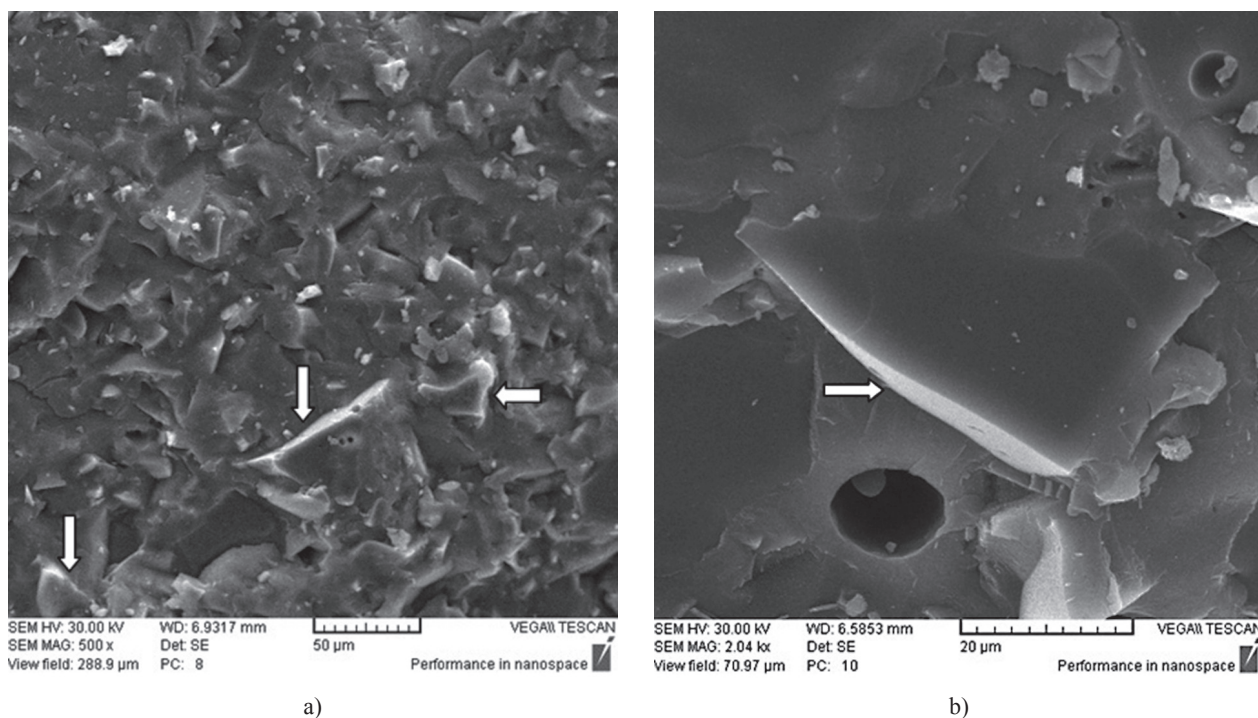


Figure 10. The microstructure of the hardened paste of phosphorus slag activated with LSS + PH at $M_s = 1$ and 5% total alkali content at: a) 500 and b) 2000 magnifications.

CONCLUSION

Experimental results show that Phosphorus slag is a very suitable precursor for alkali-activated binders considering the compromise between the compressive strength and the efflorescence formation. Activators of relatively lower alkalinity (lower pH value) are not well effective. Phosphorus slag can be activated with plain activators, but compound activators containing liquid sodium silicate result in higher 28-day compressive strengths. In addition, mix designs with relatively higher alkali contents of the type sodium (e.g. liquid sodium silicate with sodium hydroxide containing 7% total alkali content at $M_s=1.5$) and those containing higher amounts of sodium carbonate (e.g. liquid sodium silicate with sodium carbonate containing 7% total alkali content at $M_s=1.5$) suffer from severe efflorescence formation. X-ray diffraction data confirm the amorphous character of the material and FTIR spectroscopy data reveal that the material is mainly composed of C-S-H (SiQ^2). Based on SEM studies showing many partially-reacted slag particles, use of ground phosphorus slag of higher fineness may result in some microstructural improvement enhancing mechanical properties of the material.

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