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# Strength development of solidified dredged sludge containing humic acid with cement, lime and nano-$SiO_2$

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## HIGHLIGHTS

- Application of nano-$SiO_2$ to cement-solidified dredged sludge (CDS) can significantly improve its strength development.
- Roles of cement, nano-$SiO_2$, humic acid, lime and curing age on the solidification effect were evaluated.
- Using lime together with cement for solidifying dredged sludge containing humic acid had advantages over using cement alone.
- The nano-$SiO_2$ content of 1.0% was considered the most cost-effective for improving the strength development of CDS.

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## ABSTRACT

The disposal of dredged sludge (DS) poses an increasingly difficult problem for sediment dredging engineering. This study investigated the strength development of solidifying DS containing humic acid (HA) with cement, lime and nano-$SiO_2$ (NS). A range of unconfined compressive strength (UCS) and pH tests were conducted to explore the roles of cement, NS, HA, lime and curing age on the solidification effect of DS. Furthermore, microstructures and crystalline phases of typical mixes were analyzed by scanning electron microscopy (SEM) and X-ray diffraction (XRD) tests. The results showed that the addition of NS can significantly improve the strength development of cement-solidified dredged sludge (CDS). The 60-day UCS of CDS with 1.0% NS was more than twice that without NS, concurrently, the addition of NS also reduced the pH of CDS. The HA seriously affected the strength development of CDS, and the influence threshold value of HA content was in the range of 4.5–5.0%. Using lime together with cement for solidifying DS containing HA had advantages over using cement alone, and the optimum mass ratio of lime to cement is 6:9. The optimum NS content of 1.0% was determined to be the most cost-effective for improving the strength development of CDS. The microstructure and mineralogy analysis confirmed that adding NS to CDS can effectively accelerate the hydration reaction and produce more calcium silicate hydrate (CSH), leading to a significant improvement in the strength of CDS.



## 1. Introduction

Dredging is a common method for river regulation and sediment removal from the bottom of lakes. However, dredging process will produce a large amount of dredged sludge (DS), which will not only occupy a large amount of land, but also cause serious secondary pollution. Due to the characteristics of high water content, fine particles, high compressibility, low strength and organic matter [1], the treatment of DS has become a worldwide problem. Traditional sludge treatment methods mainly include filling, air drying and heat treatment, however, these methods have many disadvantages of long cycle, high cost and unsatisfactory treatment effect and so on. The solidification technology is a widely used method of DS treatment. According to adding solidifying materials to the DS, through mixing and curing, a series of hydrolysis and hydration reactions occur between the sludge, water and solidifying materials, and a certain amount cementitious substance are produced, then improve the physical and mechanical properties of the DS. Generally, DS are soft soils with very low shear strength ($C_u$ < 50 kPa) [2], if solidified DS can be converted into geotechnical materials for civil engineering construction, which can not only consume a large amount of waste DS, but also effectively solve

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the problem of shortage of soil for construction. Previous studies show that the solidified DS have been extensively used in many fields, especially in civil engineering [3–5].

Portland cement is the most widely used as soft soil solidifying material because of its easy availability and reasonable price [6]. The main mechanism of cement-solidified soil is through the hydration of cement, produces the cementitious substances calcium silicate hydrates (CSH) and calcium aluminate hydrates (CAH), and then develops the strength [7–10]. However, the cement production will bring significant environmental impacts, such as increasing greenhouse effect, energy loss and the consumption of non-renewable natural resources [11–17]. Statistics show that $CO_2$ emissions from cement industry account for 6–7% of global $CO_2$ emissions [18–20]. Furthermore, cemented soil is usually highly alkaline, which has a negative impact on groundwater and plant growth [21–22]. Quicklime has a long history as another solidifying material for soft soil reinforcement [23–26], but quicklime is seldom used alone, usually in conjunction with cement for solidifying soft soil [27–28]. Cement is responsible for the primary strength development, while quicklime can provide significant alkaline environment and neutralizes acidic substances in soft soils. Similarly, the production of quicklime will also consume a lot of natural resources, leading a negative impact on the environment. Based on the purpose of controlling cement consumption and improving the strength of solidified DS, adding a small amount of additives is a promising way.

With the rapid development of nanotechnology, application of nanomaterials in civil engineering has gradually attracted considerable scientific interest of researchers and engineers [22,29–30]. The common nanoparticles used in cementitious composites are mainly $SiO_2$, $Al_2O_3$, MgO, $TiO_2$ and carbon nanotube [22,29,31–32]. Among the nanomaterials described above, nano-$SiO_2$ (NS) is the most widely used and plays the important role. Based on the high amount of pure amorphous $SiO_2$, NS has high pozzolanic activity [33–34]. In addition, NS has high surface energy and can react with $Ca(OH)_2$ to significantly promote cement hydration [35]. The effects of NS on the physical and mechanical properties of cementitious materials have been widely studied. Lin et al. [36] found that adding NS into sludge ash–cement mortar can effectively increase the strength and hydration rate. Stefanidou and Papayianni [32] reported that NS can make the cement structure denser and then improve the strength. Gao et al. [37] and Lo et al. [38] all explored the effect of NS on the alkali-activated properties of metakaolin-based geopolymers, and results showed that the incorporation of NS can improve the compactness and strength. In the field of geotechnical engineering, Bahmani et al. [29] studied a series of engineering properties of cement-treated residual soil, they found that the addition of NS can improve the compressive strength and promote the pozzolanic reaction. Therefore, it is expected that using NS as cement admixture for solidifying DS, its strength can be significantly improved under the control of cement dosage.

In addition, DS usually contains a certain amount of organic matter, and the presence of organic matter affects the geomechanical behavior of the DS itself and solidified DS. Generally, the organic matter in DS can be divided into humic and nonhumic groups, and humic acid (HA) is considered to be the main component of humic group [39]. Previous studies have confirmed that HA may seriously inhibit the hydration process of cement-based materials [40]. This could be explained that the existence of HA decreases the pH of pore solution, and then destroys the high alkaline environment needed for cement hydration [39]. Furthermore, the HA can coat the cementitious material particles when treated with cement-based materials, and then retard the hydration process [40]. However, the strength development characteristics of DS containing HA solidified with cement and NS have not been evaluated comprehensively.

This paper attempts to investigate the effectiveness of using cement, lime and NS as solidifying materials for solidifying DS. The unconfined compressive strength (UCS) is used as a control indicator to evaluate the strength development, and the pH values of solidified DS were determined as an auxiliary analysis index. The roles of NS on the solidification effect of cement-solidified dredged sludge (CDS) were studied in detail. Additionally, the roles of cement, HA, mass ratio of lime to cement (L/C) and curing age on the strength development of CDS were also explored. The microstructure and mineralogy analysis were conducted based on scanning electron microscopy (SEM) and X-ray diffraction (XRD), and then the microscopic mechanisms affecting strength development of CDS are analyzed. The findings in this study suggest that using NS as cement admixture for solidifying DS, which can effectively improve the strength development of CDS.

## 2. Materials and methods

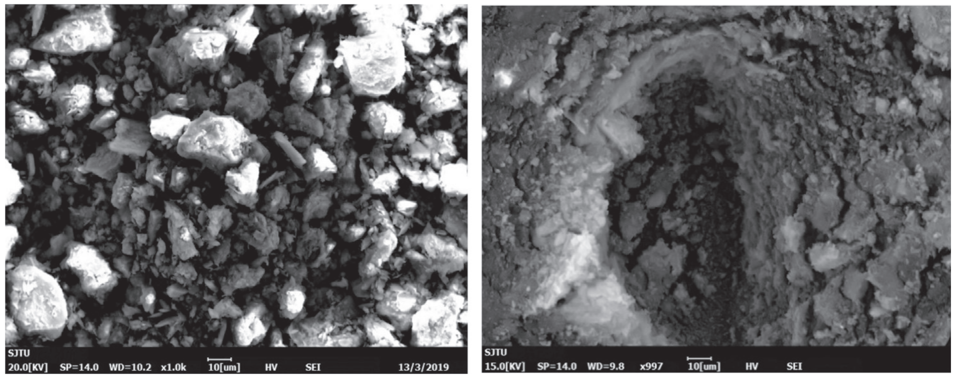
### 2.1. Materials

The DS used in this study was taken from a river dredging project in Minhang district, Shanghai, China. A series of materials characterization tests were carried out to determine the basic physical properties of DS. The DS had a liquid limit of 64.3%, plastic limit of 26.5%, and initial water content of 80–120%. The specific gravity was 2.69 and void ratio was about 2.12. Through the compaction tests, the optimum moisture content and maximum dry density was 22% and 1.73g/cm$^3$, respectively. Combined with the ASTM D4972-13 [41], the pH value of DS was determined to be 7.46. The chemical composition of DS determined by X-ray fluorescence (XRF) and shown in Table 1, which reveals that $SiO_2$ and $Al_2O_3$ were two dominant components in DS. Based on the scanning electron microscopy (SEM) and X-ray diffraction (XRD) tests, the microstructure and crystalline phase of DS are shown in Fig. 1(a) and 2, respectively. It could be seen that DS particles were irregular angled shape with porosity. The XRD pattern shows that quartz, illite and kaolinite were the main crystalline phase of DS. It is worth noting that the HA was considered to belong to the DS system, and it was used for preparing the HA-containing DS. The HA-containing DS samples were artificially synthesized by adding the designed proportions of HA powder to the DS samples. The binder used for solidifying DS are #42.5 ordinary Portland cement (OPC), quicklime and NS. The chemical composition of OPC is listed in Table 1. The quicklime white powder used in this study was obtained by grinding massive quicklime with a ball mill, and according to the information provided by the seller, the content

**Table 1**
The chemical composition of DS and OPC.

| Material | Chemical composition (%) | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $SiO_2$ | $Al_2O_3$ | $Fe_2O_3$ | $K_2O$ | CaO | $Na_2O$ | MgO | $TiO_2$ | $MnO_2$ | LOI |
| DS | 42.20 | 21.59 | 12.77 | 8.15 | 7.18 | 3.04 | 1.96 | 0.78 | 0.19 | 2.12 |
| OPC | 21.6 | 4.13 | 4.57 | 0.56 | 64.44 | 0.11 | 1.06 | – | – | 0.76 |

Notes: LOI: loss on ignition.




(a) DS (b) NS

**Fig. 1.** The microstructure of DS and NS.

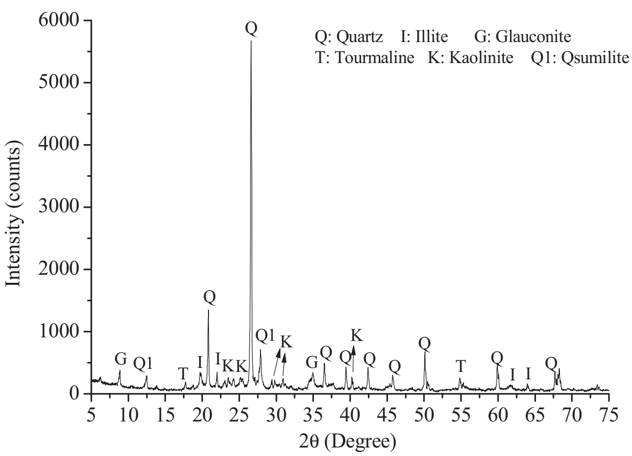



**Fig. 2.** The mineralogy of DS from XRD test.

of calcium oxide (CaO) is over 90%. The NS used was white powder and contained at least 99.8% $SiO_2$. The average particle size and surface area of NS were about 15 nm and 230 $m^2/g$, respectively. The microstructure of NS determined by SEM test is shown in Fig. 1(b).

## 2.2. Mix design and sample preparation

Table 2 presents the testing program and mix design of this study. The mix design was represented by the mass ratio of $M_s$:$M_b$:$M_w$ wherein $M_s$ is the mass of dry DS solid, $M_b$ is the mass of binder (including cement and lime) and $M_w$ is the mass of water. It is worth pointing out that when HA was added to the dry DS, the mass of dry DS includes the mass of HA, namely, HA was added to the DS in the form of internal mixing. As described in Table 2, the cement content ($C_c$) was characterized by the mass ratio of cement to dry DS solid; the lime content ($C_l$) was characterized by the mass ratio of lime to dry DS solid; the HA content ($C_h$) was characterized by the mass ratio of humic acid to dry DS solid; the total water content ($C_w$) was characterized by the mass of water to dry DS and binder ($M_s + M_b$), in terms of the natural water content of DS, the total water content of the mixture was controlled to 70%; the NS content ($C_n$) was characterized by the mass ratio of NS to the mixture ($M_s + M_b + M_c$). For the testing program shown in Table 2, series I was used to explore the influence of cement content, and series II was used to explore the role of NS compared to series I. Series III was used to explore the influence of NS content, and series IV was used to explore the role of HA compared to Series III. Series V was used to explore the influence of HA content. Series VI was used to explore the role of using lime and cement on the solidification effect of DS containing HA.

The sample preparation process can be described as follows. The DS was dried in the oven under the temperature of 105 °C ± 5 °C, then was crushed into powder by a ball mill and passed through 2 mm sieves. Combined with the mix design, the mass of raw materials and water were determined and weighed. Poured the weighed raw materials into the mixer and stirred for 5 min, then gradually added water and continued stirring for additional 5 min until the mixture was stirred evenly. The uniform DS-binder mixture was then placed into cylindrical PVC split moulds with the dimension of 50 mm in diameter and 50 mm in height. In order to control the dry density and ensure the homogeneity of samples between the different groups, the compaction process was conducted by a vibration machine to eliminate air pockets, and the height of each sample was strictly controlled to 50 mm. Furthermore, due to the water content of 70% was higher than the liquid limit of DS (64.3%), the vibration process would not affect the dry density significantly. The prepared samples together with moulds were placed in a standard curing room with the temperature of 25 °C ± 3 °C. After 10 days of curing, the solidified DS samples were demolded and sealed curing with plastic fresh-keeping films until 28 and 60 days. It is worth noting that after 7 days of curing, the samples containing HA were not strong to be demolded, thus the curing age was set at 28 and 60 days. The low strength after curing for 7 days might be that the total water content is higher than its liquid limit, and the cement-DS mixture was almost slurry form after mixing. In addition, the presence of HA seriously damaged the strength development of cement-DS mixture. In order to ensure the consistency of test results, three parallel samples were prepared for each mix and the average value was taken as the final test result, a total of 150 samples were prepared in this study.

## 2.3. Testing procedure

The unconfined compressive strength (UCS) of samples were tested as per to ASTM D4219-08 [42]. During the testing process, the vertical load was applied at a constant displacement rate of 1 mm/min until failure. Three samples were tested for each mix, and the average was taken as the strength. The pH value of samples cured for 60 days were tested using a pH tester, according to ASTM D4972-13 [41]. After UCS tests, weighed 20 g damaged sample for each mix, crushed and put into a 100 ml beaker, then 50 ml distilled water was added and stirred for 5 min with a stirring rod. After standing for 2 h, the pH value of supernatant was measured

**Table 2**
Testing program and mix design.

| Series | $M_s$:$M_b$:$M_w$ | $C_c$ (%) | $C_l$ (%) | $C_h$ (%) | $C_n$ (%) | $C_w$ (%) | Curing time (days) |
|---|---|---|---|---|---|---|---|
| I | 100:5:73.5<br>100:10:77<br>100:15:80.5<br>100:20:84 | 5<br>10<br>15<br>20 | 0 | 0 | 0 | 70 | 28, 60 |
| II | 100:5:73.5<br>100:10:77<br>100:15:80.5<br>100:20:84 | 5<br>10<br>15<br>20 | 0 | 0 | 1.0 | 70 | 28, 60 |
| III | 100:15:80.5 | 15 | 0 | 0 | 0<br>0.5<br>1.0<br>1.5<br>2.0 | 70 | 28, 60 |
| IV | 100:15:80.5 | 15 | 0 | 2.5 | 0<br>0.5<br>1.0<br>1.5<br>2.0 | 70 | 28, 60 |
| V | 100:15:80.5 | 15 | 0 | 0.5<br>1.5<br>2.5<br>3.5<br>4.5 | 1.0 | 70 | 28, 60 |
| VI | 100:15:80.5 | 13<br>11<br>9<br>7<br>5 | 2<br>4<br>6<br>8<br>10 | 3.5 | 1.0 | 70 | 28, 60 |

Notes: ($M_s$:$M_c$:$M_w$): Mass ratio of dry sludge to curing agent (including cement and lime) and water; $C_c$: cement content; $C_l$: lime content; $C_h$: humic acid content; $C_n$: nano-$SiO_2$ content; $C_w$: total water content.

with pH tester. The microstructural analyses of selected samples were conducted by employing scanning electron microscope (SEM) and X-ray diffraction (XRD). For the SEM tests, a COXEM EM-30 Plus SEM was used to acquire the microstructure images of samples. The samples for SEM tests were soaked in ethanol for 7 days, aiming to stop hydration reactions, and then freeze drying was conducted using liquid nitrogen. After sublimating for 48 h in a vacuum, the dried sample pieces not exceeding 7 mm in size were prepared for SEM testing. Before SEM testing, the samples were coated with a layer of gold on surface, then loaded into the SEM for capturing images. The granulated sample powder sieved through 75 μm sieves was used for XRD testing. The samples were scanned with the step length of 0.02° and scanning rate of 8°/min, starting from 5° to 75°. After XRD testing, the results were analyzed using MDI Jade 6.0 material analysis software.

## 3. Results and discussion

### 3.1. Role of cement on cement-solidified dredged sludge

Fig. 3 shows the effect of cement content on the unconfined compressive strength (UCS) and pH of cement-solidified dredged sludge (CDS). It could be observed that UCS increased with the increase of cement content. The main solidification mechanism in CDS is through the cement hydration, then produces the calcium silicate hydrates (CSH) and calcium aluminate hydrates (CAH), which are responsible for the strength development of CDS. Moreover, the Portlandite ($Ca(OH)_2$) also produced by cement hydration can react with clay minerals in DS, leading to the formation of CSH and CAH as well, which are responsible for the long-term strength development of CDS. After 28 days of curing, a rapid strength increase as the cement content increased to 15%. This is the reason that cement content of 15% was taken as the benchmark of other groups. When curing age increased to 60 days, the UCS increased linearly with the increase of cement content, implying that cement solidification method is one of the most effective ways for solidifying DS. The pH is an important parameter affecting the strength development of solidified soil [43]. The variation of pH with cement content is presented in Fig. 3(b). It is conspicuous that pH increased as the increase of cement content. The $Ca(OH)_2$ produced by cement hydration increased the alkalinity of CDS, then leading to the increase of pH value. The relationship between UCS and pH of CDS after curing for 60 days is shown in Fig. 4. The UCS increased with the increase of pH, implying that alkaline environment is essential to the strength development of CDS. This is attributed to the increase of pH improves the solubility of Si and Al in DS, which is conducive to the formation of CSH and CAH.

### 3.2. Role of nano-$SiO_2$ on cement-solidified dredged sludge

Figs. 5–7 show the roles of NS on the UCS and pH of CDS. After adding 1.0% NS to CDS, the contrast changes of UCS compared to that without NS is provided in Fig. 5. It is conspicuous that the UCS of CDS can be significantly improved by adding NS, Fig. 5(a) indicates that the UCS of CDS with 1.0% NS is far higher than that without NS. Furthermore, it is also observed that the 60-day UCS of CDS with 1.0% NS is more than twice that without NS, and under the condition of adding 1.0% NS, the 60-day UCS of CDS is far higher than 28-day UCS. The reasons can be explained as follows: (1) Due to the reaction between $SiO_2$ and $Ca(OH)_2$, the additional CSH was produced in CDS, leading to the significant improvement in UCS. (2) The addition of NS with high specific surface area accelerated the hydration of cement [29,44–45]. (3) The addition of NS caused many physical and mechanical changes, such as the improvement in compactness and the increase of cohesion between soil particles. Furthermore, cement hydration is a continuous process and the addition of NS is beneficial to the long-term strength development of CDS. With the progress of cement hydration, the consumption of

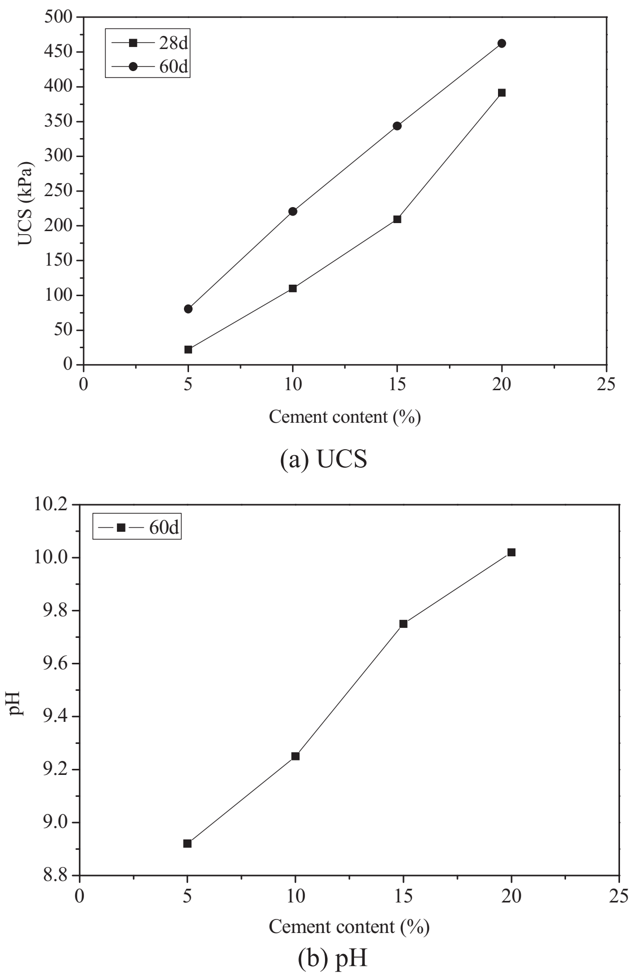



Fig. 3. Effect of cement content on the (a) UCS and (b) pH of CDS.

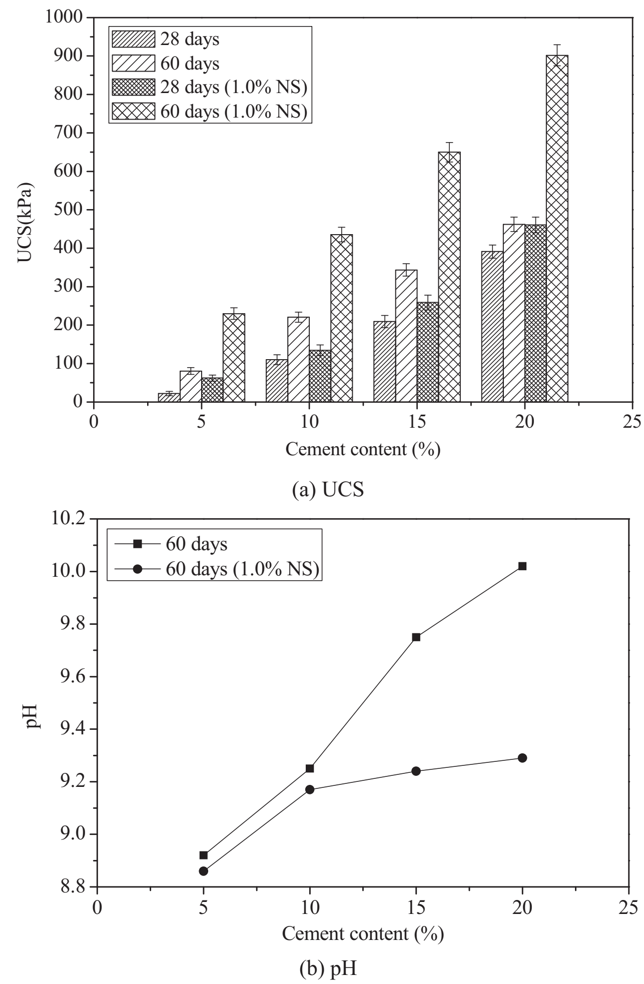



Fig. 5. Roles of adding 1.0% nano-$SiO_2$ on the UCS and pH of CDS.

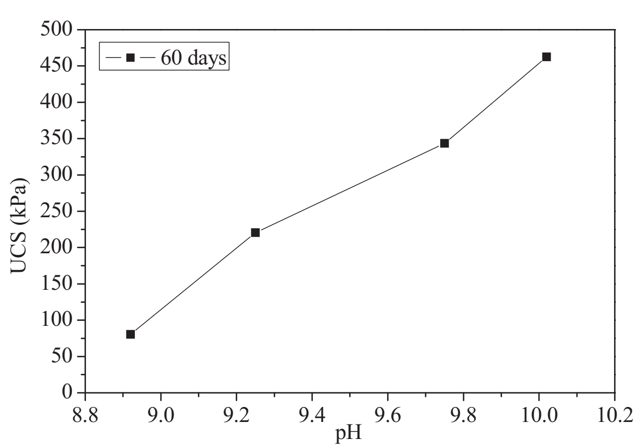
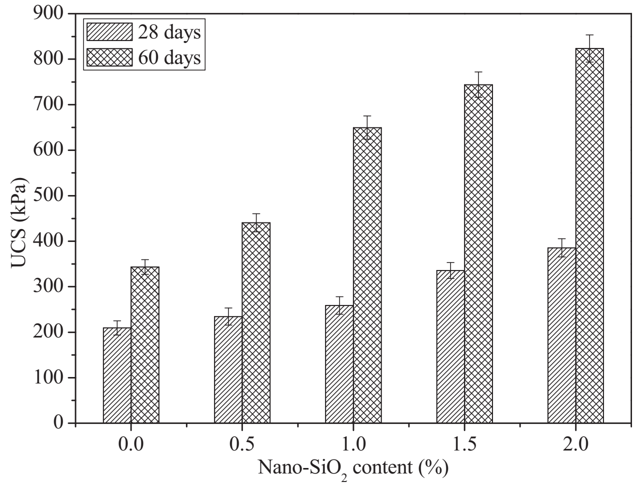



Fig. 4. The relationship between pH and UCS of CDS at 60 days.

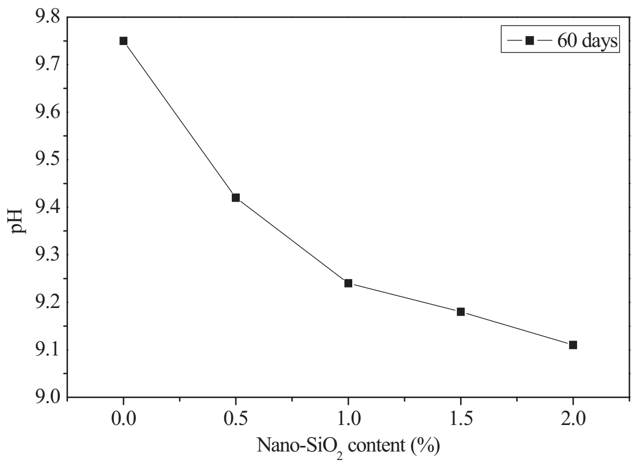
$Ca(OH)_2$ by NS accelerated the secondary hydration reaction, and then leading to the significant improvement in later strength. It could be presumed that the contribution of NS to the strength development of CDS is also related to the hydration degree of cement. A comparison of pH values is evident shown in Fig. 5(b), which reveals that the incorporation of NS decreased the pH of CDS obviously. This is attributed to the consumption of $Ca(OH)_2$ by NS through the secondary hydration reaction. This is consistent with the previous results reported by Bahmani et al. [29].

Fig. 6 shows the effect of NS content on the UCS and pH of CDS containing 15% cement content. It is clear that the UCS increased with the increase of NS content. This indicates that when using 15% cement for solidifying DS, the significant improvement in UCS can be achieved by increasing the NS content. Take the CDS with 1.0% NS as an example, its 60-day UCS is almost twice that of CDS without NS. As predicted, the pH of CDS decreased as the increase of NS content, shown in Fig. 6(b). The consumption of $Ca(OH)_2$ by NS in secondary hydration reaction was responsible for this phenomenon. However, it is conspicuous from Fig. 6(b) that the decreasing trend of pH is gradually slowed down with the increase of NS content. This indicates that adding NS is limited to reduce the pH value of CDS, and when NS content continues to increase, the pH value of CDS tends to be stable.

The relationship between UCS and pH of CDS with different NS contents is presented in Fig. 7. It is interesting found that the UCS decreased with the increase of pH value. The role of NS here can not only reduce the pH, but also improve the UCS of CDS. This is because NS consumed a large amount of $Ca(OH)_2$ and decreased the alkalinity of CDS, meanwhile, more CSH was produced by secondary hydration reaction between $SiO_2$ and $Ca(OH)_2$. Although alkaline environment is helpful to improve the UCS of CDS, noting that high alkaline also has a negative impact on the environment and the planting performance of CDS. Therefore, the “contradiction” between strength and alkalinity can be effectively alleviated to some extent by adding NS into CDS. It is desirable to use NS as cement admixture for solidifying DS, which not only improve the




(a) UCS




(b) pH

**Fig. 6.** Effects of nano-$SiO_2$ content on the (a) UCS and (b) pH of CDS.

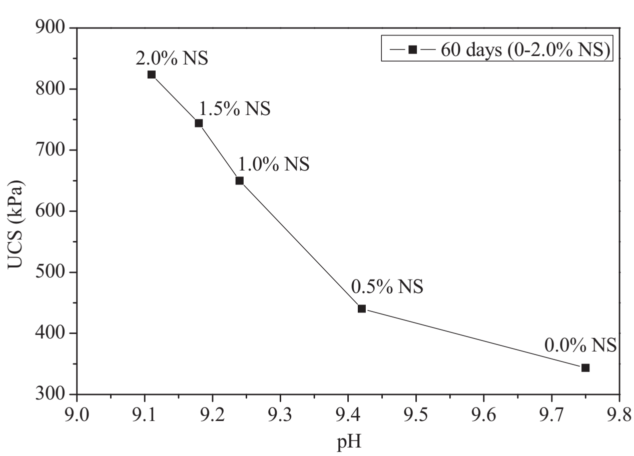



**Fig. 7.** Relationship between UCS and pH of CDS with different nano-$SiO_2$ contents.

strength development, but also can effectively control the alkaline of CDS.

### 3.3. Role of humic acid on cement-solidified dredged sludge

Fig. 8 shows the effects of NS and HA on the UCS of CDS. It is evident that the UCS of CDS decreased sharply with the addition of 2.5% HA. This indicates that HA seriously affects the strength development of CDS. The solidification effect will be greatly decreased when using cement alone for treating DS containing HA. The presence of HA reduced the pH of pore water solution in CDS, and meanwhile adsorbed calcium ions ($Ca^{2+}$) needed to produce cementitious substances, and then hindered the hydration of cement. HA can also decompose the cementitious substances that have been produced, resulting in a reduction in the final amount of cementitious substances, thereby reducing the strength of CDS. Additionally, HA also prevented the dissolution of Si and Al in DS, and then hindered the pozzolanic reaction which was responsible for the long-term strength development of CDS. This is attributed to that HA particles are much smaller than that of DS particles, and the micro-porous of HA results in its strong water holding and absorption capacity. It is also observed from Fig. 8 that the addition of NS can effectively improve the strength development of CDS containing HA, and the UCS increased with the increase of NS content. This shows that the addition of NS can weaken the side effect of HA on cement hydration. It could be presumed that due to the smaller particle size and higher surface energy, the binding ability of NS is stronger than that of HA, which not only inhibits the decomposition of cementitious substances to a certain extent, but also accelerates the hydration of cement. The above observations suggest that using NS as cement admixture for solidifying DS containing HA, which can effectively improve the strength development of CDS.

Fig. 9 shows the effects of HA content on the UCS and pH of CDS. It could be seen from Fig. 9(a) that when using 15% cement together with 1.0% NS for solidifying DS containing HA, the UCS gradually decreased with an increase in HA content. This indicates that with the increase of HA content, the hindrance to cement hydration and the decomposition of cementitious substances increased gradually, which leads to the gradual decrease of UCS. However, it is conspicuous that with the increase of HA content, the decrease of UCS tended to be stable. So, it could be presumed that there is a threshold value for the influence of HA content on the UCS of CDS. When HA content is less than threshold value, the UCS decreases with the increase of HA content; while as the HA content is greater than threshold value, the increase in HA content has little effect on the UCS. It is therefore possible that the threshold value is in the range of 4.5–5.0%. This is in line with results of Zhu et al. [46]. This can be explained that when HA content exceeds threshold value, the amount of cementitious substances is very small. At this time, the UCS of CDS mainly comes from the improvement in physical and mechanical properties caused by cement, not from the amount of cementitious sub-

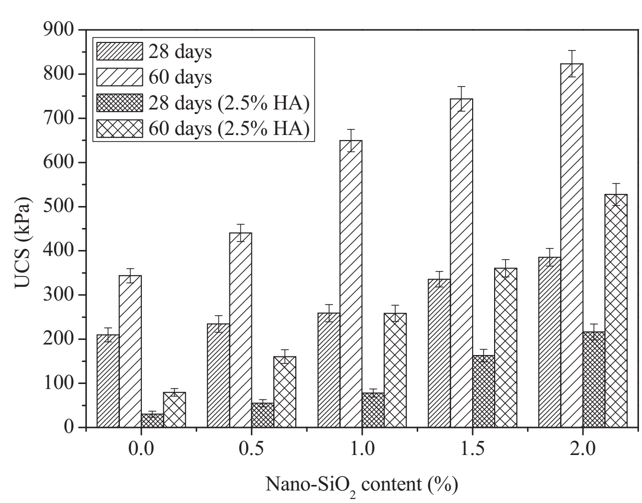



**Fig. 8.** Effects of nano-$SiO_2$ and humic acid on the UCS of CDS.

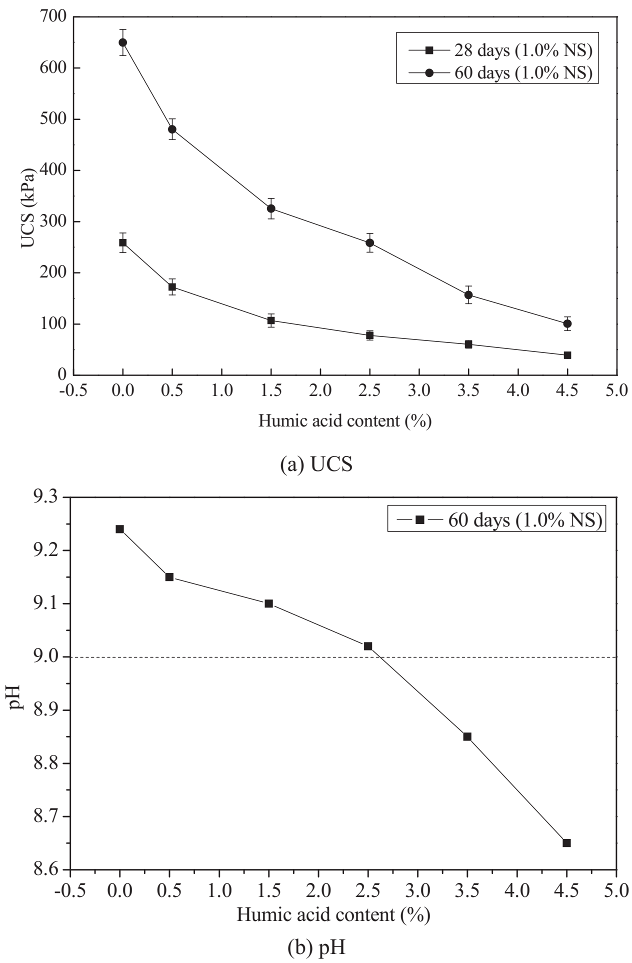



**Fig. 9.** Effects of humic acid content on the (a) UCS and (b) pH of CDS.

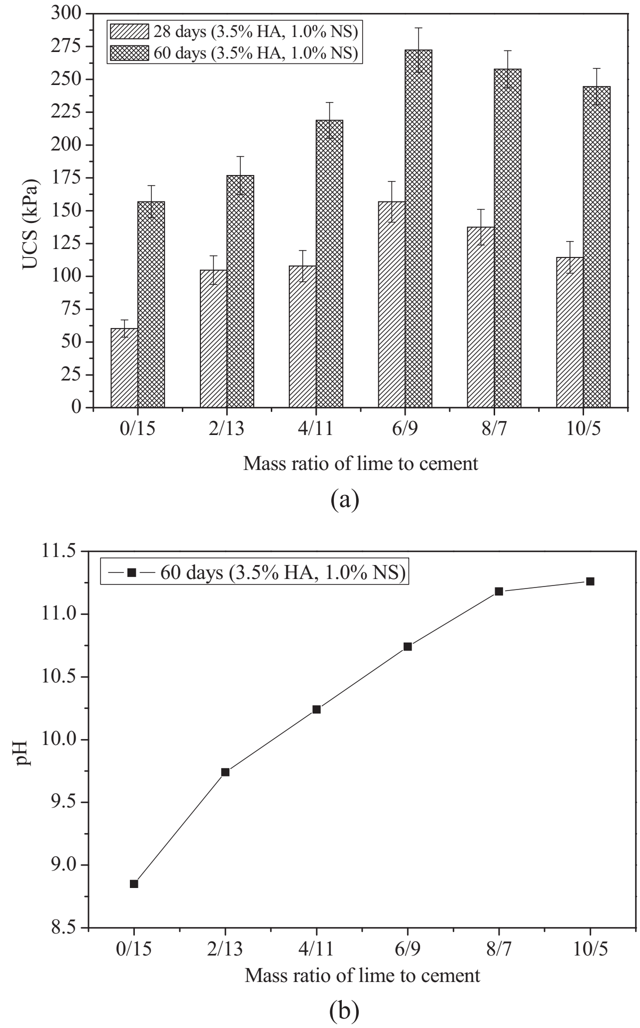



**Fig. 10.** Effects of mass ratio of lime to cement on the (a) UCS and (b) pH of CLDS.

stances. The effect of HA content on the pH of CDS is shown in Fig. 9(b). As predicted, the pH of CDS decreased with the increase of HA content. The previous research has revealed that if the pH is <9, no cementitious substance produced by cement hydration are formed [40]. If so, when HA content exceeds 2.5%, no cementitious substances formed in CDS. However, it could be clearly seen that although the HA content exceeds 2.5%, the UCS of CDS increased with curing age. This is also confirmed that the addition of NS is conducive to the strength development of CDS containing high HA content (pH < 9).

### *3.4. Role of lime on cement-solidified dredged sludge*

In order to alleviate the serious strength loss of CDS caused by the existence of HA. The effectiveness of using lime together with cement for solidifying DS containing HA was investigated. For the DS containing 3.5% HA, the effect of mass ratio of lime to cement (L/C) on the UCS and pH of cement lime-solidified dredged sludge (CLDS) is shown in Fig. 10. It could be observed from Fig. 10(a) that the UCS of CLDS increased first and then decreased with the increase of L/C, and reached the maximum as the L/C of 6:9. Compared with DS containing 3.5% HA solidified by 15% cement alone, the solidification effect can be improved significantly by using 6% lime together with 9% cement. The strong hydration reaction occurred when lime met water, and produced more alkaline $Ca(OH)_2$. Additionally, the hydration rate of lime is much faster than that of cement, so $Ca(OH)_2$ produced by lime hydration was preferentially used to neutralize the acidic substances in DS, then ensured a certain amount of cementitious substances in CLDS. However, there is an optimum L/C in CLDS, when lime is excessive, although it can further neutralize acidic substances in DS, the further reduction of cement content will also limit the strength development of CLDS. In addition, excessive lime will also produce larger expansion pressure and cause destructive volume deformation, and then seriously affect the strength development. Therefore, it is desirable to use 6% lime and 9% cement instead of 15% cement alone for solidifying DS containing HA. The variation of pH with L/C for CLDS is given in Fig. 10(b). The pH increased gradually and then tended to be flat with the increase of L/C. This indicates the alkaline environment of CLDS is formed by lime and cement together. The relationship between UCS and pH of CLDS is shown in Fig. 11. It is clear that UCS increased first and then decreased with the increase of pH, implying that there is an optimum alkaline environment for the strength development of CLDS containing HA. It is interesting seen that the optimum pH of 10.75 which corresponds to the maximum UCS of CLDS.

### *3.5. Role of curing age on cement-solidified dredged sludge*

The curing age is of great importance for the strength development of CDS [47]. The strength difference based on curing age can be used to evaluate the effect of binder content on the strength development of solidified soil [48], and then determines the opti-

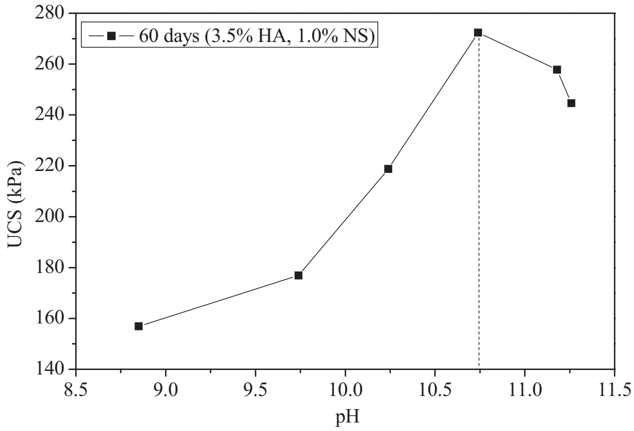



**Fig. 11.** Relationship between UCS and pH of CLDS.

mum cost-effective binder content. The strength difference (ΔUCS) and strength growth rate ($UCS_{gr}$) of CDS were defined as follows:

$$\Delta UCS = UCS_{(60)} - UCS_{(28)} \tag{1}$$

$$UCS_{gr} = \frac{UCS_{(60)} - UCS_{(28)}}{UCS_{(28)}} = \frac{\Delta UCS}{UCS_{(28)}} \tag{2}$$

where ΔUCS is the strength difference of CDS, kPa; $UCS_{(60)}$ and $UCS_{(28)}$ are the 60-day and 28-day strength of CDS, respectively, kPa; $UCS_{gr}$ is the strength growth rate of CDS.

Fig. 12 shows the ΔUCS and $UCS_{gr}$ of CDS containing 0.0% and 2.5% HA versus different NS content. For CDS without HA, as shown in Fig. 12 (a), the ΔUCS increased rapidly at first and then tended to stable with the increase of NS content. The $UCS_{gr}$ increased first and then decreased with the NS content, and reached the maximum when NS content was 1.0%. Additionally, the $UCS_{gr}$ was greater than 1.0 when NS content exceeded 1.0%. For the CDS containing 2.5% HA, as shown in Fig. 12(b), the ΔUCS increased linearly at first and then kept stable, as the NS content increased to more than 1.5%, the ΔUCS continued to increase linearly. Similarly, when $UCS_{gr}$ reached the maximum, the corresponding NS content was 1.0%, and $UCS_{gr}$ was always greater than 1.0, implying the positive role of NS on the strength development of CDS containing HA with the increase of curing age. Based on the above observations, it is suggested that using 1.0% NS as cement admixture for solidifying DS, especially DS containing HA, which will be the most cost-effective for the strength development of CDS.

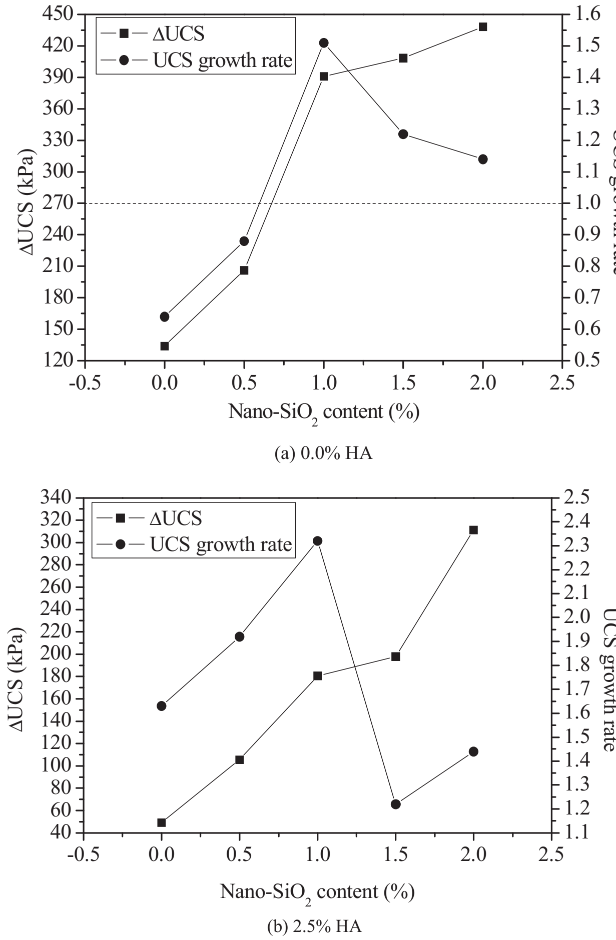



**Fig. 12.** The ΔUCS and UCS growth rate of CDS containing (a) 0.0% HA and (b) 2.5% HA versus NS content.

### 3.6. SEM analysis

Typical SEM micrographs, taken at magnification of 1000 times, for solidified DS with cement, lime and NS at 28 days are shown in Fig. 13. It is evident that with the increase of cement content, the amount of cementitious products increased and the cementation bond between cementitious products and DS particles became stronger (Fig. 13(a)–(c)). In general, strength development of cement-solidified soil depends on the cementation bond [49]. After 28 days of curing, the pores between the DS particles were filled with hydration products CSH and CAH, confirming that CSH and CAH are the main hydration products of cement. Fig. 13 (d)-(f) show the microstructure of solidified DS with 15% cement together with 1.0, 1.5 and 2.0% NS, respectively. Compared with CDS without NS, the CDS admixed NS exhibited denser microstructures. This observation is in line with results of Abbasi et al. [50]. The addition of NS accelerated the hydration of cement, and more CSH was produced. Additionally, the amount of CSH and the compactness of microstructure increased with the increase of NS content. For the CDS containing 2.5% HA, the amount of CSH and CAH was very few in the SEM image, and the microstructure was not close-knit (Fig. 13 (g)). Fig. 13 (h) shows the microstructure of DS containing 3.5% HA solidified with cement, lime and NS. Compared with CDS containing HA, the denser and cementation microstructure was evident in CLDS. The above observations are well demonstrated that the strength development of solidified DS depends on the amount of hydration products, the compactness of microstructure and the cementation degree of DS particles.

### 3.7. XRD analysis

The crystalline phases determined by XRD tests are provided in Fig. 14 for typical CDS samples at 28 days. Evidently, quartz (Q), kaolinite (K), berlinite (B) and illite (I) were detected in all tested CDS samples, indicating the main mineralogical components of DS. Furthermore, hydration products CSH and CAH were also detected in all tested samples, confirming that the CSH and CAH were the main hydration products of cement. The $Ca(OH)_2$ was detected in the DS solidified by 15% cement only, while it was absent in other CDS samples. This was attributed to the secondary hydration reaction caused by the addition of NS. Moreover, the existence of HA hindered the hydration of cement, and then very little $Ca(OH)_2$ produced. It is clear found that the additional CSH was discovered after adding 1.0% NS to CDS, which is consistent with the previous research [32,35,51]. This observation can well confirm the significant improvement in strength with the addition

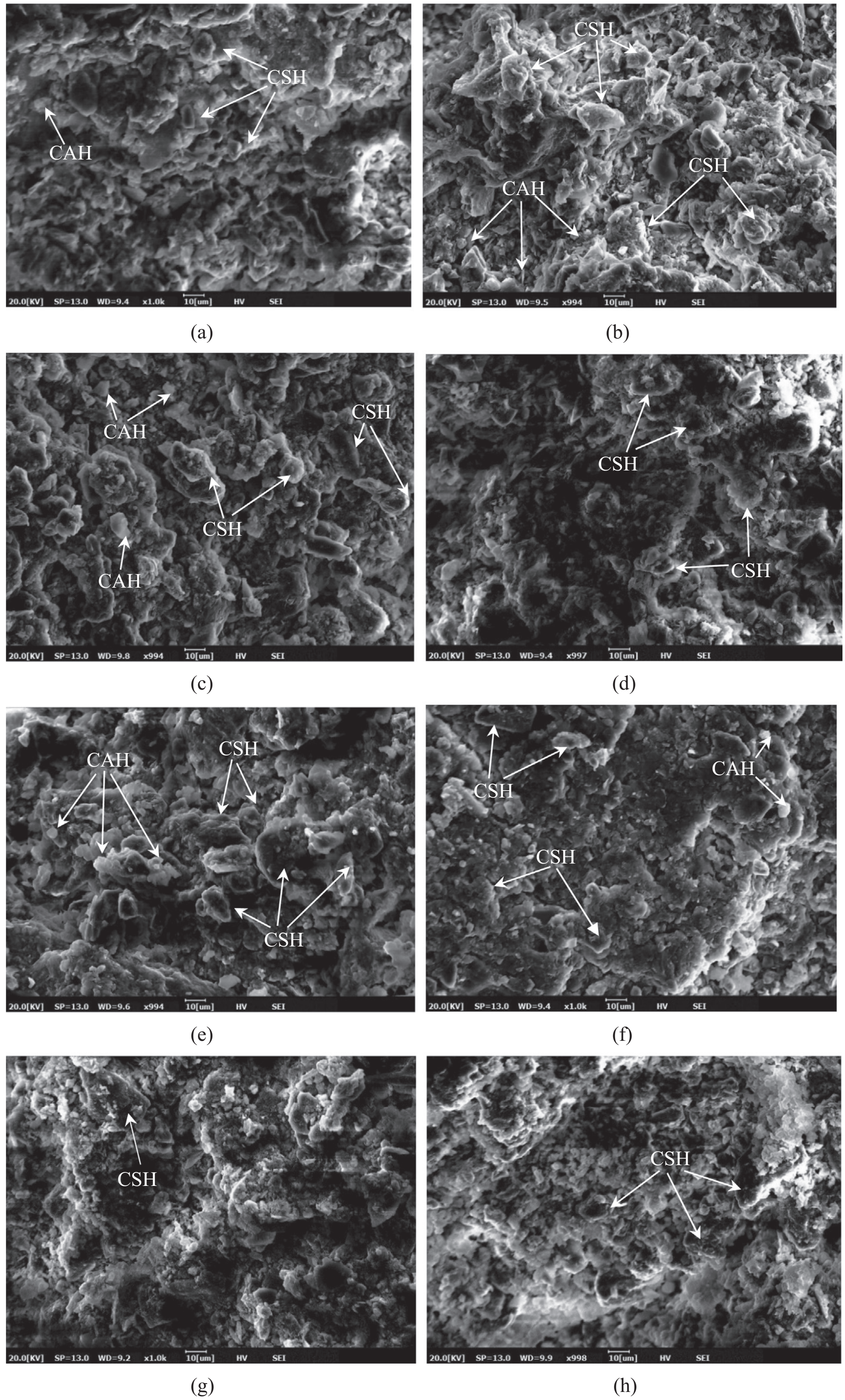



**Fig. 13.** SEM images of solidified dredged sludge with (a) 10% cement, (b) 15% cement, (c) 20% cement, (d) 15% cement + 1.0% NS, (e) 15% cement + 1.5% NS, (f) 15% cement + 2.0% NS, (g) 15% cement + 1.0% NS (containing 2.5% HA) and (h) 9% cement + 6% lime + 1.0% NS (containing 3.5% HA).

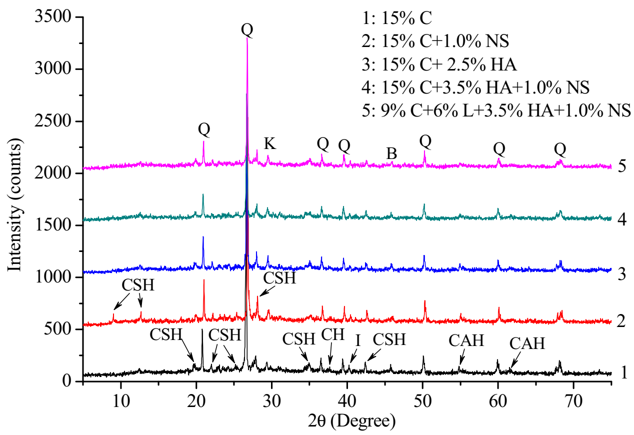



**Fig. 14.** XRD diffractograms of CDS at 28 days. The abbreviations stand for Q-quartz, K-kaolinite, B-berlinite, I-illite, CSH-calcium silicate hydrate, CAH-calcium aluminate hydrate, CH-$Ca(OH)_2$.

of NS. The CSH was also detected in the CDS containing HA, especially CLDS, implying that using the binder combination of cement, lime and NS instead of cement alone, which can effectively improve the strength development of CDS.

## 4. Conclusions

This study investigated the strength development of solidified dredged sludge (DS) containing humic acid (HA) with cement, lime and nano-$SiO_2$ (NS), and the roles of cement, NS, HA, lime and curing time were examined. Additionally, the microstructures and crystalline phases of typical mixes were analyzed by scanning electron microscopy (SEM) and X-ray diffraction (XRD) tests. The following conclusions can be drawn:

(1) The UCS of cement-solidified dredged sludge (CDS) increased almost linearly with the increase of cement content. The increase of pH significantly affected the strength development of CDS, this was attributed to the solubility of Si and Al was improved. The UCS increased with the increase of pH, confirming that alkaline environment was conducive to the strength development of CDS.
(2) Adding NS to CDS can significantly improve the UCS of CDS, and the 60-day UCS of CDS with 1.0% NS was more than twice that without NS. The addition of NS contributed to the decrease of pH value. The UCS and pH increased and decreased with the increase of NS content, respectively. Using NS as cement admixture can not only improve the strength development of CDS, but also control its pH level.
(3) The existence of HA seriously affected the strength development of CDS. The UCS of CDS containing HA can be effectively improved by the addition of NS, and increased with the increase of NS content. The UCS and pH of CDS gradually decreased with the increase of HA content, and there was an influence threshold value of HA content on the strength development of CDS, which was in the range of 4.5–5.0%. Moreover, it is desirable to use lime together with cement instead of cement alone for solidifying DS containing HA, and the optimum mass ratio of lime to cement (L/C) was 6:9. The optimum pH of cement-lime-solidified DS (CLDS) was 10.75, which corresponded to the maximum UCS of CLDS.
(4) The strength difference (ΔUCS) and strength growth rate ($UCS_{gr}$) based on the curing age were used to evaluate the strength development of CDS. The $UCS_{gr}$ increased first and then decreased with the increase of NS content, and achieved the maximum when NS content was 1.0%. So, it is suggested that using 1.0% NS as cement admixture for solidifying DS, which will be the most cost-effective for the strength development of CDS.
(5) The SEM images indicated that the strength development of CDS depended on the amount of hydration products, the compactness of microstructure and the cementation degree of DS particles. Furthermore, the main hydration products detected by XRD tests for CDS included CSH and CAH, and the addition of NS was conducive to produce the additional CSH in CDS.

## 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.

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