Flotation behaviour and surface characteristic of anosovite in a sodium oleate solution

Yijie Wang[*], Shuming Wen[*], Junhui Zhang[**], Dandan Wu[*], Yongjun Xian[*], Haiying Shen[***]

[*] State Key Laboratory of Complex Nonferrous Metal Resources Clean Utilization, Kunming University of Science and Technology, Kunming 650093, China. Corresponding authors: shmwen@126.com (Shuming WEN), 61470281@qq.com (Yongjun XIAN)

[**] Institute of Mineral Resource Comprehensive Utilization, Chinese Academy of Geological Sciences, Chengdu 610041, China

[***]Faculty of Foreign Languages and Cultures, Kunming University of Science and Technology, Kunming 650093, China

Abstract: Properties of anosovite in titanium slag, anosovite flotation response in a collector solution of sodium oleate, and adsorption behaviour of sodium oleate on the mineral surface were studied in the present work using XRD, Raman spectra, flotation tests, zeta potential analysis, FTIR and XPS. The results show that the anosovite crystal contains magnesium, and its chemical composition is $Mg_{0.09}Ti_{2.91}O_5$. The chemical bonds on the anosovite surface mainly comprise Ti-O bonds. Micro-flotation tests indicate that anosovite has better floatability at a wide pH range and the recovery reaches 88% at pH=6, when the dosage of sodium oleate is only $4 \cdot 10^{-6}$ mol/dm^3. The point of zero charge of anosovite was determined near pH 3.2 by the zeta potential measurement. In the flotation process, chemical adsorption occurs between the carboxyl of sodium oleate and the titanium sites on the anosovite surface.

Keywords: anosovite, sodium oleate, flotation, adsorption

Introduction

Titanium is mostly extracted from titanium-bearing minerals. Ilmenite and rutile are the most economically resource among titanium minerals. Most rutile concentrates are used to produce titanium sponge and titanium dioxide by chlorination. This process requires high-grade TiO_2 and low impurities (Kang and Okabe, 2013). Ilmenite concentrates are generally enriched to the titanium slag because of their low-grade TiO_2 and high contents of iron and other impurities. However, due to the limit of ilmenite concentrate quality, most titanium slag still has difficulty satisfying the

production requirements of titanium sponge and chloride-process titanium dioxide (Zhang et al., 2011). Therefore, the upgrading of titanium slag is an urgent need in the titanium industry.

Flotation can be implemented to upgrade titanium slag, as it has long served the mineral processing field as a mature technology (Bahri et al., 2016; Albrecht et al., 2016). The primary titanium mineral in the titanium slag is anosovite, which belongs to artificial mineral. The surface properties of anosovite and natural minerals have a big difference due to their different minerogenetic conditions. However, the research on flotation behaviour and surface characteristics of anosovite is limited. Thus, it is necessary to study the flotation behaviour and mechanisms between anosovite and collectors.

In the flotation process, collectors are selectively adsorbed on a valuable mineral surface, rendering the surface hydrophobic. Afterwards, the minerals adhere to bubbles and float. Therefore, the study of the collectors role on mineral surfaces is the basis of mineral flotation separation. Sodium oleate is a typical collector of oxide ore, and it is also the representative of fatty acid collectors. It has universal significance to study the adsorption mechanism of sodium oleate on the anosovite surface. In addition, sodium oleate has been applied to flotation of natural titanium minerals, such as rutile and ilmenite (Zhu et al., 2011; Wang et al., 2014; Zhang et al., 2015; Liu et al., 2015). As a result, sodium oleate was selected as the collector for flotation of artificial mineral anosovite.

In the present work, flotation tests were first conducted to reveal the effects of pulp pH and sodium oleate dosage on anosovite flotation response. The adsorption behaviour of sodium oleate on the anosovite surface was also determined by the zeta potential measurement, Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS). Overall, this study will contribute to the understanding of anosovite floatability and separation between anosovite and gangue minerals.

Experimental

Materials

The anosovite samples used in the study were from Wuding County, China. The samples were produced by the electric furnace smelting process with the raw materials of ilmenite concentrates. The chemical composition of the anosovite samples is shown in Table 1. The grade of TiO_2 was 93.45%, and the content of Mg, Ca, Si and Al impurities was low.

The X-ray diffraction (XRD) results of the anosovite ore samples are shown in Fig. 1. From the spectra, the anosovite crystal is well developed, and the main characteristic peaks are obvious. Furthermore, the anosovite crystal is doped with magnesium, and its chemical composition is $Mg_{0.09}Ti_{2.91}O_5$.

Table 1. Chemical composition of anosovite ore (wt%)

TiO_2	Fe	Cr	V	Al_2O_3	SiO_2	CaO	MgO
93.45	0.36	0.019	0.084	2.52	2.56	0.31	0.59

The Raman spectra of the anosovite ore samples are shown in Fig. 2. In the measured Raman spectra, three characteristic peaks at 169.0, 402.6 and 605.9 cm^{-1} were observed. The 169.0 cm^{-1} peak is caused by symmetric stretching vibrations of Ti-O. The 402.6 cm^{-1} peak is caused by symmetric bending vibrations of Ti-O, and the 605.9 cm^{-1} peak is caused by both symmetric stretching vibrations and bending vibrations of Ti-O (Xiao et al., 2007). Ti-O bonding is observed to be the main chemical bond on the anosovite surface.
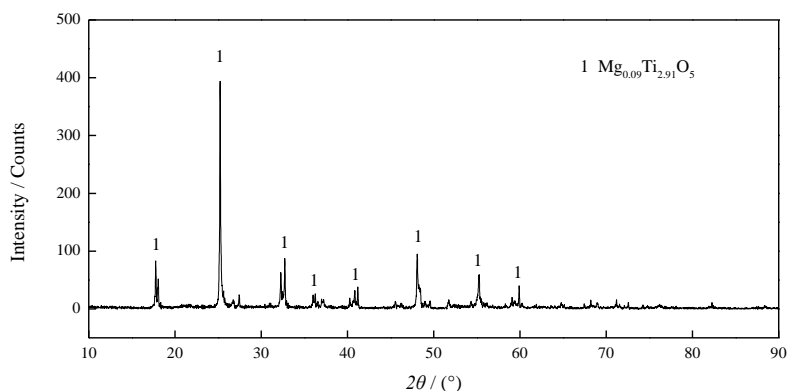

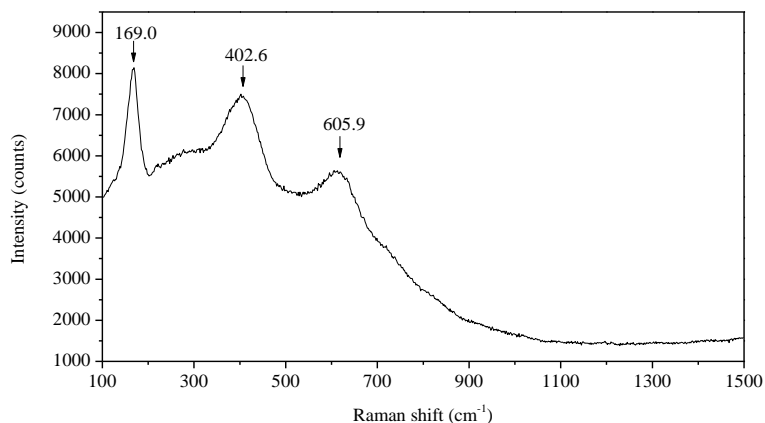Fig. 1. XRD spectra of the anosovite ore samples

Fig. 2. Raman spectra of anosovite ore samples

Flotation test

A 40-cm^3 hanging laboratory flotation machine at a revolving speed of 1900 r/min was used to test the flotation behaviour of anosovite. Deionised water with a resistivity of <18 MΩ.cm was used throughout the flotation tests, and all tests were performed at room temperature. Up to 3 g of anosovite (−140+200 µm) was transferred into the flotation cell. After stirring for 1 min, the pH value of the flotation pulp was adjusted using NaOH and HCl (analytical reagent) solutions. The collector (sodium oleate, analytical reagent) and frother (pine oil, technically pure) were then added and stirred for 3 and 1 min, respectively. Afterwards, the flotation pulp was aerated and floated for 3 min, and the product was collected and dried to calculate the recovery. Each test was performed three times and the average recovery was calculated.

XRD analysis

The mineral composition of the anosovite ore was characterised by XRD (D/Max 2200, Rigaku, Japan) with Cu-K$_\alpha$ radiation (λ = 0.154056 nm, 40 kV, 200 mA) over the 2θ range of 10° to 90° at a scanning rate of 3°/min.

Raman analysis

The LabRAM HR Evolution Raman spectrometer produced by Horiba Jobin Yvon was used for Raman spectroscopy in this study. The laser wavelength was 532 nm. The resolution was 1 cm^{-1}, and the integral number was five.

Zeta potential measurement

The zeta potential ζ was measured using a zeta potential instrument (Zeta Plus) from Brookhaven Instruments Corporation. Up to 0.1 g of 5 µm anosovite was placed in a solution with a certain pH, and sodium oleate was added to the solution. The solution was stirred for 10 min using a magnetic stirrer, and then allowed to rest for 10 min. The pH of up to 1.5 cm^3 of supernatant, pipetted by a sampler, was measured in a measurement cell. The zeta potential was measured 10 times and the average value was calculated.

FTIR analysis

The potassium bromide squash method was used in the FTIR study. One gram of anosovite (5 µm) was added to the 40 cm^3 sodium oleate solution and stirred for 5 min. Subsequently, the suspensions were filtered and rinsed three times with deionised water. Finally, the samples were air dried. The FTIR spectra (Tensor27, Bruker, Germany) were recorded in the range of 400 cm^{-1} to 4000 cm^{-1} with a spectral resolution of 4 cm^{-1} and a scan number of 10.

XPS analysis

The preparation methods of the test samples used in the XPS study were consistent with the methods used in the FTIR analysis. The XPS analysis was conducted with a PHI 5000 Versa Probe II spectrometer (ULVAC-PHI, Japan) using an Al K_α irradiation X-ray source. The pressure in the analyser chamber was 10^{-8} Pa. MultiPak Spectrum software was used to analyse the spectra. C_{1s} binding energy (284.8 eV) was used to calibrate the $Ti_{2p3/2}$ and $Ti_{2p1/2}$ peaks.

Results and discussion

Effect of pH and sodium oleate dosage on anosovite flotability

The pH value of ore pulp and the collector dosage can clearly influence the floatability of minerals. Therefore, these two factors are discussed in this section. Figure 3 shows the effect of pH on the flotation recovery of anosovite at a sodium oleate concentration of $2\cdot10^{-6}$ mol/dm^3. As shown in Fig. 3, sodium oleate demonstrates a good collector performance for anosovite at a relatively wide pH range from 4 to 9 with a maximum recovery approximately 80%. However, the recovery declines sharply at pH<4 and pH>9, indicating poor floatability of anosovite in the sodium oleate solution at this pH range. The reason may be adsorption of collectors reduced.

The effect of sodium oleate dosage on the flotation recovery of anosovite at pH = 6 is shown in Fig. 4. The results show that anosovite recovery increases with increasing sodium oleate concentration but then declines slightly. The recovery reached its highest point of 88.24% when the dosage of sodium oleate was $4\cdot10^{-6}$ mol/dm^3.

Compared with the natural titanium minerals, such as ilmenite and rutile, anosovite exhibited an excellent floatability in small amount sodium oleate solution at a relatively wide pH range. These results indicate that anosovite has a high surface activity, which is different from natural titanium minerals.
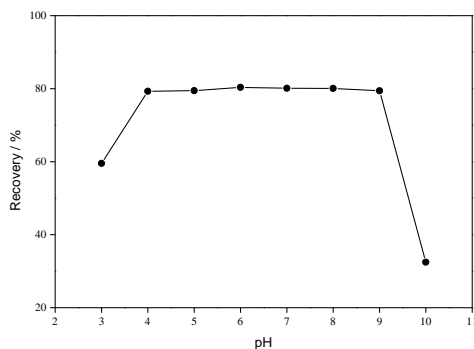

Fig. 3. Effect of pH on flotation recovery of anosovite
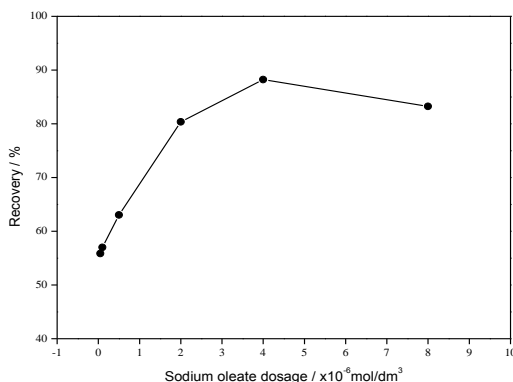at a sodium oleate concentration of $2\cdot10^{-6}$ mol/dm^3

Fig. 4. Effect of sodium oleate dosage on flotation recovery of anosovite at pH = 6

Effect of sodium oleate on anosovite surface potential

The relationship between pH value and $\log C$ of the sodium oleate solution components at C_T of $4 \cdot 10^{-6}$ mol/dm^3 was calculated, and the result is shown in Fig. 5.
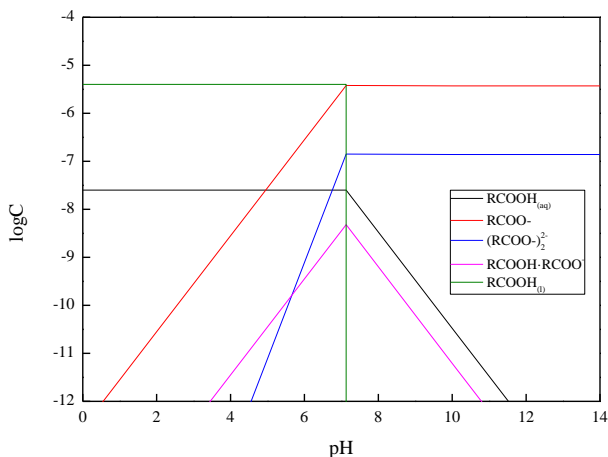

Fig. 5. Log$C$-pH diagram of sodium oleate solution components, $C_T = 4 \cdot 10^{-6}$ mol/dm^3

Figure 6 shows the zeta potential of anosovite in deionised water and sodium oleate solution. As shown in Fig. 6, when anosovite is in deionised water, the point of zero charge (PZC) can be detected near pH 3.2. However, the existence of sodium oleate shifted the anosovite PZC from pH 3.2 to 2.8.

The zeta potential of the anosovite surface was positive at pH < 3.2 and shifted in a negative direction after adding sodium oleate. This finding indicates that sodium oleate adsorbed on the surface of the anosovite. The adsorption is electrostatic adsorption or chemisorption.

At pH > 3.2, the zeta potential of anosovite in the sodium oleate solution also shifted in a negative direction compared to anosovite in deionised water, especially in the pH range in which anosovite enhances recovery. In this pH range, the concentrations of $RCOO^-$, $(RCOO-)_2^{2-}$ and $RCOOHRCOO^-$ increase rapidly, particularly those of $RCOO^-$ and $(RCOO-)_2^{2-}$, as shown in Fig. 6. Therefore, the increasing level of anion adsorption on the anosovite surface leads to a significant decrease in the zeta potential. With the increase in pH, the concentrations of $RCOO^-$ and $(RCOO-)_2^{2-}$ become stable, and the $RCOOHRCOO^-$ concentration gradually decreases. Thus, the adsorption capacity of anions on the mineral surface decreases, and the changes in the zeta potential value are no longer apparent. At pH>3.2, the ions of sodium oleate, which exhibit the same charge as the mineral surface, can effectively be adsorbed onto the mineral surfaces, indicating that the adsorption of sodium oleate on anosovite is not electrostatic adsorption but chemisorption.
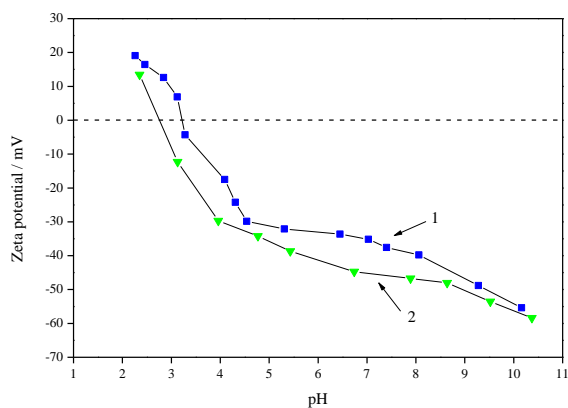

Fig. 6. Zeta potential of anosovite in deionised water (1) and sodium oleate solution (2)

FTIR study of anosovite reacted with sodium oleate

Figure 7 shows the FTIR spectra of sodium oleate. The asymmetric stretching vibrations and symmetric stretching vibrations of $-CH_2-$ in sodium oleate exhibit peak values of 2921.47 and 2851.37 cm^{-1}, respectively. The $-COO-$ characteristic peak value of 1561.15 cm^{-1} is attributed to an asymmetric stretching vibration, whereas the peaks at 1446.40 and 1425.06 cm^{-1} are attributed to symmetric stretching vibrations. The peaks at 722.10 and 698.91 cm^{-1} are attributed to bending vibrations of $-(CH_2)_n-$ (Tandon et al., 2001; Nájera, 2007; Liu et al., 2015).

The FTIR spectra of anosovite before and after reaction with sodium oleate are shown in Fig. 8, in which new absorption peaks are observed after anosovite reacted with the collector. The peaks at 2919.90 and 2854.20 cm^{-1} are $-CH_2-$ characteristic peaks of sodium oleate. However, the peaks frequency almost did not change compared with Fig. 7. This finding demonstrates that sodium oleate is adsorbed on the

anosovite surface. The new absorption peak at 1435.57 cm^{-1} is attributed to the symmetric stretching vibration of -COO-, and it shifts by 10.51 cm^{-1} in contrast with the 1425.06 cm^{-1} peak of sodium oleate. The appearance of a 1435.57 cm^{-1} peak indicates the occurrence of chemical adsorption of carboxyl on the anosovite surface.
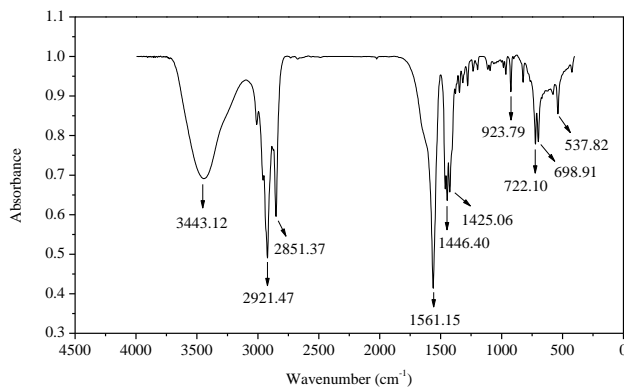
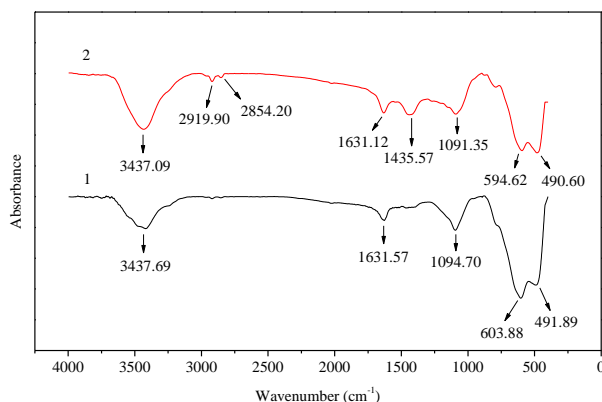Fig. 7. FTIR spectra of sodium oleate

Fig. 8. FTIR spectra of anosovite before (1) and after (2) reaction with sodium oleate

XPS study of anosovite reacted with sodium oleate

XPS can be used to study the chemical state of elements on the mineral surface, which provides adsorption information of the collector. The binding energy of Ti$_{2p}$ was measured before and after anosovite reacted with the collector sodium oleate. The results after fitting are shown in Fig. 9. The binding energies of Ti$_{2p3/2}$ and Ti$_{2p1/2}$ on the anosovite mineral surface are 458.56 and 464.26 eV, respectively (Hoang et al., 2012; Eskandarloo et al., 2016; Liu et al., 2016). After conditioning anosovite with sodium oleate, The binding energies of Ti2p changed from 458.56 and 464.26 eV to

458.92 and 464.62 eV, with an energy difference of 0.36 eV. This change in Ti_{2p} binding energy demonstrates that the chemical environment of Ti transformed and chemical adsorption occurred at the Ti sites on the anosovite surface. Further, the XPS analysis results are consistent with the FTIR spectra and zeta potential, indicating that the adsorption of carboxyl on the Ti sites result in anosovite flotation.
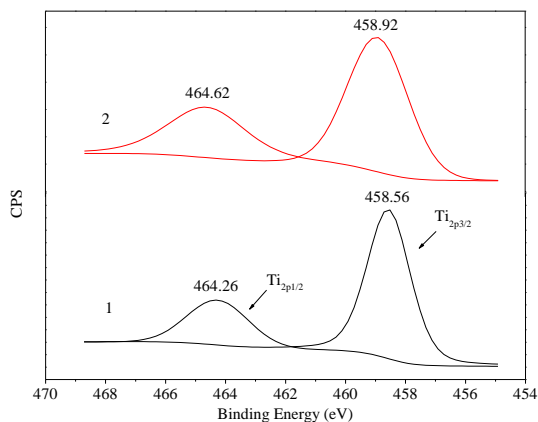

Fig. 9. Ti_{2p} XPS spectra of anosovite (1) and anosovite reaction with sodium oleate (2)

Conclusions

This work demonstrates the flotation behaviour and surface characteristics of artificial mineral anosovite in a sodium oleate solution. Analyses of the anosovite properties show that the TiO_2 grade of the anosovite ore sample is 93.45%, and its chemical composition is $Mg_{0.09}Ti_{2.91}O_5$. The Ti-O bond is the primary chemical bond on the anosovite surface. Micro-flotation tests indicate that sodium oleate exhibits a good collector performance for anosovite at a relatively wide pH range of 4 to 9. Moreover, an excellent recovery can be achieved using only a small amount of sodium oleate, suggesting that anosovite demonstrates good flotability. The PZC of anosovite was determined near pH 3.2. After anosovite reacts with sodium oleate, the zeta potential of anosovite shifts to the negative direction. Subsequently, new FTIR absorption peaks appeare, and the binding energies of Ti_{2p} change in the XPS analyses. Overall, these results indicate that chemical adsorption of carboxyl occurs at the titanium sites on the anosovite surface.

References

ALBRECHT T.W.J., ADDAI-MENSAH J., FORNASIERO D., 2016, *Critical copper concentration in sphalerite flotation: Effect of temperature and collector,* International Journal of Mineral Processing 146, 15-22.

BAHRI Z., REZAI B., KOWSARI E., 2016, *Selective separation of gallium from zinc using flotation: Effect of solution pH value and the separation mechanism,* Minerals Engineering 86, 104-113.

ESKANDARLOO H., HASHEMPOUR M., VICENZO A., FRANZ S., BADIEI A., BEHNAJADY M.A., 2016, *Bestetti M. High-temperature stable anatase-type TiO_2 nanotube arrays: A study of the structure-activity relationship,* Applied Catalysis B: Environmental 185, 119-132.

HOANG S., BERGLUND S.P., HAHN N.T., BARD A.J., MULLINS C.B., 2012, *Enhancing visible light photo-oxidation of water with TiO_2 nanowire arrays via cotreatment with H_2 and NH_3: Synergistic effects between Ti^{3+} and N,* Journal of the American Chemical Society 134, 3659-3662.

KANG J., OKABE T.H., 2013, *Removal of iron from titanium ore through selective chlorination using magnesium chloride,* Materials Transactions 54, 1444-1453.

LIU C., FENG Q.M., ZHANG G.F., 2015, *Electrokinetic and flotation behaviors of hemimorphite in the presence of sodium oleate,* Minerals Engineering 84, 74-76.

LIU J., DUAN X.L., ZHANG Y., LI Z.Q., YU F.P., JIANG H.D., 2016, *Growth, electronic structure and properties of $Rb_2Ti_{1.95}Yb_{0.05}(PO_4)_3$ crystals,* Journal of Alloys & Compounds 660, 356-360.

LIU W.J., ZHANG J., WANG W.Q., DENG J., CHEN B.Y., YAN W., XIONG S.Q., HUANG Y., LIU J., 2015, *Flotation behaviors of ilmenite, titanaugite, and forsterite using sodium oleate as the collector,* Minerals Engineering 72, 1-9.

NÁJERA J.J., 2007, *Phase transition behaviour of sodium oleate aerosol particles,* Atmospheric Environment 41, 1041-1052.

TANDON P., RAUDENKOLB S., NEUBERT R.H.H., RETTIG W., WARTEWIG S., 2001, *X-ray diffraction and spectroscopic studies of oleic acid-sodium oleate,* Chemistry & Physics of Lipids 109, 37-45.

WANG J., CHENG H.W., ZHAO H.B., QIN W.Q., QIU G.Z., 2014, *Flotation behavior and mechanism of rutile in presence of sodium oleate,* The Chinese Journal of Nonferrous Metals 24, 820-825.

XIAO P., ZHENG S.B., YOU J.L., JIANG G.C., CHEN H., ZENG H., 2007, *Structure and Raman spectra of titanium oxides,* Spectroscopy and Spectral Analysis 27, 936-939.

ZHANG J., LIU W.J., WANG W.Q., XIONG S.Q., WANG D.Z., YAN W., DENG J., 2015, *Flotation characteristics of two different types of ilmenite with sodium oleate,* Mineralogy & Petrology 109, 299-306.

ZHANG W.S., ZHU Z.W., CHENG C.Y., 2011, *A literature review of titanium metallurgical processes,* Hydrometallurgy 108, 177-188.

ZHU Y.G., ZHANG G.F., FENG Q.M., YAN D.C., WANG W.Q., 2011, *Effect of surface dissolution on flotation separation of fine ilmenite from titanaugite,* Transactions of Nonferrous Metals Society of China 21, 1149-1154.