

DEVELOPMENT OF A NEW POWDERED RESIN FOR WATER PURIFICATION IN NUCLEAR POWER PLANTS

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ABSTRACT

Conventional sulfonic cation resin which contains sulfur atoms produces corrosive gas (SO_x) during its incineration. Then weakly acidic, carboxylic resin with no sulfur was selected as an alternative for water treatment in nuclear power plants. Experimental results show that the lifetime of the carboxylic resin is longer than that of the sulfonic resin, because the flow area in the precoat layer is wider due to its weak connection force with anion resins.

A computer code was developed to simulate the filtration characteristics of the powdered resins. The code includes contraction of the precoat layer, and provides calculation results which agree within 5% of the experimental ones.

BACKGROUND

Condensate Water Cleanup System

Figure 1 shows a typical example of a condensate water cleanup system in a Japanese boiling water reactor (BWR) plant. Both a filter demineralizer and a demineralizer are used to purify condensate water. Powdered and bead ion exchange resins are applied to the filter demineralizer and the mixed bed type demineralizer, respectively. The powdered resins are customarily treated as a radioactive waste without any reuse, while bead resins are reused after chemical regeneration (1). Therefore, the spent powdered resins constitute a major fraction of radioactive waste.

Several methods of incineration technology have been developed to reduce the volume of the spent powdered resins. Recently, fuel rod failures are being cut to almost none, due to the improvement of reactor operation and fuel fabrication. Fission product nuclides from the fuel rods are almost non-existent in the primary coolant and the specific activity of spent powdered resins is much lower than that of the design value. These make a special incinerator for high activity resins unnecessary. Then the most promising method becomes burning spent powdered resins with combustible wastes by a miscellaneous solid waste incinerator which has already been installed in the nuclear power plant.

Selection of Alternative Cation Exchange Resin

Two-thirds of the powdered resins are cation exchange resins and the rest, anion exchange resins. Ion exchange resins consist of base polymer and functional groups. The former is styrene-divinylbenzene polymer and the latter is sulfonic group for conventional sulfonic resin. The sulfonic cation resin generates corrosive gas (SO_x) when it is incinerated. The SO_x gas attacks the walls of the incinerator and shortens its operating lifetime.

The authors considered that SO_x generation could be avoided by using a new cation resin which contains no sulfur atoms. The properties of various cation resins were evaluated using the literature (2, 3) to select the optimum alternative resin. Table I summarizes some typical findings. There are four types of commercially available cation resins: Sulfonic, phosphonic, carboxylic, and phenolic resins. The last three resins are preferable from the standpoint of incineration because they contain no sulfur. However, the phosphonic resin generates a corrosive product, P₂O₅, while incinerating it (4). Then the last two cation resins (carboxylic and phenolic resins) are preferable for the treatment of the spent resin.

Effective pH range, in which the resin has an ion exchange capacity, was another important factor for study from the viewpoint of water purification. The primary coolant of BWR plants is controlled in the pH range from 6.0 to 7.5. Since the phenolic resin does not satisfy the condition, the carboxylic resin is the most preferable alternative to the conventional sulfonic resin.

EXPERIMENTAL

Experimental Methods

Filtration characteristics such as crud removal efficiency and lifetime of the powdered resins were examined using sulfonic and carboxylic cation resins. Figure 2 shows a schematic of the experimental apparatus. The powdered ion exchange resins were precoat on the filter element with about 10 mm thickness after mixing cation resin, anion resin and fiber. While deionized water containing simulated crud passed through the precoat layer, crud removable efficiency, thickness of the precoat layer, and pressure drop were measured.

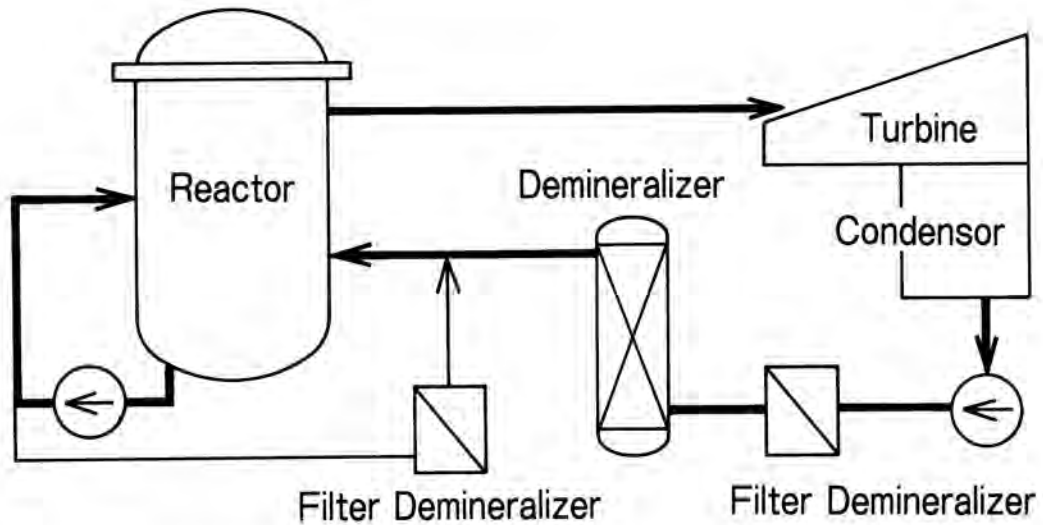


Fig. 1. Flow Sheet of a Typical Japanese BWR Plant.

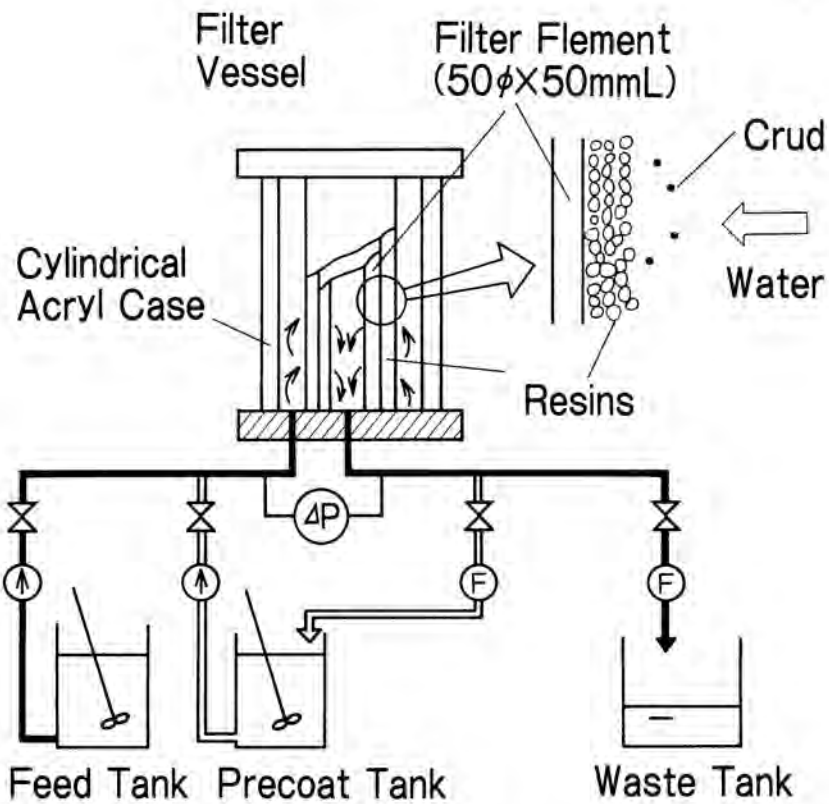


Fig. 2. Schematic Diagram of the Experimental Apparatus.

TABLE I

Comparison of Properties for Various Cation Exchange Resins.

Resin species	Sulfonic (conventional)	Phenolic	Carboxylic	Phosphonic
Structure	$\begin{array}{c} -\text{CH}-\text{CH}_2-\text{CH}- \\ \quad \\ \text{C}_6\text{H}_4 \quad \text{C}_6\text{H}_4 \\ \quad \\ -\text{CH}- \quad \text{SO}_3\text{H} \end{array}$	$\begin{array}{c} -\text{CH}-\text{CH}_2-\text{CH}- \\ \quad \\ \text{C}_6\text{H}_4 \quad \text{C}_6\text{H}_4 \\ \quad \\ -\text{CH}- \quad \text{PO}_3\text{H}_2 \end{array}$	$\begin{array}{c} -\text{CH}-\text{CH}_2-\text{CH}- \\ \quad \\ \text{C}_6\text{H}_4 \quad \text{COOH} \\ \quad \\ -\text{CH}-\text{CH}_2-\text{CH}- \\ \quad \\ \text{C}_6\text{H}_4 \quad \text{COOH} \end{array}$	$\begin{array}{c} \text{OH} \quad \text{OH} \\ \quad \\ \text{C}_6\text{H}_3 \quad \text{CH}_2 \quad \text{C}_6\text{H}_3 \\ \quad \quad \\ \text{OH} \quad \text{OH} \quad -\text{CH}_2- \end{array}$
Corrosive product after incineration	SO _x	P ₂ O ₅	none	none
Effective pH range	1-14	3-14	5-14	10-14
Ion exchange capacity (eq/kg-resin)	4	4	8	6

Table II summarizes the experimental conditions. Conventional quaternary ammonium resin was selected for the anion resin. The main composition of crud is iron, and various forms are generally known. Then Fe(OH)₃ and Fe₂O₃ were separately used to simulate the crud. The other conditions were equivalent to BWR plant operating conditions, except for crud concentration, which was increased to accelerate the filtration phenomena.

Experimental Results

Figure 3 plots the two parameters for both resin types as a function of crud loading when the crud was simulated by Fe(OH)₃. The pressure drop increases with the crud loading, because the removed crud occupies space between the powdered resins and frictional loss increases. After the pressure drop reaches a critical value (0.17 M Pa), the precoat layer in BWR plants is removed by backwashing. The critical value is determined by the mechanical strength of the filter element, on which the powdered resin was precoat. The lifetime of the powdered resins equals the time until the pressure drop reaches the critical value. Then it is preferable to increase the pressure drop as slow as possible. The following two features were observed from the graph:

1. The pressure drop of the carboxylic resin increased more slowly than that of the sulfonic resin.
2. The crud removal efficiencies were above 92% throughout the lifetime of both resins, satisfying the design value 90%.

Figure 4 plots the pressure drop and the thickness of the precoat layer when the crud was simulated by Fe₂O₃. The crud removal efficiencies of both resins are maintained above 99% throughout the lifetime. The average diameter of Fe(OH)₃ is much smaller than that of Fe₂O₃ because Fe(OH)₃ is in a colloidal form. Then Fe₂O₃ is more easily held by the precoat layer than Fe(OH)₃, and a higher crud removal efficiency is obtained. Three features were found from Fig. 4.

1. As Fe(OH)₃, the pressure drop of the carboxylic resin increases more slowly than that of the sulfonic resin.
2. The thickness of the precoat layer decreases to about a half of the initial value.
3. The lifetime for Fe₂O₃ is about 15 times longer than that for Fe(OH)₃.

Because of the experimental results, it was confirmed that the alternative carboxylic resins have satisfactory filtration characteristics. Next, filtration characteristics of powdered resin were numerically studied by developing a computer code.

CALCULATION

Filtration Model

There are many factors which affect the filtration characteristics of powdered resin: Ratio of cation to anion resin, the resin diameter, the weight ratio of fiber, and so on. A filtration model was developed to find the optimum

TABLE II

Experimental Conditions of Filtration.

Precoat conditions	Cation resin	Sulfonic and carboxylic resin
	Anion resin	Quaternary ammonium resin
	Resin particle size	30-40 μ m
	Cation/anion	2/1
	Acrylic fiber ratio	30wt%
Filtration conditions	Filtration area	90cm ²
	Filtration velocity	8m/h
	Simulated crud	Fe(OH) ₃ , Fe ₂ O ₃
	Crud concentration	5ppm (5mg/kg-water)
	Water pH	~7
	Water conductivity	~1 μ S/cm

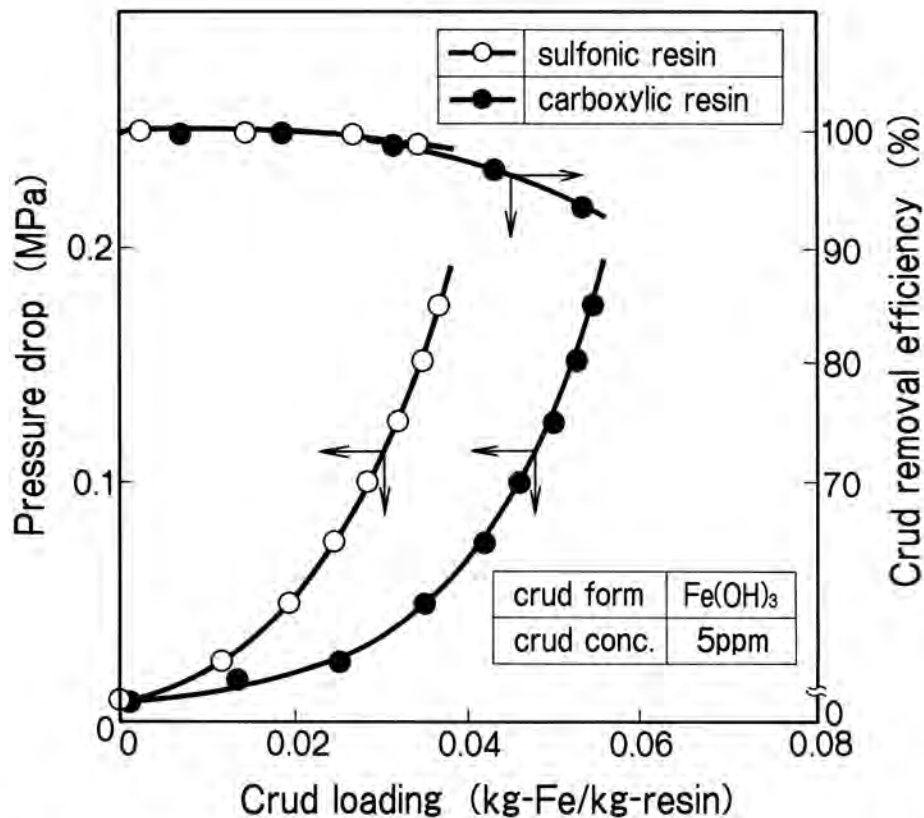


Fig. 3. Comparison of Filtration Performances for Sulfonic and Carboxylic Cation Resins.

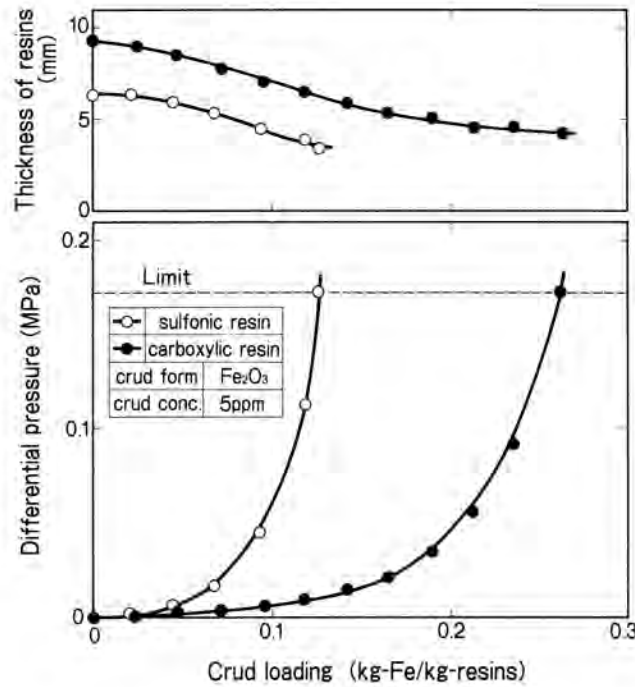


Fig. 4. Comparison of Filtration Performance for Sulfonic and Carboxylic Resin.

conditions and calculation results were compared with experimental results.

At first, the cross-section of precoat layer was observed as shown in Fig. 5. Crud particles are found to be held in the precoat layer. Water goes through the layer of the crud particles which are held in the space between the powdered resin, and the pressure drop is generated mainly by viscous friction between the flowing water and the crud particles. Then, the pressure drop increases with the amount of removed crud in the precoat layer, because viscous friction increases with the surface area of the crud particles and the water velocity. As the precoat layer is contracted as shown in Fig. 4, the pressure drop becomes much bigger due to the increase of water velocity. As a result, the pressure drop increases exponentially.

Filtration in the precoat layer is similar to deep bed filtration, which has been experimentally and theoretically studied (5, 6). The difference between powdered resins and the deep bed filtrations is that the precoat layer of powdered resins is contracted by crud loading.

Calculation Methods

Figure 6 shows the calculation method of pressure drop as a function of crud loading. The crud concentration in flowing water was evaluated by Eq. (1) of Fig. 6. The same equation for deep bed was expressed as Eq. (5).

$$\frac{\partial C}{\partial x} = -\lambda \cdot C$$

In order to evaluate the effect of contradiction, the variable was exchanged from x in Eq. (5) to ρx in Eq. (1). The removed crud could be calculated by equation (2), which was deduced from the mass balance.

Basic Eqs. of (1) and (2) can be solved by space and time integrations using K and ρ , which were experimentally measured as discussed later. The pressure drop in the precoat layer was calculated by integrating Eq. (3) in Fig. 6, the Kozeny-Carman Eq. (7), which has been widely used for calculation of the pressure drop in the deep bed. The average diameter of crud particle was selected as the representative length (d) of Eq. (3), because the pressure drop is generated by viscous friction in the crud layer.

Measurement of Constant

Constant K was evaluated from the crud concentration gradient in the precoat layer. Figure 7 shows the crud concentration distributions of carboxylic and sulfonic resins, which were measured by an X-ray micro analysis. From Fig. 7, the K value was obtained as $17 \text{ m}^2/\text{kg}$ for carboxylic resin, and as $26 \text{ m}^2/\text{kg}$ for sulfonic resin.

Figure 8 shows relationships of resin density and pressure drop. The resin density changes with not only pressure drop but also crud adsorption. Density of the strongly acidic, sulfonic cation resin is heavier than that of the weakly acidic, carboxylic cation resin, since the strongly acidic resin combines with anion resin more firmly than the weakly acidic resin. Resin density was measured at four different crud adsorption amounts. The resin density in the computer code was calculated by an interpolation method.

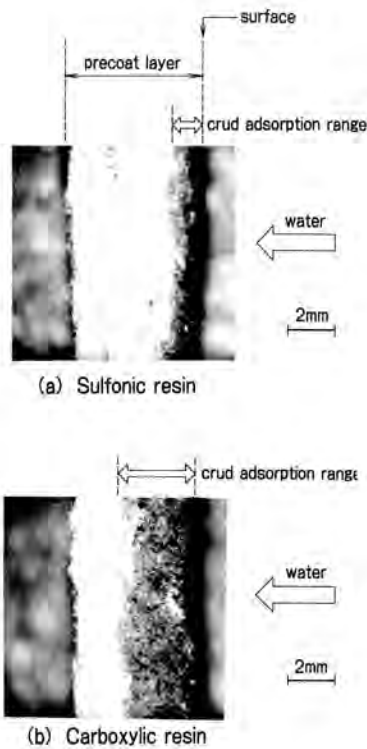


Fig. 5. Microscopic Sectional Appearance of Precoat Layer After Crud Filtration.

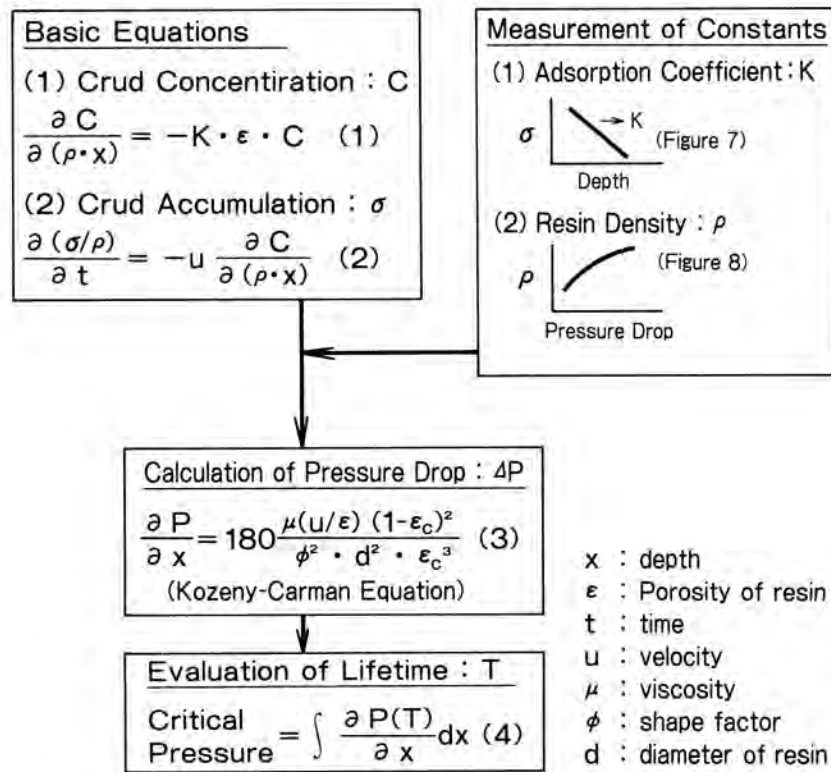


Fig. 6. Calculation Method of Pressure Drop.

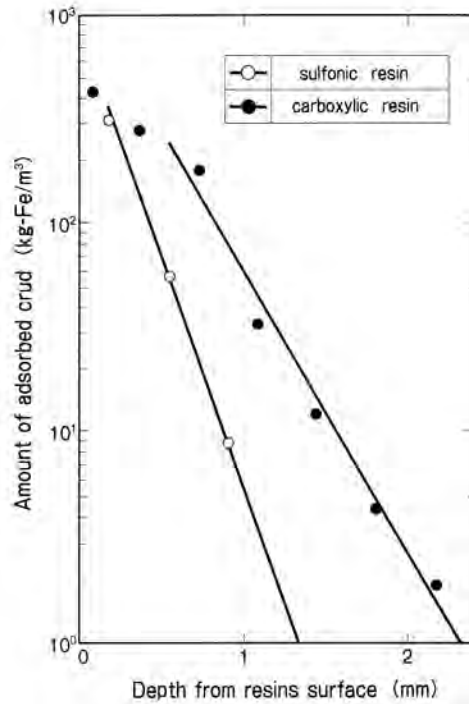


Fig. 7. Distribution of Adsorbed Crud on Resins.

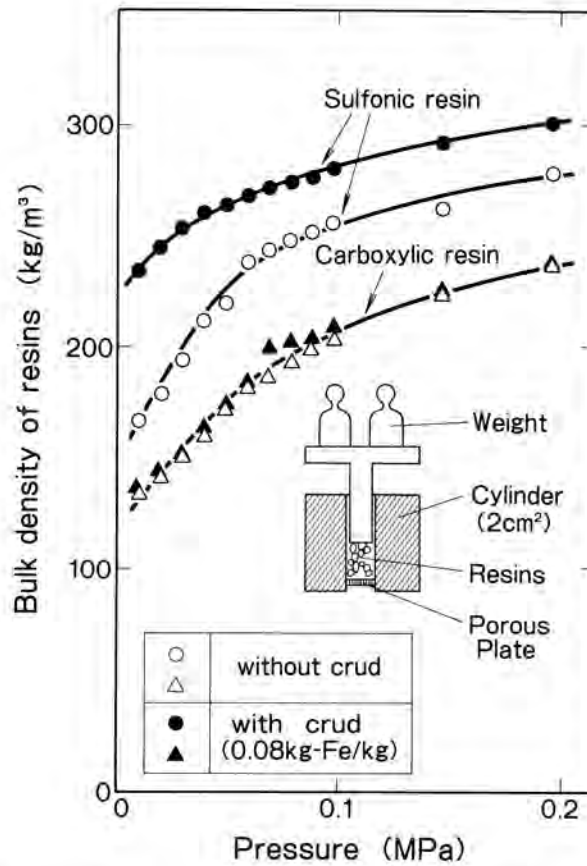


Fig. 8. Changes of Resins Bulk Density by Pressure and Crud Adsorption.

Comparison Between Experimental and Calculated Results

Figure 9 compares experimental and calculated results of pressure drop. A solid line expresses the calculated results with the contraction of the precoat layer, and the dashed line shows those without contraction. The calculated results with contraction agree with the experimental results within 5%. Without contraction, the water velocity in the precoat layer is evaluated to be smaller than the actual value, and the pressure drop increases more slowly than the actual phenomena. Since the density of carboxylic resin is smaller than that of sulfonic resin, water in the carboxylic resin flows more slowly and the pressure drop increases more slowly also.

Since good agreement was obtained, this model with contraction of the precoat layer can simulate the filtration characteristics very well.

CONCLUSIONS

Strongly acidic, sulfonic cation resin which contains sulfur atoms generates corrosive gas when it is incinerated. Then an alternative resin was selected and its filtration

characteristics were studied experimentally and numerically, as summarized below.

1. Properties of various cation resins were evaluated from the literature. Weakly acidic, carboxylic cation resin, which was characterized by the absence of sulfur atoms, was selected for the alternative resin.
2. Filtration characteristics were examined for sulfonic and carboxylic resins. Removal efficiencies of both resins were above 92% and 99% for Fe(OH)₃ and Fe₂O₃, respectively. Lifetime of the carboxylic resin was longer than that of the sulfonic resin, because the density of the former one was smaller and the flow area in the precoat layer was wider.
3. A computer code was developed to simulate the filtration characteristics of the powdered resins. When the code included the effect of the contraction, the calculation results agreed with the experimental ones within 5%.

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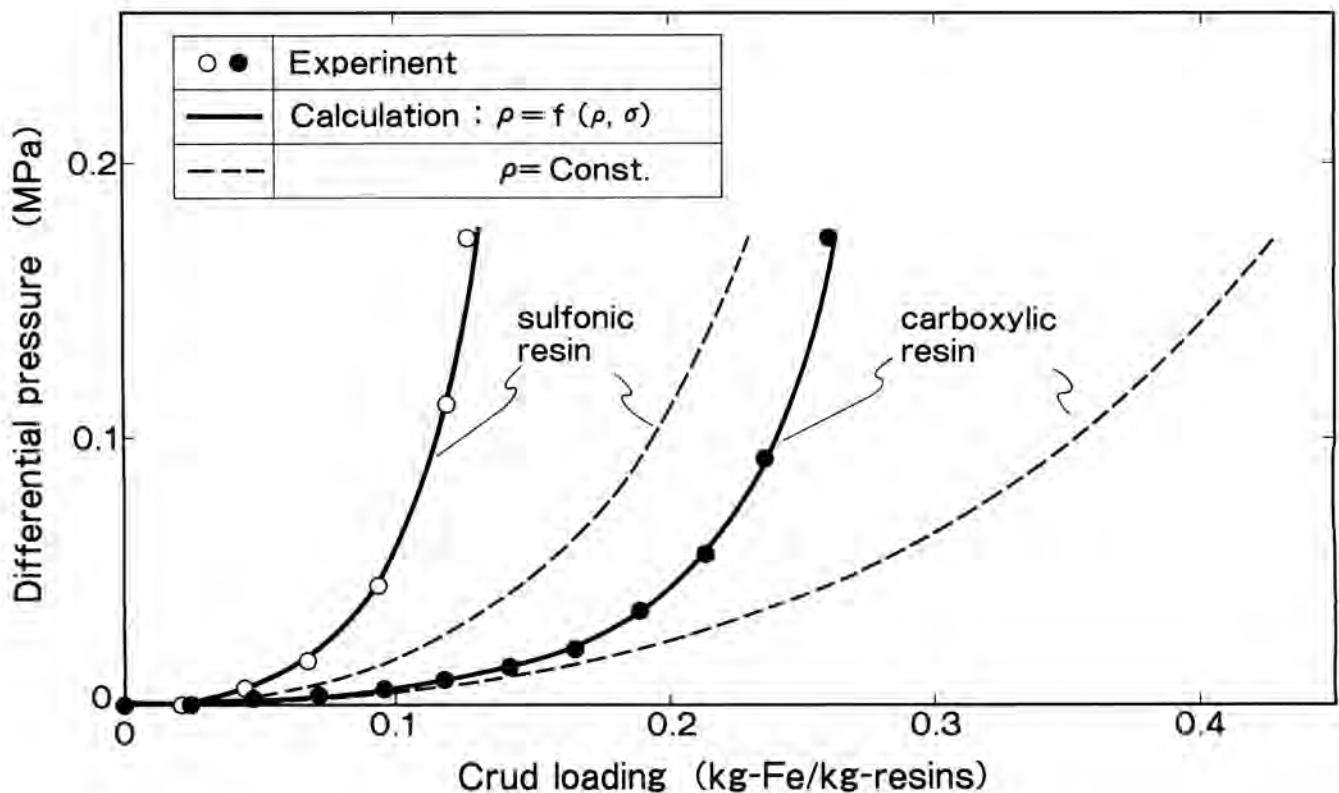


Fig. 9. Comparison of Calculated and Experimental Results.

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