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Assessment of sulphates effect on pH and pozzolanic reactions of soil-lime-natural pozzolana mixtures

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ABSTRACT

The geotechnical properties of subgrade soils may need to be enhanced for appropriateness in pavement construction using mineral additives such as cement, lime (L) and fly ash. An experimental investigation was undertaken to study the effects of sodium (Na_2SO_4) and calcium ($CaSO_4.2H_2O$) sulphates on pH and pozzolanic reactions of soil-lime-natural pozzolana (soil-L-NP) mixtures in order to choose an adequate mixture for pavement subgrade soil stabilisation. The pH was measured for different curing periods with and without sulphates. The results showed that increases and decreases in pH values depend on the type of additive and its amount, type of sulphate and its content, mineralogical composition of stabilised soil and curing period. In addition, the pH parameter can be used as an indicator to track the pozzolanic reactions process. On the other hand, clayey subgrade soils can be stabilised with Lime–Natural Pozzolana (L–NP) mixtures containing any amounts of $CaSO_4.2H_2O$ which is highly recommended. However, Na_2SO_4 with a low content has a better effect on the behaviour of these soils but become deleterious when its content is greater than 2%. In general, the addition of sulphates accelerates both the pozzolanic reactions and NP dissolution.

Introduction

High volumes of problematic soils have been not recommended to be used as materials for construction due to their low quality. Indeed, in the world, it is known that the most frequent problem for all civil engineering projects is the presence of unsuitable soils which require a special technique for their improvement such as chemical stabilisation, dynamic compaction and soil replacement. Chemical soil stabilisation has been practised for several years with the main aim to make the unsuitable soils capable of meeting the requirements of the specific engineering projects (Kolias et al. 2005). However, cement has been used as a main hydraulic binder for civil engineering projects such as road pavements, earth dams and building constructions (Mehta 1999). The production of one-metric-ton of cement leads to the emission of about one-metric-ton of CO₂ and requires large amounts of energy (Ghrici et al. 2007, Segui et al. 2013). In order to reduce both energy consumption and CO₂ emission, several researchers recommended the use of volcanic materials such as volcanic ash and NP (Hossain et al. 2007, Mfinanga and Kamuhabwa 2008, Harichane et al. 2010, 2011a, 2011b, 2011c, 2012, Zoubir et al. 2013, Segui et al. 2013, Al-Swaidani et al. 2016, Gadouri et al. 2016a, 2016b, 2016c). These mineral additives have been used in combination with L for soil stabilisation because of their economical benefits and advantageous properties. Indeed, it has been reported that the combination of volcanic ash with L produced beneficial effects on the physico-mechanical behaviour of the stabilised soil (Hossain *et al.* 2007). In addition, Harichane *et al.* (2011a) reported that for a longer curing period, shear and unconfined compressive strength values of cohesive soils stabilised with the combination of NP and L are very larger than that of the untreated soils.

According to Khemissa and Mahamedi (2014), expansive and salted soils with low resistance (strength) and high plasticity are among the problematic soils most met in the Algerian arid and semi-arid regions. It was necessary to improve these soils in order to render them acceptable for construction. For example, most of the soils used in the East–West highway project (located in the Northern territory of Algeria) have been improved using cement and/or L in order to make them able to carry the traffic loads. But, these soils caused severe damage to infrastructures in form of cracks and swelling. According to Baryla *et al.* (2000), various forms of degradation observed in road pavements are frequently related to the formation of new expansive phrases such as ettringite and/or thaumasite due to the presence of sulphate ions (SO_4^{2-}).

Furthermore, NP is found with high amounts in areas of Beni-Saf located in the West of Algeria (Ghrici *et al.* 2007). The effects of Na₂SO₄ (Gadouri *et al.* 2016a) and CaSO₄·2H₂O (Gadouri *et al.* 2016b) on geotechnical properties of clayey soils stabilised

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KEYWORDS

Clayey soil; lime; natural pozzolana; sulphate; pH value



 Table 1. Physico-mechanical and chemico-mineralogical properties of materials used.

Properties name	Chemical formula	Materials used	
Chemico-mineralogical pro	GS	RS (%)	
Calcium oxide (%)	CaO	14.43	2.23
Alumina (%)	Al ₂ O ₃	14.15	19.01
Silica (%)	SiÔ,	43.67	57.02
рН		9.18	9.05
Calcite (%)	CaCO ₃	26.0	4.0
Quartz (%)	SiO	20	30
Illite (%)	2K, O.Al, O., 24SiO, 2H, O	16.0	24.0
Kaolinite (%)	Al ₂ Si ₂ O ₅ (OH) ₄	12.0	16.0
Montmorillonite (%)	Al ₂ ((Ši ₄ ÅI)O ₁₀)(OH) ₂ .H ₂ O	20.0	-
Physico-mechanical prope			
Specific gravity (–)		2.71	2.84
Passing 80 µm sieve (%)		85.0	97.5
Liquid limit (LL, %)		82.8	46.5
Plastic limit (PL, %)		32.2	22.7
Classification system (USC	LS), (—)	CH	CL
Unconfined compressive	strength (UCS, kPa)	100	510
Chemical properties of add	litives	L	NP
CaO (%)		83.3	9.90
MgO (%)		<0.5	2.42
Fe ₂ O ₃ (%)		<2.0	9.69
Al ₂ O ₃ (%)		<1.5	17.5
SiO ₂ (%)		<2.5	46.4
CaCO ₃ (%)		<10	-
Physico-chemical propertie	CaSO ₄	Na_2SO_4	
Molar weight (g/mol)	172.2	142	
Auuay (dried)	99	99.5	
pH (50 g/L, 25 °C)	-	5–8	

with L, NP and their combination have been investigated. They have reported in their study that sulphate ions react with calcium (Ca²⁺), hydroxyl (OH⁻) and alumina [Al(OH)₄] and silica [SiO(OH)₃]⁻ compounds to form ettringite mineral.

Furthermore, the magnitude of damage caused by this mineral (ettringite) depends on the additive type and its content, the mineralogical composition of stabilised soil and the type of sulphate ions (e.g. K⁺, Na⁺, Ca²⁺, Mg²⁺,...etc.) and its concentration. Similar observations have been reported by several researchers (Kinuthia et al. 1999, Sivapullaiah et al. 2000, 2006, Le Borgne 2010, Segui et al. 2013, Aldaood et al. 2014a, 2014b, Hu et al. 2016). It has been reported that the presence of $CaSO_4 \cdot 2H_2O$ produced a beneficial effect on strength and plasticity of stabilised clayey soils (Yilmaz et al. 2009, Gadouri et al. 2016b), but the presence of Na₂SO₄ with a high concentration induced a deleterious effect and affected the stabilisation process (Kinuthia et al. 1999, Ktnuthia and Wild 2001, Gadouri et al. 2016a, Hu et al. 2016). On the other hand, NP can be used in combination with L in order to resist to sulphate attacks (Gadouri et al. 2016a) and in the improvement of general durability of clayey soils (Harichane et al. 2010).

In Algeria, intensive road networks currently built as well as large amounts of soils with insufficient or poor mechanical characteristics requires developing new hydraulic binders based on several mixtures. Di Sante *et al.* (2014) have studied the progression of physico-chemical reactions in compacted soil–lime mixtures and their effect on the mechanical and hydraulic performance with time as a method based only on pH measurement. They have reported that the method adopted in their study allowed to appropriately analyse the results obtained from both permeability and oedometer tests. On the other hand, Rao and Shivananda (2005) have assessed the effects of ambient temperature on the progress of lime-soil reactions of an expansive black cotton soil. They have reported that higher ambient temperatures do accelerate the progress of lime-soil reactions. In addition, the pH parameter was used to monitor the progression of the lime-clay reactions Al-Mukhtar et al. (2010). So, the pozzolanic reactions can be controlled by the pH value measurement because the pH value is responsible for the dissolution of silica (SiO₂) and alumina (Al₂O₃) which react with calcium (provided from lime) to form cementing agents (C-S-H and C-A-H) responsible for the development of mechanical performance (strength development), particularly, with the curing period. Conversely, the decrease in strength development can be reflected by the decrease in the pH value, and consequently the decrease in pozzolanic reactions. So, the pH can be used as a good indicator (or index parameter) to track the pozzolanic reactions process.

In this paper, according to ASTM D4972-01 (2001), the assessment of sulphates effect on pH value and pozzolanic reactions of soil-lime-natural pozzolana (soil-L-NP) mixtures has been investigated in order to develop hydraulic binders for pavement subgrade soil stabilisation.

Materials extraction and identification

In the present study, two clayey soils were obtained from Chelif town located in the west of Algeria. The grey clayey soil (GS) and red clayey soil (RS) were obtained from an embankment project site and a highway project site, respectively. However, the NP was used as an additive to improve both clayey soils. It was obtained from Beni–Saf deposit located in the west of Algeria. All these materials were extracted and transported to the laboratory for preparation and testing.

However, the NP was ground to the specific surface area of 420 m²/kg whereas the L used in this study was a hydrated lime $(Ca(OH)_2)$. It was commercially available lime typically used for construction purposes.

Moreover, two chemical compounds were used. The first is a calcium sulphate dihydrate ($CaSO_4 \cdot 2H_2O$). The second is a sodium sulphate (Na_2SO_4). The main physico-mechanical, chemico-mineralogical and physico-chemical properties of soils, additives and sulphates are summarised in Table 1.

Test procedures and samples preparation

pH measurement test

In this study, a pH meter was used for testing in order to evaluate the degree of acidity (or alkalinity) in soil materials suspended in water. The pH parameter is useful in assessing the solubility of clayey soil minerals and the mobility of ions in the soil solution. An experimental test of pH measurement was conducted on both selected clayey soils and performed according to ASTM D4972-01 (2001). The pH of both stabilised clayey soils was measured in all samples with and without sulphates. Table 2 shows a summary of 56 combinations for both GS and RS samples. In this study, according to Harichane and Ghrici (2009) and Gadouri *et al.* (2016a), 8%L, 20%NP and the combination of both (8%L + 20%NP) were selected as optimum dosages for stabilisation.

Table 2. A summary of the mix combinations tested for both clayey soils stabilised with and without sulphates.

		Mix	ture p	ropoi	rtions (%)
Sulphate type	Combinations	Soil	NP	L	Sulphate
Without sulphate	POLO	100	0	0	0
·	P0L8	92	0	8	0
	P20L0	80	20	0	0
	P20L8	72	20	8	0
Calcium sulphate	P0L0C2	98	0	0	2
$(CaSO_4 \cdot 2H_2O)$	P0L8C2	90	0	8	2
7 2	P20L0C2	78	20	0	2
	P20L8C2	70	20	8	2
	P0L0C4	96	0	0	4
	P0L8C4	88	0	8	4
	P20L0C4	76	20	0	4
	P20L8C4	68	20	8	4
	P0L0C6	94	0	0	6
	P0L8C6	86	0	8	6
	P20L0C6	74	20	0	6
	P20L8C6	66	20	8	6
Sodium sulphate (Na ₂ SO ₄)	P0L0N2	98	0	0	2
	P0L8N2	90	0	8	2
	P20L0N2	78	20	0	2
	P20L8N2	70	20	8	2
	POLON4	96	0	0	4
	P0L8N4	88	0	8	4
	P20L0N4	76	20	0	4
	P20L8N4	68	20	8	4
	POLON6	94	0	0	6
	P0L8N6	86	0	8	6
	P20L0N6	74	20	0	6
	P201 8N6	66	20	8	6

Samples preparation

Soil-L, soil-NP and soil-L-NP mixtures

For both clayey soils, several combinations of NP and L were used for their stabilisation. The air-dried soils were initially mixed with the predetermined quantity of NP and L in a dry state to obtain different mixtures. Before distilled water addition, all mixtures (soil-L, soil-NP and soil-L-NP) were sieved through a No. 10 sieve (2 mm sieve mesh openings) in order to eliminate the fractions with particles larger than 2 mm. For each mixture, 10 g (of air dried) was weighed and placed into a glass container. Thus, 10 g of distilled water was also added to each mixture and letting stand for 1 h prior to testing. All mixtures were placed into a glass container at a temperature and relative humidity of 20 \pm 2 °C and 95 \pm 5%, respectively. For all mixtures, the pH measurement was carried out in a slurry form but not on the pore water of a compacted sample. Furthermore, the samples were tested after curing for 7, 30, 60 and 120 days. The tests of all samples were repeated on three identical samples and the accepted pH value was an average of three tests carried out on each sample type.

Soil-L-sulphates, soil-NP-sulphates and soil-L-NPsulphates mixtures

In this case, the samples were mixed in the same way as presented above except that different contents of Na_2SO_4 and $CaSO_4 \cdot 2H_2O$ powders (0–6% by weight of dry soil) were also added into the soil–L, soil–NP and soil–L–NP mixtures in a dry state. In addition, the pH tests were performed after the same curing periods in the same way as presented above once the distilled water was added to the mixtures.

X-ray diffraction test and samples preparation

The X-ray diffraction (XRD) test was invited in order to investigate the mineralogical aspect of two clayey soils stabilised with L, NP and their combination. A PHILIPS PW3020 diffractometer was used for XRD analysis. The fractured samples obtained from unconfined compressive strength tests (Gadouri et al. 2016a, 2016b) were dried for 1 day at 40 °C. Before testing, the collected soil samples were crushed into a fine powder and passed through a 400 µm sieve to use as samples for the XRD test. The diffraction patterns were conducted using Cu-Ka radiation with a Bragg angle (2 θ) range of 4–60° running at a speed of 0.83 $\times 10^{-2}/2$ s. The same XRD test was adopted by Aldaood *et al.* (2014a, 2014b). In this study, the examination of the eventual formation of cementing compounds and ettringite were conducted on untreated and treated clayey soil samples after 60 days of curing. In addition, the investigation of the formation of cementing compounds and ettringite were also conducted on soil samples containing 4% of both Na_2SO_4 and $CaSO_4.2H_2O$.

Experimental results and discussion

pH variation of both untreated and treated soil samples

Figure 1 shows the changes in the pH of soil–L, soil–NP and soil–L–NP mixtures measured at different curing periods. For both clayey soils, there are marginal changes in pH values of soil–NP mixture to compare with untreated soils. In contrast, for a shorter curing period (7 days), the addition of 8%L increases the pH of both GS and RS from 9.18 and 9.08 to 12.3 and 12.35, respectively. A similar behaviour was observed by Al-Mukhtar *et al.* (2010). According to Samantasinghar (2014), the long-term pozzolanic reactions begin as an increase in hydroxyl ions (OH⁻) from the lime causes an increase in the pH of the soil water (or soil solution).

Furthermore, the pH of both clayey soils stabilised with L alone or in combination with NP decreases with curing period due to the consumption of L added by pozzolanic reactions to form cementing agents (Figures 5(g) and (h) and 6(g) and (h). The highest effect on the pH of both clayey soil samples is achieved when the combination of 20%NP + 8%L was used. In all cases, the decrease in pH value with the curing period is more pronounced with the RS than with the GS. This can be explained by the difference in chemical composition between both soils when the GS present a high amount of natural CaO (14.43%) as compared with the RS (2.23%). On the other hand, it is probably also due to the fact that RS presents a higher amount of SiO₂ and Al₂O₃, therefore, pozzolanic reactions can develop to a greater extent with RS, leading to a higher decrease in pH value.

pH variation of untreated soil samples containing various sulphate contents

Table 3 presents the results of pH variation of both untreated clayey soil samples measured under different sulphate contents at different curing periods. Both untreated soil samples showed negligible changes in the pH value upon the addition of various Na_2SO_4 contents at different curing periods. For any curing



Figure 1. Effect of 20%NP, 8%L and their combination on the pH of both clayey soils (a) GS, (b) RS.

Table 3. Changes in pH values of both untreated soil samples containing d	ifferent
contents of sulphates.	

	Soil	Combina-	pH value ı curir	measure ng perioc	d for dif ds (days)	ferent
Sulphate type	tions	7	30	60	120	
Without sulphate	GS RS	POLO POLO	9.18 9.08	9.20 9.10	9.17 8.98	9.15 9.05
Sodium sulphate (Na ₂ SO ₄)	GS RS	POLON2 POLON4 POLON6 POLON2 POLON4 POLON6	9.17 9.14 9.16 9.07 9.10 9.07	9.19 9.21 9.16 9.10 9.10 9.01	9.21 9.09 9.21 9.12 9.11 9.07	9.13 9.12 9.09 9.08 9.09 9.08
Calcium sulphate (CaSO ₄ ·2H ₂ O)	GS	POLOC2 POLOC4 POLOC6	9.54 10.07 10.15	9.25 9.80 9.91	9.15 9.42 9.61	9.14 9.20 9.32
	RS	POLOC2 POLOC4 POLOC6	9.42 9.86 10.10	9.22 9.50 9.65	9.16 9.34 9.55	9.10 9.15 9.21

periods, it is obvious to see that no rate of Na_2SO_4 has had any influence on pH of both untreated soils. In contrast, for both clayey soil samples, pH increases considerably with increasing $CaSO_4 \cdot 2H_2O$ content but decreases with curing period. For comparison, the increase in pH value with $CaSO_4 \cdot 2H_2O$ is more pronounced with the GS than with the RS. This is probably due to the high content of CaO (14.43%) of the GS to compare with that of the RS because the CaO can considerably contribute to increasing the pH value.

pH variation of Soil-NP-Sulphate mixture

Figure 2 illustrates the results of Na_2SO_4 and $CaSO_4.2H_2O$ effects on the pH of Soil–NP mixture measured at different curing periods. It is obvious to observe that for both sulphates the pH of two clayey soil samples decreases with curing period but increases with increasing sulphate contents. However, there is a slight decrease in pH values of both clayey soils with increasing Na_2SO_4 content. For both clayey soils, the sensitivity



Figure 2. Effect of different contents of Na, SO, and CaSO, 2H, O on the pH of both clayey soil samples stabilised with 20%NP (a) GS, (b) RS.

of the pH to the curing period effect is more pronounced with the CaSO₄·2H₂O than with the Na₂SO₄. In the same way, it is also more pronounced with the CaSO₄·2H₂O content than with the Na₂SO₄ content. This behaviour confirms that the sensitivity of the amorphous silica (SiO₂ from soil and/or NP) to the sulphate effect is more pronounced with divalent cations (Ca²⁺) than with monovalent cations (Na⁺). On the other hand, for a longer curing period (120 days), the CaSO₄·2H₂O effect on the pH of both clayey soils is comparable to that of the Na₂SO₄.

The pH is a better indicator for the tracking of pozzolanic reactions evolution which leads to the formation of cementing agents responsible for strength improvement. It has been demonstrated that the presence of $CaSO_4 \cdot 2H_2O$ improves considerably the strength of soil–NP mixture as compared with mixture without $CaSO_4 \cdot 2H_2O$ (Gadouri *et al.* 2016b).

pH variation of soil-L-sulphate and soil-L-NP-sulphate mixtures

The results of Na_2SO_4 and $CaSO_4 \cdot 2H_2O$ effects on the pH of soil–L and soil–L–NP mixtures measured at different curing periods are shown in Figures 3 and 4, respectively. In all cases, the pH of both soil–L and soil–L–NP mixtures increases with increasing Na_2SO_4 and $CaSO_4 \cdot 2H_2O$ content but decreases with curing period. A similar trend was observed by Shi and Day (2000) and Aldaood *et al.* (2014b) when they used Na_2SO_4 and gypsum ($CaSO_4 \cdot 2H_2O$), respectively. However, when Na_2SO_4 is present the pH of both soil–L and soil–L–NP mixtures can reach a value of approximately 13. The same value was obtained by Wang and Gillott (1991).

The increase in pH value with sulphate content is more pronounced with the Na₂SO₄ than with the CaSO₄·2H₂O. This is



Figure 3. Effect of different contents of Na₂SO₄ and CaSO₄:2H₂O on the pH of both clayey soil samples stabilised with 8%L (a) GS, (b) RS.

attributed to the sodium hydroxide (NaOH) which increases considerably the pH of soil and causes the dissolution of a large amount of alumina and silica that come into reaction with the remaining L to form cementitious products (Sridhran *et al.* 1995). It has been reported that chemical reactions between L, NP and Na₂SO₄ increase the pH of the mixture and produces an early increase in unconfined compressive strength of both GS and RS samples containing Na₂SO₄ (Gadouri *et al.* 2016a).

Contrarily to the pH variation of soil–NP mixture, for both clayey soils the sensitivity of the pH to the L and L–NP effect is more pronounced with the presence of Na_2SO_4 than with the $CaSO_4 \cdot 2H_2O$ addition. Moreover, for both clayey soils, the sensitivity of the pH to the curing period effect is more pronounced with the $CaSO_4 \cdot 2H_2O$ than with the Na_2SO_4 whereby the RS has the best results.

It has been reported that for a shorter curing period the unconfined compressive strength of both soil-L and soil-L-NP

mixtures is greater with $CaSO_4 \cdot 2H_2O$ (Mfinanga and Kamuhabwa 2008, Gadouri *et al.* 2016b) than with Na_2SO_4 (Gadouri *et al.* 2016a). This is because with Na_2SO_4 the cation exchange requirements must be met from L addition, whereas the calcium ions (Ca^{2+}) required for cation exchanges of soil are provided by Ca^{2+} from $CaSO_4 \cdot 2H_2O$ dissolution. Thus, there is a high decrease in the L content available for pozzolanic reactions in soil with Na_2SO_4 compared with that available in soil with $CaSO_4 \cdot 2H_2O$ (Mitchell 1986).

However, for a longer curing period the Na_2SO_4 with high concentrations alters only the strength of soil–NP and soil–L mixtures, whereas the soil–L–NP mixture resists to the alteration (Gadouri *et al.* 2016a). This is because the pH of these mixtures decreases with curing period which facilitates the formation of an expansive mineral (ettringite) responsible for the strength alteration.



Figure 4. Effect of different contents of Na₃SO₄ and CaSO₄·2H₂O on the pH of both clayey soil samples stabilised with the combination of 20%NP and 8%L (a) GS, (b) RS.

Effect of sulphates on the mineralogical composition of soil–NP, soil–L and soil–L–NP mixtures

Figures 5 and 6 show the XRD patterns of both GS and RS samples stabilised with 8%L, 20%NP and 20%NP + 8%L in the presence of only 4% of both Na_2SO_4 and $CaSO_4$ ·2H₂O after 60 days of curing period.

The XRD analysis indicated that the GS was composed of quartz, Montmorillonite, illite, kaolinite and calcite clay minerals, while this soil was predominantly composed of calcite (Figure 5(j)). However, the RS was contained of illite, kaolinite and quartz clay minerals, while the clay mineral was predominantly composed of quartz (Figure 6(j)). In the absence of sulphates, the identification using the XRD analysis revealed that the changes observed in the mineralogical composition of soil–L and soil–L– NP mixtures can be reflected in the formation of C–S–H and C-A-H compounds (Figures 5(g) and (h) and 6(g) and (h)). However, the formation of these compounds was not observed in XRD patterns when using the NP alone as a stabiliser of both clayey soils (Figures 5(i) and 6(i)). This can be explained by the low pH value measured in the soil-NP mixture due to the fact that NP can't react with clay minerals in the absence of L or other activators of pozzolanic reactions such as the temperature known as physical activation method. On the other hand, the formation of ettringite in both soil-L and soil-L-NP mixtures was clearly observed in XRD patterns when both Na₂SO₄ and $CaSO_4 \cdot 2H_2O$ are present (Figures 5(a), (b), (d), (e) and 6(a), (b), (d), (e)). According to Gadouri et al. (2016a), the ettringite is a calcium aluminium sulphate hydrate (C-A-S-H) type of mineral which is responsible for both the early strength increase and structural distress at later stage, as will be chemically discussed in the next section.





Effect of sulphates on pozzolanic reactions and pH variation

The addition of water $(2H_2O)$ to the $[Ca(OH)_2]$ increases the pH value of the soil solution as follows (Equation (1)):

 $Ca(OH)_{2} \rightarrow Ca^{2+} + 2OH^{-}$ (Ionisation of calcium hydroxide) (1)



Figure 6. XRD patterns of RS samples stabilised with 8%L, 20%NP and 20%NP + 8%L in the presence of 4% of both Na₂SO₄ and CaSO₄·2H₂O after 60 days of curing period.

The acceleration in the rate of pozzolanic reactions leads to the acceleration of NP dissolution which forms monosilicates $[SiO(OH)_3]^-$ and aluminates $[Al(OH)_4]$ compounds. When calcium ions (Ca²⁺) contact these compounds the C–S–H and C–A–H can be formed as follows (Equations (2) and (3)) (Shi and Day 2000):

$$Y[SiO(OH)_3]^- + XCa^{2+} + (Z-X-Y)H_2O + (2X-Y)OH^- \rightarrow C_X - S_Y - H_Z^{(2)}$$

(Formation of calcium silicates hydrates)

$$2[Al(OH)_4]^- + 4Ca^{2+} + 6H_2O + 6OH^- \rightarrow C_4AH_{13}$$
 (3)

(Formation of calcium aluminates hydrates)

The role of these compounds in the soil–L–NP mixture is to produce a layer of stable protective film that envelops the soil particles, to bind the soil particles together, to seal the voids that decrease the void index and consequently the water permeability and to improve the compactness and consequently the unconfined compressive strength of soil (Gadouri *et al.* 2016a).



Figure 7. Flow chart shows the results obtained from different mixtures for using in pavement subgrade soil stabilisation.

Roy (1986) reported that the reaction between Na_2SO_4 and $Ca(OH)_2$ in the contact of $2H_2O$ can be presented as follows (Equation (4)):

 $Ca(OH)_2 + Na_2SO_4 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + 2NaOH$ (4)

(Formation of sodium hydroxide and pH value increases up to 13)

Moreover, in the presence of H_2O , the reaction between Na_2SO_4 and soil–L or soil–L–NP mixtures leads to the formation of NaOH which develops a higher alkaline solution to compare with that of the Ca(OH)₂. The high pH developed by NaOH produces, by dissolution, a large amount of SiO₂ and Al₂O₃ which react with the remaining L to form a high amount of cementitious products responsible for the increase in soil strength.

However, the dissolution of sulphates menials (Na₂SO₄ and CaSO₄·2H₂O) increases the concentration of SO₄²– ions and then leads to the formation of ettringite (Ca₆Al₂(SO₄)₃(OH)₁₂, 26H₂O), shown as (Equations (5)–(7)):

$$Na_2SO_4 \rightarrow 2Na^+ + SO_4^{2-} \tag{5}$$

(Dissolution of sodium sulphate)

$$CaSO_4 \cdot 2H_2O \to Ca^{2+} + SO_4^{2-} + 2H_2O$$
 (6)

(Dissolution of calcium sulphate)

$$6Ca^{2+} + 2Al(OH)^{-4} + 4OH^{-} + 3(SO_4)^{2-} + 26H_2O \rightarrow Ca_6Al_2(SO_4)_3(OH)_{12}, 26H_2O$$
(7)

(Formation of ettringite mineral)

The effect of ettringite mineral $(Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O)$ on the soil–L–NP mixture is to absorb a high content of water molecules which produce a high swelling, to decrease the void volume, to improve the compressive strength in the initial period and to alter the specimens in the later stage (Gadouri *et al.* 2016a).

In this study, according to Figures 5 and 6, the formation of cementitious compounds (C–S–H and C–A–H) and ettringite is due to the presence of both Na_2SO_4 and $CaSO_4 \cdot 2H_2O$.

Sulphate type	Age (days)	Mixture and d	lesignation	Assessment and recommendations
Na ₂ SO ₄	7	(A)	(A1), P20L0N2 (A4), P20L0N4 (A7). P20L0N6	Present very low pH values (in this study, 9.22 < pH < 9.26), very low UCS values (0.07 < UCS (MPa) < 0.15) and no pozzolanic reactions (Gadouri <i>et al.</i> 2016a)
			(A2), POL8N2 (A5), POL8N4 (A8), POL8N6	Present high pH values (in this study, 12.57 < pH < 12.67), high UCS values (1.37 < UCS (MPa) < 1.79), acceleration of early pozzolanic reactions (Gadouri <i>et al.</i> 2016a)
			(A3), P20L8N2 (A6), P20L8N4 (A9), P20L8N6	Present high pH values (in this study, 12.64 < pH < 12.77), high UCS values (1.55 < UCS (MPa) < 2.76), acceleration of early pozzolanic reactions (Shi and Day 2000, Hu <i>et al</i> . 2016, Gadouri <i>et al.</i> 2016a)
	120	(C)	(C1), P20L0N2 (C4), P20L0N4 (C7), P20L0N6	Present very low pH values (in this study, 9.10 < pH < 9.20), very low UCS values (0.17 < UCS (MPa) < 0.26) and no pozzolanic reactions (Gadouri <i>et al.</i> 2016a), not recommended for pavement engineering
			(C2), POL8N2 (C5), POL8N4 (C8), POL8N6	Present high pH values (in this study, 12.34 < pH < 12.51), high UCS values (2.17 < UCS (MPa) < 3.94), decrease in pozzolanic reactions, formation of ettringite mineral (Gadouri <i>et al.</i> 2016a), recommended as materials for pavement engineering
			(C3), P20L8N2 (C6), P20L8N4 (C9), P20L8N6	Present high pH values (in this study, 12.45 < pH < 12.55), very high UCS values (4:39 < UCS (MPa) < 5.23), decrease in pozzolanic reactions and formation of ettringite mineral (Shi and Day 2000, Gadouri <i>et al.</i> 2016a), highly recommended as materials for pavement engineering
CaSO ₄ ·2H ₂ O	7	(E)	(E1), P20L0C2 (E4), P20L0C4 (E7), P20L0C6	Present intermediate pH values (in this study, 9.63 < pH < 10.35), low UCS values (0.45 < UCS (MPa) < 1.05), acceleration of early pozzolanic reac- tions (Aldaood <i>et al.</i> 2014a, 2014b, Gadouri <i>et al.</i> 2016b), cheapest and economic
			(E2), POL8C2 (E5), POL8C4 (E8), POL8C6 (E3), P20L8C6 (E6), P20L8C4 (E6), P20L8C4 (E9), P20L8C6	Present high pH values (in this study, 12.43 < pH < 12.53), low to very high UCS values (1.68 < UCS (MPa) < 5.10), acceleration of early pozzolanic reactions (Aldaood <i>et al.</i> 2014a, 2014b, Gadouri <i>et al.</i> 2016b), cheapest and economic
	120	(0)	(G1), P20L0C2 (G2), P0L8C2 (G3), P20L8C2 (G3), P20L0C4 (G5), P20L0C4 (G6), P20L8C4 (G5), P20L8C4 (G8), P20L8C6 (G9), P20L8C6	Present low to high pH values (in this study, 9.07 < pH < 12.15), extremely very high UCS values (3.93 < UCS (MPa) < 8.67), decrease in pozzolanic reactions, formation of ettringite mineral, no destruction has been observed in studied specimens (Aldaood <i>et al.</i> 2014b, Gadouri <i>et al.</i> 2016b), cheapest and economic, highly recommended as materials for pavement engineering

Table 5. Recommendations for a better selection of an adequate mixture for pavement subgrade soil stabilisation (case of clayey soils of low plasticity).

Sulphate type	Age (days)	Mixture	and designation	Assessment and recommendations
Na ₂ SO ₄	7	(B)	(B1), P20L0N2 (B4), P20L0N4 (B7), P20L0N6	Present very low pH values (in this study, 9.22 < pH < 9.35), very low UCS values (0.16 < UCS (MPa) < 0.55) and no pozzolanic reactions (Gadouri <i>et al.</i> 2016a)
			(B2), POL8N2 (B5), POL8N4 (B8), POL8N6	Present high pH values (in this study, 9.22 < pH < 9.26), high UCS values (1.03 < UCS (MPa) < 2.12), acceleration of early pozzolanic reactions (Gadouri <i>et al</i> . 2016a)
			(B3), P20L8N2 (B6), P20L8N4 (B9), P20L8N6	Present high pH values (in this study, 9.22 < pH < 9.26), high UCS values (1.59 < UCS (MPa) < 4.71), acceleration of early pozzolanic reactions (Shi and Day 2000, Hu <i>et al.</i> 2016, Gadouri <i>et al.</i> 2016a)
	120	(D)	(D1), P20L0N2	Present very low pH values (in this study, pH = 9.16), very low UCS values (UCS = 1.26 MPa), (Gadouri <i>et al.</i> 2016a), not recommended
			(D4), P20L0N4 (D7), P20L0N6	Present very low pH values (in this study, $9.13 < pH < 9.25$), all specimens have been broken (deteriorated) before UCS test due to the ettringite formation (Gadouri <i>et al.</i> 2016a), strictly not recommended for pavement engineering
			(D2), P0L8N2 (D5), P0L8N4 (D3), P20L8N2 (D6), P20L8N4	Present very low pH values (in this study, 12.63 < pH < 12.91), extremely very high UCS values (2.97 < UCS (MPa) < 8.70) (Gadouri <i>et al.</i> 2016a), highly recommended as materials for pavement engineering
			(D8), P0L8N6	Presents very low pH values (in this study, pH < 12.84), all specimens have been broken (deteriorated) before UCS test due to the ettringite formation (Gadouri <i>et al.</i> 2016a), strictly not recommended for pavement engineering
			(D9), P20L8N6	Presents very low pH values (in this study, pH 12.97), low UCS values (UCS = 2.46 MPa), decrease in pozzolanic reactions and formation of ettringite mineral (Shi and Day 2000, Gadouri <i>et al.</i> 2016a), not recommended for pavement engineering
CaSO ₄ ·2H ₂ O	7	(F)	(F1), P20L0C2 (F4), P20L0C4 (F7), P20L0C6	Present intermediate pH values (in this study, 9.45 < pH < 10.24), high UCS values (1.52 < UCS (MPa) < 3.89), formation of cementing agents by pozzolanic reactions (Aldaood <i>et al.</i> 2014a, 2014b, Gadouri <i>et al.</i> 2016b), cheapest and economic
			(F2), POL8C2 (F5), POL8C4 (F8), POL8C6 (F3), P2OL8C2 (F6), P2OL8C4 (F9), P2OL8C6	Present high pH values (in this study, 12.50 < pH < 12.62), high UCS values (2.02 < UCS (MPa) < 5.76), acceleration of early pozzolanic reactions (Aldaood <i>et al.</i> 2014a, 2014b, Gadouri <i>et al.</i> 2016b)
	120	(H)	(H1), P20L0C2 (H2), P0L8C2 (H3), P20L8C2 (H4), P20L0C4 (H5), P0L8C4 (H6), P20L8C4 (H7), P20L0C6 (H8), P0L8C6 (H9), P20L8C6	Present low to very high pH values (in this study, 9.31 < pH < 12.20), very high UCS values (4.93 < UCS (MPa) < 9.87), decrease in pozzolanic reactions, formation of ettringite mineral (Le Borgne 2010, Aldaood <i>et al.</i> 2014a, 2014b, Gadouri <i>et al.</i> 2016b), highly recommended as materials for pavement engineering

Adequate mixture for pavement subgrade soil stabilisation

The flowchart (Figure 7) and Tables 4 and 5 were proposed to be used only for cohesive soils of high or low plasticity. This flowchart can be used as the way to identify possible mixdesigns and to associate them to a label $(A_{1-9} up to H_{1-9})$ with which look up the contents presented in Tables 4 and 5. In fact, the adequate mixture for pavement subgrade soil stabilisation can be selected according to the Figure 7 based also on both Tables 4 and 5, which were obtained using the pH values and previous results of strength (e.g. Aldaood et al. 2014a, 2014b, Hu et al. 2016, Gadouri et al. 2016a, 2016b). On the other hand, Tables 4 and 5 present the different mixtures of the clayey soil of high plasticity and clayey soil of low plasticity, respectively. Both Tables 4 and 5 explain the components of Figure 7 and present detailed recommendations to choose an adequate mixture with suitable technical and economic conditions for only a longer curing period. It will be recommended only for all clayey soils stabilised with L alone or in combination with natural pozzolana in the presence of monovalent (Na2SO4) and divalent $(CaSO_4 \cdot 2H_2O)$ sulphates.

Conclusions

The effect of sulphates on pH and pozzolanic reactions of soillime-natural pozzolana mixtures has been studied in order to select an adequate mixture for pavement subgrade soil stabilisation. Based on the test results, the following conclusions can be drawn:

- In the absence of sulphates, the addition of L alone to both clayey soils produces a considerable increase in the pH value. However, a further increase was recorded when using the L in combination with NP. In all cases, the pH of both clayey soils stabilised with L alone or in combination with NP decreases with curing period. On the other hand, a negligible change in the pH value was observed when using NP alone.
- The increase in the pH value of both soil–NP and soil–L–NP mixtures with increasing sulphate content was more pronounced with the Na₂SO₄ than with the CaSO₄·2H₂O, this is due to the fact that the NaOH (from Na₂SO₄) developed a high pH value in the soil solution to compare to that developed by the Ca(OH)₂ (from L and/or CaSO₄·2H₂O). On the other hand, for the same mixtures (soil–NP and

soil–L–NP), the sensitivity of the pH to the curing period effect was more pronounced with the $CaSO_4 \cdot 2H_2O$ than with the Na_2SO_4 . In addition, it was also more pronounced with the $CaSO_4 \cdot 2H_2O$ content than with the Na_2SO_4 content. Furthermore, for both soil–L and soil–L–NP mixtures, the sensitivity of the pH to the L and L–NP effect was more pronounced with the presence of Na_2SO_4 than with the $CaSO_4 \cdot 2H_2O$ addition.

- For a shorter curing period, the Na₂SO₄ can be used as an accelerator of NP dissolution when its content is less than 2%. However, it is necessary to classify the Na₂SO₄ as a deleterious element for pavement engineering when its content is greater than 2%. Conversely, the CaSO₄·2H₂O can be used as an additive with any content for soil stabilisation. However, for any curing periods, the pH of both GS and RS samples stabilised with L alone or in combination with NP was very higher than that of samples stabilised without Na₂SO₄.
- Increases and decreases in the pH value depend largely on the type of additive used and its content, type of sulphate and its content, mineralogical composition of the stabilised soil and curing period.
- It should be noted that the use of a suitable type of treatment for pavement subgrade soil stabilisation requires respect the recommendations presented in both Tables 4 and 5.

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