Selective Separation of Scheelite from Calcite by Self-Assembly of H$_2$SiO$_3$ Polymer Using Al^{3+} in Pb-BHA Flotation

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Abstract: The flotation separation of scheelite from calcite is problematic, where sodium silicate modified by polyvalent metal ions has shown some advantages for selective depression. In this study, an Al-Na$_2$SiO$_3$ polymer was used as the depressant for the flotation separation of scheelite from calcite using a lead complex of benzohydroxamic acid (Pb-BHA) as the collector. Furthermore, a number of measurements were conducted to investigate the structure of the Al-Na$_2$SiO$_3$ polymer and its adsorption behavior with Pb-BHA complexes on the mineral surface. Flotation experiments indicated that the Al-Na$_2$SiO$_3$ polymer shows good selectivity for the flotation separation of scheelite from calcite at pH 8, where the optimum ratio of sodium silicate to aluminum sulfate was 2:1. Fourier-Transform Infrared (FTIR) and solution chemical analyses revealed that aluminum hydroxide complexes and the hydroxy moiety of silicic acid are able to self-assemble via condensation affording an Al-Na$_2$SiO$_3$ polymer, i.e., a composite aluminosilicate polymer. The zeta potential measurements and adsorption capacity measurements indicated that, upon adsorption of the Al-Na$_2$SiO$_3$ polymer and Pb-BHA complexes on the mineral surface, the Al-Na$_2$SiO$_3$ polymer had less influence on the adsorption of Pb-BHA complexes on the scheelite surface, while the opposite was true for calcite. Therefore, more Pb-BHA complexes and fewer Al-Na$_2$SiO$_3$ polymers were deposited on the scheelite surface, while fewer Pb-BHA complexes and more Al-Na$_2$SiO$_3$ polymers were adsorbed on the calcite surface. The selective separation of scheelite from calcite was attributed to the cooperative selectivity of the Pb-BHA complexes and Al-Na$_2$SiO$_3$ polymer.

Keywords: scheelite; calcite; Al-Na$_2$SiO$_3$ polymer; Pb-BHA complex; FTIR

1. Introduction

The flotation separation of scheelite from other calcium-containing minerals is problematic due to their similar physicochemical characteristics and flotation behavior [1–6]. Sodium silicate is commonly used in scheelite flotation to depress calcium-bearing gangue minerals and silicate minerals; however, the selectivity of sodium silicate for scheelite flotation is inadequate, whereby the floatability of scheelite is somewhat reduced [7–9]. Modification of sodium silicate with polyvalent metal ions,

oxalic acid, sulfuric acid, ammonium salt, and some other reagents has been proven to be effective in enhancing the depression of gangue minerals with little effect on the desired minerals [7,10–13].

The selective adsorption of sodium silicate on minerals is significantly improved by modification with polyvalent metal ions, such as Fe(II), Pb(II), Cu(II), Mg(II), and Al(III) [10,12,14–16], especially for application in scheelite flotation. The Pb-benzohydroxamic acid (BHA) complex, a novel metal-organic collector, has shown specificity toward scheelite, contributing to the flotation separation of scheelite from other calcium minerals [4,17,18]. A simplified flotation process using Pb-BHA complexes was developed to replace the energy-inefficient Petrov's process involving the use of a fatty acid to increase the recovery of scheelite and reduce the overall cost. In the new process, an Al-Na$_2$SiO$_3$ polymer was used to efficiently improve the quality of the concentrate. Compared to sodium silicate, the Al-Na$_2$SiO$_3$ polymer (sodium silicate modified by Al^{3+}) showed better selective depression of scheelite and calcite during Pb-BHA flotation, leading to the separation of scheelite from calcite [19]. The improved selectivity of the Al-Na$_2$SiO$_3$ polymer was attributed to the addition of aluminum ions; however, the structure and active species of such Al-Na$_2$SiO$_3$ polymer in slurry and mineral surfaces remained unclear. In addition, in contrast to fatty acid flotation processes requiring large masses of sodium silicate (e.g., 1–3 kg/t), little amounts of Al-Na$_2$SiO$_3$ polymer (e.g., 0.1–0.3 kg/t) are enough and effective for Pb-BHA flotation, indicating that the combined utilization of Pb-BHA complexes and such an Al-Na$_2$SiO$_3$ polymer exhibits absolute specificity toward scheelite, thus contributing to efficient and clean scheelite flotation processes. However, the competition between the Al-Na$_2$SiO$_3$ polymer and Pb-BHA complex on the minerals surface remains unclear; their adsorption behavior on scheelite and calcite requires further investigation to uncover the mechanism behind the superior selectivity of the Al-Na$_2$SiO$_3$ polymer during Pb-BHA flotation.

In this study, the structure of the Al-Na$_2$SiO$_3$ polymer was studied in detail, and the competitive adsorption mechanism of the Al-Na$_2$SiO$_3$ polymer and Pb-BHA collectors on both scheelite and calcite was elucidated by some advanced experiments. Flotation experiments of pure minerals were conducted to explore the optimal conditions for the selective separation of scheelite from calcite using the Al-Na$_2$SiO$_3$ polymer. Fourier-Transform Infrared (FTIR) and solution chemical analyses of Na$_2$SiO$_3$ and the Al-Na$_2$SiO$_3$ polymer were conducted to clarify the structure of the polymer. Zeta potential and adsorption measurements were also performed to study the adsorption behavior of Al-Na$_2$SiO$_3$ and Pb-BHA complexes on the mineral surface. A model for the adsorption of the Al-Na$_2$SiO$_3$ polymer and Pb-BHA complexes on scheelite and calcite surfaces is proposed to explain the superior selectivity of the Al-Na$_2$SiO$_3$ polymer during Pb-BHA flotation.

2. Materials and Methods

2.1. Minerals and Reagents

Pure scheelite and calcite were sourced from the Shizhuyuan mine, Hunan, China. The powder X-ray diffraction data confirmed that the samples had a purity of >97%. The −74 μm fractions of scheelite and calcite were used for the experiments. The samples used for zeta potential measurements were further ground to −2 μm in an agate mortar.

Analytical grade lead nitrate and BHA were purchased from Guangfu, Tianjin, China. Sodium silicate (SS, Na$_2$SiO$_3$·9H$_2$O) was obtained from the Zhuzhou Flotation Reagents Factory, Hunan, China. Analytical grade aluminum sulfate (Al$_2$(SO$_4$)$_3$) and terpineol were obtained from the Kemiou Chemical Research Institute, Tianjin, China. The pH was adjusted using NaOH or HCl stock solutions. Deionized water was used in all experiments.

2.2. Flotation Experiments

Pure mineral flotation tests were conducted in an XFG flotation machine at an impeller speed of 1600 rpm, with a plexiglass cell volume of 40 mL. The mineral suspension was prepared by adding 2.0 g of mineral to 30 mL of deionized water. Samples of mineral mixtures were prepared with 1.0 g of scheelite

and 1.0 g of calcite. $Pb(NO_3)_2$ was mixed with BHA, referred to as Pb-BHA, before addition. Na_2SiO_3 was mixed with $Al_2(SO_4)_3$, referred to as Al-Na_2SiO_3, before addition. The flotation experimental procedure is that previously described in the literature [19]. After 5 min of flotation, the floated and non-floated particles were collected, dried, and weighed, and the recovery was calculated.

2.3. Fourier-Transform Infrared (FTIR) Measurements

For the FTIR measurements, an Al-Na_2SiO_3 polymer with the desired mass ratio was prepared in a solution and agitated for 10 min at pH 8.0. The pulp was then centrifuged, the precipitate was washed at least three times with deionized water, and the sample was then dried in a vacuum oven at 40 °C. The FTIR measurements were conducted using a Bruker Alpha FTIR spectrometer at 20 °C in the range of 400–4000 cm^{-1}.

2.4. Zeta Potential Measurements

Zeta potential measurements were conducted using a zeta potential analyzer (ZetaPlus, Bruker, Germany) at 20 °C. Colloid particle suspensions were prepared by adding the desired reagents to 40 mL of KCl background electrolyte (10^{-3} mol/L) and agitating for 3 min. Mineral suspensions containing 0.02 g of solids and 40 mL of a KCl background electrolyte (10^{-3} mol/L) were prepared in a beaker at a given pH and desired reagent concentration. After settling for 10 min, the supernatant liquor was used for zeta potential measurements.

2.5. Adsorption Capacity Determination

The adsorption capacity toward BHA was monitored using a total organic carbon analyzer (TOC-LCPH/CN, Shimadzu Corporation, Kyoto, Japan). The -74 μm fraction of pure scheelite or calcite (2.0 g) was conditioned in a 40 mL solution using the desired reagents for the flotation tests. After that, the conditioned pulp suspension was centrifuged for 15 min, and the supernatant solution was removed for analysis. The amount of BHA adsorbed on the scheelite and calcite particles was calculated as:

$$\Gamma = (C_0 - C)V/mA \tag{1}$$

where Γ is the amount of BHA adsorbed on the mineral surface (mol/m^2), C_0 and C are the initial and residual concentrations (mol/L) of BHA, respectively, V is the volume of the solution (L), m is the amount (g) of particles per sample, and A is the specific surface area of the minerals (0.192 m^2/g for scheelite and 0.335 m^2/g for calcite, as determined by BET analysis).

3. Results and Discussion

3.1. Single Mineral Flotation Experiments

Pb-BHA complexes have proven to be selective for calcium mineral flotation, demonstrating good collecting ability toward scheelite. In Pb-BHA flotation experiments, although fluorite could not be collected, a high recovery of calcite was maintained across the tested pH range [4,18]. A depressant is necessary to enable the separation of scheelite from calcite; however, the use of Na_2SiO_3 was inefficient [19]. Different dosages of Al-Na_2SiO_3 polymer were added to investigate its effect on scheelite and calcite flotation, as shown in Figure 1. An atypical scheelite recovery curve was observed with the increasing depressant dosage, and a further detailed analysis of such a singular recovery curve will be conducted in the near future. From Figure 1, the recovery of calcite decreased rapidly with the increasing Al-Na_2SiO_3 polymer loading; at Al-Na_2SiO_3 polymer concentrations over 50 mg/L, the recovery of scheelite was higher than that of calcite, and thus, the separation of scheelite from calcite was realized. In particular, the optimum concentration of Al-Na_2SiO_3 polymer for scheelite flotation using Pb-BHA complexes as the collector was determined as 100 mg/L.
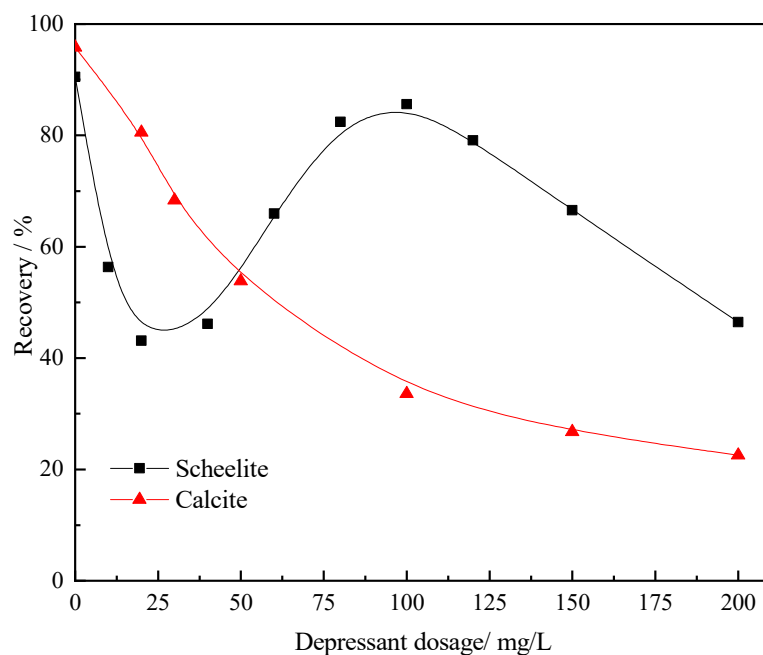
Figure 1. Effect of Al-Na$_2$SiO$_3$ polymer dosage on scheelite and calcite flotation (pH = 9.0 $\pm$ 0.1, $C_{\text{lead ion}}$ = 3 $\times$ 10^{-4} mol/L, C_{BHA} = 1.5 $\times$ 10^{-4} mol/L, $C_{\text{terpineol}}$ = 12.5 µL/L).

Figure 2 shows the effect of the mass ratio of sodium silicate to aluminum sulfate on the flotation of scheelite and calcite, where the dosage of sodium silicate was fixed at 100 mg/L. The results demonstrate that the floatability of scheelite and calcite varies with an increasing aluminum ion concentration. The addition of aluminum ions significantly improves the selectivity toward scheelite and calcite; however, excess aluminum ions have a negative impact on scheelite flotation, as seen in Figure 2, from which the optimum ratio of sodium silicate to aluminum sulfate was determined to be 2:1.
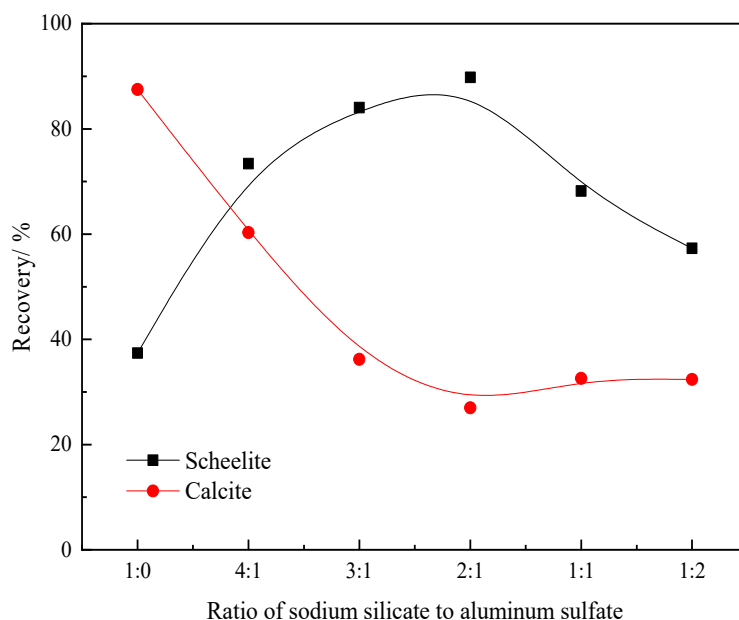

Figure 2. Effect of the ratio of sodium silicate to aluminum sulfate on scheelite and calcite flotation (pH = 8.0 $\pm$ 0.1, C_{ss} = 100 mg/L, $C_{\text{lead ion}}$ = 3 $\times$ 10^{-4} mol/L, C_{BHA} = 1.5 $\times$ 10^{-4} mol/L, $C_{\text{terpineol}}$ = 12.5 µL/L).

Figure 3 shows the effect of the Al-Na$_2$SiO$_3$ polymer on the scheelite and calcite flotation versus the pH. The results indicate that the recovery of scheelite after treatment with the Al-Na$_2$SiO$_3$ polymer

was >80% at pH 7–9; however, that of calcite was only 20–30% under these conditions. In particular, at the optimal pH of 8, the recoveries of scheelite and calcite were 89.8% and 27%, respectively.
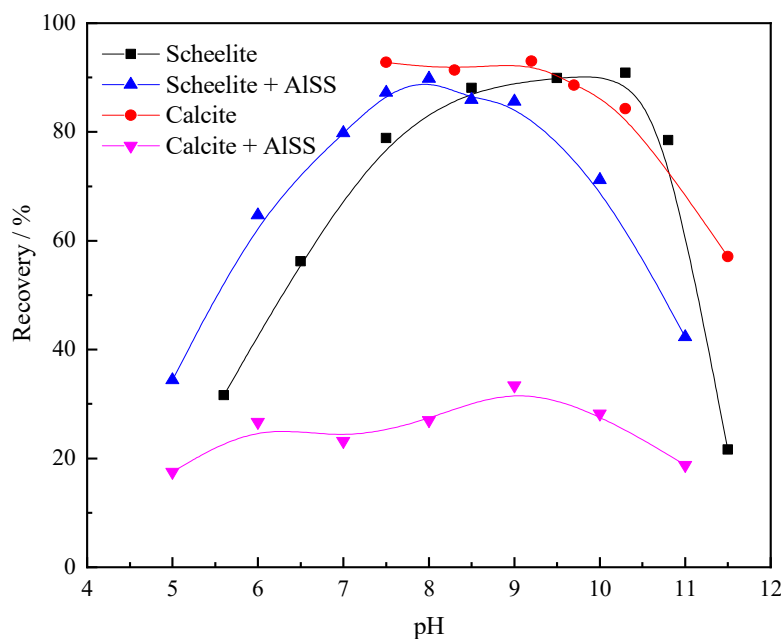

Figure 3. Effect of the Al-Na$_2$SiO$_3$ polymer on scheelite and calcite flotation with the varying pH (C_{Alss} = 100 mg/L, $C_{lead\ ion}$ = 3 × 10^{-4} mol/L, C_{BHA} = 1.5 × 10^{-4} mol/L, $C_{terpineol}$ = 12.5 μL/L).

Flotation tests of a mixture of scheelite and calcite minerals were conducted under the optimal conditions determined from the above experiments. As shown in Table 1, a concentrate with 66.10% WO$_3$ was obtained with a WO$_3$ recovery of 79.81%, demonstrating that the Al-Na$_2$SiO$_3$ polymer shows good selectivity for the separation of scheelite from calcite.

Table 1. Flotation results from mixed minerals.

Products	Yield/%	WO$_3$ Grade/%	WO$_3$ Recovery/%
Concentrate	48.30	66.10	79.81
Tailings	51.70	15.62	20.19
Feeding	100.00	40.00	100.00

3.2. Structure of the Al-Na$_2$SiO$_3$ Polymer

3.2.1. FTIR Spectroscopy

In order to gain detailed information on the structure of the Al-Na$_2$SiO$_3$ polymer, the FTIR spectra of Na$_2$SiO$_3$ and Al-Na$_2$SiO$_3$ polymer were recorded, as shown in Figure 4. As for sodium silicate, the bands at 3324.73 and 3396.63 cm^{-1} are associated with hydroxyl stretching vibrations of sodium silicate molecules, the band at 1646.20 cm^{-1} corresponds to the bending vibration of hydroxyl groups, that at 990.71 cm^{-1} is assigned to the stretching vibration of the Si–O–Si bonds of SiO$_2$$^{2-}$, and the band at 460.92 cm^{-1} is attributed to the bending vibration of the Si–O–Si bonds of SiO$_4$$^{4-}$ [20–22]. Compared to the FTIR spectrum of sodium silicate, the Al-Na$_2$SiO$_3$ polymer spectrum shows some differences. New bands are observed at 2520.54 and 586.26 cm^{-1}, while the bands at 2954.46, 2328.51, 1454.20, and 835.94 cm^{-1} have disappeared, and the rest of absorption bands have shifted to different degrees, suggesting that the sodium silicate structure has changed upon the addition of aluminum ions. The new bands at 2520.54 and 586.26 cm^{-1} are attributed to O–Al bonding and Al–OH bending vibration, respectively, while the bands at 1105.02 and 445.14 cm^{-1} are attributed to the vibration

of Si–O–Al bonds [23–27]. These bands indicate that a chemical reaction has occurred between the aluminum ions and sodium silicate, where the aluminum ions have combined with the oxygen atoms of sodium silicate to form Si–O–Al bonds.
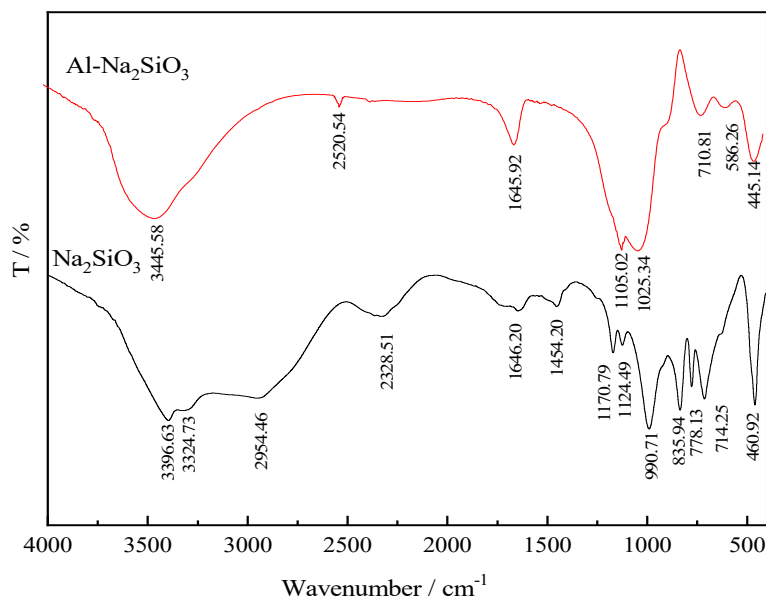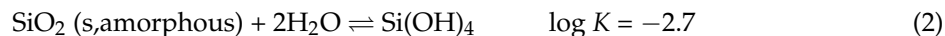

Figure 4. Fourier-Transform Infrared (FTIR) spectra of Na_2SiO_3 and the $Al-Na_2SiO_3$ polymer.

3.2.2. Self-Assembly of Sodium Silicate and Aluminum Ions in Solution

Sodium silicate is an alkali salt that undergoes severe hydrolysis in aqueous solution. Marinakis and Shergold [28] calculated the distribution of sodium silicate species in solution according to the following equilibria using the equilibrium constants determined by Lagerstrom [29]:

$$SiO_2 \text{ (s,amorphous)} + 2H_2O \rightleftharpoons Si(OH)_4 \qquad \log K = -2.7 \qquad (2)$$

$$Si(OH)_4 \rightleftharpoons SiO(OH)_3{}^- + H^+ \qquad \log K = -9.46 \qquad (3)$$

$$SiO(OH)_3{}^- \rightleftharpoons SiO_2(OH)_2{}^{2-} + H^+ \qquad \log K = -12.56 \qquad (4)$$

Based on Equations (2)–(4), the distribution of the hydrolysis species from sodium silicate at an initial concentration of 1×10^{-4} mol/L was calculated, as presented in Figure 5. In aqueous solution, sodium silicates present three major species: a neutral polyprotic $Si(OH)_4$ species prevailing at pH < 9.4, a mono-deprotonated conjugate base, $SiO(OH)_3{}^-$, which is dominant in the pH range of 9.4–12.6, and a di-deprotonated conjugate base, $SiO_2(OH)_2{}^{2-}$, which exists at pH > 12.6.

The sodium silicate species in aqueous solution may polymerize into polysilicic acid at a certain concentration [30,31]. In acidic solution, $Si(OH)_4$ may combine with H^+ to form $H_5SiO_4{}^+$. In neutral or alkaline solution, $Si(OH)_4$ may lose H^+ to form $H_3SiO_4{}^-$, favoring the polymerization reaction between $Si(OH)_4$ and $H_3SiO_4{}^-$ according to Figure 6 [31]:
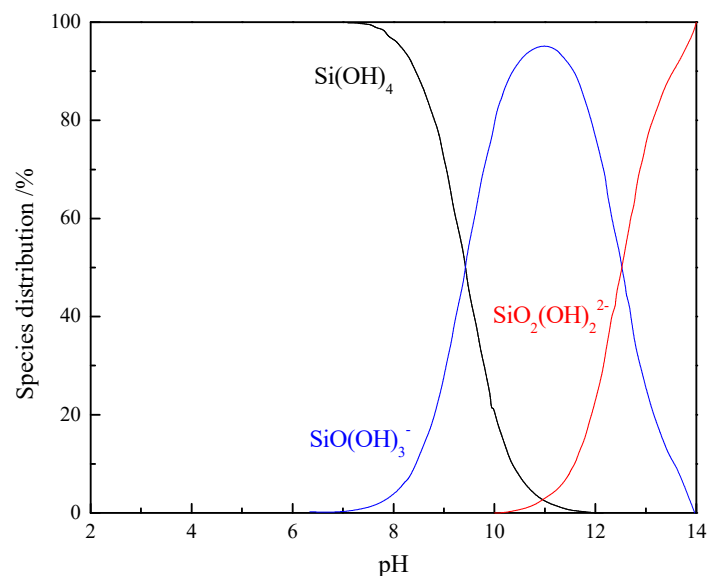
Figure 5. Speciation distribution of silicate anions as a function of the pH ($C = 1 \times 10^{-4}$ mol/L).
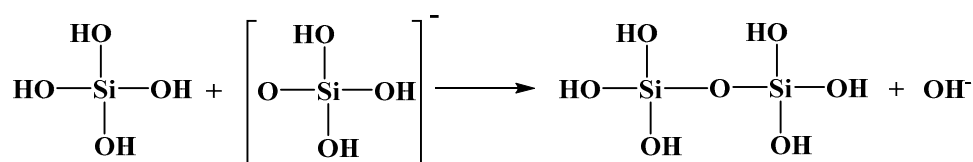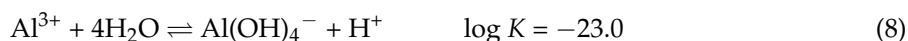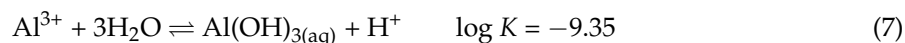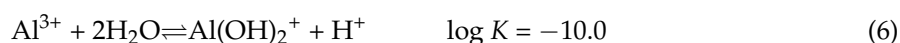

Figure 6. The polymerization reaction between $Si(OH)_4$ and $H_3SiO_4^-$.

$H_6Si_2O_7$ may react with OH^- to form $H_5Si_2O_7^-$, and then, a polymerization reaction between $H_6Si_2O_7$ and $H_5Si_2O_7^-$ proceeds to furnish a molecule with a higher degree of polymerization.

When aluminum salts enter the aqueous solution, the aluminum ions undergo a step-by-step hydrolysis reaction at pH > 3.0; at low aluminum concentrations (i.e., less than 0.001 mol/L), the majority of hydrolyzed aluminum exists as mononuclear aluminum hydroxide complexes [32–35]. The hydrolysis reactions proceed as per the equilibrium constants shown in the following equilibria [33,36–39]:

$$Al^{3+} + H_2O \rightleftharpoons AlOH^{2+} + H^+ \qquad \log K = -4.99 \qquad (5)$$

$$Al^{3+} + 2H_2O \rightleftharpoons Al(OH)_2^+ + H^+ \qquad \log K = -10.0 \qquad (6)$$

$$Al^{3+} + 3H_2O \rightleftharpoons Al(OH)_{3(aq)} + H^+ \qquad \log K = -9.35 \qquad (7)$$

$$Al^{3+} + 4H_2O \rightleftharpoons Al(OH)_4^- + H^+ \qquad \log K = -23.0 \qquad (8)$$
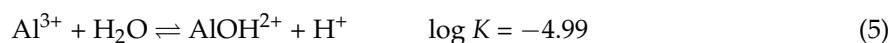
Based on Equations (5)–(8), the distribution of the hydrolysis species of aluminum ions at an initial concentration of 1×10^{-4} mol/L was calculated and plotted in Figure 7. In aqueous solution, Al^{3+} and mononuclear aluminum hydroxide complexes $Al(OH)^{2+}$ and $Al(OH)_2^+$ are predominant over the pH range of 3–6, while $Al(OH)_{3(aq)}$ species prevail across the pH range of 6–9 and $Al(OH)_4^-$ predominates at pH > 9.
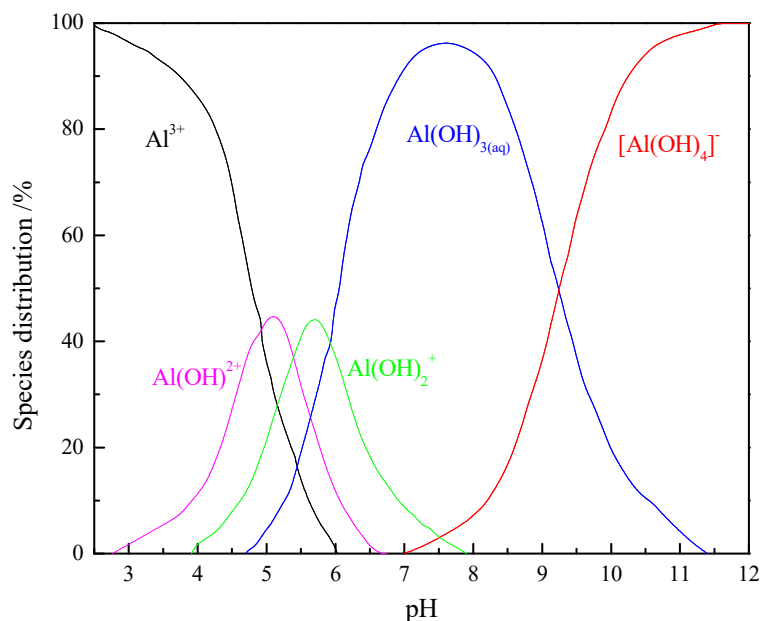
Figure 7. Speciation distribution of monomer aluminum as a function of the pH ($C = 1 \times 10^{-4}$ mol/L).

When aluminum ions are added to a solution of sodium silicate, a dehydration condensation reaction occurs between the aluminum hydroxide complexes and the hydroxy moiety of silicic acid or polysilicic acid, forming a new composite aluminosilicate polymer [40–42]. Taking the mononuclear hydrolysis species of silicic acid and aluminum as an example, under neutral and alkalescent conditions, $Si(OH)_4$ and $Al(OH)_3$ are the dominant species in solution. Such dehydration condensation reaction is speculated to proceed as Figure 8:
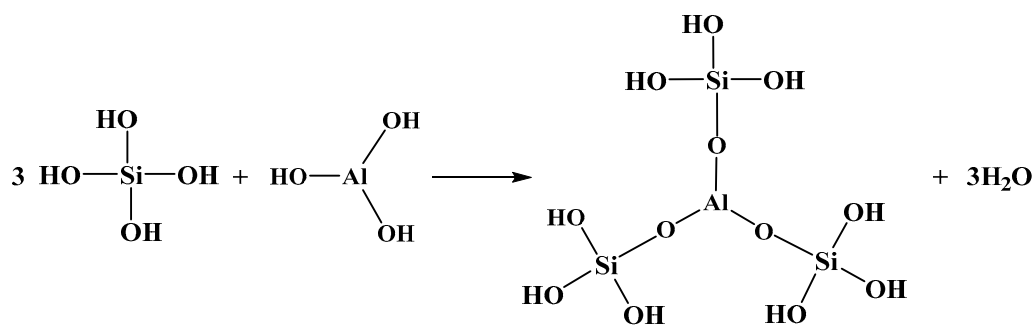

Figure 8. The dehydration condensation reaction between $Si(OH)_4$ and $Al(OH)_3$.

Under alkaline conditions, $H_3SiO_4^-$ and $Al(OH)_4^-$ are the dominant species in solution; thus, the dehydroxylation condensation reaction is speculated to proceed as Figure 9:
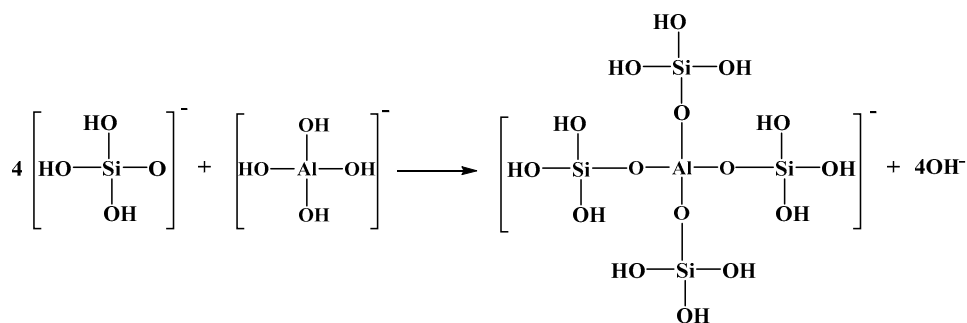

Figure 9. The dehydroxylation condensation reaction between $H_3SiO_4^-$ and $Al(OH)_4^-$.

After the condensation reaction, a new composite aluminosilicate polymer is formed, which contains Si–O–Al bonds in its structure, in agreement with the FTIR results from Figure 4. From the analysis of the above solution, when aluminum ions are added to the solution of sodium silicate, the aluminum hydroxide complexes and hydroxyl moiety of silicic acid or polysilicic acid self-assemble by dehydration or dehydroxylation condensation reactions to form an Al-Na$_2$SiO$_3$ polymer. Compared to Na$_2$SiO$_3$, the Al-Na$_2$SiO$_3$ polymer has a different structure with different physical and/or chemical properties. Indeed, the Al-Na$_2$SiO$_3$ polymer presents better selective adsorption for scheelite and calcite.

3.3. Effect of the Al-Na$_2$SiO$_3$ Polymer on the Adsorption of Pb-BHA Complexes on the Mineral Surface

The Al-Na$_2$SiO$_3$ polymer adsorbs on the surface of scheelite and calcite by chemisorption, where the oxygen atoms of Al-Na$_2$SiO$_3$ bind the calcium cations on the scheelite and calcite surface. Al-Na$_2$SiO$_3$ exhibits weak chemisorption on the scheelite surface, while it is adsorbed more powerfully on the calcite surface [19]. The Pb-BHA complex is a metal-organic collector, where the metal is the functional group that recognizes the W–O bonds on the scheelite surface. This approach is significantly different from traditional anion collectors that react with Ca sites on the mineral surface [17]. The adsorption diagram of silicic acid and Pb-BHA on the scheelite or calcite surface is shown in Figure 10. Silicic acid binds the calcium cations of the mineral surface; however, the Pb-BHA complexes recognize the oxygen bonds on the mineral surface, and thus, the adsorption of silicic acid (or Al-Na$_2$SiO$_3$ polymer) and Pb-BHA occurs at different sites. This mechanism is very different from traditional fatty acid flotation, where the fatty acid and silicic acid both react with the calcium cations on the mineral surface in a competitive manner [7,9,11,16].
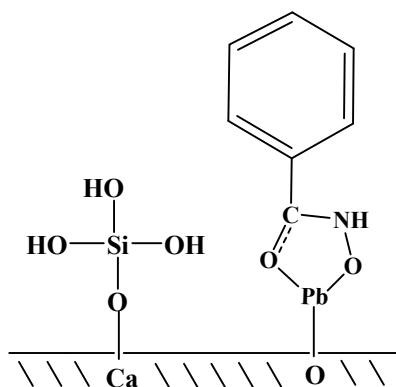

Figure 10. Adsorption diagram for silicic acid and a Pb- benzohydroxamic acid (BHA) complex on the scheelite surface.

3.3.1. Zeta Potential Measurements

The zeta potential results for Na$_2$SiO$_3$, Al-Na$_2$SiO$_3$ polymer, and Pb-BHA complex are shown in Figure 11. The Pb-BHA complex colloid exhibits a strong positive charge in the pH range of 6–10, and thus, it tends to adsorb on the negatively charged scheelite surfaces by electrostatic interactions [17]. In contrast, colloidal silicic acid and the Al-Na$_2$SiO$_3$ polymer have a negative charge, and the charge on the Al-Na$_2$SiO$_3$ polymer is more negative at about 20 mV in the pH range of 8–11, which may be attributed to the larger number of hydroxyl groups on the Al-Na$_2$SiO$_3$ polymer due to the bridging action of aluminum ions.
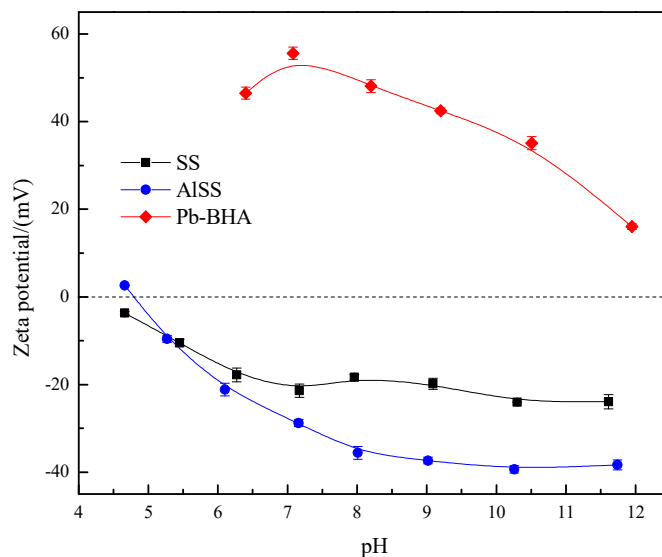
Figure 11. Zeta potential plots for Na$_2$SiO$_3$, Al-Na$_2$SiO$_3$ polymer, and Pb-BHA complex (C_{SS} = C_{AlSS} = 100 mg/L, $C_{lead\ ion}$ = 3 × 10^{-4} mol/L, C_{BHA} = 1.5 × 10^{-4} mol/L).

Compared to Na$_2$SiO$_3$, Al-Na$_2$SiO$_3$ adsorbs to a larger extent on the calcite surface than on scheelite [19]; therefore, the Al-Na$_2$SiO$_3$ polymer will also present a different influence on the adsorption of Pb-BHA complexes on the scheelite and calcite surfaces. The isoelectric point (IEP) of scheelite and calcite is circa 1.3 and 9.6, respectively; therefore, in the pH range of 7–9, the scheelite particles are negatively charged but calcite is always positively charged [8,43–45]. Figure 12 shows the zeta potential of scheelite and calcite at different concentrations of Pb-BHA after treatment with Na$_2$SiO$_3$ and the Al-Na$_2$SiO$_3$ polymer. The zeta potential of scheelite and calcite increases with the Pb-BHA dosage, indicating the adsorption of Pb-BHA on the minerals. From Figure 12a, the zeta potential of the scheelite treated with Al-Na$_2$SiO$_3$ increased remarkably compared to that with Na$_2$SiO$_3$, indicating that more Pb-BHA was adsorbed on the scheelite surface after treatment with the Al-Na$_2$SiO$_3$ polymer than with Na$_2$SiO$_3$. However, the opposite occurred for calcite, as seen in Figure 12b. Therefore, the Al-Na$_2$SiO$_3$ polymer had less influence on the adsorption of Pb-BHA complexes on the scheelite surface, while an obvious influence was observed for the calcite surface.
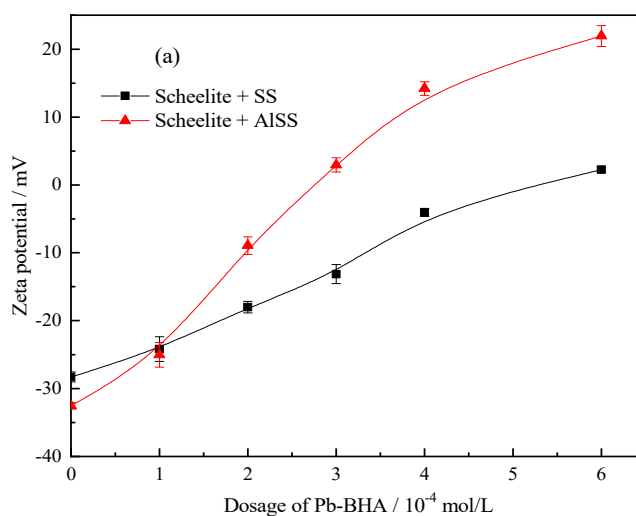

Figure 12. *Cont.*
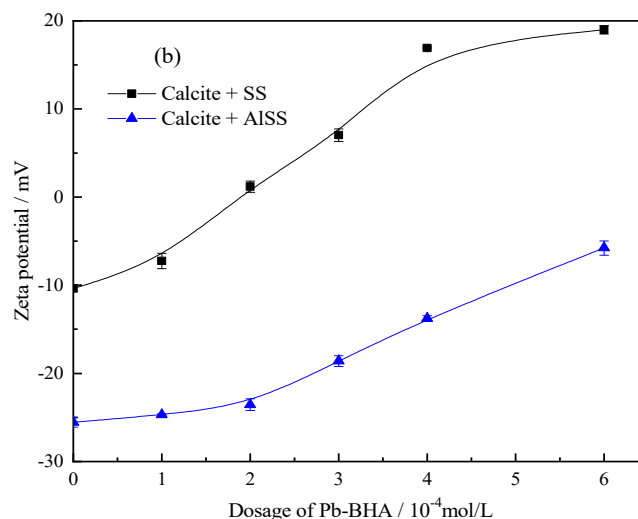
Figure 12. Zeta potential plots for (**a**) scheelite and (**b**) calcite at different concentrations of Pb-BHA after treatment with Na_2SiO_3 and the Al-Na_2SiO_3 polymer (pH = 8.0 ± 0.1, C_{Pb}:C_{BHA} = 2, C_{SS} = C_{AlSS} = 100 mg/L).

3.3.2. Adsorption Capacity

Figure 13 shows the adsorption capacity of Pb-BHA on the scheelite and calcite surface at different concentrations of Na_2SiO_3 and Al-Na_2SiO_3 polymer. The amount of Pb-BHA adsorbed on scheelite was more than that of calcite without Na_2SiO_3 or the Al-Na_2SiO_3 polymer, which is attributed to the specificity of Pb-BHA toward scheelite. Additionally, the adsorption curve shows some peaks with the increasing depressant dosage; however, herein, we focused on the different influence of Na_2SiO_3 and Al-Na_2SiO_3 polymer on the adsorption of Pb-BHA on scheelite and calcite. The results from Figure 13 indicate that the Al-Na_2SiO_3 polymer had less influence on the adsorption of Pb-BHA complexes on the scheelite surface, however, a significant influence was true for calcite, consistent with the zeta potential measurement results.
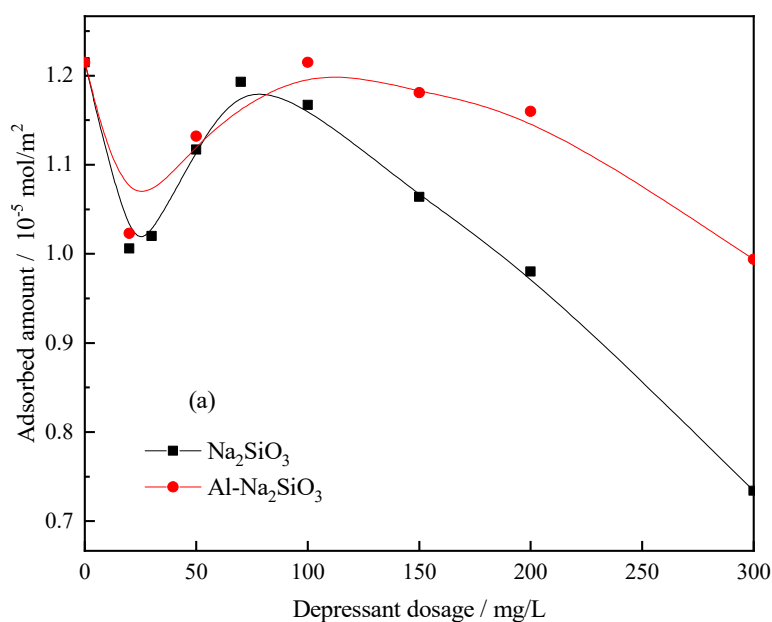

Figure 13. *Cont.*
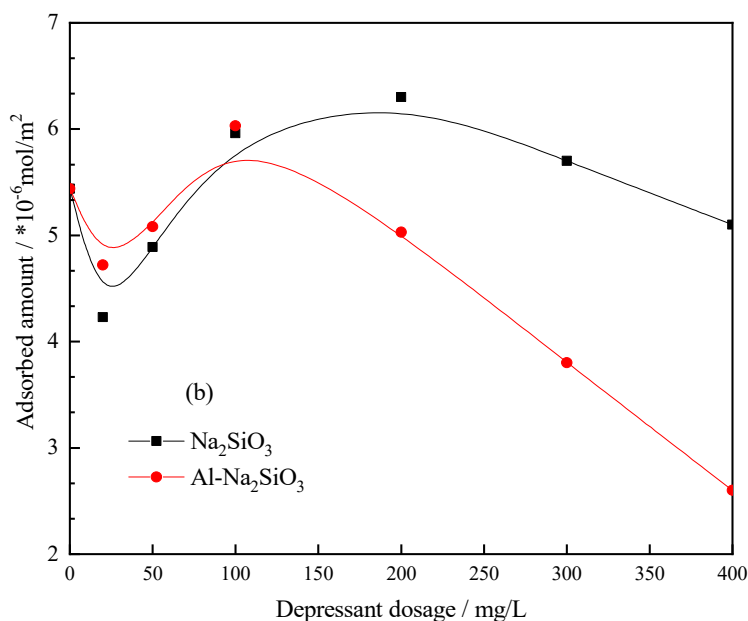
Figure 13. Pb-BHA amount adsorbed on the (**a**) scheelite and (**b**) calcite surface at different concentrations of Na_2SiO_3 and Al-Na_2SiO_3 polymer (pH = 8.0 ± 0.1, C_{Pb} = 3 × 10^{-4} mol/L, C_{BHA} = 1.5 × 10^{-4} mol/L).

3.4. Adsorption Model of the Al-Na₂SiO₃ Polymer and Pb-BHA Complexes on the Surface of Scheelite and Calcite

Based on the above analysis results, an adsorption model of the Al-Na_2SiO_3 polymer and Pb-BHA complexes on the scheelite and calcite surface was established to explain the superior selectivity of the Al-Na_2SiO_3 polymer toward scheelite and calcite during Pb-BHA flotation, as shown in Figure 14. The typical cleavage planes of scheelite expose more O atoms overall, leading to a negatively charged surface due to the dominant WO_4^{2-} species, and thus, the strongly positively charged Pb-BHA complexes can react with the O atoms of the scheelite surface more easily. In turn, the usual cleavage planes of calcite expose more Ca atoms; such dominant Ca^{2+} species result in a positively charged surface in the pH range of 7–9, and thus, the Pb-BHA complexes have more difficulty to adsorb on the calcite surface. This leads to the selectivity of the Pb-BHA complex as the collector during scheelite and calcite flotation. On the other hand, the Al-Na_2SiO_3 polymer has a larger negative charge than Na_2SiO_3 and thus, it is more difficult for the Al-Na_2SiO_3 polymers to adsorb on the negatively charged scheelite surface by electrostatic interactions, resulting in weaker chemisorption of the Al-Na_2SiO_3 polymer on the scheelite, which in turn leads to a lower amount of Al-Na_2SiO_3 polymers adsorbed on the scheelite surface. However, the opposite is true for calcite, resulting in a larger more amount of Al-Na_2SiO_3 polymers adsorbed on the calcite surface, rendering the surface strongly hydrophilic. This leads to the selectivity of the Al-Na_2SiO_3 polymer as the depressant during scheelite and calcite flotation. When selective flotation of scheelite from calcite is conducted using Pb-BHA complexes as the collector and Al-Na_2SiO_3 polymers as the depressant, their selectivity is fully exploited and reinforced by each other. More Pb-BHA complexes and fewer Al-Na_2SiO_3 polymers are adsorbed on the scheelite surface, rendering it strongly hydrophobic and floating to the surface of the slurry. Fewer Pb-BHA complexes and more Al-Na_2SiO_3 polymers are deposited on the calcite surface, rendering it strongly hydrophilic and sinking to the bottom of the slurry. Thus, the selective separation of scheelite from calcite is achieved through the cooperative selectivity of Pb-BHA complexes and Al-Na_2SiO_3 polymers.
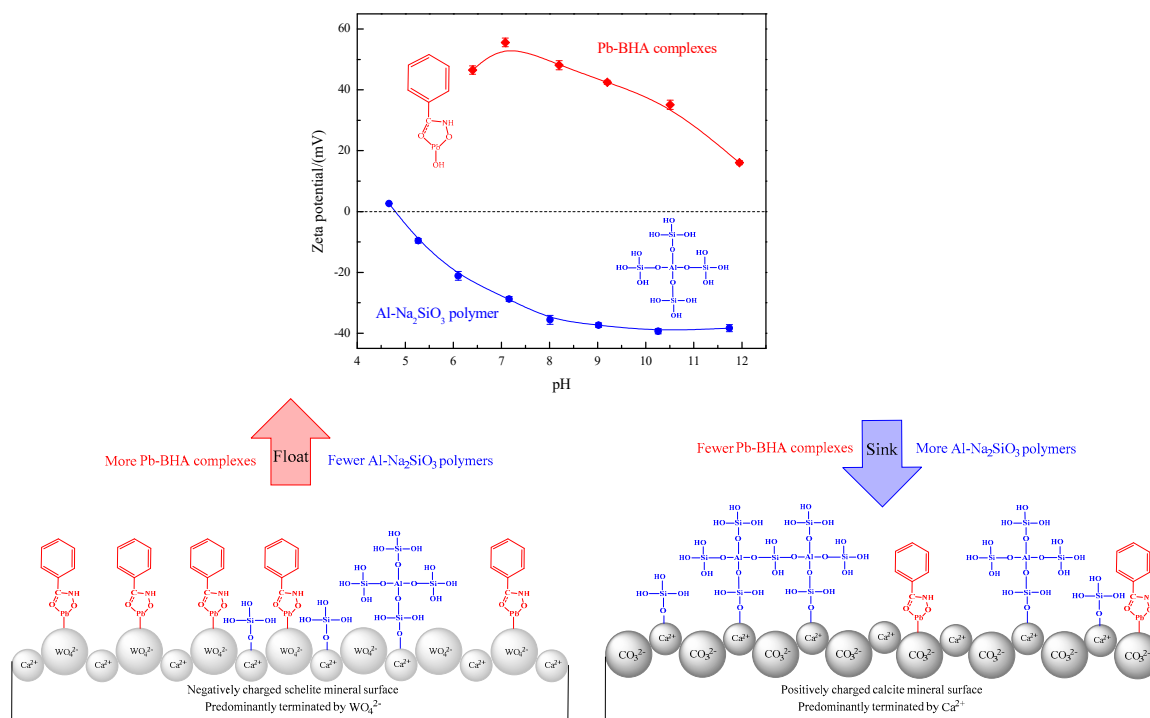
Figure 14. Adsorption model for the Al-Na$_2$SiO$_3$ polymer and Pb-BHA complexes on the scheelite and calcite surface.

In addition, based on the reverse zeta potential of Pb-BHA complexes and silicic acid colloid (or Al-Na$_2$SiO$_3$ polymer), we believe that a moderate amount of silicic acid colloid could make the zeta potential of the mineral surface more negative, which may benefit the adsorption of Pb-BHA complexes by electrostatic forces, thus providing an explanation for the increased flotation recovery and adsorbed amount curve. Certainly, this hypothesis needs further detailed studies for its clarification.

4. Conclusions

The Al-Na$_2$SiO$_3$ polymer showed good selectivity for the flotation separation of scheelite from calcite using Pb-BHA complexes as the collector at pH 8, where the optimum ratio of sodium silicate to aluminum sulfate was determined as 2:1. When aluminum ions were added to the solution of sodium silicate, the aluminum hydroxide complexes and the hydroxy moieties of silicic acid or polysilicic acid self-assembled via condensation, affording an Al-Na$_2$SiO$_3$ polymer, which is a new composite aluminosilicate polymer containing Si–O–Al bonds in its structure. The Pb-BHA complexes adsorbed more easily on the scheelite surface than on the calcite surface. On the other hand, the Al-Na$_2$SiO$_3$ polymer adsorbed with difficulty on the scheelite surface, but easily on the calcite surface. Upon adsorption of the Al-Na$_2$SiO$_3$ polymer and Pb-BHA complexes on the mineral surface, the Al-Na$_2$SiO$_3$ polymer exhibited low influence on the adsorption of Pb-BHA complexes on the scheelite surface, while the opposite was observed for calcite, which is attributed to the cooperative selectivity of Pb-BHA complexes and Al-Na$_2$SiO$_3$ polymers. More Pb-BHA complexes and fewer Al-Na$_2$SiO$_3$ polymers were adsorbed on the scheelite surface, while fewer Pb-BHA complexes and more Al-Na$_2$SiO$_3$ polymers were deposited on the calcite surface, leading to the selective separation of scheelite from calcite.

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