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Study on the Interaction between Iron(III) Hydroxide Oxide and Cation Exchange Resins

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In some nuclear power plants, ion exchange resins for condensate purification systems show increasing rust removal efficiency year by year. In order to clarify this phenomenon, resin properties and rust behavior after adsorption on the resins have been studied. An adsorption test, a dissolution test and an ion exchanging test were performed in this study, using strongly acidic cation exchange resins, amorphous iron(III) hydroxide oxide and ^{55}Fe tracer. It was found that aged cation exchange resins showed obvious property changes due to oxidative swelling, which induced better water mobility in the micropores. According to the property change, amorphous iron(III) hydroxide oxide, one of the iron rust components, is easily dissolved and diffused into resin beads, and consequently adsorption sites on aged resins are recovered rapidly compared with fresh resins. This is the reason for the superiority of the aged cation exchange resins in rust removal.

Ion exchange resins for water purification systems in power plants have to remove not only ions but also suspended solids like rust. Rust deposits on ion exchange resins, however, detract the ion exchanging functions. Backflushing and chemical regeneration are effective for recovery from fouling, and the frequency of such recovery operations varies with the conditions under which ion exchange resins have been used. Some resins require an interval of a few days between backflushing operations to retain their water purification performance, and some resins do not need such a short backflushing interval to maintain a good removal efficiency. It has been empirically found that backflushing for aged resins is not needed so frequently, because aged resins, especially cation exchange resins, have a large capacity for iron deposit ions.$^{1)}$ In this paper rust means oxides and hydroxide oxides of iron.$^{2)}$ Amorphous iron hydroxide oxide is one type of rust and the particles must be very small due to their noncrystalline form when they are released from corroded steel surface. Therefore amorphous iron hydroxide oxide is essentially harder to remove by means of resin beds than other types of rust, and this characteristic seems to control the overall performance for iron removal of ion exchange resins.$^{3)}$ In order to clarify the reason why the aged cation exchange resins show excellent performance for iron rust adsorption, iron-resin interaction was studied both in terms of cation exchange resin properties and post-adsorption behavior of amorphous iron hydroxide oxide using artificial iron rusts and a tracer.

Experimental

Ion Exchange Resins. Four kinds of cation exchange resins were used in the tests. All the resins were nuclear grade gel type, strongly acidic cation exchange resins, DIAION SK1BN, manufactured by Mitsubishi Chemical Corp., and they were sieved between 590 μm and 720 μm. Resin A was fresh and resins B, C, and D were used in actual plants for rust removal. Resins were converted to H form with 6 mol dm^{-3} hydrochloric acid, then were thoroughly rinsed with pure water.

Chemicals. Two kinds of artificial rusts were provided. One was amorphous iron(III) hydroxide oxide, prepared by neutralizing iron(III) sulfate with sodium hydroxide.$^{4)}$ The median radius of particles was 0.6 μm, and their noncrystalline form was confirmed by X-ray diffraction. Another was magnetite, manufactured by Kojundo Chemical Laboratory Co., Ltd., with a median particle radius of 1 μm. Its crystalline form was confirmed by X-ray diffraction. Benzenesulfonic acid monohydrate ($C_6H_5SO_3H{\cdot}H_2O$) of more than 97% purity, synthesized by Kanto Chemical Co., Inc., was employed for simulation of the acidic atmosphere on the cation exchange resin surface.

Procedure. Resin Properties: Water retention capacity, C_w, was calculated by the following equation.

$$C_w = (W_1 - W_2)/W_1 \times 100,$$

where W_1 is the resin weight after centrifugal dehydration, and W_2 is the weight after drying in an oven at 105 °C for 16 h. Surface pH for cation exchange resins was measured by both a pH indicator, Horiba C-1 and color identification with Thymol Blue. Zeta potential was measured by electrophoresis using a Zetasizer II for crushed resins, about 20 μm granules. Iron content was visually confirmed by electron probe microanalysis for the resins as it is. Resin beads were cut in two pieces and the cross sections were observed by JEOL 35CF, scanning electron microscope and wave length dispersive X-ray analysis. Ion exchange capacity was measured as salt splitting capacity. Ten cm^3 sample resins were packed in a glass column. After conversion with 2 mol dm^{-3} HCl to H form, 250 cm^3 of 0.9 mol dm^{-3} NaCl solution was passed through the column. The effluent was titrated with 0.1 mol dm^{-3} NaOH and Methylene Blue-Methyl Red indicator.

Adsorption Performance: The apparatus is shown in Fig. 1. There are six glass columns with 12-mm inner diameters and 30 cm^3 of cation exchange resins of various ages were packed in each column. The resins were sufficiently regenerated with hydrochloric acid to remove the iron deposits completely. Amorphous iron(III) hydroxide oxide was dispersed in deoxygenated deionized water to produce a concentration of Fe of 100 µg dm^{-3}. The pH of the solution was 5.9, in which the solubility of amorphous iron(III) hydroxide oxide is negligible. The sample water was run through the columns at a linear velocity of 108 m h^{-1} for a week. After the test, amorphous iron(III) hydroxide oxide, loosely trapped on the resin beads was thoroughly removed by sufficient scrubbing, then tightly adsorbed iron(III) hydroxide oxide was stripped by ultrasonic cleaning and extracted with 6 mol dm^{-3} hydrochloric acid. Each amount was determined by fluorescence X-rays and atomic absorption spectroscopy.

Iron Rust Dissolution: One gram of each type of rust was soaked and stirred in 0.3 dm^3 of 0.06 mol dm^{-3} benzenesulfonic acid, the pH of which was adjusted to the same pH as the cation exchange resin surface. Over the duration of the test, 1 cm^3 of solution was taken and filtered with a 0.45 µm Millipore filter, then iron in the filtrate was determined by atomic absorption spectroscopy as dissolved iron. The sample volume was taken into account to estimate the solubility.

Ion Exchange Rate: Ion exchange rate for iron(III) ion was estimated using 6.8×10^3 Bq of ^{55}Fe tracer. Five cation exchange resin beads, which were thoroughly regenerated, were soaked in 10 cm^3 of ^{55}Fe solution at room temperature for 24 h. The residual radioactivity in the solution was measured by an NaI scintillation counter.

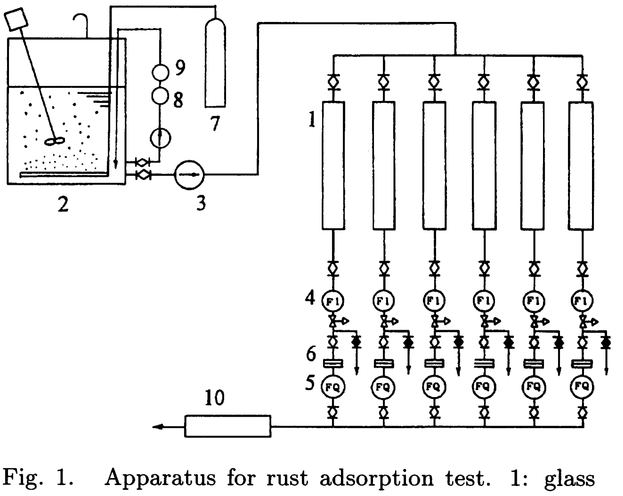

Fig. 1. Apparatus for rust adsorption test. 1: glass column, 2: tank, 3: feed pump, 4: flow indicator, 5: volume indicator, 6: Millipore filter, 7: nitrogen gas, 8: conductivity indicator, 9: oxygen indicator, 10: mixed resin bed.

Results

Resin Properties. Water retention capacities, pHs and zeta potentials for fresh and used cation exchange resins are summarized in Table 1. Water retention capacity for used resins is somewhat larger than that of fresh resins because of oxidative breaking of the main chains of the poly(styrene-co-divinylbenzene) matrix, that is, irreversible swelling. Salt splitting capacities per resin volume consequently decreased for resins B, C, and D. From their water retention capacities, the crosslinkage for the used resins was estimated as 7% of divinylbenzene (DVB). R. Kunin[5] reported that the mean diameters of micropores for cation exchange resins were 1.31 nm and 1.35 nm corresponding to 8% DVB and 7% DVB respectively. Other research[6] has reported the diameters of 3.3 and 3.6 nm for 8 and 7% DVB H-form strongly acidic cation exchange resins. Zeta potentials for cation exchange resins suggested that the used resins seemed to be more reactive with amorphous iron hydroxide oxide than fresh resins because zeta potential for amorphous iron hydroxide oxide is positive at neutral pH.[7] The used cation exchange resins showed somewhat lower pHs than fresh resins. These property changes might be due to the better water mobility for used resins attributed to the larger pore size. Figure 2 shows the iron content for various cation exchange resins. It can be seen from the figure that the iron was evenly adsorbed and the level in the resin bead increased over the period of operation. The surface of the aged cation exchange resin, resin D, as shown in Fig. 3, compared with the surface of the fresh resin, resin A, was rough, and the roughness may enhance the surface area and adsorption sites. Thus, aged cation exchange resins have affinity for amorphous iron hydroxide oxide.

Adsorption of Iron Hydroxide Oxide on the Cation Exchange Resins. To simplify the rust-resin interaction, only amorphous iron(III) hydroxide oxide was used for the column test. After a week run, the resins loaded the artificial rust were taken out for analysis. The artificial rust captured by filtration was sufficiently removed by scrubbing, then tightly adsorbed rust was separated by ultrasonic cleaning and finally residual iron, suspended solid and/or ion, were extracted with hydrochloric acid. In Table 2, the latter two types of iron are summarized. No regular pattern relating to the resin ages could be observed in tightly adsorbed iron, w_S. Fresh cation exchange resins, like resin A, have the largest w_S. Resin B has smaller w_S, probably due to surface contamination. Resin C has also smaller w_S, but has larger w_B, acid extracted iron. It suggests the iron transfer from the surface to the inside of the resin beads by the water mobility in the micropores, as described latter. Resin D, 7 years old, had large w_S again, because of surface roughness as shown in Fig. 2. For acid extracted iron, w_B, obvious differences

Table 1. Properties of Tested Resins

Resins	Age/y[a]	Water/%	Capacity[b]/equiv dm^{-3}	ζ-potential/mV	Acidity/pH
A	0	55	2.0	−49	1.8—2.0
B	1	56	1.7	−61	1.4—1.6
C	5	58	1.7	−65	1.4—1.6
D	7	58	1.7	−66	1.4—1.6

a) Gross years since in-service, including outage. b) Salt splitting capacity.

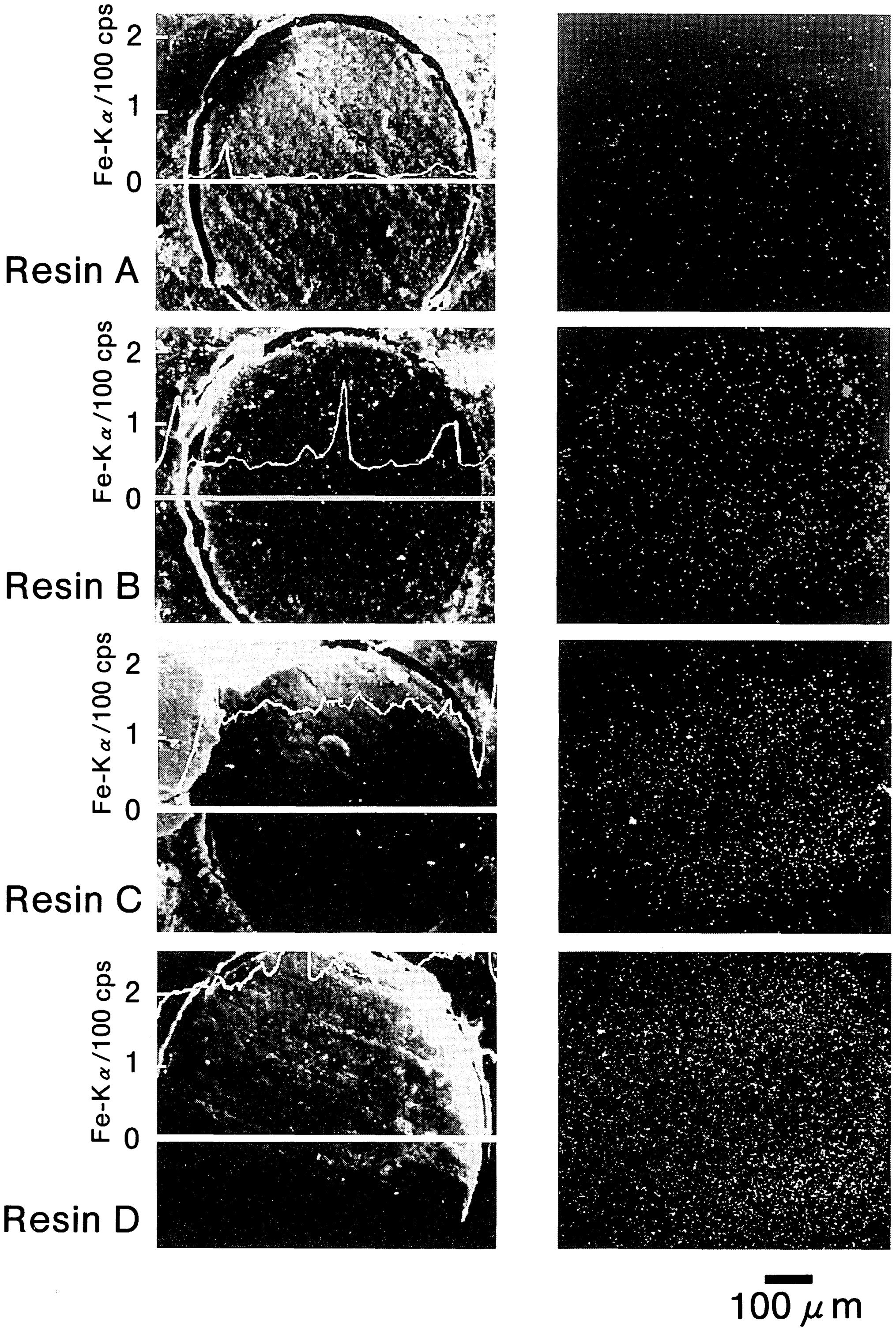

Fig. 2. Secondary electron image (left) and iron distribution (right) for the cross section of cation exchange resin beads.

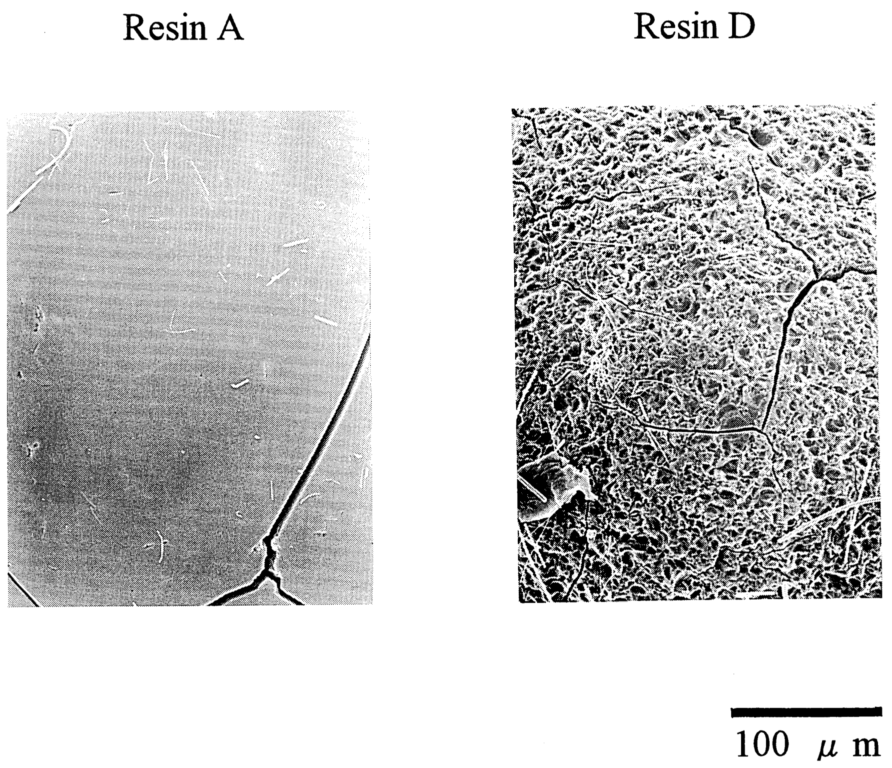

Fig. 3. Surface of fresh and aged cation exchange resins.

Table 2. Adsorption of Iron(III) Hydroxide Oxide on Cation Exchange Resins at Room Temperature

Resins	w_S [a)] $\mathrm{gFe\,dm^{-3}}$	w_B [b)] $\mathrm{gFe\,dm^{-3}}$
A	0.027	0.18
B	0.016	0.17
C	0.015	0.24
D	0.024	0.30

a) w_S: Iron stripped by USC, b) w_B: Iron extracted with 6 mol dm^{-3} HCl after USC.

can be observed between younger resins (A and B) and aged resins (C and D). From the results, aged resins that were used for more than 5 years and have larger water retention capacities, more negative zeta potentials, and lower pHs than fresh resins, were confirmed to have large capacities for amorphous iron(III) hydroxide oxide.

Dissolution Test for Artificial Rust. Because strongly acidic cation exchange resin is a copolymer of sulfonated polystyrene and DVB, the acidity of the resin surface is caused by the sulfonic group. The acidic atmosphere was accordingly simulated by benzenesulfonic acid in the dissolution test. Figure 4 shows the result of dissolution rate for amorphous iron(III) hydroxide oxide compared with that of magnetite. The vertical axis indicates the reduction ratio by dissolution for suspended iron particles in the solution, where w_0 is the initial concentration and w is the observed concentration for suspended iron. The dissolution rate for iron(III) hydroxide oxide was approximately fifty times larger than that of magnetite, and both dissolution rates were constant over the 2.5×10^4 seconds of soaking. Amorphous iron(III) hydroxide oxide is one of the main components of rusts which are produced by corrosion of carbon steels at normal temperature.[2)] It has been found through the dissolution test that amorphous iron(III) hydroxide oxide could be dissolved after adsorption on the cation exchange resin beads, but the actual rust dissolution on the cation exchange resins should not be so rapid. Rust that was stripped by ultrasonic cleaning from cation exchange resins after scrubbing was identified by X-ray diffraction as an amorphous substance, and this iron tightly adsorbed on the resins was reduced by soaking without stirring as shown in Fig. 5, where the vertical

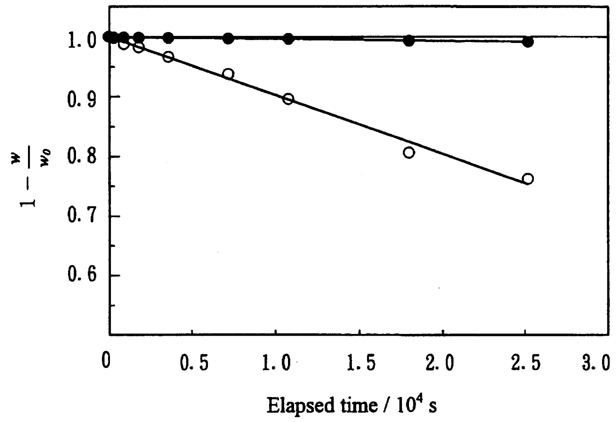

Fig. 4. Dissolution rate for artificial rusts in benzenesulfonic acid. ○: Amorphous hydroxide oxide, 520 mg as Fe. ●: Fe_3O_4, 730 mg as Fe.

axis indicates the reduction ratio for tightly adsorbed iron. The reduction rate was much smaller than the results of the simulation test, but the gradual decrease was considered to be dissolved iron on the resin surface.

Ion Exchange Rate to Fe^{3+}. The radioactivity reduction rate for bulk water by ion exchange of Fe^{3+} increased with the age as shown in Table 3. To explain the difference, the diffusivity of iron(III) ions into the resin micropores was considered. As mentioned above, used resins have larger pore diameters than fresh resins. It is well known that the Knudsen diffusivity D_k is proportional to pore radius r as follows:

$$D_k = 9.7 \times 10^3 r(T/M)^{1/2},$$

where T is temperature and M is molecular weight of the adsorbent.[8] Diffusion into the micropore is regarded as a rate determining step in the ion exchange process. In Fig. 6 the rates were accordingly plotted to the micropore diameters, $2r$, which were indicated in the literature.[6] The factor of the difference between the rates for resins A and D was 1.9, which is larger than the pore size factor, 1.1. The expansion of micropores due to irreversible swelling, however, seems to induce more rapid ion exchange certainly.

Discussion

As described above, rust, especially amorphous iron (III) hydroxide oxide, is adsorbed and dissolved on the cation exchange resin beads, and turns to iron(III) ion or much smaller particles, which can diffuse into the beads. The ability of cation exchange resins to capture iron increases with increasing duration of operation, because of micropore expansion by irreversible swelling and surface roughness by attrition. Ishigure et al. reported about a mathematical model for adsorption of CRUD, rust generated in nuclear power plants, using hematite.[9] They assumed that the rust was deposited and released from a limited number of adsorption sites on the resin beads. From our results, the recovery for the adsorption sites should be considered in addition to this model, because adsorption sites with amorphous iron(III) hydroxide oxide deposits can be recovered by dissolution of the adsorbate and the recovery rate is controlled by dissolution and ion-exchanging rates for deposited iron(III) hydroxide oxide. Adsorption sites on aged cation exchange resins, therefore, can be recovered more rapidly than those of fresh cation exchange resins and have a large capacity for iron(III) hydroxide oxide. In our consideration, aged cation exchange resins were able to adsorb more amorphous iron(III) hydroxide oxide than fresh cation exchange resins due to the affinity indicated by surface structure and properties. Also, in the case of fresh resins, the adsorbed rust interferes with the adsorption of incoming rust. The adsorption sites on aged resins, however, can be refreshed by taking the amorphous iron(III) hydroxide oxide into themselves. The relative recovery rate was calculated using the data for resin B in Fig. 5 and the data for resins B and D in Table 2. From Fig. 5, the reducing factor for a week is 0.2. Assuming that past accumulated iron has no influence on the dissolution and the diffusion process,

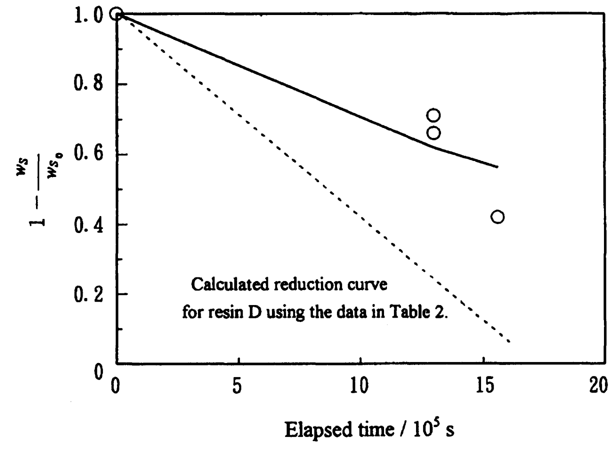

Fig. 5. Reduction curve for tightly adsorbed iron on resin B.

Table 3. Reduction Rate of ^{55}Fe by Ion Exchange for Various Resins

Resins	Water retention capacity/%	^{55}Fe reduction rate[a]/$10^{-6}s^{-1}$
A	55	3.0
B	56	5.0
C	58	5.3
D	58	5.6

a) Measurements were obtained by soaking at room temperature for 24 h.

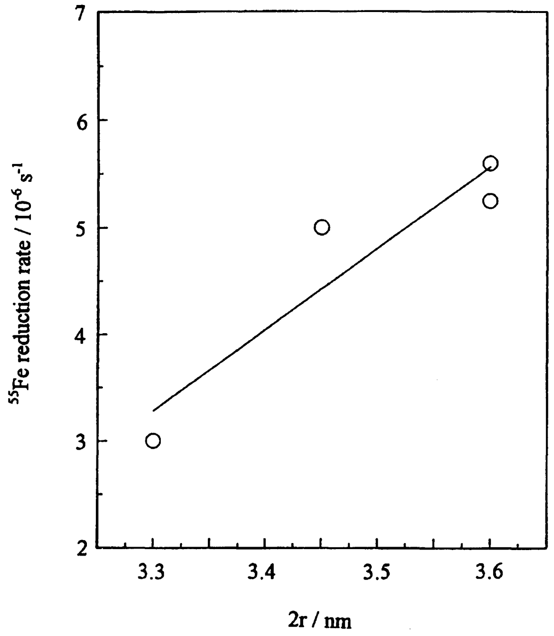

Fig. 6. Relation between micropore size and ion exchange rate.

the iron reduction for a week in Fig. 5 is comparable to the w_B for resin B in Table 2. Because the w_B for resin B which is the amount of acid extracted iron is considered to move from the resin surface to the inside in a week. Gross loaded iron for resin B in Table 2, including iron removed by scrubbing (no indication), can be calculated as w_B, 0.17 gFe dm^{-3}, divided by 0.2. Assuming the total iron calculated in this way, 0.85 gFe dm^{-3} was also loaded to other test resins, it can be applied to resin D, and a reducing factor of 0.35 for resin D was obtained. This value is 1.8 times that of resin B. So, the recovery rate for adsorption sites of resin D is about double that of resin B. Resin B was nearer to the other used resins, C and D, in pH and zeta potential, as shown in Table 1. Nevertheless the capacity of resin B for amorphous iron(III) hydroxide oxide was as small as that of fresh resin. This suggests that a few percent increase for water retention capacity of cation exchange resins induces a gain of the iron capturing ability, because only water retention capacities showed the difference between young resins (A and B) and aged resins (C and D) corresponding to the difference of the capacities for amorphous iron(III) hydroxide oxide. Generally the breakthrough curve of suspended rust shows a different pattern from a breakthrough curve to ions, that is, even though the iron leakage begins, the effluent iron level is not able to reach the inlet level. This occurs due to the balance between the iron taken in and the consumed iron. Consequently the leakage level for an aged resin bed should be lower than that for a fresh resin bed as shown in Fig. 7.

Conclusions

Interaction between amorphous iron(III) hydroxide oxide and cation exchange resins was studied and the following conclusions were obtained.

1. Physical properties for aged cation exchange resins show more affinity for amorphous iron(III) hydroxide oxide than fresh cation exchange resins due to irreversible swelling by slow oxidation.
2. Amorphous iron(III) hydroxide oxide adsorbs on the adsorption sites of cation exchange resin beads and interferes with other rust adsorption.
3. Amorphous iron(III) hydroxide oxide can be dissolved on the resin beads easily, compared with other rusts.
4. Iron(III) ion, produced by dissolution, are diffused and exchanged with the functional group on the resins.
5. Dissolution and ion exchanging process were able to recover the adsorption sites that were occupied by amorphous iron(III) hydroxide oxide, and the rates for aged resins are larger than fresh resins, due to the larger micropores formed by irreversible swelling.
6. The mechanism described above could explain why cation exchange resins improve their performance for rust removal year by year.

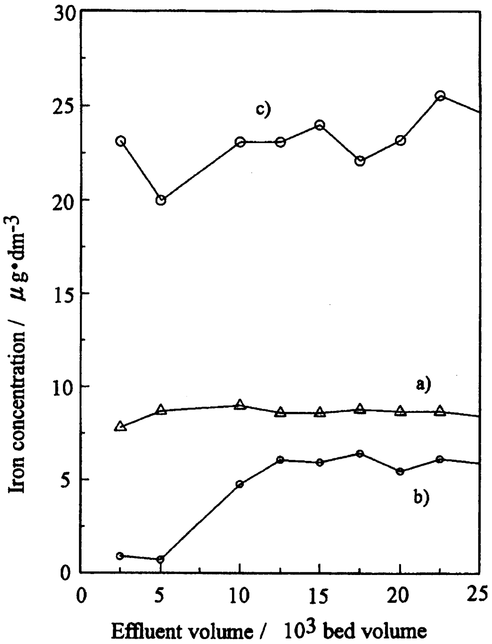

Fig. 7. Typical breakthrough curve of suspended rust. a): fresh or young resins, b): aged resins, c): inlet concentration.

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