Persulfates as repulping reagents for neutral/alkaline wet-strength broke

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ABSTRACT: Alkali metal persulfates (general formula $M_2S_2O_8$) have been found to repulp neutral/alkaline wet-strength broke. Persulfate salts effectively defibered paper made with polyamide-epichlorohydrin resins, though slower than hypochlorite. Vapor phase chromatography showed a substantially lower content of organic chlorides in the persulfate repulping liquor. Recycled handsheets from persulfate- and hypochlorite-repulped broke had about equal dry strength. In wet-strength grades made from recycled pulp without washing, residual persulfate interfered much less with wet-strength resin effectiveness than did residual hypochlorite.

KEYWORDS: Broke, calcium hypochlorite, effluents, epichlorohydrins, persulfates, reagents, recycling, repulping, sodium hypochlorite, wet strength.

For years, sodium and calcium hypochlorite [NaOCl and $Ca(OCl)_2$] have been preferred reagents for repulping bleached wet-strength broke that contains polyamide-epichlorohydrin (PAE) resin. Because of concern about chloroform, tetrachlorodibenzodioxins, and adsorbable organic halides (AOX) in mill effluents, there is growing interest in possible nonchlorinating repulping aids. We have found that persulfate ($S_2O_8^=$) salts are an effective chlorine-free alternative to hypochlorite (OCl^-) for repulping neutral/alkaline wet-strength broke *(1)*.

Nomenclature

Persulfates are salts of peroxysulfuric acid, $H_2S_2O_8$ (also known as peroxydisulfuric acid). The ammonium, potassium, and sodium salts of general composition $M_2S_2O_8$ are commercially available. The sodium salt was used in most of this work. From the different but related monopersulfuric acid, H_2SO_5 (Caro's acid), is also derived a complex monopersulfate (PMPS) of composition $2KHSO_5{:}KHSO_4{:}K_2SO_4$.

Results and discussion

Wet-strength paper, made either on a Noble-Wood handsheet machine or a laboratory pilot machine, was repulped at 1.3% consistency in a TAPPI disintegrator by TAPPI method T 205 om 88. The progress of defibering is charted in six steps; 6 represents complete defibering. Results are reported as times required for complete defibering. When defibering was incomplete within 1 h, the highest stage reached is reported (**Table I**).

pH and temperature dependence

Alkaline conditions accelerate repulping by persulfate, $S_2O_8^=$ *(1)* or monopersulfate, HSO_5^- *(1, 2)*. Persulfate repulping is more rapid at higher temperatures. In both respects, it contrasts with PAE repulping by sodium or calcium hypochlorite which has a slight negative temperature dependence *(3)* and is most effective at pH 6.5–7.0 (in the buffer region for the $HOCl{:}OCl^-$ equilibrium).

During persulfate repulping, the pH decreases to an extent depending on the reagent and the system. In buffered systems, equimolar amounts of different persulfates defibered broke at comparable rates. The decomposition routes and rates of peroxygen compounds, including persulfates, depend in complex fashion on pH, temperature, and trace metals in the system. The relative performance of two salts can vary between pH-buffered and unbuffered systems. A choice among persulfates will depend on convenience and cost-effectiveness under specific mill conditions.

Alkali has been employed as an alternative to hypochlorite, especially in unbleached kraft broke where OCl^- is consumed by bleached instead of degrading the resin *(3)*. Although

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I. Repulping of wet-strength broke with persulfate ion

Paper				Repulping conditions					
Pulp[a]	Resin[b]	% Added	%W/D	Reagent	%[c]	Added init., pH	Buffer	Temp., °C	Time, min
BK	PAE	0.5	18.6	OCl^-	0.5	7	No	54	5
BK	PAE	0.5	18.6	$S_2O_8^=$	1.85	10	No	71	10
BK	PAE	0.5	18.6	$S_2O_8^=$	1.85	7	No	71	10
BK	PAE	0.5	18.6	$S_2O_8^=$	1.85	4	No	71	50
BK	PAE	0.5	18.6	$S_2O_8^=$	1.85	7	No	54	20
BK	PAE	0.5	19.0	HSO_5^-	1.10	10	No	71	10
BK	PAE	0.5	19.0	HSO_5^-	1.10	7	No	71	40
BK	PAE	0.5	17.8	$S_2O_8^=$	1.85	10	No	71	40
BK	PAE	0.5	17.8	$S_2O_8^=$	1.85	10	Yes	71	30
BK	PAE	0.5	17.8	None	. . .	10	Yes	71	Incompl. (St.5)
BK	PAE	0.5	17.8	$S_2O_8^=$	1.85	11	Yes	71	40
BK	PAE	0.5	17.8	None	. . .	11	Yes	71	Incompl. (St.5)
BK	PA	0.75	16.0	$S_2O_8^=$	1.60	11	Yes	71	5
BK	PAE	0.5	19.2	$S_2O_8^=$	2.14	10	Yes	71	40
BK	PAE	0.5	19.2	OCl^-	0.5	6.5	Yes	54	5
BK	PAE	0.35)	18.6	$S_2O_8^=$	2.14	10	Yes	71	50
BK	+ CMC	0.15)	18.6	OCl^-	0.5	6.5	Yes	54	20
OCC	PAE	0.5	19.5	$S_2O_8^=$	2.4	10	Yes	71	Incompl, (St.5)
OCC	PAE	0.5	19.5	OCl^-	3.0	6.5	Yes	54	Incompl. (St.5)
BK/	PAE	0.3	18.0	$S_2O_8^=$	3.7	10	No	71	Incompl. (St.5)
CTMP	PAE	0.3	18.0	OCl^-	0.5	6.5	No	54	30

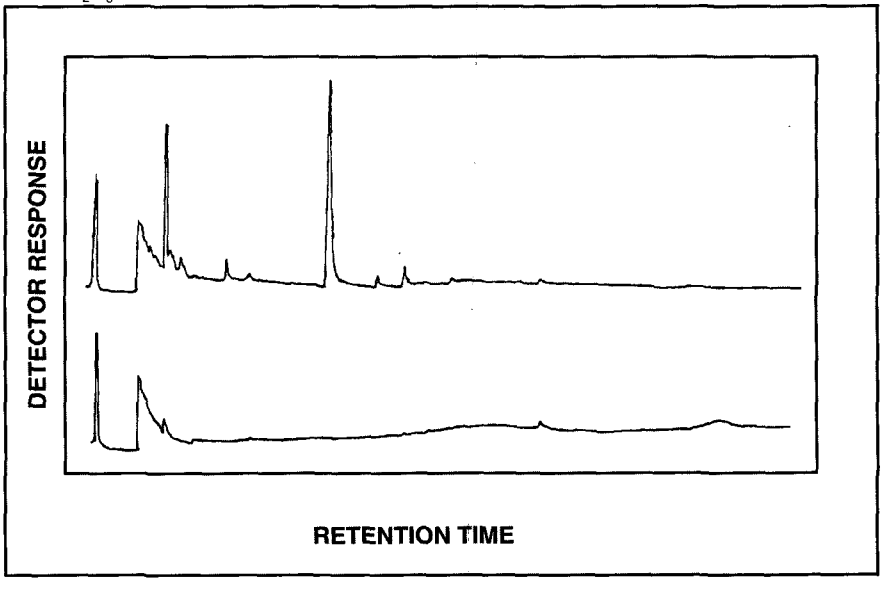
[a] BK = 50/50 or 70/30 hardwood/softwood bl. kraft; OCC = old corrugated container; BK/CTMP = 35/30 hwd. bl. kr./swd. bl. kr./CTMP.
[b] PAE = commercial polyamide-epichlorohydrin resin; PA = commercial polyamine-epichlorohydrin resin.
[c] Active anion content (not salt wgt.) as % of paper.

persulfate is more effective under moderately alkaline conditions than at neutral pH, its effect does not depend on alkaline hydrolysis. Bleached broke is defibered more rapidly by alkaline persulfate than by alkali alone at the same pH. Model compound studies with persulfates and other peroxy compounds suggest that the oxidant can attack PAE resins at either the tertiary amine crosslink sites *(4–9)* or the amide linkages in the base polymer *(10)*.

Range of application

Besides PAE resins, persulfate can degrade polyamine-epichlorohydrin resins effectively. Combinations of PAE and CMC at the right ratios can in-

1. Gas chromatography of aqueous filtrates from defibered PAE broke. Oxidant: upper, OCl^-; lower, $S_2O_8^=$.



II. Dry strength and wet-strength response of persulfate- and hypochlorite-redispersed pulps[a]

Pulp	PAE added, % of pulp	Density, kg /m³	Breaking length, km Dry	Breaking length, km Wet	Breaking length, % W/D	TAPPI brightness
Repulped broke recast into sheets after washing.						
Initial sheets:						
Waterleaf	0	446	4.74	0.16	3.3	83.3
Wet-strength (w.s.)	0.5	441	5.54	1.15	20.8	81.4
Recycled pulp from:						
Waterleaf redisp. w/water	0	429	4.25	0.19	4.4	83.6
W.s. broke redisp. w/ $S_2O_8^=$	0	424	3.98	0.14	3.6	82.8
W.s. broke redisp. w/ OCl^-	0	421	4.11	0.16	3.9	85.2
Recycled pulp from:						
Waterleaf redisp. w/ water	0.5	420	5.10	1.15	22.5	81.7
W.s. broke redisp. w/ $S_2O_8^=$	0.5	426	5.29	1.09	20.6	81.4
W.s. broke redisp. w/OCl^-	0.5	414	4.88	1.05	21.5	82.8
Repulped broke cast into sheets without washing.						
Initial sheets:						
Waterleaf	0	...	4.50	0.15	3.4	83.7
Wet-strength (w.s.)	0.5	...	5.32	1.11	20.9	82.0
Recycled broke from:						
Waterleaf redisp. w/water	0.5	...	4.22	0.88	20.7	82.0
W.s. broke redisp. w/ $S_2O_8^=$	0.5	...	3.29	0.73	22.2	82.9
W.s. broke redisp. w/ OCl^-	0.5	...	3.57	0.40	11.2	85.7

[a] 30/70 softwood/hardwood bleached kraft pulp. Sheets made in water with 100 ppm Ca hardness, 50 ppm alkalinity. Washing: 3 cycles of dispersion and filtration, + treatment with 10 ppm Na_2SO_3 (based on water) as reserve antichlor.

crease wet and dry strength more than PAE resin alone at an equal PAE resin furnish *(11, 12)*. Persulfate can degrade PAE resin-CMC combinations, though (like OCl^-) more slowly than PAE alone.

Persulfates, like OCl^-, repulp unbleached kraft or chemithermomechanical pulp (CTMP)-containing wet-strength broke more sluggishly than bleached broke. Presumably, $S_2O_8^=$ is also consumed in side reactions with lignin residues.

Organic chlorides in degradation products

Samples of PAE resin-treated paper were digested with sodium hypochlorite or sodium persulfate under their normal repulping conditions. Aqueous filtrates from the reaction mixtures were concentrated and analyzed by gas chromatography, using a Hall electron capture detector that responds only to halogen-containing compounds. **Figure 1** shows a much smaller population of organic chlorides in the $S_2O_8^=$ repulping effluent than in the OCl^- filtrate. It has not been possible to characterize the lone Cl-containing peak in the complex mixture of degradation products. Since persulfates contain no active chlorine, the remaining organochloride probably stems from the minor fraction of chloroalkyl groups pre-existing in the resin.

Strength and wet-strength response of recycled papers

Wet-strength paper containing 0.5% PAE resin was repulped with neutral hypochlorite or with hot alkaline sodium persulfate. Waterleaf made from the same batch of pulp was redispersed in water. The three recycled pulps were washed three times, treated with Na_2SO_3 antichlor, and used to make both waterleaf and wet-strength paper (**Table II**). Handsheets from hypochlorite- and persulfate-reworked pulp had similar dry strength, though the hypochlorite gave brighter sheets. Comparing the virgin and recycled waterleaf shows that more of the strength loss is due just to the operations of drying and redispersing, and to lower sheet density, than to chemical degradation of the pulp. With earlier repulping agent, the washed pulps responded normally to wet-strength resin.

To simulate worst-case conditions, a second set of recycling experiments was run without washing the redispersed pulp. In this series, the percentage wet/dry tensile strengths showed that residual persulfate had little effect on the newly added PAE resin, while residual OCl^- was detrimental. Thus, higher chemical costs of persulfate relative to hypochlorite can be at least partly offset by a reduced need for washing and/or antichlor.

Safety and regulatory considerations

Persulfates are classed as oxidizers by the U.S. Department of Transportation. Like hypochlorite salts, persulfate salts should not be stored near heat sources, combustible materials, reducing agents, acids, or bases. Manufacturers can advise on proper methods and construction materials for handling and storage *(13)*. Neoprene gloves and face and eye protection against splashes are recommended personal equipment.

Ammonium, potassium, and sodium persulfates are listed among allowable indirect additives for food packaging *(14)*.

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