



## Effect of Flocculation of Alumina Slip on the Pore Size Distribution of Cast Alumina by Polyacrylamide (PAM)

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### ABSTRACT

Tubular alumina filters were prepared by a slip casting process. The flocculation of alumina slip was studied as a function of pH and PAM concentrations. The particle size and viscosity of alumina slip were determined by using laser diffraction technique and Brookfield DV III+ viscometer, respectively. Pore size and pore size distribution of the alumina filters were measured by using Mercury Porosimeter. From the experimental results, the isoelectric point (i.e.p.) of the alumina slip showed at pH 7 and gave the largest particle size. Furthermore, the flocculation by PAM increased particle sizes, particle size distribution and viscosity of alumina slip due to polymer bridging on surface of particles. However, the addition of electrolyte in PAM solutions facilitate flocculation of particles due to the compression of electrical double layer and increase in the van der Waals attractive forces. The larger floc size resulted in bigger pore size in the filter. The average pore size of fired filter at 1500°C is in the range of 0.32 – 0.34µm.

**Keywords:** Alumina, Flocculation, Rheology, Slip casting.

### 1. INTRODUCTION

Alumina filters are used in food, agriculture and automotive industries. These filters are usually prepared by methods such as powder pressing, dip-coating, tape casting, membrane or extruding followed by partial sintering of powders [1]. Tubular forms of filters are fabricated by slip casting. The objectives of this research are to study the effects of pH and PAM concentrations on the flocculation of alumina slip, and to prepare alumina filters which could be used for

separation of colloids from drinking water, in concentration of fruit juices in the food industry and in the filtration of beverages for clarification and sterilization [2]. These filters should provide longer lifetimes and better acidic and alkaline resistance than polymer membranes.

Alumina particles can be stabilized by an electrostatic mechanism through careful pH-control (HCl and NaOH). At low pH (pH 3-5) the particles have positive surface charges

and at high pH (pH 9-11) the particles have negative surface charges. Alumina particles with the same charge repel each other and remain in dispersion. The effectiveness of the stabilization depends upon the type of mechanism that generates the repulsive forces usually derived from the interaction between electrical double layers [3]. The pH-control to isoelectric point of particles resulted in the flocculation of particles by van der Waals forces. PAM is widely known as the flocculant of oxide particles. The addition of PAM in the suspension provided attraction of nonionic polyacrylamide chains on to the particles surface in the slip which resulted in the flocculation of particles by polymer bridging [3]. A typical nonionic polyacrylamide favors be adsorbed on the zero charge of particles by hydrogen bonding. The flocculation increased particle sizes, particle size distribution and viscosity of alumina slip [4-7].

In the casting process flocculation of slip has also an effect on the solution viscosity and on the rheological properties of the slip. An increase in viscosity resulted from increase of the floc size and solids content of the slip [8-10]. Increasing floc size generates larger pores size and pore size distribution in products.

The aim of this study is to examine the flocculation behavior of alumina slip on the pore size distribution of alumina filters. The flocculation behavior may be explained in terms of the influence of pH and PAM concentrations on particle interactions.

## 2. MATERIALS AND METHODS

### 2.1 Particle size and rheological measurement

The experimental work was performed by using 99.6%  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> (Nipron Light Metal: Japan) with a specific gravity of 3.80 and the average particle size was 0.7  $\mu$ m. The 25% (w/w) of alumina powder was dispersed in

distilled water and then mixed by electric mixer (Stir-pak 50002-07 Cole-palmer) for 30 minutes. The alumina slip was adjusted pH by 0.1 M HCl and 0.1 M NaOH until the pH values were 3, 5, 7, 9 and 11, respectively. In the case of slip viscosity and particle size distribution determination, the measurements were performed immediately after the mixing step. Particle size distribution measurements were done by using the light scattering technique (Mastersizer S, Malvern). Viscosity was measured by Brookfield rheometer DV-III+ rotating-spindle. Zeta potential of alumina particles were determined by Zetasizer 3000 HAS, Malvern.

Nonionic polyacrylamide (PAM) (MW 15 million; Betz Mining Chemicals, USA) was dissolved in distilled water and mixed for 24 h. The alumina powder was dispersed in 0.04 M NaCl and adjusted to 5, 7 and 9. Finally, PAM solution was added in the alumina suspension in different concentrations.

### 2.2 Pore size distribution of green and fired tubular alumina filters

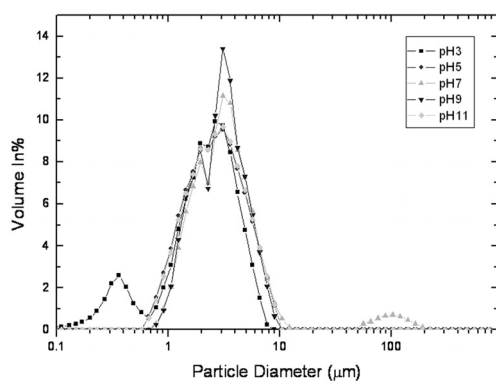
The slips were casted into plaster moulds using a casting time of 2 minutes. The mould had a diameter of 2.5 cm and a length of 15 cm. The casting samples were initially dried at room temperature for 24 h. Afterward, the samples were heated up to the sintering temperature at 1,500 °C, with heating rate of 3 °C min<sup>-1</sup> and soaking for 1 h. The pore size and pore size distribution of the green and fired filter samples were determined by Automated Mercury Porosimeters (Pore-Master-60 Quatachrome Instruments).

## 3. RESULTS AND DISCUSSION

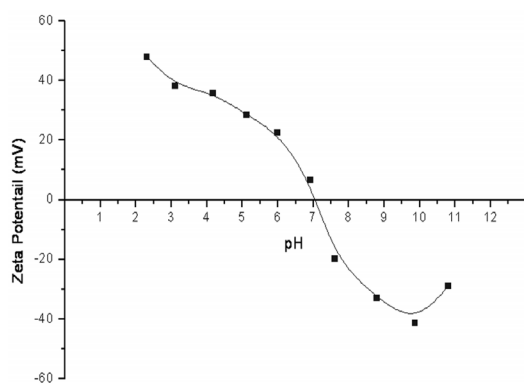
Figures 1-2 illustrated particle size distribution and viscosity of alumina slip at pH 3, 5, 7, 9 and 11. From the results of particle size and viscosity measurements, it was found that pH 7 which is the pH of zero

charge (as shown in Figure 3), gave the largest particle size and highest viscosity due to decreasing of the surface charge of particles. At this pH, van der Waals attractive force was dominant. The average particle size  $D[4,3]$  was  $9.01 \mu\text{m}$ . The increase in viscosity by increasing the particle size can mainly be attributed to the attraction between particles which renders them more resistant to flow. At below pH 7, the particles have positive surface charges and above pH 7, the particles have negative surface charges. Alumina particles with the same charge repel each other and remain in dispersion. In this condition, the small particle size was generated and provided the low viscosity.

Figure 3 showed that the zeta poten-



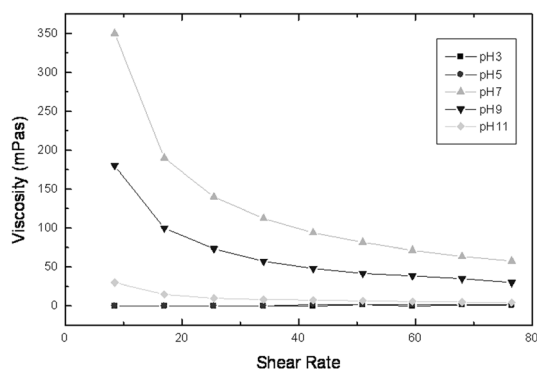
**Figure 1.** Particle size distribution of alumina slips as a function of pH.



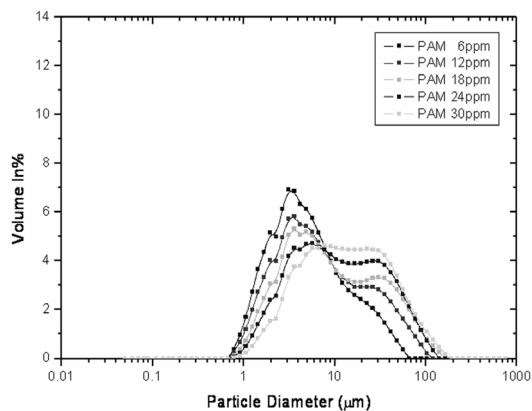
**Figure 3.** The zeta potential of alumina slips as a function of pH.

tial value decreased from 48 to -29 mV and the pH of point zero charge ( $\text{pH}_{\text{PZC}}$ ) was 7. The charge on a hydrated surface of alumina particles dispersed in water was determined by its reaction with  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$  ions. The addition of  $\text{H}_3\text{O}^+$  ions will reduce the pH and cause the uncharged surface to become protonated and positively charged. The addition of  $\text{OH}^-$  ions will remove hydrogen from the surface and produce a negative surface charge when the pH is greater than the PZC of the surface. Exchange at the surface is reversible but time-dependent, and the relative concentration of  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$  ions is determined by potential.

Particle size distribution of alumina slips at pH 7 which flocculated by PAM illustrated



**Figure 2.** Viscosity of alumina slips as a function of pH.



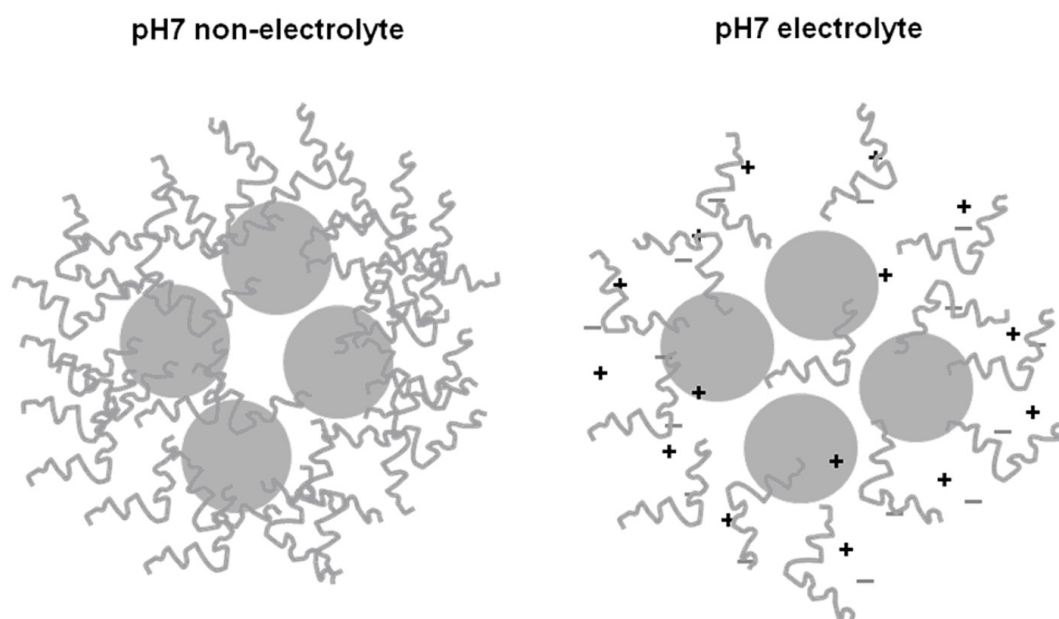
**Figure 4.** Particle size distribution of alumina slips in 0.04M NaCl and PAM at pH 7.

in Figure 4. It was found that the particle size distribution showed wide range of 1- 100  $\mu\text{m}$  and increasing of PAM concentrations was provided distinctly increase of particle size. The 30 ppm of PAM gave the largest of particle size of 20.48  $\mu\text{m}$ . The addition of PAM solution at pH of point zero charge provided attraction of nonionic polyacrylamide chains on alumina surface and flocculated by hydrogen bonding.

On the other hand, alumina which added

only PAM solutions showed the particle size distribution wider than electrolyte addition. The average particle size  $D[4,3]$  was 24.09  $\mu\text{m}$ . Electrolyte which added in the suspension at pH of point zero charge provided positive and negative ions in suspension. The adsorption of polyacrylamide chains was hindered by these ions. The flocculation models were proposed as shown in the Figure 5.

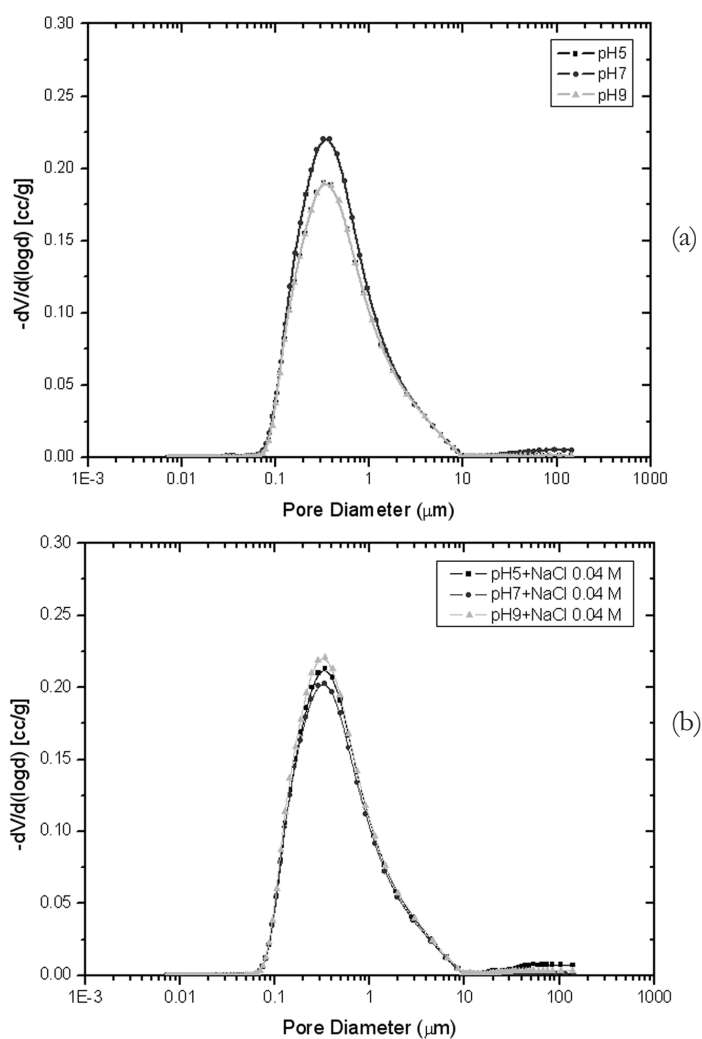
The pore size distributions of fired



**Figure 5.** Comparison of flocculation models by PAM in non-electrolyte and electrolyte conditions at pH 7.

tubular filters were shown in the Figure 6 and Table 1. The fired tubular filters were prepared in two conditions. Firstly, the filters was prepared by 25 % (w/w) alumina slip in non-electrolyte and added 30 ppm of PAM and adjusted pH at 5, 7 and 9. Secondly, the filters

was prepared by 25 % (w/w) alumina slip in 0.4 M NaCl electrolyte and added 30 ppm of PAM and adjusted pH at 5, 7 and 9. From the experimental results, it was found that the pore size distributions of both conditions were slightly different.



**Figure 6.** Comparison of pore size distribution of fired alumina filters at pH 7.  
 (a) Non-electrolyte PAM 30 ppm. (b) Electrolyte PAM 30 ppm.

**Table 1.** Average Pore Size and pore volume data of fired and green alumina filters.

Conditions	Average Pore Size ( $\mu\text{m}$ )		Pore volume (%)	
	Green	Fired	Green	Fired
Electrolyte PAM pH5	0.233	0.3369	63.55	46.63
Electrolyte PAM pH7	0.219	0.3357	61.34	45.30
Electrolyte PAM pH9	0.239	0.3395	65.32	48.80
Non-electrolyte PAM pH5	0.205	0.3232	60.12	43.25
Non-electrolyte PAM pH7	0.228	0.3445	67.98	47.51
Non-electrolyte PAM pH9	0.234	0.325	64.43	44.01

#### 4. CONCLUSIONS

The fabrication of porous tubular alumina filters which prepared by slip casting process. A correlation between pore size and flocculation was studied. The pH and PAM concentration had strong effects on the surface charges of particles and the particle size in the slip.

The pH of point zero charge of alumina slip was found at pH 7. The flocculation by PAM increased particle sizes, particle size distribution and viscosity of alumina slip due to polymer bridging on surface of particles. The addition of electrolyte in the slip at pH of point zero charge resulted in decrease adsorption of nonionic PAM on the surface particles. The average pore size of fired filters at 1500°C was in the range of 0.32 – 0.34µm.

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