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國立成功大學
National Cheng Kung University

鋇系化學過氧沉澱除硼程序之原理及應用

Principal of barium-based chemical oxo-precipitation and its application in boron removal

窮理致知
Veritas et Conscientia

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Abstract

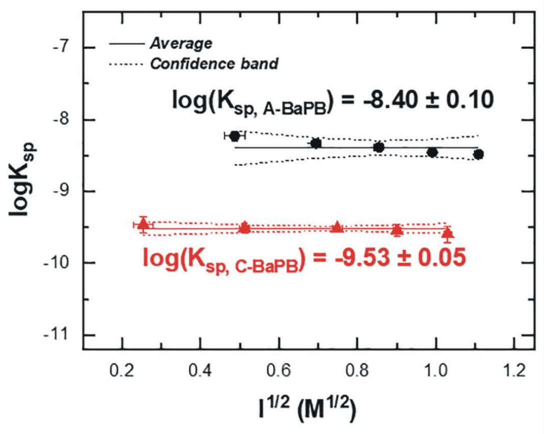
This research aims to study and engineer the barium-based COP to treat the boron-containing streams. The solubility products (K_{sp}) of the amorphous BaPB (A-BaPB, $Ba(B(OH)_3OOH)_2$) and the crystalline BaPB (C-BaPB, $BaB(OH)_2(OO)_2B(OH)_2$) were experimentally determined to be $10^{-8.40}$ and $10^{-9.53}$, respectively. The thermodynamic model that was built based on K_{sp} confirmed that A-BaPB is 10-fold soluble than C-BaPB, which drove the phase transformation through the dissolution-precipitation route. To enable the continuous treatment and minimize the sludge production, two fluidized-bed crystallizers (FBCs) were designed to immobilize A-BaPB and C-BaPB on granular supports. The FBC of A-BaPB could achieve 85.1% of boron removal (TR) and 83.7% of crystallization ratio (CR) from concentrated stream ($[B]_0$ = 46 mM (500 mg-B/L)). While the removal of boron was subject to the equilibrium solubility of A-BaPB, the sludge production rate ($\dot{m}_{slg}$) was governed by the supersaturation ratio (S) of the mixture at the bottom of the reactor. The FBC of C-BaPB aims to further eliminate the boron level from the effluent of the FBC of A-BaPB. By using granular seeds of C-BaPB as the fluidized medium of FBC, the continuous crystal growth removed 89.9% of boron from the synthetic effluent of FBC of A-BaPB ($[B]_{in}$ = 4.5 mM (50 mg-B/L)). Based on the linear relation between crystal growth rate (R_c) and relative supersaturation (S-1), the crystal growth rate of C-BaPB was mass transfer controlled, which was not altered by the superficial velocity. Ultimately, a hybrid system that integrates two FBCs for the subsequent crystallization of A-BaPB and C-BaPB was demonstrated to treat the concentrated boric acid solution ($[B]_0$ = 46 mM (500 mg-B/L)). The integrated system enabled 97.8% of boron removal and 97.4% of crystallization ratio, producing an effluent with a boron level of 7.8 mg-B/L and a turbidity of 5.5 NTU.

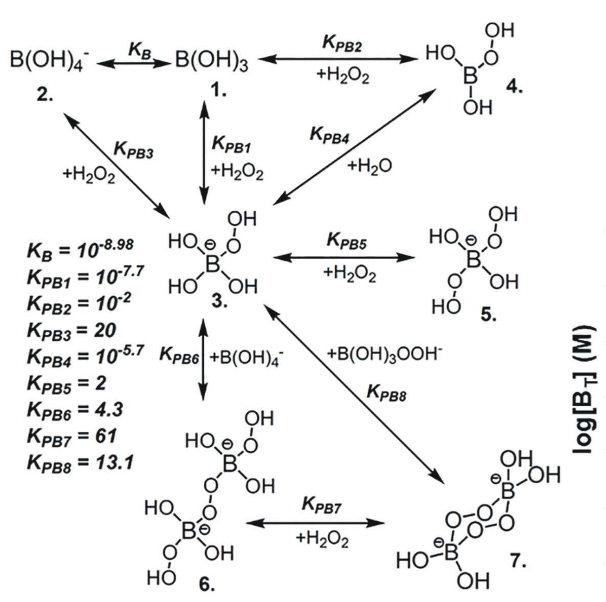
Major findings

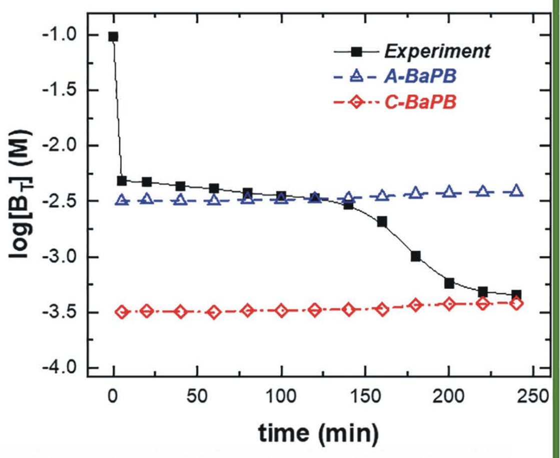
Solubility products of barium perborates (BaPBs)

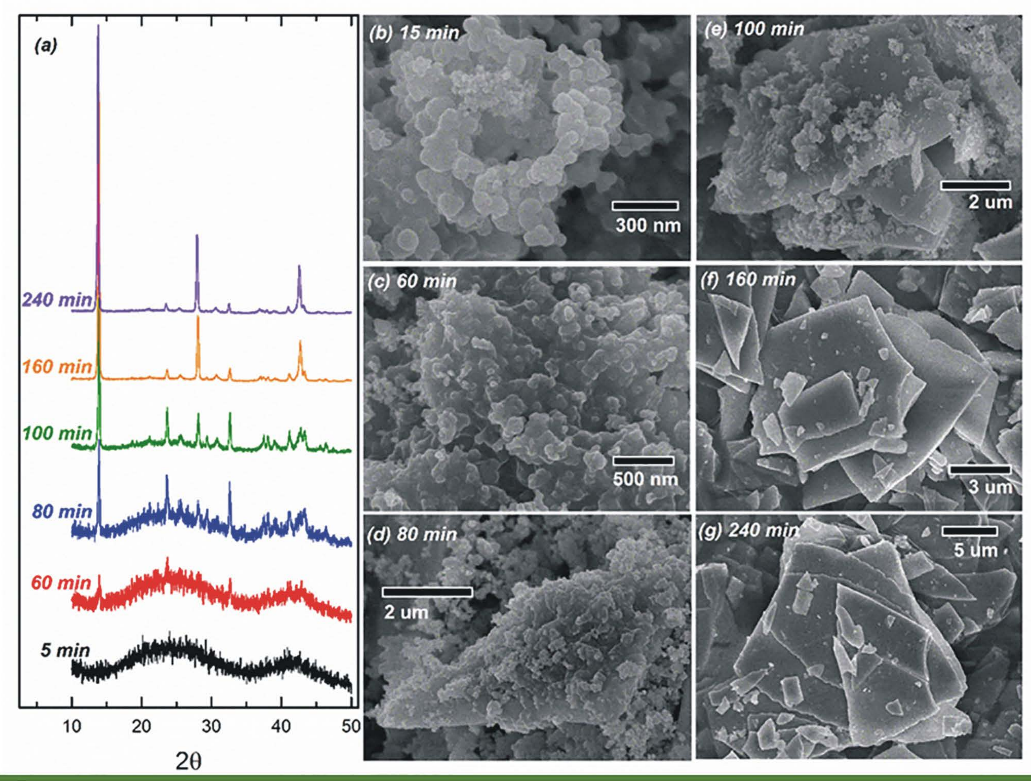
Solubility products (K_{sp}) of two kinds of BaPBs were determined:

- A-BaPB ($Ba(B(OH)_3OOH)_2$) $\log(K_{sp,A\text{-}BaPB}) = -8.40 \pm 0.10$
- C-BaPB ($BaB(OH)_2(OO)_2B(OH)_2$) $\log(K_{sp,C\text{-}BaPB}) = -9.53 \pm 0.05$





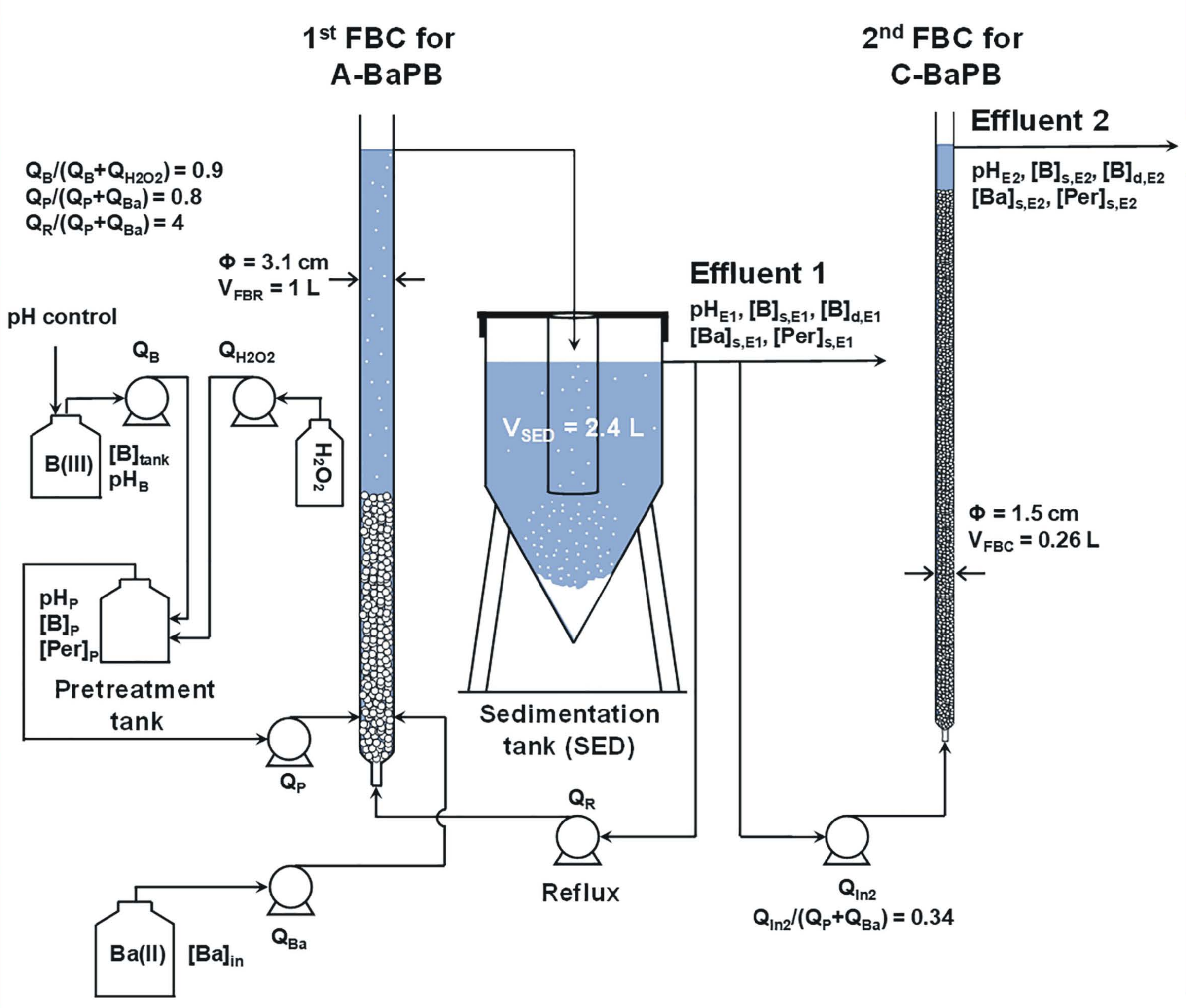




Fluidized-bed crystallization processes

- Fluidized-bed crystallizers (FBCs) were designed to remove the boron continuously in forms of granular A-BaPB and C-BaPB to minimize sludge production.
- The integration of the FBCs of A-BaPB and C-BaPB crystallized and eliminated > 97% of boron from the synthetic stream (450 mg-B/L)

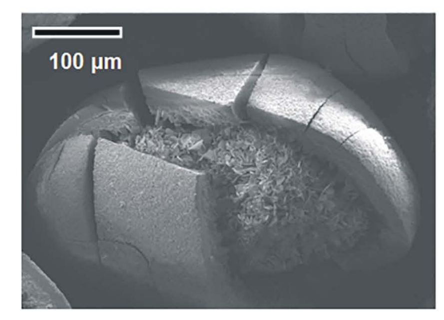
FBC system	A-BaPB	C-BaPB	A-BaPB + C-BaPB
B_{in} (mg/L)	450	70	-
L_{in} (g-B/(m²•h))	1400	405	-
HRT (min)	16	9	-
pH_E	9.9	9.4	-
B_{out} (mg/L)	70	7.6	-
Turbidity (NTU)	40	5.5	-
Total removal	79.8%	90%	97.8%
Crystallization ratio	74.8%	89%	97.4%

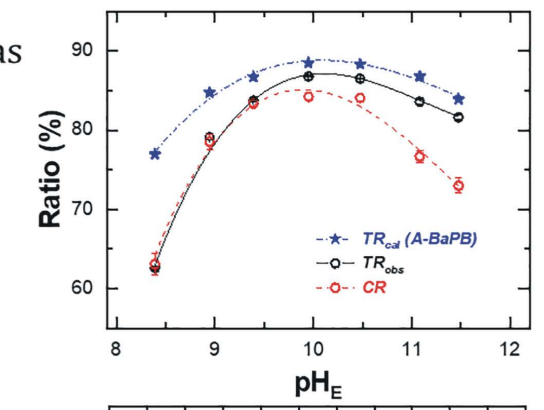


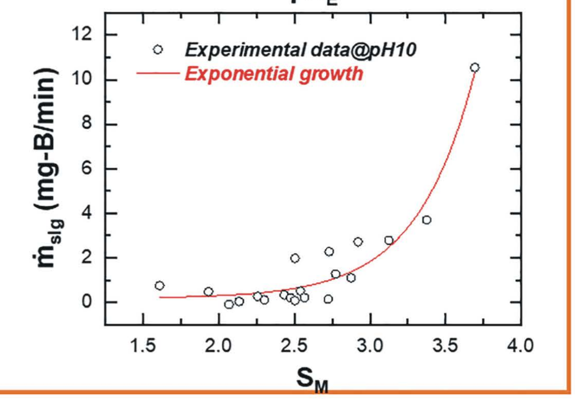
FBC of A-BaPB

Granulized ~ 85% of boron as A-BaPB from concentrated solution (450 mg-B/L)

$$S = \sqrt[3]{\frac{\{Ba^{2+}\}\{B(OH)_3OOH^-\}}{K_{sp,A-BaPB}}}$$



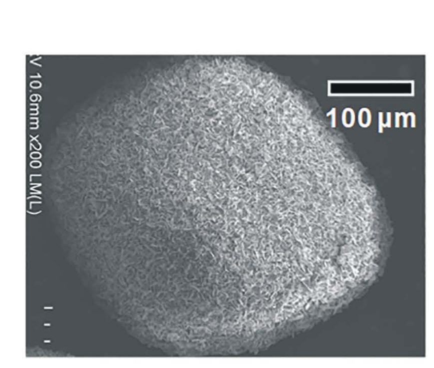


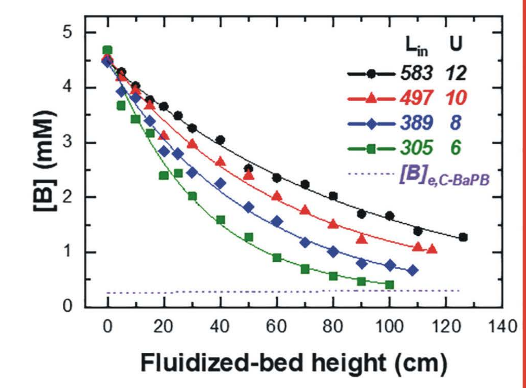


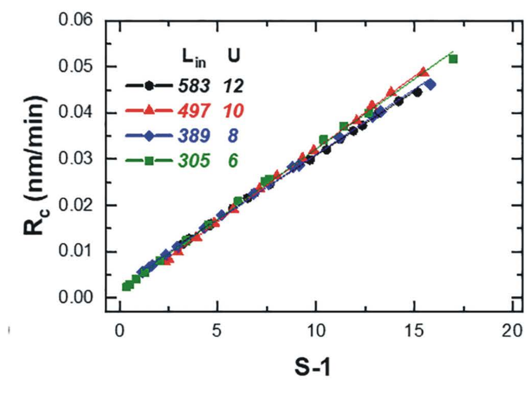
FBC of C-BaPB

C-BaPB was crystallized from the synthetic effluent of the FBC of A-BaPB (50 mg-B/L)

$$S = \sqrt{\frac{\{Ba^{2+}\}\{B(OH)_2(OO)_2B(OH)_2^{2-}\}}{K_{sp,C-BaPB}}}$$







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