Utilisation of unconventional raw materials a new approach

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SUMMARY

A new field of sulfite pulping has been evaluated by Ingruber and Allard from Acid to alkaline with the aid of hot pH measurement. At that time, high strength pulps were produced by kraft process which resulted in low yield. Kraft pulp is unfortunately dark brown in colour and it needs considerable quantities of equipment and chemicals to bleach it to a brightness suitable for printing grades. The recent knowledge of chemistry of hot alkaline pulping solutions has been reported to develop this promising field of alkaline sulfite pulping. The data for alkaline sulfite cooks of spruce northern mixed hardwoods and southern pine have been presented for a very wide range of pulp grades. To demonstrate the advantages of alkaline sulfite process for liner board, a semi commercial scale trial was made in the CIP research pilot plant. The conclusion was described that strong kraft like pulp could be made at higher unbleached yield and brightness.

Following this development, the unconventional raw materials were studied to achieve economical advantages. It was found that unconventional raw material based mills which do not have recovery system could better utilize to achieve a variety of improvements in mill operations. The pH of the pulping liquor crops quickly during the early stage of the cook, and most of the pulping is done at pH (cold) 9-10. To achieve maximum delignification, the alkali ratio is found to be derendent on the lignin content present in the raw materials. The important observations are that this process reduces total alkali charge and it emerges higher yield, easier to bleach pulp, short cooking time and stronger pulp. The high yield of this pulp is the result of preservation of carbohydrates. Alpha Cellulose is remarkably preserved during pulping. Another important observation is recorded that this pulping process eliminates the odour problem for all practical purposes and reduces water and air pollution load. Of course, an increase in yield, and lower chemical consumption for pulping, bleaching and pollution may contribute very substantially towards the economy and financial success of the mills.

ADVANTAGES AT A GLANCE—FOR NEW PROCESS

(Based on Lab. Scale Study)

1. Faster rate of delignification.
2. High pulp yield (8-10% points higher)
3. Lower Chemical consumption in pulping operation.
4. Reduction in cooking time—A net saving of time.
5. Need lower cooking temperature—A net saving in energy at higher productivity.
6. High brightness of pulp—No need to bleach for production of many grades of paper—A net saving in bleaching chemicals and equipments.
7. Light yellow colour of pulp—A net saving of yellow dye for various grades of paper.
8. Higher ash content from 1.0-3.0 percent—An inherent inorganic loading as paper - A net saving of inorganic loading chemicals.
9. Pulp strengths as kraft strengths.
10. Reduction in the odours problems.
11. Reduction in organic and inorganic load of water effluent.
12. Reduction in Chemical consumption, less pollution load.
3. Possibility of utilization of flue gases and close system of mill.

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About 35 years ago, sulfite was the dominant chemical pulping process throughout the world. In the early 1960's, many sulfite mills were forced to decide either for implementation in effective disposal of spent liquor or to shut down. The primary reason was the environmental protection. Spent liquor could no longer be discharged directly into the receiving waterways. Many small sulfite units facing the high unit cost of installing chemical recovery systems were shut down in quick succession in North America as well as in Scandinavia. Since that time, virtually all the expansion in chemical pulping capacity has been in kraft pulping. Kraft pulping has the advantage that it can be used for a wide range of wood raw materials to produce an exceptionally strong pulp.

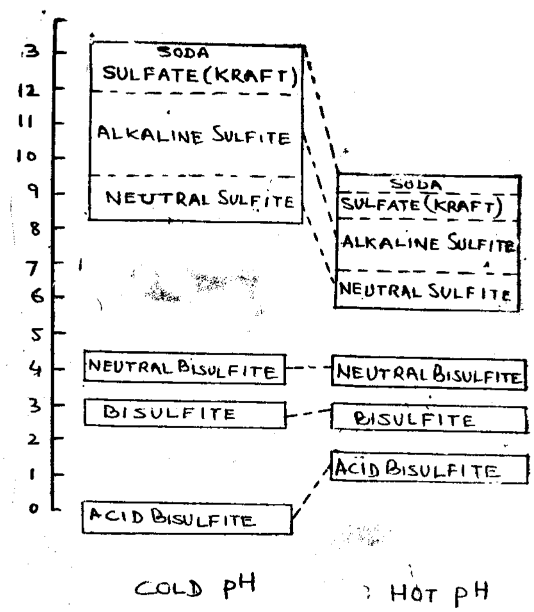
Kraft pulp is unfortunately dark brown in color, and it needs considerable quantities of equipment and chemicals to bleach it to a brightness suitable for printing grades. Since the acute oil supply crisis of 1973, the production of a strong pulp has become increasingly costly and impractical because of the large quantities of chemical used in the pulping and bleaching of kraft pulp. Another main drawback of kraft process is the emission of sulphur compounds polluting the atmosphere. With increasing cost of chemicals and capital cost of installed equipment, it is a serious doubt that kraft mill with low pulping yield and extensive bleaching requirements could be built and operated with a satisfactory return on investment. With the recent developments, there is no other single pulping process that is as versatile as sulphite. It can produce well-defined marketable pulp products over a range of 30-90% yield and over a pH range of 1-13.

A comprehensive study of sulfite pulping at varying pH levels from strongly acid to strongly alkaline were discussed[1]. By control of both temperature and hot pH, it was possible for the first time, to separate the effect of temperature and pH and to arrive at a revealing picture of the effect of cooking on pulping kinetics, chemical composition, and carbohydrate characteristics of the pulps. A comparison of the position according to cold and hot pH values measured in the cooking liquor shows that apparent gaps between processes close when the actual pH at cooking temperature is determined. Thus the total pH range of pulping processes has been covered for all practical purposes. Figure given here gives the position of all pulping processes on pH scale.

In order to arrive at a good comparison of the properties of various alkaline pulps, the cooks were conducted in 70 litre and 30 litre experimental digester units with indirect heating and forced liquor circulation. Eastern Canadian white spruce southern long leaf pine and eastern Canadian hard woods were used as a raw material mainly for alkaline su fite and kraft pulps[2]. The main conclusions were that alkaline sulfite cooks required 5-8°C higher temperature to maintain the kraft like pulping rate and the strength characteristics of alkaline sulfite pulps were satisfactory compared to kraft pulps of the same wood.

To confirm observations of small scale experiments, and to demonstrate the advantages of the alkaline sulfite process for lineiboard on a semi-commercial scale, a trial was made in the CIP Research pilot plant at Gatineau. Detailed descriptions of the pilot plant were published[3] Eastern canadian spruce-balsam chip mixture was used and it was confirmed that the alkaline sulfite process produced pulps with strength properties equivalent to those made by the kraft process.

Recently, experiments with anthraquinone have shown that the alkaline sulfite—anthraquinone approach is much more effective than the kraft anthraquinone method[4].



Following the development of alkaline sulphite pulping of softwood and hardwood, from last one year our research and development team is engaged in finding the pulping economics of the various pulping processes for conventional and unconventional raw material with and without addition of AQ to exercise the strict control on the use of cooking, bleaching and pollution treatment chemicals so as to bring down the cost of paper production which is a prime necessity for Indian pulp and paper units specially for, which do not have chemical recovery unit. In this direction, alkaline su'fite-AQ and neutral sulfite AQ process are best to be suited[5]. In this paper, we report the fundamentals of alkaline sulfite-AQ process for unconventional raw material (wheat and rice straw).

COOKING LIQUOR AND POSITION OF pH (COLD) DURING PULPING

The cooking liqour consists Na_2SO_3 and NaOH. The possible ions are Na^+, H^+, SO_3^{-2}, OH^{-1} and HSO_3^{-1} The OH^- ion differs greatly from SO_3^{-2} and HSO_3^{-1} ions in their chemical nature and course of reaction to lignin, cellulose and hemicellulose. The specific ionic ratio is essential in cooking liquor.

Ingruber and Allard have shown the position of various pulping process on the pH scale (Figure page 22). They reported that alkaline sulfite pulping was performed at pH (cold) of 13-10 while the neutral sulfite was progressed at pH (cold) of 8.5 to 10.5. The pH (cold) values are recorded during pulping at mild cooking conditions and it is found that pH (cold) in alkaline sulfite pulping drops rapidly in the early stage of the cook and most of the pulping has progressed at pH (cold) 10.5-9 for pulping temperature from 100°C to 150°C and also upto end of the cook while most of the soda and kraft pulping were performed at pH (cold) 12-10.5 for the similar range of temperature and time.

PULPING CONDITIONS AND DELIGNIFICATION

To achieve the optimum delignification, various ionic ratios have been used for the range of 0.0 to 0.9 by increasing the Na_2SO_3 content at fixed total alkali charge in the cooking liquor. It is observed that specific ionic ratio or optimum alkali ratio (OAR*) (Na_2SO_3/total alkali, both as NaOH) is essential in the cooking liquor. The OAR for wheat and rice straw were observed in the range of 0.65-0.70 and 0.45-0.50 for the lignin content of wheat and rice straw material 18.5-19.0 and 11-11.5 percent respectively. This means that OAR differs greatly and it is dependent on the following two factors:—

1. Amount of lignin in raw material.
2. Manner of combination of carbohydrates to lignin.

An increase of alkali ratio from initial to OAR re ults faster delignification but further increase above OAR, there is decreasing pattern of rate of delignification which becomes very slow for AR** 0.9 or above as has been found in the case of mono sulfite pulping[6].

An increase in total alkali charge accelerates delignification but Na_2SO_3 charge has greater effect on delignification than the total alkali charge. When pulping temperature is increased from 140°C to 160°C, then there is no sharp change in kappa number for a constant alkali charge. To achieve the kraft or soda-AQ like delignification rate, the alkaline sulphite process leads to the reduction of alkali charge or pulping time or both alkali charge and pulping time at slightly higher temperature. This means that alkaline sulfite process offers various advantages on the kraft and soda-AQ process. The one reason for these advantages is the easy imprignation of cooking liquor during pulping. It has been also noted that rate of delignification of alkaline sulfite AQ is faster than neutral sulfite AQ process.

YIELD AND GENERAL PROPERTIES OF PULP

The most interesting observation of alkaline sulfite-AQ process is very high pulp yield The total pulp yield is 8-10 percent points higher than soda-AQ and kraft. The pulp yield about 2.5-3.0 percent point higher is observed for neutral sulfite AQ at constant kappa number for the same brightness of pulp. The alkaline sulphite-AQ process gives light yellow unbleached pulp having the brightness 57-59° GE at kappa level 24-25. The brightness of this pulp can be improved by increasing total alkali charge at optimum alkali ratio. This pulp looks similar to semi-bleached pulp and has 2-3 percent high ash content than soda AQ and kraft pulp. An increase in temperature from 140-160°C, there is decrease in pulp yield about 3-4 percent. By increasing the Na_2SO_3 content to OAR, it has become clear that Na_2SO_3 used in cooking liquor is the responsible for higher brightness and ash in pulps.

To produce the 72-75 percent unbleached pulp of kappa number approximately 49-55, total alkali charge 3.5 to 5.0 percent could be used at optimum alkali ratio but resulted material has to be defibrated using defibrator. In this way this offers the possibility for semichemical pulp of straws.

*OAR = Optimum alkali Ratio
**AR = Alkali ratio

CHEMICAL COMPOSITION OF UNBLEACHED PULP

Alkaline sulfite-AQ pulp has 1.4-0.6 percent high alpha cellulose and 2-2.6 percent high ash content than kraft and soda-AQ pulps. The high yield of alkaline sulfite AQ pulp is the result of stabilization of carbohydrates. Alpha cellulose is remarkably preserved (alpha cellulose 13-11.5 percent more) in alkaline sulfite AQ when compared with kraft and soda-AQ pulps. Tnis stabilization of Carbohydrates is partly the result of mild cooking condition and partly due to drop in pH in early stage of the cooking which stabilizes the carbohydrates during pulping. The increase of ash content also contributes to high yield as a pulp.

BLEACHING OF PULP

The brightness of unbleached pulp is recorded to be 57-59°GE at pulp yield 62 percent and it looks like a semibleached pulp. Of course, no need to bleach and unbleached pulp directly can be used for various grade of writing, printing and newsprint paper.

As far as bleaching of pulp is concerned, little information is available for alkaline sulfite of softwood pulp[2] but our work is in progress on bleaching of alkaline sulfite AQ pulp for fine grade of paper from straws and bagasse.

The data available from alkaline sulfite bleaching experiments on softwood pulp show that alkaline sulfite pulp is easier to bleach, have higher brightness, suffer considerably less brightness reversion than kraft pulp. It requires less chemical to bleach and the number of bleaching stages could be reduced. The carbohydrates loss during bleaching of alkaline sulfite pulp is less than kraft and soda pulps for the same yield Results also indicate that alkaline sulfite soft wood pulp shrink less than kraft pulp. Another unexpected finding was the equalization of the viscosity.

PAPER MAKING PROPERTIES

The variation in paper making properties during beating was determined for alkaline sulfite-AQ, Soda-AQ and kraft pulps using a valley beater. All the pulps were easily beaten and slightly lower beating time (1-2 minutes) is needed to alkaline sulfite-AQ pulp. The drainage time is found to be less (2-4 minutes) for alkaline sulfite AQ pulp when compared with soda-AQ and kraft pulps. The bonding ability develops rapidly. The burst and tensile strengths are fully equal to those of soda-AQ and kraft for a fixed freeness level. The tearing strength of alkaline sulfite-AQ pulp is about 10–20 percent lower than corresponding kraft pulp. When comparing the strength properties, it has been kept in mind that yield of alkaline sulfite-AQ pulp is higher than Soda-AQ and kraft pulps for a constant kappa level.

BLACK LIQUOR AND RECOVERY

Very little information has been developed with regard of alkaline sulfite spent liquor and its by-product. Following are the main characteristics of black liquor observed from preliminary examination.

1. Low solid content
2. High content of inorganic material
3. Low viscosity
4. Low heating value
5. H_2S can not be liberated from the spent liquor

When alkaline sulfite spent liquor is compared with soda AQ kraft spent liquor. there are three fundamental significants in the field of recovery of the inorganic chemicals.

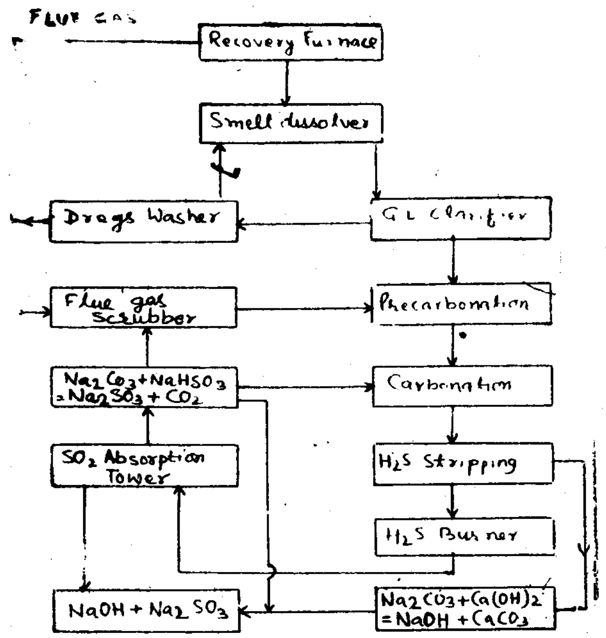
1. Volatile mercaptans cannot form methoxy group of lignin and hemicelluloses.
2. H_2S can not be librated from solutions.
3. Replacement of sulphides (oxidation state—2) by sulfites (oxidation state + 4).

From the above points, the conclusions are that losses of volatile sulphur compounds prior to the furnace will be naturally elimlnated and no liquor oxidation would be required. Lowest SO_2 emissions would be possible during the burning of alkaline sulfite spent liquor in an incinator or boiler furnace because of high Na to S ratio. In absence of Na_2S, the causticizing efficiency could be improved by about 1–3%[10].

Although a complete chemical recovery system for alkaline sulfite pulping is now available commercially[7] but one step is also complex as the equipment is required for the $H_2S—SO_2$ conversion and make up of Na_2SO_3 based cooking liquor. After combustion of the spent liquor, flue gases will mainly contain CO_2 and SO_2 and it would be possible to use effectively the flue gases for the following conversions in the green liquor :—

$$Na_2S + H_2O + CO_2 = Na_2CO_3 + H_2S$$
$$Na_2S + SO_2 + H_2O = Na_2SO_3 + H_2S$$
$$2\,NaOH + SO_2 = Na_2SO_3 + H_2O$$

Flow diagram of the Rauma chemical recovery system is given in the following figure :—



ENVIRONMENTAL PROTECTION

Alkaline sulfite-AQ process has potential advantage in the field of environmental protection.

Air Protection

Value of odour threshold[8] (limit of perceptibility by human nose) and toxicity to fish[9] of the chemicals used or formed in the kraft and alkaline sulfite pulping processes has been studied. The conclusions are that sulfide solutions is 200-1000 times offensive and 2 times more toxic than sulfite.

If in near future, air pollution regulation will force to cover the emission limit from the kraft mills, then it will offer the similar situation which was about 35 years ago in America and Scandianavia for sulfite mills. At that time, they would have either to implement of kraft odour emission or shut down the kraft mills. It may be possible to reduce kraft mill odour down to certain limit, but it is not feasible economically.

Most of the problems would simply disappear using alkaline sulfite AQ process in absence of volatile odours substances. No precautions would be necessary from the digester to liquor combustion unit. In case of alkaline sulfite, digester and evaporator condensates would be non toxic and low in odour. Burning of alkaline sulfite spent liquor in incinerator or boiler furnace will produce lowest SO_2 emissions because of the high Na to S ratio[2].

Water Protection

As it is already discussed that high yield pulp is achieved from alkaline sulfite AQ process. The ash content in the pulp is also higher than other chemical process. In this way it makes possible to reduce organic and inorganic load in spent liquor which would reduce the chemical loading in water effluent. Water effluent can be minimised by simple efficient recovery of chemicals and reuse of water in the mills. Thus it is possible to be a close system of mills for alkaline sulfite AQ process.

FUUURE LOOKS

In the consideration of costs of fibrous material, energy and chemicals, alkaline sulfite chemical pulp can be more economical to produce various grade of paper. Alkaline sulfite AQ chemical pulp has been demonstrated to be competitive with kraft with possible higher pulp yield and lower pollution loading. The number of sulfite mills staying in operation might be stablized.

Alkaline sulfite can be used for high yield pulping to achieve semi-chemical pulp. There is an alternative for TMP. Modern ground wood mills can be operated with comparable efficiency as TMP mills at lower energy requirement. CMP, CTMP and other sulfite mechanical processes are merely extensions of known high yield sulfite technology. They reflect the unusual versatility of the sulfite process.

With the recent availability of economical and reliable chemical recovery system, alkaline sulfite AQ pulping could be continued within accept-able environmental limits.

SULFITE SHUTTLES INTO SPACE

By Alwong Tappi J. Oct. 1982)

Unexpected sudden changes in world economics gave sulfite a new life. The unique surface quality of sulfite pulp fibers make it possibly a superior fiber for white paper production.

And now the space shuttle flies because of sulfite pulp. There are also additional components of the space shuttle which are constructed with carbon fibers material. In the first two space vehicles COLUMBIA and CHALLENGER constructed todate, sulfite rayon fibers were used almost exclusively in these critical components. But there is threat.

Polyacrylonitrile fibers are competing aggresively against rayon fibers for the use in the next group of space shuttles being built. Continuing research and development effort to further improve the sulfite dissolving pulp is definitely needed to maintain the competitive edge.

An interesting forestry-related experiment was carried out during the third space shuttle mission. A plant growth study was conducted to demonstrate the effect of near weight-less on the quantity and rate of lignin formation in different plant species during early stages of development. Slash pine seedlings were among the few plants selected for these tests. Results of these experiments could provide new knowledge on the effect of physical environment on the biosynthesis of lignin in trees.

IN THE COMING DECADE, THE FUTURE OF SULFITE LOOKS BRIGHT

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LITERATURE CITED

1. Ingruber, O.V., and Allard, G.A., 'The effect of hydrogen ion activity in the sulfite pulping of black spruce, tappi 50, 597-614 (1967).

2. Ingruber, O.V., and Allard, G.A., 'Alkaline sulfite pulping for 'KRAFT' strength, Pulp and Paper magazine of Canada, 74 (11) 84 (1973).

3. Anon, 'Pilot pulping plant debuts at CIP-Gatineau. Pulp Paper Mag. Can. 71, 54-56 (Aug. 21. 1970).

4. Ingruber, O.V., 'Alkaline sulfite pulping, paper presented at the AI ChE National meeting, San Francisco, Calif., Nov. 1979.

5. Bahadur Singh, Tiwari, R.N., Ashwani Sharma, Subhash Chandra, Saksena, U.L., & Chowdhary, L.N., communicated to Tappi J. and Research & Development Report, Star Paper Mills Ltd., Saharanpur.

6. Chowdhary, L N., Saksena, U.L., Subhash Chandra, Bahadur Singh, and Tiwari, R.N., Alkaline Sulfite pulping-a modified mono sulfite pulping proccss' communicated to Ippta J.

7. AlWong (Editorial view point), and Tappi and TS-CPPA Int's sulfite pulping conference, Toronto, Tappi 65 (10); 11 & 29 (1982).

8. NAPCA Report, 'Control of atmospheric emissions of the wood pulping industry, Final report, Volume 1, March, 1970.

9. Klein, L., *River Pollution, II. Causes and effect* Butterworths, London, 1962.

10. Alwong, Pulp and Paper international, 23 (1); 55 (1981).