THE EFFECT OF QUICK FREEZE PRETREATMENT ON GRINDING OF SPENT ORGANIC ION-EXCHANGE RESINS

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ABSTRACT

It has been found that the structure of bead type organic ion-exchange resins is destroyed by quick freezing. The defected resins do not recover the original structure after thawing and they can be easy to be broken at room temperature by small force. Therefore, bead type spent ion-exchange resins can be ground readily at room temperature after quick freezing the fully water-swollen resins by using liquid nitrogen or solid carbon dioxide.

The quick freeze pretreatment of cation exchange resins is very effective on grinding in particular. However, the effect of the pretreatment of anion resins is less than that of cation exchange resins. In case of anion exchange resins, the ionic form of resins affect the grindability remarkably.

INTRODUCTION

Spent organic ion-exchange resins generated from nuclear facilities such as nuclear power plants and research institutes, should be solidified by incorporating them into proper matrices, i.e. cement, bitumen, or polymer, sometimes, after incineration or wet oxidation. Spent resins exist in the form of bead (0.3-1.2 mm diameter) and powder (5-130 μm diameter). It is known that powdered resins would be better for treatment (i.e. solidification, incineration, or wet oxidation) than bead resins due to their large surface area. Especially, in case of bituminization of bead resins, size reduction is required to obtain a homogeneous waste form because of sedimentation of bead resins (1,2). The small particle size of resins have also an advantage in that resins are dried efficiently when bituminized. Then grinding for size reduction is an important process prior to bituminization of spent bead resins.

Organic ion-exchange resins cannot, however, be ground easily, as thermosetting plastic, since they are a kind of cross-linked polymers. Grinding of organic ion-exchange resins is an energy and time consuming process. Furthermore, prolonged grinding time and excessive grinding forces may cause particle size and distribution undesirable.

We have introduced a new technology, named quick freeze pretreatment into grinding of bead type spent organic ion-exchange resins. Quick freeze pretreatment is a process to destroy the structure of bead resins by quick freezing prior to grinding and facilitate the size reduction when grinding. Yoshikawa(3) have contrived the grinding process of spent resins under low temperature condition and referred to importance of quick freezing but not provided any experimental data. The purpose of this study is to observe the change of the structure of bead resins by quick freeze pretreatment and investigate the effect of quick freeze pretreatment on grinding of resins at room temperature.

PRINCIPLE OF QUICK FREEZE PRETREATMENT

All ion-exchange resins retain moisture in their pores for ion-exchanging. They still have moisture after their useful life unless they are dried out for other treatments. Usually, bead type organic ion-exchange resins have 40 - 60 wt% of moisture.

When water freezes into ice at 273 K, density decreases, i.e. from 0.999 g/cm^3 to 0.910 g/cm^3. Namely, volume of matter increases about 10 %. If water freezes in a tightly closed reservoir, volume expansion adds pressure to the reservoir. Although measurement of this freezing expansion pressure is not easy, it may be assumed that it is very high pressure up to 100 MPa. If the reservoir has not enough compressive strength, it is broken or damaged by expansion pressure.

The same principle can be applied to bead resins containing moisture inside of them. It will be possible to destroy the structure of resins to some extent by freezing expansion pressure. The resin bead, however, is not a tightly closed reservoir, but is close to a open reservoir. It is then necessary to convert resin bead from open reservoir to tightly closed reservoir. When a resin bead containing moisture quick-freezes from surface of a resin bead into inside, resin bead is covered with ice shell at the beginning of freezing and becomes closed system. Freezing expansion pressure is then exerted on resin bead during the process of freezing. And the structure of a resin bead is destroyed unless it is strong enough to stand or flexible enough to absorb the expansion volume.

It is confirmed that those conditions above mentioned can be achieved when swollen bead resins are quick-frozen by liquid nitrogen, or solid or liquid carbon dioxide.

EXPERIMENTAL

Resins

The organic ion-exchange resins used in this experiment and their properties are listed in Table I. Duolite

A101D and C20 are being used for pool water treatment at the Post Irradiation Facility(PIF) and decontamination of condensate from an evaporator at the Radwaste Treatment Facility(RWTF) in the Korea Atomic Energy Research Institute. Amberlite 77, 78 and 150 are typical ion-exchange resins used in nuclear power plants in Korea. In addition, Samyang Diaion SK1B is a Na ion form of strongly acidic cation exchange resins manufactured in Korea. Among these resins, experiments were carried out mostly with a Na ion form and a H ion form of Duolite C20 as spent cation exchange resins, and a Cl ion form, a OH ion exchange resins, and a NO_3 ion form of Duolite A101D as spent anion exchange resins. These resins were discharged from RWTF during nonactive test operation and they had no radioacivity. In case of Amberlite 77, 78, 150 and Samyang Diaion SK1B, fresh ion-exchange resins are used instead of spent ones.

TABLE I

Properties Of Organic Ion-Exchange Resins Used

Name	Function	Ionic Form	Shape	Type
Duolite				
C20	Cation-Exchange	H^+,Na^+	Beads	Gel
A101D	Anion-Exchange	OH^-,Cl^- NO_3-	Beads	Gel
Amberlite				
IRN 77	Cation-Exchange	H^+	Beads	Gel
IRN 78	Anion-Exchange	OH^-	Beads	Gel
Samyang Diaion SK1B	Cation-Exchange	Na^+	Beads	Gel

Quick Freeze Pretreatment

After removing water between resin beads, fully water-swollen resins were directly mixed with liquid nitrogen or solid carbon dioxide called in dry ice. As soon as water-swollen resins contact with liquid nitrogen or solid carbon dioxide, resins froze quickly. After quick-frozen resins were then thawed completely, grinding test was carried out on those resins.

Grinding Test

Specification of a laboratory ball mill and grind conditions used in this study are listed in Table II.

Particle Size and Distribution Analysis

Particle size and distribution of resins with larger than 100 μm diameter were measured by wet sieving using Korea Standard sieves. Those of resins with less than 100 μm diameter which were produced by grinding were analyzed by Coulter Multisizer manufactured in Coulter Electronics Co.

RESULTS AND DISCUSSION

Effects of Quick Freeze Pretreatment on Grinding of Cation Resins

The structure of resins was changed obviously by quick freezing as shown in Fig.1. So many cracks were observed inside of resin bead with quick freeze pretreatment while no crack was found in resin bead without pretreatment. As Fig.1 is a picture taken after a quick-frozen resin was thawed, it can be concluded that the resins destroyed by quick freezing do not recover its original structure after thawing. Therefore, we could investigate the effect of quick freeze pretreatment on grinding at room temperature without experimental difficulties and disturbances arising from cryogenic grinding.

Fig. 1. Microphotograph of cation exchange resins with and without rapid freeze pretreatment. (x40). a) without pretreatment; b) with pretreatment.

Figure 2 shows the experimental results on cation resins with and without quick freeze pretreatment, obtained from grinding test under condition of Table II. Fully swollen cation resins (Na ion form of Duolite C20) without pretreatment was hardly ground despite of long grinding time (above 10 hr). Furthermore, long time grinding caused bimodal distribution of particle size. On the contrary, grindability of cation resins increases dramatically by the quick freeze pretreatment. Particle size of resins with pretreatment after grinding for 30 min was 57 μm diameter (at 63.2%, cumulative % less than size) while that of resins without pretreatment even after grinding for 20 h being 588 μm (at 63.2%, cumulative % less than size). Particle size distribution of resins with pretreatment after grinding was also more uniform than that of resins without pretreatment.

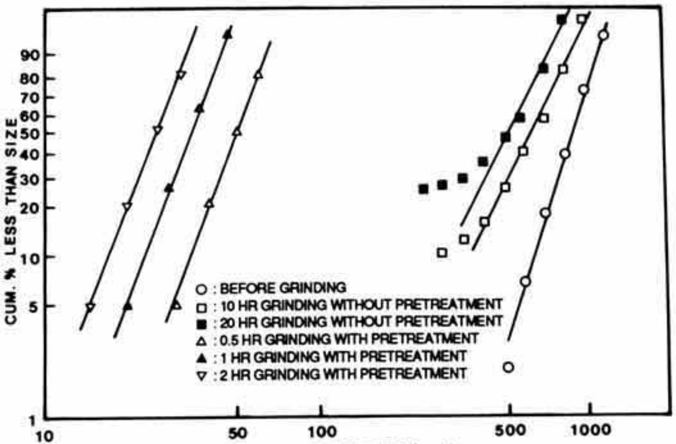

Fig. 2. Rosin-Rammler size distribution plots of cation exchange resins before and after grinding with or without pretreatment.

For comparison of grindability more detail, the following index of comminution (IC) was used(4).

$$IC = (PC/EI) \times 1000 \text{ (mg/J)}$$

Where PC is a fraction of ground resins below 75 μm in diameter (mg) and EI is the energy input (J). As a result, IC of resins with pretreatment is 8.4×10^{-3} mg/J while that without pretreatment is 4.3×10^{-5} mg/J. Cation resins with pretreatment can be ground 200 times more than resins without pretreatment.

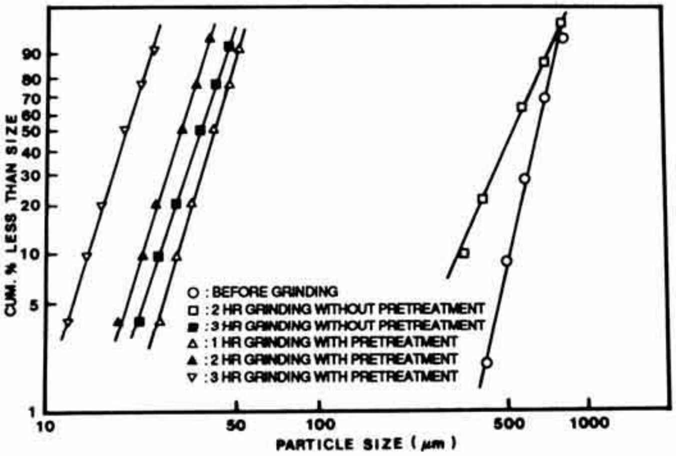

Fig. 3. Rosin-Rammler size distribution plots of anion exchange resins before and after grinding with or without pretreatment.

TABLE II

Experimental Conditions

Ball Mill	
Size: Diameter	**76 mm**
Length	**81 mm**
Material:	**SiC**
Ball	
Density:	**3.7 g/cm^3**
Shape:	**Spherical**
Diameter:	**10 mm**
Material:	**SiC**

Fractional volume loading of ball : 0.5
Fractional volume loading of resins : 0.2
Mill speed : 104 rpm

Grinding condition :	Wet grinding at room temperature

<u>Effects of Quick Freeze Pretreatment on Grinding of Anion Resins</u>

The experimental results of grinding for Cl ion form of anion resins (Duolite A 101D) is shown in Fig.3. IC of anion resins with pretreatment is 3.3×10^{-3} mg/J and that of anion resins without pretreatment being 1.1×10^{-3} mg/J. It seems that anion resins can be ground easily without pretreatment because the degree of cross-linking in anion resins is usually lower that in cation resins. The effect of pretreatment is also not so significant as compared with cation resins. This reason is that polymer chains in anion resins may absorb the expansion pressure to some extent because elasticity of anion resins is larger than that of cation resins.

The effect of ionic forms of anion resins on the grindability was also investigated. The change of median particle size (diameter) depending on grinding time for various ionic form of anion resins with and without quick freeze pretreatment is shown in Fig.3. It is known that regardless of ionic form, anion resins with pretreatment one always ground faster than those without pretreatment. And it is more important that grindability of anion resins is affected by ionic form significantly. To grind the NO_3 ion form of anion resins, for example, substitution of NO_3 ion form of anion resins into OH ion form is more desirable than quick freeze pretreatment of NO_3 ion form of anion resins at the view point of size reduction. Of course, grinding after quick freezing the anion resins which are substituted into OH ion form is the most effective.

Moisture content capacity of anion resins varies significantly according to affinity of ions in the resins with water, i.e. moisture content is 52 wt%, 70 wt%, and 45 wt% for Cl ion form, OH ion form and NO_3 ion form of anion resins (Duolite A101D), respectively. And from the fact that resins

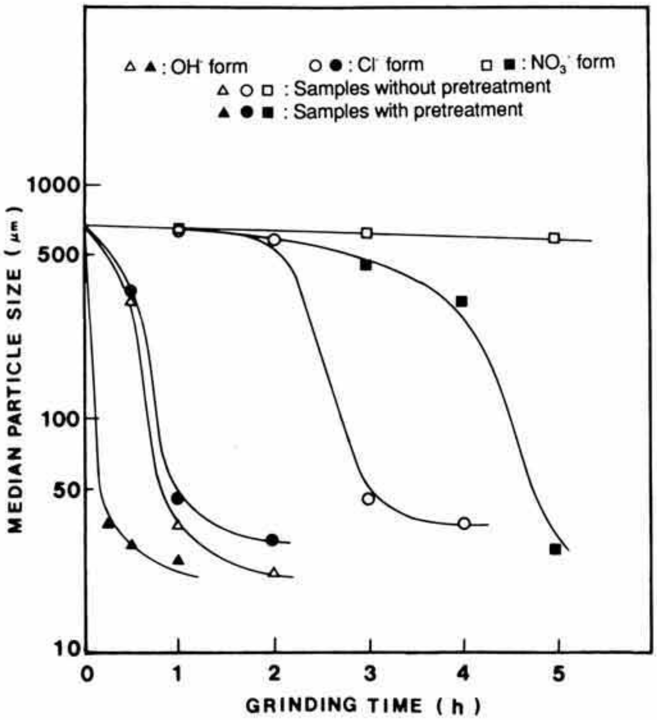

Fig. 4. Effects of ionic forms on grinding of anion exchange resins.

is ground better as moisture content of resins increases, moisture inside of the resins seems to weaken the strength of resins. In case of cation resins, grindability of H ion form resins is, however, similar to that of Na form resins in this experiment although moisture content of H ion form resins is higher than that of Na ion form resins. But it is possible to investigate the difference of grindability between H ion form and Na ion form of cation resins through more precise measurement.

Effects of Pretreatment on the Other Commercial Resins

Experimental results of several fresh commercial resins listed in Table III. The median particle size of resins with pretreatment reduced to around 50 μm within 1 h by grinding while that of resins without pretreatment was hardly changed under same condition. It is concluded clearly that quick freeze pretreatment is very effective for grinding of most bead type organic ion-exchange resins, regardless of spent ones or fresh ones.

CONCLUSION

Bead type organic ion-exchange resins can be ground readily at room temperature after quick freezing the fully water-swollen resins by using liquid nitrogen, and solid carbon dioxide. In this study, the effect of this pretreatment on grinding of spent resins has been investigated using laboratory ball mill. It has been found that the structure of bead resins is destroyed by quick freezing. The defected resins do not recover its original structure after thawing and they can be easy to be broken at room temperature by small force. The quick freeze pretreatment is very effective in grinding of cation resins in particular. However, the effect of the pretreatment on the grinding of anion resins is less than that of cation resins. In case of anion resins, the ionic form of resins affect the grindability remarkably.

TABLE III

Results Of Grinding After Quick Freeze Pretreatment For Several Kinds Of Ion-exchange Resins

Name	Particle size, μm before grinding	Particle size, μm after grinding
Amberlite		
IRN77	297-1,190	18-71 (48)
78	297-1,190	17-74 (50)
150	297-1,190	13-74 (40)
Samyang Diaion SK1B	297-1,190	27-79 (57)

* Grinding time : 1 h
* (): Median particle size

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