

# Effects of the Surface Chemical Properties of Silica Sols on the Retention and Drainage of Microparticle Systems

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## ABSTRACT

The impact of major surface chemical properties of silica sols on the retention and drainage performance of the silica based microparticle system, Compozil, was investigated using four different silica sols. And the effect of silica properties on the interactions with cationic starch and cationic polyacrylamide has also been identified. The surface charge density and the stability over pH of silica sols were increased by introducing aluminosilicate anions at surface. It was found that the charge density of silica sols determined the addition level necessary to attain the maximum retention and drainage. When silica sols were combined with cationic starch, the charge density of the product was the critical property and the degree of microaggregation was of minor importance. In the cationic polyacrylamide system the degree of colloid structure appeared to be a more critical property than the charge density of silica sols.

## 1. Introduction

Microparticle-containing retention aid systems have been increasingly used for fines retention and drainage during papermaking, especially in the manufacture of fine papers. These retention aid systems are normally based on negatively charged inorganic colloids and positively charged synthetic and natural polymers. There are two commonly used systems; colloidal silica in conjunction with cationic starch<sup>1)</sup> and bentonite together with cationic polyacrylamide.<sup>2)</sup> A third system which also have been suggested involves the in situ formation of colloidal aluminium hydroxide, which is combined with cationic potato starch.<sup>3)</sup> In this case the aluminium hydrox-

ide is believed to carry positively charged groups, which will interact with native phosphate groups on the amylopectin molecule in the potato starch. In a recent work it has also been proposed that in situ produced metalosilicate hydrosols could be used in combination with cationic starch.<sup>4)</sup>

Although these systems contain components very different in nature they obviously share some common features, for example, the mode of addition and the flocculation behaviour. The cationic compound is normally added first, which gives an initial flocculation of fillers and fibers. The formed flocs are then subjected to high shear causing partial redispersion. This is followed by the addition of the microparticle, which achieves final flocculation of the furnish.

This addition mode normally gives a high first pass retention on the paper machine.

One property of microparticle systems, which distinguishes them from other dual retention aids, is their ability to reflocculate after floc breakage. The microparticle systems do not only cause strong flocculation but also increase the dewatering rate on the wire and press section of the paper machine. It has been suggested that a small scale reflocculation after web forming, leads to higher permeability of the web which explains the dewatering effects of these chemical systems.<sup>3)</sup> Another explanation to this increased dewatering effect is that free nonadsorbed polymer in solution will decrease the dewatering. The addition of a microparticle could be beneficial for the dewatering by deposition of the polymer onto furnish components.<sup>4)</sup> It has been suggested that for dosage levels used in microparticle systems a part of the polymer can be free in solution when the microparticle is added and in polyacrylamide-bentonite system it is also possible to get fiber flocculation induced by a network formation formed in the solution between the two components.

Preparation of particles of polysilicic acid from water glass solution and aluminum or ferric salt solutions has been reported<sup>5)</sup> and the advantage of these compounds as retention aid components would be low cost of the raw materials and that the preparation is carried out at the paper mill. In a recent development microparticles are formed by partial gelation of solutions of sodium silicate solutions by the direct addition of mineral acids or solutions of e.g. aluminum or ferric salts.<sup>6)</sup> And the surface properties of silica appeared to play an important role in microparticle systems from the studies.

The present investigation has focused on the impact of certain surface chemical properties of silica sols on the retention and

drainage performance of the silica based microparticle system, Compozil. Four commercial silica sol products were used in this study and three physical properties of the silica products have been investigated; the charge density, the chemical composition on the silica particles and microaggregation of the primary silica particles. And the effect of silica properties on the interactions with cationic starch and cationic polyacrylamide has also been identified.

## 2. Materials and Methods

### 2.1 Materials

The pulp used in the experiment was a mixture of 80% of bleached hardwood kraft pulp and 20% of bleached softwood kraft pulp. After disintegration, the dry lap pulps was beaten in a Vally beater to 25° SR and a filler mixture of 70% of talc and 30% of ground limestone, 20% calculated on the pulp was added to the stock. Tap water was used throughout the experiments but deionized water was used to dilute the chemicals. The stock was prepared to a concentration of 0.5% for the retention experiments and to a concentration of 0.3% for the drainage experiments. The starch used was a quaternized potato starch (BMB-190, degree of cationic substitution = 0.048, Lyckeby Starkelsen, Sweden) and cooked at 95°C for 20 minutes at a concentration of 2% after which it was diluted to 0.5%. A commercial cationic polyacrylamide (CPAM) was used (BMB-2320, cationicity = 20 mol %, Eka Chemicals, Sweden) and dissolved to a 0.1% solution.

Four commercial anionic colloidal silica products (ACS) were used (BMA-grades, Eka Nobel) and their physical properties were evaluated. The properties of these products are shown in Table 1.

**Table 1. Properties of anionic colloidal silica products used in this study**

	Specific surface area(m <sup>2</sup> /g)	Charge density (meq/g)	Particle size (nm)	pH	Remarks
ACS1	500	0.5	5.0	10.0	
ACS2	500	0.5	5.0	9.3	surface modified
ACS3	850	0.8	3.0	8.7	surface modified
ACS4	850	0.8	3.0	8.7	surface modified + structured

## 2.2 Methods

The zeta potential of the silica sol particles was measured in a ZetaSizer 3(Malvern Instr. Ltd., UK) at different pH values.

The retention experiments were made in a Dynamic Drainage Jar (DDJ) with baffles and a standard steel screen (200 mesh, 76  $\mu$ m hole diameter). Of the total stock, 33% was fine material (fiber fines and filler) and the retention value reported are the retention of fines and filler together. The CPAM was added first to the furnish under stirring (1200 rpm). After 30 seconds the stirring was slowed down to 1000 rpm and simultaneously the ACS was added. Samples were collected after further stirring during 15 seconds. In the experiments with cationic starch the procedure was the same except that the stirring speed was kept constant (1000 rpm) during the additions of the two components.

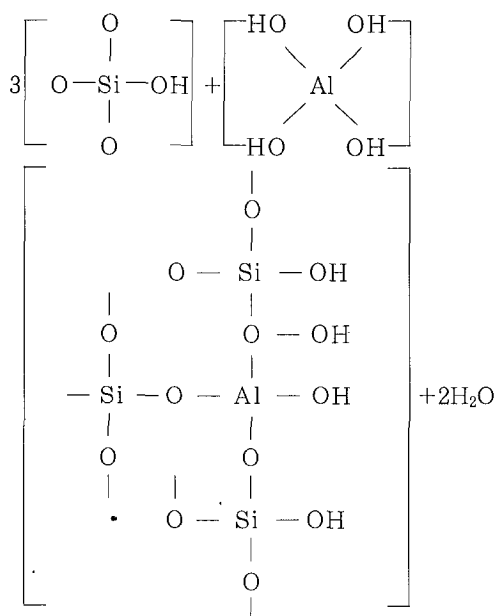
Drainage test was carried out in a CSF tester with the rear outlet stopped. 1000 mL of test stock were taken and chemicals added same as in the retention measurement in timed sequence in the DDJ. After the desired mixing time the sample was transferred to the CSF tester and the time taken for various volumes taken.

## 3. Results and Discussion

### 3.1 Effect of surface modification of ACS

ACS2, ACS3 and ACS4 contain silica sols that are surface modified with aluminate ions. The formation of the aluminosilicate anion by reaction with the surface of silica is represented in Fig. 1. In a pure silicic acid (ACS1) the silanol groups will due to their weak acid nature be neutralized at low pH. At a pH of less than 6, this type of product is no longer sufficiently charged to give effect in combination with cationic electrolyte. However, by incorporating aluminium in the surface structure a negatively charged group is created which is much less pH dependent than the silanol groups.

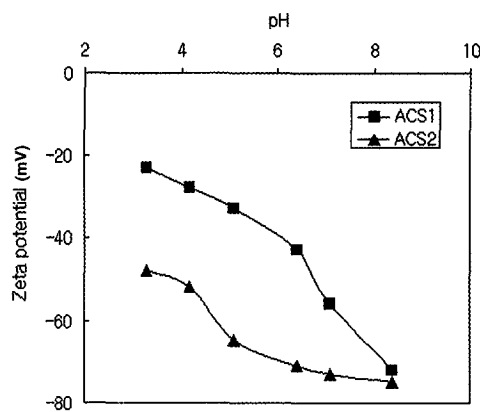
In Fig. 2 the zeta potential of the silica sols is represented as a function of pH. From this figure it can be noted that the two silica sols represent very strong negative surface charges at pH 8. With decreasing pH, the anionic charges decrease more rapidly with the unmodified silica sol compared with the modified one. In case of the unmodified silica sol the charge drops to about one third when decreasing pH to 4 from 8 while surface modified silica sol drops a little. This result could be verified in the retention and dewatering test with the two silica sols (Figs. 3 and 4). Below pH 6 hydrogen bonding occurs between the proton of the neutral silanol groups, -SiOH, and the electron-donor atoms oxygen or nitrogen in either



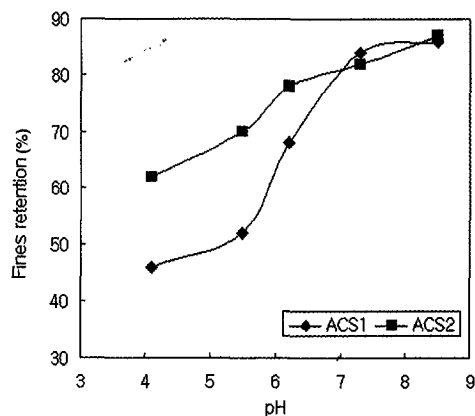
**Fig. 1. Surface modification of a silica by aluminate ion.**

hydroxyl or amide groups. When the pH is increased above 7 the silica surface becomes ionically charged and hydrogen bonding with organic molecules does not occur. This is probably because the molecule cannot approach the silica surface since it is hindered by adjacent cations,  $\text{Na}(\text{H}_2\text{O})_6^+$ . By incorporating aluminosilicate ions in the surface the surface charge will increase and hydrogen bonding at a pH less than 6 will not occur.<sup>7)</sup>

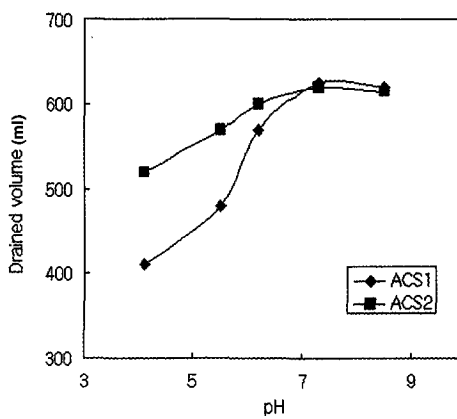
To be present as an aluminosilicate ion, each aluminium must be surrounded by and linked through oxygen to other silica atoms, this limits the maximum coverage to about 25%. As shown in Fig. 2, the surface modification resulted in high negative charges also at pH less than 6. The effect of the surface modification remains down to pH 3 where the aluminium starts to dissolve.



**Fig. 2. Zeta potential as a function of pH for the surface modified and unmodified ACSs.**



**Fig. 3. Fines retention as a function of stock pH in a starch system.**



**Fig. 4. Effect of stock pH on dewatering in a starch system.**

### 3.2 Effect of charge density of ACS

The charge density per unit weight of silica sol is related to the number of silanol groups present on the surface of the particle. This means that the surface area of the product and charge density are related to each other (Table 1).

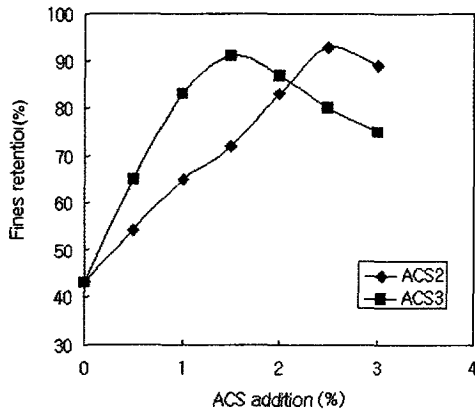


Fig. 5. Fines retention as a function of added amount of ACSs of different charge densities in a starch system.

In Figs. 5 and 6, experiments with two different silica sols are shown. These products are discrete colloids, and they were added in conjunction with 1.0% of cationic starch. From these figures it can be noted that the position of the retention maximum is shifted to approximately 60% of the addition levels of silica sol when a product with lower charge density (ACS2) was used compared to the higher charged silica sol (ACS3). Furthermore, the charge density of ACS3 (0.8 meq/g) was almost 60% higher than that of ACS2 (0.5 meq/g) and the difference for the two ACS products to attain maximum retention magnitude can solely be explained by the difference in charge densities. In conclusion, to attain the retention maximum a certain amount of negative

charges from ACS is needed to neutralize the cationic charges of the starch. When silica sol was combined with linear polymers, such as cationic polyacrylamides, the figure was similar to the starch based system and therefore charge density is an important property of silica sol.

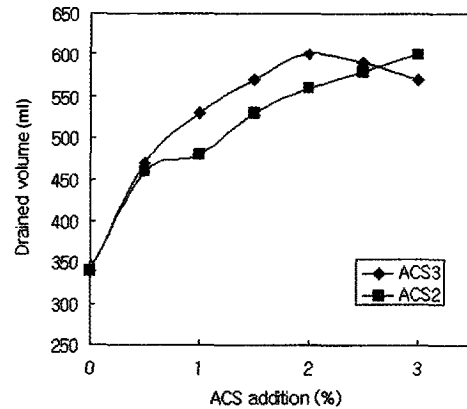


Fig. 6. Dewatering as a function of added amount of ACSs of different charge densities in a starch system.

### 3.3 Effect of microaggregation of ACS

Silica sols are often regarded to be monodisperse systems containing discrete particles in solution. There are, however, possibilities to create controlled aggregates of colloids in these systems (structured silica sols). These aggregates could have an unbranched structure, that is particles linked together in a chain. The structured silica sol is made of chemically bonded discrete particles. The necking between the particles has further strengthened the structure.

In Figs. 7 and 8, the results with four silica products are shown. ACS3 and ACS4 have the same charge density but different degree of microaggregation. When these products were combined with cationic starch, it can be seen that the performance of the products

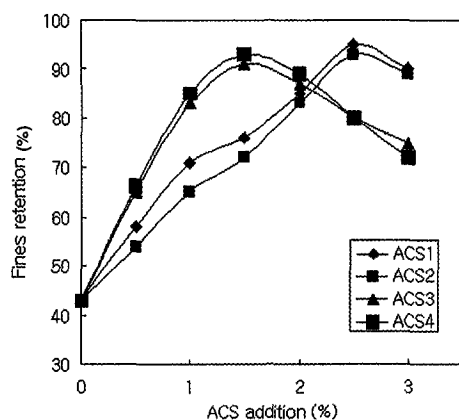


Fig. 7. Fines retention as a function of added amount of ACS in a starch system.

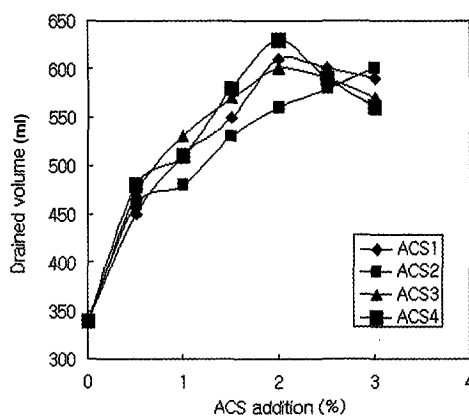


Fig. 8. Dewatering as a function of added amount of ACS in a starch system.

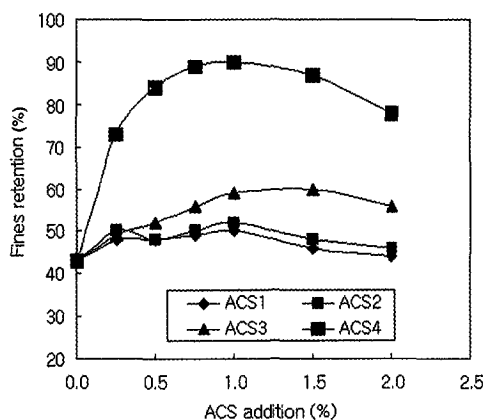


Fig. 9. Fines retention as a function of added amount of ACS in a PAM system.

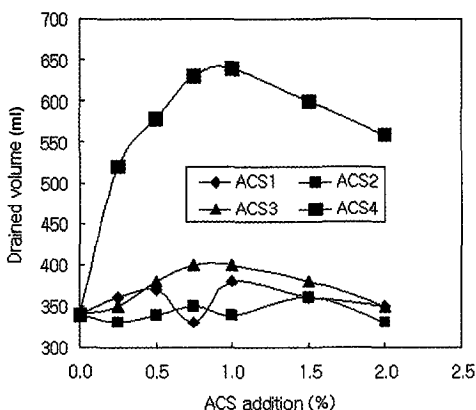


Fig. 10. Dewatering as a function of added amount of ACS in a PAM system.

is approximately the same. However, when the products were evaluated together with the cationic PAM, the result was contrary to the starch based system. In Figs. 9 and 10, it can be seen that silica sols containing discrete colloids (ACS1, ACS2, ACS3) give only a minor effect, while the product with highest degree of structure (ACS4) contributes to a very significant increase in retention and dewatering. But among the unstructured silica sols, the highly charged silica sol (ACS3) still showed better retention and drainage performance compared with lower charged

ones (ACS1, ACS2). The results from this PAM based system suggest that both charge density and the structure of ACS contribute to the performance of the system. But the structure of the ACS seems to be a much more critical property in combination with cationic PAM compared to combinations with cationic starch.

Electrostatic attractions and bridging have been assumed to be the main mechanisms of the microparticle systems.<sup>8)</sup> Therefore, the result with cationic polyacrylamide could be explained that for bridging with a open

structure such as cationic polyacrylamide, a large extended inorganic bridge is needed to fit between the loops of the adsorbed polymer.

#### 4. Conclusions

Some important surface chemical properties of silica sols in a microparticle retention system have been identified in combination with either cationic starch or cationic polyacrylamide. The impact of the surface modification, the charge density and the microaggregation of silica sols on the performance of retention and drainage were investigated.

The surface charge density and the stability over pH of silica sols were increased by introducing aluminosilicate anions at the surface. It was found that the charge density of silica sols when combined with cationic starch or cationic polyacrylamide determined the addition level necessary to attain the maximum retention. When silica sols were combined with cationic starch, the charge density of the product was the critical property and the degree of microaggregation was of minor importance. In the cationic polyacrylamide system, it was important for the silica sol to have not only a high charge density but also a high degree

of colloid structure. In this case the silica sol is needed to have a suitable dimension to give efficient bridging with the linear polymer.

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