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# **Pre-Filming Method of Reducing Metal Release from Alloy 690 for SG in Primary Water of PWR**

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# Background

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- 1) **Radioactive resources** are mainly **released metal, Co and Ni etc.** from primary water structures in PWR.
- 2) Especially, **area of SG (Steam Generator) tubes** contacting with the primary water is the **largest** among those of primary water structures.
- 3) Therefore, **reduction of metal release from SG tubes** is the **most effective** in order to reduce exposure.

# Ni Release from SG Tubes

## Steam Generator (SG)

Ni releases from SG tube to primary water.



Move to reactor core.

## Reactor Core



Ni is transformed to radioactive Co.

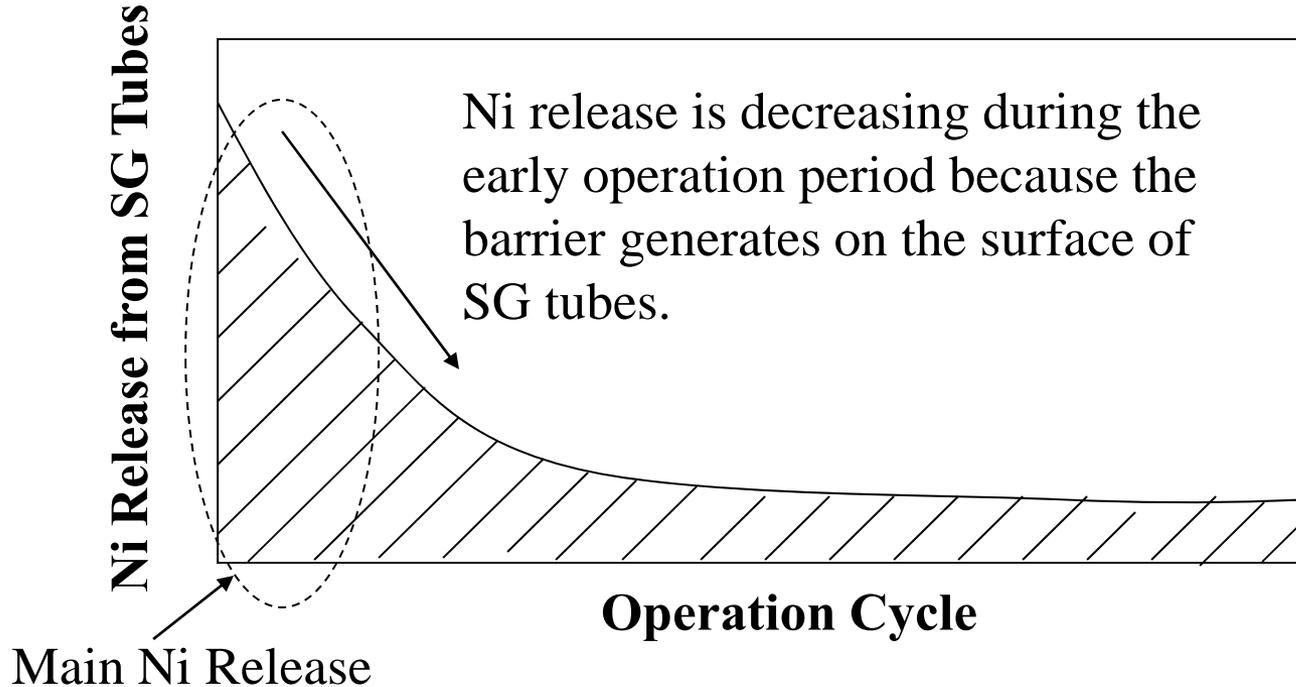
- 1) Radioactive nuclide that governs radiation effect is mainly  $^{58}\text{Co}$  which comes from Ni base alloy used as SG tube.
- 2) It is important to study the method of reducing metal release from SG tube from the viewpoint of reducing exposure.

Figure 1

Adhere to primary circuit structures.

# Ni Release from SG Tubes during Operation Cycle

Main Ni release from SG tubes occurs in the early operation period. In order to reduce total Ni release, **reduction of Ni release in the early operation period is the most effective.**



**Figure 2 Image of Ni Release from SG Tubes during Operation Cycle**

# Reduction of Ni Release by Pre-Filming on SG Tubes Surface

Pre-filming on the SG tube surface is expected to reduce Ni release in the early operation period.

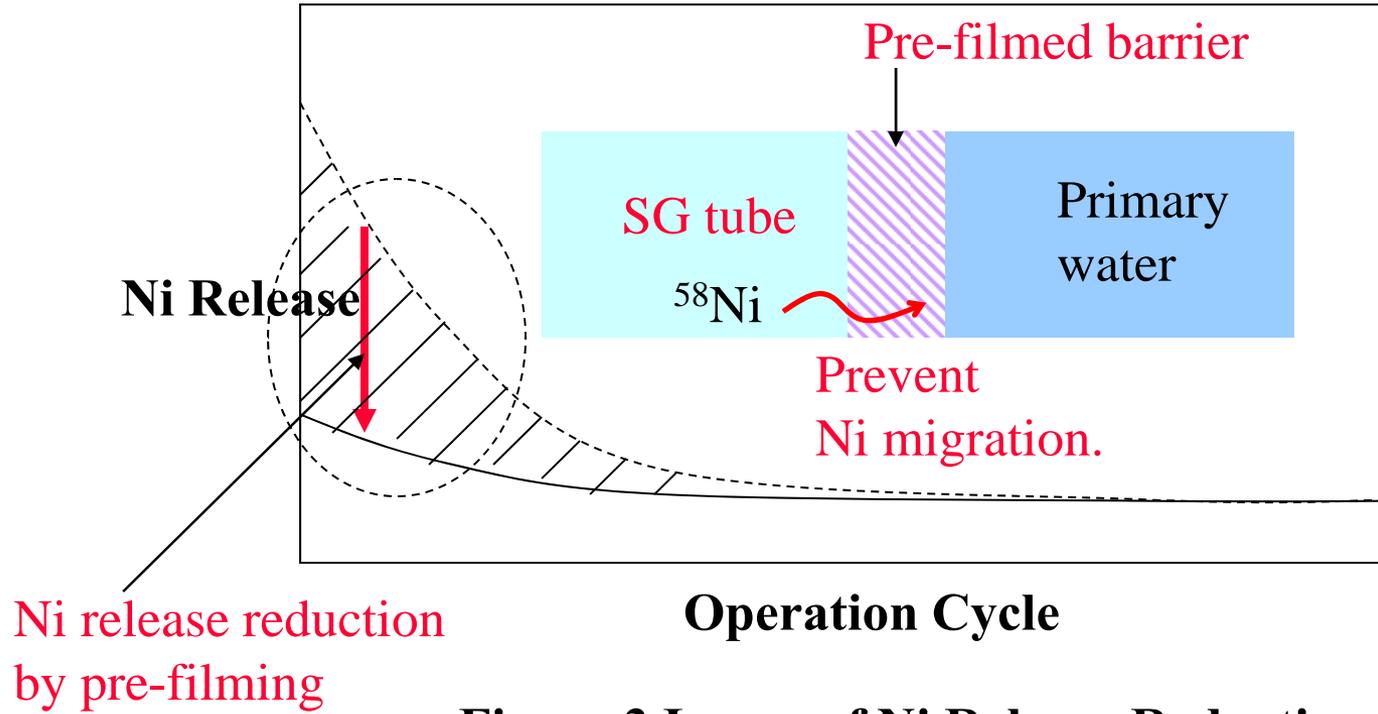


Figure 3 Image of Ni Release Reduction

# Commercial Application of Pre-Filming Method

Co release in Higashidori Nuclear Power Station, BWR, decreased by pre-filming on the surface of feed water heater tube, about 1/2 compared with other plant without pre-filming method.

(\*)Sato, Tohoku Electric Power Company, The thermal and nuclear power generation convention 2008 Sendai

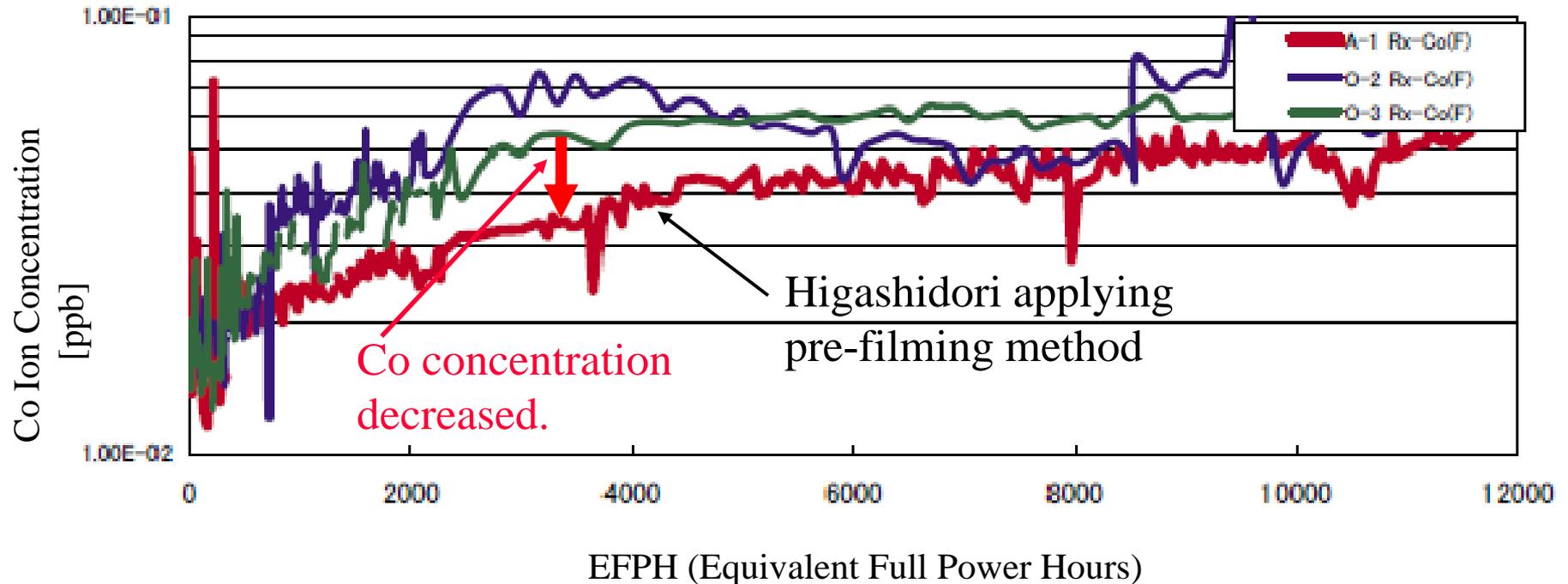
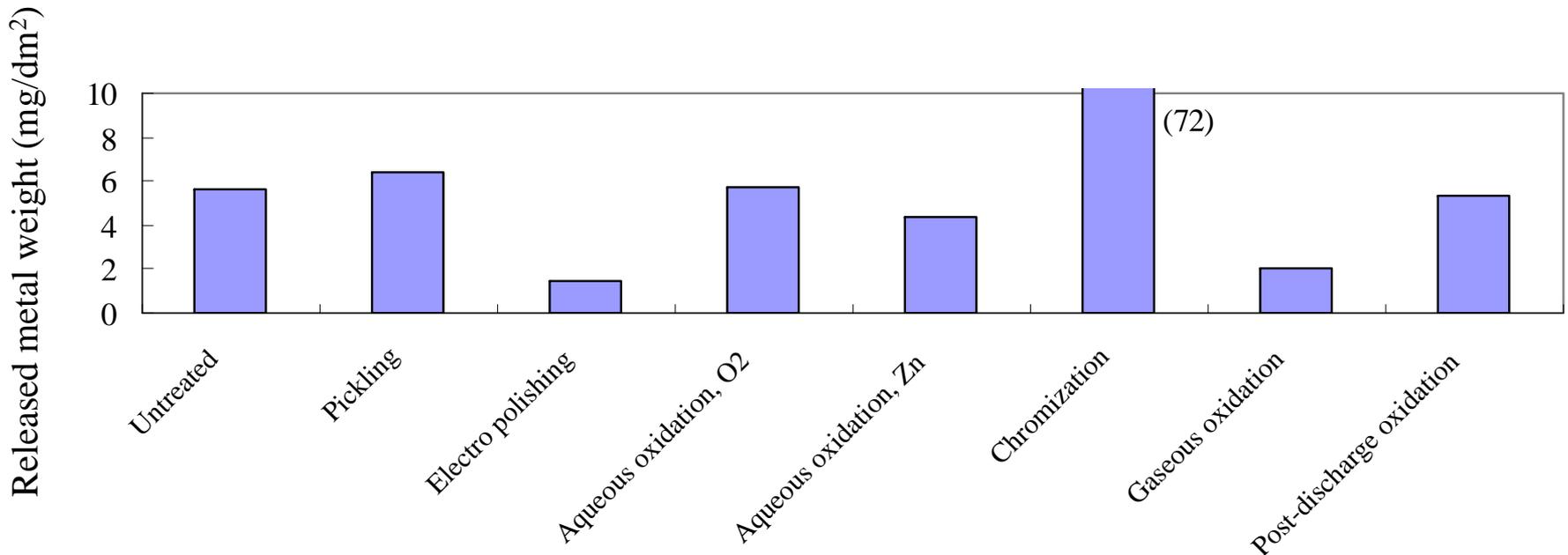


Figure 4 Process of Co Ion Concentration in Nuclear Reactor Water

# R&D of Pre-Filming Method to Alloy 690

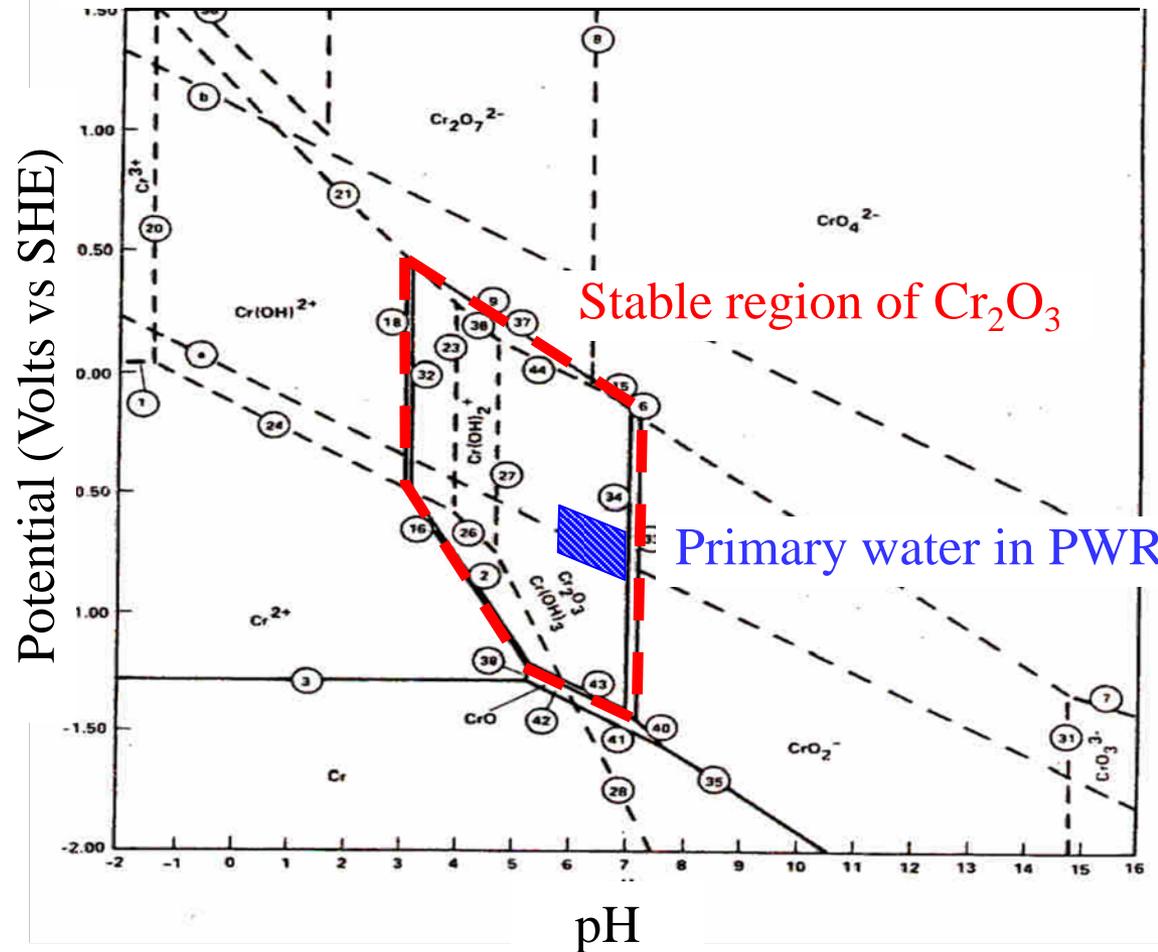
As different pre-filming method from below methods, we researched oxidation at high temperature.



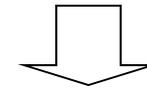
**Figure 5 Quantity of Released Metal during the Corrosion Test**

( L. Guinard, EDF, Water Chemistry of Nuclear Reactor Systems 8, BNES, 2000)

# Possibility of Cr Oxide as Pre-Film Candidate



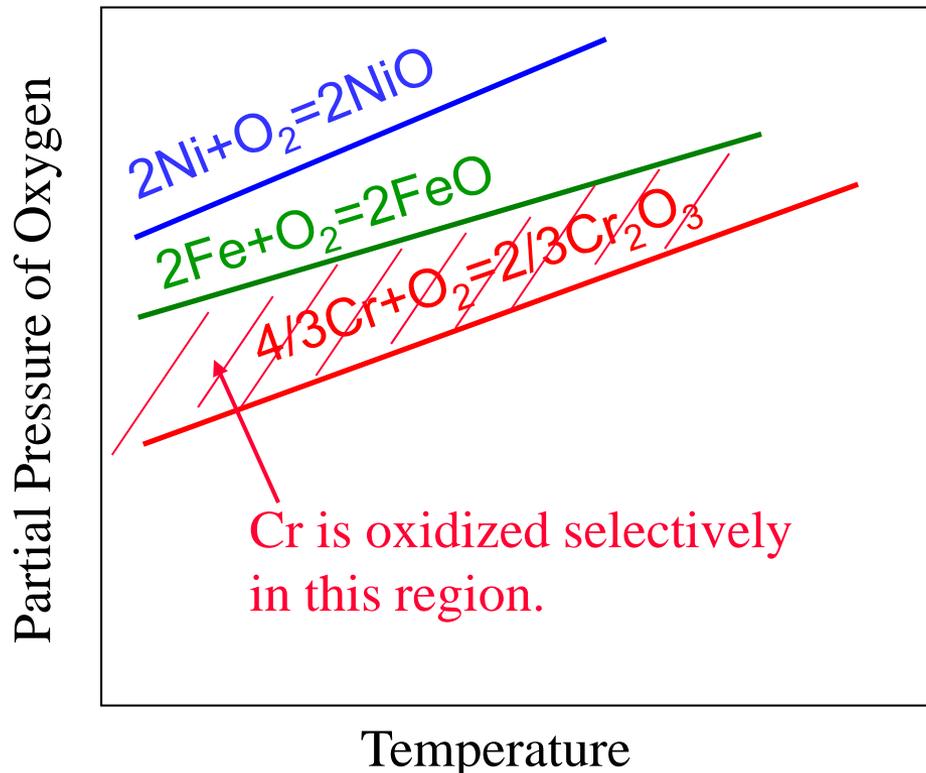
**Cr oxide is stable**  
in primary water of PWR.



We considered that  
**Cr oxide film is suitable**  
as a barrier against  
**Ni release**  
from SG tubes  
to primary water  
during operation.

Figure 6 Potential-pH Diagram of Cr in 300°C Water

# Cr Oxide on alloy 690



Alloy 690 contains 30% Cr.

We considered that **Cr oxide** can be formed on the surface of alloy 690 by control of **oxygen potential** and **temperature**.

Figure 7 Relationship between Type of Oxide and Oxidation Condition

# Objective

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- 1) Clarify the possibility of **selective oxidation of Cr in alloy 690** by controlling **oxygen partial pressure and temperature**.
- 2) Clarify the effectiveness of **pre-filming** on **Ni release reduction from alloy 690**.

# Preparation of Test Specimen

Specimen : **Alloy 690** sheet (60Ni-30Cr-10Fe)

Heat treatment

- Cold rolling
- Sampling test specimen
- Surface polishing
- **Pre-filming**

# Pre-Filming Method

- 1) Oxide film formation by oxygen at high temperature.
- 2)  $\text{H}_2\text{O}$  in  $\text{H}_2$  gas as oxygen source.

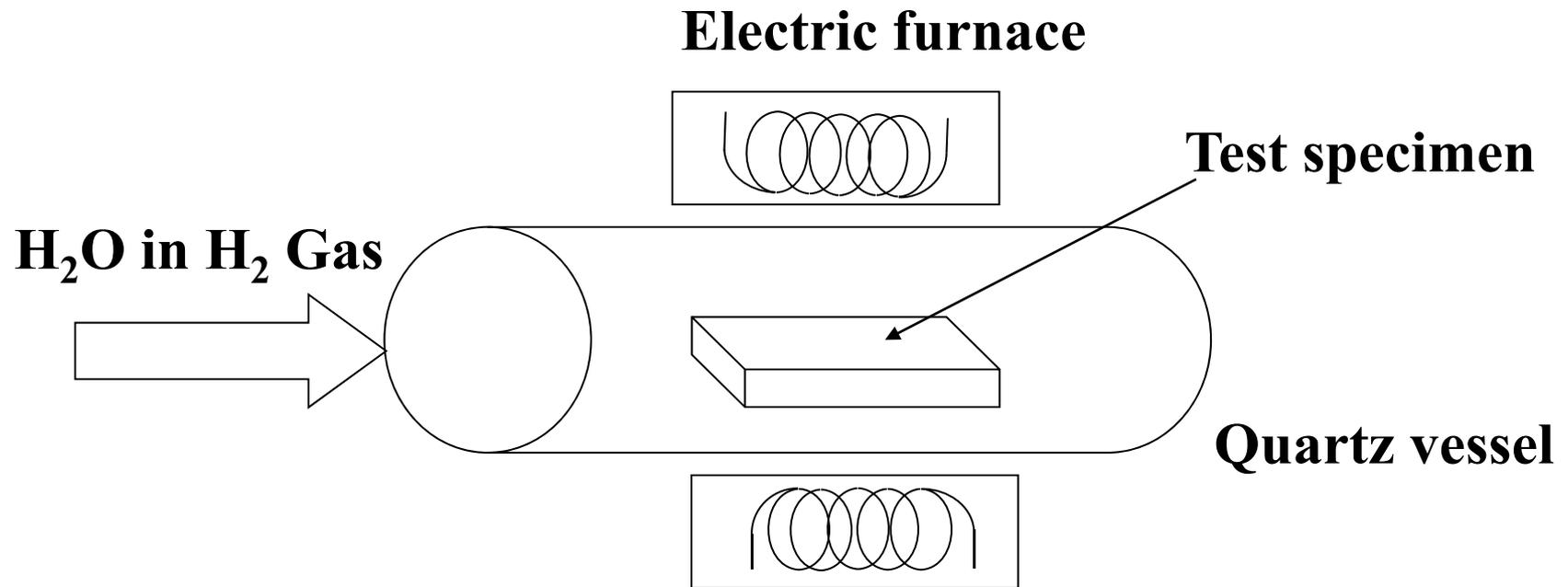
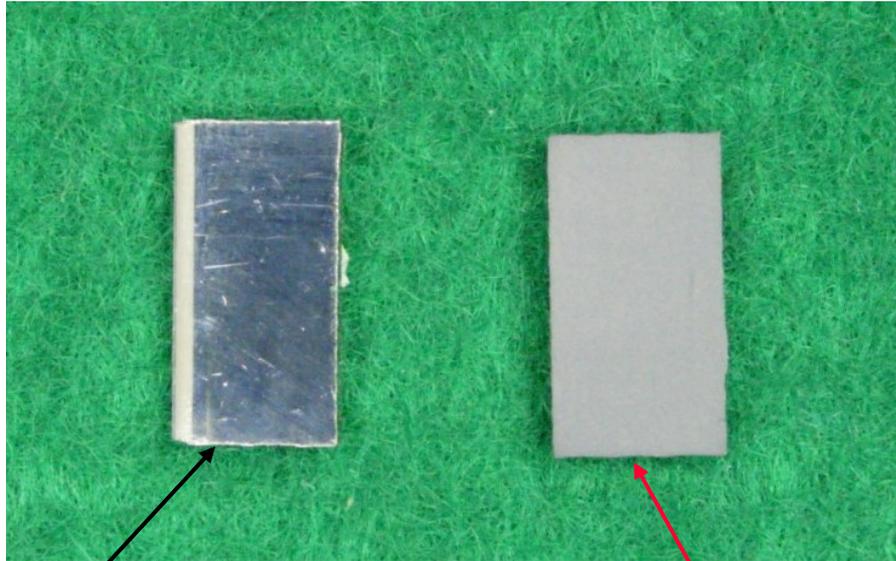


Figure 8 Pre-Filming Equipment

# Appearance of Oxide Film



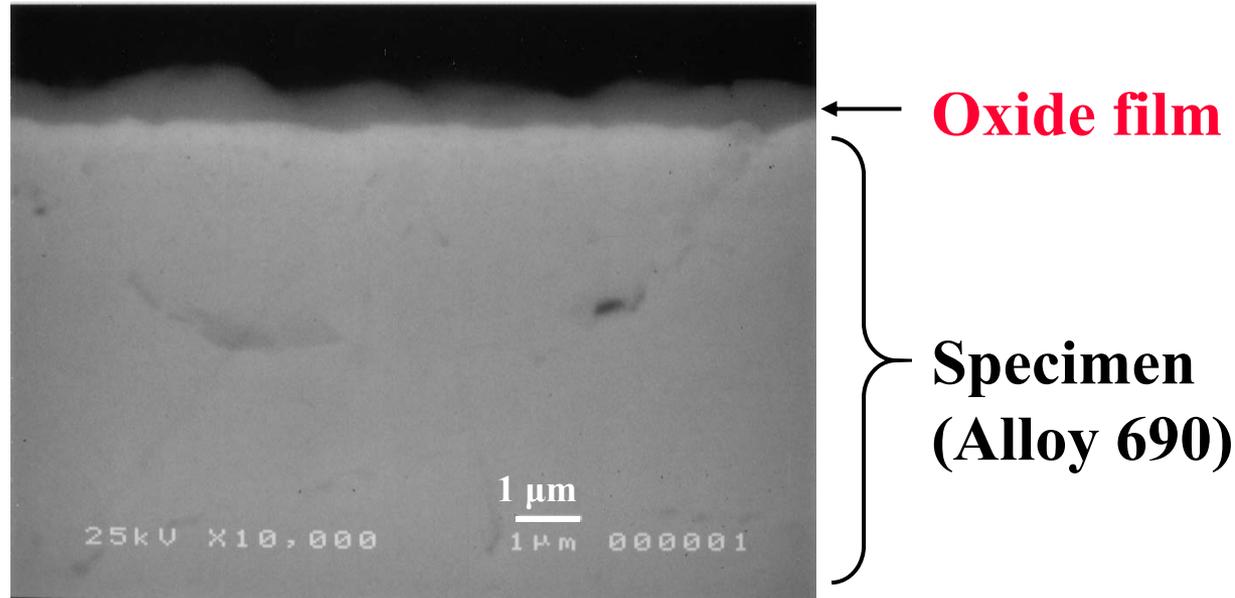
**Bare specimen  
(Before pre-filming)**

**After pre-filming**

**Photo 1 Appearance of Specimen**

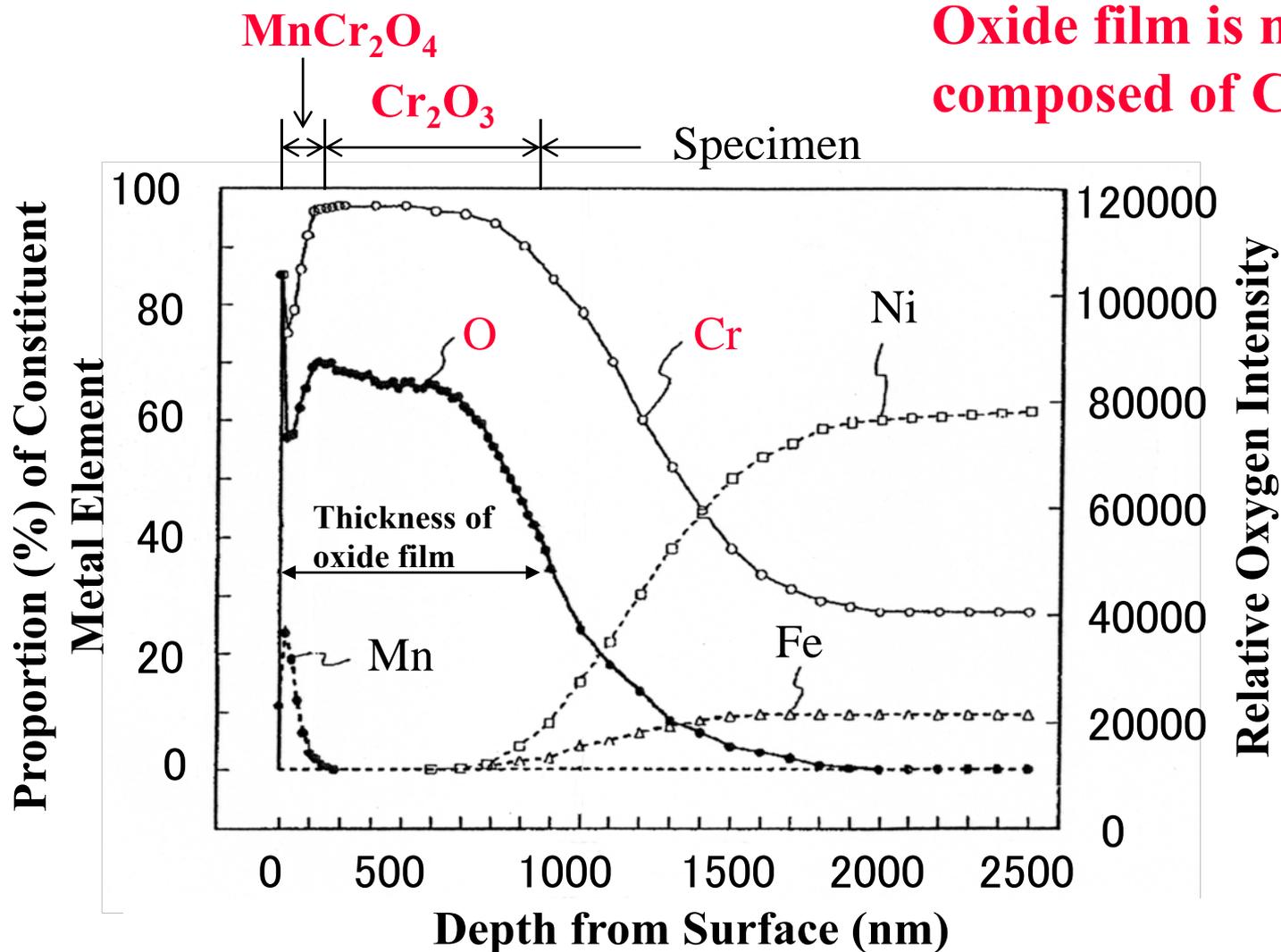
# Cross Section of Oxide Film

**Homogenous oxide film** was formed on the surface of the specimen.



**Photo 2 Cross Section of Oxide Film (SEM)**

# Composition of Oxide Film



**Figure 9 Analysis of oxide film by SIMS**

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**Ni Release Test  
on Various Thickness Oxide Film**

# Ni Release Test Method

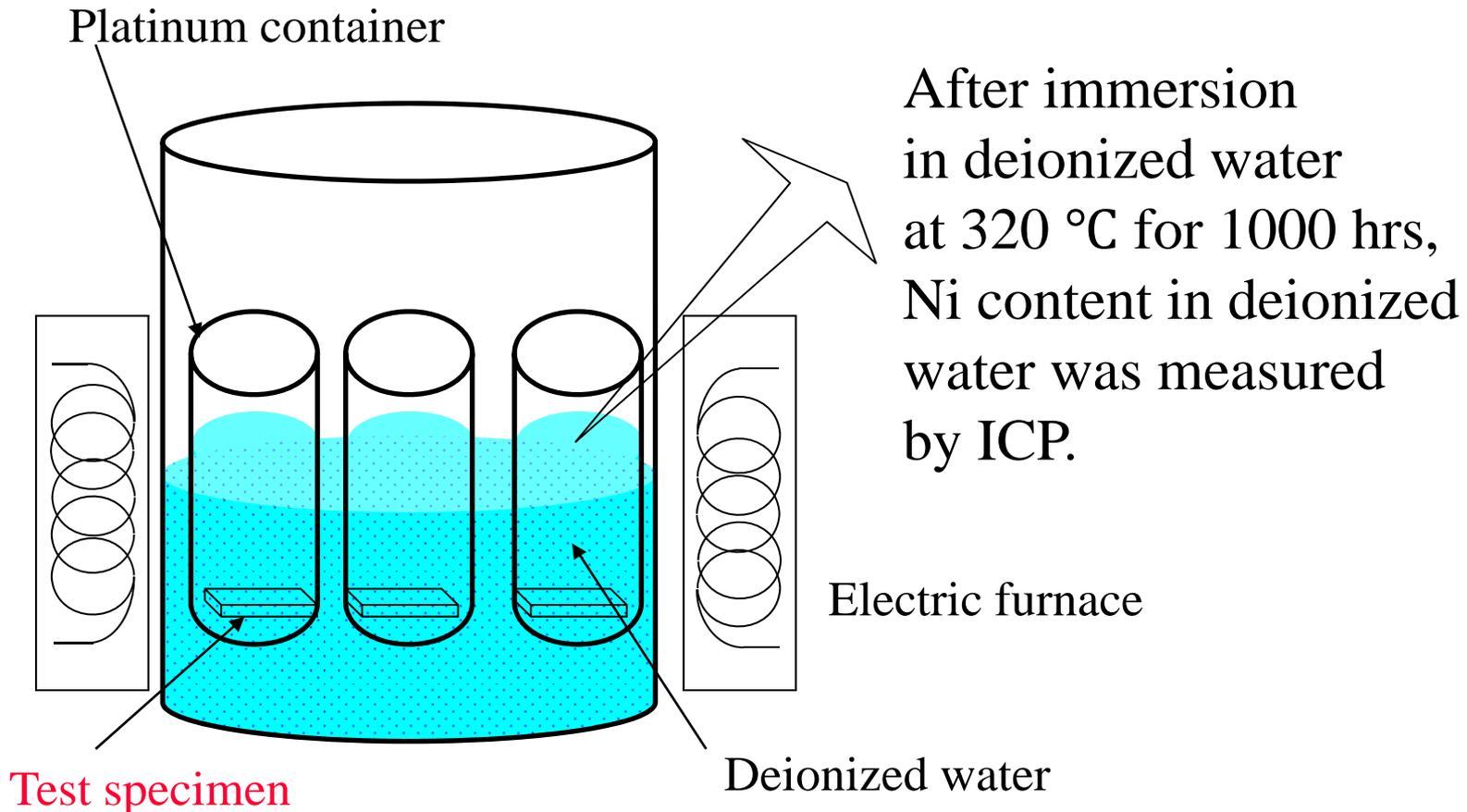
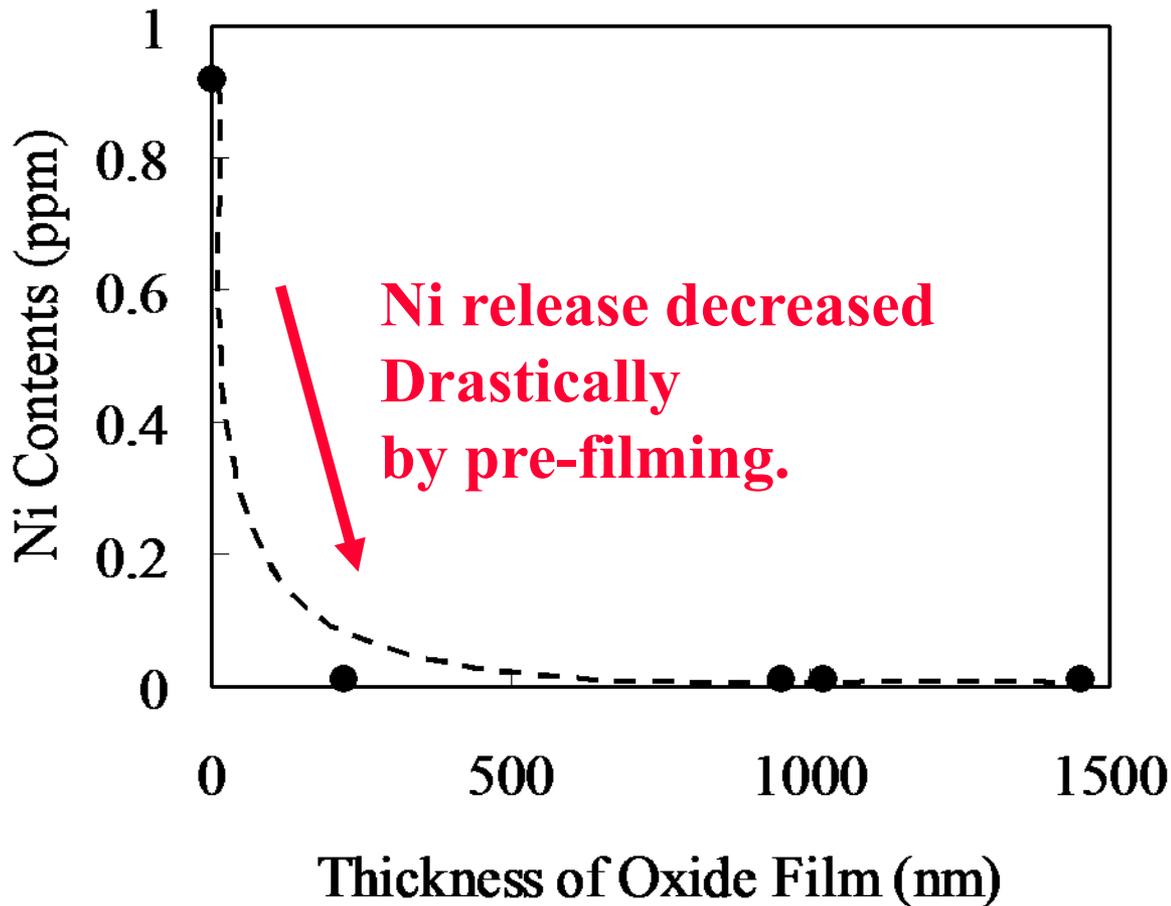


Figure 10 Ni Release Test Equipment

# Ni Release Test Result of Pre-Filmed Specimen



Ni release decreased from 0.9 ppm to 0.01 ppm by pre-filming, regardless of oxide film thickness.

Figure 11 Effect of Oxide Film on Reduction of Ni Release

# Conclusion

Following results were obtained.

- 1) **Cr oxide film can be formed on the surface of alloy 690 by using H<sub>2</sub>O in H<sub>2</sub> gas at high temperature.**
- 2) **The oxide film is mainly composed of Cr<sub>2</sub>O<sub>3</sub>.**
- 3) **Pre-filming of Cr<sub>2</sub>O<sub>3</sub> decreased Ni release from alloy 690 by a factor of 0.1.**
- 4) **Ni release from SG tubes in PWR can be expected to reduce by this pre-filming.**

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**Thank you for your attention.**