FINAL REPORT

Project Title: Yield Improvement and Energy Savings Using Phosphonates as Additives in Kraft pulp

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Sheldon Verrett, 385 Marshall Avenue, Webster Grove, MI 63119
Tel. (312) 872-2127

Contact(s): Ulrike Tschirner (612) 624-8798, e-mail : Ulrike@umn.edu
Timothy Smith (612) 624-6755, e-mail: smith463@umn.edu

Project Team: DOE-HQ contact: Gibson Asuquo, Project Manager
Beth Dwyer, Financial Assistance Officer
Sheldon Verrett (Industry contact)
Sharon Bartlett (U of Mn grant and Contract Administrator)

Project Objective: Develop a commercially viable modification to the Kraft process resulting in energy savings, increased yield and improved bleachability. Evaluate the feasibility of this technology across a spectrum of wood species used in North America. Develop detailed fundamental understanding of the mechanism by which phosphonates improve KAPPA number and yield. Evaluate the North American market potential for the use of phosphonates in the Kraft pulping process. Examine determinants of customer perceived value and explore organizational and operational factors influencing attitudes and behaviors. Provide an economic feasibility assessment for the supply chain, both suppliers (chemical supply companies) and buyers (Kraft mills). Provide background to most effectively transfer this new technology to commercial mills.

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<u>Section one:</u>

Yield improvement and energy savings using phosphonates as additives in kraft pulp: Industry overview and diffusion potential

1. Introduction

While a Kraft pulping process including the expanded use of phosphonates appears promising in a limited number of mill settings from a technical process perspective, this portion of the overall study aims to examine the market applicability of this innovation. In the following sections, we examine the feasibility of this new potential process within the framework of the innovation adoption and diffusion literature. Buyers of industrial process innovations often resist adoption because: 1. the value of these advances to the firm are obscured by technical and market uncertainties, 2. the risk associated with adoption is heightened as current operations are disrupted, 3. the task is complicated by organizational pressures to meet short term financial performance objectives, and 4. the difficulty in linking advanced technologies to market opportunity is insurmountable (Anderson et al. 1987, Christensen 1997, Dougherty and Hardy 1996, O'Connor 1998, Veryzer 1998). While these obstacles remain, a growing line of research has developed exploring the factors influencing the adoption and diffusion of an innovation - the innovation itself, how information about the innovation is communicated, time, the social/organization system into which the innovation is being introduced, etc. (Rogers, 1995). The market-based applicability component of this research aims to investigate how these major factors interact to facilitate or impede the adoption of this, and similar, innovations by Kraft mills in North America.

The market research study presented below employs a combination of secondary data collection, exploratory interviews, and internet-based survey efforts. Our approach to this study attempts to balance qualitative and quantitative research following a Sequential Exploratory Strategy as put forward by Creswell (2003a, 2003b). This process involves qualitative data collection in an effort to validate measurement constructs and surface additional dimensions impacting the research (Phase I). This technique has been used to explicate the processes that characterize a wide variety of marketing-related activities such as service encounters; personal selling; retail activity; marketing channels; and pricing (Sherry 1991). Following this effort quantitative data was collected in an attempt to explicitly test causal linkages between predictor and dependent constructs of technology adoption (phase II). Finally, based on these findings, we attempt to provide some conclusions as to the potential impact of this technology on yields, costs, and environmental/energy performance of the industry.

2. Overview of the industry

The U.S forest products industry is a world leader in the production of pulp and paper, producing 35 % of the global pulp output and almost a third of the world's paper. Domestically, it is the third largest manufacturing sector. End-consumers and businesses use its product on a daily basis and the sector employs half a million Americans. It is characterized by commodity-pricing and intense competition on cost and the mostly incremental innovation processes reflect the maturity of the sector.

Currently, the U.S. pulp and paper industry is recovering from a major economic downturn and the ensuing consolidation phase, brought on by the development of overcapacity in the late 1990s. At this time, many industry benchmarks start looking more positive – physical output and profits have started increasing and higher capacity utilization rates indicate that the sector has made a turn-around. But the industry continues facing challenges, in particular with regard to energy and material use. The most important issues the industry has to confront are international competition, energy price hikes and increasingly stringent environmental regulation.

a) Physical output, capacity utilization and employment

The U.S. pulp and paper industry is a major global player: In 1997, American pulp and paper mills accounted for more than a third of worldwide pulp production and 16% of all mills across the world (EPA 1997). The industry had a gross output of $ 155.2 billion in 2005 (BEA 2006). The production capacity utilization rates in the entire paper industry stood at 75% in 2005, with 84% for pulp and paper mills and converted paper products at 64% capacity (US Census Bureau 2007). Compared to the US average of 70%, the primary pulp and paper sector was performing relatively well. However, the pulp and paper industry is very capital intensive, i.e., the capacity usage rates closely predicts the rentability of the capital (Buongiorno and Calmel 1988). High capacity utilization rates are a more important predictor of profits than in other sectors.

Table 1: Physical Output of Paper Products, 1998 and 2002. Source: EIA, May 2006b

Physical	1998	2002
Paper Products (Thousand Tons)	87,375	82,679
Total paper	40,606	37,684
Total paperboard	45,171	43,659
Wet Machine Board	81.6	42.6
Building paper	688.6	524.4
Insulating Board	827.4	767.5

In fact, the high utilization rate at this moment is not a consequence of sustained demand, but actually reflects capacity reductions in response to weak markets. In fact, the industry suffered a major economic downturn during the last decade. Physical output fell by 5.4% between 1998 and 2002, with the paper segment the most strongly affected (Table 1). This downturn is visible in the capacity utilization rates, which were as high as 95% for the primary pulp and paper mill segment in 1997, but had fallen to 83% by the year 2000 (US Census Bureau 2007). To maintain profitability, pulp and paper manufacturers had no choice but to reduce capacity by closing the least profitable mills (BEA 2005a).

In a cross OECD comparison, the U.S. pulp and paper sector had a slightly lower than average productivity increase of 1.008 per year (Hseu and Shang 2005). Reflecting the capacity cutback in the industry, the value of shipments in paper manufacturing decreased from $ 168 billion in 1998 to $ 156 billion in 2002 (in 2000 $). This translated into a slight decrease in the share of shipment value in all of manufacturing, from 4.2 %

to 3.9 %. Capacity adjusted value of production decreased from $ 172 billion to $ 160 billion during the same time (BEA 2005b). Currently, gross output is slowly recovering after the downturn in 2001 (Table 2).

Table 2: Gross Output of Paper Products. Source: BEA, 2006

Paper products - Gross Output						
Year	2000	2001	2002	2003	2004	2005
Billion $	162.4	153.6	151.4	148.1	150.8	155.2

While production seems back on track, employment in the industry continues to decrease: According to industry sources, 70,000 jobs have been lost in the pulp and paper industry since 1997, following the closure of 101 pulp and paper mills (AF&PA 2005). The entire U.S. American paper products industry (including downstream industry) has lost 124,000 jobs between 2000 and 2005 (BEA 2006).

b) Industry structure

The pulp and paper industry is characterized by high fragmentation. The largest company, International Paper, controls a mere 11% of the market (Benway 2006). A good measure of industry concentration is the Herfindahl-Hirschman Index (HHI), which is obtained by squaring each company's market share and then adding up the results. Linerboard, recycled board and corrugating medium all have low concentration values of less than 1,000 on the HHI (Urmanbetova 2004). Bleached board used to have a moderate HHI close to the 1,000 level, but recent mergers have catapulted the HHI close to 2,000. Values larger than 1,800 indicate high concentration (DOJ 2007).

Overall, while the industry remains quite fragmented, there has been a recent consolidation trend, driven by volatile prizes. Pulp and paper products are commodities. Export prices follow demand procyclically (Rusko 2005) and price volatility and competition in the market are extremely high. Anticipating growing exports to Asia, pulp and paper manufacturers had been adding capacity during the 1980s and early 1990s.

When real exports stayed well below expectations, prices fell to historically low levels in the mid-1990s. On the one hand, given this environment, any innovation providing significant cost reductions should be welcome. One the other hand, innovations requiring major production interruptions may be disadvantaged.

One way pulp and paper companies have reacted to price volatility is by specialization (Benway 2006). A company occupying a specialized market niche generally can count on more stable prizes. In the last decade, mergers and capacity reduction were the other prevalent strategy to deal with price volatility and excess capacity. Recent years have seen major restructuring in the industry, especially in the linerboard and bleached board sector, where the three largest companies – Smurfit-Stone, Weyerhaeuser and International Paper – now control a third of the market (Utichelle 2000). All three companies have closed their least productive mills after the acquisitions or mergers. Linerboard prices are forecast to attain a minimum price of $ 530 per ton in 2007 (Scotia Capital 2007), up from $ 340 in 1998. Pesendorfer (2003) found that horizontal mergers in the paper industry in the 1980s were profitable, with merging firms increasing efficiency. In the last decade, the industry fell back on this time-tested pattern.

c) Innovativeness and productivity

The pulp and paper industry is a mature sector, whose innovative activity is primarily concentrated among suppliers rather than pulp and paper firms themselves. This is especially true in the context of industry consolidation and recession in the late 1990s, when internal R&D budgets experienced a sharp drop (TAPPI 2001). Historically, the pulp and paper industry evolved in innovative spurts, which in turn generated structural change (Toivanen 2004): In the early development stages of the industry, technical innovations created barriers of entry at several instances. Monopolistic or oligopolistic conditions reigned for a certain period of time, until patents expired, other firms caught up through imitation and standardization and government regulation undercut the concentration of market power. This generally resulted in a stronger focus on economies of scale and scope and on lowering production costs during the middle part of the last century, following a typical product life cycle. Structurally, consolidation and increased reliance on specialized machinery and material producers for innovation accompanied this process. In line with these findings, Bengston and Strees (1986) showed that intermediate inputs in the pulp and paper industry are non-neutral. Technical change of input materials has a positive effect on productivity.

The externally driven innovation mode of the pulp and paper industry is not solely a U.S. phenomenon. Diaz-Balteiro et al. (2006) found that there is no significant link between innovative activity and efficiency for Spanish pulp and paper mills, indicating that these firms rely on the acquisition of external knowledge embodied in machinery and materials. Overall, productivity increases in the U.S. pulp and paper industry appear to be determined more strongly by technical change than by efficiency increases. In a cross OECD comparison, the U.S. had average productivity increases, the lowest efficiency increase of all countries and above average technical change rates over the period of 1991 to 2000 (Hseu and Shang 2005). This means that technical innovation is the main driver of productivity growth in this sector.

Little of this technical change is radical, a typical characteristic of mature industries. In fact, when facing environmental regulation of dioxin emissions, the pulp and paper industry displayed a strong inclination towards incremental innovation (Norberg-Bohm and Rossi 1998). In a survey of Georgia pulp and paper firms, Youtie et al. (2006) found that innovation in the industry is mostly supply-chain and business-process oriented and not so much knowledge oriented. Part of this preference for incremental innovations stems from a static regulatory regime, but it also results from industry structure, in particular capital intensity, and the fact that existing production practices have not been challenged excessively by environmental regulations. There still seems leeway for improvement, before switching to a completely different technology.

The diffusion of radical technical innovations has not always followed the same paths or timelines across pulp and paper-producing countries. Recycled wood-fiber use first took off in Scandinavian and European countries before gaining importance in the U.S. and Canada, as did chlorine free bleaching. Consumer preferences and regulatory incentives are some of the important reasons for these differing pathways (Reinstaller 2005).

Currently, industry research appears to grant the most attention to energy and environmental performance, as well as product quality and production cost. The Agenda 2020 Compact between the forestry products industry and the Department of Energy defined six strategic areas for innovation, focusing on raw material supply, manufacturing costs, human capital, energy efficiency, environmental performance and new product development (TAPPI 2001).

3. Resource Use, Energy Use and Pollutant Discharge

The pulp and paper industry requires large amounts of energy, water and raw materials. It is also a major emitter of greenhouse gases and air and water pollutants toxic to humans and/or ecosystems. The last twenty years have seen major efforts by the industry to reign in energy and water consumption, as well as to address pollution issues. Currently, the possible advent of a carbon-constrained economy, combined with rising energy prices, constitute the biggest challenge for the sector.

a) Resource use and pollutant discharge

Since its beginnings, the industry has made major progress in reducing the use of virgin wood fiber and water, but remains a major consumer of both. In a paper mill, roughly 200 tons of water are needed to produce 1 ton of paper (Garner 2002). Freshwater consumption, however, is much smaller, because most mills today operate in closed circuits: they clean and reuse the water used during pulping, decreasing their production costs in the process. In fact, between the mid-1970s and the mid-1990s, the amount of water consumed to produce a ton of paper was reduced by 65% (Encyclopedia of American Industries 2007).

Recycled fiber use has become widespread in the industry, both because larger amounts have become available on the market and because the industry has realized that provisions of virgin fiber might be limited in the future due to environmental regulations or simply supply constraints. The use of recycled fiber has important implication for kraft pulping, the most widely used method of pulping in the U.S. Its importance is likely to increase in the future, driven by the greater use of recycled paper fibers (Encyclopedia of American Industries 2007). These fibers are weaker than virgin wood fibers and as their share in mill input rises, chemical pulp gains importance as an ingredient to obtain greater overall strength. Kraft pulp is also blended with weaker mechanical pulp to provide the desired strength.

The pulp and paper industry also emits a substantial amount of greenhouse gases and pollutants toxic to humans and/or ecosystems. Most of these pollutants are emitted to the air and some are discharged via water releases. In 2004, pulp and paper mills released 228.5 million pounds of chemicals reportable under the Pollution Prevention Act of 1990 (EPA 2004). In 1994, the sector emitted 31.6 million cubic tons of CO_2 (EIA 2000). A third of these emissions or 11 million metric tons of carbon (MMTC) come from electricity use, most of the rest is due to cogeneration from natural gas (8.3 MMTC), coal (7.8 MMTC) and residual fuel oil (3.7 MMTC). Overall, most criteria air pollutant emissions stem from energy use, but a considerable share of hazardous material air and water pollution is associated with chemical use. The sector's carbon intensity stood at 11.88 MMTC per quadrillion Btu.[1]

More stringent environmental regulations and a possibly carbon-restrained economy increase the likelihood of even higher portions of combined heat and power generation at pulp and paper mills in the future (Khrushch et al. 1999). Likewise, generation from biomass will gain importance. More stringent environmental regulation may also create additional incentives for introducing emission reducing process and equipment innovations.

b) Energy use

At 275 thousand GWh of primary energy use in 2002, pulp and paper production ranked 4th among all industry sectors (EIA 2006a). Only chemicals (737 thousand GWh), petroleum and coal products (693 thousand GWh) and primary metals (304 thousand GWh) – all heavy, energy-intensive industries – used more energy than pulp and paper production. Energy use is driven by boilers needed for process steam and onsite electricity generation. An overview of the forest products[2] industry's energy footprint

[1] Does not include emissions from black liquor and biomass gasification, which are considered carbon neutral.

[2] Note: EERE does not differentiate between the wood products and the pulp and paper industry, so the actual percentage could be different. Another source (EIA 2005) indicates, however, that if at all different, heating process energy use is higher for pulp and paper than for wood products, where machine drives are more important energy consumers.

(EERE 2006) shows that process heating (steam systems, heat exchangers, condensers, fired heaters, heat pumps) accounts for roughly 80% of process energy use in the machine drives account for another 19% of process energy use. Any innovation reducing the temperature or time required for cooking processes could mean major reductions in overall energy use.

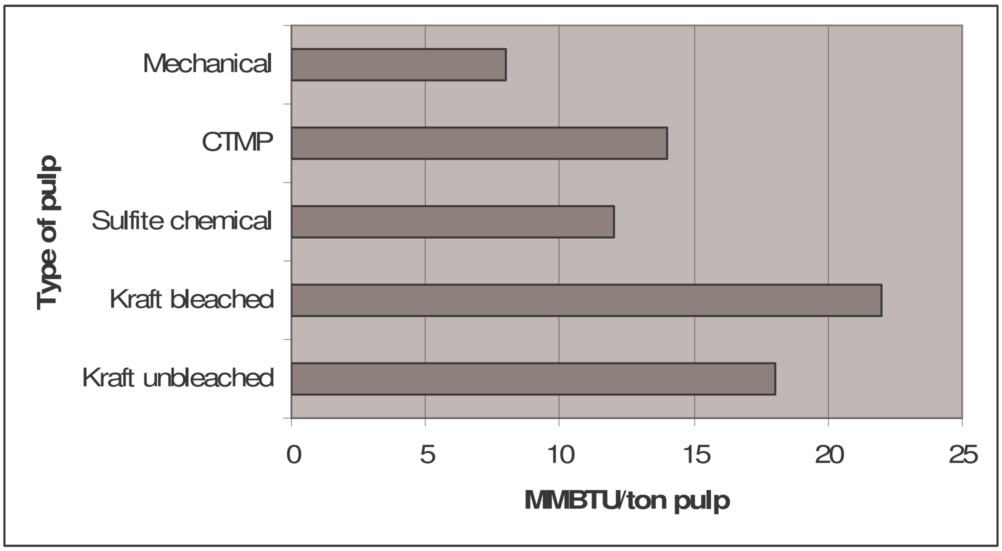
Energy costs hold a considerable share in the total expenditures of a pulp or paper mill. The industry spent about $ 3.05 billion on electricity purchases in 2002 and a total of $ 7.2 billion for all energy expenditures (EIA 2002). Pulp milling counts among the most energy-intensive manufacturing sector, with 56 thousand BTU consumed per dollar of value of shipment in 2002 (idem). Only alkalies and chlorine, fertilizer, lime and cement production are as energy-intensive or more so.

Considering these numbers, it is not surprising that the pulp and paper industry is the largest co-generator in the U.S. manufacturing industry, with almost 50 billion kWh generated on site in 1998 (EIA 2004). In the kraft pulp process, the lignin-rich black liquor remaining after the pulping process is burnt to recover added chemicals and to generate steam. Most mills use both biomass and fossil fuels for co-generation. Between 1972 and 1997, the industry has increased its share of cogeneration by almost 40% (AF&PA 1997).

Apart from biomass generation, mills draw most of their energy needs from natural gas and oil. They also buy electricity. In 2002, the sector was the fourth largest consumer both of natural gas, at 490 billion cubic feet, and electricity, at 65.5 billion kWh (EIA 2002). It also used 18 million bbl of residual and distillate fuel oil. It can be expected that the price of these fossil fuels will remain at sustained levels in the near future. Globally, demand for oil is growing at a ratio of approximately 1.6 % per year (OECD/IEA, 2002). Demand growth coincides with intensifying energy dependence throughout the OECD (OECD/IEA, 2003) and increasing uncertainty about the longevity of oil supplies and access to these supplies. In a similar fashion, average industrial prices for natural gas have increased by 50% between 2001 and 2006, from $ 5.24 per Thousand Cubic Feet in 2001 to $ 7.89 (EIA 2007). The production method most vulnerable to higher energy prices is kraft pulping, because it has significantly higher energy needs than all other types of pulping (Table 4). Rising prices for primary fuels and electricity will likely result in further increases in co-generation activities. Price signals may also focus managers attention on energy efficient process and machinery innovations.

The industry has already made some progress in reducing its energy use. Between 1973 and 1991, it attained an annual percentage decrease of 0.9% in electricity consumption. While the industry is becoming less energy intensive, the reductions (weighted for production mix) are not as large as in most other OECD countries (Farla et al. 1999). This suggests that there is still leeway for energy efficiency improvements.

Figure 1: Energy intensity for different types of pulping processes. Adapted from Garner 2002



This is also indicated by an energy assessment carried out by researchers at the Georgia Institute of Techonology (Jacobs Greenville / IPST 2006), who found that state of the art mills use about a quarter less energy than the average mill and advanced technologies could drive energy savings up to more than 40%. In terms of fossil fuel use, this translates into a 46% consumption gap between top and average performers and up to 75% savings compared to the status quo for advanced technologies.

Industry analysts see energy prices as the main driver of change at this point (Jopson 2004). Many firms already implement a number of energy management strategies. Energy efficiency programs have typically focused on technical improvements in the machinery, for instance through steam and heat recovery, ameliorated insulation or variable speed drives (CADDET 2001). Increased co-generation and fuel-switching are also classic strategies. Consistent energy management can lead to roughly 5-15% improvements in energy and water use, as well 1% raw material savings (Garner 2002). Process improvements constitute the second pathway for improved energy efficiency. Given that process heating is the main driver of energy use in pulp and paper mills, it represents an ideal target for process improvements. Cooking, evaporation and drying represent 60 to 80% of the steam required in the entire kraft pulping process (CADDET 2001). A third pathway for energy efficiency improvements is energy benchmarking and purchasing management (Francis et al. 2002).

The high capital cost of energy efficiency investments can be an obstacle to such investments. In fact, there is often a gap between actual investments and those that appear to be profitable: both consumers and firms under-invest in energy efficiency, implicitly assuming high discount rates (De Canio 1998, Golove and Eto 1996). This phenomenon is called the efficiency gap. In the business sector, an important cause of underinvestment are the hidden costs and the risks inherent in such investments. Installing energy efficient equipment can require changing the entire production process and may result in major disruption of production.

In that sense, any innovation that does not require excessive change of equipment, but instead focuses on changing inputs, might not suffer from an equally large diffusion barrier. With regard to pulp mills, it can be expected that the diffusion barrier for input innovation (e.g., chemicals, materials etc) is lower than the one for equipment innovation. Changed inputs generally require little or no changes to production processes compared to installing new equipment. In line with this argument, many R&D projects already focus on innovations not requiring changes in equipment. In particular, hopes have been set in biotechnology as a means of energy conservation in pulp and paper production (Bajpai and Bajpai 1998).

It is important to realize that most technical improvements are not installed for the sake of energy performance alone, but are often linked to other objectives, such as yield or environmental performance. In fact, energy saving technologies that also grant other benefits, such as improved process control, better environmental performance or higher product quality are more likely to gain acceptance among pulp and paper manufacturers (Nilsson et al. 1996).

4. Outlook for the diffusion of innovation in the kraft pulping sector

The literature on technology innovation distinguishes between the invention, innovation and diffusion stages (Utterback and Abernathy 1975, Nelson and Winter, 1977, Gort and Klepper 1982). Invention describes the act of coming up with a new product or process. Diffusion means the dissemination of a product beyond a small group of original suppliers and users (innovation) and ultimately, the adoption of a technology by the majority of firms and consumers. Consumer behavior, regulatory barriers, but also internal institutional barriers in firms can hinder diffusion of new technologies.

While this research borrows substantially from prior technology research, specifically the works of Chandy and Tellis (1998) and Grewal et al. (2001) focusing on "radical" innovations, these frameworks have been expanded to examine issues specific to the "non-radical" nature of this important technology and to explicitly address the unique environment associated with the kraft pulping process. Rather than relying on a single research approach, we employed a mixed research design in this project, attempting to mix the best of qualitative and quantitative research. Philosophically, mixed research takes an eclectic, pragmatic, and commonsense approach, suggesting that the researcher mix quantitative and qualitative in a way that works best for the given research question being studied in a particular context. Mixed research uses both deductive and inductive methods, obtains both quantitative and qualitative data, attempts to corroborate and complement findings, and takes a balanced approach to research.

Specifically, we employed a mixed method design in that we use a qualitative research paradigm for one phase and the quantitative research paradigm for a different phase of the study. We employ this technique primarily due to the fact that certain variables cannot be defined with indicators prior to conducting the study, because the information to do this is lacking. The purpose of Phase I of the study is to help identify this information. Therefore in this phase, we are not primarily interested in measuring variables, but rather identifying variables or clusters of variables that help explain a chemical technologies adoption in the paper industry and/or reasons for its success or failure. In that case, the researcher will often try to find indicators that make the variables measurable. By better understanding these themes we can now give an operational definition of the strength of adoption likelihood, the integration of consolidation activities between merged firms, or the degree to which process innovations are disruptive on a scale. This enables us to measure through a quantitative study the degree of adoption likelihood, and the most important contributing factors to it.

5. Phase I – Qualitative Interviews and Identification of Themes Associated with Incremental Process Adoption in the Pulp and Paper Industry

For the qualitative portion of the study we employed a “grounded theory” approach in that our goal was the development of inductive, "bottom-up," theory that is "grounded" directly in the empirical data (Galser and Strauss 1967, Strauss and Corin 1987), in this case preliminary interviews with kraft pulp/paper personnel involved in process technology adoption within their mill. Interviews were conducted between February and April 2004. Following standard interview protocol, data was collected at four company sites, and it is believed that a reasonable level of data saturation was reached through these interviews. Based in large part on the work of Higgins & Hogan exploring internal diffusion of high technology industrial innovations, interviews were scheduled across multiple functions with each mill, including engineering, general management, marketing and procurement, and research and development staff. For the purposes of this phase of the project, we searched for kaft pulp & paper mills within reasonable proximity of St. Paul, Minnesota in an effort to reduce cost and ensure exposure to mills utilizing significant aspen furnish. Accordingly, we identified mills in Minnesota, Wisconsin, Michigan and Ontario (Canada) for interviews. The mills were:

1. SAPPI, Minnesota Pulp & Paper Division, Clouquet, MN
2. Boise Paper Solutions, International Falls, MN
3. Domtar Industries Inc., Nekoosa, WI
4. International Paper Company, Kakuna, WI

Within this methodology, data analysis typically proceeds through a process of open coding (i.e., reading transcripts line-by- line and identifying and coding the concepts found in the data), axial coding (i.e., organizing the concepts and making them more abstract), and selective coding (i.e., focusing on the main ideas, developing the story, and finalizing the grounded theory). The grounded theory process is "complete" when theoretical saturation occurs, when no new concepts are emerging from the data. Table xxx provides a summary of the themes emerging from this process.

Table 3. Themes from Qualitative Data

ILLUSTRATIVE QUOTE	AXIAL CODING	SELECTIVE CODING
"In a established mill it is very hard, because one mistake goes a very long way."	Organizational Size	
"we are not adverse to trying something new if we think there is a promise for benefit for us and we don't think it will not negatively impacts our end users." "[If] a mill is almost dying…they are more likely to try something as compared to an established mill."	Institutional pressures towards innovation	
"the mill has the right to say that we don't want it. "if the dollars are high enough and there is a marketing need, then it comes [from] a higher level…it gets passed on… In that case, it is going to be a little bit easier…"	Self Governance	Organizational
"if you're going to go into that market you need to have the right equipment to do it properly…you make a decision to go to a market and you have a strategy and you need to add technology and capitol to do those	Future Market focus	
"we have a process that we like to call it the [xx] process, which is essentially using a lot of problem solving techniques to decide what are the best solutions to different issues… we like to track the savings we create, but it	Innovativeness	
"survival of this industry is to compete globally, if we don't find ways to reduce our costs…, to up quality, to hopefully gain more market share, we won't survive"	Market Turbulence	
"if you want to change the process, then there is a lot of capital involved in that, and that is not a continuing "from the standpoint of finding lower costs and making process improvement and process changes to do that or to quality improvement that don't necessarily increase costs, those are very high focus and aggressively pursued."	Technology Turbulence	Environmental
"It's now definitely more of a global competitive marketplace…Our quality needs to be better we need to be able "because competition is bigger, because you are not only consolidating, so stakes get a little higher…"	Sector Competitiveness	
"as consolidation takes place we have got more resources. You are getting bigger, Ok the you can tackle bigger projects."	Merger and Acquisition Activity	
"in terms of process conditions, that's an ongoing term, in terms of better Ti02, better clay, better defoamer, Ok, that's a ongoing process. But, if you want to change the process path, that doesn't happen often enough… that is "we like to have preferred vendors who offer a great amount of service to us… they also come and provide us with very new ideas and new technology since they already know the process, they come to us with ideas, not	Innovation Scope (Incremental/Radical)	Technical
"[process improvement] is really grounded in the mill… it can be approved or disproved at the mil level… if it's over a certain dollar amount, it'll go to corporate [for] capital and… go to the senior manager of the major division and they will say yes or no. It is mostly, I would say in my opinion, financially driven." "we are always looking for production enhancements… the more tons we make, the more we get to spread out your fixed costs across those tons, and lower the apparent cost per ton… those type of things are generally the	Innovation Breadth (process/product)	

6. Phase II – Quantitative Survey Data of Innovation in the Pulp and Paper Industry

In combination with the qualitative study described above, we developed a quantitative questionnaire utilizing a combination of previously validated multi-attribute scales and unique measures related to the kraft pulp industry to accomplish the technology adoption assessment objectives of the study. The survey was administered in August of 2005 and resulted in 43 responses from the North American Pulp and paper industry, representing a response rate of approximately 15% of mill personnel surveyed.

Specifically, constructs explored through Phase II data collection are organized into environment, technological, and organizational dimensions. The intent is to understand the relationships between the constructs, gauge their relative contribution to technology adoption, and surface industry-specific catalysts and/or barriers impacting the adoption of incremental process innovations, specifically the adoption of phosphonate additives.

a) Overview of constructs

Environmental Constructs:

We explore environmental influences on technology adoption through the constructs of market turbulence, technology turbulence, and sector competitiveness and consolidation. Preliminary research in the area of technology adoption in the pulp and paper industry has identified positive relationships between each of the above constructs and adoption.

Technological Constructs:

Innovations that contain a high degree of new knowledge compared to a current technology, and ones that represent a clear departure from existing practices are generally considered to be radical innovations (Dewar and Dutton 1986), whereas those that can be adopted with only minor changes in business practices are considered incremental (Nord and Tucker 1987). Given this definition, it becomes clear that classifying phosphonate additives neatly into one category or the other is contingent on the operational context of the adopter. Similar to radical/incremental innovations, new technologies also have the potential to operate as both a product and process innovation depending on the strategic intent of adaptors and how the technology is used by the organization. While the vast majority of recent research has focused on radical product innovation, we hypothesize that the majority of kraft mills adopting phosphonate additives will do so within the context of incremental process adoption, representing an under researched area of study.

Organizational Constructs:

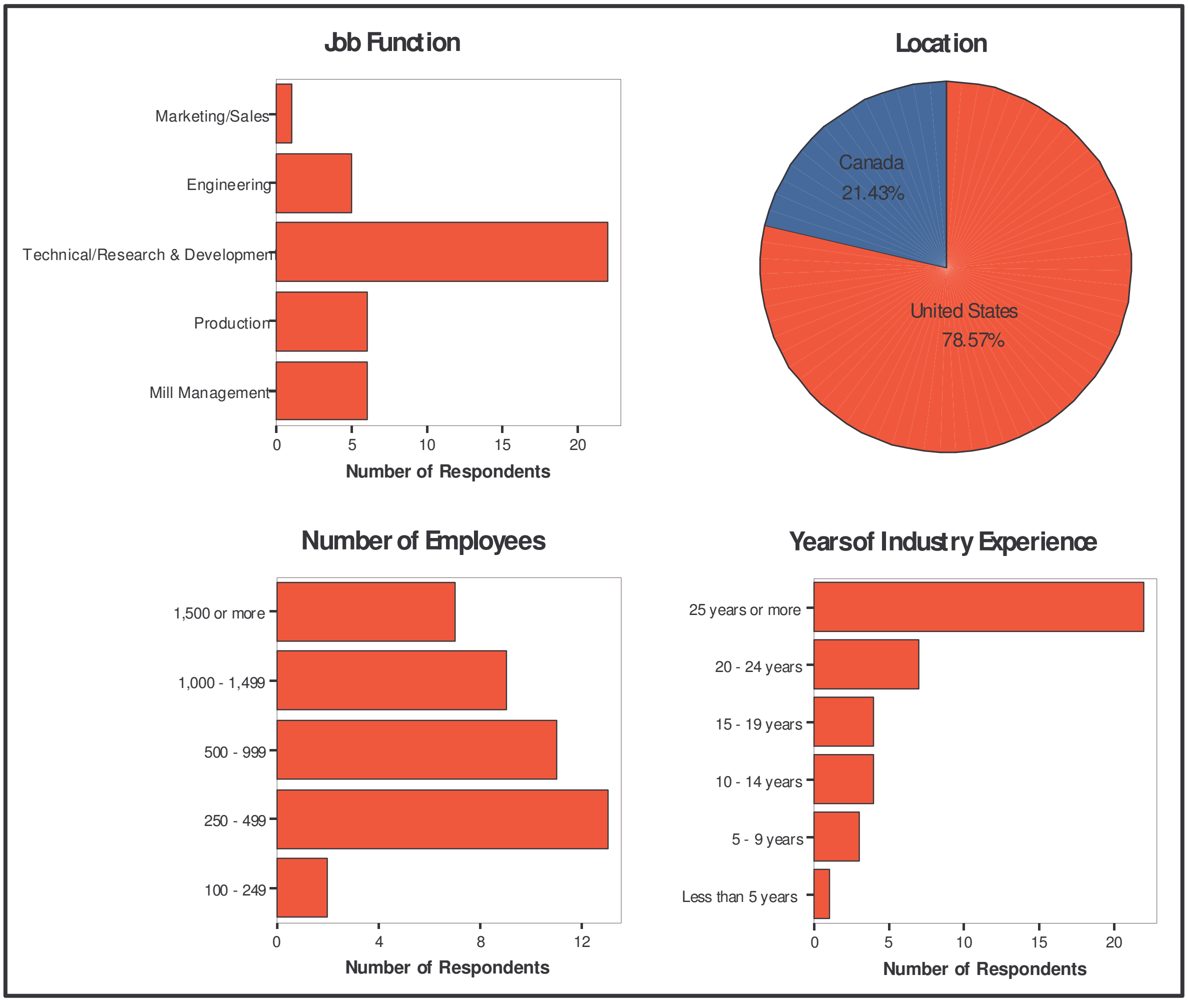
The impact of organizational factors influencing technology adoption are operationalized by the constructs of organizational size, institutional pressures toward innovation, self governance (autonomy), future market focus, and innovativeness. While much of this work has been conducted in a high-tech environment focused on radical new products, we remain interested in exploring these constructs in the pulp and paper setting.

b) Respondent Profile

Data was collected through an electronic survey during May 2005, resulting in a total of 43 responses (15 % response rate) from Kraft pulping mills in North America. Over half of respondents (56 percent) identified themselves as technical or research and development (R&D) employees; those working as engineers and in the production areas encompassed 12 and 14 percent of total respondents, respectively. Finally, 14 percent of respondents are mill managers and the remainder work in sales and marketing. As presented also in Figure 2**,** the majority of respondents represent mills within United States (78.57 percent) and the rest (21.43 percent) are located in Canada.

In terms of mill size, only 2 mills reported mill employment of less than 250 employees. About 80 percent of them have between 250 and 1500 employees with the largest category being mill size of 250 – 499 employees. The remaining 17 percent of companies have more than 1500 employees. Regarding their professional experience, over half of total respondents (53 percent) have more than 25 years working within the pulp and paper industry, and 19 percent have between 20 and 25 years of experience. Thus, the sample represents significant knowledge of the industry with over 90 percent of respondents having 10 years or more experience in the industry.

Figure 2: Profile of Respondents



c) Incremental and Radical Process Innovation

Respondents were asked to rate the importance to their organization of adopting a chemical or mechanical process technologies. More specifically, they were asked to rate the importance of adopting each technology type if it is characterized by an incremental process innovation or by a radical process innovation. On a 7-point interval scale, where 1 equals "Not at all Important" and 7 equals "Very Important", respondents considered that adopting *incremental* process innovations is significantly important for their organization. This result is true for both chemical and mechanical types of technologies.

As shown in Table 4, incremental innovation for chemical processes was rated at 5.7 and for mechanical processes was rated at 5.51, both significantly higher than the scale's neutral value of "4". When considering the importance of adopting *radical* process innovations, respondents considered them neither important nor unimportant for both, the chemical and the mechanical, technologies. Radical innovation for chemical processes was rated at 3.67 and for mechanical processes was rated at 3.81, both are not significantly different than the scale's neutral value of "4".

The above results are in concert with the actual budget allocations made by these companies on each of these types of technologies and process innovations within the last two years. As presented in Table 5 below, the majority of this budget was destined to incremental innovations in both, the chemical processes (i.e. 41.63 percent), and the mechanical processes (i.e. 36.63 percent). During the past two years, radical innovations just received about one fifth of this total budget, including 9.65 percent allocated to chemical technologies and 12.09 percent allocated to mechanical types of technologies.

Table 4. Comparison of Project Types by Importance

Importance of Technology Projects:	N	Mean	Sig. [1] (2-tailed)	Std. Error
Chemical Process Improvement Technology				
Incremental Innovation	43	5.70	0.001	0.168
Radical Innovation	43	3.67	0.193	0.246
Mechanical Process Improvement Technology				
Incremental Innovation	43	5.51	0.001	0.168
Radical Innovation	43	3.81	0.425	0.231

[1] Significance based on difference from scale neutral value of 4.

By taking a closer look to the lower and upper bounds, it is useful to consider the percentages of budget allocation in terms of median values as opposed to mean values alone. This is especially important to radical innovations in the mechanical processes improvement technology, where a median value of 5 percent possibly represents a more accurate assessment of central tendency compared to its mean value of 12.09 percent.

Table 5. Comparison of Technology Budget across Project Types

% Technology budget spent on (last 2 years):	Mean	Median	Lower Bound	Upper Bound
Chemical Process Improvement Technology				
Incremental Innovation	41.63	40	35.32	47.93
Radical Innovation	9.65	10	6.37	12.93
Mechanical Process Improvement Technology				
Incremental Innovation	36.63	35	30.02	43.23
Radical Innovation	12.09	5	6.62	17.56

d) Factors affecting technology adoption

Technology adoption was examined through a series of regression analyses for both incremental and radical innovations. The technology adoption variable (i.e. dependent variable) in our model is the product of the budget (as a mean percentage) identified to a specific innovation, multiplied by the number of projects within each specific innovation (i.e. incremental or radical). Thus, adoption is specified as

Technology Adoption X = (% of the budget destined to innovation X) * (Number of X innovation projects)

Where: X could be either incremental or radical.

Table 6 below presents the results of our analysis on the adoption of *incremental* technologies. One important organizational aspect that drives incremental innovation (0.407; p-value= 0.002) is the way a firm faces innovation opportunities, by taking risk, cannibalizing current product offerings and taking the lead within the industry. The "firm learning" capacity or knowledge shows also as a significant coefficient influencing the adoption of incremental innovations (-0.232; p-value= 0.064).

Furthermore, an important number of paper companies currently face consolidation situations and it is hypothesized that recent merger activities and the degree of integration of activities post-merger might positively impact innovation within the firm. We assess the influence that these mergers have on the company's technology adoption rates by considering several potential organizational aspects that are affected by mergers. Specifically, we are interest if (a) Technology/Production processes; (b) Pricing decisions; and (c) New product development process, after a merger influence the rate incremental innovations are adopted. Results indicate that *pricing decisions* and *new product development process,* both, significantly affect the adoption of incremental technologies.

Finally, at 90% confidence level, project champions and the size of the mills, both, were also important in the adoption of this type of technologies.

Table 6. Regression Coefficients for Model of Incremental Technology Adoption

Model: Incremental Tech Adoption (Adj. R^2 = .488)	B	Std. Error	Sig.
(Constant)	3.968	1.859	0.045
Firm Innovativeness	0.407	0.115	0.002
Firm Learning	-0.232	0.118	0.064
Technology/Production processes recently merged	0.308	0.213	0.164
Pricing decisions recently merged	0.592	0.318	0.076
New product development recently merged	-0.716	0.354	0.056
Mill size (number of employees)	-0.491	0.265	0.078
Importance of project champions	-0.438	0.249	0.093

Several other factors were also considered in the analysis, nevertheless, through the stepwise regression analyses, no significant effects were detected. One example is the level of autonomy that a mill has from its corporate office, which does not seem to affect the rate, in which either incremental nor radical, innovations are adopted.

When we specifically considered the adoption of *radical* technologies as opposed to incremental ones, several others factors present significant effects. For example, as shown in Table 7, considering the satisfaction of future customers' needs and wants is a key factor companies ponder when adopting radical technologies (0.443; p-value= 0.030). The way a firm faces innovation opportunities, by taking risk, cannibalizing current product offerings and taking the lead within the industry, also are significantly important when adopting radical innovations (0.158; p-value= 0.026). Likewise, the size of the mill is considered important when adopting radical technologies; however, neither the technological turbulence of the industry, the role of project champions nor the influence of sales systems after a recent merge, influence in any way the adoption of radical technologies.

Table 7. Regression Coefficients for Model of Radical Technology Adoption

Model: Radical Tech Adoption (Adj. R^2 = .316)	B	Std. Error	Sig.
(Constant)	-10.287	3.353	0.006
Firm Future Customer Focus	0.443	0.190	0.030
Firm Innovativeness	0.158	0.066	0.026
Sales systems recently merged	0.394	0.212	0.077
Information systems recently merged	-0.324	0.199	0.117
Mill size (number of employees)	0.622	0.265	0.029
Technology Turbulence in industry	0.191	0.112	0.104
Importance of project champions	0.283	0.201	0.173

7. Utility-based System Design Analysis

Another primary objective of this research was to examine the trade-offs associated with the potential benefits of using phosphonates as additives. Toward this end we conducted a conjoint analysis of four product attributes each having three levels of possible outcomes. Conjoint Analysis is a procedure for measuring, analyzing, and predicting customers' responses to new products and to new features of existing products. It enables us to decompose customers' preferences into "part-worth" utilities associated with each option of each product attribute. We can then recombine the part-worths to predict customers' preferences for any combination of attribute options, to determine the optimal product concept or to identify market segments that value a particular product concept highly.

This technique is particularly useful in that the analysis is conducted at the individual level and the performance gains associated with using the product can be thought of as a series of trade-offs. Based on a set of orthogonal product profiles, sixteen cost/benefit scenarios related to the use of phosphonates as additives in the pulping process were rated by respondents. In close consultation with research colleagues, profiles were developed using the following criteria:

Cook Time (at 170 degrees C) is reduced by either:

- 40 minutes
- 30 minutes
- or, 20 minutes

Yield Improvement is either:

- 1-2 percent
- 2-3 percent
- or, 3-4 percent

Bleaching Chemical Cost Savings of either:

- 30 percent (from current costs)
- 20 percent (from current costs)
- or, 10 percent (from current costs)

Price paid to suppliers for the phosphonate is either:

- $6 per air dry metric tonne (ADMT) of pulp production
- $8 per air dry metric tonne (ADMT) of pulp production
- or, $10 per air dry metric tonne (ADMT) of pulp production

Preliminary, average part-worth estimates are provided below. The average part-worth of each attribute option across the selected respondents gives a good indication of the attribute options that are attractive to the selected group of customers as a whole.

Table 8: Average Part-Worth Utilities

Criteria	**Average part-worth**
Cook Time	
40 minute reduction	12.72
30 minute reduction	10.34
20 minute reduction	0
Yield Improvement	
3-4 percent	29.04
2-3 percent	7.28
1-2 percent	0
Bleaching Cost Savings	
30 percent	6.72
20 percent	8.78
10 percent	0
Price	
$6 per ADMT	17.12
$8 per ADMT	8.66
$10 per ADMT	0

While part-worth utilities are not comparable between attributes, the differences between part-worth utilities within attributes can be compared to differences in other attribute categories. For example, the difference between $10 per ADMT and $8 per ADMT is valued, on average, by respondents similarly to the difference between bleaching cost savings of 10% and 20%. Therefore, yield improvement, particularly at improvements in the 3-4% range (against the benchmark of 1-2 %) are valued at more than two times the value of 40 minute reductions in cook time and three times the value of a 20% reduction in bleach savings (against their respective benchmarks).

8. Market potential

In order to assess the potential market impact of phosphonate additives, it is important to gain an overview of the mills prospectively amenable to phosphonate addition. As a final step in the analysis, we identified firms in which the technology examined is applicable.

A list of promising pulp and paper mills was compiled using the *2004 Lockwood Post Directory of Pulp and Paper Mills* (Beuingen et al. 2004). This industry directory lists every pulp and paper manufacturer in the US and Canada, including contact information, mill size, production volume, and different attributes about the mills' production. The two primary selection criteria were the use of a kraft pulping process and of hardwood species. The addition of phosphonates did not work equally well for softwood species. Consequently, mills using solely this wood type were eliminated from the list.

The list was further narrowed down to only those mills located within the natural range of aspen, the wood species for which the results looked most promising. In North America, aspen ranges in a continuous path from the Atlantic coast as far south as Virginia up through Canada reaching Alaska and the Arctic Circle (Johnson 1999). The initial determination was based on Isenberg's (1981) Aspen growth range map, which indicated aspen growth primarily in Canada and the northern U.S. states, including both the east and west coasts. To account for potential range shifts, this map was checked against the Aspen range depicted in a more recent map of the distribution of all forest types (U.S. Department of the Interior 2006). No significant shifts were found.

The location of aspen growth patterns was then checked against the locations of each mill and mills outside the Aspen range were eliminated from the list. In total, the final list included 43 mills. 26 of these mills were located in the United States and 17 in Canada. A database was assembled containing contact data, volume of soft and hardwood pulps used, total capacity, digesters used, power generation and amount of power purchased by the mill, if any. The mills were then called one by one to determine whether Aspen was part of the species mix used for kraft pulping. The phone calls followed a standardized script indicating the purpose of the product and inquiring after the size of the mill, the total capacity and production volume, to confirm the data found in the *Lockwood Post Directory*. The contacts were also informed that any information provided would not be disclosed in the final report; the information was only being used for a market analysis. The contacts were then asked to describe the wood species mix of hardwoods used in the mill and the percentage of each species in the total wood mix. If the mill was found to use aspen, data was collected on the quantity of aspen used, its percentage in the total wood mix and the actual tonnage of aspen used, if known.

Both making contact to and obtaining meaningful information from the mills was difficult. Although the most recent edition of the *Lockwood Post Directory* was used, in the time since its publishing in 2004 a number of mills seem to have closed. Several of the mills were concerned about trade secret information. Table 9 gives an overview of the responses.

Table 9. Results of Aspen Inquiry

	Mills within aspen range	Mills not using aspen	Mills using aspen	Mill not responding	Mills that could not be reached
US	26	7	2	2	15
Canada	17	1	3	0	14
Total	43	8	5	2	29

Only 5 mills of those willing to respond were found to use aspen. One of the Canadian mills did not specify the quantity, but less than 5% of the hardwood mix at this particular mill is aspen. Another mill in Canada was not able to give an exact number, because the amount of aspen used varies widely from year to year, depending on specialized customer orders. The third Canadian mill specializes in aspen, which makes up 75% of their hard wood mix. They use up to 250 thousand metric tons of aspen a year.

One of the U.S. mills also uses a substantial amount of aspen, namely 600 to 650 thousand cords per year. Given that a standard dry cord of aspen wood approximates 1860 – 2400 lbs, the mill uses anywhere between 500,000 and 700,000 metric tons of aspen per year. The other U.S. mill employs 40% aspen in their hard wood mix. While this mill did not specify the quantity of aspen processed, it should be in the order of 300 thousand tons per year. This number was estimated from the total hardwood kraft pulp output of 375 thousand metric tons a year and a typical Aspen pulp yield of 51% (Ahmed et al. 1998).

In hope of obtaining more information, industry associations were contacted. In Canada, PAPRICAN, the Pulp and Paper Research Institute of Canada was contacted. According to researchers at Paprican, 10 Canadian mills use aspen in hardwood kraft pulping, consuming approximately 3000 metric tons per day. This sums up to more than a million tons of aspen used for kraft pulping in Canada alone. In an effort to gain similar information for the U.S. market, the Technical Association of the Pulp and Paper Industry (TAPPI) was contacted. TAPPI did not have the information available, but suggested a few other organizations that may have access to this data. These organizations included Pulp & Paper Online, Paper Age, RISI and the Institute of Paper Science and Technology as well as the Center for Paper Business and Industry Studies departments at Georgia Tech. These organizations were then contacted and asked similar questions about aspen use in the US, unfortunately to no avail.

While the total number of responding mills in the primarily seems low (12 mills), the percentage response rate was in fact 28%. Judging by the numbers for Canada, there should be several more U.S. mills using aspen than we were able to verify. We will therefore use two estimates, a lower bound estimate for the confirmed aspen use in US mills and an upper bound estimate, extrapolating from the percentage of Canadian mills processing aspen (59%) and their average use rates (300 tons per mill per day). Given that Aspen is a more predominant species in Canada than in the U.S. regions within its range, the number obtained is likely optimistic.

Table 10 below shows that even under the lower bound estimate, almost 2 million metric tons of aspen are processed each year by North American pulp and paper mills, yielding at least 0.97 million metric tons of bleached hardwood kraft pulp, assuming a standard yield of 51%. Adding phosphonates can improve yield from 4 to 7%. This would result in additional yield between 80 thousand metric tons and 130 thousand tons for the lower bound estimate for the US and Canada combined. Assuming the higher number of mills in the U.S., production would increase between 110 thousand and 190 thousand tons per year, at constant inputs.

Table 10. Aspen use and pulp outputs

	Number of mills	Aspen used per year*	Hardwood kraft production at 51% yield*	Hardwood kraft production at 4-7 % yield improvement*
Canada	10	1.1	0.56	0.61 - 0.64
US lower bound (conf.)	2	0.8	0.41	0.44 - 0.46
US upper bound (estim.)	15	1.6	0.82	0.88 - 0.93

*million metric tons

Alternatively, keeping outputs constant, mills could reduce aspen inputs by 4 to 7%. The decreased supply cost of aspen could amount to at least 4 million $, assuming lower bounds for both cord weight and U.S. production. To this cost reduction would be added the avoided energy cost from the 15 to 35 minutes cook time reduction.

Table 10. Aspen use and pulp outputs

	Constant output*	Reduced aspen input*	Cost reduction at $60/dry cord** 7% yield improvement	Cost reduction at $60/dry cord**, 4% yield improvement
Canada	0.561	1.02 - 1.06	$ 8.8 - 26.4 million	$ 2.4 to 3.1 million
US lower bound (conf.)	0.408	0.74 - 0.76	$ 6.4 - 19.2 million	$ 1.8 to 2.3 million
US upper bound (estim.)	0.816	1.49 - 1.54	$ 12.9 - 38.5 million	$ 3.5 to 4.6 million

*million metric tons

**1 dry cord = 0.843 to 1.089 metric tons

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<u>Section two:</u>

Yield improvement and energy savings using phosphonates as additives in kraft pulp: technical evaluation and optimization

In this study seven different commercial phosphontes and number of custom made phosphonste products and product mixtures were evaluated. All of the products were provided by our industrial collaborator Solutia. The two phosphontes showing the best response as additives in the Kraft digerster were Dequest 2016 [HEDP ; (1-hydroxyethylidine)- diphosphonic acid] and Dequest 2066 [DTPMPA; diethylene triamine penta (methylene phosphonic acid)]. Information on chemical names, characterisitcs and properties of all the phosphontes used can be found at the Dequest web site: http://www.dequest.com/pages/sitemap.asp

1. Evaluation of different wood species

One of the objectives of this study was to evaluate different wood species, using a selection of commercial phosponates in the Kraft digester. A total of four hardwood species and one commercial chip mixture (southern hardwood) were evaluated using eight different phosphonate products. In addition, we studied three softwood species and one commercial mixed softwood batch (Table 1). This study was performed using a M/K lab digester. All the hardwoods showed some yield improvement at given lignin removal level (KAPPA number); for softwoods only pine and fir responded positively with respect to yield improvement (1-2%). In addition, all the hardwoods showed increase in reaction speed (KAPPA number at given H-factor), while the softwoods demonstrated little to no improvement in reaction speed. All wood species showed improvement in bleaching response at given lignin content. As will be discussed later, the improved bleaching response clearly is due to effective removal of transition metals from the pulp fiber. The best response to addition of phosphontes into the digester was observed using aspen chips. For aspen significant yield improvement (4-7%) and/or increased delignification (up to 7 points at an addition rate of 0.2% HEDP) were observed. The eight phosphonates tested showed different response; in most cases Dequest 2016 (HEDP) was the superior additive. Please see Table 1 for a detailed summary.

Table 1: Response of selected wood species to phosphonate addition to the Kraft digester

Wood Species	Phosphonate tested	KAPPA number reduction at given H-factor	Yield improvement at given KAPPA	Bleaching improvement at same starting KA	Comments
Aspen	2016, 2086 2066, 2096 6004, 2054 7000, 3000	Up to 7 points (0.2%) Up to 10 points (0.4%)	4-7%	2-3 points	Considerably better response than AQ, 2016 best performing
Alder	2016, 2086 2066, 2096 6004, 2054 7000, 3000	Up to 2 points at high KA	~ 1% at high KA	1.5 Points	AQ performed equal or better than any of the phosphonates
Birch	2016	3 points	1-2%	NA	
Maple	2016	Up to 4 points at higher KA	1-2 points	1 point	
mixed southern Hardwood	2016	Up to 1 point	1-2%		Similar in yield improvement than AQ, but less effective in increasing lignin removal
Pine	2016 2006	No change	1-2%	2-3 points	Yield same as AQ addition
Spruce	2016	No change	No change	2-3 points	
Fir	2016, 2086 2066, 2096 6004, 2054 7000, 3000	1 point at high AA	~ 2% for 2054	3 points	2054 better in yield than AQ
Mixed Softwood	2016, 2086 2066, 2096 6004, 2054 7000, 3000	No change	No change	2-3 points	

For aspen, addition of HEDP at levels of 0.1-0.2% (on wood) resulted in significantly faster lignin removal rate. At 170 ^{0}C cooking time savings of 15 - 35 minutes could be achieved. For all aspen cooks a yield improvement at given H-factor (cooking time) was observed (Figure 1). A better variable to consider for yield than H-factor is KAPPA number. The KAPPA number vs. pulp yield (Figure 2) clearly shows that HEDP is effective in achieving higher total pulp yield at a given KAPPA number (lignin content). It also becomes evident that this effect is more pronounced at higher degree of delignification (long cooking time, low KA number).

Figure 1:
Yield versus H-factor (cooking time) for aspen chips with and without addition of 0.2 % HEDP in the digester

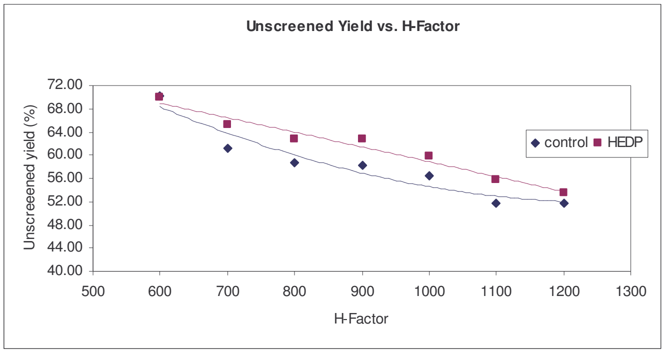
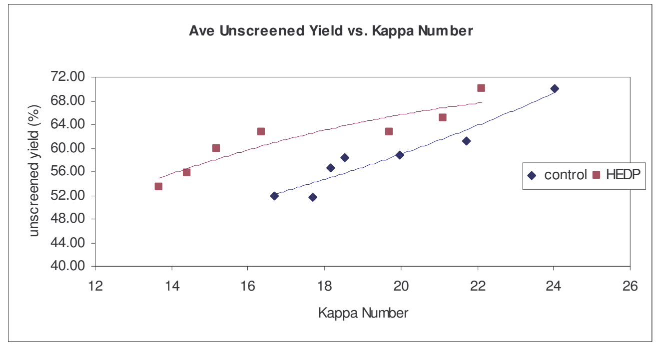


Figure 2:
Yield at given level of lignin removal for Aspen chips ; comparison between control and HEDP (0.2%) addition into Kraft digester



2. Fiber Properties

Fiber properties play an important role in establishing properties of the final paper product. Any changes in pulping technology will have to be implemented in a way that does not negatively affect fiber properties. Besides basic strength properties, beatability, brightness and opacity, pulp drainage is of importance since it affects papermachine speed and energy used for drying.

Physical properties and freeness were determined for numerous pulp samples. In all instances a slight improvement of physical properties could be observed. Table 2 shows response of aspen control and HEDP treated pulps to beating in a PFI mill. Tensile index, Burst index and Tear index either remained the same or showed a very small improvement with phosphonates in the digester. The Zero-span tensile showed up to 8 % improvement for the phosphonate pulps. These finding are supported but the fact that pulp viscosity also increased. Freeness of

phosphonate treated pulps was comparable to freeness values found for the control. We feel confident that no negative effect on papermaking properties is to be expected for the phosphonate treated pulps.

Table 2: Physical properties of aspen pulps with and without Phosphonate addition to the digester.

Pulp	PFI mill revolutions	CSF ml	Bulk cm^3/g	Tensile N×m/g	Bursting kPa×m^2/g	Tearing mN×m^2/g	Zero Span N/cm	Brightness %ISO
Control	0	692	2.33	19.0	0.66	3.60	77.9	31.4
	2,500	606	1.44	46.4	2.32	8.37	79.8	29.8
	5,000	491	1.24	56.7	3.66	9.18	82.1	27.7
	7,500	422	1.20	64.3	4.02	8.93	82.5	26.8
	10,000	338	1.15	71.9	4.75	9.04	84.3	25.8
Na_4HEDP 0.20%	0	688	2.28	20.5	0.74	4.18	80.5	36.3
	2,500	584	1.35	48.7	2.83	7.95	85.8	34.6
	5,000	482	1.21	58.0	3.41	8.88	85.2	33.7
	7,500	406	1.17	65.1	4.18	8.96	89.6	32.0
	10,000	339	1.10	72.8	4.90	9.63	91.3	30.8

3. Effect of Phosphonates on Brightness and Bleaching

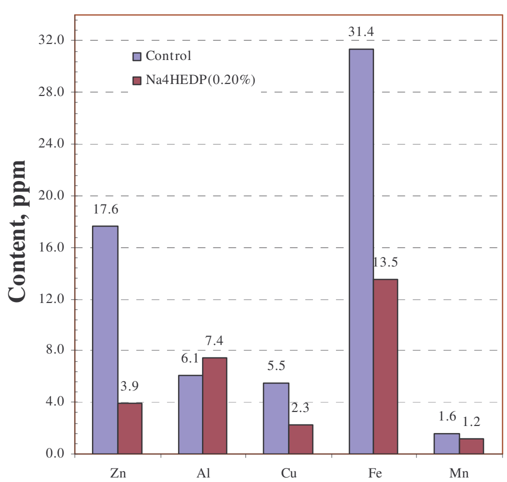


Figure 3: Change in metal content for aspen pulps with and without HEDP

Due to the chelating abilities of phosphonates improved metal removal (Figure 3) resulting in up to four points of brightness increase at given degree of delignification for the unbleached pulps out of the digester. The metal removal also resulted in improvements in bleaching response for all wood species tested. Table 3 demonstrates chemical savings for a traditional DEDED bleaching sequence after using Dequest 2016 or 2066 in the digester. In this experiment chlorine dioxide charge was reduced for the pulps with the phosphonate addition (by 0.3%), attempting to achieve the same brightness. Table 4 shows response of aspen pulps with and without phosphonates to a DEopP sequence. Here the chemical charges were kept constant. The results illustrate that with the same chemical charge final brightness is significantly higher. Another set of experiments selected pulps with the same lignin content for an ECF bleaching sequence. Even though starting KAPPA number was only 0.4 points lower for the pulps treated with HEDP in the digester the starting brightness was one point higher out of the digester. The brightness advantage was carried through all 4 stages (Table 5).

Numerous other experiments were performed and even in cases where no effect of phosphonates on lignin content was observed (for example for softwoods) a positive effect on bleaching response could be observed.

Table 3: HW-DEDED aspen wood chips

		Control	**2016(0.2%)**	**2016 (0.1%)**	**2066 (0.2%)**
Ini. KAPPA no.		22.5	16	18.1	18.6
Ini. Brightness, %		29.2	34.4	33.1	33.7
D1:	**ClO2, %**	**1.3**	**1**	**1**	**1**
	Residual, g/l	0.006	0.006	0.003	0.006
	End pH	2.95	3.21	3.61	3.73
	Brightness, %	**44.75**	**53.66**	**51.25**	**53.7**
E1:	NaOH, %	2	2	2	2
	End pH	11.84	11.8	11.87	11.87
	Brightness, %	**57.74**	**61.98**	**60.2**	**62.2**
D2:	***ClO2, %***	**0.5**	**0.4**	**0.5**	**0.5**
	Residual, g/l	0.067	0.085	0.006	0.006
	End pH	3.93	4.21	**4.21**	4.22
	Brightness, %	**83.27**	**84.1**	**83.7**	**84.8**
E2:	NaOH, %	2	2	2	2
	End pH	11.8	11.78	11.72	11.74
	Brightness, %	**82.63**	**83.38**	83.8	**84.6**
D3:	**ClO2, %**	**0.2**	**0.2**	**0.2**	**0.2**
	Residual, g/l	0.07	0.073	0.036	0.03
	End pH	5.17	5.38	4.42	4.32
	Brightness, %	**90.53**	**90.59**	**89.9**	**90.7**

Table 4:. HW-DEopP, aspen wood chips

		Control	2016(0.2%)	216(0.1%0	2066 (0.2%)
Ini. KAPPA no.		24.5	17.06	18.1	18.6
Ini. Brightness, %		28.3	35.2	33.1	33.7
***D:	**ClO2, %**	**1**	**1**	**1**	**1**
	Residual, g/l	0.003	0.003	0.003	0.006
	End pH	3.72	3.53	3.61	3.73
	Brightness, %	**38.4**	**53.81**	**51.25**	**53.7**
Eop:	NaOH, %	3	3	3	3
	O2 pressure, psi	30	30	30	30
	H2O2, %	0.5	0.5	0.5	0.5
	Residual, g/l	0.046	0.118	0.122	0.18
	KAPPA no.	5.6	4.5	5.3	4.4
	End pH	11.75	11.83	11.67	11.66
	Brightness, %	**71.22**	**79.23**	**78.8**	**79.15**
P:	**H2O2, %**	**0.6**	**0.6**	0.6	0.6
	Residual, g/l	0.007	0.011	0.08	0.24
	End pH	11.66	11.71	11.67	11.62
	Brightness, %	**79.5**	**83.43**	84.7	85.65

Table 5: Bleaching experiments Maple pulps, same starting lignin content

BRIGHTENSS % ISO	**Control**	**2066 (2%)**
Initial KAPPA	15.6	15.2
Initial brightness	35.6	36.2
D_0 0.8% ClO_2 63 ^{0}C, 25 minutes	52.6	53.6
Eop (0.3% P) 80 ^{0}C. 45 minutes, 1.07% NaOH	70	72
D_1 0.6% ClO_2 , 0.2% NaOH, 71 ^{0}C, 100 minutes	86.0	86.4
D_2 0.2% ClO_2, 75^0 C 130 minutes, 0.1% NaOH	89.4	90.1

4. **Fundamental understanding of reaction mechanisms**

   a. **Pulp composition**

One of the goals of this project was to gain understanding of the fundamental reactions involved in modifications observed with addition of phosphonates to a traditional Kraft process. Towards this goal we performed detailed carbohydrate analysis of pulps processed with and without addition of HEDP. Commercial aspen chips were processed to produce Kraft pulps with and without the addition of HEDP (0.1-0.4 % on chips). Three different H factors (705, 853 and 1000) were used, resulting in a KAPPA number range from 14 to 26. The pulps were analyzed for their carbohydrate and lignin content. Three sets of carbohydrate analysis were performed; set 1 and 2 were direct repeats (same pulp samples) the 3rd set consisted of pulps from separate runs.

Comparing glucose content at given yield we can see that the control has a distinctly lower glucose content than the HEDP treated samples (Figure 4 and 5). This comparison shows the same trend irrespectively if screened or unscreened yield are used as the basis for comparison (compare Figure 4 with Figure 5). Glucose in pulp samples originates either from cellulose or glucomannans. We found approximately 2 % mannose in the original aspen chips, but none in any of the pulp samples, indicating that the glucomannans were dissolved in the pulping process. This effect was expected, since glucomannans are easily hydrolyzed under alkaline conditions. The lack of mannans verifies that all the glucose in the pulp is derived from cellulose. The main hemicellulose type in hardwoods are xylans. Xylans consist mainly of xylose and show a distinctly stronger resistance to alkaline pulping. Comparison of xylose levels does not show a significant difference between the HEDP treated samples and the control (Figure 4 and 5 – lower set of data on the graph).

At the same time, as expected, the Klason lignin content at given yield is lower for the HEDP treated samples than for the control (Figure 6). As noted before HEDP promotes the preferential removal of lignin from the wood sample, retaining larger amounts of cellulose. Comparison of KAPPA number with Klason lignin content shows data scattered around the theoretical values (theoretically KAPPA number X 0.13 = Klason lignin)(Figure 7).

Fig. 4 Pulp composition vs screened yield(aspen)

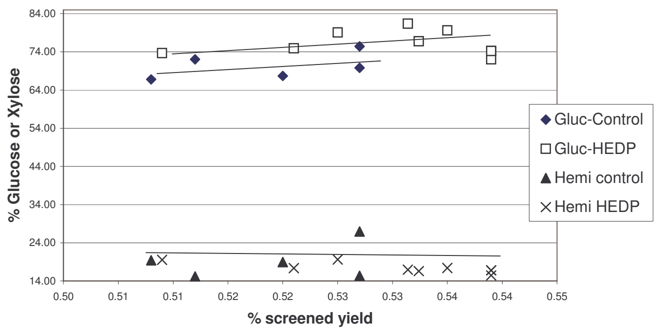


Fig. 5: Pulp compsition vs unscreened yield (aspen)

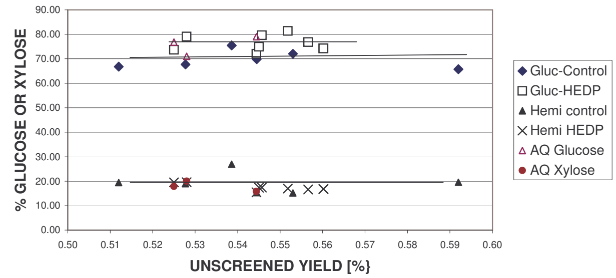


Fig. 6 Klason Lignin content at given yield (aspen)

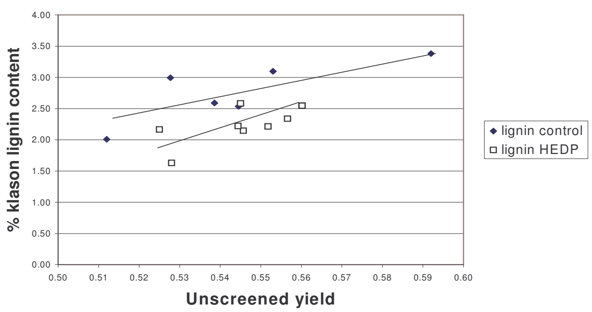
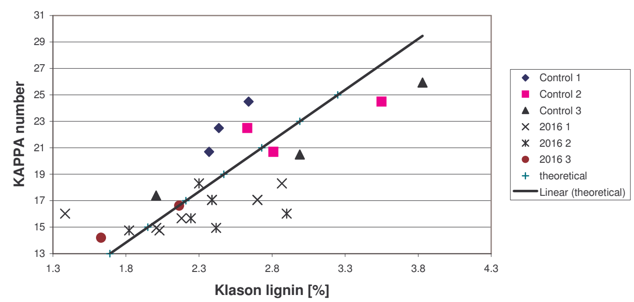


Fig. 7:KAPPA number versus Klason lignin



For comparison three samples processed with Anthraquinon as pulping additive were included into the analysis. The glucose content at given yield for these samples appears to be close to the results found for the HEDP pulps (Figure 5). The xylose content is in the same range than the control or the HEDP pulps. In addition the lignin content at given yield clearly is in the same range than the lignin content for HEDP samples. HEDP as well as Anthraquinon are promoting preferential removal of lignin during the cook, preserving the cellulose content, while hemicellulose content is not significantly changed.

b. Hexeneuronic acids

One potential reason for differences in KAPPA number, especially for hardwood pulps could be differences in formation of Hexeneuronic acid groups (HexuA groups) (Figure 8). The unsaturated residues consume $KMnO_4$ in the KAPPA number measurement, resulting in over-estimation of actual KAPPA number values. The content of HexuA groups in Kraft pulp is strongly influenced by the cooking conditions. In general, HexuA groups formed at given KAPPA numbers decrease as the cooking temperature or time is reduced, which can be achieved by increasing the concentration of OH^- and/or HS^- in cooking liquors. AQ is found to slightly reduce the formation of HexuA groups.

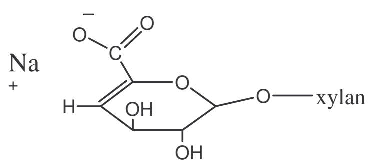


Figure 8: The structure of Hexeneuronic acid

HexuA groups in Kraft pulp can be quantified by a UV/Visible photometric method and results are presented in Table 5. HexuA group contents determined for the different pulps vary from 47 to 51µmol/g pulp. At any given H-factor level both Na_4HEDP and Na_5DTPMP treated pulps show slightly higher HexuA contents than the control, while the AQ treated pulp is slightly lower. It is confirmed that the HexuA group content is mildly decreased as H-factor increases, due to a greater decomposition of xylan at longer cooking time. Comparing HexuA's at a given KAPPA number pulps from runs with HEDP appear to have a slightly larger value than control or AQ pulps. Nevertheless, the differences are very small, and there certainly is no evidence that the reduced KAPPA number with phosphonates might be caused by lower levels of HexeA's. This finding agrees with Figure 6, showing a linear relation ship between KAPPA number and lignin content.

Table 6 HexuA contents determined by the UV/Visible method

Pulp (charge, %)	H-factor	KAPPA	HexuA (µmol/g pulp)
Control(0.0)	558	25.3	48.95
	853	17.0	48.02
Na_4HEDP(0.2)	558	17.4	50.78
	853	15.0	50.27
Na_5DTPMP(0.2)	853	16.6	48.18
AQ(0.1)	853	17.8	47.75

c. Solid-state (SS) NMR

Aspen pulp samples from different cooks (with and without phosphonate addition, different H-factors, different KAPPA numbers) were characterized using SS-NMR. Some sample spectra of CP/MAS ^{13}C-NMR at 400MHz are illustrated in Figure 9 (two aspen pulp samples and aspen wood). Assignments of principal resonances in the spectra are summarized in Table 7. Signals occurring between 60 and 110ppm are attributed primarily to carbohydrate carbon atoms, while including contributions from lignin side-chains and Lignin-Carbohydrate functionalities. Resonances in the region of 110 to 160ppm are indicative of lignin structures. In addition, the most characteristic peak for the methoxyl group at 56ppm is contributed by lignin. Prominent signals for hemicelluloses appear at 173ppm for the carbonyl group and at 20ppm for the methyl group.

Table 7 Assignments of peaks in the CP/MAS ^{13}C-NMR spectra of wood and pulp samples

δ, ppm	Lignin (S=Syringyl, G=Guaiacyl)	Cellulose and hemicelluloses
173.0	C_α=O (trace)	C=O in acetyl and -COOH groups of xylan
153.0~148.0	S 3/5 (4-O-R) (downfield)	
	S 3/5 (4-O-H), G 3/4 (upfield)	
135.0~132.0	Condensed structures:	
	S 1/4 (4-O-R), G 1 (4-O-R) (downfield)	
	S 1/4 (4-O-H), G 1 (4-O-H) (upfield)	
ca. 120.0	G 6	
ca. 114.0	G 2/5	
ca. 110.0	S 2/6	
105.0~103.0		C-1 in cellulose (downfield) and hemicelluloses
88.0		C-4 (crystalline)
84.0	C_β in β-O-4	C-4 (amorphous)
73.0 (strong)	C_α-OH in β-O-4	C-2,3,5 in cellulose and hemicelluloses
ca. 65.0	C_γ-OH	
64.0		C-6 in cellulose (crystalline)
56.0	Aryl methoxyl C	
50.0~15.0		Aliphatic C not attached to oxygen
20.0		Methyl C in acetyl groups of xylan

Signals of carbon atoms from carbohydrates (both cellulose and hemicelluloses) can be assigned . Carbon-1 occurs at ~105ppm in the most downfield range of 60~110ppm. Carbon-4 is the next, at 88~84ppm, followed by the doublet at ~73ppm of C-2, 3, 5 in the six-member ring. The aliphatic C-6 shows up in the most upfield area, i.e., at 64 ppm with an upfield shoulder. Crystallinity is known in nature as a major characteristic of cellulosic microstructure. In SS ^{13}C-

NMR spectra, the crystallinity of cellulose can be measured by the integral ratio of the C-4 peak at 88ppm (crystalline) over the C-4 peak at 84ppm. Results (Table 8) show that the crystallinity increases steadily from 0.58 of the wood sample to 0.84~0.85 of the pulp samples. Little difference between the control, Na_4HEDP, and AQ treated pulps is noticeable. It is known that amorphous areas in cellulose are preferentially attacked and dissolved during Kraft pulping, giving rise to the crystallinity increase with growing yield losses.

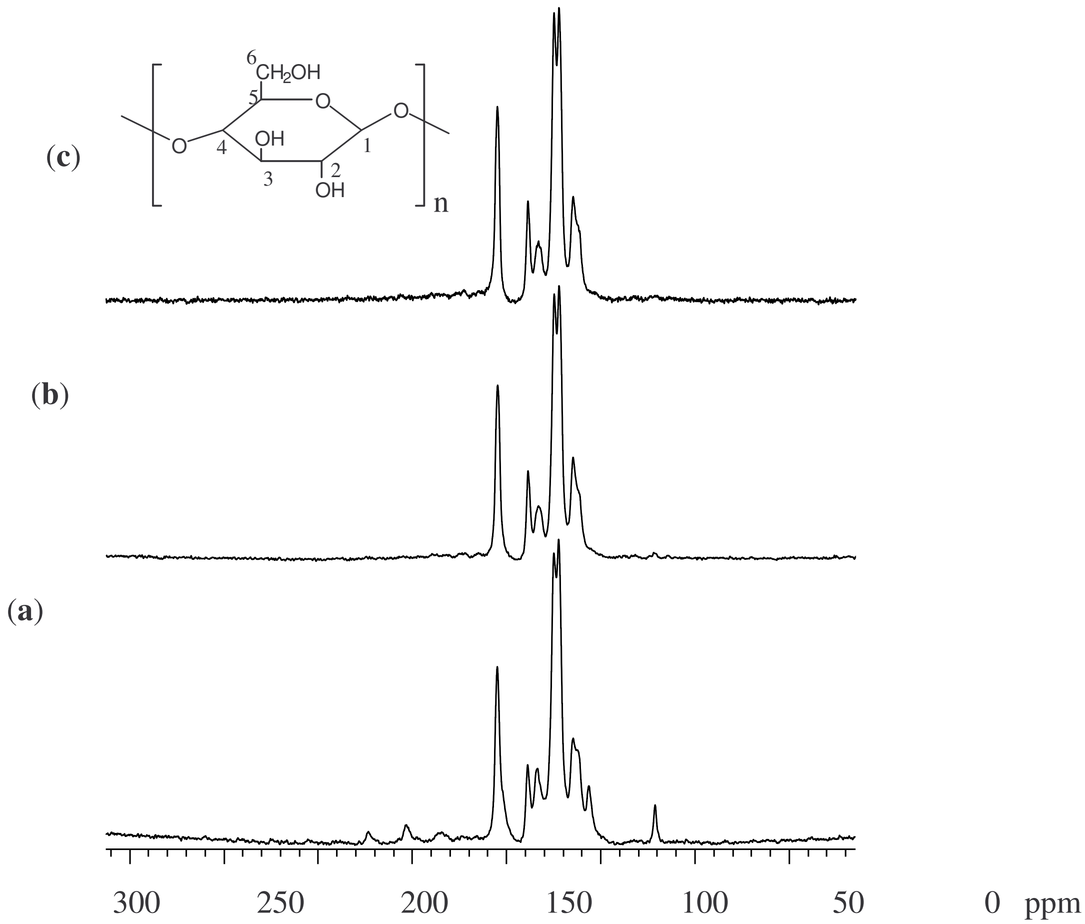


Figure 9: CP/MAS ^{13}C-NMR spectra of : (a) the aspen wood, (b) the control and (c) Na_4HEDP(0.2%) treated pulps at H-factor 853.

Table 8: Integration (total 100) of peaks in the CP/MAS ^{13}C-NMR spectra of wood and pulp samples

Chemical shift, δ (ppm)	Wood	Pulp		
		Control	Na_4HEDP(0.2%)	AQ(0.1%)
173.0	0.8	0.3	0.0	0.0
153.0~148.0	2.0	0.8	0.0	0.0
135.0~132.0	1.6	1.1	0.0	0.0
105.0~103.0	15.8	16.1	15.9	16.3
88.0	4.8	6.3	6.3	6.2
84.0	8.4	7.5	7.4	7.4
73.0	42.5	44.4	46.3	46.3
64.0	14.6	14.9	15.3	15.7
56.0	5.3	2.1	0.0	0.0
35.0~10.0	1.9	0.7	0.0	0.0
Ratio ($\frac{I\_at\_88ppm}{I\_at\_84ppm}$)	0.57	0.84	0.85	0.84
KAPPA number	n/a	20.5	14.2	16.9

Note: All pulps cooked at H-factor 853; I=Integration

d. Free Phenolic Group

The phenolic group is one of the most significant functional groups that affect both physical and chemical properties of the lignin polymers. The phenolic group is able to ionize under alkaline conditions and thus improve the solubility of the lignin in aqueous systems, an important factor in pulping. Lignin chemical reactivity in various modification processes is strongly influenced by its phenolic hydroxyl groups. During lignin degradation new phenolic groups are generated. Thus, the quantitative measurement of phenolic hydroxyl groups supplies relevant information concerning the lignin structure and reactivity as well as the extent of lignin degradation. The phenolic groups in Kraft lignin (aspen) were determined using the UV spectroscopy method, based on the difference in absorption of phenolic units in neutral and in alkaline solution. The cleaving of alkyl-aryl ether linkages during the Kraft cook leads to formation of new phenolic end groups. The phenolic hydroxyl content in the residual lignin increases during the cook. Dissolved lignin from aspen Kraft cook has 2.1-3.9 mmol/g phenolic hydroxyl groups present (Table 9).

Table 9 Free Phenolic Group for Control and HEDP cooks

H-Factor	KAPPA # HEDP	Total content OH (tot) - HEDP	H-Factor	KAPPA # Control	Total content OH (tot) - Control
600	22.11	2.1635	600	24.03	2.3146
700	28.35	2.1304	700	21.70	2.2499
800	19.69	2.7523	800	19.98	2.8528
900	16.34	2.3810	900	18.54	2.7351
1000	15.78	2.4192	1000	18.15	3.2171
1100	14.40	2.7660	1100	17.71	2.8588
1200	13.69	2.0868	1200	16.70	3.9125

By cleaving the majority of the phenylpropane-ß aryl ether structures, the Kraft pulp lignin has been changed as compared to the native lignin in wood. The residual lignin is believed to be more branched compared to the native lignin. The lower amount of phenolic groups in the black liquor lignin of HEDP cooks compared to control cooks, (Figure 10) could indicate that the HEDP lignin have been less degraded. The fact that these lignins were isolated from black liquor means that they were soluble in the alkali system of our pulping liquor. This indicates that HEDP is promoting lignin removal from the cell wall before it has reacted to the same extent than the lignin in the control runs. This theory is supported by the molecular weight distributions we found for these lignins (see the Molecular weight determination section).

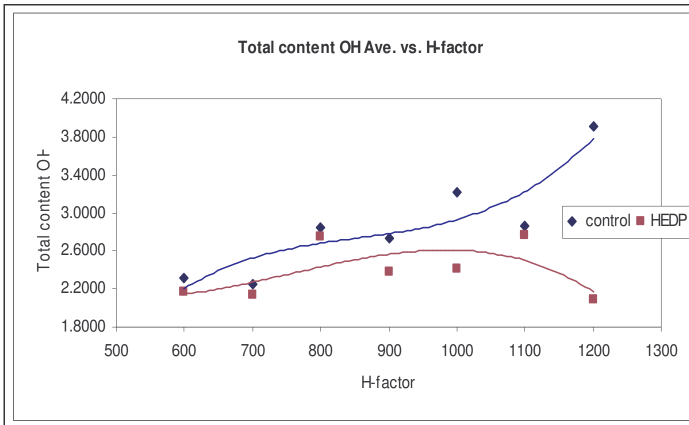


Figure 10: Free Phenolic Group Ave. vs. H-Factor: Control and HEDP cooks

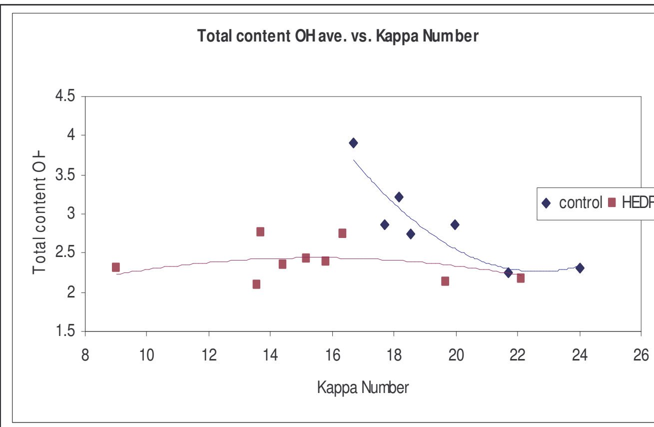


Figure 11: Free Phenolic Group Ave. vs. KAPPA Number: Control and HEDP cooks

The discrepancy of free phenolic group between control and HEDP cooks appears to be more visible when the H-factor increases (Figure 10). Phenolic groups vs. KAPPA number (Figure 11) indicate that at given KAPPA number, the cooks treated by HEDP have lower free phenolic groups compared to the control ones. For KAPPA number below 20, there is a significant difference between control and HEDP cooks in term of amount of phenolic units. However when the KAPPA number is above 20 the difference becomes negligible

e. S/G Ratio

The nature of lignin differs on the microscopic level. Hardwood lignin and softwood lignin structures are also different. The lignin in the middle lamella of softwoods has higher p-hydroxyphenyl units and contains less free phenolic hydroxyl groups than in the secondary wall Softwood does not have large number of Syringyl units. On the other hand, lignin in hardwood has a high content of syringyl units in the secondary walls and ray cells, whereas the middle lamella contains a guaiacyl-syringyl lignin. In contrast, the vessel contains a guaiacyl lignin in both the secondary wall and the middle lamella. We observed that softwoods showed no or little response to the addition of phosphonates in the Kraft process. Therefore it was speculated that the amount of Syringyl present or the Syringyl/Guaiacyl ratio could be the determining factor for response to phosphonates addition. S/G ratio for pulps cooked to different lignin content with and without HEDP was determined.

Table 10. S/G ratio for different wood chip

Wood chip	S/G ratio1	S/G ratio2	S/G ratio ave
Aspen	2.99	2.99	2.99
birch	3.82	3.12	3.47
maple	3.65	3.32	3.49

Table 10 shows S/G ratio for different wood chip. The aspen starting material S/G ratio is 2.99, birch and maple are considerably higher. Softwoods on the other hand are known to have mainly G units. This indicates that the S/G ratio of the starting material does not impact the response in the cooks. In addition to the starting material we examined S/G ratio of pulps with and without phosphonate treatment in the digester. It is known that S units react more readily, so a decrease in S/G ratio is expected as the cooking proceeds. Figure 12 and Table 11 show that the S/G ratio of HEDP cooks is slightly higher at given lignin content compared to the control cooks. This means that the phosphonates are capable of promoting removal of guaiacyl units from lignin.

Table 11: S/G ratio for Control and HEDP cooks

H-Factor	KAPPA # HEDP	S/G ratio ave HEDP	H-Factor	KAPPA # Control	S/G Ratio ave Control
600	22.11	**0.78**	600	24.03	**0.64**
700	28.35	**0.77**	700	21.70	**0.92**
800	19.69	**1.34**	800	19.98	**1.14**
900	16.34	**2.10**	900	18.54	**0.86**
1000	15.78	**1.25**	1000	18.15	**1.11**
1100	14.40	**1.13**	1100	17.71	**0.49**
1200	13.69	**1.25**	1200	16.70	**1.20**

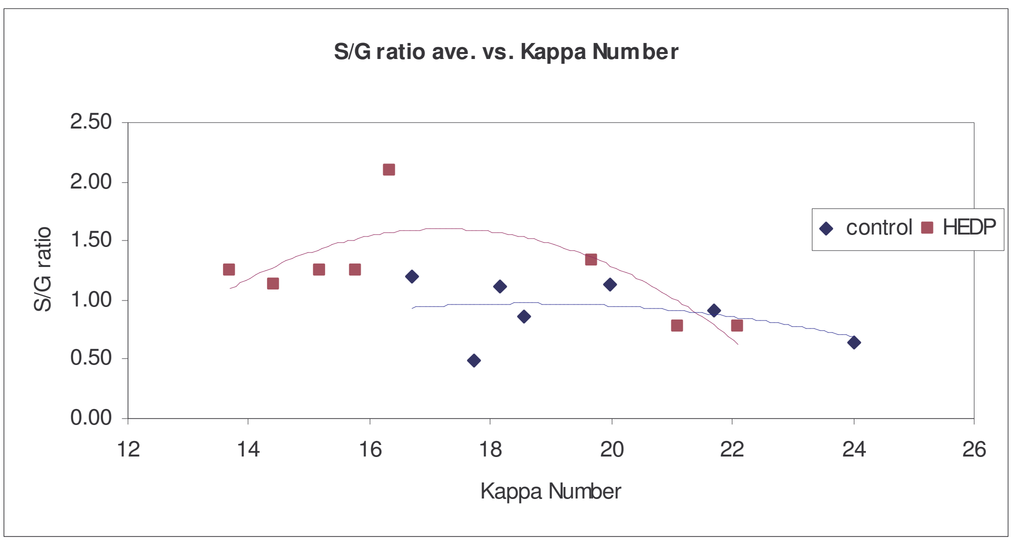


Figure 12 : S/G ratio at different levels of lignin removal for control and HEDP treated aspen pulps.

a) Black Liquor Lignin Molecular Weights

Average Molecular weight (Mw) and its distribution are an essential aspect to distinguish the polymeric properties of lignin as well as its condensed structures. We used different methods to determine the molecular weight (Mw) of black liquor lignin for both HEDP and controls cooks. The most successful attempt measured the average Mw using caustic (0.1N) as solvent. The molecular weights of black liquor lignin from runs treated with HEDP are slightly higher compared to the control pulp (Table 12 and Figure 13, 14). The relation between Mw and H-factor is not linear. The control cooks trend shows that the Mw increases up to H-factor 900 and decreases at higher H-factors. While HEDP samples show more constant Mw against H-factor. Comparing average molecular weight at given level of lignin removal indicate that at low KAPPA numbers black liquor lignin has a higher average molecular weight for cooks with HEDP in the digester. This finding agrees with the earlier presented results on free phenolic groups. HEDP appears to be capable of removing lignin at higher molecular weight levels (less degradation).

Table 12 Lignin Molecular Weight average using NaOH as solvent

	H-Factor	**KAPPA #**	**Mw ave.**		**H-Factor**	**KAPPA #**	**Mw ave.**
Control	600	24.03	12011	**HEDP**	600	22.11	12342
	700	21.7	12180		700	28.35	12443
	800	19.98	12689		800	19.69	12233
	900	18.54	12430		900	16.34	12585
	1000	18.15	12203		1000	15.78	12273
	1100	17.71	12217		1100	14.4	12302
	1200	16.7	11846		1200	13.69	12266

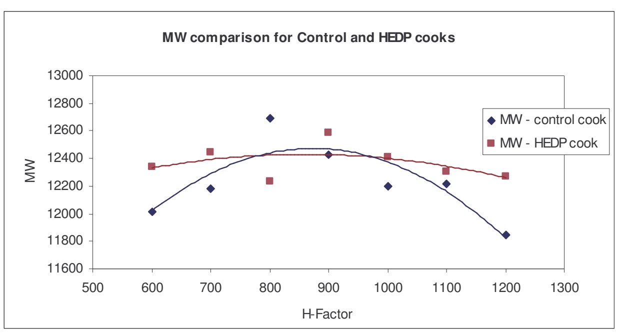


Figure 13: Average Molecular weight Mw at given H-factor for aspen

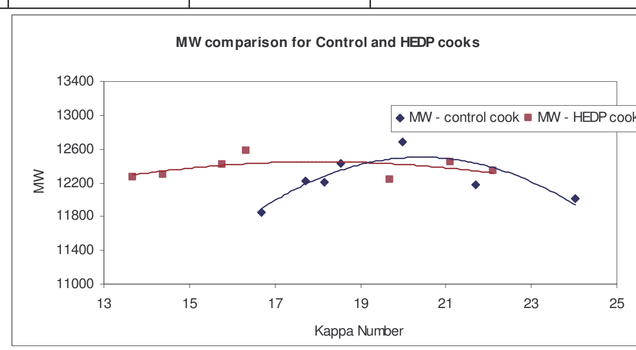


Figure 14 Lignin Molecular Weight vs KAPPA Number for aspen pulps.

5. Dispersion properties

Effect of addition of phosphonates on lignin dispersion was studied using aspen black liquor lignin. For this purpose a solution of 10 g/l of lignin was prepared using NaOH Dequest 2016 was added. Both solutions were acidified slowly, precipitated lignin was centrifuged off, washed and oven dried. Interestingly it could be seen that especially at higher pH levels lignin precipitation is considerably more pronounced in systems that contain phosphonates (Figure 15). If this effect is present in the original black liquors it could mean that lignin is removed from the solution by precipitation, thereby changing dissolved solid content of the black liquor. Since we observed reduced lignin content in pulp fibers it is assumed that lignin is not precipitated onto fibers but can be removed effectively in the subsequent washing stage.

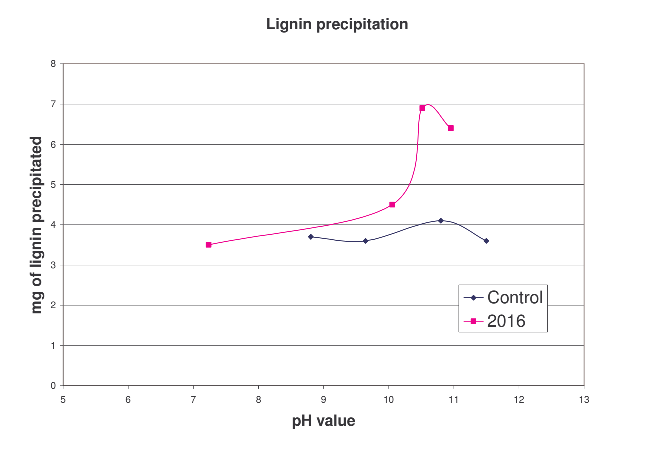


Figure 14: Lignin precipitation in black liquor systems

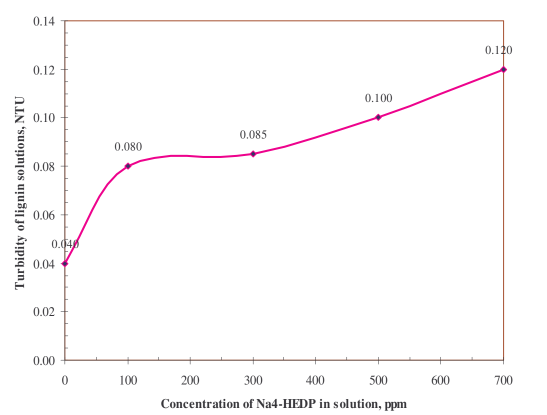


Fig. 15: Turbidity of lignin solution with increasing amount of HEDP

To confirm the above described findings we performed lignin precipitation studies at pH 8 using increasing amounts of phosphonates, determining lignin precipitation by monitoring Turbidity of the solution. Turbidity is defined as measurement of "the clarity of an otherwise clear liquid by using colorimetric scales or the cloudy or hazy appearance in naturally clear liquid caused by a suspension of colloidal liquid droplets or fine solids". HEDP (pH 11.5 at the original active acid concentration) is picked for the exploration, since other phosphonates perform essentially the same in terms of dispersing.

A homogeneous lignin solution is composed of non-dissolved but well dispersed lignin particles along with dissolved lignin as solutes. Typically, any change in turbidity or solubility is related to dispersing state alteration of the stable system. As Figure 15 shows, at pH 8.0 and room temperature turbidity increases constantly from 0.04 to 0.12NTU as HEDP increases from 0 to 700ppm in solution.

6. Penetration of cooking Liquor into chips

An attempt was made to characterize liquor penentration into wood chips and determine if there is a significant impact on liquor penetration into the chips with phosphonate addition. Test samples were prepared by adding 20 g samples of chips into bags (bags hade large number of holes) and place them into the same pressure vessel (room temperature, 50 psi). Samples were removed from the vessel at different times, chips were removed from the bag and free draining liquor was removed before weighing the chips. Even with several repeat runs standard deviations were high.

For Aspen chips there is a slightly faster penetration of HEDP containing liquor visible at short retention times (up to 10 weight % more, Figure 15)). Given longer retention times the difference becomes smaller and finally is not visible any more (60 minutes). The softwood chips did not show this effect (Figure 16). Even though the Dequest liquors were slightly above the control, the difference is considerably lower for the softwood chips (within 2%) than for the aspen chips. Considering the above mentioned variability of the test procedures none of the differences can be shown to be statistically significant.

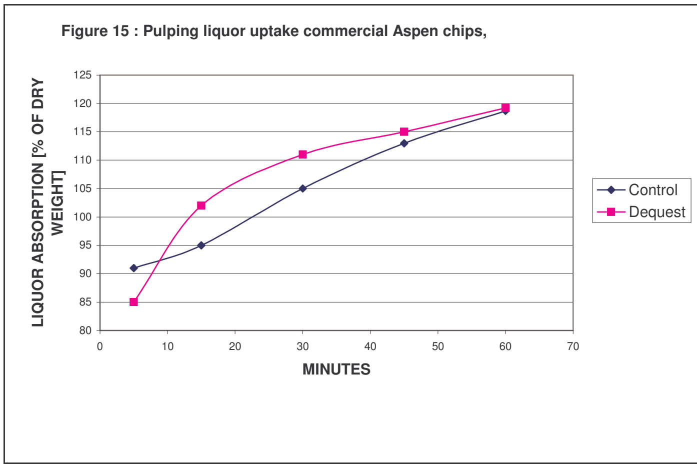


Figure 15 : Pulping liquor uptake commercial Aspen chips,

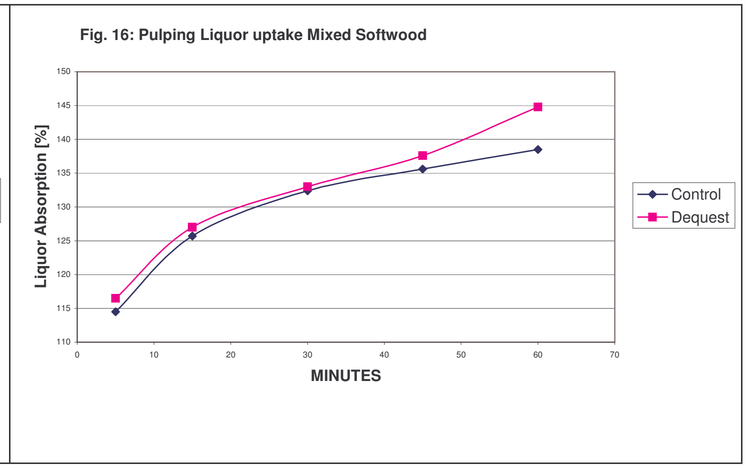


Fig. 16: Pulping Liquor uptake Mixed Softwood

7. Fate of Phosphonates in the Digester

Phosphonates are known to be resistant to heat and other harsh conditions, so we fully expected that they survive the Kraft cooking process. Experiments using variety of set-ups were used to design a reliable quantitative testing procedure using. ^{31}P NMR was selected as the most effective tool. HEDP shows only one distinct peak at 19.8 ppm in a ^{31}P NMR spectrum (see Figure 17). This peak is clearly visible in black liquor even after cooking times of up to four hours; nevertheless some minor peaks in lower regions are observed, but the majority of HEDP survives the cooking procedure. Nevertheless, not all phosphonate can be found in the liquor, a substantial amount are found to be absorbed onto the pulp. Amount of phosphonate adsorbed depends strongly on type of phosphonate used. Recirculation of black liquor will allow reduction of phosphonate addition rate.

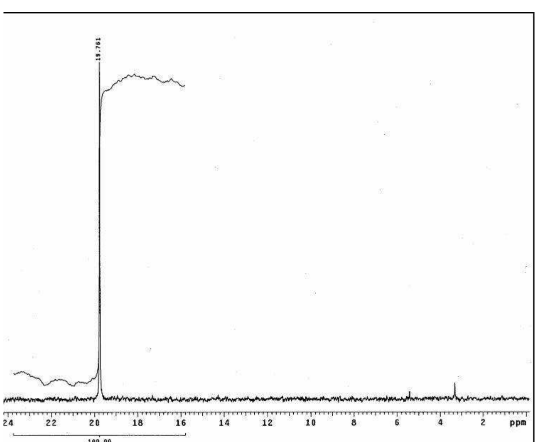


Figure 16:
^{31}P NMR spectrum of HEDP in black liquor

8. Effect of phospohonate blends and addition levels

Nearly a dozen phosphonate products were evaluated using aspen chips, the material most responsive to phosphonate addition in the pulping process. The pulping conditions used were: H-factor 1000, AA 18.0% and sulfidity 25.0% (as Na_2O).

Table 14 Pulp kappa number of individually-used phosphonate cooking at H-factor 1000, all phosphonates were supplied by Solutia (Dequest products)

	Charge, %			
Phosphonate (abbrev.)	0.00(Control)	0.03	0.20	0.50
D2006(Na_5ATMP)**		21.2	18.1	16.4
D2016(Na_4HEDP)		21.6	16.2	15.2
D2054(K_6HDTMP)		21.3	20.4	17.2
D2060S(DTPMP)		19.6	17.9	16.5
D2066(Na_5DTPMP)	20.8	19.4	17.8	15.0
D2086		19.8	16.9	15.8
D3000S		21.0	17.9	15.5
D6004		20.2	18.0	16.8
D7000(PBTC)		21.7	21.3	19.8
D2066A(Na_3DTPMP)***	17.0	16.0	14.0	13.3

The Kappa number reduction is small at 0.03% addition levels, but becomes increasingly significant (3.6~5.8 points) at 0.50% charge. D2016 (Na_4HEDP), D2066, (Na_5DTPMP), D2066A, D2060S, D2086 and D3000S seem to be superior in improving delignification. In addition, seven phosphonate blends were evaluated against both the control and each other at the same cooking conditions but varied H-factors. As illustrated in Table 15, D83A and D83B turned out to be the most effective blends, achieving kappa number decreases of up to 8 points and the highest pulp brightness. D83A outperformed D83B, attaining higher screened yields and lower rejects at both H-factor levels tested. By comparing the component ratio in D83A and

D83B, the result confirm that D2016 (Na_4HEDP) shows a clear advantages over D2086 in Kraft pulping. Phosphonate responds was based on their original components. There does not seem to be a synergistic effect in blending different products.

Table 15 Cooking results of phosphonate blends

H-factor	Phosphonate (w/w)	Charge (%)	Items assessed: Kappa number	Screened yield (%)	Rejects (%)	ISO brightness (%)
705	Control	0.0	24.8	50.5	4.8	28.3
	D78 (1:1, D2006:D2066)	0.2	18.6	52.7	3.0	31.8
	D80 (1:1, D2006:D2086)	0.1	21.3	52.6	2.6	31.0
	D83A (2:1, D2016:D2086)	0.2	17.6	52.7	2.2	33.5
	D83B (1:2, D2016:D2086)	0.2	17.6	51.3	4.7	35.9
	D84 (1:1, D2054:D2086)	0.2	17.9	52.5	2.5	31.1
	D86 (1:1, D2086:D2066A)	0.1	20.3	50.2	3.8	29.3
	D87 (1:1, D2054:2066A)	0.1	19.9	50.4	7.1	33.5
853	Control	0.0	23.2	52.6	2.8	29.0
	D78 (1:1, D2006:D2066)	0.2	18.2	53.3	2.2	31.4
	D80 (1:1, D2006:D2086)	0.1	20.0	53.0	2.3	30.9
	D83A (2:1, D2016:D2086)	0.2	15.3	54.1	1.5	33.7
	D83B (1:2, D2016:D2086)	0.2	16.7	52.5	2.6	35.2
	D84 (1:1, D2054:D2086)	0.2	16.7	52.7	1.6	31.4
	D86 (1:1, D2086:D2066A)	0.1	18.8	52.4	1.6	29.9
	D87 (1:1, D2054:2066A)	0.1	19.1	53.1	1.5	32.1

Note: Chip solids 56.0%; an average of two replicates reported for the control

9. Conclusions:

Phosphonates as additives in the Kraft pulping process have the potential to increase yield, speed of reaction and bleaching response. While only hardwood, and specifically aspen, show a significant yield improvement all wood species tested showed increased bleaching response. The increased response to bleaching is caused by lower lignin content and/or lower levels of transition metals in the pulp processed with phosphonates. For almost all wood species HEDP is the most effective phosphonate, including number of blends. HEDP does survive the Kraft pulping process and recirculation of black liquor offers one option to reduce the overall addition level. Approximately 0.15-0.2 % phosphonate (on dry wood basis) are needed to significantly improve pulping conditions. Black liquor lignin recovered after the pulping stage shows higher phenolic group content and slightly higher average Mw. This finding indicates that phosphonates are capable of aiding lignin removal at lower degree of degradation, resulting in increased speed of reaction.

In collaboration with Solutia Inc. (our industry collaborator) we are attempting to move forward to mill trials. Several European mills are currently adding very small amounts of phosphonate to the digester. While the addition levels are to small to show significant changes to yield we are hopeful that data collected at these trial will provide additional information and will allow us to move forward with a mill trail using higher levels of HEDP.

10. **Milestone Status Table:**

ID Number	Task / Milestone Description
1	Evaluation of different wood species
2	Characterization of fundamental background
2.1	Dispersion properties
2.2	Penetration into wood chips
2.3	Characterization of residual lignin
2.4	Characterization of black liquor lignin
2.5	Comparison of phosphonate responses
2.6	Optimization of process
2.7	Fate of phosphonates in the process
3.	Market study
3.1	Secondary Literature review
3.2	Model development
3.3	Interview with mill personal
3.4	Survey design and implementation
3.5	Economic feasibility assessment
4.	Analysis and final report

11. **Approved Budget Data**:

Phase / Budget Period			DOE Amount	Cost Share	Total
	From	To			
Year 1	4/1/03	3/31/04	$157,680	$ 41,145	$ 198,825
Year 2	4/1/04	3/31/05	$106,682	$ 42,190	$ 148,872
Year 3	4/1/05	3/31/06	$105,956	$ 43,277	$ 149,233
Year 4	NA				
Year 5	NA				
		Totals	$ 370,318	$ 126,612	$ 496,930