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Influences of process water chemistry on reverse flotation selectivity of iron oxides

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Abstract: It is critical for water quality in flotation as it dramatically influences the chemical/electrochemical properties of mineral surfaces and their interactions with reagents. Many potential variations could alter the water chemistry: water recirculation, mineral dissolutions, reagent additions, etc. This study aimed to identify the key elements from the recycled water sources affecting the separation efficiency in a typical industrial flotation circuit of iron oxides through a series of bench/micro flotation tests, zeta potential measurement, etc. The built-up and distribution of the dominant cations/anions in the process water from the roughers in the flotation system was also analyzed and recorded by Inductively Coupled Plasma-Optical Emission (ICP-OES) for a period of about three months when the operations were stable. The flotation results pointed out that a concentrate with a sharp increase of 6.0% Fe recovery and 2.5% SiO_2 content was obtained by using the recycled tailing water only in comparison by using fresh water. In contrast, a slight uptrend in the grade of Fe but a substantial loss of near 6.5% Fe recovery occurs by using the treated sewage water alone instead. This could attribute to the ion distributions in these water sources, in which Ca^{2+}, Fe^{n+}, Mg^{2+} or SO_4^{2-} ions were determined as the key ions influencing the flotation behaviors of the iron ore. But the competitive effects of Fe^{3+} ions were more significant than the ones of Ca^{2+} or Mg^{2+} ions. And the occurrence of starch could deteriorate the dilution of silicates in concentration induced by Fe^{3+}/Fe^{2+} ions. It can be explained by zeta potential measurement or solution chemistry of those ions, indicating that at 8.5-9.0, the coating of the precipitates of $Fe(OH)_{3(s)}$ induced by iron ions alters a reverse on the zeta potentials of quartz. The presence of SO_4^{2-} ions, however, has a positive role in reducing the possibility of slime coating on silicates due to acting as a chelating agent of iron ions.

Keywords: water chemistry, ion distribution, iron oxides, reverse flotation

1. Introduction

It is essential for water quality in flotation as it largely influences the chemistry of pulp, alters the properties of mineral surfaces, and interferes with their interactions with reagents. There are many potential variations affecting the chemistry of process water: mineral dissolutions, water recirculation, residual reagents, etc. (Muzenda, 2010; Liu et al., 2013; Michaux et al., 2018). The occurrence and built-ups of some disturbing cations/anions, for example, Na^{2+}, Ca^{2+}, Mg^{2+}, Mn^{2+}, Fe^{3+}, Al^{3+}, Cl^-, NO_3^-, SO_4^{2-}, PO_4^{3-} etc., are inevitable in the process water, which could bring unpredictable modifications on the surface chemistry of minerals and disturb their flotation behaviors (Haselhuhn et al., 2012; Li et al., 2018).

The effects of the common cations in water, such as Na^+, Ca^{2+}, Mg^{2+}, Mn^{2+}, $Fe^{2+/3+}$, Al^{3+}, etc. on the flotations of iron oxides have been recently studied in detail. Fuerstenau et al. (1963), Nevasaia et al. (1998), and Ruan et al. (2018) revealed that Ca^{2+}/Mg^{2+} ions have the promotive effects on the anionic flotation of quartz or silicates. Ofor (1996), Manono et al. (2012), and Ren et al. (2018), however, reported the competitive effects of these cations in both cationic and anionic flotation of hematite, silica, or talc gangues. These influences are greatly relevant to the type of collectors, properties of minerals themselves, and cation valence/concentrations. Table 1 summarizes the effects of cations/anions at

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different valences or concentrations in water on the flotation of iron oxides. It indicates that the cations with higher valences tend to have a more positive/negative on the mineral recoveries. Similar observations made by Flood et al. (2006) suggested that the adsorption density of polymer on silica increases with an increase in cation concentration and valence. But it could be inconsistent with the findings by Ruan et al. (2018), who mentioned that the activation abilities of the quartz of the divalent cations (Ca^{2+} or Mg^{2+}) are greater than the trivalent cations (Fe^{3+} or Al^{3+}) during anionic flotation. This can be evidenced by the investigations reported by Rao (2004), who suggested that the potential reversal triggered by metal ion adsorption could hinder the floatability of the minerals if the collector adsorption dominantly depends on electrostatic interaction.

Table 1. Differences in the effects of cations/anions at different valences or concentrations in water on the flotation of iron oxides

Cations /Anions	Type of Flotation	Minerals Floated	Differences in Cation Influences	References
Fe^{2+}, Fe^{3+}/SO_4^{2-},Cl^-	Anionic	Cassiterite	A drop in the recovery of cassiterite with an increase in concentrations and valences when the ion concentration is over 0.1 mmol/L	Cao et al., 2021
K^+, Na^+/Cl^-	-	Coal/clay	Na+ /K+ improves the combustible recovery by inhibiting clay coating or promoting the aggregation of clay.	Bai et al., 2020
Ca^{2+}, Mg^{2+}, Fe^{3+}, Al^{3+} $/Cl^-$	Anionic	Quartz	The order of the activation abilities on quartz: $Ca^{2+} \geq Mg^{2+} > Fe^{3+} > Al^{3+}$.	Ruan et al., 2018
Ca^{2+} $/Cl^-$	Cationic	Quartz	Competitive adsorption of ester amine on quartz with an increase of concentration.	Ren et al., 2018
Ca^{2+}, Mg^{2+}, K^+, Na^+/Cl^-	-	Quartz	The dissolution rate of quartznear-neutraltral pH salt-free solutions: $MgCl_2$<$CaCl_2$<NaCl~KCl.	Dove and Nix, 1999
Na^+, Ca^{2+}/Cl^-	Anionic	Quartz	Little difference in this adsorption between Na^+ and Ca^{2+}.	Nevskaia et al., 1998
Al^{3+}/SO_4^{2-}	Anionic	Silica	Al ions/species adsorbed and hinder its reaction with NaOl.	Chen et al., 2018
Mn^{2+}/Cl^-	Cationic	Silica	Competitive adsorption of Mn(OH)2.	Duarte et al., 2015
Fe^{3+}, Ca^{2+}/Cl^-	Cationic/Anionic	Spodumene and Beryl	Fe3+ ions show good activations on both minerals at a low concentration of 35 mg/l but Ca^{2+} ions can't.	Wang et al., 2007
Na^+, Mg^{2+}, Ca^{2+}, La^{3+}/Cl^-	Polymer	Silica	i) Promotive adsorption with an increase of concentration and valency strength; ii) Little effect by NaCl.	Flood et al., 2006
Ca^{2+}, Mg^{2+}, Al^{3+}, Sn^{4+} $/NO_3^-$, SO_4^{2-}, PO_4^{3-}	Anionic	Hematite	A drop in adsorption density with an increased charge of cation or anion	Ofor, 1996

Table 1 also shows the possible roles of some anions coupled with the above cations on the flotation performance of iron ore flotation. The monovalent anions, such as Cl^-, if adsorbed on certain oxides and have little influence on their floatability while the anions with higher valences tend to have more substantial roles on the flotation performances. Cao et al. (2021) reported that iron ions coupled with sulfate have more depression than chloride. Somasundaran and Grieves (1975) also found no specific adsorption of anions, Cl^-, NO_3^-, on SiO_2 or Al_2O_3 minerals but on Fe_2O_3 minerals. This is in agreement with the observations by Ofor (1996), indicating that the anion has a greater depression than cations of the same charge in the flotation of hematite and an increase in the valence of the anion leads to a drop in the adsorption of oleate on hematite. The reversal of hematite induced by the adsorption of these anions, especially SO_4^{2-} ions, could attribute to the depressions (Ferreira et al. 2004).

Studies as described before mostly focus on the influences of cations or anions with ideally prepared water samples of known chemistry and pure minerals. The process water chemistry of an industrial iron ore concentrator which involves many recycled water sources with a continuous build-up of these dissolved ions due to water recirculation has rarely been reported. What happens to the flotation behaviors of iron oxides if their accumulations in the process water occur and how they influence the flotation selectivity may not be fully understood. In this study, the relationship between the dominant anionic/cationic distributions in the recycled water sources and the flotation performance of an industrial iron ore concentrator was explored through a series of bench/micro flotation tests, zeta potential measurement, etc. The water analyses from different locations in the flotation system were also conducted by Inductively Coupled Plasma-Optical Emission (ICP-OES) for a period of about three months when the operations were stable.

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, which had been ground and pre-upgraded by magnetic separationThe ore sample was assayed by chemical analysis as shown in Table 2, which shows that it contains 55.6% Fe, 10.5%SiO_2, 1.89%CaO, 3.28% MgO, and 1.36% Al_2O_3. It was also characterized by X-ray Diffraction using Bruker D8 Discovery X-ray Diffractometer at a λ value of 1.79Å in which a cobalt source was introduced due to its advantage of identifying the powder containing iron in comparison with the other sources, for example, copper or chromite.Fig. 1presents the diffractograms of the iron ore sample, indicating that the highest peak at a 2θ of 35.3937^o was labeled by magnesium-bearing magnetite, and the other main peaks of the reference patterns were recognized as ankerite, silica, and phyllite as well.

Table 2 The chemical composition of the iron ore sample.

Item	TFe	MFe	SiO_2	CaO	Al_2O_3	MgO	S	P	Mn	K	Na
Content, %	55.6	53	10.50	1.89	1.36	3.28	0.47	0.0060	0.91	0.33	0.066

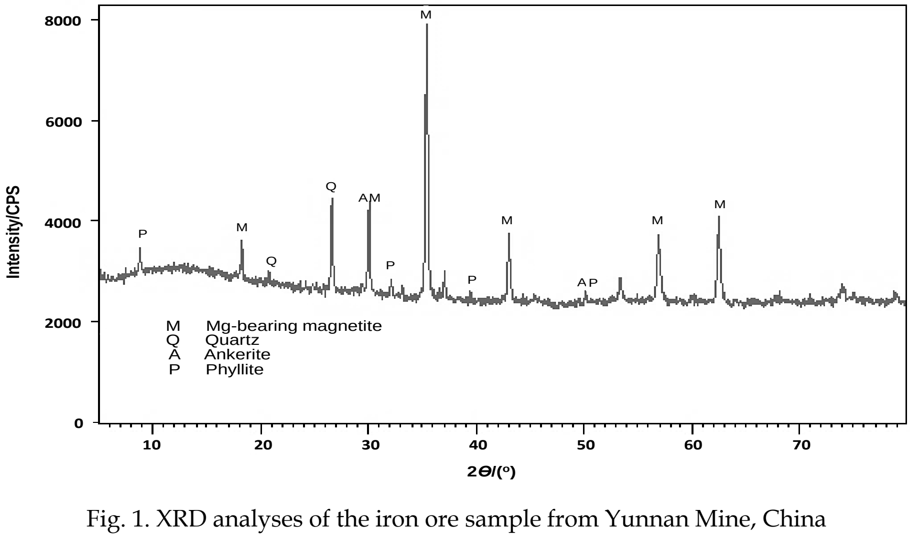


Fig. 1. XRD analyses of the iron ore sample from Yunnan Mine, China

Corn starch (S-4180) was purchased from Sigma-Aldrich. It was digested with sodium hydroxide in hot water used as flocculants. Dodecylamine (DDA), 124-22-1, was purchased from Shangdong Chemical Tech. Co. The reagents at chemical grades, such as sodium hydroxide, calcium chloride, magnesium chloride, ferric chloride, potassium thiocyanate, sulfuric acid, and sodium sulfate, were from Fisher Scientific or Sigma-Aldrich. 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. Process flow sheet of the industrial flotation process

A reverse-flotation flowsheet of an industrial iron ore concentrator with different water sources was shown in Fig. 2. The head feed for the flotation system was the concentrates from magnetic separation. The purpose of the reverse flotation is to re-upgrade the concentrates by the removal of the silicates. The iron ore sample at a range of 32-35% solid density was fed into the roughing banks. The water sources involve the internal recycled water from the dewatering units, or external water sources, the local freshwater at a flow rate of approximately 900m^3/h, and recycled water from the tailings pond and the treated sewage water plant at a flow rate of 500-1000 m^3/h which fluctuates seasonally. Sulfuric acid as pH modifier, caustic-digested starch as flocculants, and DDA as a collector were used in this process. The pH range of the pulp is from about 8.5 to 9.0 during flotation. DDA or starch concentrations are kept at a constant level based on real-time monitoring in the flotation cell. The flotation concentrate from the roughing stage was pumped to the cleaning cells where the final concentrate was produced by removing most of the silica gangues.

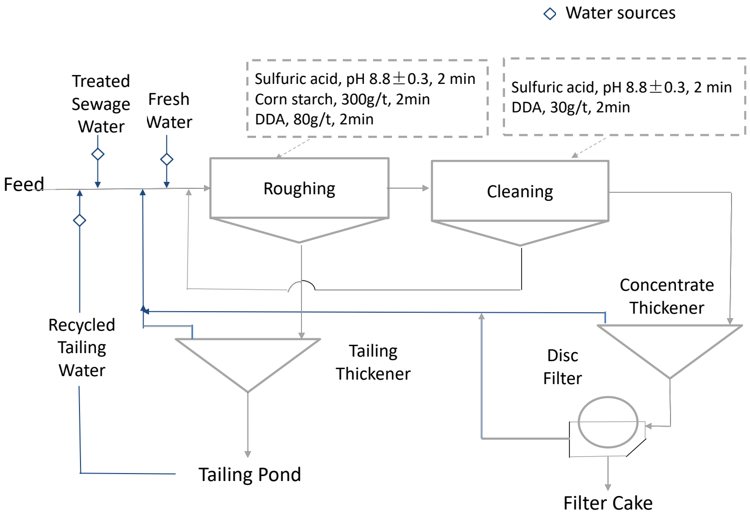


Fig. 2. The flowsheet of an industrial flotation plant of iron ores in Yunnan Mine

The water samples were taken from three water sources: the local freshwater, the water from the tailings pond, and the water from the local sewage treatment plant. The one-liter glass bottle was used to collect each water sample periodically from the industrial flotation concentrator by centrifuging and filtrating. All the samples were analyzed for the main cations and anions by a certified laboratory.

2.3. Methods

2.3.1. Bench Flotation tests

To prepare samples for bench flotation tests, 500 g of the iron ore sample was weighed and mixed with tap water at room temperature. The test was conducted by using a 1.5L cell (XF-D) for roughing and cleaning stages at an impeller speed of 1200 rpm for a certain time based on the flowsheet shown in Fig. 2. A froth depth (FH) of 15.2 cm, superficial gas velocity (Jg) of 0.75 cm/s, and collecting time (t) of 10 minutes were employed for the roughing stage but a froth depth of 11.5 cm and collecting time of 4 minutes at the same superficial gas velocity for the cleaning stage. Dodecylamine (DDA) as a collector was used to render the hydrophobicity of the silicates in the ore and enhance their attachment with bubbles. The caustic-digested starch as flocculants was introduced to flocculate and depress the iron oxides. Sodium hydroxide or sulfuric acid as pH modifiers were introduced into the tests. The concentrates, middlings, and tailings from the bench flotation tests had been filtrated, dried, weighed, and then assayed grade of Fe and content of SiO_2, respectively.

2.3.2. Zeta potential measurement

The zeta potentials of quartz were measured with the use of a ZetaPALS manufactured by Brookhaven Instruments Corporation, USA, based on the electrophoretic light scattering (ELS) technique. To prepare samples for the zeta potential measurements, a 100 mL 0.5% (5 g/L) quartz solution was mixed with a 100 mL cation chloride or/and sodium sulfate solution at a concentration of 1 mmol/L at room temperature. The mixed suspension was stirred for 10 min. Five mL of the mixed suspension was withdrawn and diluted to 100 mL with a 10^{-3} mol/L KCl solution. The pH of the diluted suspension was adjusted using HCl or NaOH, and a small aliquot of the suspension was transferred to the sample cell of the ZetaPALS for zeta potential measurements.

2.3.3. Micro-Flotation Tests

To prepare samples for a flotation test using a Hallimond cell, 1 g quartz was weighed and mixed with 100 mL distilled water. A 6 mg/L DDA as a collector was used for each test and its conditioning time was 1 min. Ferric or ferrous chloride at different concentrations or 4 mg/L starch was added and conditioned for 2 min if needed before the addition of the collector. All micro-flotation tests were performed at an air rate of 0.2 m^3/min at room temperature, and the flotation time was three minutes.

2.3.4. Solution chemistry calculation of cations

The calculations of solution chemistry of Ca^{2+}, Mg^{2+}, Fe^{3+}, or Fe^{2+} ions were conducted at a pH range from 1 to 12 by using the Visual MINTEQ17. Each cation solution at 5 mmol/L was prepared at room temperature (25℃). The ionic or precipitate species were selected in terms of Log activity. The final data were excelled and its Log C-pH curve was drawn by using the Origin 95 software.

3. Results and discussion

3.1. Chemistry of water sources and their influences on flotation selectivity of iron oxides

The water chemistry of three water sources from an industrial iron ore concentrator: the local freshwater, the water from the tailings pond, and the water from the local sewage treatment plant was shown in Table 3. It indicates that the contents of the main cations, Ca^{2+} or Mg^{2+} ions, as well as the dominant anions, Cl^- or SO_4^{2-} ions, in the recycled tailing water were obviously much higher than in the treated sewage water or freshwater. The total hardness in the tailing water is approximately seven times the one in freshwater. And only less than one-fifth of the total hardness is temporary. The presence of iron ions in the recycled tailing water is inevitable due to the dissolution of the iron ore itself and the consumption of grinding media. The detection of these ions, however, was difficult due to the formation of their precipitates occurring at a large pH range of over 3 in terms of iron ion solution chemistry (Ruan et al., 2018; Ren et al., 2018). As all water samples from these water sources at near neutral or weak alkali were anaylzed after centrifuging and filtrating the slimes, which could remove all iron precipitates.

Table 3 Chemical analysis of water sources in the industrial iron ore flotation system

Water sources	pH	Ca^{2+}, mg/L	Mg^{2+}, mg/L	Total Hardness ($CaCO_3$), mg/L	Al^{3+}, mg/L	Cl^-, mg/L	SO_4^{2-}, mg/L	Slimes, mg/L	NH_3^+N, mg/L	Acrylamide, mg/L
Fresh Water	7.9	15	5	158.7	<0.020	5.5	12.7	1	0.03	0.00029
Treated Sewage Water	6.4	128	284	783.3	<0.020	176.8	494.0	3	0.08	0.00030
Recycled Tailing Water	9.8	274.9	345.2	1154	<0.020	258.0	963.0	5.7	0.05	0.00028

Figs. 3a and 3b present the flotation selectivity of the iron ore at 8.7±0.2 by using different water sources. It indicates that the use of recycled tailing water only tends to harvest a concentrate at a higher recovery of Fe at a similar grade of Fe in comparison with the other water sources. But a sharp increase in the content of SiO_2 by near 2.5% occurs with using the recycled tailing water by contrast with using the freshwater. The curves also show a slight uptrend in the grade of Fe but a substantial loss of the recovery of Fe by using the treated sewage water alone instead. It is a benefit to use freshwater to obtain a concentrate at a relatively satisfied SiO_2 of less than 6.5%. Based on the chemical analysis from Table 3, high contents of Ca^{2+}, Mg^{2+}, SO_4^{2-}, or possible Fe^{n+} ions in the recycled tailing water could contribute to the dilution of silica in concentrates. According to the previous literature published by Taggart and Arbiter (1946), Ca^{2+} or Mg^{2+} ions at a high concentration induce a drop in the recovery of pyrochlore due to the reversal of its surface charge and hindering the adsorption of the amine on it. Identical observations have been made by Fuerstenau et al. (1963) and Brown and Ekberg (2016), indicating that the reversal of the molybdenite/quartz zeta potential attributes to the formation of the hydrolyzed products, such as $Ca(OH)^+$, $CaCO_3$, $Mg(OH)^+$, $Mg(OH)_2$, $MgCO_3$, etc.

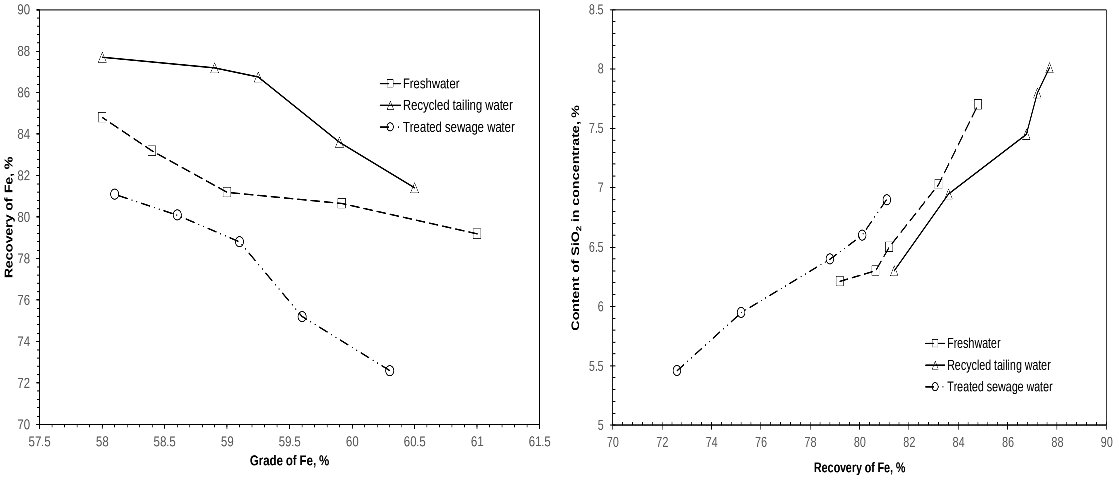


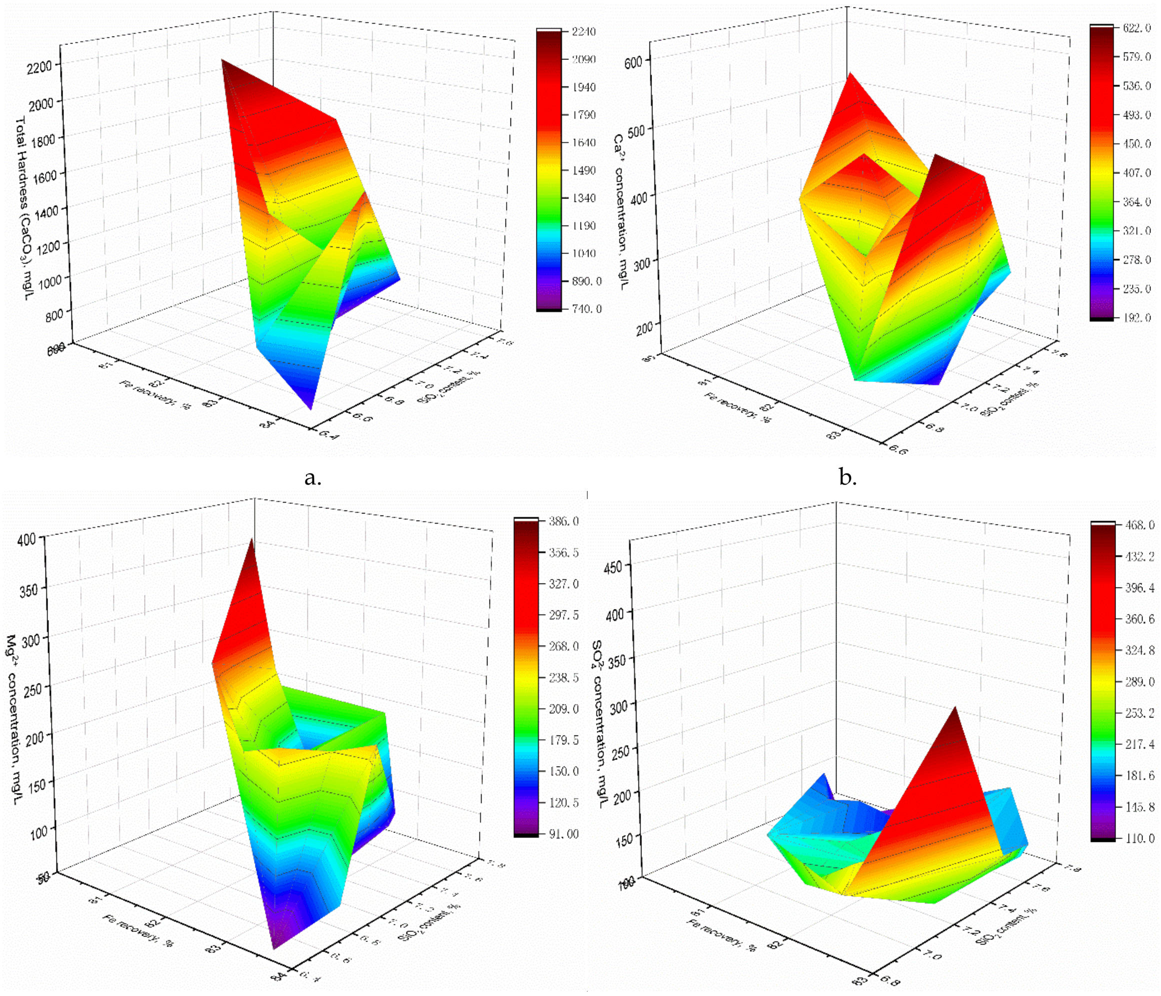
Fig. 3. Flotation performance (a. Grade of Fe vs recovery of Fe, and b. content of SiO_2 vs recovery of Fe) of the iron ore by using different water sources at a pH range of 8.7±0.2

3.2. Ion distributions in process water and its relationship with flotation properties

The records of the relationship between the flotation properties of iron oxides and total hardness, Ca^{2+}, Mg^{2+}, or SO_4^{2-} ion distribution in the process water from the roughers for a period of three months as shown in Figs. 4a-4d. The data show that the total hardness at a higher value doesn't enhance the flotation properties. And Ca^{2+} ion concentrations definitely play a negative role in influencing the iron grade/recovery. Mg_{2+} ion concentration, however, doesn't seem to have an important role in affecting the flotation behaviors of iron oxides. This may be consistent with the previous research, indicating that a drop of about 50% in the recovery of quartz was found in the presence of Ca^{2+} ions at a concentration of 80 mg/L using ester amine as collectors performed by Ren et al. (2018). The controversial observations were reported by Feng et al (2018), showing that the presence of Mg^{2+} ions induced an increase in the recovery of quartz at a pH range of 9-10. Fig. 4d also indicates that SO_4^{2-} ions seem to have positive effects on both the recovery and grade of Fe in concentrates. This probably explains an increase in the recovery of Fe and SiO_2 content in concentrates by using the recycled tailing water from Fig. 3. SO_4^{2-} ions at high content could trigger a reversal on zeta potential or a shift on the pzc of the minerals due to specific adsorption of these ions on the mineral surface, increasing their contact angle and thus promoting the flotation recovery using an amine type collector (Fuerstenau, 2005).

3.3. Influences of the main inorganic ions on flotation selectivity of iron oxides

Fig. 5 reveals the influences of cation chlorides or sodium sulfate in water on the flotation selectivity of iron oxides. The results indicate that the effects of Fe^{3+} ions were more significant than the ones of others as there is a sharp upward trend in the content of SiO_2 and a drop by approximately 5.5% in the recovery



a. b.

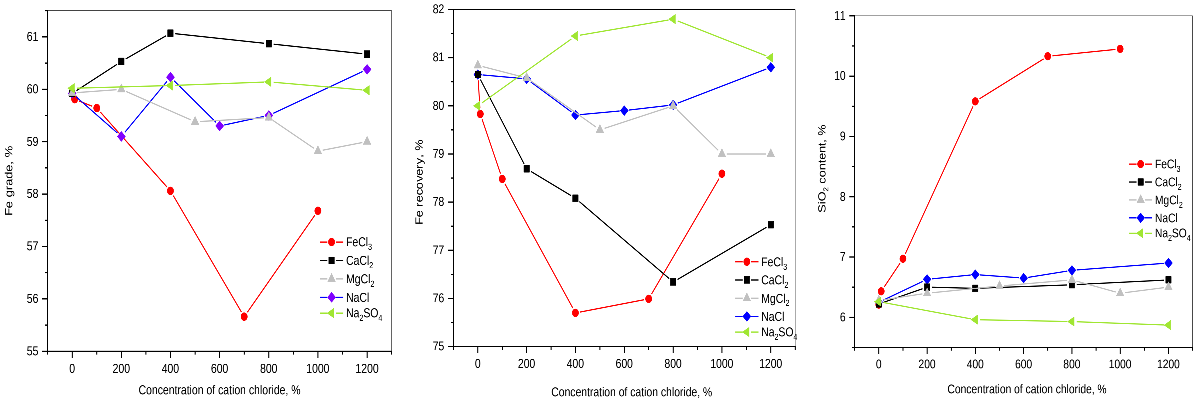
c. d.

Fig. 4. The records of ion distributions in the process water from the roughing stage on the Fe recovery or SiO2 content in concentrates in the industrial iron ore flotation plant at a period from June, 1st to August, 1st, 2021 ((a. total hardness, b. Ca^{2+}, c. Mg^{2+}, or d. SO_4^{2-})

of Fe in concentrates with increasing concentration of Fe^{3+} ions in water. While a high concentration of Mg^{2+} ions induces a slight drop in the recovery of Fe but a little in the content of SiO_2. The occurrence of Ca^{2+} ions, however, results in a gradual decrease in the flotation recovery of iron oxides. This is evidenced by the records from Figs. 4b and 4c, suggesting the competitive influences of Ca^{2+} ions but no apparent one of Mg^{2+} ions. According to the previous research (Ofor, 2017; Manono et al., 2017; Ruan et al., 2018; Ren et al., 2018), it indicates cations with a higher valence tend to influence the floatability of silica more strongly. In terms of the data from Table 3 and Figs. 3-4, a build-up of Ca^{2+} ions that occurs in the recycled tailing water may partly contribute to the fluctuations in the recovery of iron while the presence of iron ion species could also attribute to a substantial increase on the content of SiO_2. Fig. 5 also indicated that the occurrence of SO_4^{2-} ions has a positive effect on reducing the SiO_2 content and increasing the Fe recovery as an increase of 2.0% Fe recovery at a slight drop of 1.0% SiO_2 content takes place at a concentration of over 400 mg/L SO_4^{2-}. The specific adsorption of sulfate ions on silicate surfaces could reverse its zeta potentials and enhance the interaction of cationic collectors on mineral surfaces (Modi and Fuerstenau, 1960; Breeuwsma and Lyjklema, 1973).

3.4. Zeta potentials of quartz or solution chemistry in the presence of the main ions in water

The zeta potential values of the quartz pretreated with $CaCl_2$, $MgCl_2$, $FeCl_2$, or $FeCl_3$ with or without Na_2SO_4 ions as a function of pH were observed in Fig. 6. There is a reversal on the zeta potentials of quartz in the presence of Fe^{3+} or Fe^{2+} ions, while no reversal but less negative on the zeta potentials of



a. b. c.

Fig. 5. Grade Fe (a), Recovery of Fe (b), and content of SiO_2 (c) in concentrates as a function of cation chloride or sodium sulfate concentrations at a pH range of 8.7±0.2

quartz with the occurrence of Ca^{2+} or Mg^{2+} ions. This could be attributed to the coating of the precipitates or the specific adsorption of iron ion hydrolyzed species on mineral surfaces at 8.5-9.0, especially solid ferric hydroxide, which was produced at a highest amount than the other iron ion species in terms of Log C–pH curves of Fe^{3+}/Fe^{2+} ions in water as shown in Fig. 7. It is also worthy to be noted that the presence of dissolved O_2 in water could lead to the oxidation of ferrous ions and their hydrolyzed products, resulting in ferric components. Ferrous hydroxide, for example, was unstable in water as it was easily oxidized into ferric hydroxide based on the following interaction:

$$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3 \qquad (1)$$

Fig. 7 also indicated that at 8.5-9.0, Ca^{2+}, $CaOH^+$, Mg^{2+}, and $MgOH^+$ were the dominant species of Ca^{2+} or Mg^{2+} in water, which could adsorb on mineral surfaces, inducing a slight shift of its zeta potentials towards less negative. Similar observations have been made by Fuerstenau et al. (1963) and Brown and Ekberg (2016), indicating that the reversal of the molybdenite/quartz zeta potential attributes to the formation of the hydrolyzed products, such as $Ca(OH)^+$, $CaCO_3$, $Mg(OH)^+$, $Mg(OH)_2$, $MgCO_3$, etc if carbon dioxide was present in water.

A shift of the IEP of the quartz pretreated with Fe^{3+} ions in the presence of SO_4^{2-} ions towards the acidic direction from near 9.0 to 7.5 was also from Fig. 6. It can be well explained by Ferreira et al. (2004), who investigated the zeta potential of hematite in the presence of K_2SO_4 induced a reversal of hematite zeta potential at a pH range of less than 8 due to specific adsorption of sulfate ions on the mineral surfaces. Identical observations have been made by Breeuwsma and Lyjklema (1973), indicating a shift in the pzc of hematite from 8.5 to 9.5 in the presence of SO_4^{2-} ions due to specific adsorption. Over 75%

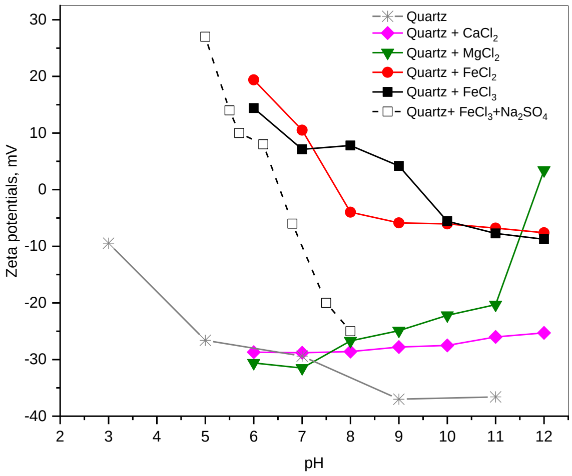


Fig. 6. The flotation recovery of the quartz pretreated by calcium or ferric chloride with or without the presence of sodium sulfate

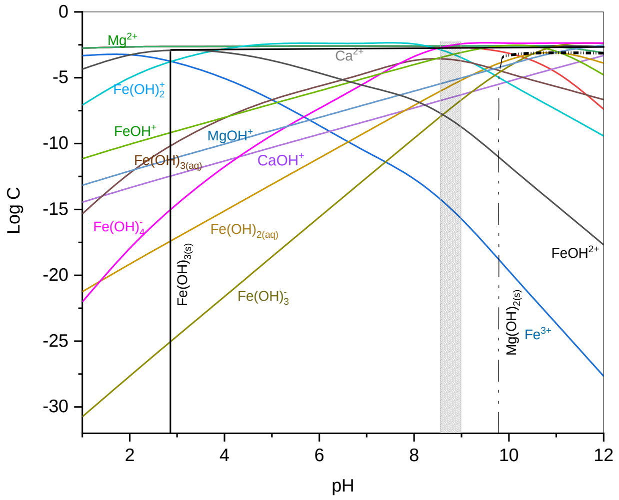


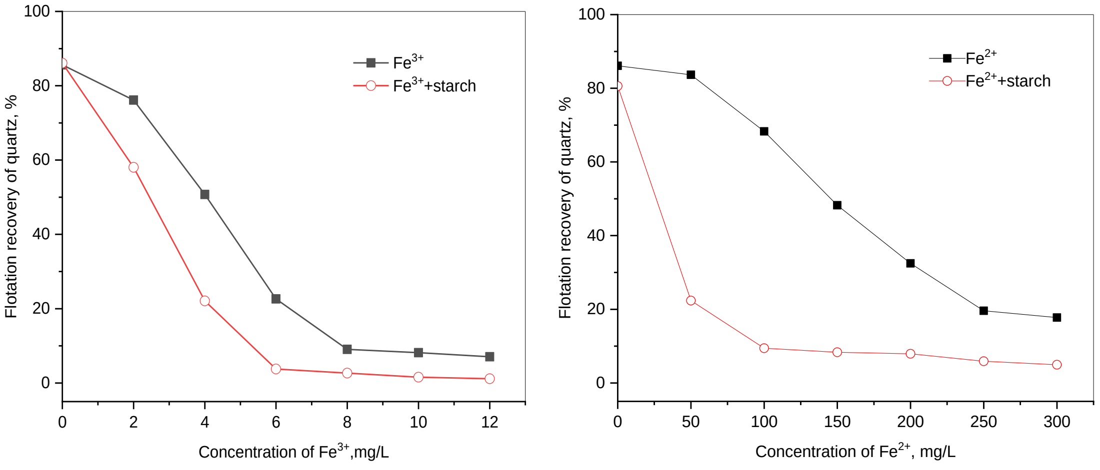
Fig. 7. Log C–pH curves of cations, such as Ca^{2+}, Mg^{2+}, Fe^{3+}, and Fe^{2+} at a concentration of 5 mmol/L in water

of free sulfate in water could be locked with iron ions due to the formation of $> \mathrm{Fe}OSO_3^-$ and $> \left(\mathrm{Fe}OOH_2{}^+\right)_2SO_4^{2-}$at this pH range (Sverjensky and Fukushi, 2006). A large number of sulfate ions in the recycled tailing water as shown in Table 2 could be beneficial to limit the function of iron ions in the cationic reverse flotation.

3.5. The possible depression mechanism of Fe^{n+} on the quartz floatability in the presence of starch

Figs. 8a and 8b show the flotation recovery of the quartz treated by Fe^{3+} or Fe^{2+} ions at different concentrations with or without starch at a concentration of 4 mg/L. The results indicated that a severe drop of over 50% in the recovery of quartz occurs in the presence of Fe^{3+} at a concentration of only 5mg/L. And the drop will be accelerated in the presence of starch. A similar downward trend in the quartz recovery as a function of Fe^{2+} ion concentrations was also observed in Fig. 8b. The addition of starch deteriorates the decrease by near 60% on the quartz recovery in comparison with the one treated by Fe^{2+} ions only. This is in accordance with the results from Figs. 5 and 6, indicating that the occurrence of iron ion species at 8.7±0.2 could coat the surfaces of quartz, which not only shields their reactions with the collector but provides the sites for flocculation by starch. This could be identified with the work by Flood et al. (2006), who suggested that the adsorption density of polymer on silica increases with an increase of cation concentration and valence.

The presence of iron ions in the recycled tailing water is inevitable due to the dissolution of the iron ore itself and the consumption of grinding media. The detection of these ions, however, was hard due



a. b.

Fig. 8. Recovery of quartz as a function of Fen+ ion concentrations with or without 4 mg/L starch at 8.7±0.2 (a. Fe^{3+}, or b. Fe^{2+})

to the formation of their precipitates at weak alkali in terms of the Log C-pH curve of Fe^{3+}/Fe^{2+} ions as shown in Fig. 7. Fig. 9 investigates the possible effects of the recycled tailing water on the flotation performance by the use of SCN$^-$ ions as iron ion cheating agents. The data show a significant drop of near 1.0% in the SiO$_2$ content in concentrates by using the recycled tailing water pretreated with SCN$^-$ ions. This could be evidenced by the presence of iron ions in the recycled tailing water, diluting the concentrate by increasing its SiO$_2$ content as shown in Fig. 5. A high concentration of over 50 mg/L of SCN$^-$ ions, however, only induce a little drop in the SiO$_2$ content, indicating that iron ion concentrations were possibly at a range from 30 to 40 mg/L. A hypothesis for the model of the slime coating was shown in Fig. 10. The modification of silicate surfaces caused by the coating of the iron hydroxides could alter the surface properties, acting as iron oxides and interacting with the starch. This could lead to a sharp increase in the SiO$_2$ content in concentrates.

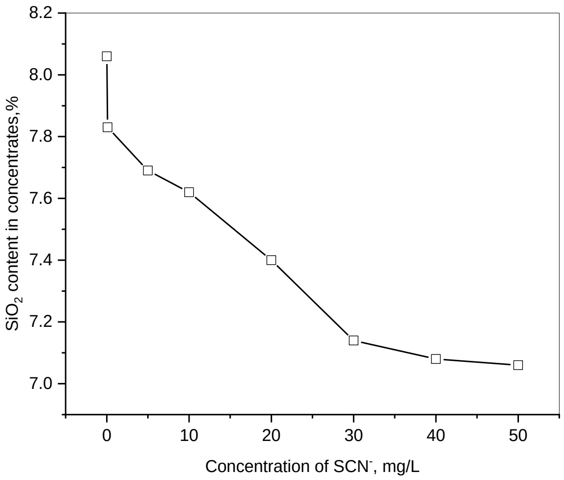


Fig. 9. Effects of SCN$^-$ ions pre-treating the tailing water on the content of SiO$_2$ in concentrates

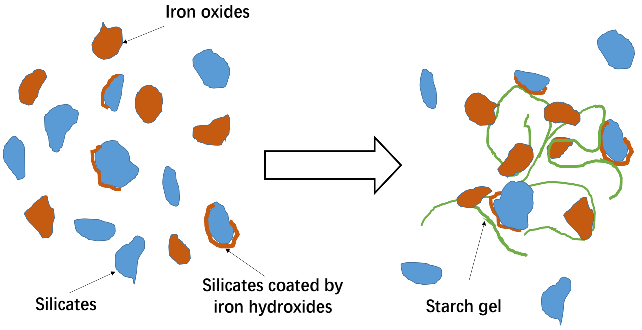


Fig. 10. The possible depression mechanism of Fen+ on the quartz floatability in the presence of starch

4. Conclusions

The flotation results showed that a sharp increase of 2.5%in the content of SiO$_2$ in concentrate occurs by using the recycled tailing water only, coupled with an increase of 6.0% recovery of Fe in comparison by using fresh water. While using the treated sewage water alone obtained a qualified concentrate but a loss of about 6.5% Fe recovery. A built-up of cations and their hydrolyzed species, especially Fe^{n+} ions, in the process water significantly contributes to the dilution of the concentrates. As ferric ion concentration increases, a sharp upward trend in the content of SiO$_2$ was observed at a loss of 5.5% Fe recovery in concentrates. And it gets worse with the presence of starch. A high concentration of Mg^{2+} ions, however, only induces a slight drop in the recovery of Fe but a little in the content of SiO$_2$. While the presence of Ca^{2+} ions results in a gradual decrease in the flotation recovery of iron oxides. This is evidenced by the records from the analyses of the process water, suggesting the competitive influences of Ca^{2+} ions but no apparent one of Mg^{2+} ions. It is also worthy to be noted that the occurrence of SO$_4^{2-}$ has a positive influence on reducing the SiO$_2$ content and increasing Fe recovery. It can be explained by zeta potential measurements and the solution chemistry of these cations, indicating that at 8.5-9.0, the precipitates of $Fe(OH)_{3(s)}$, or other ionic complexes, for example, $Fe(OH)_2^+$, Ca^{2+}, $CaOH^+$, Mg^{2+}, $MgOH^+$, etc., could coat or specific adsorb on the silicate surfaces and render a shift on its IEP. It is beneficial to use SCN^- as an iron ion chelating agent to pretreat the recycled tailing water as it reduces the possibility of the formation of ferric hydroxide avoiding the coating on silicate surfaces.

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