

# RECENT DEVELOPMENTS AND PRESENT TRENDS IN SULPHITE PULPING

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## INTRODUCTION

Ninety-four years ago the American chemist Benjamin Tilghman was granted the world's first patent on sulphite pulping. Seven years later the world's first sulphite pulp mill was started. No one can deny that great progress has been made since this time, although this has been mainly in the technological field. Chemically, the sulphite pulping is still, with a few exceptions, the same acid one-stage process it was ninety years ago, the pH of the cold cooking liquor being fixed at between 1.5 and 2 by the use of calcium base. In spite of this, the chemists and chemical engineers have skilfully found out how to use variables other than pH, such as chemical-to-wood ratio and temperature, in order to produce a variety of pulp qualities from greaseproof to dissolving pulp.

In the competition between the calcium-base sulphite pulping and the somewhat older kraft pulping method, the sulphite process had predominated for a long time. During the 1920's, however, the alkaline process became more important, and in recent decades the growth of the kraft industry has been rather spectacular, especially in the U.S.A. One of the reasons for this is the fact that pine, and to some extent hardwoods, are not very suitable for calcium base sulphite cooking, but are readily pulped by the kraft process. Another reason is the improvements in bleaching, by which the kraft pulp can now be bleached to the same brightness as sulphite pulp. Some years ago, the slow death of the sulphite pulping method was predicted. But, the last few years have given the sulphite pulp producer a new lease of life, and the sulphite process is now recovering from its decline. New modifications of the process and new methods, which are of considerable importance for the sulphite industry, have been developed. There are now some optimists who even believe that the recent developments will slowly make the sulphite method once again the dominant process.

In order to realize the significance of the developments, some of the disadvantages, and also the advantages, of the conventional sulphite process over the sulphate process must be summarized:

### *Disadvantages:*

- Limited use of pulp wood species
- Expensive pulp wood, *e.g.* spruce
- Low strength properties, especially tear
- Lower opacity
- Water pollution problems
- Longer cooking time

*Advantages:*

- Higher yield at the same *Kappa*-number
- Higher unbleached brightness
- Better bleachability
- Better beatibility

All these factors are economically important and, where industrial development is concerned, only improvements which imply better economy will count.

With this background I will discuss how the recent developments can change the picture, how some disadvantages of the old sulphite process can be cancelled, and how some advantages can be further improved.

The developments, which I have in mind are:

- (i) Soluble-base cooking
- (ii) Improved chipping
- (iii) Improved bleaching
- (iv) Continuous digestion.

### SOLUBLE-BASE COOKING

Soluble-base cooking with sodium, magnesium and ammonium bases is by no means, generally speaking, a new concept. Tilghman worked with soluble bases and the first sulphite mill used a magnesium base. However, in the last decade or two there has been a renewed interest, and considerable developments have been achieved. Soluble-base cooking has been a most popular subject for both pure and applied chemical research during recent years. The change from calcium to sodium, magnesium or ammonium will make it possible to change the sulphite process so that almost all the disadvantages, and also the advantages, can be influenced favourably. Of course, all these improvements do not occur simultaneously.

The great advantage of soluble bases is that they allow the pH to be used as an independent variable. It might, therefore, be convenient to discuss soluble-base sulphite cooking from the variable pH point of view.

The pH plays a most important rôle in chemical reactions, and sulphite pulping is no exception. It must be further considered that there are numerous reactions taking place during a sulphite cook, and that these are influenced in different ways by the change of pH. To take some examples: the sulphonation of lignin and the different behaviour of the so-called X-, Y- and Z-groups; the dissolution or hydrolysis of lignin, the hydrolysis of carbohydrates; the splitting off of different substituents of hemicelluloses, such as acetyl and glucuronic acid groups, and of sidechains, which will change the physico-chemical behaviour of the hemicelluloses. It is, therefore, easily understood that pH is a most important variable, and that by controlling this at one or several levels in a sulphite cook, new types of pulps and improvements of different types can be expected. A great number

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of different pH combinations, especially in two- and three-stage cooking is possible, but so far only a few have been extensively studied and discussed.

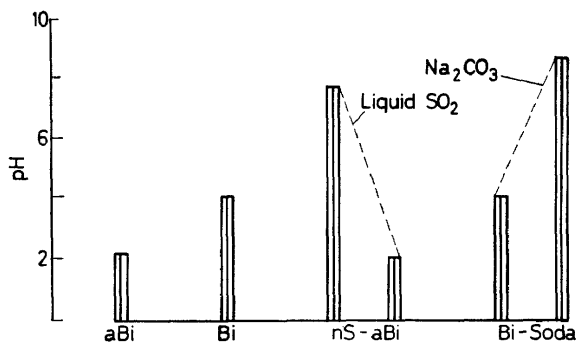


Figure 1. Some soluble base sulphite cooking methods: aBi: acid bisulphite; Bi: bisulphite; nS: neutral sulphite

Figure 1 shows graphically the new sulphite cooking methods. To the left is the conventional acid bisulphite cooking, but with soluble bases; however, this method is neither new nor very exciting. Then there is the bisulphite cooking at about pH 4. The Magnefite and Arbiso processes belong to this group. The next bars on the graph indicate a two-stage cook of the Stora type with the pH between 5 and 8 in the first stage and then, after addition of liquid sulphur dioxide, an acid stage. A modification of this method starts with pH 8, but the second stage is carried out at pH 4. Finally there is an example of the Sivola two-stage sulphite cooking starting with pH 4 and then, after addition of sodium carbonate, ending at pH 9 in the final stage. Some of the merits and limitations of these methods will now be mentioned.

### (a) One-stage acid bisulphite cooking

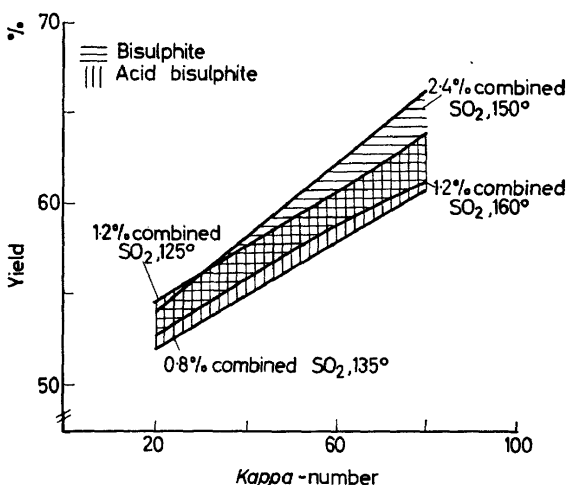
The mere substitution of a sodium, magnesium or ammonium base for a calcium base without changing the pH, does not imply much of a change in pulping. Sodium or ammonium bases give shorter cooking times than calcium and magnesium bases in paper pulp cooking, which means a higher capacity. In making dissolving pulp, sodium and ammonium will give a lower  $Kappa$ -number, *i.e.* lignin content, at a given D.P. or pulp viscosity with somewhat less chemical consumption in bleaching. The same bases also give less shives, compared with calcium or magnesium base cooking with good cooking acid impregnation. Furthermore, species, like Douglas Fir and larch, containing taxifolin will be more easily pulped by soluble bases.

### (b) One-stage bisulphite pulping (pH 4)

The one-stage bisulphite cooking at pH 4 constitutes a new development, although some of the merits of this method were mentioned as early as 1926, when Hägglund found that sodium bisulphite pulps have exceptionally

high strength and also are easy to defibrate in high yields. The cooking acid contains pure bisulphite without excess of sulphur dioxide. At a pH of about 4 and higher the interference of pinosylvin in pine heartwood on the sulphonation of the lignin is negligible. Therefore, all one- or multi-stage sulphite cooking methods with an initial pH of 4 or higher make it feasible to pulp pine. The feasibility of pulping pine is of economical importance to the industry, because pine is cheaper than spruce in many pulp producing areas, and the cost of the wood is often in the order of 50-60 per cent of the production cost of the pulp. This also explains why increased yield, even if very small, is of great importance.

It has been claimed that bisulphite cooking at pH 4 gives higher yields than the conventional sulphite process. If one means higher yield at a given degree of delignification there is only a minor difference between the two types of pulping, as shown in *Figure 2*. Both in the acid bisulphite



*Figure 2.* Unbleached pulp yield *v.* lignin-number for bisulphite and acid bisulphite softwood pulps

and the bisulphite cooking, the yield at a given *Kappa*-number can be varied somewhat by changing the cooking temperature or the chemical charge. Decreased temperature, or increased chemical charge, will increase the yield by higher hemicellulose retention in relation to the lignin dissolution. Recent investigations have shown, that this increase in hemicellulose content with higher chemical charge is almost entirely due to an increase in glucomannan and only slightly due to an increase in xylan (*Figure 3*). No explanation can be given for these observations so far.

In another sense, however, the bisulphite cooking can give higher yields. At high *Kappa*-numbers the delignification seems to be a little more selective, especially at a high chemical charge to wood ratio. A high chemical charge also gives a higher yield at the *defibration point*, which might be interpreted as a more specific delignification of the middle lamella. This point, which

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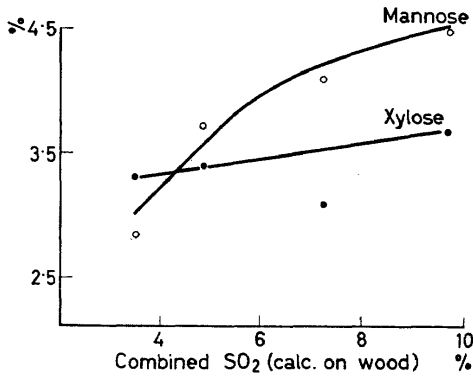


Figure 3. Hemicellulose content of bisulphite pulps v. chemical charge in pulping

roughly indicates the maximum yield of what can be denoted as chemical pulp that does not need any mechanical defibration, is in the order of 60 per cent for bisulphite pulp compared with 56 per cent for a good acid bisulphite pulp. Also bisulphite pulps in higher yields, 65–75 per cent, are surprisingly easy to refine compared with conventional sulphite or kraft pulps.

Another attractive advantage of the bisulphite pulps, especially those with sodium base, is their higher quality. The strength properties are somewhere between those of the conventional sulphite and kraft pulps as illustrated in *Figure 4*. Here the tear is plotted against tensile strength, to give the best over-all picture of the strength properties. The upper,

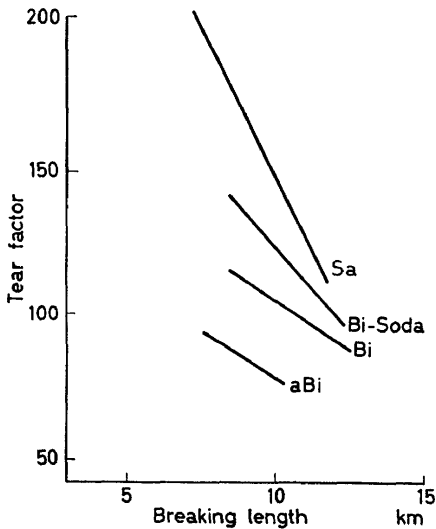


Figure 4. Strength properties of various types of bleached chemical spruce pulps in high yields: aBi: acid bisulphite; Bi: bisulphite; Sa: sulphate

left hand end point of each curve represents the unbeaten stage and the lower, right hand point approximately 550° SR freeness\*. The low tear of the sulphite pulp, which really is a pronounced disadvantage in many cases, can be increased by going over to bisulphite pulps, without losing any tensile strength. The high tear is partly due to the greater bulk of the bisulphite pulp over the conventional acid sulphite. Moreover, the tensile strength of these pulps is the same as, or sometimes even greater than, that of kraft pulps made from the same soft wood. It is, furthermore, of considerable technical importance that the initial, unbeaten tensile and burst strength of the pH 4-pulps is very great, and that these pulps, therefore, require very little beating. They are also very easily drained, a property which is of great significance for the modern fast running paper-machines, the speed of which is continuously increasing. The opacity, which also is an important pulp property for the paper-maker, is significantly higher for the pH 4-pulps than for the conventional sulphite pulps.

Some of the merits of the bisulphite pulps, especially the tensile and burst strength, are more pronounced in the higher yield range of 55–60 per cent. The lignin content is, therefore, rather high and, in many cases, too high to allow the pulps to be bleached economically in the conventional way. However, as in the case of other high yield and semi-chemical pulps, peroxide bleaching or other non-delignifying types of bleaching should be applicable. The stability of the brightness will probably not be very good. The problem of making lignin white and stable white has yet to be solved.

The results so far quoted have been obtained using softwoods. For hardwoods, at least for birch and aspen, the bisulphite cooking has been reported to give an even greater increase in strength properties, compared with the conventional acid bisulphite pulping. Also, the opacity of the product is higher. There is a limitation, however, namely that chemical hardwood pulps, at least birch pulps, can be obtained only within a very narrow *Kappa*-number range. The birch bisulphite pulps first become defibrable below a *Kappa*-number of about 40–45. On the other hand it is difficult to get pulps with lower *Kappa*-number than about 25–30 due to decomposition of the cooking liquor, resulting in a loss of bisulphite and the production of dark pulps.

It might be a little too early to state that there is a trend at present towards bisulphite cooking, but there are two mills in Norway, two in Sweden and at least one other in the United States making chemical magnesium base bisulphite (Magnefite) pulp. A new sulphite mill under construction in Sweden will also produce a similar magnesium base bisulphite pulp of both soft- and hardwood.

The bisulphite process will probably also be of great interest for semi-chemical pulps, as has been pointed out by Husband. Some years ago he showed that semi-chemical pulps of a quality at least equal to neutral sulphite semi-chemical (NSSC) pulps can be pulped in a considerably shorter time, and with less consumption of chemicals, with sodium bisulphite at pH 4 than with neutral sulphite. The pulps are brighter than the NSSC-pulps. In Russian papers, semi-chemical bisulphite pulp has also

\*SR = Schopper-Riegler : °SR defined by the construction of the equipment, which measures the ability of the pump to be drained.

been stated to be suitable both for liner† and for the corrugated medium. It would, not be surprising, therefore, if there were to be a development of semi-chemical bisulphite pulps. This is also in line with the suggestion from the Abitibi Company.

### (c) Two-stage sulphite cooking with second stage acid

Another, and perhaps stronger, trend is towards two-stage sulphite cooking. In 1953 the Söråker Mill (belonging to the Swedish Cellulose Company), in 1956 the Kramfors, and in 1958 the Ortivken Mill, all changed to two-stage pulping with sodium sulphite at pH 8 in the first stage and normal acid calcium base sulphite at pH 1.5–2 in the second stage. One reason for this was that it made the pulping of bark-damaged wood feasible. In 1955 the Stora Company Mill in Skutskär started to pulp pine wood in two stages with a pH between 4 and 8 in the first stage and pH 1.5–2 in the second stage. This is done entirely with sodium base, and with recovery of the chemicals. A new sulphite mill in Nova Scotia, which is going to pulp in the same way, is now under construction. The Mo and Domsjö Sulphite Mill, which normally runs an acid sodium bisulphite dissolving pulp, has also made plans to switch to the same two-stage process at any time. Weyerhaeuser also announced last year that their Cosmopolis mill had changed to a similar two-stage cooking process with a magnesium base.

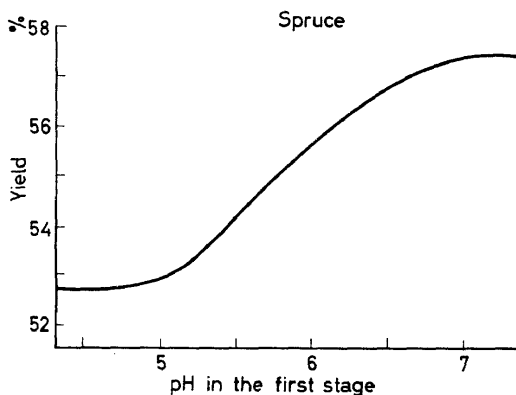


Figure 5. Unbleached yield after two-stage sulphite cooking to *Kappa*-number 20 *v.* pH in the first stage

What are the factors which make this type of two-stage cooking so attractive? It has already been pointed out that any method starting at pH 4 or higher will give a free choice of pulp wood, and that pine can be readily pulped by this process.

A greater advantage of this particular process is, however, the increase in pulp yield, as compared with that achieved in the conventional sulphite process, by the proper choice of pH in the first stage. This increase in yield at a given *Kappa*-number is due to retention of glucomannan, which is controlled by the pH in the first stage (Figure 5). Rydholm has shown †Paper for surface layers of corrugated board.

that the glucomannan retention is most probably a function of the acetyl content. The softwood glucomannan has no substituents apart from the acetyl groups. By splitting these off, the straight glucomannan chains will more easily be attached to the cellulose by hydrogen bonds. The conditions during the first stage, and especially the pH, will determine the amount of residual acetyl groups, and thus also the glucomannan retention. With a sodium base the optimum glucomannan retention will easily be attained. It has recently been shown that with a magnesium base the same glucomannan retention can also be achieved.

For softwood pulping this two-stage process obviously has great advantages in so far as the yield of paper pulps is concerned. In the manufacture of dissolving pulp with high  $\alpha$ -cellulose content, no hemicellulose retention is desired. Hardwoods, on the other hand, do not contain any glucomannan worth mentioning, and therefore no yield increase is obtained by high pH in the first stage.

Because of their high hemicellulose content these softwood two-stage pulps with high pH in the first stage are very easy to beat. They are especially suitable for the manufacture of greaseproof paper, but are useful also for other types of paper, especially if the maximum yield increase is purposely not achieved and the beating is carefully done. Under these conditions the pulp has approximately the same strength properties as a conventional acid bisulphite pulp from the same wood.

A modification of the method suggested by Rydholm involves cooking at pH 8 in the first stage, but pH 4 in the second. This would result in the same yield increase as if the second stage were more acidic, but the resulting pulp will show somewhat better strength characteristics, fully comparable with the conventional acid bisulphite pulp.

#### **(d) Two-stage sulphite cooking with an alkaline second stage**

There is also another type of two-stage sulphite cooking, which was worked out some years ago by Sivola and others, and practised industrially since about 1954 in the Finnish Rauma Mill. The last carbonate stage, at about pH 10, is typical of this process, often called the Sivola process. The preceding stage or stages are chosen according to the type of pulp to be produced and the pulpwood (*Figure 6*). For paper pulp the first stage is usually carried out at pH 4. For dissolving pulp the preceding stage is either an acid bisulphite stage, or a pH 4-stage followed by an acid bisulphite one. The latter type is of course necessary if pine has to be used. In all cases the pH increase in the last stage is accomplished by the addition of sodium carbonate. This stage is equivalent to a separate hot alkali refining stage, and from the standpoint of the quality of the pulp produced the carbonate stage can be a separate one as well. By including it as a part of the cooking process some advantages are obtained: the sodium carbonate will be a part of the chemicals in the recovery system, and, thus, the cost for chemicals will be less than with the separate stage; the organic substance dissolved in the alkaline stage will be collected in the waste liquor and burnt together with the other dissolved wood substance from the first stage, and will thus not contribute to water pollution; also the heat economy will be better.



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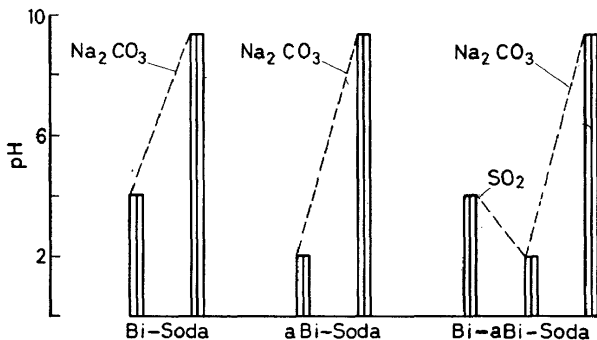


Figure 6. Various types of Sivola pulps: aBi: acid bisulphite; Bi: bisulphite

A separate hot alkali refining stage, which is a part of the bleaching sequence for dissolving pulps, will break down the hemicelluloses by peeling and dissolve them. The action of the carbonate stage in a Sivola cook is similar. The dissolution of hemicelluloses is controlled by the amount of carbonate, time and temperature. Alpha cellulose contents as high as 97%, which also is the maximum for conventional hot alkali refining, can be reached.

The two-stage bisulphite-soda cook will give paper pulps of exceptionally good strength properties, approaching those of kraft pulp. By courtesy of the Billerud Company some of their data has been made available. Figure 4 demonstrates that the bisulphite soda pulp has an intermediate position between the kraft and bisulphite pulps as far as strength is concerned.

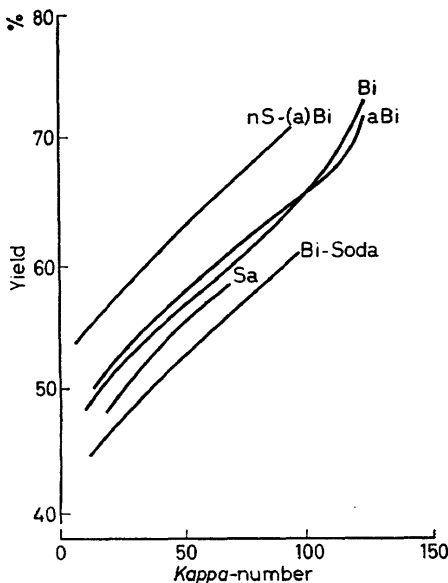


Figure 7. Unbleached yield of various types of spruce pulps v. lignin-number: aBi: acid bisulphite; Bi: bisulphite; nS: neutral sulphite; Sa: sulphate

The pulp is rather bright, and as easy to bleach as a sulphite pulp. But, unfortunately, there is a sacrifice to be made in order to get this pulp, and that lies in the low yields obtained. Bisulphite soda pulps are shown in *Figure 7* to have an even lower yield at a given  $Kappa$ -number than the kraft pulps. The relative order of pulps will still be the same after bleaching. By choosing milder conditions in the carbonate stage the yield of the carbonate pulp can be increased to that of a kraft pulp, or even higher, but, at the same time, the strength properties will be lower. The strength properties of the pulps shown in *Figure 4* were those obtained after the bleaching of the pulps shown in *Figure 7*.

By the introduction of the soluble bases, and by the utilization of the possibilities they offer, especially in making the pH an independent variable, the sulphite process can be made highly flexible with regard to the choice of pulp wood and product produced. The economically important pulp yield, which for the conventional sulphite pulp is already higher than for kraft, can be further increased, with a simultaneous increase, in some cases, in tensile strength, tear, and opacity.

### (e) Recovery

The soluble bases are expensive and the chemicals must of necessity be recovered. The recovery in magnesium-base sulphite pulping is well established and simple. For sodium bases several recovery methods have been worked out, but so far only a limited number are used commercially. These are more complicated than the magnesium recovery process, and require a rather high capital investment. It is, therefore, out of the question for a small mill making chemical pulp to install a sodium recovery system; the smallest size has a capacity of the order of 50–60,000 tons per year. However, in several countries, there is extensive work going on in order to develop simple methods for sodium base recovery. There is hope, that we, in a few years time, will develop new methods, more simple than the present ones and requiring less capital investment. Sodium bases are generally preferred to magnesium bases for greater flexibility in the cooking process and easier delignification. Interest seems at present to be divided equally between sodium and magnesium bases, but if simpler recovery methods are worked out for sodium bases they might command the greater interest.

## IMPROVED CHIPPING

It is a well-known fact that the conventional chippers damage the chips by exerting a pressure parallel to the fibres. The fibres are corrugated in the damaged area. Probably disorientation occurs where the fibres are bent. Then, during the sulphite cook, fibres are weakened by hydrolytic attack at the points of disorientation in the fibre wall. This weakening does not occur in kraft pulping. The damaged sulphite fibres will easily break into fibre fragments on beating. The freeness will be low and the strength properties of the pulp, tear, tensile, and burst, will be some 10–15 per cent lower than the pulp from undamaged hand-made chips. Logan at Anglo-Canadian has now succeeded in his development of a new type of drum chipper which will not cause any fibre damage. In industrial

operation this has increased the strength properties of the sulphite pulp by about 5–15 per cent. This is a most valuable contribution to the development of the sulphite pulp quality. It can be predicted that this basic idea in chipper design will be adopted by the sulphite industry, especially by the market pulp mills.

### IMPROVED BLEACHING

A trend which is more clearly visible for market pulp mills, as least in Scandinavia, than for integrated mills is worth mentioning briefly. The competition in the market has created an abnormal demand for high brightness, which is not always based on a demand for this high brightness from the ultimate consumers of the end products of the pulp. The use of chlorine dioxide in the final stage in sulphite bleaching has, therefore, become more common. Even typical kraft pulp bleach sequences have been adopted by the sulphite industry. One Swedish sulphite pulp mill has a five-stage operation, including two chlorine dioxide stages, and a new sulphite mill will employ a similar system.

### CONTINUOUS SULPHITE COOKING

Although this is a wood chemistry symposium I will mention a recent technical development which, however, does not yet constitute a trend. The Billerud Company in Sweden has solved the technical and chemical problems involved in continuous sulphite digestion. Their experimental continuous digester, with a capacity of about 10 tons a day, can now produce an acid bisulphite pulp of the same quality as the normal batch pulp. The sulphite liquor decomposition is not a problem in the continuous acid bisulphite pulping, but is troublesome in the continuous bisulphite pulping to low *Kappa*-numbers. The experimental digester is a twin tower arrangement, in which a variety of two-stage cooks has also been carried out successfully.

### CONCLUSION

Finally, I should like to mention that all these developments are the result of fundamental and technical research. It has been facilitated by the free exchange of ideas and results which prevails in the pulp and paper industry. However, further results are needed to get a better knowledge of the chemistry of the wood components and a better understanding of the chemistry of the technical processes. On this basis further developments will be made.

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