半導體廠氫氟廢水 $CaCl_2$加藥模式建立及減量之應用

賴明孝

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Agenda

一. 基本化學原理

二. 加藥模式建立

三. 加藥模式之實際驗證

四. 藥劑減量有效運用

五. 效益成果分享

一. 基本化學原理(1/4)

$m\ A^{n+} + n\ C^{m-} \leftrightarrow A_mC_n$, m & n=Numbers (ex. $Na^+ + Cl^- \leftrightarrow NaCl$(食鹽))

(A陽離子) (C陰離子) (鹽類分子)

K_{SP}(溶解度積常數)=$[A^{n+}]^m$ x $[C^{m-}]^n$，(水溶液中各離子飽和生成分子析出之指標)

由Lange's Handbook of Chemistry (Table 1.71)取得CaF_2、$CaSO_4$、$Ca_3(PO_4)_2$之K_{SP}(25℃):

CaF_2: K_{SP} = $[Ca^{2+}]$ x $[F^-]^2$ = 5.3 x 10^{-9}

$CaSO_4$: K_{SP} = $[Ca^{2+}]$ x $[SO_4^{2-}]$ = 4.93 x 10^{-5}

$Ca_3(PO_4)_2$: K_{SP} = $[Ca^{2+}]^3$x $[PO_4^{3-}]^2$ = 2.07 x 10^{-29}

$CaHPO_4$: K_{SP} = $[Ca^{2+}]$ x $[HPO_4^{2-}]$ = 1.0 x 10^{-7}

$Ca(H_2PO_4)_2$: K_{SP} = $[Ca^{2+}]$ x $[H_2PO_4^-]^2$ = 1.0 x 10^{-3}

TABLE 1.71 Solubility Product Constants

The data refer to various temperatures between 18 and 25°C, and were complied from values cited by Bjerrum, Schwarzenbach, and Sillen, *Stability Constants of Metal Complexes*, Part II, Chemical Society, London, 1958, and values taken from publications of the IUPAC Solubility Data Project: *Solubility Data Series*, international Union of Pure and Applied Chemistry, Pergamon Press, Oxford, 1979–1992; H. L. Clever, and F. J. Johnston, *J. Phys Chem. Ref. Data*, **9**:751 (1980); Y. Marcus, *Ibid.* **9**:1307 (1980); H. L. Clever, S. A. Johnson, and M. E. Derrick, *Ibid.* **14**:631 (1985), and **21**:941 (1992).

In the table, "L" is the abbreviation of the organic ligand.

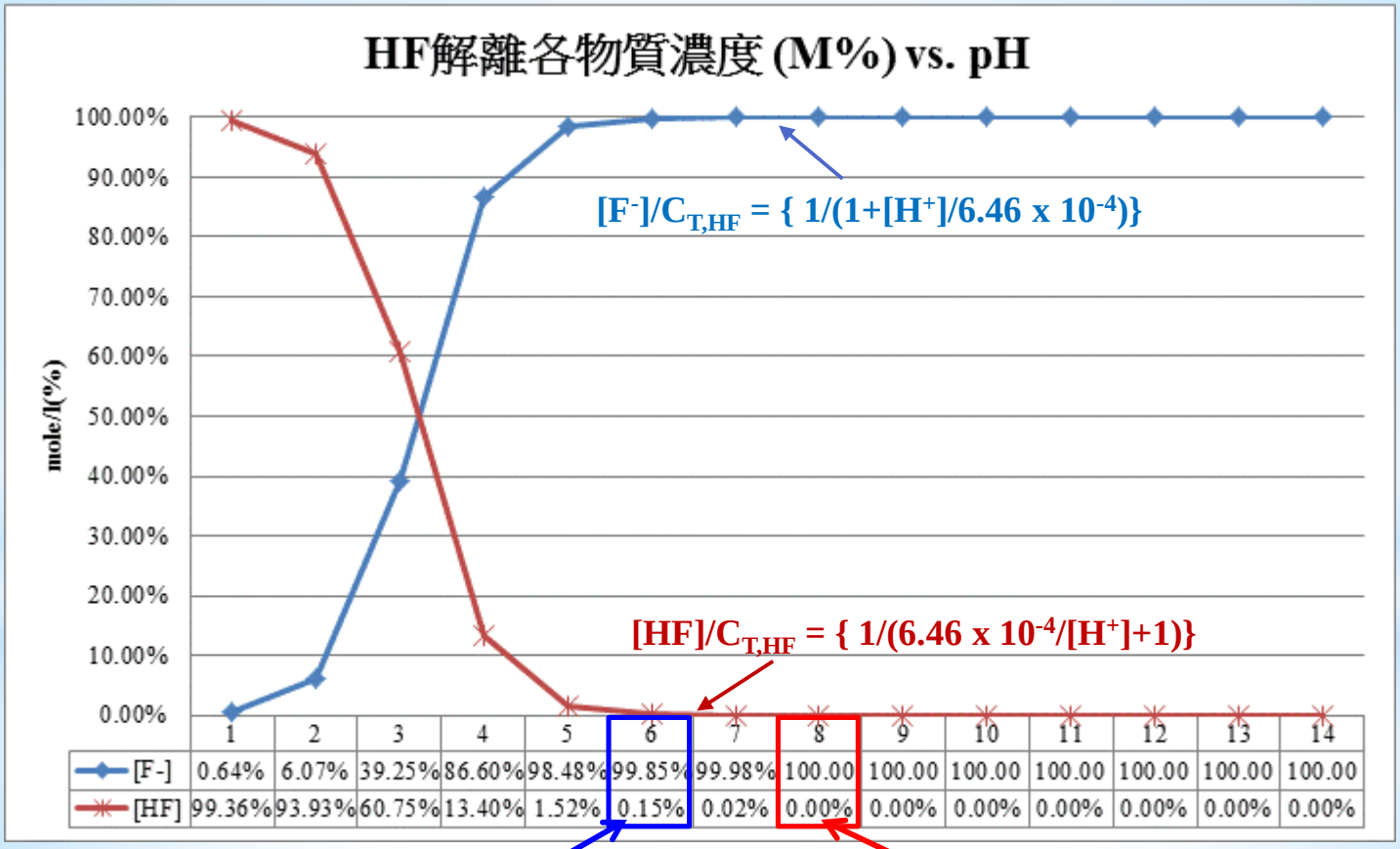
TABLE 1.71 Solubility Product Constants (*Continued*)

Compound	Formula	pK_{sp}	K_{sp}
hydroxide	$Cd(OH)_2$ fresh	14.14	7.2×10^{-15}
iodate	$Cd(IO_3)_2$	7.60	2.5×10^{-8}
oxalate 3-water	$CdC_2O_4 \cdot 3H_2O$	7.85	1.42×10^{-8}
phosphate	$Cd_3(PO_4)_2$	32.60	2.53×10^{-33}
quinaldate	CdL_2	12.30	5.0×10^{-13}
sulfide	CdS	26.10	8.0×10^{-27}
tungstate	$CdWO_4$	5.7	2×10^{-6}
Calcium			
acetate 3-water	$Ca(OAc)_2 \cdot 3H_2O$	2.4	4×10^{-3}
arsenate	$Ca_3(AsO_4)_2$	18.17	6.8×10^{-19}
benzoate 3-water	$CaL_2 \cdot 3H_2O$	2.4	4×10^{-3}
carbonate	$CaCO_3$	8.54	2.8×10^{-9}
carbonate (calcite)	$CaCO_3$	8.47	3.36×10^{-9}
carbonate (aragonite)	$CaCO_3$	8.22	6.0×10^{-9}
carbonatomagnesium	$Ca[Mg(CO_3)_2]$ dolomite	11	1×10^{-11}
chromate	$CaCrO_4$	3.15	7.1×10^{-4}
fluoride	CaF_2	8.28	5.3×10^{-9}
hexafluorosilicate	$CaSiF_6$	3.09	8.1×10^{-4}
hydrogen phosphate	$CaHPO_4$	7.0	1.0×10^{-7}
hydroxide	$Ca(OH)_2$	5.26	5.5×10^{-6}
iodate 6-water	$Ca(IO_3)_2 \cdot 6H_2O$	6.15	7.10×10^{-7}
molybdate	$CaMoO_4$	7.84	1.46×10^{-8}
niobate	$Ca(NbO_3)_2$	17.06	8.7×10^{-18}
oxalate hydrate	$CaC_2O_4 \cdot H_2O$	8.63	2.32×10^{-9}
phosphate	$Ca_3(PO_4)_2$	28.68	2.07×10^{-29}
8-quinolinolate	CaL_2	11.12	7.6×10^{-12}
selenate	$CaSeO_4$	3.09	8.1×10^{-4}
selenite	$CaSeO_3$	5.53	8.0×10^{-6}
silicate, *meta*	$CaSiO_3$	7.60	2.5×10^{-8}
sulfate	$CaSO_4$	4.31	4.93×10^{-5}
sulfate dihydrate	$CaSO_4 \cdot 2H_2O$	4.50	3.14×10^{-5}
sulfite	$CaSO_3$	7.17	6.8×10^{-8}
sulfite 0.5-water	$CaSO_3 \cdot 0.5H_2O$	6.51	3.1×10^{-7}
tartrate dihydrate	$CaL \cdot 2H_2O$	6.11	7.7×10^{-7}
tungstate	$CaWO_4$	8.06	8.7×10^{-9}

一. 基本化學原理(2/4)

$$HA(\text{酸}) \xrightarrow{Ka} H^+ + A^-(\text{酸根離子}) \qquad Ka(\text{酸解離常數}) = \frac{[H^+] \times [A^-]}{[HA]}$$, [ ] :表示mol濃度

(A). $HF \xrightarrow{Ka_{,HF}} H^+ + F^-$, $Ka_{,HF} = 6.46 \times 10^{-4} = [H^+] \times [F^-] / [HF]$; $C_{T,HF} = [F^-] + [HF]$



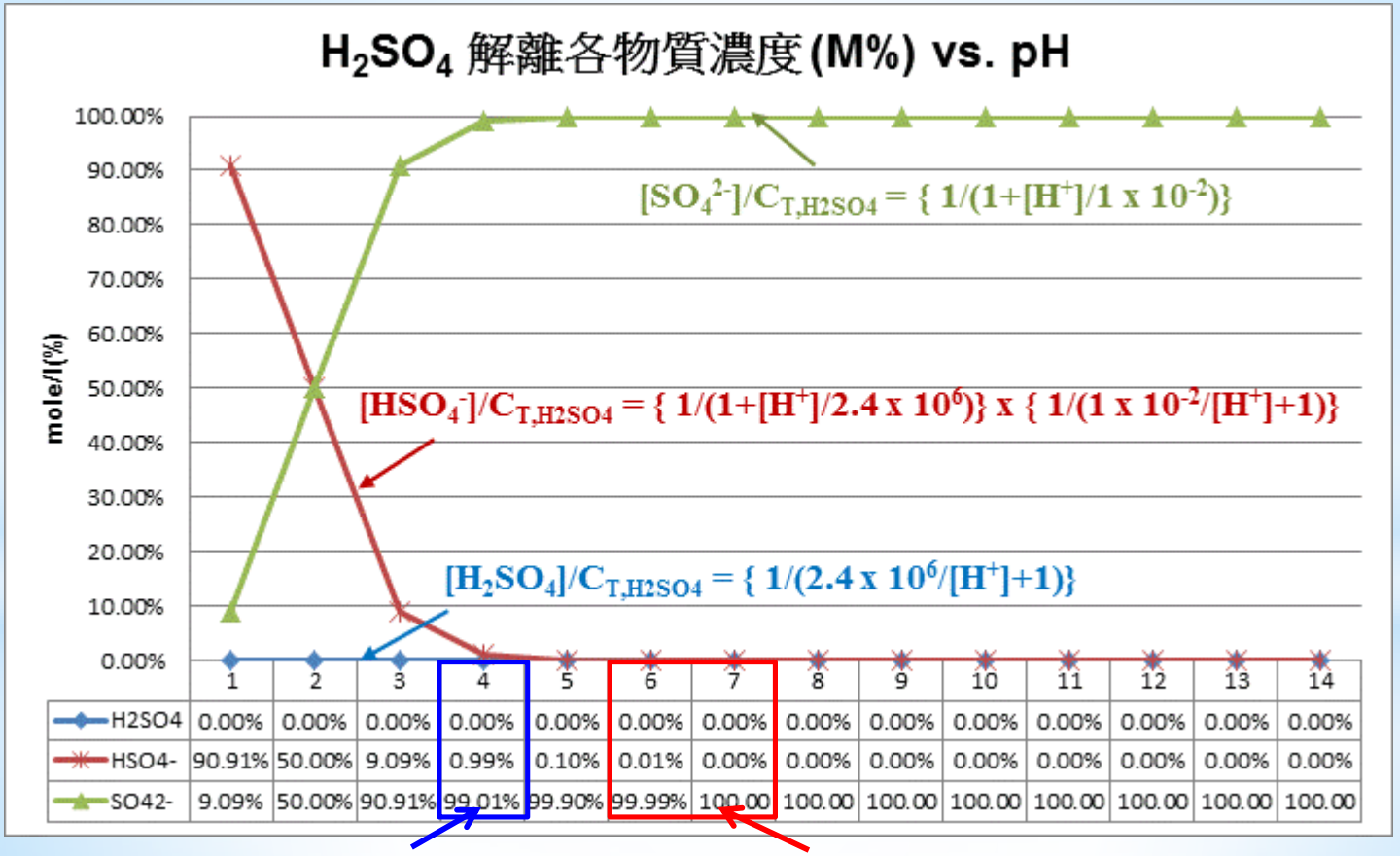
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
[F-]	0.64%	6.07%	39.25%	86.60%	98.48%	99.85%	99.98%	100.00	100.00	100.00	100.00	100.00	100.00	100.00
[HF]	99.36%	93.93%	60.75%	13.40%	1.52%	0.15%	0.02%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%

一. 基本化學原理(3/4)

(B). $H_2SO_4 \xrightarrow{Ka1_{,H2SO4}} H^+ + HSO_4^- \xrightarrow{Ka2_{,H2SO4}} H^+ + SO_4^{2-}$

$Ka1_{,H2SO4} = 2.4 \times 10^6 = [H^+] \times [HSO_4^-] / [H_2SO_4]$ ； $C_{T,H2SO4} = [SO_4^{2-}] + [HSO_4^-] + [H_2SO_4]$

$Ka2_{,H2SO4} = 1.0 \times 10^{-2} = [H^+] \times [SO_4^{2-}] / [HSO_4^-]$



	1	2	3	4	5	6	7	8	9	10	11	12	13	14
H2SO4	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
HSO4-	90.91%	50.00%	9.09%	0.99%	0.10%	0.01%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%	0.00%
SO42-	9.09%	50.00%	90.91%	99.01%	99.90%	99.99%	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00

pH=4 解離99%

pH=6.4 解離100%

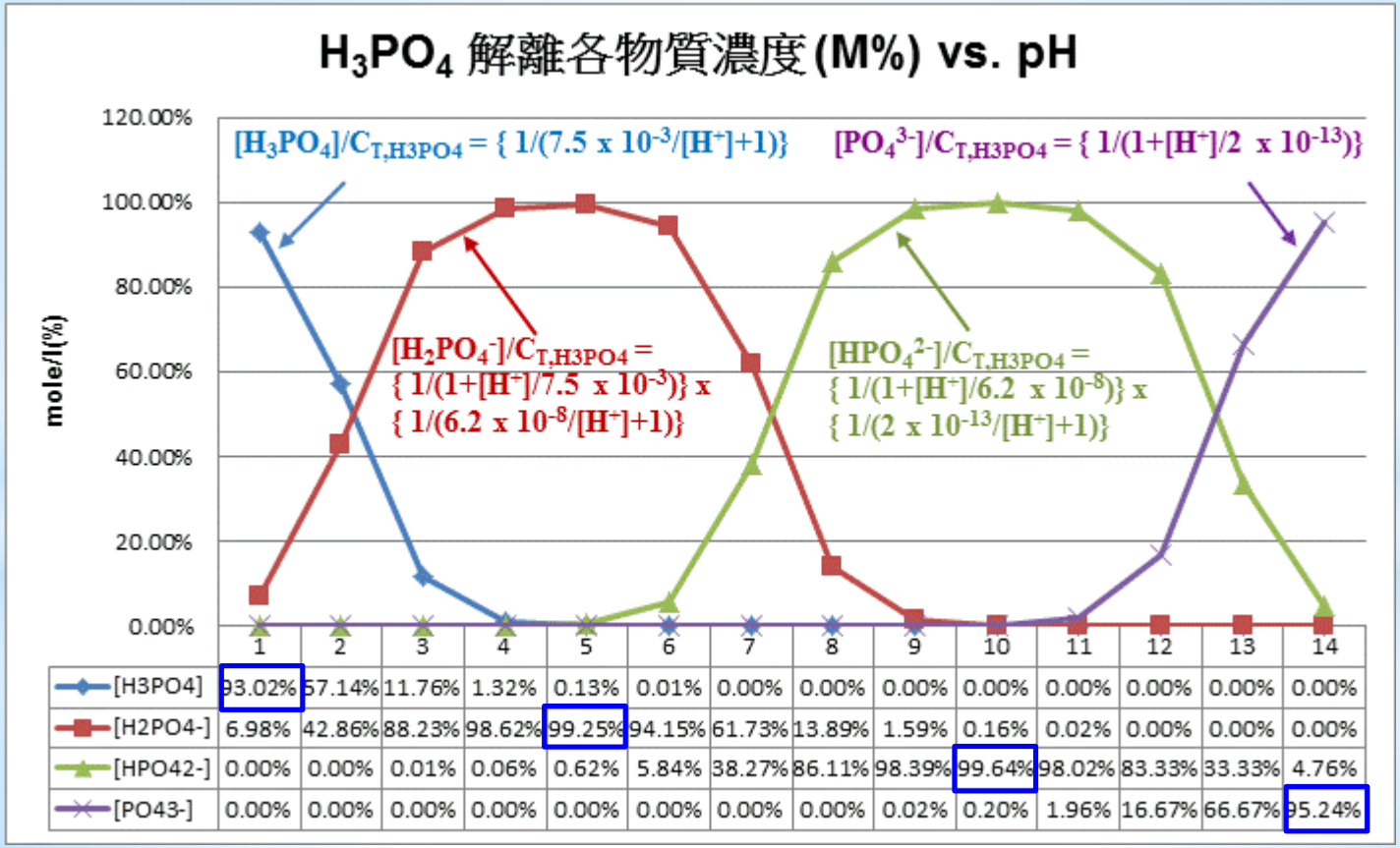
一. 基本化學原理(4/4)

(B). $H_3PO_4 \xleftrightarrow{Ka1_{,H3PO4}} H^+ + H_2PO_4^- \xleftrightarrow{Ka2_{,H3PO4}} H^+ + HPO_4^{2-} \xleftrightarrow{Ka3_{,H3PO4}} H^+ + PO_4^{3-}$

$Ka1_{,H3PO4} = 7.5 \times 10^{-3} = [H^+] \times [H_2PO_4^-] / [H_3PO_4]$; $C_{T,H3PO4} = [PO_4^{3-}] + [HPO_4^{2-}] + [H_2PO_4^-] + [H_3PO_4]$

$Ka2_{,H3PO4} = 6.2 \times 10^{-8} = [H^+] \times [HPO_4^{2-}] / [H_2PO_4^-]$

$Ka3_{,H3PO4} = 2.0 \times 10^{-13} = [H^+] \times [PO_4^{3-}] / [HPO_4^{2-}]$



二. 加藥模式建立

委外檢測處理前

$C_{T,H3PO4}$, $C_{T,H2SO4}$ & $C_{T,HF}$濃度

藉平衡常數(Ka)計算

(solution pH)影響實際解離度

(A) 實際溶解濃度

$PO_4^{3-}{}_{(Act)}$

$SO_4^{2-}{}_{(Act)}$

$F^-_{(Act)}$

(B) 最大溶解濃度

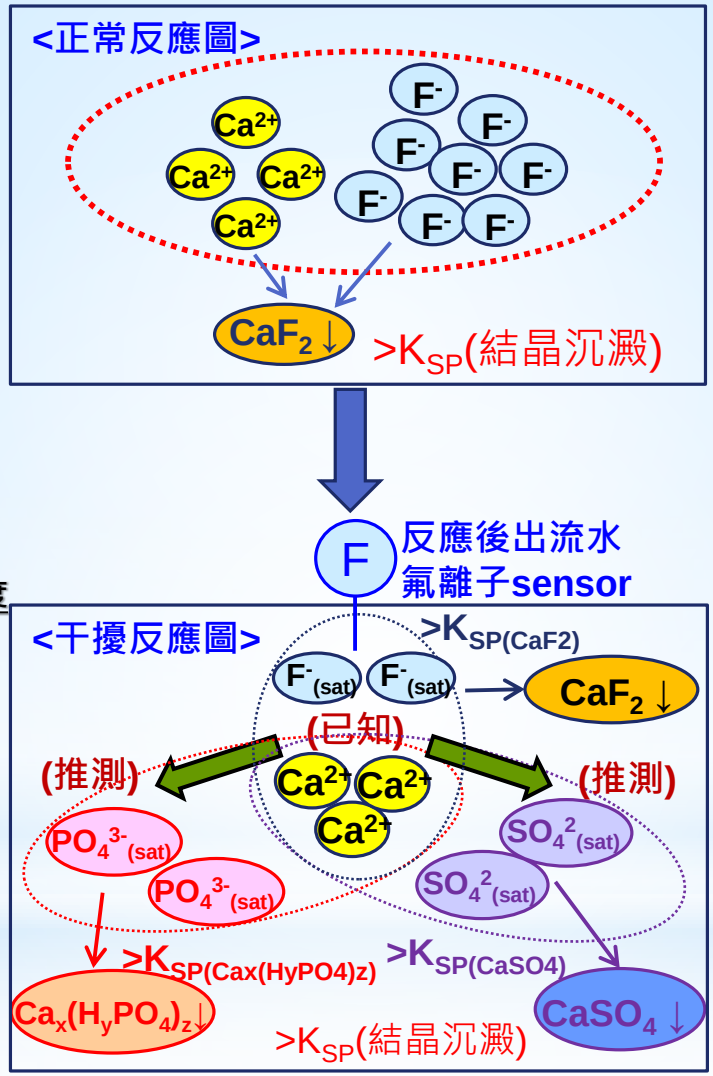
$PO_4^{3-}{}_{(sat)}$

$SO_4^{2-}{}_{(sat)}$

$F^-_{(sat)}$

(A) > (B)

[(A)- (B)]濃度差求出$CaCl_2$量需求



<不含其他酸根離子干擾之行為>

=KSP(溶解度積)➔飽和濃度指標

飽和溶液下離子濃度

$[Ca^{2+}] \fallingdotseq 44(mg/l)$; $[F^-] \fallingdotseq 41.7(mg/l)$

<含磷/硫酸根離子干擾之行為>

最終水溶液中平衡之Ca^{2+}濃度可由F^-濃度(on-line) & $KSP_{(CaF2)}$ 求得

Ca^{2+}濃度確定後，則由

$KSP_{(Cax(PO4)y)}$求得$PO_4^{3-}{}_{(sat)}$

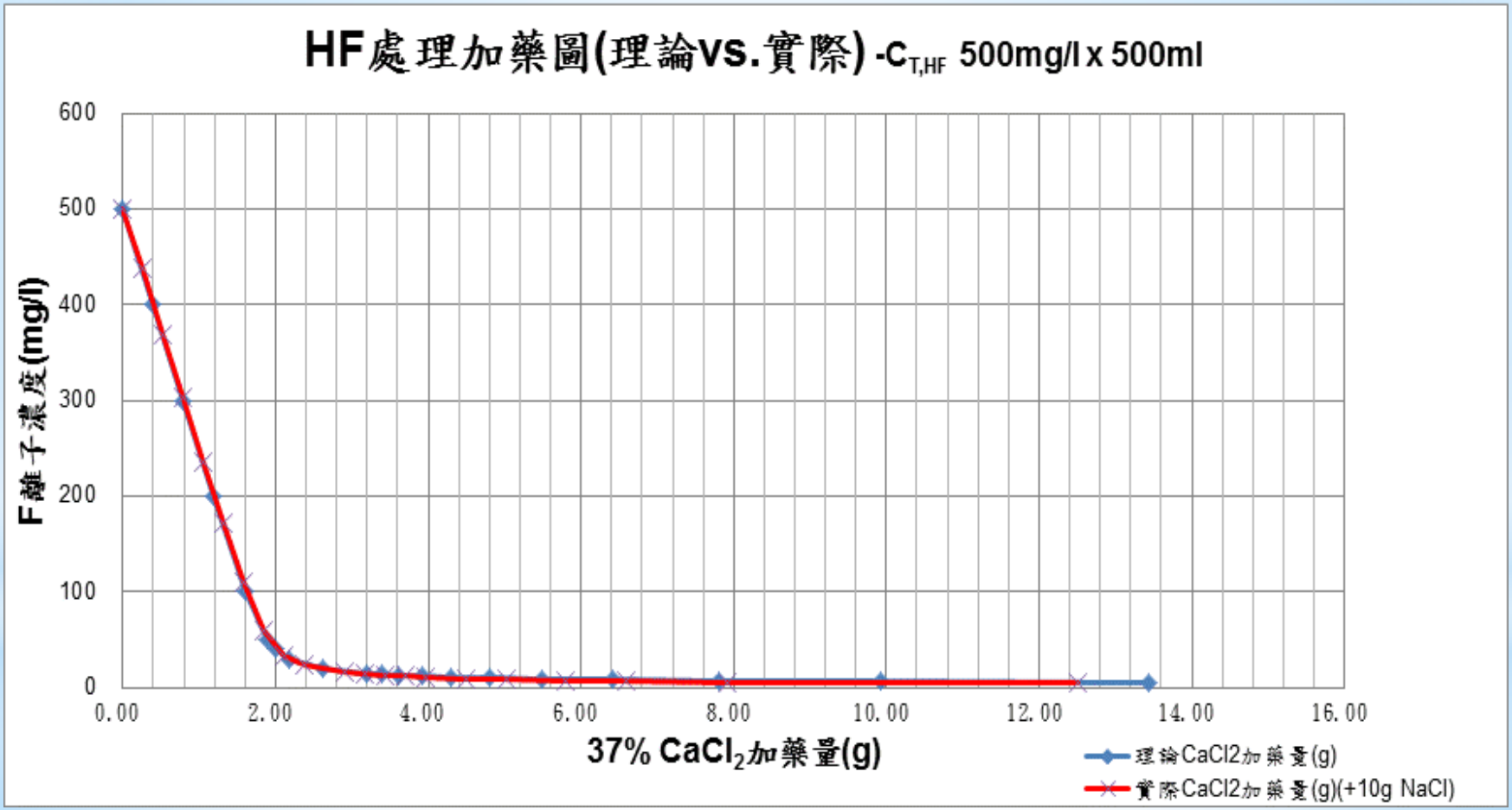
$KSP_{(CaSO4)}$求得$SO_4^{2-}{}_{(sat)}$

結論: HF處理前&後F^-濃度/PH/委外檢測PO_4^{3-}&SO_4^{2-}濃度等操作參數，即可求得$CaCl_2$總耗用量

進一步調整上述參數，以避開PO_4^{3-}&SO_4^{2-}存在下對$CaCl_2$之耗用干擾。

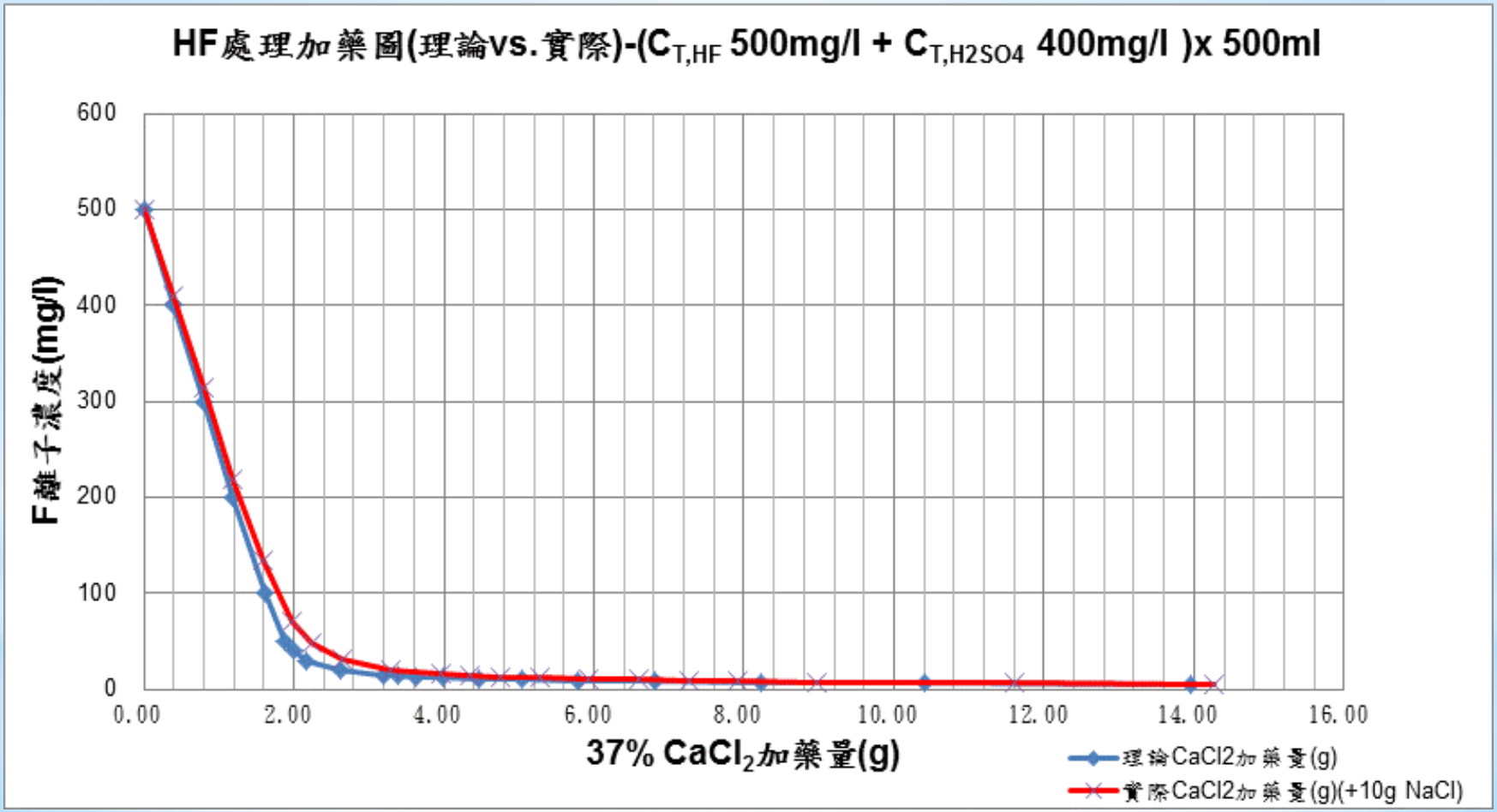
三. 加藥模式之實際驗證(1/6)

1. 以DI水配置($C_{T,HF}$:500mg/l) x 500ml+10g NaCl(提高水溶液導電度 > 3000μs/cm)，
   以定量吸管添加37% $CaCl_2$ 0.2 ml/次 ，藉以HACH F^- & pH計進行實驗量測 (keep pH=7)



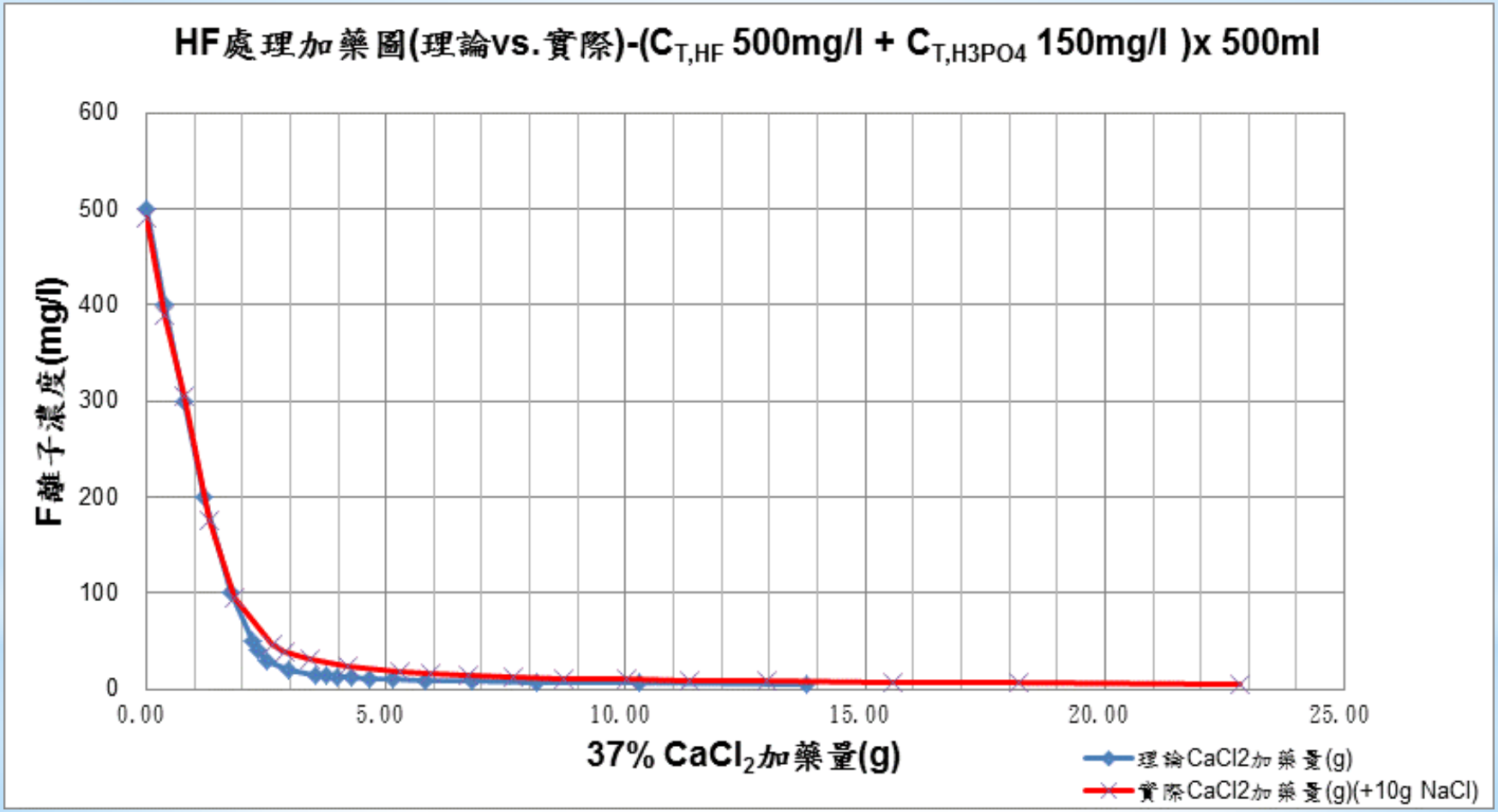
三. 加藥模式之實際驗證(2/6)

2. 以DI水配置($C_{T,HF}$:500mg/l + $C_{T,H2SO4}$:400mg/l) x 500ml+10g NaCl(提高水溶液導電度 > 3000μs/cm)，以定量吸管添加37% $CaCl_2$ 0.2 ml/次 ，藉以HACH F^- & pH計進行實驗量測 (keep pH=7)



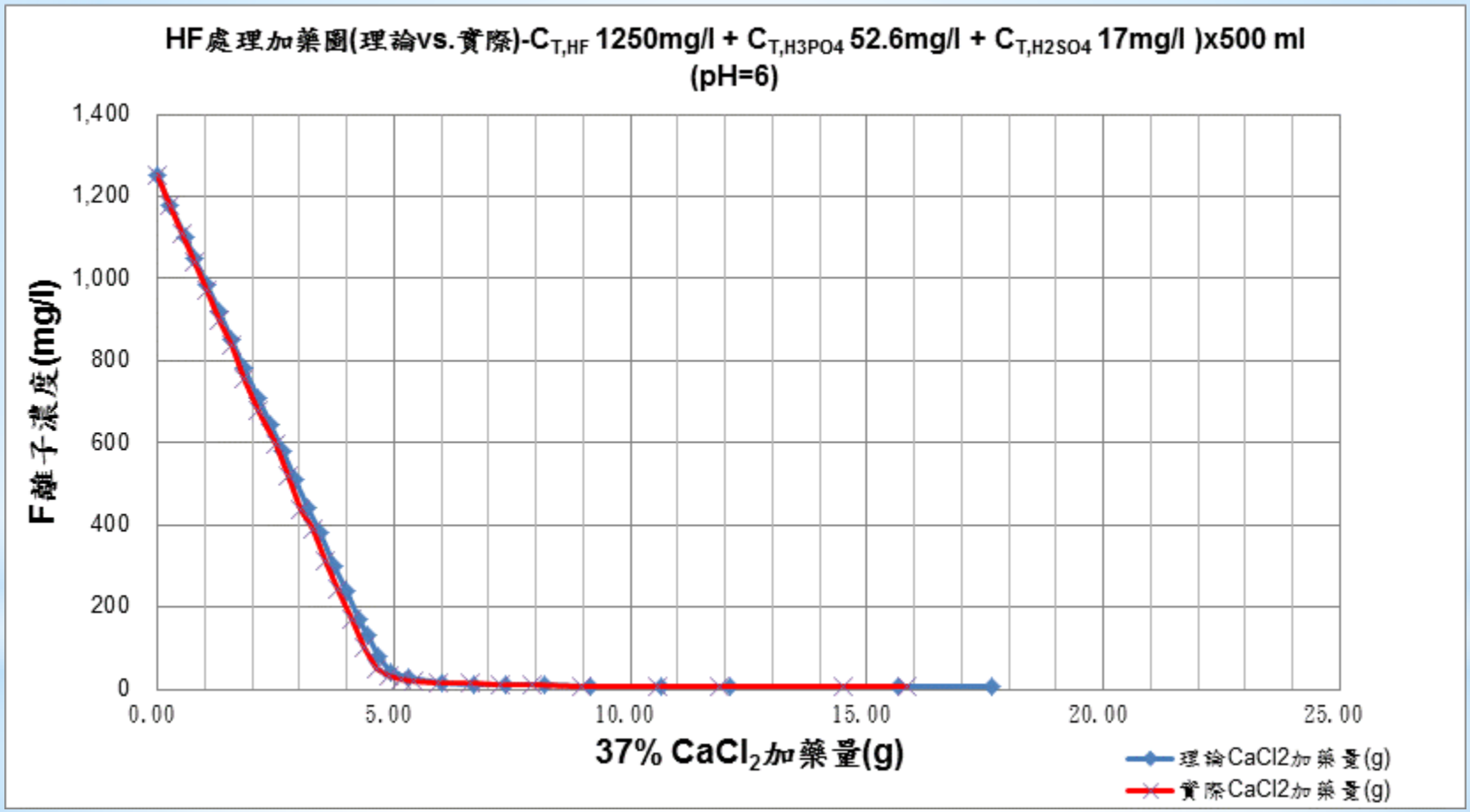
三. 加藥模式之實際驗證(3/6)

3. 以DI水配置($C_{T,HF}$:500mg/l + $C_{T,H3PO4}$:150mg/l) x 500ml+10g NaCl(提高水溶液導電度 > 3000μs/cm)，以定量吸管添加37% $CaCl_2$ 0.2 ml/次 ，藉以HACH F^- & pH計進行實驗量測 (keep pH=7)



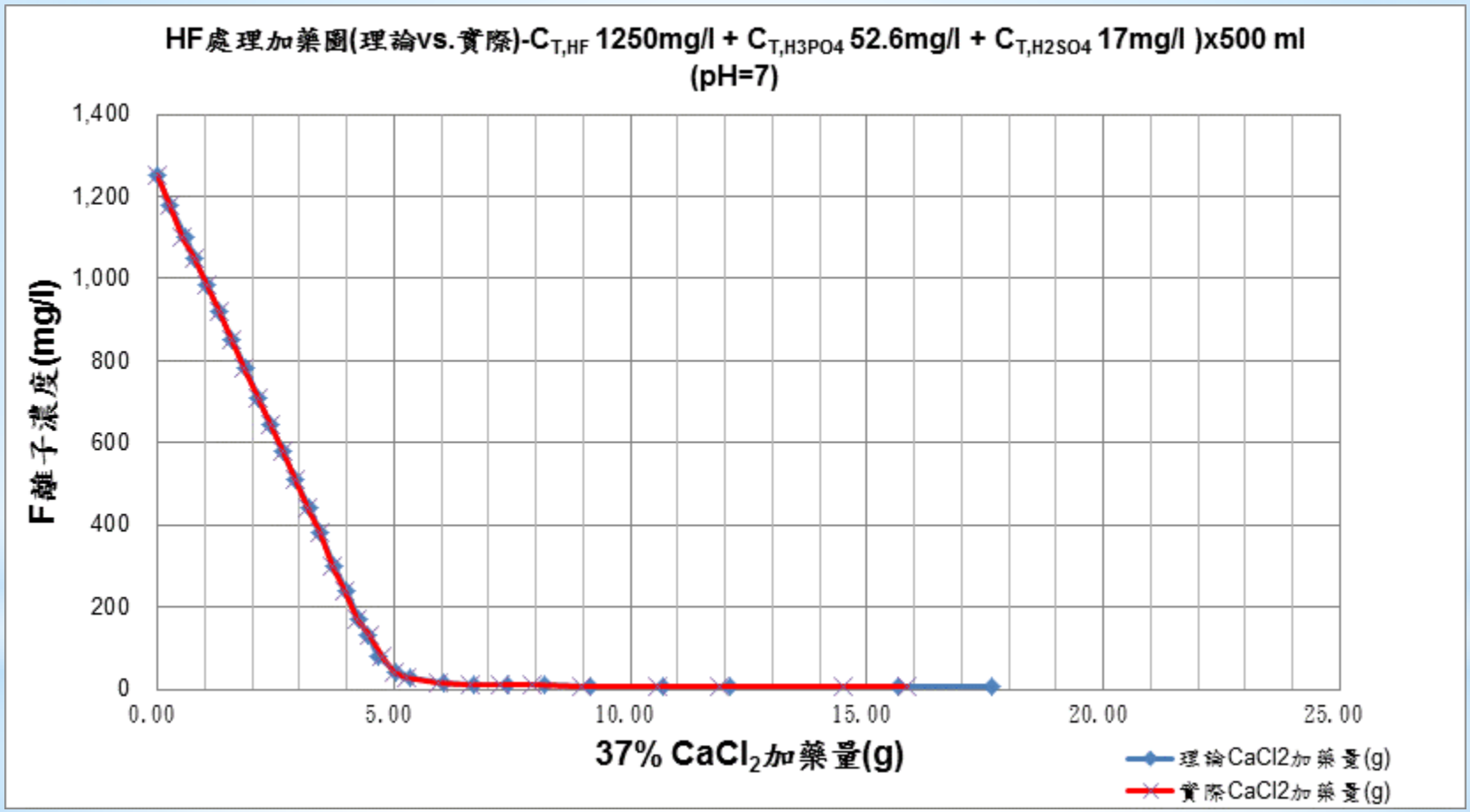
三. 加藥模式之實際驗證(4/6)

4. 取實際廢水 ($C_{T,HF}$:1250mg/l + $C_{T,H2SO4}$:17mg/l + $C_{T,H3PO4}$:52.6mg/l) x 500ml
   以定量吸管添加37% $CaCl_2$ 0.2 ml/次 ，藉以HACH F^- & pH計進行實驗量測 **(keep pH=6)**



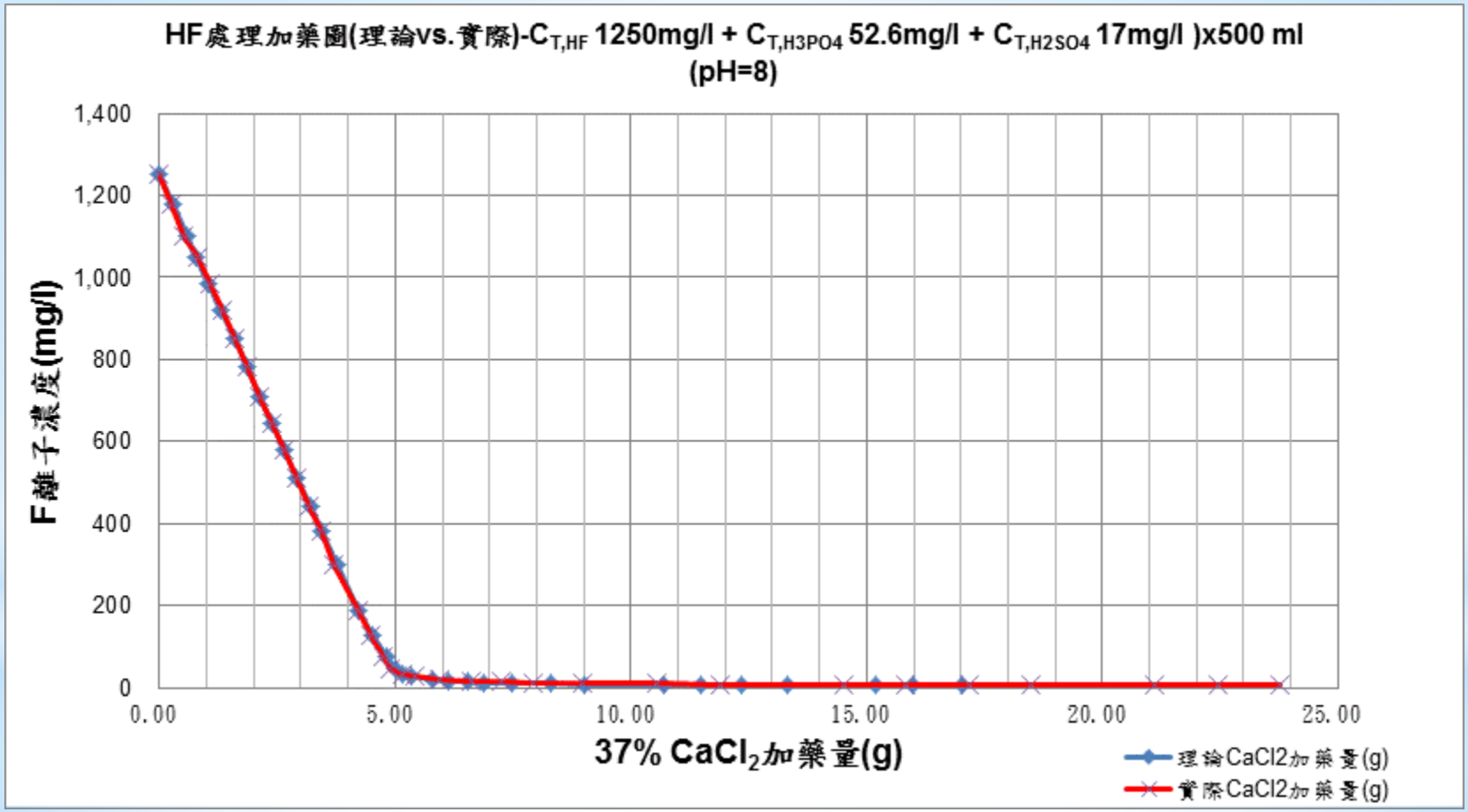
三. 加藥模式之實際驗證(5/6)

5. 取實際廢水 ($C_{T,HF}$:1250mg/l + $C_{T,H2SO4}$:17mg/l + $C_{T,H3PO4}$:52.6mg/l) x 500ml
   以定量吸管添加37% $CaCl_2$ 0.2 ml/次 ，藉以HACH F^- & pH計進行實驗量測 **(keep pH=7)**

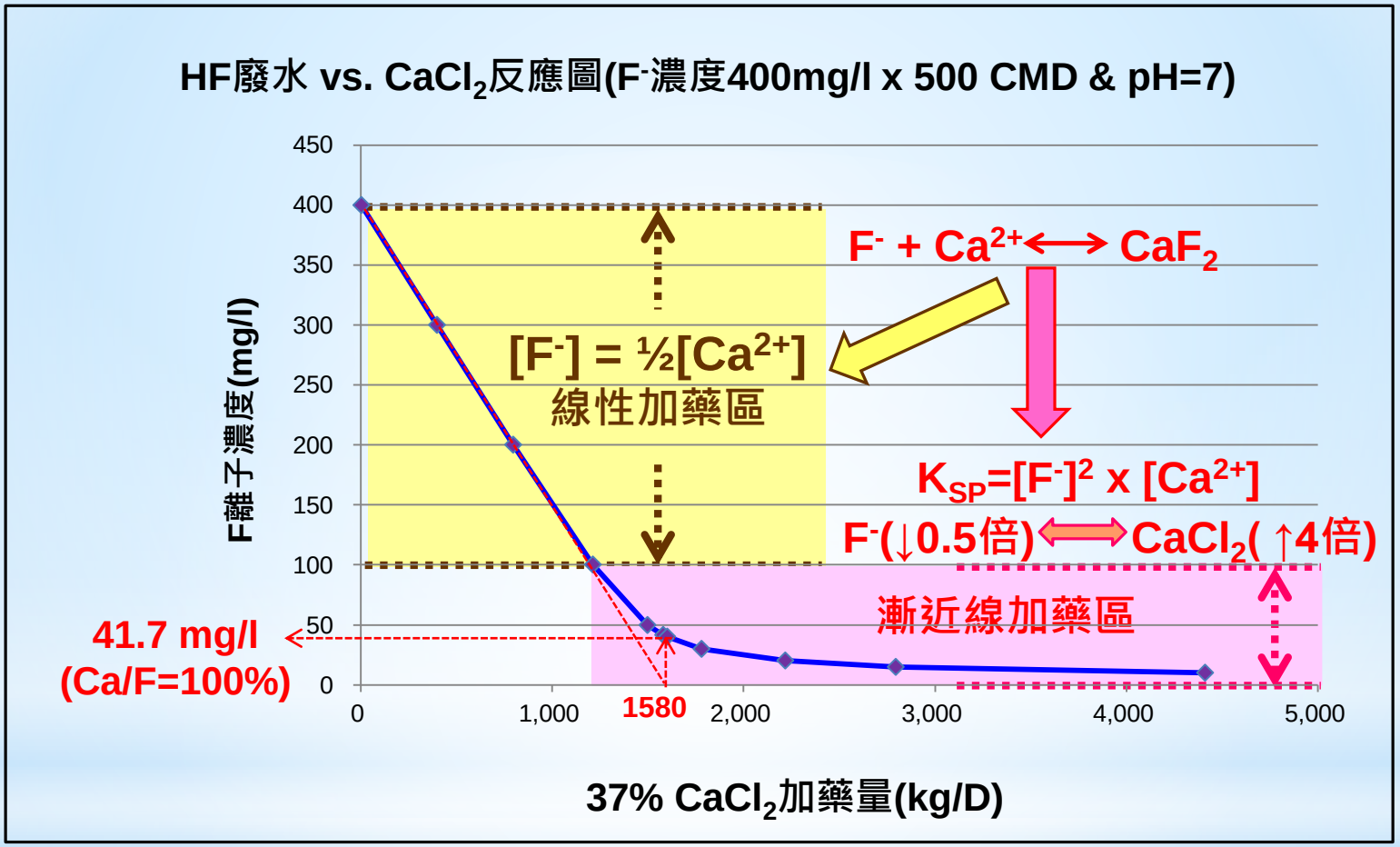


三. 加藥模式之實際驗證(6/6)

6. 取實際廢水 ($C_{T,HF}$:1250mg/l + $C_{T,H2SO4}$:17mg/l + $C_{T,H3PO4}$:52.6mg/l) x 500ml
   以定量吸管添加37% $CaCl_2$ 0.2 ml/次 ，藉以HACH F^- & pH計進行實驗量測 **(keep pH=8)**



四. 藥劑減量有效運用(1/7)



$$\text{Ca/F ratio(\%)} = \frac{\text{實際}CaCl_2\text{耗量}}{\text{F濃度當量換算之}CaCl_2\text{耗量}} \times 100\%$$

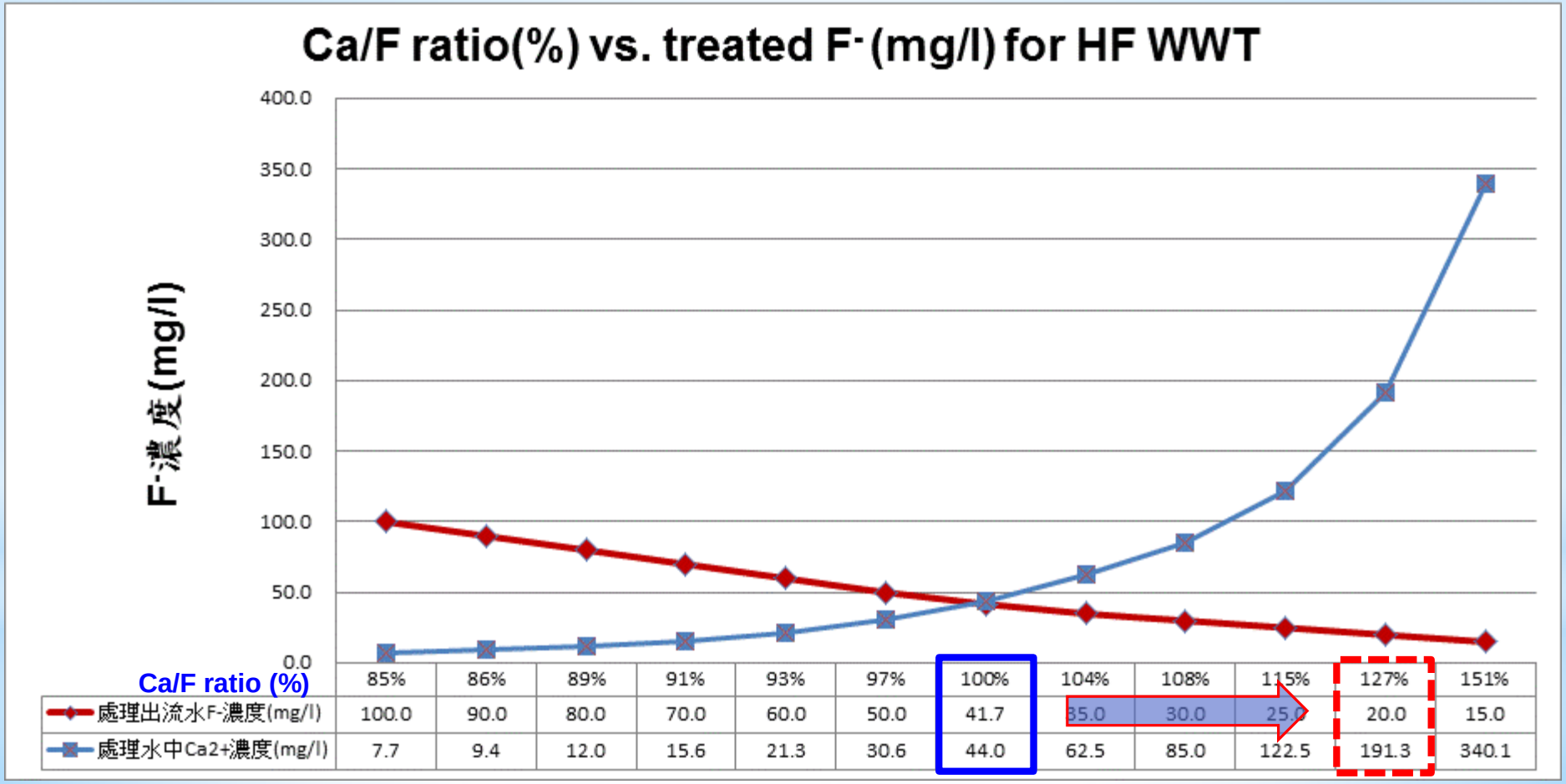
F濃度當量換算之$CaCl_2$耗量:

= 400(mg/l) x 500(CMD) / 19($M_{W,F-}$) x 1/2(mole比) x 111($M_{W,CaCl2}$) / 37(%w) / 1000(g/kg)= **1580(kg/D)**

四. 藥劑減量有效運用(2/7)

HF處理系統反應在PH=8.2下水溶液中F^- & Ca^{2+}離子之平衡濃度

CaF_2 $K_{SP}=5.31 \times 10^{-9}$ (LANGE'S HANDBOOK OF CHEMISTRY)



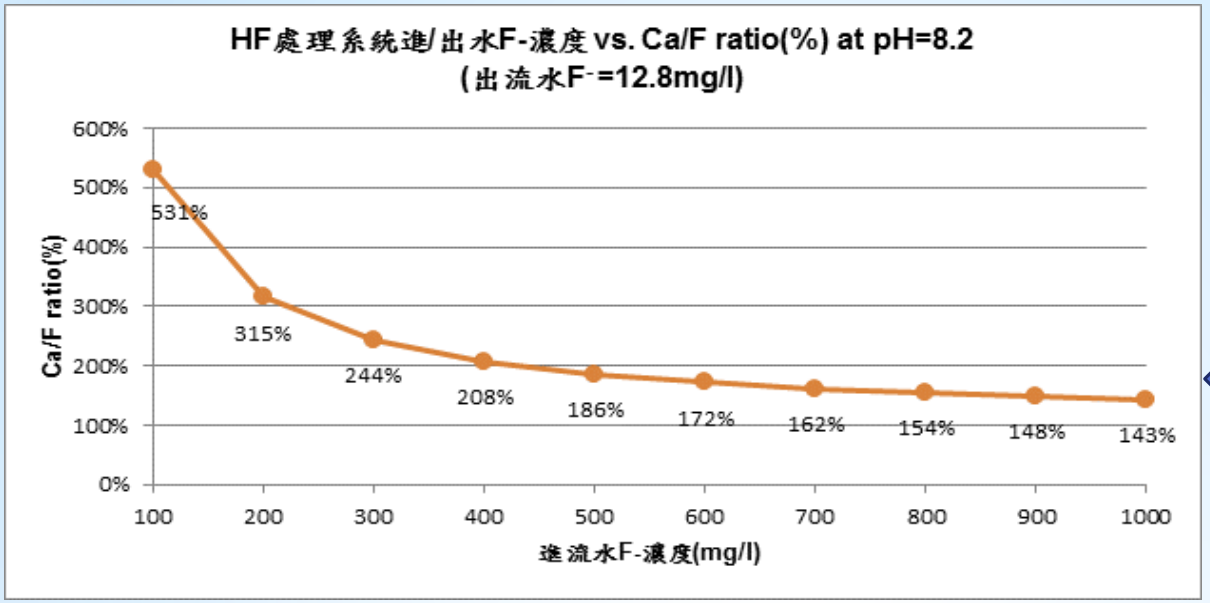
Ca/F ratio (%)	85%	86%	89%	91%	93%	97%	100%	104%	108%	115%	127%	151%
處理出流水F-濃度(mg/l)	100.0	90.0	80.0	70.0	60.0	50.0	41.7	35.0	30.0	25.0	20.0	15.0
處理水中Ca2+濃度(mg/l)	7.7	9.4	12.0	15.6	21.3	30.6	44.0	62.5	85.0	122.5	191.3	340.1

依據LANGE'S HANDBOOK OF CHEMISTRY提供之KSP則Ca/F ratio 100%(Ca/F=0.5莫耳比)狀況下，水中殘存之F^-濃度應在41.7mg/l; Ca^{2+}濃度應在44.0mg/l

四. 藥劑減量有效運用(3/7)

HF處理系統$C_{T,HF}$濃度& $F^-_{,final}$ vs. Ca/F ratio(與XX公司論文比較)

加藥模式估算



與XX公司論文提供之圖表比對趨勢類似(但高濃度F-其數值仍有差異)

所以本圖表之變動並非考慮反應時間之長短，而是因為進流水F-濃度愈高，無效加藥比例上相對愈低，所以$CaCl_2$ dosing ratio愈低

XX公司論文提供

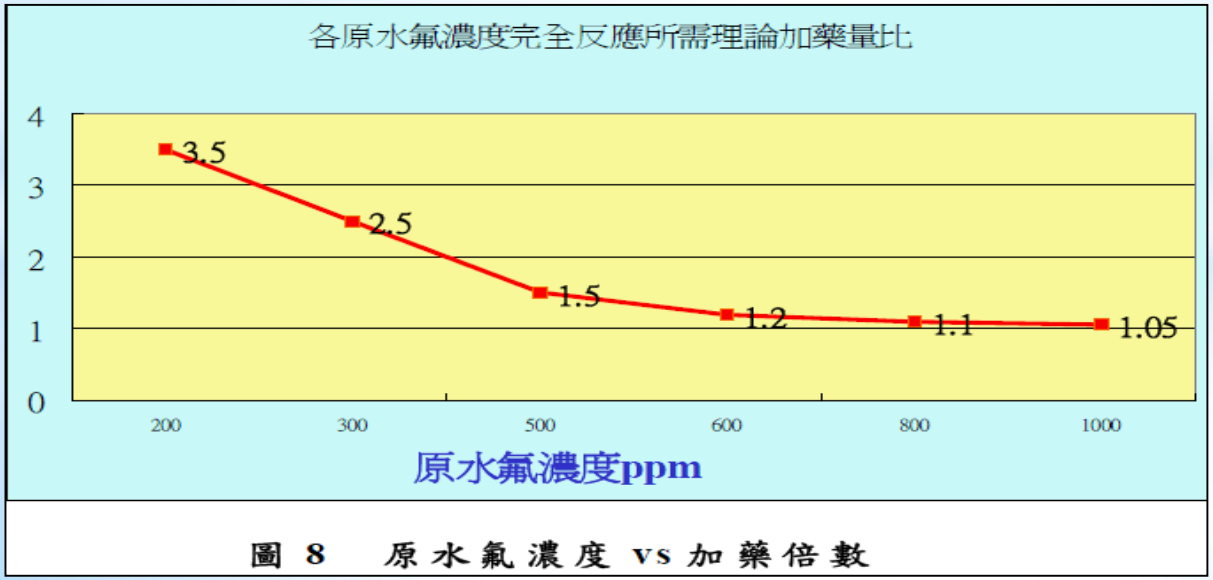


圖 8　原水氟濃度 vs 加藥倍數

四. 藥劑減量有效運用(4/7)

HF處理系統反應在PH=7下水溶液中HF濃度 vs. $CaCl_2$之加藥說明

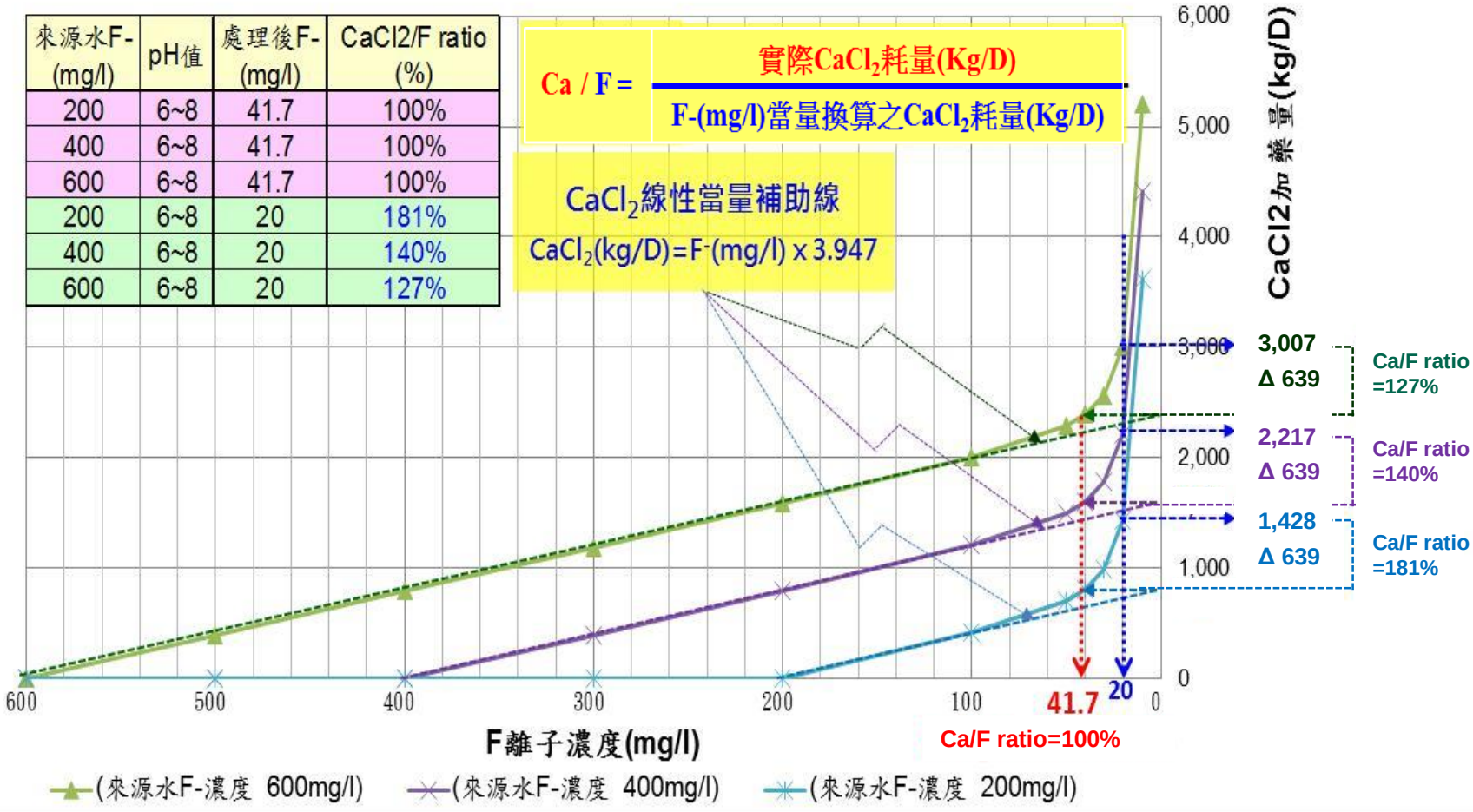
HF 處理系統$CaCl_2$加藥模擬與減量

來源水F-(mg/l)	pH值	處理後F-(mg/l)	CaCl2/F ratio (%)
200	6~8	41.7	100%
400	6~8	41.7	100%
600	6~8	41.7	100%
200	6~8	20	181%
400	6~8	20	140%
600	6~8	20	127%

$$Ca/F = \frac{\text{實際}CaCl_2\text{耗量(Kg/D)}}{\text{F-(mg/l)當量換算之}CaCl_2\text{耗量(Kg/D)}}$$

$CaCl_2$線性當量補助線

$CaCl_2(kg/D) = F^-(mg/l) \times 3.947$

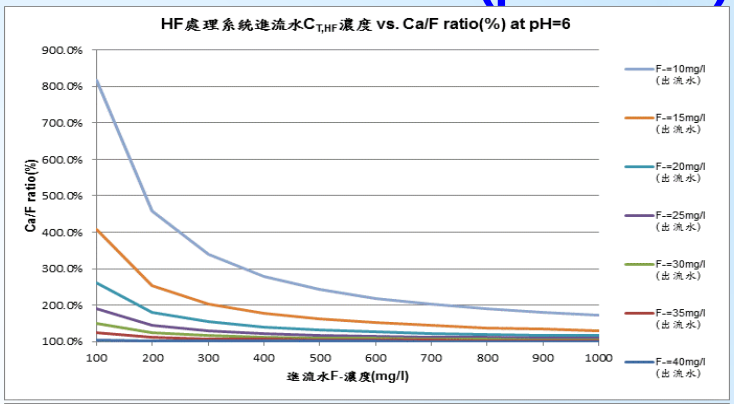


四. 藥劑減量有效運用(5/7)

HF處理系統$C_{T,HF}$來源濃度/$C_{F^-,final}$濃度vs. Ca/F ratio說明(pH=6/7/8)

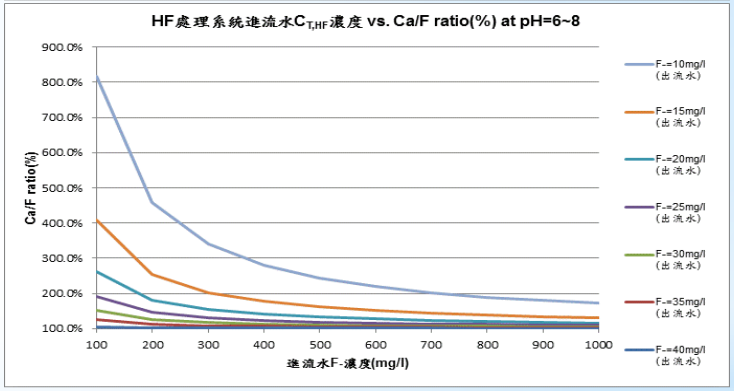
HF處理系統進/出水$C_{T,HF}$濃度 vs. Ca/F ratio(%) at pH=6

出流水 F-濃度(mg/l) / 進流水 $C_{T,HF}$濃度(mg/l)	F⁻=40mg/l (出流水)	F⁻=35mg/l (出流水)	F⁻=30mg/l (出流水)	F⁻=25mg/l (出流水)	F⁻=20mg/l (出流水)	F⁻=15mg/l (出流水)	F⁻=10mg/l (出流水)
100	105.3%	124.2%	150.6%	191.2%	261.6%	408.0%	816.9%
200	102.6%	112.0%	125.2%	145.5%	180.7%	253.9%	458.4%
300	101.7%	108.0%	116.8%	130.3%	153.8%	202.6%	338.9%
400	101.2%	105.9%	112.5%	122.7%	140.3%	176.9%	279.1%
500	100.9%	104.7%	110.0%	118.1%	132.2%	161.5%	243.3%
600	100.8%	103.9%	108.3%	115.1%	126.8%	151.2%	219.4%
700	100.6%	103.3%	107.1%	112.9%	123.0%	143.9%	202.3%
800	100.5%	102.9%	106.2%	111.3%	120.1%	138.4%	189.5%
900	100.4%	102.6%	105.5%	110.0%	117.8%	134.1%	179.5%
1000	100.4%	102.3%	104.9%	109.0%	116.0%	130.7%	171.6%



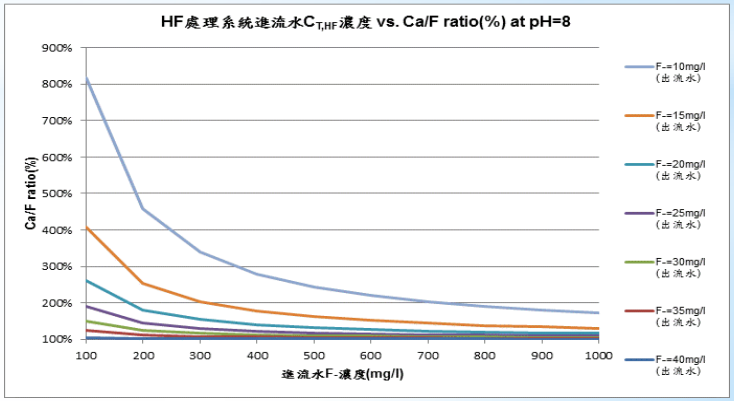
HF處理系統進/出水$C_{T,HF}$濃度 vs. Ca/F ratio(%) at pH=7

出流水 F-濃度(mg/l) / 進流水 $C_{T,HF}$濃度(mg/l)	F⁻=40mg/l (出流水)	F⁻=35mg/l (出流水)	F⁻=30mg/l (出流水)	F⁻=25mg/l (出流水)	F⁻=20mg/l (出流水)	F⁻=15mg/l (出流水)	F⁻=10mg/l (出流水)
100	105.4%	124.3%	150.8%	191.3%	261.7%	408.1%	817.0%
200	102.7%	112.2%	125.4%	145.6%	180.9%	254.1%	458.5%
300	101.8%	108.1%	116.9%	130.4%	153.9%	202.7%	339.0%
400	101.3%	106.1%	112.7%	122.8%	140.4%	177.0%	279.2%
500	101.1%	104.9%	110.1%	118.3%	132.3%	161.6%	243.4%
600	100.9%	104.0%	108.4%	115.2%	126.9%	151.3%	219.5%
700	100.8%	103.5%	107.2%	113.0%	123.1%	144.0%	202.4%
800	100.7%	103.0%	106.3%	111.4%	120.2%	138.5%	189.6%
900	100.6%	102.7%	105.6%	110.1%	118.0%	134.2%	179.7%
1000	100.5%	102.4%	105.1%	109.1%	116.2%	130.8%	171.7%



HF處理系統進/出水$C_{T,HF}$濃度 vs. Ca/F ratio(%) at pH=8

出流水 F-濃度(mg/l) / 進流水 $C_{T,HF}$濃度(mg/l)	F⁻=40mg/l (出流水)	F⁻=35mg/l (出流水)	F⁻=30mg/l (出流水)	F⁻=25mg/l (出流水)	F⁻=20mg/l (出流水)	F⁻=15mg/l (出流水)	F⁻=10mg/l (出流水)
100	105%	124%	151%	191%	262%	408%	817%
200	103%	112%	125%	146%	181%	254%	459%
300	102%	108%	117%	130%	154%	203%	339%
400	101%	106%	113%	123%	140%	177%	279%
500	101%	105%	110%	118%	132%	162%	243%
600	101%	104%	108%	115%	127%	151%	220%
700	101%	103%	107%	113%	123%	144%	202%
800	101%	103%	106%	111%	120%	139%	190%
900	101%	103%	106%	110%	118%	134%	180%
1000	101%	102%	105%	109%	116%	131%	172%



$C_{T,HF}$濃度愈高則Ca/F愈低

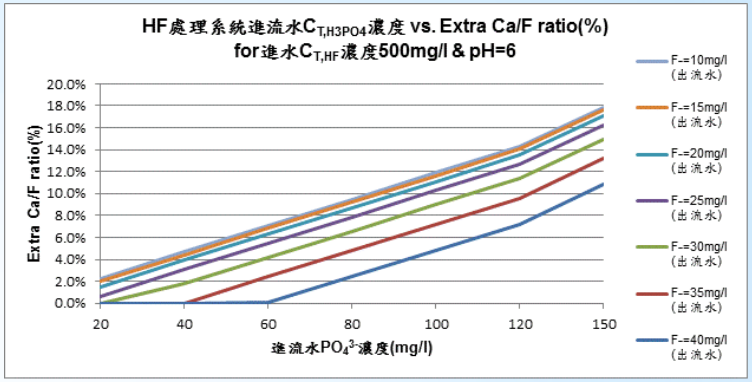
$C_{F^-,final}$濃度愈高則Ca/F愈低

四. 藥劑減量有效運用(6/7)

$C_{T,H3PO4}$干擾濃度/$C_{F-,final}$濃度vs. Extra Ca/F ratio說明(pH=6/7/8 ; $C_{T.HF}$=500mg/l)

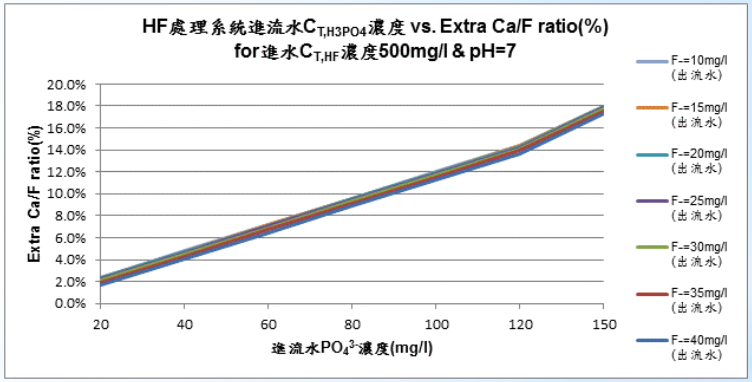
HF處理系統進流水$C_{T,H3PO4}$濃度(mg/l) vs. Extra Ca/F ratio(%) for進水$C_{T,HF}$濃度500mg/l & pH=6

出流水 F-濃度(mg/l) / 進流水 $C_{T,H3PO4}$濃度(mg/l)	F⁻=40mg/l (出流水)	F⁻=35mg/l (出流水)	F⁻=30mg/l (出流水)	F⁻=25mg/l (出流水)	F⁻=20mg/l (出流水)	F⁻=15mg/l (出流水)	F⁻=10mg/l (出流水)
20	0.0%	0.0%	0.0%	0.7%	1.5%	2.0%	2.3%
40	0.0%	0.0%	1.8%	3.1%	3.9%	4.4%	4.7%
60	0.0%	2.4%	4.2%	5.5%	6.3%	6.8%	7.1%
80	2.4%	4.8%	6.6%	7.9%	8.7%	9.2%	9.5%
100	4.8%	7.2%	9.0%	10.3%	11.1%	11.6%	11.9%
120	7.2%	9.6%	11.4%	12.7%	13.5%	14.0%	14.3%
150	10.8%	13.2%	15.0%	16.3%	17.1%	17.6%	17.9%



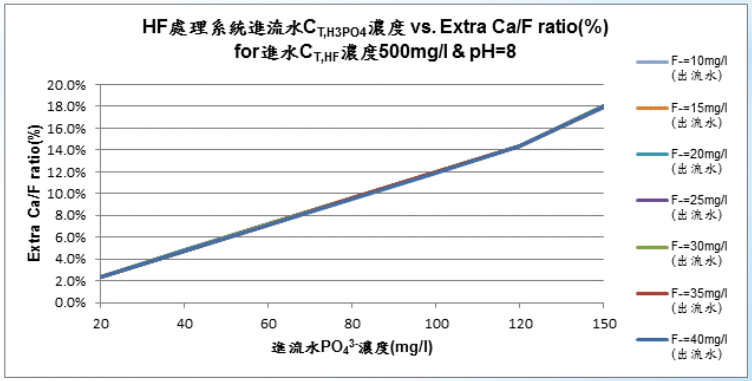
HF處理系統進流水$C_{T,H3PO4}$濃度(mg/l) vs. Extra Ca/F ratio(%) for進水$C_{T,HF}$濃度500mg/l & pH=7

出流水 F-濃度(mg/l) / 進流水 $C_{T,H3PO4}$濃度(mg/l)	F⁻=40mg/l (出流水)	F⁻=35mg/l (出流水)	F⁻=30mg/l (出流水)	F⁻=25mg/l (出流水)	F⁻=20mg/l (出流水)	F⁻=15mg/l (出流水)	F⁻=10mg/l (出流水)
20	1.7%	1.9%	2.1%	2.2%	2.3%	2.4%	2.4%
40	4.1%	4.3%	4.5%	4.6%	4.7%	4.8%	4.8%
60	6.5%	6.7%	6.9%	7.0%	7.1%	7.2%	7.2%
80	8.9%	9.1%	9.3%	9.4%	9.5%	9.6%	9.6%
100	11.3%	11.5%	11.7%	11.8%	11.9%	12.0%	12.0%
120	13.7%	13.9%	14.1%	14.2%	14.3%	14.4%	14.4%
150	17.3%	17.5%	17.7%	17.8%	17.9%	18.0%	18.0%



HF處理系統進流水$C_{T,H3PO4}$濃度(mg/l) vs. Extra Ca/F ratio(%) for進水$C_{T,HF}$濃度500mg/l & pH=8

出流水 F-濃度(mg/l) / 進流水 $C_{T,H3PO4}$濃度(mg/l)	F⁻=40mg/l (出流水)	F⁻=35mg/l (出流水)	F⁻=30mg/l (出流水)	F⁻=25mg/l (出流水)	F⁻=20mg/l (出流水)	F⁻=15mg/l (出流水)	F⁻=10mg/l (出流水)
20	2.3%	2.4%	2.4%	2.4%	2.4%	2.4%	2.4%
40	4.7%	4.8%	4.8%	4.8%	4.8%	4.8%	4.8%
60	7.1%	7.2%	7.2%	7.2%	7.2%	7.2%	7.2%
80	9.5%	9.6%	9.6%	9.6%	9.6%	9.6%	9.6%
100	11.9%	12.0%	12.0%	12.0%	12.0%	12.0%	12.0%
120	14.3%	14.4%	14.4%	14.4%	14.4%	14.4%	14.4%
150	17.9%	18.0%	18.0%	18.0%	18.0%	18.0%	18.0%



$C_{T,H3PO4}$干擾濃度愈高則Extra Ca/F愈高

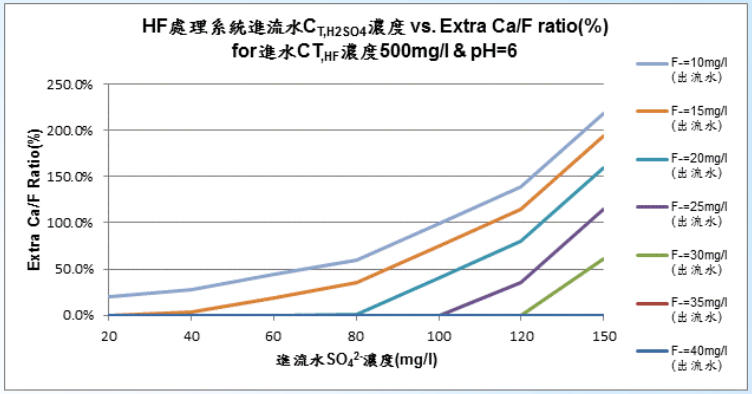
pH值愈低則Extra Ca/F影響較低

四. 藥劑減量有效運用(7/7)

$C_{T,H2SO4}$干擾濃度/$C_{F-,final}$濃度vs. Extra Ca/F ratio說明(pH=6/7/8 ; $C_{T.HF}$=500mg/l)

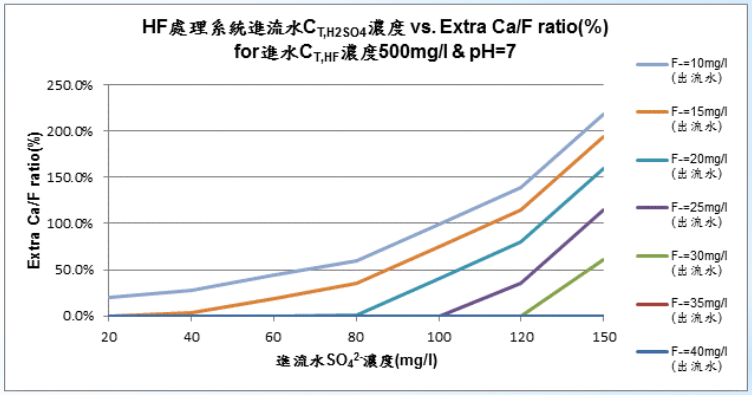
HF處理系統進流水$C_{T,H2SO4}$濃度 vs. Extra Ca/F ratio(%) for進水$C_{T,HF}$濃度500mg/l & pH=6

出流水 F-濃度(mg/l) / 進流水 $C_{T,H2SO4}$濃度(mg/l)	F⁻=40mg/l (出流水)	F⁻=35mg/l (出流水)	F⁻=30mg/l (出流水)	F⁻=25mg/l (出流水)	F⁻=20mg/l (出流水)	F⁻=15mg/l (出流水)	F⁻=10mg/l (出流水)
500	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	20.0%
600	0.0%	0.0%	0.0%	0.0%	0.0%	3.4%	27.9%
800	0.0%	0.0%	0.0%	0.0%	0.0%	19.3%	43.7%
1000	0.0%	0.0%	0.0%	0.0%	0.8%	35.1%	59.6%
1500	0.0%	0.0%	0.0%	0.0%	40.4%	74.7%	99.2%
2000	0.0%	0.0%	0.0%	35.9%	80.0%	114.3%	138.7%
3000	0.0%	0.0%	61.2%	115.1%	159.1%	193.4%	217.9%



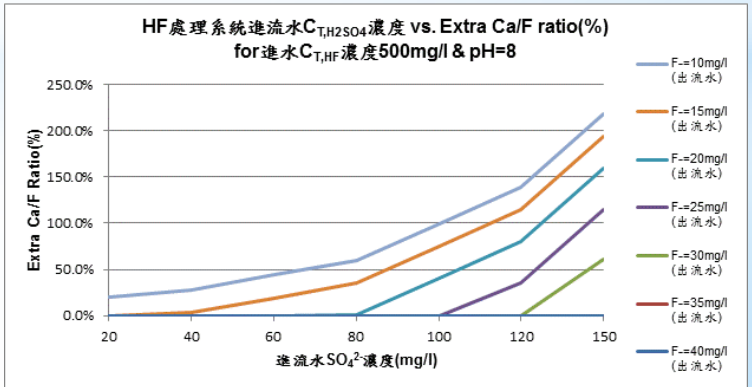
HF處理系統進流水$C_{T,H2SO4}$濃度 vs. Extra Ca/F ratio(%) for進水$C_{T,HF}$濃度500mg/l & pH=7

出流水 F-濃度(mg/l) / 進流水 $C_{T,H2SO4}$濃度(mg/l)	F⁻=40mg/l (出流水)	F⁻=35mg/l (出流水)	F⁻=30mg/l (出流水)	F⁻=25mg/l (出流水)	F⁻=20mg/l (出流水)	F⁻=15mg/l (出流水)	F⁻=10mg/l (出流水)
500	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	20.0%
600	0.0%	0.0%	0.0%	0.0%	0.0%	3.4%	27.9%
800	0.0%	0.0%	0.0%	0.0%	0.0%	19.3%	43.7%
1000	0.0%	0.0%	0.0%	0.0%	0.8%	35.1%	59.6%
1500	0.0%	0.0%	0.0%	0.0%	40.4%	74.7%	99.2%
2000	0.0%	0.0%	0.0%	35.9%	80.0%	114.3%	138.7%
3000	0.0%	0.0%	61.3%	115.1%	159.2%	193.4%	217.9%



HF處理系統進流水$C_{T,H2SO4}$濃度 vs. Extra Ca/F ratio(%) for進水$C_{T,HF}$濃度500mg/l & pH=8

出流水 F-濃度(mg/l) / 進流水 $C_{T,H2SO4}$濃度(mg/l)	F⁻=40mg/l (出流水)	F⁻=35mg/l (出流水)	F⁻=30mg/l (出流水)	F⁻=25mg/l (出流水)	F⁻=20mg/l (出流水)	F⁻=15mg/l (出流水)	F⁻=10mg/l (出流水)
500	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	20.0%
600	0.0%	0.0%	0.0%	0.0%	0.0%	3.4%	27.9%
800	0.0%	0.0%	0.0%	0.0%	0.0%	19.3%	43.8%
1000	0.0%	0.0%	0.0%	0.0%	0.8%	35.1%	59.6%
1500	0.0%	0.0%	0.0%	0.0%	40.4%	74.7%	99.2%
2000	0.0%	0.0%	0.0%	35.9%	80.0%	114.3%	138.8%
3000	0.0%	0.0%	61.3%	115.1%	159.2%	193.4%	217.9%



$C_{T,H2SO4}$干擾濃度愈高則Extra Ca/F愈高

pH值6~8則Extra Ca/F變化不大

五. 效益成果分享(1/3)

HF處理系統進/出水$C_{T,HF}$濃度 vs. Ca/F ratio(%) at pH=7

(i)

出流水 F-濃度(mg/l) / 進流水 $C_{T,HF}$濃度(mg/l)	F⁻=40mg/l (出流水)	F⁻=35mg/l (出流水)	F⁻=30mg/l (出流水)	F⁻=25mg/l (出流水)	F⁻=20mg/l (出流水)	F⁻=15mg/l (出流水)	F⁻=10mg/l (出流水)
100	105.4%	124.3%	150.8%	191.3%	261.7%	408.1%	817.0%
200	102.7%	112.2%	125.4%	145.6%	180.9%	254.1%	458.5%
300	101.8%	108.1%	116.9%	130.4%	153.9%	202.7%	339.0%
400	101.3%	106.1%	112.7%	122.8%	140.4%	177.0%	279.2%
(Ci) 500	101.1%	104.9%	110.1%	118.3%	132.3%	161.6%	243.4%
600	100.9%	104.0%	108.4%	115.2%	126.9%	151.3%	219.5%
700	100.8%	103.5%	107.2%	113.0%	123.1%	144.0%	202.4%
800	100.7%	103.0%	106.3%	111.4%	120.2%	138.5%	189.6%
900	100.6%	102.7%	105.6%	110.1%	118.0%	134.2%	179.7%
1000	100.5%	102.4%	105.1%	109.1%	116.2%	130.8%	171.7%

(Ai)

HF處理系統進流水$C_{T,H3PO4}$濃度(mg/l) vs. Extra Ca/F ratio(%) for進水$C_{T,HF}$濃度500mg/l & pH=7

出流水 F-濃度(mg/l) / 進流水 $C_{T,H3PO4}$濃度(mg/l)	F⁻=40mg/l (出流水)	F⁻=35mg/l (出流水)	F⁻=30mg/l (出流水)	F⁻=25mg/l (出流水)	F⁻=20mg/l (出流水)	F⁻=15mg/l (出流水)	F⁻=10mg/l (出流水)
20	1.7%	1.9%	2.1%	2.2%	2.3%	2.4%	2.4%
40	4.1%	4.3%	4.5%	4.6%	4.7%	4.8%	4.8%
60	6.5%	6.7%	6.9%	7.0%	7.1%	7.2%	7.2%
(j) 80	8.9%	9.1%	9.3%	9.4%	9.5%	9.6%	9.6%
100	11.3%	11.5%	11.7%	11.8%	11.9%	12.0%	12.0%
120	13.7%	13.9%	14.1%	14.2%	14.3%	14.4%	14.4%
150	17.3%	17.5%	17.7%	17.8%	17.9%	18.0%	18.0%

(Bj)

HF處理系統進流水$C_{T,H2SO4}$濃度 vs. Extra Ca/F ratio(%) for進水$C_{T,HF}$濃度500mg/l & pH=7

出流水 F-濃度(mg/l) / 進流水 $C_{T,H2SO4}$濃度(mg/l)	F⁻=40mg/l (出流水)	F⁻=35mg/l (出流水)	F⁻=30mg/l (出流水)	F⁻=25mg/l (出流水)	F⁻=20mg/l (出流水)	F⁻=15mg/l (出流水)	F⁻=10mg/l (出流水)
500	0.0%	0.0%	0.0%	0.0%	0.0%	0.0%	20.0%
600	0.0%	0.0%	0.0%	0.0%	0.0%	3.4%	27.9%
800	0.0%	0.0%	0.0%	0.0%	0.0%	19.3%	43.7%
(k) 1000	0.0%	0.0%	0.0%	0.0%	0.8%	35.1%	59.6%
1500	0.0%	0.0%	0.0%	0.0%	40.4%	74.7%	99.2%
2000	0.0%	0.0%	0.0%	35.9%	80.0%	114.3%	138.7%
3000	0.0%	0.0%	61.3%	115.1%	159.2%	193.4%	217.9%

(Dk)

估算HF處理系統所需 Ca /F ratio

假設HF處理系統操作條件如下:

1. 進流HF廢水$C_{T,HF}$濃度=700mg/l
2. 進流HF廢水$C_{T,H3PO4}$濃度=60mg/l
3. 進流HF廢水$C_{T,H2SO4}$濃度=600mg/l
4. HF處理系統反應pH=7
5. HF處理後F^-控制濃度=20mg/l

Ca/F ratio估算公式:

=(Ai) + (Bj)x500/(Ci) + (Dk)x500/(Ci)

Ex. $CaCl_2$ dosing ratio估算說明如下:

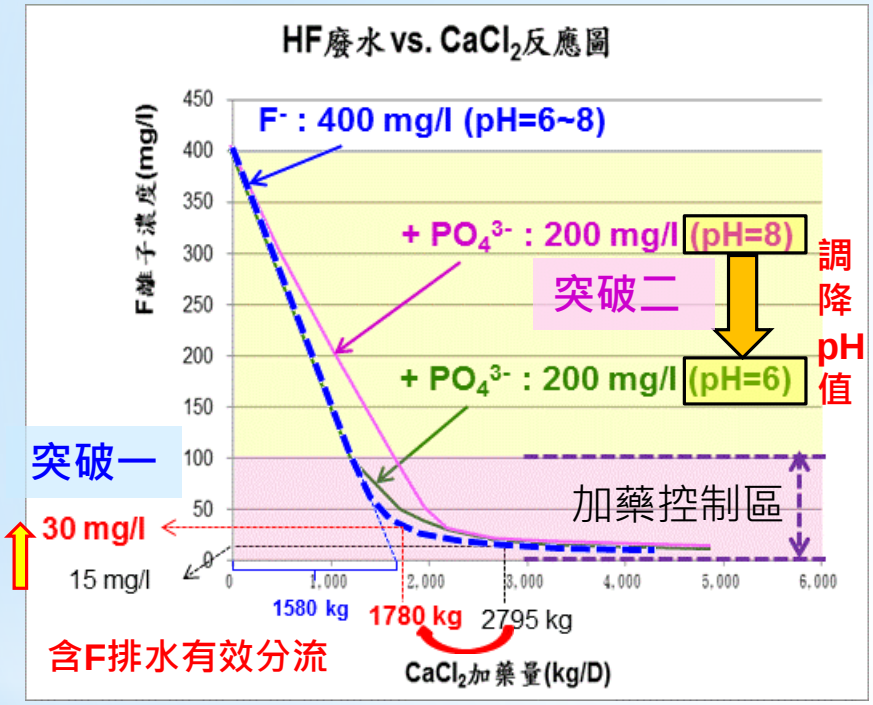
- $C_{T,HF}$(700mg/l)所需Ca/F ratio=123.1%
- $C_{T,H3PO4}$(60mg/l)所需Ca/F ratio:
  7.1% x 500mg/l / 700mg/l = 5.1%
- $C_{T,H2SO4}$(600mg/l)所需Ca/F ratio:
  0% x 500mg/l / 700mg/l = 0%

Total Ca/F Ratio:
=123.1%+5.1%+0%= 128.2%

五. 效益成果分享(2/3)

減量12%

- Methodology ---廢水-$CaCl_2$ 減量- HF廢水處理最佳化



天缺一： 過量加 $CaCl_2$ (F^-處理至低濃度區)

HF廢水 + $CaCl_2$藥劑 (KSP-1)

$$2F^- + Ca^{2+} \leftrightarrow CaF_2\downarrow$$

$[Ca^{2+}] \times [F^-]^2 = KSP\text{-}1$(溶解度積常數) ➔F降1/2; Ca增4倍

突破一：有效調高處理後F^-濃度降低$CaCl_2$用量

天缺二：過量加 $CaCl_2$ (PO_4^{3-} …干擾離子搶奪)

Ka (酸解離常數)

$$H_3PO_4 \Leftrightarrow 3H^+ + PO_4^{3-}$$

突破二：調降pH值干擾物不易形成離子搶奪$CaCl_2$

文獻化性資料

KPI	進流水F^-濃度(mg/l)	進流水PO_4^{3-}濃度(mg/l)	進流水SO_4^{2-}濃度(mg/l)	HF反應pH值	出流水F^-濃度(mg/l)	$CaCl_2$ / F dosing Ratio
Y2015	500~250	≤100	≤2000	5~8	≥30	≤120%

國內首創控制系統

KSP (溶解度積常數)

Ka (酸解離常數)

HF加藥Model

輸入水質條件

自動產出

精確$CaCl_2$耗量 (最佳化用藥)

五. 效益成果分享(3/3)

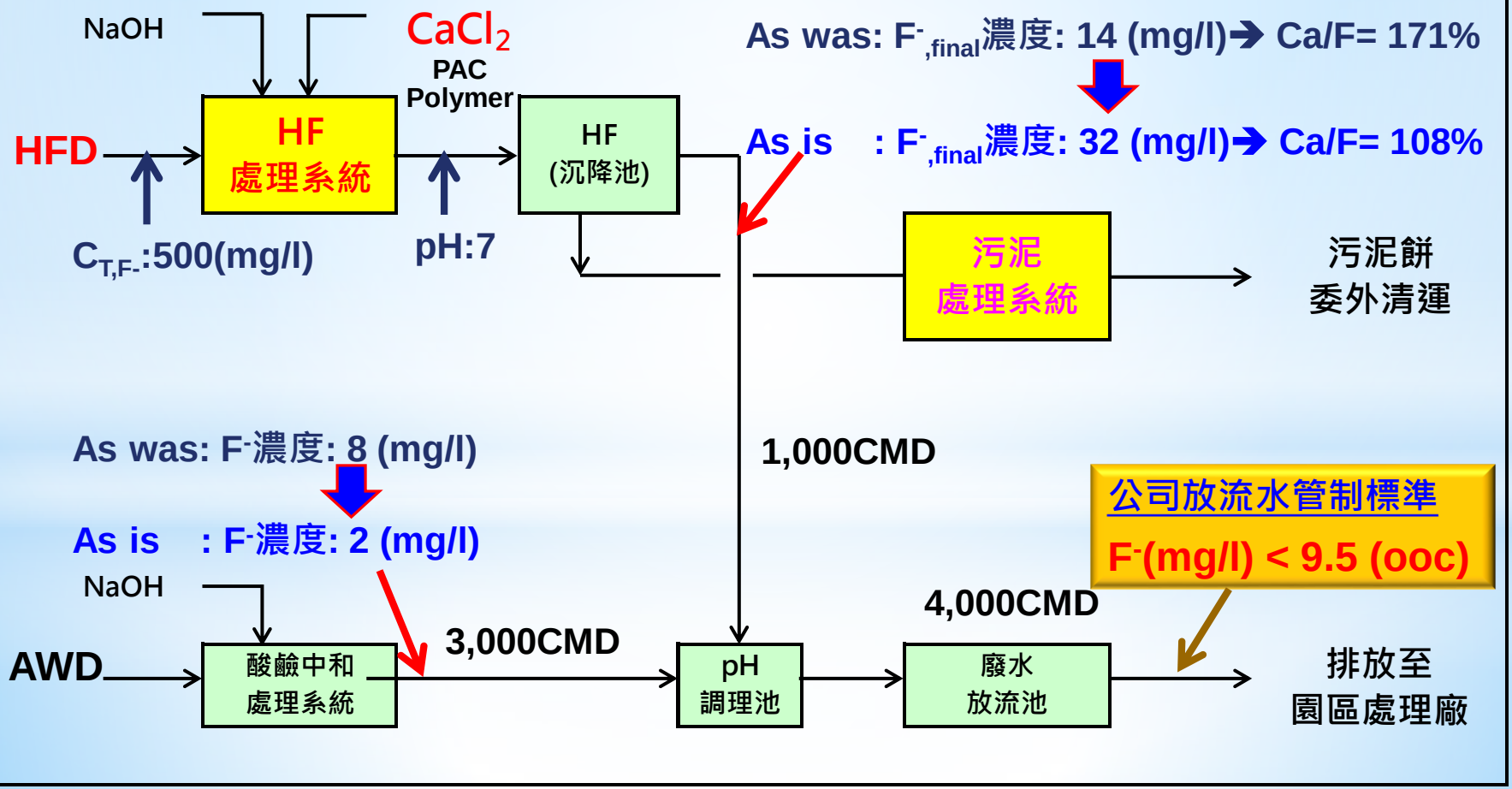
有效降低AWD廢水中F^-濃度
可降低約37.1%$CaCl_2$使用量

As was
6,765kg/D
(37%$CaCl_2$)

-37.1%

As is
4,255kg/D
(37%$CaCl_2$)

HFD & AWD 廢水處理系統流程圖



感謝各位先進的

聆聽與指教