A NEW METHOD TO ALLOW REUSE OF SPENT POWDERED ION EXCHANGE RESIN

M.Kikuchi [1], K.Funabashi [2], T.Fukasawa [2], and H.Yusa [2]

1 Nuclear Plant Design Dept.
Hitachi Works, Hitachi, Ltd.
3-1-1 Saiwai-cho, Hitachi, Ibaraki 317,

2 Energy Research Lab., Hitachi, Ltd.
1168 Moriyama-cho, Hitachi, Ibaraki 316, Japan.

ABSTRACT

A method was developed to reuse spent powdered ion exchange resin, which is estimated to be about 60% of the total radioactive waste produced in a nuclear power plant. The method forms a part of our new volume reduction system. The three key steps in the reuse are; (1) removal of solid impurities, such as crud, from resin by using an ultrasonic technique ; (2) separation of flocculating cation and anion resins by using electrolyte action ; and (3) regeneration of separated resins by using H_2SO_4 and NaOH. Pilot plant (capacity ; 9kg/h) tests demonstrated that spent resin can be regenerated with an efficiency of about 90%. The filtering performance of the regenerated resin was examined and found acceptable for practical use. Application of this reuse method reduces the spent resin volume to a level about 30% of that presently generated.

INTRODUCTION

Increasing amounts of radioactive wastes from nuclear power plants have necessitated extensive efforts to develop a better waste volume reduction system. We have previously originated a drying and pelletizing technique with which liquid and slurry wastes can be remarkably reduced in volume (e.g. to about 1/7 compared with a cement solidification system).[1],[2] Now, we have implemented a new method to reuse spent powdered ion exchange resin. When used in our volume reduction system, further reductions in the waste volume were obtained.

Figure 1 outlines the BWR plant radwaste system and the volume ratio of the main wastes. About 60% of the waste is due to powdered ion exchange resin. This resin is widely used for water treatment because of its ability to remove both ionic and solid impurities. In the case of BWR plants, large amounts of powdered ion exchange resin are used as the condensate filter demineralizer for purification of the primary cooling water. Figure 2 is a schematic drawing of such a demineralizer. The powdered ion exchange (mean diameter of 30 μm) is precoated on the filter element with a thickness of about 10 mm after mixing cation and anion resins, usually in the ratio of 2 to 1. After the pressure drop reaches a certain value due to filtering solid impurities such as crud (main composition : Fe_2O_3), the precoat layer is removed by a water back wash to the spent resin storage tank. The used powdered resin has been customarily treated as radioactive waste without any reuse since a regeneration method has not been developed, while the bead ion exchange resin is reused after chemical regeneration. The former results in the primary source of radioactive waste.

The purpose of this research work was to develop a regeneration method for powdered ion exchange resin in order to reduce the final waste volume, as well as to minimize expenses for new ion exchange resin.

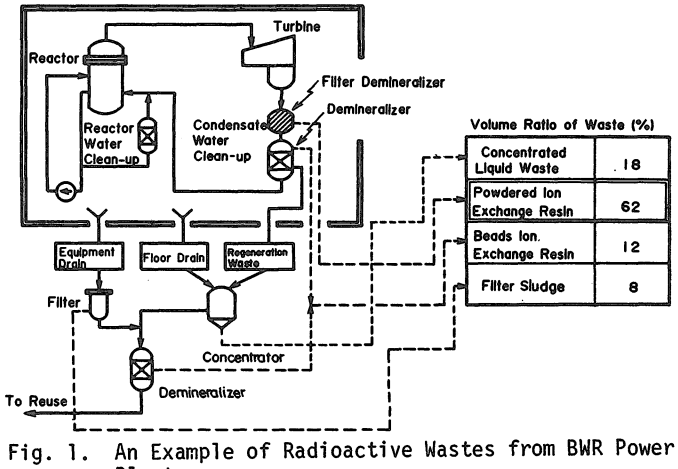


Fig. 1. An Example of Radioactive Wastes from BWR Power Plant.

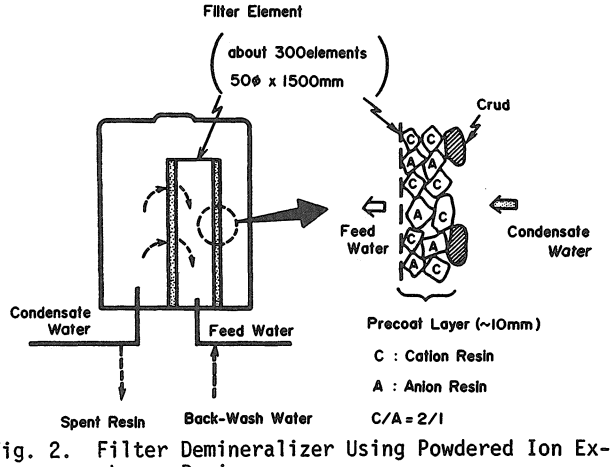


Fig. 2. Filter Demineralizer Using Powdered Ion Exchange Resin.

FLOCCULATION OF POWDERED ION EXCHANGE RESIN

Powdered ion exchange resin shows distinctive flocculation phenomena when cation resin having negative surface charge and anion resin having positive surface charge are mixed. Figure 3 reproduces a photo of the flocks and gives relationships between particle diameter and specific volume of flocks. Commercially available powdered resin (diameter : 20-250 μ m) and bead resin (diameter : 420-1200 μ m) are shown as references. The specific volume of the flocks increases as resin diameter decreases. This can be attributed to a stronger specific surface charge for smaller resins. The ability of powdered resins to form highly porous flocks provides good filter performance by reducing the pressure drop, but becomes a problem in reuse of the spent resin.[3]

An outline of the reuse process is shown in Fig. 4. The spent resin adsorbs ions such as Co^{2+} and Mn^{2+} and solid impurities such as crud. The process consists mainly of four steps : (1) removal of solid impurities such as crud from resins; (2) decomposition of flocks; (3) separation of resins into cation and anion types; (4) regeneration of separated resins. For item (1), we have already developed an ultrasonic technique which can remove crud with an efficiency of 88%[4]. Item (4) uses the same techniques as conventional chemical regeneration, such as H_2SO_4 solution treatment for cations and NaOH solution for anions. This regeneration waste containing Na_2SO_4 and radioactive ions is treated as concentrated waste. Thus the new technique should be applied to items (2) and (3) in order to provide a feasible reuse system.

The principle of the new technique to perform both decomposition and separation is described in Fig. 5. By adding a strong electrolyte such as NaOH to the flock-containing solution, functional groups which are source of surface charges on the resin are saturated, e.g. the cations with Na^+ and anions with OH^-. Since resin charges are neutralized, the flocks are easily decomposed. If the specific gravity of the electrolyte is adjusted to between that of the two resins, separation of cation and anion types can be done by a sedimentation technique.

The separation efficiency is determined by either the small amount of cation resins mixed in the floated anion resins or anion resins sedimentated with the cation resins. Within our experimental region, the efficiency is mostly determined by the former case.

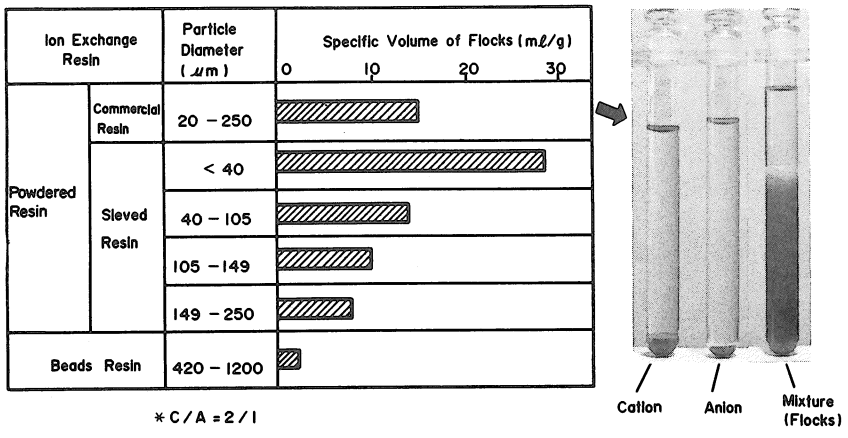


Fig. 3. Flocculation Property of Ion Exchange Resin.

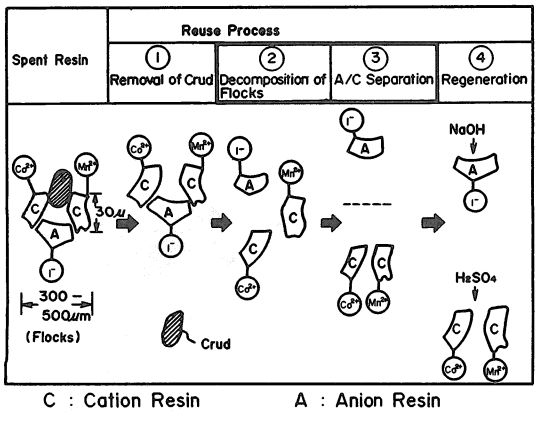


Fig. 4. Reuse Process Scheme of Powdered Ion Exchange Resin.

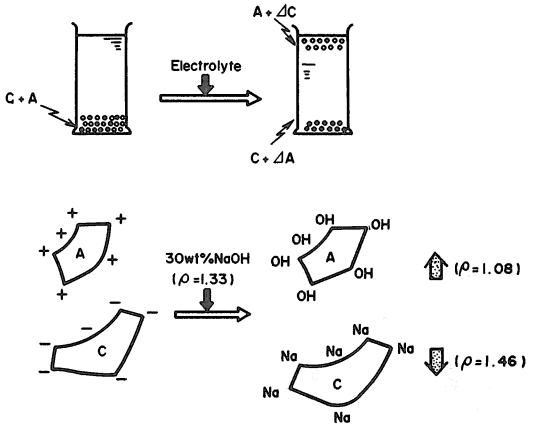


Fig. 5. Principle of Resin Separation Method.

FUNDAMENTAL EXPERIMENTS

The separation efficiencies after 5hr settling are shown for different electrolytes in Fig. 6 as a function of electrolyte ionic strength which represents the effects of both charge and concentration of electrolyte, e.g. a measure of the neutralization power of the resin surface charge. The efficiency increases as ionic strength increases above 5, independent of the kind of electrolyte. This efficiency independency suggests that neutralization of resin surface charge has an important function in the flock decomposition and separation process.

In order to increase sedimentation rate and removal efficiency, a centrifuge was applied. The result is shown in Fig. 7 when NaOH is used as electrolyte. A separation efficiency of about 85% was obtained in a 1000G centrifuge, but only 20% separation efficiency was obtained for a 5hr settling. The reduction of the electrolyte concentration is important because it directly reflects the amount of secondary waste.

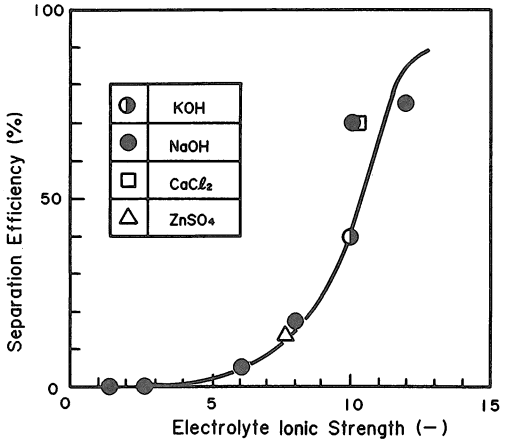


Fig. 6. Separation Efficiency for Different Electrolytes.

PILOT PLANT TESTS

Outline of Pilot Plant

Based on results from fundamental experiments, a pilot plant (treatment capacity : 9 kg/h, 1/4 actual size) was constucted. A process scheme of the pilot plant is shown in Fig. 8. The main components are two centrifuges. The primary centrifuge is a specially designed dual basket type centrifuge which combines both resin separation and rinse functions in one centrifuge.

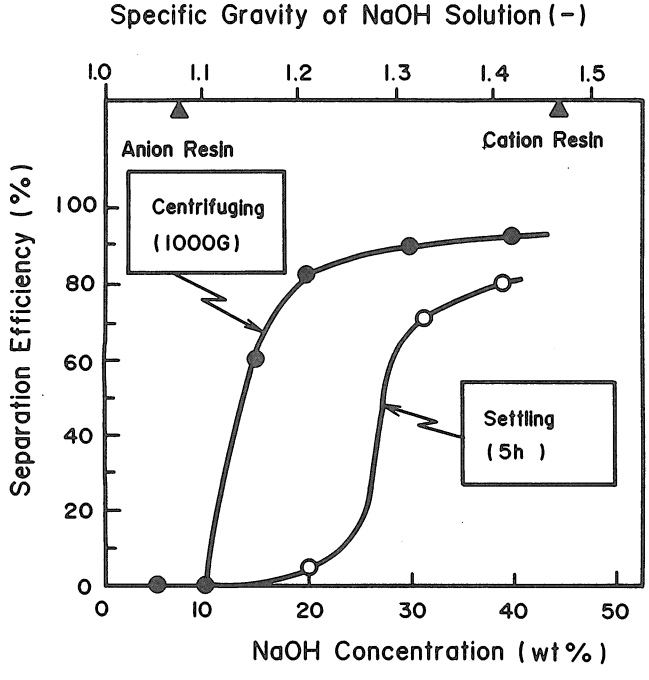
Spent resin is fed to the primary centrifuge as a NaOH slurry after the crud removal process, and cation and anion resin separation is performed. The anion resin is continuously removed from the centrifuge and fed to the secondary centrifuge as a NaOH slurry, while cation resin remains in the primary centrifuge. Then cation and anion resins are rinsed with water in two centrifuges. The anion resin is ready for reuse since it is already regenerated to the OH type by the NaOH solution. However cation resin must be treated by H_2SO_4 solution to be regenerated as an H type.

The system is operated by a computor control system. Figures 9 and 10 show photos of the pilot plant and a CRT display on the control panel during the separation process.

Test Results

The pilot plant test results are summarized in Fig. 11. The separation efficiency of 90% was obtained under operation conditions of 1500 G and a 9 kg/h feed rate. Crud removal efficiency and ion exchange capacity of resin after separation and regeneration cycles are used to evaluate the filtering performance of regenerated resin in practical use.

Crud removal efficiency was measured using 1 μm Fe_2O_3 powder solution at 10 ppm concentration. The removal efficiency of about 95%, which exceeds the design criterion (90%) was obtained at a linear



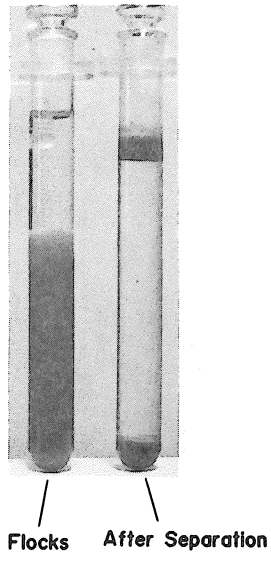


Fig. 7. Effect of Centrifugal Force on Separation Efficiency.

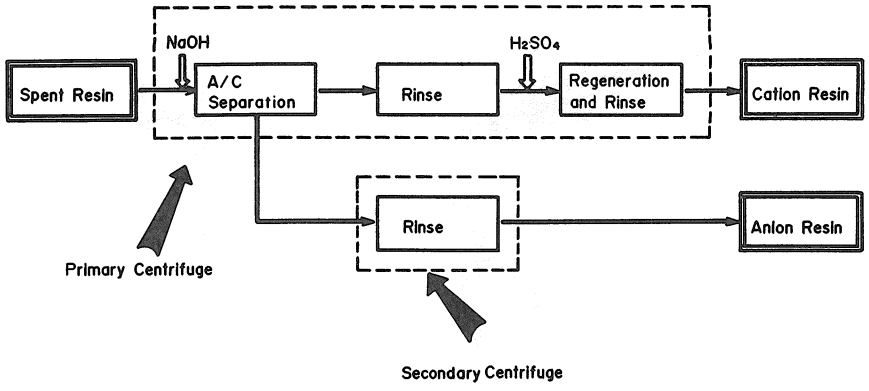


Fig.8 Process Scheme of Pilot Plant

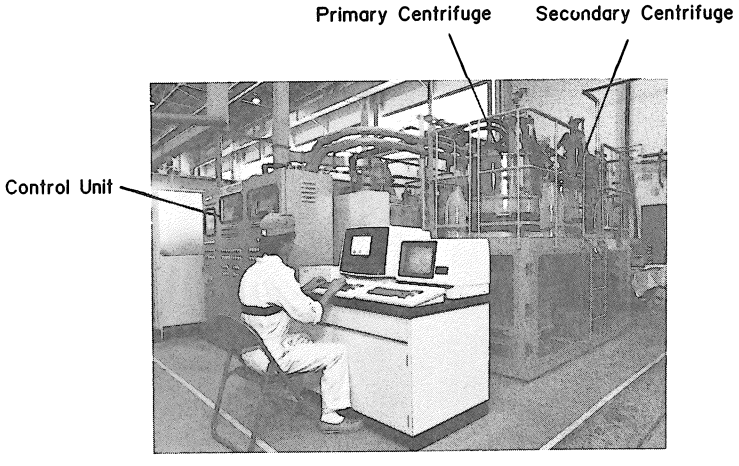


Fig.9 Pilot Plant (Capacity : 9kg/h)

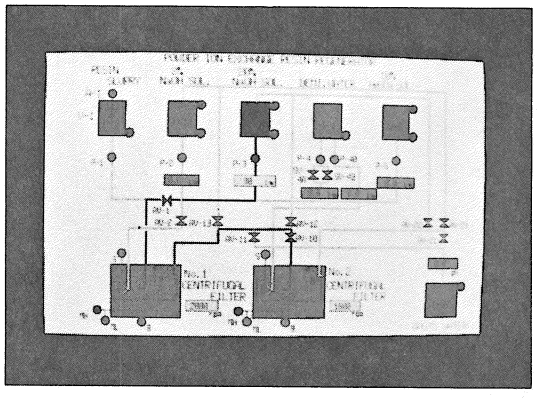
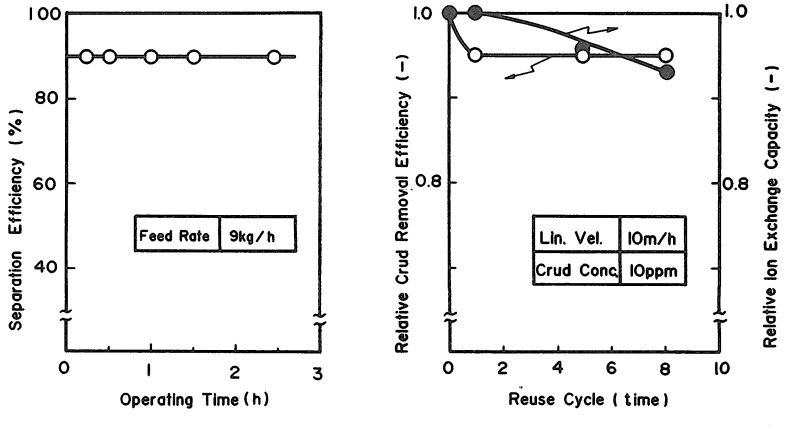


Fig.10 An Example of CRT Display of the Pilot Plant



(a) Separation Efficiency (b) Performance of Regenerated Resin

Fig.11 Pilot Plant Test Results

velocity of 10 m/h. The decrease after the first recycle might be attributed to an outflow of small amounts of minute particles. The slight decrease in ion exchange capacity, e.g. to about 93% of the value for new resin was observed. This might be due to deterioration of the anion exchange resin, which has a relatively weak functional group.

Estimation of Waste Volume

The effect of volume reduction using the new system was estimated from the pilot plant test. The results are shown in Fig. 12. Amount of spent resin is reduced in proportion to the number of reuse cycles, while the amount of concentrated liquid (Na_2SO_4 solution) increases. The results suggest that 4 recycle times are adequate and the waste volume due to spent powdered resin can be reduced to 1/3 when applying the new technique.

IMPROVED DRYING AND PELLETIZING SYSTEM

Figure 13 outlines the improved drying and pelletizing system in which the powdered resin reuse system is implemented with the previous system. In the system, reused spent powdered resin and other radioactive wastes including liquids and slurries are dried to powder by a thin film dryer, then dry powder is transformed to almond-shaped pellets by a pelletizer. These pellets are stored in the interim storage tank followed by packaging in the drum for the final disposal.

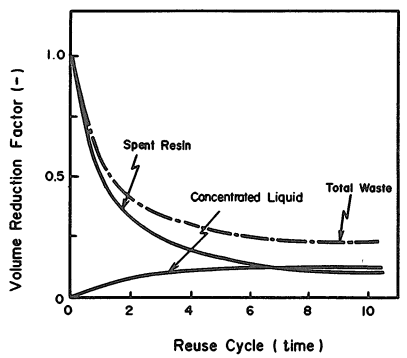


Fig.12 Volume Reduction of Radioactive Waste by Reuse of Powdered Ion Exchange Resin

Implementation of the reuse system is expected to reduce the total waste volume to about 2/3 as compared with the previous drying and pelletizing system, that is about 1/10 as compared with cement solidification method.

CONCLUSION

A new method was developed to allow reuse of spent powdered ion exchange resin which is about 60% of total radioactive waste generated in a BWR plant. For separation of flocculated cation and anion resins, the key point in the reuse process, our new technique combines centrifugation and use of strong electrolyte solution.

The pilot plant test demonstrated that a 90% separation and regeneration efficiency was obtained. Deterioration in filteration and ion exchange capability of recycled resin was at most 7% after 8 recycles. It was also demonstrated that the spent resin volume could be reduced to 1/3 when the new technique was utilized. This system can be implemented to the drying and pelletizing system for further reduction of total waste volume from nuclear power plants.

ACKNOWLEDGEMENTS

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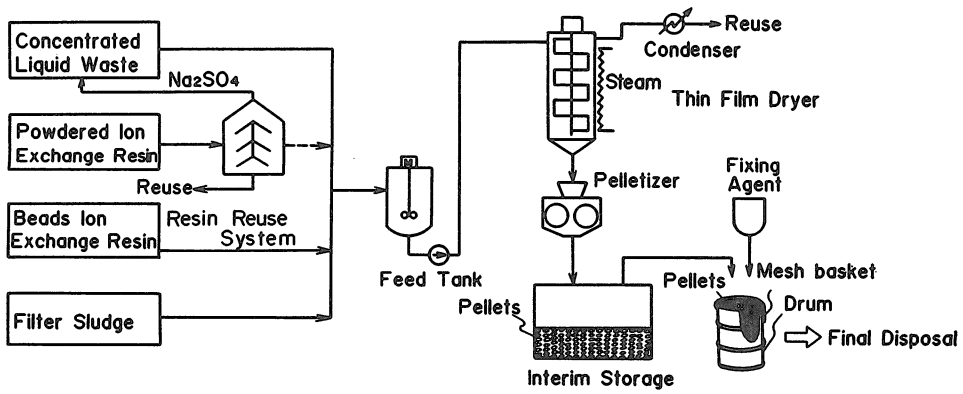

Fig.13 Improved Drying and Pelletizing System