The Effects of Cationic Valence on Wash Deinking of Newsprint

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THE EFFECTS OF CATIONIC VALENCE ON WASH DEINKING OF NEWSPRINT

by

Lawrence E. McEnroe

A thesis submitted in partial fulfillment of the course requirements for

The Bachelor of Science Degree

Western Michigan University
Kalamazoo, Michigan
April 24, 1981
ABSTRACT

The effects of cationic valence were tested against final pulp brightness in the wash deinking process on newsprint. The electrolytes used were AlCl_3, CaCl_2 and NaCl. The concentrations were varied from $8.32 \times 10^{-4}$ M to 100 times that amount on all three electrolytes. The effects were studied on the wash water and the cooking liquor separately, using deionized water as a control run. It was found that there was a noticeable loss of brightness even at the lowest level of electrolyte addition in both the wash water trials and the cooking liquor trials. The effect was greatest when the electrolytes were added to the cooking liquor for AlCl_3 and CaCl_2. It was also noticed that the addition of Al and Ca ions to cooks containing sodium silicate as a dispersing agent caused a precipitate to form, possibly lowering the effectiveness of the dispersing agent.
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INTRODUCTION

Every day we are confronted with shortages of energy and natural resources, explicitly portrayed by television, radio, newspaper and every other conceivable form of communication. This need not be emphasized. What must be emphasized, what must be thoroughly investigated is any and every way available to conserve energy and resources. Deinking technology is one area in which both energy and natural resources are conserved every day.

Because of conservation importance, it seems justifiable to spend time seeking to improve and streamline the deinking process. One area of interest, closed-system deinking, deserves considerable research as it ties energy and resource savings to the reduction of mill effluents more and more required of today's paper industry. But system closings can bring many problems such as heat build up and dissolved solids increases. This project will be dealing with the latter.

Dissolved solids include contaminants in the mill's supply of fresh water, chemicals added to the pulping stage of deinking, chemicals contained in the printed paper stock, and contaminants in recirculated water from other parts of the mill. All can cause problems in deinking ranging from corrosion to loss of pulp brightness. Specifically, it is the goal of this work to gain a better understanding of how the charge on the dissolved chemicals relates to the
detrital effect the chemicals have on deinked pulp brightness, if any.

BACKGROUND

WASHING VS FL OTATION

J. A. Clewley (1) presents a brief comparison of the advantages and disadvantages of washing and flotation deinking. Washing is the simpler of the two, relying on screening or squeezing the water away from the fiber, and the success of the process depends upon how finely the ink particles can be divided. The theoretical efficiency of 99% or more is not usually achieved due to agglomerates of ink forming and being trapped in the fibers upon de-watering. The initial cost of the wash deinking equipment is usually lower than that of the flotation process, although the costs of wash equipment are largely dependent upon environmental restrictions on effluents, and this can raise the capital cost considerably. The chemical costs for the wash system are slightly lower than those of flota-tion. The wash deinking system is, on the whole, more stable to change in conditions, such as temperature, dwell time, water hardness, and pH.

Flotation deinking normally obtains a higher yield than wash deinking, though this is usually due to retention of fines and fillers which pass through the screens of
the wash system. The flotation process uses less water than the wash process, although with proper clarification and reuse of water in wash deinking the difference becomes quite less pronounced.

Because of widespread use and acceptance of wash deinking in this country, and also because of the simplicity and control of the system, the wash process was chosen for study in this project.

WASH DEINKING

The procedure of wash deinking is not complicated, consisting of two basic steps, the cook and the wash. The mechanism of the process, however, is complicated and prone to many variables. These variables will be discussed following the details of the wash deinking procedure.

A typical cook (2,3) may contain chemicals to aid in detergency such as surfactants, chemicals to adjust the pH of the cook and swell the cellulose fibers such as sodium hydroxide, and chemicals to promote the stability of the ink/water suspension, dispersants. The cook is usually maintained at elevated temperatures to increase the solubility and suspension of the unwanted products, and to keep the temperature above the foaming temperature of the surfactant used. Mechanical action is often imparted to the stock through an impeller. This motion creates shear between the fibers, breaking loose some of the ink particles and aiding in preventing resettling of those particles already in suspension.
The wash stage consists of a series of dilutions and concentrations of the cooked pulp. Each successive step removes more of the ink particles from the stock. The washing is usually carried out in a counter-current method, with the wash water from the succeeding step being used in the previous step, the initial wash being made with the dirtiest water, the final step with fresh water. Concentration of the diluted pulp can be achieved in several ways. Sidehill screens are commonly used due to the low capital cost, but they also exhibit high water usage. Decker-style screens are also used, although no vacuum is drawn on the pulp because a sudden increase in consistency on the screen's surface would cause a fiber mat to form, the mat then effectively collecting the ink particles instead of allowing them to flow through with the wash water. For high consistency pulp washing screw presses are often used. (2)

WATER REUSE

There are many variables associated with the cook and the wash. Chemicals added to the cook, time and temperature of the cook, and screening methods of the pulp are just a few of the broad scope of variables which are encountered in a study of wash deinking. Another area, and that which is the basis of this paper, is the build-up of soluble substances in recirculated wash and cook water, notably that of mono- and polyvalent electrolytic salts.

In closing a deinking system, it is normally the wash water from the first deinking wash that is returned to the
cook. As much as a 50% savings in chemicals and steam result from closing this loop. (4) Often the wash water from the first washing stage is clarified before returning to the pulper. Inky water from the latter washing stages is collected and clarified, the clear water returning to the final wash step. The dissolved solids in this water can be removed by softening or ion-exchange, but this is seldom done on a commercial scale due to the high cost of such treatments and the huge volume of water involved. (4) Matthew (5) reported in laboratory testing that with clarification and softening the wastewater could be used over and over with no noticeable decrease in brightness. In industrial practice, the suspended solids are kept to acceptable levels by a constant purge from the system a portion of the process water, with a fresh water make-up. (1)

Matthew observed that the build-up of dissolved salts quickly causes a noticeable decrease in brightness, and that the effect increases with the number of times the water is reused. Cruea (6) determined that adding alum to the pulp causes a 17% decrease in pulp brightness as compared to pulp washed with neutral pH water. DeCeuster (8) found that the addition of 376 mg/liter CaCO₃ to the wash water produced pulp five points lower in brightness than pulp washed in uncontaminated water. This effect has been reproduced in other laboratory work (8) as well as in industrial practice (1). The build-up of dissolved solids contributes to other process problems including corrosion,
slime, foam and deposits. (4) Clearly, dissolved solids do pose problems to modern closed-system deinking, and an analysis of the effects of these solids is justified.

THEORY

SHULTZE-HARDY RULE; ZETA POTENTIAL

For many years it has been known that colloidal dispersions, such as the ink/water suspensions generated in a deinking cook, are highly sensitive to the addition of ions which carry an electrical charge opposite to that of the colloidal particles. (9) If the valency of the ions is high, the destabilizing effect is particularly great. If the surface potential of the colloid is sufficiently high, the flocculating concentrations of mono- , di-, and tri-valent ions should vary as $z_2^6$, where $z_2$ is the valency of the added ion. (10) This is known as the Shultze-Hardy rule of valence.

The destabilizing effect is due to a compression of the electrical double layer surrounding the colloidal particles as caused by the added ions. The effective thickness of the double layer, $1/k$, is the distance from the charged surface of the colloid into the solution within which the major portion of electrical interactions with the surface can be considered to occur. The effective thickness is mathematically determined as:
\[
\frac{1}{k} = \left( \frac{\varepsilon_r \varepsilon_0 \varepsilon_{0,RT}}{4\pi F^2 \sum C_i Z_i^2} \right)^{\frac{1}{2k}}
\]

\[\varepsilon_r = \text{the relative static permittivity of the sol.}\]
\[\varepsilon_0 = \text{the permittivity of a vacuum}\]
\[R = \text{the gas constant}\]
\[T = \text{the absolute temperature}\]
\[F = \text{the Faraday constant}\]
\[C_i = \text{the molar concentration of any ion in the solution phase}\]
\[Z_i = \text{the valence of the ion of concentration } C_i.\]

Thus, the effective thickness of the double layer is inversely proportional to the valence of the ions in the solution phase and to the square root of their concentrations. (11)

When the valence and concentration of a particular ion are high enough they can contract the thickness of the double layer to a point that the repulsion between two particles in suspension will not be great enough to prevent the particles from colliding and coagulating.

The zeta potential is the potential of the charged surface at the plane of shear between the particle and the surrounding solution as the particle and the solution move with respect to each other. (11) Although the zeta potential does not always correspond to the effective thickness, it can be a useful tool in determining the effect ions have on the contraction of the double layer and therefore possibly predict the occurrence of coagulation of the colloid.

APPLICATION OF SHULTZE-HARDY RULE

Applying the Shultze-Hardy rule of valence to a colloidal suspension, the resulting theoretical molar concentrations of the mono-, di-, and tri-valent cations
required to flocculate the suspension would be 100:1.6:0.13,
respectively. Although these are the ratios in an ideal
case, the charge rule seems to hold up fairly well in prac­
tice, again assuming the surface potential is high enough. (12)
The molar ratios vary somewhat depending on the actual cations
tested, but the trend remains the same. As an example, the
millimolar values for NaCl, CaCl₂, and AlCl₃ to flocculate
a solution of As₂S₃ are 51, .65, and .093 respectively. (12)
or ratios of 100:1.3:0.18.

In the case of colloidal particles with low surface
potential the effect is diminished to a certain extent. The
molar ratios of the cation required to flocculate the par­
ticles follow the Debye-Hückel approximation more closely
than the Shultze-Hardy rule of valence. (12) In the Debye­
Hückel theory the effect is on the order of z²⁻² instead of
z²⁻⁶, yielding ratios of 100:25:11 for mono-, di-, and tri­
valent cations. This, again predicts the action of cations
in experimental work with good accuracy. The effect of
multivalent anions on positively charged colloids follows
the same two theories as well as the cations, although not
as much experimental work has been done. (12)

Walkuch and Williams (13) researched the effect of
electrolytes on the coagulation of fines in dilute stock
suspensions. They determined that the fines coagulated with
mono-, di-, and tri-valent cations Na, Ca, and La in fairly
good accordance with the Shultze-Hardy rule of valence.
They found the same trends were present when measuring
the electrophoretic mobility, which is a good approximation of the zeta potential. Thus, the fines coagulated with decreasing electrophoretic mobility, showing that as the electral double layer is compressed the particles begin rapid agglomeration.

DETERGENCY

The applications of these valence rules become apparent upon an examination of the mechanics of dirt removal (ink, in particular) from a fibrous substrate (paper fibers) through detergency and the cleaning process.

Rosen (11) provides a good review of detergency. The cleaning process consists of three elements: 1) the substrate; 2) the soil; and 3) the cleaning solution or bath. In the case of deinking, the substrate is cellulose, the soil is ink particles, and the bath is water. The surfactant in the bath works to wet the substrate and the soil particles, greatly diminishing the adhesion between the two. The water interacts with the substrate and the soil particles, forming electrical double layers at the substrate/liquid and particle/liquid interfaces. These double layers usually result in charges of the same sign on the substrate and particle, causing mutual repulsion, further weakening the adhesion between them.

The major mechanism by which the soil is removed from the substrate is through the increase in the negative electrical potentials at the Stern layers (the region of strongly held counterions adsorbed close to the charged
surface on fixed sties) of both the substrate and the particles through adsorption onto them of anions in the bath. Anionic surfactants are usually the most effective for increasing the negative electric potentials, although inorganic anions, especially polyvalent ones, are also effective. (11)

The adsorption of these negative species on the particulate soil in the bath is also important because it helps to prevent agglomeration of the particles, therefore keeping the individual particles in suspension, making their eventual removal with the bath from the substrate easier. (11)

Knowing the mechanism of soil removal from the substrate, it is readily apparent how the build-up of salts, especially those with polyvalent cations, can affect the cleaning process. Rosen (11) outlines three reasons for this effect:

1. Adsorption of polyvalent cations onto the negatively charged substrate and soil reduces the negative electric potential on each, making initial separation more difficult, and reposition and agglomeration easier. This effect has been noticed with nonionic surfactants as well as anionic.

2. The polyvalent cations act as linkages or bridges between the negatively charged substrate and negatively charged particles, causing deposition. The cations may also act as linkages in connecting the soil particle and the hydrophilic group of the surfactant, leaving the hydrophobic
group of the surfactant toward the water and increasing the work of wetting the soil.

3. As the concentrations of the cations increase, the corresponding metal salts of the anionic surfactants and other anions such as phosphates or silicates in the bath may reach their saturation point and precipitate onto the substrate, shielding the soil particles there from surfactant action.

BUILDERS

Materials known as builders are added to the bath to counteract the effect of the polyvalent cations. Builders include sodium or potassium polyphosphates, especially sodium tripolyphosphate, sodium silicates, and sodium carbonates. In addition to sequestering or precipitating the cations in the bath, builders help in dispersion and deflocculation of the ink particles, and aid in buffering the solutions, usually at moderately high pH ranges.(4)

DEBATE

Whether or not the ink/fiber suspensions involved in newsprint deinking follow the theoretical behavior of colloidal suspensions outlined here is not generally agreed upon. Curea (6) claims the highest brightness occurs in washing at pH 3-6, the opposite of that claimed by theory proposed in Rosen (11). Watson (8) showed the possibility of the effect of total dissolved solids to be greater on the deinking cook instead of the washing stage, although
more evidence needed to be gathered. What seems to be in general agreement from a laboratory viewpoint is that cations play an important role in determining the quality of deinked pulps. Exactly what that role is and how it affects the process and mechanisms of deinking is what is yet to be determined.
STATEMENT OF PROBLEM

Much is yet to be learned about the actual effects of the valence levels of cations in a deinking process on the quality of the pulp obtained from a wash deinking process. Although there is experimental evidence of valence effect on perfect colloidal suspensions, there is debate as to whether or not similar effects exist on fiber/ink suspensions. It was the goal of this study to:

1. determine if there are pronounced effects on the brightness of deinked pulps by adding mono- and polyvalent cations;

2. determine, if such effects exist whether these effects are more noticeable in the cook stage or the wash stage.
EXPERIMENTAL APPROACH

In order to eliminate as many variables as possible, the wash deinking system was chosen for this experimental work. The wash system was less prone to changes in temperature and cooking chemical concentrations, and the overall process was simpler.

The newspaper, surfactant, and dispersant were the same throughout the experiment. The newspaper was the 2/11/81 edition of the Kalamazoo Gazette, sections A and E (83.5 g O.D. weight). The surfactant was Triton X-100, a nonionic surfactant with a HLB value of 13.5. Sodium silicate solution, at 38% solids, was the dispersant used.

The time, temperature, and agitation of the cook were all held constant to minimize variation in the treatment of the inked pulp. The wash sequence was also held constant.

The concentrations of ions added to the cook and the wash were varied from $8.32 \times 10^{-4}$ moles per liter to 100 times that amount. For the aluminum ion, this translated to 100 parts per million to 10,000 parts per million. The salts, $\text{AlCl}_3$, $\text{CaCl}_2$ and $\text{NaCl}$ all had the same anion to reduce the effect of the anion valence.

Ions were added to the cook and the wash water, but separately. This method allowed the determination of magnitude of the effect of each stage. In the case of the cook, the electrolyte was added with the surfactant and dispersant before the newsprint was added. For the wash stage, the desired amount of electrolyte was added to 20 liters of
deionized water in a seven-gallon polyethylene bottle.

In making the brightness pads of the final deinked pulp, a process similar to that proposed by DeCeuster (7) was used. The pulp from the final wash step was rediluted with the wash water from that step. This pulp was then poured over a plastic paper machine wire cut to fit a Buchner funnel. This way simulated more closely actual conditions of a deinking mill by avoiding the "infinite washing" of other methods using fresh water at low pulp consistencies in a sheet mold machine.
COOKING PROCEDURES

1. To a 4 liter stainless steel beaker 2.00 liters of deionized water were added.

2. The water was heated to 50°C on a laboratory hotplate.

3. The cooking chemicals (see Table I, p. 18) and the desired ion were added.

4. 83.5g O.D. newspaper (Kalamazoo Gazette, 2/11/81, sections A and E) was torn into approximately two-inch squares and placed in the cooking liquor. The paper was allowed to soak for five minutes. The consistency was 4.0%.

5. The laboratory Cowles dissolver at 40% power (as determined by a rheostat) was used to disintegrate the pulp for 30 minutes.
WASHING PROCEDURES

1. The pulp at 4.0% consistency from the cook was diluted to 1.0% with deionized water (ions added according to Table II, p. 19).

2. The diluted pulp was agitated for one minute with a variable-speed mixer to disperse the pulp evenly.

3. The pulp was poured down the laboratory sidehill screen (80 mesh) at an angle of 45°. This first pass concentrated the pulp to 3% consistency.

4. The pulp was poured down the screen a second time, concentrating the pulp to a 4% consistency.

5. Steps 1, 2, 3 and 4 were repeated twice, giving a total of three washings.

6. The pulp from the third washing step was diluted with the water removed in that step to 1.0% consistency. 350 ml of this diluted pulp was used to make a brightness pad over a six-inch plastic paper machine wire on a Buchner funnel. Five brightness pads were made from each trial.

7. The brightness pads were pressed (while wet) at 30 psi for two minutes between blotters to provide a smooth surface for testing. The pads were then allowed to air dry for two days in darkness at room temperature.
TABLE I
Cooking Liquor Formulations

<table>
<thead>
<tr>
<th>TRIAL</th>
<th>TRITON X-100</th>
<th>SODIUM SILICATE</th>
<th>ION</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>.84g (1.0%)*</td>
<td>4.39g (2.0%)</td>
<td>-</td>
</tr>
<tr>
<td>1-9</td>
<td>.84g</td>
<td>4.39g</td>
<td>-</td>
</tr>
<tr>
<td>10</td>
<td>.84g</td>
<td>4.39g</td>
<td>.222g AlCl₃ (8.32 x 10⁻⁴ M)</td>
</tr>
<tr>
<td>11</td>
<td>.84g</td>
<td>4.39g</td>
<td>2.22g AlCl₃</td>
</tr>
<tr>
<td>12</td>
<td>.84g</td>
<td>4.39g</td>
<td>22.2g AlCl₃</td>
</tr>
<tr>
<td>13</td>
<td>.84g</td>
<td>4.39g</td>
<td>.244g CaCl₂·2H₂O (8.32 x 10⁻⁴ M)</td>
</tr>
<tr>
<td>14</td>
<td>.84g</td>
<td>4.39g</td>
<td>2.45g CaCl₂</td>
</tr>
<tr>
<td>15</td>
<td>.84g</td>
<td>4.39g</td>
<td>24.5g CaCl₂</td>
</tr>
<tr>
<td>16</td>
<td>.84g</td>
<td>4.39g</td>
<td>.097g NaCl (8.32 x 10⁻⁴ M)</td>
</tr>
<tr>
<td>17</td>
<td>.84g</td>
<td>4.39g</td>
<td>.970g NaCl</td>
</tr>
<tr>
<td>18</td>
<td>.84g</td>
<td>4.39g</td>
<td>9.70g NaCl</td>
</tr>
<tr>
<td>19**</td>
<td>.84g</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>20**</td>
<td>.84</td>
<td>-</td>
<td>.222g AlCl₃</td>
</tr>
</tbody>
</table>

* % Added based on O.D. weight (83.5g) of newsprint in 2.0 liters of deionized water

** pH adjusted to 10.0 w/NaOH (10% solution)
### TABLE II

Wash Water Formulations

<table>
<thead>
<tr>
<th>TRIAL</th>
<th>ION*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>-</td>
</tr>
<tr>
<td>1</td>
<td>2.22g AlCl₃ (8.32 x 10⁻⁴ M)</td>
</tr>
<tr>
<td>2</td>
<td>22.2g AlCl₃</td>
</tr>
<tr>
<td>3</td>
<td>222g AlCl₃</td>
</tr>
<tr>
<td>4</td>
<td>2.45g CaCl₂·2H₂O (8.32 x 10⁻⁴ M)</td>
</tr>
<tr>
<td>5</td>
<td>24.5g CaCl₂·2H₂O</td>
</tr>
<tr>
<td>6</td>
<td>24.5g CaCl₂·2H₂O</td>
</tr>
<tr>
<td>7</td>
<td>0.973g NaCl (8.32 x 10⁻⁴ M)</td>
</tr>
<tr>
<td>8</td>
<td>9.73g NaCl</td>
</tr>
<tr>
<td>9</td>
<td>97.3g NaCl</td>
</tr>
<tr>
<td>10-18</td>
<td>-</td>
</tr>
<tr>
<td>19</td>
<td>-</td>
</tr>
<tr>
<td>20</td>
<td>-</td>
</tr>
</tbody>
</table>

* Indicates amount of desired electrolyte added to 20.0 liters of deionized water
BRIGHTNESS TESTING

1. All brightness tests were made on the same brightness meter using the same standard for calibration throughout the course of the study.

2. Ten brightness readings were taken on each pad: five from the top of the pad, five from the bottom.

3. The results from the brightness tests are listed in Table III, page 22. Each value is an average of 25 brightness readings (five tests per side times five pads per run), with the overall average based on the fifty total tests per trial.
RESULTS

The results of the brightness tests on the pads made from each trial are presented in Table III, page 22.

In Fig. 1, the pad brightness is plotted on the Y axis against the log of the particular ion concentration on the X axis (moles per liter), for the ions added to the wash water and not the cook water. The axes on Fig. 2 are similarly labeled, this time plotting the pad brightness against the ion concentration of ions added to the cook stage and not to the wash water.

Fig. 3 is a plot of pad brightness against the pH of the cook and wash stages for AlCl₃ addition.
### TABLE III
Brightness Tests*

<table>
<thead>
<tr>
<th>TRIAL</th>
<th>TOP BRIGHTNESS</th>
<th>BOTTOM BRIGHTNESS</th>
<th>AVERAGE</th>
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</thead>
<tbody>
<tr>
<td>Control</td>
<td>57.3</td>
<td>57.4</td>
<td>57.4</td>
</tr>
<tr>
<td>1</td>
<td>50.4</td>
<td>50.8</td>
<td>50.6</td>
</tr>
<tr>
<td>2</td>
<td>47.7</td>
<td>47.4</td>
<td>47.6</td>
</tr>
<tr>
<td>3</td>
<td>45.0</td>
<td>44.9</td>
<td>44.9</td>
</tr>
<tr>
<td>4</td>
<td>51.9</td>
<td>51.5</td>
<td>51.7</td>
</tr>
<tr>
<td>5</td>
<td>51.7</td>
<td>53.5</td>
<td>52.6</td>
</tr>
<tr>
<td>6</td>
<td>44.9</td>
<td>44.5</td>
<td>44.7</td>
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<td>7</td>
<td>52.6</td>
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<td>8</td>
<td>52.8</td>
<td>53.2</td>
<td>53.0</td>
</tr>
<tr>
<td>9</td>
<td>52.0</td>
<td>52.0</td>
<td>52.0</td>
</tr>
<tr>
<td>10</td>
<td>55.6</td>
<td>55.8</td>
<td>55.7</td>
</tr>
<tr>
<td>11</td>
<td>38.9</td>
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FIG. 1

EFFECT OF IONS IN WASH WATER

BRIGHTNESS (% of MgO)

log of ion concentration (moles/liter)
FIG. 2

EFFECT OF IONS IN COOKING LIQUOR

BRIGHTNESS (% MgO)

log of ion concentration (moles/liter)

CONTROL

$\text{NaCl}$

$\text{CaCl}_2$

$\text{AlCl}_3$
FIG. 3
BRIGHTNESS vs. pH

CONTROL

AICl₃ IN COOK

AICl₃ IN WASH
DISCUSSION OF RESULTS

The results of this study provided several points of interest.

CATIONS IN WASH WATER

Several important trends were discovered in the plot of brightness vs. log of ion concentration (Fig. 1, p. 23). Firstly, even small amounts of added electrolyte (100 p.p.m.) caused a drop of up to 6 points in final brightness over the control samples. As more electrolyte was added to the wash water the effects grew stronger. This varied from a one point drop from low concentration to high concentration upon NaCl addition to a five point difference from low concentration to high concentration for AlCl₃ addition. This effect showed as decreasing slopes from NaCl to CaCl₂ to AlCl₃. All of the decreases in brightness appeared to be linear, with the exception of the wide spread of the CaCl₂ points.

At first it was not known why the plotted points for CaCl₂ were scattered so. Later in the experiment it was observed that the calcium ions reacted with the dispersant, sodium silicate, to form an insoluble precipitate. This was proposed as a possible explanation for the deviation of the CaCl₂ points.

CATIONS IN COOKING LIQUOR

The effects of cations when added to the cooking liquor on pulp brightness were much more spectacular than the effects
on the wash.

As in the wash experiment, the effects were apparent at low concentrations. The pulp brightness reacted to the NaCl concentration much as it did in Fig. 1, with a small, steady linear decrease as the cation concentration increased. This was expected, as surface chemistry theory predicts that ion effects are inversely proportional to some power of the valence of the ion. Thus, Na\(^{+}\), with a valence of one, would yield a linear relationship.

The plots of CaCl\(_2\) and AlCl\(_3\), however, were much different than their counterparts in Fig. 1. Both appeared to rapidly affect pulp brightness at low concentrations and then level off in their effects at higher concentrations. This represented more of the power rule effect that would be expected from classical surface chemistry and the effective thickness equation discussed on page 7. The plot clearly showed that the effect of adding electrolytes to the cooking liquor on pulp brightness was far greater than the effect caused by adding the same concentrations of ions to the wash water.

Again, the CaCl\(_2\) points were somewhat erratic. It was in the cooking liquor that the precipitation of Ca with the dispersant was first noticed. The Al also caused a precipitate to form when it was used in higher concentrations. This precipitation effect was not mentioned in earlier literature and possibly has gone unnoticed until now. It was, however, noteworthy in that the more dispersant is precipitated from the cooking liquor, the less its efficiency will become.
It is possible that dispersant precipitation was the cause for some of the brightness drops when AlCl$_3$ or CaCl$_2$ was added to the cook.

BRIGHTNESS AND pH

Fig. 3, in which the final pulp brightness was plotted against the pH of the cooking liquor or wash water, was included in this report because of the similarity of the curves with those of Figs. 1 and 2. Though there appeared a strong relation between the pH of the liquid and the final pulp brightness, it was not believed to be a major factor. This belief stems from earlier work by Cruea (6) which showed the brightness of deinked pulp reached a peak at pH 4, not a decrease as suggested by Fig. 3.

TRIALS 19 AND 20

Trials 19 and 20 were run to determine if there was still an ion effect when no dispersant was added. The runs were pH adjusted to 10 with NaOH. There were several problems with these trials, including another precipitation reaction when Na OH was added to the AlCl$_3$ cooking liquor and therefore the results were inconclusive at best. Due to time restrictions, this area was not further pursued.
CONCLUSIONS

1. Adding ions caused a decrease in final pulp brightness in both the wash water and cooking liquor addition.

2. For multivalenced ions, the brightness decrease was greater when added to the cooking liquor than for those ions added to the wash water. Thus, the effects of ions was more pronounced in the cook stage, and more care should be taken to remove ions from the cook water than from the wash water.

3. The addition of Ca and Al ions to cooks containing sodium silicate as a dispersing agent caused a precipitate to form. This formation took dispersant out of solution and therefore could have lead to a lessenning of the dispersant's effectiveness.
SUGGESTIONS

1. More work should be done on a sodium silicate-free deinking system to separate the ion effects from the loss of dispersant effects.

2. The study should be repeated using buffered systems at both high and low pH ranges to determine if the assumption that the pH of the process is not a dominating factor (to correlate with the earlier work done by Cruea).

3. The concept of ion effect should be studied on a flotation deinking system as well to possibly determine which system is better suited to areas of high water hardness (Ca ions), high salinity (Na ions) or use in conjunction with an acid whitewater papermachine system (Al ions).


