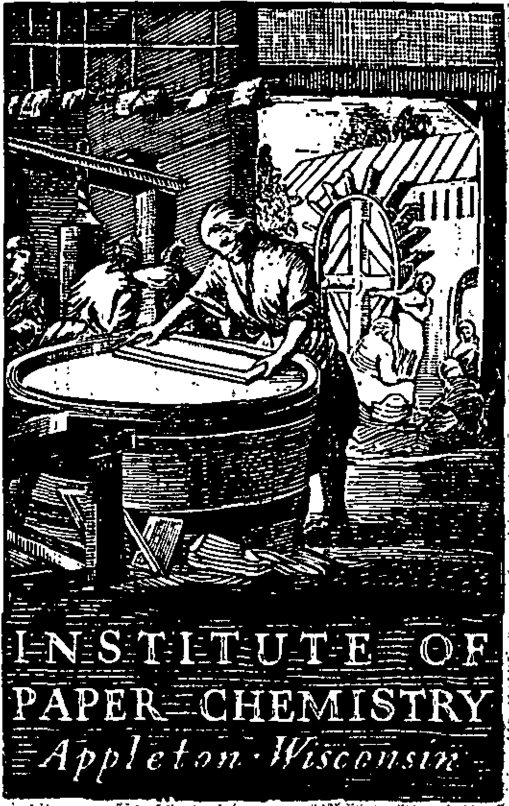
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SELECTIVE DELIGNIFICATION OF WOOD AND OTHER FIBROUS MATERIALS:

PRELIMINARY ECONOMIC ANALYSIS

Project 2500

Report Eighteen

A Progress Report
to
THE GRANTORS

August 30, 1972

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THE INSTITUTE OF PAPER CHEMISTRY
Appleton, Wisconsin

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TABLE OF CONTENTS

	Page
SUMMARY	1
INTRODUCTION	3
FORMULATION OF ANALYSIS	6
Definition of Economic Factors	7
Differential Analysis	8
DEVELOPMENT OF ANALYSIS	10
Economics of Yield	10
Chemical Costs	16
Chemical Recovery	20
Evaporation and Burning	23
Electrolytic Chlor-Alkali	34
Chlorine Dioxide Production	45
Causticizing with Lime	51
Recovery Summary	59
APPLICATION TO SPECIFIC CASES	63
Bleached Hardwood Holopulp	64
Very High-Yield Softwood Holopulp	66
Partial Recovery	69
ADDITIONAL WORK	71
High-Carbonate Recovery	71
Stoichiometric Variations	72
Pulping and Washing Operations	73
Environmental Considerations	74
Papermaking Economics	75
Final Report	75

NOMENCLATURE 77

ACKNOWLEDGMENT 80

LITERATURE CITED 80

THE INSTITUTE OF PAPER CHEMISTRY
Appleton, Wisconsin

SELECTIVE DELIGNIFICATION OF WOOD AND OTHER FIBROUS MATERIALS: PRELIMINARY ECONOMIC ANALYSIS

SUMMARY

A preliminary economic analysis of the holopulping process has been carried out. The analysis was set up on a differential basis to permit comparison with existing processes, especially kraft. The analysis was concerned with the economics of the trade-off between savings in wood costs for holopulp due to higher yield and increased chemical costs used in selective delignification. The influence of the chemical recovery system on the cost of cooking chemicals was also determined. This analysis does not include pulping and bleaching costs (other than chemical costs), environmental costs, or any value judgments regarding the use of holopulp in papermaking.

Based on current wood costs, it appears that the savings due to higher yield would be about $5-10/ADT. The increased chemical costs for holopulp over kraft tend to exceed this by a significant amount at pulping stoichiometries currently practiced. A comparison between holopulp and kraft for a bleached hardwood pulp shows excess costs for holopulp of $10-20/ADT. A similar comparison for a high-yield, unbleached softwood pulp showed break-even economics if a pulp having the requisite properties could be made at 75% yield with 4.5% ClO_2.

Analysis of the recovery system showed that the cost of caustic and chlorine would probably range from 2 to 2.5¢/lb. and that ClO_2 could be obtained for 8 to 12¢/lb. The cost of chlor-alkali was less sensitive to Na_2CO_3 in the ash than expected. On the other hand, separation of NaCl from Na_2CO_3 for separate causticizing of the Na_2CO_3 did not look economical with NaCl the dominant ash component. It appears that burning chlorine to HCl and recycling it to react with Na_2CO_3 is

more economical as long as NaCl is the major ash component. A comparison of full recovery and partial recovery gave a payout time of 3.7-4.7 years for the incremental investment in the electrolytic chlor-alkali and ClO_2 processes.

The work planned to complete this economic analysis includes an extension of the recovery cost estimate to carbonate-rich systems, a comprehensive evaluation of stoichiometric variables, a thorough evaluation of the equipment and operating costs in pulping, an evaluation of environmental costs, and a look at the economic implications of the use of holopulp in papermaking.

At this point in the study, judgments should be tempered by the realization that many important factors were not included in this preliminary analysis. Quantitative data are based on present technology and current costs. Trends in stumpage and harvesting costs; accommodation of environmental impact (land, air, and water); pulp conversion and processing costs; and the relative costs of using different materials to meet certain end-use requirements are all relevant to final assessment.

INTRODUCTION

Economic considerations must play a dominant role in the development of any process. These considerations become more compelling as the development approaches the point where decisions regarding the possibility of commercial implementation must be made. Economics serves as the ultimate yardstick in determining the success or failure of a process. This project has been concerned with examining the potential of oxidative pulping to produce holopulps by selective delignification. As part of the effort to bring the project to a logical conclusion, it was deemed necessary to make a comprehensive economic assessment of the holopulping process.

Such a comprehensive economic analysis is by its nature quantitative and comparative. It is quantitative in that it attempts to assign numerical values to process costs as well as the more intangible aspects of the process. It must also be comparative. Alternative processing schemes (such as the kraft pulping process) are available for achieving the desired product. For holopulping to be successful, it should show an economic advantage over alternatives for certain conditions. The purpose of this economic analysis is to make a quantitative comparison of holopulp with other processes so as to provide a basis for judgments regarding process feasibility.

There are certain broad elements of the holopulping process as it has evolved to date which dominate the economic picture. Holopulp is a high-yield pulp produced by selective delignification, and consequently contains a high proportion of hemicellulose. Because of this high yield, there is a reduction in the amount of wood needed to produce a given amount of pulp. The retention of the hemicelluloses results in a pulp of high bonding capability which can influence papermaking behavior and product performance. Selective delignification is achieved by the use of chemicals which have heretofore been considered as too expensive. The extent to which these chemical costs can be reduced through operation of a chemical recovery system becomes very important. Holopulping does not involve the use of sulfur, and so avoids the odor problem of the kraft mill. It also employs the same chemicals for pulping and bleaching, and so the chemical recovery system can handle the bleach effluent also. The task of the economic analyst is to quantify these various advantages and disadvantages in order to permit a comparison with conventional pulping practices.

The economics of holopulping received a good deal of attention in the last proposal. It was proposed that an economic analysis of the holopulping process be carried out to define costs, designate areas where cost reductions can be achieved, and to provide for a continuing assessment of holopulping economics. It was stated that a thorough parametric study of economic variables was needed to determine the extent to which process changes or changes in cost factors influence the overall economics. The economic analysis was to be formulated in such a way that cost comparisons with other pulping processes could be made on a differential basis.

The economic analysis was further delineated in the Amendment and Modification of the Supplemental Agreement (Number Two) resulting from the discussion of the meeting held at O'Hare Airport, Chicago, Illinois, December 28, 1971. The relevant section is quoted below.

> "1. By way of clarification, it is to be emphasized that holopulp and holopulping represent a range of pulp products and processes delineated broadly by thermomechanical defibration of wood chips along with sequential steps involving the use of caustic and oxidative treatments based mainly on the use of chlorine, chlorine dioxide, and hypochlorite. The chemical recovery system is involved then in the processing of effluent streams containing sodium and chlorine as the principal inorganic constituents leading to regeneration of the required chemicals. The economic assessment of the 'holopulping process' is to be considered in the broadest sense as a critical analysis of a range of alternate processes rather than solely the delimited processes which have been outlined in the earlier work."

This report presents the results of a preliminary economic analysis of holopulping. The economic factors related to higher yield have been defined and quantified. An analysis of the economic aspects of chemical recovery has been made. These parts of the total economic picture have been applied to a few specific cases. The comparisons were made on a differential basis as much as possible. Economic implications of papermaking and of environmental factors have not yet been included to any great extent.

FORMULATION OF ANALYSIS

The objectives of the economic analysis are to define the costs of producing holopulp, determine the extent to which these costs can be influenced by process changes and external cost factors, and to make a critical comparison with other processes. The analysis is to be formulated so that cost comparisons with other processes can be made on a differential basis (only those elements which are different are included in the analysis). Such an analysis gives the difference in cost between producing a ton of holopulp and a ton of some other pulp. The analysis is to be set up in parametric form, both with respect to unit cost factors and process variables. This permits a generalized economic analysis which can readily be applied to specific situations.

Analysis of the economics of pulping is complicated by the fact that pulp is an intermediate product whose true value ultimately derives from the paper made from it. It is relatively straightforward to compare the cost of making a unit weight of pulp by two different processes. It is much more difficult to determine the value of two different pulps. If the only comparison made is the cost of producing unit weights of pulp by two different processes, it is tacitly assumed that the pulps are equivalent in their properties. It is, of course, well known that pulps produced by different processes do have different properties and are most suited for different products. When considering a pulp having the distinctly different properties that holopulp has, it is very easy to get bogged down in quality considerations. In order to get around this difficulty, the economic analysis is carried out in two stages. In the first stage, the concern is directed toward the determination of relative costs on a unit weight-of-pulp basis. The second stage is devoted to an analysis of the comparative economics of holopulp as a papermaking material. This separation is not absolute. The interpretation of the first-stage information is aided greatly by choosing reference pulps of approximately equivalent quality.

DEFINITION OF ECONOMIC FACTORS

The biggest elements in the holopulp cost picture are:

1. the trade-off between reduced wood costs due to higher yield and the use of expensive chemicals for selective delignification, and
2. the influence of a chemical recovery system on the cost of chemicals.

Any analysis of holopulp economics should start with these elements.

The single most important factor involved in wood costs is pulp yield, the amount of pulp formed per unit weight of wood. This is determined primarily by pulping stoichiometry (the types and amounts of chemicals employed in pulping). It will also be somewhat dependent on species. The other major factor involved in wood costs is the unit cost of the wood. This is quite variable and depends on location, species, whether or not lumber wastes are employed, and the degree of selectivity required. One of the regions of uncertainty is the extent to which wood unit costs will rise due to pressure for other uses of land.

Chemical costs are determined simply as the product of the amount of chemicals used and the unit costs of the chemicals. Pulping stoichiometry is a very important factor here. As a first approximation, published market prices may be used to estimate the unit cost of chemicals. The next step is to consider the cost of chemicals in terms of a chemical recovery system.

In analyzing the costs of chemicals when recovery is employed, it is necessary to add up the individual cost elements of the recovery system and assign them to the chemicals produced. The cost elements would include the charges against capital required for equipment, utilities costs (especially electrical power for chlorate and chlorine cells and steam for liquor evaporation), operating, maintenance, and supervisory labor, and make-up and miscellaneous chemical requirements.

After these major elements are in hand, the economic analysis can be refined by including additional factors such as costs of pulping (and bleaching) besides the chemicals costs, environmental costs, papermaking costs, and product values.

DIFFERENTIAL ANALYSIS

The economic analysis is to be formulated on a differential basis to permit easy comparison of costs among the alternative processes. Such a comparison is not directly concerned with the determination of absolute costs, but rather with those factors which are different among the processes considered. All costs are formulated relative to the reference process. This technique assumes that alternative processes are available and that economics serves as a criterion for judging their merit.

The selection of a base of comparison is important in setting up a differential analysis. In this report, it will be assumed that one airdry ton each (containing 1800 lb. ovendry fiber) of both holopulp and the reference pulp is used in comparing costs. For those cost elements where plant size is important, a production rate of 500 ADT per day will be used as a basis. It is assumed that both the holopulp and the reference pulp are made from the same species for roughly the same ultimate purpose. The reference pulp would, in principle, be derived from any alternative process for making pulp. In most cases, the reference pulp would be kraft, either bleached or unbleached, depending on the specific comparison made. For those grades where kraft is not the most economical pulp, alternative reference pulps can be used.

The technique for setting up a differential analysis is rather simple. Costs are equated wherever possible and eliminated from the analysis. Only items whose costs are significantly different are included. Initial approximations of equality may then be challenged and adjusted as the analysis becomes more refined. Each major cost item is then summed to give an overall economic comparison. This provides not only for the overall economics, but it also provides a quantitative assessment of those elements which favor holopulp as well as those which are disadvantageous.

DEVELOPMENT OF ANALYSIS

As was mentioned in the previous section, the dominant elements in the holopulp cost picture are the trade-off between savings in wood costs due to higher yield and the high cost of the delignification chemicals, and the role played by the chemical recovery system in lowering chemical costs. These major factors will now be considered. First, the economics of higher yield will be examined. Next, pulping stoichiometries together with estimates of chemical cost will be combined to determine net chemicals cost for comparison with savings in wood costs. Finally, the chemical recovery system will be examined in some detail to determine its impact on chemical costs.

ECONOMICS OF YIELD

The direct effect of an increase in yield is that less wood is required to make a given amount of pulp. This is the major economic effect of an increase in yield. However, there are other factors involved. Because of the lowering in the amount of wood required, the size of the woodyard and woodroom would be reduced for plants of comparable pulp tonnage. This could lead to savings in capital charges and possibly in labor. On the other hand, an increase in yield decreases the amount of dissolved organics and thus lowers the total heat value of the liquor. Another aspect of the yield question is the validity of a comparison based on equal weights of pulp. Pulping to higher yield does not increase the number of fibers obtained from a given amount of wood. The yield increase is obtained by increasing the weight of each fiber. This gets into pulp quality and use considerations, which will be treated in detail later in this study. In this report, only the direct effect of reduced wood usage will be considered.

For any process, the cost of wood can be related to the pulp yield by the equation,

$$C_W = \frac{1800\ c_W}{y} \qquad (1) ,$$

where

$\underline{C_W}$ = cost of wood per ton of pulp, \$/ADT,

$\underline{c_W}$ = unit cost of clean wood, ¢/lb. o.d., and

$\underline{y}$ = pulp yield, %.

If holopulp is to show an economic advantage over the reference pulp, the cost of wood must be less. The advantage for holopulp can be determined by subtracting the wood costs for holopulp from the wood costs for the reference pulp. This gives

$$ADV = 1800\left(\frac{c_{W,R}}{y_R} - \frac{c_{W,H}}{y_H}\right) \qquad (2) ,$$

where $\underline{ADV}$ = the cost advantage of holopulp in \$/ADT and the subscripts $\underline{R}$ and $\underline{H}$ indicate reference pulp and holopulp, respectively.

The unit cost of wood should be approximately the same for each pulp. This assumes that the same species is used for both processes (which seems to be the only fair comparison) and that costs of the wood handling, barking, and chipping operations are comparable. Then, Equation (2) simplifies to

$$ADV = 1800\left(\frac{1}{y_R} - \frac{1}{y_H}\right) \qquad (3) .$$

It is seen that the relative cost advantage of holopulp on wood costs is dependent on three parameters: the unit cost of clean wood, the holopulp yield, and the yield of the pulp used for comparison. The advantage is linearly dependent on unit cost of wood, but depends on yield in a nonlinear manner. Figure 1 shows the advantage in wood costs as a function of the three parameters. Figure 2 shows the same data

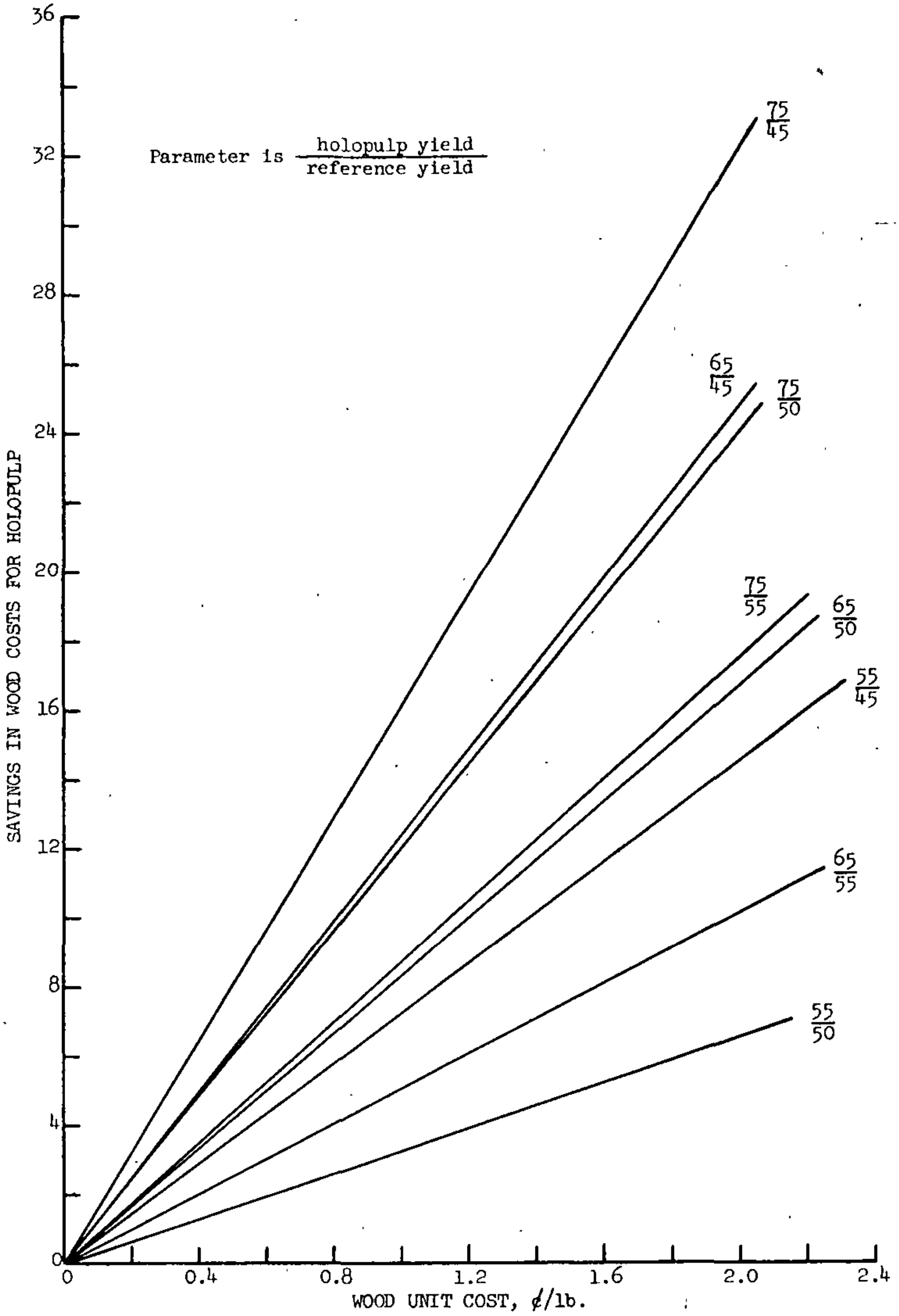


Figure 1. Data on Economic Advantage of High Yield

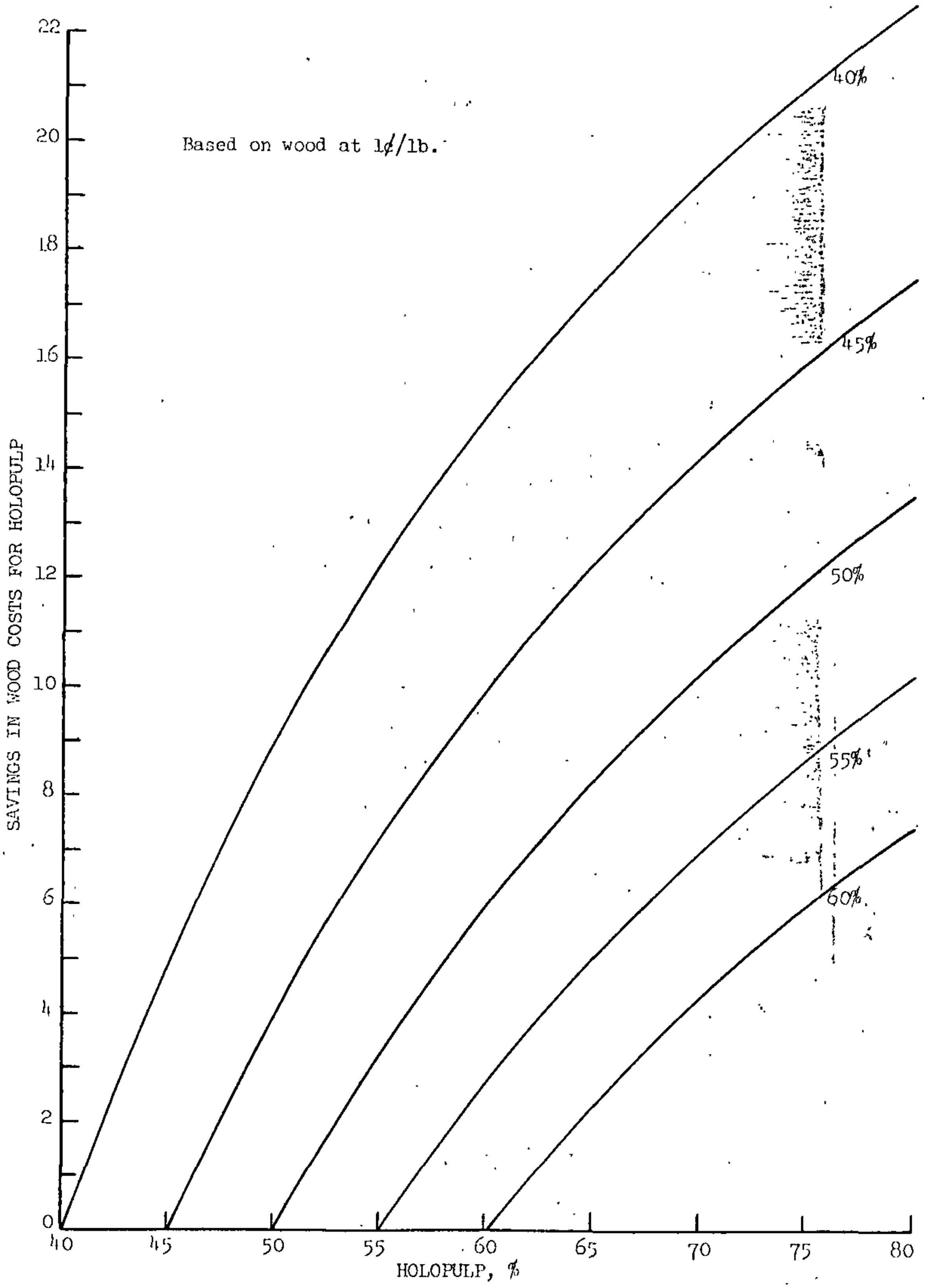


Figure 2. Working Curves for Yield Economics

plotted as a function of holopulp yield with wood unit costs of 1¢/lb. The curves in Fig. 2 may easily be used as working curves by multiplying by the actual unit wood costs. This is a consequence of the linear dependence on wood unit cost.

Figure 2 shows very clearly that the savings in wood cost are not a linear function of holopulp yield. The rate of increase in savings decreases as holopulp yield increases. It is also evident that the yield of the reference pulp with which holopulp is compared is very important. For the same difference in yield level between holopulp and the reference pulp, the cost advantage is greater the lower the yield of reference pulp. For example, with the difference between yields fixed at 15%, the cost advantage is $12.25, $10.00, $8.30, $7.00, and $6.00 at reference pulp yields of 40, 45, 50, 55, and 60%, respectively. This means that with everything else equal, it is advantageous to prepare holopulps which would compete with low-yield pulps.

In order to get a reasonable idea of the magnitude of the savings in wood costs, it is necessary to get some data on the unit cost of wood. The following data were published by the American Paper Institute in a statistical summary of June, 1971 (1).

		Costs, $/cord	
		1969	1970
Wisconsin:	Spruce and fir – roundwood	28.50	29.20
	Aspen – roundwood	16.00	16.00
Southeast:	Southern pine – roundwood	20.90	-
	Hardwood – roundwood	16.35	-
Mid-South:	Southern pine – roundwood	18.55	-
	Hardwood – roundwood	16.85	-
Louisiana:	Southern pine	17.75	17.70
	Hardwood – roundwood	17.40	17.50

Additional data taken from the textbook by Casey (2) estimate the bark content at 7-8% of the dry wood weight and the solid volume of a cord at 98 ft.^{3} Density data were given as follows:

		Density, lb. o.d./ft.^{3}
Hardwoods:	Aspen	22
	Cottonwood	23
	Yellow poplar	25
	Beech and birch	34
	Maple	32-35
	White oak	37
Softwoods:	Balsam fir	21
	Eastern white pine	21
	Eastern hemlock	24
	Jack pine	24
	Spruce	24
	Red pine	24
	Tamarack	31

Applying these data gives the following values for the unit cost for clean wood.

		Unit cost, ¢/lb. o.d.
Wisconsin:	Spruce	1.32
	Aspen	0.81
Southeast:	Southern pine	0.97
	Hardwood	0.53
Mid-South:	Southern pine	0.86
	Hardwood	0.55
Louisiana:	Southern pine	0.82
	Hardwood	0.57

It is evident that unit costs of wood vary considerably depending on species and location. For hardwoods, it appears that the unit cost ranges from 0.5 to 1¢/lb., while for softwoods the range is from 0.8 to 1.3¢/lb. It would appear that values of 0.75¢/lb. for hardwoods and 1¢/lb. for softwoods can be used in calculations. It should be noted that a unit cost of 1¢/lb. is equivalent to a cost of $36/ADT for a 50%-yield pulp.

Figure 2 can be used to estimate the potential savings in wood cost for certain cases:

Case 1: High-yield softwood holopulp for linerboard, compared with unbleached kraft for the same purpose. Assuming a holopulp yield of 75% and a kraft yield of 55%, and using 0.8 to 1.3¢ per lb. as the range of wood unit costs gives potential savings in wood costs of $7-11/ADT.

Case 2: Semibleached hardwood holopulp for use in mixed furnishes. Assuming a holopulp yield of 65% and a reference yield of 50% and 0.5-1¢/lb. as the range of hardwood unit costs gives potential savings of $4-8/ADT.

Case 3: Bleached holopulp from hardwoods. Assuming a holopulp yield of 60% and a reference yield of 45% gives potential savings of $5-10/ADT.

Case 4: Bleached softwood holopulp. Assuming a holopulp yield of 55% and a reference yield of 45% gives potential savings of $6-9.5/ADT.

These cases indicate that, in general, holopulping would generate savings in wood costs of $5-10/ADT because of higher yield. The conditions which give very high savings (high holopulp yield and low reference pulp yield) do not appear to be realistic. The unit cost of wood appears to have the greatest leverage in increasing the savings in wood cost. However, at least in North America, it does not appear that it could lead to savings in the $15-20/ADT range.

CHEMICAL COSTS

The cost of chemicals is determined in a straightforward manner. The cost of each chemical is determined as the product of the amount of chemical used and the unit cost of the chemical. The total chemical cost is obtained by summing the individual costs. In holopulping, the practice has grown up of expressing chemical consumption on the basis of the wood rather than the pulp. Thus, yield enters into the relationship. A stoichiometric factor, $\underline{S}$, defined as chemical consumed per unit weight of wood can be used to describe the amount of each chemical used. The cost of chemicals for holopulp can then be expressed quantitatively as follows:

$$C_{C,H} = \frac{1800}{y}\left(S_D c_D + S_N c_N + S_C c_C + S_H c_H\right) \tag{4}$$

where

$\underline{C}_{C,H}$ = total chemical cost for holopulp, \$/ADT,
$\underline{S}_D$ = stoichiometric factor for ClO_2, lb./lb. wood,
$\underline{S}_N$ = stoichiometric factor for NaOH, lb./lb. wood,
$\underline{S}_C$ = stoichiometric factor for chlorine, lb./lb. wood,
$\underline{S}_H$ = stoichiometric factor for hypochlorite, lb./lb. wood,
$\underline{c}_D$ = unit cost of ClO_2, ¢/lb.
$\underline{c}_N$ = unit cost of NaOH, ¢/lb.,
$\underline{c}_C$ = unit cost of Cl_2, ¢/lb., and
$\underline{c}_H$ = unit cost of hypochlorite, ¢/lb.

The above equation assumes that chlorine dioxide, caustic, chlorine, and hypochlorite are the chemicals employed in holopulping. Additional chemicals can be handled by the addition of more terms in Equation (4).

Since the terms for each chemical are simply summed in Equation (4), it is clear that from an economic standpoint, one chemical can be substituted for another in the ratio of unit costs without changing the overall cost. Thus, $\Delta\underline{S}_C = (\underline{c}_D/\underline{c}_C)\Delta\underline{S}_D$ describes quantitatively how Cl_2 could replace ClO_2 while maintaining economic equality. Unit cost ratios can be used as a guide in changing the stoichiometry to achieve a more favorable cost picture. For example, if $\Delta \underline{S}_{\underline{C}} < (\underline{c}_{\underline{D}}/\underline{c}_{\underline{C}})\Delta \underline{S}_{\underline{D}}$, the change would decrease chemical costs. As an illustration, if the cost of ClO_2 is 10¢/lb. and the cost of Cl_2 is 2.5¢/lb., then $\Delta \underline{S}_{\underline{C}} < (10/2.5)\Delta \underline{S}_{\underline{D}} < 4\Delta \underline{S}_{\underline{D}}$, and it would be economically feasible to use up to 4% Cl_2 to achieve a 1% reduction in the ClO_2 demand. While the above example is illustrative only, the general principle of using unit cost ratios to guide substitutions is valid. This principle can eventually serve as one component in a general optimization procedure.

In order to estimate the order of magnitude of the cost of holopulping chemicals, it is necessary to have some data on chemical unit costs. The following values may be used as a first approximation:

Cl_2:	4.7¢/lb.	Market price (Oil, Paint & Drug Reporter) (3)
NaOH:	4¢/lb.	Market price (Oil, Paint & Drug Reporter) (3)
NaOCl:	8.8¢/lb.	Calculated from cost of Cl_2 and NaOH
ClO_2:	13¢/lb.	Obtained from Chemetics representative.

It is expected that the holopulp recovery system should reduce chemical unit costs substantially below market prices. This will be considered in some detail in the next section. Recovery will not reduce chemical costs to a negligible level because substantial electrolysis will be involved. In order to make estimates, it will be assumed that NaOH, Cl_2, and NaOCl are available at half of the market price and that ClO_2 costs may range from 7.5 to 10¢/lb.

It is also necessary to specify the pulping stoichiometry being considered. A reasonably typical stoichiometry is 7.5% ClO_2, 12% NaOH, and 3% NaOCl. Variations on this stoichiometry can also be considered. Figure 3 presents calculated chemical costs for 12% NaOH at 2¢/lb. and 3% NaOCl at 4.4¢/lb., and levels of ClO_2 ranging from 3% to 9% at 7.5¢ and 10¢/lb. The curve for NaOH and NaOCl alone is also shown.

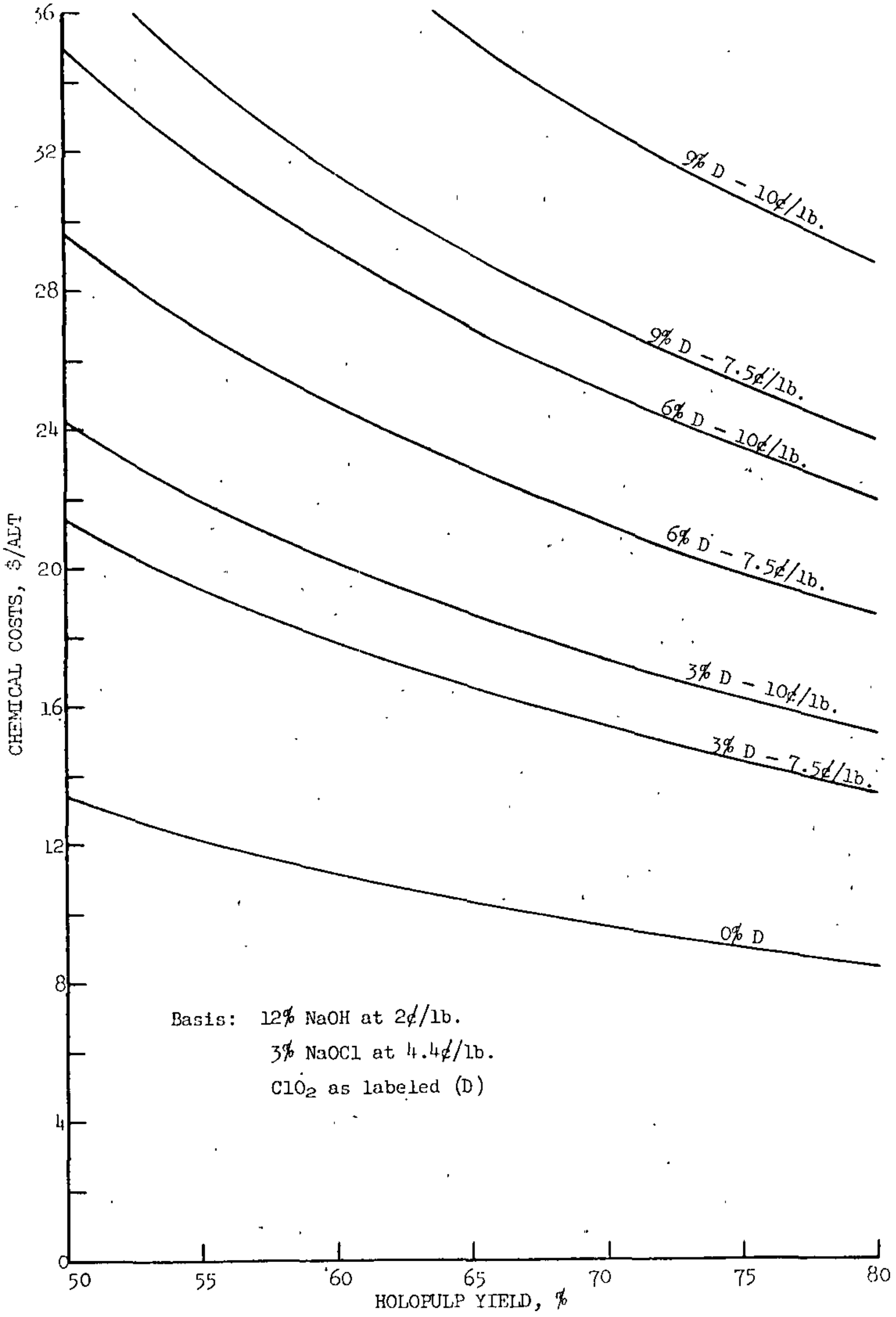


Figure 3. Calculated Chemical Costs

It is clear that the chemical costs are high in holopulping. For the stoichiometry listed above as reasonably typical, chemical costs could run \$25-30/ADT. This greatly exceeds the expected savings in wood costs of \$5-10/ADT. Care must be taken not to jump to conclusions at this point. The cost of chemicals for the reference pulp have not been included, nor have other aspects of the total economic picture. Recovery systems must be considered before making a comparison. The data in Fig. 3, however, are indicative of a potential for excessive chemical costs in holopulping which would be very difficult to recover through other advantages.

Figure 3 clearly shows that ClO_2 is responsible for a large share of the chemical costs. In addition, since ClO_2 must be generated on-site from chlorate in all cases, the inclusion of a recovery system would be expected to have a smaller effect on ClO_2 costs. In order to gain some perspective on the relationship between chemical costs and chemical consumption, it is of interest to look at the conditions where the cost of ClO_2 alone would be within the range of expected savings in wood costs. A plot of ClO_2 costs _versus_ the amount consumed for various yields and unit costs is given in Fig. 4. This shows the rapidity with which ClO_2 costs can rise. Since savings in wood costs are expected to range from \$5 to \$10/ADT, it is of interest to look at the conditions equivalent to a cost of \$10/ADT. They are 3.6%, 4.5%, and 6.0% ClO_2 consumed for a pulp yield of 65% and ClO_2 unit costs of 10, 8, and 6¢/lb., respectively, 3.8% ClO_2 at 55% yield and 8¢/lb. and 5.2% ClO_2 at 75% yield and 8¢/lb. Since ClO_2 at 6¢/lb. does not seem very relatistic even with a recovery system, it appears that ClO_2 costs exceed savings in wood costs when ClO_2 usage exceeds 4-5% on the wood (about 7% on the pulp).

CHEMICAL RECOVERY

The chemical recovery system must be considered in reaching judgments on the economics of holopulp relative to alternative processes. Chemical recovery

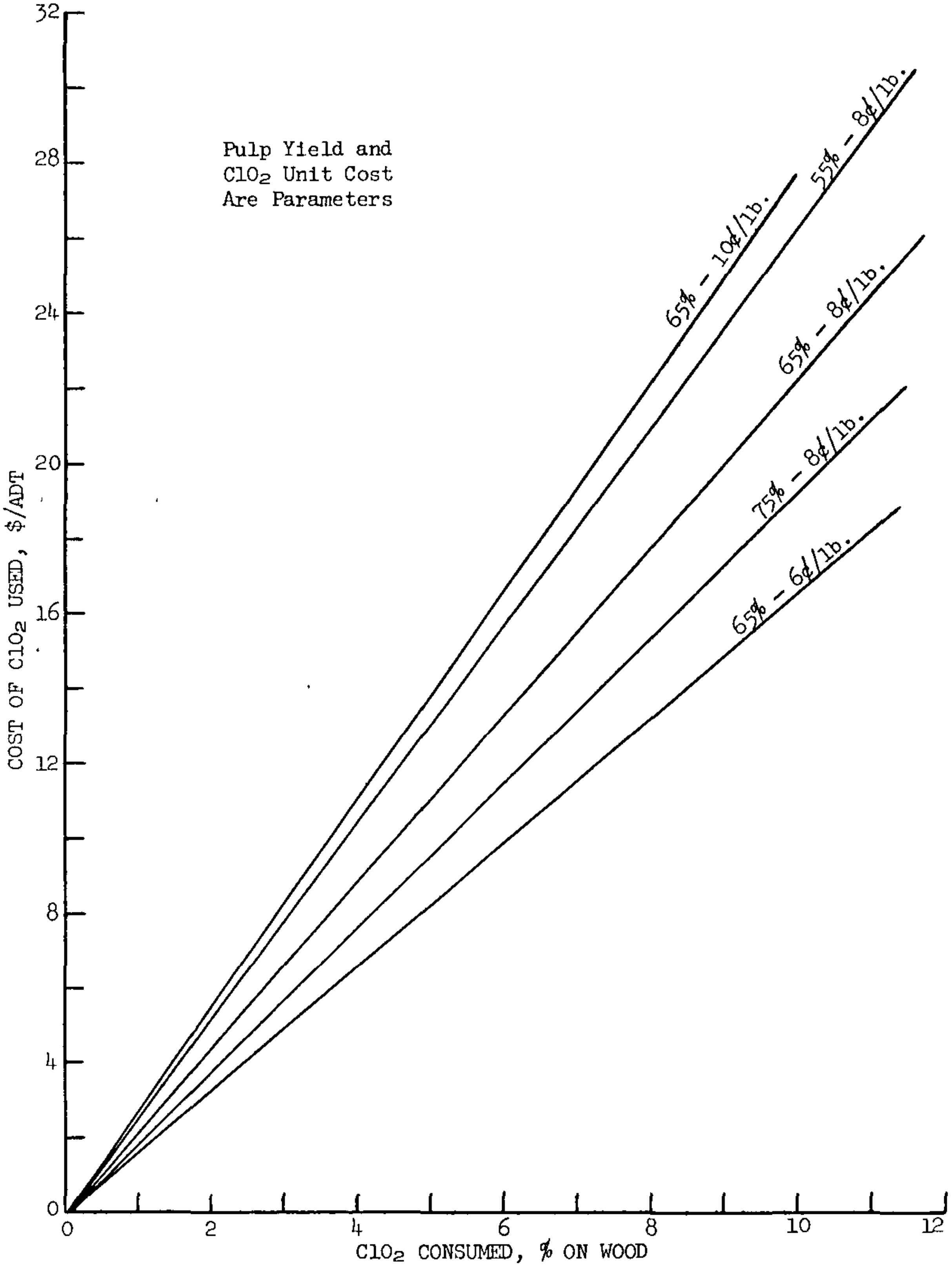


Figure 4. Cost of Using ClO_2

determines the effective cost of the chemicals employed in pulping. The chemical recovery system is responsible for the very low direct chemical costs in the kraft process. One of the hopes is that a holopulp recovery system would significantly reduce the high chemical costs discussed in the previous section.

The analysis presented in this report is quite general. It is not confined to a particular flowsheet or pulping stoichiometry. It is assumed only that the pulping step produces a spent liquor containing sodium, chlorine, and organic, with sodium present in excess on an elemental basis. The relative amounts of these components and the initial solids content of the liquor are assumed to be variables. Regardless of the details of the process flowsheet and the exact proportion of chemicals used, the recovery process can be thought of as consisting of a few major elements. These are as follows.

1. Evaporation to concentrate the liquor.
2. Combustion to produce a $NaCl$-Na_2CO_3 smelt and to generate steam.
3. Partial crystallization to separate Na_2CO_3 from $NaCl$.
4. Neutralization of Na_2CO_3 with HCl.
5. Burning H_2 and Cl_2 to form HCl.
6. Electrolysis of $NaCl$ to form $NaOH$, Cl_2, and H_2.
7. Generation of ClO_2 in a Day-Kesting process.
8. Reaction of Cl_2 with $NaOH$ to form hypochlorite.
9. Causticizing Na_2CO_3 with lime and calcining the $CaCO_3$.

All of the above elements are not necessarily included in the recovery system, nor are they all major cost items. The most expensive operations are evaporation and burning, electrolytic chlor-alkali, causticizing and calcining, and ClO_2 production. Conversion of Na_2CO_3 to $NaCl$, combustion of H_2 and Cl_2 to form HCl, and hypochlorite manufacture are costly only in terms of the chemicals used.

Separation of Na_2CO_3 from NaCl and causticization of Na_2CO_3 could be very significant because they permit a nonelectrolytic (and hence potentially cheaper) method for producing caustic.

The ultimate economic comparison is to be done on a differential basis with alternative processes. The most representative alternative process is kraft. Thus, the analysis of holopulp recovery should be made, as far as possible, on a differential basis with kraft. This is straightforward when the two processes parallel each other such as in evaporation and burning. It is not easily done when the processes are divergent. In this case, it is necessary to consider each process separately and then compare.

The following steps were used to carry out the analysis of recovery economics.

1. The relative costs of evaporation and burning were determined on a differential basis. Excess costs were charged against the chemicals produced (i.e., the smelt).
2. Costs of electrolytic chlor-alkali production were determined including allowance for Na_2CO_3 neutralization and a provision for costs of Na_2CO_3-NaCl separation.
3. The cost of producing ClO_2 with the Chemetics system was determined.
4. The cost factors for lime-causticizing systems were determined. These data were used to estimate costs for kraft as well as for holopulp.
5. The information was integrated and interpreted to give a complete overall cost picture for holopulp recovery economics.

Evaporation and Burning

This section deals with a comparison of the relative cost of producing smelt (recovered inorganics) from holopulp and kraft liquors and involves the operations of evaporation and combustion. Since the details of how these operations would be carried out in holopulping are not yet fully defined, it is necessary to make a few assumptions.

1. It is assumed that evaporation of both liquors will be carried out to 50% solids in the same type of evaporator with the same materials of construction. The only difference assumed to affect costs is a difference in the amount of water to be evaporated. It appears that this assumption gives the benefit of doubt to holopulp since the presence of chlorides in holopulp liquors could lead to corrosion problems. Thus, if anything, holopulp evaporators are likely to cost more (rather than less) than kraft evaporators at the same load. This possibility was neglected in this analysis.

2. It is assumed that the capital cost for the furnace is dependent on the total B.t.u. load only (based on the fact that fluidized bed combustion does not appear feasible for holopulp liquor so that combustion would have to be carried out under smelting conditions in some type of furnace – presumably similar to a kraft furnace). It is further assumed that any savings in burning holopulp liquor in a low-pressure boiler would be offset by the loss of the ability to generate by-product electrical power. Both the kraft and holopulp furnaces are assumed to produce low-pressure steam of equivalent unit value. The uncertainty underlying these assumptions cannot be resolved until the holopulp combustion picture clarifies.

3. It is assumed that labor costs are equivalent for the two processes and cancel each other out. This assumes that labor costs are not dependent on evaporator or furnace load. This assumption could also give the benefit of doubt to holopulp since the possibility of corrosion in the holopulp system could lead to higher maintenance costs.

With the assumptions made above, the factors which enter the economic balance are the following:

a. Capital charges for the evaporators which are taken to depend on load (lb. of water evaporated/ADT),

b. Cost of steam used in evaporators,

c. Capital charges for the furnace which are taken to depend on the B.t.u. load, and

d. Value of steam produced from the boiler.

The use of auxiliary fuel to help maintain combustion of holopulp liquor is not included in this analysis. If combustion studies do indicate the need for auxiliary fuel, an additional cost term would have to be added.

The analysis of evaporation and combustion is carried out on a differential basis with kraft, with any economic differences between the two processes expressed as $/ADT. It is possible to divide this value by the total amount of recovered inorganic (ash) per ADT giving a cost for recovering chemical in ¢/lb. Only the difference in costs between holopulp and kraft is assessed against the recovered chemical. If evaporation and burning costs are equivalent between the two processes, the recovered NaCl and Na_2CO_3 are obtained at no net cost.

The charges for both capital and steam for the evaporators are assumed to be dependent on evaporator load only. Since it is assumed that liquors from both processes are concentrated to 50% solids, the evaporator load will depend on the total solids produced per ADT and the initial solids concentration. In order to estimate the total amount of liquor solids per ADT, the loss in wood material during pulping can be equated to the organic in the liquor. This figure together with the liquor solids content gives the total amount of liquor.

$$\text{Liquor} = \frac{1800}{s(1 - X_A)}\left(\frac{1 - y}{y}\right)\frac{\text{lb. liquor}}{\text{ADT}} \qquad (5)$$

where

$\underline{s}$ = liquor solids content, lb. solid/lb. liquor,

X_A = liquor ash content, lb. ash/lb. solids, and

y = pulp yield.

The evaporator load is the amount of water which must be evaporated to bring the solids content up from the initial value, s, to the final value of 50%. This is given by

$$L_E = \frac{1800}{(1 - X_A)}\left(\frac{1 - y}{y}\right)\left(\frac{1 - s}{s}\right) - \frac{1800}{(1 - X_A)}\left(\frac{1 - y}{y}\right)\left(\frac{1 - 0.5}{0.5}\right) \qquad (6a)$$

or

$$L_E = \frac{1800}{(1 - X_A)}\left(\frac{1 - y}{y}\right)\left(\frac{1 - 2s}{s}\right) \qquad (6b)$$

where L_E = evaporator load, lb. water evaporated/ADT. This load factor can be determined for both holopulp and kraft by specifying the yields, ash contents, and solids contents for each.

It is relatively straightforward to calculate capital and steam charges once the load is known. The capital charges, C_E, are found as

$$C_E = \frac{I_E R}{P} \qquad (7)$$

where

C_E = capital charges for evaporators, \$/ADT,

I_E = evaporator investment, \$,

R = annual return factor applied to capital, including depreciation, interest, taxes, and insurance, and

P = annual production rate, ADT/yr.

The investment for evaporators is assumed to depend on the load according to the usual power law relationship. Then,

$$\frac{I_{EH}}{I_{EK}} = \left(\frac{L_{EH}}{L_{EK}}\right)^{n_E} \qquad (8)$$

where n_E = scale factor for evaporators. The difference in capital charges between the two processes is then given by

$$\Delta C_E = C_{EH} - C_{EK} = \frac{I_{EK}R}{P}\left[\left(\frac{L_{EH}}{L_{EK}}\right)^{n_E} - 1\right] \qquad (9) .$$

The costs for steam used in evaporation will be directly related to the load. Thus, the difference in operating costs for evaporation between holopulp and kraft can be written as

$$\Delta O_E = O_{EH} - O_{EK} = \frac{(L_{EH} - L_{EK})}{E_S}\,\frac{c_S}{100} \qquad (10)$$

where

O_E = operating cost for evaporation, \$/ADT,
E_S = steam economy, lb. water evaporated/lb. steam, and
c_S = unit cost of steam, ¢/lb.

The next item to estimate is the load factor for the furnace. This was assumed to be the B.t.u. load. This may be taken to be proportional to the total amount of organic in the liquor as follows.

$$L_F = 1800\left(\frac{1 - y}{y}\right)H_V \qquad (11)$$

where L_F = furnace load factor, B.t.u./ADT, and H_V = heating value, B.t.u./lb. organic.

The capital charge for the furnace is assumed to follow the same type of relation as that for the evaporators. The difference in capital charges between the two processes is then given by

$$\Delta C_F = C_{FH} - C_{FK} = \frac{I_{FK}R}{P}\left[\left(\frac{L_{FH}}{L_{FK}}\right)^{n_F} - 1\right] \qquad (12)$$

where

$\underline{C_F}$ = capital charge for furnace, \$/ADT,

$\underline{I_F}$ = furnace investment, \$, and

$\underline{n_F}$ = scale factor for furnaces.

The amount of steam produced is assumed to be directly related to the B.t.u. load. It depends on the efficiency of steam production and the enthalpy of the steam. Since steam production is a process credit, it enters this analysis as a negative operating cost. Thus, the difference in furnace operating cost between holopulp and kraft can be written as

$$\Delta O_F = O_H - O_K = -\frac{L_{FH}\eta}{h_S}\frac{c_S}{100} + \frac{L_{FK}\eta}{h_S}\frac{c_S}{100} \qquad (13a)$$

or

$$\Delta O_F = (L_{FK} - L_{FH})\frac{\eta}{h_S}\frac{c_S}{100} \qquad (13b)$$

where

$\underline{O_F}$ = operating cost for combustion, \$/ADT,

η = efficiency of steam production (fraction of total energy recovered as steam), and

$\underline{h_S}$ = enthalpy of steam, B.t.u./lb.

The final item to calculate is the amount of holopulp ash produced per ton. This is given by

$$A_H = 1800 \frac{(1 - y_H)}{y_H} \frac{X_{AH}}{(1 - X_{AH})} \qquad (14)$$

where $\underline{A_H}$ = holopulp ash (NaCl + Na_2CO_3), lb./ADT. The four cost terms can be added together, multiplied by 100 and divided by the amount of ash. The result is to express excess costs for evaporation and burning of holopulp over kraft as a unit cost on the ash. Thus,

$$c_A = (\Delta C_E + \Delta O_E + \Delta C_F + \Delta O_F)/A_H \qquad (15)$$

where $\underline{c_A}$ = differential cost of producing holopulp ash, ¢/lb.

Estimates were made of the parameters involved in these cost equations to permit a quantitative evaluation and an estimate of the differential cost of holopulp ash. The major task was to estimate the investment cost for a kraft evaporator and recovery furnace.

The evaporator investment was based on an average evaporation load of 4.6 lb. H_2O/hr.ft.^{2} taken from the TAPPI monograph on chemical recovery (4). A total of 4-2/3 lb. of water per lb. of solids will be evaporated in going from 15% solids to 50% solids. Assuming 3000 lb. solids/ADT and a 500-ADT/day plant, the evaporation rate is 292,000 lb./hr. requiring 63,100 ft.^{2} of heating surface. Figure 11-34 in Perry's "Chemical Engineers' Handbook," 4th edition (5), gives installed costs for LTV evaporators vs. total ft.^{2} of heating surface. For 63,100 ft.^{2}, the cost is $550,000 (1960 prices). Using a cost index chart in Poppers' "Modern Cost-Engineering Techniques" (6) increases this to about $700,000 for 1968 prices. A table on page 99 of Popper contains additional information for estimating costs of chemical plant equipment. For LTV evaporators, he gives \$1200/ft.^{2} as a basic unit cost (1968 prices), 0.53 as the size exponent, and 1.9 as the installation factor. This would give $\$1200 \times (63{,}100)^{0.53} \times 1.9 = \$850{,}000$ for the 500-ADT/day kraft mill evaporator. Taking these two estimates into account and the inflation which has recently taken place, it appears reasonable to assume a value of \$1 million as the investment required for the evaporators for a 500-TPD kraft system.

Data on capital cost of kraft recovery furnace systems were taken from Fig. 5-46, page 5-99 of "Control of Atmospheric Emissions in the Wood Pulping Industry" by Hendrickson, Roberson and Koogler (7), Vol. 2, Final Report on Contract No. CPA 22-69-18, March 15, 1970, by HEW (NAPCA). These curves gave estimates of \$6 million at 500 TPD and \$8.6 million at 1000 TPD for a boiler producing 600 p.s.i.g., 750° steam, and \$7.2 million and \$10.2 million at 500 and 1000 TPD, respectively, for a boiler producing 1250 p.s.i.g., 900°F. steam. Analysis of these data gave a size exponent of 0.51. The lower pressure values were used in this analysis.

A list of the values used for the parameters in Equations (6)-(15) is given below.

$I_{EK} = \$1{,}000{,}000$ $\quad$ $I_{FK} = \$6{,}000{,}000$

$n_E = 0.53$ $\quad$ $n_F = 0.51$

$P = 175{,}000$ TPY $\quad$ $R = 0.25$

$H_V = 10{,}000$ B.t.u./lb. organic $\quad$ $h_S = 1000$ B.t.u./lb. steam

$\eta = 0.5$ $\quad$ $c_S = 0.1$¢/lb.

$E_S = 5$ lb. evap./lb. steam $\quad$ $X_{AH} = X_{AK} = 0.33$

$y_H = 0.65$ $\quad$ $y_K = 0.5$

$s_H = 0.075$ $\quad$ $s_K = 0.15$

Using these values in Equations (15), (14), (13b), (12), (11), (10), (9), and (6b) gives the following estimate for $\underline{C_A}$:

$$C_A = [21.7 - 232 + 77.4 + 415]/484 = 0.58¢/\text{lb}.$$

This is about one half the market price of NaCl and shows how readily the advantage of recovery can be lost with a low-cost chemical. The two terms associated with the furnace have the biggest effect in this example. The capital cost of the kraft furnace is higher because of the higher load. This is more than offset by the increased steam production for kraft. The biggest single charge against holopulp, for the values of the parameters listed above, is the decreased steam production associated with the higher holopulp yield.

The differential costs of evaporation and burning are strongly dependent on a few key variables. Evaporation costs are influenced mainly by the initial concentration of holopulp liquor, s_H, and the unit cost of steam. Combustion charges depend on the holopulp yield and the unit cost of steam. Both are influenced by annual return factor, R. Figures 5 and 6 show the effects of these variables on evaporation and combustion costs, respectively.

It is seen in Fig. 5 that evaporation charges can rise very steeply at low solids concentration. It is clear that the possibility of serious cost penalties at low solids contents far exceeds the small savings at high solids contents. It appears that holopulp spent liquor leaving the pulping and washing operations must have a solids content of at least 7.5% if excessive costs are to be avoided. To achieve solids contents of this level will require recycling of pulping liquors, particularly for the oxidation stages and judicious use of wash water. While preliminary paper studies have indicated the possibility of reaching solids contents of 10% and nothing has been uncovered which would prevent recycling large volumes of liquor, a detailed engineering analysis of the water balance has not been carried out. Production of high solids liquor has not been demonstrated in the lab. Thus, a reasonably accurate value of the initial holopulp liquor solids content is not

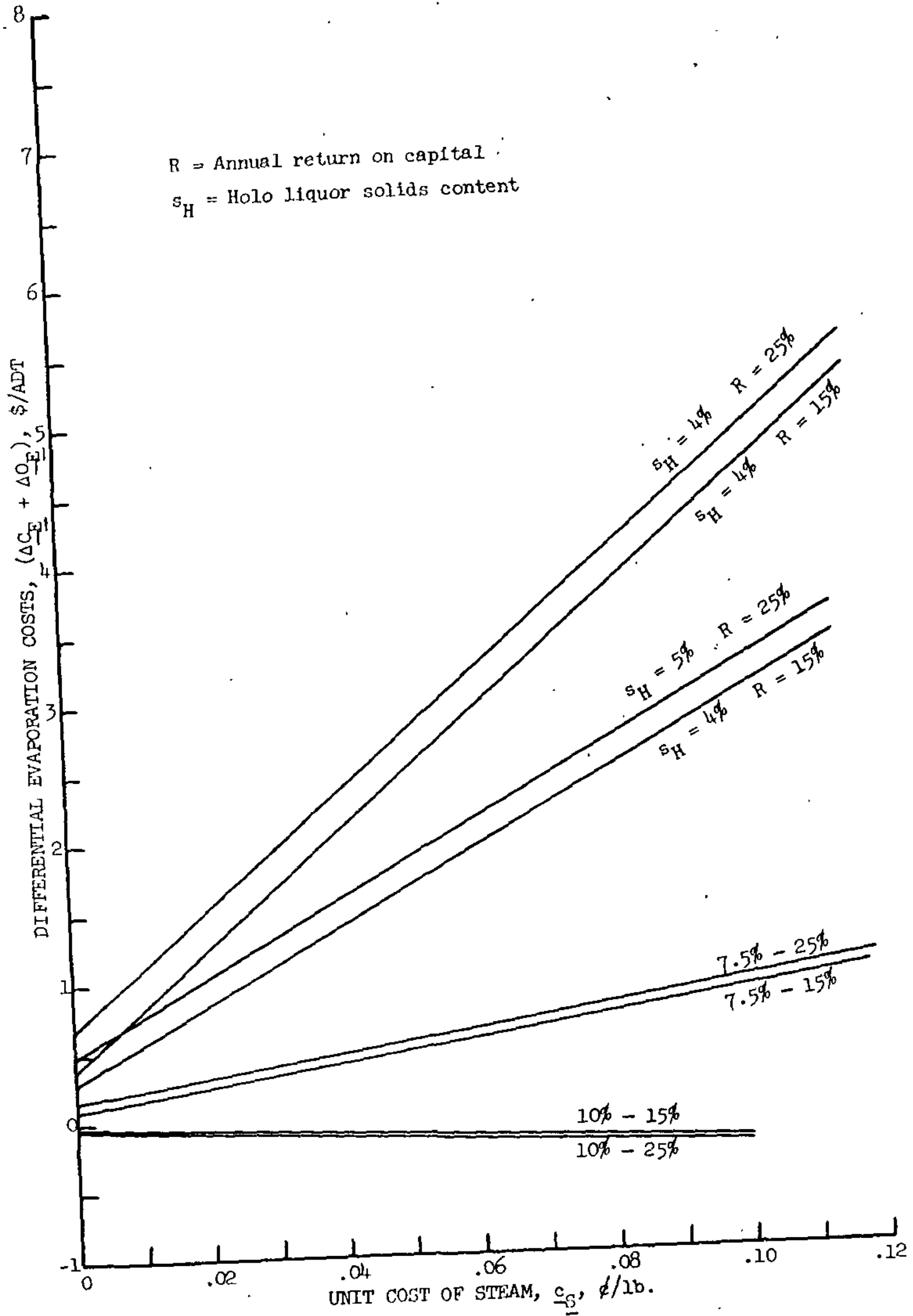


Figure 5. Holopulp Excess Evaporation Costs

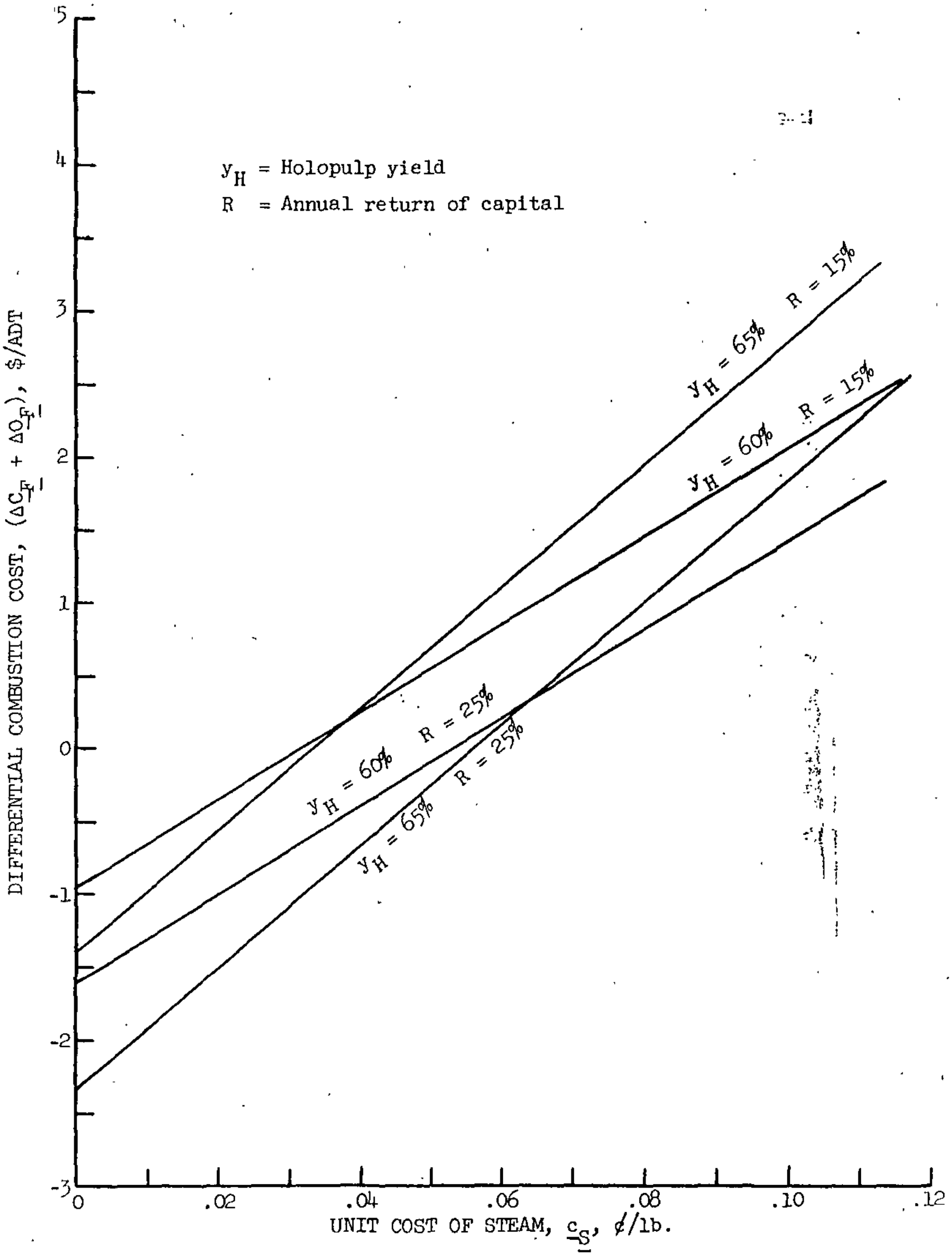


Figure 6. Holopulp Excess Combustion Costs

known at present. It is prudent to expect low solids liquors. Laboratory pulping without extensive interstage washing produces a liquor with a maximum solids content of about 1-2%. Thus, a fivefold increase in solids content would have to be achieved by recycling and other water conservation practices to reach the desired 7.5% level.

Figure 6 shows the very strong influence of steam unit costs on combustion differential costs. These curves describe that trade-off between a smaller furnace and lower steam production for holopulp, both due to the higher yield. The break-even point is dependent mainly on the unit cost of steam and the annual charge against capital. At a 15% annual charge, break-even occurs at steam unit costs of about 0.033¢/lb., while at a 25% annual charge, break-even occurs at about 0.055¢/lb. With steam costs greater than the break-even value, the differential charge for combustion against holopulp will be positive.

The net result of the economic analysis of evaporation and burning as epitomized by Fig. 5 and 6 is that it is most probable that these operations will be more costly to carry out for holopulp than for kraft. This is due to the likely higher evaporator load for holopulp and the loss in energy value due to higher yield. Under unfavorable circumstances (steam unit costs > 0.1¢/lb. and liquor solids contents < 5%), the differential cost can exceed $5/ADT, which is in the same range as the expected savings in wood costs. Even under favorable conditions, the differential cost is likely to be around $2/ADT, which would result in a charge against the recovered NaCl (and Na_2CO_3) of about 0.4-0.5¢/lb. This is nearly half of the market price for these materials.

Electrolytic Chlor-Alkali

Electrolytic processes are the only commercially attractive processes for forming chlorine and caustic from the recovered NaCl. Holopulp recovery is thus forced to electrochemical technology for processing all of the recovered NaCl. Some flexibility does exist with respect to the recovered Na_2CO_3. It may be separated from the NaCl and causticized with lime, or it may be converted to NaCl with hydrochloric acid. No realistic options other than chlor-alkali cells are available for the recovered NaCl. The integration of chlor-alkali technology into holopulp recovery was considered in some detail in Progress Report Eleven (8). In that report, it was concluded that diaphragm cells appeared more attractive. This analysis is based on diaphragm cells.

This analysis of chlor-alkali production is not carried out on a differential basis with kraft. The reason is that there is no parallel operation in the kraft process. Production of caustic by causticizing with lime will be considered a completely separate operation and will be analyzed separately. The procedure that is used here is to analyze the costs for chlor-alkali and lime-causticizing separately and assign them to the chemicals produced. The comparison can then be made.

In the present stage of the analysis, the following factors are included in the cost of chlor-alkali production:

1. Cost of the raw material (NaCl)
2. Cost of electrical power
3. Charges against capital
4. Cost of steam for caustic evaporation.

Labor costs are not included at this stage. In a commercial holopulp recovery plant, there would be chlorate cells for ClO_2 production as well as chlor-alkali cells, and labor would be split between them. In this analysis, the labor is calculated with ClO_2 economics.

The raw material cost will be the cost of the ash plus any additional charges for converting Na_2CO_3 to NaCl or for separation of NaCl from Na_2CO_3. The cost of producing the ash was discussed in the previous section. Additional charges will be considered later. It is conceivable that the raw material cost could be higher than the cost of purchased salt because it bears the full charge for increased evaporation and burning costs relative to kraft. Since these steps would need to be done for pollution control anyway, the charge would exist regardless of whether or not recovered NaCl was used. Thus, it is possible that reclaimed NaCl would be used even though it was more expensive than purchased salt by this method of calculation. These same considerations do not apply to costs of purifying the recovered material. If the costs of purification are higher than purchased salt (about 1¢/lb.), then the recovered material would not be used and purchased material would be used instead.

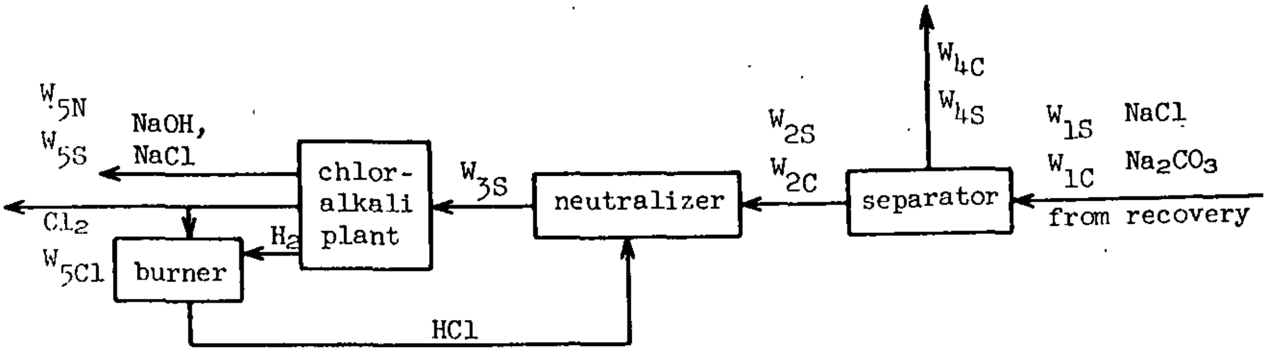
The cost of power will depend on the amount of power used and the unit cost of power. The literature gives values ranging from 2600 to 3000 kw.-hr. per ton Cl_2 or 1.3 to 1.5 kw.-hr./lb. Cl_2. This is d.c. power. It would be necessary to adjust this by the rectifier efficiency to get at the actual a.c. power used. It is possible that the use of metal electrodes would lower the power demand. However, the usual design practice with metal electrodes has been to raise the current density so as to lower capital costs rather than power demand. Some data supplied by Chemetics indicate an a.c. power level of 1.31 kw.-hr./lb. Cl_2. This seems to be a little low. Power will be on the order of 1¢/kw.-hr., ranging as low as 0.5¢/kw.-hr. in favorable locations.

A large capital investment is required for the chlor-alkali plant. This includes the investment in the cells themselves, the peripheral electrical equipment, caustic evaporator, and the equipment for handling chlorine and hydrogen. The Encyclopedia of Chemical Technology (9) lists the investment for a chlor-alkali plant at \$87,000 per daily ton Cl_2. In this analysis, capital estimates are based on 500 ADT/day x 500 lb. NaCl/ADT = 125 tons NaCl/day, which is equivalent to 76 tons Cl_2 per day. Thus, investment would be 76 x 87,000 = \$6.6 million. Popper (6) gives the following capital cost data (1967 costs) for a chlor-alkali plant: \$13,000,000 for 70,000 tons/yr. of chlorine, with a size exponent of 0.69. Then, for a 76-ton Cl_2/day plant, the cost would be $13 \times 10^6 \left(\frac{76 \times 350}{70,000}\right)^{.69} = \$6.7$ million. These two estimates agree amazingly well. It might be argued that the elimination of chlorine liquefaction facilities and sharing electrical facilities with the chlorate plant would reduce capital costs somewhat. However, this would be compensated by the fact that the cost data cited above precede the era of rampant inflation. Even if capital costs were cut 25%, the investment in the chlor-alkali plant would still be \$5 million.

Steam costs are primarily associated with the caustic evaporator. In a typical cell system, about 5 lb. water/lb. NaOH must be evaporated in order to produce 50% caustic. The cost of steam will depend on the steam economy and the unit cost of steam. This cost can be reduced by evaporating to less than 50% caustic.

In order to develop a set of cost equations for the chlor-alkali plant, it is necessary to consider the influence of ash composition. The recovered ash will contain NaCl and Na_2CO_3 in proportions dependent on the amounts of sodium and chlorine in the spent liquor. It is possible that a portion of the Na_2CO_3 (including some NaCl) may be separated out for causticizing with lime. The remaining Na_2CO_3 must be converted to NaCl by neutralization with HCl. An additional factor to consider is that some NaCl passes out of the system with the NaOH product and is not electrolyzed. The following diagram can be used to develop the necessary material balance:

ELECTROLYTIC CHLOR-ALKALI


W5N
W5S
NaOH,
NaCl
Cl2
W5Cl
burner
H2
chlor-alkali plant
W3S
neutralizer
HCl
W2S
W2C
separator
W4C
W4S
W1S
W1C
NaCl
Na2CO3
from recovery

where

$\underline{W}_{1S}$ = NaCl is ash, lb./ADT,

$\underline{W}_{1C}$ = Na_2CO_3 in ash, lb./ADT,

$\underline{W}_{2S}$ = NaCl to neutralizer, lb./ADT,

$\underline{W}_{2C}$ = Na_2CO_3 to neutralizer, lb./ADT,

$\underline{W}_{3S}$ = NaCl to cells, lb./ADT,

$\underline{W}_{4S}$ = NaCl to lime causticizer, lb./ADT,

$\underline{W}_{4C}$ = Na_2CO_3 to lime causticizer, lb./ADT,

$\underline{W}_{5S}$ = NaCl in product caustic solution, lb./ADT, and

$\underline{W}_{5N}$ = NaOH produced by electrolysis, lb./ADT, and

$\underline{W}_{5Cl}$ = net Cl_2 produced, lb./ADT.

The material balance equations over the separator are:

$$W_{2S} = W_{1S} - W_{4S} \quad (16)$$

and

$$W_{2C} = W_{1C} - W_{4C} \quad (17) .$$

The neutralization reaction can be written as $Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$.

Then,

$$W_{3S} = W_{2S} + 1.10 \cdot W_{2C} \quad (18) ,$$

and the amount of Cl_2 used to make the necessary HCl is 0.67 $\underline{W}_{2C}$. The electrolysis reaction can be written as

$$2NaCl + 2H_2O \rightarrow 2NaOH + H_2 + Cl_2 .$$

Thus,

$$W_{5N} = \frac{W_{3S} - W_{5S}}{1.46} \qquad (19) .$$

However, $\underline{W}_{5S}$ is a function of $\underline{W}_{5N}$ because of solubility limitations at a given caustic concentration. For example:

at 50% NaOH, NaCl/NaOH = 0.0624;
at 40% NaOH, NaCl/NaOH = 0.0892;
at 30% NaOH, NaCl/NaOH = 0.2113.

In general, the quantity ρ can be defined as the ratio of NaCl to NaOH in the caustic solution. Then,

$$W_{5S} = \rho W_{5N} \qquad (20) ,$$

and

$$W_{5N} = \frac{W_{3S}}{1.46 + \rho} \qquad (21) .$$

The amount of NaCl which is actually electrolyzed is given by

$$1.46\ W_{5N} = \frac{W_{3S}}{1 + (\rho 1.46)} \qquad (22) .$$

The net amount of chlorine produced by the chlor-alkali system is given by

$$W_{5Cl} = 0.888\ W_{5N} - 0.67\ W_{2C} \qquad (23)$$

or

$$W_{5Cl} = \frac{0.888\ W_{3S}}{1.46 + \rho} - 0.67\ W_{2C} \qquad (24) .$$

The economic equations can now be developed. The cost of raw material for chlor-alkali production is assigned after any separation of Na_2CO_3 from NaCl. It includes the basic cost of the recovered ash and any costs associated with the separation step that are assigned to the salt-rich stream. The cost for electrical power is given simply as the product of the amount of power used and the unit cost of power. The cost of steam is determined as the steam used times the unit cost for steam. The operating cost for chlor-alkali is then determined as the sum of the raw material, steam, and power costs. Thus,

$$O_{CA} = \frac{W_{2S} + W_{2C}}{100} (c_A + c_{S1}) + \frac{W_{5N} L_{CE} c_S}{100 E_{SCE}} + \frac{W_{3S}}{1 + (\rho/1.46)} \times \frac{0.608K}{100} \times c_p \qquad (25)$$

where

$\underline{O_{CA}}$ = operating cost of chlor-alkali system, \$/ADT,

$\underline{c_{S1}}$ = any costs associated with the separation step assigned to the salt-rich stream, ¢/lb.,

$\underline{L_{CE}}$ = load on caustic evaporator, lb. H_2O_{evap}/lb. NaOH,

$\underline{E_{SCE}}$ = steam economy of caustic evaporator, lb. H_2O_{evap}/lb. steam used,

$\underline{K}$ = power required, kw.-hr./lb. Cl_2, and

$\underline{c_p}$ = unit cost of power, ¢/kw.-hr.

The capital charges will be determined in a manner analogous to that used for the evaporator and furnace. The base line for the capital cost estimate is 500 ADT/day at 500 lb. NaCl/ADT. Provisions are made for salt loads differing from the base line. The capital charges can be written as

$$C_{CA} = \frac{I_{CA} R}{P} \left(\frac{W_{3S}/[1 + (\rho/1.46)]}{500} \right)^{n_{CA}} \qquad (26)$$

where

$\underline{C_{CA}}$ = capital charge for chlor-alkali, \$/ADT,

$\underline{I_{CA}}$ = investment in chlor-alkali for base tonnage, \$, and

$\underline{n_{CA}}$ = scale factor for chlor-alkali cells.

The total costs for chlor-alkali production are to be assigned to the chlorine and caustic soda produced. In order to determine the cost of chlorine and caustic, the operating and capital charges are added together and divided by the total weight of chlorine and caustic produced. This is given by

$$c_{CL} = c_N = \frac{(W_{2S}+W_{2C})(c_A+c_{S1}) + \frac{W_{3S}L_{CE}c_S}{(1+\frac{\rho}{1.46})E_{SCE}} + \frac{0.608W_{3S}}{1+\frac{\rho}{1.46}}Kc_p + \frac{100\,I_{CA}R}{P}\left(\frac{W_{3S}}{[1+\frac{\rho}{1.46}]500}\right)^{n_{CA}}}{\left(\frac{1.888W_{3S}}{1.46+\rho}\right) - 0.67\,W_{2C}} \qquad (27)$$

Equation (27) can be rearranged slightly by using Equation (18) to give:

$$c_{CL} = c_N = \frac{\left\{\left[1 - 0.1\left(\frac{W_{2C}}{W_{3S}}\right)\right]\frac{c_A + c_{S1}}{1+\frac{\rho}{1.46}} + \frac{L_{CE}c_S}{E_{SCE}} + 0.608Kc_p + \frac{I_{CA}R}{5P}\left(\frac{W_{3S}}{[1+\frac{\rho}{1.46}]500}\right)^{n_{CA}-1}\right\}}{1.292 - 0.67\left(1+\frac{\rho}{1.46}\right)\frac{W_{2C}}{W_{3S}}} \qquad (28)$$

where

$\underline{c_{CL}}$ = cost of producing Cl_2, ¢/lb., and

$\underline{c_N}$ = cost of producing NaOH, ¢/lb.

The cost of caustic and chlorine in the holopulp system can be obtained from Equation (28) once the values of the parameters are estimated. The following values can be assumed for a first-order estimate of chlor-alkali costs.

$W_{1S} = W_{2S} = W_{3S} = 500$ lb./ADT, $W_{2C} = 0$, $c_{S1} = 0$,
$c_A = 0.5$¢/lb., $c_p = 1$¢/kw.-hr., $c_S = 0.1$¢/lb.,
$\rho = 0.0624$, $I_{CA} = \$6.6$ million, $R = 0.25$, $P = 175{,}000$ ADT/yr.,
$K = 1.4$ kw.-hr./lb. Cl_2, $L_{CE} = 5$ lb./lb., $E_{SCE} = 2.2$ lb./lb.,
and $n_{CA} = 0.69$.

Then,

$$c_{CL} = c_N = \left[\frac{0.479 + 0.227 + 0.851 + 1.912}{1.292}\right] = 2.7\text{¢/lb.}$$

For the values of the parameters used in this example, the biggest factor involved in the chlor-alkali cost is capital charges. This is followed by electrical power, raw material and steam charges, in that order. While the cost for chlorine and NaOH could be reduced somewhat by using a lower unit power cost or a smaller capital charge factor, it appears that electrolytic chlor-alkali would cost on the order of 2¢/lb. in the holopulp system.

The cost estimate made above gave the benefit of the doubt to holopulp in at least one respect in that it assumed that the recovered ash contained only NaCl. This would not normally be the case. Typically, the recovered chemical would consist of a mixture of Na_2CO_3 and NaCl. In this case, it would be necessary to either remove the Na_2CO_3 by separation (which could involve a cost, c_{S1}) or the carbonate would have to be neutralized with HCl [giving a finite value for W_{2C} in Equation (28)]. Either method could increase the cost of chlor-alkali. A series of plots of chlor-alkali costs *versus* wt. % Na_2CO_3 in the ash is given in Fig. 7. The annual charge applied to capital, R , and the unit cost of power, c_p , are shown as parameters. The other cost parameters were held at the same values cited previously, except, of course, for the material balance quantities. They were calculated assuming a total ash of 500 lb./ADT and no separation of Na_2CO_3.

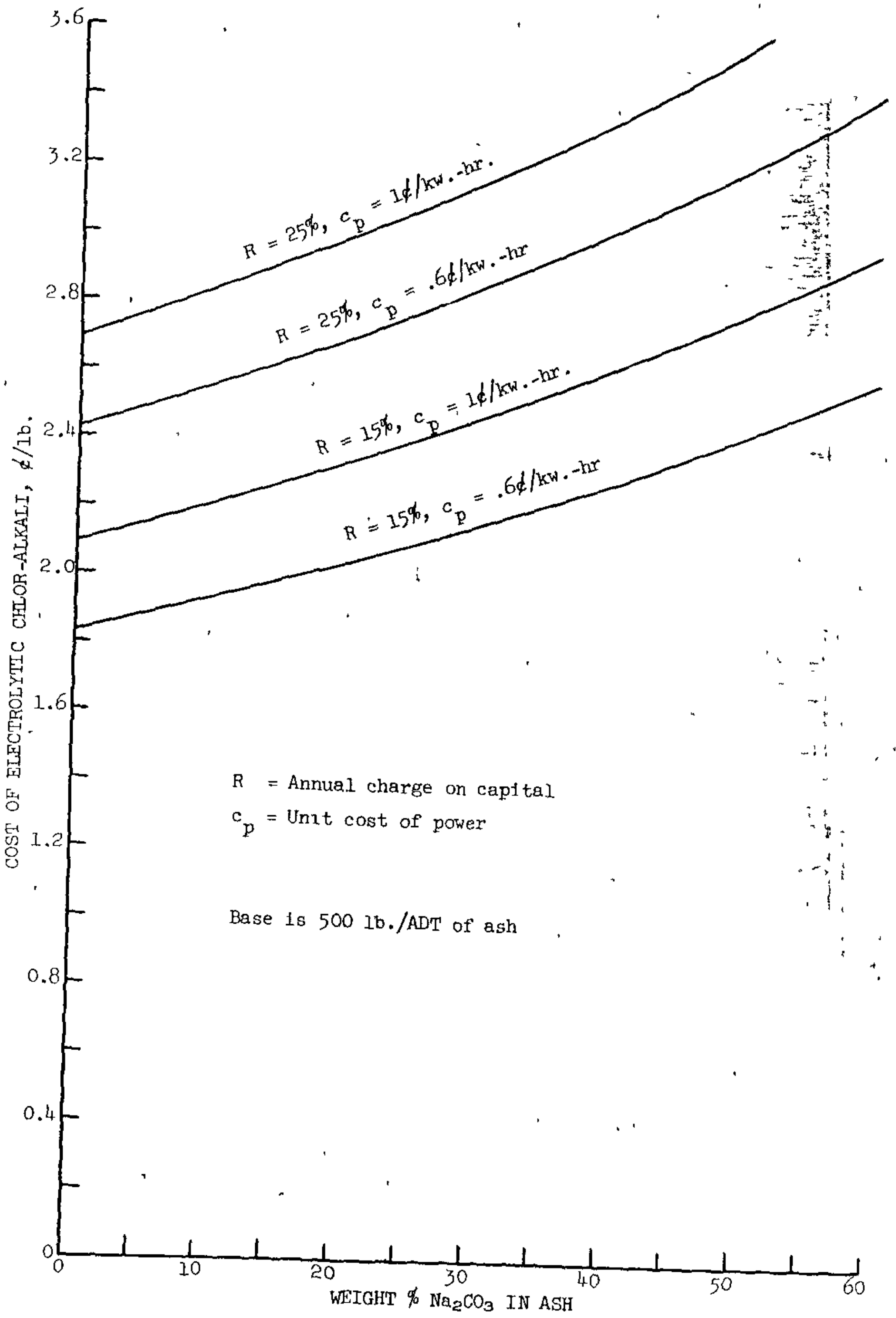


Figure 7. Cost of Electrolytic Chlor-Alkali

The calculated results in Fig. 7 show the pronounced influence of capital and power costs on chlor-alkali. Of more interest, however, is the effect of ash composition. The cost of chlor-alkali rises as the percentage of Na_2CO_3 in the ash increases. This is because a portion of the chlorine is made into HCl for neutralization and thus there is less product to bear the charges. However, the cost of chlor-alkali does not rise as steeply as might be expected. The cost rises only 17.5% for Na_2CO_3 increasing from 0 to 30% by weight. This would indicate that the neutralization technique is economically feasible over a reasonably wide range of Na_2CO_3 contents.

It is difficult to consider the cost of separation of Na_2CO_3 apart from consideration of the economics of alternative processing steps. Separation is feasible only if a second method of producing caustic is available. When this is the case, the method of assigning production costs for chlor-alkali equally between chlorine and caustic is not realistic. The cost (and value) of NaOH is determined by the second caustic-producing method and this is used to allay a portion of the chlor-alkali costs. The remainder is all assigned to the chlorine produced. In such a situation, the cost of producing chlorine would be given by:

$$c_{Cl} = \frac{\left\{[1-0.1(\frac{W_{2C}}{W_{3S}})]\left(\frac{C_A + C_{S1}}{1 + \frac{\rho}{1.46}}\right) + \frac{L_{CE}c_S}{E_{SCE}} + 0.608Kc_p + \frac{I_{CA}R}{5P}\left(\frac{W_{3S}}{500(1 + \frac{\rho}{1.46})}\right)^{n_{CA}-1} - \frac{W_{3S}c_{Na}}{1.46+\rho}\right\}}{\frac{0.888\ W_{3S}}{1.46 + \rho} - 0.67\ W_{2C}} \qquad (29)$$

where $\underline{c}_{N2}$ = cost of producing NaOH by alternative process, ¢/lb. It is also difficult to decide what portion of the separation costs should be assigned to the carbonate-rich phase and what part to the salt-rich phase. This would depend in part on the motivation for introducing the separation step. It is clear on examining Equation (28) or (29) that any charges for separation tend to appear additively in the final cost.

Chlorine Dioxide Production

If the holopulp system is to be completely closed and not dependent on disposal of by-products, chlorine dioxide must be produced by a process which does not use sulfuric acid. There is only one process of this type which has reached commercial status – the Day-Kesting process which employs HCl to react with Na_2ClO_3 in forming ClO_2. The current version of this process is that of Chemech, and the economic analysis of ClO_2 production is based on their process. The major reactions in the Chemech process are the following:

1. $NaCl + 3H_2O \rightarrow NaClO_3 + 3H_2$
2. $NaClO_3 + 2HCl \rightarrow ClO_2 + \tfrac{1}{2}Cl_2 + NaCl + H_2O$
3. $NaClO_3 + 6HCl \rightarrow 3Cl_2 + NaCl + 3H_2O$.

This last reaction is an undesired side reaction. The relative predominance of the two generator reactions (Reactions 2 and 3) can be described in terms of the generator efficiency, η, which is defined as the ratio of chlorate consumed by the desired reaction (Reaction 2) to the total chlorate reacted. It is then possible to write an overall generator reaction as follows.

$$NaClO_3 + (6 - 4\eta)HCl \rightarrow \eta ClO_2 + (3 - \tfrac{5}{2}\eta)Cl_2 + NaCl + (3 - 2\eta)H_2O \ .$$

A total of five items will be included in the economic analysis of ClO_2 production. These are as follows:

1. Capital charges
2. Cost of electrical power
3. Steam costs
4. Cost of raw materials
5. Labor costs.

The cost of ClO_2 production is determined on an absolute basis (and not relative to kraft) since there is no direct analogy in conventional pulping systems.

Most of the information on which these cost estimates are based was supplied by Chemech. An initial capital cost estimate supplied by Chemech was $7.5 million for 50 tons/day of ClO_2. About $5 million of this was for chlorate production and $2.5 million for the ClO_2 generator. Later, they also supplied cost estimates for two cases of combined chlor-alkali and ClO_2 plants as described below.

Case 1.

ClO_2 = 47 TPD as solution
Cl_2 = 80 TPD all converted to HCl
NaOH = 90 TPD as 30% solution

Capital cost: $15,700,000 which includes

land and site preparation	$100,000
steam plant	$500,000
working capital	$500,000

Operating costs (per 24-hr. day):

electrical power	764,000 kw.-hr. (a.c.)
salt (including that in NaOH)	146 tons
electrode maintenance	$980
diaphragm replacement	$40
maintenance materials	$650
steam	615 tons
water	6.2 million gallons
operating and maintenance labor	35 man-days
supervision	2 man-days.

Case 2.

ClO_2 = 38.5 TPD as gas
Cl_2 = 80 TPD all converted to HCl
NaOH = 90 TPD as 30% solution

Capital cost:	$14,400,000 which includes land and site preparation	$100,000
	steam plant	$400,000
	working capital	$500,000

Operating costs:

electrical power	664,000 kw.-hr. (a.c.)
salt	146 tons
electrical maintenance	$860
diaphragm replacement	$40
maintenance materials	$610
miscellaneous chemicals	$40
steam	390 tons
water	6.0 million gallons
operating and maintenance labor	35 man-days
supervision	2 man-days

There is reason to believe that these estimates of capital costs are too high. If the investment data from the previous section are projected to 80 TPD Cl_2, one arrives at a value for the chlor-alkali plant of $6.9 million. If this is subtracted from the total capital cost in Case 1, it gives $8.8 million for the capital cost of the ClO_2 plant. This is higher than the original estimate of $7.5 million for 50 TPD of ClO_2. It should also be noted that the difference in capital between Case 1 and Case 2 is only $1.3 million, even though the ClO_2 tonnage was reduced from 47 to 38.5 TPD and the need for a scrubber and water-chilling plant is eliminated. If it is assumed that all of the difference in capital is due to the reduction in ClO_2 tonnage only, the capital for 47 TPD of ClO_2 is \$8.3 million at a scale factor of 0.85 and \$7.2 million at a scale factor of 1. The very high investment needs for these two cases is even more disturbing since they are supposed to include significant savings due to integration of power supplies, etc. for both chlor-alkali and ClO_2 plants. The reason for a high estimate is not known. It appears unlikely that Chemech would deliberately overstate their cost estimates.

H. V. Casson of Huron Chemicals Limited has supplied capital requirements for chlorate plants using his cells. In order to supply a 47-TPD ClO_2 plant operating at 95% efficiency, a total of 78 TPD of chlorate are needed. Casson estimates \$105/annual ton at that capacity for a total of \$2.9 million for a battery limits chlorate plant. This does not include the ClO_2 generator. If the same proportion of costs between generator and chlorate plant is assumed as in Chemech's initial estimate, Casson's estimate would translate to about \$4.5 million for a 50-TPD ClO_2 plant.

At the present time, it appears best to compromise between Casson's estimate and that of Chemech and use \$6 million as the capital required for a 50-TPD ClO_2 plant. Chemech has suggested the use of a scale exponent of 0.85 in calculating capital requirements at other plant sizes.

The power required may be estimated in several ways. The difference in power required between Case 1 and Case 2 is 100,000 kw.-hr. If this is all assigned to the difference in ClO_2 production (47 - 38.5 = 8.5 TPD), it gives 5.9 kw.-hr. per lb. of ClO_2. Data on the original Chemech chlorate plant at Bellingham, Washington, indicated that between 5800 and 6000 kw.-hr./ton chlorate was required. At 95% generator efficiency, this gives 4.9 kw.-hr./lb. ClO_2. There is no fixed single value for the power requirement. It is possible to design the cells to operate at a higher current density (hence, power cost) so as to minimize capital, and vice versa. It appears reasonable to use 5 kw.-hr./lb. ClO_2 as an approximation of the power requirement.

Steam requirements can be taken from the data furnished for Case 1 and Case 2 provided that a means of separating the steam used for ClO_2 from that used for chlor-alkali is available. A large portion of the difference between Case 1 and Case 2 is due to the steam required to chill water for the ClO_2 absorber in Case 1. In addition, the generator itself requires about 3.7 lb. steam/lb. ClO_2 when 33% HCl is used as feed (information furnished by Chemech). If this factor is used to estimate the steam used in the generator, the steam requirement for Cases 1 and 2 can be broken down as follows.

	Steam Requirement, tons	
	Case 1	Case 2
Chlor-alkali plant	240	240
ClO_2 generator	175	150
Chiller	200	-
	615	390

For the conventional plant producing an aqueous solution of ClO_2, this would amount to: $(200 + 175)/47 = 8$ lb. steam/lb. ClO_2.

The only significant feed to the Chemech system is hydrochloric acid. This would be produced by burning H_2 in Cl_2 and dissolving the HCl in water. It has been assumed that the equipment for forming HCl and absorbing it is relatively small in cost compared to the uncertainty in other elements of the system so that the only significant cost of the HCl is the cost of the chlorine used to form it. That chlorine which leaves the system as Cl_2 with the ClO_2 is assumed to be a credit at the cost of Cl_2. In this case, the only raw material charge is for the chlorine used to make ClO_2 (35.5/67.5, or 0.526 lb./lb. ClO_2). The cost of other materials is neglected at this stage of the analysis.

Labor costs can be based on the information furnished by Chemech for Cases 1 and 2. They estimated 35 man-days of ordinary labor and 2 man-days of supervisory labor to be assigned partly to chlor-alkali and partly to ClO_2 production. Assuming \$40/man-day for ordinary labor and \$80/man-day for supervisory labor, this becomes

$$\frac{\$1560}{90 \text{ tons NaOH} + 50 \text{ tons } ClO_2} = \frac{1560 \times 100}{140 \times 2000} = 0.55¢/\text{lb.}$$

charged to both caustic and ClO_2 production. If all of this labor is charged against ClO_2 (based on the argument that ClO_2 leads to NaCl in ash which leads to electrolytic recovery), it becomes 1.55¢/lb.

A cost equation can be developed for ClO_2 as follows.

$$c_D = \frac{I_D R}{350,000} (P/50)^{n_D - 1} + K_D c_p + L_D c_S + 0.526\, c_{CL} + c_{DL} \tag{30}$$

where

$\underline{c_D}$ = unit cost of producing ClO_2, ¢/lb.,

$\underline{I_D}$ = investment for 50-TPD ClO_2 plant, \$,

$\underline{P}$ = ClO_2 production rate, TPD,

$\underline{K_D}$ = electrical power requirement, kw.-hr./lb. ClO_2,

$\underline{L_D}$ = steam requirement, lb. steam/lb. ClO_2,

$\underline{c_{DL}}$ = cost of labor charged to ClO_2, ¢/lb. ClO_2, and

$\underline{n_D}$ = scale factor for ClO_2 plant.

A plot of ClO_2 costs found from Equation (30) is shown in Fig. 8 for certain values of capital charge factor, $\underline{R}$, and power costs, $\underline{c_p}$. The effect of plant size is also shown. Values chosen for the other parameters are as follows:

$\underline{I_D}$ = \$6 million, $\underline{P}$ = 50 TPD, $\underline{K_D}$ = 5 kw.-hr./lb. ClO_2,
$\underline{L_D}$ = 8 lb. steam/lb. ClO_2, $\underline{C_S}$ = 0.1¢/lb. steam,
$\underline{c_{CL}}$ = 2¢/lb., $\underline{c_{DL}}$ = 1¢/lb. $\underline{n_D}$ = 0.85.

Inspection of Fig. 8 shows that the costs tend to fall in the range of 6¢ to 12¢/lb., depending on the values assumed for the parameters. To get costs as low as 6¢/lb., it is necessary to have power at only 0.3¢/kw.-hr. (3 mil power) and a total charge against capital of only 10%. This does not appear realistic. If 5 mil power and 15% capital charges are taken as minima, then the lowest ClO_2 cost is 8¢/lb. It could easily range higher. It is obvious in Fig. 8 that ClO_2 costs are not appreciably affected by plant size. This is a consequence of using 0.85 as a scale factor.

It appears that ClO_2 costs would range from 8 to 12¢/lb., depending on local conditions. Ten cents per pound does not appear to be too far off as a typical figure. These may be compared with costs of ClO_2 by the SVP process taken from an article in the September 1971 issue of Tappi (10). It was estimated that ClO_2 would cost 12.4¢/lb. with credit for by-product Na_2CO_3, and 15.6¢/lb. without credit. The investment was about \$900,000 for a 10-TPD plant.

Causticizing with Lime

In order to complete this analysis of the economics of holopulp recovery, it is necessary to determine the cost of producing NaOH by causticizing Na_2CO_3 with lime and the cost of separating Na_2CO_3 from NaCl. The cost estimate for causticizing can also be applied to kraft in the differential cost comparison with holopulp.

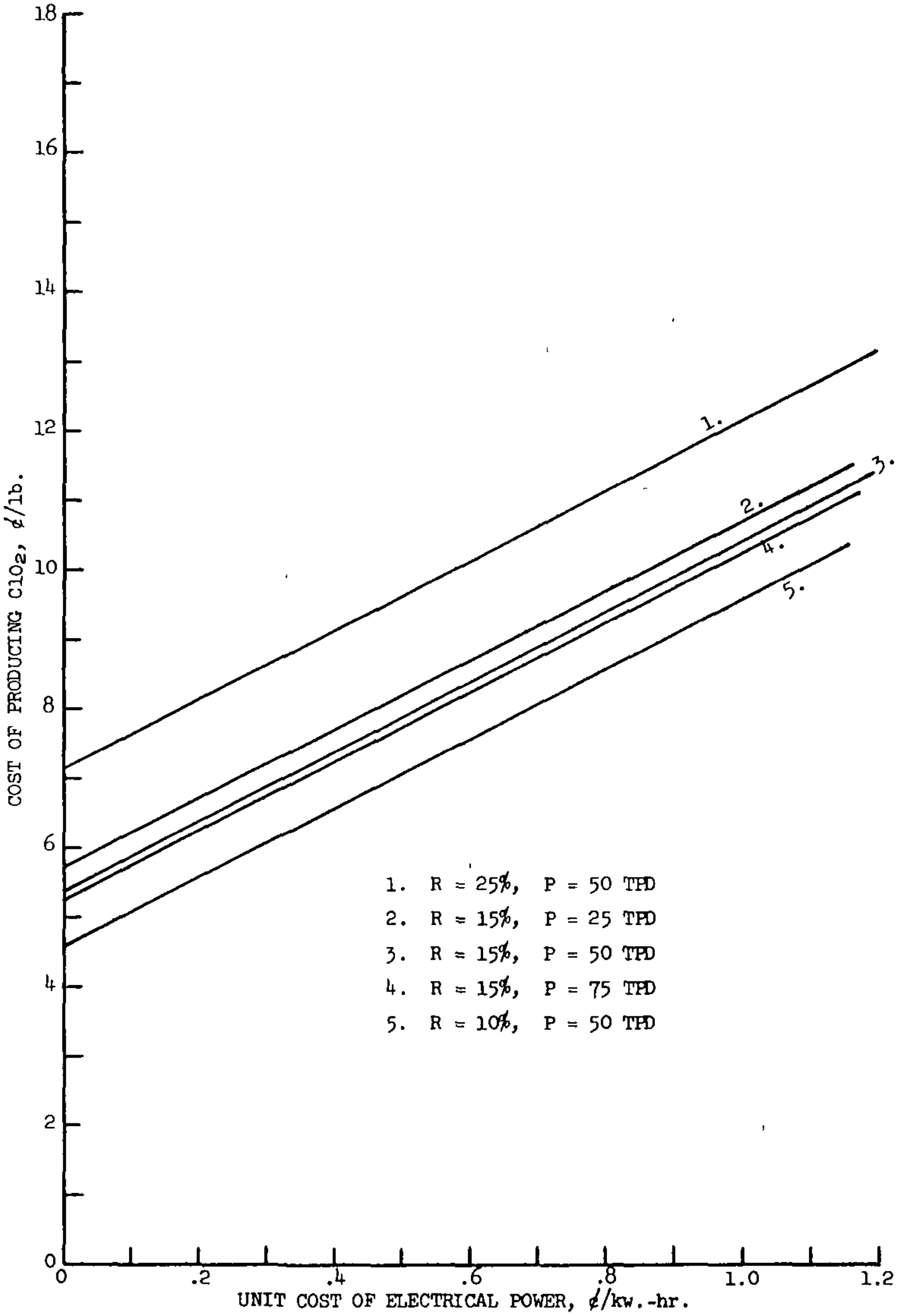


Figure 8. Cost of ClO_2

The reaction in causticizing is exceedingly simple. $CaO + H_2O + Na_2CO_3 \rightarrow 2NaOH + CaCO_3$. This reaction goes to the right because $CaCO_3$ is more insoluble than $Ca(OH)_2$. The $CaCO_3$ can be recovered to make CaO, thus closing the cycle.

In estimating the costs of producing NaOH by this method, the following factors are considered:

1. Charges against the capital investment
2. Fuel costs for the calciner
3. Raw material costs
4. Labor costs
5. Electrical power for kiln.

Data on size and horsepower for rotary-kiln installations are given in Table 20-10 of Perry's Chemical Engineers' Handbook, 4th edition (5), as a function of capacity. Approximate purchase costs of rotary kilns are given in Table 20-11. For 125 TPD of lime sludge, these tables give a size of 10½ ft. x 185 ft., 50-75 horsepower, and a 1960 purchase cost of $220,000. For 190 TPD of lime sludge, the size is 10 ft. x 300 ft.; power is 75-125 h.p., and the 1960 purchase cost is $300,000. These data would indicate a scale exponent of 0.74 for kilns. It is stated that installed costs will run 300-500% of the purchase cost. This is because the purchase cost does not include the refractory brick lining. Thus, 1960 costs for the kiln would range from $600,000 to $1 million for 125 TPD of lime sludge and from $0.9 million to $1.5 million at 190 TPD of lime sludge. It is also stated that maintenance will average 5-10% of the total installed cost per year, but is dependent largely on the life of the refractory lining. No data were found on the investment needed for the causticizing system. This consists mainly of stirred tanks and clarifiers. It is assumed that the investment would be on the same order as for the calcination system.

Fuel costs for the calciner tend to be a major operating cost. The amount of fuel required depends to a large extent on the heat recovery equipment installed in the calciner. Typically, the heat consumption for a kiln ranged from 8 to 12 million B.t.u./ton of product (CaO). The cost will depend on the heat demand and the unit cost of fuel.

The raw material includes the Na_2CO_3 which is causticized and any make-up lime that is needed. The cost of the Na_2CO_3 as supplied to the causticization system includes the cost of producing it as a recovered ash plus any additional charges for separating it from NaCl.

Labor costs can only be estimated at this stage of the analysis. It may be assumed that 6 man-days of operating labor and one of supervisory labor are required for the daily production. If, as was assumed earlier, the charges are taken as $40/man-day of operating labor and $80/man-day for supervisory labor, the total daily charge would be $320. At 500 lb. NaOH/ADT and 500 ADT/day, this comes to 0.13¢/lb. NaOH.

The electrical power cost for operating the kiln could probably be neglected from the horsepower requirements given in Perry (5). Those values were 50-75 horsepower for 125 TPD of lime sludge and 75-125 horsepower for 190 TPD of lime sludge. This amounts to about 0.5 h.p. day/ton of sludge or about 18 kw.-hr. per ton of sludge. Even at a power cost of 1¢/kw.-hr., this would be only 18¢/ton of lime sludge. Thus, this element of the cost picture can be neglected.

An equation for the cost of producing NaOH by causticizing with lime is given as follows.

$$c_{N2} = \frac{I_{LS}R}{875,000}\left(\frac{P_N}{125}\right)^{n_{LS}-1} + \frac{B}{2857}c_B + \frac{c_A + c_{sep} + M_L c_L}{0.755\,\eta_c} + c_{LSL} \qquad (31)$$

where

$\underline{c}_{N2}$ = cost of producing NaOH by causticizing with lime, ¢/lb.,

$\underline{I}_{LS}$ = investment in lime system for 125 TPD NaOH, \$,

$\underline{P}_{N}$ = actual NaOH production rate, TPD,

$\underline{B}$ = heat consumption for kiln, million B.t.u./ton CaO,

$\underline{c}_{B}$ = unit cost of fuel, ¢/million B.t.u.,

$\underline{M}_{L}$ = make-up lime requirement, lb./lb. Na_2CO_3 fed,

$\underline{c}_{L}$ = unit cost of make-up lime,

η_{C} = conversion efficiency, NaOH/(NaOH + Na_2CO_3) as Na_2O,

$\underline{n}_{LS}$ = scale factor for lime system,

$\underline{c}_{sep}$ = cost of separating Na_2CO_3 from NaCl assigned to Na_2CO_3, ¢/lb. Na_2CO_3, and

$\underline{c}_{LSL}$ = cost of lime system labor assigned to product, ¢/lb. NaOH.

It appears useful to assign a set of values to the parameters in Equation (31) in order to estimate the cost of NaOH produced in this manner, and to determine the dominating terms. The following values are assumed:

$\underline{I}_{LS}$ = \$3,000,000, $\underline{R}$ = 25%, $\underline{P}_{N}$ = 125 tons NaOH/day,
$\underline{B}$ = 10(million B.t.u./ton product), $\underline{c}_{B}$ = 40¢/million B.t.u.,
$\underline{c}_{A}$ = 0.5¢/lb. Na_2CO_3, $\underline{c}_{sep}$ = 0.5¢/lb. Na_2CO_3,
$\underline{M}_{L}$ = 0.05 lb. CaO/lb. Na_2CO_3, $\underline{c}_{L}$ = 1¢/lb.,
η_{C} = 0.90, $\underline{c}_{LSL}$ = 0.13¢/lb. NaOH.

This gives: $\underline{c}_{N2}$ = 0.857 + 0.14 + 1.548 + 0.13 = 2.675¢/lb. NaOH. This value is somewhat surprising at first glance because it indicates that the cost of preparing caustic by this method is of the same order as electrolytic caustic. The dominating terms in the cost equation are the cost of the raw materials and the capital charges. Applying these same conditions to kraft would give a cost of 1.2¢/lb. because $\underline{c}_{A}$ and

$\underline{c}_{sep}$ would be zero for kraft. It is clear that the costs of achieving a separation of Na_2CO_3 from NaCl must be kept to low levels (less than 0.5¢/lb. of Na_2CO_3) if causticizing with lime is to show any economic benefit in the holopulping process.

In comparing the cost of producing caustic by causticizing with lime [Equation (31)] with the cost of electrolytic caustic [Equation (28)], it is illuminating to look at the influence of the individual terms. In doing this, it is reasonable to neglect the costs of fuel, labor, and make-up lime in the causticizing process and the cost of steam in the electrolytic process. This leaves capital and raw material costs for both processes and, in addition, the power cost for the electrolytic process. The raw material cost is significantly lower for the electrolytic process. There are two main reasons for this:

1. The causticizing process properly bears the cost for separating Na_2CO_3 from NaCl.
2. The costs for the electrolytic process are borne by Cl_2 and NaOH. Thus, the denominator in Equation (28) is larger.

The capital investment in the chlor-alkali plant is significantly greater, but again the charges are borne by both Cl_2 and NaOH and hence the effect is not as pronounced as it would seem. Power costs are important only for the electrolytic process and this tends to make it more expensive.

The cost of separation of Na_2CO_3 from NaCl is probably the largest single factor in determining the point at which it is economical to introduce a supplementary causticizing system. It is therefore appropriate to examine the cost of achieving a separation. In the section on cost of chlor-alkali, the material balance around the separation step was given as

$$W_{2S} = W_{1S} - W_{4S} \qquad (16)$$

and

$$W_{2C} = W_{1C} - W_{4C} \qquad (17) .$$

The recovered ash was assumed to consist of NaCl and Na_2CO_3 (in the amounts of W_{1S} and W_{1C} per ADT), and this was separated into a salt-rich stream (W_{2S}, W_{2C}) and a carbonate-rich stream (W_{4C}, W_{4S}). The feed to the separation step was assumed to bear the charge, c_A , applied equally to NaCl and Na_2CO_3 by weight. (This is arbitrary; it could be assigned by mole or any other basis.) The additional cost associated with the separation step can be assigned to the carbonate-rich stream and/or the salt-rich stream in any reasonable manner. In most cases, separation would be introduced only to permit production of caustic by a lower cost direct causticization. Thus, the normal practice would be to assign all of the separation costs to the carbonate stream. In addition, since Equation (31) was set up considering only the Na_2CO_3, the separation charges should be assigned only to the Na_2CO_3 in the carbonate-rich stream and not to the NaCl which passes through as an inert. For the same reason, the separation cost should also include the ash cost of the inert NaCl in the carbonate-rich stream, W_{4S} .

The possibility of separating Na_2CO_3 from NaCl was discussed in Progress Report Fifteen (11). Solubility data for this system were presented. At higher temperatures (25°C. and up), Na_2CO_3 and NaCl are about equally soluble in the presence of both solid phases. At temperatures near 0°C., the solubility of Na_2CO_3 is greatly depressed. If the composition of the recovered ash is sufficiently different from 50% NaCl and 50% Na_2CO_3, concentration of green liquor would drop out the species present in excess and leave a solution containing about equal parts of each substance. Under pulping conditions developed previously, NaCl would be recovered as the solid phase and Na_2CO_3 in a 50-50 solution. If Na_2CO_3 were present in excess, the opposite would be true. Cooling to temperatures in the range 0-15°C. would be needed to drop Na_2CO_3 from the 50-50 solution.

In estimating the cost of separation here, it will be assumed that NaCl is present in excess and that causticizing is done on the 50% solution. It will be assumed that refrigeration is not needed. The cost of separation will include charges against capital, steam costs for concentrating, and labor costs. In addition, it will include the cost of the ash of the NaCl carried with the carbonate-rich stream.

The following cost equation can be written:

$$c_{sep} = \frac{I_{sep} R}{1750\, W_{4C}} \left(\frac{W_{1S} - W_{1C}}{240} \right)^{n_{sep}} + L_{sep} c_S + c_{sepL} + \frac{W_{4S}}{W_{4C}} c_A \qquad (32)$$

where

c_{sep} = cost of separation assigned to Na_2CO_3, ¢/lb. Na_2CO_3,
I_{sep} = investment in 60-TPD crystallizer, \$,
n_{sep} = scale factor for crystallizer,
L_{sep} = evaporation load, lb. H_2O/lb. Na_2CO_3, and
c_{sepL} = cost of labor for separation assigned to Na_2CO_3, ¢/lb.

Popper's book (6) gives an estimate of \$600,000 for the investment in a 60-TPD crystallizer with a scale factor of 0.65. The evaporation load would be strongly dependent on the initial ash composition. For an ash containing 75% NaCl, the evaporation load would be about 8 lb. H_2O/lb. Na_2CO_3. If it is assumed that the labor force for the causticizing operation could handle separation also, then $c_{sepL} = 0$. Steam costs may be taken at 0.08¢/lb. The material balance quantities are assumed to be W_{1S} = 360 lb./ADT and $W_{1C} = W_{4C} = W_{4S}$ = 120 lb./ADT. If the ash is taken to have a charge of 0.5¢/lb. and an annual capital charge factor of 25% is assumed, the unit cost of separating out Na_2CO_3 is given as

c_{sep} = 0.715 + 0.64 + 0 + 0.5 = 1.855¢/lb. Na_2CO_3.

A separation charge of this magnitude would be prohibitive for justifying the addition of a causticizing operation. The estimate would not appear to be too far out of line. The first term represents the charge against capital. The capital charge factor used (25%) may have been high, but even if it is reduced to 10%, the net cost for capital would still be 0.3¢/lb. The second term is the steam costs. Since the evaporator load is determined by solubility, it is fixed and the steam cost estimate is reasonable. It could be reduced by going to multiple-effect operation. However, this would increase the capital cost. The third term represents labor costs and was here assumed to be negligible. This may not necessarily be the case. The last term represents the ash charge for the inert NaCl entering the causticizing stream. It is governed primarily by solubility and ash unit costs, so that the estimate value seems reasonable. Thus, separation costs could range from about 1.5 to 2¢/lb. Na_2CO_3.

The cost of separation is too high to justify inclusion of a causticizing step when the ash is salt rich (0 to about 50% Na_2CO_3). For this range, it appears that electrolytic chlor-alkali with recycled HCl to neutralize the Na_2CO_3 in the ash is more economical. For ash compositions in mid-range (≈ 50% NaCl and Na_2CO_3), separation could not be achieved simply by concentrating, and cooling would also have to be employed. In this situation, it might be feasible to causticize all of the ash and then drop salt from a caustic evaporator. This same technique might well be employed for carbonate-rich ash. This requires further investigation.

Recovery Summary

A comparison of the economic effects of chemical recovery in holopulping with other recovery processes must be based on the effective cost of the chemicals produced. The holopulp recovery process is sufficiently different from conventional kraft recovery that a direct comparison of differential costs is not feasible. Only the evaporation and burning operations appear to be sufficiently parallel to permit a direct differential analysis. Accordingly, excess costs for evaporation and burning for holopulp are charged to the recovered ash from holopulp. The ash from the conventional process is assumed to be obtained at no charge (if holopulp evaporation and burning costs are less than the conventional process, holopulp ash is assessed a negative charge). From that point on, all processing charges are applied to both cases so as to determine the net cost of producing chemicals by either method.

Evaporation and burning costs tend to be higher for holopulp than for kraft. The difference is on the order of $1-3/ADT, which would result in holopulp ash costs of 0.2-0.6¢/lb. ash. Increased evaporation costs rest on the likelihood of a dilute holopulp spent liquor being produced. This is strongly dependent on pulping and washing technology and the limits have not yet been closely defined. It appears likely that the dilution will outweigh the lower solids production associated with a high-yield pulp so that the holopulp evaporator load would be higher. Holopulp should require a smaller furnace and hence a lower capital charge for the furnace due to the lower amount of solids produced per ton. However, the corollary to this is a reduction in steam production since combustible organics in the liquor would be less. The net result here is also generally unfavorable to holopulp.

The first step in regeneration of salt-rich ash is electrolytic chlor-alkali production including conversion of some chlorine to HCl and recycling it to neutralize the Na_2CO_3 in the ash. The net cost of chlorine and NaOH produced by this method is, naturally, dependent on the amount of Na_2CO_3 in the ash. The costs would range from 1.8 to 2.6¢/lb. Cl_2 and NaOH for a 100%-NaCl ash up to 2.4 to 3.4¢/lb. Cl_2 and NaOH for a 50%-Na_2CO_3 ash. The increase in cost is due to the additional amounts of chlorine which have to be recycled as HCl for Na_2CO_3 neutralization. However, the rate of increase is not as great as might be expected, and this approach to holopulp recovery seems economically justifiable over a reasonably wide range of ash compositions. The cost is dependent primarily on capital charges, electrical power costs, and the charge assessed to the ash.

Cost of chlorine dioxide produced by the Chemech process using HCl feed formed by burning chlorine from the chlor-alkali cells is estimated to range from 8 to 12¢/lb. The dominant factors in this cost picture are capital charges, electrical power costs, and the cost of chlorine for feed. These values can be compared with a range of 12 to 16¢/lb. ClO_2 estimated for the SVP process.

Costs of caustic production through the use of a lime cycle were also estimated. These are strongly dependent on the cost of the Na_2CO_3 feed. For the kraft system, where no charge is assessed to the chemicals recovered, the cost of caustic ranges from 0.8 to 1.2¢/lb. For holopulp, which would have to bear the costs assessed to the ash as well as costs for separating Na_2CO_3 from NaCl, the range in costs for NaOH is 3.7 to 4.8¢/lb. This is more expensive than electrolytic caustic production. It does not appear economically feasible to add a lime system to the holopulp recovery process when NaCl is the dominant component of the ash.

In general, the capital requirements for a holopulp recovery system will be greater than that of kraft. The major reasons for this are that electrolytic chlor-alkali systems require a larger investment than a causticizing-calcining plant and the use of a more elaborate ClO_2 process which includes on-site chlorate production. A summary of capital estimates for a 500-TPD recovery system for both kraft and holopulp is given below.

	Holopulp	Kraft
Evaporation	$ 1.2 million	$ 1.0 million
Burning	4.4 million	6.0 million
Electrolytic chlor-alkali	6.6 million	
Chemech ClO_2	6.0 million	
Causticizing with lime		3.0 million
Total:	$18.2 million	$10.0 million

APPLICATION TO SPECIFIC CASES

The preceding sections have dealt with the general problems of quantification of the savings in wood costs due to higher yields, the application of stoichiometry and unit costs to determine chemical costs, and estimation of the unit costs of chemicals produced by the recovery system. It is now desirable to apply these findings to some specific cases. The holopulp processes which will be analyzed are described in some detail in Progress Report Sixteen (12). They are as follows:

1. Bleached hardwood (red maple) holopulp to be compared with bleached hardwood kraft.
2. Unbleached, very high yield holopulps from softwoods to be compared with unbleached softwood kraft (for linerboard).
3. Comparison of the bleached hardwood process (no. 1 above) with and without full chemical recovery.

These analyses will consider only the relative economics of high yield and chemical costs. The major items which are neglected at this stage of the analysis are as follows:

1. Differences in capital and operating costs for the pulping and washing operations themselves (other than direct chemical costs) have been neglected.
2. Any advantages or disadvantages in using holopulp in papermaking have been neglected. Comparisons are made simply on the basis of an equal weight of pulp.
3. Environmental costs have not been included in the analysis up to this point. The elimination of sulfur would be expected to show some tangible benefits to holopulp.
4. No attempt has been made to forecast how the various elements in the holopulp cost picture would change in the future.

Any judgments arrived at on the basis of the cost estimates presented below must be tempered by an awareness of the incomplete nature of this economic analysis.

BLEACHED HARDWOOD HOLOPULP

A procedure for producing a bleached hardwood holopulp is described in Tables IV and VII of Progress Report Sixteen (12). This produces a shive-free bleached pulp with a yield range of from 57 to 60%, a TAPPI brightness of 88, and good brightness stability. The stoichiometry employed in pulping was as follows (based on original wood):

Alkali conditioning:	3%	NaOH
Lignin modification:	7.5% 1.33%	ClO_2 Cl_2
Alkali extraction:	7.5%	NaOH

and for bleaching,

Chlorine dioxide-chlorine:	0.77% 0.38%	ClO_2 Cl_2
Alkali extraction:	1.2%	NaOH
Chlorine dioxide:	0.4%	ClO_2

This gives total chemical consumption as follows:

8.67% ClO_2

11.7% NaOH

1.71% Cl_2

Combustion of the liquor from such a process would give an ash containing 63% NaCl and 37% Na_2CO_3.

The cost of chemicals for holopulp is given by

$$\frac{18}{0.57 \rightarrow 0.6}\left[0.0867(8 \rightarrow 12) + (0.117 + 0.0171)(2.24 \rightarrow 3.28)\right] = \frac{\$29.80 \rightarrow 46.70}{\text{ADT}}$$

where Cl_2 and NaOH costs are read from Fig. 7 and a range of 8 → 12¢/lb. was used for ClO_2.

The savings in wood costs due to higher yield can be estimated from Fig. 2 once a value of the yield for bleached hardwood kraft is given. An experimental yield of 46% was determined for bleached kraft pulp from the same wood supply as the holopulp. Assuming 46% yield for the reference and a holopulp yield range of 57-60%, Fig. 2 shows a range in savings of \$7.6 → \$9.2/ADT at a wood cost of 1¢/lb. Assuming a range in wood unit costs from 0.6 to 1¢/lb. gives a range of potential savings of \$4.6-\$9.2/ADT.

The cost of chemicals for the bleached hardwood kraft is estimated as follows. A laboratory cook of these chips was described on page 107 of Progress Report Twelve (13). The chemical charge was 15% active alkali as Na_2O and 28% sulfidity, to give an unscreened yield of 50.3% and 1.6% rejects. On a differential basis, there is no charge for the Na_2S used because it does not require further processing after incineration. The NaOH is a cost item because it requires the use of the lime system. Thus, the chemical cost for making unbleached hardwood kraft is estimated as $\frac{18}{0.503} \times 0.139 \times (0.8 \rightarrow 1.2) = \$4\text{-}\$6/\text{ADT}$. This is based on previous estimates of 0.8 to 1.2¢/lb. as the cost of NaOH for kraft pulping. The estimate of bleaching cost is based on the use of "market" values for bleaching chemicals (no recovery of bleaching chemicals) and the bleaching conditions described in Appendix V of Progress Report Sixteen (12). The following consumption data are expressed as percent on o.d. original pulp.

Chlorination:	2.5% Cl_2 at 4.7¢/lb.
Alkali extraction:	1.7% NaOH at 4¢/lb.
Hypochlorite:	0.75% available Cl_2 at 8.8¢/lb.
Chlorine dioxide:	0.6% ClO_2 at 12¢/lb.

Final yield = 46%.

This gives the following estimate of bleaching chemical costs as

$$\frac{18 \times 0.503}{0.46} [0.025 \times 4.7 + 0.017 \times 4 + 0.0075 \times 8.8 + 0.006 \times 12] = \$6.40/\text{ADT}.$$

Adding together the pulping and bleaching costs gives $10.4-$12.4/ADT as the expected range in chemical costs for bleached hardwood kraft in this differential analysis.

This preliminary cost comparison can now be made by deducting the kraft chemical costs from the holopulp chemical costs and then comparing the excess holopulp chemical costs against the savings in wood cost. The relevant data are as follows:

	Holopulp chemical cost:	$29.80 → $46.70/ADT
less	Kraft chemical cost:	$10.40 → $12.40/ADT
	Excess holopulp chemical cost:	$19.40 → $34.30/ADT
less	Savings in wood cost:	$ 9.20 → $ 4.60/ADT
	Excess holopulp cost:	$10.20 → $29.70/ADT

It is seen that the cost of bleached hardwood holopulp exceeds the cost of bleached kraft by a significant amount. The excess cost is expected to range from about $10 to $30 per ADT depending on cost parameters. This is the amount by which the increased chemical cost of holopulp exceeds the savings in wood costs. If this holopulp is to show a net economic advantage, this cost deficit must be made up by the factors heretofore neglected in this analysis, such as environmental or papermaking or product cost advantages.

VERY HIGH-YIELD SOFTWOOD HOLOPULP

The second case for which a specific cost comparison with kraft is desired is a very high-yield unbleached softwood holopulp which could be suitable for linerboard or other grades of that type. Pulping studies of this possibility have served to bracket conditions, but have not yet defined a specific set of process conditions as optimum. However, it appears worthwhile to examine the potential economics of such a pulp.

The following stoichiometries, taken from Table II of Progress Report Sixteen (12) are used in this analysis:

Oxidant, % ClO_2:	4.5	6.0	7.5	9.0
Alkali, % NaOH:	15	15	15	8
Yield, %:	75	72	68	73
Kappa number:	87.0	76.3	62.3	61.4
Na_2CO_3, % of ash:	80.5	74.7	68.3	62.2

The cost of chemicals for these cases would be the sum of the chlorine dioxide and the caustic costs. A dominant feature of all these cases is the fact that Na_2CO_3 is the major component of the ash. This is an aspect of recovery for which the technical details have not yet been worked out. The most promising approach would seem to be causticizing all of recovered ash and then separating out the NaCl in the caustic evaporator. If this is technically feasible, it would lead to a relatively low-cost caustic and a higher cost for chlorine and hence ClO_2. The increased cost for chlorine and chlorine dioxide would be due to the fact that electrolytic costs would not be apportioned to the NaOH by weight. It is difficult to be precise about ClO_2 and NaOH unit costs for this situation; however, it would appear realistic to use costs of 1.2-1.6¢/lb. for NaOH and 9-14¢/lb. for ClO_2. Then the chemical costs per ADT for the cases described above are:

ClO_2:	$ 9.75 → 15.10	13.50 → 21.00	17.90 → 27.80	20.00 → 31.10
NaOH:	$ 4.32 → 5.76	4.50 → 6.00	4.77 → 6.35	2.37 → 3.16
Total:	$14.07 → 20.86	18.00 → 27.00	22.67 → 34.15	22.37 → 34.26

The chemical costs for producing a softwood unbleached kraft at 50% yield may be estimated at $4-6/ADT. (Estimate is the same as the hardwood estimate without the bleaching cost.) Then the net increase in chemical cost for holopulp for these cases is:

$10.07-$14.86 $14.00-$21.00 $18.67-$28.15 $18.37-$28.26

The estimated savings in wood costs can be determined from Fig. 2 assuming a reference yield of 50% and a unit cost range of 0.8-1.3¢/lb. for softwood. This gives the following range in savings in wood costs for the cases considered:

$9.60-$15.60 $8.80-$14.30 $7.60-$12.35 $9.08-$14.76

These cost data may be summarized as follows. $/ADT:

ClO_2 used, %	4.5	6.0	7.5	9.0
NaOH used, %	15	15	15	8
Yield, %	75	72	68	73
Holopulp chemical cost	14.07-20.86	18.00-27.00	22.67-34.15	22.37-34.26
Kraft chemical cost	4-6	4-6	4-6	4-6
Excess chemical cost	10.07-14.86	14.00-21.00	18.67-28.15	18.37-28.26
Savings in wood cost	15.60- 9.60	14.30- 8.80	12.35- 7.60	14.76- 9.08
Net excess cost	-5.53 - 5.26	-0.30-12.20	6.32-20.55	3.61-19.18

The most interesting numbers are for the first case where the net excess cost for holopulp is estimated to range from -$5.50 to +$5.25 per ADT. This indicates that for these conditions holopulp could cost less to produce than kraft. If a satisfactory linerboard can be produced from holopulp made at 75% yield and with 4.5% ClO_2, it could be economically attractive. The favorable economic picture disappears as ClO_2 usage reaches 6% or higher.

This analysis is very preliminary. The economics of recovery of high-carbonate ash is not totally worked out. Tall oil recovery and possible differences in recovery of tall oil between holopulp and kraft were ignored. The cost of the refiners needed to complete fiber liberation was also neglected. However, the crude comparison made indicates there is an economic potential if useful pulps can be produced at yields of about 75% with ClO_2 limited to 4.5% on the wood.

PARTIAL RECOVERY

At the conclusion of the section on chemical recovery, an estimate of the capital requirements for a holopulp recovery system was made. The capital estimate was distinctly higher than that of a kraft system of comparable tonnage. A large part of the capital required was for the electrolytic chlor-alkali cells and for ClO_2 production. In order to minimize capital investment, it is possible that totally closed-loop operation would be avoided. In this situation, evaporation and burning of the spent liquor would be carried out for pollution control purposes and the ash disposed of. The electrolytic plant would be eliminated. Purchased chlorine, caustic, and chlorate (for ClO_2 generation) would be used. It is assumed that an SVP ClO_2-generating system would be installed to minimize by-products. The Na_2SO_4 from the SVP generator could either be disposed with the liquor ash or sold as a by-product. It is of interest to compare the economics of such a system with that using a complete recovery process. The bleached hardwood holopulp discussed above will be used for making this comparison.

In comparing the economics of full and partial recovery, yield economics does not enter in. It is assumed that cooking conditions are equivalent. It is likewise assumed that evaporation and combustion costs are the same. The difference shows up in the chemical costs for the two methods plus the possible cost for disposing of the ash.

The chemical consumption data for the bleached hardwood holopulp were 8.67% ClO_2, 11.7% NaOH, and 1.71% Cl_2 with a final yield of 57-60%. The chemical cost for this process was estimated to range from $29.80 to $46.70 per ADT for the system employing chemical recovery. For the case of partial recovery, chemical costs can be calculated using market prices and assuming 12¢/lb. for ClO_2 with credit for Na_2SO_4 by-product and 16¢/lb. for ClO_2 without by-product credit. Then the chemical cost estimate becomes:

Chlorine dioxide:	8.67% at 12-16¢/lb.	=	31.20 → 43.90, $/ADT
Alkali:	11.7% at 4¢/lb.	=	14.02 → 14.78, $/ADT
Chlorine:	1.71% at 4-7¢/lb.	=	2.40 → 2.54, $/ADT.

This means that chemical costs without recovery are $14-$18 per ADT higher than they are with a full recovery system. The savings in capital costs would be $7.8 million for the Chemech system and $7.0 million for the chlor-alkali plant less $3.3 million for the SVP plant of the desired capacity. This is a capital saving of $11.5 million for a 500-TPD holopulp plant. The annual cost of the higher chemical cost due to incomplete recovery is 500 TPD x 350 days/yr. x ($14-18/ADT) = $2.45 → $3.15 million. This gives a payout time on the incremental investment for a full recovery system of 3.7 to 4.7 years, which is not extremely attractive.

The conclusion that the large investment in electrolytic technology gives a relatively low return must be tempered by the realization that the cost of disposing of the ash was neglected. Since the ash would be soluble, it is unlikely that simple landfill techniques could be used without contaminating groundwater or surface water supplies. In addition, since the ash would contain about one third Na_2CO_3 and two thirds NaCl, it would be difficult to sell as a by-product. Problems in ash disposal could well provide the impetus for full recovery.

ADDITIONAL WORK

The economic analysis presented in this report is preliminary in nature. While it has examined in some detail the trade-off in savings in wood costs vs. the use of expensive delignification chemicals, and the effect of chemical recovery on chemical costs, there are many aspects of the economic picture which have been treated only superficially or ignored. These will have to be included in the economic analysis in order to meet the objective stated in the proposal. The following work on economics is planned for the remainder of this project.

HIGH-CARBONATE RECOVERY

The technology and economics of recovery when the ash is predominantly Na_2CO_3 will be examined. This situation is important in the high-yield softwood pulping process where greater amounts of alkali are used. It is also the direction that the recovery system will take as ClO_2 usage is curtailed in favor of additional alkali. Once the recovery technology for Na_2CO_3-rich ashes is defined and quantified, it will be possible to determine chemical costs over the full range of ash contents.

The analysis of separation of Na_2CO_3 from NaCl presented in this report showed that it is quite costly to separate by concentration only. Concentration would drop the species present in the greatest amount and would leave behind a solution containing nearly equal parts of each compound. This is not really what is desired. Chilling a saturated solution would result in the crystallization of most of the Na_2CO_3. However, this would involve refrigeration and would also be expensive. What would be desired would be a method for dropping out the minor component of the ash. It appears that this could be accomplished by causticizing the ash solution directly and then dropping the NaCl by concentrating the caustic solution. There are some potential technical problems to this approach (such as the behavior of carryover lime particles) which must be evaluated before caustic production can be costed.

STOICHIOMETRIC VARIATIONS

As was stated earlier in this report, the economic analysis of holopulp is not to be restricted to the particular conditions employed in the laboratory studies, but rather is to encompass a wide range of pulping variables broadly delineated by the steps of thermomechanical defibration and sequential treatments with the chemicals ClO_2, NaOH, Cl_2, and NaOCl. There are two major aspects to the problem of a multivariable analysis of the economics of pulping stoichiometry:

a. Relating the stoichiometric variables to the ash composition and describing the effect of ash composition on chemical cost.

b. Relating the stoichiometric variables to the effect on wood, particularly yield, lignin content, and pulp properties.

The first item will be completed with the extension of the current economic analysis of recovery to carbonate-rich ash compositions. The second item will require more ingenuity.

In order to estimate the effect of stoichiometric variables on yield, etc., it is planned to use the data of Stone and Clayton (14) published in the Pulp and Paper Magazine of Canada in June, 1960. This provides information on relative rates of lignin and carbohydrate removal by kraft and soda liquors. It can be used to estimate the effects of strong alkali treatments before oxidation with ClO_2. By combining the information obtained from Stone and Clayton with information generated in this program on the selectivity and extent of delignification with ClO_2 and alkali, it should be possible to generate a simple mathematical model relating stoichiometry to yield and lignin content. It may also be possible to predict pulp properties to a limited extent. The combination of the stoichiometric model, the wood cost information presented in this report, and the extended description of chemical costs as a function of ash composition can then be used to examine a wide range of stoichiometric variables.

PULPING AND WASHING OPERATIONS

The only economic variables considered in the analysis of pulping up to this time have been wood and chemical costs. The capital costs of the pulping (and bleaching) vessels, the washers, and refiners have been neglected in the analysis. Likewise, operating variables such as steam consumption, electrical power requirements, and labor have been ignored. The differences between the cooking aspects of holopulping and kraft are profound and it is likely that there would be significant economic differences also. For example, holopulping tends to be an atmospheric pressure operation, while kraft cooking is carried out at elevated pressures. Holopulping employs a sequential treatment with chemicals, possibly with interstage washing, while kraft is (except for bleaching) essentially a single-vessel process. Refiners are needed for defibering chips before oxidation in holopulping. This step does not exist in conventional kraft. Additional differences could be associated with materials of construction due to differences in corrosiveness of the chemicals employed.

This is an aspect of the comparative economics of holopulping which has not received adequate treatment in previous analyses. The differences in cost are likely to be significant. Thus, it is necessary to broaden the comparative economic evaluation of the pulping operation beyond simply chemical costs and wood costs.

ENVIRONMENTAL CONSIDERATIONS

The environmental situation must be included in any comprehensive economic evaluation. Environmental advantages have long loomed as one of the plus factors in holopulping. The elimination of sulfur from the pulping system should eliminate the odor problem long associated with kraft. There appears to be little doubt that the process itself should be essentially odor free and not plagued with the need to control very small amounts of extremely odorous chemicals. It is necessary to determine what the economic value of odor-free operation is. The complete range of air pollution problems of a holopulp mill is a little less clear. A potential exists for emission of chlorine compounds during the pulping steps, during evaporation and burning, and from leaks, cell gas exhausts, etc. All indications are that these should be minor and controllable. The economic implications of this control remains to be determined.

The state of the water pollution situation of a holopulp mill is not too well clarified at present. It is certain that there would be some effluent due to incomplete washing of the pulp. The extent of this and the characteristics of such an effluent remain to be determined. It is known that evaporator condensates have a substantial BOD load and would require treatment of some sort. A large unknown is the general behavior of the holopulp fiber in the papermaking system. The long-term stability of the retained hemicellulose and the extent to which the system will shed fines are just two aspects of the problem. The environmental consequences of using holopulp fibers in papermaking must be considered.

It is clear that the economic implications of environmental problems must be considered for holopulp. Environmental costs for holopulp should be compared with cost estimates for conventional processes. The economic advantage of odor-free operation should be quantified as much as possible. The complete air emission situation should be assessed and control costs estimated. The water pollution picture should be defined and comparative costs estimated. This evaluation would include the costs of bleach effluent disposal for conventional processes.

PAPERMAKING ECONOMICS

The analysis to date has been based on comparisons of costs for equal weights of pulp. Since pulp is an intermediate whose value is ultimately determined by the product into which it is made (and hence by the particular properties of the pulp), equal weights of pulp do not necessarily have the same value. A comprehensive economic analysis must take this factor into consideration.

There are three broad aspects to the economics of the use of holopulp. They are as follows:

1. The amount of pulp required to make a particular product.
2. Runnability considerations related to its performance on a paper machine.
3. Product quality factors.

The first item is probably the simplest to consider and may well have the biggest influence on economics. If less holopulp is required to make a given product (if the desired properties can be obtained with a lighter basis weight sheet), this would be an economic advantage to holopulp. The converse would act as a cost penalty. In a similar vein, if the use of holopulp would permit extension of the amount of low-cost material used in the sheet (for example, groundwood), the net furnish could show a cost advantage. Some of these aspects are under study in the laboratory and will be factored into the cost analysis.

Certain factors such as ease of drainage, ease of drying, ability to withstand pressing, wet web strength, etc. which affect the productivity of a paper machine would influence the cost of papermaking and hence affect the worth of the pulp. These would be included in the analysis.

Product quality factors are difficult to quantify. Any obvious feature of holopulp which might give it added value will be included.

FINAL REPORT

At the end of this work, a comprehensive report on the economics of holopulp will be issued. It will include those items of future work discussed above plus the critical elements of this report. This should serve as an overall summary of the economic status of holopulping.

NOMENCLATURE

A_H = holopulp ash, lb./ADT

ADV = cost advantage of holopulp, \$/ADT

B = heat consumption in calcining, million B.t.u./ton product

$C_{C,H}$ = chemical cost for holopulp, \$/ADT

C_E = evaporator capital charge, %/ADT

C_F = capital charge for furnace, \$/ADT

C_W = cost of wood per unit weight of pulp, \$/ADT

c_A = differential cost of producing holopulp, ¢/lb.

c_B = unit cost of fuel, ¢/million B.t.u.

c_{CL} = unit cost of chlorine, ¢/lb.

c_D = unit cost of chlorine dioxide, ¢/lb.

c_{DL} = cost of labor charged to ClO_2, ¢/lb. ClO_2

c_H = unit cost of hypochlorite, ¢/lb.

c_L = unit cost of make-up lime, ¢/lb.

c_{LSL} = cost of lime system labor assigned to NaOH, ¢/lb. NaOH

c_N = cost of producing electrolytic NaOH, ¢/lb.

c_{N2} = cost of producing NaOH by causticizing with lime, ¢/lb.

c_p = unit cost of electrical power, ¢/kw.-hr.

c_S = unit cost of steam, ¢/lb.

c_{S1} = costs associated with separation step and assigned to salt-rich stream, ¢/lb.

c_{sep} = cost of separating Na_2CO_3/NaCl assigned to Na_2CO_3, ¢/lb.

c_{sepL} = cost of separation labor assigned to Na_2CO_3, ¢/lb.

c_W = unit cost of clean wood, ¢/lb.

E_S = steam economy, lb. water evaporated/lb. steam

E_{SCE} = steam economy for caustic evaporator, lb. evapd./lb. steam

H_V = liquor heating value, B.t.u./lb. organic

h_S = enthalpy of steam, B.t.u./lb.

I_{CA} = investment in chlor-alkali plant of 80 TPD Cl_2, \$

I_D = investment for 50-TPD ClO_2 plant, \$

I_E = evaporator investment, \$

I_F = furnace investment, \$

I_{LS} = investment in lime system for 125 TPD NaOH, \$

I_{sep} = investment in a 60-TPD crystallizer, %

K = electrical power requirement for chlor-alkali, kw.-hr./lb. Cl_2

K_D = electrical power requirement for ClO_2, kw.-hr./lb. ClO_2

L_{CE} = load on caustic evaporator, lb. evaporated/lb. NaOH

L_D = steam requirement for ClO_2 generator, lb. steam/lb. ClO_2

L_E = evaporator load, lb. water evaporated/ADT

L_F = furnace load factor, B.t.u./ADT

L_{sep} = crystallizer evaporator load, lb. H_2O/lb. Na_2CO_3

M_L = make-up lime requirement, lb./lb. Na_2CO_3 fed

n_{CA} = scale factor for chlor-alkali plant

n_D = scale factor for ClO_2 plant

n_E = scale factor for evaporator

n_F = scale factor for furnace

n_{LS} = scale factor for lime system

n_{sep} = scale factor for crystallizer

O_{CA} = operating cost of chlor-alkali system

O_E = operating cost for evaporator, \$/ADT

O_F = operating cost for combustion, \$/ADT

P = annual pulp production rate, ADT/yr.; actual ClO_2 production rate, TPD

P_N = actual NaOH production rate, TPD

R = annual return factor applied to capital

S_C = stoichiometric factor for Cl_2, lb./lb. wood

S_D = stoichiometric factor for ClO_2, lb./lb. wood

S_H = stoichiometric factor for hypochlorite, lb./lb. wood

S_N = stoichiometric factor for NaOH, lb./lb. wood

s = solids content of liquor, lb. solid/lb. liquor

W_{1S} = NaCl in ash, lb./ADT

W_{1C} = Na_2CO_3 in ash, lb./ADT

W_{2S} = NaCl to neutralizer, lb./ADT

W_{2C} = Na_2CO_3 to neutralizer, lb./ADT

W_{3S} = NaCl to cells, lb./ADT

W_{4S} = NaCl to causticizing system, lb./ADT

W_{4C} = Na_2CO_3 to causticizing system, lb./ADT

W_{5S} = NaCl in electrolytic caustic solution, lb./ADT

W_{5N} = electrolytic NaOH, lb./ADT

W_{5Cl} = net amount of chlorine produced, lb./ADT

X_A = ash content, lb./lb. liquor

y = pulp yield, lb. pulp/lb. wood or %

η = efficiency of steam production; ClO_2 generator efficiency

η_C = causticizing efficiency, $NaOH/(NaOH + Na_2CO_3)$ as Na_2O

ρ = weight of NaCl per unit weight NaOH in electrolytic caustic

Δ = difference or change operator

subscript H refers to holopulp

subscript K refers to kraft

subscript R refers to reference pulp

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LITERATURE CITED

1. American Paper Institute. Monthly statistical summary. Vol. XLIX, no. 6, June, 1971.
2. Casey, J. P. Pulp and paper: chemistry and chemical technology. 2d ed. Vol. 2. Wood-pulp. New York, Interscience, 1960.
3. Chemical Marketing Reporter (Oil, Paint and Drug Reporter). New York, Schnell Publishing Company.
4. TAPPI Monograph Series No. 32. Chemical recovery in alkaline pulping processes: a project of the Alkaline Pulping Committee. R. P. Whitney, ed. New York, Technical Association of the Pulp and Paper Industry, 1968.
5. Perry, J. H. Chemical engineers' handbook. 4th ed. New York, McGraw-Hill, 1963.
6. Chemical Engineering. Modern cost-engineering techniques. Herbert Popper, ed. p. 99. New York, McGraw-Hill, 1970.
7. Hendrickson, E. R., Roberson, J. E., and Koogler, J. B. Control of atmospheric emissions in the wood pulping industry. Vol. 3 (final report). p. 5-99. Gainesville, Fla., Environmental Engineering, Inc., and Greenville, S.C., J. E. Sirrine Co., March 15, 1970. 250 p.
8. Grace, T. M., Project 2500, Report Eleven. Appleton, Wis., The Institute of Paper Chemistry, July 15, 1970.
9. Encyclopedia of Chemical Technology. H. F. Mark, J. J. McKetta, Jr., and D. F. Othmer, eds. 2d ed. New York, Interscience, 1963.
10. Partridge, H. deV., Atkinson, E. S., and Schulz, A. C., Tappi 54, no. 9:1484-7 (1971).
11. Grace, T. M. Project 2500, Report Fifteen. Appleton, Wis., The Institute of Paper Chemistry, Oct. 4, 1971.
12. Jamieson, R. G., and Nicholls, G. A. Project 2500, Report Sixteen. Appleton, Wis., The Institute of Paper Chemistry, Aug. 7, 1972.
13. Jamieson, R. G., and Nicholls, G. A. Project 2500, Report Twelve. Appleton, Wis., The Institute of Paper Chemistry, May 18, 1971.
14. Stone, J. E., and Clayton, D. W., Pulp Paper Mag. Can. 61, no. 6:T307-13 (1960).

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