

Effects of $\text{Ca}^{2+}/\text{Mg}^{2+}$ ions in recycled water on the reverse flotation properties of iron oxides

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Abstract: Water quality, particularly hardness, plays an important role in affecting the floatability of minerals as it interferes with the chemical/electro-chemical characteristics of mineral surfaces and their interactions with flotation reagents. It could become unpredictable when water sources characterized by different calcium or magnesium ion distributions were involved. This study aimed to identify the role of $\text{Ca}^{2+}/\text{Mg}^{2+}$ ions in the recycled water on the cationic reverse flotation selectivity of iron oxides through a series of bench/micro flotation tests, zeta potential, powder contact angle, and Fourier Transform Infrared (FTIR), etc. The results pointed out that the use of recycled tailing water deteriorates the flotation selectivity and dilutes the concentrates. This can be largely attributed to the presence of Ca^{2+} ions at higher concentrations as they induce a drop in the Fe recovery and an increase in SiO_2 content while an increase in the content of Mg^{2+} ions seems to have little effect on the quality of concentrate. As evidenced by the data from micro-flotation, powder contact angle, zeta potentials, and FTIR, a hydrophilic colloidal layer formed by Ca-based hydrolyzed compounds, such as $\text{Ca}(\text{OH})^+$ or $\text{CaCO}_{3(s)}$, etc., on quartz could change its zeta potentials and disturb its interactions with a cationic collector. They also play a role in weakening the flocculation of starch on hematite probably by pre-locking the acidic groups on the starch remnants and contracting their configurations, thus preventing their adsorption on mineral surfaces. However, magnesium ions seem to be beneficial to in strengthening the flocculation of starch on hematite as magnesium-based species could act as adsorption bridges of between starch and mineral surfaces.

Keywords: recycled water, calcium/magnesium ions, hematite, reverse flotation

1. Introduction

To save freshwater, lessen its impact on the environment, and save operating expenses, recycled water must be used in a mineral processing plant. Typically, tailing dams, thickener overflows, dewatering and filtration units, or occasionally sewage water treatment plants are the water sources for recycling. The quality of the recycled water, however, has significant effects on flotation, as there are many potential variations in the recycled water, especially water hardness, disturbing ions/compounds, pH, etc., which could alter the chemistry of a flotation system and consequently lead to the loss in selectivity (Haselhuhn et al., 2012; Gao et al., 2021; Corin, et al., 2024).

The hardness of water as an indicator of water quality, varies according to the types or locations of water sources. This could bring some unpredicted alternations in the pulp chemistry disturbing the flotation performance. The effects of calcium or magnesium ions on direct or reverse flotation properties of iron oxides have been investigated in detail as shown in Table 1. It shows that the positive or negative effects of these cations during mineral flotation were relevant to types of collectors and floated minerals. The occurrence of both Ca^{2+} and Mg^{2+} ions induces an increase in the quartz or silicate recovery when using an anionic collector, and Ca^{2+} ions seem to have a stronger influence than Mg^{2+} ions (Nevasaia et al., 1998; Flood et al., 2006; Ruan et al., 2018; Feng et al., 2018). However, these cations could have a role in deteriorating the cationic flotation selectivity of talc, silica, or hematite (Ofor, 1996; Ren et al., 2018). It is also to be noted that in the anionic flotation of hematite the disturbance of Ca^{2+} or Mg^{2+} ions on the adsorption of oleate on mineral surfaces was observed by Ofor (1996). The adsorption of these ions-

based hydrolyzed compounds could have a role in affecting the interactions between mineral surfaces and collectors by modifying or reversing the surface charges of minerals and causing its unpredicted interferences (Rao, 2004). The recovery of pyrochlore is further reduced by high concentrations of Ca^{2+} or Mg^{2+} because they prevent the amine from adhering to the surface reversing the charge sign from negative to positive (Taggart and Arbiter, 1946). According to the previous findings performed by Brown and Ekberg (2016), the ζ -potential sign reversal may be caused by the products of $\text{Ca}(\text{OH})^+$ or/and CaCO_3 , or Mg^{2+} , $\text{Mg}(\text{OH})^+$ / $\text{Mg}(\text{OH})_2$ onto the mineral surfaces. A hydrophilic colloidal layer forms on the mineral surface, the precipitation of these cations, such as metal hydroxides, carbonate, or sulfates, may contribute to the zeta potential sign reversal on mineral surfaces (Santos et al., 2024).

Table 1. The possible effects of $\text{Ca}^{2+}/\text{Mg}^{2+}$ ions in water on the reverse/direct flotation of iron oxides

Type of Collector	Minerals Floated	Main Results or Conclusions	References
Anionic	Quartz /silica	Enhancing the adsorption of the collector on quartz by Ca^{2+} or Mg^{2+} ions, and the order of the activation abilities on quartz: $\text{Ca}^{2+} \geq \text{Mg}^{2+}$	Ruan et al., 2018
Cationic		Weakening the adsorption of ester amine on quartz by Ca^{2+} or Mg^{2+} ions	Ren et al., 2018
Anionic		Strengthening the adsorption of anionic collector on quartz	Nevskaia et al., 1998
Anionic		Positively affecting on the adsorption of sulfonate on quartz.	Fuerstenau et al. 1963
Polymer		Promoting the adsorption of polymer with the presence of Ca^{2+} or Mg^{2+} ions	Flood et al., 2006
Anionic		Hematite	Disturbing the adsorption of oleate on mineral surfaces by Ca^{2+} or Mg^{2+} ions

Starch is practically used in the reverse flotation of iron ores serving two functions: it acts as flocculants to collect fine particles and as a depressant to prevent amine adsorption at the mineral surface, maintaining their hydrophilic (Shrimali et al., 2018; Yang et al., 2023; Andrade et al., 2024). Thermal or/alkali gelatinization is the common method to prepare starch solution before its use. The acidic groups resulted from starch digestion could contribute to the interactions with mineral surfaces (Tang and Liu, 2012). In addition to gelatinization degree, concentration, particle size, temperature, water quality, especially calcium or magnesium ions could have also an important role in flocculation characteristic on fine particles (Li et al., 2022; Zhang et al., 2023; Andrade et al., 2024; Wang and Liu, 2024). Studies as described before mostly focus on the influences of calcium or magnesium ions on mineral surfaces or their interactions with cationic/anionic collectors. The effects of Ca^{2+} or Mg^{2+} ions in water on the flocculation of iron oxides using starch as flocculants have been had little mentioned. However, the common solvent chosen for the previous studies on the effects of gelatinization or flocculation characteristics was distilled water or deionized water (Zhang et al., 2023; Andrade et al., 2024; Wang and Liu, 2024). In practices, commercial starch preparation has been incorporated with local freshwater, tap water, and even recycled water that is distinguished by different components, particularly Ca^{2+} and Mg^{2+} ions, for use in local flotation concentrators of iron ores. In this study, the distributions of magnesium or calcium ions in the recycled water and their influences on the cationic reverse flotation properties of iron oxides, especially the flocculation characteristics of starch on particles were investigated in this work through a variety of bench/micro flotation tests, zeta potentials, powder contact angle, and FTIR analysis.

2. Materials and methods

2.1. Materials

An iron ore sample collected from an iron mine in Yunnan, China, was at a size range of about 87.6% passing 74 microns. It was also characterized by X-ray Diffraction using Bruker D8 Discovery X-ray

Diffractionmeter with cobalt source at a λ value of 1.79\AA as shown in Fig. 1(a). The main peaks of the reference patterns were labeled by Mg-bearing magnetite, ankerite, silica, and phyllite as well. The ore sample contains 55.6% Fe, 10.5% SiO_2 , 1.89% CaO, 3.28% MgO, and 1.36% Al_2O_3 . The distributions of iron or SiO_2 were assayed as shown in Fig. 1 (b). The pure quartz was also collected from Yunnan Mine, China, which XRD-typical peaks were present shown in Fig. 1 (b). It contains 99.64% SiO_2 at a size range of $<45\ \mu\text{m}$. The powder of pure hematite (99+ %, $<5\ \mu\text{m}$), 1309-37-1, was purchased from Sigma-Aldrich.

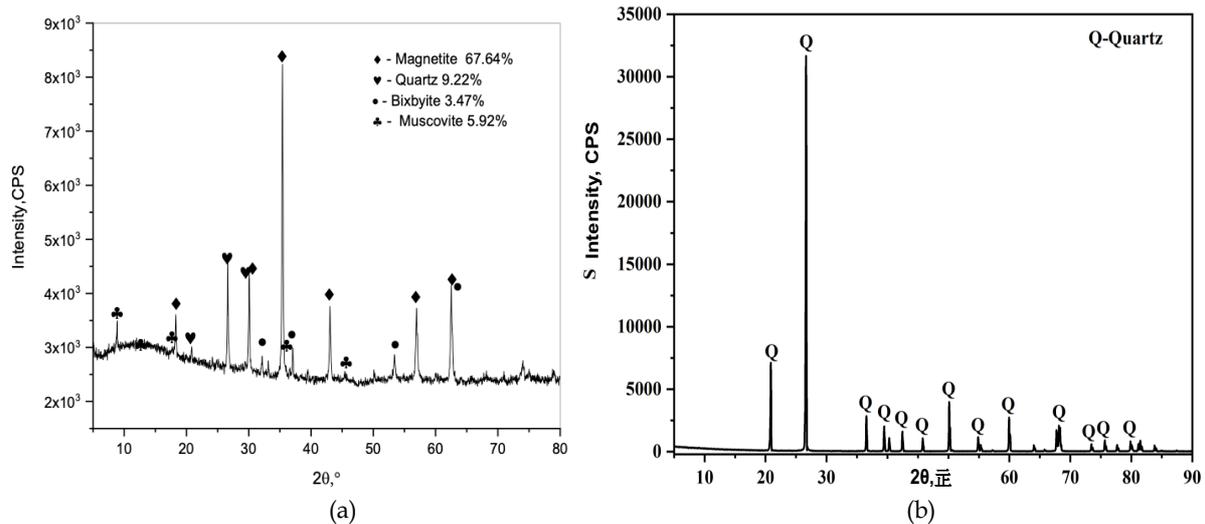


Fig. 1. The XRD analyses of the iron ore sample (a) and the pure quartz sample (b)

Corn starch with a product number of S-4180 was purchased from Sigma-Aldrich. It was caustic-digested with sodium hydroxide in hot water used as flocculants/depressants of iron oxides. Dodecylamine (DDA), 124-22-1, was purchased from Shangdong Chemical Tech. Co. The reagents at chemical grade reagents were used for all the tests, such as anhydrous ethanol, sodium hydroxide, potassium chloride, calcium chloride, magnesium chloride, hydrochloric acid and sulphuric acid were all from Fisher Scientific or Sigma-Aldrich.

2.2. Water samples from an industrial flotation process of the iron ores

The iron ore at a range of 32-35% solid density was fed into the roughing banks in the industrial flotation system. Its concentrate from the roughing stage was pumped to the cleaning cells where the final concentrate was produced by removing most of silica gangues using sulphuric acid as pH modifier, 300 g/t caustic-digested starch as flocculants, and 100 g/t DDA as collector. The pH of the pulp is 8.7 ± 0.2 during flotation. Total hardness of the process water from the rougher banks were monitor periodically. Several barrels of the water sources recycling in the plant, including the local freshwater, tailing water, and treated sewage water were sampled, sealed and transported from the local concentrator in Yunnan, China. The removal of the slimes and residues of the organic reagents from the water sample were also conducted before chemical analyses and flotation tests. The ionic distributions of different water sources in the industrial flotation system of the iron ore are shown in Table 2. The data indicate that in terms of CaCO_3 calculations, the total hardness in the tailing water is approximately seven times the one in the freshwater. The concentrations of ions, especially Ca^{2+} and Mg^{2+} ions from the recycled tailing water were much higher than the ones from other water sources.

2.3. Methods

2.3.1. Bench flotation or micro-flotation tests

A reverse flotation system using starch as flocculants and DDA as a collector was employed for all the flotation tests of the iron ore or hematite samples. Bench flotation tests were conducted using a 1.5 L cell (XF-D) at an impeller speed of 1100 rpm. 500 g of the iron ore sample was weighed and mixed with deionized water. The froth depth (FH) of about 8.5 cm, superficial gas velocity (J_g) of 0.75 cm/s, and

collecting time (t) of 10 minutes for each test were employed. 100 g/t DDA as a collector, 300 g/t caustic-digested starch as flocculants, and sodium hydroxide or sulfuric acid as pH modifiers were used for all the tests. The concentrate and tailing from the bench flotation tests were filtrated, dried, weighed, and then assayed the grade of Fe and SiO₂, respectively.

Table 2. Inorganic components of different water sources in an industrial flotation system

Item	Freshwater	Recycled Tailing Water	Treated Sewage Water
pH	7.9	9.8	6.4
Cl ⁻ , mg/L	5.5	258.4	176.5
SO ₄ ²⁻ , mg/L	12.7	963.0	494.2
Ca ²⁺ , mg/L	15.0	196.5	121.3
Mg ²⁺ , mg/L	5.0	134.7	107.8
Total Hardness (CaCO ₃), mg/L	158.7	1154.0	783.3

A Hallimond tube was employed for the micro-flotation tests using deionized water. 1 g hematite or quartz was weighed and mixed with 100 mL 120 mg/L starch or 30 mg/L DDA with the absence/presence of Ca²⁺/Mg²⁺ ions at different concentrations, respectively. After conditioning three minutes, an air rate of 0.2 m³/min was pumped into the tube. The collecting time was one minute. Each test was performed at room temperature.

2.3.2. Powder contact angle measurement

Tensiometer K100, Kruss Instrument., Germany, was used to measure the contact angle of hematite or quartz powder treated with starch or DDA in the presence or absence of Ca²⁺/Mg²⁺ ions by using ADVANCE software. A 100 mL 2% w/v hematite or quartz suspension with calcium or magnesium ions at 100 mg/L or not was mixed with 100 mL 120 mg/L of the starch or 30 mg/L DDA solution, respectively. The mixture was stirred for ten minutes, and then it was filtered and allowed to dry at room temperature in a vacuum container. A sample weighing 1.5 g was collected for the measurement. The solvent chosen for the capillary constant and contact angle measurements of hematite were anhydrous ethanol and deionized water, respectively. The powder contact angle of the samples was calculated based on the Eq. (1) as follows (Tohry et al., 2020), in which c is the powder capillary constant (mm⁵), ρ is the density of the liquid (g/mL), σ is the surface tension of a liquid (mN/m), η is the viscosity of liquid (mPa · s), k is the slope of the line of m² to time t, and θ is the contact angle (°).

$$\theta = \arccos \frac{k\eta}{c\rho^2\sigma} \quad (1)$$

2.3.3. Zeta potential measurement

A Zetasizer Nano ZS90, manufactured by Malvern Instrument in the UK, was applied to measure the zeta potentials of pure hematite, starch, or their mixture when calcium or magnesium ions were present or not. A 100 mL 2% w/v hematite suspension (containing 2 g hematite) with the absence/presence of Ca²⁺ or Mg²⁺ ions at 100 mg/L was treated with 100 mL 120 mg/L of starch solution. The mixture was gently shaken in a thermostated circular shaker for ten minutes. A 10⁻³ mol/L KCl solution was employed to dilute 5 mL of the mixture into 100 mL and a small aliquot of the mixed suspension was transferred to the sample cell for zeta potential measurements. The pH of the diluted suspension was adjusted using HCl or NaOH.

2.3.4. FTIR analysis

A Bruker Alpha Fourier transform infrared spectrometer was employed to analyze the hematite or its blends with starch in the absence/presence of calcium or magnesium ions. At a resolution of 4 cm⁻¹, the spectra were acquired on the samples in KBr pellets that ranged from 4000 cm⁻¹ to 400 cm⁻¹. Each sample was prepared in the form of KBr (potassium bromide) pellets containing 10-15 mg solids samples for the FTIR analysis at room temperature.

3. Results and discussion

3.1. Flotation performance of the iron ore using different water sources

Fig. 2(a) presents the flotation performance of the iron ore sample using different water sources at 8.7 ± 0.2 . It obtains a concentrate at the highest recovery of Fe (86.75%) produced using recycled tailing water than with the other water sources at a similar grade of Fe. However, its SiO_2 content reaches nearly 7.87%, much higher than the freshwater or treated sewage water. The curves also show a slight upward trend in the grade of Fe but a loss of the recovery of Fe by using the treated sewage water compared with the freshwater. The use of freshwater produced a concentrate with the lowest SiO_2 content of about 6.5%. Based on the chemical analysis from Table 1, the high content of total hardness, or $\text{Ca}^{2+}/\text{Mg}^{2+}$ in the recycled tailing water could contribute to the dilution of silica in concentrates. It is in accordance with the data from the process water analysis in Fig. 2(b), revealing that an increase on SiO_2 content and a sharp drop on iron recovery in concentrates occurs as total hardness of the process water increases. A concentrate at 8.2% SiO_2 content and near 80% Fe recovery was obtained with the hardness at over 2000 mg/L. It seems to be beneficial to use the low hardness water as the lower the water hardness is, the better the concentrate quality was obtained.

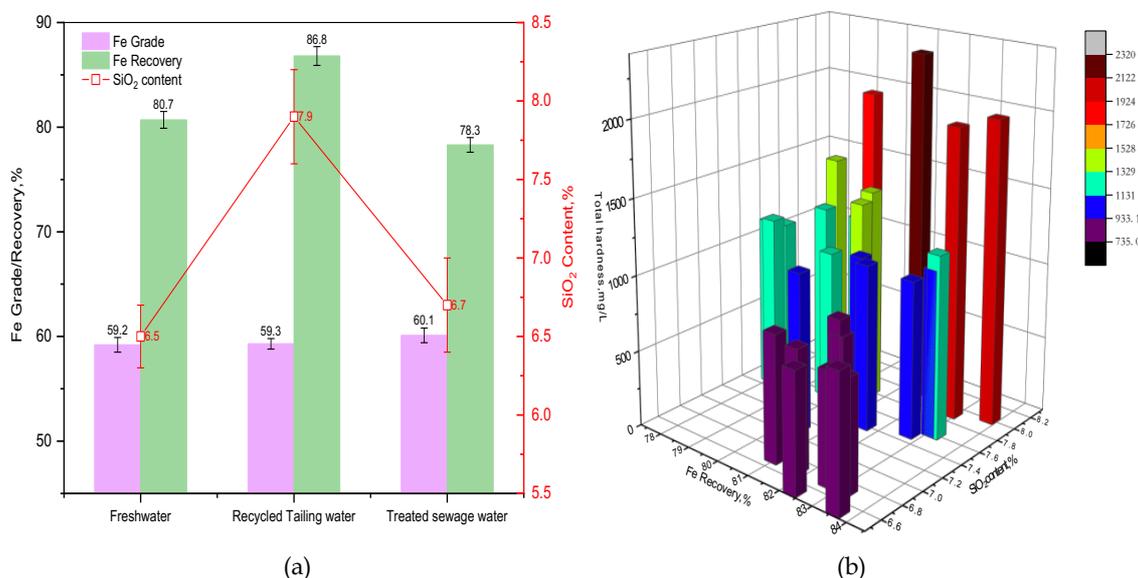


Fig. 2. Flotation performance of the iron ore using different water sources at $\text{pH } 8.7 \pm 0.2$ (a) and the relationship between total hardness in the process water from the industrial flotation system and iron recovery/ SiO_2 content in concentrates (b)

3.2. Influences of $\text{Ca}^{2+}/\text{Mg}^{2+}$ ions on flotation properties of iron oxides

Fig. 3 (a) provides the effects of total hardness on the flotation performance of the iron ore sample. The data show a drop by approximately 5% in the Fe recovery and an increase by about 1.0% in the SiO_2 content with increasing total hardness from 150 to near 1000 mg/L calculated as CaCO_3 . A slight downward trend on the Fe grade were also observed as total hardness in water reaches 1000 mg/L. It can be explained by the results from Fig. 3(b), indicating that Ca^{2+} or Mg^{2+} ions play different roles in affecting the flotation properties of the iron ore. Ca^{2+} ions were more significant than Mg^{2+} ions as a sharper drop in Fe recovery and an increase in SiO_2 content occur with increasing Ca^{2+} ion concentrations. But it changes a little on both Fe recovery and SiO_2 content for the presence of Mg^{2+} ions. At 8.7, the adsorption of the calcium-based hydrolyzed species, such as Ca^{2+} , $\text{Ca}(\text{OH})^+$, $\text{CaCO}_{3(s)}$, etc., could induce surface modification of minerals and influence their interactions with the collectors (Baes and Mesmer, 1976; Ren et al., 2018).

The influences of calcium or magnesium ions on hematite or quartz recovery have been investigated as shown in Fig. 4. It shows a slight increase in hematite recovery as Mg^{2+} ionic concentration increases. However, a severe drop of over 50% occurs with increasing Ca^{2+} ionic concentrations. It is consistent with the results from Fig. 3(b), suggesting the depressing effects of Ca^{2+} ions but the promotive ones of

Mg^{2+} ions in the hematite recovery. It is interesting to note that the presence of calcium ions also has a depression on quartz recovery when its concentration was over 100 mg/L as shown in Fig. 3(b). However, Mg^{2+} ions seem to be beneficial to recover quartz as an increase in quartz recovery takes place when its concentration increases. In terms of the data from Table 1 and Fig. 2, a build-up of Ca^{2+} ions in the recycled tailing water may contribute to the dilution of SiO_2 gangues. This could be relevant to the adsorption of Ca-/Mg-based hydrolyzed products on these minerals and disturb their interactions with starch or DDA. According to the previous literature investigated by Ofor (1996) and Rao (2004), a reversal on mineral surface charges contributes to the formation of the hydrolyzed products, such as $Ca(OH)^+$, $CaCO_3$, $Mg(OH)^+$, $Mg(OH)_2$, $MgCO_3$, etc.

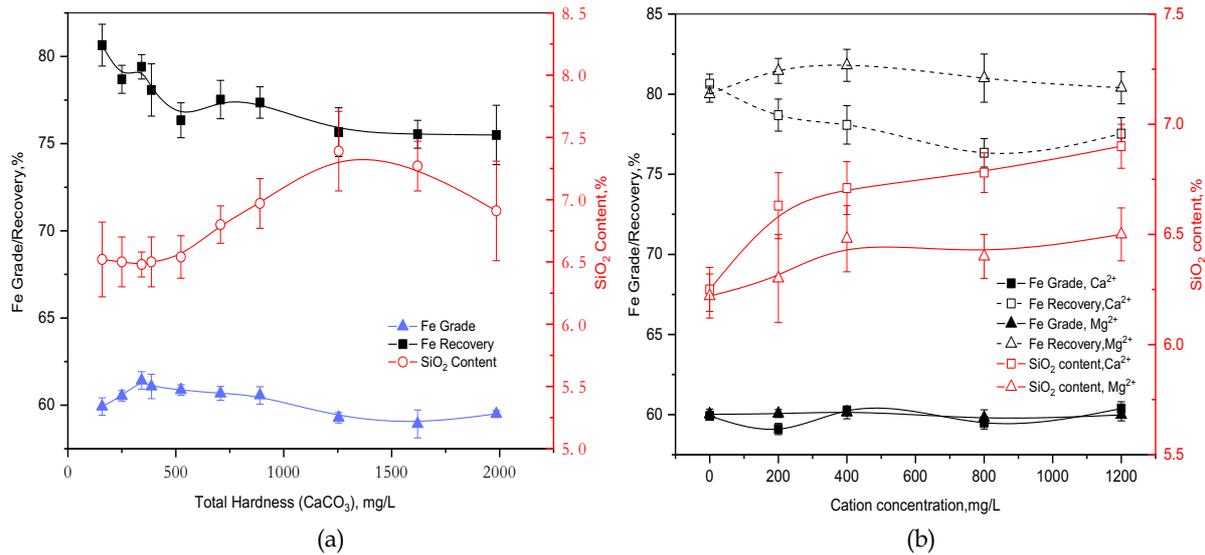


Fig. 3. Flotation performance of the iron ore as a function of total hardness (a) or Ca^{2+}/Mg^{2+} ion concentration (b) at 8.7 ± 0.2

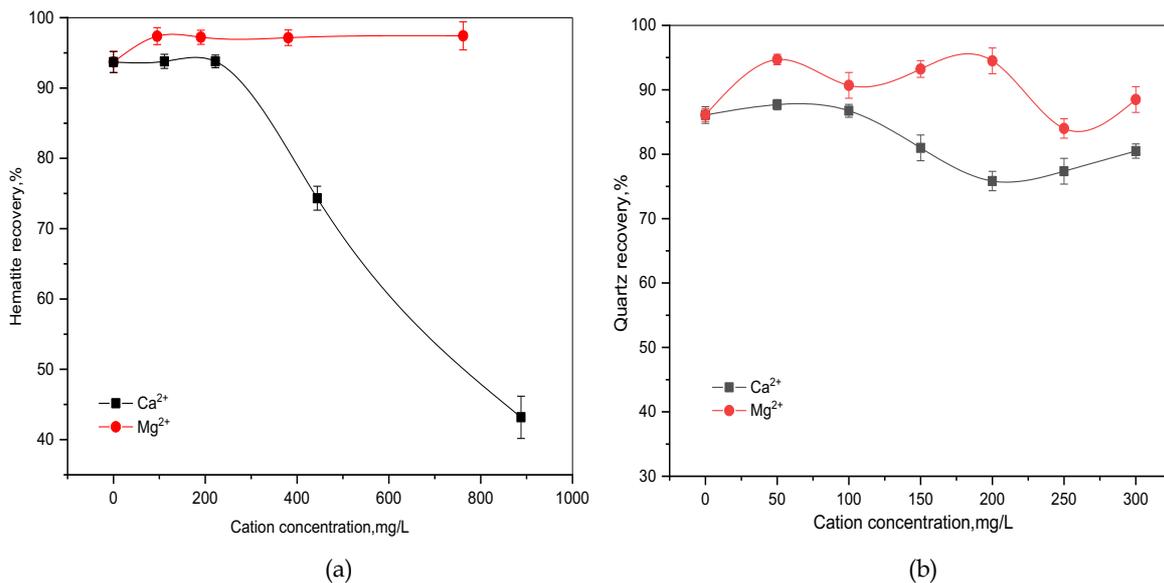


Fig. 4. Flotation performance of pure hematite flocculated with starch (a) or quartz treated by DDA (b) as a function of Ca^{2+}/Mg^{2+} ion concentration at 8.7 ± 0.2

3.3. Contact angle of hematite or quartz with the absence/presence of Ca^{2+}/Mg^{2+} ions

Table 3 displays the comparison of the contact angles of hematite particles flocculated with starch or quartz treated by DDA in the absence/presence of calcium or magnesium ions. It shows that the lowest contact angle (66.53°) was obtained from the hematite treated by starch with the occurrence of

magnesium ions, which could be a benefit to increasing the strong flocculation of starch due to an increase of hydrophilicity on mineral surfaces. However, an increase in the contact angle from 73.79° to 83.08° was observed from the particles with starch in the presence of calcium ions compared with one without any cation. This is well in agreement with the results from Figs. 3 and 4, indicating that the occurrence of calcium ions could weaken the flocculation of starch but magnesium ions could strengthen the adsorption of starch on hematite. Table 3 also shows the contact angle of quartz particles treated by DDA with the occurrence of Ca²⁺ or Mg²⁺ ions, suggesting that an increase by 3.77° in the contact angle of quartz was observed with the use of Mg²⁺ ions but a slight change with Ca²⁺ ions. It is followed by the results from Fig. 4(b), revealing that Ca²⁺ ions at low concentrations (100 mg/L) could influence a little quartz recovery while Mg²⁺ ions have a positive effect on improving the quartz recovery as they increase the hydrophobicity of quartz with the presence of the cationic collector. This could largely be attributed to the disturbances of their cation hydrolysed species on the interactions between quartz and DDA or hematite and starch.

Table 3. The contact angle of hematite flocculated starch or quartz treated by DDA in the absence/presence of Ca²⁺/Mg²⁺ ions

Minerals	Conditioning Type	Contact angle,°
Hematite	Non	79
	Starch	74
	Starch + Mg ²⁺	67
	Starch + Ca ²⁺	83
Quartz	Non	43
	DDA	59
	DDA + Mg ²⁺	63
	DDA + Ca ²⁺	61

3.4. Zeta potentials of hematite or quartz with the absence/presence of Ca²⁺/Mg²⁺ ions

Fig. 6 illustrates the zeta potentials of quartz or its mixture with DDA in the absence/presence of Ca²⁺ or Mg²⁺ ions. It indicates that a shift towards a less negative side on the zeta potentials of quartz presents when Ca²⁺/Mg²⁺ ions were added. Ca²⁺ ions reduce the charges of quartz more significantly than Mg²⁺ ions at a large pH range. With the presence of the cationic collector, a reversal on the zeta potentials of quartz surfaces occurs but it became less substantial if the cations were present. It is worth noting that calcium ions induce a sharp drop in the positive charges of quartz treated by DDA. This could be consistent with the results from Fig. 4(b), mentioning that calcium ions play an important role in deteriorating the quartz recovery. This is in accordance with the previous research explored by Taggart and Arbiter (1946) and Breeuwsma and Lyklema (1973), reporting that Ca²⁺ ions obtained a decrease 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. The precipitation of their hydrolyzed compounds, such as Ca(OH)⁺, CaCO₃, etc., may contribute to the ζ-potential sign modification on mineral surfaces due to the formation of a hydrophilic colloidal layer on the mineral surface, delaying the collector adsorption (Fuerstenau et al., 1963; Ren et al., 2018). A little effect on quartz recover with the presence of magnesium ions could be attributed to only a small number of Mg²⁺ or Mg(OH)⁺ adsorbed on mineral surfaces found by Feng et al. (2018).

3.5. FTIR of starch-flocculated hematite or DDA-treated quartz with the absence/presence of Ca²⁺/Mg²⁺ ions

Fig. 7(a) shows the FTIR spectra of the hematite particles or their blends with starch in the presence of calcium or magnesium ions. The curves show that a new peak at 2070 cm⁻¹ or 1292/1475 cm⁻¹ occurs on the curve of the hematite treated by starch with Mg²⁺ or Ca²⁺ ions, respectively, which could be attributed to the involvement of calcium- or magnesium-based compounds in the interactions between starch and mineral surfaces. Calcium hydroxyl or precipitates could deactivate the acidic groups from the caustic-digested starch, weakening its flocculation capacity on particles by contracting the starch

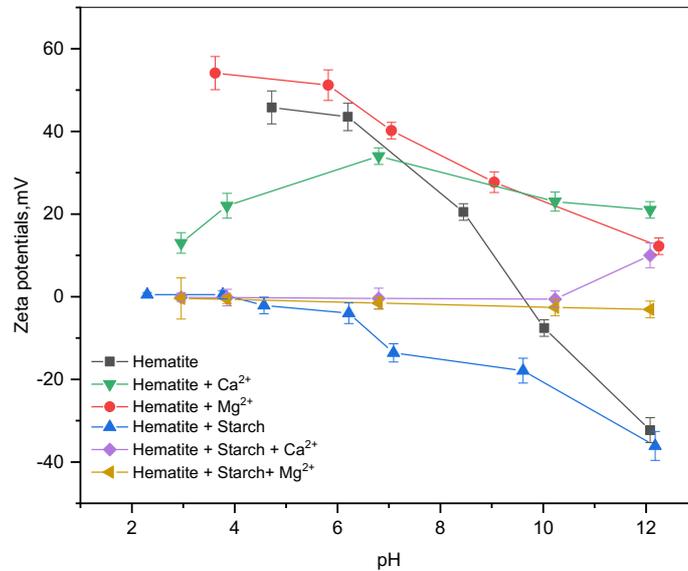


Fig. 5. The zeta potentials of hematite using starch with the absence/presence of Ca²⁺/Mg²⁺ ions

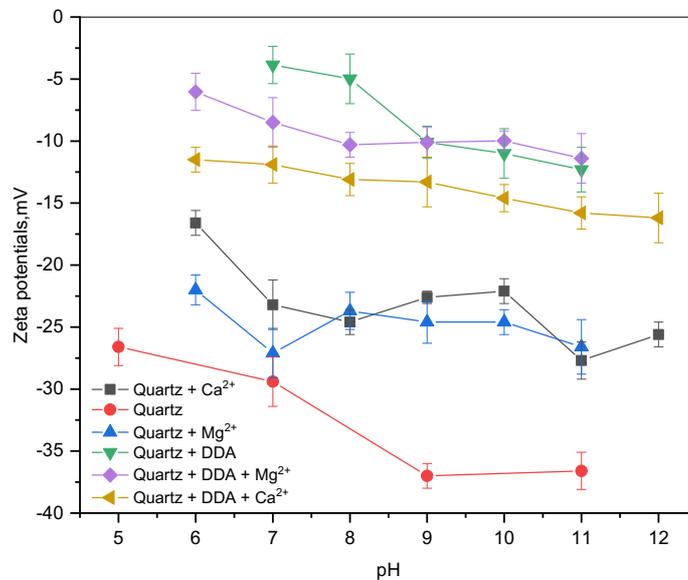


Fig. 6. The zeta potentials of quartz using DDA with the absence/presence of Ca²⁺/Mg²⁺ ions

configuration and disturbing its adsorption on mineral surfaces. This is in coincidence with the results from Table 2 and Figs. 3-5, indicating a negative effect on the iron oxide flocculation of starch with the presence of calcium ions. However, the occurrence of the peak at near 1300 cm⁻¹ and the stretch of -COOH or C-OH at over 1390 cm⁻¹ from the curve of hematite using starch treated by magnesium ions were observed, which suggests that the presence of Mg²⁺, Mg(OH)⁺, Mg(OH)₂, or MgCO₃ compounds could enhance the flocculation of starch on hematite (Fuerstenau et al., 1963; Baes and Mesmer, 1976). It is probably due to either their magnesium-based products could act as an adsorption bridge between mineral surfaces and starch by attracting the adsorption of the acidic groups on the starch chain pieces and anchoring the active sites on hematite. This is in line with the previous research reported by Wang et al. (2022), which demonstrated the presence of -CH₂-O-Al²⁺ when caustic starch and aluminum sulfate were combined at a mass ratio of 1:1.

Fig. 7(b) also provides the spectra of quartz or its mixture with DDA in the presence of Ca²⁺/Mg²⁺ ions. It indicates that the typical peaks of calcium hydrolyzed products at 1360 cm⁻¹ and 1400 cm⁻¹ occur but no apparent peaks for magnesium-based species on the curve of quartz conditioned with DDA. This means that the hydrophilic layer coated by calcium-based precipitates on quartz could disturb the

adsorption of DDA, which is in agreement with the results from Figs. 4(b) and 6(b). However, the adsorption of magnesium-based products, for example, Mg^{2+} or/and $Mg(OH)^+$, could be weak and easily be removed with little effect on recovering the quartz during flotation.

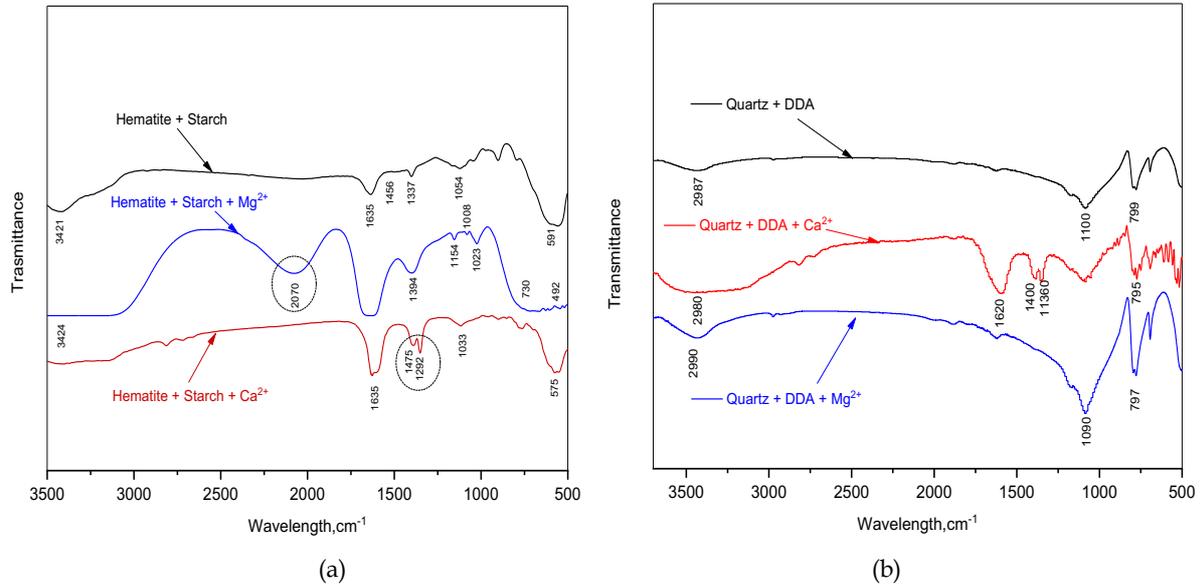


Fig. 7. The FTIR curves of hematite flocculated with starch (a) or quartz treated by DDA (b) in the absence/presence of Ca^{2+}/Mg^{2+} ions

A hypothesis of the role of Ca^{2+} or Mg^{2+} ions in affecting the flotation properties of iron oxides is shown in Fig. 8. The formation of a hydrophilic colloidal layer on quartz by hydrolyzed Ca-based compounds, like $Ca(OH)^+$, $CaCO_3$, etc., may alter the zeta potentials of quartz surfaces and interfere with their interactions with DDA. Since the electrostatic adsorption of the dominant hydrolyzed products of DDA, such as RNH_3^+ , $RNH_2(s)$, or $RNH_3^+ \cdot RNH_2$, could be hindered by these positive charged calcium-based species coating on the originally negative-charged quartz at a pH range of near 8.7 (Han et al., 2016). But the small coverage of magnesium hydrolyzed products on quartz seems to have a less influence on the interactions with the collectors. Probably as a result of pre-locking the acidic groups on the starch remnants and constricting their configurations, calcium-based species could also have a competitive role in the flocculation of starch on hematite. It is interesting to note that magnesium-based species, for example, $Mg(OH)^+$, Mg^{2+} , $Mg(OH)_2$, etc., may serve as adsorption bridges between the surfaces of hematite and starch strengthening the adsorption of starch on particles.

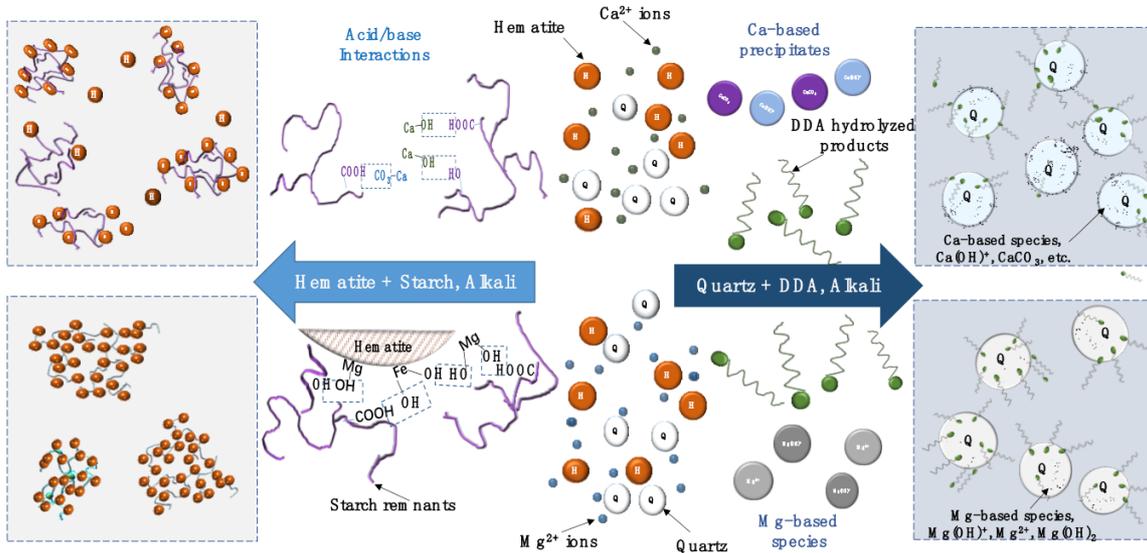


Fig. 8. A hypothesis about the effects of Ca^{2+}/Mg^{2+} ions on quartz or hematite recovery during flotation

4. Conclusions

Different water sources with varying contents of calcium or magnesium ions re-cycling in an industrial reverse flotation system of iron ore cause a fluctuation in the flotation performance of iron oxides. With the objective of identifying the possible influences of these ion distributions in these water sources and stabilizing the system, a series of tests, including flotation tests, zeta potentials, powder contact angle, and FTIR analysis were conducted. The results show that a sharp increase of 1.35% in the content of SiO₂ in concentrate occurs by using the recycled tailing water, coupled with an increase of 6% recovery of iron in comparison to using the freshwater. The high content of calcium or magnesium ions in the recycled tailing water could contribute to it. As evidenced by the results from powder contact angle, zeta potentials, and FTIR, Ca²⁺ ions, can dilute the concentrate severely by reducing the recovery of Fe and increasing the content of SiO₂. This could be attributed to the coating of a hydrophilic colloidal layer induced by calcium-based precipitates on quartz surfaces or/and the pre-locking of the acidic groups of the caustic-digested starch by acid-based interactions weakening its flocculation performance on particles. But magnesium-based compounds could act as adsorption bridges between mineral surfaces and starch enhancing their interaction, as these species could preferentially adsorb onto mineral surfaces.

Acknowledgments

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