# The Effect of Zn Addition On The CRUD Structure

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## 1. Introduction

A deposition of corrosion products on fuel rods from the coolant circulated in a nuclear power plant (NPP) is commonly known as CRUD (Chalk River Unidentified Deposit). With the high temperatures reached in the reactor core, there is a high probability of the reactor reaching a sub-cooled nucleate boiling state. As CRUD formation is the function of reactor power and coolant temperature, it is predominantly formed around micro-bubbles that occur alongside the sub-cooled nucleate boiling.

CRUD causes several reactor integrity problems. The first is B accumulation in CRUD, which creates an axial offset anomaly in the reactor core by absorbing neutrons. Another problem is radioactivity increasing on the inner surfaces of primary systems. After Co and Ni, which are dissolved in primary systems are deposited on fuel cladding, they are irradiated by neutrons and become radioactive isotopes, such as Co-60 and Co-58. These isotopes escape from fuel cladding and replace CRUD in the primary system's inner face.

However there have been many technologies applied for the mitigation of CRUD such as high pH operation, the use of enriched boric acid, H injection, chemical purification, magnetic filtering, and injection of metal ions such as Zn. In this study, we checked the effect of Zn on the formation of CRUD by SEM. Also we checked ICP results from simulated coolant.

## 2. Methods and Results

we set up an experimental device that can simulate the real phenomenon on the upper position of nuclear fuel cladding and thus make artificial CRUD. It is designed to simulate coolant encounters with SUS-304 foil at 320℃ and 150bar during 5days. We kept the flow rate at 2.5ml/min, so as to maintain the concentration of boron and corrosion products.

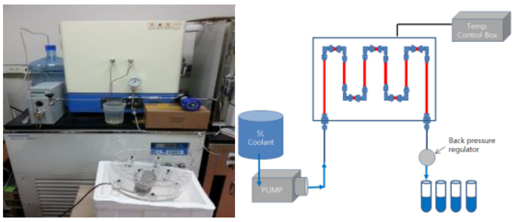


Figure 1. CRUD experiment

Two kinds of simulated coolant were injected into system to confirm Zn effect on CRUD structure and size. Composition and concentration data are shown in Table1. To get an obvious ion concentration change and rapidly make CRUD, we made three-times-higher ion (Fe, Cr, Ni, Co, and Zn) concentrations, except for B and Li.

| Elements | B | Li | Fe*3 | Cr*3 | Ni*3 | Co*3 |
|---|---|---|---|---|---|---|
| ppm | 1000 | 3 | 25.68 | 2.37 | 1.35 | 0.24 |
| mg | 5720 | 18.14 | 25.68 | 2.37 | 1.35 | 0.24 |

| Elements | B | Li | Fe*3 | Zn*3 | Cr*3 | Ni*3 | Co*3 |
|---|---|---|---|---|---|---|---|
| ppm | 1000 | 3 | 25.68 | 3 | 2.37 | 1.35 | 0.24 |
| mg | 5720 | 18.14 | 25.68 | 3 | 2.37 | 1.35 | 0.24 |

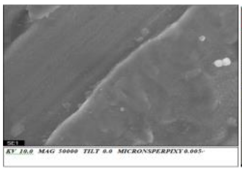
Table 1. Ion composition and concentration of simulated coolant (top: no Zn addition, bottom: Zn addition)

The two photos bellow(Figure 2) show the results of semples. Depending on the location of the pipe samples were taken of each. From the sample 0 to 5, these samples had temperature deviation and location difference when they existed in heater. Because we wanted to examine the CRUD structure and particle size changes depending on position for real reactor.


Figure 2. CRUD experiment samples.

Zn is known for mitigating Alloy 600 PWSCC and decreasing primary system radioactivity. Zn has substitution reactions with divalent cations (Fe, Ni, Co, etc). It forms a strong protective film on the system's inner surface. Because of this protective film, we can control the depositing of corrosion and radioactive isotopes (Co-58, Co-60, etc.) on CRUD.

To confirm Zn effect, we performed SEM and XRD analysis for each samples. For the reference, we got SUS-304 SEM/EDX analysis data(Figure 3).




| Matrix Correction | Wt% | At% |
|---|---|---|
| O K | 03.48 | 11.19 |
| NiL | 10.76 | 09.44 |
| AlK | 00.29 | 00.56 |
| SiK | 00.51 | 00.94 |
| TIM | 02.37 | 00.60 |
| CrK | 16.20 | 16.05 |
| FeK | 66.39 | 61.23 |

Figure 3. SUS-304 SEM/EDX results for reference.

The following pictures are SEM images for each specimen. As the sample number increase from 0 to 5, the condition for specimen is more close to real condition for upper side of reactor.

From these images, for the first, we can find the difference of CRUD particle size depending on sample number and Zn existence. As the number of samples is increased, the particle size is also increased(From 100nm to 400nm). It means that the upper side of reactor has bigger size of CRUD deposit particles than lower side. From the Zn existence, the Zn added experiment shows small and compact form of CRUD deposit particles compare to No Zn samples. It mean the strong protective film on the system's inner surface that we predicted as a Zn effect.

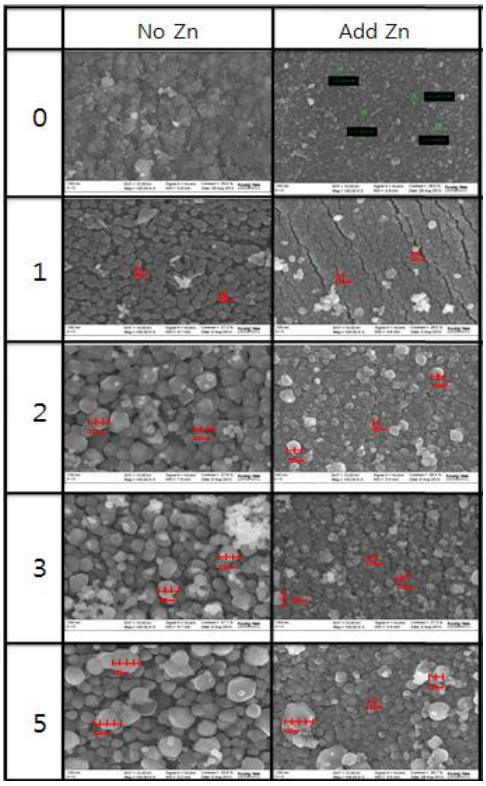



Figure 4. CRUD SEM images depending on sample number and Zn addition

We also did XRD and EDX analysis for each specimens. However, from these results, we couldn't find the existence of Zn and Co exactly. Each specimens has too small amounts of elements to analysis.

Following one is representative XRD result throughout all samples.

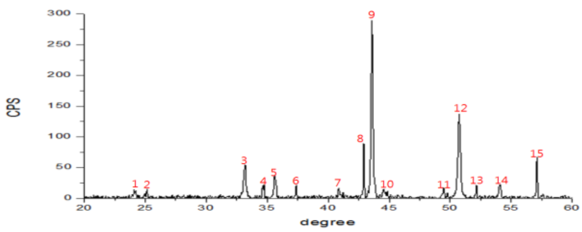


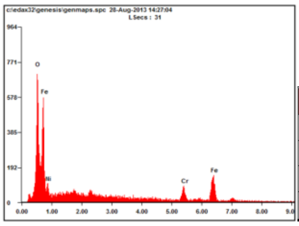

Figure 5. XRD spectrum for Add Zn_2 sample

From the Peak intensity and degree, we find out Iron Oxide, NiO and Iron austenite but Iron austenite is just a metal part from SUS-304.

| Peak Number | Degree | D-value | material |
|---|---|---|---|
| 3 | 33.220 | 2.6962 | Iron Oxide JCPDS Card(33-664) |
| 5 | 35.580 | 2.5211 | |
| 14 | 54.080 | 1.6944 | |
| 6 | 37.380 | 2.4038 | NiO JCPDS Card(14-481) |
| 8 | 42.920 | 2.1054 | |
| 9 | 43.580 | 2.0751 | Iron austenite JCPDS Card(31-691) |
| 12 | 50.720 | 1.7984 | |

Table 2. Add Zn_2 XRD spectrum analysis

Following Figure is EDX data for Add Zn_2 sample. This one also doesn't have any Zn or Co data.



| Matrix Correction: ZAFElement | Wt% | At% |
|---|---|---|
| O K | 10.30 | 28.48 |
| NiL | 07.01 | 05.28 |
| CrK | 12.65 | 10.76 |
| FeK | 70.04 | 55.47 |

Figure 6. EDX data for Add Zn_2 sample

## 3. Conclusions

The fact that CRUD has different formation with the Zn existence in coolant is obviously known. Some plants currently use Zn injection to get advantage of reducing activity on primary system.

In this study, we simulated whole parts of the reactor core from bottom part to upper part by 5 parts of SUS-304 pipes and two kinks of coolants(with Zn and without Zn). By taking a specimen from each pipes, we find out that the formation of CRUD is different for Zn existence and location. When the Zn is added, the CRUD depositions are more compactly arranged then another.

For the EDX and XRD data, because it contains too small amount to analysis, we couldn't find Co and Zn elements. However, by the XPS analysis, we can get a Co and Zn data from those samples.

## REFERENCES

[1] Brian Cox, Friedrich Garzarolli, Al Strasser, Peter Rudling. The effects of Zn injection(PWRs and BWRs) and Noble Metal Chemistry(BWRs) on fuel performance- an update