

Received March 2, 2020; reviewed; accepted May 1, 2020

Effect of grinding media on the flotation behavior of fluorite using sodium oleate as a collector

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Abstract: Grinding, an essential procedure before flotation, to some extent, determines the flotation behavior of minerals. In this study, the effect of grinding media on the flotation behavior of fluorite using sodium oleate (NaOl) as a collector was investigated via micro-flotation experiments, zeta potential measurements, scanning electron microscopy-energy dispersive spectrometry (SEM-EDS) and X-ray photoelectron spectroscopy (XPS) analyses. The results indicated that, compared with the fluorite particles ground by ceramic media, the ones ground by cast iron media adsorbed less NaOl, resulting in lower flotation recovery. The lower flotation recovery of fluorite particles ground by cast iron media resulted from the coating of the hydrophilic Fe precipitates generated in the grinding, including Fe(0), Fe(OH)₂, and Fe(OH)₃ on their surfaces. These Fe precipitates may cover the Ca active sites and increase the hydration membrane which can inhibit the further NaOl adsorption. This research reveals the effect of grinding media on the flotation behavior of fluorite and guides for media selection in disposing of fluorite ore.

Keywords: fluorite, grinding media, flotation, Fe precipitates

1. Introduction

Grinding is an important mineral preparation process for flotation. The collisions between mineral particles and media in the grinding process result in the size reduction and fresh surface exposure of minerals. It is well known that flotation is a beneficiation method based on the physicochemical characteristics of mineral surfaces (Guo et al., 2019). Therefore, to some extent, grinding media determines the flotation behavior of minerals (Li and Gao, 2017). It is well known that using the cast iron media in grinding has a detrimental effect on the flotation of sulfide minerals (Adam et al., 1984; Peng et al., 2003a, 2003b; Deng et al., 2013; Long et al., 2020). Also, it is believed that using inert grinding media, such as ceramic and zirconia media, can improve the flotation recovery of sulfide minerals compared with cast iron media which results in the generation of iron oxyhydroxide species coating on the mineral surfaces (Huang and Grano, 2006; Bruckard, 2011; Corin et al., 2018; Deng et al., 2019). However, most researches have been mainly focused on the deteriorating effect of cast iron media on the sulfide minerals. The effect of cast iron media on the flotation behavior of non-sulfide minerals has been ignored.

Fluorite, a typical non-sulfide mineral, is widely applied in chemical, material, metallurgical, and other industrial fields (Zheng 2009). Flotation is the most commonly used beneficiation method for fluorite ore (Aliaga et al., 2006; Zhou et al., 2013; Peng et al., 2014). With the depletion of high-grade and easy beneficiated fluorite resources, the low-grade, complicated, and finely disseminated raw fluorite ores which are difficult to be beneficiated should be efficiently used. However, using these ores result

in the decrease of the fluorite powder quality. A great number of researches mainly have focused on flotation reagents and processes (Zhang and Song, 2003; Song et al., 2006; Zhang et al., 2018). However, the effect of grinding media on the flotation behavior of fluorite has been also ignored.

Globally, cast iron media is the most widely used in industrial grinding because of its cheap price. However, because of the dissolution and corrosion of cast iron media, the effect and mechanism of cast iron media in grinding on the flotation of fluorite are still unclear. In this study, the effect and mechanism of cast iron media on the fluorite flotation were investigated using ceramic media as a comparison to cast iron media. In this purpose, micro-flotation experiments, zeta potential measurements, scanning electron microscopy-energy dispersive spectrometry (*SEM-EDS*), and X-ray photoelectron spectroscopy (*XPS*) analyses were performed to reveal its effect and mechanism.

2. Materials and methods

2.1. Materials

The fluorite samples used in this study were collected from the Jiangxi Province, China. Lump crystals of fluorite were first hand-ground to -1.7 mm and then hand-selected for the highly pure parts. After that, the highly pure parts (200 g) were ground in a tumbling mill equipped with a 1.5 dm³ ceramic pot. The tumbling mill was the same type as Li and Gao's research work (Li and Gao, 2017; 2018). The ceramic pot was placed on two rotating rods, and the rods were connected with the belts which were motivated by an electric motor. For each grinding, the grinding concentration and media filling rate were 50% and 50%, respectively. Ceramic and cast iron ball were used as the grinding media in parallel. The diameters of the ceramic ball were 20 mm, 12 mm, and 8 mm, respectively, with the mass ratio of 8:5:6. As for the cast iron media, the diameters were 15 mm and 10 mm, respectively, with a mass ratio of 3:2. The grinding time for the ceramic and cast iron media was 4 min and 2 min, respectively. After the grinding, the products were screened to collect the -75+38 μm fractions for the micro-flotation experiments, *SEM-EDS* and *XPS* analyses. The -38 μm fractions were further ground to -5 μm for the zeta potential measurements. The size distributions of the classified fluorite particles (-75+38 μm) ground by ceramic and cast iron media were measured by Mastersizer 2000 (Malvern Panalytical Ltd., UK), and the results are shown in Fig. 1. It can be seen From Fig. 1 that there was no significant difference in the particle size distributions between the two fluorite particles. The chemical analysis (Table 1) indicates that the CaF₂ grade of fluorite samples was 99.10% without Fe element. The XRD results (Fig. 2) further indicated the high purity of the samples.

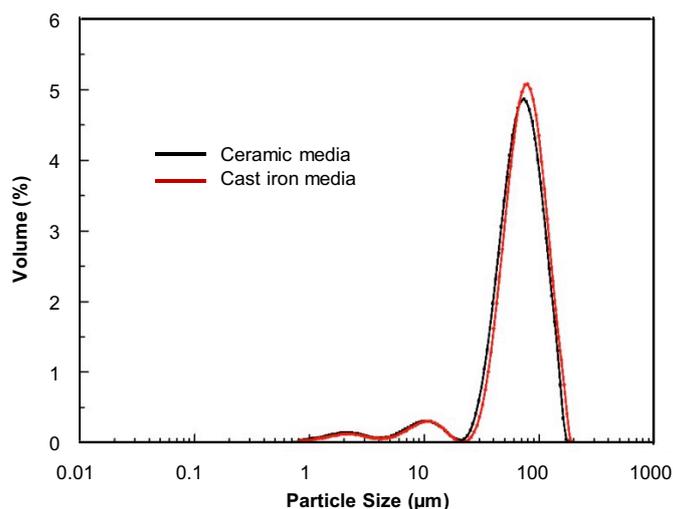


Fig. 1. Particle size distributions of fluorite particles ground by ceramic and cast iron media in parallel

Table 1. Chemical analysis of the fluorite samples (%)

Sample	CaF ₂	SiO ₂	MgO	Al ₂ O ₃	TFe
Fluorite	99.10	0.35	0.11	0.15	-

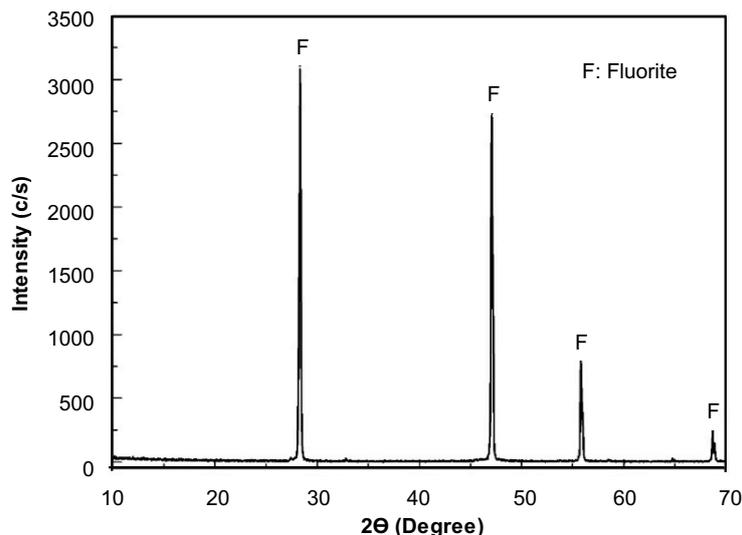


Fig. 2. XRD patterns of the fluorite samples

Sodium oleate ($C_{17}H_{33}CO_2Na$, NaOl), an analytical grade pure reagent bought from Shanghai Maikun Chemical Co., Ltd., Shanghai, China was used as a collector. Analytical grade hydrochloric acid (HCl) and sodium hydroxide (NaOH) bought from Sinopharm Chemical Reagent Co., Ltd., China, were used as the pH modifiers. Deionized water (DI, resistivity $18.2 M\Omega \times cm$) used in all the experiments and analyses was produced by an ultra-pure water machine (Chongqing Qianyan Water Treatment Equipment Co., Ltd, China).

2.2. Methods

2.2.1. Micro-flotation experiments

Micro-flotation experiments were carried out in an XFGC flotation machine (Jilin Exploration Machinery Plant, Fig. 3) equipped with a $40 cm^3$ plexiglass cell at an impeller speed of 1600 rpm. This machine is widely used for micro-flotation experiments (Jin et al., 2018; Huang et al., 2019). For each experiment, 2 g of $-75+38 \mu m$ fluorite was added to the cell with $35 cm^3$ of DI water. Then, the pulp was mixed for 2 min to obtain the homogenous suspension. After that, the pH modifier and collector were added sequentially and stirred for about 2 min and 3 min, respectively. Then, the froth of the suspension was collected for about 4 min. Finally, the froth and tailing were collected, filtered, dried, and weighted, separately. Each flotation experiment was repeated three times and finally averaged. The flotation recovery was calculated using Eq. 1:

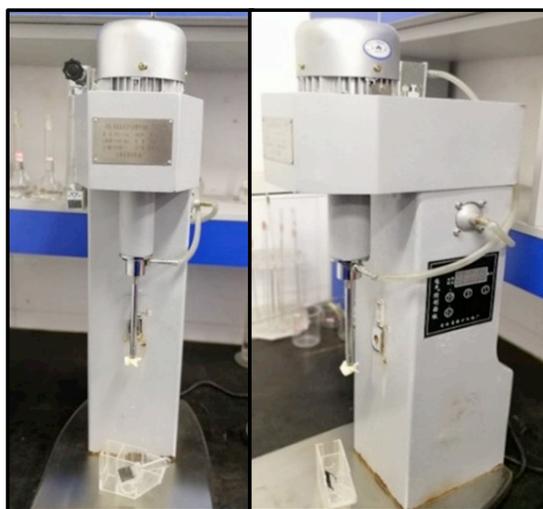


Fig. 3. Snapshots of the XFGC flotation machine

$$\varepsilon = \gamma = \frac{m_1}{m_1 + m_2} \quad (1)$$

where ε is the flotation recovery; γ is the flotation yield; m_1 is the quality of froth (g); m_2 is the quality of tailing (g).

2.2.2. Zeta potential measurements

Zeta potential measurements were conducted using a Malvern Zetasizer Nano ZS90 instrument equipped with a rectangular electrophoresis cell. For each measurement, 0.05 g of -5 μm fluorite and 35 cm^3 of 10^{-2} mol/dm³ KCl were mixed and stirred for 2 min to obtain the suspension. After that, the pH modifier and collector were added and stirred for about 2 min and 3 min, respectively, which were consistent with the micro-flotation experiment. Subsequently, the suspension was settled for about 10 min to allow the coarse particles to settle down. The supernatant of the suspension was taken and transferred into the rectangular electrophoresis cell for measurements. Each measurement was automatically performed in triplicate at 25°C with a measurement error of ± 2.0 mV.

2.2.3. SEM-EDS analysis

SEM-EDS analysis was used to investigate the surface morphology and surface elements of the fluorite particles ground by ceramic and cast iron media in parallel. The analysis was conducted using a JEOL JSM-6610 scanning electron microscope and a Bruker QUANTAX200-30 energy dispersive spectrometer. Before the analysis, the fluorite particle surfaces were sputter-coated with a layer of gold. The magnification of SEM was adjustable from 5 to 300000 times.

2.2.4. XPS analysis

XPS is an important surface analysis technology and has already been widely used in mining engineering (Yao et al., 2018; Yao et al., 2020). Fluorite particles ground by ceramic and cast iron media were tested in parallel using the ThermoFisher, ESCALAB 250 XI instrument. The energy resource of the instrument was Al K α X-ray ($h\nu=1486.6$ eV) with 12.5 kV operating voltage and 16 mA current. The analytical chamber vacuum was maintained at about 8×10^{-10} Pa during the analyses. All the binding energies were referenced to the neutral C1s peak at 284.8 eV to compensate for the surface-charging effect.

3. Results and discussion

3.1. Micro-flotation experiments

Figure 4 shows the effect of NaOl concentration on the flotation recoveries of fluorite particles ground by ceramic and cast iron media in parallel. It can be seen from Fig. 4 that the two curves of the fluorite flotation recoveries show a similar trend. With the increase of NaOl concentration, the flotation recoveries of fluorite first increased and then decreased. The maximum flotation recoveries of fluorite particles ground by ceramic and cast iron media are 87.4% and 81.3%, respectively, at 1.0×10^{-4} mol/dm³ NaOl concentration which may be caused by the monolayer adsorption of the collector on the fluorite surface (Mielczarski et al., 1993; Gao et al., 2016). However, when the NaOl concentration was higher than $1.0 \cdot 10^{-4}$ mol/dm³, the flotation recovery decreased which may be caused by the multilayer adsorption of the collector on the fluorite surface or the formation of micelles (Wang et al., 2005). Within all the experimental NaOl concentrations, the fluorite particles ground by ceramic media showed a higher flotation recovery than those ground by cast iron media, indicating that the fluorite ground by ceramic media had a better floatability.

Figure 5 shows the effect of solution pH value on the flotation recoveries of fluorite particles ground by ceramic and cast iron media in parallel. The flotation recoveries of both the two curves have a similar trend, but a higher flotation recovery of fluorite ground by ceramic media was observed. With the increase of solution pH value, the recovery curves seem to have a very slight increase and then a sharp decrease. The recoveries begin to decrease at high solution pH values (pH > 10), which may be caused by the competition for the adsorption of Ca active sites on the mineral surfaces between the oleate ions and the abundant OH⁻ (Li and Gao, 2017).

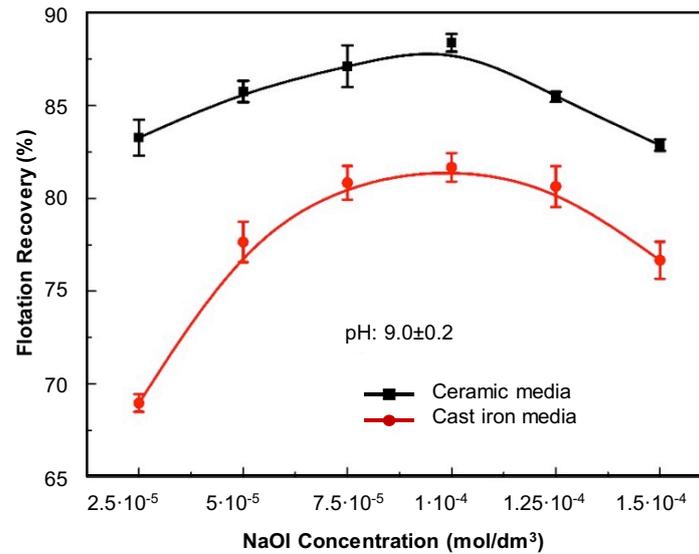


Fig. 4. Effect of NaOl concentration on the flotation recoveries of fluorite ground by ceramic and cast iron media in parallel

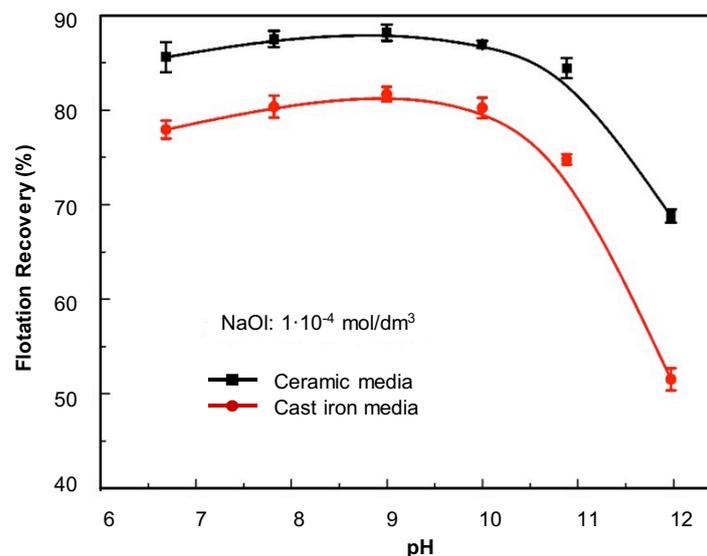


Fig. 5. Effect of solution pH value on the flotation recoveries of fluorite ground by ceramic and cast iron media in parallel

3.2. Zeta potential measurements

Figure 6 shows the effect of solution pH value on the zeta potentials of fluorite particles ground by ceramic and cast iron media in the absence and presence of NaOl. In the absence of NaOl, the IEPs (isoelectric points) of fluorite particles ground by ceramic and cast iron media were found to be as 8.5 and 8.9, respectively, and the zeta potentials of fluorite decreased with the increasing the solution pH value, which is in agreement with the previous reports (Gao et al., 2015; Jiang et al., 2018). However, it was also observed a slightly higher zeta potential of fluorite particles ground by cast iron media, which may result from the coating of the Fe precipitates generated in the grinding (Yu et al., 2017). In the presence of NaOl, the zeta potentials of fluorite particles shifted to the negative direction, indicating the adsorption of the anionic carboxylate functional group in NaOl onto the fluorite surfaces (Feng et al., 2015; Xu et al., 2014; Deng et al., 2019). Figure 6 also shows that the fluorite particles ground by cast iron media still had a higher zeta potential than those ground by ceramic media. However, it can also be

seen that the zeta potentials of fluorite particles ground by cast iron media shifted towards less negative, indicating that the fluorite ground by cast iron media adsorbed less NaOI on their surfaces.

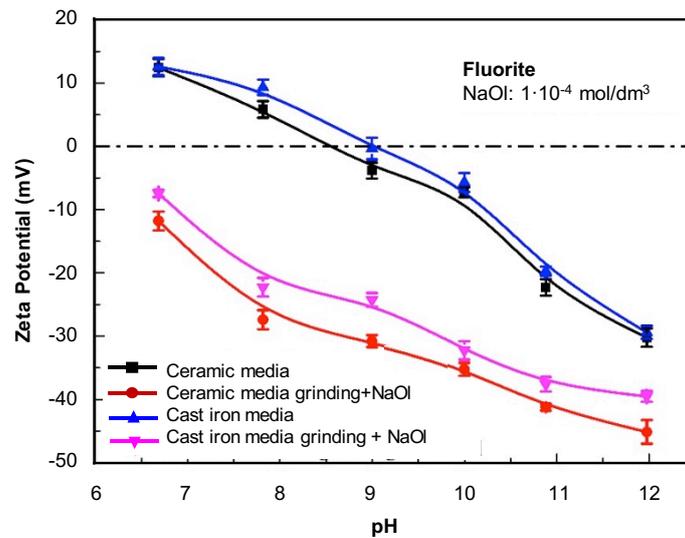


Fig. 6. Effect of solution pH value on the zeta potentials of fluorite ground by ceramic and cast iron media in parallel

3.3. SEM-EDS analysis

Figure 7 shows the SEM-EDS images of fluorite particles ground by ceramic and cast iron media in parallel. From Fig. 7(a) and Fig. 7(c), it can be seen that the surfaces of fluorite particles ground by ceramic media were smoother than those ground by cast iron media. Fig. 7(c) also shows that there were small particles coating on the surfaces of fluorite particles ground by cast iron media. Fig. 7(b) shows the EDS spectra of fluorite particles ground by ceramic media. From the spectra, it can be known that there was no Fe element detected on the surfaces of fluorite particles ground by ceramic media. As for the spectra of fluorite particles ground by cast iron media shown in Fig. 7(d), Fe element was detected which may originate from the Fe contaminations in the grinding process.

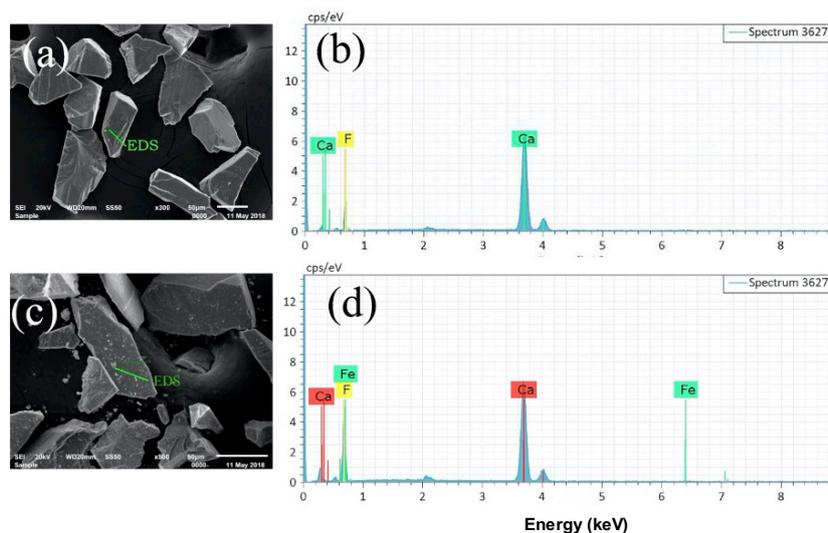


Fig. 7. SEM and EDS images of fluorite particles ground by (a) and (b) ceramic media, (c) and (d) cast iron media

3.4. XPS analysis

To further reveal the element composition and state of the small particles on the fluorite surfaces, XPS analyses were performed, and the results are shown in Fig. 8. It can be seen from Fig. 8 that elements of C, Ca, and F were all detected on both the surfaces of fluorite particles ground by ceramic and cast iron

media. The element of C originates from the background of XPS analyses (Dong et al., 2019; Feng et al., 2020), while the elements of Ca and F originate from the chemical composition of fluorite. Additionally, in the spectra of fluorite ground by cast iron media, Fe2p peak was also detected, but no Fe peak was detected in the case of ceramic media.

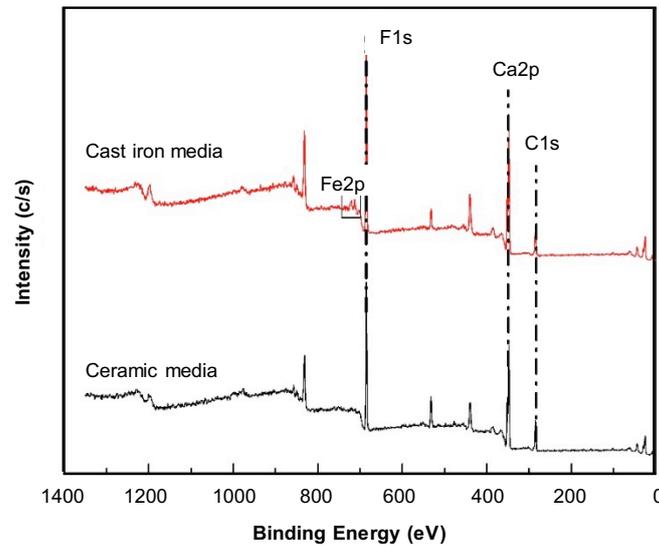


Fig. 8. XPS survey spectra of fluorite ground by ceramic and cast iron media in parallel

Table 2 presents the contents of elements calculated from the XPS survey spectra on the surfaces of fluorite ground by ceramic and cast iron media in parallel. It can be seen from Table 2 that the Fe element was not detected on the surfaces of fluorite particles ground by ceramic media. However, in the case of cast iron media, the contents of Fe element were 2.58%, which further proved the Fe contaminations in the cast iron media grinding process.

Table 2. Contents of elements on the surfaces of fluorite ground by ceramic and cast iron media in parallel

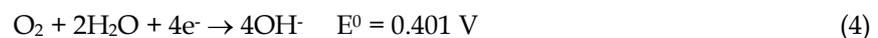
Grinding media	Ca	F	C	Fe
Ceramic media	31.30	37.43	31.27	-
Cast iron media	30.71	35.01	31.70	2.58

To analyze the Fe element state of the small particles on the surfaces of fluorite particles ground by cast iron media, the narrow spectra of Fe2p are shown in Fig. 9. From Fig. 9, it can be seen that the peak at 712.0eV was assigned to the Fe2p_{3/2} (Thermo Scientific XPS database). After peak-fitting and separation, five different peaks appeared in the spectra. The peaks at 708.1eV, 709.2eV, and 712.2eV are assigned to the Fe(0), Fe(OH)₂, and Fe(OH)₃, respectively, while the peaks at 715.0eV and 716.2eV are attributed to the satellites of Fe(OH)₂ and Fe(OH)₃, respectively (Buckley and Woods, 1984; Li and Iwasaki, 1992; Yang et al., 2016; Rabieh et al., 2017; NIST XPS database; Thermo Scientific XPS database). Fe(0) maybe is the worn parts of the cast iron media on the surfaces of fluorite. Fe(OH)₂ and Fe(OH)₃ can be identified most likely from the galvanic interactions between grinding media which are shown as follows (Rabieh et al., 2017; Yao et al., 2019; Hu et al., 2020; Zhang et al., 2020):

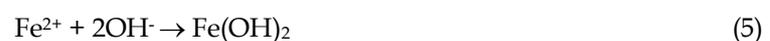
- Anodic oxidation:



- Cathodic reduction:



- Hydroxylation:





where E^0 is the standard half-cell reduction potential. It has already been reported that these Fe hydroxy precipitates ($\text{Fe}(\text{OH})_2$, $\text{Fe}(\text{OH})_3$) are hydrophilic (Yu et al., 2017; Yao et al., 2019). Coating of these precipitates on the surfaces of minerals may on one hand cover the Ca active sites that inhibit further collector adsorption (Stone et al., 1984; Gao et al., 2012; Jin et al., 2008). On the other hand, coating of these hydroxy precipitates can increase the hydrophilicity of minerals (Zhang et al., 2020); and hence the hydration membrane on the mineral surfaces increases which result in the NaOl more difficult to be adsorbed (Hu, 1989; Tian et al., 2018).

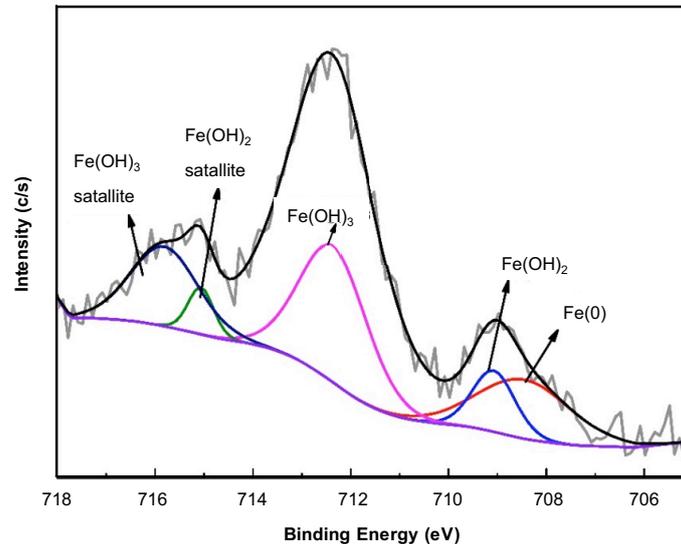


Fig. 9. XPS narrow spectra of Fe2p on the surfaces of fluorite particles ground by cast iron media

4. Conclusions

In this study, the effect of grinding media on the flotation behavior of fluorite using NaOl as a collector was investigated. The results for micro-flotation experiments indicated that the fluorite particles ground by cast iron media showed a lower flotation recovery than those ground by ceramic media. The zeta potential results of the particles exhibit that, compared with the fluorite particles ground by ceramic media, the ones ground by cast iron media adsorbed less NaOl on their surfaces. SEM-EDS analysis proved that there were Fe precipitates coating on the surfaces of fluorite particles ground by cast iron media, but not in the case of the ones ground by ceramic media. XPS analysis further revealed that the Fe precipitates were $\text{Fe}(0)$, $\text{Fe}(\text{OH})_2$, and $\text{Fe}(\text{OH})_3$. These Fe precipitates may cover the Ca active sites and increase the hydration membrane on the surfaces of fluorite particles ground by cast iron media which can inhibit the further NaOl adsorption.

Acknowledgments

The author would like to thank the National Natural Science Foundation of China (Project No. 51704214 & 51704215) and the Shiyanjia Lab (www.shiyanjia.com) for the XPS tests.

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