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# Chemical analysis of fuel crud obtained from Korean nuclear power plants

Jei-Won Yeon [a,*], In-Kyu Choi [b], Kyoung-Kyun Park [a], Hyoung-Mun Kwon [c], Kyuseok Song [a]

[a] *Nuclear Chemistry Research Division, Korea Atomic Energy Research Institute, 1045 Deadeok-daero, Yuseong-gu, Daejeon 305-353, Republic of Korea*
[b] *Nuclear Fuel Cycle Process Development Division, Korea Atomic Energy Research Institute, 1045 Deadeok-daero, Yuseong-gu, Daejeon 305-353, Republic of Korea*
[c] *Post Irradiation Examination Facility, Korea Atomic Energy Research Institute, 1045 Deadeok-daero, Yuseong-gu, Daejeon 305-353, Republic of Korea*

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## ABSTRACT

Crud samples were obtained from two different kinds of used fuels in PWRs. The constituent elements were analysed according to the shapes of crud particles by SEM and EPMA. The principal elements of octahedral crystal particles were identified as Ni and Fe, where the ratio (Fe/Ni) was approximately 2. The major element of the observed needle-like structures was determined to be Ni. In addition, Zr composed the main element of particles shaped like broken fragments sized at 10–50 μm in diameter. The round particles less than 20 μm in diameter were identified as Si-containing compounds. We also found the Zn element in a series of fuel crud samples obtained from a plant. Zn was mainly detected in the hard crud, inner layer of crud, but not on the surface of crud. It was observed that there is an inverse relationship between the Ni and Zn contents in the hard crud.

## 1. Introduction

In pressurised water reactors (PWRs), the pH of the reactor coolant has been controlled in order to increase the solubility of crud (Chalk River unidentified deposits) when passing through the reactor core for the purposes of reducing crud deposition on the fuel surface [1]. Originally, it was a good concept to mitigate the crud deposition on fuel rods under the normal fuel burn-up condition. However, modern PWRs operate under high fuel burn-up conditions, so that the fuel performs with higher duty for longer residence times suffer from unfavourable $pH_T$ conditions <6.9, in early stages of operation, and undergo subcooled boiling towards the top of the reactor core [2,3].

Therefore, the amount of crud on fuel rods increases with the increase in corrosion products of structural materials, and the increase of crud deposition promoted by subcooled boiling [4]. Accompanying the transition to higher duty cores have been some crud-related incidents causing anomalous and unanticipated core behaviour in PWRs, fuel integrity problems, and adverse radiological events. In order to mitigate these crud-related incidents, many innovative strategies have been developed [4–9] including elevated pH operation with enriched boric acid (EBA), ultrasonic cleaning, low hydrogen control, zinc addition, purification of coolant, and surface treatment of fuel cladding. If the chemical and structural information on crud were available with the application of these technologies, it would be a useful tool to effectively enhance the performance of these technologies [10,11].

In the present work, we observed various crud samples obtained from the ultrasonic cleaning of fuels and from scraping out the surface of used fuels, respectively. Several kinds of particles were observed in crud obtained from ultrasonic cleaning. The principal elements of octahedral crystal particles were identified as Ni and Fe, where the ratio (Fe/Ni) was approximately 2. The major element of the needle-like structures was identified as Ni. In addition, Zr composed the majority of broken-shaped fragments. The round particles were identified as silica-containing compounds. Finally, we found the Zn element in a series of fuel crud samples obtained from a PWR plant. Zn was mainly detected in the hard crud, inner layer of crud, but not on the surface of crud. Our results on fuel cruds were similar to those previously reported by Byers and Deshon [3].

## 2. Experimental

Crud samples were obtained from two different used fuels in Korean PWRs. The relevant fuel data are summarised in Table 1. Two kinds of analyses were applied to the crud samples. One is a surface analysis for the crud obtained during the ultrasonic cleaning of fuels. The second is a chemical analysis for the crud scraped from the fuels. The crud for surface analysis was sampled in the fuel storage pool during the ultrasonic cleaning of fuels, and the crud for chemical analysis was obtained from fuels by hot cell work after cooling down in a storage pool. During the ultrasonic cleaning, deposited crud on the fuel rods was removed from the fuel cladding, so the samples are actually mixed crud. On the other hand, in a hot cell, crud samples were collected and divided into two kinds. One was soft crud obtained by scrubbing fuel surface

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* Corresponding author. Tel.: +82 42 868 8158; fax: +82 42 868 8148.
*E-mail address:* yeonysy@kaeri.re.kr (J.-W. Yeon).

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**Table 1**
Spent fuel data used for the crud analysis.

| Fuel assembly mark | A | B | C | D | E |
|---|---|---|---|---|---|
| Reactor producer | FRM[a] | FRM | FRM | FRM | WH[b] |
| Loaded cycle | 10, 11 | 10, 11 | 12, 13 | 12, 13 | 12, 13, 14 |
| Burn-up, designed (MW d/Mt U) | 41,996 | 41,996 | 44,994 | 44,994 | 40,531 |
| Clad material | Zircaly-4 | Zircaly-4 | Zirlo | Zirlo | Zircaly-4 |
| Coolant | $H_2O$ | $H_2O$ | $H_2O$ | $H_2O$ | $H_2O$ |
| Effective full power days | 433, 444 | 433, 444 | 484, 475 | 484, 475 | 426, 430, 410 |
| Date of discharge | 2002.9.10 | 2002.9.10 | 2005.10.26 | 2005.10.26 | 2003.5.10 |
| Related figures | 4[a] | 3 and 4 | 2 | 4[b] | 6–8 |

[a] FRM: Framatome.
[b] WH: Westinghouse.

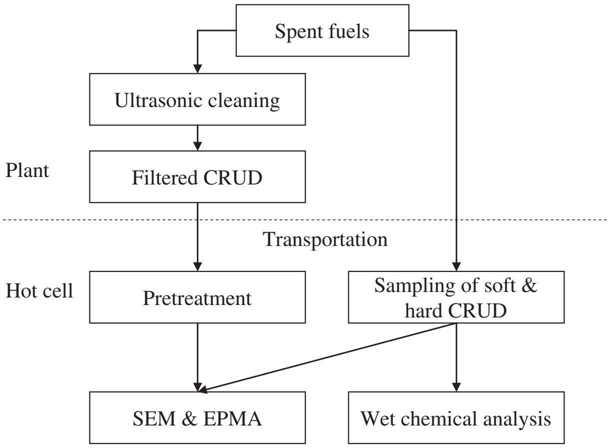


**Fig. 1.** Process of crud sampling and analysis.

with filter paper, and the other was hard crud, strongly attached on the cladding, but sampled by a metal scraper. We sampled the soft crud first, and then the two hard crud samples were collected at different parts of a fuel surface. The crud sampling processes are shown in Fig. 1.

For the surface analysis of radioactive crud, SEM (Scanning Electron Microscopy, Philips model XL-30) with EDS (Energy Dispersive X-ray Spectroscopy, EDAX DX-4) and shielded EPMA (Electron Probe Micro Analyzer, CAMECA SX-50R) were used. The analysis data were obtained from the scanning of the full screen, unless the analysis points were designated. For the chemical analysis of crud, soft and hard crud samples were dissolved in concentrated $HNO_3$ and HCl mixed solutions, respectively. Subsequently, the elemental analysis was carried out by Inductively Coupled Plasma–Atomic Emission Spectrometer (ICP–AES) for both samples.

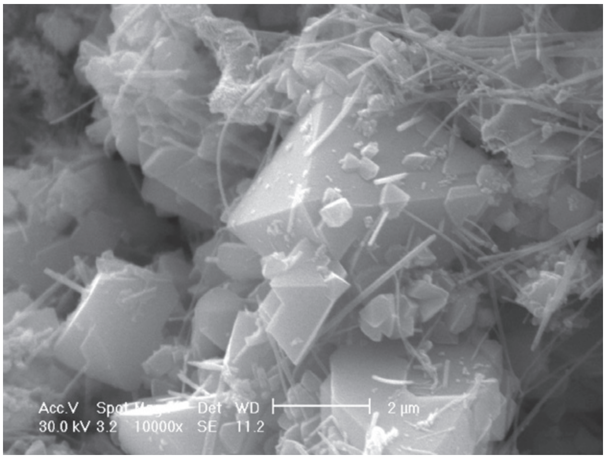
## 3. Results and discussion

### 3.1. Cruds obtained from ultrasonic cleaning of fuels

Recently, ultrasonic cleaning of fuels has been regarded as a promising technique to mitigate the axial offset anomaly (AOA) [6]. This technique is basically to remove the fuel crud, which deposits corrosion products on the surface of fuels, during the overhaul period of nuclear power plants. It has been reported [3,12] that the fuel crud is composed of several kinds of components such as nickel ferrite, nickel oxide, metallic nickel and other constituents. However, as the fuel crud is removed by the fuel bundle in a cleaning rack equipped with ultrasonic generators, all of the components of crud are completely mixed during the cleaning process.

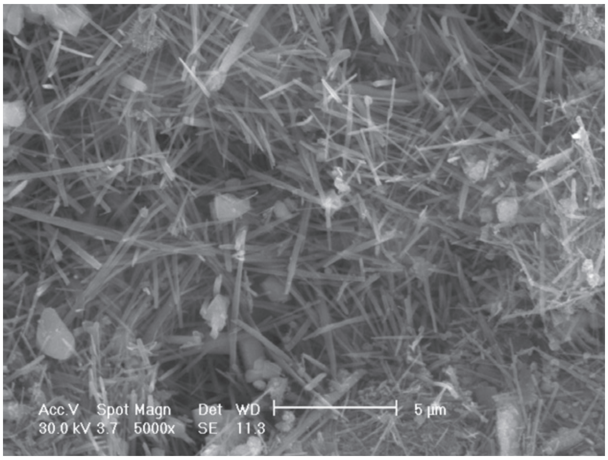
Nickel ferrite has been reported [3,12] as the most common component of fuel crud. Nickel ferrite crystals are typically blocky and have well-defined crystal faces. We found several kinds of particles in the crud sample. Well-defined octahedral crystals were observed in crud samples as shown in Fig. 2. Elemental analysis particularly for these crystals was carried out. The values in the table of Fig. 2 have been normalised so that the sum of the Ni, Fe, Cr, Mn and Zr concentrations equaled 100%. Besides Zr, which is the major element of fuel cladding, the major elements of the crud were Fe and Ni where the ratio (Fe/Ni) was approximately 2. It is deduced that the major component of these crystals is $NiFe_2O_4$, due to the stoichiometric Ni:Fe ratio. As nickel ferrite has a well-defined octahedral crystal structure, it is assumed that nickel ferrite is formed by the crystallisation process from Ni and Fe ions as corrosion products of structural materials, such as stainless steels and nickel based alloys. Although nickel ferrite is observed on the surface of steam generator tubing materials such as alloy 600 [13], it is deduced that nickel ferrite is not transported from the outsides of reactor core, but formed directly on the surface of fuel rods due to the layered structure composed of $NiFe_2O_4$, NiO and $ZrO_2$ [3].

In addition to the octahedral crystals regarded as a nickel ferrite, the Zr element was observed in the crud sample. As $ZrO_2$ is known as a sole compound containing Zr in crud, it is an indication of existence of $ZrO_2$. During the fuel cleaning process, the $ZrO_2$ layer was removed from the fuel cladding and mixed into the crud.



| Element | Cr | Mn | Fe | Ni | Zr | Total |
|---|---|---|---|---|---|---|
| At % | 0.72 | 1.95 | 46.07 | 25.91 | 25.35 | 100 |

**Fig. 2.** A SEM photo of an octahedral crystal compound in a crud sample, and the chemical composition at that area measured by EPMA. The unit at.% refers to atomic%.



| Element | Si | Cr | Mn | Fe | Ni | Zr | Total |
|---|---|---|---|---|---|---|---|
| At % | 2.76 | 2.48 | 3.76 | 33.54 | 53.55 | 3.91 | 100 |

**Fig. 3.** Photos and elemental composition of the needle-like structures in a crud sample. The unit at.% refers to atomic%.

Therefore, it is thought that some fine $ZrO_2$ fragments were contained in the analysis range of SEM–EDS.

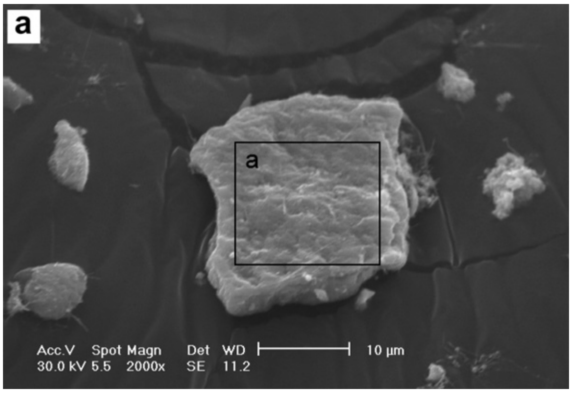
As shown in Fig. 3, needle structures were detected in the crud sample. The thickness of the needles were less than 0.4 μm and the length was approximately 10 μm. The major element of the needles was Ni as shown in the table of Fig. 3. The values in the table have been normalised so that the sum of the Ni, Fe, Zr, Mn, Cr, and Si concentrations equaled 100%.

In PWRs, nickel oxide NiO was detected in crud from both high and low duty cores. When Ni content was high compared to Fe content, NiO needles were reported to form in the crud [3]. Besides needles, there were some grain particles in the sample, and Fe element was observed. Therefore, it is thought that the compound of the needle-like material shown in Fig. 3 is NiO, and other particles are Fe-containing oxides.

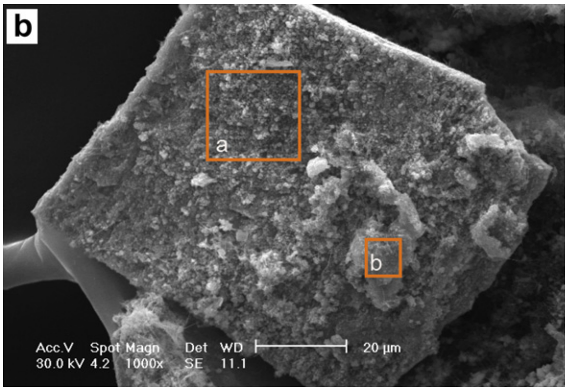
On the other hand, there is another compound having the needle structure in crud. Sawicki and Allsop [11] found thin needles in AOA-affected PWR cores which were identified as bonaccordite, $Ni_2FeBO_5$. Moreover, from the Fe element observed in the table of Fig. 3, it is also possible that the needle structure could be regarded as bonaccordite. Therefore, with the data we obtained, we only conclude that the main compound of the materials shown in Fig. 3 could be the mixture of NiO and Ni–Fe oxides or $Ni_2FeBO_5$.

In addition, as previously stated, the layered structure of crud supports the idea that needle-like structures formed on the fuel rods, and were not transported from the outside of the core. Therefore, it is deduced that the needle-like structure, whether NiO or $Ni_2FeBO_5$, is formed in the vicinity of the boiling points on the surface of fuel rods.

In the crud samples, some fragments were observed as shown in Fig. 4. Unlike $NiFe_2O_4$ and the needle-like NiO structures previously observed, the materials look like broken fragments of some oxide layers. Compared to other particles, the size of these fragments were large, approximately 10–50 μm in diameter. As listed in the table of Fig. 4, Zr content of the fragments was generally over 80 atomic%, where the fragments definitely came from oxide layers of cladding material. It was reported [3] that there are two kinds of $ZrO_2$ layers formed on fuel rods. One is a stable oxide layer as a protective film of a Zircaloy cladding. The other $ZrO_2$ layer is formed within the crud as the degradation product of the protective $ZrO_2$ film. Moreover, the latter layer is generally observed as oxide particles with a size of less than 3 μm in diameter. Therefore, we propose that the bigger $ZrO_2$ fragments do not come from the inside of crud, but from a breakaway of the stable oxide layer on cladding during the severe ultrasonic cleaning process.



| Element | Si | Cr | Mn | Fe | Ni | Zr | Total |
|---|---|---|---|---|---|---|---|
| At % | 8.52 | 0.47 | 0.43 | 1.44 | 0.66 | 88.47 | 100 |



| Element | Si | Cr | Mn | Fe | Ni | Zr | Total |
|---|---|---|---|---|---|---|---|
| a | 2.33 | 0.46 | 0.72 | 1.91 | 2.23 | 92.35 | 100 |
| b | 3.65 | 0.28 | 0.68 | 11.0 | 6.34 | 78.04 | 100 |

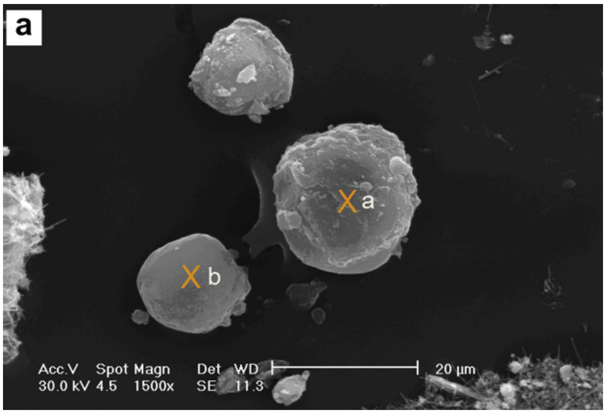
**Fig. 4.** Photos and elemental composition of the fragments in a crud sample. Numerical values shown are expressed as atomic%.

Some particles, where the major element was Si, were also found in the crud obtained during the ultrasonic cleaning process. Fig. 5 and the attached table show SEM photos of the round particles and their chemical constituents. Although the average content of Si in crud was around 10 atomic%, the content of Si in Si-rich particles was over 40 atomic%. It has been reported [14] that the Si ingredient is introduced from impurities of chemical additives, and storage racks of spent fuels and filter materials into reactor coolant. It is also known that Si can be observed in association with Ca.

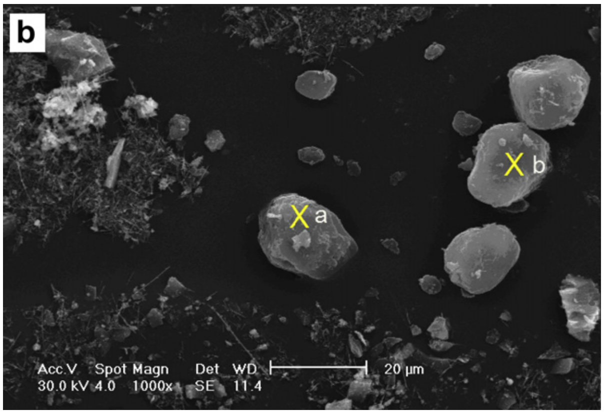
### 3.2. Soft and hard cruds collected from fuel rods

Two kinds of crud samples were collected from fuel rods. One is a soft crud obtained by scrubbing the fuel rods with ashless filter paper. Fig. 6 shows the surface morphology of the soft crud observed from one side. Even though the chemical content listed in the table of Fig. 6 varied along each measurement point, the main elements were Ni and Fe. Soft crud was composed of various micro-particles.

The second sample type is a hard crud, which was strongly attached on the fuel cladding. Hard crud was also sampled from a

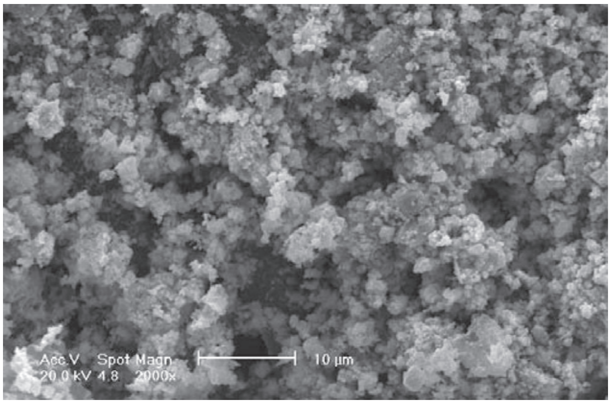


| Element | Si | Ca | Cr | Fe | Ni | Zr | Total |
|---|---|---|---|---|---|---|---|
| a | 64.42 | 8.98 | 2.56 | 6.45 | 9.16 | 8.43 | 100 |
| b | 43.35 | 11.59 | 3.16 | 11.0 | 13.64 | 17.26 | 100 |



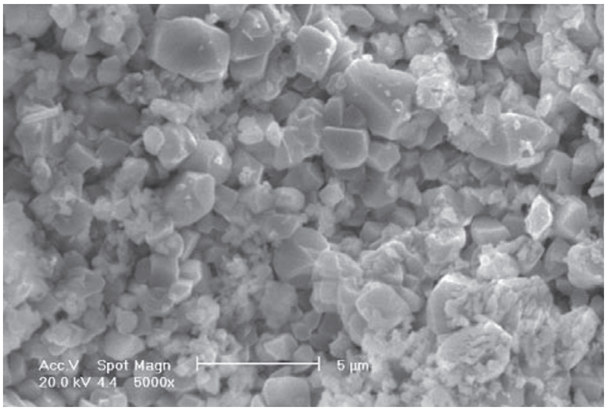
| Element | Si | Ca | Fe | Ni | Zn | Total |
|---|---|---|---|---|---|---|
| a | 73.37 | 6.16 | - | - | 20.34 | 100 |
| b | 78.20 | 10.03 | 6.01 | 5.76 | - | 100 |

**Fig. 5.** Photos and elemental composition of the particles in a crud sample. Numerical values shown are expressed as atomic%.



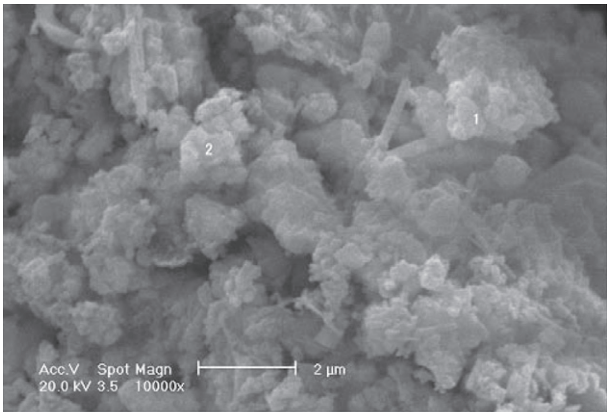
| Element | Fe | Ni | Cr | Zn | Total |
|---|---|---|---|---|---|
| Atomic % | 55.3 | 36.8 | 5.5 | 2.4 | 100 |

**Fig. 6.** Particle image and elemental composition of the soft crud.



| Element | Cr | Fe | Ni | Zr | Total |
|---|---|---|---|---|---|
| Atomic % | 0.73 | 2.88 | 3.02 | 89.16 | 100 |

**Fig. 7.** Crystalline side of the hard crud crust and its elemental composition.



| Element | Cr | Fe | Ni | Zr | Total |
|---|---|---|---|---|---|
| Point 1 | 7.0 | 44.3 | 45.1 | 3.6 | 100 |
| Point 2 | 5.6 | 28.1 | 56.0 | 10.3 | 100 |

**Fig. 8.** Non-crystalline side of the hard crud crust with analysis of indicated points. Numerical values shown are expressed as atomic%.

fuel rod by a metal scraper, and it was collected as pieces of crust. Figs. 7 and 8 are the SEM images showing both sides of a hard crud crust, respectively. One side shown in Fig. 7 is composed of small particles less than 3 μm in diameter. Since the main element of this side is Zr, this side is thought to be in contact with the fuel cladding. Fig. 8 shows the other side of the crud crust. This side was found to be a rugged texture, of which the major elements were Ni and Fe. From the analysis of the major elements, this side is thought to be exposed to the reactor coolant.

Two kinds of cruds were used for the chemical analysis by ICP–AES. One is a soft crud obtained by a scrubbing of the surface of the fuels with ashless filter paper. The other is hard crud, which is strongly attached on the fuel cladding. We analysed one soft and two hard crud samples. The results of the chemical analysis for these samples are listed in Table 2. In the soft crud sample obtained from the outer layer of crud, the major elements were Ni, Cr and Fe. The Zr content in the sample was very low. Conversely, in both hard crud samples, Fe is a major element, and it was remarkable to be observed in the presence of Zn.

Normally, Zn is injected into a coolant for reducing the radioactivity of said coolant, or for mitigating a corrosion of steam generator tubes [8]. Sometimes Zn is unintentionally added into the coolant as impurities of chemical additives or structural materials. Although a considerable amount of Zn was found in crud samples

**Table 2**
Elemental analysis data of the soft and hard cruds measured by ICP–AES. Unit is wt.%.

| Crud | Element | | | | | | | |
|---|---|---|---|---|---|---|---|---|
| | Co | Cr | Fe | Mn | Ni | Zn | Zr | Total |
| Soft | 0.0 | 8.3 | 29.1 | 0.0 | 60.6 | 0.6 | 1.4 | 100 |
| Hard 1 | 0.2 | 9.1 | 71.4 | 1.5 | 11.3 | 4.7 | 1.8 | 100 |
| Hard 2 | 0.1 | 9.3 | 61.7 | 0.5 | 5.5 | 22.3 | 0.6 | 100 |

obtained from one of the power plants surveyed, no Zn addition was attempted into the coolant until 2008 in Korean PWRs. In Table 2, a relationship was observed between Ni and Zn contents in the hard crud. Ni content was higher than Zn content in hard crud sample 1. Inversely, in sample 2, Zn content was higher than Ni. There were no considerable changes in other minor contents of both samples of hard cruds. It is reported [15] 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 temperatures. Therefore zinc ferrite is observed in the inner layer of crud, namely in hard crud. The relationship between Zn and Ni contents in both crud samples shows a good agreement with that previously reported by Byers et al. [12].

On the other hand, it is known that Ni in an outer layer of crud can remain as NiO or Ni metal [12]. The result that Zn content is very low in soft crud means no exchange reaction has occurred between Zn ions and NiO even at high temperatures. In addition, Zr content in the soft and hard cruds was very low compared with those samples obtained from an ultrasonic cleaning process. It is suggested that Zr-containing layers in hard crud would not be removed completely by the scraping process.

## 4. Conclusions

It is confirmed that the fuel crud contains many elements including Ni, Fe, Cr, Co, Zr, and Si, identified by using SEM–EDS, EPMA and ICP–AES. The major constituent element of the observed needle-like structures was identified as Ni. The stoichiometric Ni:Fe ratio of the crystal with octahedral structure was measured at 1:2 by using SEM–EDS. From the elemental analyses, it was deduced that these materials are composed of NiO and $NiFe_2O_4$, respectively. Many crud fragments of 10–50 μm diameter were contained in the crud samples. The main element composing them was identified as Zr. Since zirconium oxide is the only zirconium compound found in crud, the major component of fragments is likely to be $ZrO_2$, which comes from the oxidation of fuel cladding material. In Zn-containing crud, Zn content was closely related with Ni content. Ni content was observed to be relatively low in the Zn-rich crud, whereas Ni content was high in Zn-poor crud. This relationship agrees with the results previously reported Byers et al. [12], which indicated that Ni ions in nickel ferrite were replaced with Zn ions in the coolant. In some crud, the Zn element was generally observed in the inner layer, and rarely observed in the outer layer. This phenomenon is best explained by the fact that the Ni compound in the outer layer is mainly Ni or NiO, which are not replaced by Zn ions. The Si element in crud was observed as Si-rich particles. These particles were determined to contain approximately 10 atomic% of Ca. The analytical results of the crud used in this work were quite similar to those reported [3,12] for cruds which had been collected from PWRs in the USA.

## Acknowledgments

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