New Dynamics Drive ClO_2 Technology Developments in Post Cluster Rule Era

Today's bleached chemical pulp mills are focusing on ways to increase ClO_2 plant capacity and efficiency to meet changing economic demands and market conditions.

— *By Ken Patrick, Editorial Director*

This December the U.S. EPA's Cluster Rules will have promulgated seven years ago. During the decade leading up to promulgation in 1997, the pulp and paper industry in this country anticipated significant capital spending in the wake of these "unified" water, air, and solid waste regulations.

However, by the time the first phases of the new rules became reality, a large number of mills had already adopted the chlorine dioxide based pulp bleaching technology the EPA would generally endorse with its new effluent legislation. Most U.S. chemical pulp mills, at least those that were economically sound and production-viable at the time, were installing or had already installed enough ClO_2 generation capacity to come into compliance with the Cluster Rules.

John Sokol

"In fact, some mills put in a little more capacity than they needed at the time," says John Sokol, manager, ClO_2 technology, Pulp and Paper North America, Eka Chemicals. "Thus there really hasn't been a big push for new ClO_2 capacity in recent years," he adds. Table 1 shows the installed ClO_2 generator base at North American pulp mills, including one in Mexico. Some units still in operation were installed in the 1950s and 1960s, but the overwhelming number were installed in the late 1980s and 1990s, reflecting the rapid conversion away from chlorine to chlorine dioxide bleaching leading up to and immediately following passage of the Cluster Rules.

In fact, 101, or approximately 75%, of the installations in Table 1 occurred from the mid-1980s (when dioxins and other chlorinated organics were first discovered in effluent discharges of some pulp mills bleaching with elemental chlorine) through 1997 when the Cluster Rules were finally passed.

Changing Dynamics

According to Sokol, dynamics driving today's chlorine dioxide activities and technologies have shifted in recent years. Rather than just reacting to the Cluster Rules, today's mills are looking for ways to get more production and efficiency from their ClO_2 generators and to better position them toward changing market conditions and demands.

"For example, some mills we've worked with lately have been traditional hardwood mills and need incremental ClO_2 capacity to switch to or add softwood as markets change," he says. "Right now their interest is getting the most they can from their ClO_2 plants. Some mills want to push the name plate capacity as far into the over-design range as possible, while still maintaining safe operations."

Beyond safety, however, there is another important consideration when pushing ClO_2 generation capacity, Sokol explains. "There's no free lunch with these units, in that you generally pay back capacity in terms of efficiency loss. Generator efficiency tends to drop as it's pushed past design capacity, and ClO_2 production costs go up correspondingly."

"Most of these mills are trying to increase ClO_2 output without creating new capital spending," Sokol continues. "And since they really don't want to lose generator efficiency either, this presents somewhat of a dilemma. This is where a new concept we are developing comes into play."

New Approach

Previously known as the Chlorine Dioxide Concept in Europe and the ATF (across the fence) concept in North America, Eka's new approach to high efficiency operation of on-site ClO_2 plants is now being called, more simply, Eka ClO_2. The concept is already being used at a dozen pulp and paper mills in Europe, Scandinavia, and South America, and is currently being developed at the first U.S. mill.

To illustrate the thinking behind Eka Chlorine Dioxide, Sokol tells of a prior meeting with a chief executive of a U.S. paper company. "In that meeting he told us that when you guys come in, we get really good ClO_2 efficiency for the 24 or so hours you're here. But as soon as you leave, it falls back to where it was before. He wanted to know how the mill could maintain the higher efficiency day in and day out." This subsequently gave birth to Eka's new approach to ClO_2 plant operations.

With this new approach, Eka remotely monitors a mill's ClO_2 plant around the clock, ensuring that it is running properly and performing at maximum efficiency, that the plant's chemicals inventory is current, and that the mill's ClO_2 needs are being met in the most effective manner possible. In addition, Eka can handle all routine maintenance for the ClO_2 plant. The net goal of the program is to reduce a mill's ClO_2 plant operating costs and ensure an uninterrupted, reliable supply of ClO_2 to its bleach plant.

Sokol explains that the Eka ClO_2 program in Europe is being staffed by some 20 people who are in 24-hour contact with the mills they serve. The U.S team currently consists of five specialists who work closely with ClO_2 plant operators at the mill where the program is being piloted in North America.

"At this time, we're remotely monitoring just about everything that goes on in the mill's ClO_2 plant, but we are not yet set up to control it remotely. We work directly with the plant's operators, who are mill employees and are very familiar with the quirks and 'personality' of their system. We look at chemical levels, chemical usage, mill uptime and downtime, and, in general, overall performance of the plant.

"We started out supplying the mill with monthly reports on the plant's operation. Right now we are transitioning to weekly and daily reports so that operators will have the feedback they need to keep things at maximum efficiency. During the day we talk to the operators by phone about how the plant is running and any specific problems that might have come up.

"The best way to run at maximum efficiency is slow and steady. Keep it running level and even in all the tanks. Avoid heavy production followed by slow periods of operation. This has meant a significant change in practices and habits for some mill employees. But, overall, things are going very smooth at our first remote operation in the U.S.

"The mill is still handling all logistics for the plant. They tell us, for example, when rail cars are received and we then make sure they get the chemicals they need when they need them. But the plan is to eventually transition mill personnel as much 'out of the loop' as possible, so that all they have to be concerned about is the level of chlorine dioxide in the storage tanks.

"We're handling more and more of the maintenance issues for the mill's ClO_2 plant. In this regard, we can do certain capital projects they really can't justify as capital items on their books right now. So, essentially, they're getting capital work done as operating expense items, which makes the mill's accountants and everyone else happy. We use our own people or subcontractors to do the maintenance work at these plants," Sokol explains.

At first both Eka and the mills had some concerns about the "big brother" aspects of the program. "We were gathering a lot of data about the ClO_2 plants, and the mills wanted to know specifically what we were going to do with all of that information. Now we've learned to trust each other and, in most cases, this is no longer a concern."

Sokol believes that, in the near future, remote monitoring of a mill's ClO_2 plant will progress toward true outsourcing (similar to the on-site PCC plants at some paper mills today), "where we actually own the plant and staff it with our people. It's certainly a doable thing, but, of course, there are some people and legal issue that will have to be worked out first," he notes.

Outsourcing operations such as the ClO_2 plant allows a mill to focus on what it does best, its core business—making pulp and paper—rather than running a chemicals operation, Sokol emphasizes.

Evolving ClO_2 Technologies

Also driven by changing dynamics, Sokol explains that ClO_2 generation technologies have evolved dramatically in recent years. In the 1950s, he notes, plants generated chlorine dioxide, chlorine, and sodium sulfate (salt cake). All three were valuable products for a mill.

In the mid-1980s, however, when the industry first began moving away from chlorine based pulp bleaching, the chlorine product was no longer so desirable. The industry then began using methanol chemistries, rather than salt (sodium chloride) as the reducing agent, to eliminate chlorine production, which considerably increased the amount of salt cake produced.

In the kraft pulping process, salt cake is added to thick black liquor just before incineration in the recovery boiler, where it is converted to sodium sulfide, an important ingredient in the makeup of raw white cooking liquor. Generally, using methanol as the reducing agent in today's ClO_2 generators has resulted in more salt cake than a mill's chemical recovery process can handle, creating a salt cake disposal problem.

In the 1990s, Sokol continues, "we started using hydrogen peroxide chemistry, which has reduced the salt cake production. But because mills have gone to such high levels of ClO_2 substitution (100% in most cases) and tightened up their recovery loops, maintaining just the right balance of sodium sulfate is still a delicate matter in many cases."

The next step in the evolution of ClO_2 generation is to better integrate sodium sulfate into a mill's processes, Sokol says, adding that Eka has already been "looking closely at how to best manage a mill's sodium and sulfur balance." For example, he says that electrolytic processes already exist, "with which we can convert salt cake into usable acid and caustic," but they are currently too expensive and have high maintenance requirements.

"The scale of an electrolytic process would be too small at just one mill. It's far outside the expertise area of a pulp and paper mill, which wouldn't, understandably, have the chemical know-how to operate such a plant. But in the future it might be possible for a chemical company such as Eka to collect salt cake from several mills and convert it in a central processing facility. Such a facility would have the proper economics of scale and could process the salt cake cost effectively," Sokol points out.

Currently, some mills with low flow effluent receiving streams have to land fill excess salt cake, which can be very costly. The by-product is not pure sodium sulfate, Sokol points out. Because it is typically contaminated with acid and chlorate, land filling is more restrictive and costly. Other mills with sufficient water flow may have permits to sewer certain amounts of the salt cake, but disposal can still be a problem for these mills. One area of the Cluster Rules to be worked on later is COD discharge, which includes salt cake, Sokol says.

Rising energy costs are also becoming a major concern with ClO_2 plants, he notes. "Right now the process is very energy intensive. A lot of heat is required to generate the steam and to evaporate high volumes of water in the process. "In the recent past, energy costs really haven't been a major driver in this area. But today it has suddenly become one. Eka is currently exploring ways to reduce energy requirements of the ClO2 plant, and I believe some significant breakthroughs are on the horizon."

MACT II—Methanol vs Peroxide

Another concern on the horizon is MACT II, pending air regulations that include methanol emissions. The amount of work that will have to be done to meet MACT II requirements for methanol storage tanks could be considerable, according to Sokol.

The cost for converting methanol storage and waste methanol tanks will likely be high, but there could also be some expensive work in relation to fugitive emissions from pump seals, sample points, etc. Because methanol is considered a Class I flammable liquid, some stringent electrical codes have to be met.

"When we first started doing methanol processes, to be 100% safe in relation to electrical codes, we diluted the methanol feed into the ClO_2 plant from 100% down to 20%, which turned out to be too stringent. It was over-kill. We found other ways to meet code requirements without diluting the methanol. Still, when doing a retrofit at an older ClO_2 plant today, we have to be very careful in relation to the electrical codes," Sokol explains.

Hydrogen peroxide doesn't fall under MACT II, so there would be no compliance issues with this process chemistry. "But peroxide has its own set of quirks and requirements in regard to safety," Sokol continues. "As with any other chemical, you have to handle peroxide properly and with the right degree of safety to meet requirements. But whether methanol is better, or peroxide, depends on your operating perspective."

Sokol notes that he has conducted several studies converting ClO_2 plants from methanol to peroxide and back again. With peroxide, bleach plant effluent BOD (biological oxygen demand) going to waste treatment is typically about 25% lower than with methanol, he points out, because there is a considerable amount of un-reacted methanol and organic by-products that enter the bleachery with the methanol solution and exit with the effluent.

"This can take a load off of secondary treatment, but depending on how a mill does its balance sheets, this has more or less value. Peroxide and methanol technologies are basically the same. The generators look the same, automation is the same, etc.," Sokol says. Methanol is the dominant technology right now, he adds, because it met the needs of immediately getting rid of the chlorine by-product beginning in the mid-1980s.

Initially, peroxide was relatively expensive compared with methanol, Sokol continues. But, today, peroxide prices have fallen, and all things considered, overall costs of the two approaches are similar. Peroxide chemistry is a much faster process than methanol, he adds, and depending on equipment at a mill, it might be possible to get more capacity from a peroxide system.

Maintenance

In the 1980s, Sokol says, "we switched to titanium as our workhorse material of construction for ClO_2 generators. If treated right, this material will last almost forever. We've opened up units that have been running for 10 years and could still see original machining marks on the circulation pump casing interior.

"Titanium is an excellent material for these systems as long as there is chlorate in them to change an oxidizing environment to a reducing environment. If a unit is started up, for example, with only sulfuric acid in it, it will not last anytime at all. As long as you maintain a chlorate residual, the reactor will have a very long operating life.

"It's all a matter of maintenance. And this is an area where mills have matured quite a bit in recent years. Some ClO_2 generators out there have been operating for 35-40 years now, and will continue to run for many more years if properly maintained. This is where the maintenance aspect of our Eka Chlorine Dioxide program could be especially valuable," Sokol points out.

COUNTRY	LOCATION	YEAR SUPPLIED	CAPACITY (TPD)
U.S.	Rayonier Inc., Fernandina Div.	1955	8.0
U.S.	Weyerhaeuser Co., Cosmopolis Mill	1960	10.0
Canada	UPM-Kymmene, Miramichi Inc.	1965	11.0
U.S.	International Paper, Augusta Mill	1966	10.0
U.S.	Sappi Fine Paper, North America Somerset Mill	1968	14.0
Canada	Parsons & Whittemore Inc., St. Anne-Nackawic Pulp Co.	1969	16.0
Canada	International Paper, Cariboo Pulp & Paper	1972	16.0
U.S.	Georgia-Pacific Port Hudson Division	1972	10.0
U.S.	Bowater Newsprint, Coosa Pines Operations	1977	11.0
U.S.	International Paper, Franklin Mill	1977	12.0
U.S.	Appleton Papers Inc.	1978	5.0
U.S.	International Paper, Courtland Mill	1978	10.0
Canada	Domtar Espanola Mill	1982	34.0
Canada	Nexfor Inc., Fraser Papers Inc.	1983	13.0
Canada	Tembec Inc., AV Cell Inc.	1983	8.0
U.S.	Georgia-Pacific, Camas Mill	1983	20.0
U.S.	Georgia-Pacific, Crossett Mill	1984	30.0
U.S.	Georgia-Pacific, Leaf River Mill	1984	30.0
Canada	Western Pulp Ltd., Squamish Oper.	1985	30.0
U.S.	International Paper, Georgetown Mill	1985	80.0
U.S.	Stora Enso, Wisc. Rapids Pulp Div.	1986	40.0
U.S.	Weyerhaeuser, Kingsport Operations	1986	5.0
U.S.	International Paper, Riegelwood Mill	1986	25.0
Canada	Domtar Communication Papers Div.	1987	24.0
Canada	NorskeCanada Ltd. - Crofton Div.	1987	40.0
Canada	Weyerhaeuser Canada Ltd.	1987	60.0
U.S.	International Paper, Pensacola Mill	1987	34.0
Canada	Canadian Forest Products, Northwood Pulp Mill	1988	50.0
Canada	Nexfor Inc., Fraser Papers, Thurso Pulp	1988	15.0
Canada	Pope & Talbot, Harmac Pulp Oper.	1988	45.0
Canada	Tembec Inc., Marathon Pulp	1988	21.0
U.S.	Georgia-Pacific, Camas Mill	1988	15.0
U.S.	Georgia-Pacific, Crossett Mill	1988	45.0
U.S.	Georgia-Pacific, Leaf River Mill	1988	30.0
U.S.	International Paper, Androscoggin Mill	1988	40.0
Canada	Tembec Inc., Specialty Cellulose Div.	1988	3.0
Canada	Howe Sound Pulp & Paper Ltd Partnership	1989	35.0
Canada	International Paper, Weldwood of Canada Hinton Div.	1989	32.0
Canada	Smurfit-Stone-La Tuque	1989	25.0
Canada	NorskeCanada Ltd.- Elk Falls Div.	1989	34.0
Canada	Pope & Talbot, Mackenzie Pulp Oper.	1989	30.0
Canada	Weyerhaeuser (Grande Prairie Mill)	1989	33.0
U.S.	KPS Investment Funds, Blue Ridge Paper Products Inc.	1989	35.0
U.S.	Weyerhaeuser, Flint River	1989	50.0
U.S.	Domtar Industries Inc., Ashdown Mill	1989	25.0
U.S.	International Paper Co.	1989	40.0
Canada	Abitibi-Consolidated, Fort Francis Div.	1990	25.0
Canada	Nippon Unipac Holding, Daishowa-Marubeni Peace River Mill	1990	29.0
U.S.	Buckeye Technologies, Buckeye Fla.	1990	30.0
U.S.	Georgia-Pacific, Naheola Mill	1990	65.0
U.S.	International Paper, Courtland Mill	1990	30.0
U.S.	Weyerhaeuser Paper Co.	1990	20.0
Canada	Irving Pulp & Paper, Saint John Mill	1990	25.0
U.S.	Bowater Newsprint, Coosa Pines Oper.	1990	32.0
U.S.	International Paper Co.	1990	36.0
U.S.	International Paper, Eastover Mill	1990	23.0
U.S.	Weyerhaeuser, Columbus Mill	1990	32.0
U.S.	MeadWestvaco, Wickliffe Mill	1990	15.0
U.S.	Weyerhaeuser, Bennettsville Operations	1990	16.0
Canada	Bowater Canadian Forest Prod. Inc.	1991	60.0
Canada	Weyerhaeuser Co. Dryden Mill	1991	30.0
Canada	Kimberly-Clark Corp., Nova Scotia	1991	33.0
Mexico	Pondercel S.A. de C.V.	1991	11.0
U.S.	Boise Cascade, Jackson	1991	30.0
U.S.	Domtar Industries Inc. Ashdown Mill	1991	25.0
U.S.	Gulf States Paper Corp.	1991	50.0
U.S.	International Paper, Augusta Mill	1991	40.0
U.S.	International Paper Co. Bastrop Mill	1991	40.0
U.S.	Potlatch Corp., Cypress Bend Mill	1991	25.0
Canada	Tembec Inc., Smooth Rock Falls Div.	1991	16.0

COUNTRY	LOCATION	YEAR SUPPLIED	CAPACITY (TPD)
U.S.	Rayonier Inc., Jesup Mill	1991	60.0
U.S.	Weyerhaeuser Co.	1991	32.0
Canada	Canadian Forest Products Ltd., Intercontinental Pulp Mill	1991	55.0
U.S.	Potlatch, Idaho Pulp & Paperboard	1991	36.0
Canada	Tembec Skookumchuck Operations	1992	20.0
U.S.	Boise Cascade, Wallula Mill	1992	36.0
U.S.	Bowater Newsprint Calhoun Oper.	1992	20.0
U.S.	Georgia-Pacific, Wauna Mill	1992	45.0
U.S.	MeadWestvaco Corp.	1992	25.0
U.S.	MeadWestvaco, Rumford Mill	1992	40.0
U.S.	International Paper, Riverdale Mill	1992	35.0
Canada	SFK Pulp Funds	1992	37.0
U.S.	Domtar Industries Inc., Nekoosa Mill	1992	20.0
U.S.	Georgia-Pacific, Brunswick Operations	1992	60.0
U.S.	Georgia-Pacific, Port Hudson Division	1992	18.0
U.S.	International Paper, Riegelwood Mill	1992	50.0
Canada	International Paper, Cariboo Pulp & Pape	1992	16.0
U.S.	Weyerhaeuser, Pulp-Paperboard Div.	1992	16.0
Canada	Smurfit-Stone Container Canada Inc., Pontiac Div.	1993	20.0
Canada	Alberta-Pacific Forest Industries Inc.	1993	15.0
U.S.	Boise Cascade, Paper Div.	1993	40.0
U.S.	Smurfit-Stone - West Point Mill	1993	18.0
U.S.	Georgia-Pacific, Old Town Mill	1993	20.0
Canada	Celgar Pulp Co.	1993	40.0
U.S.	Georgia Pacific, Brunswick Operations	1993	65.0
Canada	Domtar, Norkraft Mill	1993	25.0
U.S.	International Paper, Quinnesec Mill	1994	30.0
U.S.	Weyerhaeuser, Plymouth Mill	1994	35.0
U.S.	Georgia-Pacific, Port Hudson Div.	1994	60.0
U.S.	Glatfelter - Spring Grove Mill	1994	15.0
U.S.	Weyerhaeuser, Johnsonburg Oper.	1994	25.0
U.S.	Boise Paper Solutions – Louisiana Oper.	1994	12.0
Canada	Kimberly-Clark Inc., Canada	1995	35.0
Canada	Western Pulp Ltd. Partnership	1995	15.0
Canada	Domtar Cornwall Business Center	1995	56.0
U.S.	International Paper, Franklin Mill	1995	30.0
U.S.	Preco Corp., Eastern Paper - Lincoln Mill	1995	8.5
U.S.	Nexfor Fraser Paper, Gorham Mill	1996	30.0
Canada	Weyerhaeuser, Prince Albert Pulp & Paper	1996	50.0
U.S.	Bowater, Catawba Operations	1996	20.0
U.S.	Sappi Fine Papers	1996	26.0
U.S.	International Paper, Riverdale Mill	1996	20.0
U.S.	Finch, Pruyn & Co,. Glens Falls Mill	1996	20.0
U.S.	MeadWestvaco Publishing Paper Div.	1996	52.0
Canada	Kruger Wayagamack Inc.	1997	14.0
U.S.	Weyerhaeuser, Hawesville Operations I	1997	40.0
U.S.	MeadWestvaco Corp., Covington Mill	1997	50.0
U.S.	MeadWestvaco Corp., Luke Mill	1997	34.0
U.S.	International Paper, Ticonderoga Mill	1997	16.0
U.S.	Sappi Fine Paper North America, Somerset Mill	1998	50.0
U.S.	Weyerhaeuser, Bennettsville Operations	1998	40.0
U.S.	MeadWestvaco, Wickliffe Mill	1998	20.0
U.S.	Domtar Industries, Woodland Mill	1998	42.0
Canada	Cascades, Les Industries Paperboard Intl -Fjordcell	1999	12.0
U.S.	Simpson Tacoma Kraft Co.	1999	30.0
U.S.	Parsons & Whittemore Inc., Alabama River Pulp Co.	1999	36.0
U.S.	Sappi Fine Paper North America, Muskegon Mill	1999	10.0
U.S.	Tembec Inc.,St. Francisville Operations	1999	18.0
U.S.	Georgia-Pacific Palatka Pulp & Paper Operations	2000	54.0
U.S.	Appleton Papers Inc.	2000	10.0
U.S.	Boise Paper Solutions	2000	32.0
U.S.	Smurfit-Stone, Containerboard Mill Div.	2000	30.0
U.S.	Parsons & Whittemore Inc., Alabama River Pulp Co.	2000	45.0
U.S.	MeadWestvaco, Evadale Mill	2000	65.0
U.S.	Smurfit-Stone Container, Brewton Mill	2000	35.0
U.S.	Kimberly-Clark, Everett Mill	2000	10.0
U.S.	Pope & Talbot, Halsey Mill	2000	35.0
U.S.	Abitibi-Consolidated, Lufkin Mill	2001	20.0
		TOTAL	**4098.5**

Table 1. Installed base of chlorine dioxide generators in the North American pulp and paper industry. (Note: mills are identified by "common" industry location terminology rather than specific city, state, province location. Some mill locations are not included.) Source: Based on Fisher International data.