DEVELOPMENT OF WET-OXIDATION TREATMENT SYSTEM FOR FILTER BACKWASH SLUDGE AND ION EXCHANGE RESINS

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ABSTRACT

Decomposition of organic compounds contained in filter backwash sludge and spent ion exchange resins is considered effective in reducing the waste volume. A system using the wet-oxidation process has been studied for the treatment of the sludge and resins stored at Tsuruga Power Station Unit 1, 357MWe BWR, owned by The Japan Atomic Power Company. Compared with various processes for treating sludge and resin, the wet-oxidation system is rather simple and the process conditions are mild.

Waste samples collected from storage tanks were processed by wet-oxidation and appropriate decomposition of the organic compounds was verified. After the decomposition the residue can be solidified with cement or bitumen for final disposal. When compared with direct solidification without decomposition, the number of waste packages can be reduced by a factor of a few dozens for the sludge and three for the resin. Additional measures for conditioning secondary waste products have also been studied, and their applicability to the Tsuruga Power Station was verified.

Some of the conditions studied were specific to the Tsuruga Power Station, but it is expected that the system will provide an effective solution for sludge and resin treatment at other NPPs.

INTRODUCTION

Filter backwash sludge (FS) and spent ion exchange resin (IEX) are generated by the water cleanup and liquid waste treatment systems of NPPs. It is a general practice in Japan to store these wastes in tanks unless their activity is acceptable for final disposal at the existing LLW disposal site. Investigations on the treatment of these wastes have accelerated in recent years in parallel with progress on the conceptual design of a disposal site that will receive higher activity waste, such as activated metals, FS and IEX.

Decomposition of organic compounds contained in FS and IEX is considered effective in reducing waste volume and saving disposal capacity and cost. In addition, their decomposition eliminates the potential impact of cellulose contained in these wastes, namely, the possibility that degradation products may increase nuclide solubility at the disposal site (1).

The Japan Atomic Power Company (JAPC) undertook an investigation on the treatment of FS and IEX stored at its Tsuruga Power Station (Tsuruga PS) Unit 1, a 357 MWe BWR plant. This is the first commercial LWR plant in Japan and it has been in operation since 1969. The volumes of the stored FS and IEX are comparatively large (i.e., 260m^3 of FS and 280m^3 of IEX) and the dose rates at the surfaces of the tanks range from a few to dozens of mSv/hr.

A series of experiments with the wet-oxidation (WetOx) process have been conducted at the Tsuruga PS by the collaboration of JAPC and JGC Corp. since 1999. The WetOx process has the advantage of safe treatment of higher activity wastes because the process is simple and decomposition occurs under water at 100 degrees centigrade. Moreover, it ensures a compact system that can be installed in the available space within the existing radioactive waste (RW) treatment facility of the Tsuruga PS.

OUTLINE OF THE WetOx PROCESS

Since the early 1980s, JGC Corp. has been developing the WetOx process using hydrogen peroxide as an oxidant and ferric and/or ferrous ions as a catalyst (2-4). In this process, organic compounds are chemically decomposed by the oxidation in an aqueous solution. This WetOx system was used at a NPP in the USA to treat chemical decontamination liquid containing EDTA, an organic chelating agent.

A schematic flow of the WetOx process is shown in Fig. 1. Waste is mixed with water to adjust its concentration in the waste feed tank and then transferred into the reactor tank. Depending on the waste to be treated, sulfuric acid may be added to keep pH value below 4 during the reaction. The decomposition reaction begins by the addition of the catalyst and 35% hydrogen peroxide after heating up to 100 degrees centigrade. The reaction is maintained by the continuous supply of the oxidant. The waste may be added during the reaction, if necessary, until the reaction is deactivated by an increase in salt concentration.

The secondary products are residual liquid and off-gas. The residual liquid is neutralized with caustic soda and then drained out for further conditioning. The off-gas consists of vapor and non-condensable gas. The vapor is condensed and received in the distillate tank. The condensate may be further processed, reused or released according to the user's requirement. The non-condensable gas may be transferred by the off-gas blower for further treatment.

The following features of the WetOx process have been reported:

- High volume reduction by the decomposition of organic compounds
- Mild process conditions: 100 degrees centigrade, atmospheric pressure
- Compact system: vessels and pumps only, no pretreatment, and simple off-gas treatment

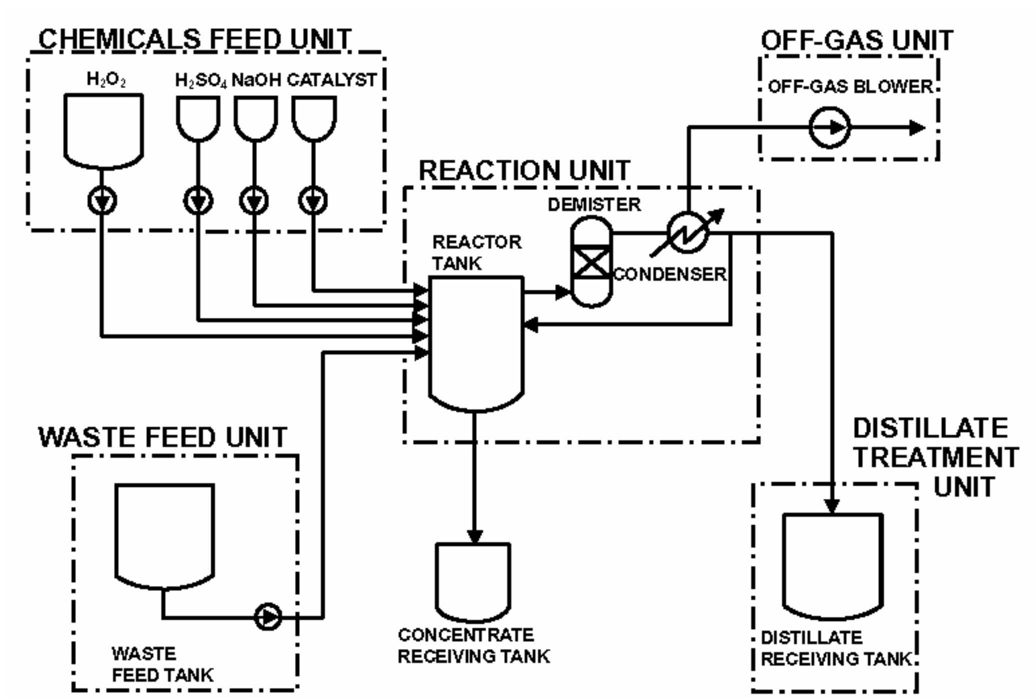


Fig. 1. Schematic flow of the wet-oxidation system

EXPERIMENTS

The experiments on FS and IEX treatment at the Tsuruga PS include: 1) sampling and analysis of wastes stored in tanks, 2) decomposition of sampled wastes in laboratory scale apparatus, 3) decomposition of simulated wastes using a pilot plant, and 4) studies on secondary products conditioning.

The main points of the experiments are as follows:
- Evaluation of the wastes to be decomposed
- Evaluation of the process parameters
- Study on conditioning and solidification of the residual liquid
- Study on Tie-in conditions with the existing RW facility for the treatment of the secondary products

Wastes to be decomposed

The wastes stored in five FS storage tanks and four IEX storage tanks were studied through an analysis of their samples. The operation record of the Tsuruga PS was also considered. Their components, volumes and activity concentrations are shown in Table I. The dominant nuclide is ^{60}Co and its concentration ranges from 1 x 10^9 to 10^{11} Bq/ton for FS and 1 x 10^{11} Bq/ton for IEX.

FS consists of filter aids (cellulose-based and diatomaceous earth-based), metal oxides and ion exchange resins, where the main component is the cellulose-based filter aid. The resin found in FS is transferred to the FS storage tank during backwash of the condensate demineralizers. The components other than the cellulose and the resin are inorganic and are not decomposed. The composition differs depending on the tank, so the process parameters, such as reaction time and oxidant addition, may require adjustment for each tank. The standard composition of the simulated waste used in the experiments has been determined for each tank, based on sample analysis.

The IEX consists of resin and metal oxides, and the total volume is estimated to be approximately 280m^3. The IEX storage tanks have received spent resin from the reactor water clean up, spent fuel pool clean up, liquid RW treatment, and condensate demineralizers without separating them according to their sources. For this reason, the total volume of the stored IEX is relatively large when compared with other NPPs where spent resins with low activity are incinerated or solidified and only those with high activity are stored in tanks. In the case of the Tsuruga PS, it is expected that volume reduction will result in large cost savings.

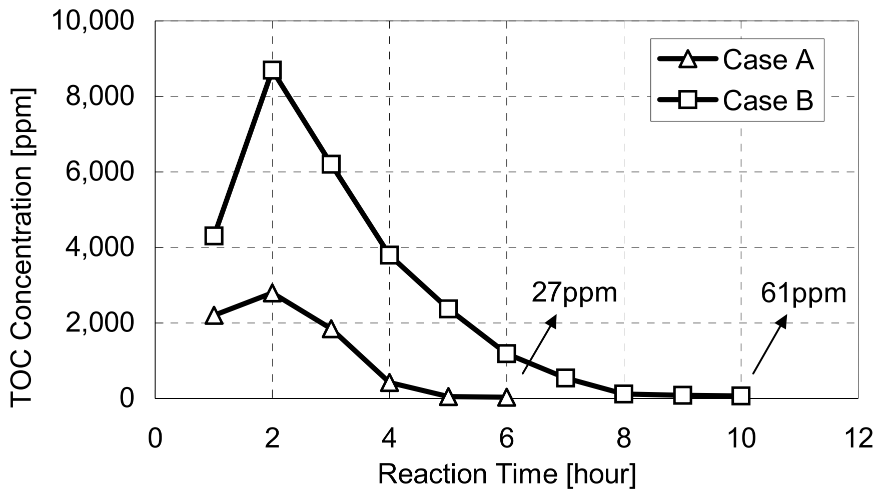
Table I. Contents of FS and IEX storage tanks

	FS storage tanks	IEX storage tanks
Contents	Filter aids - Cellulose base - diatomaceous earth base, etc. Ion exchange resins Metal oxides	Ion exchanger resins Metal oxides
Total volume of waste (mass)	260m^3 (270 ton-wet)	280m^3 (205 ton-wet)
Co-60 activity concentration	1 x 10^{+9} – 10^{+11} Bq/ton-wet	1 x 10^{+11} Bq/ton-wet

Decomposition by the WetOx process

Fig. 2. shows typical decomposition data evaluated in the TOC concentration. The data is obtained by decomposing simulated FS using a pilot plant with a reactor capacity of 0.15m^3. The process parameters

such as the oxidant feed rate were determined in advance through bench scale experiments.
The TOC concentration decreases with the reaction time, and more than 95% of the initial organic compounds are decomposed in 6-8 hours. Experiments on FS samples show the same result, i.e., the organic compounds are decomposed to a TOC concentration of less than a few tens of ppm. Although it is observed that the resin is a little more stable than the cellulose-base filter aid, IEX is decomposed to the same level in 6 hours by adjusting the waste concentration supplied.



Case A: Cellulose 10.9kg, IEX 2.3kg, 35%H_2O_2 Feed Rate 32L/h
Case B: Cellulose 3.3kg, IEX 4.8kg, 35%H_2O_2 Feed Rate 17L/h

Fig. 2. TOC concentration during WetOx reaction for simulated filter sludge

Conditioning of the residual liquid

The residual liquid contains sodium sulfate and inorganic sludge. It can be solidified with cement or bitumen widely adopted in NPPs. Compared with the direct solidification of FS and IEX, solidification after WetOx treatment reduces the number of waste packages by a factor of a few dozens for FS and by about three for IEX.

It is important to demonstrate that the waste forms produced do not affect the nuclide retention of the engineered barrier of the disposal site. The nuclide retention can be assessed by a distribution coefficient -Kd (a ratio of nuclide concentrations between the solid and water). Kd was determined under the simulated disposal condition, using a mixture of the residual liquid and engineered barrier material.

Fig. 3. shows the relationships between the reaction time, TOC concentration and Kd values for ^{60}Co and ^{63}Ni, which were obtained using residual liquid of the simulated FS decomposition. While the TOC concentration of the residual liquid decreases with the reaction time, the Kd value exponentially increases. The correlation shows that the decomposition to a few dozens of ppm satisfies the disposal conditions, the Kd values adopted from the safety assessment of the LLW disposal site.

Further volume reduction of the residual liquid

Additional treatment measures were studied to achieve higher volume reduction of the residual liquid. First, a cementation system using a mixer equipped with a heater was considered. This system concentrates all contents of the residual liquid by evaporation in the mixer. After evaporation, the concentrated residual liquid is solidified with cement in the mixer.

Second, a combination of filtration and selective ion exchange using inorganic media was considered. It removes particulate radioactivity, such as cobalt, by filtration and traps cesium ions in the inorganic selective ion exchange media. Treated water containing the sodium sulfate has less activity and can be sent to the plant water treatment system.

When such processes are selected, the radiation protection measures must be taking into account for operation and handling within the plant and transportation and disposal since the resultant products have high dose rates.

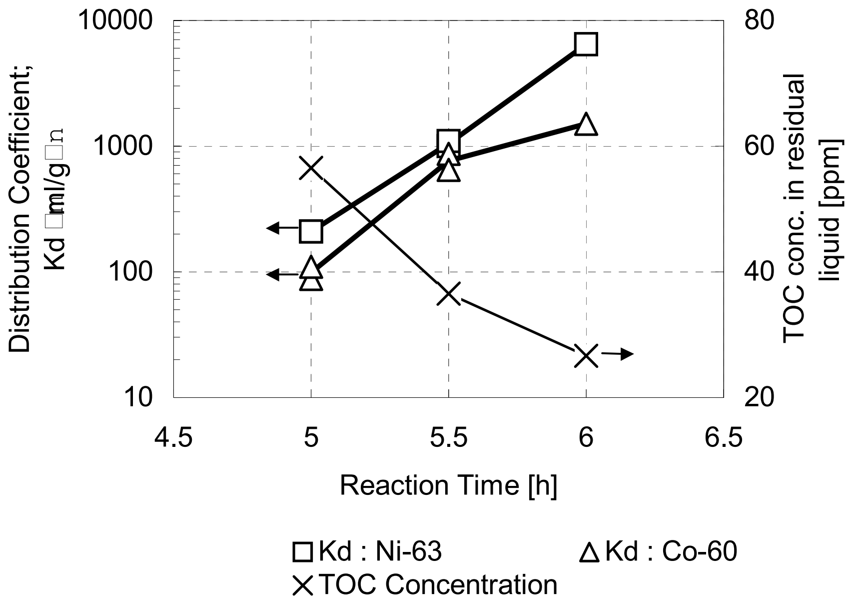


Fig. 3. Development of TOC concentration and distribution coefficient with reaction time (Decomposition of simulated filter sludge)

Conditioning of the distillate

The distillate recovered from the off-gas condenser may be treated, reused or released. The Tsuruga PS plans to transfer the distillate to the existing RW treatment system for reuse as plant make up water. The distillate will be treated by evaporation in the existing RW facility. Measures to eliminating trace amounts of organic compounds in the distillate were studied since organic compounds cannot be removed by the plant's evaporator and may affect the nuclear reactor.

A catalytic combustion system was studied to evaluate its performance. When the off-gas is not treated by the catalytic combustion, the TOC concentration of the distillate peaks at about 300ppm in the early stage of the reaction and drops down to a few tens of ppm as the decomposition proceeds. It is observed that the TOC concentration in the distillate is lowered to less than 1ppm when the catalytic combustion is installed. The system effectively removes organic compounds, and the distillate can be treated in the same manner as other liquid wastes to be reused in the plant.

CONCLUSION

The WetOx system has been studied for the treatment of the filter sludge and ion exchange resin, specifically those stored at the Tsuruga PS. The system provides an effective solution to the treatment of these wastes, which enables the decomposition of organic compounds and ensures high volume reduction performance. Compared with direct solidification without decomposition, the volume reduction ratio in terms of waste packages is estimated at a few dozens for the filter sludge and three for the ion exchange resin. The volume of the resin can be reduced to a ratio of nine by installing an additional system, but radiation protection measures to deal with the high dose rates of resultant products must be considered.

It has been found that the WetOx process is suitable for sludge and resin treatment at the Tsuruga PS. Although some of the conditions studied are specific to the Tsuruga PS, it is expected that the system will provide an effective solution for sludge and resin treatment at other NPPs.

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