# Formation Of CRUD and the Effect Of Zn on the CRUD Composition

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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).It has been an issue for NPP as increasing the level of radioactivity in reactor coolant system (RCS) and generating reactor imbalance of power distribution due to boron (AOA) and carrying on excess burden to the coolant purification system for a few decades. 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, especially the composition change to see the effect of Zn (50 ppm).

## 2. Experimental procedures

From significant numbers of lab studies and field experiences reported, Zn addition is known to be an effective method to reduce CRUD formation in RCS. The mechanism of Zn in coolant system on CRUD is assumed that Zn has the highest site preference energy for the formation of deposit like CRUD among all other cations in coolant system. Hence, Zn can replace these cations such as Fe, Ni with itself from oxide layer. And Zn has the highest site preference energy for tetrahedral sites, while Cr has the highest site preference energy for octahedral sites. Therefore, Zn is incorporated into inner oxide layer which mainly consists of chromites and becomes very stable and protective oxide films which composed of Zn-Cr phase. The results of this effect of Zn addition reduce the metal release and corrosion rate of RCS materials. Moreover, incorporation of Zn in tetrahedral sites inhibits the cobalt deposit into oxide layer because Zn site preference energy for tetrahedral sites is higher than that of Co. This is mechanism that how Zn reduces the radiation fields. The primary purpose of Zn addition into PCS is to reduce dose rate, to mitigate the PWSCC initiation, to reduce the generating of corrosion products and CRUD deposition on fuel surfaces.

In this study, we simulated the environment of the primary reactor coolant system by making a device as shown in figure 1. The solution contains B, Li, Fe, Zn ,Cr ,Ni and Co in distilled water.

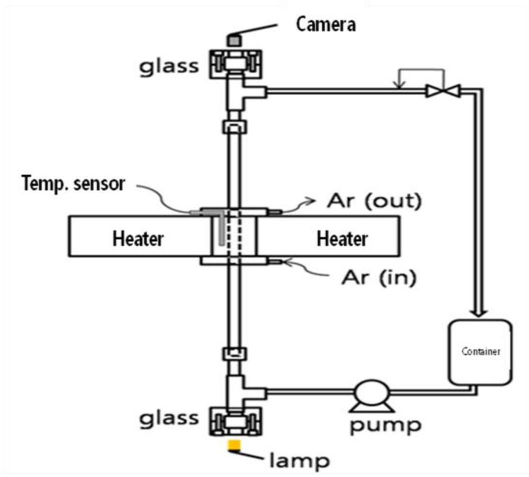

Figure 1. A diagram of CRUD experimental apparatus.

Ni, Cr and Fe are typical compositions of CRUD. These ions in the coolant are deposited by the difference of solubility that depends on temperature. Figure 2 shows the dependency of the solubility of Fe and Ni. The solubility of Zn also depends on temperature and pH of the water. When the pH is fairly neutral, Zn in water is insoluble. But its solubility increases with increasing acidity. Because we used boron acid for solution, its solubility was increased. The solubility of Zn is very low at the RCS due to the high temperature of 350℃. Current NPP use the Zn concentration of 40ppb. In this experiment used 50ppm to get a distinct Zn effect on the CRUD.

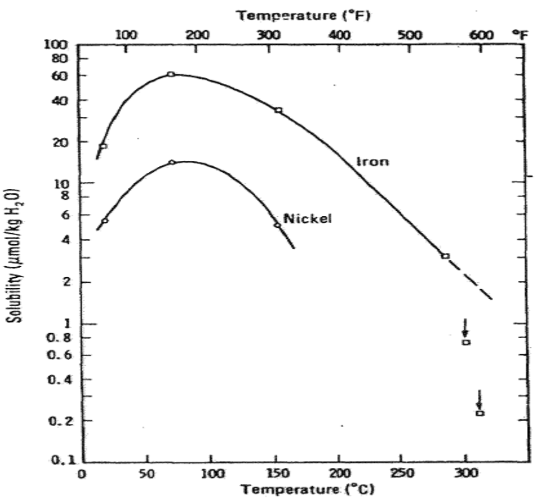

Figure 2. Solubility of nickel and iron with respect to temp.

We used a long-glass plate for CRUD deposition. Figure 3 shows the system apparatus used and the CRUD formed on the glass. The inner pressure was kept around 120 bar and the outside heater was maintained at 400℃ for one week. On the surface of the glass, brown deposits were observable. We analyzed the deposits using XRD and XPS to get the information of the structure and the composition of CRUD.

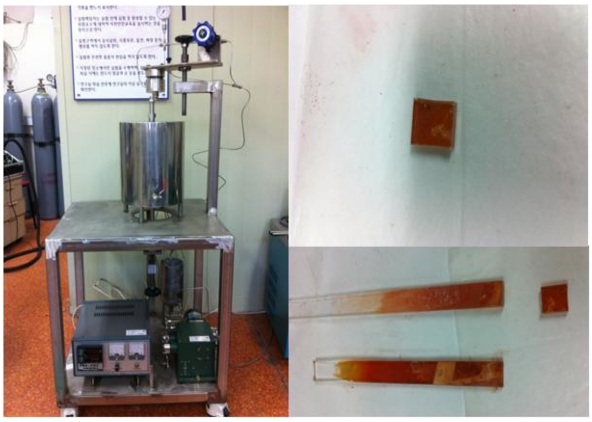

Fig 3. CRUD experiment device(left) / CRUD sample(right)

### 3. Results and Conclusions

Normally CRUD in NPP without Zn is usually composed of two layers. The outer layer is known as $NiFe_2O_4$ and the inner layer as $FeCr_2O_4$. When there exists some Co in the solution, Fe in $FeCr_2O_4$ is receptive to Co and $CoCr_2O_4$ appears.

XRD peaks of the CRUD obtained by this study indicated the existence of a spinel structure $Fe_2O_3$ and $NiFe_2O_4$ (Figure 4 and Figure 5). We could not find the inner Cr rich layer. XPS result indicated no Co peak for CRUD composition. From this result, Zn in the solution seemed to reduce some portion of Co. In future studies, by changing the metal ion composition in aqueous solution and adjusting the temperature of coolant, we plan to track the change of the composition of CRUD.

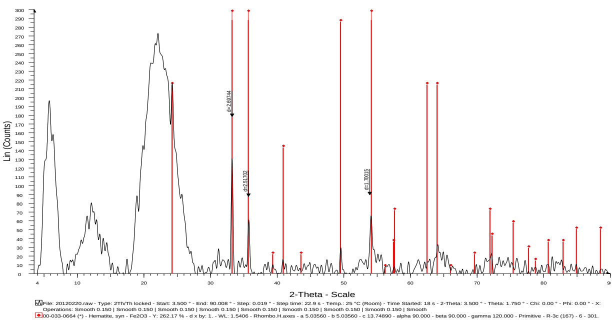


Figure 4. $Fe_2O_3$ Peak in XRD analysis result

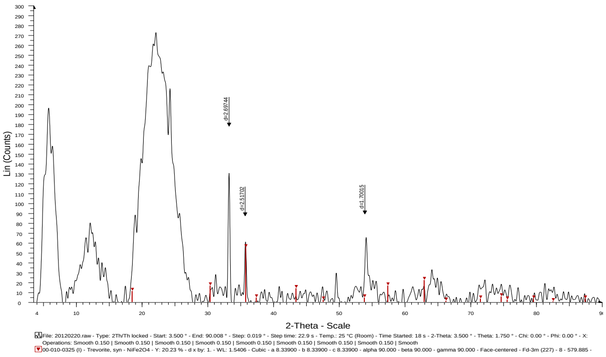


Fig 5. $NiFe_2O_4$ Peak in XRD analysis result

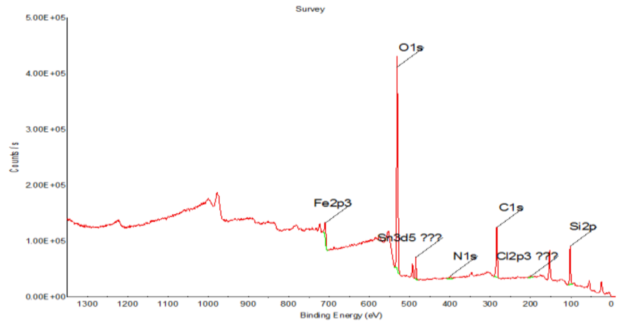


Figure 6. XPS peaks of CRUD

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