

## Effects of calcium ions on starch gelatinization and particle flocculation

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**Abstract:** While interfering ions in water play a crucial role in altering starch's adsorption behavior on hematite, their effects on starch gelatinization properties have not been fully understood. The purpose of this research is to investigate how  $\text{Ca}^{2+}$  affects the morphology of caustic-gelatinized starch and its effectiveness in flocculating iron oxides. A series of tests and measurements were employed, including batch flotation, sedimentation, turbidity, viscosity, zeta potentials, Fourier Transform Infrared, powder contact angle, and surface force calculations. The results demonstrate that calcium ions inhibit starch gelatinization, as evidenced by increased turbidity and reduced viscosity. This reduces floc size and settling rate, ultimately weakening starch's flocculation efficiency. The mechanism likely involves calcium-mediated re-entanglement of stretched starch chains through interactions with the functional sites generated during alkaline gelatinization. The formation of Ca-starch crosslinking diminishes the starch gel's ability to flocculate fine particles.

**Keywords:** starch, gelatinization, calcium, particle, flocculation

### 1. Introduction

Due to its eco-friendly and cost-effective properties, starch has been extensively applied as a flocculant in iron ore flotation (Peres and Correa, 1965; Weissenborn et al., 1995). Starch gels are typically prepared through thermal treatment, alkaline digestion, or both. Gelatinization is a complex process involving the disruption of starch granule crystallinity and subsequent formation of a viscous sol-gel (Yang and Montgomery, 1996; Roberts and Cameron, 2002). Beyond gelatinization parameters (e.g., starch/NaOH ratio, water content, heating temperature, or gelatinization time), water quality could also be shown to modify gel properties, thereby influencing starch's flocculation performance (Patel and Seetharaman, 2006; Li et al., 2007; Tang and Liu, 2012).

Many researches in the food and biological applications focus on the influence of cations on starch gelatinization. It demonstrates that metal ions of different valences distinctly modify starch gel properties, including gelatinization temperature, solubility, and viscosity (Smasundaran and Natarajan, 1988; Brown et al., 1995; Fan et al., 2017; Zhong et al., 2022; Abedi et al., 2024). While monovalent ions like  $\text{Na}^+$  affect polysaccharide gel properties (Reyniers et al., 2019; Zhang et al., 2019), divalent cations ( $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ) exhibit more pronounced effects, enhancing viscosity, solubility, and swelling capacity but reducing gelatinization temperature (Zhong et al., 2022; Abedi et al., 2024). In contrast, trivalent ions ( $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ ) increase maize starch's gelatinization temperature through glycosidic bond cleavage and form stable starch complexes that inhibit digestion (Zhang et al., 2024; Zhuang et al., 2024). These effects could be attributed to multiple mechanisms: disruption of intra-granular hydrogen bonds, interactions with hydroxyl groups, and metal-starch complexation (Szymońska et al., 2015; Wang et al., 2017; Zhong et al., 2022; Wang et al., 2023).

Unlike previous findings in food or biological areas, these metal ions may exhibit fundamentally different effects on starch-induced particle flocculation in mineral flotation systems. Sodium ions, for example, have little effect on the particle flocculation process of starch as monovalent ions are insufficient to overcome the repulsive forces between particles (Ganz, 1965; Oosten and Breda, 1990; Antisari et al., 2010). But  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions can enhance flocculation selectivity due to the formation

of large and stable particle flocs (Zhang et al., 2007). Trivalent ions are different cases, in which their impact was concentration-dependent: beneficial for flocculation at low levels yet inhibitory at high levels (Fu et al., 2023; Wang et al., 2024). Precipitation of these cations as metal hydroxides, carbonates, or sulfates could reverse surface  $\zeta$ -potentials, thereby interfering with polysaccharide adsorption on mineral particles (Somasundaran et al., 1988; Fornasiero and Ralston, 2006; Liu et al., 2013).

Although the above highlighted the importance of these cations in modifying the structure and properties of the starch gel in food or biological industry, the nature of  $\text{Ca}^{2+}$  disturbance on starch pasting properties and flocculating particle capacity during mineral flotation was not fully understood. Local freshwater sources, particularly those with varying hardness components, are routinely employed for starch preparation in flotation processing plants. These ionic constituents can fundamentally reshape the starch digestion process while simultaneously altering flocculation efficiency. To identify how  $\text{Ca}^{2+}$  influences the gel configurations of starch and their effectiveness in flocculating particle, batch flotation tests, turbidity tests, viscosity tests, settling tests, powder contact angle measurement, FTIR, and zeta potential analysis were conducted.

## 2. Materials and methods

### 2.1. Materials

The iron oxide ore sample at grades of 55.6% Fe and 10.5%  $\text{SiO}_2$  was obtained from a Yunnan iron mine (China) for flotation experiments. XRD characterization was performed using a Bruker D8 Discovery diffractometer (Co-K $\alpha$  radiation,  $\lambda = 1.79 \text{ \AA}$ ). Fig. 1 shows the diffraction pattern, with identified peaks corresponding to magnetite ( $\text{Fe}_3\text{O}_4$ ), ankerite [ $\text{Ca}(\text{Fe,Mg})(\text{CO}_3)_2$ ], quartz ( $\text{SiO}_2$ ), and phyllosilicate minerals.

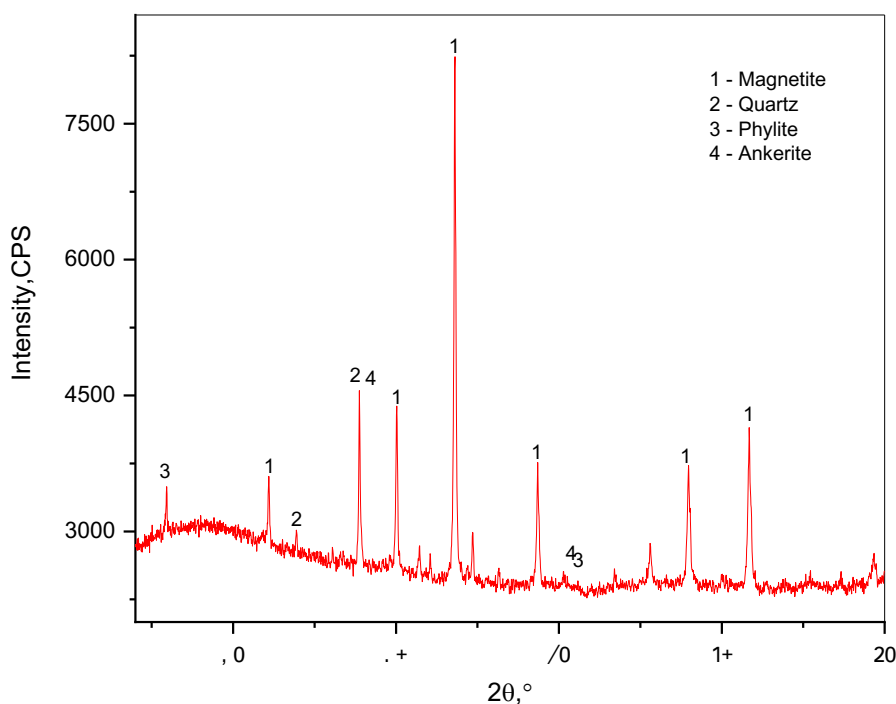


Fig. 1. The XRD data from the ore sample in a Yunnan Iron mine, China

High-purity hematite powder at  $\text{Fe}_2\text{O}_3 > 99\%$  (particle size  $< 5 \mu\text{m}$ ) sourced from Sigma-Aldrich) was used for all measurements, contact angle determination, and FTIR spectroscopy. Analytical-grade reagents,  $\text{CaCl}_2$  ( $\geq 99\%$ ),  $\text{KCl}$  (99.4%),  $\text{NaOH}$  (98.8%), and  $\text{HCl}$  (99%), were obtained from Fisher Scientific. Dodecylamine ( $> 97\%$ ) served as the collector. The gelatinization process employed corn starch (Sigma-Aldrich) and sodium hydroxide in a 5:3 weight ratio (starch: $\text{NaOH}$ ), a ratio previously optimized by Tang and Liu (2012). Before gel preparation, predetermined concentrations of calcium ions were introduced into deionized water, which served as the universal solvent for all experimental procedures and analytical measurements.

## 2.2. Methods

### 2.2.1. Turbidity and viscosity of the starch gel

Turbidity measurements of starch suspensions were conducted using a VWR Scientific 66120-200 turbidimeter. Starch gels were prepared by mixing a 5:3 (w/w) starch-to-NaOH ratio in 200 mL of deionized water containing  $\text{Ca}^{2+}$  (0, 1, 2, 4, or 8 mmol/L). The suspensions were gently agitated for 30 min at  $25 \pm 1$  °C. Measurements were performed in triplicate, with mean values reported.

The viscosity of starch gels with or without  $\text{Ca}^{2+}$  during alkali digestion was measured using a Cannon-Fenske Routine Viscometer (Model 51310, USA). Samples were prepared identically to the turbidity tests and diluted 3-fold before analysis. Efflux times between the marked lines were recorded for deionized water ( $t_0$ ) and starch solutions ( $t$ ). The viscometer was rinsed with deionized water and ethanol, then dried between trials. Dynamic viscosity ( $\eta_r$ ) was calculated using Eqs. 1–2, accounting for starch concentration ( $c$ ) and the Kramer constant ( $\beta$ ).

$$\eta_r = t/t_0 \quad (1)$$

$$\frac{\ln \eta_r}{c} = [\eta] + \beta [\eta]^2 c \quad (2)$$

### 2.2.2. Sedimentation test and floc size analysis

The settling rate of starch-induced hematite flocs with or without  $\text{Ca}^{2+}$  was evaluated using a glass graduated cylinder (250 mL capacity, 28 cm tall  $\times$  4 cm diameter). Starch gels were prepared by digesting 2000 mg of starch with 1200 mg of NaOH in 200 mL of deionized water, slightly conditioning for 30 min. For settling tests, a 100 mL aliquot of 100 mg/L starch solution was combined with 150 mL of hematite suspension (2% w/v, equivalent to 3 g hematite), followed by agitation in a temperature-controlled shaker for 10 min. Interface settling times were recorded at  $25 \pm 1$  °C. Floc size distributions (0.1–1000  $\mu\text{m}$ ) were also analyzed using a BT-9300S laser granulometer.

### 2.2.3. Batch flotation test

Batch flotation tests were conducted in a 1.5 L XF-D flotation cell operating at 1160 rpm with a superficial gas velocity ( $J_g$ ) of 0.85 cm/s. Starch gels containing varying  $\text{Ca}^{2+}$  concentrations (prepared as described previously) were introduced at 300 g/t ( $\approx$ 100 mg/L), along with 80 g/t dodecylamine collector, to 500 g ore samples in 1.5 L water (natural pH  $\approx$ 8.5). Following 10 minutes of flotation (10 cm froth depth), concentrates and tailings were vacuum-filtered, oven-dried, weighed, and analyzed for iron content.

### 2.2.4. Powder contact angle measurement

The contact angles of starch-induced hematite flocs were measured using A K100 tensiometer (Krüss GmbH, Germany) with ADVANCE software. Starch gels (100 mg/L) were prepared in  $\text{Ca}^{2+}$ -containing deionized water (0–8 mmol/L) following standard NaOH pasting procedures. For testing, 100 mL starch gel and 150 mL hematite solution (2% w/v, 3 g hematite) were mixed (10 min, 25°C), then, filtered, and vacuum-dried. Measurements were performed on 1.5 g samples based on Eqs. 3 (Tohry et al., 2020),

$$\theta = \arccos \frac{\eta}{c \rho^2 \sigma} \cdot \frac{m^2}{t} \quad (3)$$

where the parameters were used in the contact angle calculations:  $m$  = mass of liquid absorbed by capillary action (g),  $c$  = powder capillary constant ( $\text{mm}^5$ ),  $\rho$  = liquid density (g/mL),  $\sigma$  = surface tension (mN/m),  $\eta$  = viscosity (mPa  $\cdot$  s),  $t$  = time (s), and  $\theta$  = contact angle (°). Anhydrous ethanol and deionized water are reference liquids to determine the capillary constant and contact angle.

### 2.2.5. Zeta potential measurement

A Malvern Zetasizer Nano ZS90 was employed to determine the zeta potentials of hematite, starch gel (with/without  $\text{Ca}^{2+}$  during/after gelatinization), and their mixtures. For  $\text{Ca}^{2+}$ -modified starch gels, 100 mL of 2 mmol/L  $\text{CaCl}_2$  solution was used during or after alkali digestion (5:3 of starch to NaOH weight

ratio). Flocculation samples were prepared by mixing 100 mL starch solution with 150 mL hematite suspension (2% w/v, 3 g Fe<sub>2</sub>O<sub>3</sub>) in a temperature-regulated shaker (25±1°C, 10 min). Before zeta potential analysis, 5 mL aliquots were diluted to 100 mL with 1 mM KCl electrolyte solution, followed by pH adjustment.

### 2.2.6. FTIR analysis

FTIR characterization of calcium chloride, starch gel prepared with/without calcium ions, and its induced hematite flocs by using a Bruker Alpha FTIR spectrometer. Alkali-induced gelatinization of starch was conducted in calcium-enriched deionized water (2 mmol/L Ca<sup>2+</sup> concentration). An aliquot of the starch was collected for direct FTIR analysis. Then 150 mL of hematite solution (2% w/v, 3 g Fe<sub>2</sub>O<sub>3</sub>) was added to either Ca<sup>2+</sup>-containing or Ca<sup>2+</sup>-free starch gel, followed by 10-minute conditioning. After centrifuging, filtrating, and drying, the powdered samples (10-15 mg) were mixed with KBr and pressed into pellets for FTIR measurement over the spectral range of 4000-400 cm<sup>-1</sup>.

### 2.2.7. Surface force calculations in hematite-starch interaction

The extended Derjaguin-Landau-Verwey-Overbeek (DLVO) theory was applied to assess interfacial interactions in the hematite-starch system. The total interaction energy ( $V_T$ ) was calculated as follows (Loveland et al., 1996; Xie et al., 2021),

$$V_T = V_d + V_e + V_{Born} + V_{AB} \quad (4)$$

where  $V_d$ ,  $V_e$ ,  $V_{Born}$ , and  $V_{AB}$  represent the van der Waals, electrostatic, Born repulsion, and Lewis acid-base hydration energies, respectively.

Considering a spherical particle interacting with a planar surface, the short-range van der Waals energy can be evaluated through the Hamaker approximation as follows:

$$V_d = - \frac{(\sqrt{A_{11}} - \sqrt{A_{33}})(\sqrt{A_{22}} - \sqrt{A_{33}}) r_p}{6H} \quad (5)$$

where  $A_{11}$ ,  $A_{22}$ , and  $A_{33}$  denote the Hamaker constants for hematite (1), starch (2), and water (3) in vacuum, respectively;  $H$  represents the surface separation distance (m) between hematite and starch;  $r_p$  is the radius (m) of the hematite particle.

$V_e$ ,  $V_{Born}$ , or  $V_{AB}$  can be calculated by the Eqs (6) - (8) (Peçanha et al., 2019; Zhang et al., 2022),

$$V_e = \pi \epsilon_r \epsilon_0 r_p [2\psi_1 \psi_2 \ln \left( \frac{1+e^{-kH}}{1-e^{-kH}} \right) + (\psi_1^2 + \psi_2^2) \ln (1 - e^{-2kH})] \quad (6)$$

$$V_{Born} = \frac{A_{123} \sigma_{Born}^6}{7560} \left[ \frac{8r_p H}{(2r_p + H)^7} + \frac{6r_p - H}{H^7} \right] \quad (7)$$

$$V_{AB} = 2\pi r_p \lambda_{AB} V_{AB(H=H_0)} \exp \left[ \frac{H_0 - H}{\lambda_{AB}} \right] \quad (8)$$

here the Stern potentials  $\psi_1$  and  $\psi_2$  (approximated by zeta potentials, in V) represent the surface charges of hematite and starch, respectively. The dielectric constant of water  $\epsilon_r$  is  $6.95 \times 10^{-10}$  C/(V m), while the Debye length  $1/\kappa$  is calculated as  $0.304\sqrt{C}$ , where  $C$  is the electrolyte concentration (mol/L). Key parameters include the attenuation length  $H_0$  (m), hydrophobic interaction constant  $\lambda_{AB}$  (J/m<sup>3</sup>), and natural logarithm base  $e$ . All energies are normalized to thermal energy units  $K_B T$ , with  $K_B = 1.381 \times 10^{-23}$  J/K at  $T = 298$  K.

## 3. Results and discussion

### 3.1. Flotation tests

The role of calcium ions on the flotation performance of iron oxides was investigated as shown in Fig. 2. There is a negative effect in enhancing the separation selectivity of the iron ore as calcium ion concentration increases. At low concentrations of Ca<sup>2+</sup> ions, there is a slight increase by about 1% in iron grade but a sharp drop with increasing calcium ion concentration at over 2 mmol/L. A substantial decrease of over 5% in iron recovery occurs when calcium ion concentration reaches 10 mmol/L. The interactions between the acidic groups in the starch gel produced by alkali treatment and calcium-based species by forming complexes between metal ions and starch molecules could be attributed to this drop (Li et al., 2015; Szymońska et al., 2015; Zhong et al., 2022; Wang et al., 2023; Tang et al., 2024). The

resulting entangled structures of the starch segments could hinder the adsorption of starch and hematite.

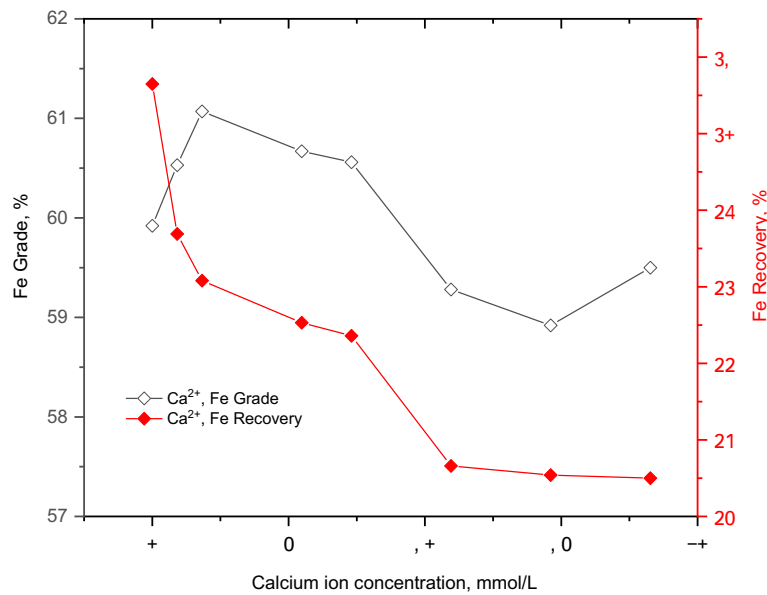


Fig. 2. The results from batch flotation tests if starch was gelatinized with different concentrations of  $\text{Ca}^{2+}$  ions

### 3.2. Flocculating behaviors of the starch gel with $\text{Ca}^{2+}$ ions

Fig. 3 provides the size fractions of the starch-induced hematite flocs when calcium ions were present during starch alkali-digestion. The results demonstrate that the original particles at a size range of over 90% passing 5  $\mu\text{m}$  were flocculated by the starch gel without calcium ions to form the flocs at 90% passing 58.09  $\mu\text{m}$ . Calcium ions significantly reduce floc particle sizes. The higher the ionic concentration is, the smaller the floc size is. The starch solution with 8 mmol/L  $\text{Ca}^{2+}$  ions almost loses its flocculating capacity on fine particles as the dominant size fraction of the particle flocs was 90% passing only 3.76  $\mu\text{m}$ . It could contribute to the loss in the flotation recovery of the iron oxides as  $\text{Ca}^{2+}$  ion concentration increases from Fig. 2. This can be explained by the settling data as seen from Fig. 4, indicating that  $\text{Ca}^{2+}$  ions can largely lower their settling rates with increasing  $\text{Ca}^{2+}$  ion concentrations. It is also worth to note that the interface line of the flocs' settlement was difficult to observe in the first 75 seconds if the  $\text{Ca}^{2+}$  ion concentration reached 8 mmol/L.

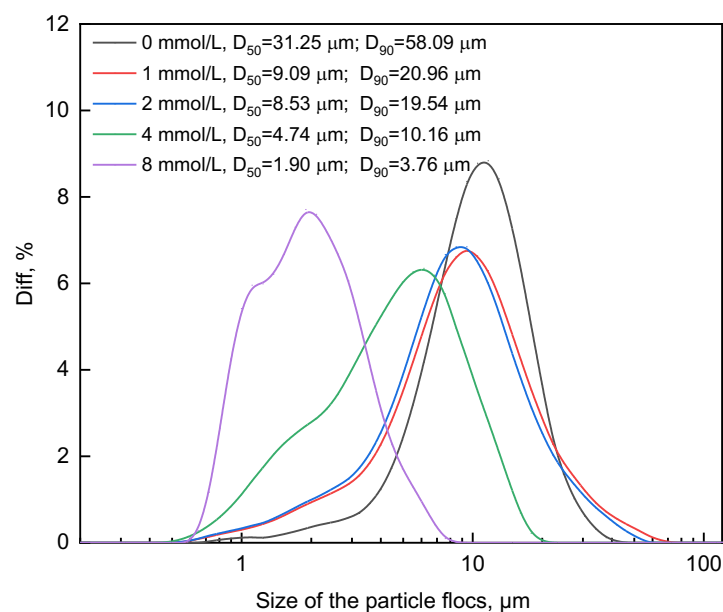


Fig. 3. Size analyses of the starch-induced hematite flocs when  $\text{Ca}^{2+}$  ions occur during starch gelatinization

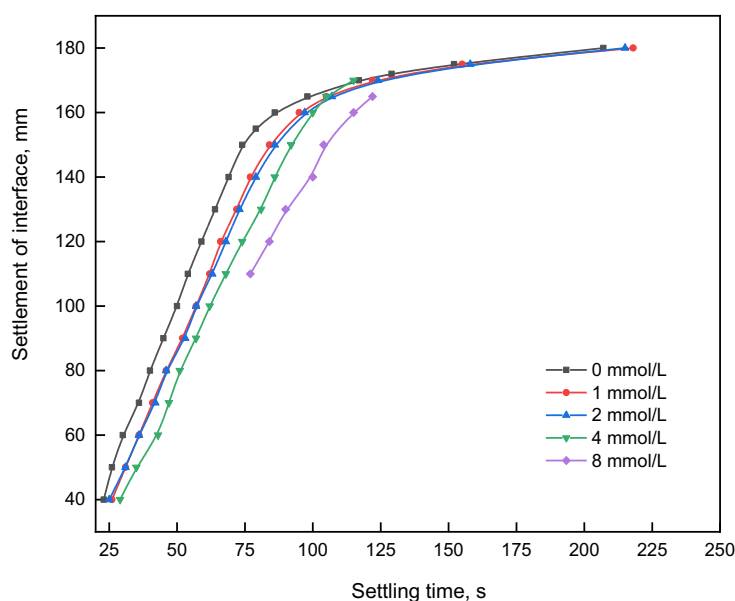


Fig. 4. Floc settling behaviors induced by  $\text{Ca}^{2+}$ -modified starch

### 3.3. Contact angle measurements

Fig. 5 displays the changes on surface wettability of hematite induced by the starch gelatinized with  $\text{Ca}^{2+}$  ions. Without calcium ions, the contact angle decreases by  $5.6^\circ$  when the particles are treated by starch. The contact angle rises slightly as the  $\text{Ca}^{2+}$  concentration increases from 0 to 4 mmol/L. At 8 mmol/L  $\text{Ca}^{2+}$ , the contact angle reaches  $83^\circ$ , suggesting reduced hydrophilicity of the starch-adsorbed particles rather than enhanced hydrophilicity. This is consistent with the trends observed in Figs. 2–4, pointing out that calcium ions weaken the effectiveness in flocculating the particles of starch. As a result, mineral surfaces become less hydrophilic, slowing floc settling. This differs from the effects of these metal ions in the pulp, as they may interact with mineral surfaces, starch, or both. Previous studies (Zhang et al., 2007; Wang et al., 2023) report that divalent metal ions can promote starch adsorption on minerals when present during flocculation—an effect not observed here.

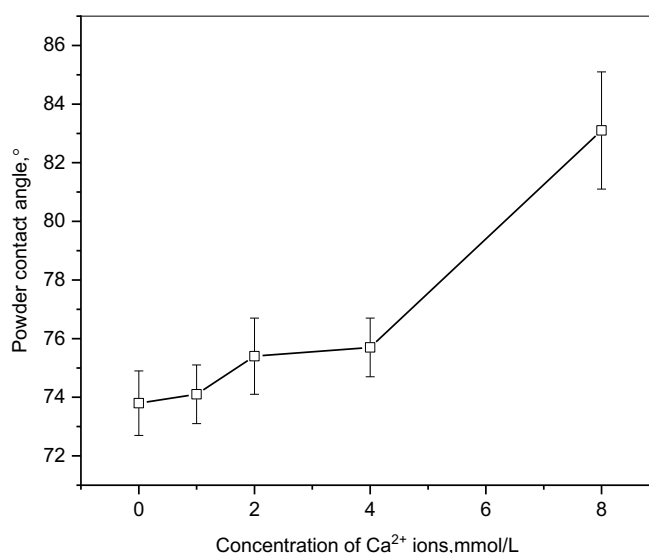


Fig. 5. The contact angles of the hematite treated by the starch gel with calcium ions at different concentrations

### 3.4. Morphological characteristics of the starch gel with $\text{Ca}^{2+}$ ions

Fig. 6 exhibits a significant increase in the turbidities of the starch gel with an increase in  $\text{Ca}^{2+}$  ion concentration. It reaches approximately 450 NTU at over 4 mmol/L  $\text{Ca}^{2+}$  ions, which induces a less

transparent solution than the one without calcium ions. Some white precipitates were also observed in the solution if the calcium ion concentration was 8 mmol/L, which could be attributed to  $\text{Ca}(\text{OH})_2$  formation at alkali. The bonding of hydroxide ions with calcium ions at high concentrations could hinder the break-up of starch granules during caustic digestion, affecting the transparency and gelatinization degree.  $\text{Ca}^{2+}$  ions at low concentrations, however, only a slight increase in turbidity occurs, suggesting that the presence of calcium ions could increase the possibility of intertwining among the long-chain residues due to the cross-link interactions between Ca-based species and the acidic sites resulting from alkali digestion. Evidenced by the results from Fig. 7, a drop in the viscosity of the starch gel occurs with increasing  $\text{Ca}^{2+}$  ion concentration. This explains the data from Figs. 2-5, revealing that the pre-occupying of the functional sites on the starch fragments by calcium-based complexes could weaken its flocculating capacity. It is worth to note that the starch gel almost loses viscosity when calcium ions are over 8 mmol/L. The deactivation of alkali by bonding with  $\text{Ca}^{2+}$  ions at high concentrations could contribute to uncompleted gelatinization of the starch solution with many entangled configurations, producing a starch sol-gel with less transparency in comparison with the one without calcium ions shown in Fig. 6. Ciesielski and Krystyjan (2009) reported that iron or nickel ions had a devastating effect on the viscosity of starch gels as metal hydroxide adheres to starch micelles. These divalent metal ions could adsorb selectively on starch derivatives (Khalil and Farag, 1998). Similar observations found by Fu et al. (2023) confirmed the formation of Pb-, Al-, or Fe-starch complexes. However, it conflicts with the research in the biological area explored by Abedi et al. (2024), revealing that calcium ions can increase the starch viscosity. This could be related to the difference in the gelatinization condition of starch for its use in mineral flotation or food preparation.

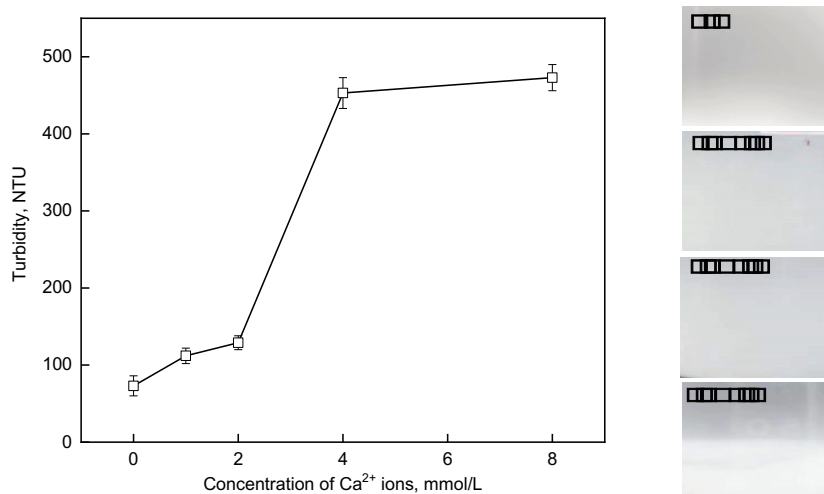


Fig. 6. Turbidity of the starch gel bearing various contents of calcium ions

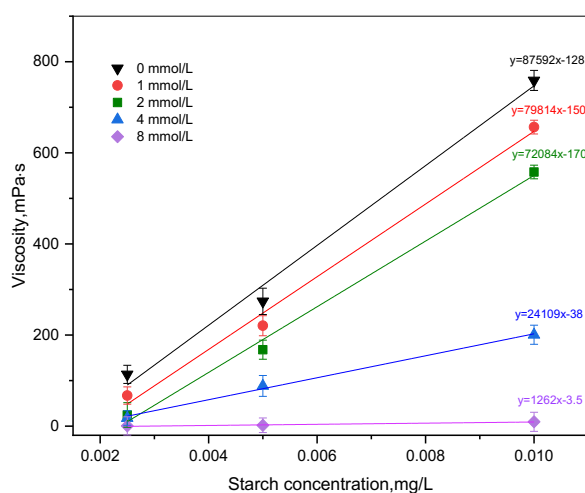


Fig. 7. The viscosity of the starch gel bearing various contents of calcium ions

### 3.5. Zeta potential measurements

Fig. 8a presents the zeta potentials of the starch treated by calcium ions during or after alkali gelatinization. The results show that the starch gel becomes less negative-charged if calcium ions were present compared to the one without any ions. But a shift towards the more positive side occurs when calcium ions were added directly into the starch solution after caustic gelatinization. It reveals that when introduced during the gelatinization stage,  $\text{Ca}^{2+}$  ions form coordination complexes with alkali-generated functional groups (e.g., carboxylates), thereby stabilizing starch's charge properties against ionic interference. However, these cations occurring after alkali gelatinization decrease the negative-charged density of starch and even reverse it. It differs from the unexpected invasion of these cations during starch degradation inducing the alternation of physicochemical gel structures (Tang et al, 2024). Similar findings reported by Zhi et al. (2023), mentioned that divalent cations induced a significant charge reversal in resistant starch particles, resulting in a net positive potential (+12.9 mV from initial -18.6 mV).

The disturbance of  $\text{Ca}^{2+}$  introduction during alkaline starch gelatinization on hematite's zeta potentials is also demonstrated in Fig. 8b. A shift towards a more positive side in hematite zeta potentials was induced by the  $\text{Ca}^{2+}$ -modified starch. This means that the invasion of calcium-based species preoccupy the functional sites of the starch remnants and hinder their adsorption on mineral surfaces (Tang and Liu, 2012; Abedi et al., 2024). This corresponds to the data from Figs. 4-7, indicating that calcium ions during starch gelatinization decreasing the negative-charged density of starch, reduce the floc sizes, and slow the settling rates, consequently weakening the surface wettability of hematite.

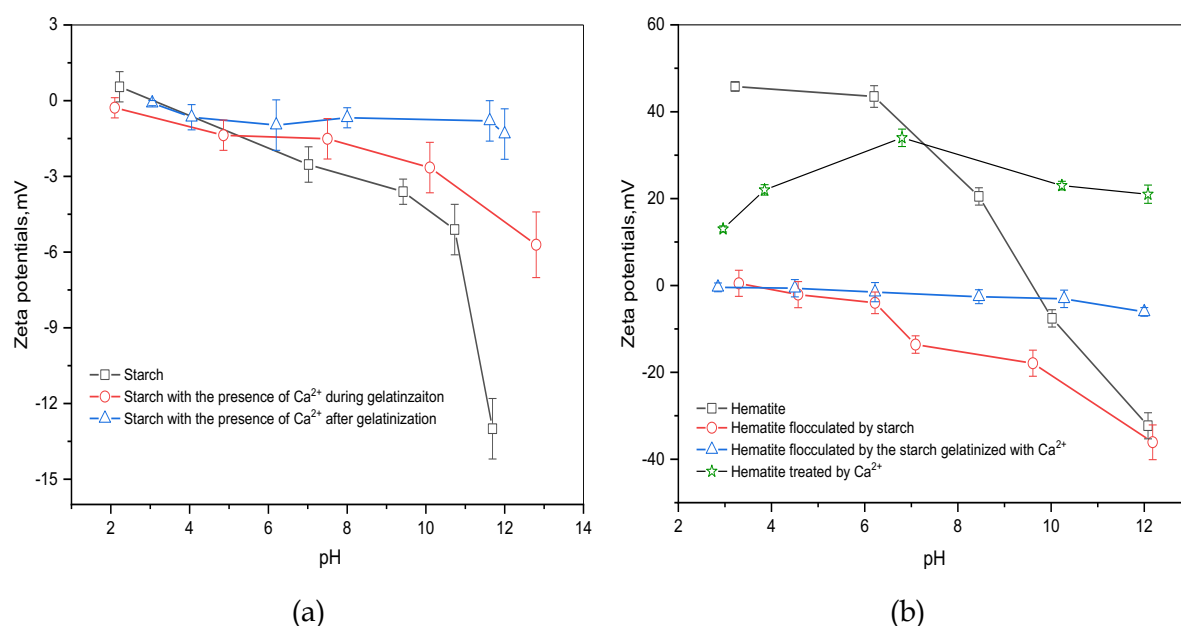


Fig. 8. Effects of  $\text{Ca}^{2+}$  ions on starch zeta potential (a) and hematite potentials induced by starch or  $\text{Ca}^{2+}$ -starch (b) ( $10^{-3}$  mol/L KCl)

### 3.6. FTIR analysis

Fig. 9 displays the FTIR spectra of hematite flocculated by a sodium hydroxide-gelatinized starch suspension in deionized water containing 2 mmol/L  $\text{Ca}^{2+}$  ions. A distinct peak at  $1394\text{ cm}^{-1}$  is observed in the spectrum of the  $\text{Ca}^{2+}$ -starch, which is absent in the spectrum without  $\text{Ca}^{2+}$  ions. This peak is likely associated with the formation of Ca-starch complexes in comparison with the peak at  $1390\text{ cm}^{-1}$  in the spectrum of  $\text{CaCl}_2$ . The interaction of calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) or calcium carbonate ( $\text{CaCO}_3$ ) with active groups (e.g.  $-\text{COOH}$  or  $\text{C}-\text{OH}$ ) may stretch these bonds at near  $1692\text{ cm}^{-1}$  (Liu et al., 2002). This is consistent with the above results depicted in Figs. 4-7, which suggest the formation of the complexes among  $\text{Ca}(\text{OH})_2$  or  $\text{CaCO}_3$  compounds and the acidic sites on the starch chains. This pre-occupation leads to the contraction or coiling of the long-chain configurations, compromising mineral surface



adsorption efficiency. Similar  $-\text{CH}_2\text{-O-Al}^{2+}$  complexation was found by Wang et al. (2024) in alkali starch- $\text{Al}_2(\text{SO}_4)_3$  systems.

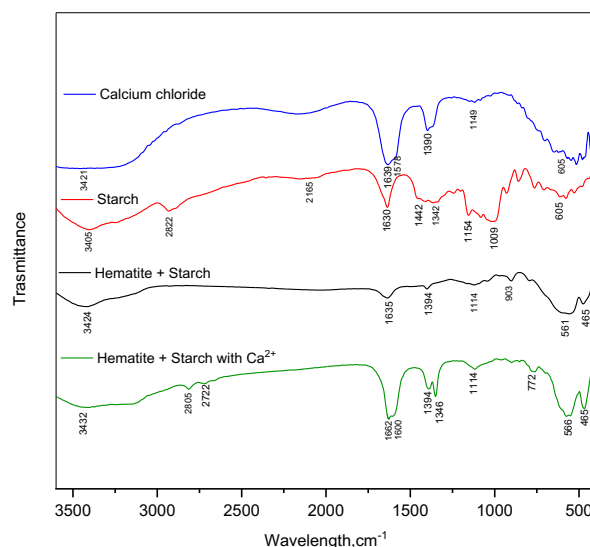


Fig. 9. The FTIR spectra of native starch,  $\text{CaCl}_2$ , and hematite flocculated by starch gel prepared with/without 2 mM  $\text{Ca}^{2+}$  during alkaline digestion

### 3.7. Interaction force calculation between hematite and starch

Fig. 10 calculates the interaction forces between hematite and starch gelatinized with or without  $\text{Ca}^{2+}$  based on the extended DLVO theory (Eqs. 4-8) related to the experimental conditions. The total  $V_T$  ( $K_B T$ ) between hematite and the starch was less attractive with the addition of  $\text{Ca}^{2+}$  ions, primarily due to the weakened attraction between the starch and mineral surfaces. This shift towards the positive side correlates with the intrusion of  $\text{Ca}^{2+}$  in the caustic-gelatinized starch, altering the physicochemical properties of the starch remnants as shown in Figs. 6-8. It indicates that the presence of calcium ions in the alkali digestion of starch could harm the effectiveness on flocculating fine hematite as it reduces the negatively charged density and viscosity of the starch gel, resulting in a decrease in particle floc size and settling rates. Cross-linking reactions involving  $\text{Ca}(\text{OH})_2/\text{CaCO}_3$  compounds and carboxyl groups produced during alkaline gelatinization could lead to steric hindrance, where the resulting condense configurations block active binding sites and consequently deteriorate flocculation performance (Tang et al., 2024).

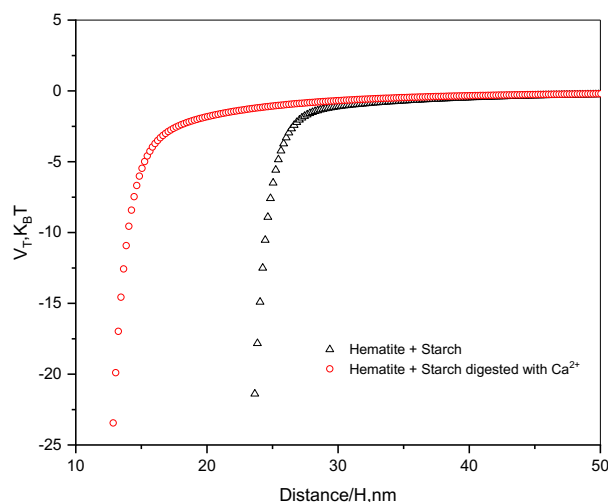


Fig. 10. Potential energy  $V_T$  ( $K_B T$ ) vs distance  $H$  of hematite-starch gelatinized with or without  $\text{Ca}^{2+}$  at pH 7 (Parameters used in  $V_T$  calculation: particle = 1000 nm,  $\theta_{\text{hematite}} = 79.4^\circ$ ,  $\theta_{\text{starch}} = 60.0^\circ$ , 1 mM KCl, Peçanha et al., 2019).

A hypothesis on the influences of calcium ions on the gelatinization properties of starch and its particle flocculation capacity was shown in Fig. 11. It demonstrates that the presence of calcium ions during starch caustic-digestion has a negative role in strengthening the flocculation performance of starch on mineral surfaces. Since the formation of the cross-linking between calcium-based precipitates, for example,  $\text{Ca}(\text{OH})_2$  or  $\text{CaCO}_3$ , and the acidic groups ( $-\text{COOH}$  or  $\text{OH}$ ) produced during alkali gelatinization. This reduces the negative-charged density, re-entangles the stretched long-chain remnants, and consequently, hinders their adsorption on particles.

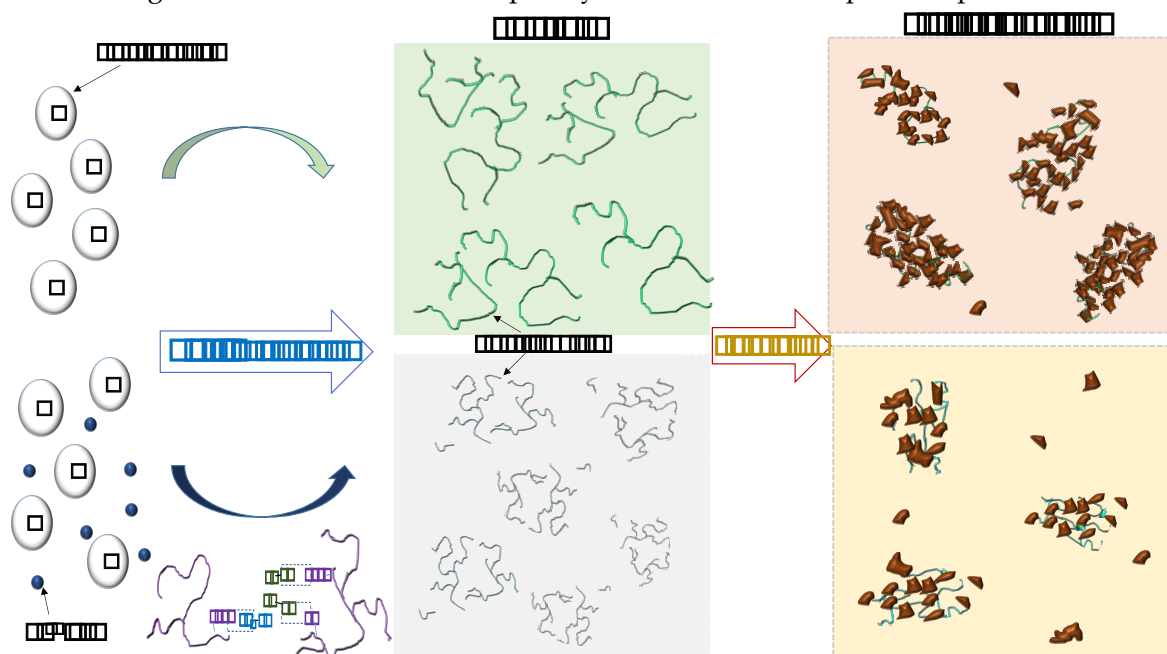


Fig. 11. The possible flocculation behaviors of Ca-modified starch on flocculation behaviors

#### 4. Conclusions

This study demonstrates that the starch gel exhibited different flocculation performance on particles when calcium ions at various concentrations were present during its gelatinization. The reduced viscosity of the incompletely gelatinized starch suspension, caused by calcium ionic disturbance, can be attributed to a decrease in particle floc sizes and settling rates. This is supported by data from batch flotation tests, zeta potentials measurements, and FTIR analysis, indicating that the introduction of these cations during the alkali digestion of starch lowers its negative charge density, entangles the long-chain structure, and consequently diminishes its flocculation capacity due to interactions between calcium-based species and the acidic groups that typically serve as anchor sites after caustic digestion. The cross-linking of Ca-starch entangles extended long-chain segments and obstructs active groups, preventing their adsorption on mineral surfaces. The findings suggest that water sources with low calcium ion content are preferable for preparing starch gel in ore flotation processes.

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