台電 BWRs/PWRs 水化學控制最適化進展

台電核發處 核能化學組
朱方

中華民國98年12月16日

大綱 I

- BWR/PWR 水化學控制為什麼需要最適化(Optimization)？
- BWR/PWR 水化學控制最適化(OWC)關鍵參數
- 從ECP及pH酸鹼值控制看臺電 BWR/PWR水化學最適化控制策略的形成與進展
- *OWC in Taipower BWRs*

核一、二廠目前IGSCC Mitigation Program

- HWC-L：0.5 ppm (2006第四季) → HWC-M：1.2/1.1/1.0 ppm (2009下半年)
- IGSCC mitigation effectiveness evaluation
- After HWC ：
  - 乾井管路Dose Rate變化 → Shutdown dose rate mitigation strategies after HWC-M.
  - FW Fe變化, RW Cu變化
  - Application of BWRVIP-75-A for inspection relief of external piping (ECP < -230mV, HWC availability > 80%) F.O.I=1/6 (when ECP=- 300 mV,HWC avail.=100%)
  - Possible hydrogen demand change after power uprate(1.7% MU → 3% S)

國際接軌, 46 members BWR chemistry monitoring and assessment program

- 美國核能界促進方案(Initiatives)下，35部US BWRs至今 HWC/NMCA/OLNC + DZO 無悔策略 (2008 德國柏林國際核電廠水化學會議)

核一、二廠未來 Possible IGSCC mitigation improvements

- HWC availability increasing (target 95%)
- Hydrogen injection during plant start-up
- NMCA/OLNC

大綱 II

- OWC in Taipower PWRs

Primary side

- Improved Maanshan's RCS Li-B control program
- Zinc addition project at Maanshan has been suspended based on the calculation by WH VIPER/BOA code
- A campaign of shutdown chemistry control optimization since MS-2 EOC-16

Secondary side

- Maanshan's steam generator sludge pile management program

SG sludge source term reduction method

FW Fe control (Hydrazine , ETA Addition)

Consideration on adding Dispersant during SG wet layup in RFO

SG sludge removal method

Modified ASCA

國際接軌, 129 members PWR chemistry monitoring and assessment program??

大綱 III

- Other Interesting Topics on EAC mitigation from Water Chemistry Perspective
  - Corrosion Fatigue of Stainless Steel in Low ECP BWR/PWR Environment

    1998 Estimation of Fatigue Strain Life Curves for Austenitic SS in LWR Environments by ANL O. Chopra
    1999 Robin Jones EPRI , cumulative fatigue usage factor(CUFs) may >1 in 60 Years
    2001/2002 Fatigue Crack Initiation in Austenitic SS in LWR Coolant-A Review by ANL O. Chopra , Bill Shack

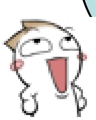
    2002 /2004 /2006 Corrosion fatigue crack growth of 304 SS by SERCO UK David Tice
    2007/2008/ 2009 Corrosion fatigue behavior (Initiation & Propogation) of Austenitic SS in LWR Environments by Switzerland PSI H.P. Seifert , S. Ritter

    Water Chemistry Parameters (NWC vs. HWC) only have a little effect

  - IASCC mitigated by HWC

  - PWR PWSCC Chemical Mitigation

    Elevated DH_2 benefit on PWSCC growth rate
    However , (Molander of Studsvik , Macdonald of Penn. State Univ., Japan) all indicate elevated DH_2 accelerates initiation of PWSCC
    Decreased DH_2 Japan , JAPC
    Zn Addition
    Li concentration (The effect of Li concentration on PWSCC growth rate show no or little influence. But,higher Li on initiation of PWSCC has not been investigated)

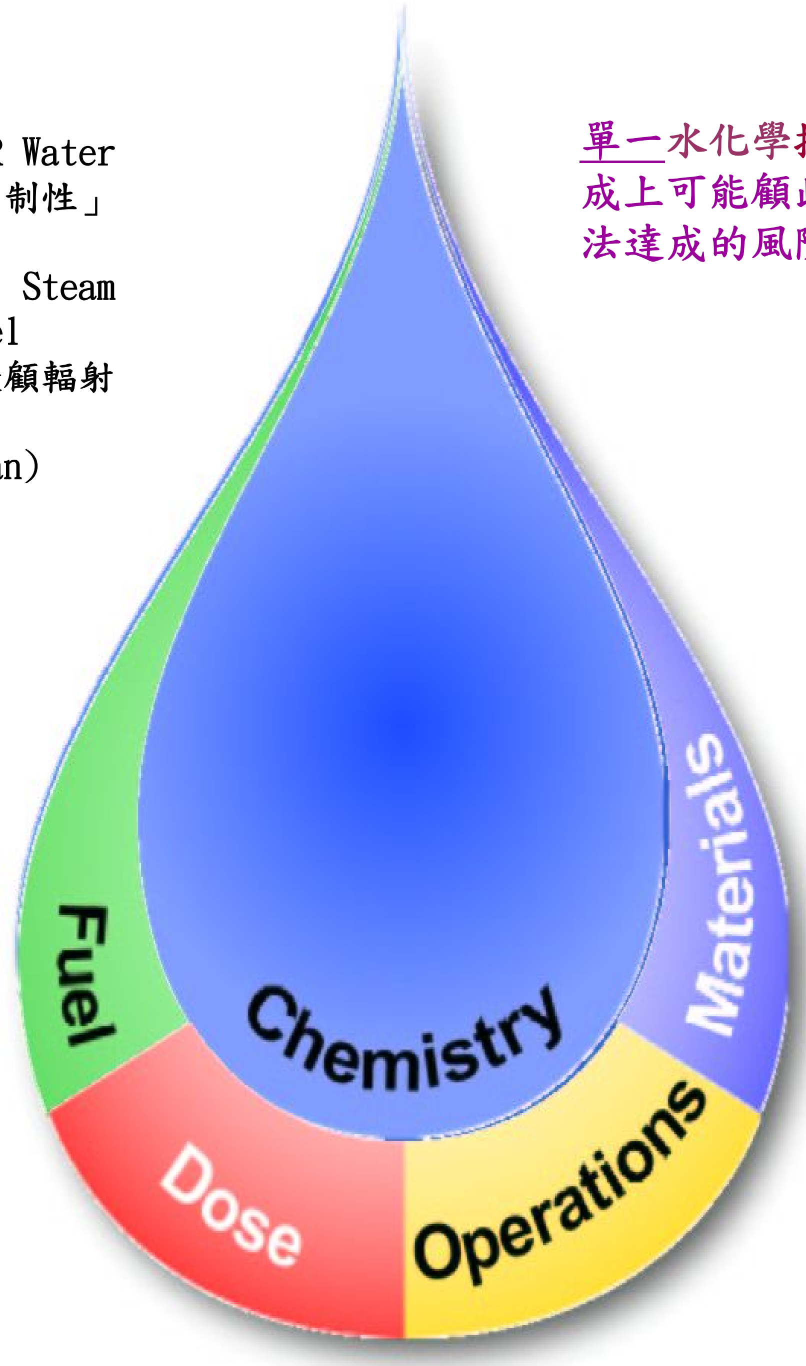


Some times the effects of these environmental parameters on PWSCC initiation and growth are different
------ by Molander of Studsvik NPC'08 Berlin

  - SCC of stainless steel in stagnant lines attached to PWR RCS piping and components

    Oxygen entrapped inside , high oxidizing environment

臺電核一二三廠依據EPRI BWR/PWR Water Chemistry Guidelines內唯一「強制性」要求,已建立以保護電廠資產(例如 Structure Material Integrity , Steam Generator Tube Integrity , Fuel Failure Free 等)為首要目標且兼顧輻射場劑量抑低之策略性水化學計畫 (Strategic Water Chemistry Plan)



單一水化學控制方式在各別目標達成上可能顧此失彼,增加各別目標無法達成的風險

美國的笨蛋(STUPID)詼諧文化

- 笨蛋 ，問題在經濟　　　199?　　美國柯林頓競選總統

  笨蛋 ，問題在經濟　　　2007　　台灣馬英九競選總統

  笨蛋應非罵人之髒話

  而是振聾發聵、醍醐灌頂、點醒眾生之意

- 笨蛋 ，電廠水化學最適化控制關鍵是ECP & pH

  日本JAPC前執行副總(顧問)Dr.Meguro解釋BWR/PWR機組如何分別以ECP(Electrochemical Corrosion Potential，電化學腐蝕電位)及pH 酸鹼值之水化學方式來控制最影響 Structure Integrity與 Capacity Factor的材料劣化問題: IGSCC(應力腐蝕龜裂)+FAC (流体加速腐蝕/薄化)

  ---2007 亞洲核電廠水化學與腐蝕研討會

  --- 2008 德國柏林國際核電廠水化學會議

從ECP及pH酸鹼值控制看臺電 BWR / PWR 水化學最適化控制策略的形成與進展

核一，二廠 (BWR)

ALARA (Purer Better) Chemistry (NWC)

水質控制 紀元

不鏽鋼/鎳基合金 IGSCC

Additive Chemistry (HWC/NMCA/OLNC)

(水質 + **ECP** ↓)控制 紀元

碳鋼管路 *FAC* **concern**

FW 注氧(ECP↑) / 管路薄化監測計畫

Impact on 乾井 Radiation Source Term

Co-60 Deposit

DZO 加鋅水化學

Fuel Crud/Corrosion concern

Under *Limits* of 2008 年EPRI BWR Water Chemistry 指引

Impact on MSLR

HP Skyshine Management Program

核三廠 (PWR)

一次側**Additive Chemistry (加氫，氫氧化鋰，硼酸)**

鎳基合金 PWSCC / Primary Coolant Activity / AOA

(水質 + ECP↓+ pH_T 微鹼) 控制最適化

+ DZA 加鋅水化學

二次側**Additive Chemistry (全揮發性處理，加聯胺) 加乙醇胺ETA)**

鎳基合金 IGA/ODSCC, 碳鋼 FAC → Fouling of S/G

(水質+ ECP↓↑+ Bulk pH 鹼性控制最適化 Crevice pH 趨中性)

ECP(Electrochemical Corrosion Potential，電化學腐蝕電位）↓ 愈低愈好 ???

ECP of 不鏽鋼/鎳基合金 ↓ IGSCC ↓ Co-60 Deposit ↑（except 加鋅）

ECP of 碳鋼 ↓ FAC ↑

BWR Bulk Water pH 酸鹼值↑↓，Crevice pH 酸鹼值↑↓

PWR Bulk Water pH 酸鹼值 ↑，Crevice pH 酸鹼值↑↓

HWC Effectiveness for IGSCC Mitigation

- **成效評估 (HWC決策前)**

依據實驗室或In-Plant Bypass Loop Autoclave或In-reactor IGSCC initiation/growth
304 SS specimen 數據 (CERT / Fracture Mechanics CT / LPRM DCB)
Crack Growth Rate Reduction F.O.I (HWC crack growth rate÷NWC crack growth rate= 1/xx)

Toshiba 依據庫藏ECP vs. 304 S.S. crack growth rate 關係圖評估Chinshan and Kuosheng FW H2 0.5 ppm 時

CS RPV bottom 150→ 0.0 mV 1/11
KS RPV bottom 100→ -100 mV 1/25

工研院材化所 Kuosheng RWCU bypass loop ECP/CGMS FW H2 0.5 ppm 時 ECP=-120 mV, CTspecimen F.O.I.= 1/5

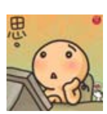
GE in-plant DCB specimen inside LPRM in upper core bypass region (close to top guide) F.O.I.= 1/10

GE in-plant DCB specimen in BHDL F.O.I.= 1/22

- **成效追蹤 (HWC執行後)**
  - **Spain GARONA NPP, *Stub Tube* (Furnace Sensitized 304 SS) HWC-M (1 ppm), ECP -245 mV UT inspection** 深度 F.O.I.= 1/10
  - 根據加氫前後In-reactor *core shroud* UT Inspection 裂縫長度/深度量測 (by BWRVIP)

Six Plants – NWC
Two Plants – HWC
Two Plants – NMCA

F.O.I.= 1/2 ?



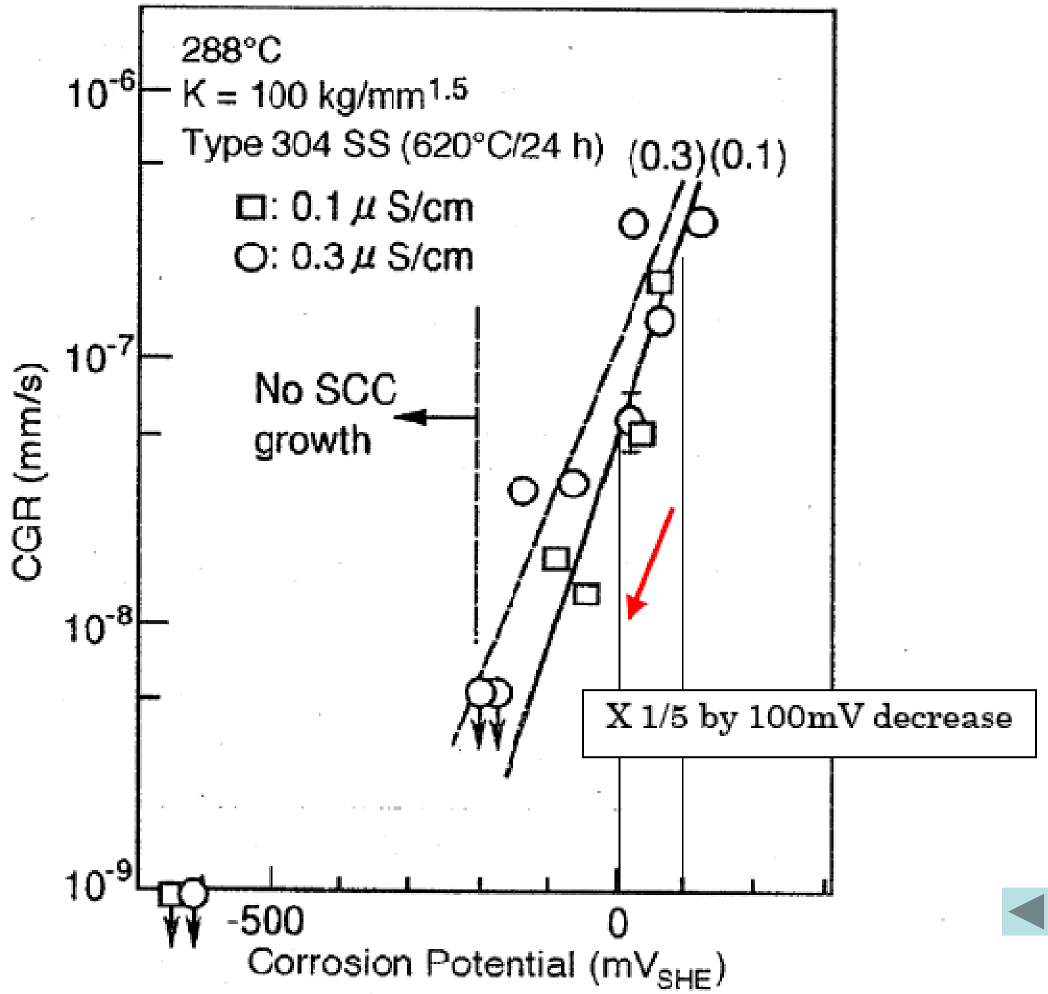


FIGURE 7. *Effects of E_{corr} and conductivity on CGR of sensitized type 304 SS.*

Fig.10 Correlation between crack growth rate and ECP of sensitized type 304 stainless steel

(1) Kikuchi et al. (1997)

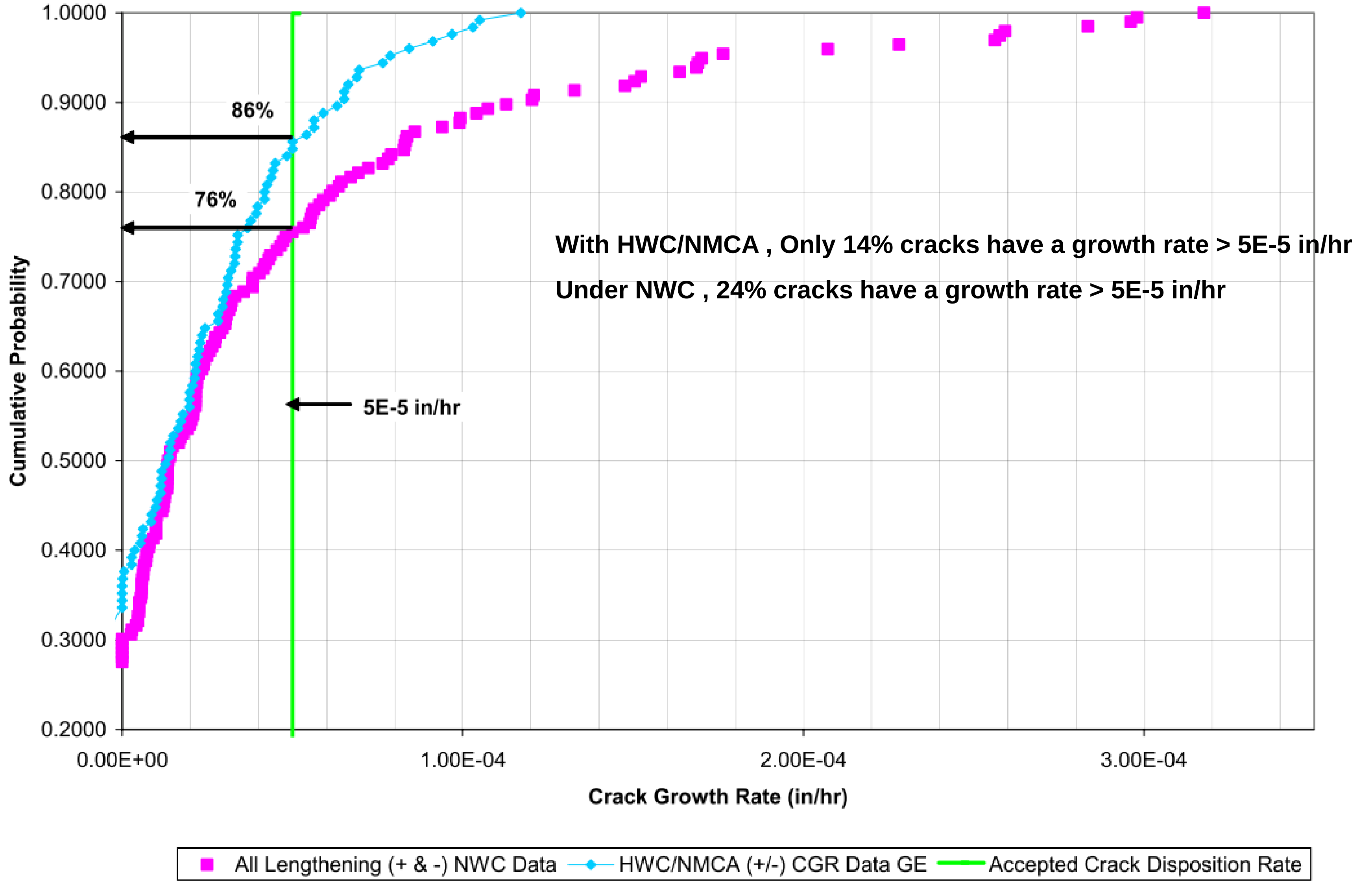


Figure 2-42
Lengthening CGR distribution NWC vs. HWC/NMCA for all plant [2-102]

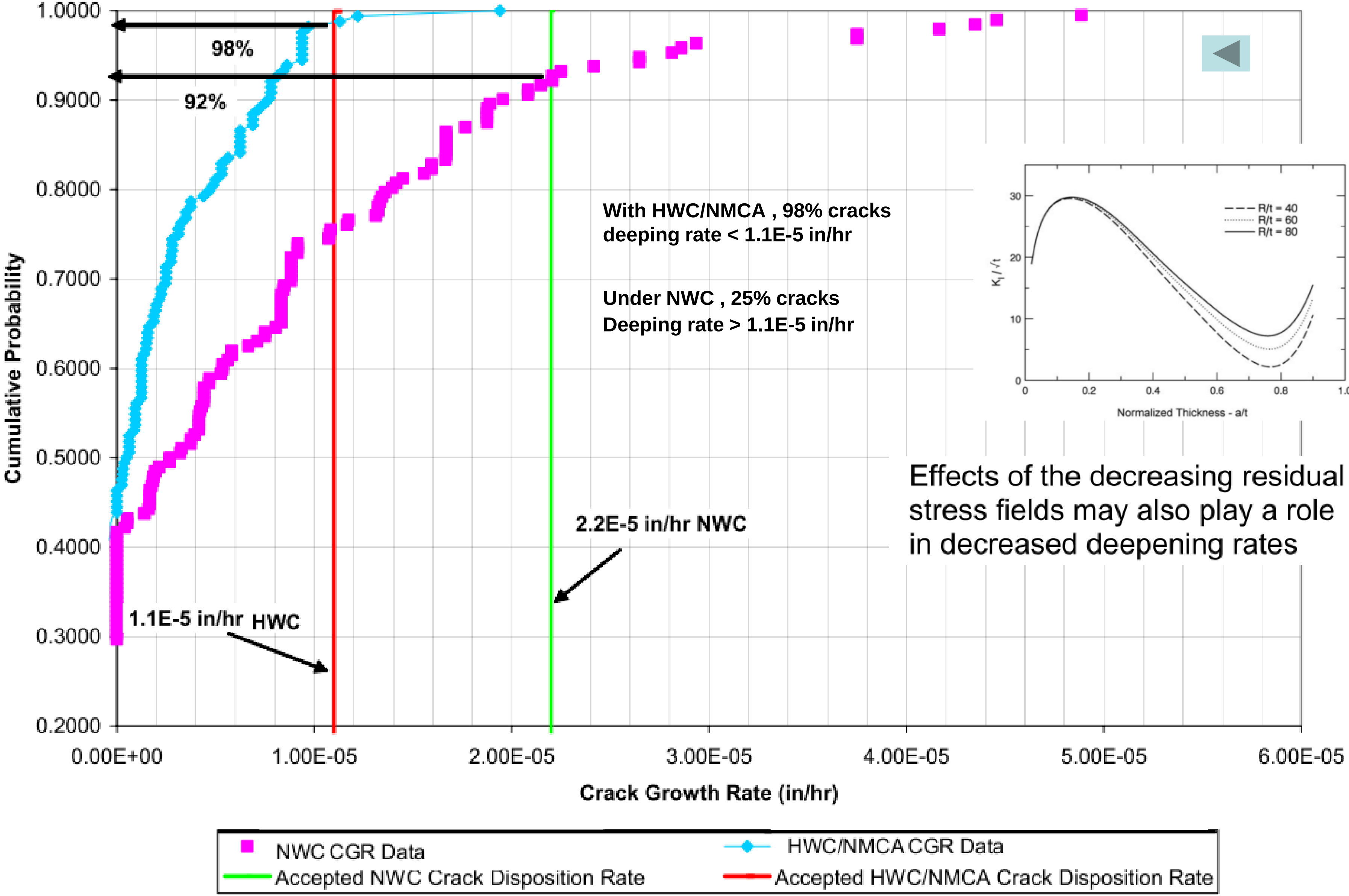
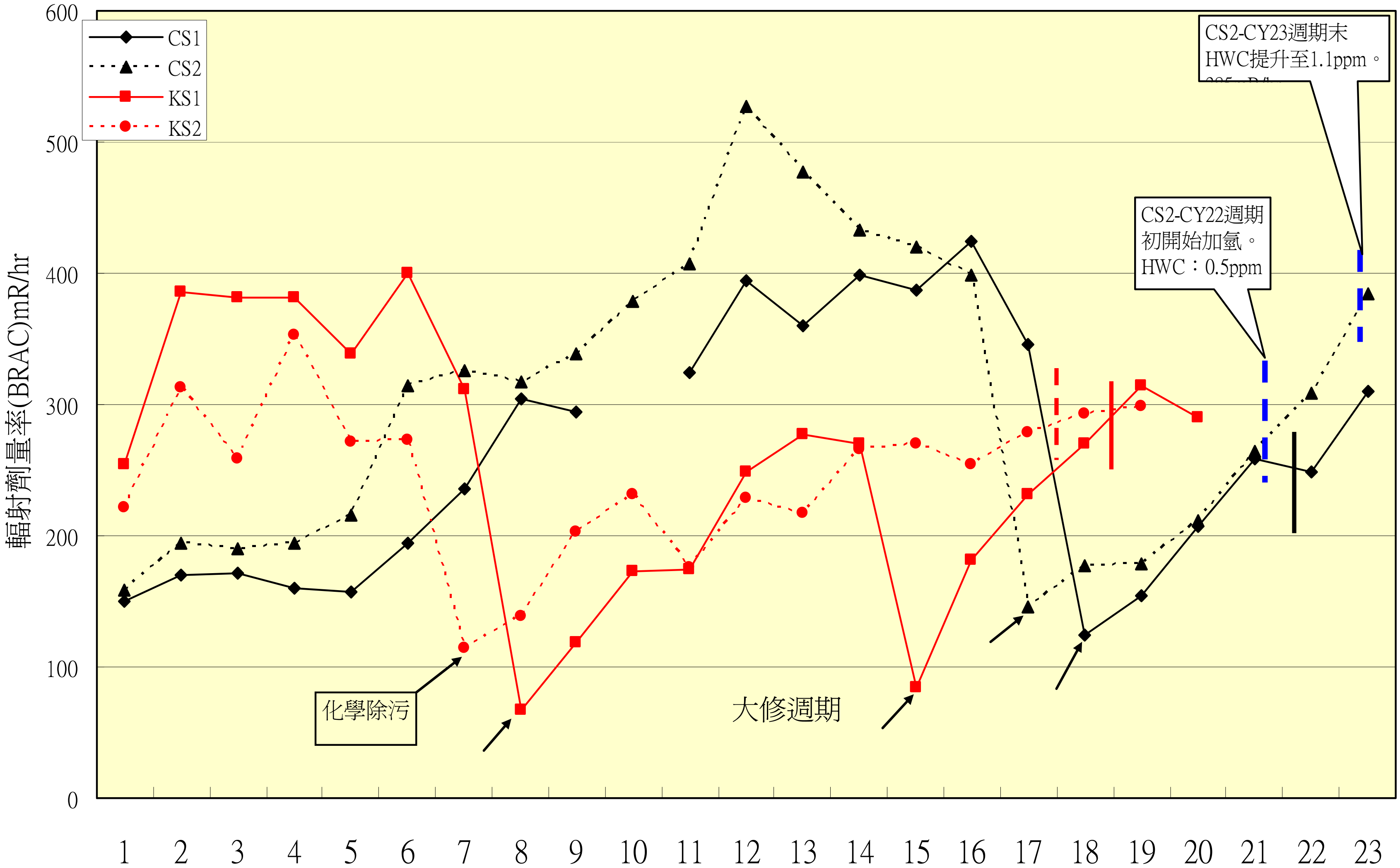


Figure 2-43
Depth CGR distribution NWC vs. HWC/NMCA for all plant [2-102]

核一、二廠四部機組再循環管路輻射劑量率(BRAC)趨勢圖



Shutdown Dose Rate Mitigation Strategies after HWC-M

- (proactive 未雨綢繆 DZO + 系統化學除汙 + DZO) strategy-------核發處

  Based on USBWRs/GE/EPRI post-HWC 經驗與建議

- Reactive (臨渴掘井) strategy--------核一廠

  a consideration on DZO will not be made until much higher dose rate increasing and untolerable after moderate hydrogen injection(> 1.0 ppm)

- (乾井Shielding +系統化學除汙) strategy--------核二廠

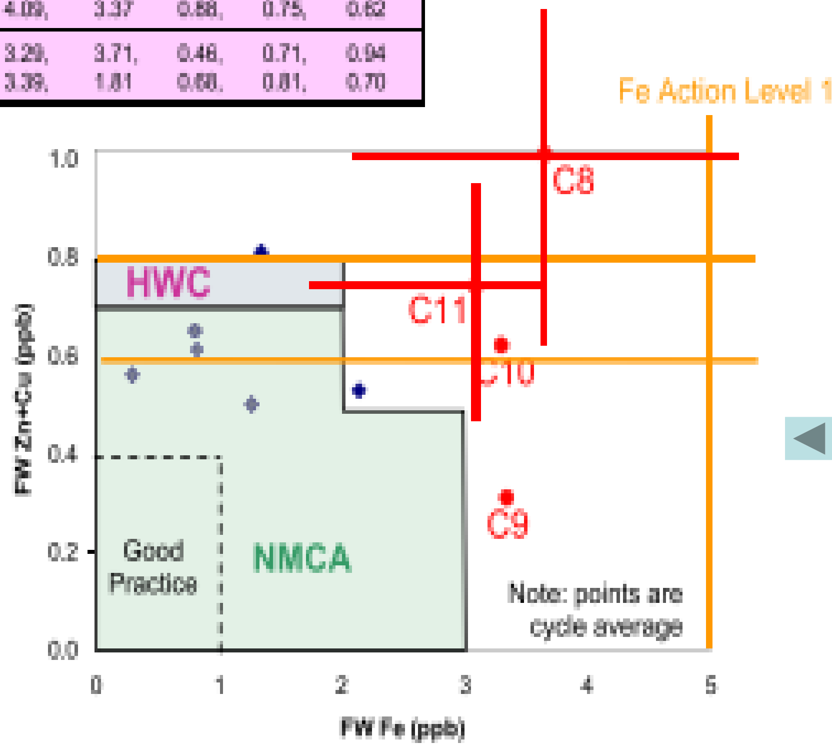
  1. DZO 對燃料護套 Crud/Corrosion 疑慮澄清

     To Whom ? and On What ?

     EPRI燃料部門 FRP and Limits on FW Fe,Cu,Zn

  2. 核二廠燃料護套破損 without adding anything to RW. 加DZO後,如發生Fuel Failure ,增加肇因分析複雜困難度.

	Cycle Avg. FW Fe (ppb)	Cycle Avg. FW Zn+Cu (ppb)	Quarterly Avg. FW Fe (ppb)	Quarterly Avg. FW Zn+Cu, ppb (Cu~0.2 ppb)
River Bend C8	3.65	1.01	5.37, 3.72, 2.18, 3.17, 4.09, 3.37	1.33, 1.28, 0.94, 0.88, 0.75, 0.62
River Bend C11	3.09	0.74	2.90, 3.29, 3.71, 3.45, 3.39, 1.81	0.46, 0.71, 0.94, 0.68, 0.81, 0.70
Needed (Quarterly Ave)	2.0	≥ 0.5		
Needed (Quarterly Ave)	3.0	< 0.5		
FitzPatrick C17	2.14	0.53		
LaSalle-1 C11	1.35	0.81		
Grand Gulf C15	1.27	0.50		
PB-2 C18	0.30	0.56		
CGS C18	0.83	0.61		
VY C25	0.81	0.65		



Red bars in the figure are ranges of quarterly average Fe (horizontal) and Cu+Zn (vertical) for RB Cycles 8 & 11. Data points for RB Cycles 9 & 10 are cycle averages. Diamond points are cycle averages of other BWRs shown in the Table. Vertical orange line is FW Fe AL 1 of 5 ppb, and horizontal lines are limits of Cu+Zn for NMCA and Mod-HWC plants, respectively, in 2004 BWR Chemistry Guidelines

圖1:核一廠一號機CPD、CDE、FW不溶鐵變化趨勢

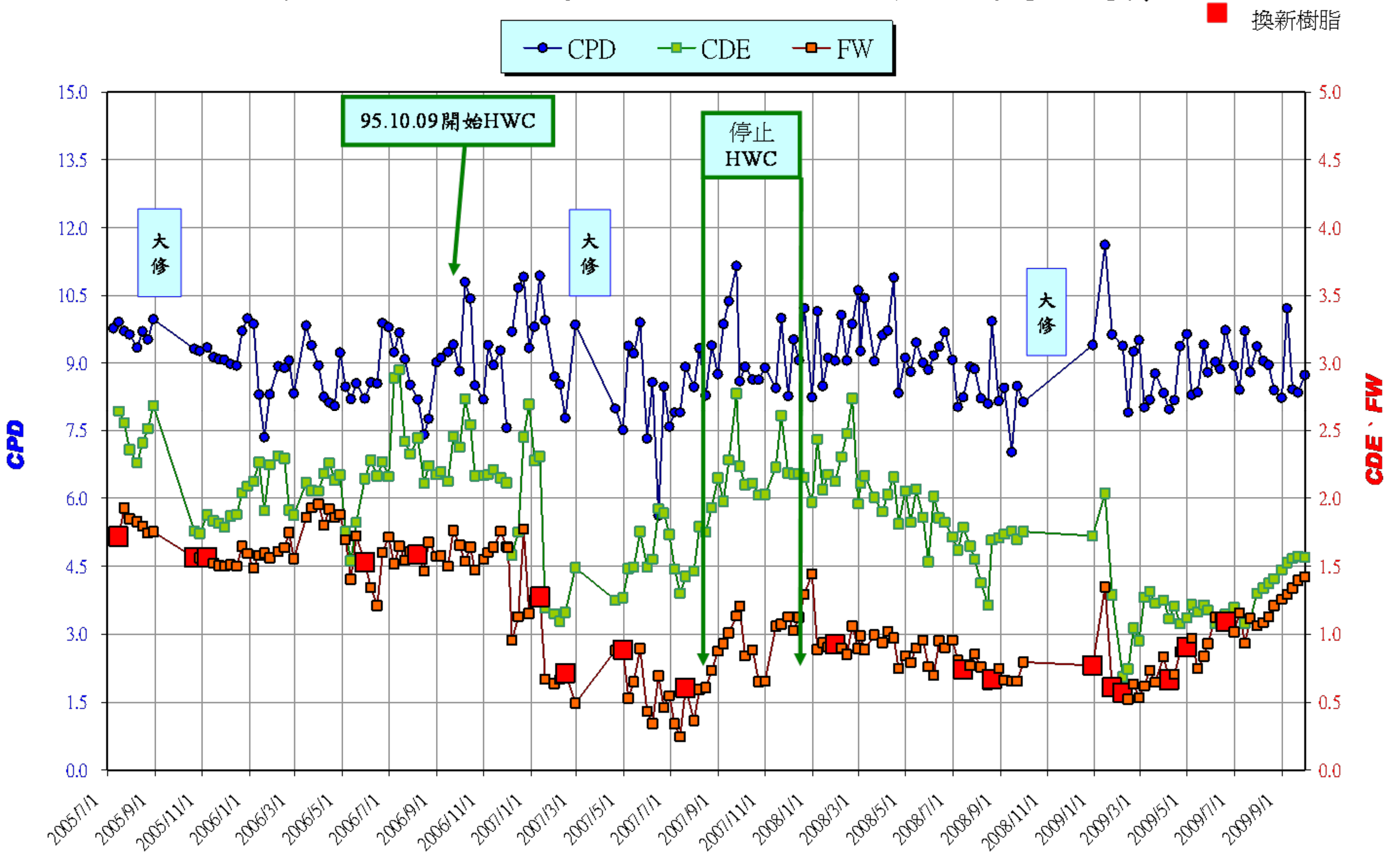


圖2:核一廠二號機CPD、CDE、FW不溶鐵變化趨勢

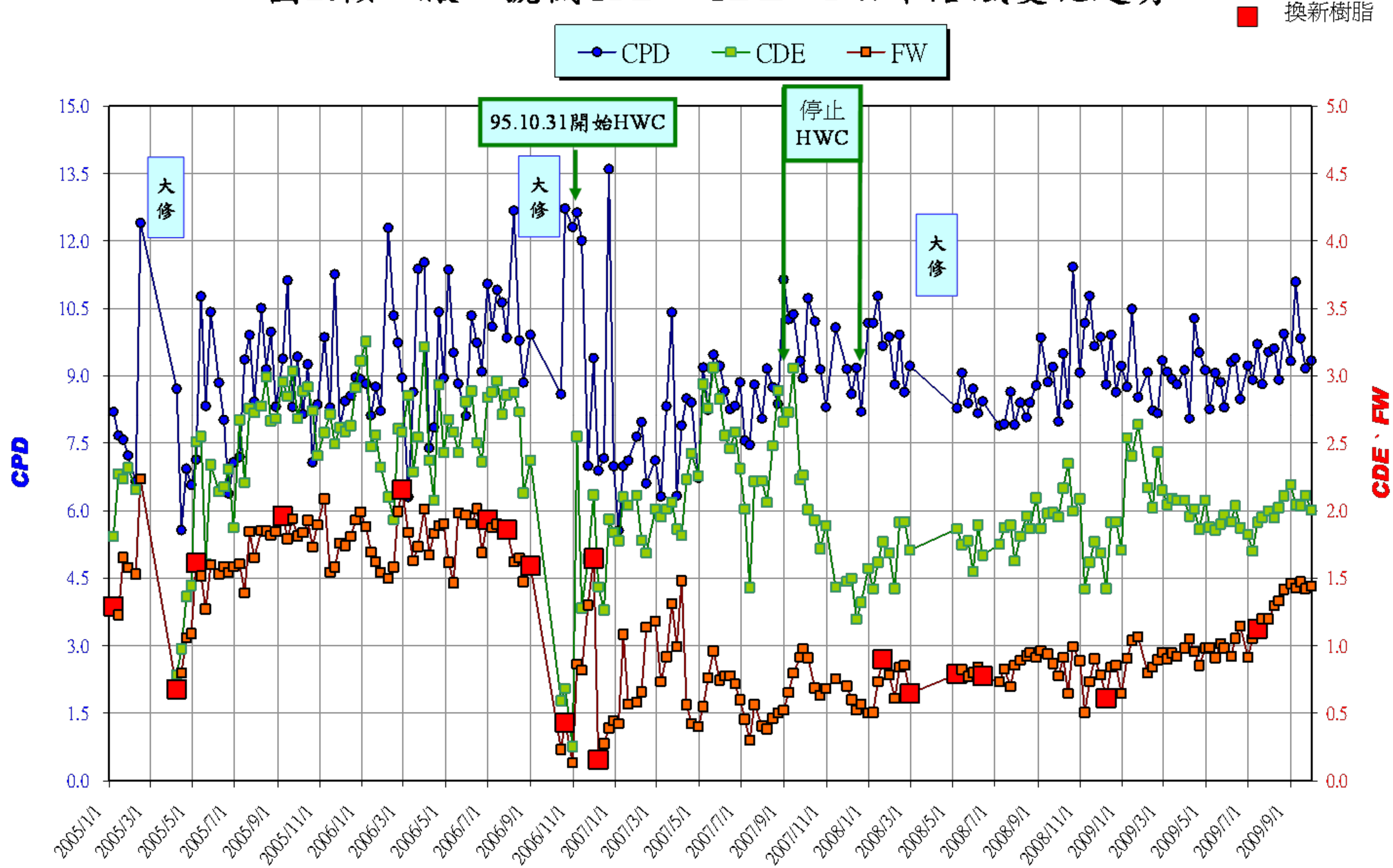
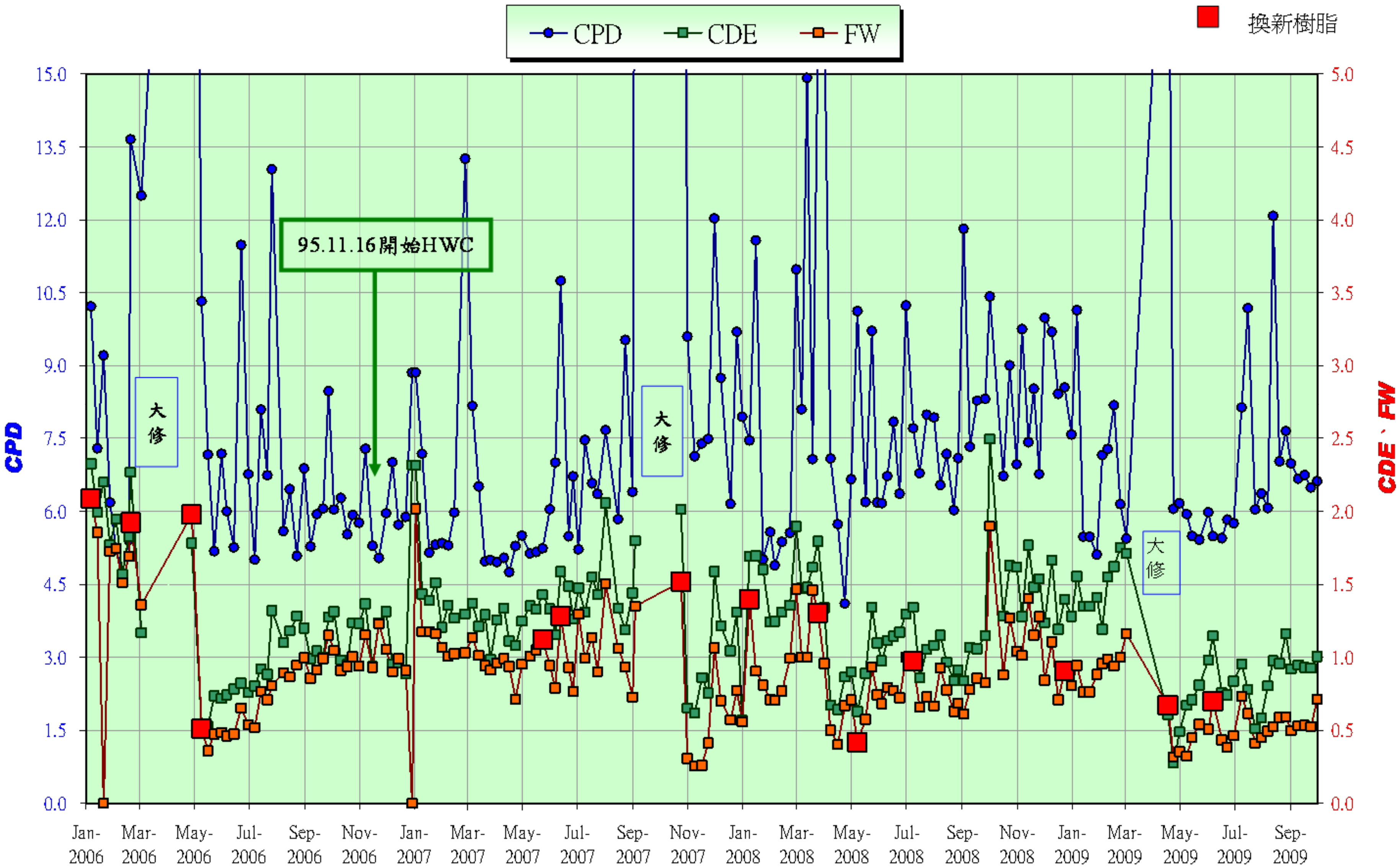


圖3:核二廠一號機CPD、CDE、FW不溶鐵變化趨勢



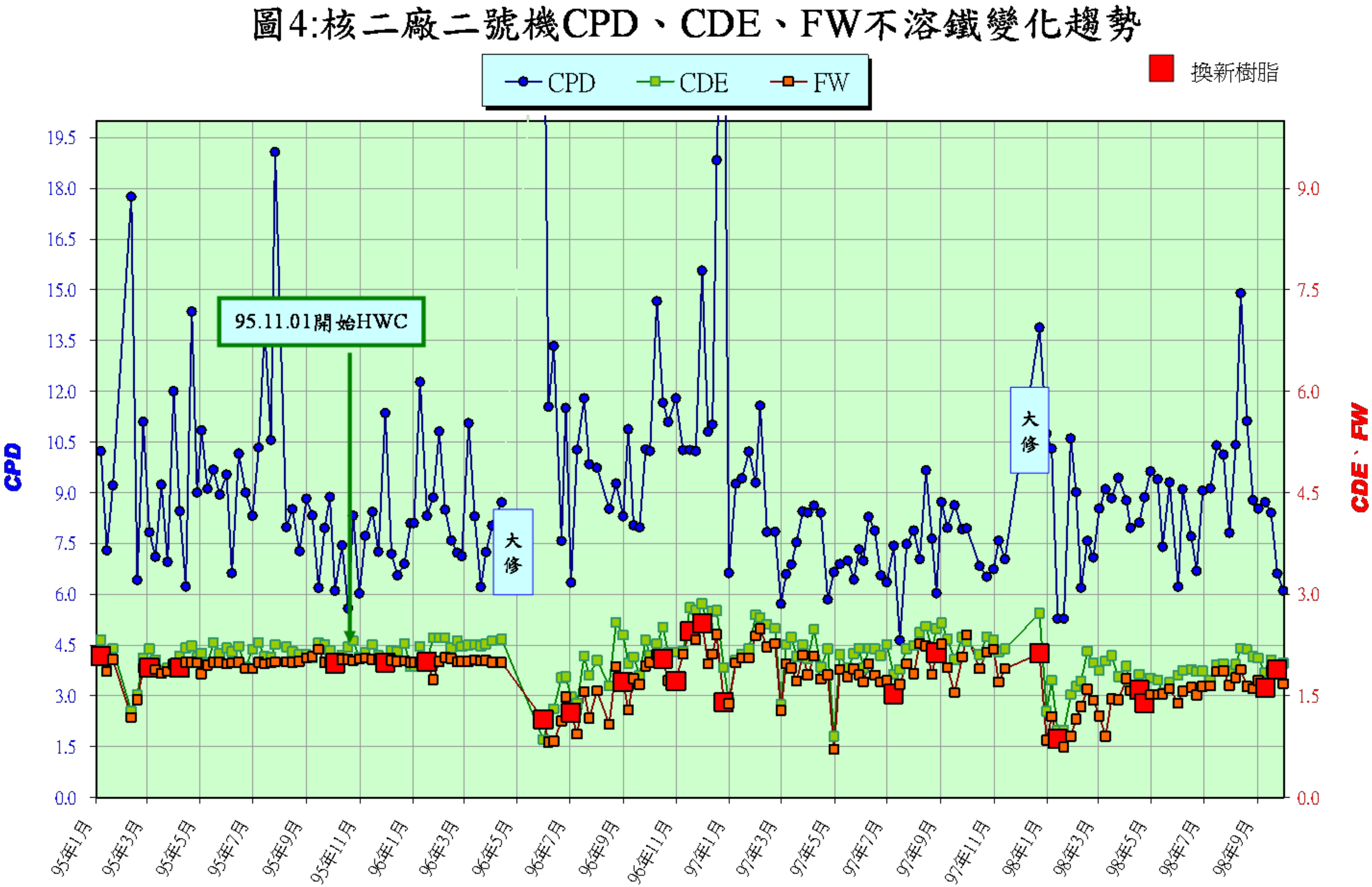


圖4:核二廠二號機CPD、CDE、FW不溶鐵變化趨勢
CPD
CDE
FW
換新樹脂
95.11.01開始HWC
大修
大修
大修
CPD
CDE、FW
19.5
18.0
16.5
15.0
13.5
12.0
10.5
9.0
7.5
6.0
4.5
3.0
1.5
0.0
9.0
7.5
6.0
4.5
3.0
1.5
0.0
95年1月
95年3月
95年5月
95年7月
95年9月
95年11月
96年1月
96年3月
96年5月
96年7月
96年9月
96年11月
97年1月
97年3月
97年5月
97年7月
97年9月
97年11月
98年1月
98年3月
98年5月
98年7月
98年9月

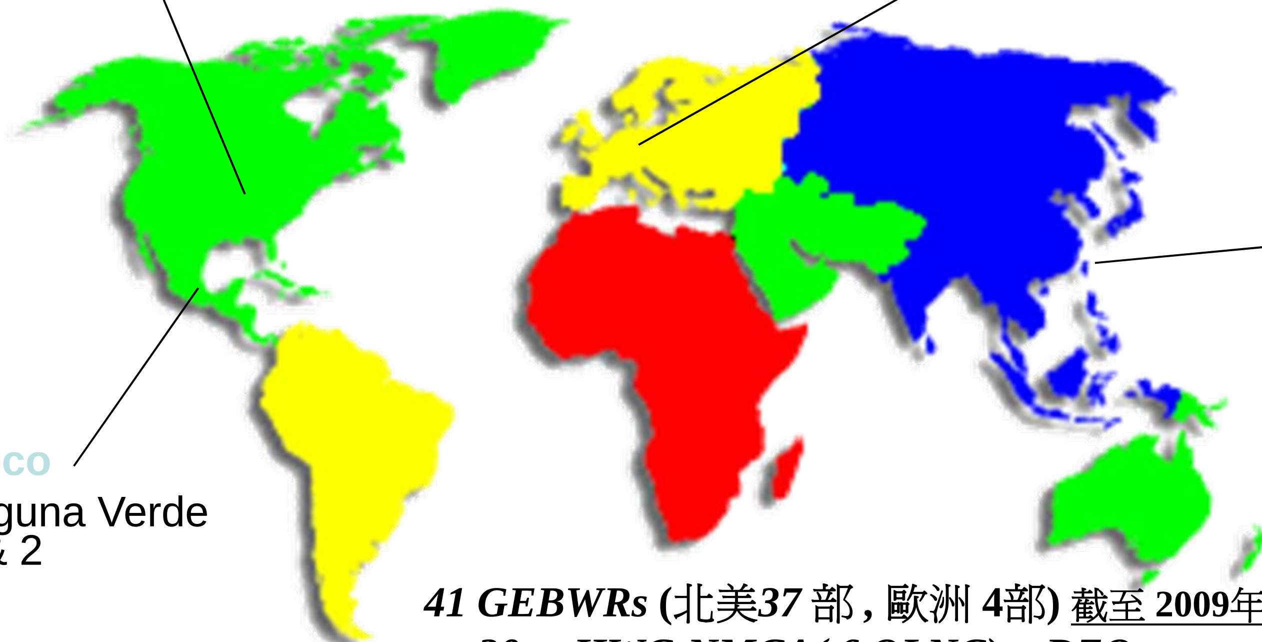
Kuosheng	Unit 1	Unit 2
Feedwater Iron (ppb)	**0.92**	**1.9**
Feedwater Zinc (ppb)	**0.003**	**0.006**
Feedwater Copper (ppb)	**0.06**	**0.09**
Reactor Water Conductivity (uS/cm)	**0.079**	**0.082**
Reactor Water Zinc (ppb)	**0.92**	**0.85**
Reactor Water Copper (ppb) before HWC	**1.8**	**1.9**
Reactor Water Copper (ppb) after HWC	**1.2**	**0.8**
Soluble Reactor Water Co-60 (uCi/ml)	**8.7 E-5**	**7.1 E-5**

It is believed that soluble copper is being reduced to a less soluble form in reducing regions of the reactor coolant system*. *Large increases in soluble RW copper are observed when the hydrogen injection system is taken out of service.

46 Participating BWRs

United States
- 35 BWRs

Europe
- Cofrentes
- KKL (not included)
- KKM
- Santa Maria de Garoña
- Ringhals 1 (new in 2009)



Asia
- **Chinshan 1 & 2**
- **Kuosheng 1 & 2**

Mexico
- Laguna Verde 1 & 2

***41 GEBWRs* (北美*37* 部 , 歐洲 4部) 截至 2009年06月資訊**

30 HWC-NMCA(6 OLNC) + DZO

11 HWC-M + DZO

- **過去四年 ,US Nuclear Industry 開始 *major initiatives(促進方案)*.
  其中 3項衝擊到水化學.**

1. Starting in 2004 , *Materials Degradation Initiative*

目標: controlling corrosion process

Key Part: EPRI Water Chemistry Guidelines

HWC 35/35 BWRs

HWC-M (ECP ≤ -230 mV) 8 BWRs

NMCA/HWC (ECP ≤ - 450 mV) 27 BWRs

OLNC/HWC 5 BWRs

希望經由ECP控制, 避免RPV Internals IGSCC 重大維修

2. Starting in 2005 , *Radiation Protection Initiative RP2020*

目標: to meet tighter regulatory limits in the future.

Key Part: Radiation Source Term Reduction

Water Chemistry is important in controlling the the effects of source term

FW Fe 接近半數BWRs ≤ 0.5 ppb

FW DZO injection 35/35 BWRs (except VY)

3. Starting in 2006 , *Fuel Integrity Improvement Initiative*

目標: Zero Fuel Failure by 2010

(包括考量水化學可能形成Fuel Crud and potential effects on fuel cladding corrosion)

高階主管認知後，水化學決策由上↓下

2008 EPRI BWR Water Chemistry Guidelines 建議

FW Fe 季平均值 < 3.0 ppb

< 2 ppb (when FW Zn > 0.5 ppb , Fw Cu < 0.05 pp)

< 2 ppb (when Fw Cu > 0.05 ppb, FW Cu+Zn > 0.5 ppb)

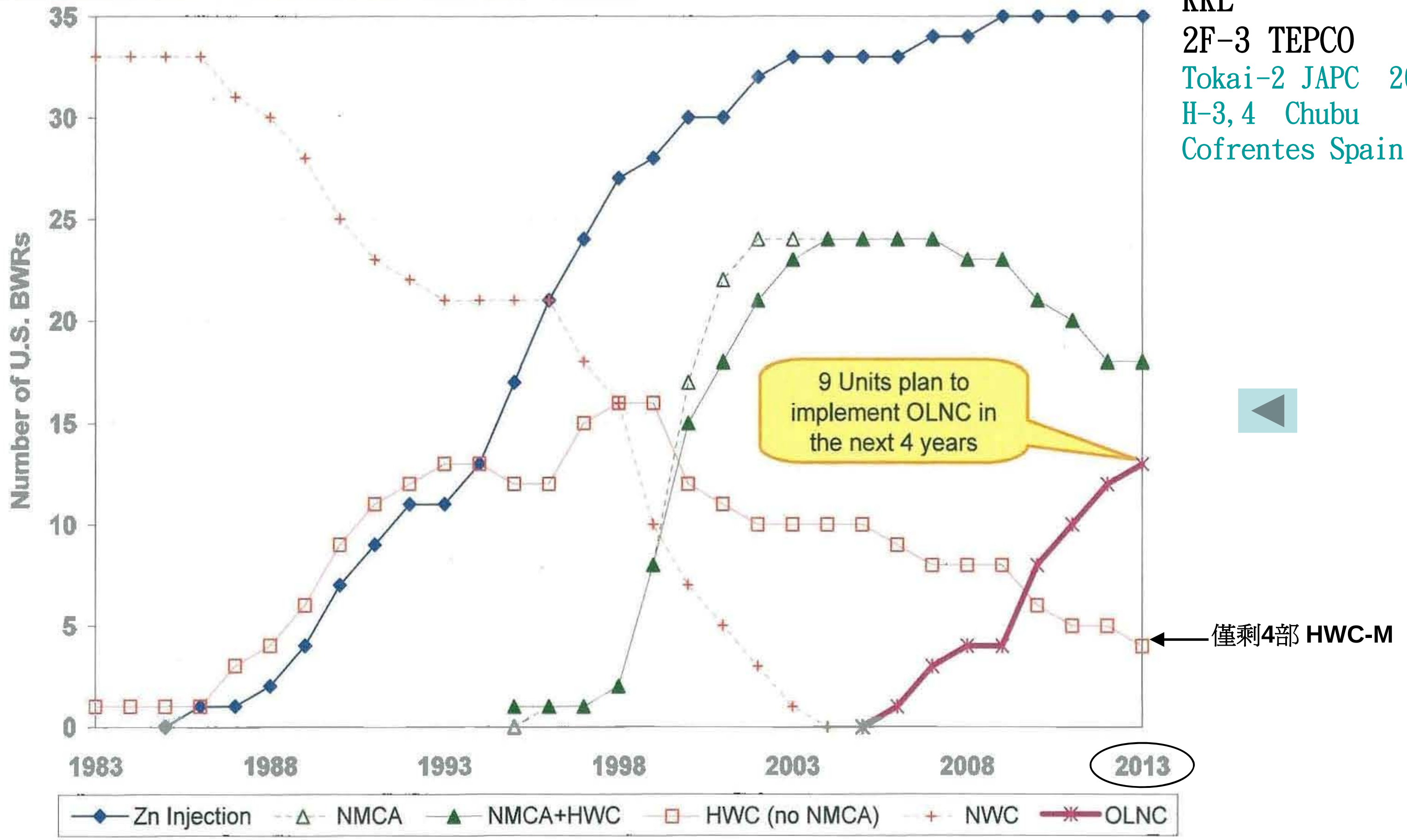
FW Zn 季平均值 < 0.6 ppb for HWC-M plants

FW Cu 季平均值 < 0.1 ppb

RW Si 季平均值 ≤ 300 ppb for Zn injection (good practice)

BWR Chemistry Trends in U.S.

Outside US
NMCA/OLNC
KKM
KKL
2F-3 TEPCO
Tokai-2 JAPC 2010
H-3,4 Chubu
Cofrentes Spain



EPRI ELECTRIC POWER RESEARCH INSTITUTE

日本 HWC during Startup (HDS/DSHWC)

- JAPC Tokai-2 (BWR-5) 與台電關係友好
  HWC during Startup / RWCU H_2 injection one hour before plant startup
  RWCU H_2 stop half hour after rated Rx water T/P
  HDS 發表於 2005 亞洲核電廠水化學會議 (韓國主辦)
  2007/ 9月 亞洲核電廠水化學會議(台電主辦)

- Chugoku Shimane-2 (BWR-5) Kuosheng Sister
  HDS Mini-tests in start-up of Cycle-15
  will be automated in start-up of Cycle-17
  發表於 2008 德國柏林國際核反應器水化學會議

美國 HWC during Startup (EHWC)

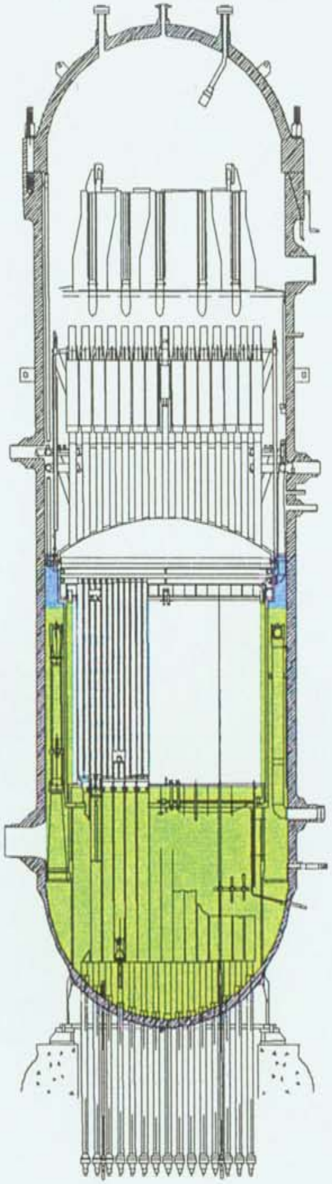
BWRVIP Chemical(Hydrazine)Injection to extend IGSCC mitigation from 93 C to 5% Power

↓

Hydrogen during Startup
(Early HWC)

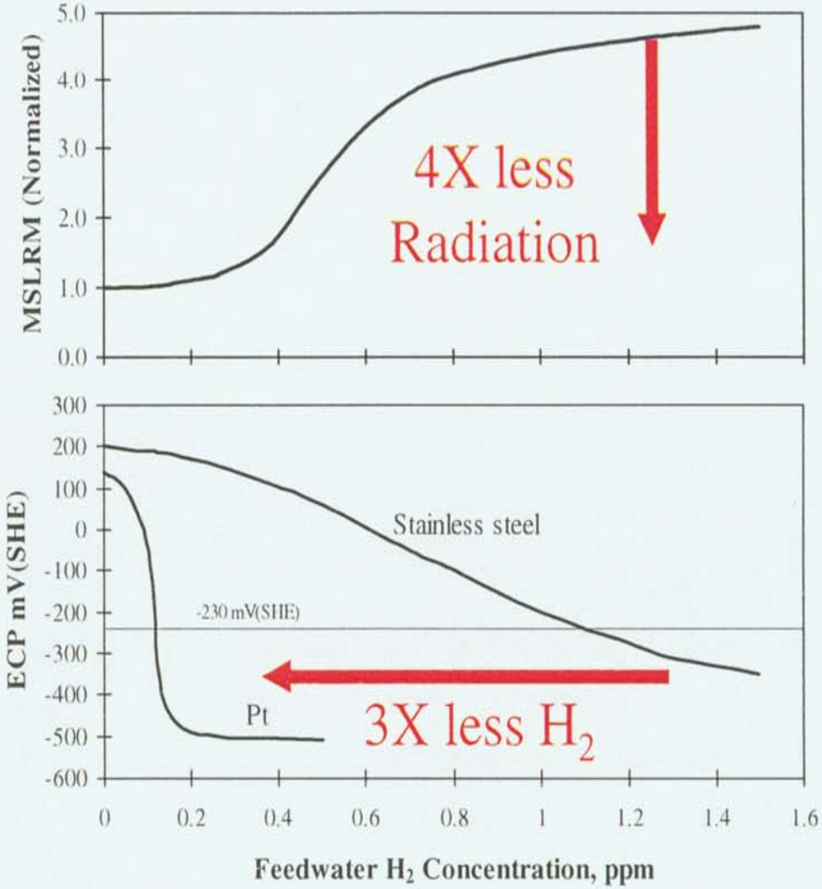
Exelon PB-2 2010 demon.

NobleChem™ Benefits Over HWC



Green Region of Mitigation with 1 - 1.6 ppm H2

Blue Additional Region of Mitigation with NMCA & ~0.4 ppm H2



2013年前,US 4部HWC-M機組仍堅持不考慮NMCA/OLNC的理由

- *Questions on its effectiveness: Knowledge GAP*

  1. Although GEH has demonstrated that ECP is reduced following OLNC application , they have not demonstrated that it is being deposited in all areas where IGSCC mitigation is desired. There are also questions about whether enough noble metal deposits into low flow regions such as the annulus between the N2 nozzle and its thermal sleeve to provide IGSCC mitigation of nozzle and thermal sleeve welds. These welds are mitigated with Mod-HWC.
  2. Crack flanking is not a concern with Mod-HWC. OLNC is intended to eliminate the crack flanking concern with Classic NMCA, but primary evidence that it does comes from KKM, where the shroud cracks are still growing, although at a slower rate

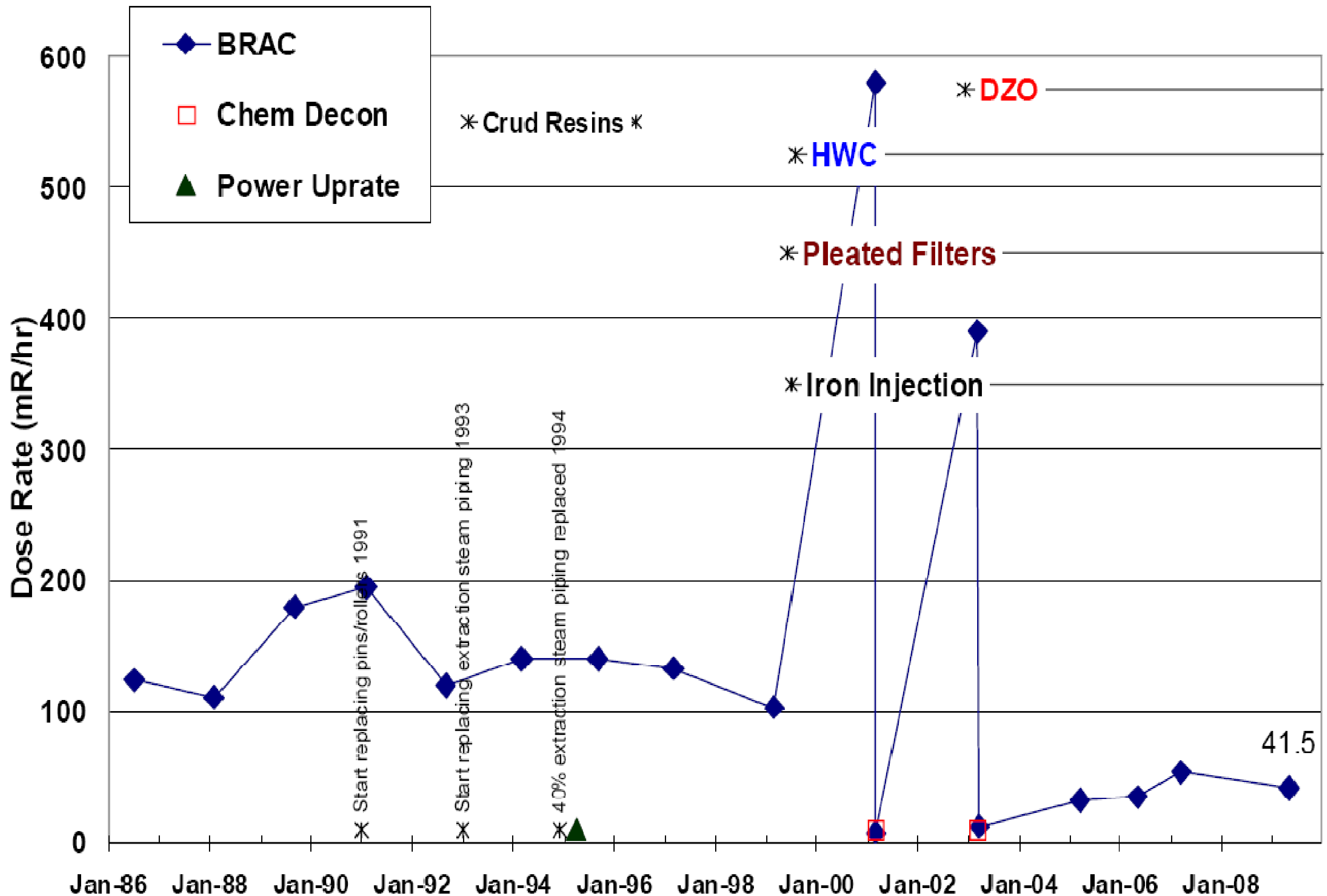
- *Fuel Design groups are concerned :*

  about the potential effects of noble metals on fuel corrosion (although none have been seen so far) and on hydrogen pickup by fuel channels, a factor in channel bow. Again, there is no theory and no evidence that suggests that either Mod-HWC or noble metal HWC causes or aggravates this situation, but the Susquehanna fuels people would rather not add noble metals

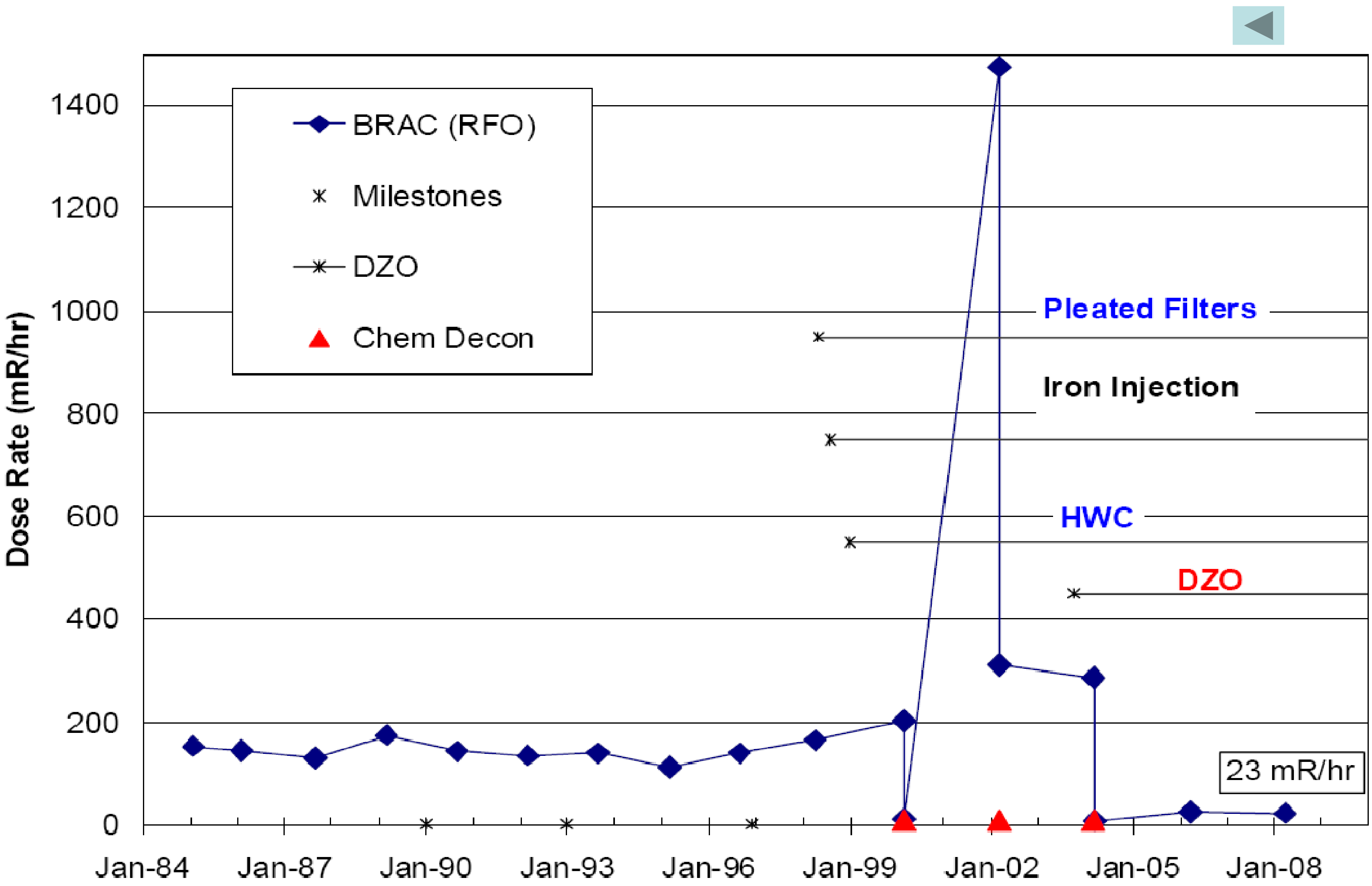
- Satisfied with shutdown radiation fields which have remained very low since the last round of chemical decontaminations, and satisfied with N-16 impact control.

- Two units has increased its capacity to inject hydrogen to ~110 scfm, sufficient to provide ~2.2 ppm FW H_2 following their Extended Power Uprate

Susquehanna 2



Susquehanna 1



核三廠化學組希望藉由一次側水化學控制來改善電廠營運問題

- Core CIPS/AOA deviation more than -3% (MS-1 CY-16,17 and MS-2 CY-16)

  RCS Li-B control **was changed from modified pH chemistry to elevated constant pH (pHt 7.3) chemistry with Li concentration below 3.5 ppm since June 2006 (cycle-17 for both units)**

- high radiation dose rate of SG channel head

  Improved RCS Li-B control ▶

  RCS 5 ppb of Zn ☹

- WH type RCP No.1 seal abnormal leakoff events

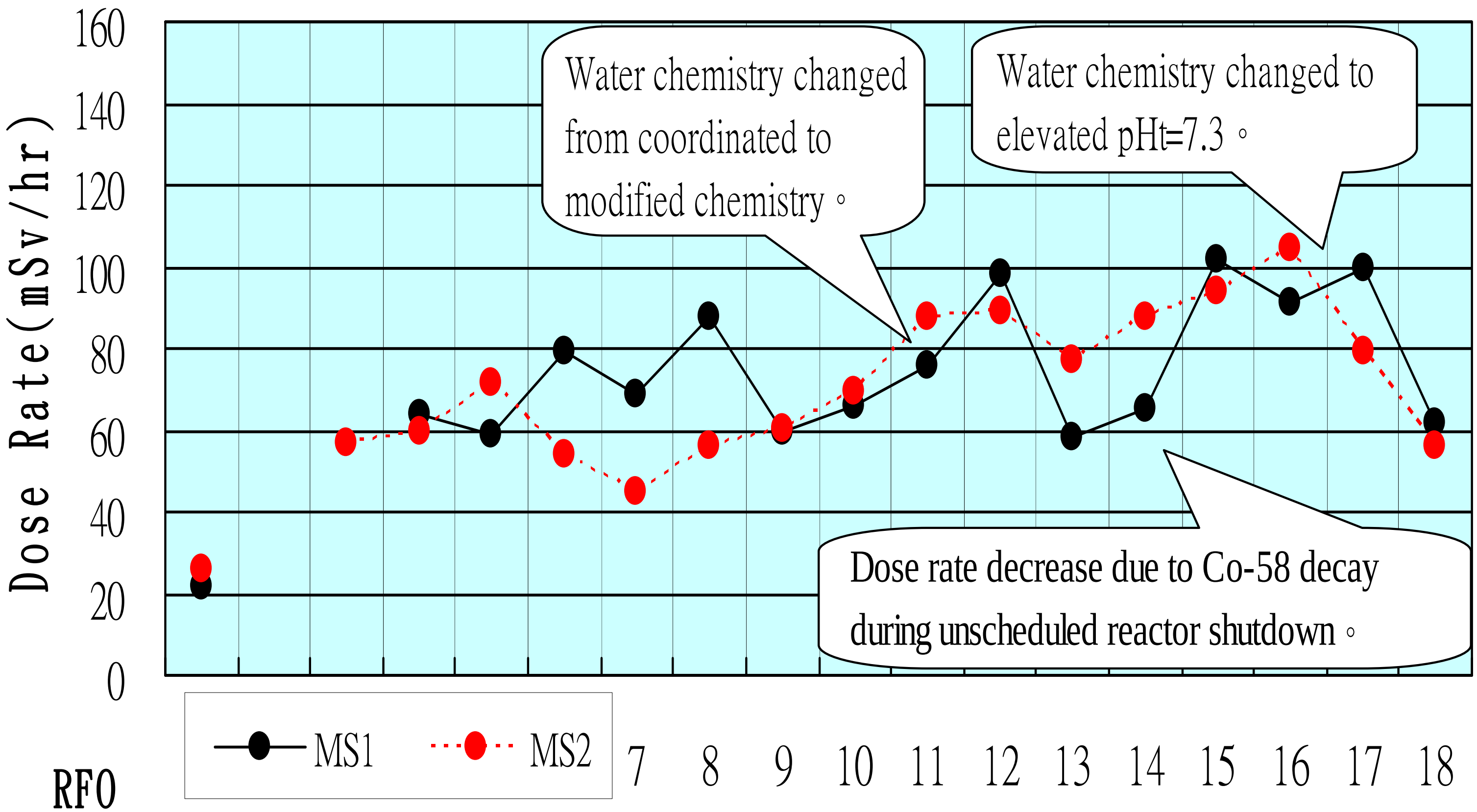
  by a maneuver on *RCS chemistry in the end of cycle thru pH changes* (note:pH drop from 7.3 to 7.2) in addition to an increasing the amount and frequency of reactor make-up water , thereby disturbing the seal steady state conditions with a flushing action caused by cooler and oxygenated water. ▶

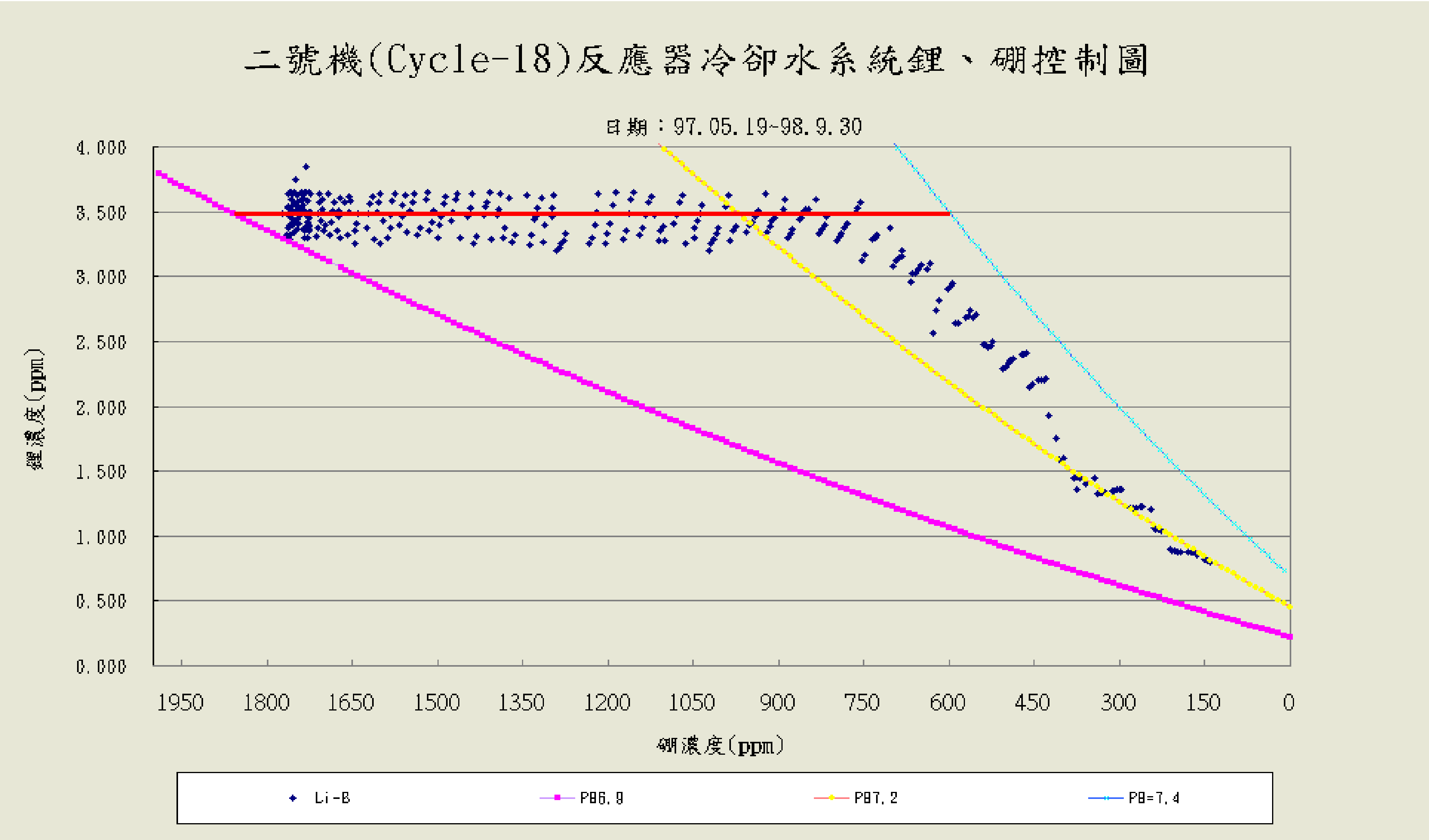
- **大修人員劑量**

  Through a campaign of *<u>shutdown chemistry control optimization</u>* since MS-2 EOC-16 , personal exposure for the work of RPV head open has been decreased from 73.67 man-mSv to 22.63 man- mSv exposed in MS-1 EOC-18

◀

Maanshan#1#2 S/G Channel head Dose Rate Trend





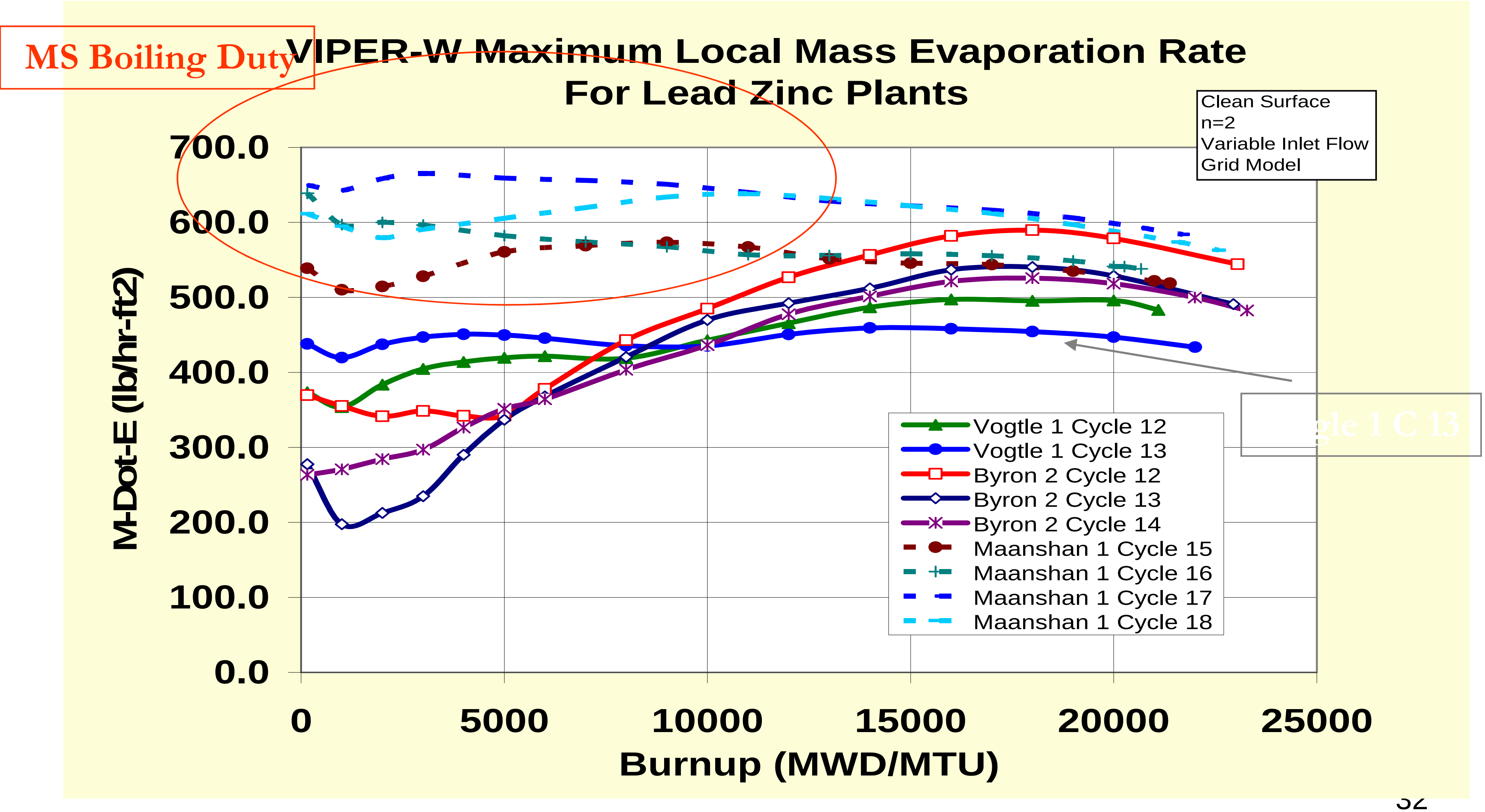
Maanshan 二號機CY-18 RCS酸鹼值長期維持於Tref300℃的 pH_T7.3已至燃料末期。

酸鹼值的控制非常小心謹慎

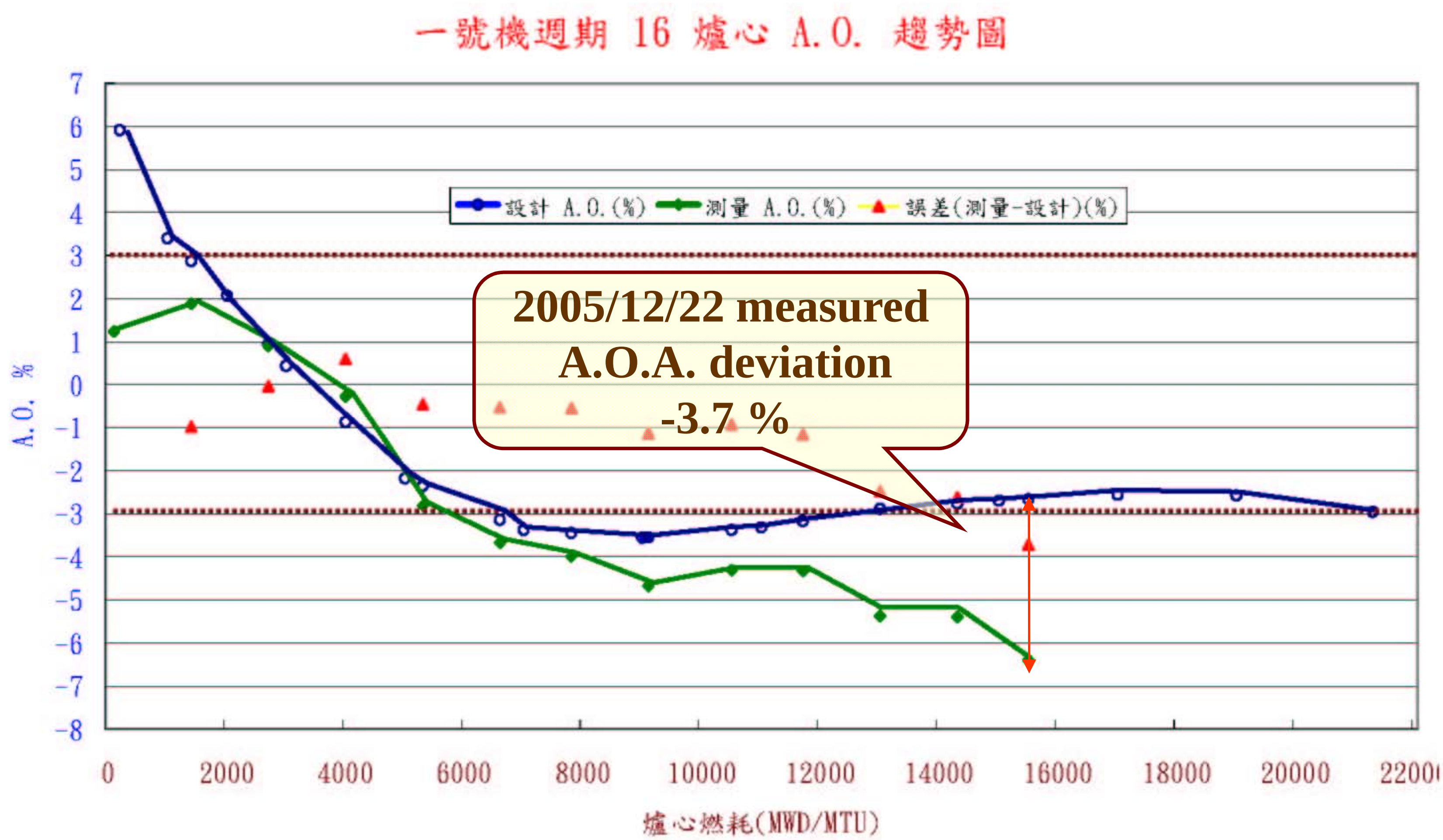
MS : High Sub-Cool Boiling Duty

High Duty Core Index = 260

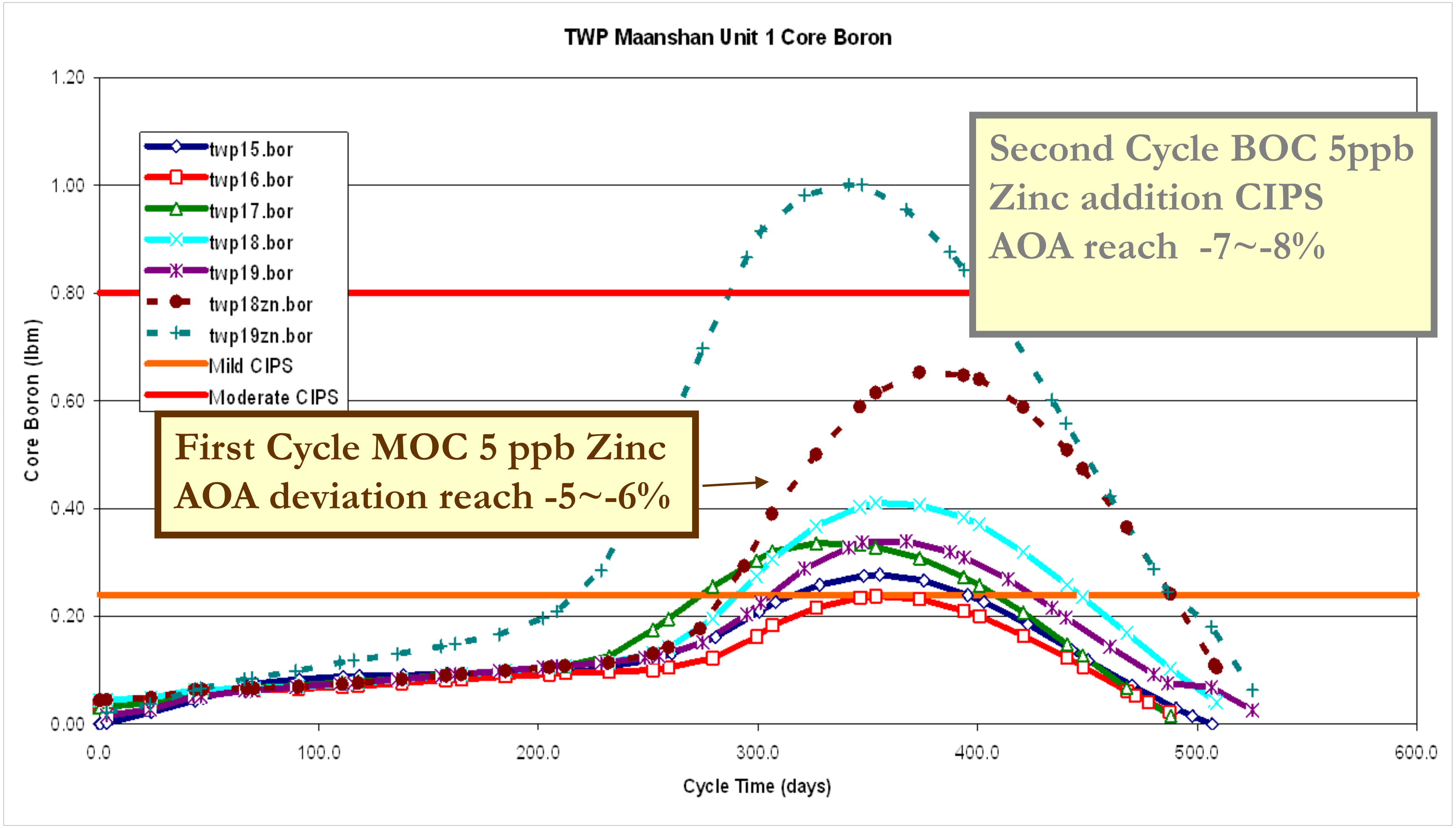
High Coolant Temperature Thot =621.5°F



MS is now operating in CY18
MS CY16、CY17 got CIPS AOA problem



MS can't survive at even 5 ppb Zinc Addition Calculated by WH VIPER/BOA Code



TPC has suspended the MS DZO project 

- TPC has suspended the DZO project account of following considerations:

① Inherent Constraints of NSSS HD condition.

② High surveillance cost for Zinc addition, including Fuel inspection, Fuel clean and Core design CIPS-Risk assessment.

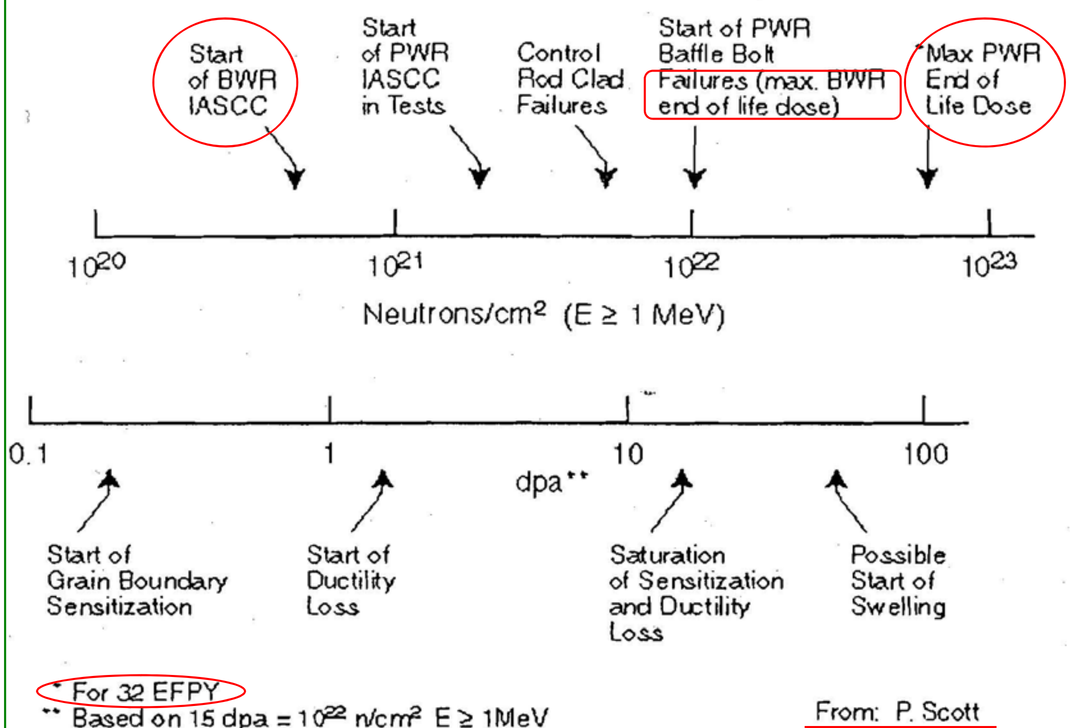
③ Need much more fuel cost for reducing the F△H in core design(4~8 million/cycle)

Comparison of Field Observations to Changes in Microstructure

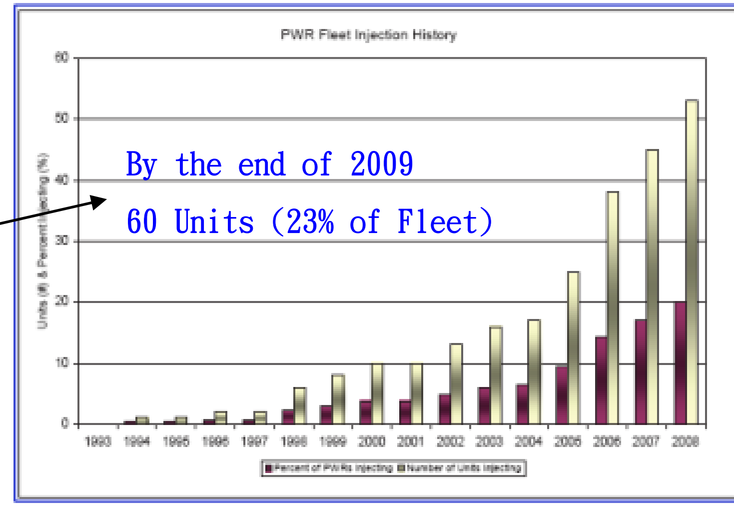
HWC抑低core shroud不鏽鋼(exposed to < 5xE20 n/cm2 neutron irradiation) IGSCC growth rate的效果雖已報告於BWRVIP-14,對接受更高中子通量下(例如機組延役至60年)之不鏽鋼是否仍能享受HWC的benefit？後續BWRVIP-99 研究指出5xE20 n/cm2 to 3xE21 n/cm2 高中子通量下HWC 仍具benefit。Followup to BWRVIP-99,phase 1結果顯示up to 6.7 dpa(1 dpa=7xE20 n/cm2) HWC仍能降低不鏽鋼ECP,但高於此中子通量後,HWC似乎無效。

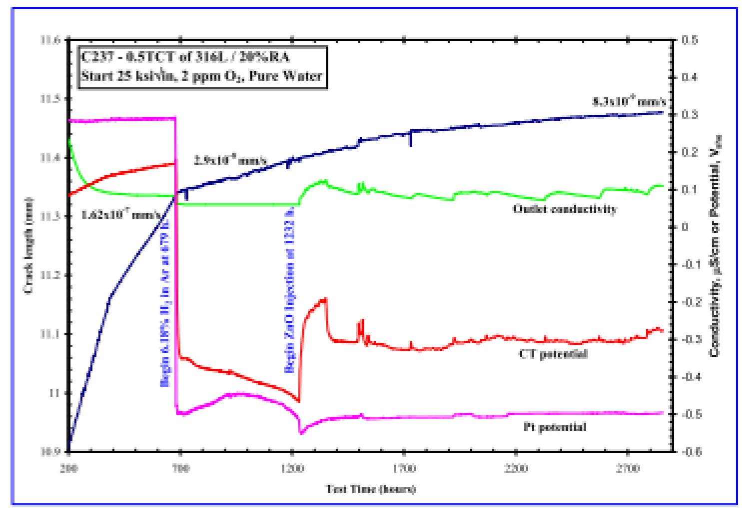
HWC mitigates IASCC in SS at moderate Ks (~15 ksi√in) but may be less effective at higher stress intensities (~18ksi√ in).

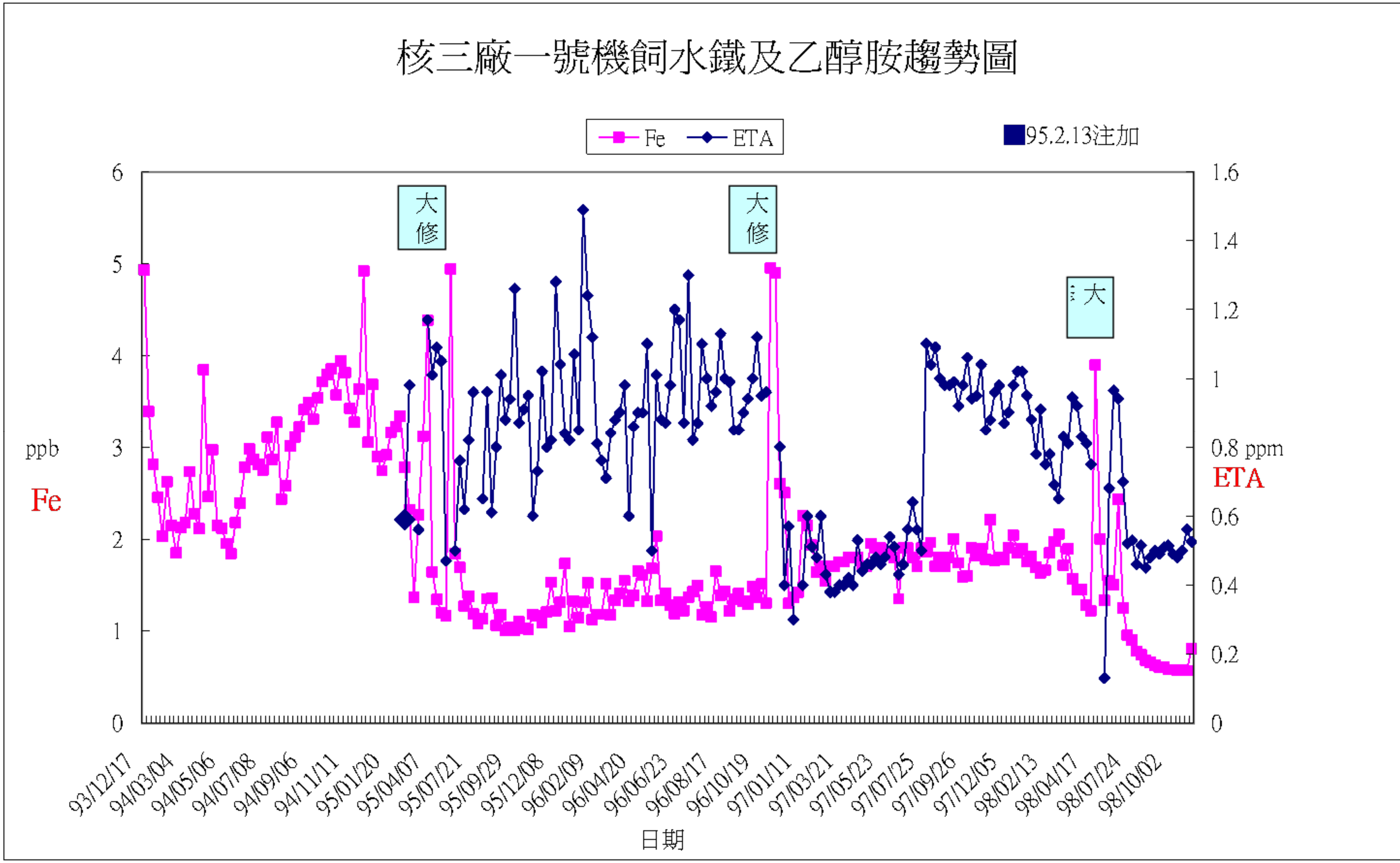
HWC is effective for non-irradiated stainless steels even at high K values



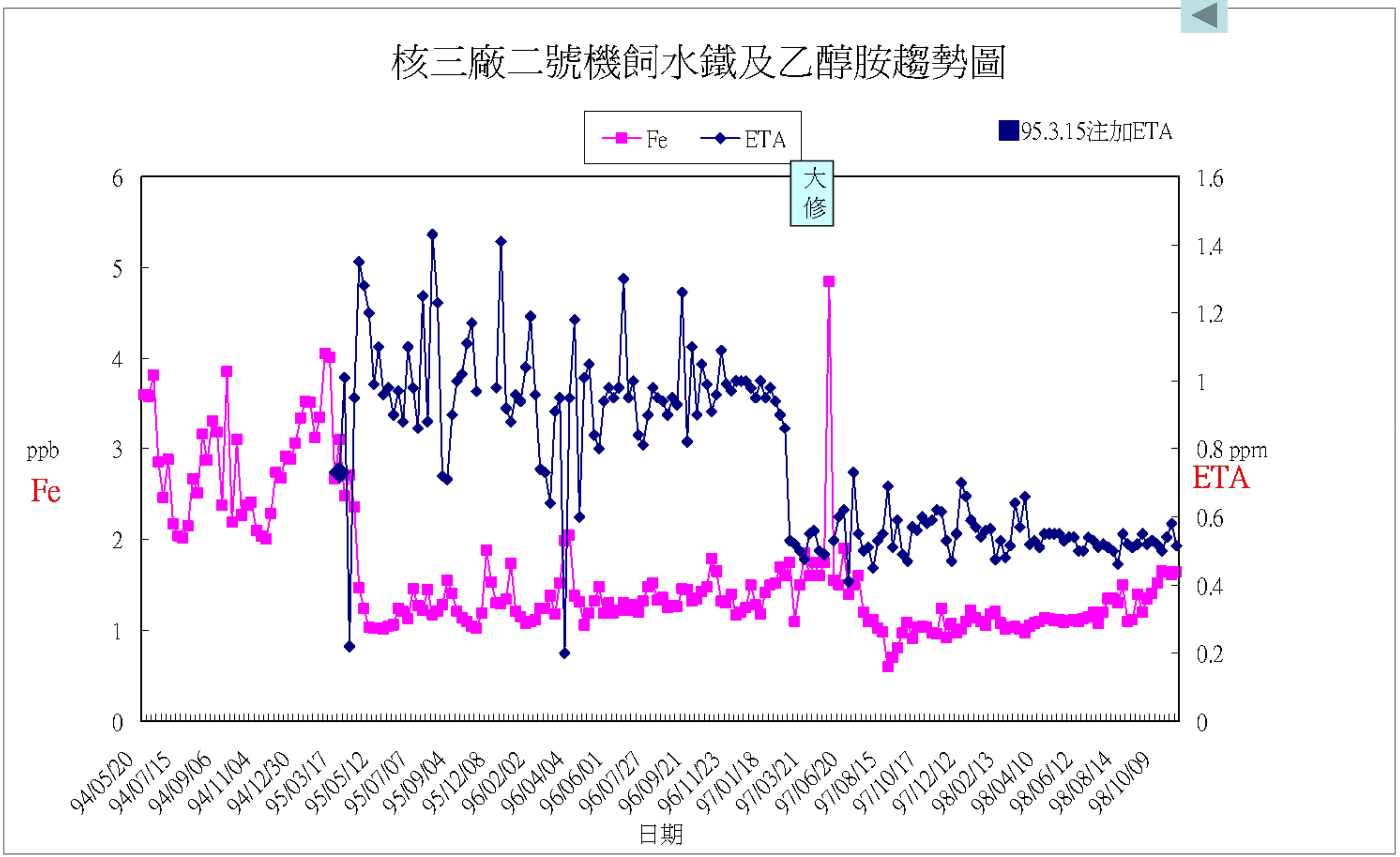
- Soluble Zinc Added for Exposure Reduction
  - Zinc addition in BWRs since 1986
  - Zinc addition in PWRs initiated in 1994
  - 50+ PWR plants worldwide now inject zinc
  - Fuel effect concerns currently limit maximum concentration
- Field and Laboratory Data Suggest Zinc Addition May Mitigate PWSCC
  - Clear effect for stainless steel
  - Steam generator tube inspection data show clear benefit for slowing time to initiation in Alloy 600
  - Picture less clear for mitigation of crack growth rate in Alloy 600 and 82/182 weld metals







核三廠一號機飼水鐵及乙醇胺趨勢圖
Fe
ETA
95.2.13注加
大修
大修
大
ppb
Fe
0.8 ppm
ETA
6
5
4
3
2
1
0
1.6
1.4
1.2
1
0.6
0.4
0.2
0
93/12/17
94/03/04
94/05/06
94/07/08
94/09/06
94/11/11
95/01/20
95/04/07
95/07/21
95/09/29
95/12/08
96/02/09
96/04/20
96/06/23
96/08/17
96/10/19
97/01/11
97/03/21
97/05/23
97/07/25
97/09/26
97/12/05
98/02/13
98/04/17
98/07/24
98/10/02
日期


核三廠二號機飼水鐵及乙醇胺趨勢圖
Fe
ETA
95.3.15注加ETA
大修
ppb
Fe
0.8 ppm
ETA
6
5
4
3
2
1
0
1.6
1.4
1.2
1
0.6
0.4
0.2
0
94/05/20
94/07/15
94/09/06
94/11/04
94/12/30
95/03/17
95/05/12
95/07/07
95/09/04
95/12/08
96/02/02
96/04/04
96/06/01
96/07/27
96/09/21
96/11/23
97/01/18
97/03/21
97/06/20
97/08/15
97/10/17
97/12/12
98/02/13
98/04/10
98/06/12
98/08/14
98/10/09
日期

END

謝謝

敬請指教