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Electrokinetic and flotation behavior of rutile in the presence of lead ions and aluminium ions

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Abstract: The effects of Pb(II) ions and Al(III) ions on the electro kinetic and flotation behavior of rutile were investigated by micro-flotation tests, zeta potential measurements and solution chemistry analysis. Micro-flotation results indicate that the Pb(II) ions can effectively improve the flotation recovery of rutile while the Al(III) ions significantly inhibit the flotation of rutile. Zeta potential measurements reveal that a collector styrene phosphoric acid (SPA) can adsorb on the rutile surface after the addition of Pb(II) ions, but hardly adsorb on the rutile surface after the addition of Al(III) ions. Pb(II) ions adsorb on the rutile surface in the form of $\text{Pb}(\text{OH})^+$ and $\text{Pb}(\text{OH})_{2(s)}$, and the latter one is the main reason that activates rutile flotation. Al(III) ions adsorb on the rutile surface mainly in the form of $\text{Al}(\text{OH})_{3(s)}$, which prevent the direct interaction between the rutile and the collector, resulting in a decrease of rutile flotation recovery.

Keywords: lead ions, aluminium ions, rutile, flotation

1. Introduction

Rutile is a crucial raw material for the extraction of titanium and the production of titanium dioxide. Titanium dioxide products are widely used in military aviation, aerospace, navigation, machinery, chemical industry, and seawater desalination (McNulty, 2007; Stanaway, 1994). Rutile is an oxidized mineral of formula TiO_2 and is usually collected by flotation with collectors for oxidizing ore, such as fatty acids, phosphate and hydroxamate collectors (Diebold, 2003; Llewellyn and Sullivan, 1982; Madeley and Graham, 1966; Wang et al., 2016; Wang et al., 2014). The composite collector composed of the mixture of styrene phosphoric acid (SPA) and fatty alcohol shows a good flotation performance for rutile. The mechanism of the adsorption of this composite collector on rutile is the association effect of fatty alcohol with strong hydrophobicity and the chemisorption of SPA on rutile surface. This adsorption increases the hydrophobicity of rutile surface, thereby enhancing the rutile flotation performance (Liu and Peng, 1999).

In industrial flotation, there are many kinds of metal ions in the pulp. These unavoidable ions have a great influence on the flotation behaviour of minerals, especially the oxide minerals (James and Healy, 1972; Li et al., 1982). Some metal ions can activate mineral flotation. However, some metal ions can inhibit mineral flotation (Cooke, 1949; Fan and Rowson, 2000; Lazaridis et al., 1992; Scott and Smith, 1993; Shi et al., 2013). There are several viewpoints of the activation mechanism of multivalent metal cations in mineral flotation. Fuerstenau proposed that metal ion hydroxyl complex is the main component of activation (Fuerstenau and Raghavan, 1976; Fuerstenau and Palmer, 1976). James holds

the point that the surface precipitation of metal hydroxide is the main active component (Ejtemaei et al., 2012; James and Healy, 1972; Jie et al., 2014; Luo et al., 2017b). According to the adsorption capacity and theoretical analysis of metal ions, the solubility product of metal hydroxide in the interface is smaller than that in solution. Therefore, the metal hydroxide will preferentially occur hydroxide precipitation on the mineral surface than in the solution, and then play an active role. Hu Yuehua and other scholars also hold this view (Hu and Wang, 1987) Sun Chuanyao, Yin Wanzhong and other scholars have studied the effect of different metal ions on the floatability of five kinds of sodium silicate minerals. They found that small radius metal cations mainly adsorb on the mineral surface in the form of hydroxide precipitation, while the large radius metal cations are mainly in the form of hydroxyl complex. For metal cations with medium valence and radius, both hydroxide precipitates and hydroxyl complexes exist (Lin et al., 2003; Nagaraj and Brinen, 1997; Yin and Sun, 2002). The inhibition effect of metal ions on mineral flotation are caused by the fact that metal ions consume collector or hinder adsorption on the mineral surface (Ananthapadmanabhan and Somasundaran, 1985; Deng et al., 2017; Fuerstenau et al., 1988).

In previous studies, we found that lead ions and aluminium ions have different influence on the flotation behaviour of rutile. In the presence of composite collector of SPA and fatty alcohol, lead ions could improve the flotation recovery of rutile, whereas aluminium ions could reduce the rutile recovery. The activation effect of lead ions on the flotation of rutile and ilmenite have been studied (Chen et al., 2017; Li et al., 2016). However, the inhibition mechanism of aluminium ion on the flotation of rutile is still unclear.

The present work, studies the role of lead ions and aluminium ions on the flotation behaviour of rutile using micro-flotation, zeta potential, and solution chemistry analysis. Compared to the previous studies (Li et al., 2016; Xiao et al., 2017), the effects of lead ions and aluminium ions on electro kinetic and flotation behaviour of rutile are systematically compared. Furthermore, solution species are discussed in detail to delineate their effect on the flotation behaviour of rutile in the studied system.

2. Materials and methods

2.1. Samples and reagents

The ore samples of rutile were obtained from Zaoyang of Hubei Province, China. The samples were crushed and ground in a porcelain mill with an agate ball. Then, the powder samples were sieved, and the -0.074 +0.038 mm size fraction was chosen for micro-flotation tests. The ore was analysed via a chemical method, and phase-examined using powder X-ray diffraction (XRD). The XRD patterns of the rutile sample shown in Fig. 1 are in agreement with the previous values reported by Li and Xiao (Li et al., 2016; Xiao et al., 2017). The chemical compositions of the samples are listed in Table 1. Based on the results it was determined that the purity of rutile is very high and meets the criteria for micro-flotation.

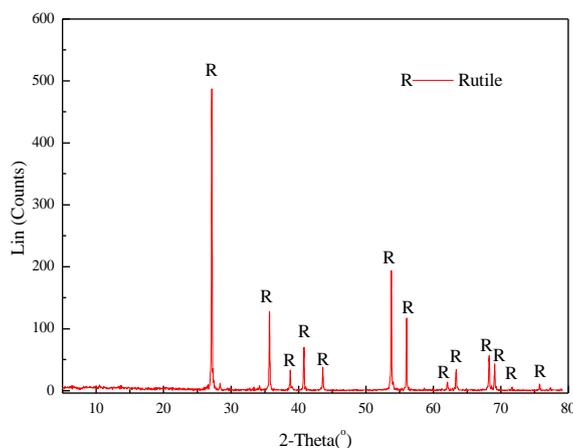


Fig. 1. XRD patterns of the rutile sample

The mixture of styrene phosphoric acid (SPA) and octanol (OCT) was used as the composite collector for the micro-flotation tests. Lead nitrate (PbNO_3) and aluminium chloride hexahydrate ($\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$)

were used as the source of lead ions and aluminium ions. HCl and NaOH were used as pH modifiers. All the reagents used in the experiments were of analytical grade, and the water used was distilled water.

Table 1. Chemical composition of rutile ore

TiO ₂	FeO	Fe ₂ O ₃	SiO ₂	CaO	MgO	Al ₂ O ₃	Other
93.8	1.43	1.23	1.97	0.15	0.31	0.79	0.32

2.2. Micro-flotation tests

The micro-flotation tests were carried out in a 40 mL plexiglass cell using an XFG-type flotation machine. 2.0 g of mineral samples was used for each experiment and the spindle speed was kept at 1600 rpm. The pulp was continuously stirred for 1 min after adding pH modifiers, then for 3 min after adding metal ions, and 3 min after adding collector. The pH of the solution was measured before the flotation, and the flotation was conducted for 3 min. The concentrate and tailing samples were collected separately and filtered, dried, and weighed to calculate the flotation recovery. All of the flotation tests were completed three times, and the average recovery and the standard deviation were reported.

2.3. Zeta potential measurements

Zeta potential measurements were performed in 1×10^{-3} mol/L KNO₃ background electrolyte solution using the Coulter Delsa440sx Zeta analyzer instrument. The samples were ground to $-5 \mu\text{m}$ before measurement. The suspensions were prepared by adding 20~30 mg samples to the beaker with 40 mL of the electrolyte solution. Then pH regulators were used to adjust the pH. Next, the respective reagents were added in the order of lead nitrate (aluminium chloride hexahydrate) and SPA. Then the suspensions were magnetically stirred for 15 min in the presence of different concentration of reagents at various pH values and then settled for 5 min. After that, the supernatant was obtained for zeta potential measurements. Each sample was tested for three times, and the average value was taken as the final result. The standard deviation in each case was also calculated and reported.

3. Results and discussion

3.1. Micro-flotation results

The objective of this study is to investigate the effects of lead ions and aluminium ions on the flotation of rutile in the presence of the composite collector (SPA and OCT). The flotation results of rutile as a function of pH values with 600 mg/L collector (300 mg/L SPA, 300 mg/L OCT) in the presence and absence of lead ions and aluminium ions are shown in Fig. 2. In the absence of metal ions the rutile shows a good flotation recovery (over 70%) in the pH range 2-9. This good recovery is attributed to the strong collecting capacity of the composite collector for rutile. In the presence of lead ions, the recovery of rutile further increases, especially in the range of pH8.5-11. It reaches the maximum value, approximately 84%, at a pH of 11. Compared to the condition of the absence of lead ions, the rutile recovery increases by roughly 8% in the pH range of 2-10. In the presence of lead ions, the flotation recovery is significantly higher at a pH of approximately 11. In the presence of aluminium ions, the flotation recovery of rutile decreases sharply with the increase of pH, and remains constant after reaching approximately 3% at a pH of 5.3, which means the flotation of rutile is almost inhibited.

The flotation recovery of rutile as a function of lead ions and aluminium ions concentration in the presence of 600 mg/L collector (300 mg/L SPA, 300 mg/L OCT) at pH 5.5 is shown in Fig. 3. The flotation results demonstrate that the recovery of rutile increases slightly and then decreases slightly with the increase of lead ions initial concentration. It means that the low concentration of lead ions has an activation effect on rutile. However, with the increase of aluminium ions initial concentration, the flotation recovery of rutile decreases rapidly, and when the aluminium ions concentration reached 1×10^{-3} mol/L, the rutile is completely inhibited.

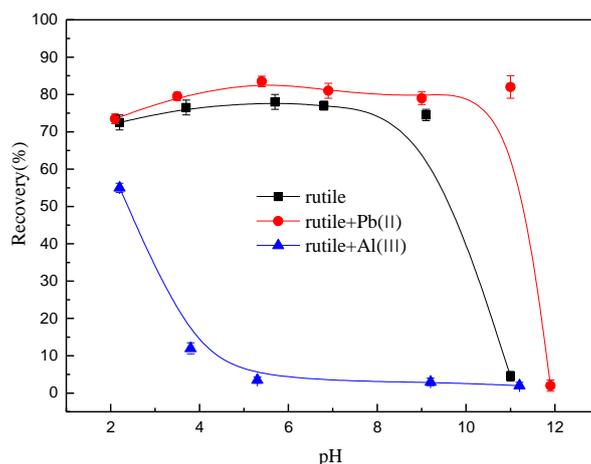


Fig. 2. Flotation recovery of rutile as a function of pH ($C_{\text{collector}} = 600 \text{ mg/L}$, $C_{\text{SPA}} = 300 \text{ mg/L}$, $C_{\text{OCT}} = 300 \text{ mg/L}$; $C_{\text{Pb(II)}} = 10^{-4} \text{ mol/L}$; $C_{\text{Al(III)}} = 10^{-3} \text{ mol/L}$)

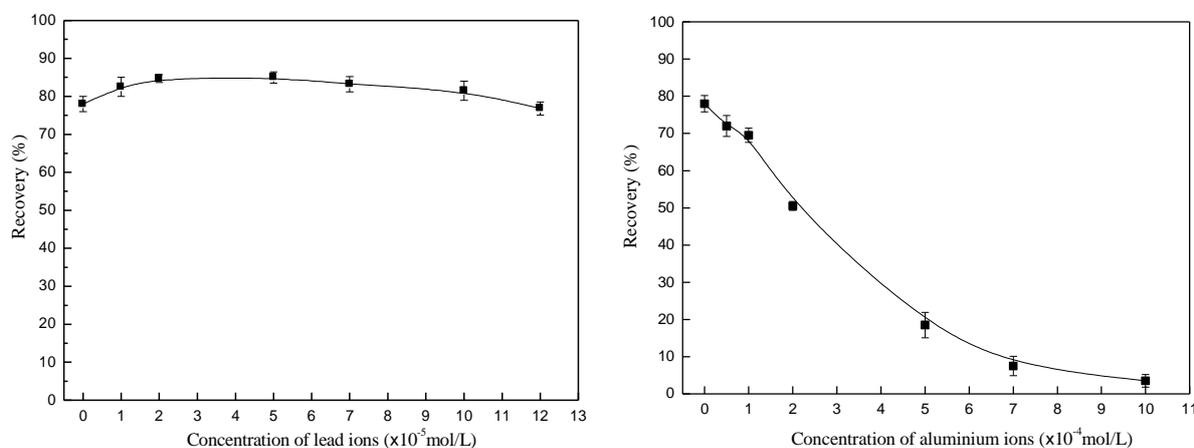


Fig. 3. Flotation recovery of rutile as a function of Pb(II) and Al(III) concentration at pH 5.5 ($C_{\text{collector}} = 600 \text{ mg/L}$, $C_{\text{SPA}} = 300 \text{ mg/L}$, $C_{\text{OCT}} = 300 \text{ mg/L}$)

3.2. Zeta potential results

The zeta potential of rutile as a function of pH in the absence and presence of lead ions are shown in Fig. 4. The point of zero charge (PZC) of rutile occurs at pH 4.1. When $\text{pH} > \text{PZC}$, the charge of rutile surface switches from positive to negative, which is in agreement with the previous values reported (Parks, 1965; Wang et al., 2016; Xiao et al., 2017). In the presence of 300 mg/L SPA, the zeta potential of rutile shifts to more negative at acidic, indicating that the adsorption of SPA on rutile surface has happened. When $\text{pH} < 4$, anionic collector SPA adsorbs on rutile surface through electrostatic forces. In the pH range between 4 and 9, SPA adsorbs on rutile surface via specific adsorption. The zeta potential of rutile in the presence of OCT was also measured, the results indicate OCT has almost no effect on the electro kinetic behaviour of rutile. In the presence of lead ions, the zeta potential of rutile becomes more positive at the same pH value. When $\text{pH} < 4.1$, the positive shift is lower, which is attributed to the fact that the positive surface charge of rutile hinders the adsorption of lead ions. However, when $\text{pH} > 4.1$, the negative charge on the mineral surface is favourable to the adsorption of lead ions (Chen et al., 2017; Liu et al., 2016). In the presence of lead ions, the zeta potential of rutile surface decreases obviously in the presence of SPA. This reduction indicates that SPA can interact with the adsorption products of lead ions on rutile surface and adsorb on rutile surface together, and enhance the flotation of rutile.

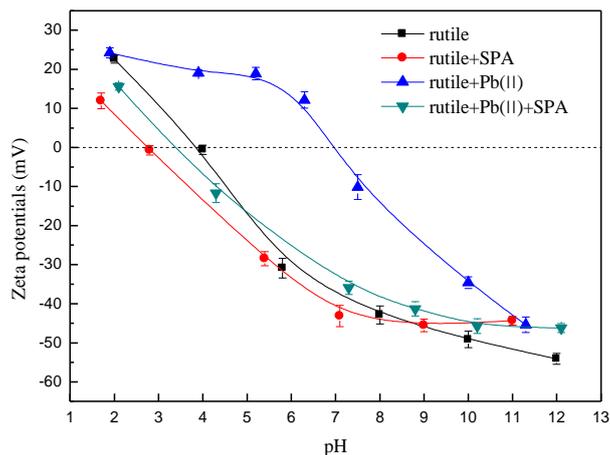


Fig. 4. Zeta potentials of rutile as a function of pH in the presence of Pb(II) (CSPA = 300 mg/L; CPb(II) = 10^{-4} mol/L)

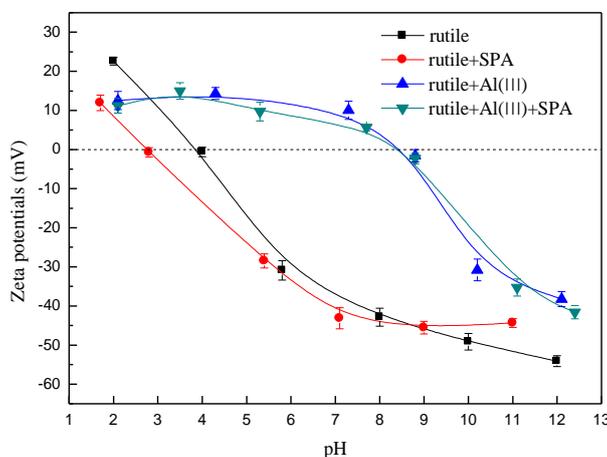


Fig. 5. Zeta potentials of rutile as a function of pH in the presence of Al(III) (CSPA = 300 mg/L; CAI(III) = 10^{-3} mol/L)

The zeta potential of rutile as a function of pH in the absence and presence of aluminium ions are shown in Fig. 5. In the presence of aluminium ions, the zeta potential of rutile decreases slightly when $\text{pH} < 4$, indicating that the positive charge on the surface of the mineral hinders the adsorption of aluminium ions. The zeta potential significantly increases when $\text{pH} > 4$, indicating that the aluminium ions have adsorbed on the surface of the rutile (Fang et al., 2017; Fuerstenau and Pradip, 2005). In the presence of aluminium ions, there is no significant negative shift in the zeta potential of rutile in the presence of SPA. It means that the SPA hardly adsorbs on the surface of rutile in the presence of aluminium ions, and the aluminium ions can inhibit the flotation of rutile. This is consistent with the flotation results shown in Fig. 2.

3.3. The species distribution of SPA, lead ions and aluminium ions in solution

The species distribution diagrams of SPA (1×10^{-3} mol/L), lead ions (1×10^{-4} mol/L) and aluminium ions (1×10^{-3} mol/L) as a function of pH are shown in Fig. 6~Fig.8.

In the solution system of 1×10^{-3} mol/L SPA, $\text{C}_6\text{H}_5\text{C}_2\text{H}_2\text{PO}_3\text{H}_2$ is the main species when $\text{pH} < 2$, and $\text{C}_6\text{H}_5\text{C}_2\text{H}_2\text{PO}_3\text{H}^-$ specie dominates at $\text{pH} 2-8$, whereas SPA is predominantly in the form of $\text{C}_6\text{H}_5\text{C}_2\text{H}_2\text{PO}_3^{2-}$ when $\text{pH} > 8$. It suggests $\text{C}_6\text{H}_5\text{C}_2\text{H}_2\text{PO}_3\text{H}^-$ is the main components of SPA that interacts with rutile. When $\text{pH} > 9$, the concentration of $\text{C}_6\text{H}_5\text{C}_2\text{H}_2\text{PO}_3\text{H}^-$ drops below 1×10^{-4} mol/L, the competition adsorption of OH^- reduces the adsorption of SPA on rutile surface, thus the rutile recovery

decreases (Wang et al., 2013). Meanwhile, the enhanced electrostatic repulsion between negatively charged rutile and homogeneously charged collector anions might prevent the interaction between rutile and SPA anions (Feng et al., 2017).

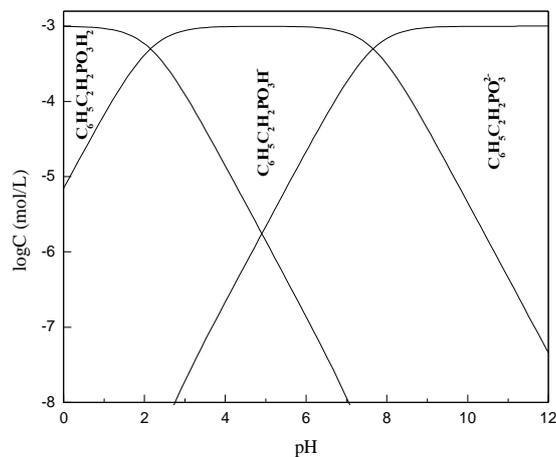


Fig. 6. Species distribution diagrams of 1×10^{-3} mol/L SPA as a function of pH

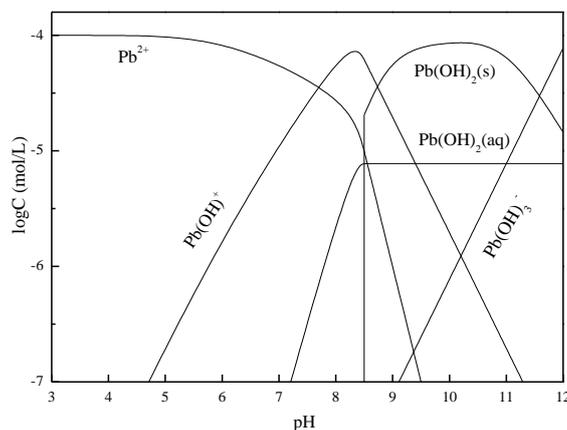


Fig. 7. Species distribution diagrams of 1×10^{-4} mol/L Pb(II) as a function of pH

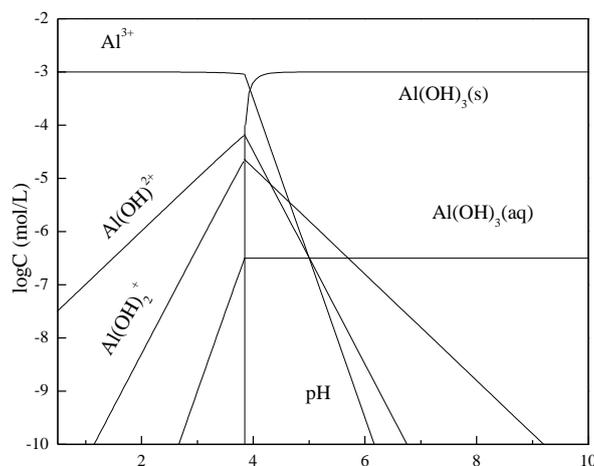


Fig. 8. Species distribution diagrams of 1×10^{-3} mol/L Al(III) as a function of pH

Fig. 8 shows the distribution diagram of Al^{3+} species in aqueous solution. When $pH < 4$, aluminium ions in solution are primarily present as Al^{3+} , and only a few aluminium ions adsorb on the surface of

rutile due to the electrostatic repulsion. The adsorption of Al^{3+} species can change the zeta potential and the number of active sites on the rutile surface. A large number of aluminium ions are present in the solution in the form of Al^{3+} , and consumes SPA concentration, thus inhibiting the flotation of rutile (Fang et al., 2017; Liu et al., 2015). When $\text{pH} > 4$, aluminium ions exist in the form of $\text{Al}(\text{OH})_{3(s)}$ which has a strong adsorption activity. The $\text{Al}(\text{OH})_{3(s)}$ precipitation could coat on the rutile surface and prevent the direct interaction between mineral and collector, resulting in the decrease of rutile flotation recovery (Alvarez-Silva et al., 2016; Deng et al., 2017; Fuerstenau et al., 1988).

Lead ions adsorb on the rutile surface in the form of $\text{Pb}(\text{OH})^+$ and $\text{Pb}(\text{OH})_{2(s)}$, while aluminium ions adsorb on the rutile surface mainly in the form of $\text{Al}(\text{OH})_{3(s)}$. The ion species present on the rutile surface can change the surface properties. However, Pb^{2+} species make the interaction between collector molecules with the rutile surface more efficient while Al^{3+} species make the interaction less efficient. This difference may be attributed to the fact that the interaction between SPA and Pb is stronger than that of Ti, while the interaction between SPA and Al is weak and even ineffective (Fang et al., 2017; Luo et al., 2017a). The $\text{Pb}(\text{OH})^+$ and $\text{Pb}(\text{OH})_{2(s)}$ species interact with the Ti-OH on the rutile surface and form surface complex Ti-O-Pb+. This adsorption greatly enhances the interaction between rutile surface and SPA, and promotes the floatability of the rutile (Li et al., 2016).

Fig. 7 shows the distribution diagram of Pb^{2+} species in aqueous solution. In the pH range of 3–4.5, lead ions in solution are primarily present as Pb^{2+} . And the adsorption amount of lead ions on rutile surface is very small (Li et al., 2016) because of the electrostatic repulsion. In the pH range of 4.5–9, lead ions in solution are primarily present as Pb^{2+} and $\text{Pb}(\text{OH})^+$. While Pb^{2+} decreases with the rise of pH, $\text{Pb}(\text{OH})^+$ increases at the same time. Because the rutile surface is positively charged, lead ions adsorb on rutile surface via specific adsorption in the form of $\text{Pb}(\text{OH})^+$ (Li et al., 2016; Xiao et al., 2017). In the pH range of 9–11.5, lead ions in solution are primarily present as $\text{Pb}(\text{OH})_{2(s)}$. Therefore, the metal hydroxide will preferentially generate hydroxide precipitation on the mineral surface rather than in the solution. This hydroxide precipitation can play an active role (Ejtemaei et al., 2012; James and Healy, 1972; Jie et al., 2014; Luo et al., 2017b). Consequently, lead ions adsorb on rutile surface in the form $\text{Pb}(\text{OH})_{2(s)}$ in the pH range of 9–11.5. When the $\text{pH} > 11.5$, negatively charged lead species $\text{Pb}(\text{OH})_3^-$ becomes dominant due to the hydrolysis reaction. As a result, a positive shift in the zeta potential of rutile decreases because of the adsorption of $\text{Pb}(\text{OH})_3^-$ (Chen et al., 2017; Liu et al., 2016).

4. Conclusions

In the presence of lead ions, the floatability of rutile was enhanced with SPA and OCT as a composite collector. In the presence of aluminium ions, the flotation recovery of rutile was significantly decreased with the increase of pH, and the flotation of rutile was inhibited as well.

A positive shift of the rutile zeta potential was observed after the addition of lead ions and aluminium ions. SPA can adsorb on the surface of rutile after the action of lead ions, but it cannot easily adsorb on the surface of rutile after the action of aluminium ions.

Lead ions adsorb on rutile surface in the form of $\text{Pb}(\text{OH})^+$ and $\text{Pb}(\text{OH})_{2(s)}$, especially in the form of $\text{Pb}(\text{OH})_{2(s)}$ species which activates rutile flotation. Aluminium ions adsorb on the rutile surface mainly in the form of $\text{Al}(\text{OH})_{3(s)}$ which can coat on the rutile surface and prevent the direct interaction between mineral and collector, resulting in the decrease of rutile flotation recovery.

Lead is toxic for humans and causes significant environmental pollution, so removal of lead(II) ions from aqueous solution after rutile flotation is necessary. We would remove lead(II) ions from aqueous solution using adsorbents such as activated carbon, zeolite and diatomite. Meanwhile, we would further search and study the metal ions that have the activation effect on rutile to replace lead ions.

Acknowledgments

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References

ALVAREZ-SILVA, M., URIBE-SALAS, A., WATERS, K.E., FINCH, J.A., 2016. *Zeta potential study of pentlandite in the*

- presence of serpentine and dissolved mineral species. *Minerals Engineering*. 85, 66-71.
- ANANTHAPADMANABHAN, K., SOMASUNDARAN, P., 1985. *Surface precipitation of inorganics and surfactants and its role in adsorption and flotation*. *Colloids and Surfaces*. 13, 151-167.
- CHEN, P., ZHAI, J., SUN, W., HU, Y., YIN, Z., 2017. *The activation mechanism of lead ions in the flotation of ilmenite using sodium oleate as a collector*. *Minerals Engineering*. 111, 100-107.
- COOKE, S., 1949. *The flotation of quartz using calcium ion as activator*. *Transactions of the American Institute of Mining and Metallurgical Engineering*. 184, 306-309.
- DENG, R., HU, Y., KU, J., ZUO, W., YANG, Z., 2017. *Adsorption of Fe (III) on smithsonite surfaces and implications for flotation*. *Colloids and Surfaces A*. 533, 308-315.
- DIEBOLD, U., 2003. *The surface science of titanium dioxide*. *Surface Science Reports*. 48, 53-229.
- EJTEMAEI, M., IRANNAJAD, M., GHARABAGHI, M., 2012. *Role of dissolved mineral species in selective flotation of smithsonite from quartz using oleate as collector*. *International Journal of Mineral Processing*. 114, 40-47.
- FAN, X., ROWSON, N., 2000. *The effect of Pb (NO₃)₂ on ilmenite flotation*. *Minerals Engineering*. 13, 205-215.
- FANG, C., CHANG, Z., FENG, Q., XIAO, W., YU, S., QIU, G., WANG, J., 2017. *The Influence of Backwater Al³⁺ on Diaspore Bauxite Flotation*. *Minerals*. 7, 195.
- FENG, Q., ZHAO, W., WEN, S., CAO, Q., 2017. *Activation mechanism of lead ions in cassiterite flotation with salicylhydroxamic acid as collector*. *Separation and Purification Technology*. 178, 193-199.
- FUERSTENAU, D., RAGHAVAN, S., 1976. *Some aspects of the thermodynamics of flotation*. *Flotation--A. M. Gaudin Memorial*.
- FUERSTENAU, D.W., PRADIP, 2005. *Zeta potentials in the flotation of oxide and silicate minerals*. *Advances in Colloid & Interface Science*. s 114-115, 9-26.
- FUERSTENAU, M., LOPEZ-VALDIVIESO, A., FUERSTENAU, D., 1988. *Role of hydrolyzed cations in the natural hydrophobicity of talc*. *International Journal of Mineral Processing*. 23, 161-170.
- FUERSTENAU, M., PALMER, B., 1976. *Anionic flotation of oxides and silicates*. *Flotation--A. M. Gaudin Memorial*.
- HU, Y., WANG, D., 1987. *Mechanism of adsorption and activation flotation of metallic ion on oxide mineral-water interface*. *Journal of Central South Mining Institute*. 5, 38-48.
- JAMES, R.O., HEALY, T.W., 1972. *Adsorption of hydrolyzable metal ions at the oxide – water interface. I. Co (II) adsorption on SiO₂ and TiO₂ as model systems*. *Journal of Colloid and Interface Science*. 40, 42-52.
- JIE, Z., WEIQING, W., JING, L., YANG, H., QIMING, F., HONG, Z., 2014. *Fe (III) as an activator for the flotation of spodumene, albite, and quartz minerals*. *Minerals Engineering*. 61, 16-22.
- LAZARIDIS, N., MATIS, K., STALIDIS, G., MAVROS, P., 1992. *Dissolved-air flotation of metal ions*. *Separation Science and Technology*. 27, 1743-1758.
- LI, H., MU, S., WENG, X., ZHAO, Y., SONG, S., 2016. *Rutile flotation with Pb²⁺ ions as activator: adsorption of Pb²⁺ at rutile/water interface*. *Colloids and Surfaces A*. 506, 431-437.
- LI, Y.-k., ZHANG, Z.-h., SUN, J., 1982. *About of flotation activation law and mechanism of calcium and iron ions on beryl and spodumene*. *Chinese Journal of Rare Metals*. 1, 31-411.
- LIN, H., YIN, W., SUN, C., 2003. *XPS analysis on adsorption law of metal ion on surface of silicate minerals*. *Nonferrous Met. Min. Metall*. 19, 21.
- LIU, C., FENG, Q., ZANG, G., MA, W., MENG, Q., CHEN, Y., 2016. *Effects of lead ions on the flotation of hemimorphite using sodium oleate*. *Minerals Engineering*. 89, 163-167.
- LIU, Q., PENG, Y., 1999. *The development of a composite collector for the flotation of rutile*. *Minerals Engineering*. 12, 1419-1430.
- LIU, W., ZHANG, S., WANG, W., ZHANG, J., YAN, W., DENG, J., FENG, Q., HUANG, Y., 2015. *The effects of Ca (II) and Mg (II) ions on the flotation of spodumene using NaOL*. *Minerals Engineering*. 79, 40-46.
- LLEWELLYN, T.O., SULLIVAN, G.V., 1982. *Froth flotation of rutile*. *Google Patents*.
- LUO, N., WEI, D., SHEN, Y., HAN, C., ZHANG, C., 2017a. *Elimination of the adverse effect of calcium ion on the flotation separation of magnesite from dolomite*. *Minerals*. 7, 150.
- LUO, X., WANG, Y., MA, M., SONG, S., ZANG, Y., DENG, J., LIU, J., 2017b. *Role of dissolved mineral species in quartz flotation and siderite solubility simulation*. *Physicochem. Probl. Miner. Process*. 53(1), 1241-1254.
- MADELEY, J., GRAHAM, K., 1966. *Flotation of rutile with anionic and cationic collectors*. *Journal of Applied Chemistry*. 16, 169-170.
- MCNULTY, G., 2007. *Production of titanium dioxide*, *Proceedings of NORM V international conference, Seville, Spain*. Citeseer, pp. 169-189.

- NAGARAJ, D., BRINEN, J., 1997. *SIMS analysis of flotation collector adsorption and metal ion activation on minerals: recent studies*. Transactions of the Indian Institute of Metals. 50, 365-376.
- PARKS, G.A., 1965. *The Isoelectric Points of Solid Oxides, Solid Hydroxides, and Aqueous Hydroxo Complex Systems*. Chemical Reviews. 65.
- SCOTT, J., SMITH, R., 1993. *Calcium ion effects in amine flotation of quartz and magnetite*. Minerals engineering. 6, 1245-1255.
- SHI, Q., ZHANG, G., FENG, Q., Ou, L., Lu, Y., 2013. *Effect of the lattice ions on the calcite flotation in presence of Zn (II)*. Minerals Engineering. 40, 24-29.
- STANAWAY, K., 1994. *Overview of titanium dioxide feedstocks*. Mining engineering. 46, 1367-1370.
- WANG, J., CHENG, H.-W., ZHAO, W.-Q., QIU, G.-Z., 2016. *Flotation behavior and mechanism of rutile with nonyl hydroxamic acid*. Rare Metals. 35, 419-424.
- WANG, J., HENG, H., ZHAO, H.-B., QIN, W.-Q., W., QIU, G.-Z., 2014. *Flotation behavior and mechanism of rutile in presence of sodium oleate*. Chin J Nonferrous Met. 24, 820.
- WANG, P.-P., QIN, W.-Q., REN, L.-Y., QIAN, W., LIU, R.-Z., YANG, C.-R., Zhong, S.-p., 2013. *Solution chemistry and utilization of alkyl hydroxamic acid in flotation of fine cassiterite*. Transactions of Nonferrous Metals Society of China. 23, 1789-1796.
- XIAO, W., CAO, P., LIANG, Q., PENG, H., ZHAO, H., QIN, W., QIU, G., WANG, J., 2017. *The activation mechanism of Bi³⁺ ions to rutile flotation in a strong acidic environment*. Minerals. 7, 113.
- YIN, W.-Z., SUN, C.-Y., 2002. *X-ray photoelectron spectrometric analysis on surface property of silicate minerals*. Journal-Northeastern University Natural Science. 23, 156-159.