UDK 620.18:669.053.4:546.47
Original scientific article/Izvirni znanstveni članek

ISSN 1580-2949
MTAEC9, 55(3)467(2021)

PREPARATION OF CALCIUM SULFATE HEMIHYDRATE WHISKERS FROM COMPLEX JAROSITE WASTE

PRIPRAVA KALCIJ-SULFATNIH POLHIDRATNIH KRATKIH VLAKEN IZ KOMPLEKSNIH JAROZITNIH ODPADKOV

Hongbin Tan[1,3*], Xiaoling Ma[1], Faqin Dong[2], Yufeng Li[2], Jinming Wang[2], Feihua Yang[4]

[1]State Key Laboratory of Environment-friendly Energy Materials, School of Materials Science and Engineering, Southwest University of Science and Technology, Mianyang Sichuan 621010, China
[2]Key Laboratory of Solid Waste Treatment and Resource Recycle, Ministry Education, Southwest University of Science and Technology, Mianyang Sichuan 621010, China
[3]Shaanxi Engineering Center of Metallurgical Slag Resource, Shaanxi University of Technology, Hanzhong Shaanxi 723000, China
[4]State Key Laboratory of Solid Waste Reuse for Building Materials, Beijing Building Materirals Academy of Science Research, Beijing 100041, China

Prejem rokopisa – received: 2020-12-29; sprejem za objavo – accepted for publication: 2021-03-15

doi:10.17222/mit.2020.251

Complex jarosite waste was obtained from zinc metal hydrometallurgical process, which contained gypsum and ammonium jarosite ($NH_4Fe_3(SO_4)_2(OH)_6$). The influence of impurity ions (Fe^{3+} and NH_4^+) on the calcium sulfate hemihydrate (HH) morphology was studied using pure gypsum as the raw material, respectively. HH crystals with a high aspect ratio were obtained without the impurity ions. The diameter increased and the aspect ratio of the HH decreased, while the addition of iron sulfate and ammonia sulfate increased. Ammonium iron (NH_4^+) can be removed by using calcium oxide to decompose the ammonium jarosite in the waste and then to wash the sediment with tap water. The sediment (calcified jarosite sediment) mainly contained $CaSO_4{\cdot}2H_2O$ and $Fe(OH)_3$. The influence of cultivating time on HH crystals growth was researched by using the sediment as raw materials. The diameter of the whiskers increased, while the hydrothermal time increased. The whiskers were obtained, with high *a* aspect ratio (10–60), large diameter (1–4 μm) and smooth surface, after the sediment was treated at 140 °C for 6 h in pH = 5 solution.

Keywords: complex jarosite waste, calcium sulfate hemihydrate, whiskers, morphology, impurity ions

Kompleksni jarozitni odpadki, ki vsebujejo mavec in amonijev jarozit ($NH_4Fe_3(SO_4)_2(OH)_6$), nastajajo med hidrometalurško izdelavo kovinskega cinka. Avtorji v članku opisujejo študijo vpliva ionov nečistoč (Fe^{3+} in NH_4^+) na morfologijo kalcij-sulfatnega polhidrata (HH) z uporabo mavca kot osnovne surovine. Kristali HH z velikim velikostnim razmerjem med dolžino in premerom so nastajali brez prisotnosti ionov nečistoč. Premer kristalov HH se je povečeval in velikostno razmerje se je zmanjševalo z dodatkom železovega fosfata oziroma amonijevega sulfata. Nitratno železo se lahko odstrani z uporabo kalcijevega oksida in pri tem pride do razpada amonijevega jarozita v odpadkih. Usedlino, ki vsebuje v glavnem $CaSO_4{\cdot}2H_2O$ in $Fe(OH)_3$ se nato lahko izpere z vodo. Avtorji so analizirali čas rasti HH kristalov z uporabo usedline kot osnovne surovine. Premer kratkih vlaken (viskerjev) raste s povečevanjem časa hidrotermalnega procesa. Pridobljena vlakna so imela razmerje med dolžino in premerom (10–60), premer (1–4 μm) in gladko površino po obdelavi usedline pri 140 °C po 6-tih urah pri kislosti raztopine pH = 5.

Ključne besede: kompleksni jarozitni odpadki, kalcij-sulfatni polhidrat, vlakna, morfologija, ioni nečistoč

1 INTRODUCTION

Presently, 75 % of world's zinc metal is produced through hydrometallurgical route, for example, a calcining and leaching process.[1] In the processes, leaching at high temperature and acid concentration is carried out to avoid losses of the metal zinc. Under these conditions, iron associated with the ferrite is also dissolved, which must be removed from the solution before electro-winning, because iron concentrations > 20 mg/L, in combination with arsenic and cobalt, significantly diminish the current efficiency leading to poor zinc deposition.[2]

In hydrometallurgical processes, iron is commonly precipitated as hematite (α-Fe_2O_3), goethite (mostly as α-FeO(OH), with less as β-FeO(OH)) or as various jarosite-type compounds. The most widely employed is the jarosite method, which also eliminates alkaline ions and sulphates in the system.[2]

During the jarosite processes, Fe(III) compounds of the type $MFe_3(SO_4)_2(OH)_6$, where M is usually mono-valent Na^+, K^+, NH_4^+, H_3O^+, Ag^+ or divalent cations, such as Pb^{2+} is precipitating, and a huge amount of jarosite residue/waste is released.[3] Moreover, some jarosite waste contains gypsum because the calcium carbonate is added in zinc sulfate solution to neutralize the acid in the jarosite processes. This jarosite residue, as a solid waste, dumps in large stockpiles exposed to a weathering process without any treatment. This jarosite waste not only takes up massive amounts of land, but also presents a great environmental risk, as it contain significant zinc and lead, as well as some arsenic, cadmium, and such toxic ingredients have the potent to be solved in rain water.[4]

*Corresponding author's e-mail:
hb-t@163.com (Hongbin Tan)

Table 1: Chemical composition of as received jarosite waste (*w*/%)

SO_3	Fe_2O_3	CaO	SiO_2	ZnO	PbO	Na_2O	Al_2O_3	MgO	As_2O_3	K_2O	others
37.54	36.79	8.1	5.45	5.31	1.89	1.88	0.79	0.55	0.44	0.42	0.84

How to effectively treat the jarosite waste has become the focus of researchers. Salinas et al.[2] used NaOH to decompose the ammonium jarosite and obtained $(NH_4)SO_4$ and Na_2SO_4 mixed solution and $Fe(OH)_3$ sediment. The jarosite waste can also be decomposed by using calcium oxide to obtain calcified jarosite (calcified method), which calcified jarosite contain iron hydroxide ($Fe(OH)_3$), calcium sulphate dihydrate (DH, $CaSO_4 \cdot 2H_2O$, gypsum) and ammonia sulfate ($(NH_4)_2SO_4$). The main chemical reaction can be simplified in the following Equation (1).[5,6]

$$2NH_4Fe_3(SO_4)_2(OH)_6 + 3Ca(OH)_2 + 2H_2O \rightarrow \rightarrow (NH_4)_2SO_4 + 6Fe(OH)_3\downarrow + 3CaSO_4 \cdot 2H_2O\downarrow \quad (1)$$

The high-value-added ammonium sulfate can be easily recovered by filtering the calcified jarosite. The calcified method is optimal for the complex jarosite treatment, because the waste contains gypsum. How to recycle the calcified jarosite sediment (CJS) is a new challenge because the sediment is also complex, as it contains $CaSO_4 \cdot 2H_2O$, $Fe(OH)_3$ and a minor amount of $(NH_4)_2SO_4$ residue.

Calcium sulphate dihydrate (DH, gypsum) is often used as raw materials to prepare calcium sulfate hemihydrates (HH) whiskers in hydrothermal condition. HH whiskers are single-crystal fibers with a diameter of 1–5 μm and an aspect ratio of 30:80. HH whiskers, with typical high-strength, low-cost, non-toxic, energy-saving and environmentally friendly material, are widely used as the reinforcing agent in many fields, such as in rubbers, plastics, adhesives, friction materials and papermaking.[7–10] Whiskers, with a high aspect ratio, are beneficial for improving the strength of composites, where the whiskers can hinder the crack growth as a bridge. Luo et al.[11] prepared HH whiskers by using a $CaCl_2$-Na_2SO_4 slurry and aging at 130–160 °C. The morphology of HH crystals is usually influenced by the process parameters (for example, reaction time, impurity ions, etc).[12–14] Mao et al.[15] investigated the effects of Fe^{3+} on the crystal morphology and size of the calcium sulfate whiskers in aqueous HCl-$CaCl_2$-H_2SO_4 solutions at 102 °C (the boiling point of the solution). The result indicated that the HH was not obtained and the DH phase formed in the presence of a 2.67-mM concentration of Fe^{3+} ions. The influence of Fe^{3+} on the DH crystal morphology has also been affirmed in the simulated condition of the phosphoric acid product.[16, 17] The $[NH_4SO_4]^-$ ion pairs can form by adding NH_4^+ in the $CaSO_4$-H_2O system. The $[NH_4SO_4]^-$ ion pair replaces the free SO_4^{2-} as the dominant reactants for the HH nucleation. They carry the SO_4^{2-} and decouple them at the nucleation sites for nucleus formation, where the ion pairs will influence the HH nucleation formation and growth.[18]

The calcified jarosite sediment (CJS) would be used to prepare HH whiskers because it contains calcium sulphate dihydrate. On the other hand, if the particle size of the HH would be far larger than iron hydroxide, the mixture can be separated by the size-sieve method and the purity of the HH product would be improved. Impurity ions (Fe^{3+} and NH^{4+}) present in the calcified jarosite sediment, which would influence the HH crystals growth. There is currently limited work reported on the influences of impurity ions (Fe^{3+} and NH^{4+}) on the HH morphology in the autoclaved hydrothermal condition. Moreover, the underlying mechanism of HH whiskers from the calcified jarosite has not been revealed.

In this work, the influences of impurity ions (Fe^{3+} and NH^{4+}) on the HH morphology were studied in the autoclaved hydrothermal condition, and influencing mechanism of impurity ions on the HH growth was studied. And the HH whiskers, with high aspect ratio and smooth surface, were prepared from the calcified jarosite sediment (CJS).

2 EXPERIMENTAL PROCEDURE

2.1 Raw materials

Starting materials used were jarosite waste (Industrial grade, Hanzhoung Zinc Industry Co., Ltd., Hanzhong, China). calcium sulphate dehydrate (gypsum, DH), iron sulfate, ammonia sulfate, calcium oxide and sulphuric acid (Chemical grade, Tianli Chemical Co. Ltd., Tianjing, China), polycarboxylic acid (Industrial grade, Muhu building materials Co., Ltd., Beijing, China).

XRD pattern and chemical composition of the as received jarosite waste are shown in **Figure 1** and **Table 1**, respectively. The jarosite waste consisted mainly of am-

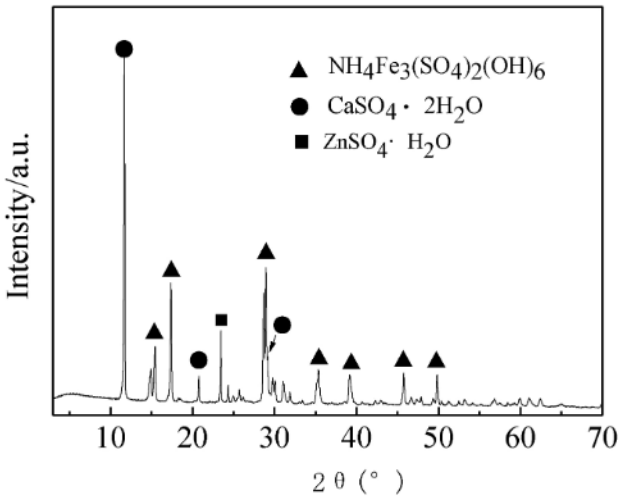

Figure 1: X-ray diffraction pattern of as received jarosite waste

monium jarosite [$(NH_4)Fe_3(SO_4)_2(OH)_6$] and gypsum ($CaSO_4{\cdot}2H_2O$) phases and mainly contained 37.54 *w*/% SO_3, 36.79 *w*/% Fe_2O_3, 8.10 *w*/% CaO and 5.45 *w*/% SiO_2, etc.

2.2 Waste treatment and whisker preparation

The jarosite waste, calcium oxide, water and 0.5 *w*/% polycarboxylic acid were placed in a mill, the mixture was ground for 2 h and aged at room temperature for 24 h to obtain calcified jarosite, and the solution pH of mixture was about 12. And then, the calcified jarosite was filtered and washed with tap water until the pH of filtrate solution was about 7. After that, distilled water was added to the product, and the solution pH value was changed by adding sulphuric acid to neutralize the redundant calcium oxide, which the solution pH was about 5. Finally, the sample was filtered and then dried at 60 °C for 24 h to obtain calcified jarosite sediment (CJS).

Some 2.0 g of gypsum (or CJS) and 40 mL of water were added into a 50 mL Teflon stainless-steel autoclave. To some of the solution, iron sulfate and ammonia sulfate were added. The reaction systems were aged at 140 °C for different times. Finally, the autoclave was cooled to room temperature naturally, and the samples were filtered, washed with hot water and dried at 100 °C for 12 h.

2.3 Sample characterization

Chemical composition of the raw material was identified with an X-ray fluorescence spectrometer (XRF, Axios-Poly, PANalytical, the Netherlands). The morphologies of the samples were characterized by scanning electron microscopy (SEM, TM-1000, Hitachi, Japan). The aspect ratios of the samples were calculated using a statistical method. The phases of the samples were identified with an X-ray powder diffraction (XRD) spectrometer (X'pert PRO, PANalytical, Netherlands) using Cu-K_α radiation (k = 0.154178 nm). The Raman spectra were measured using a Renishaw InVia Raman spectrophotometer with an argon ion laser (k = 514.5 nm) as the excitation light.

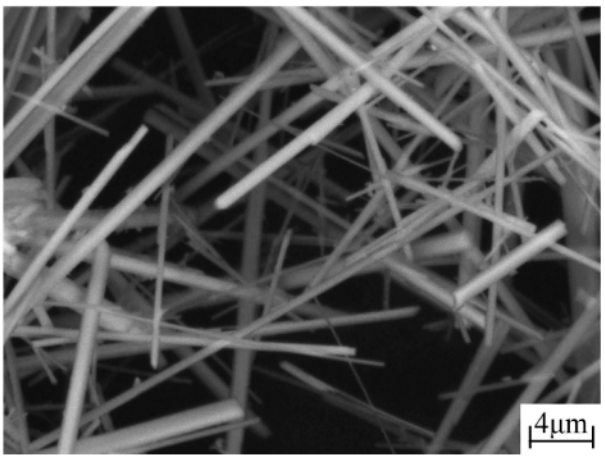

Figure 2: Scanning electron microscope micrograph of the sample prepared by using calcium sulphate dehydrate

3 RESULTS AND DISCUSSION

The SEM micrograph of the sample prepared using DH is shown in **Figure 2**. The whiskers were obtained

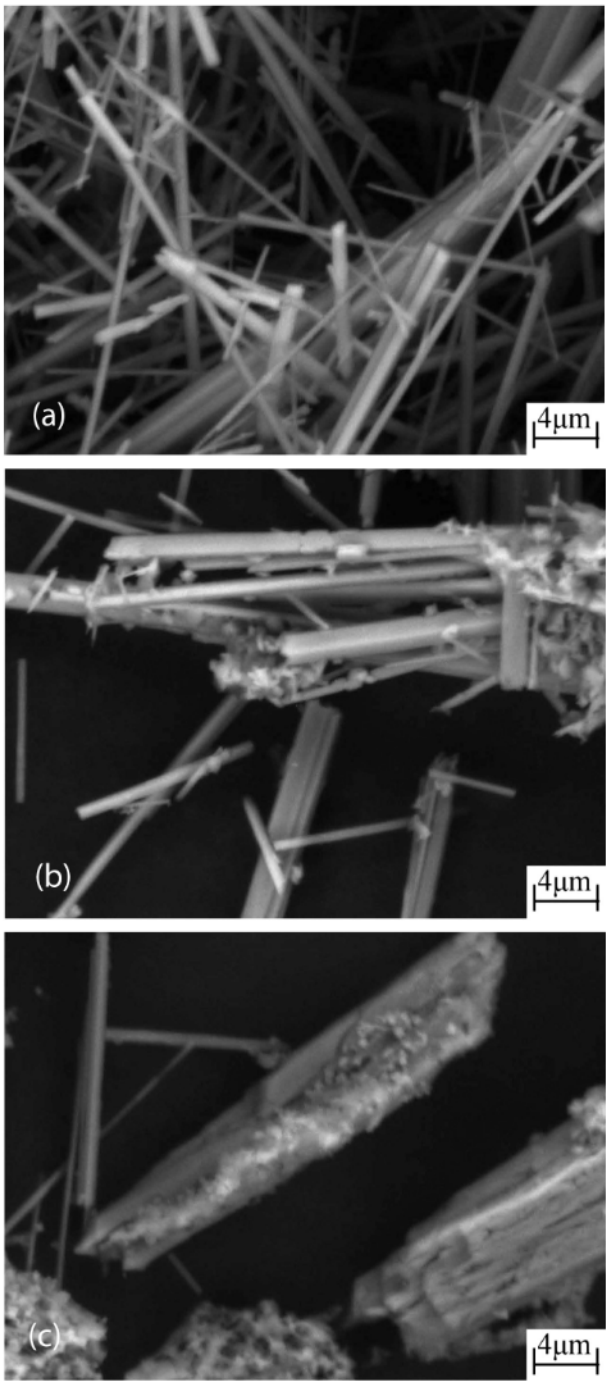

Figure 3: Scanning electron microscope micrographs of the samples prepared by adding different content iron sulfate in calcium sulphate dehydrate: a) 5 *w*/%, b) 10 *w*/%, c)15 *w*/%

with a smooth surface (about 0.4–1μm in diameter and an average aspect ratio of 50).

The dissolution-recrystallization theory is frequently used as the formation mechanism of calcium sulfate hemihydrates (HH) crystals. A three-stage process would be involved for whiskers formation. First, the crystal nucleus of the HH forms; second, self-assembly of HH possibly aggregates co-oriented along their *c* axes; finally, the crystals grow along their *c* axes and form acicular crystals.[19] HH usually crystallizes in the one-dimensional (1D) shape in free condition because the crystal lattice of HH is consists of calcium and sulfur oxygen tetrahedron chains (–Ca–SO_4–Ca–SO_4–). These chains are hexagonally arranged and form a framework parallel to the c axis, where one water molecule is attached to every two calcium sulfate molecules.[20]

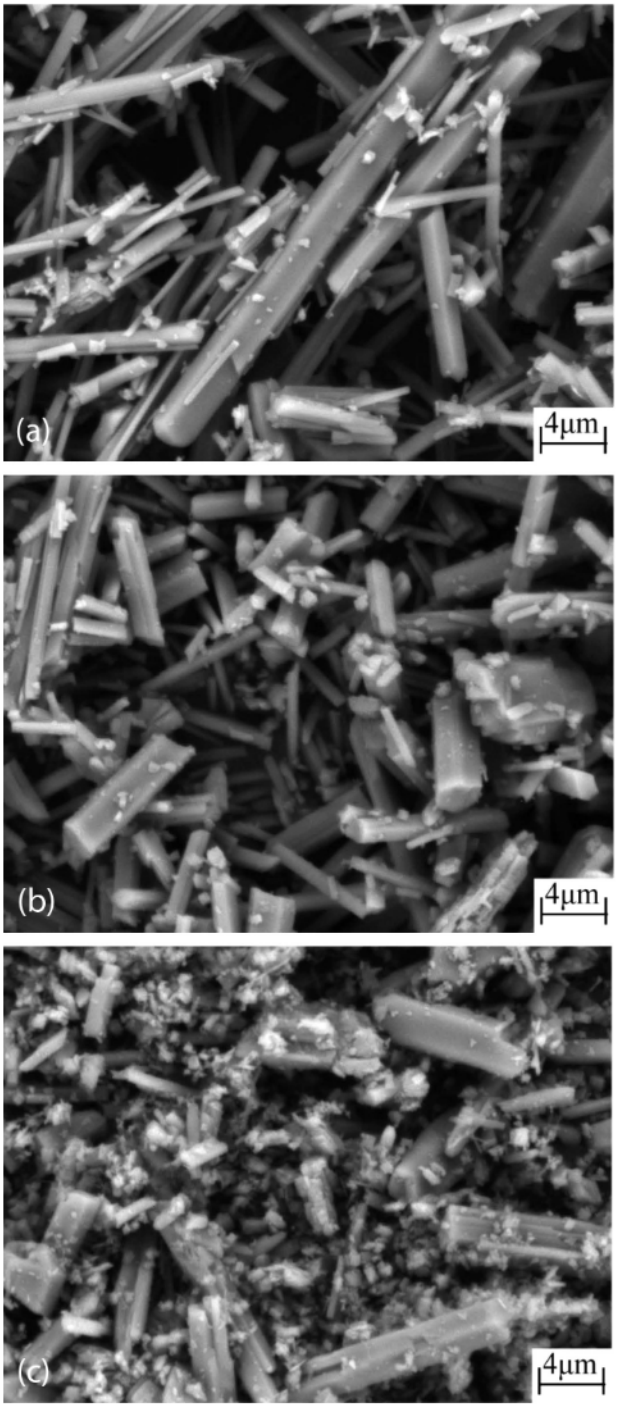

Figure 4: Scanning electron microscope micrographs of the samples prepared by adding different content ammonia sulfate in calcium sulphate dehydrate: a) 5 *w*/%, b) 10 *w*/%, c) 15 *w*/%

The SEM micrographs of the samples prepared by adding different contents of iron sulfate in DH are shown in **Figure 3**. The diameters of the whiskers increased and the aspect ratio decreased, while the amount of iron sulfate increased. Some coarse whiskers and a little of fascicular crystals, which grew together without separation, were observed by adding a 5 *w*/% iron sulfate. A lot of fascicular crystals were obtained and only a few whiskers were observed by adding 15 *w*/% iron sulfate.

The SEM micrographs of the samples prepared by adding different contents of ammonia sulfate in DH are shown in **Figure 4**. The diameter of whiskers also increased, and aspect ratio decreased, while the addition of ammonia sulfate increased. The crystals were obtained with about 1–3μm in diameter and 5 for the average aspect ratio by adding a 10 *w*/% ammonia sulfate. The average aspect ratio was about 3 and some columnar crystals cannot be observed by adding a 15 *w*/% ammonia sulfate.

The aspect ratio of the crystals decreased, while the content of impurity ions (Fe^{3+} and NH^{4+}) increased, because the additives changed the surface energy of HH and consequently inhibited the growth along the [001] direction.[15] According to the above results, iron sulfate and ammonia sulfate can influence the HH crystals growth. Moreover, the influence of ammonia sulfate on HH crystals growth was bigger than iron sulfate.

The solution pH value was controlled at 12 when jarosite waste reacted with calcium oxide, which with a high pH value was an advantage to decompose the am-

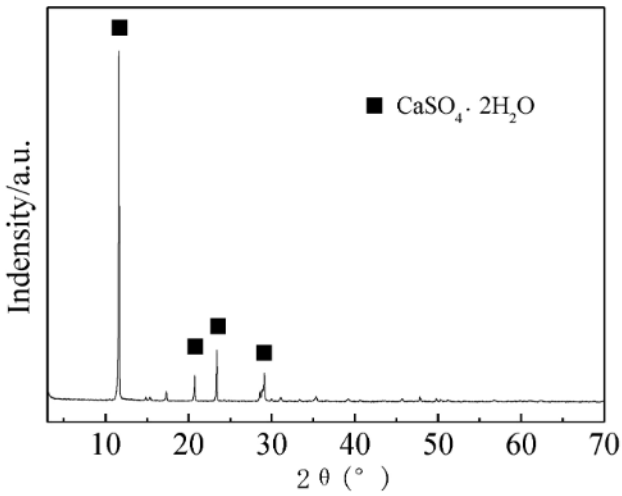

Figure 5: X-ray diffraction pattern of calcified jarosite sediment

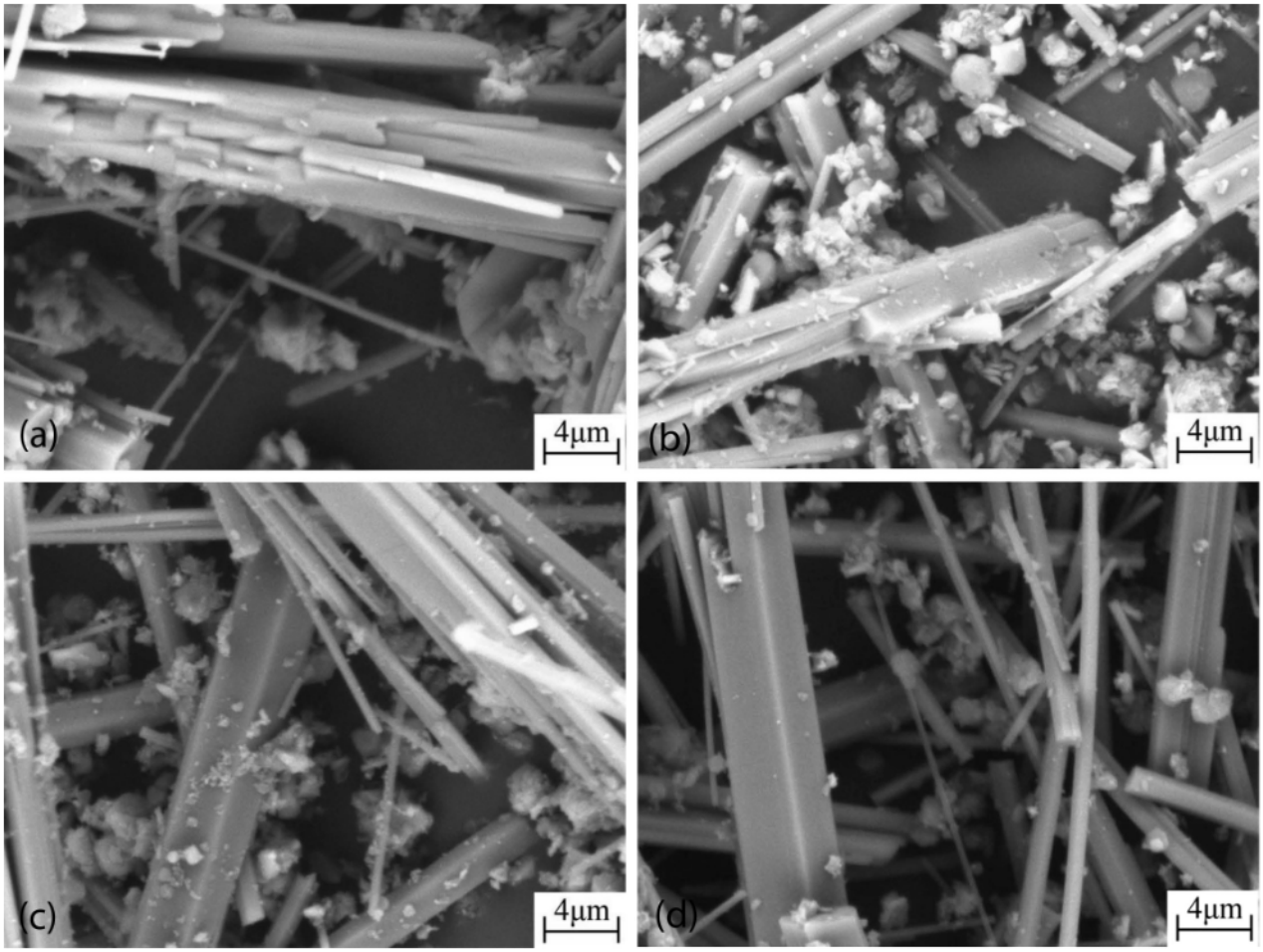

Figure 6: Scanning electron microscope micrographs of the calcified jarosite sediment based samples prepared at 140 °C for different time: a) 1 h, b) 2 h, c) 4 h, d) 6 h

monium jarosite.[21] The NH_4^+ can be removed by filtering and washing the calcified jarosite with water. After the product was washed, the solution pH value of calcified jarosite sediment (CJS) was about 5 by adding sulphuric acid, because calcium oxide can be retained in the CJS and low pH value was advantage to gypsum dissolution in hydrothermal system, which helped HH whiskers growth.[22] On the other hand, the pH value of CJS was not too low because the iron hydroxide can dissolve in low pH solution.

The XRD pattern of the CJS is shown in **Figure 5**. The phases of the CJS consisted mainly of $CaSO_4{\cdot}2H_2O$. According to Equation (1) in Introduction Part, the iron hydroxide was not detected by XRD because iron hydroxide was an amorphous phase.[5,6] The ammonia sulfate was also not been detected by XRD, because it was highly soluble in water and was washed out.

The SEM micrographs of the CJS based samples prepared at 140 °C for different times are shown in **Figure 6**. Some fascicular crystals (whiskers) with a high aspect ratio, thin diameter and smooth surface, were obtained in the sample after hydrothermal treatment for 1 h. A little of iron hydroxide (or others substances) grains adhered to the whiskers' surfaces. The fascicular crystals reduced and the diameter of whiskers increased in the samples while hydrothermal time increased. The whiskers were obtained with about 1–4 μm in diameter and 30 in aspect ratio for a hydrothermal time of 2 h.

The fascicular crystals were not observed in the sample after 6 h, and the whiskers were obtained with about 1–4 μm in diameter and 10:60 in aspect ratio. On the other hand, the grain diameter (about 1 μm) of iron hydroxide (or others substances) did not change while hydrothermal time extended.

Fascicular crystals were observed possibly because a little of impurities (such as, Mg^{2+}) can promote DH to dissolve and obtain high super-saturations solution.[23,24] Some thin HH crystals possibly dissolved and other crystals grew, while the curing time increased. As a result, fascicular crystals were not observed in the sample after 6 h.

The XRD pattern of the CJS based sample prepared at 140 °C for 2 h is shown in **Figure 7**. The peaks of sample presented analogous diffraction angles, indicating that the main phase of the sample was HH ($CaSO_4{\cdot}0.5H_2O$). The phase of HH is mainly affected by

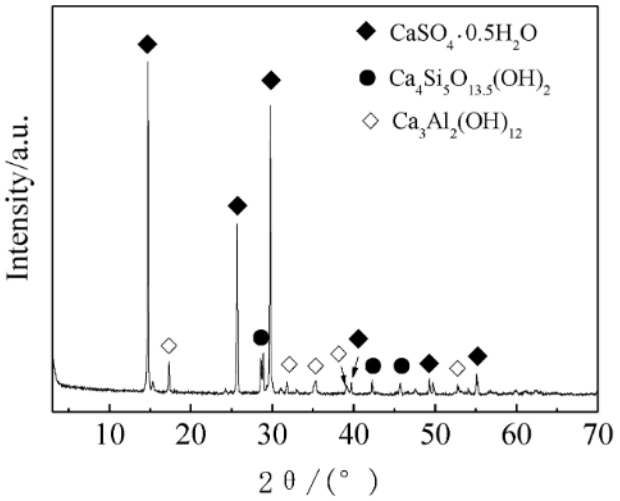

Figure 7: X-ray diffraction pattern of the calcified jarosite sediment based sample prepared at 140 °C for 2 h

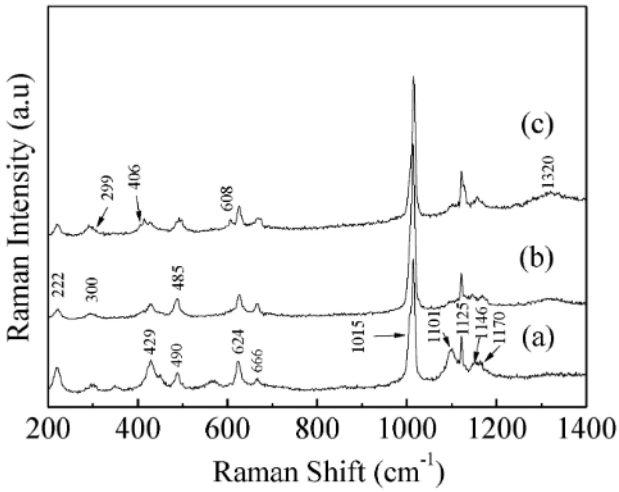

Figure 8: Raman spectra of calcified jarosite sediment based samples prepared at 140 °C for: a) 2 h, b) 4 h, c) 6 h

temperature. HH will be obtained from DH at 103–105 °C in H_2O hydrothermal conditions.[23] Moreover, calcium silicate hydroxide (PDF: 29-0381, $Ca_4Si_5O_{13.5}(OH)_2$) and katoite (PDF: 24-0217, $Ca_3Al_2(OH)_{12}$) were detected.

The Raman spectra of the CJS-based sample prepared at 140 °C for different time are shown in **Figure 8**. The combination of a strong Raman peak at 1015 cm^{-1} with distinguished peaks at (1101, 1125, 1146, 1170, 429, 490, 624, 660) cm^{-1} (**Figure 8a**) indicate the formation of $CaSO_4{\cdot}0.5H_2O$ at hydrothermal times of (2, 4, 6) h.[25] The phase of $CaSO_4{\cdot}0.5H_2O$ did not change while the hydrothermal time increased. The peaks at (485, 222, 300) cm^{-1} (**Figure 8a**) indicate the formation of FeOOH at hydrothermal times of (2, 4, 6) h.[26] The peaks at (1320, 608, 406, 299) cm^{-1} (**Figure 8c**) acknowledge the formation of Fe_2O_3 after a hydrothermal time of (2, 4, 6) h.[27] The content of Fe_2O_3 increased, the content of FeOOH decreased, and color of sample changed from yellow to brown, while the hydrothermal time increased. Further research is needed to continue to define the structures of Fe_2O_3 and FeOOH.

According to the Raman spectra, the iron hydroxide transitioned to iron (hydr)oxides (FeOOH and Fe_2O_3) after the hydrothermal treatment. The $CaSO_4{\cdot}2H_2O$ had completely transitioned to $CaSO_4{\cdot}0.5H_2O$ and the phase did not change when the hydrothermal time increased.

According to the above results, the influence of NH_4^+ and Fe^{3+} on the HH crystals growth can be weakened by washing the calcified jarosite sediment and controlling the hydrothermal solution pH value, respectively.

The iron (hydr)oxides and HH crystals could be separated by size-sieve method to improve HH product purity when the CJS was treated under hydrothermal conditions for 6 h. The HH crystals can be used to reinforce composites and iron (hydr)oxides can be used as raw materials of iron. To reduce hydrothermal time and to obtained nano-size particles of iron (hydr)oxides, further research continues to define these dependencies, which would be favorable for the separation of iron and sulfur with low cost. Moreover, to eliminate toxic waste metals (Zn, Cd…) in the HH product needs further research.

4 CONCLUSIONS

The diameter of the HH crystals increased and the aspect ratio decreased, while the addition content of ammonia sulfate and iron sulfate increased, respectively. A lot of fascicular crystals were obtained and only a few whiskers were observed by adding 15 *w*/% iron sulfate. The average aspect ratio was about three and some irregular particles were observed by adding 15 *w*/% ammonia sulfate.

The ammonium jarosite can be decomposed by using calcium oxide to obtain calcified jarosite. The NH_4^+ can be removed by washing the calcified jarosite sediment with water. The influence of Fe^{3+} on the HH crystals growth can be weakened by controlling the solution pH value. The whiskers were obtained, with a high aspect ratio (10–60) and a large diameter (1–4 μm), when the calcified jarosite sediment was treated at 140 °C under hydrothermal conditions for 6 h in pH = 5 solution.

Acknowledgements

This work was supported by the Research Fund of the Sichuan Science and Technology Program of China (2020YFS0334), Natural Science Foundation of Southwest University of Science and Technology (19zx7130) and State Key Laboratory of Solid Waste Reuse for Building Materials (SWR-2021-001).

5 REFERENCES

[1] P. K. Senapati, B. K. Mishra, Rheological characterization of concentrated jarosite waste suspensions using Couette & tube rheometry techniques, Powder Technol., 263 (**2014**), 58–65

[2] E. Salinas, A. Roca, M. Cruells, F. Patino, D. A. Cordoba, Characterization and alkaline decomposition–cyanidation kinetics of industrial ammonium jarosite in NaOH media, Hydrometallurgy, 60 (**2001**) 3, 237–246

[3] M. Kerolli-Mustafa, I. Bacic, L. Curkovic, Investigation of jarosite process tailing waste by means of raman and infrared spectroscopy, Materialwiss. Werkst., 44 (**2013**) 9, 768–773

[4] S. H. Ju, Y. F. Zhang, Y. Zhang,P. Y. Xue, Y. H. Wang, Clean hydrometallurgical route to recover zinc, silver, lead, copper, cadmium and iron from hazardous jarosite residues produced during zinc hydrometallurgy, J. Hazard. Mater., 192 (**2011**) 2, 554–558

[5] F. Patiño, M. U. Flores, I. A. Reyes, M. Reyes, J. Hernández, I. Rivera, J. C. Juárez, Alkaline decomposition of synthetic jarosite with arsenic, Geochem. Trans., 14 (**2013**) 2, 1–9

[6] F. Patiño, M. Cruells, A. Roca, E. Salinas, M. Pérez, Kinetics of alkaline decomposition and cyanidation of argentian ammonium jarosite in lime medium, Hydrometallurgy, 70 (**2003**) 1–3, 153–161

[7] X. Feng, Y. Zhang, G. L. Wang, M. Miao, L. Y. Shi, Dual-surface modification of calcium sulfate whisker with sodium hexametaphosphate/silica and use as new water-resistant reinforcing fillers in papermaking, Powder Technol., 271 (**2015**), 1–6

[8] B. H. Guan, L. Yang, H. L. Fu, B. Kong, T. Y. Li, L. C. Yang, α-calcium sulfate hemihydrate preparation from FGD gypsum in recycling mixed salt solutions, Chem. Eng. J., 174 (**2011**) 1, 296–303

[9] G. M. Jiang, W. Y. Fu, Y. Z. Wang, X. Y. Liu, Y. X. Zhang, F. Dong, Z. Y. Zhang, X. M. Zhang, Y. M. Huang, S. Zhang, S. H. Lv, Calcium sulfate hemihydrates nanowires: one robust material in separation of water from water-in-oil emulsion, Environ. Sci. Technol., 51 (**2017**) 18, 10519–10525

[10] G. M. Jiang, J. X. Li, Y. L. Nie, S. Zhang, F. Dong, B. H. Guan, Immobilizing water into crystal lattice of calcium sulfate for its separation from water-in-oil emulsion, Environ. Sci. Technol., 50 (**2016**) 14, 7650–7657

[11] K. B. Luo, C. M. Li, L. Xiang, H. P. Li, P. Ling, Influence of temperature and solution composition on the formation of calcium sulfates, Particuology, 8 (**2010**) 3, 240–244

[12] X. Mao, X. Song, G. Lu, Y. Xu, Y. Sun, J. Yu, Effect of additives on the morphology of calcium sulfate hemihydrate: Experimental and molecular dynamics simulation studies, Chem. Eng. J., 278 (**2015**), 320–327

[13] J. W. Mao, G. M. Jiang,Q. S. Chen , B. H. Guan, Influences of citric acid on the metastability of α-calcium sulfatehemihydrate in $CaCl_2$ solution, Colloid. Surface. A., 443 (**2014**), 265–271

[14] B. Kong, J. Yu, K. Savino, Y. G. Zhu, B. H. Guan, Synthesis of α-calcium sulfate hemihydrate submicron-rods in water/n-hexanol/CTAB reverse microemulsion, Colloid. Surface. A., 409 (**2012**), 88–93

[15] X. L. Mao, X. F. Song, G. M. Lu, Y. Z. Sun, Y. X. Xu, J. G. Yu, Effects of metal Ions on crystal morphology and size of calcium sulfate whiskers in aqueous HCl solutions, Ind. Eng. Chem. Res., 53 (**2014**) 45, 17625–17635

[16] A. Kruger, W. W. Focke, Z. Kwela, R. Fowles, Effect of Ionic Impurities on the Crystallization of Gypsum in Wet-Process Phosphoric Acid, Ind. Eng. Chem. Res., 40 (**2001**) 5, 1364–1369

[17] D. Hasson, J. Addai-Mensah, J. Metcalfe, Filterability of gypsum crystallized in phosphoric acid solution in the presence of ionic impurities, Ind. Eng. Chem. Res., 29 (**1990**) 5, 867–875

[18] G. M. Jiang, H. L. Fu, K. Savino, J. J. Qian, Z. B. Wu, B. H. Guan, Nonlattice cation-SO_4^{2-} ion pairs in calcium sulfate hemihydrate nucleation, Cryst. Growth. Des., 13 (**2013**) 11, 5128–5134

[19] X. Wang, L. S. Yang, X. F. Zhu, J. K. Yang, Preparation of calcium sulfate whiskers from FGD gypsum via hydrothermal crystallization in the H_2SO_4-NaCl-H_2O system, Particuology, 17 (**2014**), 42–48

[20] Q. Han, K. B. Luo, H. P. Li, L. Xiang. Influence of disodium hydrogen phosphate dodecahydrate on hydrothermal formation of hemihydrate calcium sulfate whiskers, Particuology, 17 (**2014**), 131–135

[21] M. E. Elwood Madden, A. S. Madden, J. D. Rimstidt, S. Zahrai, M. R. Kendall, M. A. Miller, Jarosite dissolution rates and nanoscale mineralogy, Geochim. Cosmochim. Acta., 91 (**2012**), 306–321

[22] F. Li, J. L. Liu, G. Y. Yang, Z. Y. Pan, X. Ni, H. Z. Xu, Q. Huang, Effect of pH and succinic acid on the morphology of α-calcium sulfate Hemihydrate synthesized by a salt solution method, J. Cryst. Growth., 374 (**2013**), 31–36

[23] E. T. M. J. Martynowicz, G. J. Witkamp, G. M. Rosmalen, The effect of aluminium fluoride on the formation of calcium sulfate hydrates, Hydrometallurgy, 41 (**1996**), 171–186

[24] L. C. Yang, Z. B. Wu, B. H. Guan, H. L. Fu, Q. Q. Ye, Growth rate of a-calcium sulfate hemihydratein K-Ca-Mg-Cl-H_2O systems at elevated temperature, J. Cryst. Growth., 311 (**2009**) 20, 4518–4524

[25] C. Paluszkiewicz, J. Czechowska, A. Slosarczyk, Z. Paszkiewicz, Evaluation of a setting reaction pathway in the novel composite TiHA-CSD bone cement by FT-Raman and FT-IR spectroscopy, J. Mol. Struct., 1034 (**2013**), 289–295

[26] M. K. Sinha, S. K. Sahu, P. Meshram, L. B. Prasad, B. D. Pandey, Low temperature hydrothermal synthesis and characterization of iron oxide powders of diverse morphologies from spent pickle liquor, Powder Technol., 276 (**2015**), 214–221

[27] A. A. Ayachi, H. Mechakra, M. M. Silvan, S. Boudjaadar, S. Achour, Monodisperse α-Fe_2O_3 nanoplatelets: Synthesis and characterization, Ceram. Int., 41 (**2015**) 2, 2228–2233