

## Influences of magnesium ions in water on gelatinization characteristics of starch and its flocculation behaviors on particles

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**Abstract:** It is inevitable for the occurrence or built-ups of disturbing cations, especially  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  ions, in process water during the flotation of iron oxides by using starch as flocculants. In addition to alkali concentrations and temperature, water quality could have an essential role in changing the physicochemical properties of the starch solution and consequently disturbing its flocculation performance on particles. This study aims to identify the effects of magnesium ions on the gelatinization characteristics of starch and its flocculation properties on particles through a series of tests, such as flotation tests, settling tests, size analyses, zeta potentials, powder contact angle, Fourier Transform Infra-Red (FTIR) and X-ray Photoelectron Spectroscopy (XPS) measurement. All results show that magnesium ions at  $\leq 4$  mmol/L have a positive role due to enlarging the sizes of the particle flocs and accelerating their settling rates. The occurrence of  $\text{Mg}^{2+}$  ions at higher concentrations during starch gelatinization only obtains a starch sol-gel with entangled configurations and preoccupied active sites, resulting in the slower settling rate of the particle flocs and less hydrophilicity on mineral surfaces. It could be attributed to the cross-link interactions of magnesium-based precipitates with the acidic groups, especially carboxyl groups on the starch remnants. The suitable acid/base interactions between  $\text{Mg}(\text{OH})_2/\text{MgCO}_3$  compounds with these groups in the starch suspension could be beneficial for enhancing the flocculation of hematite as they could build bridges among the pieces and enlarge their sizes as a "load carrier" for aggregation with minerals. However, too much cross-linking could re-entangle the remnants, block their adsorption sites on mineral surfaces, and eventually, weaken the flocculation capacity of starch.

**Keywords:** starch, magnesium ions, gelatinization, flocs, hematite, alkali

### 1. Introduction

It is well known that the gelatinizing properties of starch directly influence the flocculation performance of particles. The popular method to prepare a starch solution for its use in flotation is caustic digestion using sodium hydroxide (Rao and Narasimhan, 1985; Peçanha et al., 2019; Wang and Liu, 2021; Yang et al., 2023). Starch granules can swell and break up rapidly at room temperature to form a sol-gel in the presence of alkali (Knill and Kennedy, 2003; Roberts and Cameron, 2002). Many variations could influence the physicochemical properties of the starch solution during gelatinization: alkali concentration, weight ratio of starch to alkali, temperature, digestion time, etc. Any change in the influences its flocculation effectiveness on particles. Pinto et al. (1992) and Peres and Correa (1996) found less than 10% floatability of hematite by using the caustic-digested starch with a 4-weight ratio of starch to NaOH. Turrer and Peres (2010) also reported that the starch suspension treated by sodium hydroxide at a 5-weight ratio of starch to alkali recovered over 65% Fe recovery at about 1% silica. In addition, Rocha et al. (2019) showed that a concentrate at Fe recovery by over 70% from an iron ore tailing was harvested if an 8-weight ratio of starch to NaOH was chosen to digest. But Tang and Liu (2012) demonstrated that the maximum recovery of fine hematite was achieved by using the starch solution gelatinized by sodium hydroxide at 0.4 N/g starch. The above suggests that various alkali

concentrations or weight ratios of starch to alkali could affect the flocculation properties of starch on particles.

Temperature is also a factor affecting the alkali degradation of starch. The water at different temperatures from 84°C to 95°C have been exploited to gelatinize the starch, coupled with sodium hydroxide at various concentrations. Weissenborn et al. (1995) investigated different flocculation recoveries of fine particles with the occurrence of the starch treated by 0.10 mol/L NaOH at 90-95°C [12]. Yang and Wang (2008) and Li et al. (2022) also studied the adsorption of fine hematite using the starch digested with 0.2 M NaOH or a 2-weight ratio of starch to NaOH at 75°C. There seem to be distinct differences in the physicochemical nature of the starch sol-gel from alkali digestion with various alkali concentrations or temperatures. Niemelä (1990) revealed a starch treated with 1M and 3 M sodium hydroxide at 175 °C and found that mixtures of carboxylic acids, up to 40-60% of the original mass of the starch, were produced. The similar observations reported by Jebber et al. indicated that various carboxylic acids (formic, acetic, glycolic, lactic, 2-hydroxybutanoic, 2-hydroxy-2-methylpropanoic, and 2-hydroxypentanoic acids) were isolated from alkali-degraded starch.

However, distilled water or deionized water was the common solvent selected for the above investigations on the effects of gelatinization conditions, for instance, the weight ratio of starch to sodium hydroxide and temperature [5-19]. In practice, local freshwater, tap water, and even recycled water characterized by various components, especially  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions, has been commercially introduced into starch preparation for its use in local flotation concentrators of iron ores. What happens to gelatinization properties of starch if water sources characterized with different qualities, especially water hardness ( $\text{Ca}^{2+}/\text{Mg}^{2+}$  ions content) or pH were involved? Many publications focus on the competitive or promotive effects of  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  ions on the flotation properties of iron oxides. For instance, Feng et al. (2018) showed that the presence of  $\text{Mg}^{2+}$  ions induced an increase in the recovery of quartz at a pH range of 9-10. A drop of about 50% in the recovery of quartz, however, was found in the presence of  $\text{Ca}^{2+}$  ions at a concentration of 80 mg/L using ester amine as collectors performed by Ren et al. (2018). Ruan et al. (2018) have indicated that the occurrence of both  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  plays a positive effect on the flotation recovery of quartz at near 9.5-10.5. These cations significantly influence flotation performance by reversing surface charge and modifying surface compositions on minerals. Fuerstenau et al. (1963) have found that the hydrolyzed cationic species produced from multivalent cations can reverse the negative charge sign of quartz and cause undesirable entrainment by interacting with the sulfonate collector. A high concentration of  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  also induces a drop in the recovery of pyrochlore due to the reversal of its surface charge from negative to positive and hindering the adsorption of the amine on it (Turrer and Peres, 2010). This is evidenced by the finding reported by Brown and Ekberg (2016), suggesting that the adsorption of  $\text{Ca}(\text{OH})^+$ ,  $\text{CaCO}_3$ ,  $\text{Mg}(\text{OH})_2$  and  $\text{MgCO}_3$  onto the mineral surfaces could be responsible for the  $\zeta$ -potential sign reversal. These precipitates contribute to the  $\zeta$ -potential sign reversal on mineral surfaces due to the formation of a hydrophilic colloidal layer on the mineral surface, preventing the adsorption of collector or depressing naturally hydrophobic minerals (Trahar and Senior, 1991; Tohry et al., 2005; Liu et al., 2013).

Although the influences of  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  ions in water on the floatability of mineral surfaces have been well explored, their disturbances on starch gelatinization and its flocculation behaviors of particles were little mentioned. In addition to alkali concentrations and temperature,  $\text{Ca}^{2+}/\text{Mg}^{2+}$  ion content in water could have an essential role in changing the physicochemical properties of the starch solution and consequently disturbing its flocculation performance on particles. In this study, the disturbance of magnesium ions in water on the gelatinization characteristics of starch and its flocculation properties were investigated through a series of tests, for instance, batch-flotation tests, settling rate tests, size analysis, zeta potential, and XPS measurements, were conducted.

## 2. Materials and methods

### 2.1. Materials

An iron oxide ore sample collected and sampled from an iron mine in Yunnan, China, was at a size range of about 87.6% passing 74 microns. The ore contains 55.6% Fe, 10.5%  $\text{SiO}_2$ , 1.89%  $\text{CaO}$ , 3.28%  $\text{MgO}$ , and 1.36%  $\text{Al}_2\text{O}_3$ . The iron ore sample was characterized by X-ray Diffraction using Bruker D8 Discovery X-ray Diffractometer with cobalt source at a  $\lambda$  value of 1.79 Å as shown in Fig. 1. The typical

peaks of the reference patterns were labelled by Mg-bearing magnetite, ankerite, silica, and phyllite. The pure hematite sample (99+ %, < 1  $\mu\text{m}$ ), CAS1309-37-1, was purchased from Sigma-Aldrich.

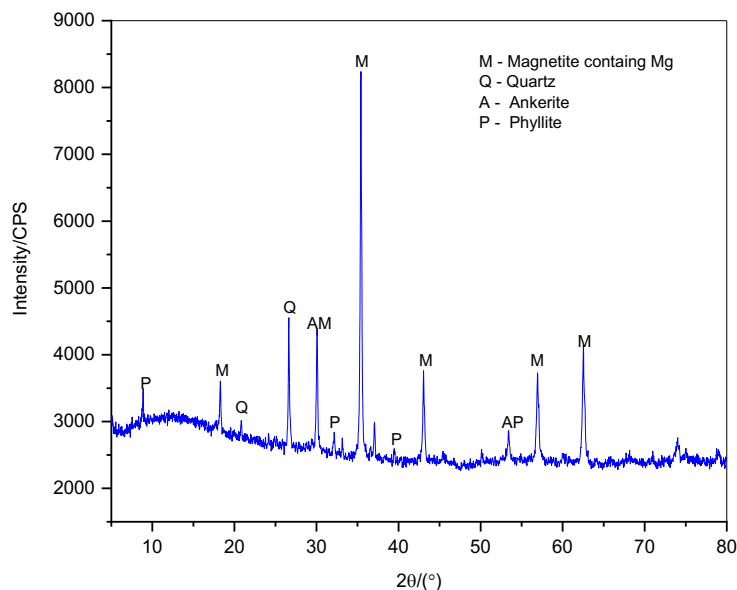


Fig. 1. XRD analysis of the iron ore sample from Yunnan, China

$\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  ( $\geq 98\%$ ), 7786-30-3, was from Fengchuan Chemical Co., Tianjin. Potassium chloride (99.4%), P217-500, sodium hydroxide (97%), and sulfuric acid (96.8%) were from Fisher Scientific. Deionized water was used for all the tests and measurements. Corn starch, S-4180, was purchased from Sigma-Aldrich. Sodium hydroxide (98.8%), S318-1, was purchased from Fisher Scientific. Starch was gelatinized by sodium hydroxide at a 5/3-weight ratio of starch to NaOH, which is considered an optimal ratio according to previous research (Tang and Liu, 2012). The presence of magnesium ions during starch gelatinization was done using magnesium ion solution at different concentrations to digest starch at the above weight ratio of starch to NaOH, slightly shaking for 20 minutes at room temperature. This section can be also divided by subheadings. Provide sufficient detail to allow the work to be reproduced. Methods already published should be indicated by a reference: only relevant modifications should be described.

## 2.2. Methods

### 2.2.1. Batch flotation tests

The sample for flotation tests was prepared by mixing 500 g of the iron ore sample with deionized water at room temperature. The test was conducted with a 1.5L cell (XF-D) for roughing and cleaning stages at an impeller speed of 1200 rpm. A froth depth (FH) of 15.2 cm, superficial gas velocity ( $J_g$ ) of 0.75  $\text{cm}^3/\text{s}$ , and collecting time ( $t$ ) of ten minutes was employed for the roughing stage at a froth depth of 11.5 cm. The collecting time was four minutes at the same superficial gas velocity for the cleaning stage. Dodecylamine as a collector at a concentration of 80 g/t was employed. The caustic-digested starch as flocculants at a dosage of 300 g/t (approximately 100 mg/L) was prepared with magnesium ions at different concentrations. All tests were conducted at natural pH (near 8.5). The concentrate, middling, and tailing from the flotation tests were filtrated, dried, weighed, and then assayed the grade of Fe and  $\text{SiO}_2$ , respectively.

### 2.2.2. Settling tests

The settling tests of the particle flocs produced from the caustic-digested starch were performed using a 250 mL graduated cylinder (280 mm high and 40 mm in diameter). To prepare the sample, 2 g starch granules were caustic-digested with 1.2 g NaOH in 200 mL deionized water containing magnesium ions at a particular concentration, stirring for 20 min. Then 2.5 mL 1% w/v the starch solution was

withdrawn and diluted into 250 mg/L by deionized water. A 100 mL 250 mg/L starch sol-gel was mixed with a 150 mL 2% w/v hematite suspension, in which the mixture contains 3g of hematite at 100 mg/L starch concentration. It was agitated slightly in a thermostated circular shaker for 10 min at 25±1 °C. After conditioning, the settling test was conducted. Each test was repeated three times. The average result was recorded.

### 2.2.3. Size analysis

The size distributions of the caustic-digested starch and its induced particle flocs were measured by a BT-9300S laser particle size analyzer, identifying the size ranging from 0.1 µm to 1200 µm. Before starch gelatinization, the deionized water bearing magnesium ions at a concentration of 2, 4, 8, or 12 mmol/L was prepared. 2 g starch granules were caustic-digested with 1.2 g NaOH in 200 mL of the deionized water containing magnesium ions at a specific concentration, stirring for 20 min before size analysis. A certain amount of the starch suspension was withdrawn to measure its size ranges. Then 1 mL 1% w/v the starch sol-gel was also collected and mixed with a 100 mL 2% w/v hematite suspension. After shaking slightly in a thermostated circular shaker for 10 min at 25±1 °C, the size analysis of the mixture was conducted.

### 2.2.4. Powder contact angle measurement

The contact angle of hematite powder flocculated by the starch sol-gel in the absence/presence of Mg<sup>2+</sup> ions during alkali digestion was measured by Tensiometer K100, Kruss Instrument., Germany. The data were analyzed by ADVANCE software. Before preparing the samples for the contact angle measurement, the deionized water characterized by 1 or 10 mmol/L Mg<sup>2+</sup> ions was prepared for alkali gelatinization. A starch gel was produced by mixing 2 g starch granules with 1.2 g NaOH in 200 mL of deionized water with or without magnesium ions. Then 1 mL 1% w/v the starch sol-gel was mixed with 100 mL 2% hematite solution and the mixture was stirred for 10 min before being filtrated and dried in a vacuum container at room temperature. A 1.5 g sample was collected for the measurement. Anhydrous ethanol and deionized water were the solvents selected for the capillary constant and contact angle measurement of hematite, respectively. Every sample was repeated three times. The powder contact angle of the samples was calculated in terms of the following Eqs. (1) - (3) (Tohry et al., 2005),

$$m^2 = \frac{c\rho^2\sigma\cos\theta}{\eta}t \quad (1)$$

$$k = \frac{c\rho^2\sigma\cos\theta}{\eta} \quad (2)$$

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

in which  $m$  represents the mass of residue liquid in the tube due to the suction by capillary force (g),  $c$  represents the powder capillary constant (mm<sup>3</sup>),  $\rho$  is the density of liquid (g/mL),  $\sigma$  is the surface tension of liquid (mN/m),  $\eta$  is the viscosity of liquid (mPa·s),  $t$  is time (s),  $k$  is the slope of the line of  $m^2$  to time  $t$ , and  $\theta$  is the contact angle (°).

### 2.2.5. Zeta potential measurement

The zeta potentials of the alkali-digested starch or its flocs of hematite were measured by a Zetasizer Nano ZS90, Malvern Instrument, UK. The technique is based on electrophoretic light scattering (ELS), known as Laser Doppler Velocimetry (LDV). To prepare the starch samples for the zeta potential measurements, 2 g starch granules were caustic-digested with 1.2 g NaOH in 200 mL of the deionized water characterizing of 0, 1, or 10 mmol/L Mg<sup>2+</sup> ions, stirring for 20 min. Then a 1 mL 1% w/v starch solution was withdrawn and mixed with a 100 mL 2% w/v hematite suspension, conditioning in a thermostated circular shaker for 10 min. 5 mL of the mixed suspension was collected and diluted to 100 mL with a 10<sup>-3</sup> mol/L KCl solution. A small aliquot of the suspension was transferred to the sample cell of the Zetasizer for zeta potential measurements. The pH of the diluted suspension was adjusted using H<sub>2</sub>SO<sub>4</sub> or NaOH.

## 2.2.6. FTIR measurement

The FTIR analysis of the starch in the presence/absence of magnesium ions during gelatinization was performed by a Bruker Alpha Fourier transform infrared spectrometer. The spectra were obtained on samples in KBr pellets ranging from 4000  $\text{cm}^{-1}$  to 400  $\text{cm}^{-1}$  at a resolution of 4  $\text{cm}^{-1}$ . The powder samples of natural starch or magnesium chloride were prepared in the form of KBr (potassium bromide) pellets containing 10-15 mg solids samples. The alkali-gelatinized starch solution sample was prepared by using deionized water containing magnesium ions at a content of 1 mmol/L. A certain amount of the starch suspension was transferred to do the FTIR measurement.

## 2.2.7. XPS measurement

The XPS measurement of hematite flocculated by the caustic-digested starch with the occurrence of magnesium ions was conducted on PHI5000 VersaprobeIII XPS at a vacuum of  $\leq 4.78 \times 10^{-6}$  Pa with the energy of 1486.6 eV, ULVAC-PHI.INC, Japan. To prepare the caustic-digested starch sample for the XPS measurements, the deionized water with 1 mmol/L  $\text{Mg}^{2+}$  ions was employed in the starch gelatinization. Then a certain amount of the starch solution was diluted into 200 mg/L in 100 ml deionized water and mixed with 100 mL of 2% hematite suspension, lightly agitating for 20 min. The suspension was centrifuged, filtered, and dried at room temperature. A small amount of the powder was collected and sampled to analyse the XPS.

## 3. Results and discussion

### 3.1. Flotation performance of iron ore using starch with $\text{Mg}^{2+}$ ions during gelatinization

Fig. 2 investigated the flotation selectivity of the iron ore using starch with the occurrence of magnesium ions at different concentrations during alkali digestion. It shows an upward trend in the iron recovery coupled with a slight drop in  $\text{SiO}_2$  content in concentrate using the starch with magnesium ions at a concentration range of  $< 4$  mmol/L but a sharp drop by 3.6% and 1.2% in the iron recovery and grade with a further increase of magnesium ion concentration from 4 to 8 mmol/L. It indicated that the occurrence of  $\text{Mg}^{2+}$  ions during starch gelatinization at lower concentrations could be beneficial for increasing the Fe recovery and lowering the  $\text{SiO}_2$  content of concentrates. Magnesium ions at higher concentrations, however, tend to disturb the flocculation of starch on particles. This could be attributed to the pre-cross-link interactions between magnesium-based compounds and the function groups on the starch remnants, affecting their adsorptions on fine particles. According to the previous literature investigated by Khraisheh et al. (2005),  $\text{Mg}^{2+}$  ions could substantially enhance CMC's adsorption onto talc by entangling the carbon chain in CMC but inhibit the adsorption of CMC at high concentrations. Li et al. (2015) also found that the higher charge density of cations could attract starch-OH groups and destabilize starch granules.

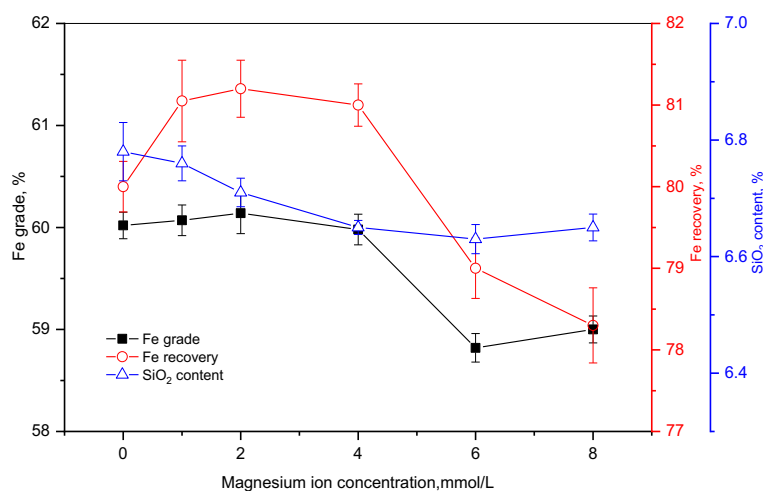


Fig. 2. The flotation performance of the iron ore using starch with the presence of  $\text{Mg}^{2+}$  ions at different concentrations during starch gelatinizing

### 3.2. Settlement of the particle flocs using starch with $Mg^{2+}$ ions during gelatinization

Fig. 3 presents the interface settlement of the particle flocs of hematite using the starch sol-gel with the absence/presence of  $Mg^{2+}$  ions during gelatinization. As can be seen, a faster sedimentation of the flocs in comparison the one without magnesium ions occurs with an increase of magnesium ion content from 0 to 4 mmol/L but a slower one took place with the occurrence of magnesium ions at over 4 mmol/L. The slowest settlement of the particle flocs was obtained by the starch sol-gel in the presence of  $Mg^{2+}$  ions at 12 mmol/L, and it still haven't reached the end of the settlement at 150 seconds. This is well in agreement with the results from Fig. 2, suggesting that the occurrence of  $Mg^{2+}$  ions at low concentrations during starch gelatinization tends to enhance the starch viscosity, enlarge the flocs sizes, and consequently accelerate their settling rates. According to the previous research reported by Subramanian and Natarajan (1988) and Pavlovic and Brandao (2003), iron ions interacted with causticized starch directly during adsorption on hematite. Fu et al. (2023) also indicated that  $Pb^{2+}$ ,  $Al^{3+}$ , and  $Fe^{3+}$  ions could coordinate with starch molecules and form metallic-starch complexes. There could be a cross-link between magnesium-based precipitates, probably  $Mg(OH)_2$  or  $MgCO_3$ , and the acidic groups, for example, carboxyl groups, in the starch solution, affecting the configuration, size, and charge of the starch remnants, and eventually altering the flocculating capacity of the caustic-digested starch on hematite.

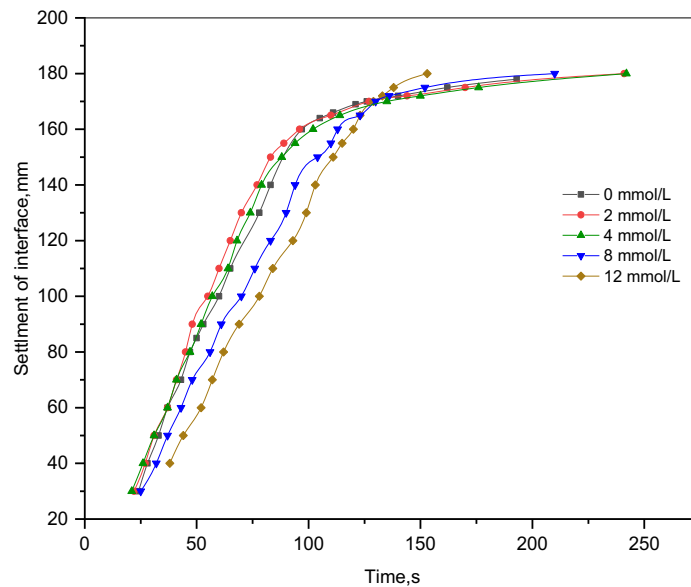


Fig. 3. The settling test of the particle flocs of hematite using the starch sol-gel with the presence of  $Mg^{2+}$  ions during starch preparation

### 3.3. Size analyses of starch and its induced particle flocs with $Mg^{2+}$ ions during gelatinization

Fig. 4 provide the size distributions and the cumulative yield of the particle flocs using the starch with the absence/presence of magnesium during starch gelatinization. It indicated that the maximum volume fraction of the particle flocs produced from the starch solution treated by 0, 2, 4, 8, or 12 mmol/L  $Mg^{2+}$  ions occur near 10  $\mu m$ , 34  $\mu m$ , 35  $\mu m$ , 4.0  $\mu m$  or 2.5  $\mu m$ , respectively. This means that magnesium ions at a concentration of < 4 mmol/L tend to induce an upward trend in the dominant volume fraction of the floc sizes but a drop when magnesium ion concentration reaches 8 mmol/L. There is little flocculation of the starch from treatment by 12 mmol/L  $Mg^{2+}$  ions on the hematite powder (99% of <1  $\mu m$ ) as its  $D_{90}$  is only at 2.5  $\mu m$ . Fig. 4 also showed that the  $D_{90}$  of the particle flocs produced from the starch solution treated by 0, 2, 4, 8, or 12 mmol/L  $Mg^{2+}$  ions occur near 17.85  $\mu m$ , 58.09  $\mu m$ , 62.40  $\mu m$ , 8.45  $\mu m$ , or 5.05  $\mu m$ , respectively. It suggests that the occurrence of magnesium ions at a concentration of less than 4 mmol/L during alkali gelatinization seems to enlarge the visual sizes of the particle flocs but a sharp drop occurs with an increase of magnesium ion concentrations from 4 mmol/L to 12 mmol/L. This can be consistent with the size analyses of the starch in the presence of  $Mg^{2+}$  ions as

shown in Fig. 5. A growth of 12.8% on  $D_{90}$  of the starch with  $Mg^{2+}$  ions at 2 mmol/L but a significant reduction by 16.8% drop with 12 mmol/L takes place in comparison with the one of the starches without  $Mg^{2+}$  ions. The acidic groups, such as carboxyl or hydroxyl groups on the starch fragments could contribute to the base/acid interactions with metal hydroxides (Oosten, 1990; Tang and Liu, 2012). The formation of the cross-linking between magnesium-based precipitates and the hydroxyl or acidic groups on the starch remnants produced from alkali digestion could be attributed to it, triggering the entanglement of configurations and affecting the size distributions.

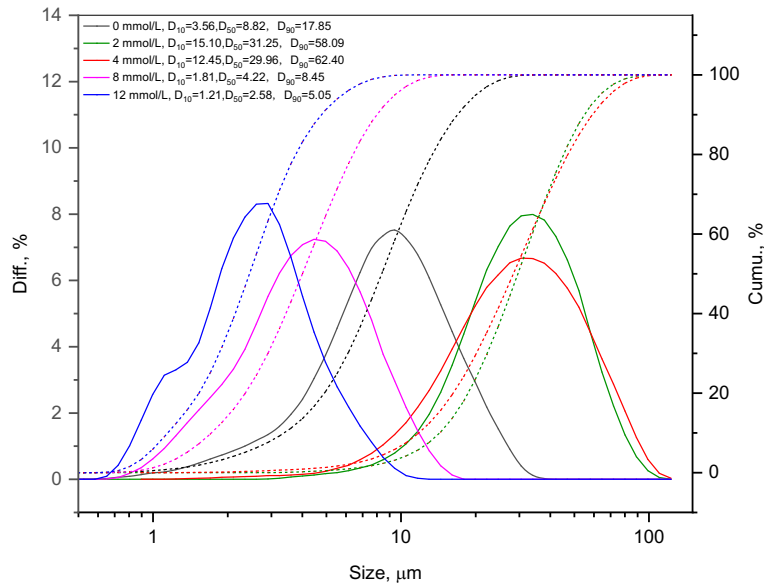


Fig. 4. The diffraction (solid line) or cumulative (dash line) percent of the particle flocs induced by the starch from alkali digestion in the absence/presence of  $Mg^{2+}$  ions

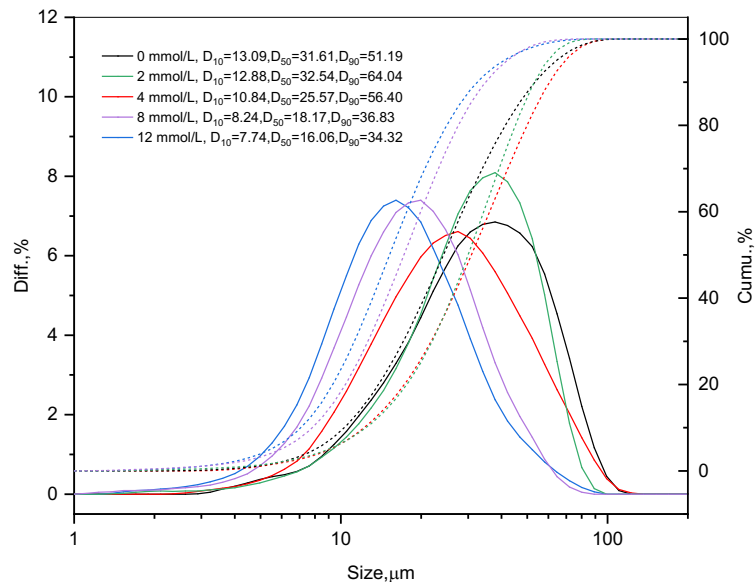


Fig. 5. The diffraction (solid line) or cumulative (dash line) percent of the starch solution from alkali digestion in the absence/presence of  $Mg^{2+}$  ions

### 3.4. Contact angles of particle flocs using starch with $Mg^{2+}$ ions during gelatinization

Fig. 6 illustrates the contact angles of the hematite treated by the starch prepared with 1 or 10 mmol/L  $Mg^{2+}$  ions during alkali-gelatinization. It shows a drop of  $5.56^\circ$  on the contact angle of the particles flocculated by the starch without magnesium ions. There is a further drop of  $1.13^\circ$  on the contact angle of the particles using the starch suspension with the occurrence of  $Mg^{2+}$  ions at 2 mmol/L during starch

gelatinization. But an increase of  $3.73^\circ$  when magnesium ion concentration reaches 8 mmol/L compared with the one without  $Mg^{2+}$  ions. This is well in agreement with the results from Figs. 2-4, indicating that the occurrence of magnesium ions at lower concentrations during starch gelatinization strengthens the adsorption of starch on mineral surfaces, increasing the hydrophilicity of mineral surfaces and accelerating the settling rates of the flocs. The appearance of magnesium ions at higher concentrations, however, tends to weaken its flocculation on particles, increasing the hydrophobicity of mineral surfaces and lowering the settling rates of the flocs instead.

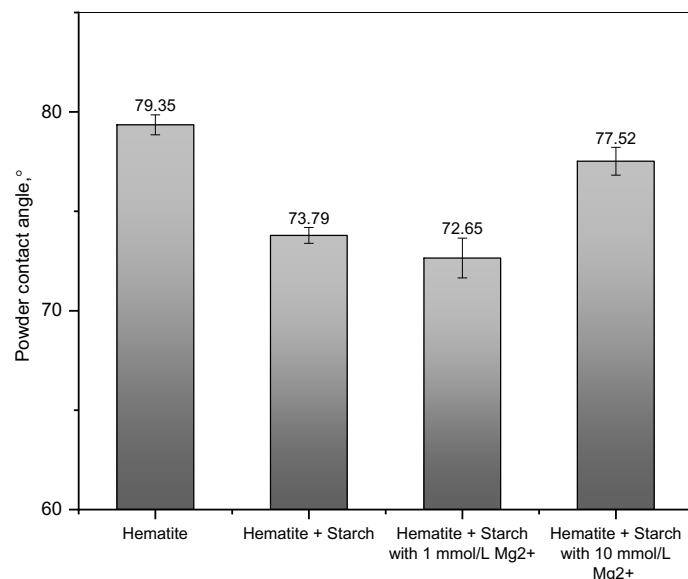


Fig. 6. The contact angles of the hematite powder treated by starch with the presence/absence of magnesium ions during alkali digestion

### 3.5. Zeta potentials of starch or its induced particle flocs with $Mg^{2+}$ ions during gelatinization

Fig. 7 exhibits the zeta potentials of the caustic-digested starch with the absence/presence of magnesium ions. The results show no substantial change in the zeta potentials or isoelectric points of the starch at a pH ranging from 2 to 10, regardless of magnesium ionic concentration. It could be attributed to neutralizing the charge coming from the acidic groups, such as  $-COOH$  or  $-OH$ , on the chains of starch fragments by magnesium-based species. The findings reported by Tang and Liu (2012) and Chandar and Somasundaran (1987) mentioned that the presence of carboxyl or hydroxyl makes causticized starch very slightly negatively charged. Fig. 7 also demonstrates the difference in the zeta potentials of hematite treated by the caustic-digested starch with the absence/presence of magnesium ions during its gelatinization. It illustrates a slight shift toward the less negative side on the zeta potentials of the particle flocs induced by the starch from alkali-gelatinization in the deionized water bearing  $Mg^{2+}$  ions at 10 mmol/L compared with the one without  $Mg^{2+}$  ions. But little change in the zeta potentials of hematite using the starch with the occurrence of magnesium ions at 1 mmol/L at 6.5-10. This suggests that the formation of light cross-linking between magnesium-based precipitates with the acidic heads on the fragments could affect little the charge of mineral surfaces treated by the starch with the occurrence of magnesium ions at low concentrations during starch gelatinization. However, the more deactivations of these acidic groups in the starch sol-gel preoccupied with more magnesium-based products could disturb the adsorption of the starch on hematite, inducing a shift towards negative side on the zeta potentials of particles using the starch with an increase of magnesium ion concentrations. Those acidic groups acting as “anchor sites” between starch and mineral surfaces could have a substantial influence on the adsorption performance of the starch on hematite as they have the capacity to provide a “load carrier” for aggregation with minerals. The preoccupation of these “anchor sites” could block their adsorption on mineral surfaces and weaken the flocculation capacity of starch. This is consistent with the results from Figs. 2-6, suggesting that during alkali gelatinization of starch, magnesium ions tend to precipitate as magnesium hydroxide or carbonate, which could easily interact



with these acidic groups produced by alkali intrusions on the starch granules in the presence of  $O_2$  in water. This cross-linking among them could affect the size, configuration, and charge of the remnants, consequently changing the flocculation properties of particles.

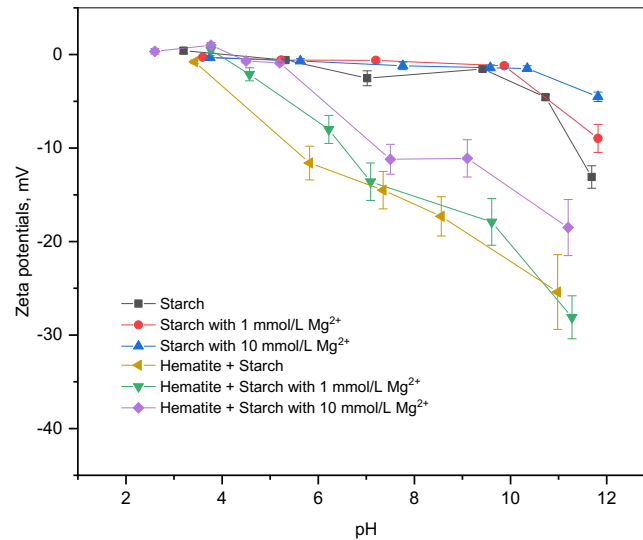


Fig. 7. The zeta potentials of the starch with the absence/presence of  $Mg^{2+}$  ions during alkali gelatinization or its particle flocs

### 3.6. FTIR and XPS of starch its induced particle flocs with $Mg^{2+}$ ions during gelatinization

Fig. 8 shows the FTIR spectra of the original starch, magnesium chloride, and starch suspension from pre-gelatinization with sodium hydroxide using deionized water with or without  $Mg^{2+}$  ions. A new peak at  $2070\text{ cm}^{-1}$  occurs on the curve of the starch sol-gel in the presence of magnesium ions compared with the one without  $Mg^{2+}$  ions. It could be relevant to the adsorption of magnesium compounds on the starch chains as there is a similar peak at  $2288\text{ cm}^{-1}$  on the curve of  $MgCl_2$ . Magnesium hydroxide or carbonate can take part in the interactions with the resulting acidic groups or hydroxyl from alkali digestion, inducing the occurrence of the peak at  $2070\text{ cm}^{-1}$  and the stretch of  $-COOH$  or  $C-OH$  at nearly  $1390\text{ cm}^{-1}$  (Chandar et al., 1987; Liu et al., 1989). This could explain the results from Figs. 4-7, revealing the presence of  $Mg(OH)_3$  or  $MgCO_3$  compounds, which occupied those acidic sites on the chain pieces, contracting or twisting the stretched configurations and weakening the adsorption of the starch on mineral surfaces. This is compatible with the findings reported by Wang et al. (2022) which showed the existence of  $-CH_2-O-Al^{2+}$  when the caustic starch was mixed with aluminum sulfate at a mass ratio of 1:1.

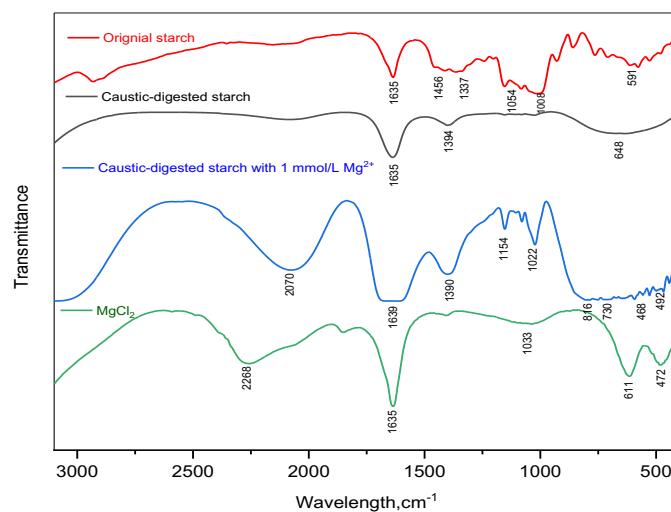


Fig. 8. FTIR of the caustic-digested starch with the absence/presence of  $Mg^{2+}$  ions at a pH value of 7

Fig. 9 displays the XPS at O1s, C1s, Fe 2p, and Mg 2p of hematite treated by the starch solution from alkali digestion with the presence/absence of  $Mg^{2+}$  ions. It indicates the presence of Mg-O/Mg-OH or Mg- $CO_3$  on the hematite surfaces with the occurrence of magnesium ions during starch gelatinization from the curve at the Mg 2p site. Coupled with the results at O1s and C1s, severe changes in the position and % area of -C=O, -COO- or -OH occur, suggesting that the cross-link interactions of Mg $CO_3$  or Mg(OH) $_2$  on the starch remnants during gelatinization disturb their adsorptions on mineral surfaces. This could induce the residence of Mg-O or Mg- $CO_3$  products on hematite, evidenced by the strength of -COO- or C-O- peak on the curves (Lefevre, 2006; Fjtemaei, 2016). A hypothesis on the cross-linking mechanism of magnesium-based precipitates with the acidic groups (-COOH or -OH) on the chains of the starch remnants was shown in Fig. 10. At alkali, magnesium ions often precipitate in the form of Mg(OH) $_2$  or Mg $CO_3$ , which could involve into the base/acid interactions with the active groups on the starch fragments, especially carboxylic groups, produced from alkali treatment (Tang and Liu, 2012). At lower concentrations of magnesium ions, slight cross-linking between these magnesium-based

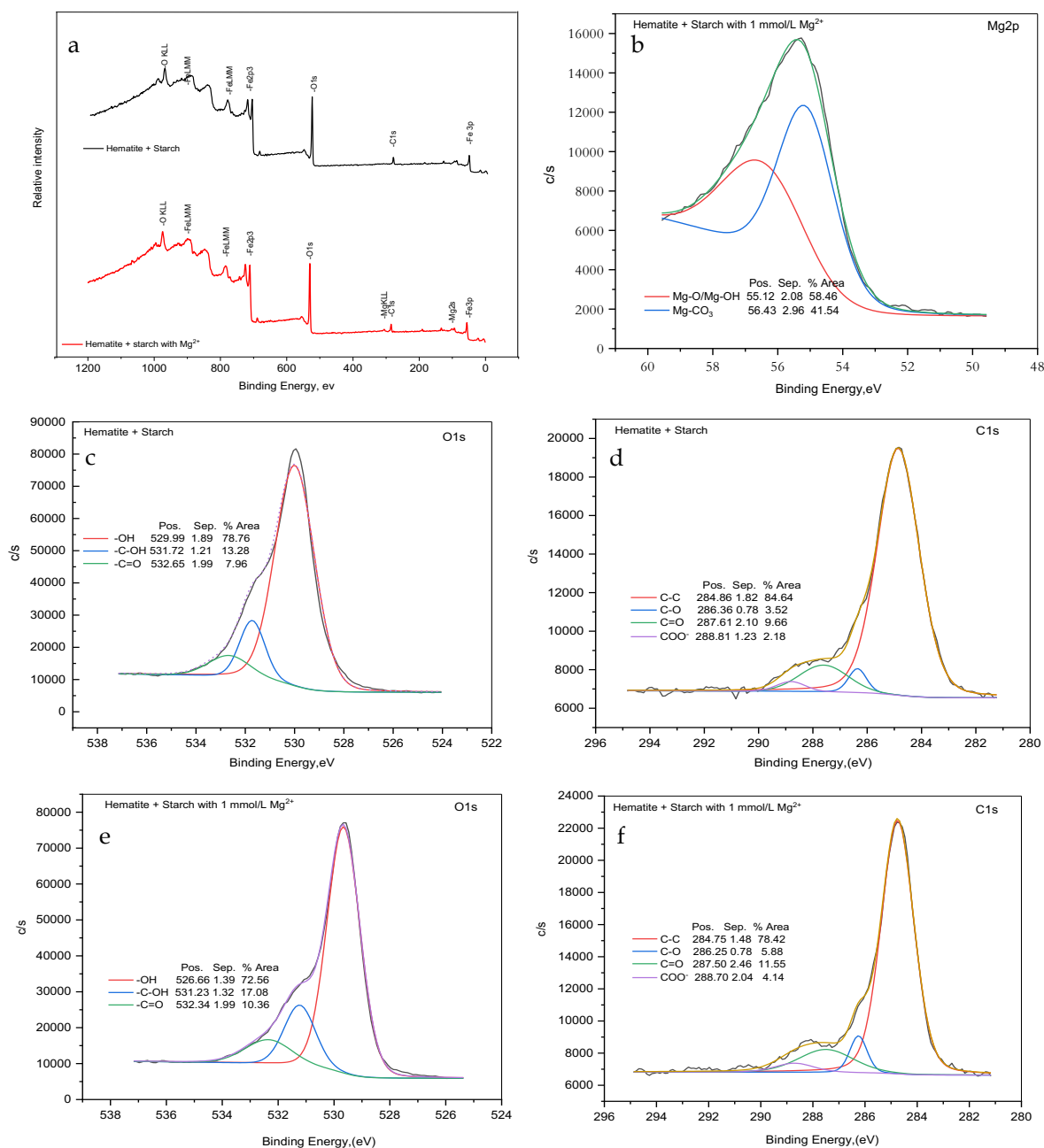


Fig. 9. XPS spectra of the caustic-digested starch in the absence/presence of 1 mmol/L  $Mg^{2+}$  ions at a pH 7 (the entire XPS spectrum, or Mg 2p, O 1s, C 1s, or Fe 2p XPS spectrum)

compounds with these acidic groups could enlarge the size of the starch remnants and increase the settling rates of the particle flocs, strengthening the flocculation on hematite. But magnesium ions at higher concentrations could induce more cross-link interactions, which could contract the stretched configurations and deactivate the functional groups of the starch sol-gel, disturbing the adsorption of starch on mineral surfaces.

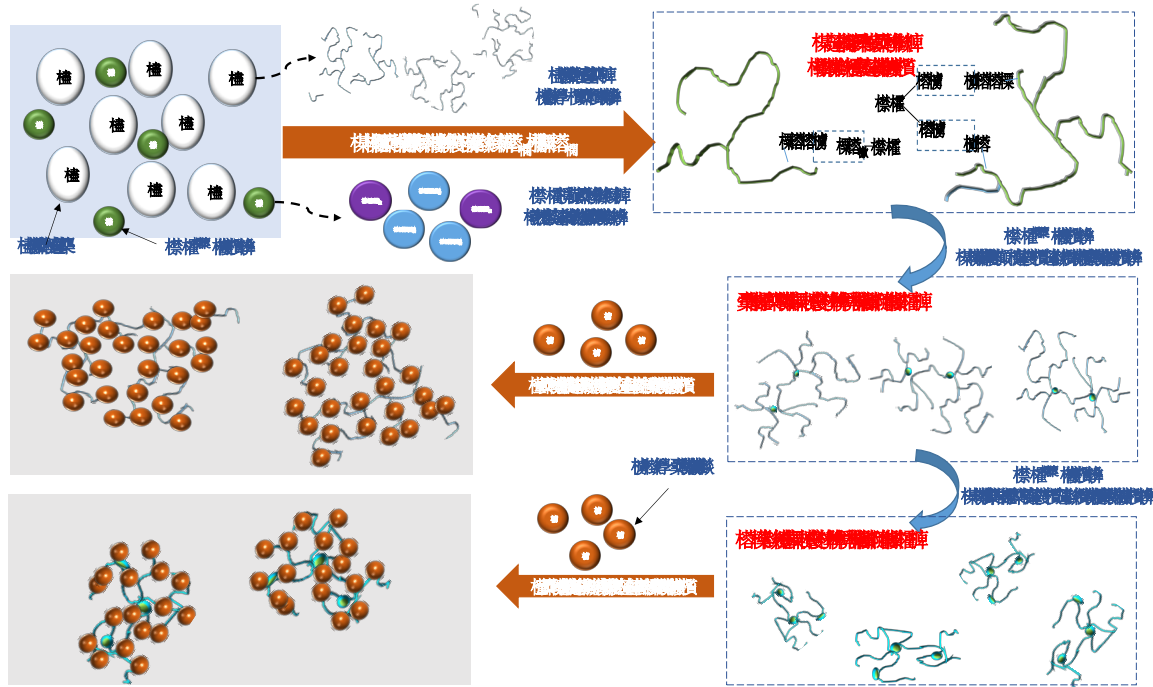


Fig. 10. The possible cross-linking mechanism of magnesium-based precipitates with the acidic groups on the starch remnants during alkali digestion and its effects on flocculation behaviours

#### 4. Conclusions

It was shown that the starch from alkali gelatinization treated by magnesium ions possessed an alteration in its size, charge, and configuration, consequently affecting its flocculating capacity on mineral particles.  $Mg^{2+}$  ions at a concentration of less than 4 mmol/L seem to have a positive effect on enhancing the flocculation of starch on particles by enlarging the remnant sizes and accelerating the settling rates of particle flocs. However,  $Mg^{2+}$  ions at higher concentrations tend to disturb the flocculation of starch on particles due to entangling the stretched configurations, reducing the floc sizes, and lowering its settling rates. At alkali, magnesium ions are found in the form of magnesium hydroxide or carbonate precipitates, which could interact with the active groups in the starch sol-gel, for example, carboxyl groups produced from alkali digestion. The formation of cross-linking between these magnesium-based species with the acidic groups, especially carboxyl groups, in the starch solution could be attributed to the changes in the flocculation capacity of starch on particles. Light cross-link interactions among them could link the starch pieces slightly and increase the visual sizes of the particle flocs while over-cross-linking could deactivate the acidic groups, tightening the stretched structure, and eventually, blocking the adsorption on mineral surfaces.

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