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

2009 ISOE North American ALARA Symposium

January 12, 2010

Sumitomo Metal Industries, Ltd.
Akihiro Uehira
Manabu Kanzaki
Kazuyuki Kitamura
Hiroyuki Anada

Contents

Background

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.**

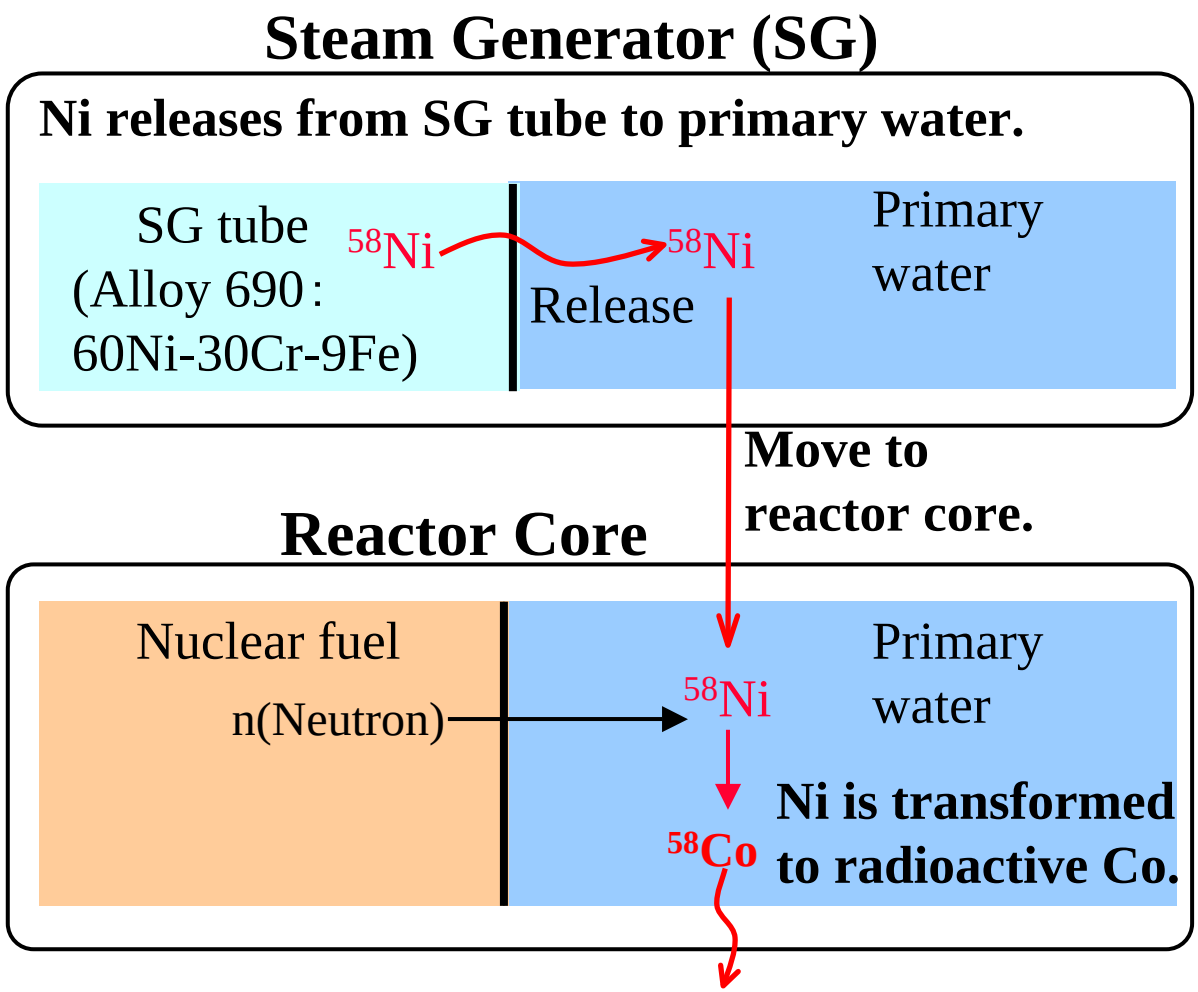
4) **We consider that pre-filming method of SG tubes is possible method to reduce metal release.**

Expected Benefit by Pre-filming SG Tubes

Table 1 Expected Benefit

Content	Expected benefit
Radiation management	Dose rate decrease
Plant performance	Clean up time during outage decrease Cost reduction
Fuel reliability	Reduction of AOA (Axial Offset Anomaly)

Ni Release from SG Tubes



1) Radioactive nuclide that governs radiation effect is mainly ^{58}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

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.

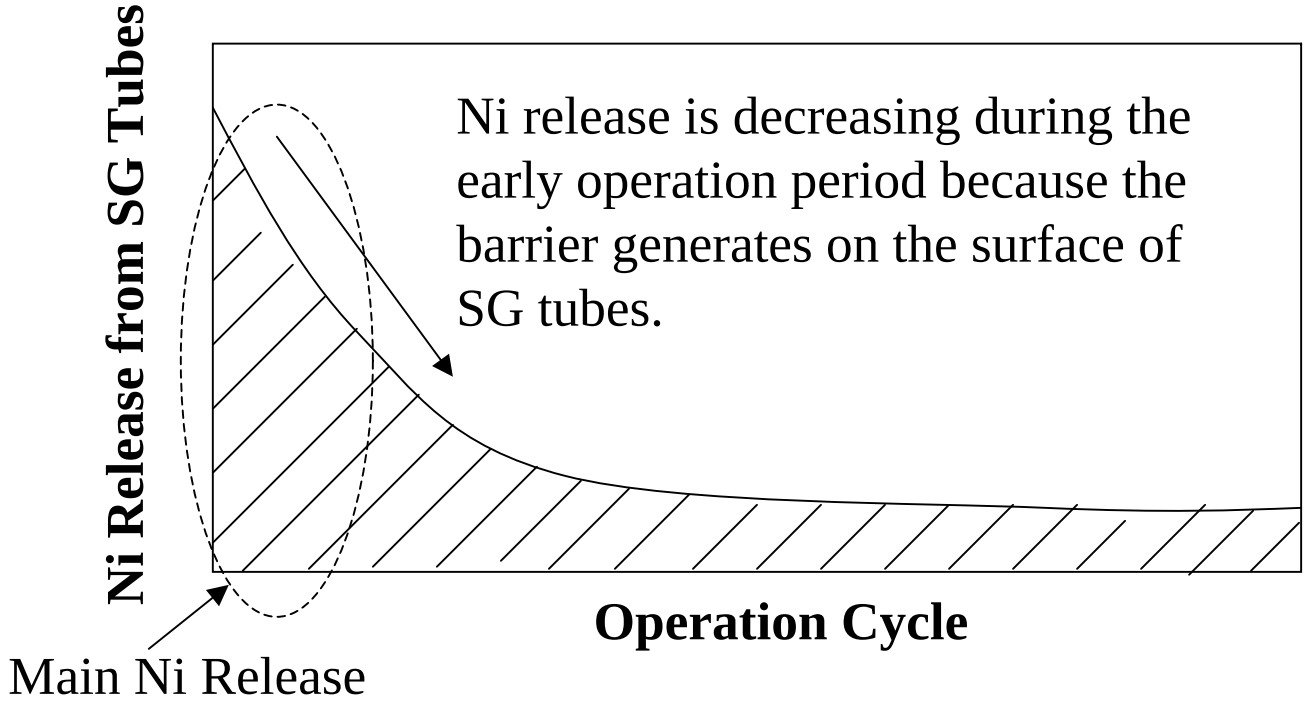


Figure 2 Image of Ni Release from SG Tubes during Operation Cycle

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.

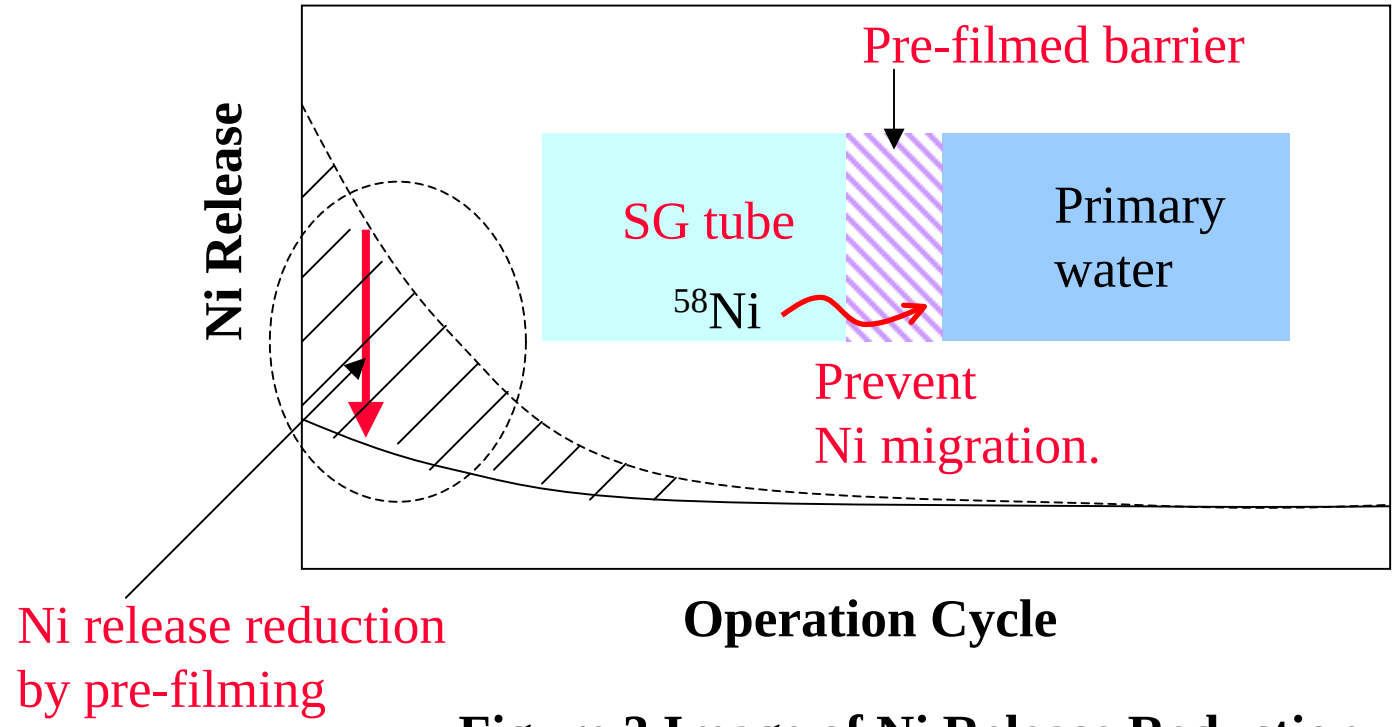


Figure 3 Image of Ni Release Reduction

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

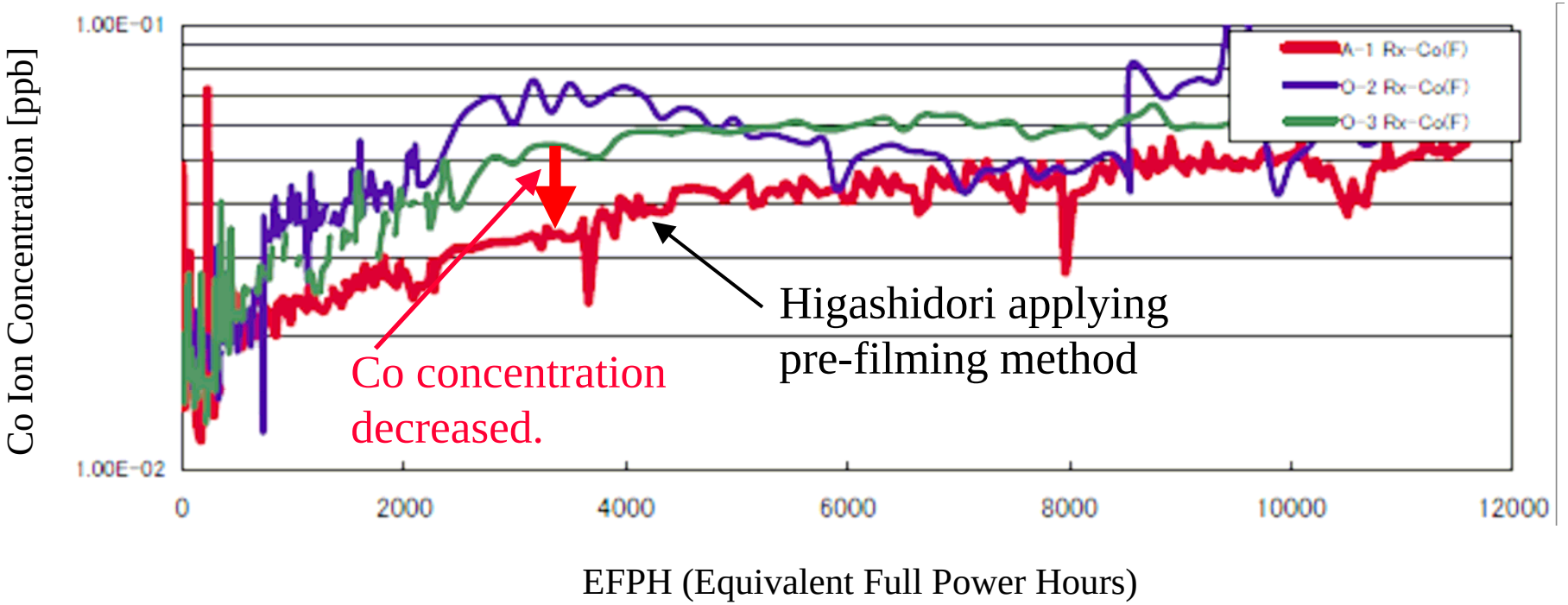


Figure 4 Process of Co Ion Concentration in Nuclear Reactor Water

R&D of Pre-Filming Method to Alloy 690

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

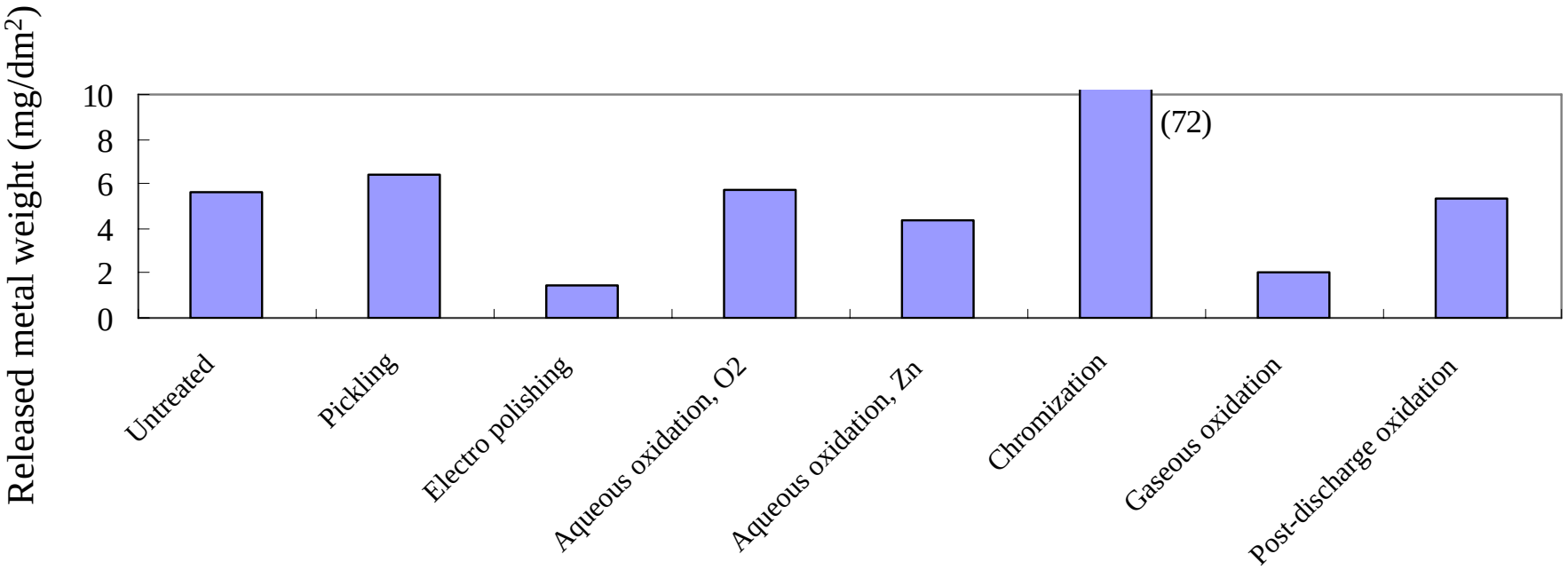


Figure 5 Quantity of Released Metal during the Corrosion Test

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

Possibility of Cr Oxide as Pre-Film Candidate

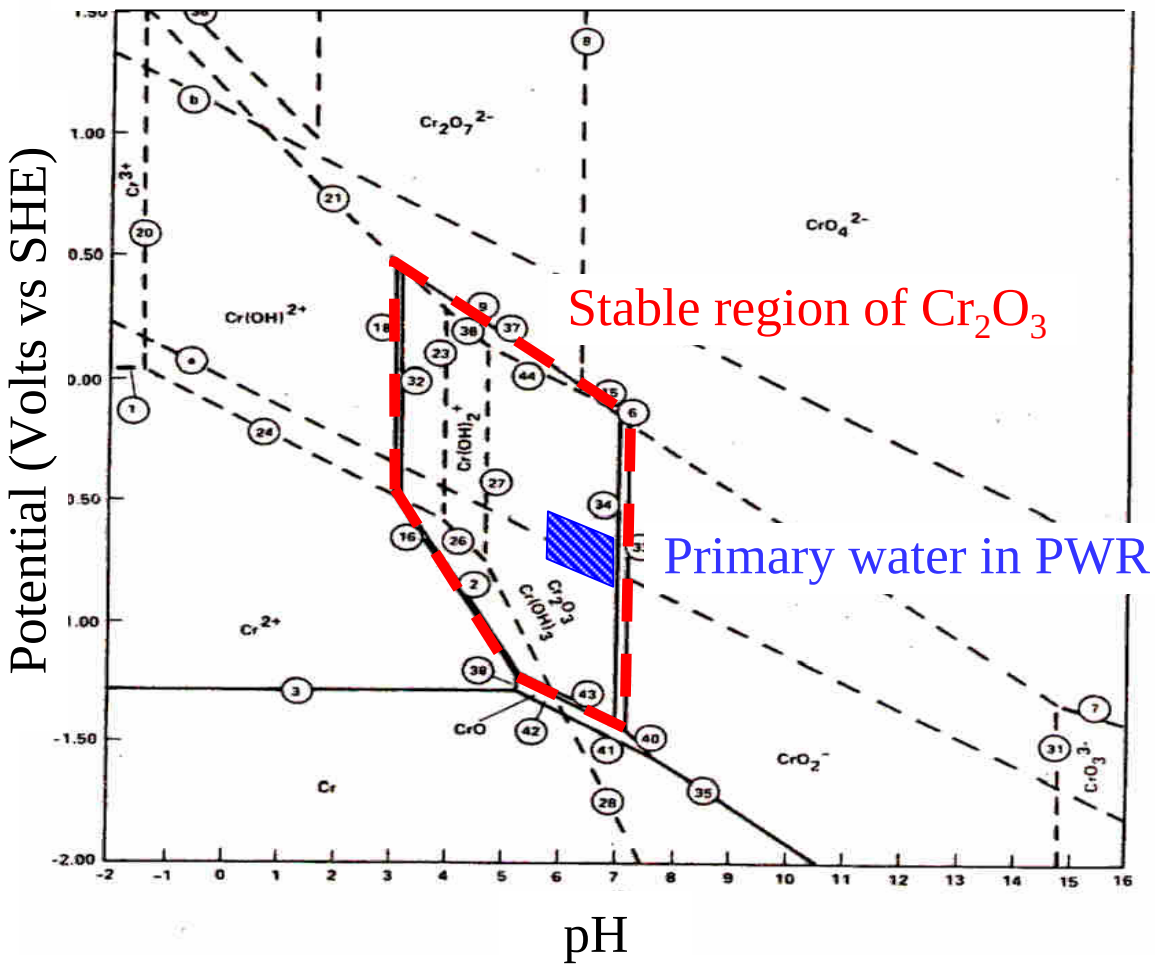
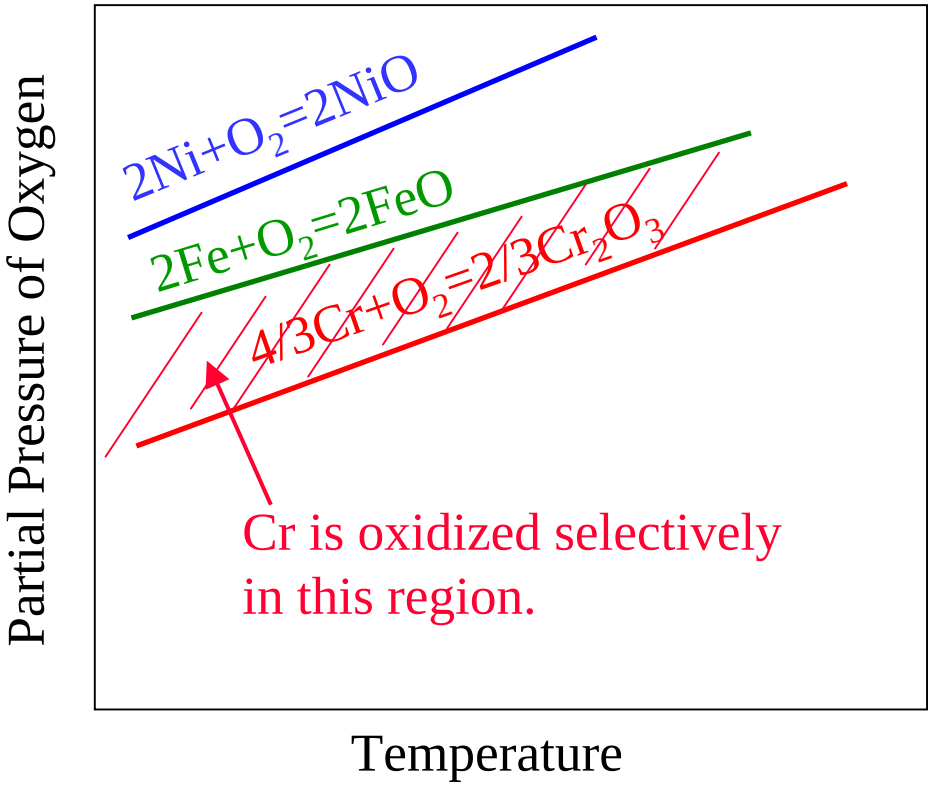


Figure 6 Potential-pH Diagram of Cr in 300℃ Water

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.

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 temperature and partial pressure of oxygen.

Figure 7 Relationship between Type of Oxide and Oxidation Condition

Objective

1) Clarify the possibility of selective oxidation of Cr in alloy 690 by controlling temperature and partial pressure of oxygen .

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) **H_2O in H_2 gas as oxygen source.**

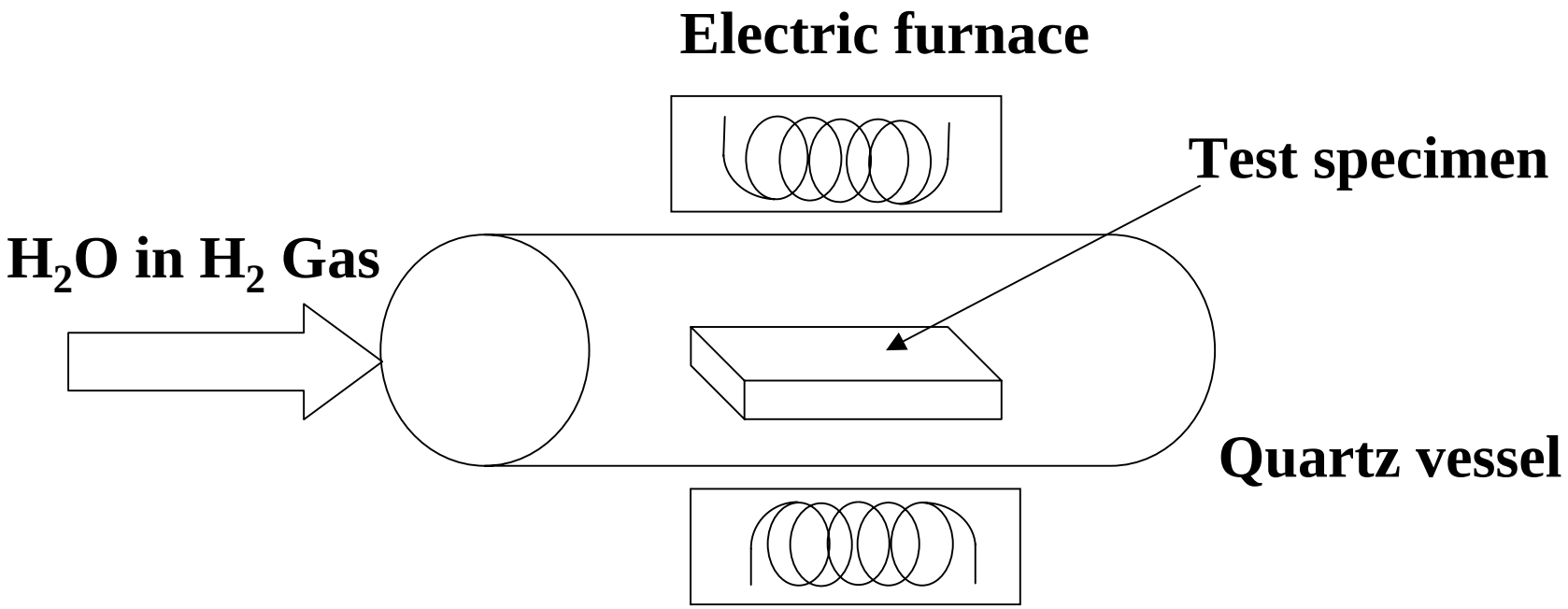
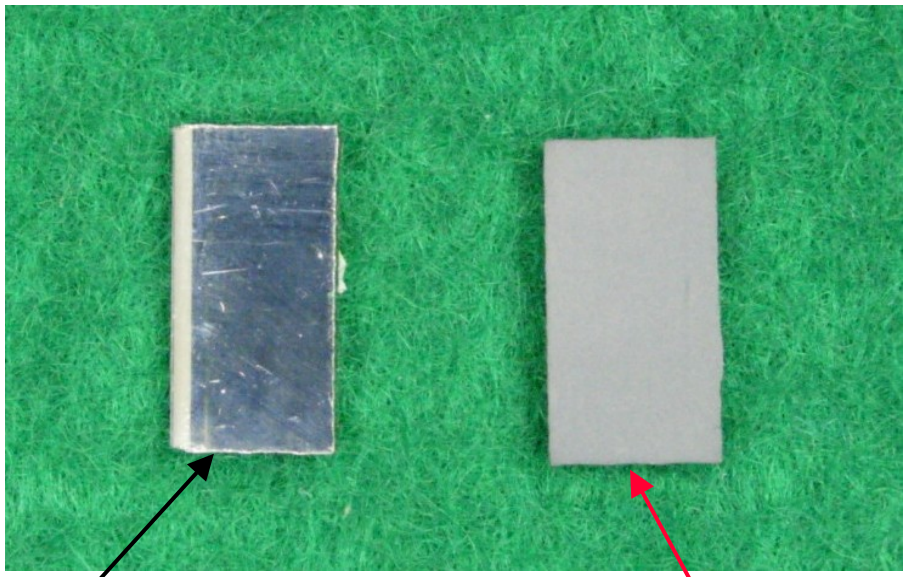


Figure 8 Pre-Filming Equipment

Appearance of Oxide Film



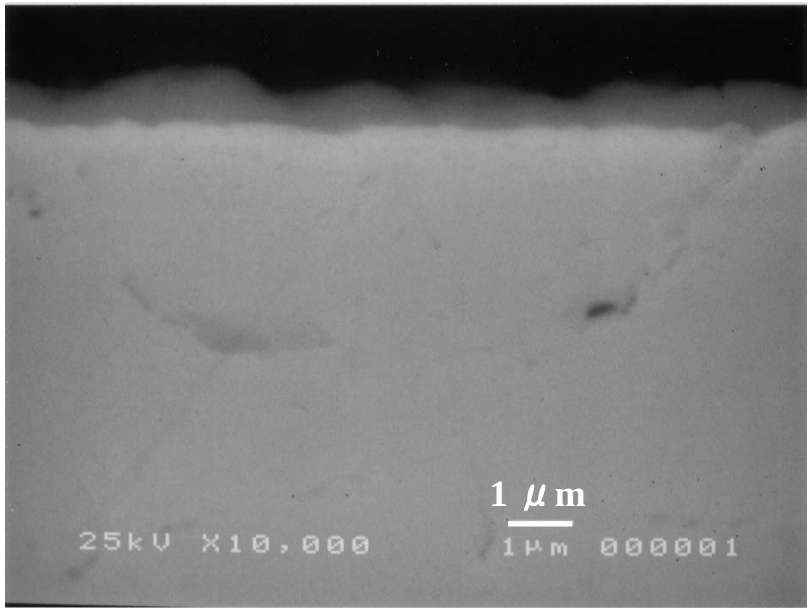
Bare specimen
(Before pre-filming)

After pre-filming

Photo 1 Appearance of Specimen

Cross Section of Oxide Film

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



Oxide film

Specimen (Alloy 690)

Photo 2 Crosse Section of Oxide Film (SEM)

Composition of Oxide Film

Oxide film is composed of Cr_2O_3 and $MnCr_2O_4$.

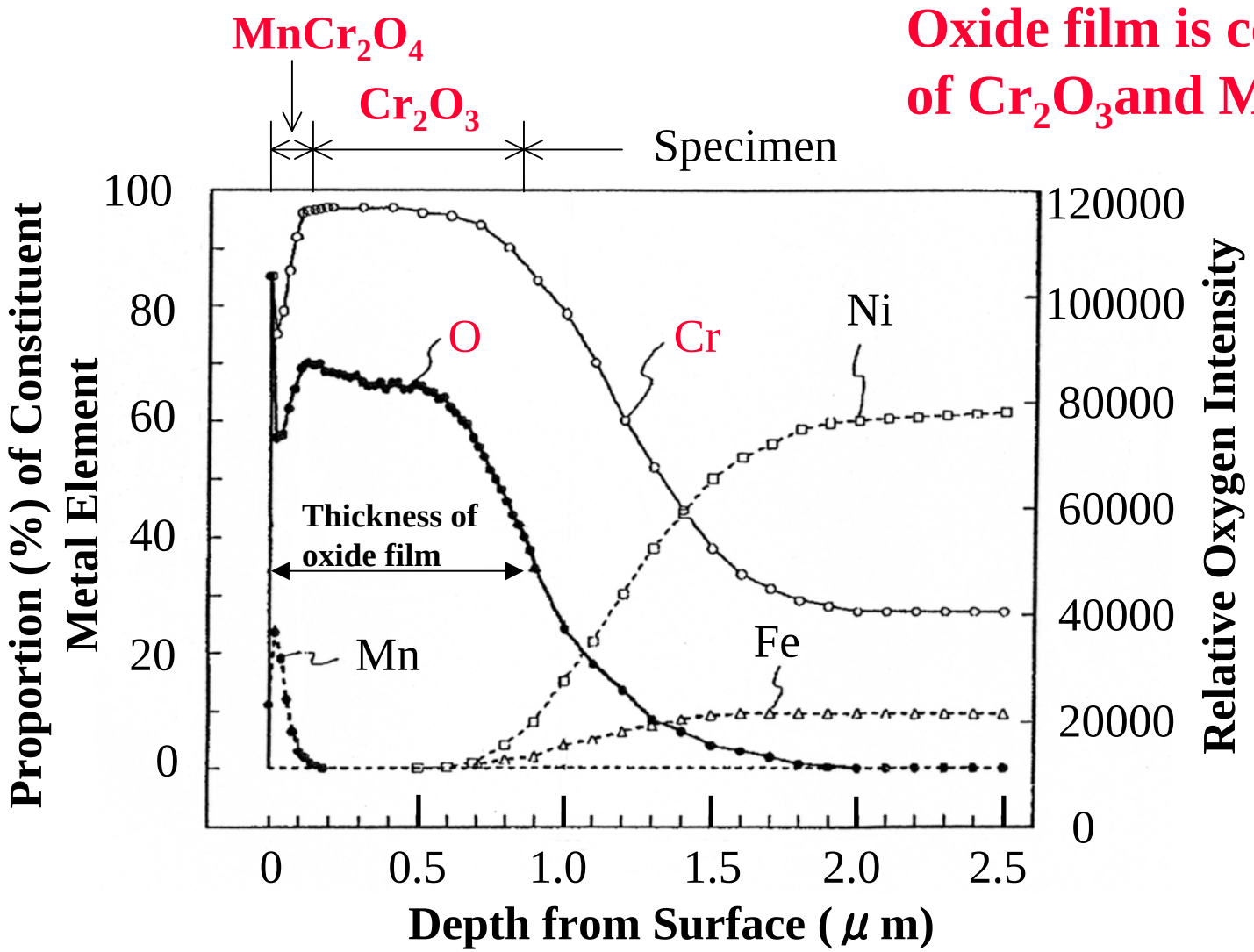
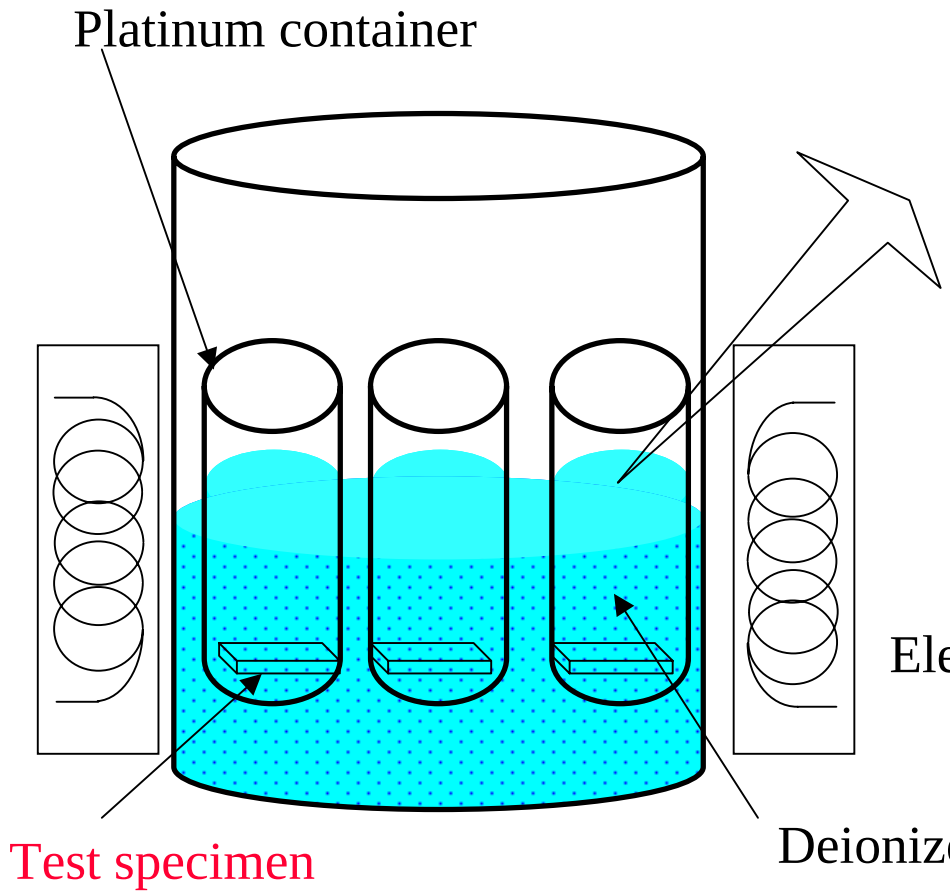


Figure 9 Analysis of oxide film by SIMS

Ni Release Test
on Various Thickness Oxide Film

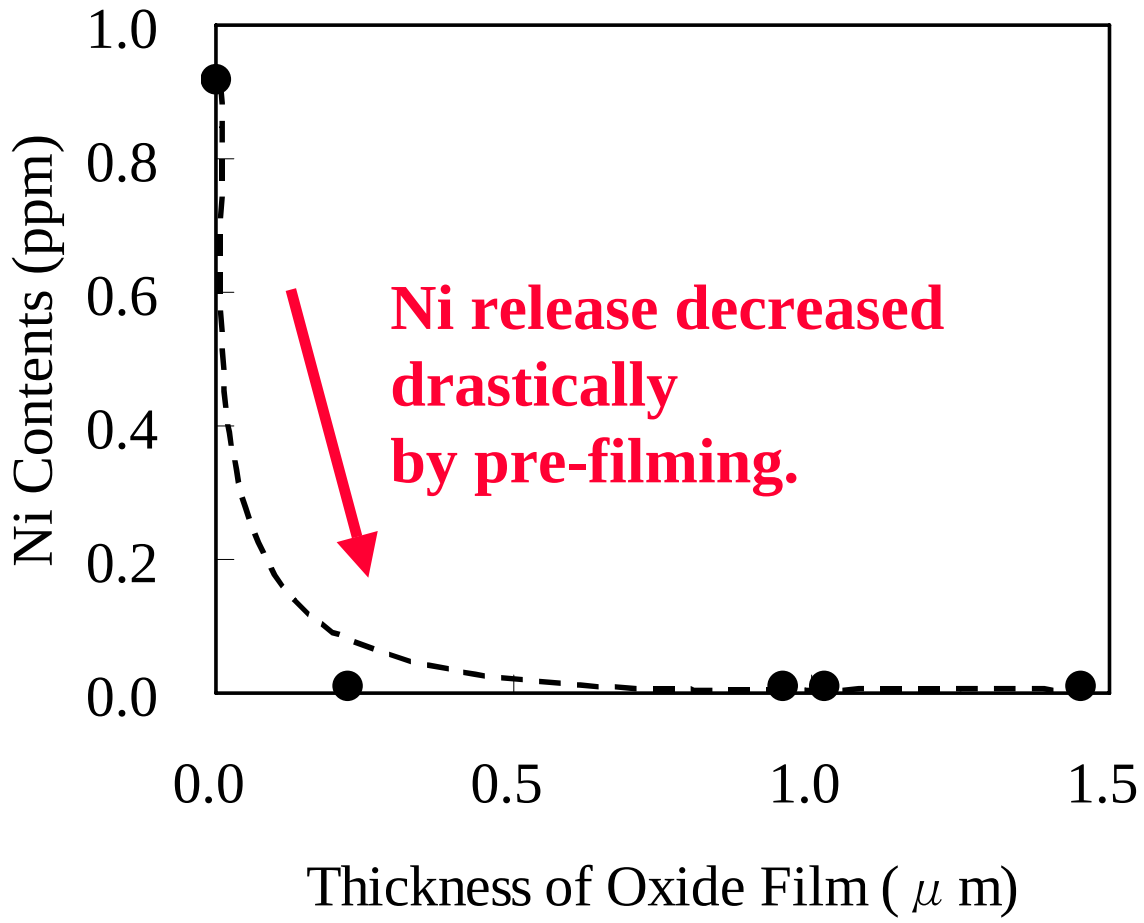
Ni Release Test Method



After immersion
in deionized water
at 320 degree C for 1000 hrs,
Ni content in deionized
water was measured
by ICP.

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_2O in H_2 gas at high temperature.**

2) **The oxide film is composed of $Cr_2O_3$and $MnCr_2O_4$.**

3) **Pre-filming 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.**

Thank you for your attention.