Journal of Building Engineering 42 (2021) 103070

Contents lists available at ScienceDirect

Journal of Building Engineering

journal homepage: www.elsevier.com/locate/jobe

Performance of leonardite humic acid as a novel superplasticizer in Portland cement systems

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ARTICLE INFO

Keywords:
Chemical admixtures
Cement hydration
Humic acid
Leonardite
Superplasticizer

ABSTRACT

Significance of superplasticizers (SPs) in sustainable development of concrete industry is well known regarding to reduced water and Portland cement content of the mixtures. Development of eco-efficient alternative types of SPs is needed. A humic-acid based superplasticizer derived from leonardite (LHA) as a natural organic matter was examined in terms of its plasticizing performance and influence on hydration as well as properties of Portland cement (PC) in comparison with lignosulfonate- (LS) and naphthalene-based admixture (NA). The impact of LHA on hydration of Portland cement was investigated for various dosages of addition by isothermal calorimetry and thermo-gravimetric analysis of hardened pastes. In addition, effect of admixtures on setting time of PC pastes as well as flow and compressive strength of mortars were also studied. Experimental results indicated that LHA has similar impact on early hydration kinetics and setting time of PC when compared to NA. However, LS caused dramatic retardation on PC hydration. LHA addition was also increased the degree of hydration of PC both at 7 and 28 days, and this increasing was more pronounced at 7 days. LHA showed a comparable plasticizing performance to the other admixtures as measured by flow of mortars for 0.3% equivalent solid dosage. Compressive strength of mortars with LHA addition was higher than that of control PC mortar at 3, 7 and 28 days of age for all the dosages tested. LHA was found to have a considerable potential for use as superplasticizer in cementitious systems with its reasonable effects on hydration and properties of PC.

1. Introduction

Critical role of water reducing agents and especially superplasticizers for the reduction of environmental impact of cementitious materials industry is widely accepted as regarding to their help to reduce water/cement ratio (w/c) and accordingly Portland cement (PC) content of concrete mixtures. In last two decades, superplasticizers have also become essential component especially of concrete mixtures containing large volume supplementary cementing materials such as fly ash, ground granulated blast furnace slag or natural pozzolans [1–7]. It is well known that the combined use of superplasticizers and supplementary cementing materials provides cost-effective high-performance concrete with improved durability and reduced CO_2 footprint [8–10].

Starting from the use lignosulfonates as the first dispersants included as natural polymer-based water-reducing agents to concrete mixtures in 1930s, dispersing chemical admixtures have been progressively improved by synthesizing polymeric dispersants as high-range water reducers (superplasticizers) such as polynaphthalene sulfonates (PNS) and polymelamine sulfonates (PMS) as well as poly-carboxylic acids (PCA) [11]. Their synthesis involves several chemical processing steps including energy-intensive acid treatments of naphthalene and melamine raw materials at a high temperature and pressure conditions. According to Environmental Product Declaration (EPD) document published for concrete superplasticizers by European Federation of Concrete Admixtures Association (EFCA) as a result of the life cycle assessment study, global warming potential and total use of non-renewable energy resources of superplasticizers are reported as 1.88 kg CO2-Eq. and 31.4 MJ for 1 kg of superplasticizer, respectively [12]. It is obvious that there is a need for development and use of cost-effective and eco-efficient alternative superplasticizers to reduce their environmental impact.

In recent years, the use of humic acid-based dispersants in various areas other than cementitious systems, has been reported in published literature [13–16]. Humic acids (HAs) are natural biopolymers consisting of highly functionalized carbon [17], and they have strong steric repulsion between its molecules like PCA, accordingly proposed as

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https://doi.org/10.1016/j.jobe.2021.103070
Received 7 May 2021; Received in revised form 1 July 2021; Accepted 3 August 2021
Available online 5 August 2021

Table 1
Oxide composition and physical properties of CEM I 42.5R type Portland cement.

Chemical Composition	(%)
SiO_2	17.78
Al_2O_3	4.59
Fe_2O_3	3.73
CaO	62.94
SO_3	4.87
MgO	2.41
Na_2O	1.08
K_2O	1.00
TiO_2	0.34
MnO	0.07
P_2O_5	0.07
Loss on ignition	1.05
Physical Properties	
Specific gravity	3.13
Blaine fineness (cm^2/g)	3469
Initial setting time (min)	212
Final setting time (min)	316
Residue on 45 μm *sieve (%)*	4.8
Residue on 90 μm *sieve (%)*	0.5
Compressive strength of mortars	
2 days (MPa)	23.7
28days (MPa)	46.5

environment-friendly, non-toxic and well-performed dispersing agent [18]. HA can be obtained from various sources such as extraction from peats or leaching from leonardite as natural organic matter [19–21]. On the other hand, Gao et al. [22] has recently reported the use of HA as dispersion stabilizer for multi-walled carbon nanotubes in cement composites. However, the published literature is lack of reports comparing humic acid (HA) obtained from leonardite as an alternative type of superplasticizer to widely used types of superplasticizers in terms of plasticizing performance and impacts on PC hydration. One of the aims of this study is to meet this need.

Leonardite is a natural organic matter occurred around lignite mines and it has a similar structure to lignite. It is known that lignite and coal-related materials has been used as clay dispersant in water-based drilling fluids [23–25]. On the other hand Leonardite differs from lignite with a higher oxygen content caused by a larger number of carboxyl and phenolic groups available in leonardite [26]. HA can be obtained from leonardite as a low-cost raw material by treating with hot sodium or potassium hydroxide solution and then precipitating solid HA by hydrochloric acid treatment. Due to strong acidity of HA (pH $<$ 2), commercially available HAs are produced by only treating with hot alkali hydroxide solution and separating the insoluble solid part to finally obtain a HA solution as a liquid sodium or potassium humate having a high pH value ($>$11) [21]. HA solutions are known to use in agriculture as soil conditioner and fertilizer [27,28]; in water treatment as adsorbent for heavy metal ions [29,30]; in medicine as anti-viral and anti-bacterial and UV-protecting agent [31,32].

In this study, it was aimed to examine the performance of humic-acid based admixture obtained from leonardite as a new potential type of superplasticizer for cementitious systems in comparison with a lignosulfonate-based (LS) and a naphthalene-based admixtures (NA). HA solution was obtained as a commercial product manufactured by alkali treatment of leonardite with potassium hydroxide, which is in use for agricultural applications. Plasticizing performance of HA as well as its impact on hydration and properties of Portland cement systems were compared to LS and NA. The impact of HA on hydration of PC was investigated by isothermal calorimetry and thermal analysis of PC pastes. In addition, the effects of HA on setting time of PC as well as flow and compressive strength development of PC mortars were evaluated in comparison with LS and NA.

Table 2
Physical and chemical properties of admixtures.

Properties	LS	NA	LHA
Active ingredient	Lignosulfonate	Naphthalene sulfonate	Humic acid
Solid content, (%)	32	35	26
Color	Brown	Brown	Brown
Density (kg/liter)	1.14	1.13	1.10
CaO, %[a]	4.77	0.25	1.18
SO_3, %[a]	1.99	13.79	1.50
Na_2O, %[a]	2.88	7.35	$<$0.01
K_2O, %[a]	1.85	0.04	9.28
Equivalent alkali (Na_2O+0.658 K_2O), %[a]	4.10	7.38	6.11

[a] Determined by X-ray Fluorescence technique on dry solid part of admixtures, and then calculated by mass of liquid admixture.

2. Experimental

2.1. Materials

A CEM I 42.5R type standard Portland cement (PC) in accordance with EN 197-1 was used in the study. Its oxide composition and physical properties are shown in Table 1.

Humic acid-based solution which is used in fact as a soil supplement in agriculture as produced from leonardite as a natural organic matter was obtained from a local commercial supplier (Ekodoga Ltd.) and notated as LHA hereafter. Two commercial water reducing admixtures in liquid forms, a lignosulfonate derivative (BASF Pozzolith) notated as LS and a naphthalene-based product (BASF Master Rheobuild) notated as NA, were also used as traditional type of water reducers for comparison with HA. Some basic characteristics of admixtures declared by their manufacturers are shown in Table 2. The relatively higher K_2O content of LHA indicated that it is a potassium humate solution, not a sodium humate, which is advantageous due to lower contribution of K_2O to the equivalent alkali content with a multiplication factor of 0.658. This could be preferential against the risk of a potential alkali-aggregate reaction in the case of usage with a reactive aggregate.

A washed river sand having a similar gradation to the standard sand in accordance with EN 196-1 is used in preparation of mortar mixtures.

2.2. Methods

In the experimental approach of the study, it was aimed to assesses the water reducing performance of HA obtained from leonardite as a natural resource and its influence on hydration of PC in comparison with LS and NA admixtures.

The PC pastes with and without admixtures were prepared by using 0.4 w/c for the determination of hydration kinetics by isothermal calorimetry; degree of hydration by differential thermal and thermogravimetric analysis (DTA/TGA) of hardened pastes; and setting time tests. The admixtures were added to mixing water in liquid dosages of 0.5%, 1.0% and 1.5% by mass of PC during preparation of cement pastes and mortars. A neat PC paste and mortar without admixture were also prepared as reference blank samples.

Hydration kinetics of PC was measured in absence and presence of admixtures by using TAM Air Microcalorimeter in isothermal condition at 25 °C according to ASTM C 1679. A handheld household mixer and deionized water were used to prepare cement pastes. The fresh pastes were immediately placed in plastic vials with closed lid to prevent evaporation and then into calorimeter. Loading of specimens into calorimeter were completed in 2 min after the end of mixing. Thermal power as mW/g of PC present in the cement paste was recorded for 72 h as a measure of rate of hydration (rate of heat evolution) and plotted against time starting from initial contact between the cement and the mixing water. Cumulative heat of hydration curves of the cement pastes was also obtained as the area under thermal power vs. time curves by

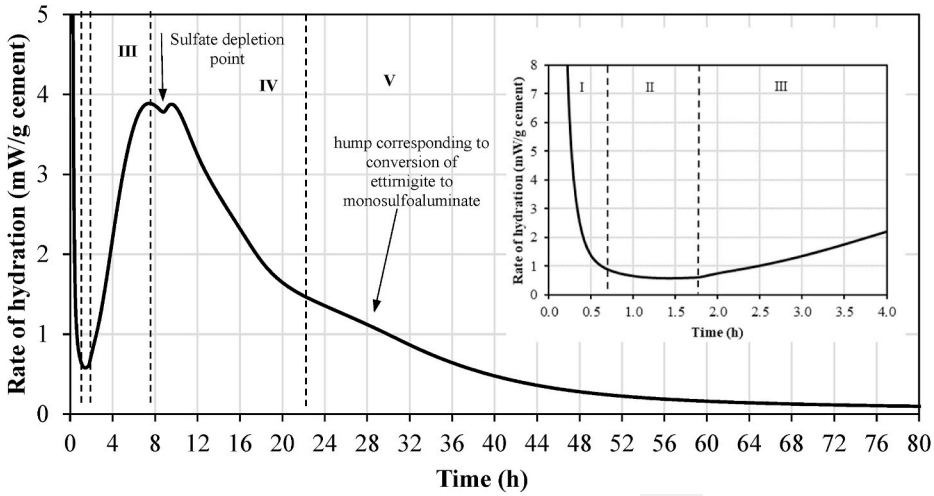

Fig. 1. Rate of hydration curve of PC used in the study and relevant stages of hydration.

integration.

Degree of hydration of PC in hardened cement pastes were determined from the amount of chemically bound water by DTA/TGA of hardened cement pastes at 7 days and 28 days of hydration in accordance with the method proposed by Pane and Hansen [33]. For this purpose, the cement pastes prepared for isothermal calorimetry were also placed into plastic syringes and the ends of the syringes were closed with lids to prevent moisture loss and carbonation. The plastic syringes were kept at room temperature until the test days. The hardened pastes were removed from the syringes and immediately crushed and sieved to obtain particles smaller than 800 μm. The samples then analyzed thermally by using Shimadzu DTG-60H TGA device between room temperature and 1100 °C at a heating rate of 10 °C/min. The amount of chemically bound water was obtained by mass loss between temperature range of 140–1100 °C as percentage with respect to ignited mass of paste, and then degree of hydration of PC pastes was calculated by normalizing this percentage mass loss to its maximum value of 0.23 for a typical ordinary PC in accordance with the method proposed by Pane and Hansen [33].

Initial and final setting times of PC with and without admixtures were determined on pastes prepared with 0.4 w/c by using an automatic vicat device in accordance with EN 196-3. Mortar mixtures were prepared with 0.5 w/c ratio and 2.75 sand/cement ratio for flow test on fresh mortars and compressive strength of hardened mortars by using a standard mixer in accordance with EN 196-1. A washed river sand having a comparable gradation to the CEN reference sand according to EN 196-1. Flow of fresh PC mortars was determined as stated by ASTM C1437 as a percentage change in diameter of fresh mortar after 25 times of dropping of flow table. To determine the compressive strength development of mortars, fresh mortars were placed into 50 mm cubic molds in two layers and compacted by a shaking table after each layer. The specimens within molds were cured by sealing with plastic stretched film and a wet cloth for 24 h. The specimens were then removed from the molds and allow to wet curing in water bath at 21 ± 1 °C up to test days. The specimens were tested for compressive strength (as average of 6 specimens for each testing age) under the loading rate of 0.5 MPa/s at 3, 7 and 28 days of age.

3. Results and discussion

3.1. Hydration kinetics

Hydration kinetics of ordinary PC is examined by heat release caused by exothermic reaction of clinker phases, mainly alite (C_3S) and tricalcium aluminate (C_3A) under five stages, which are shown in Fig. 1 with

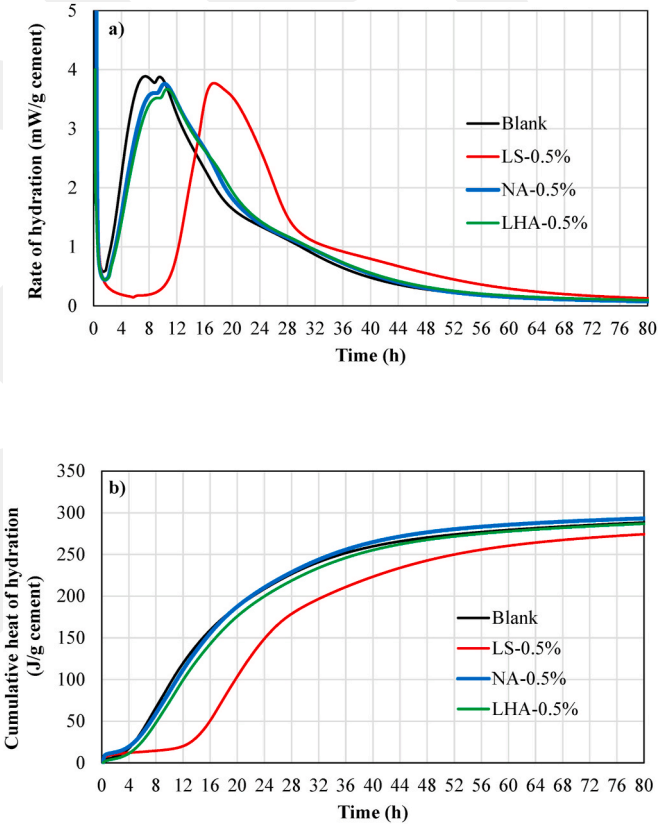

Fig. 2. a) Rate of hydration and **b)** Cumulative heat of hydration of cement pastes with 0.5% liquid dosage of admixtures.

the related points for PC used in the study with 0.4 w/c at 25 °C.

Stage I is the first peak caused by wetting of cement particles and fast dissolution of anhydrous phases including formation of ettringite owing to high reactivity aluminates in presence of calcium sulfate. The first stage is flowed by Stage II consisting of the rapid decrease in rate of reaction and then the induction period. Stage III starts including the second main peak corresponding to hydration of calcium silicates, mainly C_3S, resulting in precipitation of main products (C–S–H and CH). The hydration then decelerates again in Stage IV in which another peak arises corresponding to sulfate depletion point, faster dissolution of C_3A and formation of ettringite. Stage V, the last stage, is characterized by a

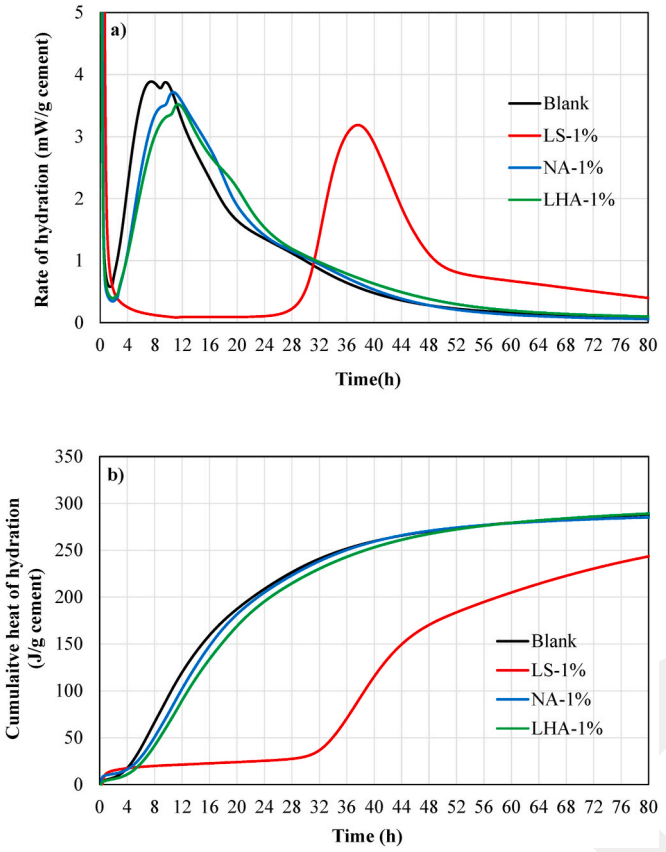

Fig. 3. a) Rate of hydration and **b)** Cumulative heat of hydration of cement pastes with 1% liquid dosage of admixtures.

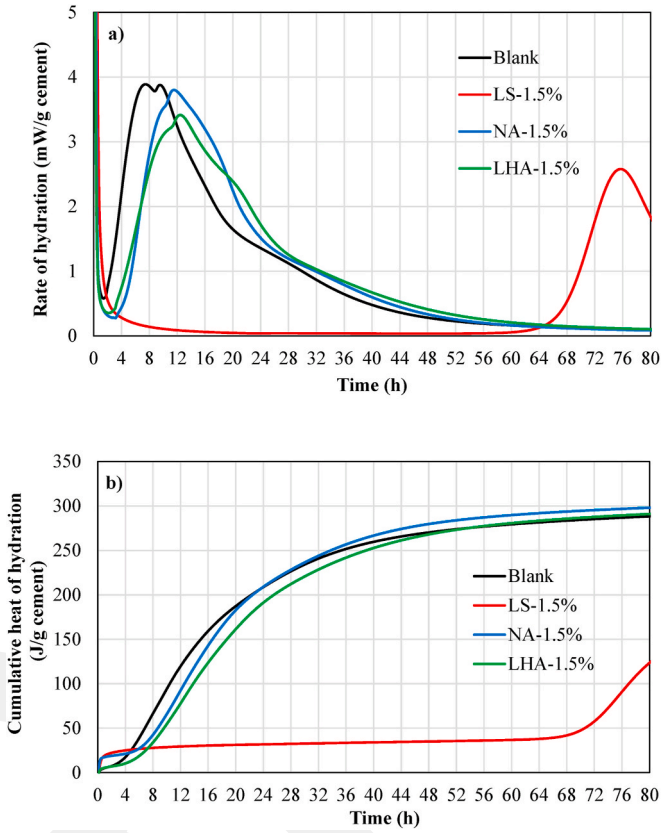

Fig. 4. a) Rate of hydration and **b)** Cumulative heat of hydration of cement pastes with 1.5% liquid dosage of admixtures.

relatively slow reactions controlled by diffusion of species through the hardened products, also including a third peak as a broad hump in heat flow profile indicating the conversion of ettringite (AFt) to monosulfohydrate (AFm) [11].

Hydration kinetics of PC was examined in presence and absence of admixtures by isothermal calorimetry test of cement pastes with 0.4 w/c at 25 °C to observe the influence of LHA on hydration kinetics comparatively with respect to LS and NA. Plots of hydration rate and cumulative heat of hydration of cement pastes with liquid dosage of admixtures varying between 0.5 and 1.5% as well as blank PC paste without admixture are given in Figs. 2–4.

It is well known that water reducers and superplasticizers generally not only retard the hydration of PC with a prolonged induction period in Stage II, but can also change the slope and height of acceleration peak in Stage III along with shifting the sulfate depletion point in Stage IV. The retardation of hydration is commonly attributed to the adsorption of admixture molecules on cement phases which causes i) interaction and complexation with calcium ions, ii) decrease in rate of dissolution, nucleation and growth of hydration products and iii) disruption of the balance between silicates, aluminates, and sulfates. Mechanisms of i) and ii) result in prolonging the induction period and reduction in peak height whereas mechanism iii) generally causes shifting or disappearing of sulfate depletion point [11,34].

As can be seen from Fig. 2, hydration of PC was not affected considerably with addition of LHA and NA for their liquid dosage of 0.5% since they exhibited comparable rate of hydration (Fig. 2a) and heat of hydration curves (Fig. 2b) with a very slight prolonging of induction period in Stage II. However, 0.5% LS addition resulted in a significantly prolonged induction period (Stage II) and accordingly shifting of main hydration peak to the right. This also reduced the heat of hydration especially at early hours when compared to LHA and NA samples. In the case of 0.5% LS addition, sulfate depletion point disappeared, and double peak formation converted to a single peak by their merging (Fig. 2a). Lignosulfonates as midrange water reducers are already known as inducing considerable retardation attributed mostly to the adsorption of residual sugar content in lignosulfonates remained from the production process [34]. Since LHA addition exhibited modifications in calorimetric signature of PC hydration similar to NA addition for a low dosage of admixtures (0.5% liquid dosage), it can be concluded that LHA addition modifies the hydration process in all the stages similarly to NA by mechanisms triggered by their adsorption on cement compounds as mentioned above.

For 1% liquid dosage of admixtures, LHA showed a similar rate of hydration profile to NA as well as slightly delayed and lower maximum peak point when compared to blank sample (Fig. 3a). On the other hand, 1% LS addition prolonged the end of induction period (Stage II) to longer than 24 h (Fig. 3a) at which the corresponding heat of hydration was dramatically lower than the other pastes as seen from Fig. 3b. At the end of 80 h, heat of hydration of LHA and NA samples was in the same level as blank sample whereas heat of hydration of LS sample remained as lower. In addition, broad hump formation in hydration rate curve of PC (Fig. 1) was observed earlier and became more evident in the case of 1% LHA addition (Fig. 3a) when compared to blank and NA samples, which indicates an earlier conversion of AFt to AFm. Minard et al. [35] have explained this conversion mechanism as precipitation of more stable monosulfohydrate (AFm) due to impoverishment of the calcium ion concentration in pore solution, which is a very slow transformation indicated by a weak thermal activity in rate of hydration curve. Therefore, it seems that LHA, unlike NA and NS, acts in way that makes the conversion from AFt to AFm earlier.

Increasing the liquid dosage of admixtures to 1.5% caused a further reduction in maximum rate of hydration of LHA sample when compared to blank and NA samples as seen from Fig. 4a. On the other hand, LS

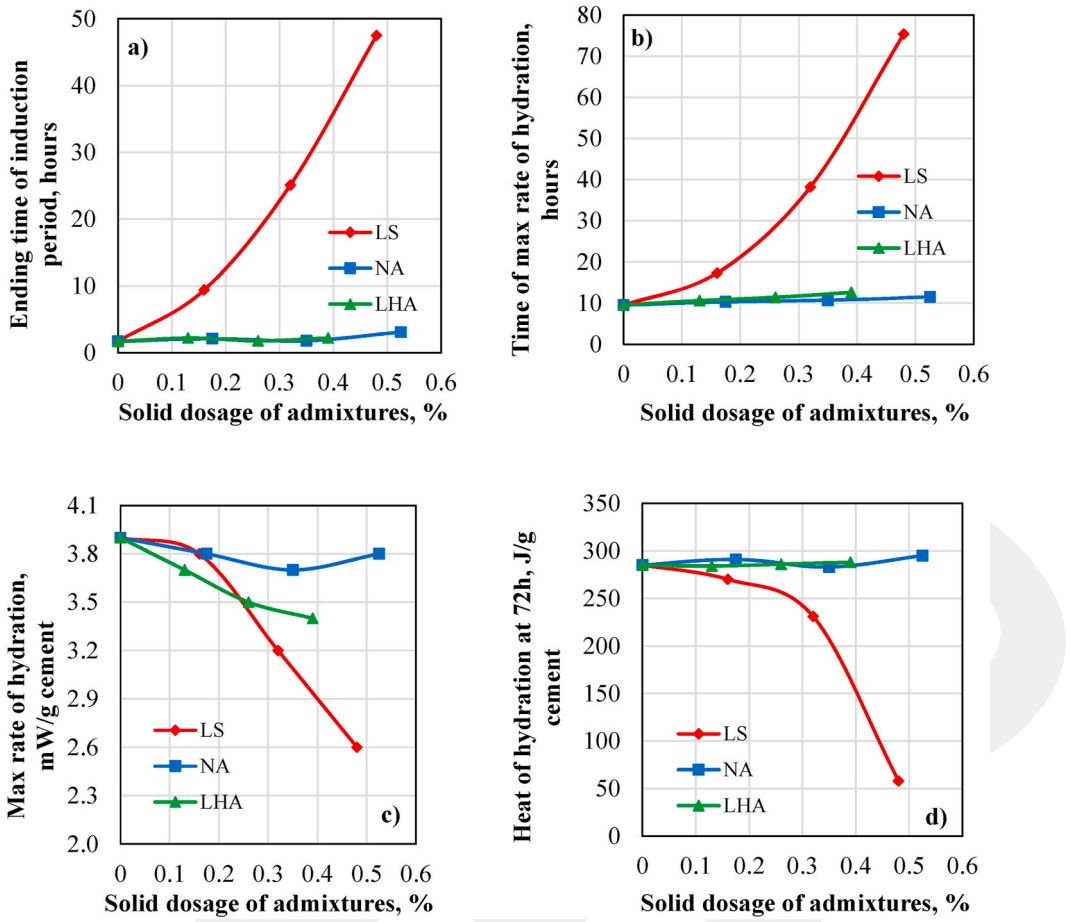

Fig. 5. Characteristic parameters of hydration kinetics for cement pastes depending on solid dosage of admixtures, **a)** Ending time of induction period, **b)** time of max rate of hydration, **c)** max rate of hydration, **d)** Heat of hydration at 72 h

exhibited an extremely delayed exothermic peak with a lower height due to prolonged end of induction period up to 60 h.

Comparing the heat of hydration of cement pastes for 1.5%liquid dosage of admixtures (Fig. 4b), it can be seen that LHA addition resulted in a slightly lower heat of hydration than NA and blank sample before 48 h, however it reached up the blank sample thereafter. A more evident and earlier conversion of AFt to AFm was also observed at 1.5% dosage of LHA in Fig. 4a, similarly to the case for 1% dosage.

Since the solid content of admixtures is variable as shown in Table 2, the effects of corresponding solid dosage of admixtures on the parameters of hydration kinetics attained from calorimetry results, e.g. ending time of induction period, time of maximum rate of hydration, maximum rate of hydration and heat of hydration at 72 h, are given in Fig. 5 in order to compare LHA to the other admixtures effectively for a given solid dosage.

LHA showed a similar impact on PC hydration to NA with increasing solid dosage in terms of ending time of induction period (Fig. 5a), time of maximum rate of hydration (Fig. 5b) and heat of hydration at 72 h (Fig. 5d). Both did not change these parameters considerably with their increasing solid dosages whereas LS caused dramatic increases in ending time of induction period and time of maximum rate and accordingly remarkable decreases in heat of hydration. On the other hand, LHA addition decreased the maximum rate of hydration of PC in a little bit more extent than NA and LS for a solid dosage lower than 0.2%. (Fig. 5c). However max hydration rate of PC with LHA was significantly higher than LS and somewhat lower than NA for solid dosages more than approximately 0.25%. The impact of superplasticizers on hydration of Portland cement and the compatibility between them are generally attributed to the level of their adsorption onto cement compounds, more specifically C_3A regarding to sulfate-admixture competition for adsorption [36–38]. Therefore, similar impacts of LHA addition to that of NA on PC hydration can be associated with its comparable adsorption level onto cement compounds.

3.2. *Setting time and degree of hydration*

Influence of solid dosages of admixtures on initial and final setting time of PC pastes was demonstrated in Fig. 6. As can be seen from Fig. 6, initial and final setting of PC prolonged in reasonable ranges with increasing dosage of LHA and NA, while LS additions resulted in abnormal delays in setting. Comparing LHA and NA in terms of setting time, it can be concluded that they show similar delays in initial setting time with increasing solid dosages, however LHA causes a longer final setting time (~3 h later) than NA for a solid dosage of 0.3%. The results are in agreement with hydration kinetics data above and with previously reported data on LS and NA type superplasticizers by other researchers [34,39]. Consequently, LHA has a quite similar impact on setting characteristics of PC when compared to naphthalene-based superplasticizer NA.

Degree of hydration of PC cement pastes at 7 days and 28 days depending on solid dosage of admixtures as determined by DTA/TGA of hardened pastes are given Fig. 7.

As seen from Fig. 7a for 7 days of age, PC with LHA addition exhibited an obviously higher degree of hydration (as determined from amount of chemically bound water) when compared to NA and LS at 7 days. Degree of hydration of PC increased with increasing solid dosage of LHA. In addition, comparing the trends of degree of hydration with increasing dosage of admixture at 28 days as seen from Fig. 7b, LHA was

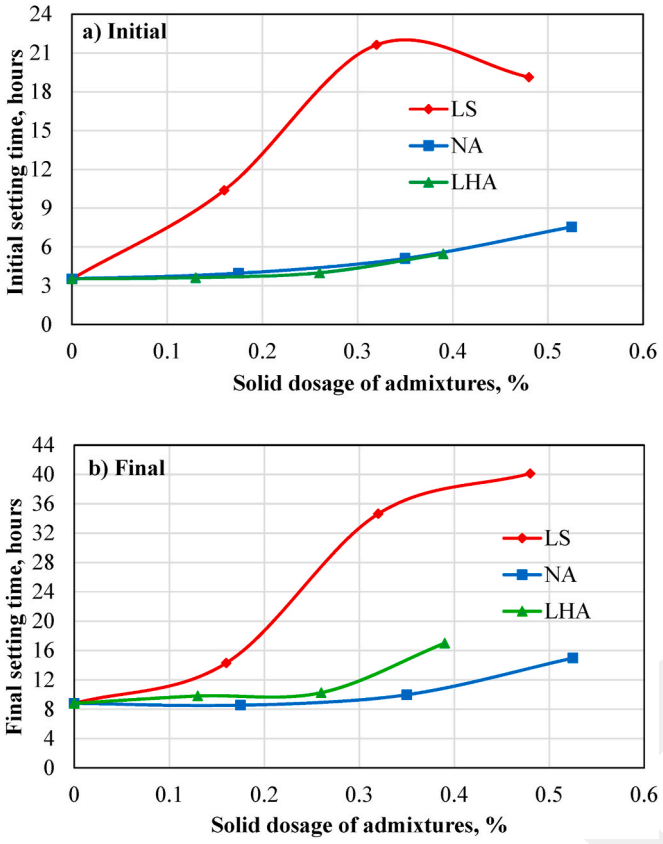

Fig. 6. Setting times of cement pastes depending on solid dosage of admixtures, **a)** Initial setting time, **b)** Final setting time.

between LS and NA for relatively low dosages whereas it is above the others for dosages >0.3%. The increased degree of hydration especially observed for LHA at 7 days as well as LHA and LS at 28 days could be associated with possible formation of additional products such as organo-mineral phases because of interaction between AFm phase with superplasticizing agents. Tendency of some polycarboxylates and naphthalene-based superplasticizers to intercalate into AFm phases has been shown in published literature [11,40,41]. The authors believe that formation of such organo-mineral phases and their growth by extending age of pastes could be responsible for increased content of chemically bound water and increased degree of hydration.

3.3. Flow of fresh mortars

Performance of admixtures to enhance the flow of fresh mortars prepared with 0.5 w/c was examined by measuring the flow of fresh mortars for varying solid dosages, and the results are given in Fig. 8. LHA addition provided a lower flow value than LS and NA for a given solid dosage lower than approximately 0.2% whereas it has a comparable plasticizing ability to LS and NA corresponding to 105% flow for a solid dosage of approximately 0.3%. Trend of curves indicates that efficacy of LHA and LS to provide higher flow values was reduced for solid dosages higher than 0.3%, however plasticizing ability of NA continues to increase with increasing dosage. On the other hand, all the admixtures resulted in a similar flow value of PC mortar at a solid dosage of 0.3% which seems to be their equivalent dosage. Consequently, it seems that plasticizing ability of LHA and LS is limited under approximately 110% flow value even if their dosages are furtherly increased beyond 0.3% solid dosage. However, NA has a performance to provide higher flow values when its solid dosage increased up to more than 0.5%.

3.4. Compressive strength of mortars

Fig. 9 shows the effect of solid dosage of admixtures on compressive strength of PC mortars prepared with a constant w/c of 0.5 at 3,7 and 28 days. Compressive strength of mortars with LHA addition was higher than that of the blank mortar regardless of the dosage whereas LS or NA addition resulted in higher or lower strength depending on type and dosage of admixtures as well as age of mortars.

As can be seen in Fig. 9a, impact of LHA addition on 3-day compressive strength of mortars with increasing solid dosage was very similar to that of LS addition, e.g. approximately 18% increase in

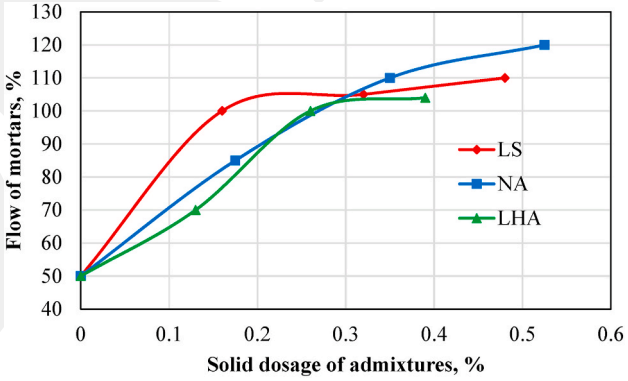

Fig. 8. Flow of cement mortars depending on solid dosage of admixtures.

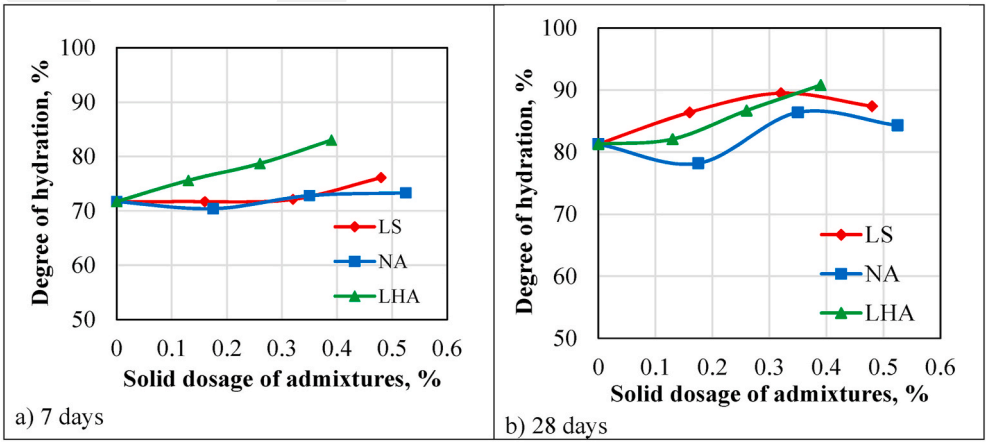

Fig. 7. Effect of solid dosage of admixtures on degree of hydration of Portland cement as determined by TGA analysis at **a)** 7 days and **b)** 28 days.

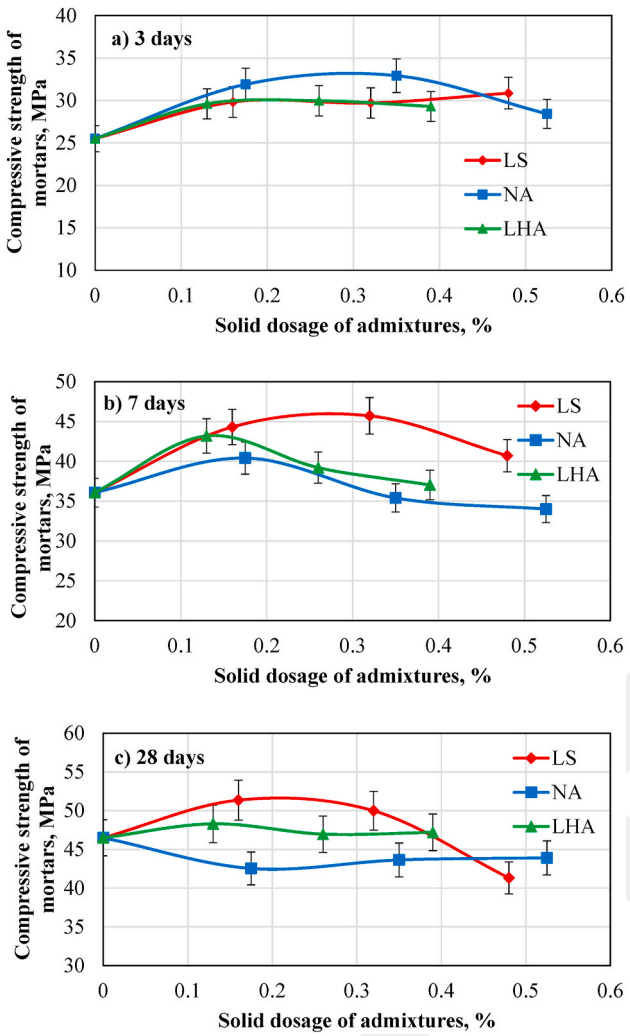

Fig. 9. Compressive strength of cement mortars depending on solid dosage of admixtures **a)** 3 days, **b)** 7 days **c)** 28 days.

strength for the dosages tested. On the other hand, NA addition resulted in about 30% higher 3-day compressive strength up to 0.3% solid dosage even though it showed a slightly higher strength than the blank mortar at approximately 0.5% solid dosage. It is interesting to observe that compressive strength of mortar with relatively high dosage of LS admixture was comparable to those of mortars with LHA and NA despite the significant retardation effect of LS and lower heat of hydration indicated by hydration kinetics and setting time data shown in Figs. 5d and 7, respectively. This can be attributed to the effect of sugar species commonly available in commercial lignosulfonate water reducers on hydration and strength development PC systems as reported in published literature [11,34,42]. Zhang et al. [42] have shown that sugar species such as sucrose and saccharide in lignosulfonate-based admixtures can first inhibit Portland cement hydration and retard setting by poisoning of calcium silicate hydrate nuclei, however they are not negatively influential on compressive strength of fully set cementitious systems. There are also reports published in literature for superplasticizers without sugar species, concluding that less amount of hydrates may be sufficient for a superplasticized PC system to achieve the same strength due to easier filling of pores after setting with a dispersed structure and well distributed cement particles when compared to a blank sample [43,44].

Comparing LHA to NA, 3-day compressive strengths of mortars with varying solid dosages (Fig. 9a) were in agreement with their similar influences on hydration characteristic determined for the first 72 h of hydration by isothermal calorimetry (Fig. 5) as well as on setting time of PC (Fig. 7).

The addition of LHA resulted in a slightly higher 7-day compressive strength than that of NA, however the strength of mortar with LS addition was remarkably higher when compared to LHA and NA addition for dosages higher than 0.2%. A parabolic trend of compressive strength variation with increasing dosage of admixtures was observed for all the types. The maximum 7-day compressive strength of mortars was provided by LS, NA and LHA addition at their approximate dosages of 0.25%, 0.18% and 0.13%, respectively. Regarding the effect of superplasticizers dosage on the amount of hydrates corresponding to a given strength of hardened cementitious systems, there are two effects acting inversely with increasing dosage of superplasticizer in the published literature as proposed by Legrand and Wirquin [43,44]. One of the effects is the dispersing effect of superplasticizers on the cement particles enhancing their homogenous distribution and making filling of pores by hydration products easier. One another influence is physico-chemical action of superplasticizers on cementitious hydrates, changing their morphology and growth to bond with each other [43]. The later one cannot be detected by calorimetry. Due to these opposite effects competing each other, there would be an optimal value for dosage of admixtures providing the highest strength for a given w/c. The parabolic trends in compressive strength of mortars (Fig. 9) as a function of dosage of admixtures can be explained with these competing effects. In addition, the reductions in compressive strength of mortars after an extreme point depending on solid dosage of admixtures could also be associated with possible air entraining side effect of plasticizing agents [11,45,46]. A defoaming agent was not used in preparation of mortars, air-entraining effect of admixtures could be considerable in the case of no or insufficient amount of defoamers in composition of commercial admixtures. This fact could also be valid for LHA not containing any defoaming agent in its composition.

Regarding the influence of admixtures on compressive strength of mortars at 28 days shown in Fig. 9c, LHA addition did not caused a significant change in strength regardless of dosage whereas the mortar with LS exhibited a slightly higher or lower strength than the blank and LHA mortar depending on its dosage. On the other hand, the effect of admixtures on 28-day compressive strength of mortars was limited within a range of ±10% approximately.

Considering the compressive strength results together with isothermal calorimetry data indicating heat of hydration of cementitious systems (Figs. 2–5), it was observed that there is no direct correlation between them. A higher heat of hydration does not necessarily mean a higher mechanical strength in hardened cementitious system since formation of some hydration products does not contribute strength significantly while releasing considerable level of heat.

4. Conclusions

Based on the experimental results obtained in this study for humic acid-based superplasticizer derived from leonardite as a natural organic matter, the following conclusions can be drawn:

1. For all the tested dosages, the impact of humic-acid based superplasticizer derived from leonardite (LHA) on calorimetric signature of hydration of PC was so similar to that of naphthalene-based NA, without significant differences in the duration of induction period and the heat of hydration at the end of 72 h. An earlier conversion of ettringite to monosulfoaluminate observed in calorimetry was only characteristic difference in the case of LHA addition. LS caused dramatically longer retardations on early hydration of PC when compared to LHA, especially at relatively higher dosages.
2. For the equivalent dosage of admixtures providing a similar flow value of fresh mortars (0.3% solid dosage), LHA exhibited a somewhat comparable setting behavior with NA, unlike dramatic delays

in setting (more than 24 h in final setting with respect to the blank) caused by LS addition.
3. LHA addition resulted in increased degree of hydration of PC at 7 days as measured by chemically bound water content of hardened pastes, which was additionally higher than LS and NA. This was also the case at 28 days of age for solid dosages >0.3%.
4. LHA addition provided flow of mortar similar to NA and LS for approximately 0.3% equivalent solid dosage. For higher fluidity level of mortar corresponding to 110% or more flow value, efficacy of LHA and LS was found to be lower than NA.
5. LHA addition resulted in higher compressive strengths of mortars when compared to blank PC mortar at early and later ages for all the tested dosages. Comparing LHA with LS for the dosage of 0.3%, compressive strength of mortar with LHA addition at 3 days was similar with LS addition as being 18% higher than blank mortar. However, the mortar with NA exhibited higher compressive strength than with LHA and LS at 3 days for 0.3% dosage of admixtures.
6. Comparing LHA to NS and NA for the equivalent solid dosage providing the same level of flow in fresh mortars (0.3% solid dosage for 105% flow), it can clearly be suggested that LHA has a considerable potential to use as a superplasticizer in cementitious systems with its reasonable influences on hydration and properties of PC.
7. Regarding the potential industrial manufacturing of humic-acid based superplasticizers from leonardite as natural raw material, uniformity of the raw material would be critical in terms of qualitative stability of the superplasticizer. This concern should be taken into consideration for potential applications.

Author statement

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Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

References

[1] C.B. Cheah, et al., The engineering performance of concrete containing high volume of ground granulated blast furnace slag and pulverized fly ash with polycarboxylate-based superplasticizer, Construct. Build. Mater. 202 (2019) 909–921.
[2] P.R. de Matos, M. Foiato, L.R. Prudencio, Ecological, fresh state and long-term mechanical properties of high-volume fly ash high-performance self-compacting concrete, Construct. Build. Mater. 203 (2019) 282–293.
[3] H. AzariJafari, et al., Studying effects of chemical admixtures on the workability retention of zeolitic Portland cement mortar, Construct. Build. Mater. 72 (2014) 262–269.
[4] M. Sahmaran, I.O. Yaman, Hybrid fiber reinforced self-compacting concrete with a high-volume coarse fly ash, Construct. Build. Mater. 21 (1) (2007) 150–156.
[5] A. Duran-Herrera, et al., Evaluation of sustainable high-volume fly ash concretes, Cement Concr. Compos. 33 (1) (2011) 39–45.
[6] N.V. Chernysheva, et al., Composite gypsum binders with silica-containing additives, IOP Conf. Ser. Mater. Sci. Eng. 327 (2018), 032015.
[7] M.Yu Elistratkin, K.M. I, Analysis of the factors of increasing the strength of the non-autoclave aerated concrete, Construct. Mater. Prod. 1 (1) (2018) 10.
[8] N. Spiratos, M. P, N.P. Mailvaganam, V.M. Malhotra, C. Jolicoeur, Superplasticizers for Concrete, Canada, 2006.
[9] P.-C. Aitcin, *High-performance Concrete*. Modern Concrete Technology, E. & F.N. Spon. xxxii, London ; New York, 1998, 591 p.
[10] Y.F. Houst, et al., Design and function of novel superplasticizers for more durable high performance concrete (superplast project), Cement Concr. Res. 38 (10) (2008) 1197–1209.
[11] Aitcin, P.-C. and R.J. Flatt, Science and technology of concrete admixtures, in Woodhead Publishing Series in Civil and Structural Engineering Number 59. 2016, Woodhead Publishing is an imprint of Elsevier,: Cambridge, UK. p. 1 online resource.
[12] E.F.o.C.A. Association, Environmental Product Decleration, 2015 (United Kingdom).
[13] M.S. Ata, P. Wojtal, I. Zhitomirsky, Electrophoretic deposition of materials using humic acid as a dispersant and film forming agent, Colloid. Surface. Physicochem. Eng. Aspect. 493 (2016) 74–82.
[14] F.d. Souza, S.R. Bragança, Humic acid as dispersant of an alumina suspension and its rheological behaviour, Mater. Res. 21 (2) (2018).
[15] G.H. Zhang, H. Hao, J.F. Zhu, Synthesis of coal-water slurry dispersant based on humic acid, in: Advanced Materials Research, Trans Tech Publ, 2012.
[16] K. Zhang, et al., Synthesis of a novel humic acid-based polycarboxylic dispersant for coal water slurry, Int. J. Green Energy 14 (2) (2017) 205–211.
[17] G. Davies, et al., Humic Substances : Structures, Properties and Uses, Special publication, Cambridge, 1998. RSC. xii, 259 p.
[18] Y. Han, et al., Stability of carboxyl-functionalized carbon black nanoparticles: the role of solution chemistry and humic acid, Environ. Sci. Nano 4 (4) (2017) 800–810.
[19] M. Kaemmerer, et al., Extraction of humic substances from leonardite and their calcium complexation properties, Agrochimica 44 (3–4) (2000) 123–131.
[20] L. Cavani, C. Ciavatta, C. Gessa, Identification of organic matter from peat, leonardite and lignite fertilisers using humification parameters and electrofocusing, Bioresour. Technol. 86 (1) (2003) 45–52.
[21] F.D. Meng, et al., Leonardite-derived humic substances are great adsorbents for cadmium, Environ. Sci. Pollut. Control Ser. 24 (29) (2017) 23006–23014.
[22] Y. Gao, et al., Dispersion of multi-walled carbon nanotubes stabilized by humic acid in sustainable cement composites, Nanomaterials 8 (10) (2018) 858.
[23] V.C. Kelessidis, C. Papanicolaou, A. Foscolos, Application of Greek lignite as an additive for controlling rheological and filtration properties of water-bentonite suspensions at high temperatures: a review, Int. J. Coal Geol. 77 (3–4) (2009) 394–400.
[24] H. Shen, W.Y. Zhang, Synthesis of lignite graft polycondensate as drilling fluid additive and its influence on the properties of water-bentonite suspensions, Chem. Technol. Fuels Oils 53 (6) (2018) 922–932.
[25] L. Zhang, et al., Experimental study on the influence of coal powders on the performance of water-based polymer drilling fluid, Energy Explor. Exploit. 38 (5) (2020) 1515–1534.
[26] G. Ricca, et al., Structural investigations of humic-acid from leonardite by spectroscopic methods and thermal-analysis, Geoderma 57 (3) (1993) 263–274.
[27] I. Ben Salah, et al., Optimization of humic acid liquid fertilizer production from lignite: effect on wheat and barley seeds germination, Recent Adv. Environ. Sci. Euro-Mediterranean Surrounding Reg. (2018) 1375–1377. Vols I and Ii.
[28] R. Selladurai, T.J. Purakayastha, Effect of humic acid multinutrient fertilizers on yield and nutrient use efficiency of potato, J. Plant Nutr. 39 (7) (2016) 949–956.
[29] Y.H. Wang, S.H. Lin, R.S. Juang, Removal of heavy metal ions from aqueous solutions using various low-cost adsorbents, J. Hazard Mater. 102 (2–3) (2003) 291–302.
[30] W.W. Tang, et al., Impact of humic/fulvic acid on the removal of heavy metals from aqueous solutions using nanomaterials: a review, Sci. Total Environ. 468 (2014) 1014–1027.
[31] R. Klöcking, et al., Development of an innovative peat lipstick based on the UV-B protective effect of humic substances, Mires Peat (2013) 11.
[32] R. Klöcking, B. Helbig, Medical aspects and applications of humic substances, in: Biopolymers Online, A. Steinbüchel (Eds.), 2005.
[33] I. Pane, W. Hansen, Investigation of blended cement hydration by isothermal calorimetry and thermal analysis, Cement Concr. Res. 35 (6) (2005) 1155–1164.
[34] Ramachandran, V.S., Concrete admixtures handbook : properties, science, and technology. second ed. Building Materials Science Series. 1995, Park Ridge, N.J., U.S.A.: Noyes Publications. xxx, 1153 pages.
[35] H. Minard, et al., Mechanisms and parameters controlling the tricalcium aluminate reactivity in the presence of gypsum, Cement Concr. Res. 37 (10) (2007) 1418–1426.
[36] M.M. Alonso, F. Puertas, Adsorption of PCE and PNS superplasticisers on cubic and orthorhombic C(3)A. Effect of sulfate, Construct. Build. Mater. 78 (2015) 324–332.
[37] O. Burgos-Montes, et al., Compatibility between superplasticizer admixtures and cements with mineral additions, Construct. Build. Mater. 31 (2012) 300–309.
[38] F. Puertas, T. Vazquez, Early hydration cement. Effect of admixtures superplasticizers, Mater. Construcción 51 (262) (2001) 53–61.
[39] J.M. Torrents, J. Roncero, R. Gettu, Utilization of impedance spectroscopy for studying the retarding effect of a superplasticizer on the setting of cement, Cement Concr. Res. 28 (9) (1998) 1325–1333.
[40] C. Giraudeau, et al., Surface and intercalation chemistry of polycarboxylate copolymers in cementitious systems, J. Am. Ceram. Soc. 92 (11) (2009) 2471–2488.
[41] A. Habbaba, Z. Dai, J. Plank, Formation of organo-mineral phases at early addition of superplasticizers: the role of alkali sulfates and C3A content, Cement Concr. Res. 59 (2014) 112–117.
[42] L.H. Zhang, et al., Effects of saccharide set retarders on the hydration of ordinary Portland cement and pure tricalcium silicate, J. Am. Ceram. Soc. 93 (1) (2010) 279–287.
[43] C. Legrand, E. Wirquin, Influence of superplasticizer dosage on the quantity of hydrates needed to obtain a given strength for very young concrete, Mater. Struct. 27 (167) (1994) 135–137.

[44] C. Legrand, E. Wirquin, Study of the strength of very young concrete as a function of the amount of hydrates formed - influence of superplasticizer, Mater. Struct. 27 (166) (1994) 106–109.
[45] B. Łaźniewska-Piekarczyk, The influence of selected new generation admixtures on the workability, air-voids parameters and frost-resistance of self compacting concrete, Construct. Build. Mater. 31 (2012) 310–319.
[46] B. Łaźniewska-Piekarczyk, The methodology for assessing the impact of new generation superplasticizers on air content in self-compacting concrete, Construct. Build. Mater. 53 (2014) 488–502.