Supplementary

Solubility approximation of vivanite, ferrous phosphate octahydrate

$Fe^{2+} + H_2O = Fe(OH)^+ + H^+$ $K_1 = 10^{-9.51}$

$Fe^{2+} + 2H_2O = Fe(OH)_{2(aq)} + 2H^+$ $K_2 = 10^{-20.61}$

$Fe^{2+} + 3H_2O = Fe(OH)_3^- + 3H^+$ $K_3 = 10^{-32.6}$

$Fe^{2+} + H_2PO_4^- = FeH_2PO_4^+$ $K_4 = 10^{2.7}$

$Fe^{2+} + PO_4^{3-} + 2H^+ = FeH_2PO_4^+$ $K_4' = K_4/(K_{a2}K_{a3}) = 10^{22.2}$

$Fe^{2+} + HPO_4^{2-} = FeHPO_4$ $K_5 = 10^{3.6}$

$Fe^{2+} + PO_4^{3-} + H^+ = FeHPO_4$ $K_5' = K_5/K_{a3} = 10^{15.9}$

$H_3PO_4 = H^+ + H_2PO_4^-$ $K_{a1} = 10^{-2.1}$

$H_2PO_4^- = H^+ + HPO_4^{2-}$ $K_{a2} = 10^{-7.2}$

$HPO_4^{2-} = H^+ + PO_4^{3-}$ $K_{a3} = 10^{-12.3}$

$P_T = [PO_4^{3-}] + [HPO_4^{2-}] + [H_2PO_4^-] + [H_3PO_4] + [FeH_2PO_4^+] + [FeHPO_4]$

$$= [PO_4^{3-}](1 + \frac{[H^+]}{K_{a3}} + \frac{[H^+]^2}{K_{a2}K_{a3}} + \frac{[H^+]^3}{K_{a1}K_{a2}K_{a3}}) + [Fe^{2+}][PO_4^{3-}](K_4'[H^+]^2 + K_5'[H^+])$$

$Fe_T = [Fe^{2+}] + [Fe(OH)^+] + [Fe(OH)_{2(aq)}] + [Fe(OH)_3^-] + [FeH_2PO_4^+] + [FeHPO_4]$

$$= [Fe^{2+}](1 + \frac{K_1}{[H^+]} + \frac{K_2}{[H^+]^2} + \frac{K_3}{[H^+]^3}) + [Fe^{2+}][PO_4^{3-}](K_4'[H^+]^2 + K_5'[H^+])$$

Solubility of vivianite

$Fe_3(PO_4)_2 \cdot 8H_2O = 3Fe^{2+} + 2PO_4^{3-} + 8H_2O$ $K_{sp} = 10^{-36}$

Since,

$K_{sp} = [Fe^{2+}]^3 \times [PO_4^{3-}]^2 = 10^{-36}$

$[Fe^{2+}]\ [Fe^{2+}]^2 \times [PO_4^{3-}]^2 = 10^{-36}$

$[Fe^{2+}]^{1/2}\ ([Fe^{2+}] \times [PO_4^{3-}]) = 10^{-18}$

$[Fe^{2+}] \times [PO_4^{3-}] = 10^{-18}[Fe^{2+}]^{-1/2}$

$Fe_T = [Fe^{2+}] + [Fe(OH)^+] + [Fe(OH)_{2(aq)}] + [Fe(OH)_3^-] + [FeH_2PO_4^+] + [FeHPO_4]$

$$= [Fe^{2+}](1 + \frac{K_1}{[H^+]} + \frac{K_2}{[H^+]^2} + \frac{K_3}{[H^+]^3}) + [Fe^{2+}]^{-1/2}10^{-18}(K_4'[H^+]^2 + K_5'[H^+])$$

Assume $Fe_T = 10^{-3}\ M$

$$\alpha x + \beta x^{-1/2} - 10^{-3} = 0$$

$$\alpha = 1 + \frac{K_1}{[H^+]} + \frac{K_2}{[H^+]^2} + \frac{K_3}{[H^+]^3}$$

$$\beta = 10^{-18}(K_4'[H^+]^2 + K_5'[H^+])$$

Solve $x = [Fe^{2+}]$

$$[PO_4^{3-}] = (\frac{10^{-36}}{[Fe^{2+}]^3})^{1/2}$$

$$[HPO_4^{2-}] = \frac{[H^+]}{10^{-12.3}}[PO_4^{3-}]$$

$$[H_2PO_4^-] = \frac{[H^+]^2}{10^{-12.3} \times 10^{-7.2}}[PO_4^{3-}]$$

$$[H_3PO_4] = \frac{[H^+]^3}{10^{-12.3} \times 10^{-7.2} \times 10^{-2.1}}[PO_4^{3-}]$$

$$[FeH_2PO_4^+] = 10^{22.2} \times [Fe^{2+}][PO_4^{3-}][H^+]^2$$

$$[FeHPO_4] = 10^{15.9} \times [Fe^{2+}][PO_4^{3-}][H^+]$$

Solubility ferrous hydroxide

$Fe(OH)_{2(s)} = Fe^{2+} + 2OH^-$ $\quad K_{sp} = 10^{-16.3}$

$$[Fe^{2+}] = \frac{K_{sp}[H^+]^2}{K_W^2}$$

$$Fe_T = [Fe^{2+}](1 + \frac{K_1}{[H^+]} + \frac{K_2}{[H^+]^2} + \frac{K_3}{[H^+]^3}) + [Fe^{2+}][PO_4^{3-}](K_4'[H^+]^2 + K_5'[H^+])$$

$$= [Fe^{2+}]\alpha + [Fe^{2+}]^{-1/2}\beta$$

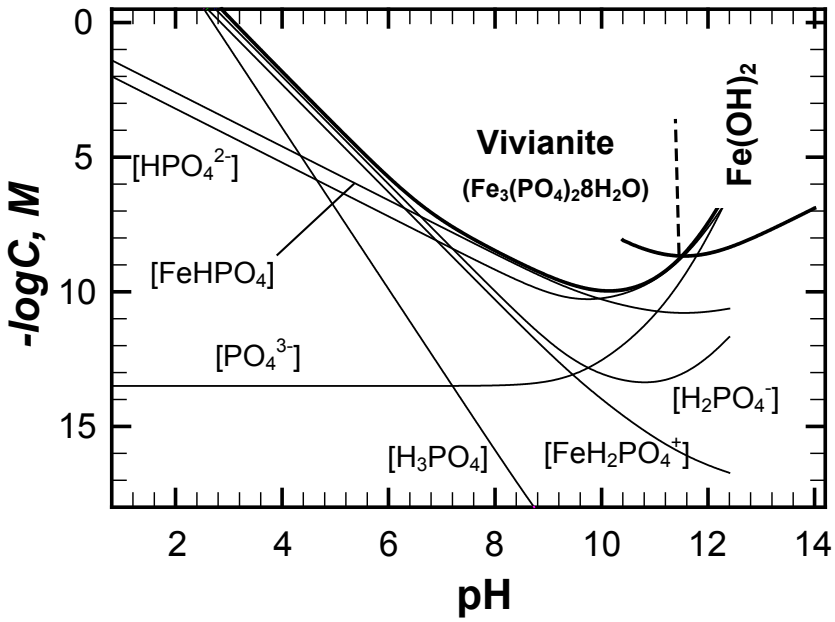

Fig. S1 Speciation of soluble phosphate contributing to precipitation of vivianite ($Fe_T = 10^{-3}$ M)

Fig. S2 Apparatus of fluidized-bed reactor

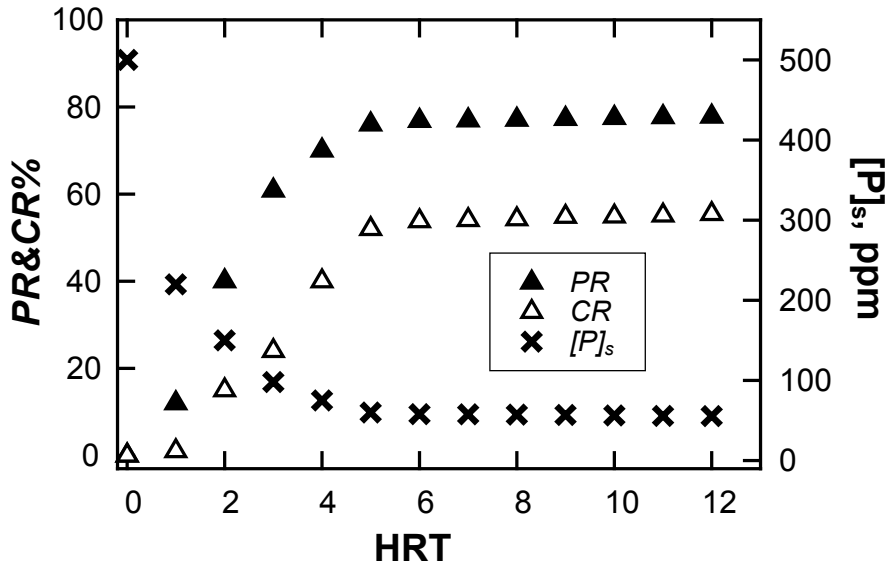

Fig. S3 The efficiency of phosphate removal (PR), crystallization ratio (CR) and the soluble $[P]_s$ in the effluent from a FBC reactor by creating vivianite (ferrous phosphate) pellets. ([Fe]/[P] = 1.5, U = 40 m h^{-1}, pH 5.5)

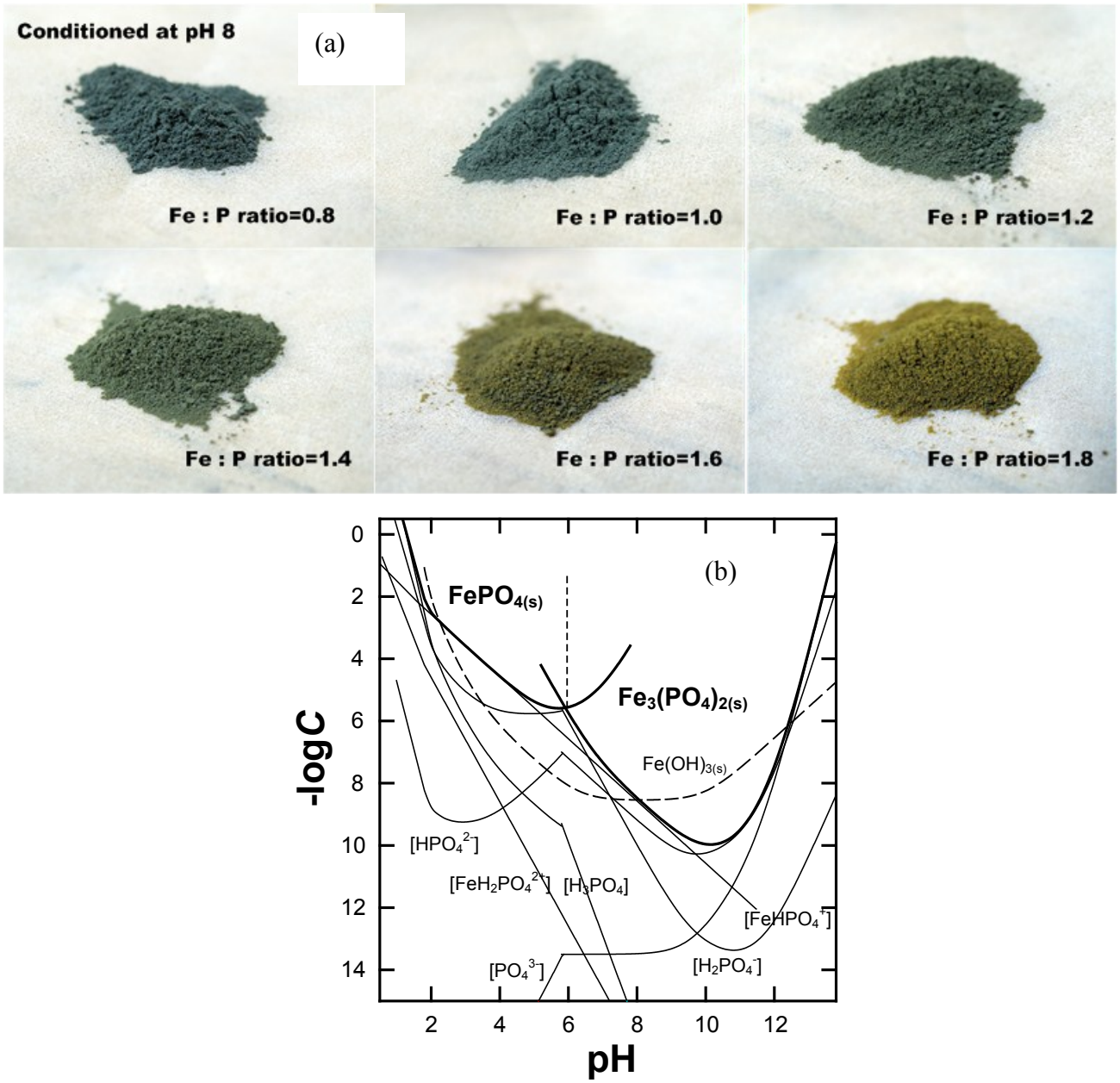

Fig. S4 (a) Ferrous phosphate sludge of jar test at different molar ratio of Fe(II) to P. (b) Solubility of $FePO_4$, vivianite and $Fe(OH)_3$.

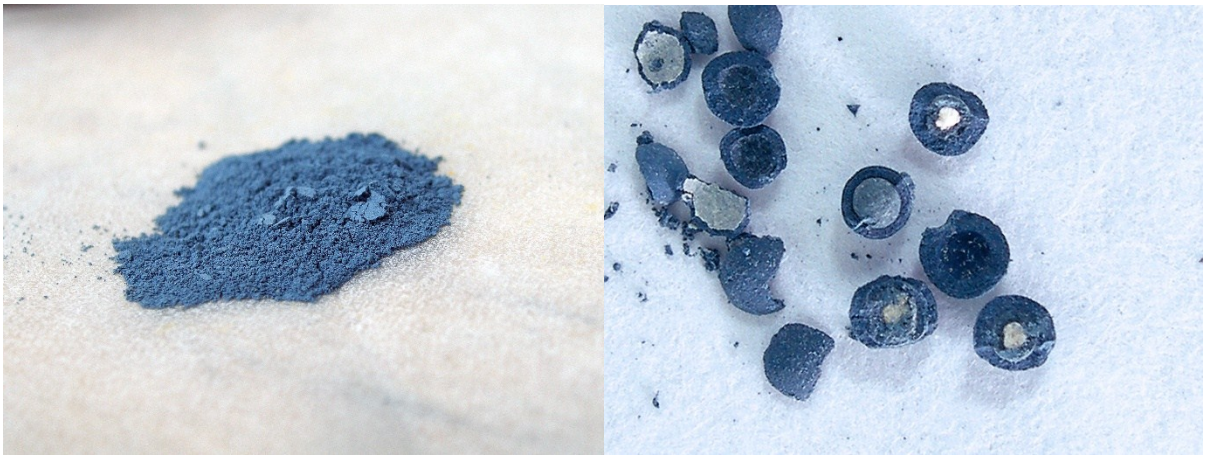

Fig. S5 Products of vivianite sludge and crystal pellets from jar test and FBC reactor, respectively.

Table S1 The iron concentrations in the filtered and unfiltered samplings under various FBC conditions

	Iron conc. (ppm)			Iron conc. (ppm)			Iron conc. (ppm)	
pH	filtered	unfiltered	Upflow (m/h)	filtered	unfiltered	Fe(II)/P	filtered	unfiltered
4.79	95.23	126.99	11.46	135	154	1	36	41
5.12	67.24	94.57	21.01	101	121	1.2	48	50
5.2	51.75	72.95	30.56	78	89	1.5	55	61
5.37	32.75	52.01	40.11	78	89	1.75	78	89
5.48	28.25	50.12	49.66	68	78	2	203	218
5.58	10.45	25.47	59.21	65	76	2.25	280	295
5.72	9.43	17.77				2.5	382	401
5.85	5.24	9.93						
6.02	3.64	5.94						
6.25	1.25	2.09						
6.5	0.975	1.82						
6.8	0.633	1.15						
7.3	0.32	0.59						
7.52	0.19	0.57						

Table S2 The other elements measure in the ICP

ICP other elements				
Ag (Silver)	Al (Aluminium)	B (Boron)	Ba (Barium)	Bi (Bismuth)
Ca (Calcium)	Cd (Cadmium)	Co (Cobalt)	Cr (Chromium)	Cu (Copper)
Ga (Gallium)	In (indium)	K (Potassium)	Li (Lithium)	Mg (Magnesium)
Mn (Mangenese)	Na (Natrium)	Ni (Nickel)	Pb (Lead)	Sr (strontium)
Ti (Titanium)	Zn (Zinc)			