Influence of pH and salt solution on the sedimentation properties of fine bauxite tailings

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Abstract: Bauxite tailings slurry is a type of solid waste produced in the process of bauxite washing and beneficiation. It has poor engineering properties, that is, self-consolidation settlement unusually cannot be completed during several decades. To investigate the sedimentation properties of bauxite tailings, bauxite tailings slurry, phyllite residual soil, and kaolinite, we conduct sedimentation tests on these materials in varying pH and salt solution environments. The influence mechanism of the surface electrical properties of clay particles on the settlement of tailings slurry is investigated using the zeta potential test. The findings reveal that increases in the cation concentration and valence state lead to compression of the electric double layer on the surface of three types of soil particles, resulting in a decline in the repulsive potential energy and an increase in the gravitational potential energy. This in turn contributes to a reduction in the settling stable void ratio. As the pH increases, the zeta potentials of the three soils gradually decrease from positive to negative. A change in the pH at the isoelectric point, PZC_{edge}, triggers the transformation of the kaolinite mineral arrangement. When the pH is either greater than or less than the isoelectric point, an increase or decrease in the pH results in expansion of the electric double layer of the clay particles and an increase in the pore content. The results of this study suggest that bauxite tailings mud is more likely to settle in an acidic environment than in an alkaline environment, thus an acidic settling environment should be utilized for bauxite tailings produced in industrial production.

Keywords: tailings slurry, sedimentation properties; zeta potential, pH, salt solution

1. Introduction

As a waste material resulting from mining and mineral processing, tailings slurry possesses engineering characteristics that include an exceptionally high water content and challenging consolidation and settlement processes. To address the disposal of tailings slurry, artificial construction of tailings dams is commonly employed for storage purposes. However, artificial dams have significant risks and environmental drawbacks (Sun et al., 2020; Kossoff D et al., 2014). Therefore, a thorough understanding of the sedimentation behavior of tailings is essential.

Fine mine tails mostly consist of clay minerals, such as kaolinite, illite, vermiculite, mica, and quartz (Liu et al., 2020; Zheng et al., 2021; Shriful Islam, 2021). Clay minerals are usually charged on the surface (Mitchell et al., 2005), which results in larger diffuse double layers forces compared to the particle gravity. Thus, it is challenging to consolidate fine mail tailings under gravity stress, and they maintain a mud state for several decades (Shamsai et al., 2007). The diffuse double layers are strongly affected by the chemical environment, and the increasing electrolyte concentration or decreasing dielectric constant can restrain the thickness of the diffuse double layers (Di et al., 1994; Sridharan et al., 1982). It is expected that the influence of dissolved salts in the liquor on high solids tailings flocculation will be significant. This will depend on how certain cations interact with the tailings surface and the polymer molecule. (Liu et al, 2020; Peng and Di, 1994). When the ionic strength is high, divalent cations such as calcium can compress the electrical double layer and reduce the distance between particles. This can facilitate coagulation and increase the effectiveness of subsequent flocculant addition. However, as the salt

concentration increases, the polymer molecule in solution also contracts. This contraction occurs because counter-ions shield the electrostatic fields around charged functionalities, causing the polymer chains to coil. Usually, this process increases the movement of polymer chains in the liquor, which enhances the mobility of polymers adsorbed on the surface. In the case of adsorbing an anionic polymer onto a quartz surface, which is a common phase in tailings slurries, molecular dynamic simulations indicate that increased NaCl salinity would enhance adsorption. However, the subsequent decrease in the polymer's radius of gyration could limit the achievable aggregate sizes. (Quezada et al, 2018). Therefore, the sedimentation of clay is strongly affected by the chemical environment.

The sedimentation structure of clay depends on the pH and salt solution concentration. The kaolinite support forms edge-face flocculation in sediment in an acidic environment. It is more complex in the alkaline environment. It possesses a dispersed structure on the contrary flocculation in a high ion concentration environment (Nasser et al., 2006; Kaya et al., 2006). The isoelectric pH also has a strong effect on the sedimentation structure of kaolinite. Increasing the ion concentration can weaken flocculation when the pH of the solution is less than the isoelectric pH. In contrast, it can promote flocculation when the pH of the solution is greater than the isoelectric pH (Wang et al., 2006; Rand et al., 1977). The coagulation between particles increased in the presence of various ions, which was directly related to their higher valences. As the ion valences increased, their ability to coagulate Na-montmorillonite particles and compress the electric double layer was also enhanced (Liu et al.,2017). Bentonite is more strongly affected by the ion concentration, and increasing the ion concentration can restrain the stable sedimentation height because of the abundant diffuse double layers on its surface (Gajo et al., 2007; Thyagaraj et al., 2013; Witteveen et al., 2013).

The presence of inorganic ions had a significant impact on the interaction between polymer flocculants and clay particles during tailings settling. The study found that the introduction of 8 mM Mg^{2+} or Ca^{2+} increased the settling rate of oil sands tailings when using 20 ppm H-PAM. (Sworsk et al., 2000). The increase in flocculation was attributed to the improved bridging between particles and polymers, which was facilitated by divalent cations. (Long et al., 2006). (Mpofu et al., 2003) found that a kaolinite suspension treated with 500 g/ton of H-PAM showed enhanced flocculation in the presence of 0.001 M Ca^{2+} at pH 10.5 and 0.001 M Mn^{2+} at pH 7.5. Additionally, (Mietta et al., 2009) observed increased agglomeration of kaolinite even in the absence of flocculant with the introduction of NaCl and $MgCl_2$ at concentrations up to 1 M and 0.5 M, respectively. The increased agglomeration of kaolinite in the presence of NaCl and $MgCl_2$ was attributed to the decreased electrical repulsion between kaolinite particles in salt solutions. On the other hand, the presence of adsorbed Fe^{3+} on clay minerals could significantly alter the surface chemistry of the minerals, thereby affecting their settling characteristics. Jun et al. observed that the interactions between pure kaolin and coal were less significant compared to those between kaolin doped with iron and coal. (Chen et al., 2020).

Polymer flocculants have been utilized to accelerate the sedimentation of fine mine tailings in industrial operations (Liu et al., 2020; Dong et al., 2023). The geotechnical properties of soil stabilized with organic polymers, such as failure strength, permeability, swelling and shrinkage, durability, and stability, have been extensively studied. When evaluating the impact of polyvinyl alcohol (SH polymer) on recycled granite residual soil, it was found that the impact resistance of soil samples improved significantly, and the soil microstructure was more tightly bonded (Yuan et al.,2022). Researchers have conducted extensive studies at both laboratory and industrial scales to investigate the flocculation of fine clay particles by polymers with the aim of improving the efficiency of solid-liquid separation. (Mierczynska et al.,2013; Mpofu et al.,2005; Cengiz et al.,2009).Polymer flocculants promote sedimentation of mine tailings via polymer chains, which adsorb the clay particles on the surface, causing the fine particle flocculate to form aggregates, and increasing the gravity weight results expedites the sedimentation (Bian et al., 2018; Ji et al., 2023; Moudgil et al., 1987). The polymer dosage is an essential factor influencing the efficiency of solid-liquid separation. There is an optimal dosage for mine tailings. A dosage lower than the optimal dosage results in the insufficient coverage of the particle surface, while a larger than optimal dosage results in surplus polymer chains (Wu et al., 2020; Masliyah et al., 2011). These phenomena can reduce the efficiency of sedimentation of mine tailings. Novel polymer flocculants have been studied to promote the sedimentation of fine mine tailings based on non-ionic polyacrylamide (Gumfekar et al., 2018; Rey et al., 1988). Ionic polyacrylamide enhances the

settlement of mine tailings because the particle surface absorbs the ions (Liu et al., 2018). However, the efficiency of the solid–liquid separation is very low, and it continues to impose high operational and capital costs (Joseph-Soly et al., 2019).

In conclusion, the chemical environment is a critical determinant of the settlement and consolidation processes. To gain further insights into the settlement mechanism of tailings slurry, a series of studies were conducted by comparing three types of clay minerals. The purpose was to explore the influence of the surface electrical properties of clay minerals on the settlement of tailings slurry in different salt solution environments, as well as its evolution and internal mechanisms. Sedimentation, nuclear magnetic resonance, and zeta potential tests were employed. The findings of this research offer a profound understanding of the characteristics of tailings slurry.

2. Materials and methods

2.1. Materials

For this experiment, three types of soil samples were selected . The mine tailings was obtained from the third phase of the washing workshop of China Aluminum Guangxi Branch, located in Pingguo City, Guangxi Zhuang Autonomous Region, China. Phyllite residual soil was collected from Longsheng County, Guangxi Zhuang Autonomous Region, while kaolinite was taken from Baoding City, Hebei Province, China. Table 1 provides essential information about the physical and chemical properties of the three samples, including their specific surface area, liquid plastic limit, and specific gravity.
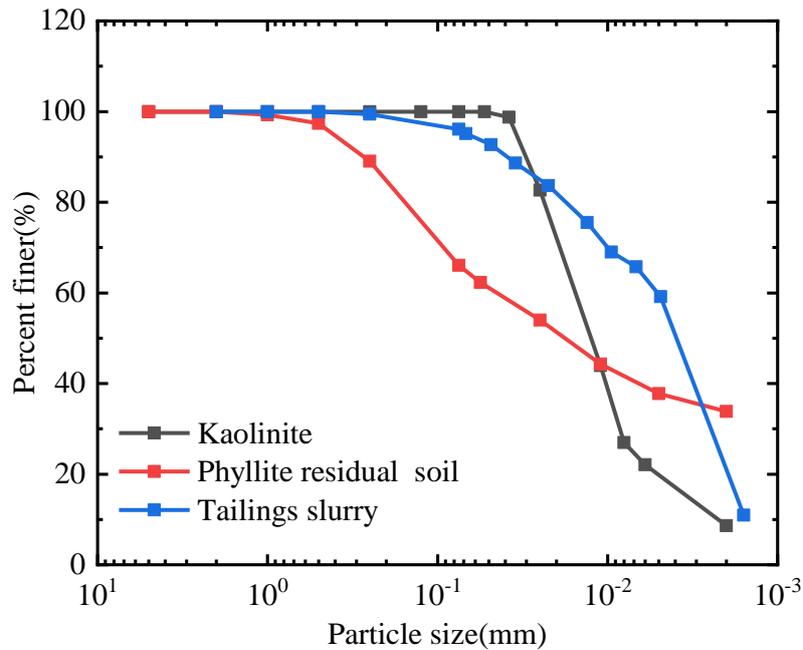
Fig. 1. Particle gradation curve of three soils

Table 1. Physical property indices of the three samples

Soil sample	Specific surface area S (m^2/g)	Cation exchange capacity CEC (mmol/100 g)	Liquid limit	Plastic limit	Specific gravity	Granulometric composition (%)		
						grit 2–0.075	powder particle 0.075–0.005	clay particle ≤ 0.005
Tailings slurry	55.09	8.44	52.20	29.3	2.74	3.93	36.89	59.18
Phyllite residual soil	51.43	8.70	70.00	32.80	2.88	33.90	28.36	37.74
Kaolinite	1.23	55.47	54.40	29.5	2.73	0.00	78.94	21.06

Additionally, Fig. 1 shows the particle distribution curve of the samples. It is evident that all three soils contain a substantial amount of clay particles. The chemical compositions of the Tailings slurry, Phyllite residual soil and Kaolinite are tested via X-ray fluorescence (XRF) spectrometry, and the results are listed in Table 2. The corresponding X-ray diffraction (XRD) results are shown in Fig. 2(a), (b) and (c), respectively for the mud, cement and metakaolin. The XRD patterns of tailings slurry and phyllite residual soil are similar. Both of them contain kaolinite and quart, amongst which kaolinite is the predominant mineral component. The Kaolinite mainly contains kaolinite,quartz, Orthoclase, illite and Albite. The proportion of specific minerals is shown in Table 3. Initial zeta potential of three minerals as shown in Table 4.

Table 2. X-ray fluorescence spectrum analysis

Soil sample	Al_2O_3 /%	CaO/ %	Fe_2O_3/ %	K_2O/ %	MgO/ %	MnO/ %	Na_2O/ %	P_2O_5/ %	SiO_2/ %	TiO_2/ %
Tailings slurry	0.87	0.61	19.02	0.91	1.07	0.09	0.40	0.15	37.14	2.06
Phyllite residual soil	25.63	0.35	22.11	0.02	0.55	0.07	0.13	0.19	33.22	3.86
Kaolinite	14.43	1.57	0.14	3.49	1.16	0.02	5.43	0.02	70.70	0.02

(a) Tailings slurry

(b) Phyllite residual soil
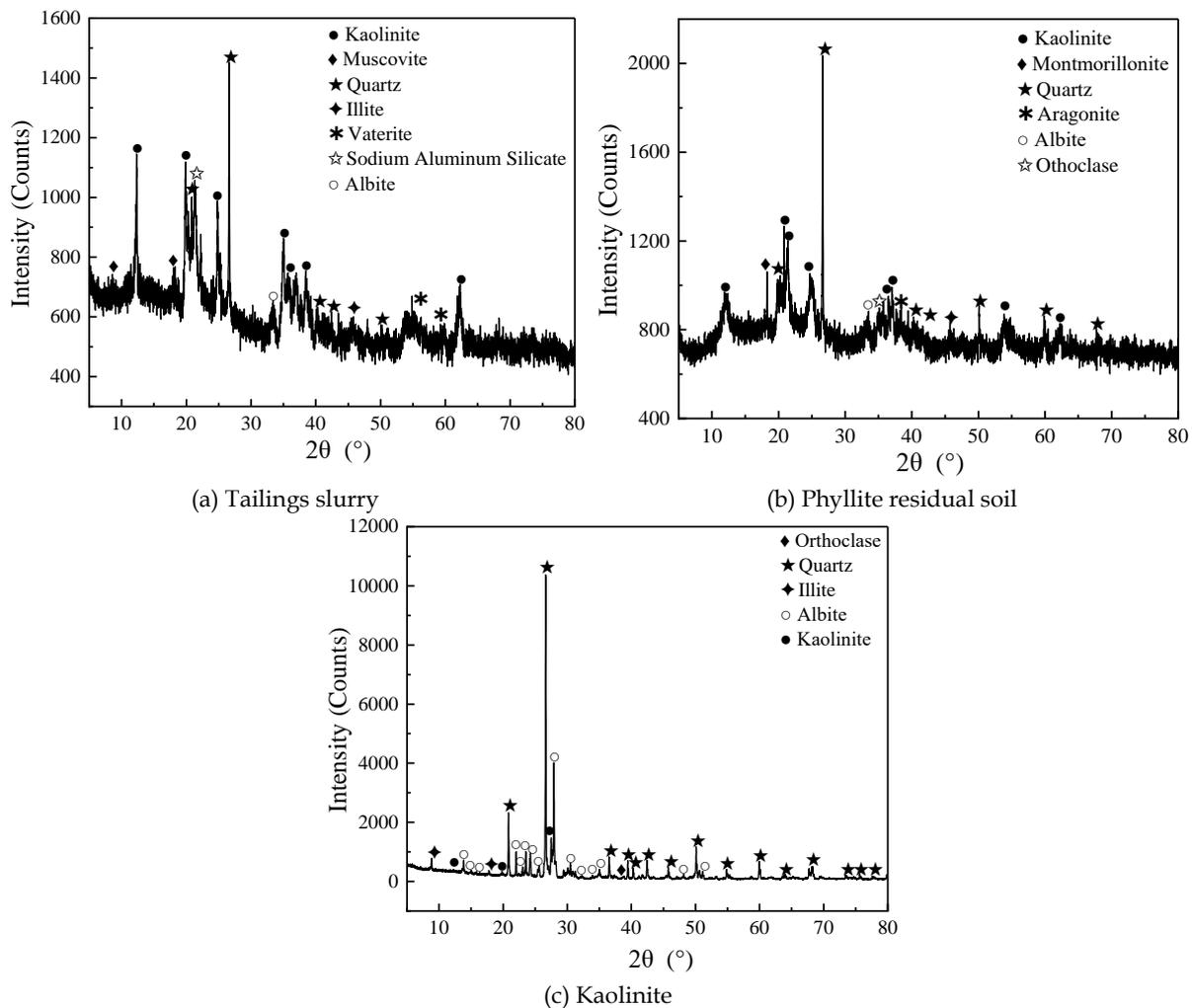
(c) Kaolinite

Fig. 2. XRD spectrums for the materials used in the experiments: (a) For the tailings slurry; (b) phyllite residual soil; (c) For the Kaolinite

Table 3. Analysis of mineral components

Soil sample	mineral component(%)								
	gibbsite	kaolinite	diaspore	goethite	quartz	anatase	microcline	vermiculite	illite
Tailings slurry	41	23	9	7	6	2	2	8	1
Phyllite residual soil	34.5	28.5	0	24.5	12.5	0	0	0	0
Kaolinite	0	90.3	0	0	9.7	0	0	0	0

Table 4. Initial zeta potential

Soil sample	Tailings slurry	Phyllite residual soil	Kaolinite
Initial zeta potential (mV)	-7.89	-2.35	-16.25

2.2. Sedimentation experiment

The inorganic ions used in this research were Na^+ and Ca^{2+}, which were obtained from sodium chloride (NaCl) and calcium chloride ($CaCl_2$), respectively. Concentrations of 0.1, 0.5, 1.0, and 2.0 mol/L were used. The pH value was adjusted by adding dilute hydrochloric acid and alkaline solutions (NaOH, $Ca(OH)_2$) of the corresponding cation to simulate different soil environments. A pH gradient (3, 5, 7, 9, 11, and 13) was established within each cation concentration range. Subsequently, free sedimentation experiments were conducted in a measuring cylinder with a volume of 50 mL. The changes in the mudline were recorded based on predetermined time intervals during the experiment.

2.3. Microanalysis

The zeta potentials of the three types of soil suspension samples, with varying concentrations and pH values, were measured using electrophoresis light scattering by a Malvern Zetasizer Nano (ZS-90, UK). Approximately 0.5 mL of suspension was added to the sample pool, and ultrasonic oscillation was carried out for 3 minutes. An electric field was applied through electrodes in the measuring cell, and the zeta potential was calculated by measuring the motion velocity of the charged particles.

3. Experiment results and analysis

3.1. Settlement test results

Fig. 3 shows the settlement results for the tailings slurry samples in sodium chloride solutions with different concentrations and pH values. It shows that the tailings slurry exhibited three settlement stages, namely, a flocculation stage, a hindered settlement stage, and a self-weight consolidation stage, which is similar to previous research results (Guo et al., 2015). It can be seen from Fig. 3(a) that the settlement process of the tailings slurry remained consistent within a pH range of 3–9. However, at a pH value of 11, the duration of the initial settlement stage was significantly prolonged, resulting in a delayed start of the final self-weight consolidation stage for the tailings slurry. Moreover, it should be noted that the duration of the settlement stage was the longest, when the pH value was 13. Fig. 3(b) shows the sedimentation process for a sodium chloride concentration of 0.5 mol/L, and the sedimentation result is similar to that shown in Fig. 3(a). However, as observed from Fig. 3(c), the effect of the pH on the flocculation stage was not significant, and the growth of the sedimentation stage was hindered when the pH was 9 and 13. The results presented in Fig. 3(d) indicate that the sedimentation process of the tailings slurry remained relatively consistent when the sodium chloride concentration was 2 mol/L and the pH was 3–11. However, at a pH value of 13, there was a significant increase in the duration of the initial sedimentation stage of the tailings slurry.

Fig. 4 shows the settlement results for the tailings slurry under different calcium chloride solution concentrations and pH values. As depicted in Fig. 4(a), the settlement process of the tailings slurry differed in an acidic environment. The duration of the initial settlement stage of the tailings slurry increased in an alkaline environment and increased with increasing pH. There was a delay in the beginning of the final self-weight consolidation stage of the tailings slurry. The settlement results for

(a) 0.1mol/L (b) 0.5mol/L (c) 1mol/L (d) 2mol/L
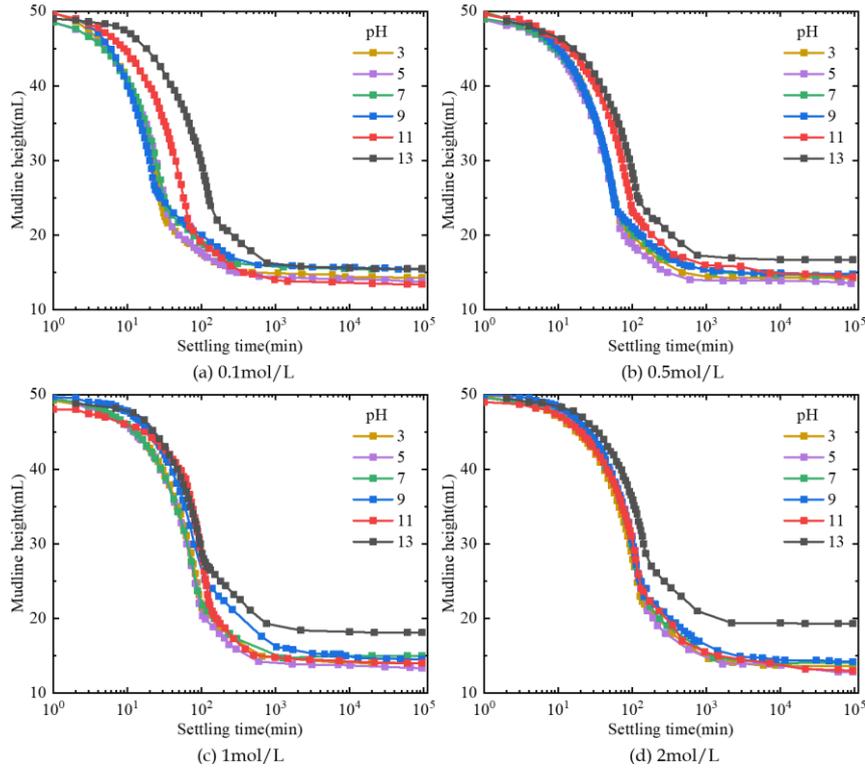
Fig. 4. Settlement curves for tailings slurry under different pH values and NaCl concentration

(a) 0.1mol/L (b) 0.5mol/L (c) 1mol/L (d) 2mol/L
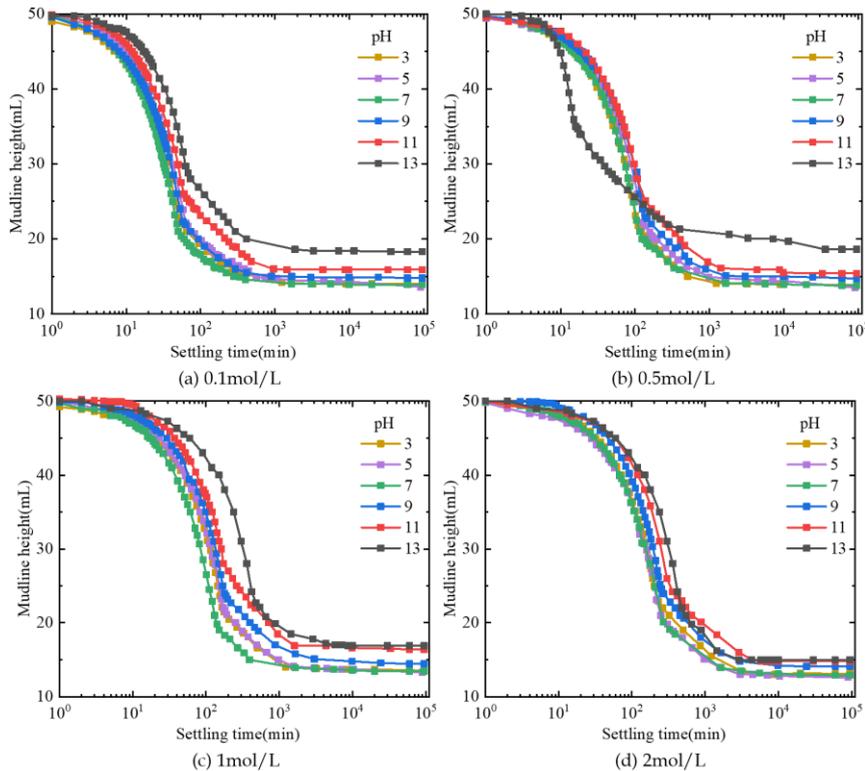
Fig. 4. Settlement curves for the tailings slurry under different pH values and different $CaCl_2$ concentrations

the other calcium chloride solution concentrations were similar to that for the 0.1 mol/L concentration. In the acidic environment, the pH change had little effect on the settlement results, while the duration of the initial settlement stage of the tailings slurry increased as the pH increased in the alkaline environment.

The settlement results for the phyllite residual soil are illustrated in Fig.5. The influence of the pH on the process is depicted in Figs. 5(a) and (b). The pH did not affect the final settling height. When the pH reached 13, the initial settlement stage of the phyllite residual soil was significantly prolonged, thereby delaying the beginning of the final self-weight consolidation phase. The increase in the calcium chloride concentration had a significant impact on the final settling height, and the pH played a crucial role. Notably, the solution with a pH value of 13 exhibited the highest final settling height. However, it should be emphasized that no definitive laws governing the change in pH were identified.

Fig. 6 shows the settlement results for the $CaCl_2$ concentrations under different pH values. As seen in Fig. 6(a), when the concentration of the calcium chloride solution was 0.1 mol/L and the pH was 13, the initial settlement stage of the phyllite residual soil was the longest, which delayed the phyllite residual soil from entering the final self-weight consolidation stage. Under pH values of 3–11, the process of the phyllite residual soil entering the self-weight consolidation stage was mutual consistency. Under the other three concentration conditions, the phyllite residual soil exhibited a similar settlement process with the concentration of 0.1 mol/L.
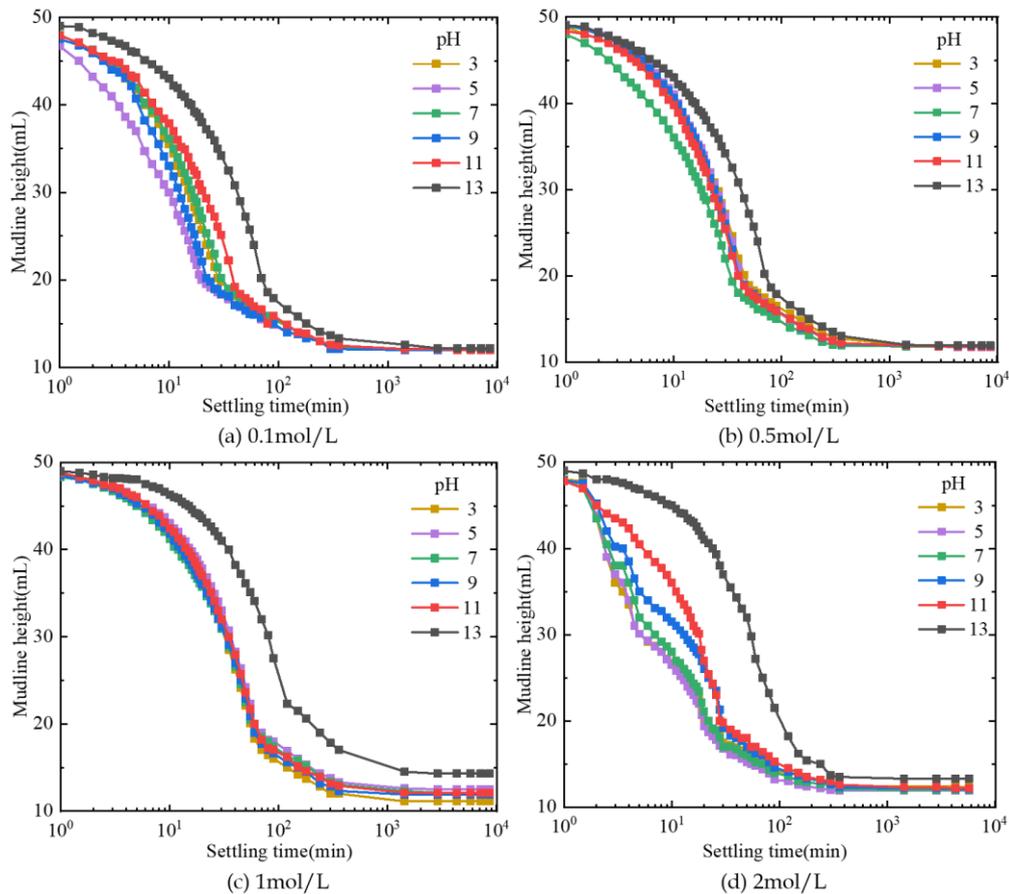
Fig. 5. Settlement curves for phyllite residual soil under different pH values and different NaCl concentrations

The settlement results for the commercial kaolinite clay are shown in Figs. 7 and 8. There is a significant difference in the settlement results compared to those of the tailings slurry and phyllite residual, that is, for a solution pH of 13, the initial settlement stage was the shortest. The initial settlement stage of the commerce kaolinite clay sedimentation was accelerated by the solution with a pH of 13, while this solution hindered the sedimentation of the tailings slurry and phyllite residual. The primary reason for this is the differences in the irregularities of the particle surfaces. Similarly, the self-weight consolidation stage of the commerce kaolinite clay was similar under pH values of 3–11.
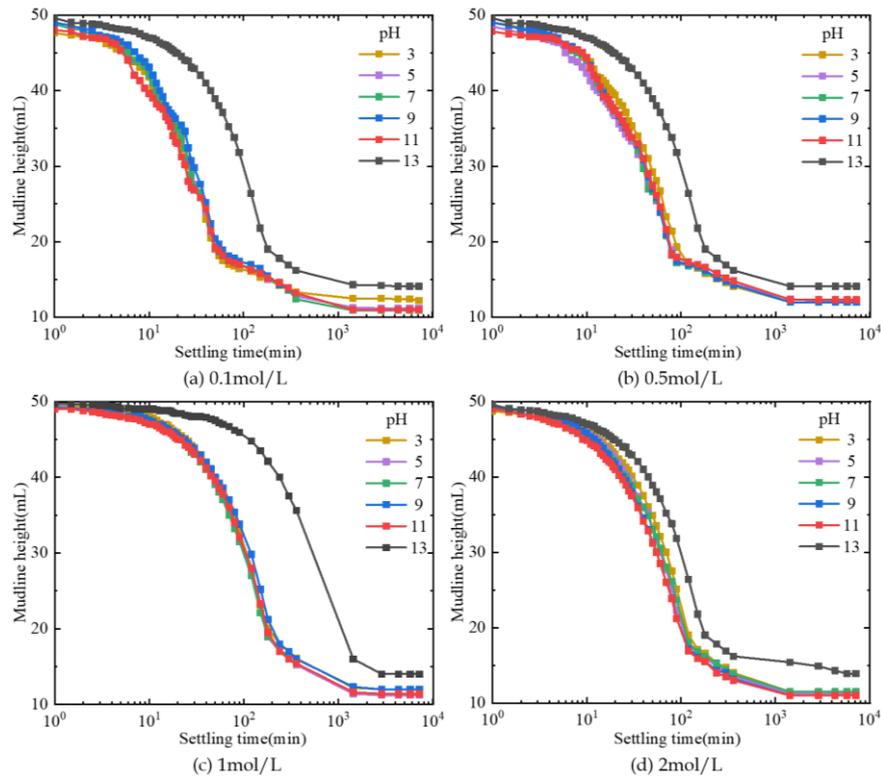
Fig. 6. Settlement curves for phyllite residual soil under different pH values and $CaCl_2$ concentrations
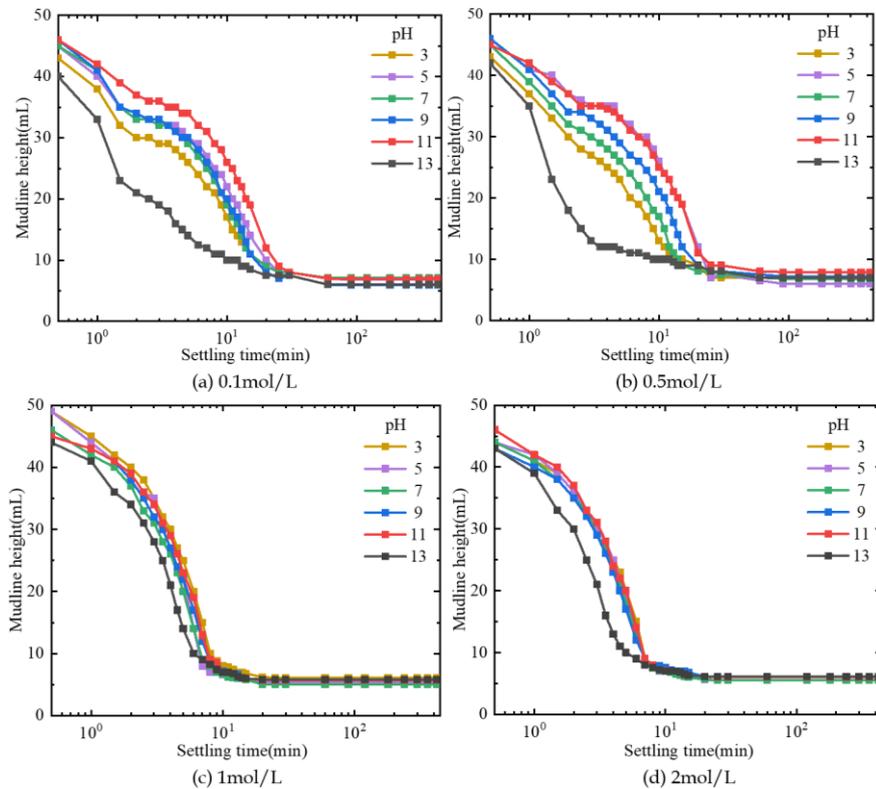
Fig. 7. Settlement curves for kaolinite under different pH values and NaCl concentrations

The relationships between the flocculation sedimentation rate, V_t, and pH for the phyllite residual clay, commercial kaolinite clay, and tailings slurry suspension are illustrated in Fig. 9 and 10. As shown in Fig. 9(a), the flocculation sedimentation rates of the phyllite residual clay and tailings slurry exhibited

a slight decrease with increasing pH. The flocculation sedimentation rate of the commercial kaolinite clay remained constant when the pH of the solution was less than 11. The flocculation sedimentation rate of the commercial kaolinite clay exhibited a significant increase when the pH was 13. The pH of the solution had a similar impact on the three samples in the 1 mol/L NaCl solution as it did in the 0.1 mol/L solution. The flocculation sedimentation rate was lower in the 0.1 mol/L NaCl solution than in the 1 mol/L NaCl solution, while maintaining the same pH value. The CaCl$_2$ solution exhibited a similar trend to that of the NaCl solution (Fig. 10). When the pH was between 3 and 13, the flocculation sedimentation rates of the phyllite residual soil and tailings slurry were similar, while the flocculation sedimentation rate of the kaolinite consistently surpassed the other two.
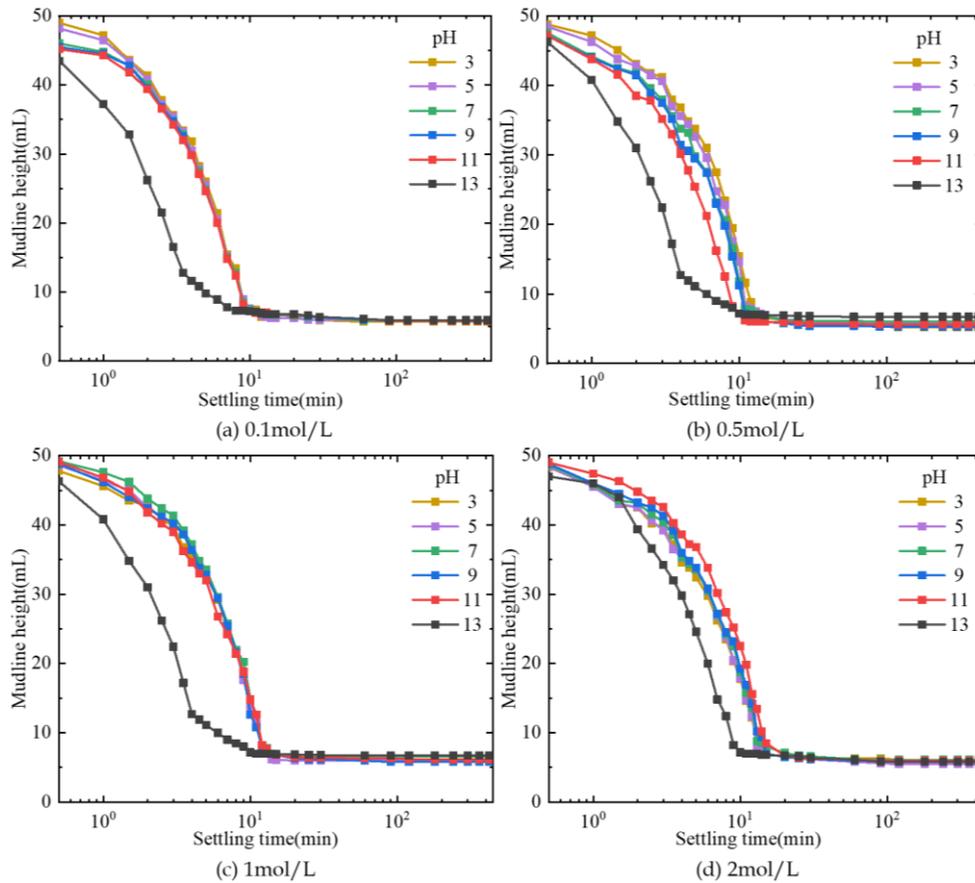
Fig. 8. Settlement curves for kaolinite under different pH values and CaCl$_2$ concentration
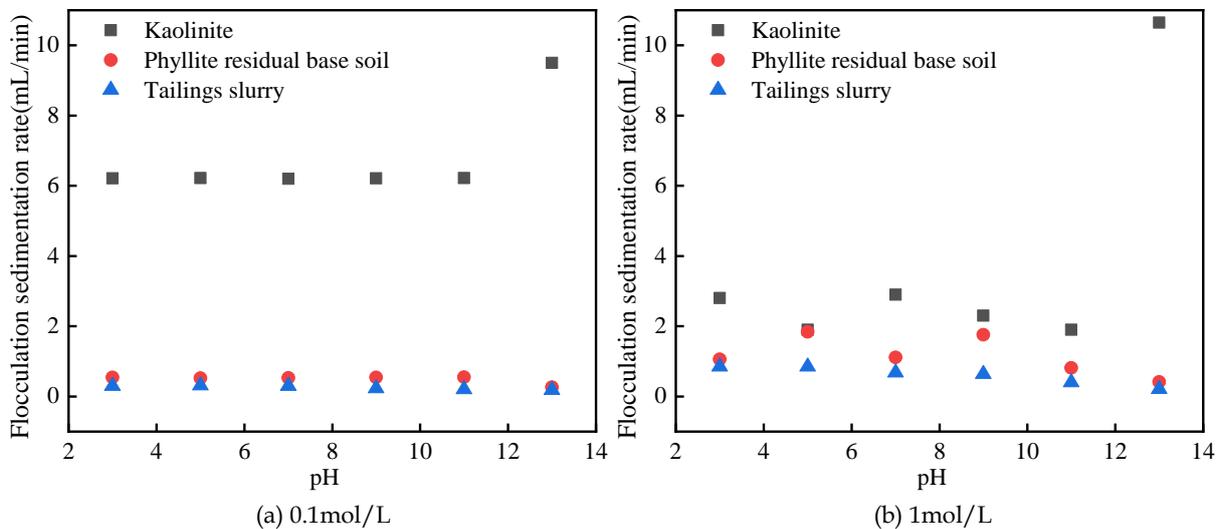
Fig. 9. Flocculation sedimentation rates of the three types of soil in NaCl solutions with different pH values
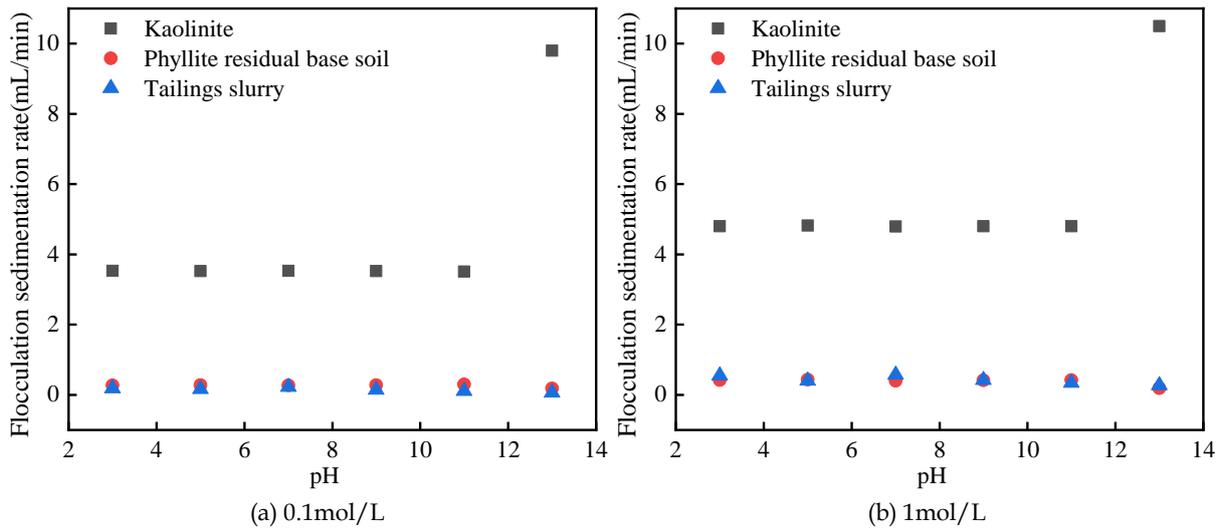
Fig. 10. Flocculation sedimentation rates of the three types of soil in CaCl$_2$ solutions with different pH values

Fig. 11 illustrates the settlement stable void ratios (e$_s$) of the three samples in solutions with different pH levels. It can be seen that in a solution with the same pH, the e$_s$ of the tailing slurry was the greatest and that of the commercial kaolinite clay was the least. The impact of pH was minimal in the 0.1 mol/L NaCl solution compared to the 1 mol/L solution (Fig. 11(a)). The variation trend of e$_s$ was not evident due to the change in the pH of the solution. In the 1 mol/L NaCl solution, as shown in Fig. 11(b), the e$_s$ value increased as the pH increased. Fig. 12 displays the e$_s$ values in CaCl$_2$ solutions with various concentrations. The impact of pH on e$_s$ was analogous to that observed for the NaCl solutions. The increase in the e$_s$ values of the phyllite residual soil and tailings slurry gradually accelerated with increasing pH, whereas the sedimentation stable void ratio of the kaolinite did not change obviously with increasing pH. For a solute with the same pH, the ions of e$_s$ of the tailing slurry was the largest and that of the commercial kaolinite clay was the smallest. This is consistent with the results (Jeldres et al., 2017) that with the increase of salt solution concentration, the particle grid becomes denser, the flocculation effect is better, and the initial sedimentation rate increases.
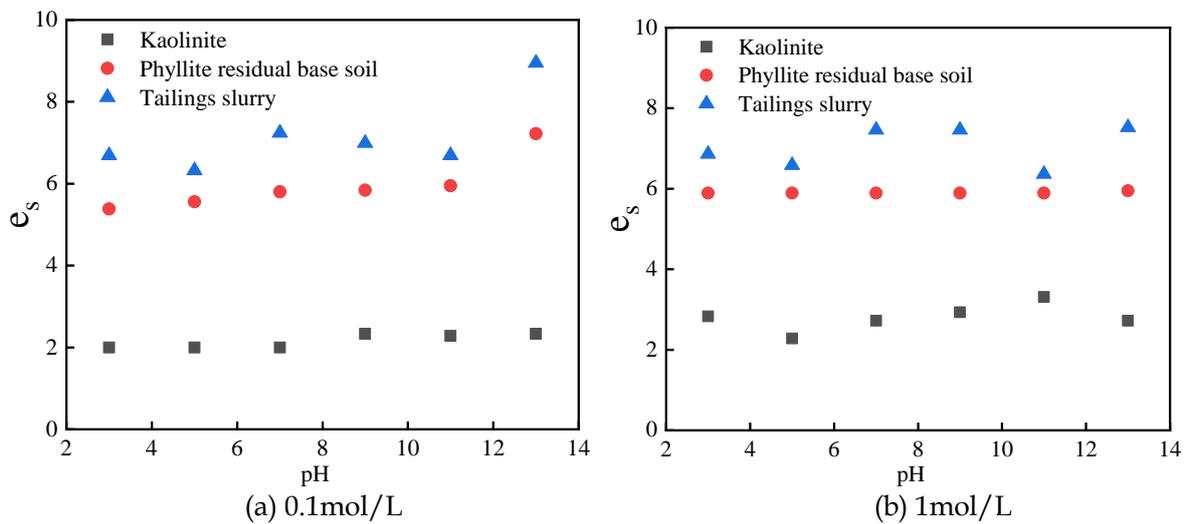
Fig. 11. The settling stable void ratios of the three soils in NaCl solutions with different pH values

3.2. Zeta potential test

Fig. 13 depicts the zeta potential of phyllite residual soil, kaolinite, and tailings slurry under varying cation concentration conditions. Figure 13 illustrates that for all three soils, the absolute value of the zeta potential decreases with increasing ion concentration, resulting in a progressively narrower range of variation. When the sodium ion concentration of a sodium chloride solution was increased from 0.01

(a) 0.1mol/L   (b) 1mol/L
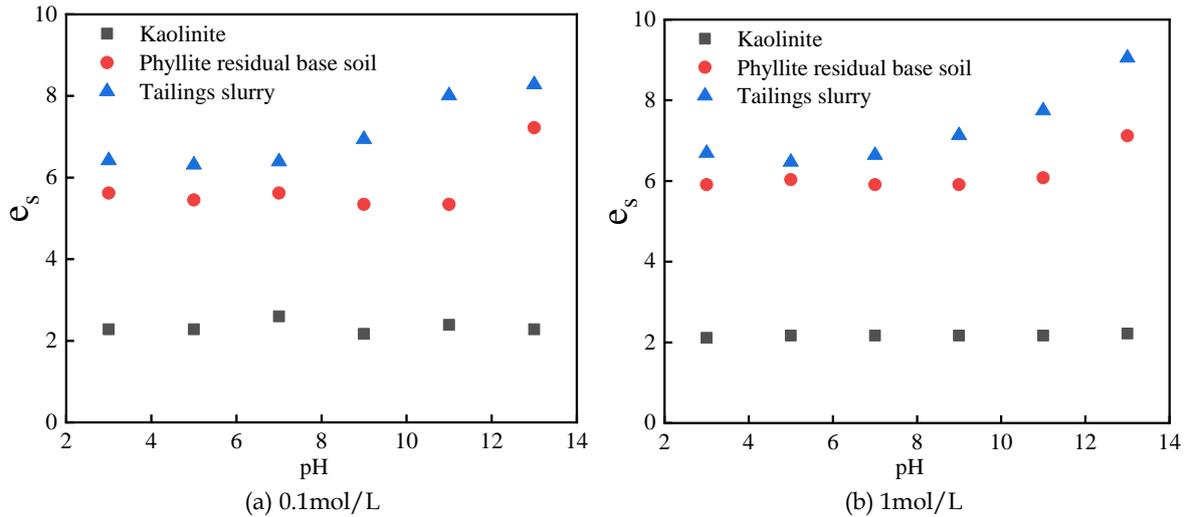
Fig. 12. The settling stable void ratios of the three soils in CaCl$_2$ solutions with different pH value

mol/L to 0.2 mol/L, the zeta potential of the kaolinite suspension increased from −43.9 mV to −26.4 mV. The increase in the cation valence led to a significant decline in the absolute value of the zeta potential for the kaolinite suspension. When the concentration of calcium ions was increased from 0.01 mol/L to 0.2 mol/L, the zeta potential of the kaolinite suspension increased from −12.2 mV to −3.24 mV. For thephyllite residual soil, when the sodium ion concentration was increased, the Zeta potential decreased from +6.09 mV to +1.03 mV. Conversely, when the calcium ion concentration was increased, the zeta potential decreased from +16.65 mV to +5.00 mV. The change trend of the clay's zeta potential was identical to that of the kaolinite, with the exception that the absolute value of the zeta potential was marginally lower than that of the kaolinite under equivalent conditions. This discrepancy is noteworthy.

The observations revealed that the transition from monovalent Na$^+$ to divalent Ca^{2+} had in a more substantial impact on the zeta potential of the kaolinite suspension, followed by the tailings slurry, and the zeta potential of the phyllite residual soil suspension was the least affected by the change in ions. When the ion concentration exceeded 0.01 mol/L, the zeta potential difference of the phyllite residual soil suspension in a calcium ion and sodium ion environment did not exceed 3.7 mV. The absolute values of the zeta potential of the kaolinite and tailings slurry suspensions decreased as the calcium ion concentration increased from 0 mol/L to 0.01 mol/L, and the decrease was more significant than that observed in the presence of sodium ions. An ion concentration within 0.05–0.2 mol/L resulted in a smaller decrease in the absolute values of the zeta potential of both the kaolinite and tailings slurry suspension in the calcium ion environment compared to that in the sodium ion environment. In summary, it was observed that calcium ions had a more pronounced influence on the zeta potentials of the kaolinite and tailings slurry suspensions at low concentrations. However, as the concentration increased, the effect of the calcium ions gradually decreased compared to that of the sodium ions.
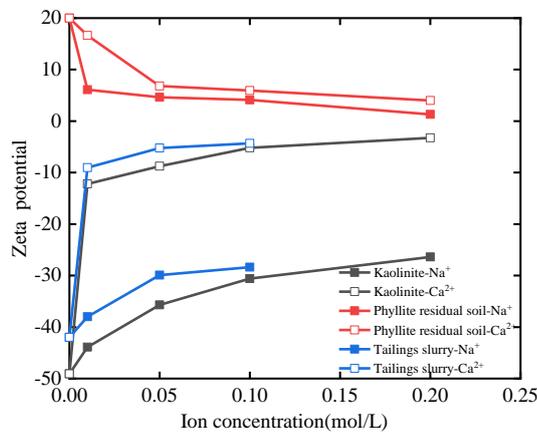
Fig. 13. Zeta potentials of the three soils under different cation concentrations
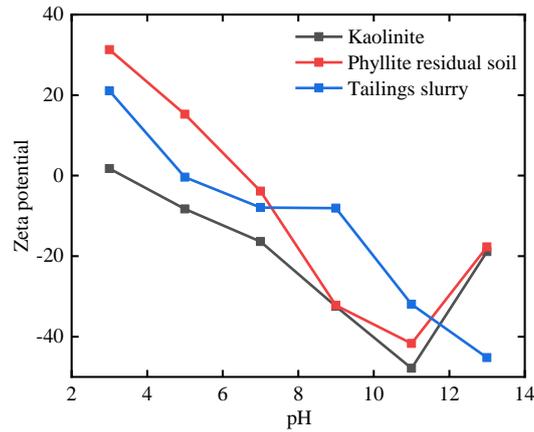
Fig. 14. Zeta potentials of the three soils under different pH values

Fig. 14 depicts the changes in the zeta potential of phyllite residual soil and kaolinite suspensions in response to pH changes. As illustrated in Fig. 14, increasing the pH from 3 to 11 resulted in a decrease in the zeta potentials of all three soil suspensions. The abrupt increase in the absolute value of the zeta potential observed at a pH of 13 was a characteristic feature of the phyllite residual soil and kaolinite suspensions. The zeta potential of the phyllite residual soil suspension gradually decreased within the pH range of 3–11, from 31.30 mV to −41.71 mV. Similarly, the zeta potential of the kaolinite suspension also consistently decreased, from 1.73 mV to −47.88 mV, within the same pH range. Furthermore, the zeta potential of the tailings slurry suspension exhibited a corresponding decrease from 21.01 mV to −31.97 mV, within the specified pH interval. The zeta potential of the tailings slurry suspension was primarily situated within the phyllite residual soil and kaolinite interface. When the pH exceeded 7, the zeta potential of the tailings slurry suspension reached the minimum absolute value. The absolute value of the zeta potentials of the kaolinite and phyllite residual soil decreased when the pH reached 13, whereas the absolute value of the zeta potential of the tailings slurry continued to increase.

4. Discussion

Kaolinite is composed of a silicon-oxygen tetrahedral layer (T surface) and a silicon-oxygen octahedral layer (O surface) connected by oxygen atoms, as seen in Fig. 15. Each particle has three surfaces : T surface, O surface and end surface (E surface). The charge density of the T plane is a fixed value, which is only related to the area of the T plane. The E-plane and O-plane in the solution due to protonation and deprotonation, so that the charge is variable charge, E-plane and O-plane are defined as HD surface.

The variation in the HD surface charge of the clay minerals was significantly influenced by the pH of the environment. The changes in the pH value resulted in modifications of the crystal structure of the clay minerals. Rand (Melton et al., 1977) observed that when the pH level exceeds PZC_{edge}, the kaolinite edges and surfaces have a negative charge, resulting in the electric double layer repulsion of the particles
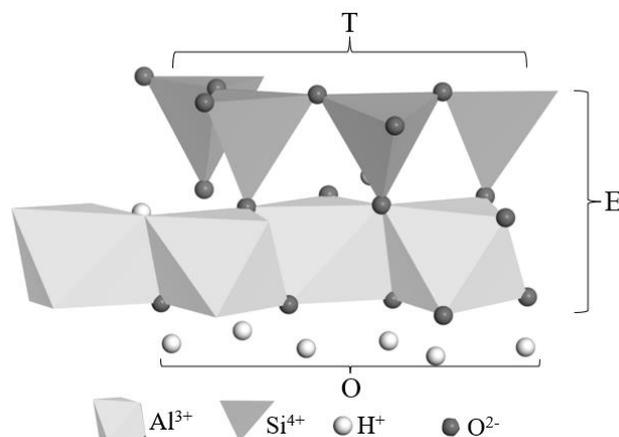
Fig. 15. Molecular structure of kaolinite layer (James K. M, Kenichi S, 2005)

becoming dominant, facilitating the formation of a face-to-face (FF) arrangement structure. Conversely, when the pH level is less than or equal to PZC_{edge}, the kaolinite edge is negatively charged, while the surface base band has a positive charge, thereby allowing the interparticle Coulomb attraction to assume the leading role. The formation of an edge-to-surface (EF) structure and an edge-to-edge (EE) structure (transition structure) is straightforward.

According to Stokes' law (Kang et al., 2019), when the particle shape is spherical, the flocculation sedimentation rate can be calculated using the following equation:

$$v = \frac{(\rho_p - \rho_f)g}{18\mu_f} D_p^2 \tag{1}$$

where ρ_p is the solid density; ρ_f is the liquid density; g is the acceleration due to gravity; μ_f is the coefficient of the dynamic viscosity of the solution; and D_p is the diameter of the spherical particle.

The clay particles in this study were examined within a water-rich medium, resulting in suspensions that exhibited properties consistent with colloidal behavior. According to the Derjaguin–Landau–Vervey–Overbeek (DLVO) theory of charged colloid stability, the alteration of the repulsive potential energy and gravitational potential energy between the particles primarily influences the stability of colloids. When two clay particles approach each other, the diffusion layer of the electric double layer initially overlaps, resulting in the disruption of counterion balance within the diffusion layer. This produces osmotic repulsion from the overlapping region towards the non-overlapping area. The concurrent occurrence of these processes result in the emergence of an electrostatic non-equilibrium state, giving rise to electrostatic repulsion. The combination of these two factors constitutes the repulsion between particles (Alagha et al., 2013). The respective calculation formula is as follows:

$$V_r = \frac{64\pi R n_0 k_B T \gamma_0^2}{\kappa^2} e^{-\kappa x} \tag{2}$$

where R is the particle radius; n_0 is the electrolytic concentration; k_B is the Deby parameter; T is the temperature (K); γ_0 is the surface potential parameter of the colloidal particles; κ is the Deby parameter; and x is the shortest distance between the particles.

According to the DLVO theory, the total potential energy, V, between the particles is defined as the sum of the gravitational potential energy (V_r) and the repulsive potential energy (V_v), i.e., $V = V_r + V_v$. The aggregate potential energy of the particles tends towards zero when the interparticle distance is extremely large; that is, the force between the particles becomes exceedingly weak and becomes negligible. As the interparticle distance decreases, it first reaches the secondary potential well, where the particles interact and coagulate reversibly, but the state is unstable. When the external conditions change, the particles separate again, and the interparticle distance decreases further and reaches the maximum energy barrier. As particles do not possess sufficient energy to cross this barrier, the particle state is stable at this point. Once the particles acquire sufficient energy, they overcome the barrier and enter the primary potential trap. Then, the interaction between the particles results in a more stable and irreversible aggregation.

With increasing ion concentration, the compression effect of the cations on the electric double layer of the particles is amplified, resulting in the particles being unable to form large flocculation clusters and dispersion and settlement of these particles in smaller clusters, thereby reducing the flocculation sedimentation rate. According to Equation (1), increasing the ion concentration also increases the density of the solution, enhancing the buoyancy of the particles and slowing down the flocculation sedimentation rate. As the valence state of the ions increased, the electric double layer of the particles experiences sharp compression, further reducing the flocculation sedimentation rate under the presence of divalent calcium ions. This is significant because the coiling of polymer chains is notably pronounced when exposed to calcium salt (Huber et al., 1993). Even at low concentrations (0.001 M), the intrinsic viscosity decreases to a level indicating a physical limit of coiling (Arinaitwe et al., 2013). In the context of low solids feedwell flocculation, the presence of minimal amounts of calcium cations in the slurry can negatively impact settling rates. This is most evident in the lower molecular weights, highlighting a reduced bridging capacity (Costine et al., 2018).Concurrently, the sensitivity to the cation valence increases, which is reflected by the increase in the absolute value of the slope of the fitting curve. Finally, due to the variation in the kaolinite mineral content across the three soils, for the same ion concentration, the flocculation sedimentation rate of kaolinite is the greatest, followed by the tailings slurry, and that

of the phyllite residual soil is the lowest. Furthermore, the flocculation sedimentation rate sensitivity of the three types of soil also decreases as the kaolinite content decreases.

As the cation concentration increases, the thickness of the electric double layer around the particles is compressed, leading to a reduction in the repulsive potential energy between them. This in turn causes a decrease in the energy barrier. Simultaneously, the compression of the electric double layer results in a decrease in the particle spacing and an increase in the gravitational potential energy. Consequently, the particles are more likely to form surface-to-surface (E-E) stacking flocs, with a vertical arrangement that results in a lower void ratio. This is consistent with the research results (Liu et al., 2020) that it is easier to produce higher aggregate porosity at high salt solution concentration. Therefore, in a cationic environment, the settlement void ratios of the three types of soil decrease with increasing ion concentration. As the valence state of the ion increases, the compression effect on the electric double layer intensifies, making the aforementioned effect more pronounced. Consequently, the sedimentation stable pore ratio is smaller in an environment containing divalent calcium ions.

The chemical environment primarily affects the properties of the clay minerals. Thus, for the same ion concentration, the order of the settlement stability pore ratios of the three soils is as follows: phyllite residual soil > tailings slurry > kaolinite. This indicates that there is a positive correlation between the kaolinite mineral content and the stability pore ratio.

With increasing pH (3–11), the flocculation sedimentation rate of kaolinite marginally decreases, while the e_s gradually increases. Similar trends were observed for the flocculation sedimentation rates of the phyllite residual soil and tailings slurry, albeit with a more pronounced decline. As the pH value of the solution increases, the bridging interaction (e.g. through hydrogen bonds) increases, and the effective binding sites before the particles increase, which helps to enhance the flocculation behavior (Chen et al., 2021). The settlement stable pore ratio initially decreases and then rebounds. At a given pH, the phyllite residual soil has a higher gravel content and lower kaolinite mineral content, resulting in a consistently higher settlement stable pore ratio compared to the other two types of soil. When the pH reaches 13, the high concentration of sodium ions in the solution compresses the electric double layer on the particle surface, leading to an increase in the gravitational potential energy governed by the van der Waals force and a corresponding decrease in the electrostatic repulsion potential energy. This prompts the transition from a more dispersed and disordered state to an orderly arrangement of longitudinal stacking and sedimentation. Consequently, the flocculation sedimentation rate of the kaolinite increases and the stable void ratio of the sedimentation decreases. Concurrently, the settlement stable void ratio and flocculation sedimentation rate of the phyllite residual soil and tailings slurry also decrease.

5. Conclusions

In this study, the sedimentation characteristics of tailing slurry, phyllite residual soil, and commercial kaolinite were investigated in various chemical environments. Subsequently, the variations in the zeta potential in these distinct chemical environments were determined via zeta potential testing. The following conclusions were drawn.

With increasing pH, the e_s of the tailings slurry and phyllite residual soil initially decreased and then rebounded, whereas the settling stable pore of the kaolinite gradually increased. The flocculation sedimentation rate remained stable throughout this process. However, at a pH of 13, the settling stable pore ratio of the phyllite residual soil sharply increased and the flocculation sedimentation rate significantly decreased. This was not consistent with the behavior of the kaolinite. The clay minerals, being the primary constituents of the three soils, had surface charges that were susceptible to pH fluctuations. Consequently, at the pH values corresponding to the isoelectric points of the three soils, the particles aggregated to form a dense edge (E-E) arrangement of flocs.

The presence of cations impeded the formation of large-sized flocs, and consequently, these particles only shrank in a single-particle dispersion manner, resulting in a smaller flocculation sedimentation rate. Under the pH–cation coupling effect, the flocculation sedimentation rate and sedimentation stable void ratio of the ore tailings slurry were consistent with those of the other two soils. When the pH reached PZC_{edge} (pH = 5), the flocculation sedimentation rate and sedimentation stable void ratio reached their minimum values.

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