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Preparation of zeolite sheets using a papermaking technique

Part I *Dual polymer system for high retention of stock components*

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Zeolite is generally used in the form of beads or pellets in various industrial fields. These types of use, however, have some serious disadvantages such as a pressure loss in the reaction tower or a powdering of the zeolite through beads rubbing against each other. Therefore, in this study, the zeolite sheets were prepared by using a papermaking technique intending the manufacture of the honeycomb structure which improved these defects to a great extent. Typical composites of sheetmaking stuffs were pulp (9%), zeolite (61.5%), kaolin (18%) and glass fiber (11.5%). When 0.5% polydiallyldimethylammonium chloride (cationic retention aid) and 0.5%–1.0% anionic polyacrylamide (anionic retention aid) with high molecular weight (4.0×10^6) on these solids were added, the retention of inorganic compounds was higher than 90%. The drainage time was adequately short. These results suggest that the method can be applied to the industrial production.

1. Introduction

Zeolite, which is a hydrated alkali-aluminium silicate, has a characteristic three-dimensional structure [1]. A number of artificial zeolites are presently commercially available. They have been used in various applications such as desiccants, adsorbents, molecular sieves, ion exchangers and catalysts [1–4]. In general, zeolites have usually been used as beads or pellets [1, 5]. However, their use can have serious disadvantages, such as a pressure loss in the reaction tower, powdering of the zeolite if the beads rub against each other and difficulties in repacking them. It is considered that these disadvantages can be overcome by creating a honeycomb structure of the zeolite [6–9]. To make the honeycomb, an extrusion method has usually been applied [5]. This method is useful for certain bulking agents, e.g. zirconium derivatives, but it is useless for zeolites because the characteristic porous structures are easily destroyed by the high extrusion pressure. It is very difficult to improve the extrusion methods because of the rheological properties of the dispersed zeolite system. Thus, papermaking techniques are applied to prepare the zeolite sheet instead of the extrusion method [10–12]. These are particularly suitable for producing the large area of the honeycomb structure that is necessary, for example, to remove the large quantities of NO_x and SO_x generated in power plants, but detailed studies of this papermaking technique have not been carried out [11, 12]. In this study, suitable conditions to keep a higher retention of fillers were searched for, and sheets containing 90–95% of zeolite, kaolin and glass fiber and 5–10% of cellulosic pulps were successfully prepared with the aid of cationic and anionic polymer retention aids.

2. Experimental

2.1. Materials

The pulps used were unbleached softwood kraft pulp (NUKP), bleached hardwood kraft pulp (LBKP) and linter pulp which were beaten to a Canadian Standard Freeness (CSF) of 313 ml, 309 ml and 333 ml respectively in a TAPPI (Technical Association of Pulp and Paper Industries, Ltd.) standard beater. Inorganic materials (fillers) were zeolite (Y type), kaolin and glass fiber kindly presented by Mitsubishi Heavy Industry.

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Poly (diallyldimethylammonium chloride) (PDADMAC) and anionic polyacrylamide (A-PAM) were used as retention aids. The charge density (CD) was determined by polyelectrolyte titration using a fluorescent indicator [13] and the molecular weight (MW) was estimated by size exclusion chromatography [14]. The CD and MW of PDADMAC were 5.8 meq/g and 2.2×10^5 respectively, and the values for A-PAM were 0.83 meq/g and 4.0×10^6 as well.

2.2. Retention of the flocculant

To 25 ml of 0.2% pulp suspension, 0–5.5 ml of 0.1% PDADMAC, 25 ml of 2.0% inorganic suspension [zeolite : kaolin : glass fiber (5.5 : 1.5 : 1)] and 0–5.5 ml of 0.1% A-PAM were added in this order with gentle stirring. After 5 min, these mixtures were filtered through a membrane filter with a pore size of 0.5 μm. The concentrations of unadsorbed PDADMAC and A-PAM in the filtrate were determined by polyelectrolyte titration [13] using a fluorescent indicator.

The retentions of PDADMAC and A-PAM were determined by subtracting the amount in the filtrate from the charged amount.

2.3. Turbidity

25 ml of PDADMAC (0–0.02%) were mixed with the same volume of 0.2% pulp slurry, followed by the addition of 25 ml of a 2.0% suspension containing zeolite : kaolin : glass fiber with a weight ratio of 5.5 : 1.5 : 1 and 25 ml of 0–0.02% A-PAM with vigorous stirring. After 30 seconds, the suspension was poured into a graduated cylinder with a height of 35 cm and a diameter of 1.8 cm. The cylinder was turned up and down 10 times and then allowed to stand for 30 minutes. About 25 ml of sample was then withdrawn from a depth of 10 cm and its turbidity was measured in the photoelectron turbidimeter.

2.4. Preparation of sheets with high contents of zeolite

250 ml of pulp slurry was mixed with 0–55 ml of 0.1% PDADMAC, followed by the addition of 250 ml of inorganic suspension and 0–55 ml of 0.1% A-PAM in that order. Handsheets with a grammage of 275 g/m^2 were prepared according to TAPPI method - 205. The wet sheets were pressed under 350 kPa for 5 minutes and dried in a convection oven at 105 °C for 30 minutes.

2.5. Retention

The retention was estimated from the ash contents of the sheets determined by igniting the sheets in an electric furnace at 700 °C for 20 minutes. These values were corrected for the weight losses of the fillers themselves by heating them at 700°C.

2.6. Drainage times

The times required for water drainage from a stock suspension through a wire mesh screen of a standard laboratory sheet-making machine were determined with a stopwatch.

3. Results and discussion

3.1. Adsorption of retention aids

PDADMAC and A-PAM were added to the suspension sequentially to improve the retention of the solids. Almost all PDADMAC was adsorbed by the solids at a level of addition below 1% because of the anionic nature of the stock. The retention of A-PAM onto solids with various amounts of PDADMAC is shown in Fig. 1. In the absence of PDADMAC, A-PAM was still adsorbed very well at the low addition level, but only half was adsorbed at the 1% addition level. These phenomena seemed to depend on the existence of a small amount of cationic material originating from Fe^{2+} and Mg^{2+} on zeolite [1].

The retention of A-PAM increased with increasing amount of pre-added PDADMAC.

3.2. Turbidity

Fig. 2 shows the effects of the retention aids on the turbidity of the supernatant fraction at a depth of 10 cm in

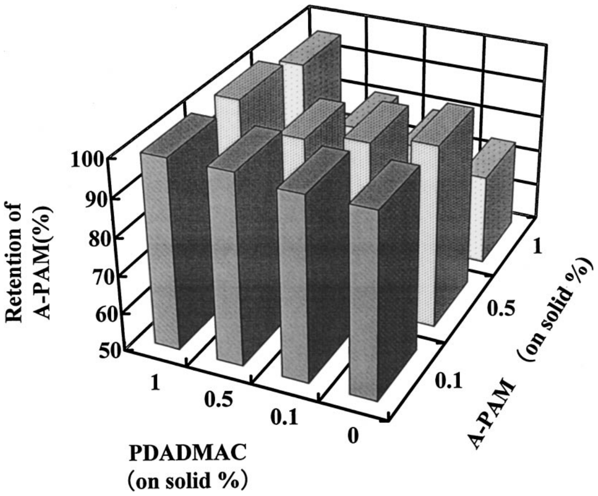

Figure 1 The retention of A-PAM on the solids, the conditions of the preparation of the zeolite sheet; NUKP 5.5%, Avicel 3.5%, zeolite 61.5%, kaolin 18%, and glass fiber 11.5%.

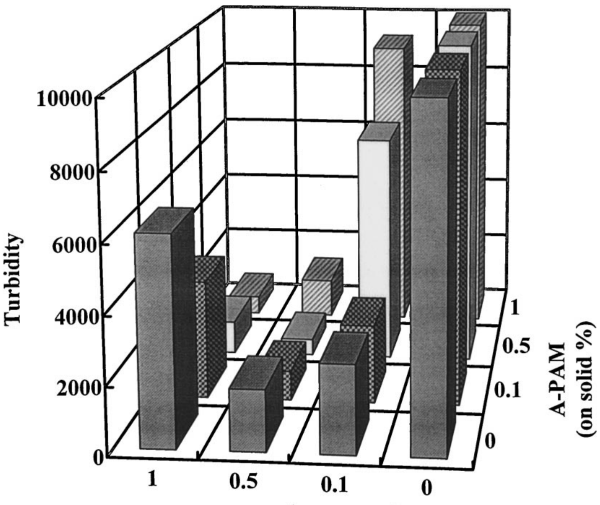

Figure 2 The effects of the retention aids on the turbidity of the suspensions of NUKP and fillers, the conditions of the preparation of the zeolite sheet, NUKP 5.5%, Avicel 3.5%, zeolite 61.5%, kaolin 18%, and glass fiber 11.5%.

a sedimentation cylinder containing the sample. When A-PAM was added alone to the slurry, the turbidity was the same as in the blank test indicating that this was no effect on the flocculation. It is thought that polymer bridges were hardly formed since the zeolite, kaolin and pulp had anionic charges. The turbidity decreased when PDADMAC was added alone to the suspension, but the aggregated fillers became separated from pulp fibers in the sedimented materials. This phenomenon indicates that it is difficult to make a zeolite sheet with a high retention. On the other hand, the fillers were fixed onto the pulp fibers and also the turbidity decreased when both PDADMAC and A-PAM were added successively to the suspension. It is suggested that the dual polymer system involving the sequential addition of cationic polymer (CP) followed by anionic polymer (AP) is useful for the formation of comprehensive flocs and thus for the preparation of a sheet with a high retention of filler.

The lowest turbidity was obtained using about 2.5 times more charges of CP than AP, probably because solids such as zeolite and fibers are negatively charged.

3.3. The effects of the retention aids on the retention

Fig. 3 shows the effect of the retention aids on the retention of the fillers. The ratio of the fillers was zeolite : kaolin : glass fiber (5.5 : 1.5 : 1). When only PDADMAC or A-PAM was added to the suspensions, the retention was about 20% or less, but when both PDADMAC and A-PAM were added to the suspensions, the retention of the fillers was greatly increased. The retention of the fillers was more than 90% when PDADMAC was added at a level of 0.1% or 0.5% on solids, followed by the addition of A-PAM at 0.5% or 1.0%. When PDADMAC was applied in much larger quantities, the retention began to decrease. This seems to be attributable to the lower bridging efficiency of A-PAM between solid particles because of the flatter conformation of A-PAM on the solids on which PDADMAC is densely adsorbed.

3.4. The effects of the pulp contents on the retention

Pulp fibers are merely forming and reinforcing materials for the preparation of the zeolite sheet, and then are eventually burned up. Therefore, it is important to prepare a satisfactory sheet with a fiber content which is as low as possible.

Fig. 4 demonstrates the effects of fiber content on the retention of the fillers. We expected that the retention of the fillers would increase with increasing content of pulps, but the results indicated that the retention of the fillers had a maximum value at a pulp content of 5–10%.

Even when the pulp content with respect to the solid phases was only 2%, the retention of the fillers was more than 80%, but it was difficult to take the wet sheet off the wire because of the low sheet strength.

3.5. The effects of the retention aids on the retention of the fillers and on the drainage time

Fig. 5 gives the effects of the retention aids on the retention of the fillers and on the drainage time. With water alone without any solids, the drainage time was 4 seconds.

The retention of the fillers in the sheet was 90.8% when 0.1% PDADMAC and 0.5% A-PAM, calculated with respect to the total solids, were sequentially added to the slurry, but the drainage time was 27.7 s which is very long compared with that (4 s) of water alone. When 0.5% PDADMAC and 0.5% or 1.0% A-PAM were added to the suspensions, the retention of the filler in the sheet was 91.8% or 92.9% respectively, and the drainage time was 13 s, indicating a large improvement. It was thought that, in the case of 0.5% PDADMAC and 0.5% A-PAM, the drainage time was reasonable because of the good flocculation conditions of the pulp

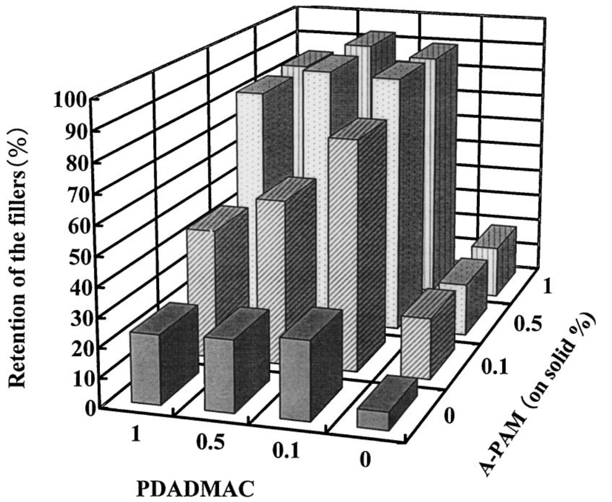

Figure 3 The effects of the retention aids on the retention of the fillers in the sheet, the conditions of the preparation of the zeolite sheet, NUKP 5.5%, Avicel 3.5%, zeolite 61.5%, kaolin 18%, and glass fiber 11.5%.

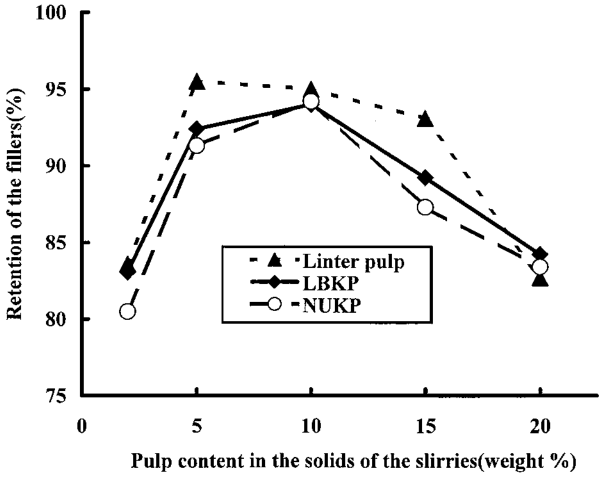

Figure 4 The effects of the pulp content on the retention of the fillers in the sheets, the conditions of the preparation of the zeolite sheet, pulp 2–20%, zeolite 68.5–50.5%, kaolin 18%, and glass fiber 11.5%, the addition level of the retention aids (On solids), PDADMAC 0.5%, A-PAM 1.0%: (♦), LBKP; (○), NUKP; (▲) linter pulp.

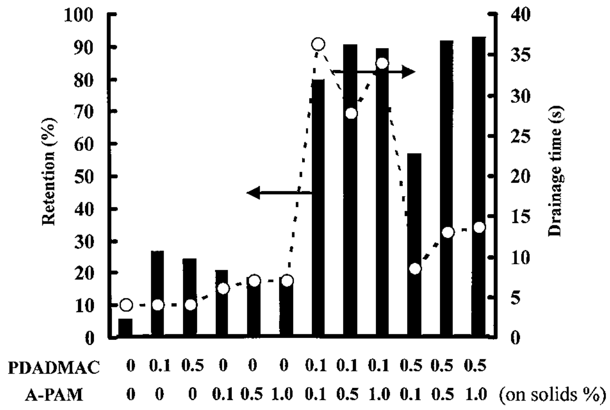

Figure 5 The effects of the retention aids on the retention of the fillers and the drainage time in sheet formation, the conditions of the preparation of the zeolite sheet, NUKP 5.5%, Avicel 3.5%, zeolite 61.5%, kaolin 18%, and glass fiber 11.5%: (■), Retention; (○), drainage time.

and the inorganic fillers. The maximum retention of the fillers, 92.9%, and the shortest drainage time, 13 s, were also achieved when 0.5% PDADMAC and 1.0% A-PAM were added to the suspension. The ratio of the cationic charges to anionic charges on the polymers (cationic/anionic) was then about 2 which was close to the value of 2.5 which gave the lowest turbidity of the supernatant, as described earlier. This suggests that the ratio of the charge amounts is one of the most important factors in the preparation of the zeolite sheet with high retention.

3.6. The effects of the pulp content on the drainage time

Fig. 6 shows the effect of the pulp content on the drainage time. When the pulp content was 5%, calculated with respect to the total solids, the shortest drainage time was obtained because of the smaller amounts of hygroscopic swollen pulp fibers, but the drainage time was elongated at a pulp content of 2%, due to the higher resistance to drainage created by the passage of much unretained filler particles through the wire mesh screen.

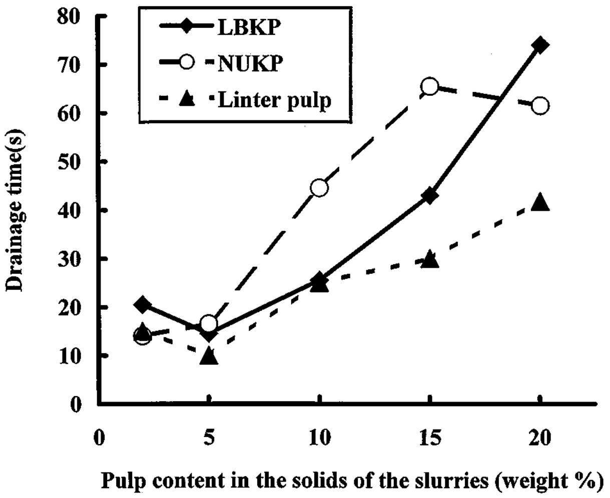

Figure 6 The effects of the pulp content on the drainage time during sheet formation, the conditions of the preparation of the zeolite sheet, pulp 2–20%, zeolite 68.5–50.5%, kaolin 18%, and glass fiber 11.5%, the addition level of the retention aids (On solids), PDADMAC 0.5%, A-PAM 1.0%: (♦), LBKP; (○), NUKP; (▲) linter pulp.

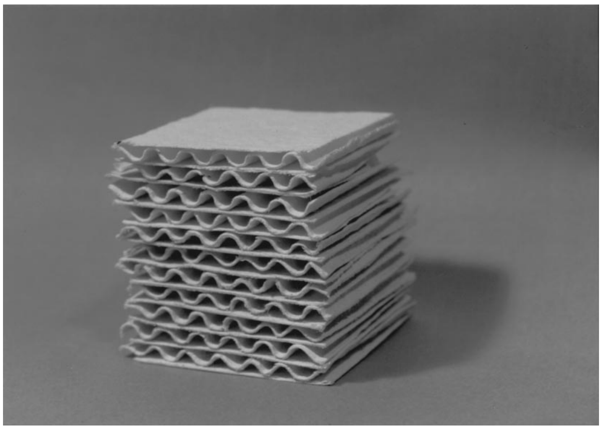

Figure 7 Honeycomb structure made of zeolite sheets.

3.7. The effects of the kinds of pulp

Figs 4 and 6 illustrate the effects of the kind of pulp on the retention of the fillers and on the drainage time, respectively.

Fig. 4 indicates that the retention of fillers was higher in the order: linter pulp > LBKP > NUKP which conversely had the lower charge density. It is considered that the retention of fillers was influenced by the conformation of the polymers when they were adsorbed onto the solid surfaces. Fig. 6 also indicates that the linter pulp was most favourable for the drainage time, and for the retention of the filler.

3.8. Attempt to prepare the honeycomb from zeolite sheet

Since satisfactory results were obtained on the filler retention and the drainage, a succeeding study was attempted to prepare the honeycomb structures.

After some of zeolite sheets prepared using papermaking technique were corrugated and the corrugated and original sheets were dipped into colloidal silica, they were piled up alternately and, then, ignited in an electric furnace at 700°C for 20 minutes to remove pulps and to sinter the zeolite particles each other. The hard honeycomb made only of inorganic materials was obtained. Fig. 7 shows the honeycomb prepared using zeolite sheet in the laboratory.

This honeycomb structure of zeolite sheet prepared using a papermaking technique is expected to overcome the disadvantages of beads and pellets and to apply to various industrial fields.

Further details on the strength and the function of the honeycombs will be reported in the following articles.

4. Conclusions

The retention of stock components was improved satisfactorily by using a dual polymer system involving the sequential addition of PDADMAC followed by A-PAM with high molecular weight. This system formed comprehensive flocs and made it possible to prepare a sheet with a high content of filler. In particular, the addition of 0.5% PDADMAC and 0.5% or 1.0% A-PAM, calculated with respect to the total solids, to the suspensions of the pulp and fillers led to the highest retention of the fillers and the shortest drainage time. It is in practice interesting that the filler retention exceeds 90%

when only small amounts of pulps and flocculants are present.

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References

1. A. DYER, "An Introduction to Zeolite Molecular Sieves" (John Wiley & Sons, New York, 1988).
2. J. A. C. SILVA and A. RODIGUES, *AICHE J.* **43** (1997) 2524.
3. S. REGE, J. PADIN and R. YANG, *ibid.* **44** (1998) 799.
4. J. YANG and C.-H. LEE, *ibid.* **44** (1998) 1325.
5. T. FUKUSHIMA, *Shokubai.* **39** (1997) 281.
6. A. KODAMA, M. GOTO, T. HIROSE and T. KUMA, *J. Chem. Engineering of Japan* **26** (1993) 530.
7. *Idem., ibid.* **27** (1994) 644.
8. *Idem., ibid.* **28** (1995) 19.
9. Y. MITSUMA, Y. OTA and T. HIROSE, *ibid.* **31** (1998) 482.
10. T. KURATA, *SEN-I GAKKAISHI.* **48** (1992) 545.
11. H. ONABE, *Japanese J. Paper Tech.* **29**(4) (1986) 28.
12. I. KATOU, *ibid.* **29**(4) (1986) 35.
13. H. TANAKA and Y. SAKAMOTO, *J. Polym. Sci. Chem.* **31** (1993) 2687.
14. A. SWERIN and L. WAGBERG, *Nord. Pulp Paper Res. J.* **1994** (1994) 9; H. TANAKA, A. SWERIN, L. SWERIN and L. ODBERG. *Langmuir.* **10** (1994) 3466.

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