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Pressurized Oxygen-Hot Alkali Pulping System

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Hot Alkali Pulping System

by

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Abstract

This study concerns the area of pulping, using an oxygen-hot caustic-magnesium carbonate system. The literature study includes the use of a similar system by French scientists in the bleaching of pulps. The few who have worked in the pulping field using oxygen are also cited, but apparently no one has investigated an oxygen-hot caustic-magnesium carbonate pulping system.

In this study, red pine chips have been treated under varying conditions of oxygen pressure and magnesium carbonate concentrations and tested for brightness, yield, permanganate number, mullen and tensile strength. It was found that the oxygen-caustic pulping system had no advantages over the hot caustic system. The oxygen-hot caustic-magnesium carbonate system though, seems to produce a brighter pulp with equal or better strength properties.

Recommendations have been made, which include the study of the reaction mechanism of this system.

Table of Contents

Intoduction

In the past few years French and Russian scientists have been studying the feasibility of bleaching with a pressurized oxygen-alkali system. The oxygen-alkali process is supposed to delignify the pulp, as is the chlorination and extraction stages of a conventional bleaching process. The high cost of elemental chlorine is the primary reason for the attempt to find an alternate method of delignification and bleaching.

Many of the French studies have been puplished recently in the United States. Scientists A. Robert et al.(1) credited Russian workers with the initial successes in delignification with the oxygen-alkali system. The Russians varied their caustic concentration from 4 per cent to 10 per cent, the oxygen pressure from 70 psig to 140 psig, the temperature from 90 degrees centigrade to 120 degrees centigrade, and the reaction time from 20 minutes to 60 minutes. They found the process to be equivalent to the chlorination

and extraction stages of the bleaching process except for a considerable loss in strength properties. Because of the strength loss, the French scientists attempted to improve on the Russian process.

The French found that the addition of about 1 per cent magnesium carbonate (on the pulp) to the caustic solution, preserves the pulp strength characteristics, yet does not decrease the oxygen's effect in bleaching. The results concerning the variation of process variables which have been published by the French are found in Table I.

The French also expanded on the Russian theory of a reaction mechanism. The Russian mechanism is stated in the French workers' article as follows: 1) the caustic swells the pulp, making it more accessible to the oxygen; 2) lignin, its by-products, and color agents react with the alkali and become accessible to the oxygen; 3) caustic soda dissolves some of the lignin, tannin, polyuronic acids and polysaccharides; 4) the oxidation process produces aromatic and aliphatic

acids which combine with the caustic and become inactive. The French felt that the addition of magnesium carbonate to the alkali seemed to protect the cellulose from degradation.

A similar bleaching process was patented in the United States in 1967. R.C. Wade (2) bleached pulp with a solution of an alkali metal-borohydrite at a pH of 9, then treated the fiber with ozone in an acid medium.

Work in pulping with a pressurized oxygen-caustic system has been minimal. A Canadian patent of 1958 seems to be the first work done in this area. G.C. Harris (3) pulped many different species of wood with pressurized oxygen and sodium bicarbonate at a pH of 7 to 9, a temperature of 125 degrees centigrade to 175 degrees centigrade, and a cooking pressure of 1000 psig to 1100 psig. He discovered with further work with sodium bicarbonate that it formed precipitates with dissolved lignin and it discolored the pulp.

A united States patent by M.M. Gaschke and M.L. Spector (4) outlined the pulping of bagasse under pressurized oxygen

in ammonium hydroxide at a pH of 9 to 12, a temperture of 80 degrees centigrade to 170 degrees centigrade, and a pressure of 5 psig to 500 psig. The process resulted in a high yield pulp of high quality and, although no experimental data could be found, the authors claim that their system is applicable to common wood species also.

A Russian scientist, Surewicz Nowakowski (5), in an article published in the United States, revealed his work with the oxygen-caustic pulping process. He found that the delignification process was inhibited in this system, and that excess caustic was consumed during the cook. The resulting pulp was brighter but it was also low in strength properties.

It should be noted that the pulping system of Nowalkowski does not include a catalyst of any kind. His poor results correspond with the early failure of the French bleaching system which did not include the magnesium carbonate catalyst. Because of the recent success of the French bleaching system

with a catalyst, it seems logical that a pulping system identical to the Russian system, except for the addition of magnesium carbonate, would prove successful.

Table I

Summary of French experimentation with bleaching process variables.

Change	Yield	Brightness	Rate of Delignification	Strength	Caustic Consumption
addition of catalyst	increase	no chg.	increase	increase	no chg.
increase in reaction temp	decrease	increase	increase	decrease	increase
increase in oxy press.				decrease	increase
increase in soda conc.		increase	increase	decrease	
increase in consistency	no chg.		no chg.		

Experimental

General

This study was carried out at Western Michigan University's Paper Technology Department, Kalamazoo, Michigan, from September 1968 to March 1969.

Objective

The purpose of this study was to determine if favorable characteristics could be imparted on red pine chips using a hot caustic-oxygen pulping system or a hot caustic-oxygen-magnesium carbonate pulping system.

Approach

Initially, a bomb system had to be developed which could retain oxygen and nitrogen pressures of 30-60 psi and internal cooking pressures of perhaps 150 psi. The nitrogen system was used as a control to be compared to the experimental systems. Cooks would then be made and evaluated by testing for yield, brightness, permangenate number, tensile and mullen.

The literative indicated that preliminary cooks using a hot caustic-oxygen pulping system would not result in an improved pulp over that made with the hot caustic-inert gas pulping system. But, as in the bleaching system, a strength and brightness increase may be seen with the addition of magnesium carbonate to the experimental system.

Bomb Design

Four 1.5 liter stainless steel bombs used in the oil bath cooker were modified for use in this study. Holes were bored just below the sealing cap for spring check valves to be inserted. No other alterations would be made on the bombs, for tempereture and pressure guages could not be read while the bomb was in the rotating frame of the oil bath. It was felt that temperature and pressure would be held fairly constant throughout the study with the use of the oil bath cooker.

It must be noted here that the time spent in designing and construction of the bomb, and experimenting with oxygen-oil combination temperatures and bomb sealing capabilities

was great. Certainly the experiment would not have been conducted under a danger of possible explosions, and it was felt that a mixture of hot oil and pure oxygen could be highly combustible and explosive. Once the oil-oxygen -heat experiments were considered favorable, four trial cooks were made with chip alkali suspensions under both oxygen and nitrogin pressure to determine if leakage occurred.

Each experiment and trial indicated that no danger would be involved if precautions were taken; especially in sealing the bombs with circular rings made of dry lap pulp and tightening the bomb caps securely.

<u>Materials</u>

Materials, other than the bombs, oil bath and tools needed in the cooking operation, are as follows:

caustic-pellets	80 mesh screen
red pine wood chips	Noble and Wood Proportioner
Magnesium carbonate	British Sheet Mold and corresponding materials (pressing and drying apparatus)
distilled water	

testing instruments

beakers

balances

Pulp Process Simulation

The modified 1.5 liter bombs were pressurized prior to cooking. The area above the liquor-chip mixture was evacuated as best possible of air with the gas used in each experiment. The cap was then sealed and the bomb pressurized through the spring-check valve. The bombs were then placed in the oil bath frame and then into the hot oil.

The oil was at the cook temperature when the bombs were placed in it. The temperature of the liquor-wood system could not reach this temperature immediately, but it would a very short time later. Thus, the cooking time data in the table of results were calculated from the time the bombs were dropped into the oil bath to the time they were taken out.

The bombs were then dropped into a cold water bath and

allowed to cool off for about an hour.

An attempt was made to simulate the industry's procedure in handling their pulp from their blow tank. The experimental pulp was rinsed out of the individual bombs into an eighty mesh wire screen, and washed with hot water (eighty degrees centigrade) for exactly five minutes. Because the yields were low (thirty-fifty percent), no agitation or refining needed to simulate the blowing or blow plate process. It was felt that if the pulp was cooked to a higher yield and agitation was required to break up the chips, control would be lost in comparing strength characteristics of one cook to another.

The washed pulp was then dispersed in cold water and placed in a Noble and Wood proportioner. Handsheets were made on the British Sheet Mold. The pulp was not refined in any way before handsheets were made, for again, it was felt that control of strength properties would be lost.

Testing Methods

Once the handsheets were made and air dried for at least two days in a constant temperature and humidity room, tests were run on the pulp. They were weighed(for bases weight and yield results), tested for brightness, mullen and a modified tensile (five cm/in elongation ten kg. load) Permangenate numbers were run on an apparatus in a pulp mill, so the resulting valves could be related to industrial results.

It was hoped that other evaluations could be run on the pulp, but time did not permit it.

Results

Hot Caustic System *vs* Hot Caustic-Oxygen System

	Trial # 1		Trial # 2	
	40# O_2	20# N_2	30# O_2	30# N_2
Cook Time hr.	2	2	3	3
Cook Temp ^0C	175°	175°	175°	175°
Caustic-Wood Ratio	1.2	1.2	0.6	0.6
Yield (%)	33	34	32	35
Brightness	48.2	47.2	47.5	45.2
Ten (modif.)	19	25	14	24
Mullen	1	2	3/4	2
Basis Wt.	2.4g	2.4g	2.4g	2.4g
K-Number	15	15	23	21

Both trials were conducted to determine the effect of pressurized oxygen in a hot caustic cook. The literature search seemed to indicate that no advantages would be obtained by introducing oxygen into a pulping system.

The caustic to wood ratio (dry caustic on oven dry wood) in trial number one is very high and would not be used in the industry. Even so, pulps of comparable quality were propuced. The oxygen pulp is one point brighter and significantly weaker; six points lower in the modified tensile test and one point lower in mullen. The slight difference in the yield should be considered negligible because of the experimental error involved with its determination.

Although the differences in the test results between the two cooks are small, each procedes in a corresponding, logical direction. The oxygen cook produced a pulp of a higher brightness and a lower strength with a possible lower yield.

Because of the high caustic to wood ratio, a second trial was run. This cook was made with a 0.6 caustic to wood ratio and a three hour cook time. The results were much more significant. The oxygen pulp was lower in yield by three percent, higher in brightness by two point three points, lower in modified tensile by ten points and lower in mullen by slightly over a point. The oxygen pulp was also lower in permangenate number by two points.

The results of the second trial supported the findings of the first cook in every case, even at a greater significance. Although brightness is increased by the use of oxygen, the yield is decreased, and so is the strength. The same results could be obtained be cooking the pulp a little longer. So, it must be stated that no advantages could be obtained by pressurizing a bomb with oxygen.

Hot Caustic-Nitrogin-Magnesium Carbonate System <u>vs</u>

Hot Caustic-Oxygen-Magnesium Carbonate System

	Trial # 1		Trial # 2	
	30# O_2 1% $MgCO_3$	30# N_2 1% $MgCO_3$	30# O_2 1% $MgCO_3$	30# N_2 1% $MgCO_3$
Cook Time hour	2 2/3	2 2/3	2½	2½
Cook Temp. °C.	175°	175°	175°	175°
Caustic Wood Ratio	0.7	0.7	0.7	0.7
Yield (%)	38	38	40	40
Brightness	45.1	42.3	45.0	42.7
Ten.(Modif)	73	58	75	60
Mullen	12.5	9.5	12	10
Basis Wt.	3.3	3.3	3.3	3.3
K-number	-	-	20	24

The next two cooks were run to determine the effect magnesium carbonate had on the two initial pulping systems, the oxygen-caustic and nitrogin-caustic. Literature seardh results from bleaching studies indicated that advantages could be obtained by adding dry magnesium carbonate to the caustic solution prior to cooking.

The correct cook temperature, cook time and caustic to wood ratio were now set for these trials and the remaining trials: 175° centigrade, 2¼-2 3/4 hour, and 0.7. The first trial showed that the oxygen-magnesium carbonate pulp was higher in brightness by three points, equal in yield and slightly stronger; thirteen points in modified tensile and three points in mullen. Thus, strength and yield were improved by the addition of magnesium carbonate to the pulping system under oxygen pressure, while the brightness was not affected!

Although it is difficult to compare the results of the caustic-nitrogin-magnesium carbonate pulp to those of the

previous experiment because of different caustic to wood ratios, slower cooking time and heavier handsheets; careful examination indicates that there was no significant improvement in brightness or strength results because of the addition of magnesium carbonate. This would indicate that the oxygen and magnesium carbonate must be in combination to improve pulp quality.

A second trial was run under the same conditions except for a slight decrease in the cooking time. The results correlate exactly with those of the first trial. Permangenate numbers were also run of these samples and showed that the oxygen-magnesium carbonate pulp were lower by four points. Thus, magnesium carbonate addition to the caustic does not seem to increase yield.

Effect of Cook Temperature on the Oxygen Magnesium Carbonate System

	30# O_2 1% $MgCO_3$	30# N_2 1% $MgCO_3$
Cook Time Hour	2½	2½
Cook Temp °C.	150°	150°
Caustic Wood Ratio	0.7	0.7
Yield(%)	60	61
Brightness	35.5	31
Ten.(Modif)	30	27
Mullen	5	5
Basis Wt.	3.3	3.3
K-number	-	-

This experiment was run to determine the effect a lower cooking temperature would have on the oxygen-magnesium carbonate system. The resulting pulp was in the sixty percent yield range and had to be agitated for an acceptable pulp to be produced. Because of this agitation, and the possible uneven effect on strength, a comparison of strength tests may not be considered valid. This oxygen-magnesium carbonate system yielded a pulp of higher brightness (over four points).

Oxygen Pressure and Magnesium Carbonate Concentration Variations

Trial # One

	$45\#O_2$		$15\#O_2$	
	1% $MgCO_3$	3% $MgCO_3$	1% $MgCO_3$	3% $MgCO_3$
Cook Time Hour	2½	2½	2½	2½
Cook Temp ($^oC.$)	175°	175°	175°	175°
Caustic Wood Ratio	o.7	o.7	0.7	0.7
Yield(%)	42	41	50	49
Brightness	44.5	46.2	41.4	42.1
Ten.(Modif)	80	74	55	53
Mullen	12	12	9	7
Basis Wt.	3.3	3.3	3.3	3.3
K-number	19	18.5	20.5	20

Oxygen Pressure and Magnesium Carbonate Concentration Variations

Trial # Two

	$45\#O_2$		$15\#O_2$	
	1% $MgCO_3$	3% $MgCO_3$	1% $MgCO_3$	3% $MgCO_3$
Cook Time Hour	2½	2½	2½	2½
Cook Temp (° C.)	175°	175°	175°	175°
Caustic Wood Ratio	0.7	0.7	0.7	0.7
Yield(%)	44.0	40	51	46
Brightness	42.1	43.8	38.8	39.1
Ten. (Modif)	79	77	64	56
Mullen	11	12	8	7
Basis Wt.	3.3	3.3	3.3	3.3
K-number	--	--	--	--

The final two trials were conducted to determine the effect a change in oxygen pressure and magnesium carbonate concentration would have on resulting pulp properties. Two trials were run produce more conclusive results.

Both trials indicated that an increase in oxygen pressure from fifteen psi to forty psi would decrease the yield by about seven percentage points, increase the brightness by three points, and increase the strength by thirty points in modified tensile and three points in mullen.

Magnesium carbonate concentration was increased from one percent to three percent. This increase resulted in a slightly lower yield(one-four percentage points), and a higher brightness (one point).

Conclusions

1. No advantages are seen by adding oxygen to the hot caustic pulping system.
2. The addition of magnesium carbonate to the oxygen system results in a stronger pulp, while other properties remain the same.
3. The addition of magnesium carbonate to a system without oxygen has no effect.
4. Increasing the oxygen pressure of the hot caustic-oxygen-magnesium carbonate system decreases yield, increases brightness and increases strength.
5. Increasing the concentration of magnesium carbonate in this system has an identical effect.

Recommendations

1. Because of the small amount of pulp yielded for each section of a trial (possibly 140 grams), beater runs and succeding tests were out of the question. In future work it is recommended that enough pulp be produced to run these tests.
2. Other tests which could be run are lignin determinations, and degree of polymerization using possibly intrinsic viscosity.
3. Future work could include cost studies on whether the addition of oxygen and a catalyst to a pulping system would be a cheaper method of obtaining an increase in brightness.
4. Future work could include an investigation into the oxygen-magnesium carbonate mechanism
    a) Finding the optimun pulping conditions for this system.

b) Using other magnesium compounds in the system.

c). Using other carbonate compounds in the system.

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