Supplementary Information

Insight into the mineralizer modified and tailored scorodite crystal characteristic and leachability for arsenic-rich smelter wastewater stabilization

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Table S1 Detailed results compare with the literature data for arsenic leachability.

Conditions	Arsenic leachiability	Reference
pH=5 and 22 °C	0.5 mg/L	1
pH=5 and 22 °C	0.35 mg/L	2
pH=6 and 22 °C	0.96 mg/L	2
pH=7 and 22 °C	5.87 mg/L	2
, At neutral pH and 22 °C, 24 weeks	5.9 mg/L	3
pH=2.8-5.3	<0.5 mg/L	4
pH=7 and 22 °C	3.6 mg/L	5
pH=3.0, 30 °C	4.0 mg/L	6
pH=3.0, 70 °C	1.0 mg/L	6
n(Fe/As)=0.8-3.0, pH=4.0	0.6-6.3 mg/L	6
NaF mineralizer, pH=2.5	0.39 mg/L	This work

References：

1. S. Singhania, Q.K. Wang, D. Filippou, G.P. Demopoulos. Acidity, Valency and Third-Ion Effects on the Precipitation of Scorodite from Mixed Sulfate Solutions under Atmospheric-Pressure Conditions, metallurgical and materials transactions b, 2006, 37B, 189-197.
2. G.P. Demopoulos. On the preparation and stability of scorodite, Arsenic Metallurgy Edited by R.G. Reddy and V. Ramachandran TMS (The Minerals, Metals & Materials Society), 2005
3. M-C. Bluteau, P.G, Demopoulos. The incongruent dissolution of scorodite-Solubility, kinetics and mechanism. Hydrometallurgy, 87, 2007, 163-177.
4. E. Krause, V.A. Ettel, Solubilities and stabilities of ferric arsenate compounds. Hydrometallurgy, 22, 1989, 311-337.
5. M-C. Bluteau, L. Becze, G.P. Demopoulos, the dissolution of scorodite in gypsum-saturated waters: Evidence of Ca-Fe-AsO_4 mineral formation and its impact on arsenic retention, Hydrometallurgy, 97, 2009, 221-227.
6. X.B. Min, Y.P. Liao, L.Y. Chai, Z.H. Yang, S. Xiong, L. Liu, Q.Z. Li, Removal and stabilization of arsenic from anode slime by forming crystal scorodite, Trans. Nonferrous Met. Soc. China, 25, 2015, 1298-1306.

Table S2. The concentration of pre-treatment, leachability and composition of solid precipitates at various mineralizers ($Na_2SiO_3 \cdot 9H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, and NaF) and temperature (120 °C, 150 °C, and 180 °C) for 25h.

Sample	Washing steps (pre-treatment)/ mg/L			As-leachability/mg/L			Solid precipitates/%				
	Al	Fe	As	Al	Fe	As	Al	Na	Fe	As	n(Fe/As)
120-Al[a]	ND[b]	ND	0.04	ND	ND	1.22	2.41	1.11	25.27	26.86	1.26
150-Al	ND	ND	ND	ND	ND	1.49	1.86	1.30	31.27	25.85	1.62
180-Al	ND	ND	0.10	ND	ND	3.10	1.38	0.76	33.71	27.20	1.66
Sample	Si	Fe	As	Si	Fe	As	Si	Na	Fe	As	n(Fe/As)
120-Si	3.5	ND	0.25	114.9	4.3	12.46	0.55	2.20	20.88	28.54	0.98
150-Si	1.7	ND	0.11	102.8	1.9	4.81	0.27	4.31	23.95	29.70	1.08
180-Si	1.4	ND	ND	101.6	2.7	4.64	0.68	5.52	28.65	28.63	1.34
Sample	F	Fe	As	F	Fe	As	F	Na	Fe	As	n(Fe/As)
120-F	0.5	ND	ND	6.2	ND	1.49	0.044	1.71	23.84	31.61	1.01
150-F	1.1	ND	ND	8.5	0.13	0.39	0.030	1.32	23.75	29.18	1.09
180-F	1.7	ND	ND	9.7	ND	0.55	0.014	1.17	28.37	27.53	1.38

[a] The sample was obtained from $Al(NO_3)_3 \cdot 9H_2O$-modified at 120 °C, other sample descriptions are similar.

[b] The ND expressed as undetected, the fluoride (F^-) concentration was measured by Ion Chromatograph and the other elements was analyzed by ICP-OES.

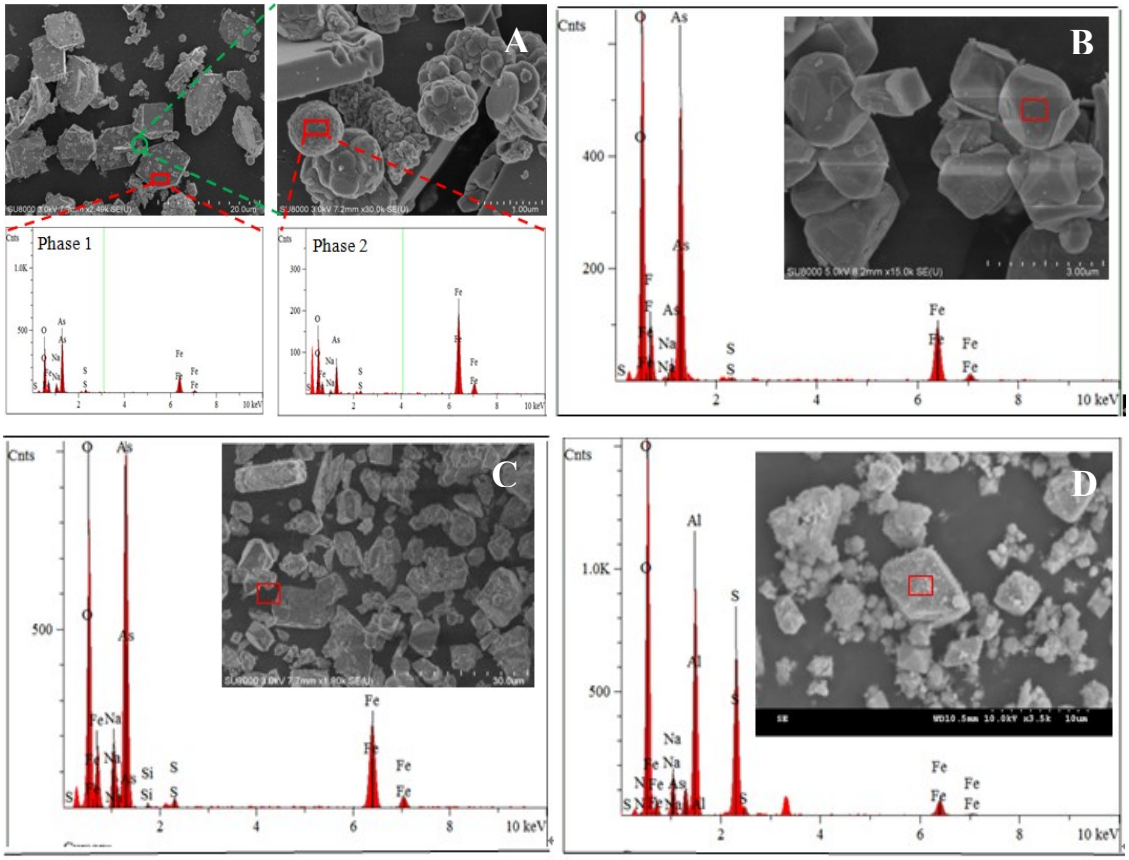

Fig. S1. SEM images and particles surface composition of solid precipitate at various mineralizers (A)H_2O control group, (B)NaF-modified, (C)$Na_2SiO_3 \cdot 9H_2O$-modified, and (D)$Al(NO_3)_3 \cdot 9H_2O$-modified for 180 ^oC. conditions.

Table S3. SEM-EDS for particles surface phase composition of solid precipitate at various mineralizers for 180 °C.

Experimental group		Element content (wt%)							
		Fe	O	As	F	Al	Si	S	n (Fe/As)
H_2O control group	Phase 1	29.0	30.5	33.5	/	/	/	/	1.2
	Phase 2	44.1	43.0	11.1	/				5.3
NaF-modified	Phase 1	23.3	41.0	30.5	0.00	/	/	/	1.0
$Na_2SiO_3 \cdot 9H_2O$-modified	Phase 1	27.0	33.1	31.8	/	/	0.4	0.8	1.1
$Al(NO_3)_3 \cdot 9H_2O$-modified	Phase 1	5.6	51.3	5.9	/	17.9	/	14.5	1.4

Table S4. The majority of XRD patterns of solid precipitate at various mineralizers and hydrothermal mineralization temperature.

mineralizers	Hydrothermal mineralization temperature/^{o}C[a]		
	120	150	180
H_2O control group	S	F, S, B	F, S, B,G
$Na_2SiO_3 \cdot 9H_2O$-modified	S	F, S, B,G	F, S, B,G
$Al(NO_3)_3 \cdot 9H_2O$-modified	F, S, B	F, S, B	F, S, B
NaF-modified	S	S	F, S, B,G

[a] "S" refers to the SD phase (scorodite); "F" refers to the FAsH phase ($FeAsO_4 \cdot 0.75H_2O$); "G" refers to the goethite phase (PDF NO. 81-0462) "B" refers to the BFAS phase ($Fe(AsO_4)_{1-x}(SO_4)_x(OH)_x \cdot (1-x)H_2O$).

Table S5 the semi-quantitative how much of each phase (scorodite, FAsH, BFAS, and goethite) in solid samples via JADE software.

Sample	Temperatures/^{o}C	Phase composition/%			
		Scorodite	FAsH	Goethite	BFAS
H_2O control group	120	100	-	-	-
	150	77.04	8.01	-	14.75
	180	71.48	12.74	7.90	7.52
$Al(NO_3)_3 \cdot 9H_2O$-modified	120	87.24	9.04	-	3.10
	150	84.78	4.72	-	8.39
	180	82.97	10.24	-	11.62
$Na_2SiO_3 \cdot 9H_2O$-modified	120	100	-	-	-
	150	74.31	11.14	1.41	12.04
	180	69.01	12.47	1.94	14.71
NaF-modified	120	100	-	-	-
	150	100	-	-	-
	180	79.47	5.48	5.19	9.79