Preparation of Simulated Crud Based on the Elemental Composition of Crud Obtained from Spent Nuclear Fuel Rods

Sang-Hyuk Jung, Jei-Won Yeon*, Jaesik Hwang, Euo-Chang Jung, Kyoung-Kyun Park, Kyuseok Song
Nuclear Chemistry Research Division, Korea Atomic Energy Research Institute,
Daeduk daero 1045, Yuseong-gu, Daejeon 305-353, Korea
** Corresponding author: yeonysy@kaeri.re.kr*

1. Introduction

Since nuclear power plant operation practice shifts to long-term fuel cycle such as from 12 month operating cycle to 18-24 month operating one, it was occasionally observed that the amount fuel crud (Chalk River Unidentified Deposit) increased on the surface of fuel cladding. An increase of fuel crud has been reported to create an axial offset anomaly (AOA) phenomena and an increase in the dose rate [1]. In order to mitigate the fuel crud formation, various techniques have been developed including higher pH operation, use of EBA (enriched boric acid), hydrogen injection, zinc addition, purification of coolant, and surface treatment of fuel cladding [2].

In particular, the chemical analysis of fuel crud is an important subject relative to the determination of optimal reactor coolant chemistry. Recently, the development of a new analysis technique using laser spectroscopy commenced for the analysis of fuel crud. In developing this technique, it is necessary to establish the emission spectrum database of crud samples with various chemical compositions.

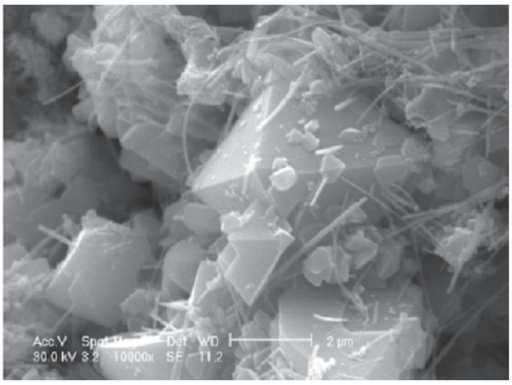
In this study, we analyzed the elemental composition and crystal structure of the crud samples [3] obtained from the ultrasonic cleaning of fuels and scraping out directly from the surface of spent fuels, respectively. And then, on the basis of the analysis results of fuel crud, Ni-Fe-Zn simulated cruds were prepared by the high-temperature steam method previously developed [4-5]. The elemental composition and crystal structure of simulated cruds were confirmed by ICP-AES and XRD, respectively.

2. Methods and Results

For the preparation of simulated crud, $Ni(OH)_2$, $Zn(OH)_2$ and $Fe(OH)_3$ were mixed with various molar ratios. And then, the mixtures were dried at 50°C for 24 h and were compressed by a pellet maker of 5.5 metric tones for 2 min. Each mixed hydroxide pellet was isolated with a vacuum quartz tube. The pellets in the quartz tubes were heat treated at 500°C for 8 h. The elemental composition analysis of simulated crud is carried out using inductive coupled plasma - atomic emission spectroscopy (HORIBA, ULTIMA 2C). The structure analysis of simulated crud was carried out by using X-ray diffraction (BRUKER-AXS, D5000) in the range between 20° and 70° using Cu Kα (λ=1.5409Å) radiation.

2.1 Analysis of elemental composition of crud obtained from spent nuclear fuel

For the preparation of simulated crud, we analyzed the elemental and structural information on the crud of the spent fuels. Fig. 1 shows the surface morphology a fuel crud sample, with the elemental composition table, from the ultrasonic cleaning of fuels. From the analysis of the data [3], it is deduced that the major component of the crystal is $NiFe_2O_4$, due to the stoichiometric Ni:Fe ratio.



Element	Cr	Mn	Fe	Ni	Zr
At. %	0.72	1.95	46.07	25.91	25.35

Fig. 1. A SEM image of a crystal compound in a crud sample, and the chemical composition at that area measured by EPMA [3].

Table 1 shows the results [3] of the chemical analysis for hard cruds. It is confirmed that the constituent element of hard crud is Co, Cr, Fe, Mn, Ni, Zn and Zr. The major elements were Fe, Ni and Zn. Relationship was observed between Ni and Zn contents. Ni content was higher than Zn content in hard crud sample 1. Inversely, in hard crud sample 2, Zn content was higher than Ni. It was known that Ni ions in nickel ferrite, which is formed in the inner layer of crud, could be replaced by Zn ions in coolant to form zinc ferrite at high temperature. From this relationship between Zn and Ni in crud, we found that the elemental compositions of two hard cruds were reasonable.

Table 1. Elemental analysis of the hard cruds measured by ICP-AES

Crud	Element (wt. %)						
	Co	Cr	Fe	Mn	Ni	Zn	Zr
Hard1	0.2	9.1	71.4	1.5	11.3	4.7	1.8
Hard2	0.1	9.3	61.7	0.5	5.5	22.3	0.6

2.2 Preparation and characterization of simulated crud

The simulated cruds with various molar ratios of Ni, Zn and Fe were prepared on the basis of the elemental and structural data described the previous section.

Table 2 shows the elemental composition of simulated crud with various molar ratios of Ni, Zn and Fe. It was confirmed that the molar ratios of the simulated crud were almost the same as the controlled ratios.

Table 2. Molar ratios of Ni-Zn-Fe mixed oxides

Sample (mixing molar ratios)	Molar ratios (measured by ICP-AES)		
	Ni	Zn	Fe
Ni: Zn: Fe = 1: 0: 2	1.12	0	2
Ni: Zn: Fe= 0.75: 0.25: 2	0.80	0.27	2
Ni: Zn: Fe = 0.5: 0.5: 2	0.49	0.53	2
Ni: Zn: Fe = 0.25: 0.75: 2	0.27	0.86	2
Ni: Zn: Fe = 0: 1: 2	0	1	2

Fig. 2 shows that 5 different X-ray diffraction patterns of simulated cruds. From these XRD patterns, the crystal structures of the cruds were identified as the mixture of NiO, Fe_2O_3, $NiFe_2O_4$, ZnO and $ZnFe_2O_4$, respectively. It was confirmed that the inversely relationship between Zn and Ni in the simulated cruds.

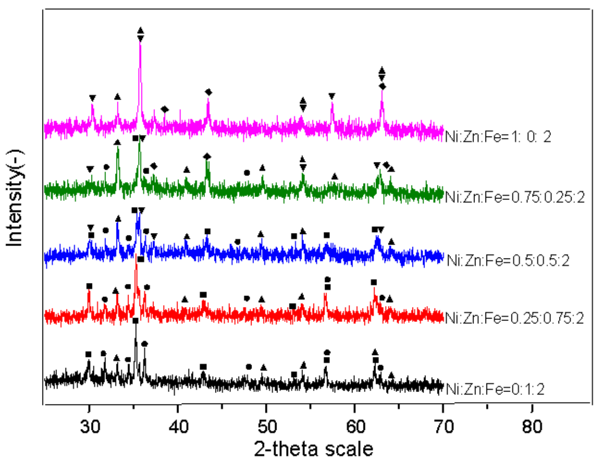


Fig. 2. X-ray diffraction patterns of the simulated crud with various molar ratios of Ni, Zn and Fe. Peaks corresponding to NiO (◆), Fe_2O_3 (▲) $NiFe_2O_4$ (▼), ZnO (●), $ZnFe_2O_4$(■).

3. Conclusions

From the analysis of crud samples of the spent fuels, we found the nickel ferrite crystal in Ni-Fe based crud, and zinc ferrite in Ni-Zn-Fe based crud, respectively. And there was an inverse relationship between Ni and Zn in Ni-Zn-Fe based crud. Based on the analysis data, we prepared 5 different simulated cruds and confirmed their crystal structures and the relationship between Ni and Zn.

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