A survey of chlorine dioxide generation in the United States

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There is plenty of room for improvement in the processes used to produce chlorine dioxide. With its impact on the environment and bleaching costs, mills will spend more time reviewing the operations of their chlorine dioxide generation plants.

In 1986 and 1987, the Pulp Bleaching Committee of TAPPI's Pulp Manufacture Division conducted surveys of chlorine dioxide generator operations in the United States. This report covers the major areas of concern in the pulp mills' chlorine dioxide plants. The committee's goal was to characterize the state of the art in the production of chlorine dioxide and thereby identify areas for improvement.

The survey covers the types of generator, capacity, safety and control features, and performance with respect to consumption, maintenance record, and the use and credit taken for by-products.

Of the 76 mills producing chlorine dioxide, 33 participated in this survey. Several of the 33 mills had at least two types of generators. All current types of generators are represented in the survey returns. The mills were coded by number to protect their anonymity.

Types and distribution of generators

The types of generators reported were the Mathieson, Solvay, R_2, SVP/R_3, R_8/SVP-CH_3OH, and the Lurgi HCl processes. **Table I** shows these types differentiated by the reaction equation, reducing agent used, and the nature of the generator effluent.

The survey provided information on 44 generators. The distributions by type and geographical region are shown in **Figs. 1 and 2.** The predominant generators in the southeastern United States are the SVP/R_3 and the R_2. The R_2 was economically attractive, initially, because of its ability to utilize the acid effluent in the adjacent tall oil plants and because of the popularity of hypochlorite bleaching. As sulfur emissions were reduced, R_2s were cascaded into R_3/SVPs (*13*), or the R_2s were shut down. Unfortunately, the number of respondents from the other regions was small, and based on our knowledge of the installations, these distributions are not representative. We predict that more mills will be converting to the more efficient processes to achieve saltcake balance, reduce hypochlorite production, and increase chlorine dioxide production.

Production rate calculations

There was diversity in the method of determining production rate. Fifty-nine percent of the respondents calculated the operating rate by the quantity of the chlorine dioxide solution produced, 24% by the quantity of solution used. Eleven percent determined the production based on quantity of chlorate used, and 5% determined it based on the change in inventory in the storage tanks. The method of calculation may explain some of the discrepancies in the reported raw material consumption figures.

The capacity of the generator

Figure 3 shows the operating range and average generator capacities. The largest generator reported produces 30 tons/day, the smallest 2 tons/day. Thirty-five percent of the respondents indicated that they had insufficient design capacity installed to satisfy the bleach plant demands.

Generator systems, protective equipment, and instrumentation safety

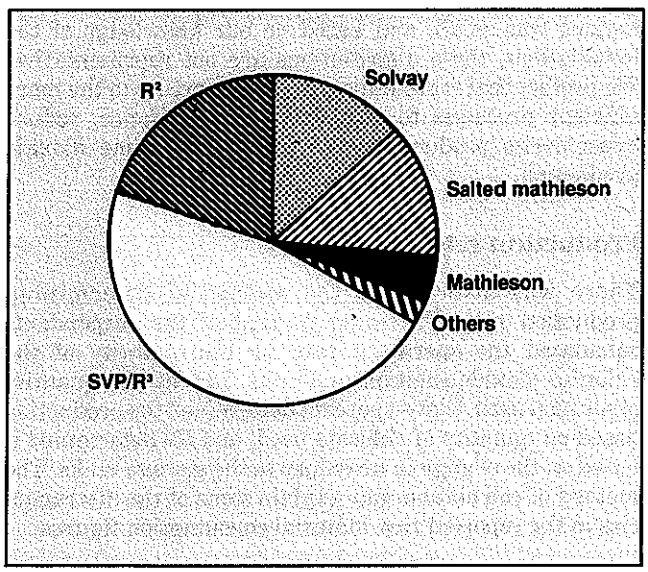
Generation systems should have the ability to detect a potential or actual upset and alert the operator to the need for a shutdown of the chemical and utility feeds and to vent the equipment prior to explosive damage. The activation of interlock will depend on the mode of

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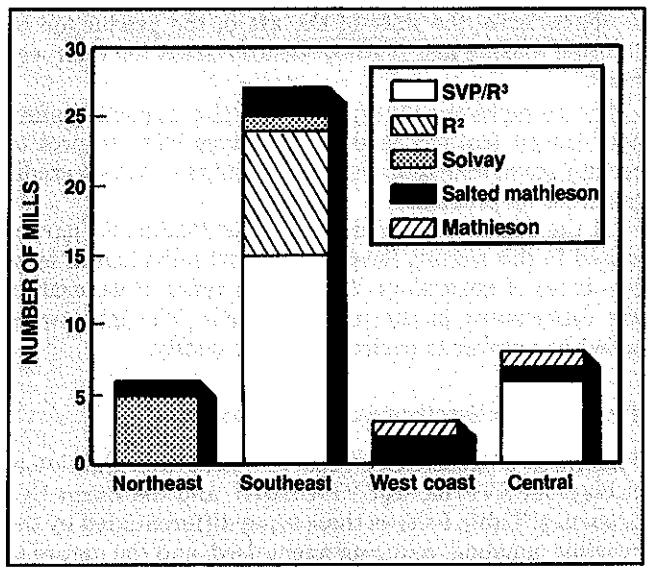
I. Details on chlorine dioxide generation processes

Process	Reaction equation	Reducing agent	Effluent produced	Comments
Mathieson	$SO_2 + 2NaClO_3 + H_2SO_4 \rightarrow 2ClO_2 + 2NaHSO_4$	SO_2	30–40% sulfuric acid	ClO_2 stripped from reactors with air. Excess saltcake causes imbalance for mills trying to reduce sulfur emissions (*1*).
Solvay	$4NaClO_3^a + CH_3OH + 2H_2SO_4 \rightarrow 4ClO_2 + 3H_2O + HCOOH + 2Na_2SO_4$	Methanol	30–40% sulfuric acid	ClO_2 stripped from reactors with air. Excess saltcake causes imbalance for mills trying to reduce sulfur emissions (*2*).
R_2	$NaClO_3 + NaCl + H_2SO_4 \rightarrow ClO_2 + \frac{1}{2}Cl_2 + Na_2SO_4$	Chloride ion from NaCl	30–40% sulfuric acid and chlorine (used for hypochlorite make-up)	ClO_2 stripped from reactors with air. Excess saltcake causes imbalance for mills trying to reduce sulfur emissions (*3*).
SVP/R_3	$NaClO_3 + NaCl + H_2SO_4$ $ClO_2 + \frac{1}{2}Cl_2 + Na_2SO_4 + H_2O$	Chloride ion from NaCl	Cl_2 as hypochloriate	Anhydrous saltcake added to recovery cycle (*4–6*).
R_6/SVP-HCl Lurgi Chemetics	(a) $NaCl + 3H_2O \rightarrow NaClO_3 + 3H_2$ (b) $Cl_2 + H_2 \rightarrow 2HCl$ (c) $NaClO_3 + 2HCl_2 \rightarrow NaCl + ClO_2 + \frac{1}{2}Cl_2 + H_2O$	Hydrochloric acid	Requires on-site chlorate cells to receive recycled salt (solid or in solution)	(*7–10*)
R_6/SVP-CH_3OH	$3NaClO_3 + 2H_2SO_4 + 0.85CH_3OH \rightarrow ClO_2 + Na_3H(SO_4)_2 + H_2O + 0.05CH_3OH + 0.6CHOOH + 2CO_2$	Methanol	Lower amounts of saltcake than other processes	Highly acidic saltcake (*11,12*).

1. Chlorine dioxide generator types



2. Generator type by geographical area



operation—atmospheric in the case of the R_2, Solvay and Mathieson, vacuum for the R_3/SVP or R_8/SVP-CH_3OH—and whether or not the stripping medium is air or steam. The use of safety features is summarized in **Fig. 4**.

The explosion lid movement detectors are only installed on the atmospheric units. Fourteen generators were fitted with explosion lid detection switches, two of which were tied into the shutdown of the unit. Fourteen generators have the integrity of the equipment protected by a rupture disc. Only four generators did not have the ability to air purge (R_2, Mathieson, Solvay) or water quench (R_3/SVP, R_8/SVR-CH_3OH) the reactors after a decomposition.

Only three installations lacked the ability to detect the high gas temperature created after a decomposition. Twenty-one of the generators had this feature tied into the interlocked shutdown of the unit. Ten units could not detect the increased gas pressure produced by a decomposition. Only 16 units interlocked a high gas-pressure reading with the unit shutdown.

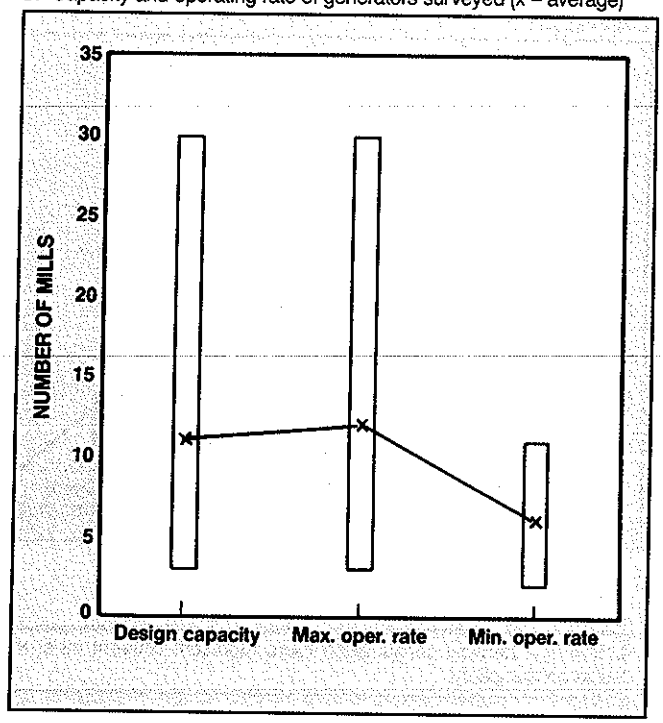
Fourteen units were set up to detect a high concentration in the chlorine dioxide solution; only one of these units interlocked this variable with the shutdown.

Eight units could detect a high flow of the reducing agent, SO_2/CH_3OH; four of these units were interlocked to shut down on a high flow or concentration signal.

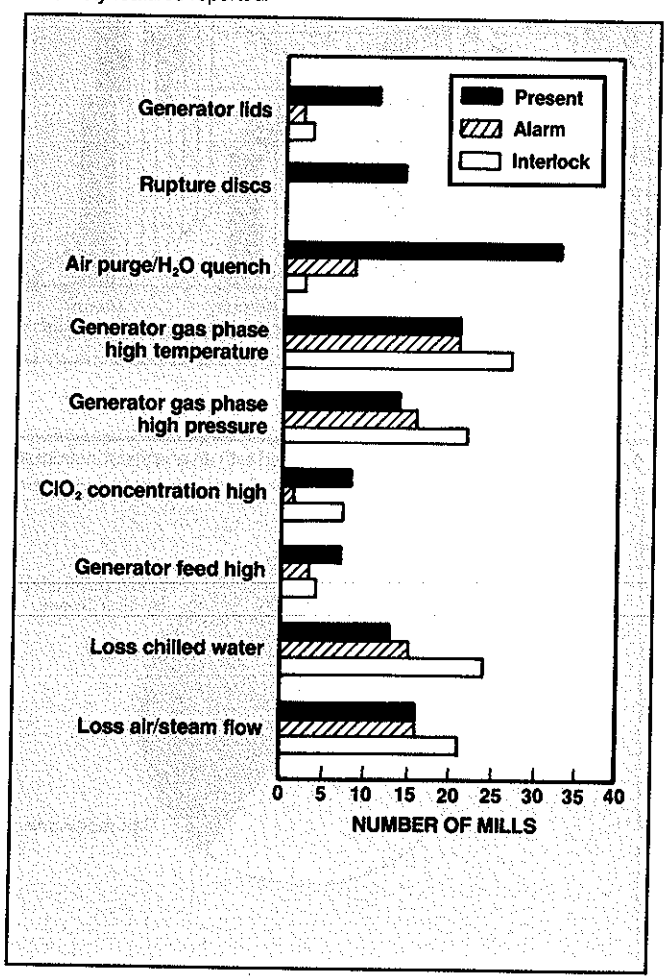
Only five units did not indicate low chilled-water flow to the chlorine dioxide absorption tower, and 21 of the units shut down the unit on receiving such a signal.

Seven units do not alarm when the air or steam for the chlorine dioxide gas diluent is absent. Only 16 units interlock this feature with the shutdown.

3. Capacity and operating rate of generators surveyed (x = average)



4. Safety features reported.



Instrumentation

The instrumentation used in chlorine dioxide systems is equally divided between electronic and pneumatic at about 40% each. There is a move to computer or microprocessor control, with about 10% now using one of these methods.

System availability and downtime

The average availability of the systems was 89%. Less than 1% of downtime was due to decompositions. Slightly more than 1% was due to boil-outs and equipment failures. The major portion of the downtime, about 3%, was due to bleach plant outages. Two percent of downtime was due to outages other than bleach plant, and 3% was due to pulp mill furnish changes.

Chemical consumption

The chemical consumption figures reported on all processes show a significant variation from designed consumption. Design values should be set at the level of performance guaranteed plus an additional 2–3% for losses due to the frequency of startup, shutdown, and decompositions in the generator.

Based on this premise, the raw material chemical consumptions in tons per ton of chlorine dioxide produced are shown in **Figs. 5–8.**

Obviously, there is room for significant improvement in performance of all the processes that produce the expensive chlorine dioxide bleaching agent.

Performance of the older units

The degree of satisfaction with existing atmospheric generators was mixed. The respondents reported their operations as being 12% poor, 28% satisfactory, 50% good, and 10% excellent. There were 13 mills with generators in service more than 15 years, 8 mills with 20 years or more, and 3 mills with 30 years or more. Several mills had replaced existing units rather than converting to processes with less problematic by-products. There was at least one Mathieson generator continuing to operate with a chlorate scrubber.

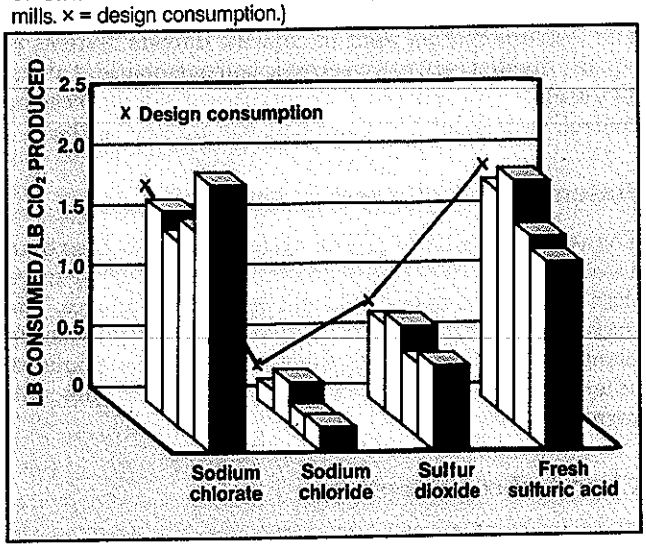
Chlorine dioxide solution quality and storage

The chlorine dioxide solution concentration was reported from 6.9 to 10.4 g/L, with storage tank solution temperatures from 40°F to 55°F. Chlorine in the chlorine dioxide solution obviously varies with the process as does the pH of the chlorine dioxide solution. Both of these variables are useful troubleshooting aids for the chlorine dioxide process and the bleach plant, so it is surprising that there were so many mills that had no values recorded on these variables.

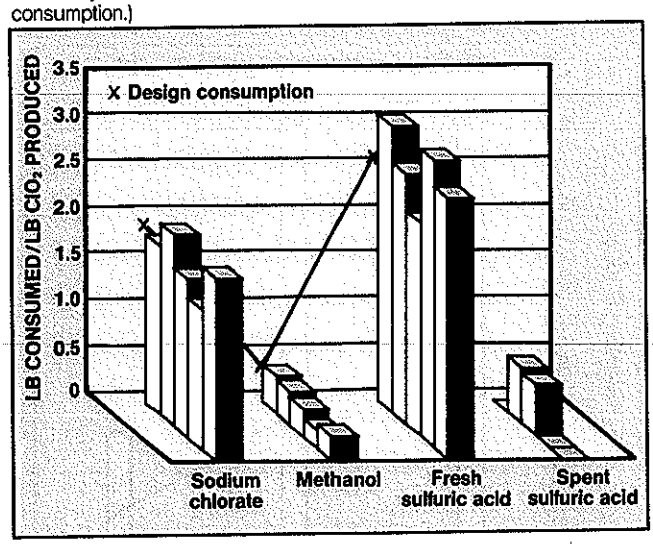
Chlorine dioxide storage is a buffer between the bleach plant demands and the ability of the chlorine dioxide generator to supply product. The range was from 4 hours to 79 hours, with an average of 11 hours.

Fiber reinforced plastic was reported as a material of construction for 41% of the chlorine dioxide storage tanks, with the remainder being constructed of tile lined steel.

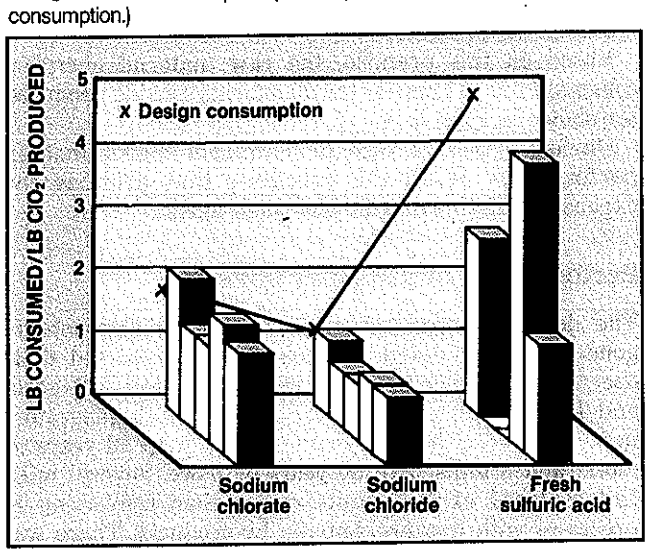
5. Salted Mathieson chemical consumption (Bars represent different mills. × = design consumption.)



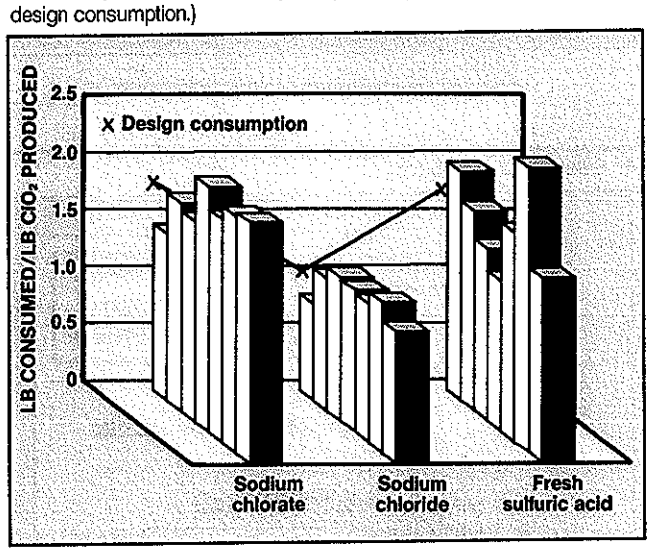
6. Solvay chemical consumption (Bars represent different mills. × = design consumption.)



7. R_2 chemical consumption (Bars represent different mills. × = design consumption.)



8. SVP/R_3 chemical consumption (Bars represent different mills. × = design consumption.)



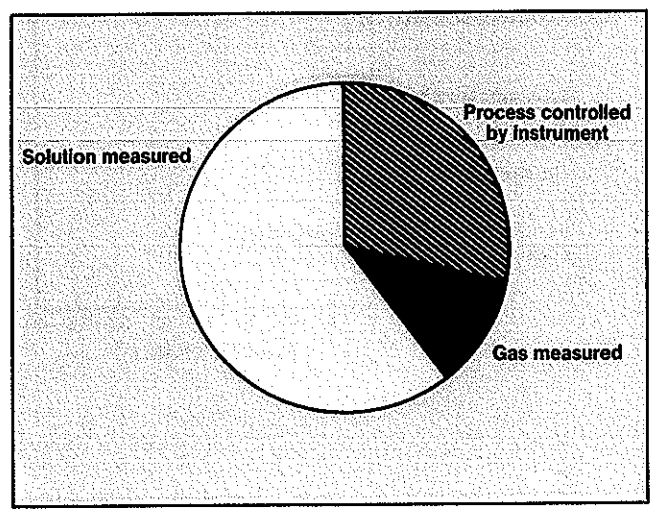
The tank volumes range from 11,000 to 343,000 gallons.

Thirty-three percent of the tanks have the gas space swept with air, 18% have their vent gases scrubbed. A surprising 33% reported occasional lifting of the explosion lids due to decompositions in the storage tank, and two mills reported that decompositions had caused damage to the tanks.

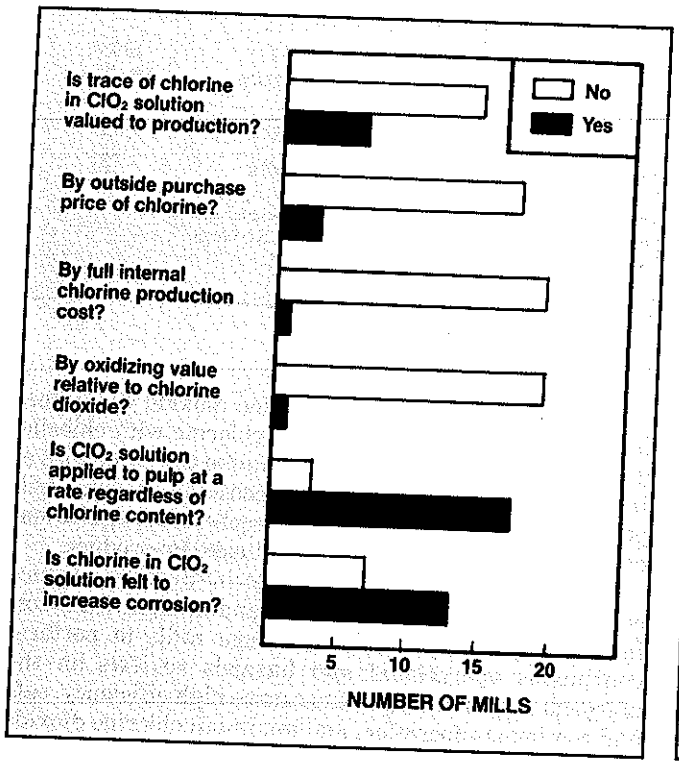
The potential for decompositions to occur in the tank is a function of the concentration and temperature of the chlorine dioxide solution. The ability to limit the destructive power of decomposition is a function of the storage tank design parameters (*14*).

As shown in **Fig. 9**, the use of a chlorine dioxide solution analyzer was reported in 17 installations. Eight of these use the instrument to control the process. Three installations use the analyzer to measure the gas concentration from the reactor. Eight mills plan to install analyzers in their process in the future.

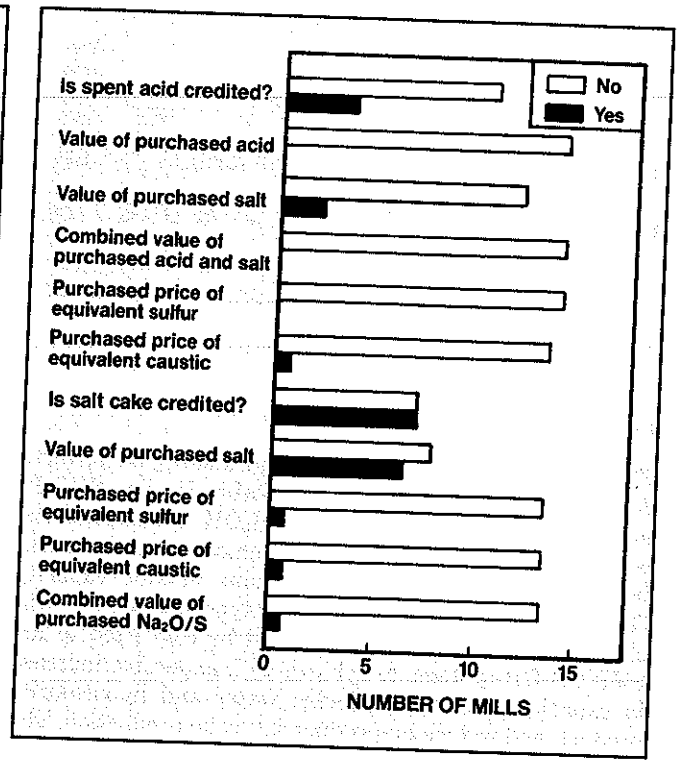
9. Chlorine dioxide concentration measured with an analytical instrument.



10. Chlorine in chlorine dioxide: measurement, value, and mill impact



11. Value of acid and saltcake generated in chlorine dioxide production.



Spent acid handling and storage

The spent acid effluent showed 0.5–6% chlorate loss to the recovery cycle. The preferred material of construction for 74% of the effluent storage tanks is fiber reinforced plastic. Glass- and tile-lined tanks were less popular at 18% each. The majority of the tanks are fitted with explosion lids and are air purged. Decompositions in the tanks and crystallization of the spent effluent were for pH adjustment, 23% added it to the tall oil plant, 3% were neutralizing it, and 55% added it to the recovery cycle. Of these, six mills added it to the weak black liquor, three mills reported adding to the strong black liquor, and eight added to the white liquor. Sixty percent of mixing was accomplished mechanically, with 40% being handled with a venturi mixer. One mill reported problems with hydrogen disulfide generation. Only five mills used a hydrogen sulfide analyzer.

Value of chlorine dioxide by-products

Only seven mills credit chlorine at the outside purchase price. Eleven mills credit the chlorine in the hypochlorite at the outside purchase price for chlorine, and one mill credited it at its oxidizing value equivalent to chlorine dioxide.

Value of the chlorine in chlorine dioxide

Figure 10 shows the responses to questions on the presence of chlorine in the chlorine dioxide solution. Six mills believe that this is of benefit to the bleaching process, three gave it the value of the outside purchase price of chlorine. One mill credits it with the internal production cost of chlorine, and one takes credit for its oxidizing value relative to chlorine dioxide. Seventeen mills apply the chlorine dioxide solution to the pulp at an oxidizing equivalent regardless of the chlorine content. Thirteen of the respondents believe that the presence of chlorine in the chlorine dioxide increases the rate of corrosion of the equipment, making it an expense instead of a credit.

The value of spent acid effluent

Figure 11 shows the responses to questions on spent acid value. Only six mills credit the value of the spent acid effluent to the chlorine dioxide process. Three of those take credit at purchase price of equivalent sulfur, and one credits it at the purchase price of equivalent caustic. No mills reported a cost assigned against the process because of excess spent acid effluent.

Fourteen mills that produced salt cake from SVP/R_3 gave value for the produced salt cake: 72% at the value of purchased salt cake, 7% at the value of purchase price of equivalent sulfur, 14% at the purchase price of equivalent caustic, and 7% at the combined value of purchased Na_2O/S.

Steam cost

Sixteen mills assigned the cost of steam consumed in the chlorine dioxide plant to the process: 63% at full manufacturing cost, and 37% at the incremental cost.

II. Distribution of generators by type and total installed daily capacity; 1988–1989

	No. of generators					Total tons per day
	SVP/R_3	Mathieson	Solvay	R_2	HCl	
Eastern U.S.	667 (38%)	72 (9%)	87 (13%)	197 (23%)	...	1128
Western U.S.	46 (3%)	33 (8%)	9 (1%)	4 (1%)	15 (1%)	106

III. Estimated impact of environmental legislation on the daily chlorine dioxide demand

	1988–1989, tons/day	1991[a], tons/day	1994[b], tons/day
Eastern U.S.	1128	1342	1501
Western U.S.	106	212	251

[a]Assumes 50% ClO_2 substitution in the chlorination stage.
[b]Assumes 75% ClO_2 substitution in the chlorination stage.

Conclusion

The distribution of generators by type and region in North America in 1988–89 is shown in **Table II**. The SVP/R_3 generators include six R_3/SVP CH_3OH. Because of the concerns about dioxin, $TOCl_2$, and chloroform, there will be a significant increase in chlorine dioxide capacity (**Table III**), and the distribution by type of generator will change dramatically. R_3/SVPs will be converted to R_3/SVP CH_3OH systems to achieve an inexpensive increase in capacity, eliminate chlorine water and hypochlorite product, and reduce by-product salt cake production. The R_2 generators will convert to Solvay systems to obtain additional capacity for incremental capital expenditure.

The large capacity of the chlorine dioxide generators installed plus the displacement of chlorine with chlorine dioxide will encourage mills to examine the economics of the HCl process. These processes consume chlorine, will permit the purchase of the electrochemical equivalent caustic soda, and have no excess saltcake by-product.

The mills' total dependence on chlorine dioxide to reduce contamination of the environment and its significant cost impact on bleaching will encourage mills to perform continuous operational and hazards reviews on the chemical preparation plant to ensure high efficiency, safe and continuous operation, and minimum chlorine dioxide costs.□

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