PSN-2009-0865
CDCC-2009-100493 Rev2

2009 ISOE Asian ALARA Symposium
Aomori Japan

Precise control of Fe concentration in feedwater for Co-60 concentration reduction

Sep. 9 2009

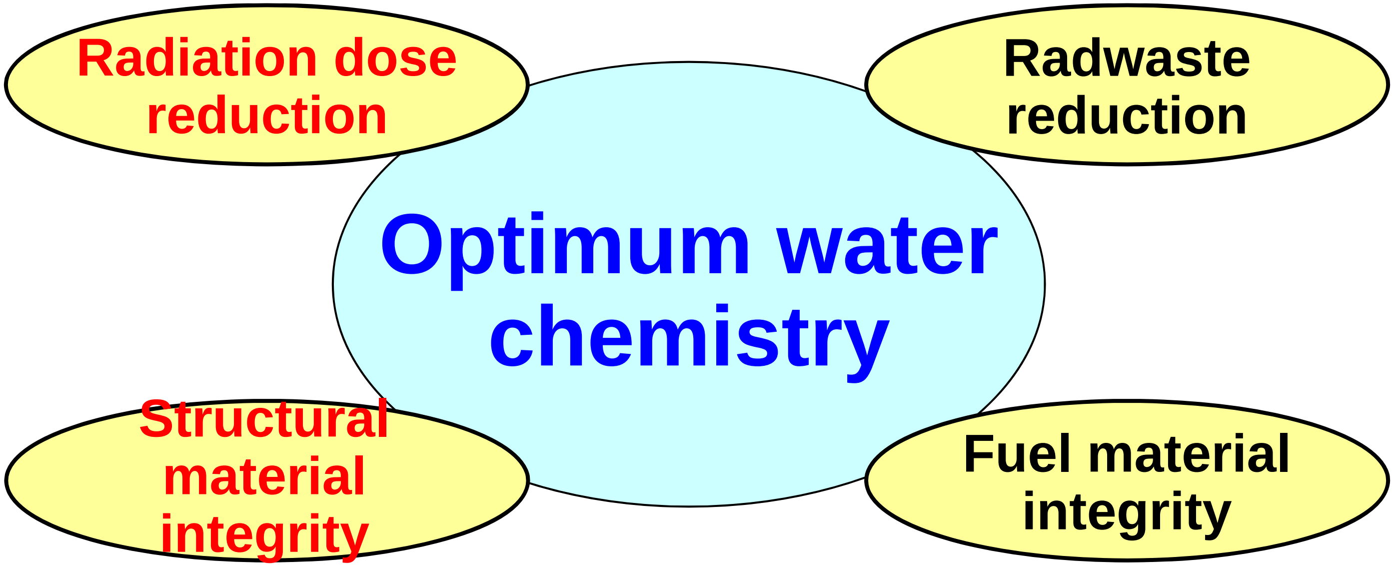
Kenji Yamazaki

Chemical System Design & Engineering Dept.
Power Systems Company
Toshiba Corporation

Contents

1. Background and Introduction

Radiation reduction

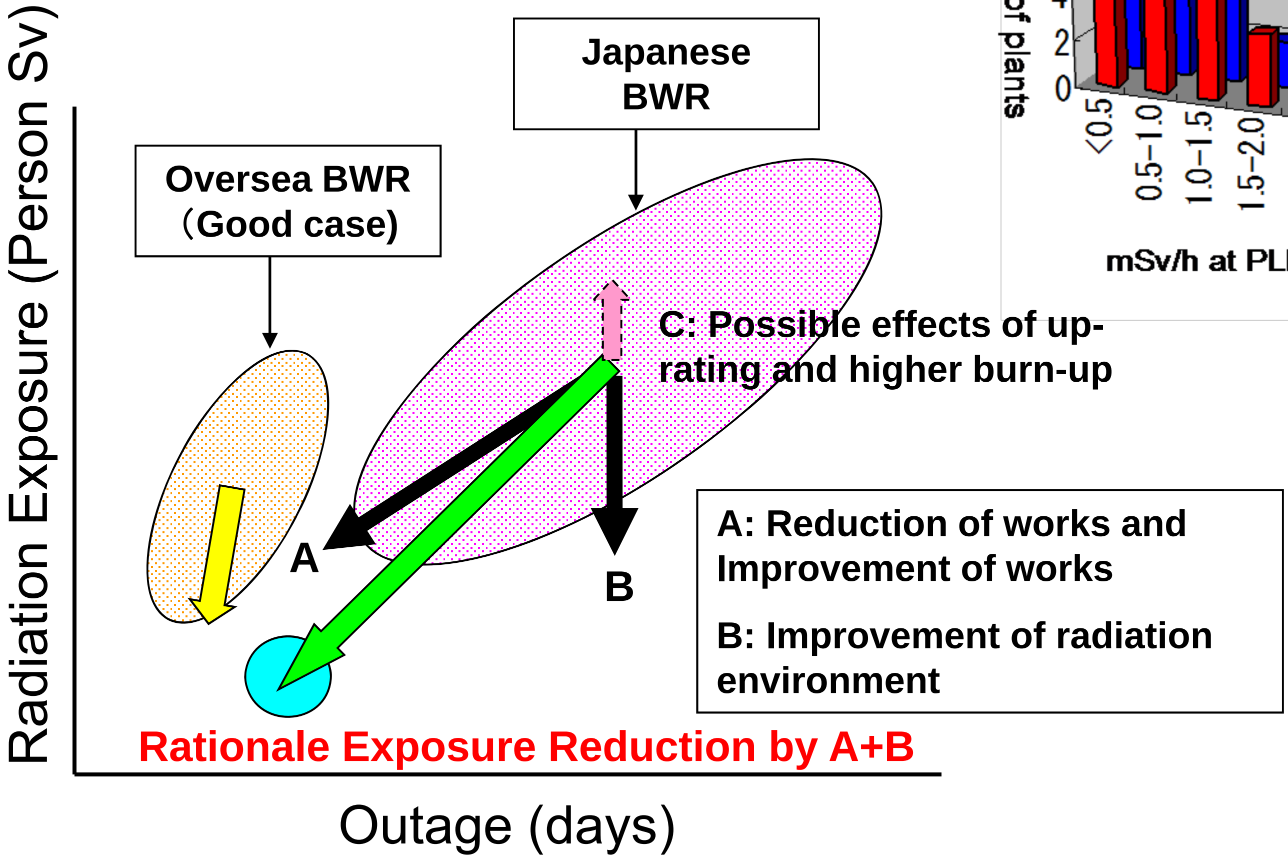


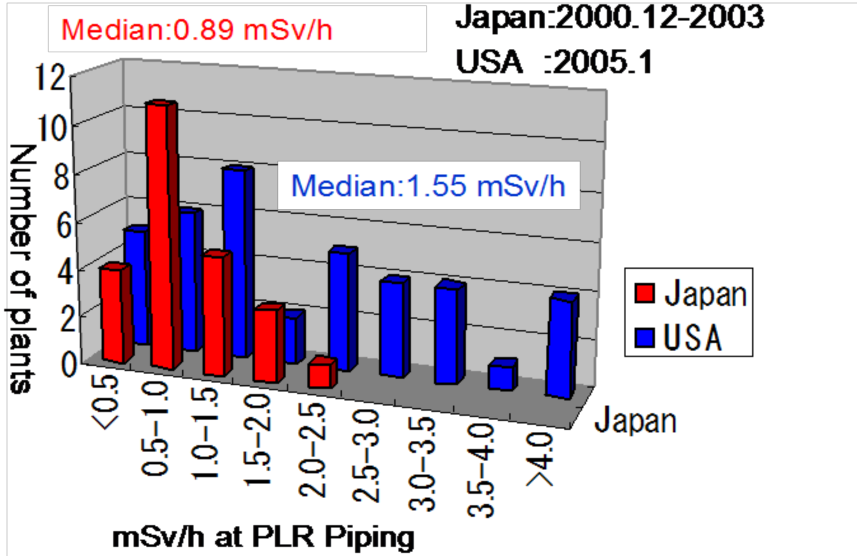
Secure and Reliable Operation

At aged BWR plants, radiation dose reduction for maintenance repair works, and mitigation of SCC are most important roles of water chemistry

1. Background and Introduction

Importance of radiation level reduction

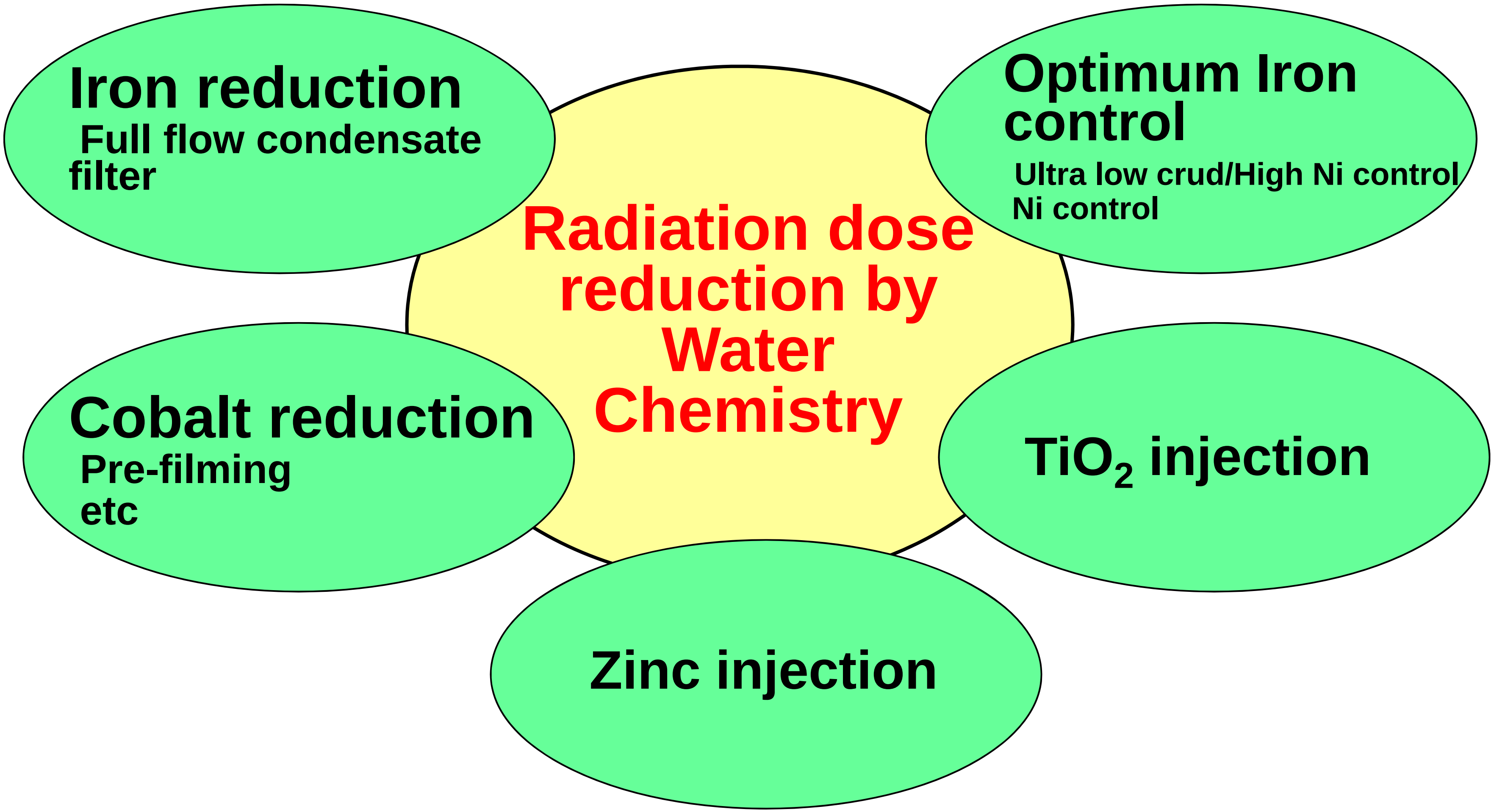




From Y. Hayashida 2007 ISOE Asian Symposium, Seoul Korea Sep 12-14 2007

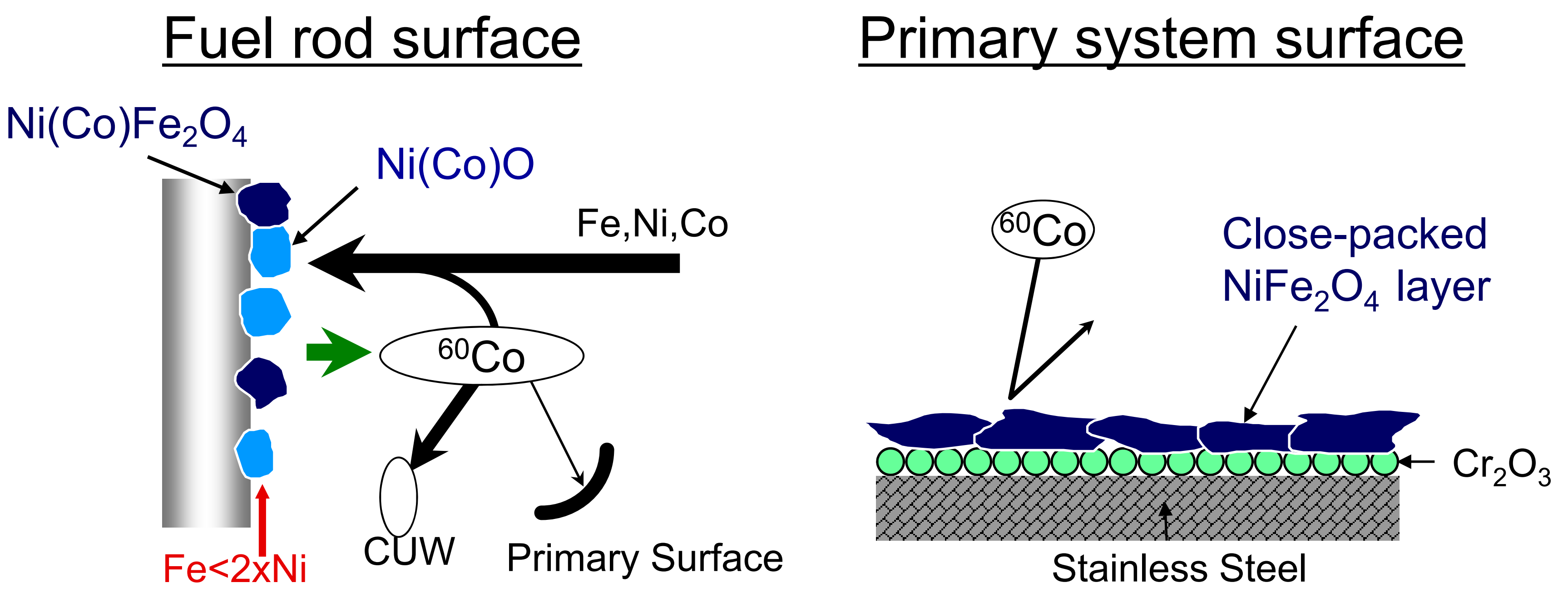
1. Background and Introduction

Water Chemistry plays a significantly important role for ALARA



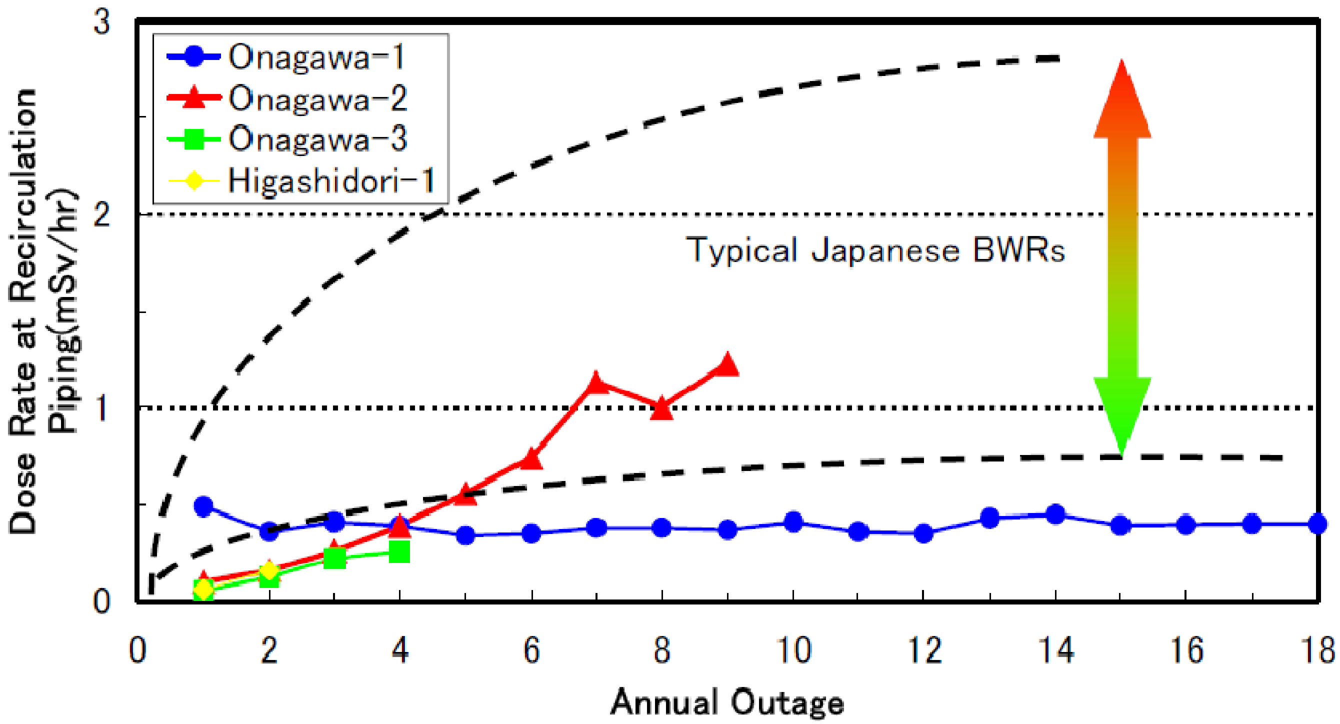
2. Experience with Ultra-Low-Fe/High Ni control

Schematic drawing of "Ultra-Low Crud High Ni control" chemistry



- Ni(Co)O is formed on fuel rod surface due to deficiency of iron (Fe<<2xNi) and Co-60 concentration in primary water is higher than Fe/Ni ratio control plants.
- Close-packed $NiFe_2O_4$ layer on primary system surface suppresses Co-60 deposition on the surfaces.
- Totally, Co-60 on primary surface (dose rate) can be suppressed low.

2. Experience with Ultra-Low-Fe/High Ni control



Minoru Saito et al. "Experiences and Optimization of Feedwater iron Control in Tohoku electric Power BWRs", Int. Conf. on Water Chemistry of Nuclear Reactor Systems Berlin, Germany Sep.15-18 (2008)

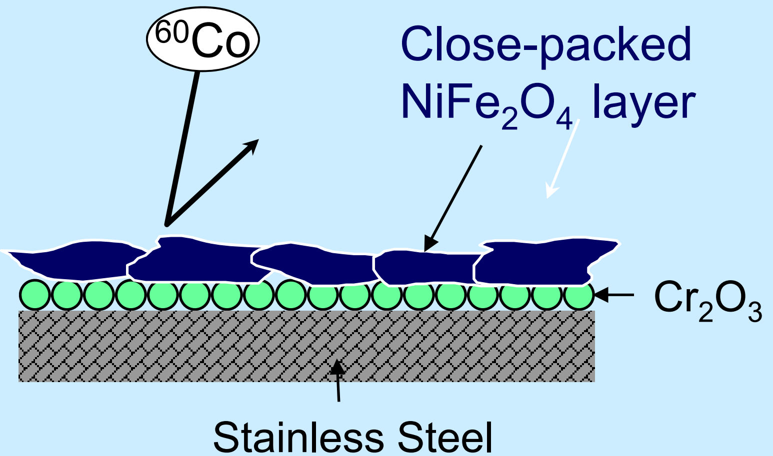
- Extremely low radiation level was achieved up to 4th cycle operation
- Radiation level increased for a long term operation.
- Evaluation of causes and improvement of water chemistry control were initiated.

2. Experience with Ultra-Low-Fe/High Ni control

Evaluation of experiences of Ultra-Low-Crud- High Ni Control of BWR plants

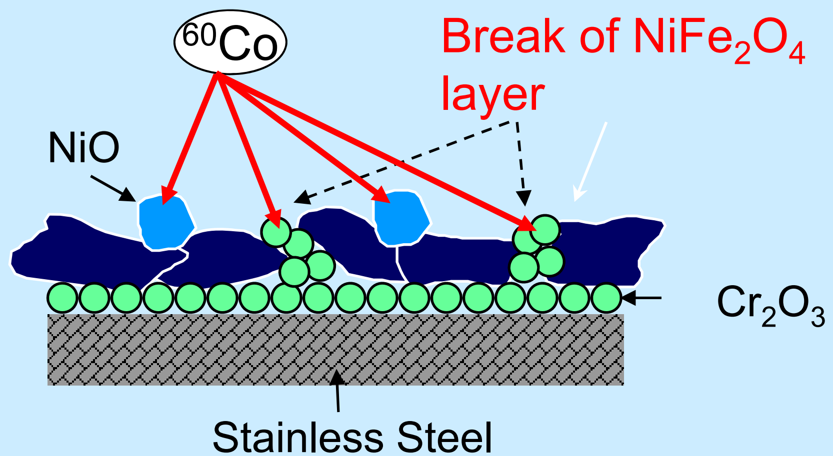
Primary system surface

Early cycles plant operation



As expected, close-packed $NiFe_2O_4$ layer on primary system surface suppresses Co-60 deposition on the surfaces.

After long plant operation

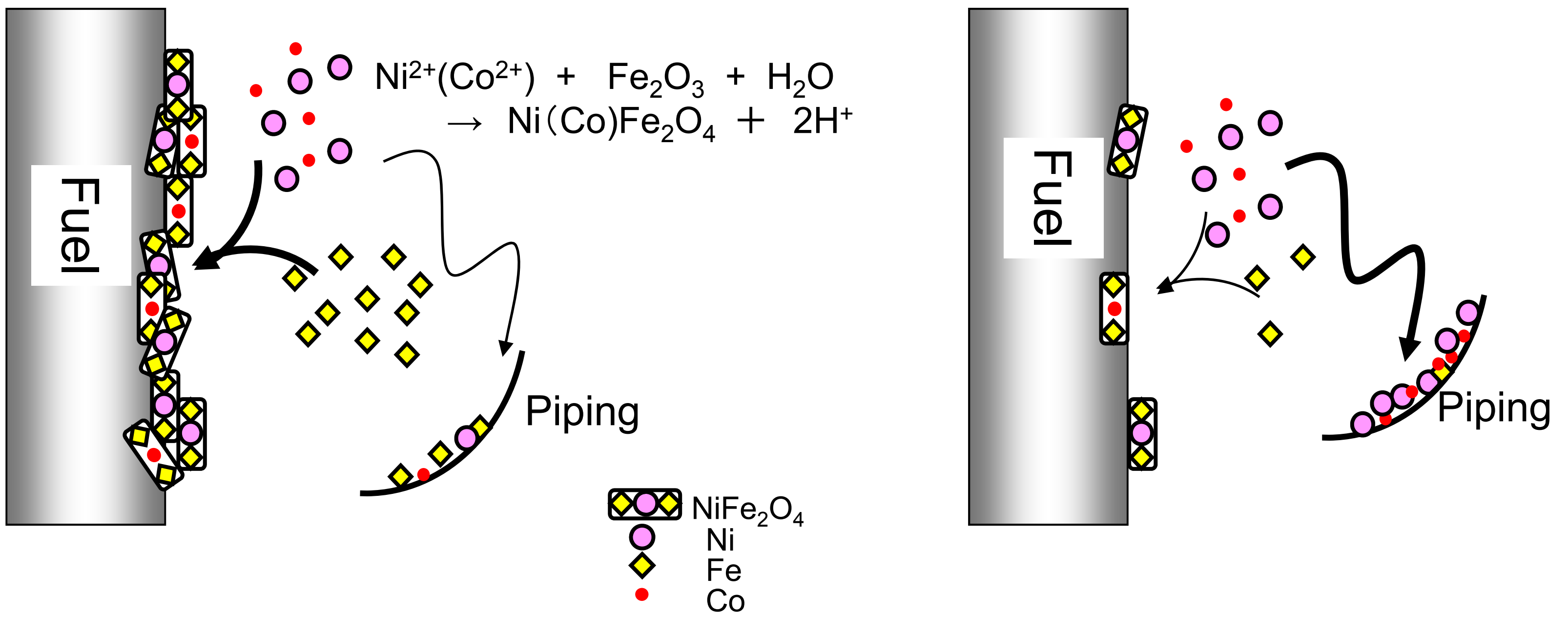


NiO and break of $NiFe_2O_4$ layer were observed.Too high Ni concentration in primary water is attributed to these unexpected phenomena.
It is concluded that Co-60 is incorporated in NiO and Cr_2O_3 (and excess $NiFe_2O_4$)

3. Ni control by precise feedwater iron control

Ni concentration control by Fe solution injection

Optimum Fe conc. **Too low Fe con.**



Ni(Co) fixed on fuel rods as $Ni(Co)Fe_2O_4$
→Ni(Co) conc. low
→Ni(Co) deposition on piping lowered
→Exposure low

Ni(Co) does not fixed on fuel rods
→Ni(Co) conc. high
→Ni(Co) deposition on piping high
→Exposure high

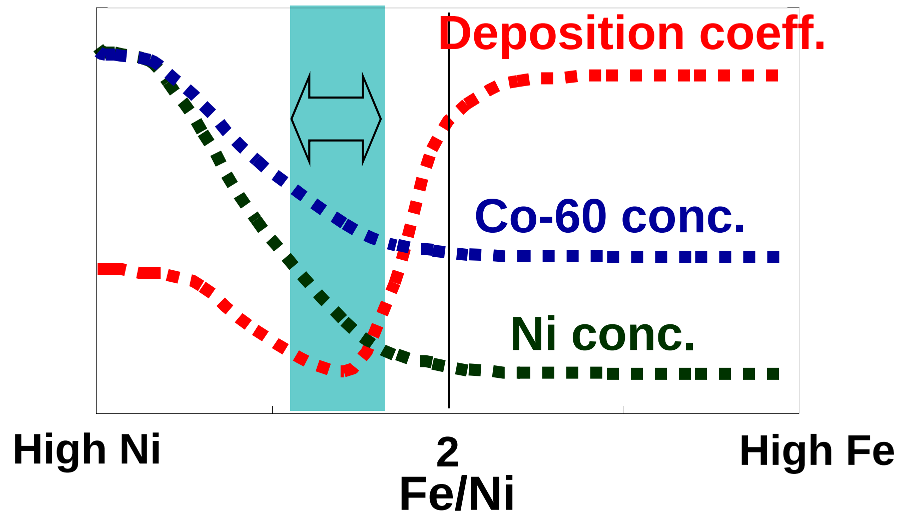
3. Ni control by precise feedwater iron control

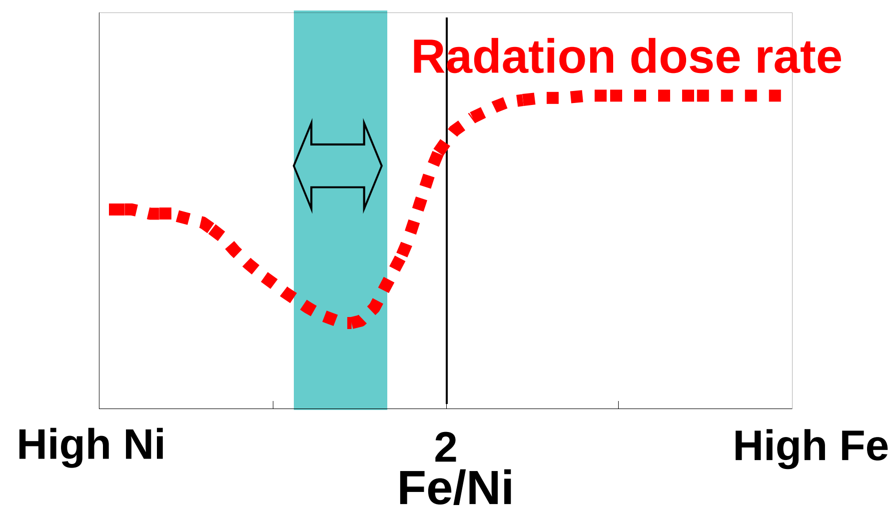
Precisely control feedwater Fe concentration, corresponding to Ni input: Range of ⟺ in the right Fig.

Ni concentration in primary water is controlled in optimum range.

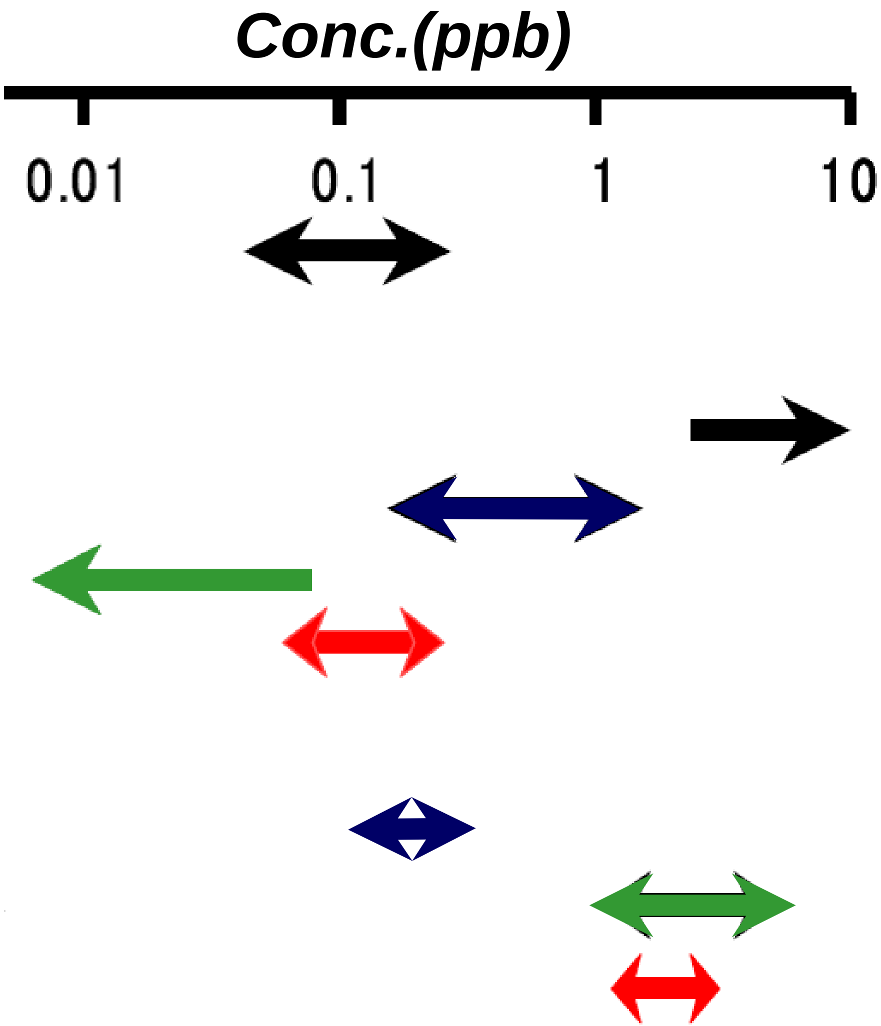
Co-60 concentration and deposition coefficient on primary surface are reduced.

Radiation dose rate on primary surface can be minimized.





Ni and Fe concentration control ranges for types of water chemistry



Feedwater

Ni concentration

Fe concentration

High crud plant

Low crud plant Ni/Fe control

Ultra low crud high Ni

Ni concentration control

Reactor water

Ni concentration

Low crud plant Ni/Fe control

Ultra low crud high Ni

Ni concentration control

3. Ni control by precise feedwater iron control

[1] Issues to be solved

Fe concentration in feedwater should be precisely controlled.

Iron compound and its injection method should be improved.

[2] Goals

Feedwater iron concentration : 0.1 – 0.2 ppb(+- 10%)

Efficient reaction with nickel and cobalt

Affinity with Zircaloy fuel rod surface

Minimum release from fuel surface

[3] Approach

To achieve the above goals, four tests were performed:

(1)Concentration stability in prepared solution

(2)Reactivity of iron with nickel (cobalt)

(3)Deposition on fuel rod surface

(4)Deposition loss on feedwater heater

Fe compounds for tests

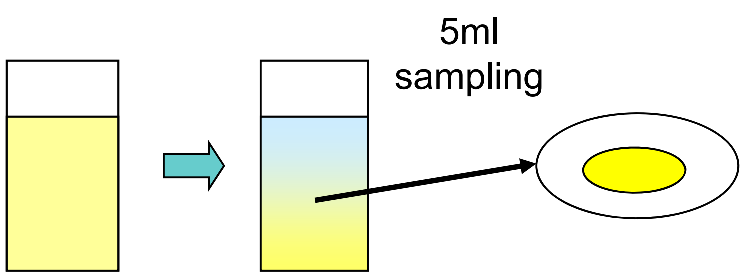
- Fe compounds were subjected to the tests.
- Compounds are selected in categories A: insoluble form (inorganic), B: low solubility (organic), C: high solubility (organic)

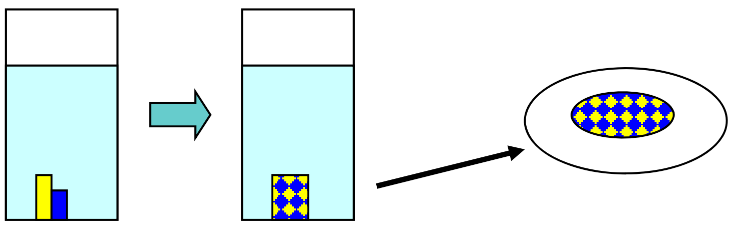
Category	No.	Name	Chemical formula	Vender	Memo
Gr.A	1	a oxyhydroxide	αFeOOH	A	Consists of Fe, H and O Insoluble
	2	γ oxyhydroxide	γFeOOH	A	
	3	Iron hydroxide oxide	FeO(OH)	C	
	4	Magnetite	Fe_3O_4	C	
Gr.B	5	Iron oxalate dihydrate	$FeC_2O_4 \cdot 2H_2O$	B	Consists of Fe, H, O and C Low solubility
	6	Iron fumarate	$FeC_4H_2O_4$	B	
	7	Iron acetate	$Fe(OH)(CH_3COO)_2$	B	
Gr.C	8	Iron lactate trihydrate	$Fe(CH_3CHOHCOO)_2 \cdot 3H_2O$	A	Consists of Fe, H, O and C High solubility
	9	Iron lactate trihydrate	$Fe(CH_3CHOHCOO)_2 \cdot 3H_2O$	B	
	10	Iron citrate n-hydrate	$FeC_6H_5O_7 \cdot nH_2O$	C	

Procedures of tests on stability and reactivity

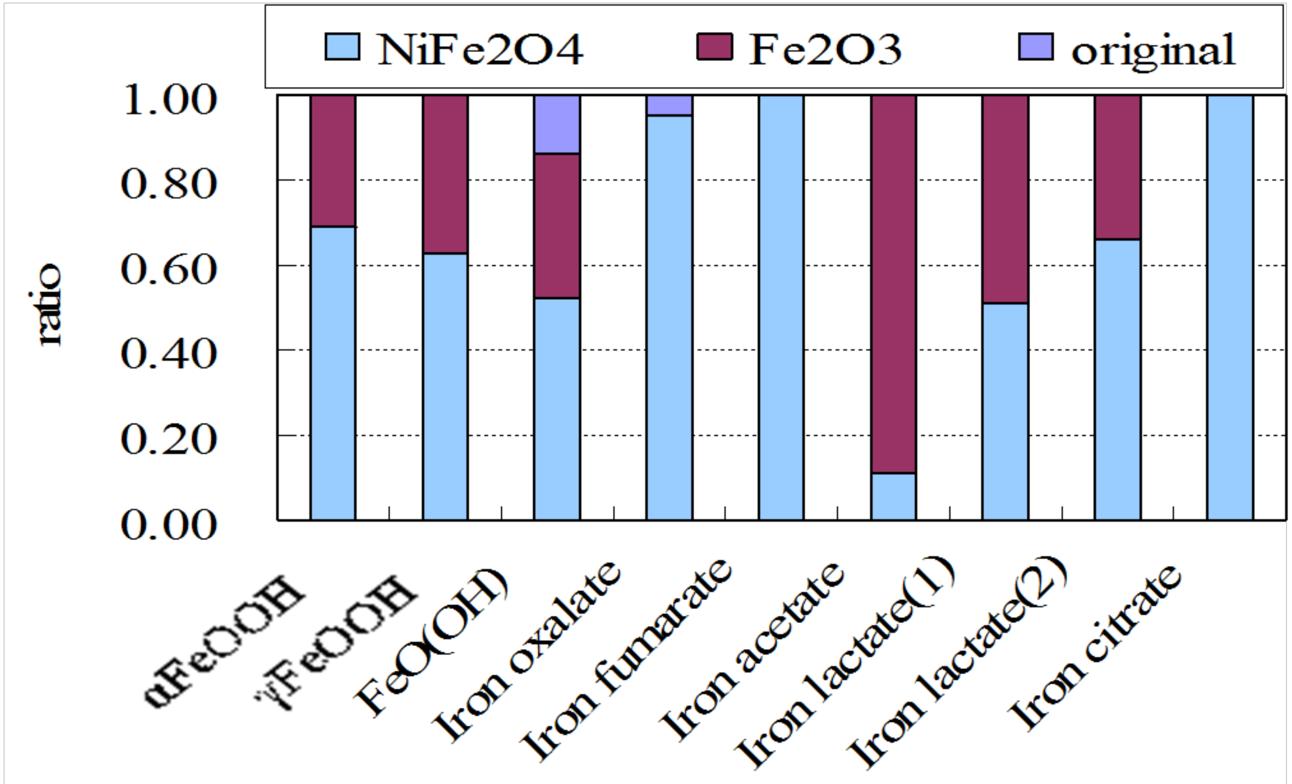
Fe (150ppm) in 500ml water
↓
Stirring by ultrasonic 10min.
↓
Stand for 17h @ R.T.
↓ **Filtration (0.1mm)**
XRF Analysis

Fe compound 2.5mg(as Fe) with/without $NiSO_4$ 2.5mg(as Ni) in 15ml water
↓
Stirring by ultrasonic 10min.
↓
558K x 17h
↓
Filtration(0.1um)
↓
XRD and XRF analysis





Results of tests on reaction with nickel



Reactivity with Ni(Co)
iron oxalate,iron fumarate,iron citrate
>αFeOOH,γFeOOH,FeOOH,iron lactate
>iron acetate

Procedure of tests on fuel rod surface deposition

Water(250ml/min.) with Fe injection(2.5ml/min.)

↓

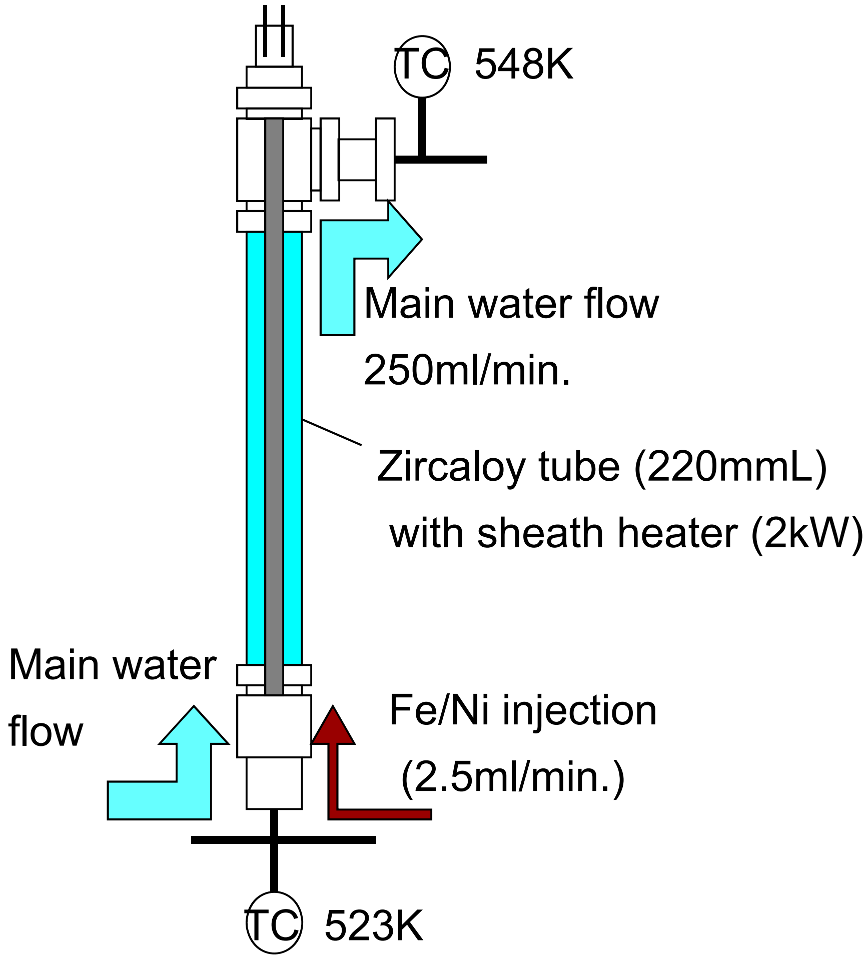
Fe/Ni=100/10ppb

↓

Heated on the fuel surface for 96h

↓

Fe deposition on the fuel analyzed by XRF and XRD



Results of tests on fuel rod surface deposition (Example)

Test condition

Test coupon：Zircaloy2
12.27mmφ, 220mm L

Temperature: 250℃ (inlet)

Pressure：7MPa

Flow rate：250mL/min

Heat ：2KW（sheath heater）

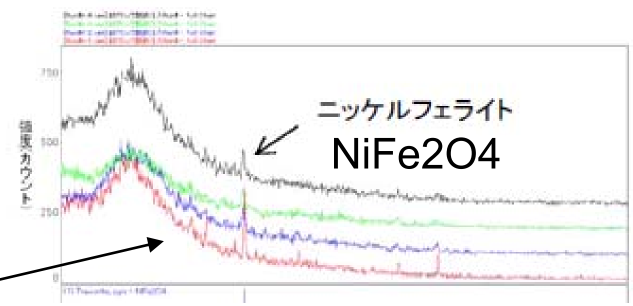
Outlet quality：20%

Iron compound：Iron Oxalate

Visual observation of fuel rod test coupon after a deposition test

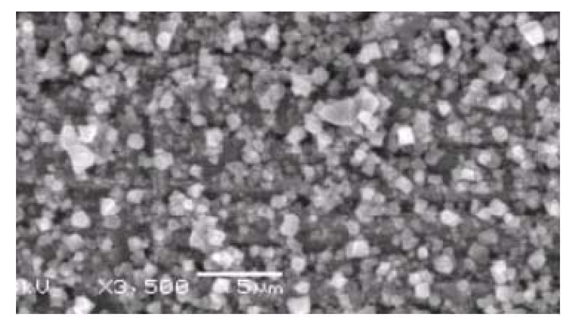
Oxide structure (XRD)

Ni ferrite ⇒ High reactivity with Ni



Oxide feature (SEM)

Uniform, close-packed deposition⇒
Minimum release



5 μm

Procedure of tests on feedwater heater train deposition loss

Fe compound (150ppm) solution

↓

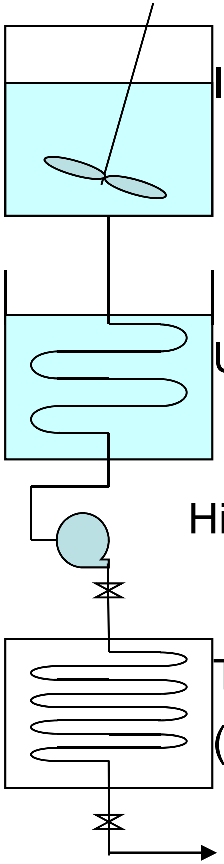
Sent to thermostatic oven(2.5ml/min.)

↓

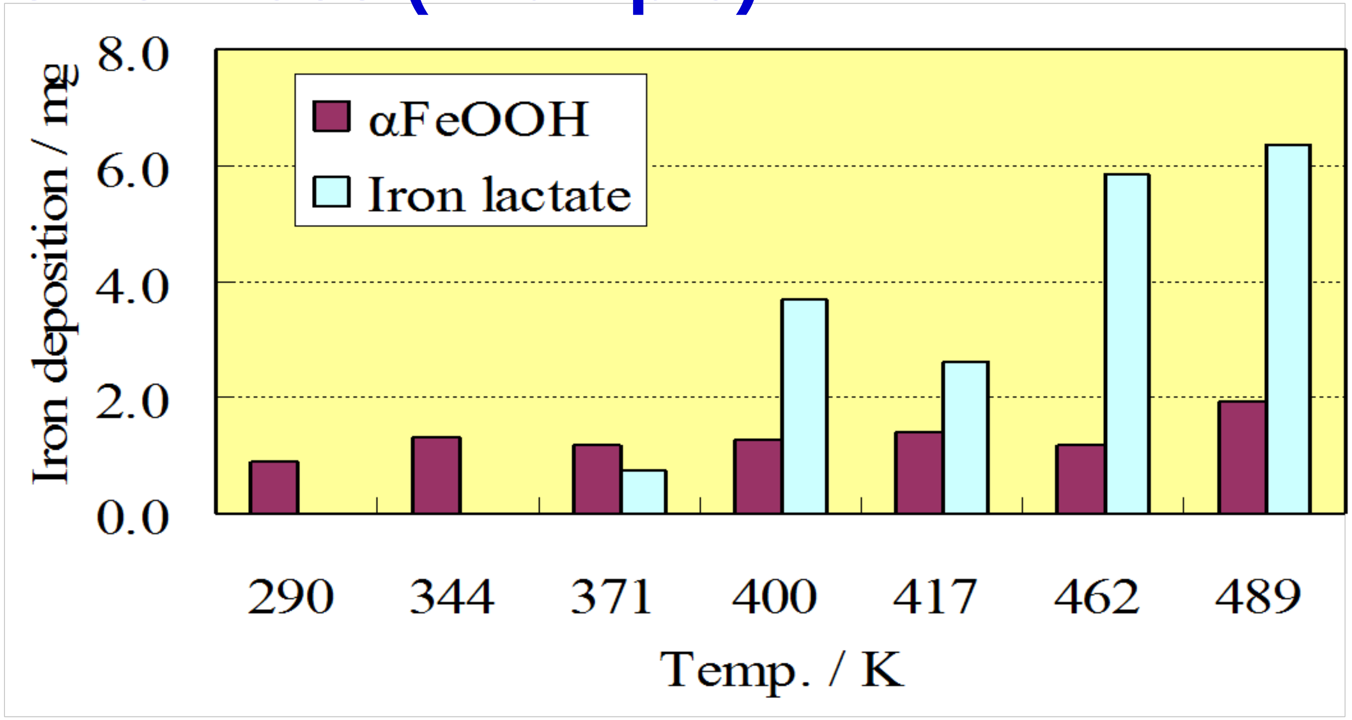
Heated (290 ~489K) for 3h

↓

Fe deposition in the pipe analyzed by XRF



Results of tests on feedwater heater train deposition loss (Example)



αFeOOH: low in wide temperature range
Iron lactate: very low at low temp. but high at high temp.

Effectiveness of iron injection

	Test results			Total effectiveness
	Reactivity (Ni/Co)	Fuel Deposition	Deposition Loss	
αFeOOH	~70%	~75%	~15%	~45%
Iron oxalate	~95%	~80%	~40%	~46%
CF bypass*	~70%	~80%	~20%	~45%

***Test results of CF bypass are estimated value.**

Total effectiveness = (Reactivity) X (Fuel Deposition) X (1-Deposition Loss)

If it is possible to inject at high temperature point (close to RPV), iron citrate my be also candidate.

The effectiveness same as CF-bypass is obtained by iron compound injection

Ni concentration control by Fe injection

[1] Several kind of iron compounds were tested by following experiments;

(1)Stability test

(2)Ni(Co) reaction test

(3)Depositin loss test

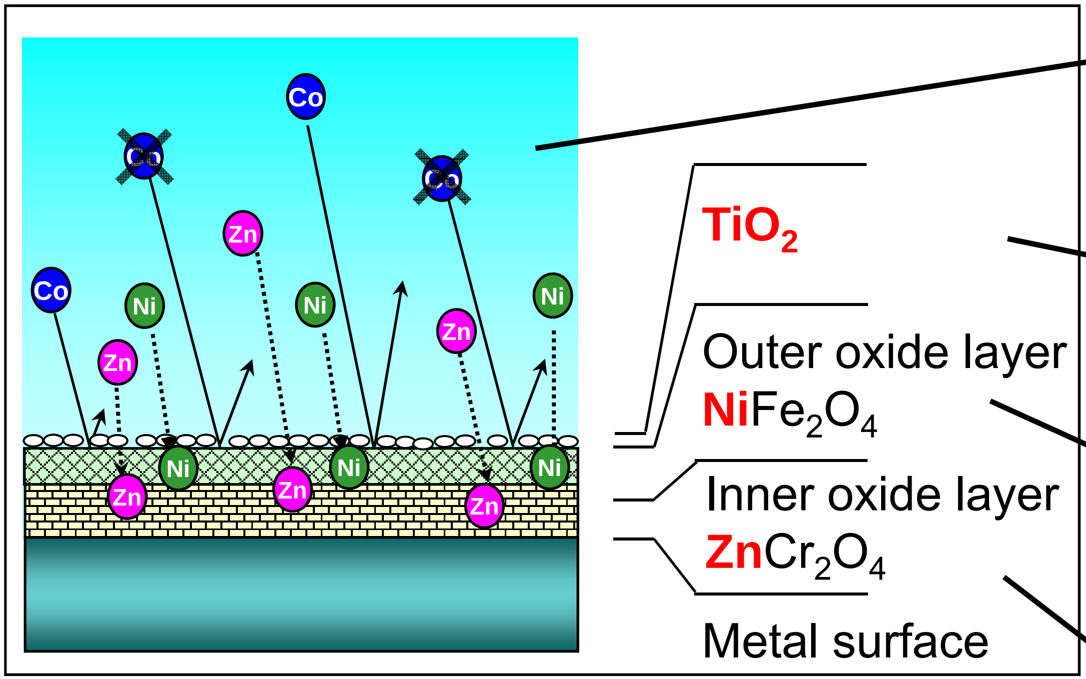
(4) Fuel surface deposition test

[2] αFeOOH and iron oxalate are the candidate as the injected compound.

4. Conclusion

Optimum reactor water Ni control is moved to "intermediate high" concentration, from "high concentration".

Radiation dose rate can be minimized by synergistic effects of Ni, TiO_2 and Zn.



Co-60 reduction by Ni control (precise Fe control)

Co-60 deposition reduction and mitigation of SCC by TiO_2

Co-60 deposition reduction by Ni control (precise Fe control)

Co-60 deposition reduction by Zinc injection

TOSHIBA

Leading Innovation >>>