PRE-CONCENTRATION OF VANADIUM-BEARING MICA FROM STONE COAL BY ROASTING-FLOTATION

Jiayan TANG[*], Yimin ZHANG[*,**], Shenxu BAO[*], Chun LIU[*]

[*] College of Resources and Environmental Engineering, Wuhan University of Technology, Wuhan 430070, China

[**] College of Resources and Environmental Engineering, Wuhan University of Science and Technology, Wuhan 430081, China

Abstract: In China, stone coal is an important source of vanadium. The use of roasting–floatation for the pre-concentration of vanadium bearing mica from vanadium bearing stone coal was investigated based on its mineralogical characteristics. The results showed that the vanadium occurred in mica minerals and the main gangue minerals were coal, calcite, and quartz. The pre-concentration process comprises three key steps: roasting, desliming, and flotation. The coal was completely removed by roasting at 700 °C for an hour. Slime was concentrated and the subsequent flotation pulp was improved by desliming. Calcite was removed by reverse flotation and mica was concentrated by positive floatation. During the process, the grade of V_2O_5 was increased from 0.71% to 1.14%, and 46.18% of the tailings were rejected. The leaching rate of vanadium was increased from 30.49% of raw ore to 69.15% of the concentrate which was an increase of about 40% at the same leaching process. This technique may promote the efficient utilization of stone coal resources.

Keywords: roasting; flotation; vanadium bearing mica; stone coal

Introduction

Vanadium is an important material used mostly in steel industry. Approximately 80% of world's vanadium is used in steel alloys, and the other 20% in the chemical industry (Moskalyk and Alfantazi, 2003). The gross reserve of V_2O_5 in stone coal is 118 teragrams, which is 6.7 times more than that in vanadium–titanium magnetite, accounting for >87% of the vanadium reserves in China and exceeding the total vanadium reserves in other countries (Bin, 2006; Zhu et al., 2012; Wang et al., 2014). Therefore effective utilization of stone coal is very important for the vanadium industry.

Currently, techniques used to extract vanadium from stone coal mainly include direct acid leaching, roasting-acid leaching, roasting-alkali leaching, calcified roasting-carbonate leaching, and low salt roasting-cyclic oxidation (He et al., 2007; Wang et al., 2008; Zhang et al., 2009; Li et al., 2010; Zhang et al., 2011). However, the composition of stone coal is extremely complex and the grade of V_2O_5 in stone coal is relatively low, generally 0.13%–1.2%. For this reason, there are some problems with the processing techniques, such as inability to process large quantities, low recovery in production, high energy consumption and high reagent consumption. The present report shows that if the V_2O_5 grade of stone coal is improved from 0.7% to 0.8%, the cost of producing 1 t of V_2O_5 will increase profits by 29% (Ning et al., 2010, Zhao et al., 2013). Hence, the vanadium pre-concentration of stone coal may improve vanadium recovery and reduce production costs. Furthermore, the vanadium pre-concentration can facilitate utilization of resources below cut-off grade (0.5% V_2O_5). Currently, over 60% of the stone coal resources are below the cut-off grade and therefore cannot be economically exploited (Deng et al., 2010).

Gravity separation and flotation separation are effective methods of pre-concentrating vanadium from stone coal. Wu et al. attempted to use flotation to pre-concentrate the vanadium bearing mineral (Wu et al., 2008). However, because of coating of carbonaceous mudstone on the surfaces of mineral particles, differences in the floatability of minerals decreased significantly and flotation separation was not satisfactory. Zhao et al. attempted to pre-concentrate the vanadium-bearing mineral from decarburization stone coal by gravity separation with a shaking table, and achieved good results (Zhao et al., 2013, Zhao et al., 2016). However, the processing capacity was small. Wang et al. attempted to pre-concentrate vanadium from low-grade stone coal by the method of desliming-flotation (Wang et al., 2014).

The objective of this study was to pre-concentrate vanadium from low-grade stone coal from Hubei Province. Mineralogical studies were performed to confirm the main occurrence of vanadium and gangue minerals. The designed pre-concentrate vanadium process includes roasting, desliming and flotation.

Experimental

Materials

The experimental sample was obtained from Teng-da Mining and Metallurgy Co. Ltd., Hubei Province, China, and was crushed to below 2 mm size through a laboratory jaw crusher and a roll crusher. Sodium oleate was used as a Ca-mineral collector. Dodecylamine (DDA) was used as a V-mineral collector. Sodium silicate, sodium fluosilicate, sodium hexametaphosphate, lead nitrate, and sulfuric acid served as regulators.

Procedure

The pre-concentration process of stone coal vanadium is shown in Figure 1. Crushed materials (200 g) were first roasted for an hour in a SXZ-10-Bmuffle furnace with a heating rate of 8°C/min. The sample was then wet-ground in a HLXMB-240 × 300 laboratory rod mill at 50 wt% solids. Desliming concentration was 2% and particle size was -0.02 mm. Flotation experiments were carried out in a 0.5 dm^3 flotation cell at an agitation speed of 1 Concentrate 992 rpm. and tailings were filtered, dried, weighed, and the production rate, grade, and recovery of products were calculated.
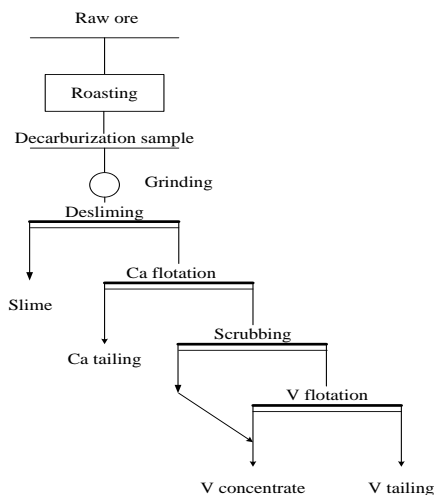
Fig. 1. Roasting-flotation and pre-concentration process
flow-sheet of vanadium

Methods

- Determination of vanadium grade was measured in accordance with Test Methods of Vanadium in Coal Standard (GB/T19226-2003).
- Chemical analysis was performed with a Xios advanced X-ray fluorescence (XRF) analyzer.
- Mineral phase composition was determined using a D/Max-IIIA X-ray diffractometer.
- Sizing analysis was conducted on sub-samples of feed and test products using laboratory wet and dry screening methods.
- Microstructure was observed using a Leica DMLP polarization microscope and JSM-5610LV scanning electronic microscopy (QEMSCAN)
- Vanadium phase was measured using a Energy dispersive spectrum analysis (EDS)

Results and discussion

Mineralogical characteristics

The XRF chemical analysis of stone coal indicated that the main components of the raw ore were SiO_2, C, Al_2O_3, and CaO, the content of V_2O_5 was only 0.71% (Table 1).

According to XRD analysis, the main mineral phases presented in the ore samples were quartz, calcite, mica, pyrite, and feldspar (Figure 2).

Table 1. Chemical composition of the raw ore and roasted sample (%)

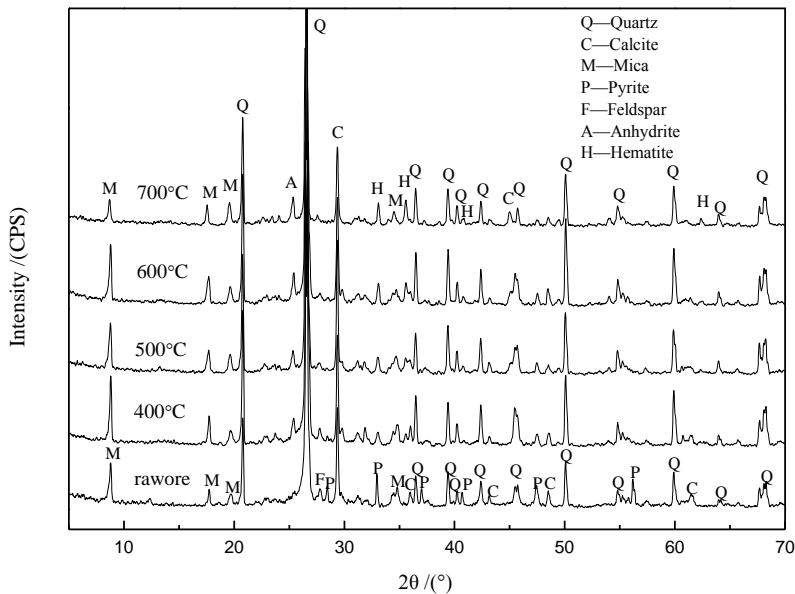| Component	V_2O_5	SiO_2	Al_2O_3	Fe_2O_3	K_2O	Na_2O	CaO	MgO	S	TC
Raw ore	0.71	49.28	8.91	4.99	3.02	0.38	6.26	2.18	3.86	13.44
Roasted ore	0.82	54.31	10.59	5.67	4.90	0.35	7.35	3.13	1.92	2.72

Fig. 2. XRD pattern of raw ore and roasted ore at different temperatures

Because stone coal was formed under deoxidized conditions (Chen et al., 2008), the V generally exists as V(III). Meanwhile, V(III) easily replaces Al^{3+} in the dioctahedron of mica group minerals because they have a similar ionic radius, electro negativity, and the same coordination number (Zhang et al., 2012). In vanadium-bearing coals, about 90% of vanadium occurs in muscovite (Ren et al., 2012). The EPMA of the raw ore confirms that the vanadium occurs in muscovite, illite, and biotite (Table 2). Hence, utilizing the flotation characteristics of minerals to separate the vanadium-bearing mica could be a viable way to pre-concentrate vanadium.

Table 2. EPMA results of raw ore (%)

SiO_2	V_2O_3	Al_2O_3	FeO	MgO	CaO	Na_2O	K_2O	Mineral
0.19	0.20	0.07	56.68	0.00	0.00	0.00	0.00	Pyrite
0.00	0.00	0.00	0.00	1.10	65.93	0.00	0.00	Calcite
98.35	0.00	0.00	0.00	0.00	0.00	0.00	0.00	Quartz
51.08	3.48	27.22	0.23	4.53	0.02	0.07	9.52	Muscovite
33.63	2.43	18.57	0.21	3.06	0.35	0.00	0.00	Illite
56.94	0.00	25.25	0.00	0.10	6.51	6.82	0.98	Anortho
40.78	1.31	17.6	1.36	21.9	0.02	0.02	8.48	Biotite

Optical images of raw ore are shown in Figure.3. These, clearly suggest it is mainly composed of coal, quartz, calcite, pyrite, and mica. Carbon is disseminated in mud cementation matter and covers the surfaces of other minerals, which renders differences in the floatability of various minerals less pronounced. So it is necessary to first decarburize the samples by roasting.
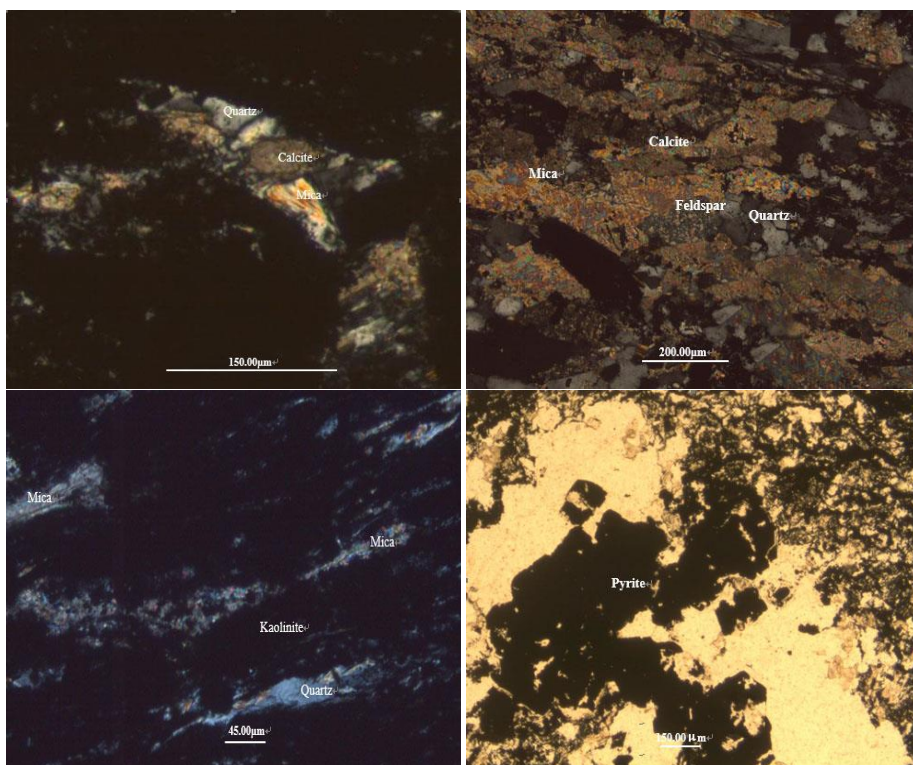

Fig. 3. Optical micrographs of ore samples

Roasting decarburization

As shown in Figure 4, decarburization was satisfactory when temperature exceeded 550°C and lasted 1 h where the fixed carbon content tended to reach 0%. In order to ensure the carbonaceous material had been completely removed, and the higher roasting temperature also can improve leaching rate, the roasting temperature should be 700°C.
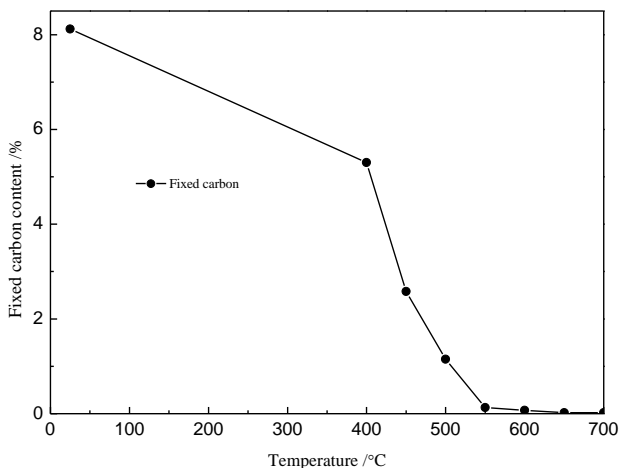

Fig. 4. The fixed carbon content of roasted ore at different temperatures

Table 1 shows the transformation of chemical between the raw ore and the roasted ore. The grade of V_2O_5 increased to some extent after roasting decarburization.

The mineral phase transformation during the roasting process is clearly shown on XRD diagram. Figure 2 shows that the diffraction peak of pyrite disappeared, and the diffraction peaks of anhydrite and hematite appeared at 400 °C. As temperature increased, the diffraction peak intensities of anhydrite and hematite gradually increased indicating relative increase in content. Anhydrite was generated by reaction of CaO from calcite decomposition with SO_2 from pyrite oxidation.

Grinding

Mineral monomer dissociation is an important parameter for flotation (Zhang et al., 2013). Increasing mineral dissociation degree is the key to improve separation effects. In general, the increase of grinding fineness can improve the monomer dissociation degree. Table 3 shows that when the content of -0.074 mm particle increased from 70% to 90%, the degree of mica liberation increased but only by 5.98%. Considering the cost of grinding, the best grinding fineness was determined to be -0.074 mm 70–80%.

Table 3. Degree of mica liberation (%)

Particle size (-0.074mm)	Single	Intergrowth			
		>3/4	3/4–1/2	1/2–1/4	<1/4
70%	70.68	11.49	8.34	5.65	3.84
80%	73.97	10.25	7.90	4.29	3.59
90%	76.66	9.76	6.82	3.94	2.82

Desliming

Hematite, and clay minerals such as meta-kaolinite can produce mud easily after roasting, decarburization, and grinding. The primary and secondary slime with a large specific surface and surface activity can consume a lot of flotation reagents in flotation (Kang and Lv., 2006). Slime can cover the surface of the mineral with no selectivity, which significantly reduces the separation efficiency.

Scattering desliming was used in this study. The desliming concentration was 2%. The particle size and element distribution of grinding product were studied in order to determine the best desliming fineness. The particle size distribution is shown in Table 4. The grade of CaO and Fe_2O_3 first increased, and then decreased with the decrease in particle size, peaking at -0.038 + 0.030 mm. But the grade of vanadium had the opposite trend. The V_2O_5 grade and recovery of -0.020 mm product were 1.12% and 14.31% respectively. Thus, -0.020 mm products could be directly regarded as concentrate and the settlement time was calculated by the Stokes formula.

Table 4. Particle size and element distribution of ground sample

Size fraction(mm)	Yield(%)	Grade(%)		
		V_2O_5	CaO	Fe_2O_3
+0.15	2.35	1.02	0.73	4.14
-0.15+0.104	8.42	1.05	0.96	4.15
-0.104+0.074	14.68	1.03	2.18	4.14
-0.074+0.045	22.65	0.62	3.87	5.21
-0.045+0.038	21.2	0.6	4.77	5.89
-0.038+0.030	6.81	0.54	6.46	10.39
-0.030+0.020	11.1	0.84	4.25	6.98
-0.020+0.015	6.08	1.03	2.35	6.43
-0.015	6.71	1.2	1.83	6.08
Total	100.00	0.80	3.48	5.76

Flotation

The mineralogical study of raw ore has shown that calcite is the main acid-consuming gangue mineral. It can increase acid consumption during acid leaching processes. At weak alkalinity (pH = 7–8), using the fatty acid as collector and sodium silicate as inhibitors, calcite and silicate minerals can be separated. Flotation tests were designed

to work with the pH range of 6–11, and using sodium oleate, sodium silicate, and lead nitrate. The effects of pulp pH on the grade and recovery of CaO were investigated (Fig. 5(a)). Results indicated that the optimum pH was 8.5-9.0. At a pulp pH was 9. 500 g/t sodium silicate showed a strong inhibition effect for silicate minerals (Figure 5(b)). As shown in Figure 5(c), when the dosage of lead nitrate was above 400 g/Mg, recovery remained unchanged and the increase in the amplitude of the grade of CaO was small. As shown in Figure 5(d), as dosage of sodium oleate increased, the grade of CaO decreased, while the recovery increased gradually. When sodium oleate dosage increased from 300 g/Mg to 500 g/Mg, the recovery increased to only 53.20%. Therefore, the dosage of sodium oleate was set to 300 g/Mg.
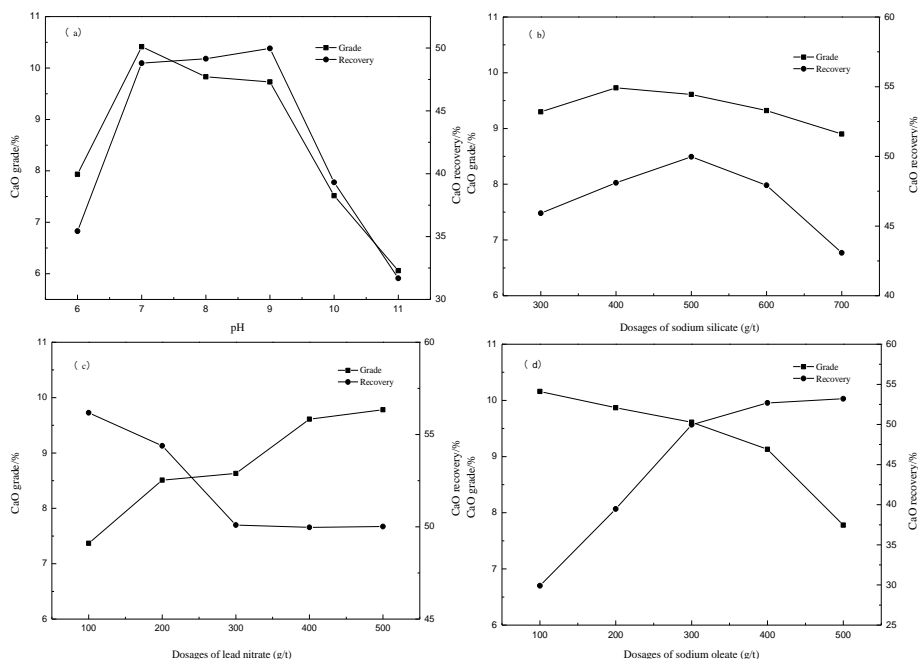

Fig. 5. Effects of (a) pulp pH, (b) sodium silicate dosage, (c) lead nitrate dosage, and (d) sodium oleate dosage on the grade and recovery of CaO

The main task in flotation of mica, is to separate mica from quartz, feldspar and other minerals. Generally, this can be realized using the cationic collector in acidic medium. However, in the reverse flotation of calcite, residual lead nitrate reagent can cause adverse effects on flotation of mica. Pb^{2+} can be adsorbed on the surface of mica, reducing its surface electronegativity and hindering the adsorption of cationic collectors on the surface of mica. For this reason, the reagent removal should be performed before flotation.

Pulp pH is an important factor for the mica flotation. The PZC of mica, quartz and feldspar are very similar. The PZC of mica is about 1.0 (Xu et al., 2013). The PZC of

quartz is about 2.0 (Besra et al., 2000). The PZC of feldspar is about 2.0 (Lv et al., 2012). For this reason, the pH of pulp was adjusted to 2.

Sodium silicate, sodium fluosilicate and sodium hexametaphosphate are the common silicate inhibitor. As shown in figure 6, sodium silicate and sodium hexametaphosphate could improve the grade of V_2O_5 in concentrate but the recovery declines. When adding sodium silicofluoride as inhibitor, the grade and recovery of V_2O_5 in concentrate could be improved. For these reasons, sodium fluosilicate was selected as an inhibitor and its dosage was set to 300 g/Mg.
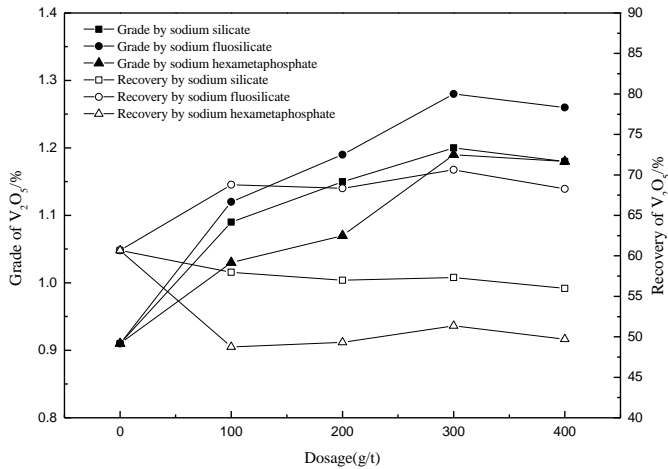

Fig. 6. Effects of sodium silicate, sodium fluosilicate and sodium hexametaphosphate on the grade and recovery of V_2O_5 in concentrate

The entire flow process of the experiment was carried out according to the technological and optimum process parameters (Table 5). The final concentrate, including slime and V concentrate was determined. The grade of V_2O_5 was 1.14% and the recovery of V_2O_5 was 73.66%. The production rate of tailings was 46.18% and vanadium loss was about 26.34%.

Table 5. Overall process test results

Product	Yield (%)	V_2O_5 grade (%)	V_2O_5 recovery (%)
Slime	10.01	1.07	12.90
Ca tailing	16.38	0.48	9.47
V concentrate	43.81	1.15	60.76
Tailing	29.80	0.47	16.87
Decarburization sample	100.00	0.83	100.00

Effect of flotation on vanadium leaching

Pre-concentration of vanadium-bearing mica from stone coal by roasting-flotation is designed to increase the concentration of vanadium-bearing mineral. However, its ultimate purpose is to facilitate extraction of vanadium. The vanadium leaching rates of the raw ore, the decarburization sample and the concentrate were investigated using a direct acid leaching process with 15% H_2SO_4, liquid-solid ratio of 2:1, leaching temperature of 95°C and the leaching time of 6 h. The leaching rates of raw ore, decarburization sample and concentrate were 30.49%, 50.47%, and 69.15%, respectively.

Conclusions

A roasting–flotation technique was used for the pre-concentration of vanadium from low-grade stone coal based on its mineralogical characteristics. Mineralogical study indicated that the vanadium is distributed in the form of isomorphism replacement in mica. The designed pre-concentrate vanadium process includes roasting, desliming and flotation. Throughout the process, the grade of V_2O_5 increased from 0.71% to 1.14%, and 46.18% of the raw ore was rejected. The leaching rate of vanadium increased from 30.49% of raw ore to 69.15% of vanadium concentrate, which means that it increased by approximately 40%. In this way, the pre-concentration process may facilitate more efficient utilization of stone coal.

Acknowledgments

References

BIN Z.Y., *Progress of the research on extraction of vanadium pentoxide from stone coal and the market of the V_2O_5*, 2006, Hunan Nonferrous Metals, 1, 16-20.

BESRA L., SENGUPTA D.K., ROY S.K., *Particle characteristics and their influence on dewatering of kaolin, calcite and quartz suspensions*, 2000, International Journal of Mineral Processing, 59, 89-112.

CHEN T.J., QIU G.Z., ZHU D.Q., *Valence variation and oxidation kinetics of vanadium during vanadium-bearing stone coal roasting*, 2008, Mining and Metallurgical Engineering. 28, 64-67.

DENG Z.G., WEI C., FAN G., LI M.T., LI C.X., LI X.B., *Extracting vanadium from stone-coal by oxygen pressure acid leaching and solvent extraction*, 2010, Transactions of Nonferrous Metals Society of China, 20, 118-122.

HE D.S., FENG Q.M., ZHANG G.F., OU L.M., LU Y.P., *An environmentally-friendly technology of vanadium extraction from stone coal*, 2007, Minerals Engineering, 20, 1184-1186.

KANG W.Z., LV Y.T., *Effect of ultrasonic treatment on slime characteristics*, 2006, Journal of China University of Mining & Technology, 35, 783.

LI M.T., WEI C., FAN G., WU H.L., LI C.X., LI X.B., *Acid leaching of black shale for the extraction of vanadium*, 2010, International Journal of Mineral Processing, 95, 62-67.

LV Z., WEI M., WU D.Y., LIU C.M., ZHAO D.K., FENG A.S., *A new technology for processing niobite ore found in Jiangxi province*, 2012, International Journal of Mining Science and Technology, 22, 579-583.

MOSKALYK R.R., ALFANTAZI A.M., *Processing of vanadium: a review*, 2003, Minerals Engineering, 16, 793-805.

NING H., HUANG G., YUAN A.W., WANG X., ZHOU X.Y., *Comprehensive utilization technology for low grade stone coal containing vanadium*, 2010, Nonferrous Metals, 3, 025.

REN L., ZHANG Y.M., BIAN Y., LIU X., LIU C., *Investigation of quartz flotation from decarburized vanadium-bearing coal*, 2015, Physicochemical Problems of Mineral Processing, 51, 755-767.

WANG L., SUN W., LIU R.Q., GU X.C., *Flotation recovery of vanadium from low-grade stone coal*, 2014, Transactions of Nonferrous Metals Society of China, 24, 1145-1151.

WANG M.Y., XIANG X.Y., ZHANG L.P., XIAO L.S., *Effect of vanadium occurrence state on the choice of extracting vanadium technology from stone coal*, 2008, Rare Metals, 27, 112-115.

WU H.L., ZHAO W., LI M.T., DENG G.Z., GE H.H., WEI C., *New craft study on enriching vanadium by means of priority coal flotation from high carbon stone-coal*, 2008, Journal of the Chinese Rare Earth Society, 26, 530-533.

XU L.H., WU H.Q., DONG F.Q., WANG L., WANG Z., XIAO J.H., *Flotation and adsorption of mixed cationic/anionic collectors on muscovite mica*, 2013, Minerals Engineering, 41, 41-45.

ZHU X.B., ZHANG Y.M., HUANG J., Liu T., WANG, Y. *A kinetics study of multi-stage counter-current circulation acid leaching of vanadium from stone coal*, 2012, International Journal of Mineral Processing, 114, 1-6.

ZHANG X.Y., YANG K., TIAN X.D., QIN W.Q., *Vanadium leaching from carbonaceous shale using fluosilicic acid*, 2011, International Journal of Mineral Processing, 100(3), 184-187.

ZHANG Y.M., BAO S.X., LIU T., CHEN T.J., HUANG J., *The technology of extracting vanadium from stone coal in China: history, current status and future prospects*, 2011, Hydrometallurgy, 109(1), 116-124.

ZHAO Y.L., ZHANG Y.M., LIU T., CHEN T.J., BIAN Y., BAO S.X., *Pre-concentration of vanadium from stone coal by gravity separation*, 2013, International Journal of Mineral Processing, 121, 1-5.

ZHAO Y.L., ZHANG Y.M., Song, S.X., CHEN T.J., BAO S.X., Behaviors of impurity elements Ca and Fe in vanadium-bearing stone coal during roasting and its control measure, 2016, International Journal of Mineral Processing, 148, 100-104.

ZHANG Y.M., HU Y.J., BAO S.X., *Vanadium emission during roasting of vanadium-bearing stone coal in chlorine*, 2012, Minerals Engineering, 30, 95-98.

ZHANG H.J., LIU J.T., CAO Y.J., WANG Y.T., *Effects of particle size on lignite reverse flotation kinetics in the presence of sodium chloride*, 2013, Powder Technology. 246, 658-663.