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Investigation on high gradient magnetic separation for CRUD material in nuclear reactor

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Abstract

In this study, we investigated high-gradient magnetic separation as a method for separating crud in high-temperature, high-pressure water inside a nuclear reactor. Corrosion products in the coolant circulate through the system and attach to the reactor core, where they are activated by neutron irradiation. The activated corrosion products then desorb from the core and circulate through the cooling system again. The corrosion product in the reactor water or piping system is called crud. Crud is the main source of radiation exposure for radiation workers. Removal and recovery of crud is important in decommissioning plants that have been in operation for service life, and new technologies are also desired. A method for separating activated ions adsorbed on ion exchange resins in nuclear reactors using magnetic separation is developed. In this method, the ion exchange resin is washed with acid, the activated ions are adsorbed from the washing water using adsorbents, and then separated magnetically. Rudimentary experiments were conducted to investigate the possibility of this method.

Keywords: high gradient magnetic separation, nuclear reactor, activated corrosion products, crud, radiation exposure of radiation worker

1. INTRODUCTION

Although highly corrosion-resistant materials are selected for the water supply system inside the nuclear reactor, some corrosion occurs in the high-temperature environment inside the reactor. This corrosion product circulates in the system while being dispersed in the coolant and attaches to the reactor core where it is irradiated with neutrons and becomes radioactive. The activated corrosion products peel off, re-circulate within the system and adhere to, for example, pipes. Such corrosion products deposited in the reactor water or on piping systems are called crud. This radioactive crud increases radiation levels in the environment and is a contributory cause of radiation exposure to radiation workers [1].

Another problem is that the heat exchange efficiency is reduced due to crud adhesion. Therefore, the establishment of crud removal technology is one of the important issues.

In addition, crud removal and recovery is important for decommissioning and continued operation of a plant that has been in operation for service life, and the development of new technologies for this purpose is also desirable.

We are therefore investigating the possibility of magnetic separation as a separation technology for crud in nuclear reactors. The results of this study will be reported.

2. CRUD

TABLE. 1
COMPOSITION OF CRUD IN PWR AND BWR.

Reactor type			BWR	PWR
Wetted area ratio of stuructural materials			Stainless steel 38～42% Carbon steel 16～20% Zircaloy 40～44% Inconel ＜1%	Inconel 65～70% Zircaloy 25～28% Stainless steel 4～6% Other alloys ＜1%
CRUD	Chemical form	Outer layer	α−Fe_2O_3 (Major), Fe_3O_4, $NiFe_2O_4$	Fe_3O_4 (Major), $NiFe_2O_4$ $FeCr_2O_4$
		Inner layer	Fe_3O_4 (Major), α−Fe_2O_3 $NiFe_2O_4$, $FeCr_2O_4$	$FeCr_2O_4$, Fe_2CrO_4
	chemical composition ratio		Fe 80 ～90% Cr+Ni 10～20%	Cr+Ni 60～80% Fe 20～40%

2.1. Chemical Composition of Crud

Crud comes from "Chalk River Unidentified Deposits," which are deposits found at the Chalk River nuclear reactor in Canada [2]. It is now a general term for metal oxides with a diameter of 0.45 μm or larger [3]. Table 1 shows a comparison of crud composition between Boiling Water Reactors (BWRs) and Pressurized Water Reactors (PWRs) [1]. As can be seen from this table, the main components are magnetite in PWRs and hematite in BWRs. These materials correspond to iron oxide scale in the water supply of thermal power plants [4].

2.2. Mechanism of Radioactive Crud Accumulation

Fig.1 shows an outline of the crud activation and accumulation process. Metals with high corrosion resistance are selected for the materials that make up the reactor, but they corrode slightly in high temperature environments (Fig. 1①). As a result, corrosion products

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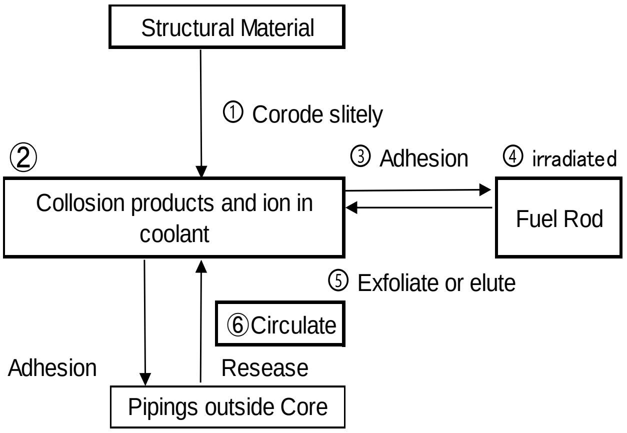


Fig. 1. Radioactivity accumulation mechanism in Primary Cooling System

and ions circulate through the system in the cooling water (Fig. 1②). When these materials reach the reactor core and adhere to the surface of the fuel rods (Fig. 1 ③), the fuel rod surfaces are irradiated with neutrons and then the materials become radioactive (Fig. 1 ④). This activated corrosion product peels off or elutes (Fig. 1⑤). These are recirculated through the system and adhere to the tubes (Fig. 1⑥).

The problem is that the radioactive isotopes accumulated in the piping system during this process increase the ambient air dose [5].

2.3. Radioisotope Nuclides in Crud

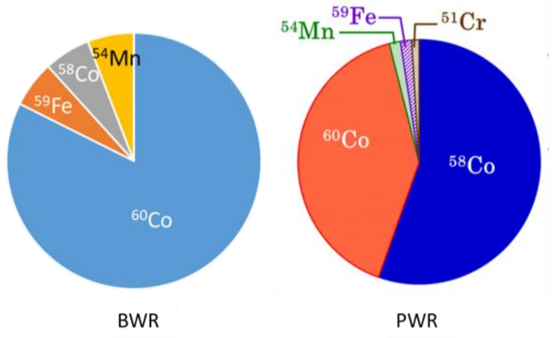
Fig.2 shows the RI nuclides that cause the problem of elevated air dose in BWRs and PWRs [1]. It also shows the nuclear reactions in which they are produced. The half-lives are also given in brackets. "y" and "d" indicate the year and day, respectively. ^{60}Co is a problem for BWRs and ^{58}Co and ^{60}Co are a problem for PWRs. However, the half-life of ^{58}Co is 71 days, which is shorter than that of ^{60}Co, and it is a nuclide that decays in a relatively short time. Therefore, ^{60}Co is also the main nuclide in PWRs.

3. DIFFERENCE OF PWR AND BWR

Fig. 3 and 4 show schematic diagrams of PWR and BWR, respectively.

In a PWR, primary cooling water and secondary cooling water exchange heat in a steam generator, which is then guided to a turbine where the secondary cooling water generates electricity. Because the turbine is rotated by secondary cooling water that is not in direct contact with the nuclear fuel, the air dose in the secondary system is low.

On the other hand, in a BWR, the turbine is rotated by water vapor that comes into contact with the nuclear fuel in the reactor core, so although the structure is simple, the system is also radioactively contaminated. As a result, workers are exposed to more radiation than in a PWR.



^{59}Co（n, γ）^{60}Co(5.3y)、 ^{58}Ni(n,p)^{58}Co(71d)、 ^{54}Fe(n,p)^{54}Mn(313d)、 ^{58}Fe（n, γ）^{59}Fe(45d)

Fig. 2. Radionuclides in the crud together with the nuclear reactions in which they are produced.

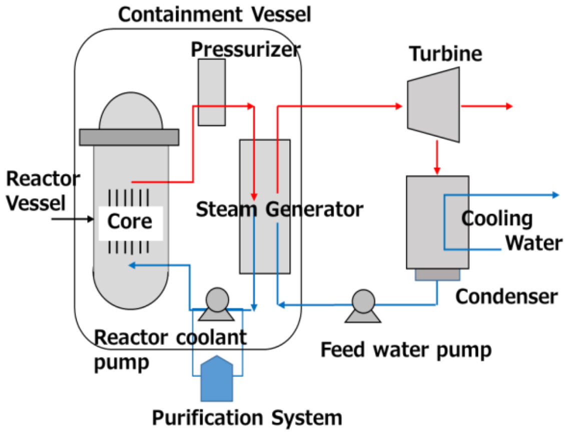


Fig. 3. Schematic diagrams of PWR

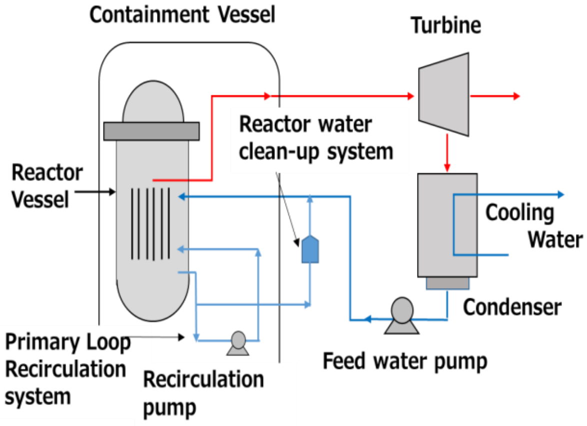


Fig. 4. Schematic diagrams of BWR.

4. CURRENT PROCESSING METHOD

4.1. BWR

The crud is basically treated with filters and ion exchange resins [6]. BWRs are equipped with “reactor water clean-up systems” as shown in Fig.3, which treat 2-4% of the total coolant [6]. Precoated filters and ion exchange resins are used [6]. Here, the activated crud is adsorbed. Ion exchange resin is used here, but it cannot be used during operation due to high temperature and high pressure (~285°C, ~7 MPa) and requires cooling.

For this reason, when this system is used, a problem arises that causes a decrease in the operating rate of the nuclear reactor. Therefore, in Europe and other countries, attempts have been made to install magnetic filters using electromagnets to operate under high-temperature and high-pressure conditions [7]. However, as mentioned above, since the main component of the crud is hematite, the current situation is that the separation efficiency cannot necessarily be said to be high. We believe that there is a possibility of introducing superconducting magnetic separation here.

4.2. PWR

Although the amount of radioactive crud in PWR is 1/2-1/3 of that of BWR (several ppb) [6], it still increases the air dose. For this reason, a “chemical volume control system” for the primary cooling system is installed to remove crud (PWR is divided into primary and secondary cooling systems). It extracts a part (17t/h in 1100MW class PWRs [6]) of the primary cooling water, which has several functions (e.g. adjustment of boron concentration), some of which are removal of corrosion products. This system is operated continuously. Ion exchange resins are used for this separation, but this results in highly concentrated radioactive waste, exchange resin.

The ion exchange resin is basically incinerated to reduce its volume and transported to vitrified waste storage center for high level radioactive waste.

Before incineration, it is necessary to wait for the RI to decay. This is because incineration concentrates RI. If it were possible to separate RI, it would be possible to incinerate without waiting for this, and there would be no need to store waste ion exchange resin.

This series of investigations clarified the field of application of superconducting high-gradient magnetic separation systems in nuclear reactors. As a short-term goal, we decided to consider the use of a high-gradient magnetic separation system to separate RI from radioactive ion exchange resins for PWR applications. The long-term goal is to implement high-gradient magnetic separation systems in BWRs.

5. USED ION EXCHANGE RESIN

Fig.5 shows the processing flow of the highly radioactive used ion exchange resin that we are considering. First, the waste ion exchange resin is washed with acid. After washing, the radioactive isotopes have been removed, so the resin can be incinerated. The problem is the wash water (containing radioactive isotopes) after washing.

The proposed post-washing process is shown in the area surrounded by the dashed line. First, the acidic wash water is neutralized. After neutralization, micro-iron^{TN} [8] powder is added to adsorb ^{60}Co or ^{58}Co ions, and the adsorbed micro-iron^{TN} is magnetically separated. If the processing volume increases in the future, the processing speed will be increased with a superconducting magnetic separator. The volume of the contaminated waste (exchange resin) can be greatly reduced and thus easily stored in the waste storage facility.

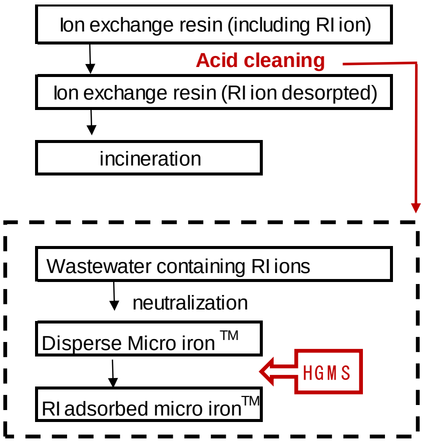


Fig. 5. Flow chart of used ion exchange resin processing, After acid cleaning, High Gradient Magnetic Separation (HGMS) will be used.

6. BASIC EXPERIMENTS

We conducted basic experiments to confirm the effectiveness of the flow proposed in Fig. 5. The following three basic experiments were carried out. First, we investigated whether there were any problems in handling the desorption process of radioactive ^{60}Co from ion exchange resins, then we demonstrated the ability of the adsorbent to adsorb cobalt ions, and finally we investigated the possibility of magnetic separation of the adsorbent. In other words, experiments were conducted to confirm the feasibility of the proposed process.

6.1. Handling of RI ^{60}Co Ions

It was necessary to confirm whether the radioisotope ^{60}Co could be adsorbed and desorbed on ion exchange resin without any problems. Therefore, an experiment was carried out to see whether ^{60}Co could be desorbed without any problems using hydrochloric acid. The actual condition of the experiment is shown in Fig. 6. The left is a photograph of an aqueous solution of ^{60}Co ions and an ion exchange resin. The right shows ^{60}Co ions being removed from an ion exchange resin using hydrochloric acid. It was confirmed that the radioactive substance ^{60}Co could be desorbed without any problem.

6.2. Performance Test of Adsorbing Material

The major influence on the proposed flow is the adsorption capacity of the adsorbent for cobalt ions. Therefore, the difference in the adsorption capacity of cobalt ions between micro iron and magnetite was compared at around pH 7. pH 7 is assumed to be a situation where the solution is neutralized. The results are shown in

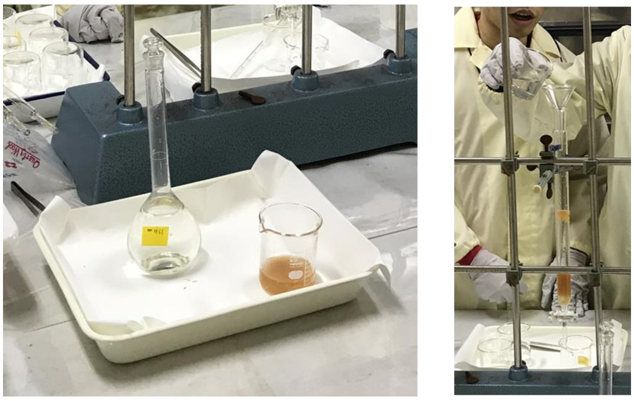


Fig.6. Adsorption and desorption test of cobalt-60 using ion exchange resin.

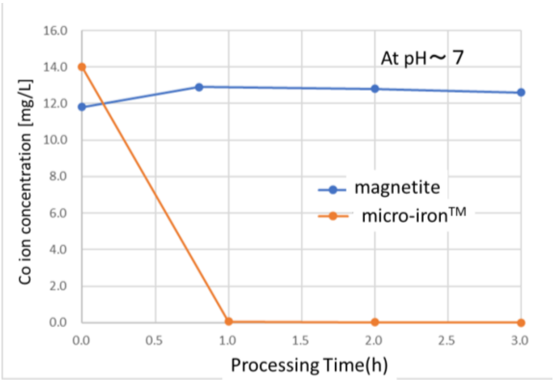


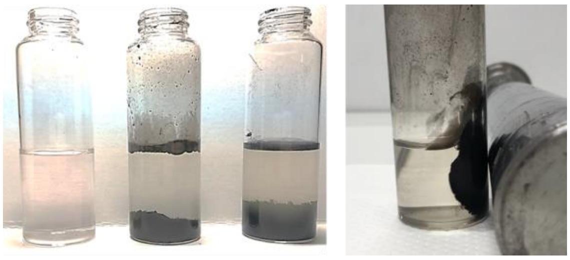
Fig. 7. Comparison of the adsorption efficiency of cobalt ions between adsorbents and magnetite.

Fig. 7, and it became clear that micro iron^{TN} effectively absorbs cobalt ions. The volume of the solution is 200 mL and the weight fraction of adsorbent is 20 g/L in both cases.

6.3. Magnetic Separation Test

Fig.8 shows an experiment in which adsorption by an adsorbent and magnetic separation were carried out on a solution containing dissolved cobalt ions (500 ppm). In Fig.8(a), the left shows a solution containing cobalt ions, the center shows a solution in which micro-iron^{TN} was dispersed and stirred for 30min., the right shows a solution in which the same amount of magnetite was dispersed and stirred. Co ions appear pink. When the adsorbent is dispersed and stirred, the solution becomes transparent, indicating that the cobalt ions have been adsorbed. With magnetite, the color of the cobalt ions remains in the solution, indicating that it has low adsorption capacity.

After adsorption, a separation experiment was carried out using a neodymium magnet (0.5T) as shown in Fig.8(b). It was confirmed that cobalt ions could be successfully adsorbed and separated out using a neodymium magnet (0.5T) as a result, it was confirmed that cobalt ions could be successfully adsorbed and separated.



(a) (b)

Fig. 8. Adsorption of cobalt ions and magnetic separation of the adsorbent. (a) From the left, cobalt aqueous solution, adsorbent dispersion, and magnetite dispersion. (b) Magnetic separation of the adsorbent after cobalt adsorption.

7. CONCLUSION

Crud generated in nuclear reactors increases the radiation exposure of maintenance workers. Therefore, crud treatment methods were investigated. It was suggested that installation of a magnetic separation system in the water circulation system in BWRs and magnetic separation of cobalt adsorbed on ion exchange resin in PWRs would be promising. Based on this, the use of magnetic separation to regenerate ion exchange resin was investigated and shown to be feasible.

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