New, improved kraft pulp quality

Keywords
baskets, batch digesters, bloucing, cellulose fiber, continuous digesters, hardwoods, kraft pulping, kraft pulps, pulp properties, quality, softwoods, tear strength, tensile strength

ABSTRACT
The papermaking potential of kraft pulps is largely determined by the quality of the fibres produced in pulping and bleaching operations. Among the characteristics of importance, physical strength is the truly unique aspect of kraft pulps, especially those made from softwoods. This paper reviews recent developments in research on kraft pulp strength delivery: the relative strengths of mill-made pulps, where strength is missing, why, and what can be done about it. In an era of ever-increasing demands for high-quality kraft pulps, every effort must be made to maximize pulp strength on all kraft mill fibre lines.

INTRODUCTION
Kraft pulping is the world's foremost process for delignifying lignocellulosic materials. It has occupied that position for the past three decades, and was a prominent wood pulping process long before that. In fact, one of kraft's strengths is its familiarity - there are thousands of competent kraft pulping practitioners around the world, and the conventional chemistry and equipment of the process are not defined by national borders.

Kraft pulping climbed to its Number One ranking because it is the process of choice to produce the strongest wood pulps from any lignocellulosic material. Most chemical pulpers have no trouble envisioning that kraft pulping will be with us for many decades to come.

All that is not to suggest, however, that the kraft process is ideal in every respect. A kraft mill is complicated to build and to operate. Enormous amounts of investment capital are required, and manufacturing costs are high.

An unfortunate aspect of kraft pulping is that it renders wood fibres brown at the same time as it dissolves much of the lignin, and so multi-stage bleaching is needed to make the pulp white (about 60% of kraft pulp is bleached). This bleaching brings with it serious environmental pressures - especially in recent years - which are focused on the escape of chlorinated organic compounds into the aquatic environment.

It is this latter problem, particularly with respect to the unintended formation of chlorinated dioxin compounds, which is now putting considerable stress on kraft pulping and bleaching operations. The trend is strongly towards more internalization of waste chemical streams, whatever their ori-
gin, within the chemical recovery sides of Kraft mills /1/. In turn, greater demands are placed on pulping itself, on further delignification (e.g., with oxygen) prior to conventional bleaching, and on the minimization of bleaching demands, especially as pertains to the use of chlorine.

In a fortunate accident of timing, Kraft pulping entered a kind of renaissance in the 1980s. Part of the impetus derived from the development of extended delignification /2, 3/, which is now the "leading edge" of new Kraft pulping technology, both continuous and batch /4, 5/. It is also true that many of the new processes of the 1970s proved not to be truly competitive. Not to be forgotten is the sheer momentum created by the versatility, endurance, and ubiquity of the Kraft process worldwide.

It is the hallmark of Kraft pulping that it produces pulps which are strong. Physical strength, more than bleached brightness or freedom from extraneous materials, is the truly unique attribute of Kraft pulps, particularly those from softwoods.

From the mid-1970s through the 1980s, a large body of new knowledge was built on how anthraquinone (AQ) and similar redox catalysts affected alkaline pulping processes such as Kraft. At Pulpex, we contributed in several ways to this new field, one of which was to assess the strength characteristics of alkaline-AQ pulps from a wide range of wood species.

In this work, we followed the conventional wisdom of using Kraft pulping as the "control", i.e., the benchmark against which to measure the merits of the new or modified processes. As a result, we accumulated a large amount of data on Kraft pulping and on unbleached Kraft pulps from many wood species, which we added to that already in our files from earlier work.

The assembly of pulp quality data from the literature suffers from the inevitable differences in experimental procedures and testing methods. By contrast, our information was all obtained via the same methodology, and in the same equipment. We conducted the pilot-plant Kraft pulping in a systematic way as regards chip quality, pulping liquor composition, cooking conditions, pulp processing, and physical and optical testing of the pulps. Because more than three-quarters of Canada's Kraft pulp production is to bleachable grades, most of our work has dealt with bleachable pulps.

With this database of Kraft pulp strength in hand, it was logical to want to compare the physical properties of the pilot-made pulps with those of their industrial counterparts, the unbleached pulps produced in Kraft mills. These comparisons began on an ad hoc basis, but quickly showed that there were consistent and large strength differences. In fact, we had to divide what was ostensibly one kind of pulp into two strength categories: mill-made pulps, and pilot- or lab-made pulps /6/.

Systematic work was begun, with several questions serving as objectives: Where is the potential strength of mill-made Kraft pulp being lost? What is the magnitude of such strength loss? Can means be found to eliminate or minimize the problem?

The progression of research followed a path of discovery which is illustrated here in point form:

- Differences in the conventional physical properties of mill-made and pilot-made unbleached Kraft pulps were characterized /6/.
- The strength loss problem was defined as occurring only in softwood operations /6/.
- The strength loss problem was localized in the digester area (i.e., it was already present in the blown pulp coming to brown stock processing lines) /7/.
- A wide range of Kraft mills — batch and continuous — were found to be well below their pulp strength potentials. The situation was generic, and a significant part of the problem lay in digester discharge mechanics /8, 9/.
- Hanging basket experiments proved that the Kraft softwood pulp from never-blown, cooked chips inside batch digesters at the end of cooking was much stronger than that blown from the same mill cooks /8, 9/.
- The advent of liquor displacement technology for batch digesters brought with it the opportunity to discharge such digesters in a gentler manner. Pumped discharge was tried, and it worked — three-quarters of the pulp strength otherwise lost in hot blowing was regained /10, 11/.

Work continues, now on a broader front and by a handful of research groups, on how best to deliver pulp strength from Kraft digesters, where else strength is being lost along the fibre lines of Kraft mills, and what's the ultimate strength attainable from a given chip furnish.

These topics are addressed below. Each topic is posed as a question, discussed in "highlight" form, and accompanied by references to the detailed scientific information which underlies the general observations and conclusions.

RESULTS AND DISCUSSION

How different are mill-made and pilot-made Kraft pulps?

The answer is that they are surprisingly different in quite a few ways. In how they respond to beating, for example, pairs of mill-made and pilot-made pulps may beat alike, but more often the pilot-plant pulp is progressively more difficult to beat to a given freeness. Fig. 1 shows the latter kind of response for PFI beating of pine/spruce pulps at kappa numbers in the mid-30s. In no case have we seen a pilot-plant pulp which was easier to beat than its mill counterpart.

In tensile strength, mill-produced softwood Kraft pulps can be notably inferior to their pilot-plant controls, but...
not always. Fig. 2 illustrates two kinds of behaviour: Case A, with a substantial tensile strength deficit across the beating range, and Case B, where only a very slight difference was found. The very modest deficit in tensile strength shown in Case B is often characteristic of pulps from Kamyr continuous digesters. It is not always true, however. This points out the difficulty in trying to generalize observations of this kind with total reliability.

As a general means of judging a pulp's overall mechanical strength, tear—tensile performance has been useful over the years /12—14/, and is now in common use. When applied to the comparison of unbleached mill and pilot-plant softwood kraft pulps, tear—tensile curves show that the mill pulps are considerably and consistently weaker /6, 8, 9/.

Tear—tensile curves have become the comparison tool of choice in this work, because they most reliably define strength differences of real consequence to the subsequent papermaking use of so many kinds of kraft pulps. In the cases shown in Fig. 3, the strength gap, illustrated as the difference in tear index at a mid-range breaking length, was found to be no less than 20% and as high as 35%. Based on similar comparisons we've made at many other mills, this gap has rarely been less than 15% /8/. Horng and Forde /15/ reported a value of 25% in their study of a kraft batch digester operation.

The examples in Fig. 3 demonstrate that, regardless of the types of conventional digesters studied, the unbleached softwood pulps coming from them are weaker than they should be. Note that these plots could equally well be interpreted as showing tensile strength deficiencies at constant tearing resistance.

When the pairs of pulps in Fig. 3 were compared in tear index versus bulk, the results were entirely analogous: the mill-produced pulps always had much lower tear indexes at any bulk value.

In all the ensuing work, the term "pulp strength delivery" was coined to focus on what percent of the potential pulp strength inherent in a given wood fibre furnish was emerging at a mill's brown stock washers. More specifically, strength delivery is the ratio of the tear index of the mill-made pulp to that of its corresponding reference pulp (usually a pilot-plant pulp), both interpolated at a constant, mid-range breaking length. The concept is diagrammed in Fig. 4.

Other differences in the physical properties of unbleached mill and pilot-plant Kraft kraft pulps were illustrated in an earlier report /6/, including stretch performance (mill-made pulps initially have more stretch, but quickly lose this advantage upon beating), and fibre length (blown mill pulps usually have lower average fibre lengths than unbleached pilot-plant pulps).

Apart from quantifying the shortfall in the strength of mill-made Kraft softwood pulps, this type of analysis also provides a general framework for adjusting the results of small-scale pulping research to those which are achievable in current mill systems. It should be obvious now that the physical properties of laboratory and pilot-plant softwood Kraft pulps are likely to be much better than can be expected in mills. When new pulping processes or techniques are being evaluated, it is reasonable to assume that the mill-scale versions will produce pulps no stronger than, and possibly quite inferior to, the small-scale products. The ability to "scale" between the research results and their likely implications in industrial operations is fundamental to the usefulness of laboratory and pilot-plant experimentation.

Are softwood and hardwood Kraft pulping operations equally affected by strength loss problems?

Curiously, hardwood operations appear to have an immunity to pulp strength loss. In each of the half-dozen hardwood mills we've examined over the years, whether batch or continuous, the pairs of mill-made and pilot-made pulps have been alike in physical properties /6/. Fig. 5 shows typical cases.

All of these hardwood cases are characterized by furnish dominated by "short-fibred" hardwoods, commonly aspen or the maples. Because the softwood cases always show the
strength delivery problems, one must assume that the much shorter, more flexible hardwood pulp fibres somehow accommodate themselves to the rigors of digester discharge without undergoing measurable fibre damage.

On a speculative basis, a digester cooking only white birch (whose average fibre length in the wood is roughly double that of aspen) might be a candidate to produce unbleached hardwood pulp with inferior strength delivery. To date, we have been unable to test this proposition in a Canadian mill.

Where, exactly, is the strength delivery problem located?

This question was tackled by sampling pulp after every unit operation along a typical brown stock process line, no matter how innocuous that unit appeared at first glance (Fig. 6)/7/. The mechanical strength properties of the pulp did not change appreciably from the blow tank to the brown stock decker, and certainly not approaching the magnitude of the strength deficits cited above.

This should not be surprising — virtually no chemistry and hardly any significant mechanical action occur along such a process line. When these samples were compared in tear—tensile, tear—bulk, and stretch—tensile plots, the same conclusion was reached: the samples were virtually alike. Therefore, we concluded that the maximum strength of unbleached kraft softwood pulp is already established when it reaches the brown stock washers. At best, it then remains unchanged through the rest of the mill. (In fact, it generally declines through a bleach plant, but that part of the story will be told elsewhere).

Thus, optimum kraft pulp strength is determined in the digester area itself. Efforts to improve the strength of these pulps need to concentrate on digester inputs (chips, liquor, heat), operating practices during cooking (especially temperature and chemical gradients), and the mechanics of transferring the cooked chips from the press vessel to the fibre line of the mill after cooking is completed.

How many kraft mills have strength delivery problems?

Apparently, all the softwood ones! In investigations spanning most of the 1980s, every mill we studied had a substantial strength deficit. Fig. 7 illustrates a broad range of strength delivery cases in bleachable-grade softwood mills /8/. More than double this number of digester operations have now been examined, and the picture remains essentially unchanged. A few cases are relatively better than the average in Fig. 7: examples are a high-kappa linerboard base stock operation in a batch digester plant /16/ and softwood sawdust pulp from an M & D continuous digester, both at 87% strength delivery. A bisulphite mill making bleachable-grade softwood pulp had almost no strength delivery problem /17/, demonstrating that the story from kraft mills is not necessarily true in other pulping processes. Several other investigators have found similar results, but few have published their data. Two reports in the mid-1980s concern batch /15/ and continuous /18/ digesters. One can go back through the literature and find a few other examples, but the best work was that done in the late 1950s and early 1960s which led to the development of wash zones at the bottoms of Kamyr continuous digesters /19—21/. An answer to pulp strength loss upon discharge in that era, the work has proved not to be a total solution, in that there is still a widespread strength delivery problem in modern continuous digester systems.
How strong is the pulp still in the form of cooked chips inside a Kraft digester at the end of pulping?

The problem of sampling fully-cooked chips still inside an industrial digester, without damaging the material, generally has been approached by suspending a chip-filled, perforated steel basket inside a batch digester during cooking, then retrieving it after the digester contents have been blown. In continuous digesters, Annergren et al. /21/ responded to the same challenge by piping a specially-designed sampling device through the lower wall of an early Kamyr digester.

The hanging of baskets (Fig. 8) in batch digesters has a long history in the chemical pulping industry, but the record of results is largely relegated to the private files of pulp and paper companies. An early reference to "basket cooking" /22/ contains little numerical information, but does describe the technique and its possibilities.

A hanging basket offers a means of isolating a small unit volume inside a mill's batch digester, thereby providing access to key results which otherwise would be impossible to obtain directly: the degree of delignification at that location, the pulp yield, and the strength of never-blown pulp. While there may be questions about whether such a unit volume truly represents the entire contents of the mill's digester, there is no doubt that the basket technique subjects real mill chips to real mill cooking conditions.

We began our hanging basket experiments in a bleachable-grade softwood Kraft pulp mill equipped with directly-steam-pulped batch digesters of two sizes: 127 m³ and 215 m³ /23/. A schematic diagram of the set-up is shown in Fig. 9, and the strength delivery results are listed in Table 1. In the very first experiment, the startling conclusion was clear: the strength of the never-blown basket pulp was far superior to that of the pulp blown from the digester.

In all succeeding experiments at that mill and at several others, the same general result was true. Whereas the position of the basket (Table 1) and the type of batch operation /8/ influenced the strengths of the basket pulps relative to their (external) pilot-plant reference pulps, the basket pulps were nevertheless always much stronger than the corresponding blown pulps. Obviously, the system and conditions of discharge were the major cause of the missing pulp strength.

The blow-line sampler results in Table 1 pointed out another facet of this type of research: it is possible to sample the discharging pulp in a completely improper way, ending up with material which no longer reflects the true strength of the pulp arriving at the mill's brown stock washers. We stopped doing blow-line sampling.

A fortuitous basket experiment in an indirectly-heated batch digester provided an unusually good example of how resistant cellulose fibres are to chemical degradation in Kraft cooking /8/. A dropped basket had to be cooked twice before it was finally rescued from the digester. Despite a kappa number of 21 and a viscosity of 21 mPa.s, the twice-cooked basket pulp still retained 89% of the tear-tensile strength of its (once-cooked) pilot-plant reference pulp, whereas the (once-cooked) blow tank pulp had only 79% strength delivery (Fig. 10). This demonstrated, unintentionally but dramatically, that although their chemical resistance is high, the fibres are not nearly so robust when subjected to the highly turbulent flow regime of hot blowing.

More recent work with triple hanging baskets has extended the general picture of pulp strength inside Kraft batch digesters at the end of cooking, but the overall conclusion remains the same: never-blown basket pulps are considerably stronger than the corresponding pulps hot-blown from digesters. This generality holds true across a wide range of softwood species, and is not affected by whether the digester is heated directly or indirectly /8/.

One might reasonably assume from this that the pulp (in cooked chip form) coming to the discharge system of a continuous digester is also much stronger than the pulp which reaches the washers. Certainly, continuous digesters can have strength deliver problems every bit as serious as batch digesters (Fig. 7). Whether the problem in continuous digesters is equally heavily weighted to fibre damage during discharge remains untested in modern equipment.

What do the fibres themselves tell us about strength loss?

To gain further insight into the effects of blow-line flow on Kraft fibres, we examined the fibres in a polarized light microscope. We looked at matched
Fig. 10. Twice-cooked basket pulp was weaker than either conventional (kappa 31⁄2) or deliberately overcooked (kappa 20) pilot-plant reference pulps from the same mill chips. Nevertheless, the basket pulp remained significantly stronger than once-cooked, hot-blown mill pulp 7⁄8.

sets of fibres from pilot-plant pulps, basket pulps, and blown mill pulps. A wide range of softwood species were represented.

Figure 11 illustrates the general observations we made 7⁄8. The fibres from pilot-plant and basket pulps (i.e., unblown fibres, A) were relatively straight, and had frequent but small dislocations along their lengths. These dislocations were not gross defects, and caused no significant changes in the direction of the fibre axis. Fibres from blown mill pulps (B), on the other hand, exhibited at least twice as many dislocations per unit length, and up to half of the most severe defects showed axis changes and collapse of the cell wall.

If fibre wall damage of this severity is a routine consequence of blown discharge, then it is no wonder that blown fibres will fail more readily 7⁄23, and papers made from them will exhibit inferior mechanical strength properties.

How can the cooked chips be removed from a kraft digester without significantly damaging the fibres?

This was the obvious challenge posed by the knowledge of the superior strength properties of the basket pulps. Fortunately, also in the mid-1980s, liquor displacement technology was just beginning to be applied to kraft batch digester operations 7⁄24. Quite apart from its advantages in heat economy and in-digester washing, the technology potentially rendered the fully cooked chips less hot and lower in final consistency after the final liquor displacement was complete. This suggested new discharge possibilities.

In the kraft industry, the discharge techniques offered were based on maintaining the pressure in the digester with steam 7⁄25, or pressurizing with compressed air 7⁄24, and then blowing. We experimented with the former type, but found that it offered no improvement in pulp strength delivery 7⁄10.

Instead, we reasoned that it was feasible to render the liquor-displaced, cooked chip mass into a fully pumpable form, and then pump the material to the "blow" tank under conditions designed to minimize all fibre impacts. In applying this approach in the mill, accelerated Sunds “cold-blow” practices of digester filling and cooking were followed 7⁄10. At the end of cooking, however, the displacement of hot black liquor was extended to a theoretical volume of 100%.

The major difference in our system was in the discharge technique and equipment. Specifically, the bottom of a 215 m³ directly-steamed digester was fitted with a new gate valve (for isolation purposes only) and inlet piping to a centrifugal stock pump mounted directly below the digester, as shown schematically in Fig. 12. The pump was designed to transport the suspension of cooked chips and fibre in black liquor at a consistency of 5—7% and a flow rate not exceeding 2—3 m³/h. The mixing zone in the conical section of the digester was controlled via brown stock washer filtrate injection through the same ports used in the liquor displacement operation. From the pump outlet, a new transfer line, 80 cm in diameter, led to a side-wall entry into the existing "blow" tank.

After the cooking and hot black liquor displacement were completed, most of the residual overpressure was removed from the digester via the top relief valve. Then the bottom gate valve was fully opened, the pump was started, and the suspension of cooked material in weak black liquor was pumped from the digester. Pumping from the digester took about 16 minutes to complete. By direct measurements, the consistency of stock in the transfer line was 5—7%, and the temperature was 85—95 °C. Pumping effectively disintegrated most of the cooked chips; the material in the transfer line was primarily fibrous pulp, mixed with fully-cooked, pin-chip-sized particles.

Figure 13 demonstrates the overall strength improvement attributable to
pumped discharge. Based on averages, the pumped pulps had 84% strength delivery (pilot-plant pulps = 100%), whereas the blown pulps were at the 69% level. The basket pulps in this mill averaged 93% strength delivery, so pumping allowed us to regain three-quarters of the strength that was otherwise lost during blown discharge.

If, instead, the average tear-tensile strength of the hot-blown pulp was taken as 100% performance, then the pumped pulps were typically 20% stronger, with some results higher still (Fig. 14).

It should be noted that blowing with compressed air in an RHD system was reported to offer improved brown stock strength too /24/. More recently, pulp strength studies in the same mill, using the pilot-plant referencing technique, have established that the strength delivery is 90% + /26/.

What remains to be done in pulp strength delivery studies?

Surprisingly, perhaps, the field remains wide open. Very few people are active in such investigations, yet the subject's importance in the kraft pulp industry is enormous. Here are some of the possibilities:

- A way must be found to circumvent the strength delivery problems of continuous digesters. Although it is once again well-known that most of them are not as good as they might be, uncertainty remains as to whether the strength shortfall is mainly due to cooking problems within the digesters (i.e., chemistry) or problems in discharge mechanics (i.e., physics). Work is underway in this field. The reinvention of through-the-wall sampling /21/ would greatly help to characterize the strength of the fully cooked chips as they come to the discharge systems of continuous digesters, and thus provide as key a piece of information as basket pulps provide in batch systems.

- What other digester discharge techniques might be appropriate? This topic can lead to endless speculation, but improvements in the discharge systems of industrial batch digesters (e.g., air blowing, pumping) show real promise. As ever more delignification is attempted in kraft pulping, and as more papermaking fibres are recycled, all means of maximizing the original strength in the fibres should be encouraged.

- Hanging basket experimentation has now advanced from single units to assemblies of three /26, 27/. Multiple baskets provide spatial information within a given batch digester cook as regards kappa numbers, pulp yields, and pulp strength. As results become available from such work, traditional questions concerning relationships between variability in kappa number and variability in pulp strength may be answered.

Perhaps it is time for a more precise measurement tool than kappa number. We do not know, for example, the distribution of residual lignin content in the pulp fibre-by-fibre. An automatic analyzer, similar to a Kajani FS-200 instrument but able to do "optical kappa numbers" /28/ on several tens of thousands of fibres in a few minutes, would be ideal. It could open up a whole new era in the understanding of the variability of kraft delignification.

Even so, the probable outcome in terms of mill operations is that kappa number differences within a digester will have to be rather large — say, 10 units or more — before this potential source of strength reduction overshadows that associated solely with digester discharge. The strength of mill-made pulps seems not nearly as sensitive to kappa number as has usually been thought /29/. It remains likely, however, that the impact of physical and chemical factors will continue to determine the strength performance of mill-made kraft pulps.

- Although digester operations account for the biggest strength drop along the fibre lines of normal bleachable-grade kraft softwood mills, other processes have effects too. Oxygen delignification is a commonly suspected one, yet detailed information on strength delivery from high-consistency and medium-consistency O₂ systems is lacking. With ever-increasing numbers of such systems in mills, it is vital to know what they do to pulp strength, and what operating conditions (and equipment?) minimize strength loss.

- A similar general argument holds for all bleach plant operations. It is a certainty that most bleach plants operating on softwood kraft pulps induce some strength loss, perhaps 10% in a tear-tensile sense across a typical five-stage sequence. Yet we
lack well-founded information on which bleaching stages are the most critical to pulp strength delivery, by what amounts, and for what reasons. Are newer types of pulp mixing and transport devices having unintended effects in the chemical and physical environments of real bleach plant operations? A thorough investigation of these considerations is important if one's goal is to deliver the utmost physical strength in the fibres emerging from the bleached end of a kraft mill.

Ultimately, it's the performance of the pulp in papermaking operations, and then the end-use behaviour of the paper itself, which are the crucial tests of the value of most kraft pulps. In an increasingly quality-conscious marketplace, there will be no relief from the demands now placed upon kraft pulps. Interior wood furnishes, old digester equipment, more stressful pulping and bleaching conditions (chiefly for environmental reasons), pressure for higher production rates to justify huge capital investments — none of these will provide acceptable excuses for diminished kraft pulp quality.

What's really required is the philosophy of a "Holy Grail" of kraft pulp quality — that magical combination of all the best options in both the overall process control schemes with the least amount of untested physical forces on fibres as they are processed from wood into pulp and then paper.

If kraft is strong, then this philosophy could be termed "kraftest!" Getting there is the challenge.

SUMMARY

Relative to the physical properties of pilot-plant unbleached softwood kraft pulps, mill-made pulps were found to have considerable and consistent strength deficits. For example, they were usually about 25% weaker in tear-tensile strength. This finding led to a broad characterization of "pulp strength delivery" in kraft mills. Hanging basket experiments in batch digesters then established that the strength losses were mainly due to fibre degradation during blowdown discharge. An alternative — pumped discharge — was engineered for a batch digester operating with liquor displacement technology, and three-quarters of the missing pulp strength was regained. Pulp strength delivery studies are now being extended to bleaching, to the fingering puzzle of continuous digester operations, and to a much closer look at the interaction between variability in cooking and its consequences in pulp performance.

EXPERIMENTAL METHODS AND MATERIALS

These have been written in detail in several of the references cited. See especially references 8, 9—10, 16, 17, and 30.

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