

Received April 2, 2021; reviewed; accepted June 22, 2021

## Buffering of pulp pH and its influence on process water chemistry during iron ore flotation

Min Tang <sup>1</sup>, Qingfei Xiao <sup>2</sup>

<sup>1</sup> State Key Lab of Complex Nonferrous Metal Resources Clean Utilization, Department of Mineral Processing, Kunming University of Science and Technology, Yunnan, China, 650093

<sup>2</sup> Department of Mineral Processing, Kunming University of Science and Technology, Yunnan, China, 650093

Corresponding authors: mtang-kmust@foxmail.com (Min Tang), 13515877@qq.com (Qingfei Xiao)

**Abstract:** It is inevitable for the occurrences of pulp pH buffering during pH control in flotation as the minerals with acidic/alkali properties tend to interact with pH modifiers and restore the pulp pH. This could result in some disturbing ions and alter the water/pulp chemistry. The purpose of this study was to identify the influences of pulp pH buffering on process water chemistry through a series of pH buffering tests, bench flotation experiments, ore dissolution tests, zeta potential measurement, and X-ray diffraction (XRD) analysis. The built-up and distribution of the dominant cations in the process water from different locations in an industrial flotation system of the iron ore were analyzed and recorded by Inductively Coupled Plasma-Optical Emission (ICP-OES) at a period of about six months when the operations were stable. The data showed that a near five-minute buffer of pulp pH at a range from near 7.9 to 8.9 occurred before it reached a stable value. At this period, the dissolution of Ca/Mg from the iron ore was dominant. And, the pulp pH at a lower value tended to induce more dissolved Ca<sup>2+</sup> and Mg<sup>2+</sup> ions. These divalent cations seem to have different influences on the flotation properties of iron oxides at the same concentrations, indicating a positive effect on the recovery of iron oxides with the presence of Mg<sup>2+</sup> ions but an opposite effect if Ca<sup>2+</sup> ions occurred. The presence of sulfate, however, tended to restore the floatability of silicate depressed by Ca<sup>2+</sup> ions.

**Keywords:** pulp pH, buffering, water chemistry, mineral dissolution, iron oxide

### 1. Introduction

Process water quality of a flotation system of iron oxides is critical as it greatly influences the chemistry of mineral surfaces and the interactions between minerals and reagents. The occurrences and built-ups of disturbing ions, especially metal ions (Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Fe<sup>3+</sup>, Al<sup>3+</sup>, etc.) in the pulp during the recycling of process water in a mineral processing plant could re-alter the process water chemistry and influence the flotation selectivity (Michaux et al., 2008; Muzenda, 2010; Liu et al., 2018).

The disturbances of metal ions at different valences/concentrations in flotation have been extensively investigated in the literature (Fuerstenau et al., 1963; Fuerstenau and Palmer, 1976; Nevasaia, et al., 1998; Chen et al., 2018; Ruan et al., 2018). The cations at higher valences tend to have more significant influences on the flotation properties, regardless of type of flotation, anionic or cationic flotation. Flood et al. (2006) reported that the more promotive adsorption of polymer on silica occurs by the cations at a higher concentration/valence. Ofor (1996) also found the more depressive effects of the cations at a higher valence on hematite recovery during anionic flotation. Those effects could be attributed to the potential reversal on mineral surfaces induced by the adsorption of these cations and hinder/enhance the interactions of collectors on them. These findings were explained in detail by Fuerstenau et al. (1963) and Rao (2004), and it was suggested that the potential reversal resulted from adsorption of metal ions could hinder the floatability of the minerals if the collector adsorption dominantly depends on electrostatic interaction.

Mineral dissolution as one of the main sources for the occurrence of these disturbing ions in process water has also been explored (Abeidu and Kholeif, 1976; Chou et al., 1989; Parapari et al., 2017), and it was revealed that the dissolution rates of these ions were probably affected by the water/pulp chemistry, especially pulp pH. Chou et al. (1989) stated that the dissolution rates of calcite, aragonite, witherite, magnesite, and dolomite were pH-dependent. Zhu et al. (2011) also found that  $\text{Fe}^{2+}/\text{Fe}^{3+}$ ,  $\text{Ti}^{4+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  ions dissolved from ilmenite and titanite at a pH of 5.8 by using sulfuric acid. Similar investigations have been done by Abeidu and Kholeif (1976), and Parapari et al. (2017), indicating that  $\text{Fe}^{2+}/\text{Fe}^{3+}$  or  $\text{Ti}^{4+}$  ions dissolved from ilmenite treated by sulfuric acid at a pH range of 6.0-6.3.

The control of pulp pH, however, is a complex and non-instantaneous process due to the alkali or acidic properties of minerals themselves. Most of the researches about pH buffering has focused on the areas of soils or fine rock minerals such as clay, silicate, or carbonate minerals. Breemen and Wielemaker (1974) found that silicate minerals, carbonates, and gibbsite presented strong buffering upon the addition of strong acid under slightly alkaline to slightly acid conditions. Jeon and Nam (2019) evaluated the pH buffering capacity of kaolinite and montmorillonite, indicating that the addition of acid can decrease the basal site density of these minerals by dissolving substituted octahedral cations. The observations by Lacroix et al. (2014) also showed the differences in the buffering potentials of typical silicate minerals.

The above literature has revealed a lot about the buffering capacity and its application of soils or rock minerals but little about the dissolved ions resulted from the buffering and their effects on water chemistry. These effects in water/pulp chemistry in flotation, however, could be significant as these ions adsorbed on mineral surfaces, alter their properties, and eventually, disturb their interactions with flotation agents. In this study, the relationship between pulp pH buffering and process water chemistry, especially metal ion concentrations, was investigated through a series of pH buffering tests, ore dissolution tests during pH control, and bench flotation experiments. An effort was also made to identify how the buffering of pulp pH influences the chemistry of process water, especially metal ion distributions, and eventually, the flotation performance of iron oxides.

## 2. Materials and methods

### 2.1. Materials

An iron oxide ore sample was collected from an iron mine in Yunnan, China, and it was at a size range of about 87.6% passing 74  $\mu\text{m}$ . The chemical composition of the sample is presented in Table 1. The iron ore sample was also 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 where the main peaks of the reference patterns were identified as Mg-bearing magnetite, ankerite, silica, and phyllite as well. The dominant metal distributions in different crystal structures of Mg-bearing-magnetite, ankerite, silica, and phyllite from the iron ore sample were identified further by using the AAS instruments from the Analytical Center of Kunming University of Sci & Tech (KUST), Kunming, China. The results also indicated that the dominant Fe sources were Mg-bearing magnetite and magnetite. The dominant source of Mg and Mn is from Mg-bearing magnetite while the only source of Ca and Al was from ankerite and phyllite, respectively.

Table 1. The chemical composition of the iron ore sample from Yunnan, China

Item	TFe	$\text{SiO}_2$	CaO	MgO	$\text{Al}_2\text{O}_3$	Mn	K	Na
Content (%)	55.60	10.50	1.89	3.28	0.91%	0.91	0.33	0.066

Corn starch (99.0%) with a product number of S-4180, which contains about 73% amylopectin and 27% amylose, was purchased from Sigma-Aldrich. Chemical-grade reagents, such as sodium hydroxide (S318-1, 98.8%), calcium chloride (10043-52-4, 96%), magnesium chloride (7791-18-6, 99%), sodium sulfate (7757-82-6,  $\geq 99\%$ ), and sulfuric acid (7664-93-9, 99.9%), were purchased from Fisher Scientific. The quartz (95%) at a size range of 90% passing 37  $\mu\text{m}$  obtained from Kunming Minerals Co was used for the zeta potential measurements. A cationic collector, dodecylamine (DDA, 124-22-1, /°C 155.0~158.0 (2.0)) was from Shandong Chemical Tech. Co., China.

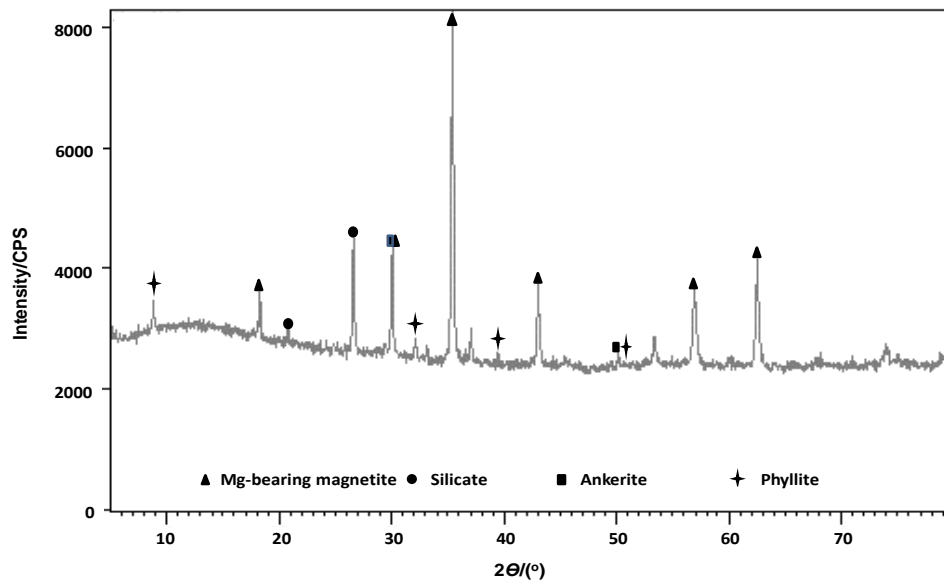


Fig. 1. The results from XRD analysis of the iron ore sample from an iron mine in Yunnan, China

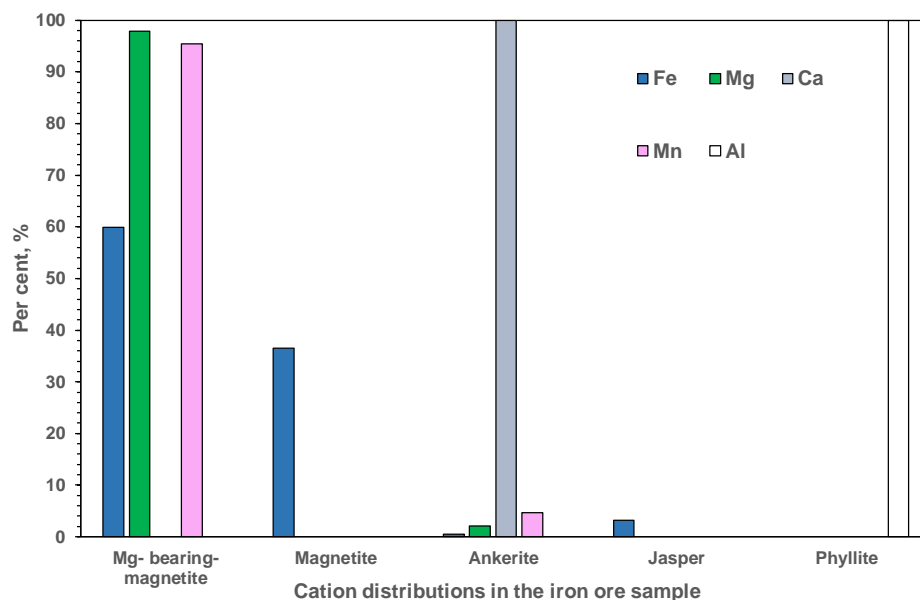


Fig. 2. Cation distributions in the different minerals from the iron ore sample identified by AAS measurement

## 2.2. Process flow sheet of the industrial flotation process

A typical reverse flotation flowsheet of the industrial iron ores from a mineral processing plant in Yunnan Mine, China is shown in Fig. 3. The ore at a solid density range of 32-35% fed into the roughing process. The pH value of the pulp at this stage is  $8.7 \pm 0.2$  adjusted by  $H_2SO_4$ . DDA or caustic-digested starch concentrations were kept at a constant level with an error bar of less than 5.0% based on a real-time monitor in the flotation cell. The flotation concentrate from the rougher was pumped into the cleaners where the final iron concentrate was collected by removing residual silica gangues further.

When the operating conditions were stable, the water samples were collected at four locations through the entire flotation system: local freshwater ①, the rougher cell ②, the cleaner cell ③, and the overflow from the dewatering unit ④. All water chemistry data presented refer to these location numbers. A one-dm<sup>3</sup> glass bottle was used to collect each water sample periodically from the industrial flotation process. All samples after being centrifuging and filtrating for the removal of slimes were analyzed by the ICP-OES equipment from the certified laboratory of Analytical Center of KUST, Kunming, China. Each test was repeated three times and averaged the results.

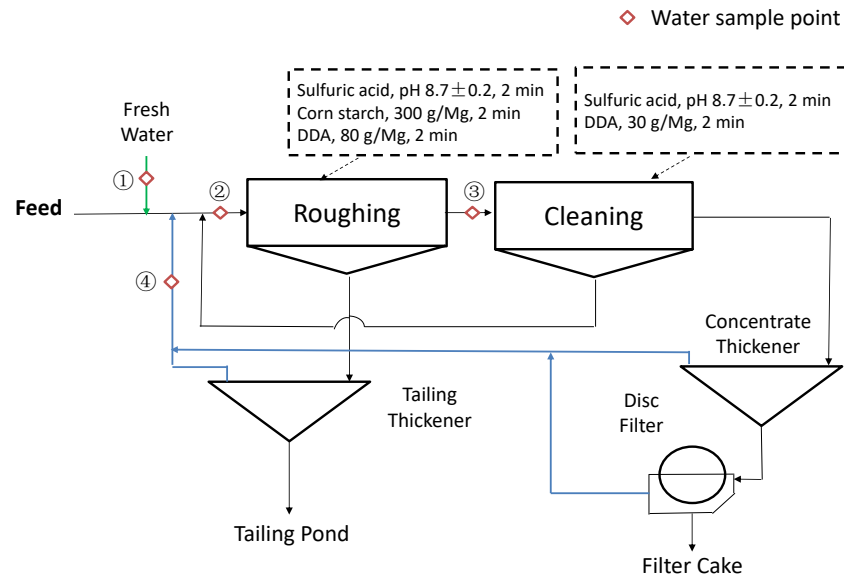


Fig. 3. The flowsheet of the reverse cationic flotation of the iron ores in Yunnan, China

## 2.3. Methods

### 2.3.1. pH buffering test/Bench flotation experiments

To prepare the sample to do the pH buffering/bench flotation experiments, 500 g of the iron ore sample was mixed with distilled water at room temperature. A 1.5 dm<sup>3</sup> flotation cell at an impeller speed of 1200 rpm was introduced to do the pH buffering tests. The pH of the pulp was measured as a function of the conditioning time of H<sub>2</sub>SO<sub>4</sub> by using a pH analyzer (PHS-3C, Leici, China). Each test was repeated three times and averaged their results.

The bench flotation experiments were conducted in a 1.5 dm<sup>3</sup> cell (XF-D) for the roughing process and a 0.5 dm<sup>3</sup> cell (XF-D) for the cleaning process at the same impeller speed as one of the pH adjustment tests. A froth depth (FH) of 15.2 cm, superficial gas velocity ( $J_g$ ) of 0.75 cm/sec, and collecting time ( $t$ ) of 10 min was employed for the roughing stage but a froth depth of 11.5 cm and collecting time of 4 min at the same superficial gas velocity for the cleaning stage. DDA as a collector and caustic-digested corn starch as flocculants were employed at the same concentration as the ones of the industrial flotation plant as shown in Fig. 3. The pH range in the pulp was 8.7±0.2 adjusted by H<sub>2</sub>SO<sub>4</sub>. The final concentrate was filtrated, dried, weighted, and assayed the grade of Fe and SiO<sub>2</sub>, respectively.

### 2.3.2. Ore dissolution test

To prepare the iron ore sample for the dissolution/flotation experiments, the bulk of the iron ore was thoroughly mixed, and then splitted into standard test samples at a weight of 500±0.02 g. An iron ore sample was mixed with distilled water in a 1.5 dm<sup>3</sup> flotation cell (XF-D) at room temperature. The mixture was pre-agitated for 10 min at an impeller speed of 1200 rpm before the pH adjustment. Then, H<sub>2</sub>SO<sub>4</sub> at the same concentration as one of the industrial flotation processes at a pH value of 8.7±0.2 was added into the pulp as a function of conditioning time. The dissolution tests were conducted as a function of the conditioning time of H<sub>2</sub>SO<sub>4</sub>. The pulp from each test was filtrated three times by using different types of filter papers to remove the slimes. The final water samples collected after centrifuging from the cell after filtrating and centrifuging were identified for the main cations, for example, Fe<sup>n+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup>, Al<sup>3+</sup>, or Mn<sup>2+</sup>, by using the ICP-OES instrument from the certified laboratory of Analytical Center of KUST, Kunming, China.

### 2.3.3. Zeta potential measurements

The zeta potentials of quartz were measured with a ZetaPALS zeta potential and particle size analyzer manufactured by Brookhaven Instruments Corporation, USA. The technique is based on electrophoretic

light scattering (ELS), also known as Laser Doppler Velocimetry (LDV). To prepare samples for the zeta potential measurements, a 100 cm<sup>3</sup> at 0.5% solids ratio (5 g/dm<sup>3</sup>) quartz suspension mixed with 100 cm<sup>3</sup> of CaCl<sub>2</sub>/MgCl<sub>2</sub> solution. The mixed suspension was stirred at room temperature for 10 min. Then, sodium sulfate at a concentration of 1 mmol/dm<sup>3</sup> added into the solution at room temperature if needed. Five cm<sup>3</sup> of the mixed suspension was withdrawn and diluted to 100 cm<sup>3</sup> with a 10<sup>-3</sup> mol/dm<sup>3</sup> NaCl solution. The pH of the diluted suspension was adjusted by using H<sub>2</sub>SO<sub>4</sub> or NaOH, and a small aliquot of the suspension was transferred to the sample cell of the ZetaPALS for zeta potential measurements. And, the error for the measurements was about ±1.5 mV.

### 3. Results and discussion

#### 3.1. Ca<sup>2+</sup>/Mg<sup>2+</sup> ion distributions in process water and its relationship with the flotation recovery

Figure 4 presents the statistical records on the distributions of the dominant cations (Ca<sup>2+</sup>/Mg<sup>2+</sup>) in the roughing process and their relationship with the flotation recovery of iron in concentrates at an iron grade of 60.0±0.3% in an industrial iron ore flotation plant at a certain period when the operations were stable. The control of the iron grade at this level in concentrates could make the iron recovery comparable under different cation distributions in the process water. The data show that Ca<sup>2+</sup> ions at higher concentrations tend to obtain a concentrate at a lower recovery of iron while Mg<sup>2+</sup> ions at higher concentrations seem to have a more positive effect on the flotation recovery. It is following the previous investigations reported by Ren et al. (2018), which showed a drop by about 50% in the recovery of quartz in the presence of Ca<sup>2+</sup> ions at a concentration of 80 mg/dm<sup>3</sup> using ester amine as collectors. Feng et al (2018) found that the presence of Mg<sup>2+</sup> ions induced an increase in the recovery of quartz at a pH range of 9-10. It is also worthy to be noted that the content of these cations in the process water was not stable, ranging from 170 mg/dm<sup>3</sup> to 480 mg/dm<sup>3</sup>. This could attribute to the Ca/Mg dissolutions and their accumulations in the process water with recycling.

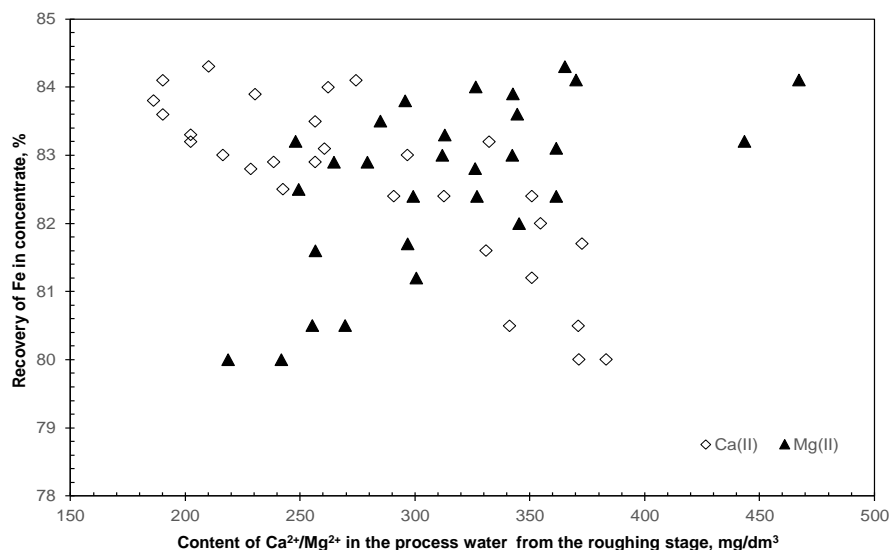


Fig. 4. The statistical records of Ca<sup>2+</sup>/Mg<sup>2+</sup> ion distributions in the process water from the roughing process vs the grade/recovery of Fe in concentrate in the industrial flotation system of the iron ore at a period from June 1<sup>st</sup> to Nov 23<sup>rd</sup>, 2018

#### 3.2. Pulp pH and its relationship with Ca<sup>2+</sup>/Mg<sup>2+</sup> ion concentrations in process water

The relationship between Ca<sup>2+</sup>/Mg<sup>2+</sup> ion distributions in the process water and the pulp pH measured from the roughing stage was presented in Fig. 5. The pH of the process water from the rougher was measured before analysing the cation concentrations. It indicated that the occurrences of both Ca<sup>2+</sup> and Mg<sup>2+</sup> ions were sensible to the pulp pH and the pH at lower values tend to produce high content of cations. The concentrations of Mg<sup>2+</sup> ions seem to be much higher than the ones of Ca<sup>2+</sup> ions at the same pH. According to the previous literature, Ca/Mg dissolution and surface complexation from ilmenite,

titanaugite or dolomite is pH-dependent. In terms of the data from XRD/AAS analyses as shown in Figs. 1 and 2, the substitution and distribution characteristics of Mg/Ca show that Mg-bearing-magnetite and ankerite could be their main sources.

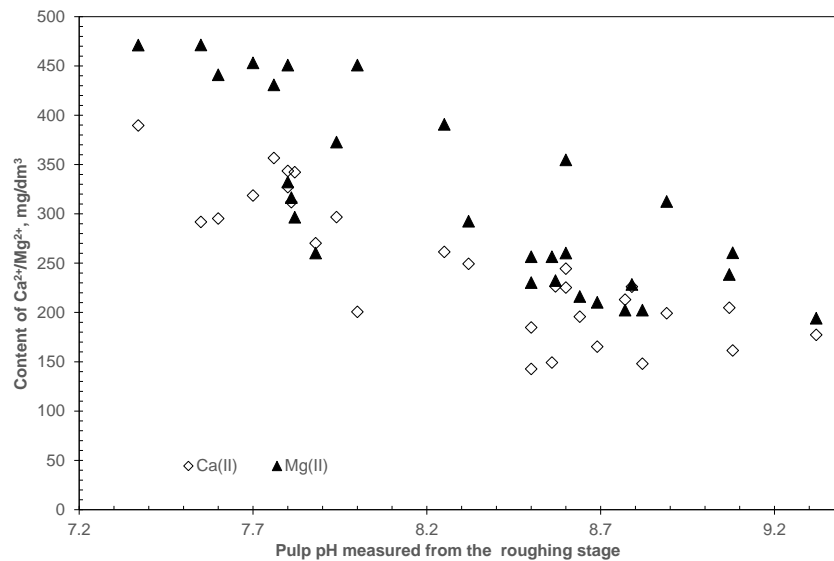


Fig. 5. The statistical records of  $\text{Ca}^{2+}/\text{Mg}^{2+}$  ion distributions in the process water from the roughing process vs the measured pulp pH in the industrial flotation system of the iron ore at a period from June 1<sup>st</sup> to Nov 23<sup>rd</sup>, 2018

### 3.3. Buffering of pulp pH and its relationship with cation dissolutions

Figure 6 provides the buffering of pH and its relationship with the cation dissolutions, for example,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Fe}^{n+}$ ,  $\text{Al}^{3+}$ , or  $\text{Mn}^{2+}$ , in the process water from dissolution tests which were conducted under the same conditions as the roughing process of the industrial mineral processing plant. It is clear that the presence of metal ions, especially  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  ions, is sensitive to the pH buffering as a significant change in their contents occurs at this time. An approximately threefold increase in the content of  $\text{Ca}^{2+}/\text{Mg}^{2+}$  was observed in the first minute of the pH buffering with the addition of  $\text{H}_2\text{SO}_4$  in comparison with the one without any addition. Then, its content continuously increased until it reached a plateau in another minute. While a little change in the content of  $\text{Fe}^{3+}$ ,  $\text{Al}^{3+}$ , or  $\text{Mn}^{2+}$  ions took place in the pulp. According to Chen and Tao (2004), Zhu et al. (2011), and Wang et al (2018),  $\text{Fe}^{2+}/\text{Fe}^{3+}$ ,  $\text{Ca}^{2+}$ ,

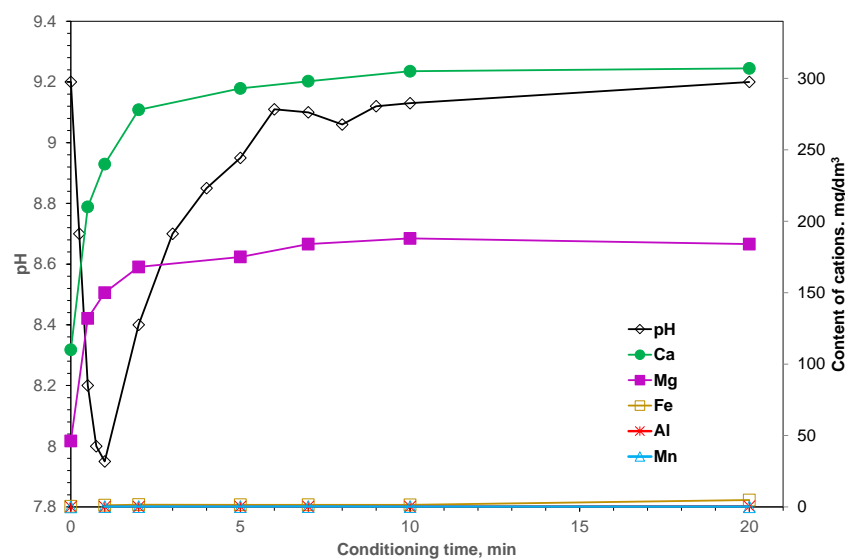


Fig. 6. The value of pulp pH as a function of conditioning time by using  $\text{H}_2\text{SO}_4$  at a dosage of 1500 g/Mg which is the same concentration as the one in the roughing process of the industrial mineral processing plant

Mg<sup>2+</sup> dissolutions from carbonates, ilmenite, or spodumene were affected by pH and stirring time. As evidenced by Riina et al. (2011), it is a slow dissolution rate of iron ions from magnetite resulted from oxalic acid, sulfuric acid, or nitric acid at a certain concentration and temperature. However, it is hard to identify iron ion concentration dissolved from the minerals due to the precipitation of iron ions at pH 8.5-9.5, which could be removed with solid particles by centrifuging and filtrating during water sample collection. The low dissolution rate of Mn and Al could be attributed to their low contents and substitution characteristics in the iron ore sample in terms of the XRD/AAS analyses.

The dissolution rates of Ca<sup>2+</sup>/Mg<sup>2+</sup> at the first minute of the pH buffering were estimated in Fig. 7. The results showed that at a period of fewer than 60 sec, the dissolution rate of Mg<sup>2+</sup> ions (2.36 mg/dm<sup>3</sup> per sec) was faster than the one of Ca<sup>2+</sup> ions (1.83 mg/dm<sup>3</sup> per sec). Mg<sup>2+</sup> ion concentrations were almost twice as many as Ca<sup>2+</sup> ion ones at the natural pH of the pulp without any addition of acid. It indicated that the dissolution of Mg<sup>2+</sup> ions was more likely to take place than one of Ca<sup>2+</sup> ions due to the chemical and substitutional characteristics of these cations as shown in Figs. 1 and 2. This was also consistent with the data from Figs. 4 and 5 in which the averaged content of Mg<sup>2+</sup> ions was relatively higher than the one of Ca<sup>2+</sup> ions. Michalowski and Asuero (2012) and Pokrovsky (1998) focused on the Ca<sup>2+</sup>/Mg<sup>2+</sup> dissolutions from dolomite or calcite, indicating that a few factors could affect the dissolutions, such as pH, temperature, CO<sub>2</sub> concentration, Ca/Mg ratio, etc. Ruiz-Agudo et al. (2010a and 2011b) also found that Mg<sup>2+</sup> ions with high charge density tend to have a strong solvation capacity from dolomite than Ca<sup>2+</sup> ions. And, the formation of mono-/bi-dentate or even polynuclear surface complexes of Mg<sup>2+</sup> ions on magnetite/maghematite face sites was observed if Mg<sup>2+</sup> ions at excessive concentrations were present.

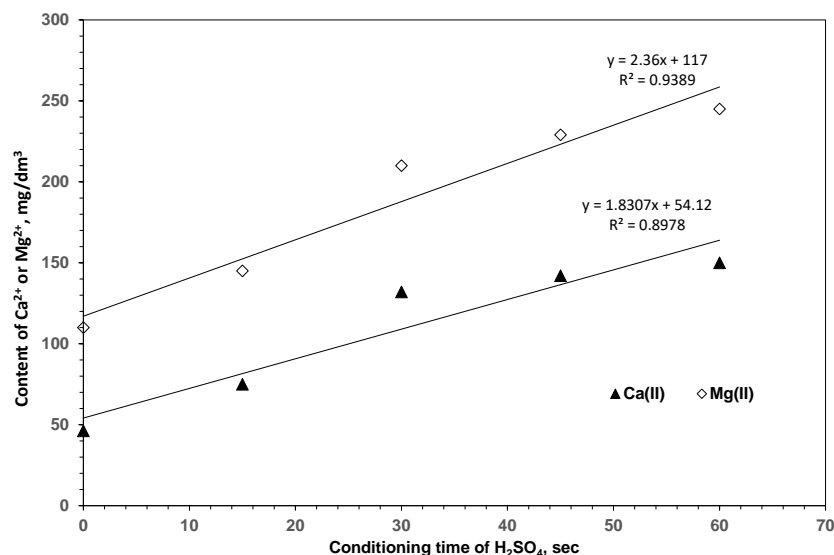


Fig. 7. Ca/Mg dissolution rates from the iron ore during pulp pH buffering by using H<sub>2</sub>SO<sub>4</sub> as an acidic pH modifier

### 3.4. The roles of Ca<sup>2+</sup>/Mg<sup>2+</sup> ion concentrations in the water on the flotation properties

Figure 8 provides the influences of Ca<sup>2+</sup>/Mg<sup>2+</sup> ions at different concentrations in water on the flotation performance of iron oxides. It shows that there is a more negative effect on both iron grade and recovery with the occurrence of Ca<sup>2+</sup> ions at higher concentrations. The presence of Mg<sup>2+</sup> ions, however, seems to enhance the flotation recovery of iron oxides, as Mg<sup>2+</sup> ions at higher concentrations tend to obtain better recoveries of iron oxides. This is in agreement with the data from Fig. 4, indicating that a large amount of Ca<sup>2+</sup> ions could contribute to the deterioration of flotation behaviours of iron oxides while a certain amount of Mg<sup>2+</sup> ions could have a positive effect on the flotation performance. This can be explained by the findings by Feng et al (2018), which showed that the presence of Mg<sup>2+</sup> ions induced an increase in the recovery of quartz at a pH range of 9-10. Ren et al. (2018) also indicated a drop by about 50% on the recovery of quartz in the presence of Ca<sup>2+</sup> ions at a concentration of 80 mg/dm<sup>3</sup> using ester amine as collectors. Ruan et al. (2018) and Feng et al (2018), however, suggested that the presence of

both  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions induced an increase in the recovery of quartz by using an amine-type collector. Taggart and Arbiter (1946) found that  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  ions at high concentrations induce a drop in the recovery of pyrochlore due to the reversal of its surface charge resulted from the adsorption of these cations on mineral surfaces.

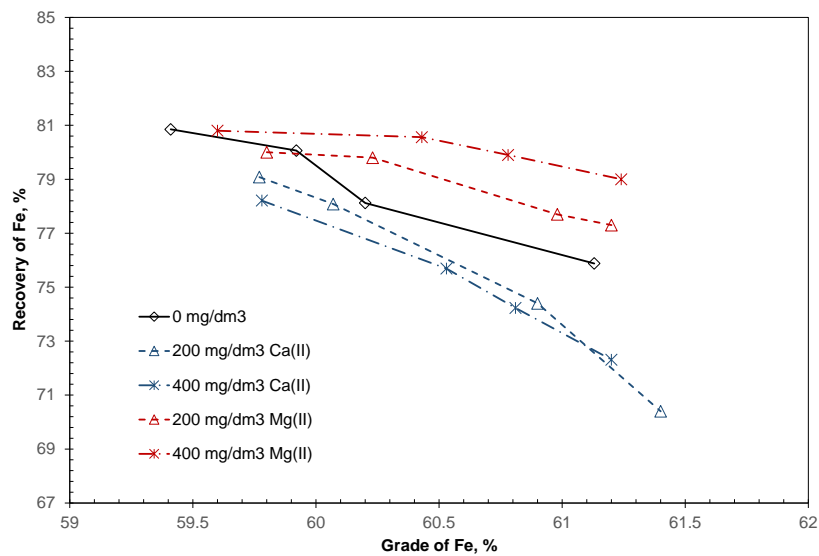


Fig. 8. The results from bench flotation experiments with the presence of  $\text{Ca}/\text{MgCl}_2$  at different concentrations in water

### 3.5. Influences of $\text{SO}_4^{2-}$ ions on the role of $\text{Ca}^{2+}/\text{Mg}^{2+}$ ion in the water

Figure 9 reveals the influences of  $\text{SO}_4^{2-}$  ions on the role of  $\text{Ca}^{2+}/\text{Mg}^{2+}$  ions in the flotation. The data indicate that  $\text{SO}_4^{2-}$  ions have a positive effect on the flotation recovery of iron oxides with the occurrence of  $\text{Ca}^{2+}$  ions as it increases both the grade and recovery of iron in concentrates with increasing the sulfate concentrations. While it does not show any benefit for the one if  $\text{Mg}^{2+}$  ions were present. The more sulfate ions only induce the worse flotation results with the presence of  $\text{Mg}^{2+}$  ions. These results were well in agreement with the zeta potentials from Fig. 10. It indicates that the zeta potentials of quartz treated by calcium or magnesium chloride with or without the presence of sulfate at a certain concentration. The results show a shift towards less negative on the zeta potentials of the quartz, regardless of cation type. This shift becomes less serious if sulfate ions were present. And the zeta

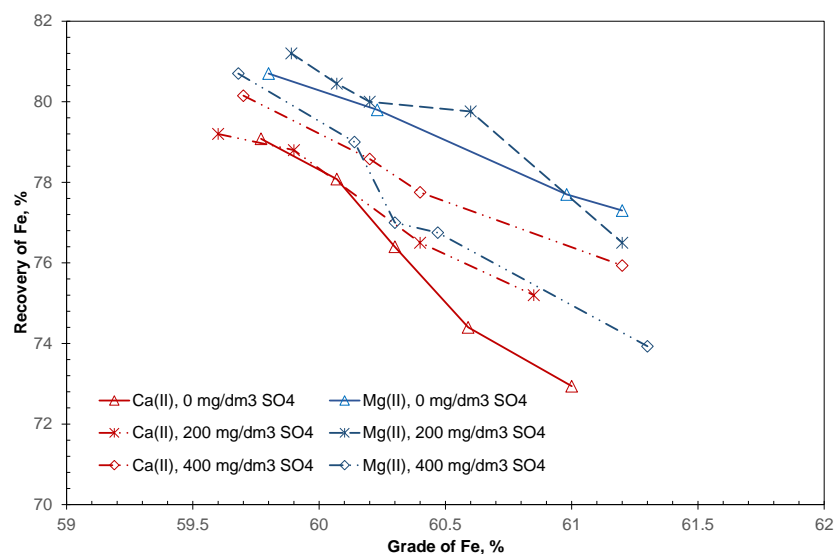


Fig. 9. Flotation performance of the iron ore pretreated with  $\text{CaCl}_2$  or  $\text{MgCl}_2$  at a concentration of  $200 \text{ mg/dm}^3$   $\text{Mg}^{2+}/\text{Ca}^{2+}$  ions as a function of sulfate concentrations



potentials of quartz treated by  $\text{Ca}^{2+}$  ions are more negative than the ones of  $\text{Mg}^{2+}$  ions with the occurrence of  $\text{SO}_4^{2-}$  ions. The specific adsorption of  $\text{SO}_4^{2-}$  ions on the quartz pre-treated by  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$  ions could contribute to the decrease in the zeta potentials. This is consistent with the results from Fig. 9, indicating that the competitive effect of  $\text{Ca}^{2+}$  ions on the mineral surfaces was disturbed by the addition of  $\text{SO}_4^{2-}$  ions. The formation of  $\text{CaSO}_4$  probably contributes to the improvement in the flotation recovery of iron oxides because of the limitation of  $\text{Ca}^{2+}$  ion activation on the mineral surfaces. It also contributes to the negative shift of zeta potentials on the quartz surface pre-coated by  $\text{Ca}^{2+}$  ions in terms of Log C-pH curve of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , or  $\text{SO}_4^{2-}$  ions (Fig. 11). The binding of sulfate ions with calcium ions probably limits the activity of these anions and eventually adversely affects the flotation selectivity. Similar observations have been made by Davila-Pulido and Uribe-Salas (2014), indicating that surface precipitation of  $\text{CaSO}_4$  decreased the hydrophobicity of sphalerite. Modi and Fuerstenau (1957) and Breeuwsma and Lyjklema (1973) proposed that there was specific adsorption of sulfate ions on positively charged corundum or hematite.

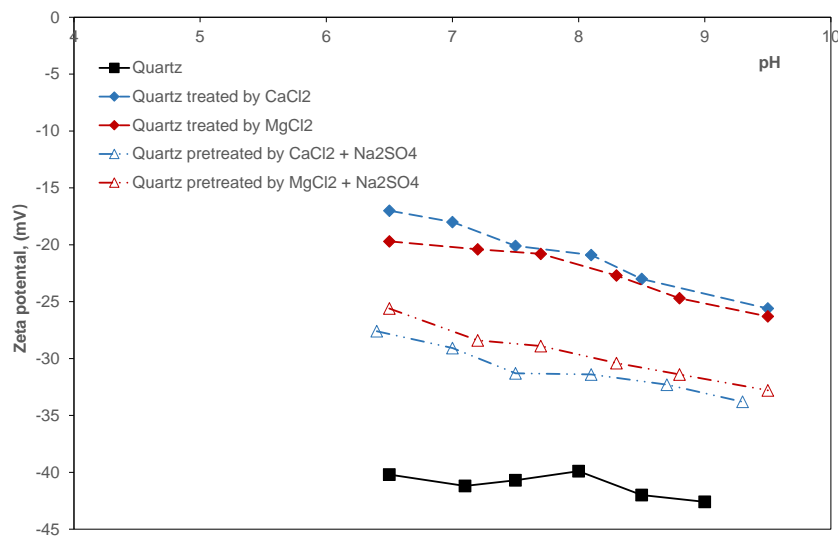


Fig. 10. Zeta potentials of quartz treated with  $\text{CaCl}_2$  or  $\text{MgCl}_2$  at a concentration of  $200 \text{ mg/dm}^3$   $\text{Ca}^{2+}/\text{Mg}^{2+}$  ions in the absence or presence of  $\text{Na}_2\text{SO}_4$  at a concentration of  $200 \text{ mg/dm}^3$

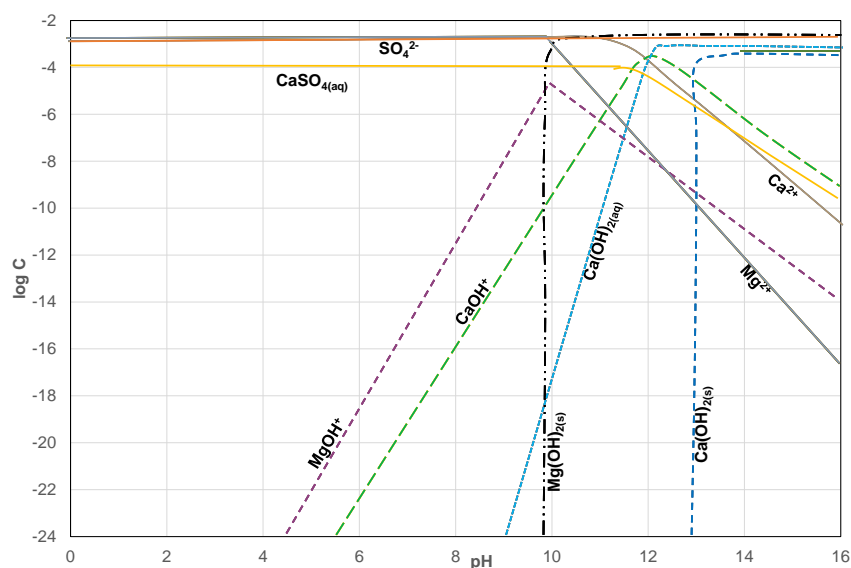


Fig. 11. Log C-pH curve of  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ , or  $\text{SO}_4^{2-}$  ions at a concentration of  $1.5 \times 10^{-3} \text{ mol/dm}^3$  in the distilled water (Modified from Ruan et al., 2018; Ren et al., 2018)

#### 4. Conclusions

A near five-minute buffering of pulp pH at a range from near 7.9 to 8.9 before it became stable was observed during pH adjustment in the iron ore flotation. At this period, the dissolution of  $\text{Ca}^{2+}/\text{Mg}^{2+}$  ions from the iron ore was dominant but the one of  $\text{Al}^{3+}$  or  $\text{Mn}^{2+}$  was a little. The content of  $\text{Ca}^{2+}/\text{Mg}^{2+}$  ions dramatically increases in the first two minutes and then gradually reaches a plateau in the second two minutes.  $\text{Mg}^{2+}$  ion concentration was approximately twice as many as  $\text{Ca}^{2+}$  ion one through the pulp pH buffering period. And, the pulp pH at a lower value seems to trigger more dissolved  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  ions. It is worthy to be noted that iron concentrations are hard to identify at weak alkali due to the formation of iron hydroxide precipitates. This is evidenced by the records of process water chemical analyses from the local industrial concentrator, which indicate that the cation distributions are largely relevant to the pulp pH measured. The flotation experiments also showed that these divalent cations showed different influences on the reverse flotation selectivity of the iron ore. While  $\text{Ca}^{2+}$  ions showed a negative effect on the flotation performance,  $\text{Mg}^{2+}$  ions a positive one. Additionally, the anions in the process water, especially  $\text{SO}_4^{2-}$  ions, had a substantial influence on the role of these cations in the flotation. As sulfate ion concentrations increased, the recovery of iron oxides increased with the presence of  $\text{Ca}^{2+}$  ions but it decreased if  $\text{Mg}^{2+}$  ions were added. This could be contributed to the formation of  $\text{CaSO}_4$ , limiting the depression capacity of  $\text{Ca}^{2+}$  ions on mineral surfaces.

#### References

- ABEIDU, A.M., KHOLEIF, T., 1976. *Modification of the anionic flotation behavior ilmenite, magnetite, enstatite and anorthite*. J. Chem. Technol. Biotechnol. 26, 719-728.
- BREEMEN, N.V., WIELEMAKER, W.G., 1974. *Buffer Intensities and Equilibrium pH of Minerals and Soils: I. The Contribution of Minerals and Aqueous Carbonate to pH Buffering 1*. Soil Sci. Soc. Am. J. 38, 55-60.
- BREEUWSMA, A., LYKLEMA, 1973. *Physical and chemical adsorption of ions in the electrical double layer of hematite*. J. Colloid Interface Sci. 43, 437-448.
- CHEN, G., TAO, D., 2004. *Effect of solution chemistry on floatability of magnesite and dolomite*. Int. J. Miner. Process. 74, 343-357.
- CHEN, Y., TONG, X., FENG, X., XIE, X., 2018. *Effect of Al(III) ions on the separation of cassiterite and clinocllore through reverse flotation*. Miner. 8, 347-358.
- CHOU, L., GARRELS, R.M., WOLLAST, R., 1989. *Comparative study of the kinetics and mechanisms of dissolution of carbonate minerals*. Chem. Geol. 78, 269-282.
- DAVILA-PULIDO, G.I., URIBE-SALAS, 2014. *Effect of calcium, sulfate and gypsum on copper-activated and non-activated sphalerite surface properties*. Miner. Eng. 55, 147-153.
- ESPIRITU, E.R.L., DA SILVA, G.R., AZIZI, D., LARACHI, F., WATERS, K.E., 2018. *The effect of dissolved mineral species on bastnaesite, monazite and dolomite flotation using benzohydroxamate collector*. Colloids. Surf. A: Physicochem. Eng. Asp. 539, 319-334.
- FENG, Q., WEN, S., ZHAO, W., CHEN, H., 2018. *Interaction mechanism of magnesium ions with cassiterite and quartz surfaces and its response to flotation separation*. Sep. Purif. Technol. 206, 239-246.
- FLOOD, C., COSGROVE, T., HOWELL, I., REVELL, P., 2006. *Effects of electrolytes on adsorped polymer layers: Poly(ethylene oxide) - Silica system*. Langmuir 22, 6923-6930.
- FUERSTENAU, M.C., MARTIN, C.C., BHAPPU, R.B., 1963. *The Role of Hydrolysis in Sulfonate Flotation of Quartz*. Reprinted from Trans. 226, 449-454.
- FUERSTENAU, M.C., PALMER, B.R., 1976. *Anionic flotation of oxides and silicates*. In: Society of Mining Engineers of AIME. Mineral Processing Division (Eds.), Gaudin, A.M., Fuerstenau, M.C. American Institute of Mining, Metallurgical, and Petroleum Engineers, New York, USA.
- JEON, I., NAM, K., 2019. *Change in the site density and surface acidity of clay minerals by acid or alkali spills and its effect on pH buffering capacity*. Sci. Re-UK. 9878, 1-10.
- JOLSTERA, R., GUNNERIUSSON, L., HOLMGRE, A., 2012. *Surface complexation modeling of  $\text{Fe}_3\text{O}_4\text{-H}^+$  and magnesium (II) sorption onto maghematite and magnetite*. J. Colloid Interf. Sci. 386, 260-267.
- LACROIX, E., BROVELLI, A., HOLLIGER, C., BARRY, D.A., 2014. *Control of groundwater pH during bioremediation: Improvement and validation of a geochemical model to assess the buffering potential of ground silicate minerals*. J Contam. Hydrol. 160, 21-29.
- LIU, W., MORAN, C.J., VINK, S., 2013. *A review of the effect of water quality on flotation*. Miner. Eng. 53, 91-100.

- MUZENDA, E., 2010. *An investigation into the effect of water quality on flotation performance*. Int. J. Chem. Mole. Nucl. Mater. Metal. Eng. 4, 562-566.
- MICHAUX, B., RUDOLPH, M., REUTER, M.A., 2008. *Challenges in predicting the role of water chemistry in flotation through simulation with an emphasis on the influence of electrolytes*. Miner. Eng. 125, 252-264.
- MIICHALOWSKI, T., ASUERO, A.G., 2012. *Thermodynamic modeling of dolomite behavior in aqueous media*. J. Chem. Thermodyn. 1-12.
- MODI, H.J., FUERSTENAU, D.W., 1957. *Streaming potential studies on corundum in aqueous solutions of inorganic electrolytes*. J. Phys. Chem. 61, 640-643.
- NEVASAIA, D., GUERRERO-RUIZ, A., LOPEZ-GONZALEZ, J.D.D., 1998. *Adsorption of polyoxyethylenic nonionic and anionic surfactants from aqueous solution: Effects induced by the addition of NaCl and CaCl<sub>2</sub>*. J. Colloid Interface Sci. 205, 97-105.
- OFOR, O., 1996. *Effect of inorganic ions on oleate adsorption at a Nigerian hematite - Water interface*. J. Colloid Interface Sci. 179, 323-328.
- PARAPARI, P.S., IRANNAJAD, M., MEHDILO, A., 2017. *Effect of acid surface dissolution pretreatment on the selective flotation of ilmenite from olive and pyroxene*. Int. J. Miner. Process. 163, 49-60.
- POKROVSKY, O.S., 1998. *Surface speciation of Ca and Mg carbonate minerals in aqueous solutions: a combined potentiometric, electrokinetic, and DRIFT surface spectroscopy approach*. Mineral. Mag. 62, 1196-1197.
- RAO, S.R., 2004. *Electrical characteristics at interfaces*, In: *Surface Chemistry of Froth Flotation*. 2nd ed. Kluwer Academic/Plenum Publishers, New York, USA.
- REN, L., QIU, H., ZHANG, Y., NGUYEN, A., ZHANG, M., WEI, P., LONG, Q., 2018. *Effects of alkyl ether amine and calcium ions on fine quartz flotation and its guidance for upgrading vanadium from stone coal*. Powder Technol. 338, 180-189.
- RIINA, S., MARJU, M., JUHA, J., ANTTI, H., 2011. *Acidic dissolution of magnetite: Experimental study on the effects of acid concentration and temperature*. Clay Miner. 59, 136-146.
- RUAN, Y., ZHANG, Z., LUO, H., XIAO, C., ZHOU, F., CHI, R., 2018. *Effects of metal ions on the flotation of apatite, dolomite and quartz*. Miner. 8, 1-12.
- RUIZ-AGUDO, E., KOWACZ, M., PUTINS, C.V., PUTINS, A., 2010. *Role of background electrolytes on the kinetics and mechanism of calcite dissolution*. Geochimica et Cosmochimica Acta 74, 1256-1267.
- RUIZ-AGUDO, E., UROSEVIC, M., PUTINS, C.V., RODRIGUEZ-NAVARRO, C., 2011. *Ion-specific effects on the kinetics of mineral dissolution*. Chem. Geol. 281, 364-371.
- TAGGART, A.F., ARBITER, N., 1946. *The chemistry of collection of non-metallic minerals by amine-type collectors*. Trans. AIME. 169, 266-269.
- WANG, Y., ZHU, G., ZHANG, L., LU, D., WANG, L., ZHAO, Y., ZHENG, H., 2018. *Surface dissolution of spodumene and its role in the flotation concentration of a spodumene ore*. Miner. Eng. 125, 120-125.
- ZHU, Y., ZHANG, G., FENG, Q., YAN, D., WANG, W., 2011. *Effect of surface dissolution on flotation separation of fine ilmenite from titanite*. Trans. Nonferrous Met. Soc. 21, 1149-1154.