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## Hydrochloric acid leaching for upgrading flotation concentrate from a low-grade bauxite ore

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**Abstract:** Bauxite is the major raw material for alumina production, and its  $\text{Al}_2\text{O}_3$  grade improvement or desilication is a necessary process for production of high-grade alumina concentrates from bauxite ores. In practice, flotation presents an effective method for the processing of such ores. However, it is not sufficient to produce a concentrate product with high  $\text{Al}_2\text{O}_3$  grade from the ores with a single flotation process, especially from these containing abundant carbonate minerals. In this investigation, hydrochloric acid leaching was used to remove dolomite impurity from the flotation concentrate of a bauxite ore, to improve its  $\text{Al}_2\text{O}_3$  grade and  $\text{Al}_2\text{O}_3/\text{SiO}_2$  (A/S) ratio. Effects of three dominant parameters on the leaching performance, that is leaching time, leaching temperature and hydrochloric acid concentration, were investigated in details. When these parameters were optimized, the aluminum concentrate assaying 67.41%  $\text{Al}_2\text{O}_3$  with 66.84% recovery and 7.44 A/S ratio was obtained from the bauxite ore assaying 42.94%  $\text{Al}_2\text{O}_3$  with 2.48 A/S ratio. It was concluded that hydrochloric acid leaching proved an effective method for upgrading of flotation concentrate from a low-grade bauxite ore containing carbonate minerals.

**Keywords:** *bauxite ore, hydrochloric acid leaching, concentrate upgrading, carbonate minerals*

### Introduction

Aluminum minerals are used as a raw material for aluminum metal refining and other industrial processes (Hyun et al., 2005), and they mainly exist in forms of gibbsite, boehmite and diaspor. There are abundant bauxite resources in China, especially in Yunnan, Shandong and Liaoning provinces, but they are basically composed of diaspor (Jiang et al., 2001; Huang et al., 2008). With the development of alumina industry and other bauxite-consuming industries, the shortage for high-quality bauxite resources is increasingly serious in the recent years (Lusty et al., 2016). However, it is

interesting to note that at least 90% of the bauxite resources in China are characteristic of high silica and low alumina, with a small mass ratio for  $\text{Al}_2\text{O}_3$  to  $\text{SiO}_2$  components (A/S ratio) (Zhao et al., 2013).

Numerous investigations have been performed on development and utilization of medium and low-grade bauxites, with remarkable progress achieved (Rayzman et al., 2003; Feng et al., 2008; Ma et al., 2009). It is well known that the Bayer process has been the principal method for the alumina production from bauxite ores in the world (Ma et al., 2012), and for the ores with the sufficiently high A/S ratio, they have been directly treated with the process (Massola et al., 2009; Jiang et al., 2010). However, for the medium and low-grade bauxite ores, its promotion for the A/S ratio is inevitably required to meet the Bayer process. Thus, the  $\text{Al}_2\text{O}_3$  grade improvement to higher than 60% or desilication for the bauxite ores has been a principle task for production of a high-grade alumina concentrate, and this is usually achieved through either washing or flotation.

Flotation is known as a highly versatile method and it is widely used for mineral processing, and direct flotation is reported effective for desilication of bauxite (Wang et al., 2004; Pan et al., 2012). However, it is usually difficult and even impossible to obtain a high-grade concentrate product through a single flotation process, especially for bauxite ores containing abundant carbonate minerals. This is due to the fact that the carbonate and aluminum minerals have similar floating properties (Liu and Liu, 2004). In fact, in recent years chemical processes have been investigated to dissolve gangue minerals from the ores and improve their  $\text{Al}_2\text{O}_3$  grades, with significant advances (Mendelovici, 2004). However, until today such investigations as dissolving carbonate minerals in the bauxite ore for improving the A/S ratio of alumina concentrate products have been rarely reported.

In the present investigation, desilication of a low-grade bauxite ore was performed with the flotation process to produce an alumina concentrate, with its A/S ratio further improved using hydrochloric acid leaching to dissolve the carbonate minerals in the concentrate. The effects of three dominant parameters on the leaching performance, that is the leaching time, leaching temperature and hydrochloric acid concentration were investigated, and then a flotation-leaching process was proposed for processing of the bauxite ore.

## **Experimental**

### **Material**

The material used in the investigation was obtained from Chengjiang Area in Yunnan province of China, with its chemical and mineral compositions illustrated in Tables 1 and 2, respectively. It should be noted that the chemical composition for the bauxite ore in Table 1 and the qualified concentrate product in Table 4 are both achieved by combining the volumetric (for components with content >1%) and atomic absorption (content <1%) methods.

Table 1. Chemical composition of bauxite ore from Yunnan province (wt. %)

Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	TiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O	LOI	Total
42.94	17.30	2.42	2.13	7.53	6.38	1.07	0.47	19.76	100.0

Table 2. Mineral composition of bauxite ore from Yunnan province (wt. %)

Bauxite minerals (Al <sub>2</sub> O <sub>3</sub> )		Silicate minerals and quartz (SiO <sub>2</sub> )			Carbonate minerals	Ti and iron impurities		Other minerals
Diaspore	Boehmite	Kaolinite	Quartz	Muscovite	Dolomite	Anatase	Geothite	
Al <sub>2</sub> O <sub>3</sub> ·H <sub>2</sub> O	Al <sub>4</sub> [Si <sub>4</sub> O <sub>10</sub> ](OH) <sub>8</sub>	SiO <sub>2</sub>	K[Al <sub>2</sub> [AlSi <sub>3</sub> O <sub>10</sub> ](OH) <sub>2</sub> ]	CaMg[CO <sub>3</sub> ] <sub>2</sub>	TiO <sub>2</sub>	FeO(OH)		
37	4	12	11	4	22	2	3	5

As shown in Table 1, the material had Al<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> grades of 42.94% and 17.30%, respectively, and thus its A/S ratio was as low as 2.48. The main impurity components in the material were SiO<sub>2</sub>, CaO, MgO, TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub>. It can be seen from Table 2, the XRD analysis of the material indicated that the Al<sub>2</sub>O<sub>3</sub> value was distributed in diaspore and boehmite, and the SiO<sub>2</sub> components were mainly distributed in silicate minerals (kaolinite and muscovite) and quartz. The material had a high content of carbonate mineral (dolomite). It is clear that this material presented a typically refractory low-grade bauxite ore.

## Methods

As shown in Fig. 1, the bauxite ore with particle size below 2 mm was firstly ground to the required particle size of 85% below 0.074 mm, and then it was processed with flotation under the optimized conditions through single factors tests as detailed in Fig. 2. Specifically, in the roughing flotation process, the material was fully mixed in a flotation cell of 1.5 dm<sup>3</sup> (XFD-15, made in Jiangxi province of China), and 1500 g/Mg sodium carbonate (i.e. 1500 g sodium carbonate for 1 Mg of material) as a modifier was added to the cell and agitated for 5 minutes. Then, 600 g/Mg sodium silicate as depressant, a new collector H2 of 200 g/Mg and 10 g/Mg terpeneol as a frother were sequentially added to the cell at a time intervals of 5, 5 and 3 minutes. The material was roughed for 5 minutes, and then was further scavenged and cleaned at the same time intervals as in the roughing process for the reagents. As a result, five flotation products, i.e. concentrate, middling-1, middling-2, middling-3 and tailings were produced, as shown in Fig. 1 and Table 3.

The concentrate had a low Al<sub>2</sub>O<sub>3</sub> grade (Table 3) due to the abundant presence of carbonate mineral (dolomite) interfused in the product. Thus, the concentrate was transferred into a reaction kettle and leached using hydrochloric acid under the optimized conditions as detailed in the present investigation. The leaching temperature was adjustable in the reactor, and a ceramic filter was applied for a solid-liquid separation of the residue from the leaching process. The solid phase from the filtering process was washed three times with clean water to remove the residual acid from the

residue, and then it was dried at 85 °C for 10 hours, weighed and analyzed. This clean residue was mixed with middling-1 and 80 wt.% of middling-2, to produce the concentrate product as shown in Fig. 1.

It is noteworthy that the reaction kettle (WHFCS-1L, made in Shandong province of China) was operated under atmospheric-pressure (0.1 MPa), at a fixed stirring speed of 300 rpm.

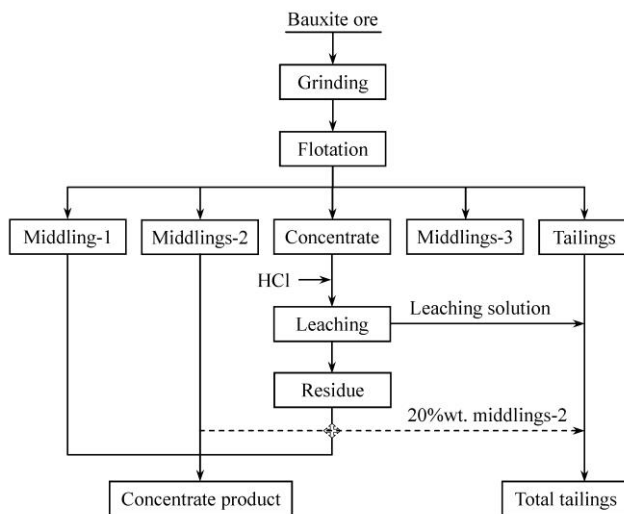


Fig. 1. Processing of bauxite ore with flotation-hydrochloric acid leaching

## Results and discussions

### Open-circuit flotation processing of bauxite ore

The material was firstly processed in an open-circuit flotation flowsheet under the optimized conditions, as illustrated in Fig. 2. According to the procedure shown in the flowsheet the following products were obtained: a high mass weight concentrate of low  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  grades but a high A/S ratio of 10.56, and middling-1 and middling-2 of much higher  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  grades and much smaller A/S ratios in comparison with those of the concentrate. It is clear that the concentrate, middling-1 and middling-2 should be considered for quality improving, as they have much higher A/S ratios compared to the middling-3 and the tailings, which have an A/S ratio smaller than 2.0.

The XRD analysis of the flotation concentrate indicates that the content of abundant carbonate minerals of dolomite significantly reduces the A/S ratio in the concentrate. As these minerals react with hydrochloric acid (Reddy et al., 1999), the hydrochloric acid leaching of the concentrate was carried out, to improve its  $\text{Al}_2\text{O}_3$  grade and A/S ratio.

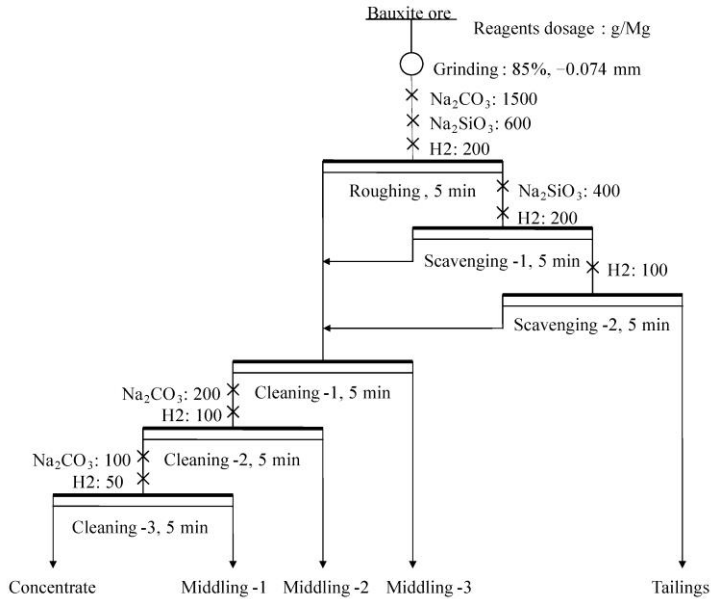


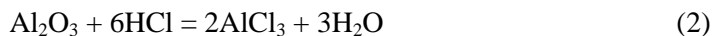
Fig. 2. Open-circuit flotation flowsheet for bauxite ore under optimized conditions

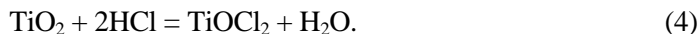
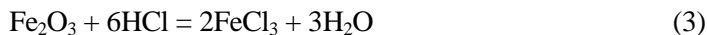
Table 3. Flotation results of bauxite ore under optimized conditions

Products	Mass weight (%)	Grade (%)		Al <sub>2</sub> O <sub>3</sub> recovery (%)	A/S ratio
		Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>		
Concentrate	42.33	41.20	3.90	40.62	10.56
Middlings-1	10.15	63.81	12.37	15.08	5.56
Middlings-2	12.05	52.33	11.45	14.69	4.57
Middlings-3	12.44	37.06	19.68	10.74	1.88
Tailings	23.03	35.18	43.25	18.87	0.81
Material	100.0	42.94	17.30	100.0	2.48

### Hydrochloric acid leaching of flotation concentrate

Before the investigations, the main reactions that may occur in the leaching solution are briefly discussed. As mentioned above, the dominant impurity in the concentrate was determined as dolomite of a chemical formula of CaMg(CO<sub>3</sub>)<sub>2</sub>, and, as shown in Table 1, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> and Fe<sub>2</sub>O<sub>3</sub> are other three components in the concentrate. The main reactions occurring in the leaching solution are given as (Yildirim, 2008; Li et al., 2013):





### Effect of leaching time

An effect of leaching time on the process performance was firstly investigated at 50 °C and in 2 mol/dm<sup>3</sup> hydrochloric acid concentration. The leaching time has a significant effect on the performance of this operation (Fig. 3). The Al<sub>2</sub>O<sub>3</sub> grade is significantly improved with increase in the leaching time from 30 to 90 minutes, beyond which it approaches to the maximum. This is also reflected in the A/S ratio, and it is dramatically increased from around 18.5 after 30 minutes of leaching to the highest value of 22.5 after 90 minutes of leaching. It is noteworthy that the increase in the leaching time results in very slight reduction in the Al<sub>2</sub>O<sub>3</sub> recovery, and a very small amount of Al<sub>2</sub>O<sub>3</sub> is dissolved in the leaching solution.

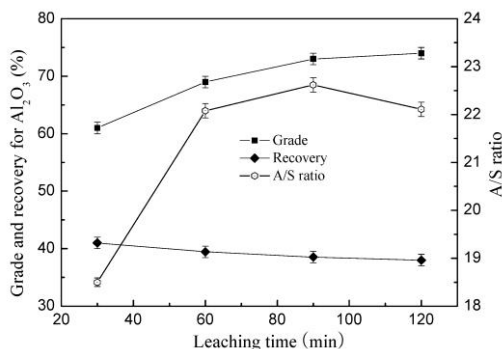


Fig. 3. Effect of leaching time on leaching performance (50 °C leaching temperature, 2 mol/dm<sup>3</sup> HCl)

It is clear that dolomite is effectively dissolved in hydrochloric acid, and it reacts in a very short time. In fact, it is observed that leaching bubbles of CO<sub>2</sub> are instantaneously produced after the concentrate is placed into the leaching reactor. As seen in Fig. 3, the leaching time of 90 minutes is sufficient to dissolve dolomite in the concentrate.

### Effect of leaching temperature

The leaching temperature presents another dominant factor that affects the leaching performance, and this is apparently illustrated in Fig. 4. It can be seen that the temperature influences leaching as positively as time does. The Al<sub>2</sub>O<sub>3</sub> grade and A/S ratio are significantly improved with increase in the leaching temperature from 30 to 70 °C, beyond which they approach to the maximums, and, the Al<sub>2</sub>O<sub>3</sub> recovery is slightly reduced as the leaching temperature is increasingly improved.

The temperature affects the leaching efficiency of dolomite in the concentrate because a high reaction temperature would provide more energy to break down the chemical bonds of dolomite, and thus improves its leaching rate.

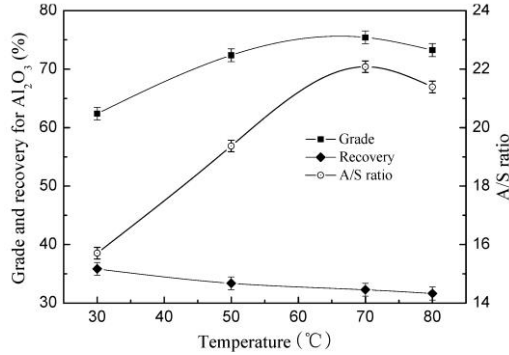


Fig. 4. Effect of leaching temperature on leaching performance (90 minutes leaching time, 2 mol/dm<sup>3</sup> HCl)

### Effect of hydrochloric acid concentration

Under the optimized leaching time, that is 90 min, and temperature (70 °C) as determined above, the effect of hydrochloric acid concentration on the leaching performance was investigated.

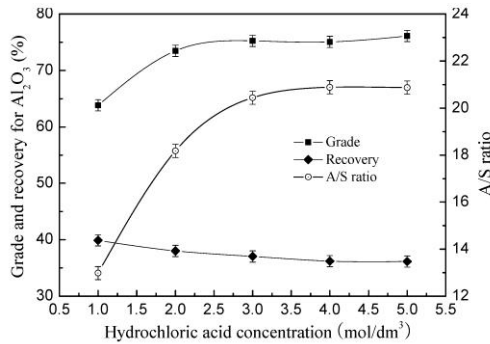


Fig. 5. Effect of hydrochloric acid concentration on leaching performance (90 minutes leaching time, 70 °C leaching temperature)

When the concentration of HCl varies from 1.0 to 3.0 mol/dm<sup>3</sup>, the Al<sub>2</sub>O<sub>3</sub> grade and A/S ratio are significantly improved, and after that, they approached to the maximums. As seen in Fig. 5, at the critical HCl concentration of 3.0 mol/dm<sup>3</sup>, the Al<sub>2</sub>O<sub>3</sub> grade and A/S ratio reach the highest values of 75.24% and 20.44, respectively. With further increase in the concentration of HCl, the visible improvements in the leaching performance were not observed. It seems that 3.0 mol/dm<sup>3</sup> hydrochloric acid is appropriate for removal of dolomite from the concentrate.

## Production of qualified concentrate with flotation-leaching process

It can be seen that for the concentrate product achieved with the flotation flowsheet shown in Fig. 2, its  $\text{Al}_2\text{O}_3$  grade and A/S ratio may be significantly improved with hydrochloric acid leaching. As shown in Fig. 5, a leaching residue assaying 75.24%  $\text{Al}_2\text{O}_3$  with an A/S ratio reaching as high as 20.44 is obtained from the concentrate after 90 minutes of leaching at 70 °C with 3.0 mol/dm<sup>3</sup> hydrochloric acid concentration. However, its  $\text{Al}_2\text{O}_3$  recovery (40.01% to material) is insufficient from the economical point of view.

To improve the  $\text{Al}_2\text{O}_3$  recovery from the material, the leaching residue is combined with middling-1 and 80 wt.% of middling-2, to produce a qualified concentrate product as shown in Fig.1. From Table 4, with the flotation-hydrochloric acid leaching process, a qualified concentrate product containing 67.41%  $\text{Al}_2\text{O}_3$  was achievable from the material, at A/S ratio of 7.0, and this process achieved a high  $\text{Al}_2\text{O}_3$  recovery reaching 66.84% (40.01% from the residue, 15.08% from middling-1 and 11.75% from middling-2 as illustrated in Table 3) from this refractory low-grade bauxite ore. It should be noted that this concentrate product is composed of leaching residue, and middling-1 and 80 wt.% of middling-2 as illustrated in Fig. 1 and Table 3.

Comparing Tables 1 and 4, the contents for CaO and MgO components are significantly reduced in the concentrate product, and it is obvious that this is due to the fact that the dolomite is effectively removed in the leaching process.

Table 4. Chemical composition of qualified concentrate product (wt.%)

$\text{Al}_2\text{O}_3$	$\text{SiO}_2$	A/S ratio	$\text{Fe}_2\text{O}_3$	$\text{TiO}_2$	CaO	MgO	LOI	Total
67.41	9.06	7.44	13.74	3.89	2.32	0.39	3.19	100.0

## Conclusions

(1) The carbonate and aluminum minerals present a similar floatability in the flotation of bauxite ore, and such bauxite ores with abundant carbonate minerals cannot be effectively utilized in practice, with a single flotation process as currently applied.

(2) These carbonate minerals in the ores may be effectively removed with hydrochloric acid leaching, and combining the flotation process, a qualified concentrate product with high  $\text{Al}_2\text{O}_3$  recovery and A/S ratio is achievable. For instance, the flotation-hydrochloric acid leaching process of the bauxite ore obtained a qualified concentrate product containing 67.41%  $\text{Al}_2\text{O}_3$ , at an  $\text{Al}_2\text{O}_3$  recovery and A/S reaching 66.84% and 7.44, respectively, from the ore assaying 42.94%  $\text{Al}_2\text{O}_3$  with a very low A/S ratio of 2.48.

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## References

- FENG, Q. M., LU, Y. P., OU, L. M., ZHANG, G. F., 2008, *Beneficiation Practice of Bauxite*, Metal Mine., 10, 1–12.
- HUANG, C. B., ZHANG, L., WANG, Y. H., LAN, Y., 2008, *Separation of aluminosilicates and diasporite from diasporic-bauxite by selective flocculation*, J. Cent. South Univ. T. 15, 520–525.
- HYUN, J., ENDOH, S., MASUDA, K., SHIN, H., OHUA, H. S., 2005, *Reduction of chlorine in bauxite residue by fine particle separation*, Int. J. Miner. Process. 76, 13–20.
- JIANG, Y. R., XUE, Y. L., CAO, X. F., XIA, Z., 2001, *Distribution behavior of collector in the desilication system of bauxite flotation*, J. Cent. South Univ. T. 8, 125–129.
- JIANG, Y. R., ZHAO, B. N., ZHOU, X. H., ZHOU, L. Y., 2010, *Flotation of diasporite and aluminosilicate minerals applying novel carboxyl hydroxamic acids as collector*, Hydrometallurgy, 104, 112–118.
- LI, G., LI, Z. H., MA, H. W., 2013, *Comprehensive use of dolomite-talc ore to prepare talc, nano-MgO and lightweight CaCO<sub>3</sub> using an acid leaching method*, Appl. Clay Sci. 86, 145–152.
- LIU, Y., LIU, Q., 2004, *Flotation separation of carbonate from sulfide minerals, I: Flotation of single minerals and mineral mixtures*, Miner. Eng. 17, 855–863.
- LUSTY, P. A. J., GUNN, A. G., 2016, *Challenges to global mineral resource security and options for future supply*, Global Miner. Res. Security, 393, 265–176.
- MASSOLA, C. P., CHAVES, A. P., LIMA, J. R. B., ANDRADE, C. F., 2009, *Separation of silica from bauxite via froth flotation*, Miner. Eng. 22, 315–318.
- MA, J. Y., LI, Z. B., XIAO, Q. G., 2012, *A new process for Al<sub>2</sub>O<sub>3</sub> production from low-grade diasporic bauxite based on reactive silica dissolution and stabilization in NaOH-NaAl(OH)<sub>4</sub> media*, Aiche J. 58, 2180–2191.
- MA, S. H., WEN, Z. G., CHEN, J. N., 2009, *An environmentally friendly design for low-grade diasporic-bauxite processing*, Miner. Eng. 22, 793–798.
- MENDELOVICI, E., 2004, *Acid and thermal treatments of lateritic bauxites*, J. Therm. Anal. Calorim. 75, 957–964.
- PAN, X. L., YU, H. Y., DONG, K. W., TU, G. F., BI, S. W., 2012, *Pre-desilication and digestion of gibbsitic bauxite with lime in sodium aluminate liquor*, Int. J. Min. Met. Mater. 19, 973–977.
- REDDY, B. R., MISHRA, S. K., BANERJEE, G. N., 1999, *Kinetics of leaching of a gibbsitic bauxite with hydrochloric acid*, Hydrometallurgy, 51, 131–138.
- VIKTOR, L. R., ILYA, Z. P., VIKTOR, M. S., 2003, *Extracting Silica and Alumina from Low-Grade bauxite*, Jom, 55, 47–50.
- WANG, Y., HU, Y., HE, P., GU, G., 2004, *Reverse flotation for removal of silicates from diasporic-bauxite*. Miner. Eng. 17, 63–68.
- YILDIRIM, M., 2008, *Dissolution Kinetics of Icel-Aydincik Dolomite in Hydrochloric Acid*, S. Afr. J. Chems. -Afr. T., 61, 127–132.
- ZHAO, A. C., LIU, Y., ZHANG, T. A., LU, G. Z., DOU, Z. H., 2013, *Thermodynamics study on leaching process of gibbsitic bauxite by hydrochloric acid*, Trans. Nonferrous Met. Soc. China, 23, 266–270.