



Science
Press

Available online at www.sciencedirect.com



ScienceDirect

Trans. Nonferrous Met. Soc. China 28(2018) 1036–1044

Transactions of
Nonferrous Metals
Society of China

www.tnmsc.cn



A new mixed-valent iron arsenate black crystal

Jin-qin YANG¹, Qing-zhu LI^{1,2}, Li-yuan CHAI^{1,2}, Qing-wei WANG^{1,2}, Hui LIU^{1,2}, Xiao-bo MIN^{1,2}, Rui-yang XIAO^{1,2}

1. School of Metallurgy and Environment, Central South University, Changsha 410083, China;
2. National Engineering Research Centre for Control and Treatment of Heavy Metal Pollution, Central South University, Changsha 410083, China

Received 8 November 2017; accepted 15 March 2018

Abstract: Scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) is the most popular phase for arsenic (As) immobilization while the reductive dissolution of Fe(III) to Fe(II) will promote As release. In the present study, an equilibrium between Fe(III) and Fe(II) was achieved in scorodite preparation system by introducing certain alcohol (methanol, ethanol, isopropanol or tert-butanol), and thus a new mixed-valent iron arsenate black crystal formulated as $\text{Fe}(\text{II})_{5.2}\text{Fe}(\text{III})_{8.8}(\text{HAsO}_4)_4(\text{AsO}_4)_8 \cdot \text{H}_2\text{O}$ was prepared. In comparison with scorodite, the black crystal has higher As content (36.4%, mass fraction) and lower crystal water content (0.73%, mass fraction). Additionally, the leaching concentration of As can be lower than the threshold value (5 mg/L) regulated by identification standards for hazardous wastes of China (GB 5080.3–2007). Therefore, this new mixed-valent iron arsenate crystal could be classified as a non-hazardous and promising As-bearing phase in environmental applications.

Key words: arsenic; iron; crystal; arsenic immobilization; hazardous wastes

1 Introduction

Arsenic (As) is a notorious environmental toxicant known as both a carcinogen and an atherogen in human beings [1,2]. Groundwater with elevated As levels as the source of drinking water poses a health threat in many parts of the world [3–5], especially in China, where 19.6 million people live in high-risk areas [6]. Since As is a short-life cycle element, structural incorporation of As in some mineral phases can get rid of As contamination in water environment. Nowadays, Fe–As bearing phases as alternatives of calcium arsenate have been concerned, such as kaňkite ($\text{FeAsO}_4 \cdot 3.5\text{H}_2\text{O}$) [7], kamarizaite ($\text{Fe}_3(\text{AsO}_4)_2(\text{OH})_3 \cdot 3\text{H}_2\text{O}$) [8], scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) [9], bukovskýite ($\text{Fe}_2(\text{AsO}_4)(\text{SO}_4)(\text{OH}) \cdot 7\text{H}_2\text{O}$) [10], hilarionite ($\text{Fe}_2(\text{SO}_4)(\text{AsO}_4)(\text{OH}) \cdot 6\text{H}_2\text{O}$) [11,12], sarmientite ($\text{Fe}_2(\text{AsO}_4)(\text{SO}_4)(\text{OH}) \cdot 5\text{H}_2\text{O}$) [13], tooeleite ($\text{Fe}_6(\text{AsO}_3)_4\text{SO}_4(\text{OH})_4 \cdot 4\text{H}_2\text{O}$) [14,15]. Because of advantages of low solubility, low water content (15.6%, mass fraction) and high As content (32.5%, mass fraction), scorodite has been accepted as the most

suitable solid for As immobilization [9,16]. However, the stability of scorodite in reducing environments is problematic [17,18]. For example, the reductive dissolution of Fe(III) to Fe(II) in scorodite by ferric reducing microorganisms can promote the mobilization of As [18–21]. Since As mobilization is dependent on redox behaviors of Fe, it arouses our great interests that whether there are some mixed-valent iron arsenate compounds containing both Fe(II) and Fe(III). Apart from As, the mixed-valent iron oxide magnetite $\text{Fe}(\text{III})_2\text{Fe}(\text{II})\text{O}_4$ can be formed by a number of different biological and inorganic mechanisms [22,23]. As a byproduct of microbial Fe(III) respiration, magnetite can be produced by the dissimilatory iron-reducing bacteria and covered from many modern and ancient environments including sediments and soils and even meteorites [24]. Accordingly, it is very likely that some mixed-valent iron arsenate phases will be found in association with scorodite under the function of ferric reducing microorganisms.

To our knowledge, there are only three mixed-valent iron arsenate crystals reported in literatures.

Foundation item: Project (51634010) supported by the Key Project of National Natural Science Foundation of China; Project (51304251) supported by the National Natural Science Foundation of China; Project (201509050) supported by Special Program on Environmental Protection for Public Welfare of China

Corresponding author: Li-yuan CHAI; Tel: +86-731-88830875; Fax: +86-731-88710171; E-mail: chailiyuan@csu.edu.cn
DOI: 10.1016/S1003-6326(18)64741-7

Danonite ($\text{Fe(II)}_{10}\text{Fe(III)}_4(\text{AsO}_4\text{H})_4(\text{AsO}_4)_8 \cdot \text{H}_2\text{O}$) is a synthetic crystal, which was hydrothermally synthesized from the oxidation of symplectite ($\text{Fe}_3(\text{AsO}_4)_3(\text{H}_2\text{O})_8$) at pH=5 under 200 °C and 24 h [25]. Césarferreiraite ($\text{Fe(II)}\text{Fe(III)}_2(\text{AsO}_4)_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}$) is a laueite-group mineral and was found from Eduardo pegmatite mine, Conselheiro Pena Municipality, Minas Gerais, Brazil [26]. Bendadaite ($\text{Fe(II)}\text{Fe(III)}_2(\text{AsO}_4)_2(\text{OH})_2 \cdot 4\text{H}_2\text{O}$) is an arthurite-group mineral and was found from the Phosphate Pegmatite Bendada in Central Portugal, the Granite Pegmatite of Lavra do Almerindo in Brazil and the Veta Negra Mine in Chile, etc [27]. Although césarferreiraite and bendadaite were found in different mine zones, they grew on scorodite or were overgrown by scorodite crust. Scorodite as a weathering product of arsenopyrite was formed at high φ_h and low pH from concentrated Fe(III) and As(V) solutions [28–31]. The co-existence with scorodite suggests that césarferreiraite and bendadaite may be formed under similar conditions but the equilibrium between Fe(II) and Fe(III) oxidation states is necessary. Accordingly, an equilibrium of Fe(II) and Fe(III) could be explored in the preparation system of scorodite to prepare some mixed-valent iron arsenate crystals for As immobilization. In this study, some reducing alcohol was introduced into scorodite system to implement partial reduction of Fe(III) and thus a new mixed Fe(II) and Fe(III) arsenate crystal ($\text{Fe(II)}_{5.2}\text{Fe(III)}_{8.8}(\text{AsO}_4\text{H})_4(\text{AsO}_4)_8 \cdot \text{H}_2\text{O}$) was generated. In comparison with scorodite, this new crystal has higher As content (36.4%, mass fraction), much lower crystal water content (0.73%, mass fraction) and better filterability. Besides, the leaching concentration of As ($\rho(\text{As}) < 5 \text{ mg/L}$) suggests that this new crystal could be classified as non-hazardous waste, and thus is a

promising As-bearing phase in environmental applications.

2 Experimental

2.1 Materials and batch experiments

Sodium arsenate ($\text{Na}_3\text{AsO}_4 \cdot 12\text{H}_2\text{O}$), ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), ferric sulfate ($\text{Fe}_2(\text{SO}_4)_3 \cdot x\text{H}_2\text{O}$), nitric acid (HNO_3), sulfuric acid (H_2SO_4), isopropanol (IPA, $\text{C}_3\text{H}_8\text{O}$), methanol (MeOH , CH_3OH), ethanol (EtOH , $\text{C}_2\text{H}_6\text{O}$), tert-butanol (TBA, $\text{C}_4\text{H}_{10}\text{O}$) were used to prepare reaction solutions. The composition of reaction solutions was shown in Table 1, and the reaction was conducted in a high-pressure hydrothermal autoclave. The reaction temperature (140–200 °C) and reaction time (1–24 h) were investigated in the reaction solution containing 0.15 mol/L Fe, 0.10 mol/L As, ~1.3 mol/L concentrated HNO_3 and 50% IPA. Unless otherwise noted, the reaction temperature and time are 200 °C and 12 h, respectively.

2.2 Characterization

Powder XRD patterns were recorded on a Rigaku D/Max-RB diffractometer with Cu K_α radiation. Surface morphologies, microstructures and element distribution were analysed by using scanning electron microscope–energy dispersive spectrometer (SEM–EDS), high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SEAD). The X-ray absorption spectroscopy (XAS) measurements were carried out using beamline 07A1 at Taiwan Light Source (TLS), China. The scan step-sizes were 2.0, 0.6, and 0.06 eV/step for pre-edge, edge and post-edge regions, respectively. Both As and Fe K-edge data were collected

Table 1 Compositions of reaction solutions

$\rho(\text{Fe})/(\text{mol} \cdot \text{L}^{-1})$	$\rho(\text{As})/(\text{mol} \cdot \text{L}^{-1})$	$\rho(\text{HNO}_3)/(\text{mol} \cdot \text{L}^{-1})$	Volume fraction/%	Solid phase	Sample label
0.315	0.21	~2.6 HNO_3	0	Scorodite	Scorodite- HNO_3
0.315	0.21	~1.3 H_2SO_4			Scorodite- H_2SO_4
0.15	0	~1.3 HNO_3	50, IPA	Fe_2O_3	Fe_2O_3
0	0.10	~1.3 HNO_3	50, IPA	—	—
0.15	0.10	~0.65 H_2SO_4	50, IPA	—	—
0.15	0.10	~1.3	50, MeOH 50, EtOH 50, IPA 50, TBA 50, IPA	Black crystal	MeOH
0.15	0.10	~1.3			EtOH
0.15	0.10	~1.3			IPA
0.15	0.10	~1.3			TBA
0.15	0.10	~1.3			50% IPA
0.195	0.13	~1.56	40, IPA	Black crystal	40% IPA
0.225	0.15	~1.82	30, IPA		30% IPA
0.255	0.17	~2.08	20, IPA		20% IPA
0.285	0.19	~2.34	10, IPA		10% IPA
0.30	0.20	~2.47	5, IPA		5% IPA

in transmission mode for the title crystal and scorodite. Thermogravimetric (TG) analysis was carried out under a nitrogen atmosphere from room temperature to 900 °C with a heating rate of 10 °C/min. Mössbauer spectra were recorded at room temperature in transmission mode and ^{57}Co was a Mössbauer source. Inductively coupled plasma-optical emission spectroscopy (ICP-OES) was used to determine the composition of the title crystal after the digestion by concentrated HNO_3 .

2.3 Quantitative element analysis of Fe and As

Approximately 250 mg of samples were dissolved in an Erlenmeyer flask by adding 15 mL of concentrated HNO_3 . A heating procedure was employed at 70 °C over a period of 12 h to dissolve solid samples [32]. Deionized water was subsequently added to make up to 100 mL for ICP-OES analysis.

2.4 TCLP tests

The short-term stability was tested by a modified US EPA Method 3111 Toxicity Characteristic Leaching Procedure (TCLP) [33]. A 1000 mL extraction fluid ($\text{pH}=4.93\pm 0.05$) was prepared by mixing 5.7 mL acetic acid ($\text{CH}_3\text{CH}_2\text{OOH}$) and 64.3 mL NaOH (1 mol/L) in deionized water. Samples were mixed with the extraction fluid at a mass-to-volume ratio of 1:20 in a 50 mL volumetric flask and then continuously shaken at 30 °C for (18 ± 2) h [34]. The filtrates were analyzed for As concentration by ICP-OES.

3 Results and discussion

Scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) can be synthesized by hydrothermal precipitation [35,36]. Here, scorodite in cyan color (labelled as scorodite- HNO_3 , seen in Fig. 1(a)) was synthesized in HNO_3 system, where $\text{Fe}(\text{NO}_3)_2$,

Na_3AsO_4 and HNO_3 were mixed in deionized water. Correspondingly, blackish green scorodite (labelled as scorodite- H_2SO_4 , seen in Fig. 1(b)) was synthesized in H_2SO_4 system, where $\text{Fe}_2(\text{SO}_4)_3$, Na_3AsO_4 and H_2SO_4 were used. When isopropanol (IPA) was introduced into the preparation system of scorodite- HNO_3 , some black crystals (Fig. 1(c)) were interestingly synthesized when IPA volume fraction varied from 5% to 50% (Fig. 2(a)). In addition, black crystals with similar XRD pattern but better crystallinity can be synthesized under longer time (Fig. 2(b)) and higher temperatures (Fig. 2(c)). Figure 2(c) showed that amorphous phase was formed when the temperature was below 160 °C, and black crystals synthesized at 160–200 °C were well-crystallized. As shown in Fig. 3, the black crystal synthesized at 200 °C is flower-like microsphere but has a monolithic spherical surface when it was synthesized at 160 and 180 °C. When IPA was replaced by methanol (MeOH), ethanol (EtOH) or tert-butanol (TBA), the resultant solids were all in black color and their XRD characteristics have no meaningful change (Fig. 4). However, no solid was formed in the absence of Fe, and Fe_2O_3 was obtained in the absence of As. Furthermore, there is no solid formation when IPA was introduced into the preparation system of scorodite- H_2SO_4 . This means that Na_3AsO_4 , $\text{Fe}(\text{NO}_3)_3$, HNO_3 and alcohol (MeOH, EtOH, IPA or TBA) are distinctive combination for the synthesis of black crystals.

Different from pyramidal scorodite- HNO_3 (Fig. 1(d)) and scorodite- H_2SO_4 (Fig. 1(e)), the well-crystallized black crystal is flower-like microsphere (Fig. 1(f)). Besides, selected area electron diffraction (SAED) patterns (Figs. 5(c)–(f)) of black crystals displayed same regular hexagon of monocrystalline phase, which differs from the polycrystalline diffraction ring of scorodite- HNO_3 (Fig. 5(a)) and scorodite- H_2SO_4 (Fig. 5(b)). As

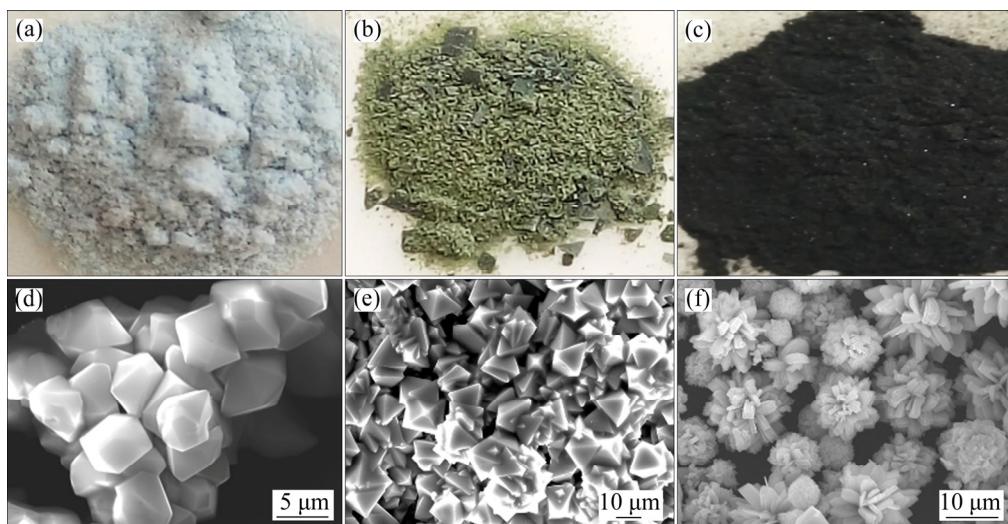


Fig. 1 Photos (a, b, c) and SEM images (d, e, f) of scorodite- HNO_3 (a, d), scorodite- H_2SO_4 (b, e) and black crystal (c, f)

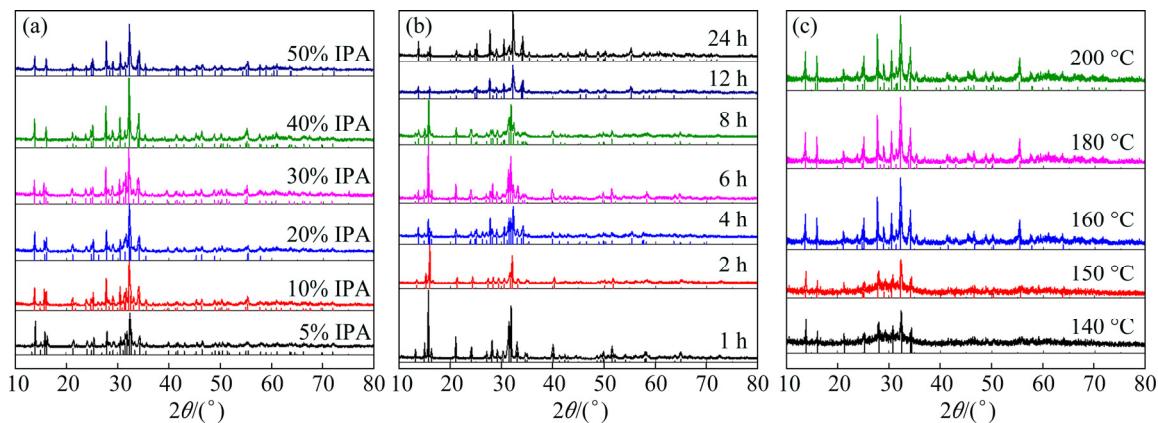


Fig. 2 XRD patterns of black crystals synthesized under different conditions of IPA volume fraction (a), reaction time (b) and reaction temperature (c)

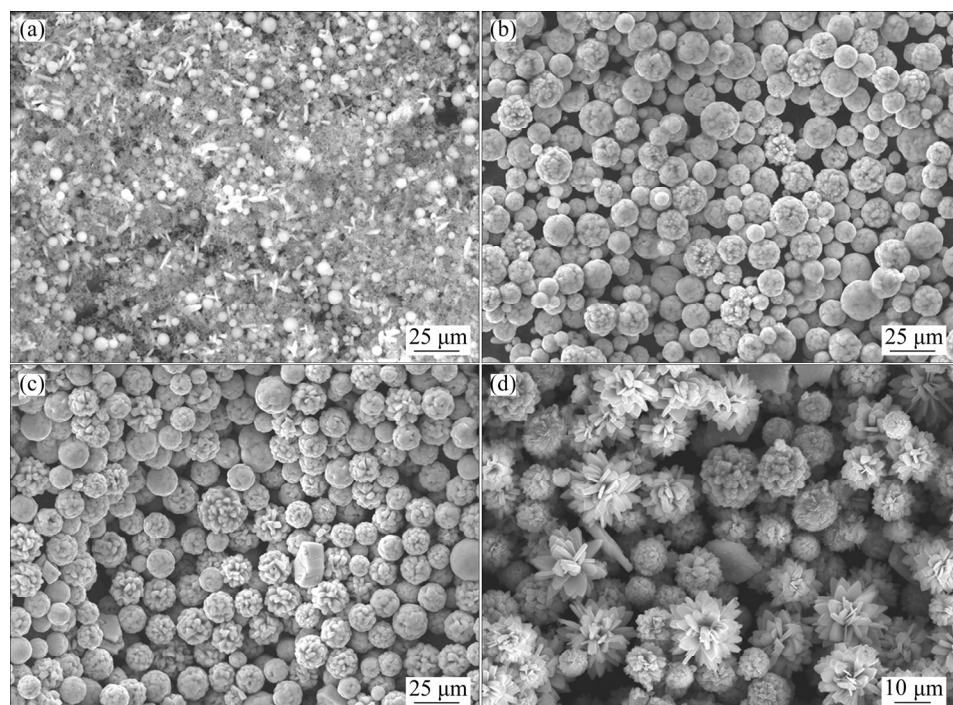


Fig. 3 SEM images of black crystals synthesized at different temperatures: (a) 140 °C; (b) 160 °C; (c) 180 °C; (d) 200 °C

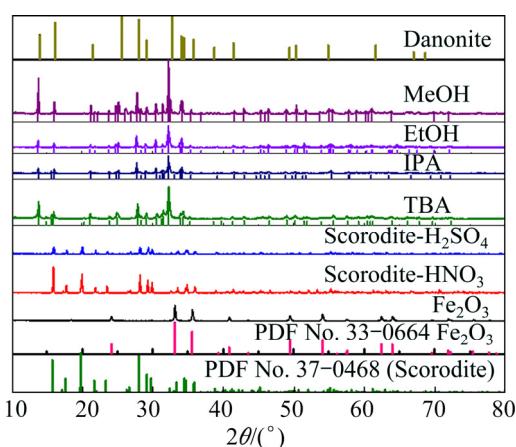


Fig. 4 XRD patterns of scorodite-HNO₃, scorodite-H₂SO₄, Fe₂O₃ and black crystals synthesized at 200 °C in the presence of MeOH, EtOH, IPA and TBA

shown in Fig. 4, the strongest eight XRD lines for black crystals are located at $2\theta=13.9^\circ$, 16.0° , 21.2° , 25.2° , 27.8° , 30.5° , 32.3° , 34.2° , which are different from scorodite (PDF No. 37-0468) but close to danonite ($\text{Fe}(\text{II})_{10}\text{Fe}(\text{III})_4(\text{AsO}_4\text{H})_4(\text{AsO}_4)_8\cdot\text{H}_2\text{O}$) [25]. Danonite is a mixed-valent iron arsenate crystal and its theoretical Fe/As molar ratio is ~ 1.17 , Fe(III)/Fe(II) molar ratio is 0.4 and crystal water content is 0.73%.

In order to identify whether the black crystal is danonite, more characterizations were conducted in the following. Firstly, CHN elemental analysis indicates that the black crystal did not contain N and C elements. EDS analysis in Fig. 6 indicated that the black crystal mainly consisted of Fe, As and O. Subsequently, the valence of Fe and As in the black crystal was confirmed respectively by Fe and As K-edge X-ray absorption near

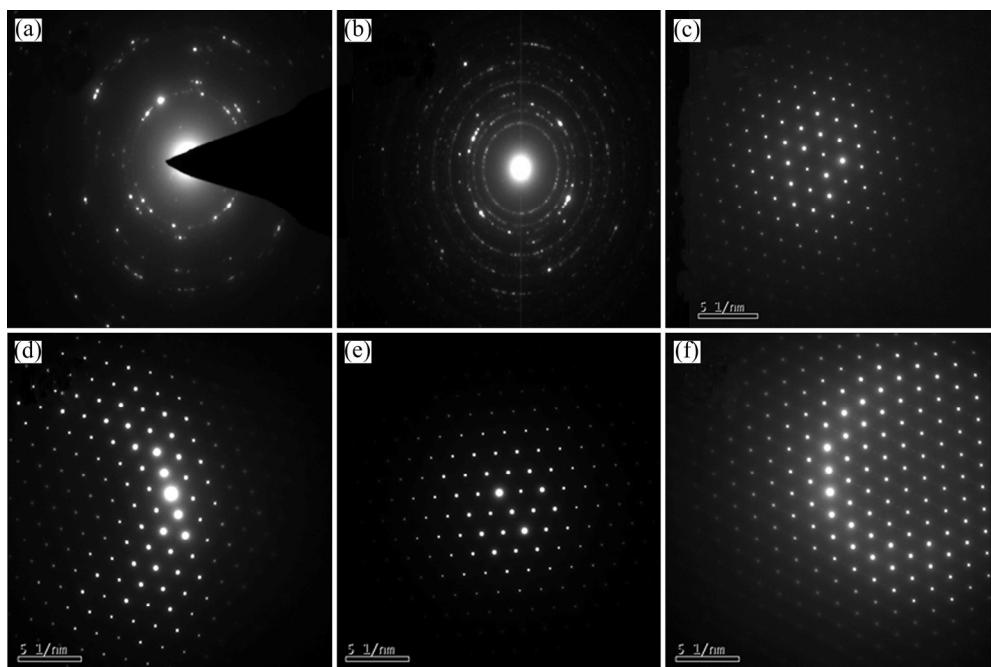


Fig. 5 SAED patterns of scorodite-HNO₃ (a), scorodite-H₂SO₄ (b) and black crystals (c–f) synthesized at 200 °C

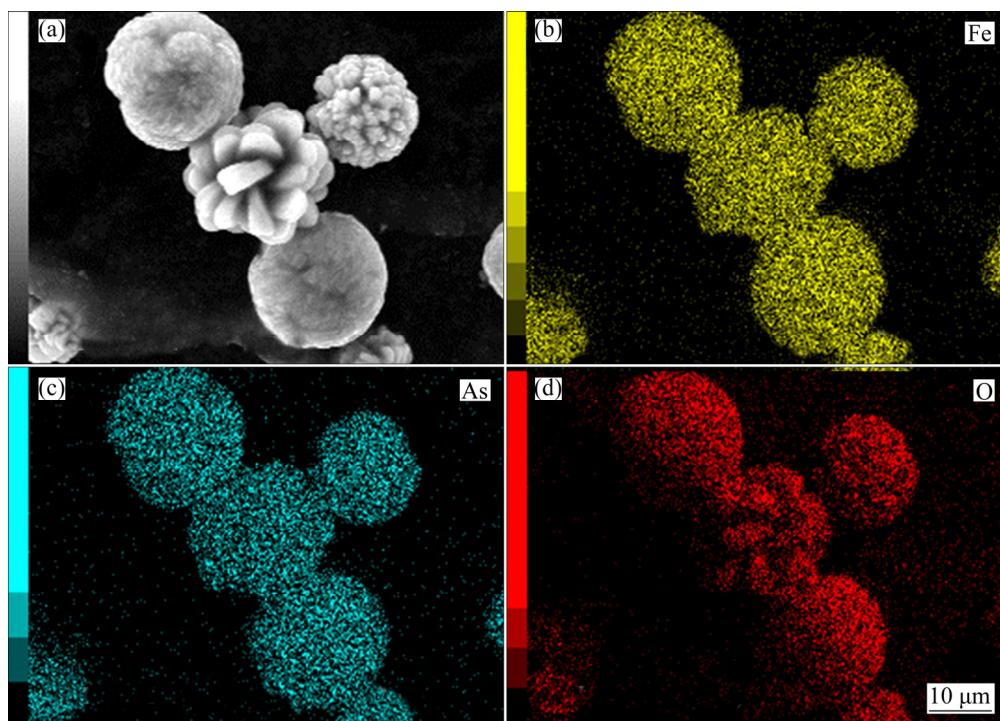


Fig. 6 SEM image of black crystal synthesized at 200 °C (a) and corresponding elemental mapping images of Fe (b), As (c) and O (d)

edge structure (XANES) spectroscopy, and compared with scorodite. As shown in Fig. 7(a), energy location of the edge and white line of As K-edge was coincident with that of scorodite, which proved that As in the black crystal is pentavalent. However, edge energy of Fe K-edge of the black crystal was 3.6 eV lower than that of scorodite (Fig. 7(b)), which indicated that Fe in the black crystal is not only trivalent. Mixed trivalent Fe(III) and

divalent Fe(II) were further confirmed by Mössbauer spectroscopy. As shown in Fig. 8, fitted curve is obtained by superimposing three doublets, one corresponding to Fe(III) and other two to Fe(II). The relative absorption spectral areas are 63.1% for Fe(III) and 36.9% for Fe(II), and thus the Fe(III)/Fe(II) molar ratio is ~1.7, which is much higher than that in danonite (0.4). It is very likely that the black crystal is a new mixed-valent iron arsenate

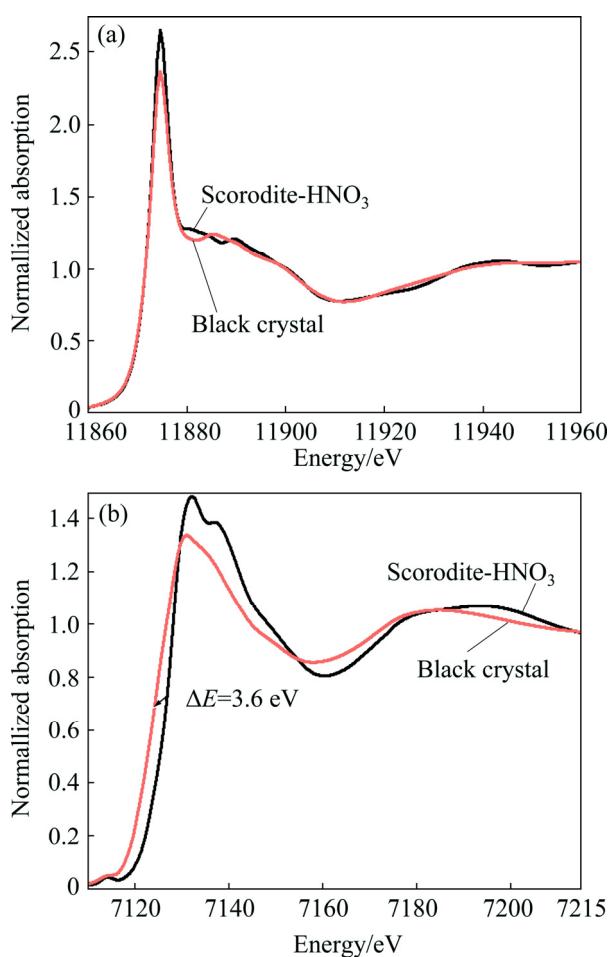


Fig. 7 XANES spectra of As (a) and Fe (b) K-edge of scorodite-HNO₃ and black crystal synthesized at 200 °C

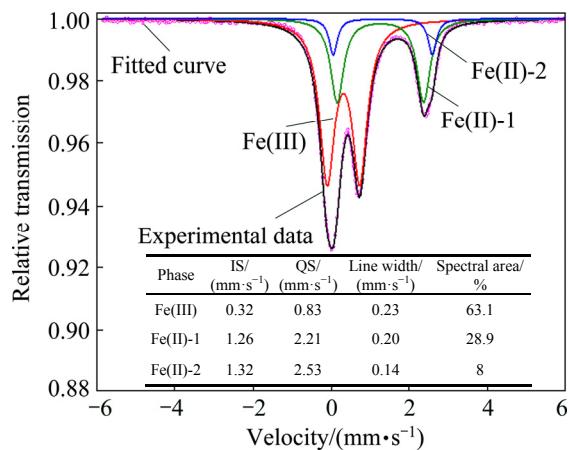


Fig. 8 Mössbauer spectroscopy of Fe in black crystal synthesized at 200 °C (IS is isomer shift and QS is quadrupole splitting)

crystal. However, its single-crystal structure was hard to be determined by X-ray crystallography method because the crystal size was too small (<20 μm). Therefore, quantitative element analysis and thermogravimetric (TG) analysis were respectively conducted to determine the

Fe/As molar ratio and crystal water content. The results of quantitative element analysis were shown in Table 2 and the Fe/As molar ratio of scorodite samples determined by this method is equal to the theoretical value (1.0), which means that this method is suitable for the Fe/As molar ratio determination. The Fe/As molar ratio of black crystals synthesized under different conditions is 1.11–1.22, and the average is 1.16, which is very close to the Fe/As molar ratio in danonite. In addition, the crystal water content of black crystals was determined by TG and shown in Fig. 9. The continuous loss of water was observed in the range of 100–400 °C, and the water losses are 0.88%, 1.18% and 1.52% when the black crystal was respectively synthesized at 200, 180 and 160 °C. The crystal water content of the black crystal is much lower than scorodite but is very close to the theoretical value of danonite (0.73%), especially when the black crystal was synthesized at 200 °C. Therefore, the black crystal synthesized in this study is

Table 2 Quantitative element analysis results of black crystals synthesized under different conditions and scorodite

Sample	ρ(Fe)/(mg·L ⁻¹)	ρ(As)/(mg·L ⁻¹)	Fe/As molar ratio
50% IPA	19.88	23.72	1.12
40% IPA	20.25	23.58	1.15
30% IPA	19.80	22.68	1.17
20% IPA	20.08	22.76	1.18
10% IPA	21.48	24.38	1.18
5% IPA	20.25	22.30	1.22
4 h	21.33	24.39	1.17
6 h	20.53	24.13	1.14
8 h	20.01	22.95	1.17
12 h	18.88	22.81	1.11
Average	20.25±0.75	23.37±0.77	1.16±0.03
Scorodite	19.85±0.73	26.25±1.31	1.02±0.02

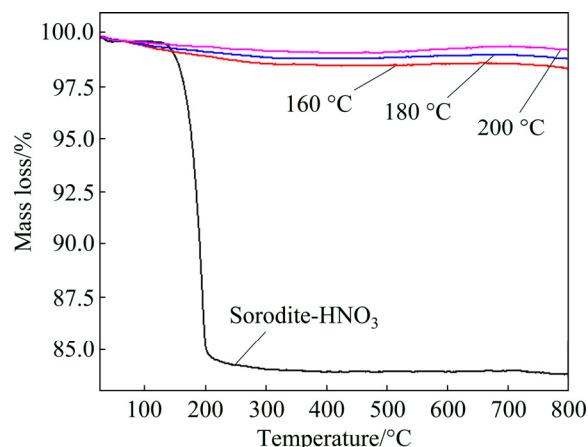


Fig. 9 TG results of scorodite-HNO₃ and black crystal synthesized at 160, 180 and 200 °C

very close to danonite except much higher Fe(III)/Fe(II) molar ratio in black crystals. The empirical formula of the black crystal is derived as $\text{Fe(II)}_{5.2}\text{Fe(III)}_{8.8}(\text{AsO}_4\text{H})_4\cdot(\text{AsO}_4)_8\cdot\text{H}_2\text{O}$ and the relative molecular mass is 2471.1 g/mol.

In the quantitative element analysis experiments, approximate 250 mg of black crystal samples were dissolved by concentrated HNO_3 and mixed with deionized water to 100 mL. Before ICP-OES determination for Fe and As concentrations, solutions were all diluted by deionized water with a volume ratio of 1:40. According to the empirical formula of the black crystal, the theoretical concentrations of As and Fe in the final solution are respectively 22.74 and 19.78 mg/L, which are in consistence with the experimental results listed in Table 2. This indicates that the derived formula is believable. Based on this formula, the As content is theoretically 36.4% and much higher than that in scorodite (32.5%). Moreover, the crystal water content of black crystal is theoretically 0.73% and much lower than that in scorodite (15.6%). Since scorodite has been accepted as the most suitable solid for As immobilization, the potential of the black crystal should also be evaluated for As immobilization. As shown in Fig. 10, As leaching concentrations of black crystals synthesized in the presence of 5%–50% IPA were lower than 35 mg/L. The lowest As leaching concentration was ~2.5 mg/L, which was lower than the threshold value (5 mg/L) regulated by identification standards for hazardous wastes of China (GB 5080.3–2007) [37]. This means that the black crystal could be classified as non-hazardous waste and thus is a promising phase for As storage. When IPA volume fractions were 60% and 70%, As leaching concentrations of resultant solids were respectively 35.76 and 56.45 mg/L, which were higher than that of black crystals. This is because that Fe-oxides/hydroxides were formed and As was possibly

absorbed when IPA volume fraction was higher than 50%. Consequently, IPA is important to partially reduce Fe(III) to Fe(II); however, it should be replaced by other reducing agents to promote the easy formation of the black crystal in the process of As removal from wastewaters. Therefore, the black crystal calls for more research to determine its crystal structure and develop new synthesis method for promoting its applications in both As immobilization and As removal from wastewaters.

4 Conclusions

- 1) A new black crystal was synthesized by introducing methanol (MeOH), ethanol (EtOH), tert-butanol (TBA) or isopropanol (IPA) into the preparation system of scorodite- HNO_3 .

- 2) The new black crystal is flower-like microsphere, displays regular hexagon of monocrystalline phase and has the strongest eight XRD lines at $2\theta=13.9^\circ$, 16.0° , 21.2° , 25.2° , 27.8° , 30.5° , 32.3° and 34.2° .

- 3) The new black crystal differs from scorodite but close to danonite in many aspects including XRD patterns, Fe/As molar ratio and crystal water content. However, the significant difference in Fe(III)/Fe(II) molar ratio implies that the black crystal is a new mixed Fe(III) and Fe(II) arsenate crystal $(\text{Fe(II)}_{5.2}\text{Fe(III)}_{8.8}\cdot(\text{AsO}_4\text{H})_4\cdot(\text{AsO}_4)_8\cdot\text{H}_2\text{O})$.

- 4) The new black crystal has higher As content (36.4%) and much lower crystal water (0.73%), besides, the lowest As leaching concentration in TCLP tests was lower than the threshold value (5 mg/L) regulated by identification standards for hazardous wastes of China (GB 5080.3–2007).

- 5) New preparation methods should be developed to promote the applications of the new black crystal in both As immobilization and As removal.

References

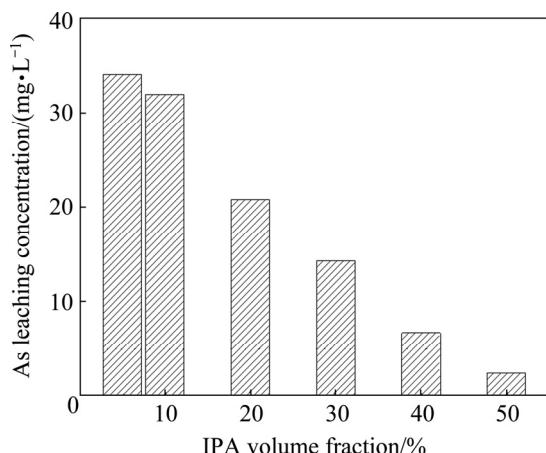


Fig. 10 As leaching concentration of black crystals synthesized under different IPA volume fractions

- [1] PERAZA M A. Subcytotoxic inorganic arsenic effects on mitochondria in a human proximal tubule cell line: Implications on mechanism of cell death [D]. Tucson, Arizona: The University of Arizona, 2003.
- [2] SLYEMI D, BONNEFOY V. How prokaryotes deal with arsenic [J]. Environmental Microbiology Reports, 2012, 4(6): 571.
- [3] VAN G A, WIN K H, ZAW T, NAING W, MEY J L, MAILLOUX B. Confirmation of elevated arsenic levels in groundwater of Myanmar [J]. Science of the Total Environment, 2014, 478(8): 21–24.
- [4] MUKHERJEE A, FRYAR A E, SCANLON B R, BHATTACHARYA P, BHATTACHARYA A. Elevated arsenic in deeper groundwater of the western Bengal basin, India: Extent and controls from regional to local scale [J]. Applied Geochemistry, 2011, 26(4): 600–613.

- [5] SOENTGEN J. Arsenic. Environmental chemistry, health threats and waste treatment [J]. *GAIA—Ecological Perspectives for Science and Society*, 2011, 20(3): 199–201.
- [6] RODRÍGUEZLADO L, SUN G, BERG M, ZHANG Q, XUE H, ZHENG Q, JOHNSON C A. Groundwater arsenic contamination throughout China [J]. *Science*, 2013, 341(6148): 866–868.
- [7] ČECH F, JANSA J, NOVÁK F. Kaňkite, $\text{FeAsO}_4 \cdot 3\text{H}_2\text{O}$, a new mineral [J]. *Neues Jahrb Mineral Monatsh*, 1976, 9: 426–436.
- [8] CHUKANOV N V, PEKOV I V, MÖCKEL S, MUKHANOVA A A, BELAKOVSKY D I, LEVITSKAYA L A, BEKENOVA G K. Kamarizaite, $\text{Fe}_3^{3+}(\text{AsO}_4)_2(\text{OH})_3 \cdot 3\text{H}_2\text{O}$, a new mineral species, arsenate analogue of tinticite [J]. *Geology of Ore Deposits*, 2010, 52(7): 599–605.
- [9] FILIPPOU D, DEMOPOULOS G P. Arsenic immobilization by controlled scorodite precipitation [J]. *JOM*, 1997, 49(12): 52–55.
- [10] MAJZLAN J, LAZIC B, ARMBRUSTER T, JOHNSON M B, WHITE M A, FISHER R A, PLÁŠIL J, LOUN J, ŠKODA R, NOVÁK M. Crystal structure, thermodynamic properties, and paragenesis of Bukovskýite, $\text{Fe}_2(\text{AsO}_4)(\text{SO}_4)(\text{OH}) \cdot 9\text{H}_2\text{O}$ [J]. *Journal of Mineralogical & Petrological Sciences*, 2012, 107(3): 133–148.
- [11] LIU J, HE L, DONG F, FROST R L. Infrared and Raman spectroscopic characterizations on new Fe sulphoarsenate hilarionite ($\text{Fe}(\text{III})_2(\text{SO}_4)(\text{AsO}_4)(\text{OH}) \cdot 6\text{H}_2\text{O}$): Implications for arsenic mineralogy in supergene environment of mine area [J]. *Spectrochimica Acta (Part A): Molecular & Biomolecular Spectroscopy*, 2017, 170: 9–13.
- [12] PEKOV I V, CHUKANOV N V, YAPASKURT V O, RUSAKOV V S, BELAKOVSKY D I, TURCHKOVA A G, VOUDOURIS P, MAGGANAS A, KATERINOPoulos A. Hilarionite, $\text{Fe}_2^{3+}(\text{SO}_4) \cdot (\text{AsO}_4)(\text{OH}) \cdot 6\text{H}_2\text{O}$, a new supergene mineral from Lavrion, Greece [J]. *Geology of Ore Deposits*, 2014, 56(7): 567–575.
- [13] FROST R L, PALMER S J, XI Y. The molecular structure of the mineral sarmientite $\text{Fe}_2(\text{AsO}_4,\text{SO}_4)_2(\text{OH})_6 \cdot 5\text{H}_2\text{O}$ —Implications for arsenic accumulation and removal [J]. *Journal of Molecular Structure*, 2011, 1004(1–3): 88–93.
- [14] CHAI L, YUE M, LI Q, ZHANG G, ZHANG M, WANG Q, LIU H, LIU Q. Enhanced stability of tooeelite by hydrothermal method for the fixation of arsenite [J]. *Hydrometallurgy*, 2017, 175: 93–101.
- [15] CHAI L, YUE M, YANG J, WANG Q, LI Q, LIU H. Formation of tooeelite and the role of direct removal of As(III) from high-arsenic acid wastewater [J]. *Journal of Hazardous Materials*, 2016, 320: 620–627.
- [16] TWIDWELL L. A guide to recent literature focused on scorodite for containment of arsenic [R]. Butte: Montana Tech of the University of Montana, 2015.
- [17] YUAN Z, ZHANG D, WANG S, XU L, WANG K, SONG Y, XIAO F, JIA Y. Effect of hydroquinone-induced iron reduction on the stability of scorodite and arsenic mobilization [J]. *Hydrometallurgy*, 2016, 164: 228–237.
- [18] PAPASSIOPI N, VAXEVANIDOU K, PASPALIARIS I. Investigating the use of iron reducing bacteria for the removal of arsenic from contaminated soils [J]. *Water Air & Soil Pollution Focus*, 2003, 3(3): 81–90.
- [19] WANG Y, LIU X H, SI Y B, WANG R F. Release and transformation of arsenic from As-bearing iron minerals by Fe-reducing bacteria [J]. *Chemical Engineering Journal*, 2016, 295: 29–38.
- [20] REVESZ E, FORTIN D, PAKTUNC D. Reductive dissolution of scorodite in the presence of *Shewanella* sp.CN32 and *Shewanella* sp. ANA-3 [J]. *Applied Geochemistry*, 2015, 63: 347–356.
- [21] CUMMINGS D E, CACCAVO F, FENDORF S, ROSENZWEIG R F. Arsenic mobilization by the dissimilatory Fe(III)-reducing bacterium *Shewanella alga* BrY [J]. *Environmental Science & Technology*, 1999, 33(5): 723–729.
- [22] JIMENEZ-LOPEZ C, ROMANEK C S, BAZYLINSKI D A. Magnetite as a prokaryotic biomarker: A review [J]. *Journal of Geophysical Research Biogeosciences*, 2010, 115: 512–514.
- [23] HUBER F, SCHILD D, VITOVA T, ROTHE J, KIRSCH R, SCHÄFER T. U(VI) removal kinetics in presence of synthetic magnetite nanoparticles [J]. *Geochimica et Cosmochimica Acta*, 2012, 96(11): 154–173.
- [24] LOVLEY D R, STOLZ J F, NORD G L, PHILLIPS E J P. Anaerobic production of magnetite by a dissimilatory iron-reducing microorganism [J]. *Nature*, 1987, 330(6145): 252–254.
- [25] MATTIEVICH E, de AMORIN H S, DO AMARAL M R Jr, TORRES-TAPIA E C, DOMINGUEZ A B. A new synthetic mixed valence iron arsenate [C]//*Hyperfine Interactions*. Rio de Janeiro: 1998: 368–371.
- [26] SCHOLZ, CHUKANOV R, FILHO N V M, ATENCIO L A D, LAGOEIRO D, BELOTTI L, CHAVES F M, ROMANO M L S C, BRANDÃO A W, BELAKOVSKIYI P R. Césarferreiraite, $\text{Fe}^{2+}\text{Fe}_2^{3+} \cdot (\text{AsO}_4)_2(\text{OH})_2 \cdot 8\text{H}_2\text{O}$, from Eduardo Mine, Conselheiro Pena, Minas Gerais, Brazil: Second arsenate in the laueite mineral group [J]. *American Mineralogist*, 2014, 99(4): 607–611.
- [27] KOLITSCH U, ATENCIO D, CHUKANOV N V, ZUBKOVA N V, MENEZES FILHO L A D, COUTINHO J M V, BIRCH W D, SCHLÜTER J, POHL D, KAMPF A R. Bendadaite, a new iron arsenate mineral of the arthurite group [J]. *Mineralogical Magazine*, 2010, 74(3): 469–486.
- [28] DOVE P M, RIMSTIDT J D. Solubility and stability of scorodite, $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$: Reply [J]. *American Mineralogist*, 1985, 70(7): 838–844.
- [29] DRAHOTA P, FILIPPI M. Secondary arsenic minerals in the environment: A review [J]. *Environment International*, 2009, 35(8): 1243–1255.
- [30] DASGUPTA D R. Occurrence of scorodite in a pegmatite in Bhilwara District, Rajasthan, India [J]. *Mineralogical Magazine*, 1966, 35(273): 776–777.
- [31] GONZALEZCONTRERAS P, WEIJMA J, WEIJDEN R V D, BUISMAN C J N. Biogenic scorodite crystallization by *Acidianus sulfidivorans* for arsenic removal [J]. *Environmental Science & Technology*, 2010, 44(2): 675–80.
- [32] KOSSOFF D, WELCH M D, HUDSON-EDWARDS K A. Scorodite precipitation in the presence of antimony [J]. *Chemical Geology*, 2015, 406(1): 1–9.
- [33] U.S. EPA. Method 1311: Toxicity characteristic leaching procedure [EB/OL] 2015-05-01. <http://www3.epa.gov/epa-waste/hazard/testmethods/sw846/pdf/1311.pdf>.
- [34] OPIO F K. Investigation of Fe(III)–As(III) bearing phases and their potential for arsenic disposal [D]. Kingston, Ontario, Canada: Queen's University, 2013.
- [35] LIU Z H, YANG X F, LIU Z Y, LI Y H, LI Q H. Effects of synthesis methods for scorodite on its leaching stability [J]. *Chinese Journal of Process Engineering*, 2015, 15: 412–417.
- [36] DUTRIZAC J E, JAMBOR J L. The synthesis of crystalline scorodite, $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ [J]. *Hydrometallurgy*, 1988, 19(3): 377–384.
- [37] GB 5080.3–2007. Identification standards for hazardous wastes—Identification for extraction toxicity [S]. (in Chinese)

一种新型混合价态铁的砷酸盐黑色晶体

杨锦琴¹, 李青竹^{1,2}, 柴立元^{1,2}, 王庆伟^{1,2}, 刘恢^{1,2}, 闵小波^{1,2}, 肖睿洋^{1,2}

1. 中南大学 冶金与环境学院, 长沙 410083;
2. 中南大学 国家重金属污染防治工程技术研究中心, 长沙 410083

摘要: 臭葱石($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$)是应用最广泛的固砷相, 但 $\text{Fe}(\text{III})$ 还原溶解为 $\text{Fe}(\text{II})$ 会促进砷的释放。本研究向臭葱石的制备体系中引入某种醇(甲醇、乙醇、异丙醇或叔丁醇)使 $\text{Fe}(\text{III})$ 和 $\text{Fe}(\text{II})$ 达到平衡并制备出一种新型混合价态铁的砷酸盐黑色晶体, 其分子式为 $\text{Fe}(\text{II})_{5.2}\text{Fe}(\text{III})_{8.8}(\text{AsO}_4\text{H})_4(\text{AsO}_4)_8 \cdot \text{H}_2\text{O}$ 。与臭葱石相比, 该黑色晶体具有较高的砷含量(36.4%, 质量分数)和较低的结晶水含量(0.73%, 质量分数)。另外, 砷的浸出浓度可以低于中国危险废物鉴别标准规定的阈值(5 mg/L)。因此, 这种新型混合价态铁的砷酸盐晶体可以被归为一种在环境应用上极具前景的非毒性含砷相。

关键词: 砷; 铁; 晶体; 固砷; 危险废物

(Edited by Wei-ping CHEN)