Influence of dissolved ions on alum cationicity under alkaline papermaking conditions

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ABSTRACT: The isoelectric point of alum when titrated with NaOH under moderate shear was at approximately pH 7.7. In the presence of calcium ion the isoelectric point was increased to above pH 8, the effect being greater with increasing Ca^{++} levels. This effect was somewhat offset by the presence of additional sulfate ion. With Ca^{++} present the available or effective cationicity of alum and poly aluminum chloride were similar at pH 8.

KEYWORDS: Alkaline papermaking, aluminum sulfate, calcium, cations, isoelectric point, papermaking, pH, sulfates.

Alum is being widely recommended for use in alkaline papermaking. Benefits claimed include improved sizing with alkenyl succinic anhydride *(1–4)*, prevention of alkenyl succinic anhydride deposits *(5)* and improved drainage and retention *(2, 6, 7)*. Recent reports of alum exhibiting cationic behavior under alkaline papermaking conditions *(2–4)* offer an explanation, at least in part, of the performance observed.

The generally accepted theories on alum chemistry do not provide for alum cationicity under typical alkaline papermaking conditions; i.e., pH of about 8. Indeed, the literature is rich in studies of alum chemistry under acidic to near-neutral conditions, and much of this is directed toward elucidating rosin sizing mechanisms. Clearly, a better definition of the charge characteristics of alum under alkaline papermaking conditions is needed. This would provide a more clear perspective for interpreting some of the more recent literature

Effect of shear on alum charge, methods of measurement

The tendency for the pH to drift after incremental additions of alkali to alum, particularly in the pH range 5 to 9, is well known. Collins *et al. (8)* developed the data for **Fig. 1** by treating alum with NaOH and allowing the samples to stand for 24 h. Strazdins *(9)* found the titratable cationic charge of the alum precipitates to increase with increasing shear, and attributed this effect to a limiting of alum floc aggregation. The charge/total cationicity/pH relationship for alum is obviously time and shear dependent, and selecting conditions for studying this relationship is necessarily somewhat arbitrary.

Figure 2 shows the electrophoretic mobility of alum titrated with NaOH as a function of pH at two different levels of shear. Values were recorded after 3 min in a medium speed blender and after 9 min of rapid magnetic stirring. In addition to reaching equilibrium pH more rapidly, the higher shear lowered the isoelectric point for alum from slightly above to slightly below pH 8. The isoelectric point from the blender experiments, *ca.* pH 7.7, is in reasonable agreement with the pH 7.5 reported by Collins *(8)*, and the blender was used for subsequent studies.

Effect of sulfate, calcium, magnesium

The effects of sulfate, calcium, and magnesium ion on the pH/mobility relationship for alum were determined. (See **Fig. 3.**) Sulfate (as Na_2SO_4) had no effect on the isoelectric pH, while Ca^{++} and Mg^{++} (as chlorides) increased the isoelectric point to the region of pH 9. At pH 8 alum and $CaCl_2$ individually are anionic with silica, but when mixed, after prior adjustment to pH 8, become cationic. (See **Fig. 4.**) Thus, Ca^{++} imparts cationicity to alum under alkaline papermaking conditions, and the effect appears to be independent of addition sequence.

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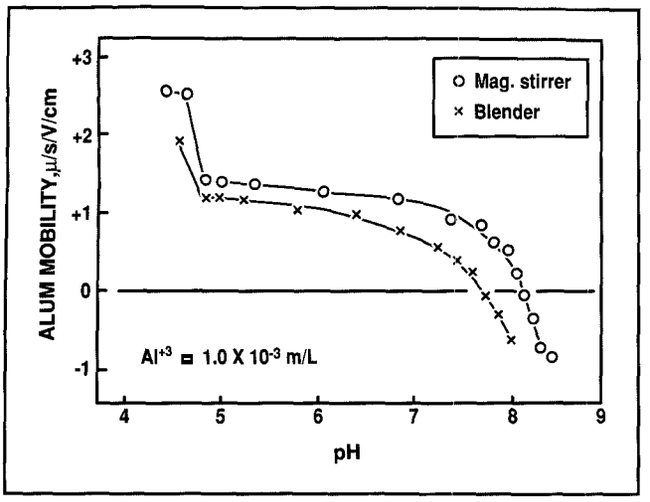
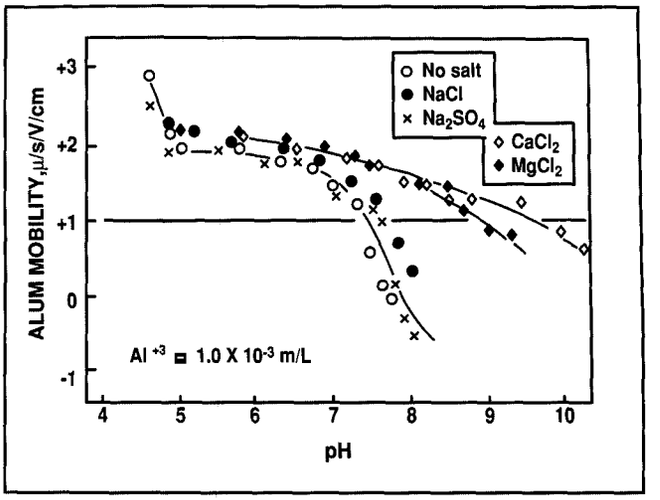
2. Electrophoretic mobility of alum as a function of pH. Al^{+3} = 1.0 x 10^{-3} m/L, 150 ppm NaCl.



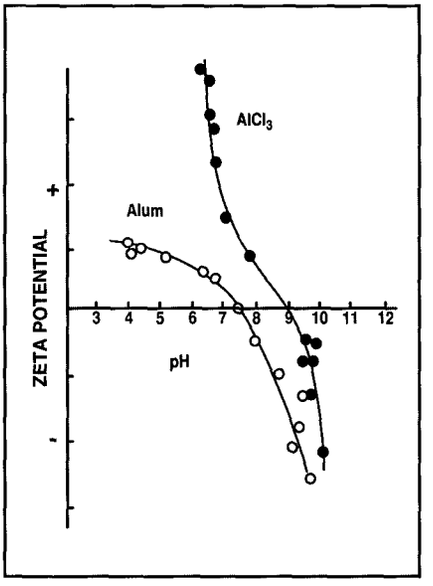
3. Effect of $SO_4^=$, Ca^{++}, Mg^{++} on the mobility of alum as a function of pH. Al^{+3} = 1.0 x 10^{-3} m/L; NaCl = 150 ppm; Na_2SO_4 = 180 ppm; $CaCl_2$ = 140 ppm; $MgCl_2$ = 120 ppm.



The isoelectric pH for alum was shown to increase with increasing levels of added Ca^{++}. (See **Fig. 5.**) Of particular significance is the appreciable cationicity of alum at pH 8 with as little as 25 ppm added $CaCl_2$ (22.5 ppm as $CaCO_3$). This level of soluble Ca^{++} is easily exceeded in the headbox filtrates of alkaline fine paper mills using $CaCO_3$ filler. (See **Table I.**) It should be noted that there was some difficulty with the reproducibility of the isoelectric "endpoint" when this was at a pH of about 9 or higher. This can be seen from a comparison of Figs. 3 and 5.

Added $CaCl_2$ had no effect on the stoichiometry of alum neutralization with NaOH. (See **Fig. 6.**) The only differences noted in potentiometric titrations were slightly higher pH values at alum neutralizations above 100% (3/1 OH/Al ratio) with $CaCl_2$ present.

1. Zeta potential (arbitrary scale) of alum and $AlCl_3$ as a function of pH *(8)*



I. Analysis of headbox filtrates from fine paper mills using $CaCO_3$ filler

Mill	*pH*	*Total hardness, ppm $CaCO_3$*	*Alkalinity, ppm $CaCO_3$*
I	7.9	95	125
II, a	7.7	100	185
, b	7.7	111	270
III, a	7.5	118	168
, b	7.6	128	155
IV, a	7.9	147	144
, b	7.9	152	148
V	8.0	100	146
VI, a	7.9	96	152
, b	7.9	98	133
VII	7.8	174	155
VIII	7.7	175	240
Avg. 12 machines		125	168

Effect of carbonate, sulfate with calcium present

In the presence of Ca^{++}, identical isoelectric pHs were observed when alum was titrated with NaOH and with Na_2CO_3. (See **Fig. 7.**) This result indicates that carbonate has no specific effect on alum cationicity.

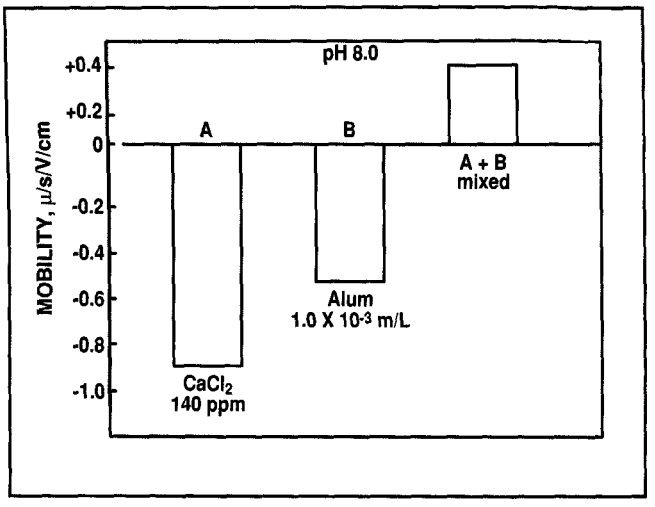
Sulfate ion reduced alum charge and lowered the isoelectric pH when Ca^{++} was present. (See **Fig. 8.**) This effect was not observed in the absence of Ca^{++}. (See Fig. 3.) However, even at 200 ppm Na_2SO_4 (135 ppm as $SO^{4=}$), alum was still cationic at pH 8. Sulfate levels in alkaline papermaking systems are not expected to be high enough to seriously reduce alum/Ca^{++} cationicity.

Total available cationicity

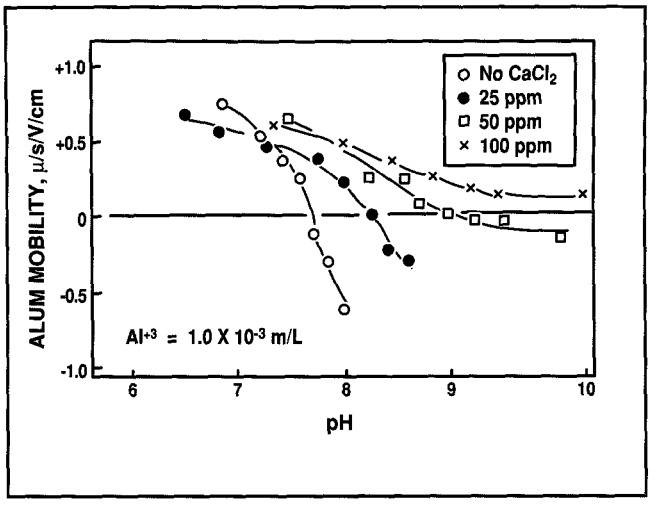
The total available cationicity of alum was measured by direct titration with polyvinyl sulfate potassium salt (PVS-K) after incremental additions of NaOH. This was done with magnetic stirring, and the results with no Ca^{++} present agree with Strazdins *(9)*. With Ca^{++} added, the increase in total cationicity is greatest at the higher (1.5 to 3.0) OH/Al ratios. (See **Fig. 9.**) This effect is more clearly seen when cationicity is plotted versus pH. (See **Fig. 10.**)

The total available charge of alum was also studied in terms of its capacity

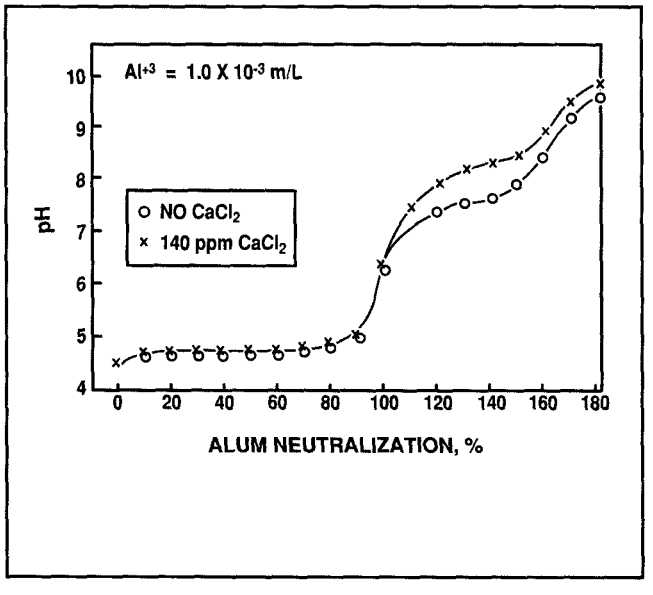
4. Mobility of alum and $CaCl_2$ individually at pH 8 and mixed after prior pH adjustment to 8



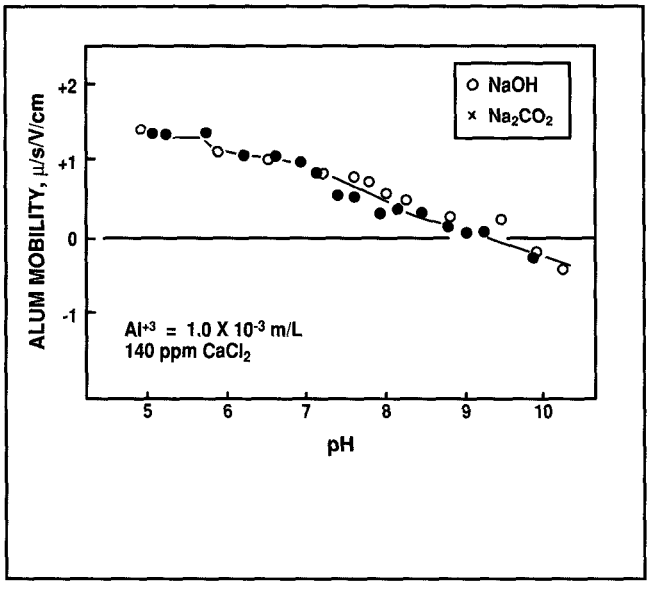
5. Effect of Ca^{++} level on the mobility of alum as a function of pH. Al^{+3} = 1.0 x 10^{-3} m/L; 150 ppm NaCl included in each condition.



6. Potentiometric titration of alum with NaOH with and without 140 ppm $CaCl_2$ added. Al^{+3} = 1.0 x 10^{-3} m/L; NaCl = 250 ppm.



7. Mobility/pH relationship for alum titrated with NaOH and with Na_2CO_3 in the presence of Ca^{++}. Al^{+3} = 1.0 x 10^{-3} m/L; $CaCl_2$ = 140 ppm.



to neutralize anionics in simulated papermaking furnishes. Furnishes were prepared at pH 4, alum added and measurements made after incremental additions of NaOH—see Experimental section.

Effect with fiber

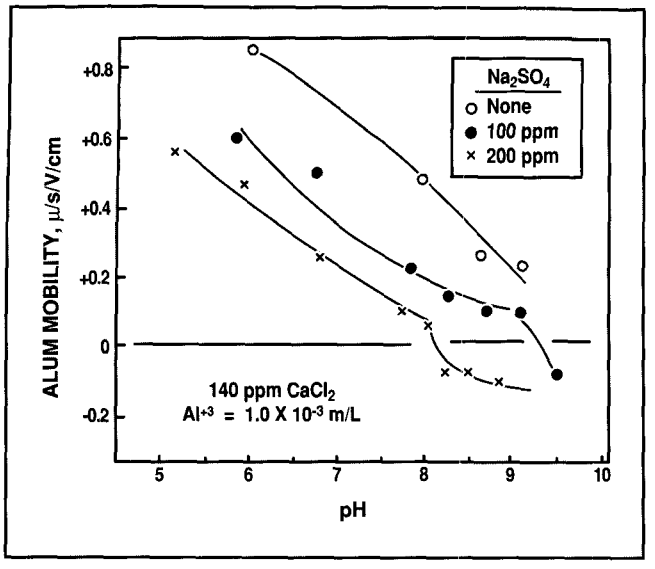
The effects of alum and Ca^{++}, individually and together, on the cationic demand of a bleached kraft pulp are shown in **Fig. 11**. In the absence of calcium, the reduction of fiber cationic demand by alum is maximum at or slightly above pH 5. Note that alum reduced cationic demand up to about pH 10, despite its demonstrated anionicity above *ca.* pH 7.7. (See Fig. 2.) This may be due to a shielding of fiber charge by $Al(OH)_3$ deposition as proposed by Strazdins *(1)*.

Addition of $CaCl_2$ alone lowered the cationic demand of the fiber, the effect being maximum in the neutral-alkaline pH range. With Ca^{++} present, alum further lowered the cationic demand with the maximum reduction being in the 5 to 6 pH range. Consistent with the previous mobility findings, Ca^{++} significantly increased the effectiveness of alum in the higher pH range.

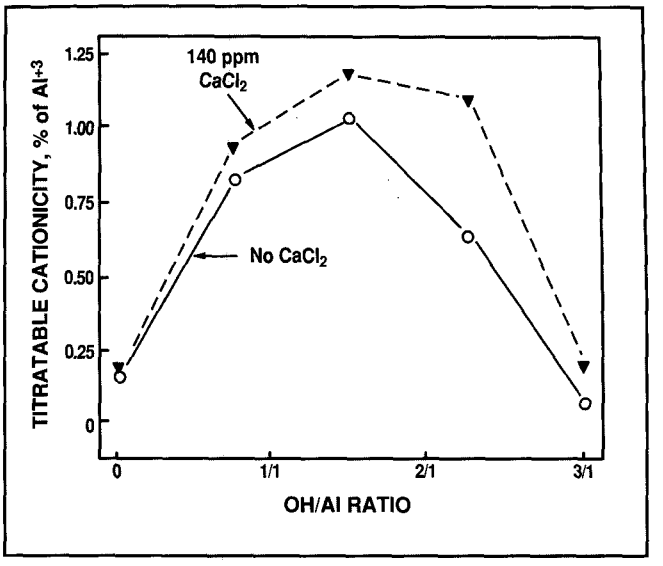
Fiber plus lignin sulfonate

The above procedures were repeated with 1.0% sodium lignin sulfonate added

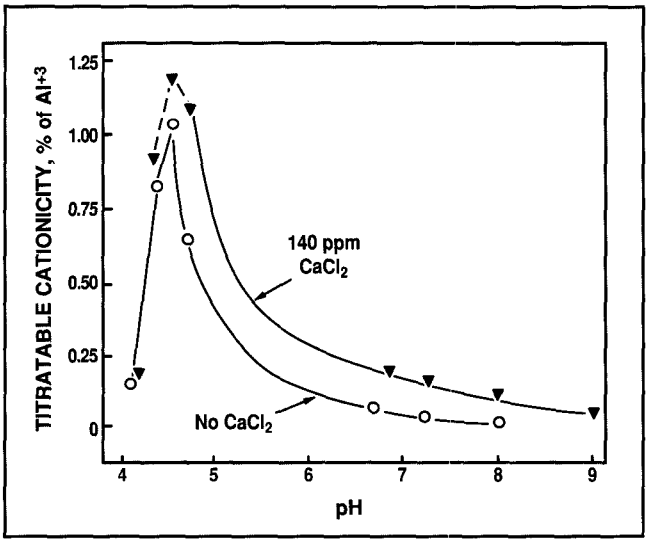
8. Effect of $SO_4^=$ on alum cationicity in the presence of Ca^{++}. $CaCl_2$ = 140 ppm.



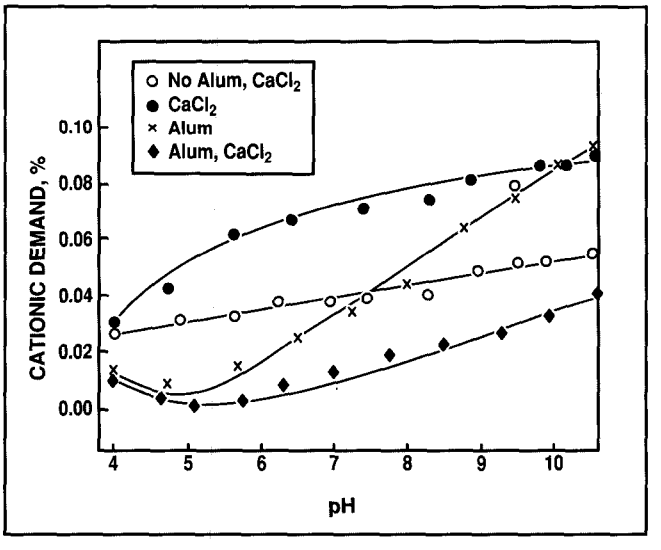
9. Effect of Ca^{++} and OH/Al ratio on titratable alum cationicity. Al^{3++} = 1.0×10^{-3} m/L, $CaCl_2$ = 140 ppm where added.



10. Effect of Ca^{++} and pH on titratable alum cationicity (from data of Fig. 9)



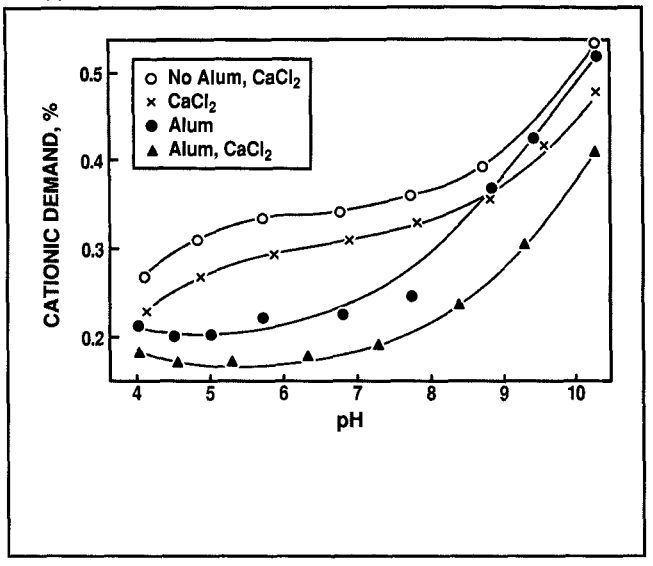
11. Effect of alum and Ca^{++} on cationic demand of a bleached kraft furnish. 50/50 HWD/SWD, 0.6% cons.; alum = 1.25% on fiber; NaCl = 150 ppm; $CaCl_2$ = 140 ppm when added.



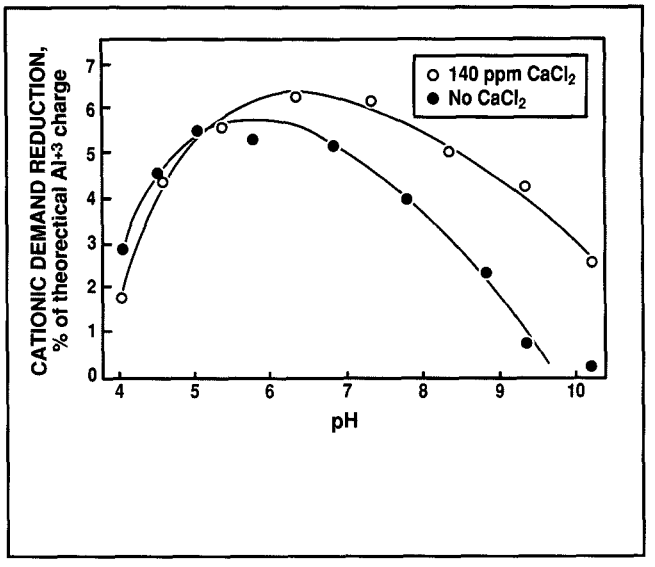
on fiber. (See **Fig. 12.**) In the absence of Ca^{++}, the results with alum were parallel to those with fiber only (Fig. 11): maximum cationic demand reduction at pH 5 to 6, some activity up to about pH 10. Ca^{++} alone gave a constant cationic demand reduction regardless of pH. With added Ca^{++}, alum effectiveness remained substantial up to pH 10.

From the data of Fig. 12, cationic demand reductions were calculated as a percentage of the theoretical, based on total availability of the Al^{+3} charge. **Figure 13** shows the apparent charge contribution of alum (% Al^{+3} charge), with and without Ca^{++}, as a function of pH. The effect of Ca^{++} was to increase alum cationicity significantly as the pH was increased above about 6. The maximum charge contributions of about 6% are in good agreement with the literature *(9)*. However, the effective pH range is much broader than that found for directly titratable alum cationicity. The cationic demand reductions at neutral-alkaline pH cannot be attributed simply to shielding of fiber charge by coating with $Al(OH)_3$ as the predominant source of anionicity was sodium lignin sulfonate.

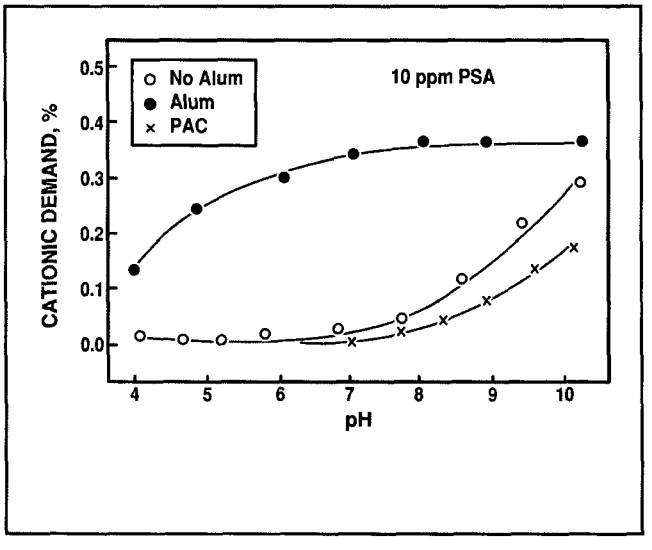
12. Effect of alum and Ca^{++} on cationic demand of a bleached kraft furnish with added sodium lignin sulfonate. 50/50 HWD/SWD, 0.6% cons.; sod. lignin sulf. = 1.0% on fiber; alum = 1.25% on fiber; $CaCl_2$ = 140 ppm when added.



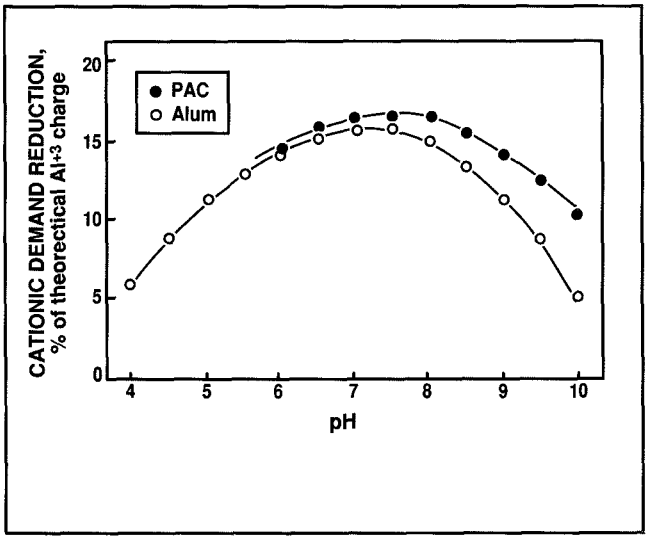
13. Available cationicity of alum as a function of pH (from data of Fig. 12)



14. Effect of alum and PAC on cationic demand of a bleached kraft furnish containing poly sodium acrylate (PSA) and Ca^{++}. 50/50 HWD/SWD, 0.6% cons.; $CaCl_2$ = 140 ppm; poly sodium acrylate = 10 ppm (0.17% on fiber); alum = 1.25% of fiber; PAC added at equal Al^{+3} to alum.



15. Available cationicity of alum and PAC with Ca^{++} present (from data of Fig. 14)



Comparison of alum, poly aluminum chloride

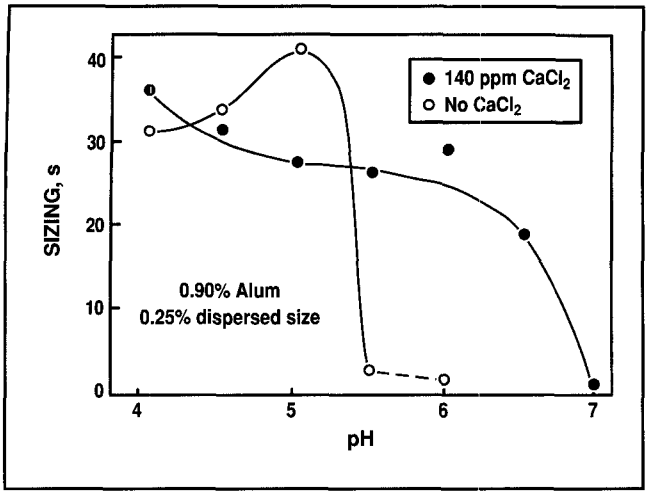
Alum and poly aluminum chloride (PAC) were compared for cationic demand reduction in a furnish containing calcium and poly sodium acrylate, a commonly used anionic dispersant. (See **Figs. 14 and 15.**) Higher cationicity of PAC versus alum (equal Al^{+3} basis) is evident only at neutral-alkaline pH, and is modest (*ca.* 10%) at the typical alkaline papermaking pH of 8.

In comparing Figs. 10, 13, and 15, it is readily seen that the total available alum cationicity and the pH of maximum cationicity vary widely with the conditions employed. This is clear evidence that *actual alum performance* will vary according to the specific application and prevailing conditions.

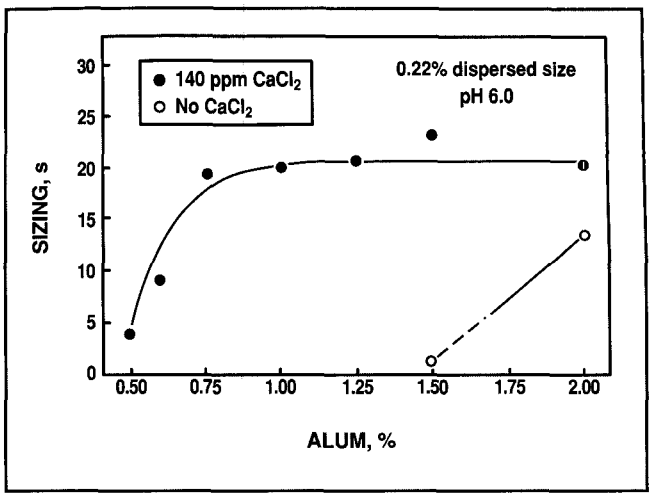
Application to rosin sizing

Suitable wet-end conditions for efficient performance of rosin sizes are determined principally by the chemistry of aluminum *(10)*. In general, where dispersed size and alum alone are used, maximum sizing occurs in the 4.5 to 5.0

16. Effect of Ca^{++} and pH on sizing with dispersed rosin and alum. 50/50 HWD/SWD bleached kraft, 70 g/m²; 0.90% alum; 0.25% dispersed size (solids); 140 ppm $CaCl_2$ (when added) based on volume of 0.6% cons. fiber.



17. Effect of Ca^{++} on sizing with dispersed rosin and alum at pH 6. Conditions identical to Fig. 14 except: 0.22% dispersed size; pH = 6.0.



pH range. Efficient sizing at higher or near-neutral pH requires additional cationicity than that available from alum alone. This can be provided by substituting poly aluminum chloride for alum *(11, 12)*, or by separate addition of a cationic polymer *(13)* or by using a cationic rosin dispersion *(14)*. Gorham and Thode *(15)* found that $CaCl_2$ increased the cationic charge of rosin-alum precipitates. In the current context, and regardless of practical value, will sufficient Ca^{++} ion permit efficient sizing with a conventional dispersed size–alum system at near-neutral pH?

Figure 16 shows that Ca^{++} (140 ppm $CaCl_2$) increased the maximum effective pH for a conventional dispersed size–alum system from approximately pH 5 to about pH 6. Also, at a constant pH of 6, better sizing was obtained with added $CaCl_2$ regardless of the alum level. (See **Fig. 17.**) Similar results, not reported here, were obtained with an anionic polyacrylamide dry strength resin.

Conclusions

Ca^{++} ion increases the cationicity of alum at pHs above about 5, and extends the isoelectric point of alum to higher pH, depending on the Ca^{++} concentration. The results clearly demonstrate that alum has a net cationic charge under typical alkaline papermaking conditions (pH 8, $CaCO_3$ filler), confirming recent reports. It is also likely that alum precipitates are amphoteric under neutral-alkaline conditions. Differences in the cationicity of alum and poly aluminum chloride are greatly reduced by the presence of Ca^{++}.

Good sizing with alum and dispersed size in the presence of Ca^{++} ion at pH 6 is a validation of the findings in papermaking terms.

Since the charge on alum is somewhat dependent on shear and time in the papermaking system, it is impossible to predict its exact cationic value. In general, however, it is expected that the later the alum is added, the higher the available cationicity will be. In furnishes very low in Ca^{++}, alum performance may be enhanced by "hardening" the system such as by adding $CaCl_2$ or CaO (lime).

Experimental

Alum mobilities were determined from a solution of commercial alum in distilled water, $Al^{+3} = 1.0 \times 10^{-3}$ m/L. The appropriate salts were added prior to the alum. Silica (MIN-U-SIL) was added at 20 mg/L as charge indicator substrate. Increments of 0.10 *N* NaOH (or Na_2CO_3) were added to adjust pH or alum neutralization. Where magnetic stirring was used, a moderate vortex was maintained for 9 min after each NaOH increment, and measurements made. When the blender was used, mixing was continued for 3 min at approximately one-half of full speed after each NaOH increment. Where fiber was used, this was a 50/50 blend of bleached HWD/SWD kraft, 0.6% consistency, refined separately to a combined CS freeness. of 500–510 mL. The pulp was first adjusted to pH 3.8–4.0. Addition sequence was salts, sodium lignin sulfonate (Marasperse N-22) or poly sodium acrylate. If necessary, pH was readjusted to 3.8–4.0. Alum, dry papermakers alum basis, was added at 1.25% based on oven-dry fiber. Where poly aluminum chloride was used, this was on an equal Al basis to alum. A propeller-type agitator was used, and a moderate vortex maintained for 4 min after each NaOH increment, and measurements made.

Cationic demand was measured by titration with poly-diallyl dimethyl ammonium chloride (poly-Dadmac) to a zero mobility end point. ■

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