# Selective flotation of witherite from calcite using potassium chromate as a depressant

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**Abstract:** Witherite has been widely used as an industrial and environmental source of barium, with calcite being the primary associated carbonate mineral. However, few studies have been conducted to effectively concentrate witherite from barium ores. In this work, with the treatment of potassium chromate ($K_2CrO_4$) and sodium oleate (NaOL), witherite was selectively separated from calcite through selective flotation at different pH conditions. In addition, contact angle, Zeta potential, adsorption and X-ray photoelectron spectroscopy measurements were performed to characterize the separation mechanisms. The results demonstrated that NaOL had a strong collecting ability for both witherite and calcite; nevertheless, witherite could be effectively selected from calcite with the highest recovery at pH 9 in the presence of $K_2CrO_4$. From the XPS measurements, NaOL and $K_2CrO_4$ were found to be primarily attached to the surfaces of witherite and calcite through chemisorption. The presence of $K_2CrO_4$ on the surface of calcite adversely influenced the NaOL adsorption, which could make the flotation separation efficient and successful.

*Keywords:* witherite, calcite, selective flotation, sodium oleate, potassium chromate

## 1. Introduction

Barium minerals have become the focus of scientific studies in terms of geology and beneficiation for many years, which primarily study the generation and separation of barite ores, i.e., the form of barium sulfate. Previous studies reported that barium mineralization occurs widely in the Lower Cambrian black shale (Pi et al., 2004). For a long time, barite has been the main barium mineral source in many parts of China. With the continuous improvement of exploitation technology, witherite has appeared in the shape of carbonate. More than 40 witherite deposits or witherite-barite deposits have been discovered in the Yangtze ore regions and other parts of southwestern China (Lü et al., 2004), attracting various scholars to conduct scientific investigation and experimental research on this infrequent mineral.

Witherite, also referred to as barium carbonate ($BaCO_3$), is a significant type of inorganic nonmetallic mineral that possesses favorable stability in thermodynamics with crystal modification upon heavy metal carbonates (Nagajyothi et al., 2016; Ivan et al., 2013). In general, there are three common polymorphisms of $BaCO_3$: hexagonal, orthorhombic, and cubic. Nevertheless, only the orthorhombic phase is relatively stable under ambient condition (Reto et al., 2006; Earnest et al., 1989).

As the main mineral components in rocks, carbonates are observed widely in sediments and inorganic components, among which heavy metal carbonates, especially barium carbonate, have been of considerable interest for research. Due to the close relationship between aragonite and the needle-like subunit, witherite has attracted immense attention in terms of technological process and economic values (Yu et al., 2004; Guo et al., 2012; Zhu et al., 2012), *e.g.*, there are persistently increasing applications in industry for producing barium salts, ceramics pigment and optical glass (Lv et al., 2007; Thongtem et al., 2010). However, the high-cost and energy-inefficient preparation processes on the basis

of barite have led to the application of witherite as stock materials (Hu et al., 2014; Gao et al., 2011; Zhang et al., 2011).

In addition, $BaCO_3$ is widely utilized in synthesizing barium ferrites and ferroelectric materials as a precursor in a relatively low-cost and high-efficiency way (Sreedhar et al., 2012; Jiao et al., 2010; Alavi et al., 2008). In recent years, various chemical and physical methods have been used to synthesize barium nanoparticles using witherite as raw materials, such as solid-state decomposition, microemulsion-based method (Li et al., 2006), reversed micelles (Karagiozov et al., 2005), and self-organized formation methods (Xie et al., 2005). In general, there is a growing demand for witherite in the modern industry. Therefore, the beneficiation and purification of witherite from other gangues are of great significance.

With a relatively narrow distribution in the whole world, a rare effective method has been found to concentrate witherite in barium ore. Calcite is one of the main gangue minerals in witherite ore (Gao et al., 2017; Yang et al., 2008; Barkhordari et al., 2009). The surface chemical properties of witherite and calcite are similar due to that fact that they both belong to carbonate minerals. NaOL has been widely used in the flotation of semisoluble salt-type minerals, such as scheelite, calcite, fluorite, barite, and celestite (Martinez et al., 2003, Li and Gao, 2018 and 2017; Gao et al., 2018a), showing a pronounced collecting power but a poor selectivity of the valuable minerals. Therefore, efficient calcite depressants are supposed to be utilized for improving the selectivity in the separation of whither and calcite by modifying the mineral surface characteristics. Depressants for calcite in previously published papers are mainly focused on water glass (Gao et al., 2016a; Wang et al., 2016; Haisheng et al., 2017), phosphates (Gao et al., 2018; Yongxin and Changgen, 1983) and some hydrophilic colloids (Liu et al., 2016; Ozcan and Bulutcu, 1993; Shi et al., 2014; Tian et al., 2017). These depressants are reported to improve the flotation selectivity with some effect, but depress witherite to a large extent at the same time. Therefore, there is a considerable demand for developing more selective depressants with high performance for the separation of witherite from calcite. Potassium chromate has been widely used as a depressant for gelena in flotation. Meanwhile, potassium chromate has depressing effects on calcite, pyrite, etc. (Huangpu, 1985; Zhang et al., 2008). In a previous work, potassium chromate was used as a depressant for calcite for the separation of fluorite and calcite. Fluorite and calcite could be separated effectively by flotation when the potassium chromate concentration was $9\times10^{-5}$ mol/L by using NaOL as the collector (Yu, 2015).

The purpose of this study is to investigate the separation of witherite from calcite using potassium chromate as a depressant. Consequently, batch flotation tests of single minerals and artificial mixtures composed of witherite and calcite single minerals were performed, with sodium oleate (NaOL) and potassium chromate ($K_2CrO_4$) being the collector and depressant, respectively. In addition, ultraviolet spectrophotometry, X-ray photoelectron spectroscopy (XPS), Zeta potential and contact angle measurements were performed to explain the mechanism.

## 2.    Materials and methods

### 2.1.  Materials

Witherite single mineral sample was obtained from Chengkou county in Sichuan province, China. High grade minerals were crushed to -2 mm by roll crushing milling and were ground in a conical ball mill with steel balls as the media under wet condition. Finally, -0.100 mm +0.074 mm particle size fraction was collected. According to the Chinese national standard (GB/T 1614-2011, Barium Carbonate for Industrial Use; a Chinese national standard had been made to define the determination method of $BaCO_3$ and impurities content in industrial barium carbonate), the barium carbonate content of witherite single mineral was analyzed to be approximately 92%. X-ray fluorescence (XRF) analysis indicated 72.44 wt.% BaO, 0.94 wt.% CaO, 2.78 wt.% $SiO_2$, and 0.78 wt.% MgO. The X-ray diffraction pattern of witherite single mineral is shown in Fig. 1a. The main minerals in the witherite single mineral were witherite and barytocalcite according to the X-ray diffraction pattern. The contents of these two minerals could be calculated according to the contents of BaO and CaO analyzed by XRF. The witherite single mineral contained approximately 91 wt.% of witherite, 5 wt.% of barytocalcite, and 4 wt.% of other gangue minerals.

The calcite single mineral sample was obtained from Wuling county in Chongqing city, China. It was also handled via the same method applied for witherite. X-ray fluorescence (XRF) analysis indicated 55.16 wt.% CaO, 0.65 wt.% $SiO_2$, and 0.24 wt.% $Al_2O_3$. Fig. 1b displays the X-ray diffraction pattern of calcite. Combining with XRF analysis, the content of calcite in the sample was greater than 98.50 wt%.
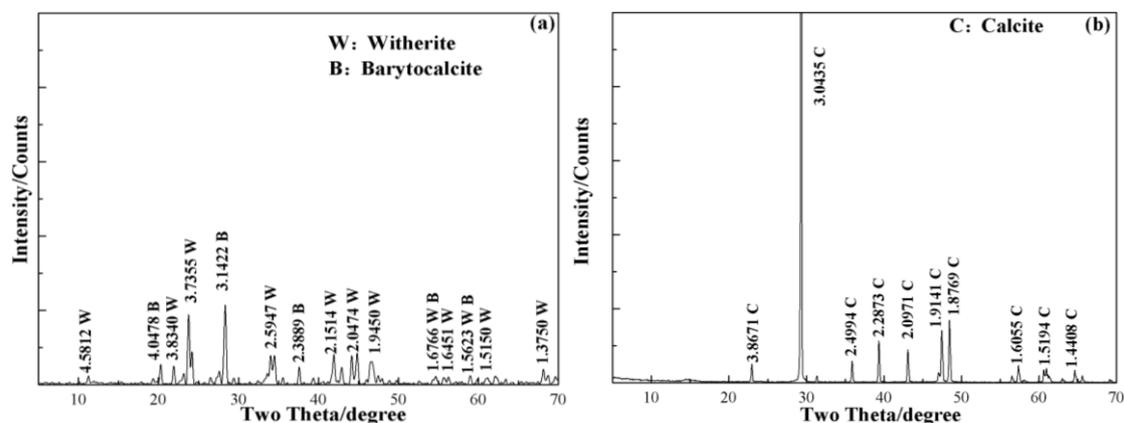


Fig. 1. XRD patterns of single minerals: (a) witherite; (b) calcite

Sodium oleate (NaOL) and potassium chromate ($K_2CrO_4$) were used as the collector and depressant, respectively, and both were purchased from Sinopharm Chemical Reagent Co., Ltd. Hydrochloric acid (HCl) or sodium hydroxide (NaOH) solutions were used to adjust the pH value of the slurry, while deionized water was applied for all experiments. All reagents were of analytical grade and used without further purification.

## 2.2. X-ray diffraction analysis

The mineral composition of single mineral samples was determined by using a D8 Advance model X-ray powder diffractometer (Bruker Corporation, Stuttgart, Germany), with Cu Kα radiation (λ=1.5406 Å). The data of the samples were collected with 2θ values ranging from 5° to 70° at a scan speed of 1°/min.

## 2.3. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) of the samples was performed on a Thermo Electron Corporation (Waltham, MA, USA) VG Multilab 2000 with a monochromatic Al X-ray source operating at 300 W. The survey was scanned from 0 to 1100 eV with a pass energy of 100 eV and steps of 1.0 eV. Only 1 sweep was carried out. 1.0 g of single mineral samples with a fraction of -74 μm was added into 30 mL of deionized water. Then, the slurries were conditioned using the same procedure as the flotation tests with and without desired reagents. After stirring for 10 min and washing twice with deionized water, the slurries were filtered and dried in a vacuum desiccator controlled at a temperature below 30°C for 24 h.

## 2.4. Ultraviolet spectrophotometry

The adsorption amount was recorded on an A360 ultraviolet spectrophotometer (AOE Instruments (Shanghai) Co., Ltd, Shanghai, China). 2.5 g of mineral sample was mixed with 25 mL of deionized water in the flotation cell for 1 min. Then, the desired concentration of reagents was added to the pulp in order and conditioned for 2 min for each reagent at room temperature (25 °C). The solid phase was separated from the solution using a H2050R-1 high-speed centrifuge (CENCE Instruments Co., Ltd., Hunan, China). Next, the supernatant of the solution was used to measure the residual NaOL concentration using the spectrophotometer with the wavelength set at 192 nm, which is the characteristic adsorption band of NaOL (Zheng et al., 2017).

### 2.5. Zeta potential measurements

The tested sample particles were ground to -2.0 μm in an agate mortar, and 20 mg of the sample was added into 100 mL of deionized water. The Zeta potentials were measured using a Malvern Zetasizer Nano ZS90 (Malvern Instruments, Malvern, UK). All measurements were conducted in a 0.1 mol/L NaCl background electrolyte solution. The pH value of the suspension solution was adjusted by HCl or NaOH solutions. The measurements were performed at 25 ℃.

### 2.6. Contact angle measurements

The contact angles of single minerals treated or untreated by the reagent to assess the wettability were measured on a GBX MiniLab ILMS (GBX Scientific Instruments, Romans, France), whose operating principle is the Washburn technique (Qiu et al., 2016; Chibowski et al., 2002; Chau, 2009). 10 g of mineral samples were added into 200 mL of deionized water, and then the slurries were conditioned using the same procedure as the flotation tests with and without desired reagents. After stirring for 10 min and washing twice with deionized water, the slurries were then filtered, and dried in a vacuum desiccator controlled at a temperature below 30°C. Each value reported was the average of three separate determinations.

### 2.7. Batch flotation tests

The flotation tests for single minerals or the artificial mixture composed of 60 wt% witherite and 40 wt% calcite were conducted in an XFG-35 laboratory mechanical flotation cell with a volume of nearly 35 mL (Gao et al., 2016a and 2016b; Gao et al., 2018a). First, 2.5 g of mixture was added along with 25 mL of deionized water into the flotation cell for 1 min at an impeller speed of 1800 rpm. Second, HCl or NaOH was added into the pulp to adjust the solution pH. Next, $K_2CrO_4$ and NaOL were added to the pulp in order, with a condition time of 2 min for each reagent. The total flotation time was 3 min, with the concentrates being collected by manual scraping. The concentrates as well as the unfloated products remaining in the cell were collected, dried and weighed to calculate the flotation recoveries. The element contents of Ba and Ga in the concentrate were measured by XRF. Contents of witherite and calcite in the artificial mixture flotation concentrate were calculated according to the element contents of Ba and Ga. The recoveries of witherite and calcite were calculated according to their contents in the concentrate.

## 3.    Results and discussion

### 3.1. Wettability of witherite and calcite

To assess the wettability of witherite and calcite, the contact angles of single minerals treated or untreated by the collector and depressant were measured under the condition of different pH values. The effect of $K_2CrO_4$ and NaOL on the wettability of witherite and calcite powder is shown in Fig. 2.
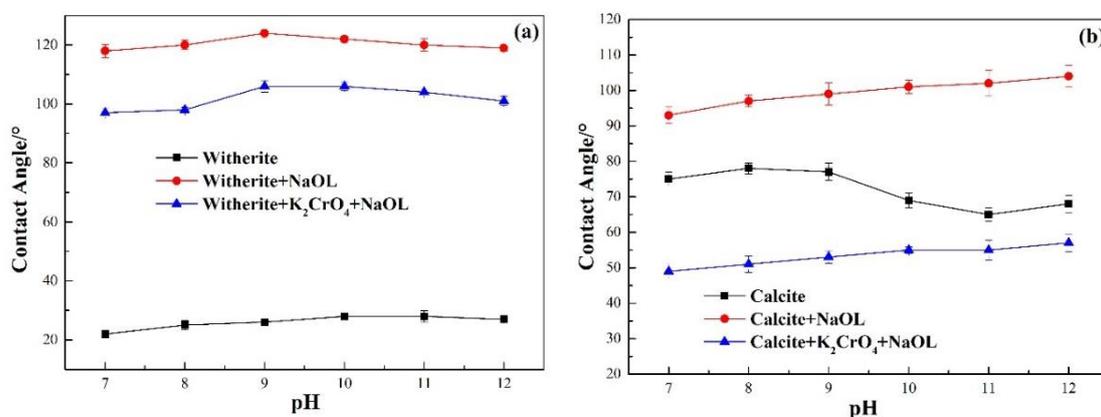


Fig. 2. Powder contact angle of single minerals treated
or untreated by the collector and depressant: (a) witherite; (b) calcite

Under neutral condition, the initial contact angle of witherite powder was 22° while the initial contact angle of calcite powder was 75°, which agreed with the result of Przemyslaw B. et al. (2017). When treated by NaOL, the contact angles of witherite and calcite were increased from 22° to 118° and from 75° to 93°, respectively, implying that witherite and calcite became extremely hydrophobic. While $K_2CrO_4$ was attached on the surface, the contact angle of calcite was decreased fiercely to 49°. Compared with calcite, the contact angle of witherite was decreased in a relatively slight extent, indicating that $K_2CrO_4$ had little effect on depressing witherite.

## 3.2. Batch flotation of single mineral and artificial mixture

To investigate the collecting and depressing effects of $K_2CrO_4$ and NaOL on witherite and calcite, batch tests of single minerals and artificial mixture were conducted, and the results are shown in Fig. 3.
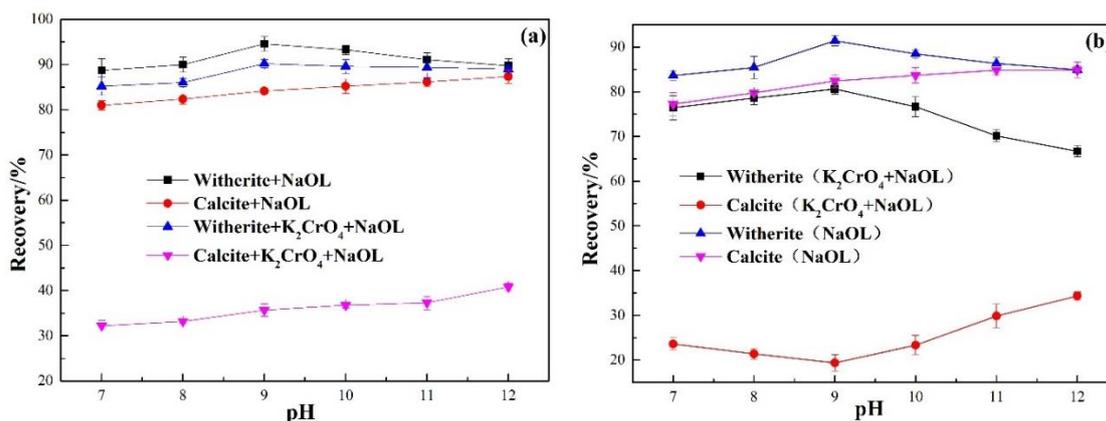


Fig. 3. Recovery of flotation on single mineral and artificial mixture: (a) single mineral; (b) artificial mixture

The recoveries of both witherite and calcite were at a high level when 25 mg/L NaOL was used as the collector within the pH range of 7 to 12, reaching the maximum at pH 9. Once 15 mg/L $K_2CrO_4$ was added into the pulp as the depressant, calcite showed a poor floatability while witherite was quite hydrophobic, with the optimal pH value being still 9, which agreed with the contact angle tests. The recoveries of the artificial mixture were identical to single mineral flotation, *e.g.*, the recoveries of witherite and calcite were both at a high level when NaOL was used as the collector in the pH range from 7 to 12. However, after the addition of $K_2CrO_4$, the difference in the recovery of witherite and calcite was observed, with the greatest difference being found at pH 9, indicating the best separation efficiency under this condition. It should be noted that NaOL had a decent collecting ability for both witherite and calcite. In addition, pH and $K_2CrO_4$ played an important role in the separation between witherite and calcite.

## 3.3. Zeta potential measurement

The Zeta potentials of witherite and calcite before and after being treated by $K_2CrO_4$ or NaOL or $K_2CrO_4$+NaOL are shown in Fig. 4.

From the electrokinetic phenomenon of witherite and calcite suspensions shown in Fig. 4, the minerals were negatively charged within pH 7 ~ 12. Once treated by $K_2CrO_4$ or NaOL or $K_2CrO_4$+NaOL, the zeta potentials of witherite and calcite were shifted down, becoming more negatively charged, probably due to the adsorption of $K_2CrO_4$ and NaOL on the mineral surfaces.

Specifically, Fig. 4(a) illuminated that the decrease in the zeta potentials of witherite with the intercalation of NaOL was greater than those treated by $K_2CrO_4$, reflecting the better adsorption of NaOL on witherite *vs.* $K_2CrO_4$, opposite to that of calcite shown in Fig. 4(b). The zeta potential curve of "witherite +$K_2CrO_4$+NaOL" was very close to that of "witherite +NaOL", indicating that preadsorbed $K_2CrO_4$ slightly influenced the adsorption of NaOL on witherite. The zeta potential curve of calcite treated by "$K_2CrO_4$+NaOL" was very close to that of "calcite + $K_2CrO_4$", reflecting better adsorption of $K_2CrO_4$ on calcite *vs.* NaOL. Moreover, the adsorption efficiency of witherite was the strongest at pH of

9 and 10, while that of calcite became stronger gradually with increasing pH, consistent with the results of the flotation tests.
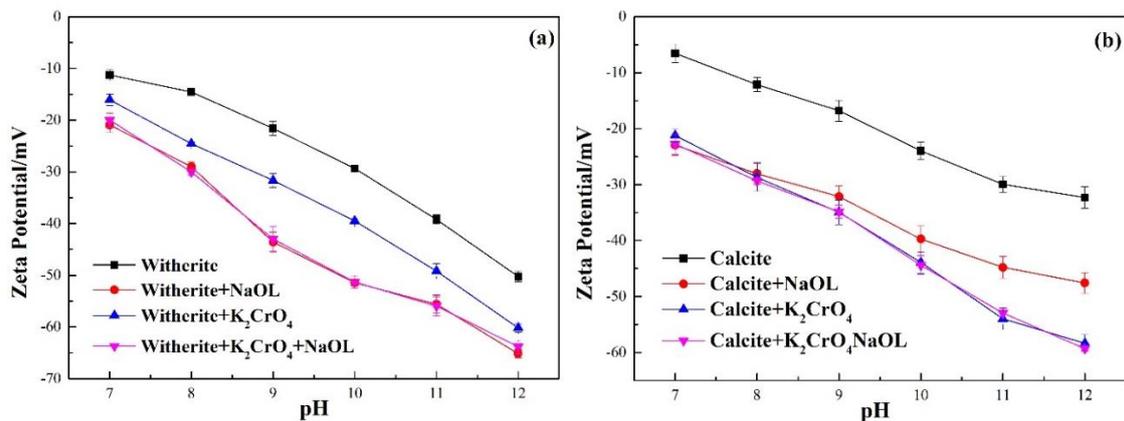


Fig. 4. Zeta potentials of witherite and calcite before and after being treated by $K_2CrO_4$ or NaOL or $K_2CrO_4$ + NaOL. (a) witherite; (b) calcite

### 3.4. Adsorption measurement of the collector

The adsorption difference of the collector on the different mineral surfaces is the premise for implementing mineral separation via forth flotation. This difference could be intuitively reflected by the apparent adsorption amount. Table. 1 shows the adsorption amounts of NaOL on witherite and calcite analyzed using a UV spectrophotometer.

Table 1. The adsorbed rates of sodium oleate attached on the surface

| Reagent regime | Abs | Residual rate/% | Adsorbed rate/% |
|---|---|---|---|
| NaOL | 0.361 | 100.00 | 0 |
| $BaCO_3$+NaOL | 0.088 | 23.55 | 76.45 |
| $BaCO_3$+$K_2CrO_4$+ NaOL | 0.112 | 31.02 | 68.98 |
| $CaCO_3$+ NaOL | 0.147 | 40.72 | 59.28 |
| $CaCO_3$+$K_2CrO_4$+ NaOL | 0.309 | 85.60 | 14.40 |

NaOL showed an out-bound adsorption on both witherite and calcite, in accordance with the high recovery in single mineral flotation. It should be noted that the adsorption rate on witherite was higher than that on calcite, indicating a better collecting ability for witherite. However, an almost 45% descend of NaOL adsorption was observed on the calcite surface in the presence of $K_2CrO_4$. In contrast, only a slight decrease of approximately 7.47% for witherite was found. To sum up, the attachment of $K_2CrO_4$ on calcite surface had a beneficial effect on the depression of NaOL adsorption, making the flotation of calcite more moderate to separate from witherite.

### 3.5. XPS analysis

As a surface-sensitive technique, XPS has been widely applied in the analysis of mineral surface properties (Chen et al., 2014; Peng et al., 2012; Wang et al., 2014; Zhao et al., 2015). Table.2 summarizes the atomic compositions of witherite and calcite interfaces before and after $K_2CrO_4$ and NaOL treatments. With the addition of $K_2CrO_4$ and NaOL, the atomic concentrations of C, O, and Cr were increased but that of Ca was decreased on the surface of calcite, indicating an obvious adsorption of $K_2CrO_4$ but a small adsorption of NaOL. For witherite, contrary to the result of calcite, there was a noticeable augment in the atomic concentration of C and a small increase in the atomic concentration of Cr, along with a decrease in the concentrations of Ba and O, which identify ther high adsorption of NaOL and the small amount of adsorbed $K_2CrO_4$.

The XPS high-resolution spectra of C 1s, Ca 2p or Ba 2p on witherite and calcite with and without the treatments of $K_2CrO_4$ and NaOL are shown in Fig. 5 and Fig. 6, respectively. Fig. 5 indicated that the binding energies of C 1s peaks in calcite were located at 288.30 and 283.92 mV, which were shifted to other values with the addition of $K_2CrO_4$ and NaOL, implying that there was a weak chemisorption of NaOL on the surface of calcite. The binding energies of Ca 2p appeared at approximately 345.78 and 349.28 mV and were shifted to smaller values at approximately 345.39 and 349.15 mV after the treatments of $K_2CrO_4$ and NaOL, implying that $K_2CrO_4$ could chemisorb with Ca atoms on the surface of calcite. These phenomena illuminated that the addition of $K_2CrO_4$ and NaOL changed the chemical circumstance of Ca atoms on the surface but seldom changed that of superficial C.

Table 2. Atomic concentration of elements on the mineral interfaces by XPS

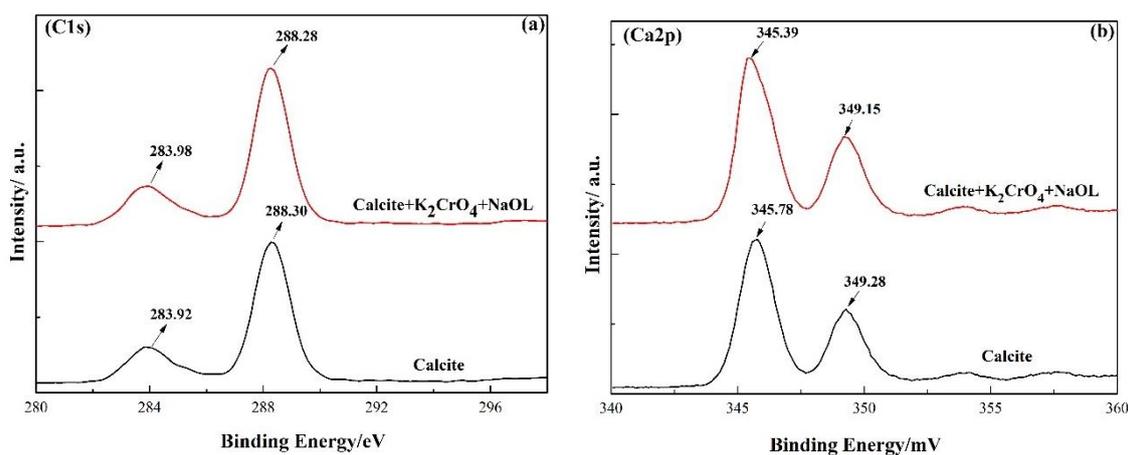| Samples | Atomic concentration of elements/% | | | | |
|---|---|---|---|---|---|
| | Ca | Ba | C | O | Cr |
| Calcite | 17.41 | / | 24.92 | 57.67 | 0 |
| Calcite+K₂CrO₄+NaOL | 11.93 | / | 26.79 | 58.96 | 2.37 |
| Δ | -5.48 | / | 1.87 | 1.29 | 2.37 |
| Witherite | / | 17.58 | 28.45 | 53.97 | 0 |
| Witherite+K₂CrO₄+NaOL | / | 9.07 | 47.78 | 42.71 | 0.44 |
| Δ | / | -8.51 | 19.33 | -11.26 | 0.44 |

"*Δ*"- *The variation of atomic concentration*



Fig. 5. XPS high-resolution spectra of C 1s, Ca 2p on calcite with and without the treatment of $K_2CrO_4$ and NaOL: (a) C 1s; (b) Ca 2p
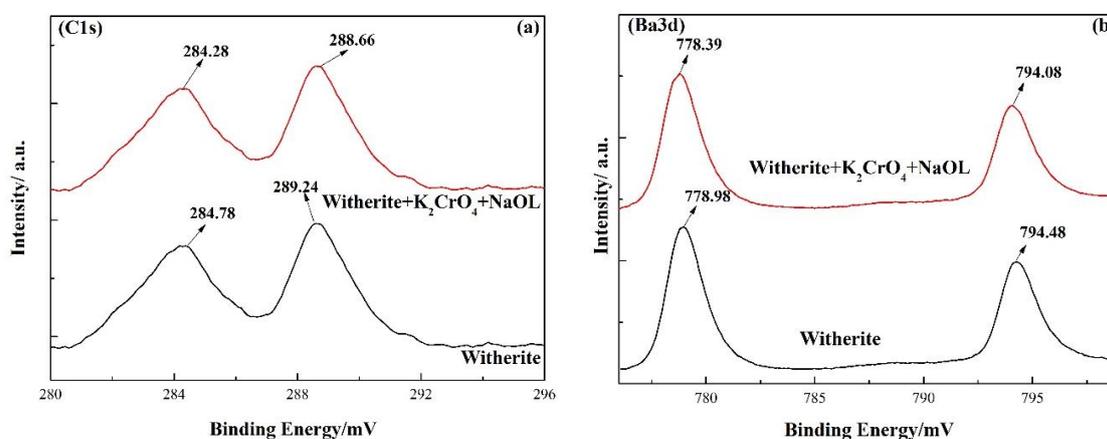


Fig. 6. XPS high-resolution spectra of C 1s, Ba 3d on witherite with and without the treatment of $K_2CrO_4$ and NaOL: (a) C 1s; (b) Ba 3d

Fig. 6 shows that the binding energies of C 1s and Ba 3d of witherite experienced a notable change before and after the addition of $K_2CrO_4$ and NaOL. Specifically, the binding energy of C 1s on witherite treated by $K_2CrO_4$ and NaOL was located at 289.24 and 284.78 mV, significantly different from the binding energies of 288.66 and 284.28 mV without the treatments, which can be attributed to the carboxyl or carbonyl groups of sodium oleate (Jin et al., 2016; Takahagi et al., 1984). The findings could reveal that sodium oleate was chemisorbed on the surface of witherite effectively. In addition, the great changes in binding energy of Ba 3d from 794.48 and 778.98 mV to 794.08 and 778.39 mV indicated the chemical interaction between the anionic molecules and superficial barium atoms. These performances clarified that sodium oleate had a high negative charge and could combine with the barium atoms effortlessly with a fantastic collectability on witherite in the absence or presence of potassium chromate.

## 4.  Conclusions

Witherite and calcite showed a slight difference in the flotation behaviors when NaOL was used as the collector during batch flotation experiments of single minerals, with a slightly higher recovery being observed for witherite. The flotation experiments for artificial mixtures showed that the difference in the recovery of witherite and calcite became more conspicuous in the presence of $K_2CrO_4$, reaching the maximum at pH 9. These findings were in agreement with the results of contact angle measurements.

Witherite showed a better adsorption capability for NaOL *vs.* $K_2CrO_4$, contrary to the result of calcite on account of the zeta potential measurement. In addition, the addition of $K_2CrO_4$ had a good effect on the depression of NaOL adsorption on calcite surface, but poorly influenced the adsorption on witherite surface.

XPS measurements confirmed that NaOL had a strong chemical interaction with witherite in the presence of $K_2CrO_4$ but had weak and even absent adsorption on the calcite surface under the same circumstance. In addition, NaOL and $K_2CrO_4$ were found to be adsorbed on the surfaces of witherite and calcite via chemical interaction with barium or calcium atoms. With the treatments of $K_2CrO_4$ and NaOL, witherite can be separated from calcite effectively by the means of forth flotation.

## Acknowledgments

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