Supporting information

Text S1

First, 300 mL AAPS was added to a beaker immersed in a water bath. The pH was adjusted to the pre-set values (0.5, 1.0, 1.5, 2.0, and 2.5) at 25 °C by adding 100 g/L $Ca(OH)_2$ solution with a peristaltic pump. After liquid-solid separation, the neutralized solution was sampled for analysis. Second, $Fe_2(SO_4)_3{\cdot}xH_2O$ pre-dissolved in 100 mL distilled water was added to the neutralized solution under the condition of n_{Fe}/n_{As}=1.5, and the obtained solution was placed in an autoclave. After reaction at 160 °C for 10 h, a liquid-solid separation was executed on the slurry, and the filtrate was collected and analyzed. The neutralization and hydrothermal residues were washed three times with hot water and dried at 60 °C for 24 h.

The precipitation efficiency of the elements was calculated using Eq. (S1):

$$\text{Precipitation efficiency}=\left(1-\frac{m_d \times w_d}{V \times c}\right)\times 100\% \tag{S1}$$

where m_d and w_d are the mass (g) and elemental content (%) of the neutralizing or hydrothermal residues, respectively, and V and c are the volume (L) and elemental concentration (g/L) of AAPS and neutralized solutions, respectively.

Text S2

To verify the feasibility and determine the optimal conditions for selective precipitation of As as $FeAsO_4$ from AAPS, detailed studies of the thermodynamic properties of the Cd^{2+}-Zn^{2+}-Fe^{3+}-AsO_4^{3-}-SO_4^{2-}-H_2O system in the pH range of 0–5.0 were conducted. According to the literatures [1−5], 35 species (H^+, OH^-, AsO_4^{3-}, $HAsO_4^{2-}$, $H_2AsO_4^-$, H_3AsO_4, Cd^{2+}, $Cd(OH)^+$, $Cd(OH)_2$(aq), $Cd(OH)_3^-$, $Cd(OH)_4^{2-}$, Cd_2OH^{3+}, $Cd_4(OH)_4^{4+}$, $CdSO_4$(aq), Zn^{2+}, $Zn(OH)^+$, $Zn(OH)_2$(aq), $Zn(OH)_3^-$, $Zn(OH)_4^{2-}$, $Zn_2(OH)^{3+}$, ZnH_2AsO_4, $ZnHAsO_4$(aq), $ZnAsO_4^-$, $ZnSO_4$(aq), Fe^{3+}, $FeOH^{2+}$, $Fe(OH)^{2+}$, $Fe(OH)_3$(aq), $FeH_2AsO_4^{2+}$, $FeHAsO_4^+$, $Fe(SO_4)^+$, $Fe(SO_4)^{2-}$, SO_4^{2-}, HSO_4^-, and H_2SO_4) were assumed to exist in the solution. Additionally, six insoluble compounds, namely $FeAsO_4$, $Fe(OH)_3$, $Cd_5H_2(AsO_4)_4$, $Cd_3(AsO_4)_2$, $ZnHAsO_4$, and $Zn_3(AsO_4)_2$ were assumed to exist. These inventories yielded 35 equilibria and 11 mass-balance equations (Table S1). Considering the properties of the solid phases that may be in equilibrium with the solution, different combinations of these equations were established based on the mass balance and the rule of solubility product, as listed in Table S2. The calculations were performed using Microsoft Excel based on the Newton-Raphson iteration method.

Table S1 Equilibrium reactions, constants, and mass balance equations for the Cd^{2+}- Zn^{2+}-Fe^{3+}-AsO_4^{3-}-SO_4^{2-}-H_2O system (25 °C)

No.	Equilibrium reactions	Equilibrium constants	Equations
1	$H_2O=H^++OH^-$	10^{-14}	$10^{-14}=[H^+][OH^-]$
2	$H_3AsO_4=H^++H_2AsO_4^-$	$10^{-2.22}$	$10^{-2.22}=[H^+][H_2AsO_4^-]/[H_3AsO_4]$
3	$H_2AsO_4^-=H^++HAsO_4^{2-}$	$10^{-6.89}$	$10^{-6.89}=[H^+][HAsO_4^{2-}]/[H_2AsO_4^-]$
4	$HAsO_4^{2-}=H^++AsO_4^{3-}$	$10^{-11.50}$	$10^{-11.50}=[H^+][AsO_4^{3-}]/[HAsO_4^{2-}]$
5	$Cd^{2+} + OH^-=CdOH^+$	$10^{4.17}$	$10^{4.17}=[CdOH^+]/[Cd^{2+}][OH^-]$
6	$Cd^{2+}+2OH^-=Cd(OH)_2(aq)$	$10^{8.33}$	$10^{8.33}=[Cd(OH)_2(aq)]/\{[Cd^{2+}][OH^-]^2\}$
7	$Cd^{2+}+3OH^-=Cd(OH)_3^-$	$10^{9.02}$	$10^{9.02}=[Cd(OH)_3^-]/\{[Cd^{2+}][OH^-]^3\}$
8	$Cd^{2+}+4OH^-=Cd(OH)_4^{2-}$	$10^{8.62}$	$10^{8.62}=[Cd(OH)_4^{2-}]/\{[Cd^{2+}][OH^-]^4\}$
9	$2Cd^{2+}+OH^-=Cd_2OH^{3+}$	$10^{4.6}$	$10^{4.6}=[Cd_2OH^{3+}]/\{[Cd^{2+}]^2[OH^-]\}$
10	$4Cd^{2+}+4OH^-=Cd_4(OH)_4^{4+}$	$10^{23.2}$	$10^{23.2}=[Cd_4(OH)_4^{4+}]/\{[Cd^{2+}]^4[OH^-]^4\}$
11	$Cd^{2+}+SO_4^{2-}=CdSO_4(aq)$	$10^{2.46}$	$10^{2.46}=[CdSO_4(aq)]/\{[Cd^{2+}][SO_4^{2-}]\}$
12	$Fe^{3+}+OH^-=FeOH^{2+}$	$10^{11.87}$	$10^{11.87}=[FeOH^{2+}]/\{[Fe^{3+}][OH^-]\}$

to be continued

Continued

No.	Equilibrium reactions	Equilibrium constants	Equations
13	$Fe^{3+}+2OH^{-}=Fe(OH)_2^{+}$	$10^{21.17}$	$10^{21.17}=[Fe(OH)_2^{+}]/\{[Fe^{3+}][OH^{-}]^2\}$
14	$Fe^{3+}+3OH^{-}=Fe(OH)_3(aq)$	$10^{29.67}$	$10^{29.67}=[Fe(OH)_3(aq)]/\{[Fe^{3+}][OH^{-}]^3\}$
15	$FeH_2AsO_4^{2+}=Fe^{3+}+H_2AsO_4^{-}$	$10^{-4.26}$	$10^{-4.26}=[Fe^{3+}][H_2AsO_4^{-}]/[\ FeH_2AsO_4^{2+}]$
16	$FeHAsO_4^{+}=Fe^{3+}+HAsO_4^{2-}$	$10^{-9.74}$	$10^{-9.74}=[Fe^{3+}][HAsO_4^{2-}]/[FeHAsO_4^{+}]$
17	$Fe^{3+}+SO_4^{--}=FeSO_4^{+}$	$10^{2.03}$	$10^{2.03}=[FeSO_4^{+}]/\{[Fe^{3+}][SO_4^{2-}]\}$
18	$Fe^{3+}+2SO_4^{2-}=Fe(SO_4)_2^{-}$	$10^{2.98}$	$10^{2.98}=[Fe(SO_4)_2^{-}]/\{[Fe^{3+}][SO_4^{2-}]^2\}$
19	$Zn^{2+}+OH^{-}=ZnOH^{+}$	$10^{4.40}$	$10^{4.40}=[ZnOH^{+}]/\{[Zn^{2+}][OH^{-}]\}$
20	$Zn^{2+}+2OH^{-}=Zn(OH)_2(aq)$	$10^{11.30}$	$10^{11.30}=[Zn(OH)_2(aq)]/\{[Zn^{2+}][OH^{-}]^2\}$
21	$Zn^{2+}+3OH^{-}=Zn(OH)_3^{-}$	$10^{14.14}$	$10^{14.14}=[Zn(OH)_3^{-}]/\{[Zn^{2+}][OH^{-}]^3\}$
22	$Zn^{2+}+4OH^{-}=Zn(OH)_4^{2-}$	$10^{17.66}$	$10^{17.66}=[Zn(OH)_4^{-}]/\{[Zn^{2+}][OH^{-}]^4\}$
23	$2Zn^{2+}+OH^{-}=Zn_2OH^{3+}$	$10^{5.0}$	$10^{5.0}=[Zn(OH)_4^{-}]/\{[Zn^{2+}]^2[OH^{-}]\}$
24	$ZnH_2AsO4^{+}=Zn^{2+}+H_2AsO_4^{-}$	$10^{-0.51}$	$10^{-0.51}=[Zn^{2+}][H_2AsO_4^{-}]/[ZnH_2AsO_4^{+}]$
25	$ZnHAsO_4(aq)=Zn^{2+}+HAsO_4^{2-}$	$10^{-1.81}$	$10^{-1.81}=[Zn^{2+}][HAsO_4^{2-}]/[ZnHAsO_4(aq)]$
26	$ZnAsO_4^{-}=Zn^{2+}+AsO_4^{3-}$	$10^{-7.31}$	$10^{-7.31}=[Zn^{2+}][AsO_4^{3-}]/[ZnAsO_4^{-}]$
27	$Zn^{2+}+SO_4^{2-}=ZnSO_4(aq)$	$10^{2.38}$	$10^{2.38}=[ZnSO_4(aq)]/[Zn^{2+}][SO_4^{2-}]$
28	$H_2SO_4=HSO_4^{-} + H^{+}$	$10^{3.00}$	$10^{3.00}=[HSO_4^{-}][H^{+}]/[H_2SO_4]$
29	$HSO_4^{-}=SO_4^{-} + H^{+}$	$10^{-1.99}$	$10^{-1.99}=[SO_4^{2-}][H^{+}]/[HSO_4^{-}]$
30	$FeAsO_4(s)=Fe^{3+}+AsO_4^{3-}$	$10^{-20.24}$	$10^{-20.24}=[Fe^{3+}][AsO_4^{3-}]$
31	$Fe(OH)_3(s)=Fe^{3+}+3OH^{-}$	$10^{-37.40}$	$10^{-37.40}=[Fe^{3+}][OH^{-}]^3$
32	$Cd_5H_2(AsO_4)_4(s)=5Cd^{2+}+2HAsO_4^{2-} +2AsO_4^{3-}$	$10^{-49.73}$	$10^{-49.73}=[Cd^{2+}]^5[HAsO_4^{2-}]^2[AsO_4^{3-}]^2$
33	$Cd_3(AsO_4)_2(s)=3Cd^{2+}+2AsO_4^{3-}$	$10^{-22.66}$	$10^{-22.66}=[Cd^{2+}]^3[AsO_4^{3-}]^2$
34	$ZnHAsO_4(s)= Zn^{2+}+HAsO_4^{-}$	$10^{-5.34}$	$10^{-5.34}=[Zn^{2+}][HAsO_4^{-}]$
35	$Zn_3(AsO_4)_2(s)=3Zn^{2+}+2AsO_4^{3-}$	$10^{-27.55}$	$10^{-27.55}=[Zn^{2+}]^3[AsO_4^{3-}]^2$
No.	**Mass balance equations of the system**		
36	$[Cd]_T^0=[Cd^{2+}]+[CdOH^{+}]+[Cd(OH)_2(aq)]+[Cd(OH)_3]^{-}+[Cd(OH)_4^{2-}]+2[Cd_2OH^{3+}]+4[Cd_4(OH)_4^{4+}]+[CdSO_4(aq)]$		
37	$[Zn]_T^0=[Zn^{2+}]+[ZnOH^{+}]+[Zn(OH)_2(aq)]+[Zn(OH)_3^{-}]+[Zn(OH)_4^{2-}]+2[Zn_2OH^{3+}]+[ZnH_2AsO_4^{+}]+[ZnHAsO_4(aq)]+[ZnAsO_4^{-}]+[ZnSO_4(aq)]$		
38	$[As]_T^0=[AsO_4^{3-}]+[HAsO_4^{2-}]+[H_2AsO_4^{-}]+[H_3AsO_4]+[FeH_2AsO_4^{2+}]+[FeHAsO_4^{+}]+[ZnH_2AsO_4^{+}]+[ZnHAsO_4(aq)]+[ZnAsO_4^{-}]$		
39	$[Fe]_T^0=[Fe^{3+}]+[FeOH^{2+}]+[Fe(OH)_2^{+}]+[Fe(OH)_3(aq)]+[FeH_2AsO_4^{2+}]+[FeHAsO_4^{+}]+[Fe(SO_4)^{+}]+[Fe(SO_4)_2^{-}]$		
40	$[S]_T^0=[SO_4^{2-}]+[HSO_4^{-}]+[H_2SO_4]+[Fe(SO_4)^{+}]+2[Fe(SO_4)_2^{-}]+[CdSO_4(aq)]+[ZnSO_4(aq)]$		
41	$[Fe]_T^0-[Fe]_T=[As]_T^0-[As]_T$		
42	$[Cd]_T^0-[Cd]_T=5/4\{[As]_T^0-[As]_T\}$		
43	$[Cd]_T^0-[Cd]_T=3/2\{[As]_T^0-[As]_T\}$		
44	$[Zn]_T^0-[Zn]_T=[As]_T^0-[As]_T$		
45	$[Zn]_T^0-[Zn]_T=3/2\{[As]_T^0-[As]_T\}$		
46	$[As]_T^0-[As]_T=4/5\{[Cd]_T^0-[Cd]_T\}+\{[Zn]_T^0-[Zn]_T\}$		

Table S2 System of equations depending on the nature of the solid phase

System No.	Solid phases	Constraint conditions
1	No solid	(1)−(29)+(36)−(40)
2	$FeAsO_4$	(1)−(30)+(36)−(37)+(39)+(40)−(41)
3	$Fe(OH)_3$	(1)−(29)+(31)+(36)−(38)+(40)
4	$FeAsO_4$+$Fe(OH)_3$	(1)−(31)+(36)−(37)+(40)
5	$Cd_5H_2(AsO_4)_4$+$Fe(OH)_3$	(1)−(29)+(31)−(32)+(37)+(40)+(42)
6	$ZnHAsO_4$+$Fe(OH)_3$	(1)−(29)+(31)+(34)+(36)+(40)+(44)
7	$Cd_3(AsO_4)_4$+$Fe(OH)_3$	(1)−(29)+(31)+(33)+(37)+(40)+(43)
8	$Zn_3(AsO_4)_4$+$Fe(OH)_3$	(1)−(29)+(31)+(35)−(36)+(40)+(45)
9	$FeAsO_4$+$Cd_5H_2(AsO_4)_4$+$Fe(OH)_3$	(1)−(29)+(30)−(32)+(37)+(40)
10	$FeAsO_4$+$ZnHAsO_4$+$Fe(OH)_3$	(1)−(29)+(30)−(31)+(34)+(36)+(40)
11	$FeAsO_4$+$Cd_5H_2(AsO_4)_4$+$ZnHAsO_4$+$Fe(OH)_3$	(1)−(29)+(30)−(32)+(34)+(40)
12	$Cd_5H_2(AsO_4)_4$+$ZnHAsO_4$+$Fe(OH)_3$	(1)−(29)+(31)−(32)+(34)+(40)+(46)
13	$Cd_5H_2(AsO_4)_4$+$Cd_3(AsO_4)_4$+Fe(OH)	(1)−(29)+(31)−(33)+(37)+(40)
14	$Cd_5H_2(AsO_4)_4$+$Cd_3(AsO_4)_4$+$ZnHAsO_4$+$Fe(OH)_3$	(1)−(29)+(31)−(34)+(40)
15	$Cd_5H_2(AsO_4)_4$+$Cd_3(AsO_4)_4$+$Zn_3(AsO_4)_4$+$Fe(OH)_3$	(1)−(29)+(31)−(33)+(35)+(40)

Table S3 The average grain size of hydrothermal As residues at various pH values calculated by Scherrer formula

pH	0.5	1.5	2.0	2.5
Average particle size/nm	33.5	33.7	17.6	14.9

References

[1] SPEIGHT J G. Lange's handbook of chemistry [M]. New York: McGraw-Hill, 2005.

[2] SMITH R M, MARTELL A E. Critical stability constants V4 inorganic complexes [M]. New York: Plenum Press, 1976.

[3] CHAI Li-yuan, CHANG Hao, WANG Yun, et al. Equilibrium of hydroxyl complex ions in Cd^{2+}-H_2O system [J]. The Chinese Journal of Nonferrous Metals, 2007, 17(3): 487−491. DOI: 10.19476/j.ysxb.1004.0609.2007.03.024. (in Chinese)

[4] MAGALHÃES M, CLARA F, de JESUS J D P. The chemistry of formation of some secondary arsenate minerals of Cu(II), Zn(II) and Pb(II) [J]. Mineralogical Magazine, 1988, 52(368): 679−690. DOI: 10.1180/minmag.1988.052.368.12.

[5] LIU Shu-fen, YANG Sheng-hai, ZHANG Xian-pan, et al. Removal of cadmium and arsenic from Cd-As-Pb-bearing dust based on peroxide leaching and coprecipitation [J]. Hydrometallurgy, 2022, 209: 105839. DOI: 10.1016/j.hydromet.2022.105839.