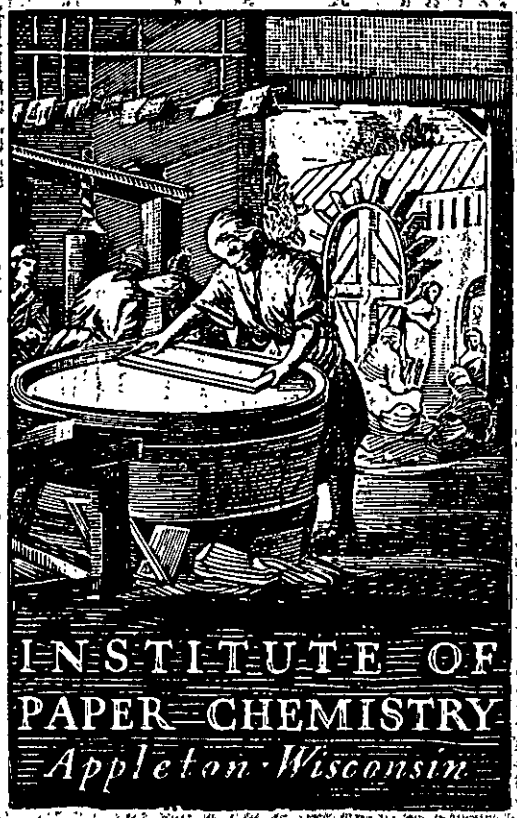

CONFIDENTIAL

SELECTIVE DELIGNIFICATION OF WOOD AND OTHER FIBROUS MATERIALS: CHEMICAL RECOVERY

Research Grant
Project 2500

Report Fifteen
A Progress Report
to
THE GRANTORS

October 4, 1971

THE INSTITUTE OF PAPER CHEMISTRY
Appleton, Wisconsin

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SUMMARY

The work of the past year has confirmed the validity of retention concepts. A recovery process based on evaporation and burning of the spent liquor to produce sodium chloride and sodium carbonate, causticization of the carbonate, electrolytic processing of the chloride, and ClO_2 generation by the Chemech method appears workable. The process should be essentially closed with no major air pollution problems and minimum effluent problems.

Studies of evaporation showed that the chlorine compounds were nonvolatile. There is no discernible odor. There is a problem with BOD in the condensate.

Combustion of spent liquor does produce sodium chloride and sodium carbonate. Small amounts of HCl and NaCl vapor are given off during combustion. These may be scrubbed from the flue gas with liquor. Heating values of the spent liquor are adequate to support combustion. Feasibility studies of fluidized bed combustion are incomplete.

It has been shown that separation of NaCl and Na_2CO_3 can be achieved. The presence of large amounts of chloride do not affect the causticization reaction. The step of using HCl to convert Na_2CO_3 to NaCl for electrolysis may be eliminated.

There appear to be no major technical problems in ClO_2 production.

INTRODUCTION

Chemical recovery in holopulping was first discussed in Appendix II of Progress Report Five in June, 1968. The major elements of a recovery system were outlined. The proposed system consisted of evaporation and combustion of the spent liquor to obtain a mixture of sodium chloride and sodium carbonate, with regeneration of the cooking chemicals through electrolytic chlor-alkali production and chlorine dioxide generation. Experimental evidence was presented which indicated that sodium chloride and sodium carbonate were the combustion products from holopulp spent liquors, but the work was not conclusive. It was shown that a self-contained recovery process required a method of chlorine dioxide generation which did not use sulfuric acid. It appeared that some version of the Day-Kesting process was most suitable for chlorine dioxide production. Electrolytic chlor-alkali production would serve both to generate caustic acid and to provide hydrochloric acid for the Day-Kesting reactor. The importance of the sodium and chlorine balance in closing the recovery cycle was brought out. The possibility of separation of Na_2CO_3 from NaCl for separate causticization was mentioned as was the use of HCl to convert Na_2CO_3 to NaCl for electrolytic caustic production. The basic concept of the holopulp recovery system has remained essentially the same since that time.

The recovery system was analyzed in much more detail in Progress Report Eleven of July, 1970. Each major area of the process was evaluated and the areas of greatest uncertainty identified. It was concluded that the biggest unknowns lay with the evaporation and combustion of the spent liquor since minimal laboratory work had been done and it was not possible to borrow directly from existing technology since those liquors had not previously existed. Another major problem area

concerned water usage in the pulping step and the resultant dilution of the spent liquor. A third problem was considered to be uncertainties regarding chlorine dioxide generation technology.

In the area of evaporation, it appeared that the greatest need was to determine if there were potential pollution problems associated with evaporation of the holopulp spent liquor. In particular, data on chlorine emissions as non-condensable gases and with condensate were needed. It was also felt that information on tendencies for solids precipitation, foaming, and scaling was needed along with data on the rheological properties of the liquor.

Several critical problems were associated with the combustion step. One was a need to conclusively establish sodium chloride and sodium carbonate as the combustion products. A second was to determine if there is a significant emission problem from chlorine-containing gases. A third problem lay with the need to determine the proper temperature range for carrying out the combustion and the type of furnace to be used. It was pointed out that process advantages could accrue if it could be established that the combustion could be carried out at temperatures below the melting point of the recovered material.

The water balance problems were related to the need for minimum use of water in pulping and washing. One approach would be to establish that liquors could be recycled in the pulping steps without adversely affecting performance. A second approach would involve demonstrating that the oxidation could be carried out at high consistencies using gaseous ClO_2. A determination of minimum interstage washing needs was also considered necessary.

The most suitable method for generating ClO_2 appeared to be the Chemech process. Some uncertainty existed as to its feasibility due to a lack of knowledge

of process details. The uncertainties were resolved in a subsequent meeting with Chemech, which will be discussed later in this report.

The main role of the process evaluation of Progress Report Eleven was to identify the major problem areas as a focus for further development work. A clearer definition of the research objectives for the past year was made at the meeting held in Chicago in June, 1970. The outline of proposed work presented at that meeting is given below.

OUTLINE OF PROPOSED WORK

I. Combustion of Spent Liquor

It is essential to demonstrate quantitatively that sodium and chlorine can be recovered as a mixture of sodium chloride and sodium carbonate. The potential for emission of gaseous chloro-compounds must be studied. Means for carrying out the combustion operation must be examined.

A. Thermodynamic Studies

Theoretical determinations of the distribution of combustion products based on thermodynamic equilibrium relationships would be used to obtain insights into combustion behavior and to aid in interpreting experimental results.

B. Experimental Combustion Studies

A flow reactor would be used to carry out combustion of liquors to provide for quantitative determination of combustion products. Two types of liquors would be used.

1. Synthetic liquors would be used to permit combustion studies to proceed apart from pulping work and to permit direct control of compositional variables.

2. Actual composite pulping liquors will be used to verify combustion behavior.

C. Heat of Combustion Measurements

Heats of combustion of spent liquors will be determined by bomb calorimetry.

D. Fluidized Bed Studies

If low-temperature combustion is found to be feasible, preliminary studies on the possibility of fluid bed combustion would be initiated.

E. Evaluation of Results

Upon completion of this work, a detailed evaluation of the combustion step would be made. This would permit a decision on how spent liquor combustion would be carried out on a pilot or commercial scale.

II. Evaporation of Spent Liquor

It is necessary to determine if the presence of compounds in condensate and noncondensable gases would interfere with their disposal or reuse. Data related to evaporator design and operation must be obtained.

A. Analysis of Condensate and Noncondensable Gases

This would involve identification and quantification of organic and chloro-compounds in the condensate and noncondensable gases.

B. Study of Evaporation Parameters

Data would be obtained on liquor viscosities, boiling-point rise, foaming tendency, scaling tendency, and corrosiveness of the liquors.

III. Water Balance over Pulping Process

A. Effect of Liquor Recycle

Pulping studies would determine if liquor recycle increases chemical consumption or otherwise interferes with pulping reactions.

B. Determination of Dewatering Limitations

The ability to dewater the material at each step in the sequence and the effect of mechanical dewatering action on pulp properties would be determined.

C. Evaluation of Washing Needs

The effects of omitting washing between various pulping steps would be determined.

D. Evaluation of Water Balance

At the conclusion of this work, an assessment of the water balance would be made. This would make possible a definition of system configuration and equipment for carrying out pulping and washing.

IV. Other Aspects of Pulping Process

A. High-Consistency Operation

1. Batch experiments would be carried out using chlorine dioxide-chlorine gas mixtures containing at least one-half mole of chlorine per mole of chlorine dioxide at very high consistency.

2. Following oxidation, other process steps would be carried out with the objects of minimizing water addition and determining pulp properties.

3. Data from the above would be used as input in water balance evaluations.

B. Extension of process knowledge

1. Completion of fiberization work

2. Species sensitivity

V. Surveys

A. Chlorine Dioxide Generation

1. Discussions planned with Chemech

2. Monitoring of new chlorine dioxide developments will be continued.

B. Equipment

1. A survey of available techniques for carrying out washing at high overall consistencies would be made.

2. A survey of available approaches to carrying out very high-consistency oxidations would be initiated.

To a large extent, the work of the past year has followed the above outline. This report is concerned strictly with work on recovery. Work on pulping and the water balance was carried out in another phase of this project and will not be discussed here. The major part of the work was directed toward evaporation and combustion. Some work to demonstrate the feasibility of alternative regeneration schemes has also been carried out. In addition, a review of the status of chlorine dioxide generation technology based on discussions with Chemech is included.

SPENT LIQUORS

PREPARATION

Two batches of spent liquor were prepared in the laboratory by pulping fiberized red maple at different conditions. Details of the pulping conditions are listed in Table I where the two liquors are designated as Liquor A and Liquor B. These liquors, prepared under controlled conditions, were used for the studies on evaporation and the small-scale combustion work. Additional liquor was collected and combined with the remainder of Liquors A and B for the bench-scale fluidized bed work.

TABLE I

PULPING CONDITIONS FOR SPENT LIQUORS

	Red Maple	
	Liquor A	Liquor B
Fiberized wood, o.d., g.	803.3	1036
Chlorine dioxide, g.	73.9	79.7
Chlorine, g.	0.0	78.8
Oxidation temperature, °C.	40-52	31.5-37
Oxidation time, hr.	4	4-5/6
NaOH, g.	72.3	93.2
Extraction temp., °C.	80	83
Extraction time, hr.	1	1
Hilex (containing 0.0525 g. of NaOCl/ml.), ml.	536	691
NaOH, g.	4.02	5.20
Bleaching temp., °C.	39	43
Bleaching time, hr.	2	2
Yield, %	64.6	65.0
Spent liquor		
From oxidation, g.	16,156	24,330
From extraction, g.	18,077	13,900

TABLE I (CONTD.)

PULPING CONDITIONS FOR SPENT LIQUORS

	Red Maple	
	Liquor A	Liquor B
From bleaching, g.	16,959	11,260
Total, g.	51,192	49,490
Total volume, kg.	51.2	49.5
Solids, %	0.803	1.07
pH of combined liquor	5.0	1.8
Na^+/Cl^- ratio	1.44	0.787

CHARACTERIZATION

A summary of the major characteristics of the spent liquors is presented in Table II. The most important data are concerned with the total solids content and the total chlorine and total sodium content since these define the basis for material balances during evaporation and combustion experiments. It is obvious that there is an anomaly in the composition of spent Liquor B determined from the pulping stoichiometry and that measured experimentally. The cause of this discrepancy is unknown. It is believed that it is most likely due to the loss of some of the oxidation liquor during the preparation step. The true composition is that found experimentally.

Neutralization curves for these spent liquors are presented in Fig. 1. These were obtained by titrating 50-ml. samples of the liquors with 0.1N caustic. In order to illustrate the amount of caustic which would be required to affect the pH on a commercial scale, the stoichiometric conditions may be used to express the milliequivalents of NaOH in terms of percent NaOH on the original wood. These data are presented in Table III.

TABLE II

CHARACTERIZATION OF SPENT LIQUORS

Actual Data	Liquor A	Liquor B
Total solids, %	0.803	1.07
Total chlorine, %	0.122	0.232
Total sodium, %	0.116	0.168
pH	5.0	1.8
Moles Cl/mole Na	0.68	0.89

Calculated from Pulping Stoichiometry	Liquor A	Liquor B
Total solids, %	0.812	1.22
Total chlorine, %	0.127	0.315
Total sodium, %	0.120	0.166
Moles Cl/mole Na	0.69	1.23

TABLE III

CAUSTIC REQUIRED TO NEUTRALIZE LIQUORS

Spent Liquor A

pH	5.0	6.0	7.0	8.0	9.0	10.0	11.0
NaOH added (% of original wood)	0.	1.1	1.5	1.75	1.96	2.36	3.06

Spent Liquor B

pH	1.8	3.0	5.0	7.0	9.0	11.0
NaOH added (% of original wood)	0.	2.3	5.95	7.5	8.2	9.45

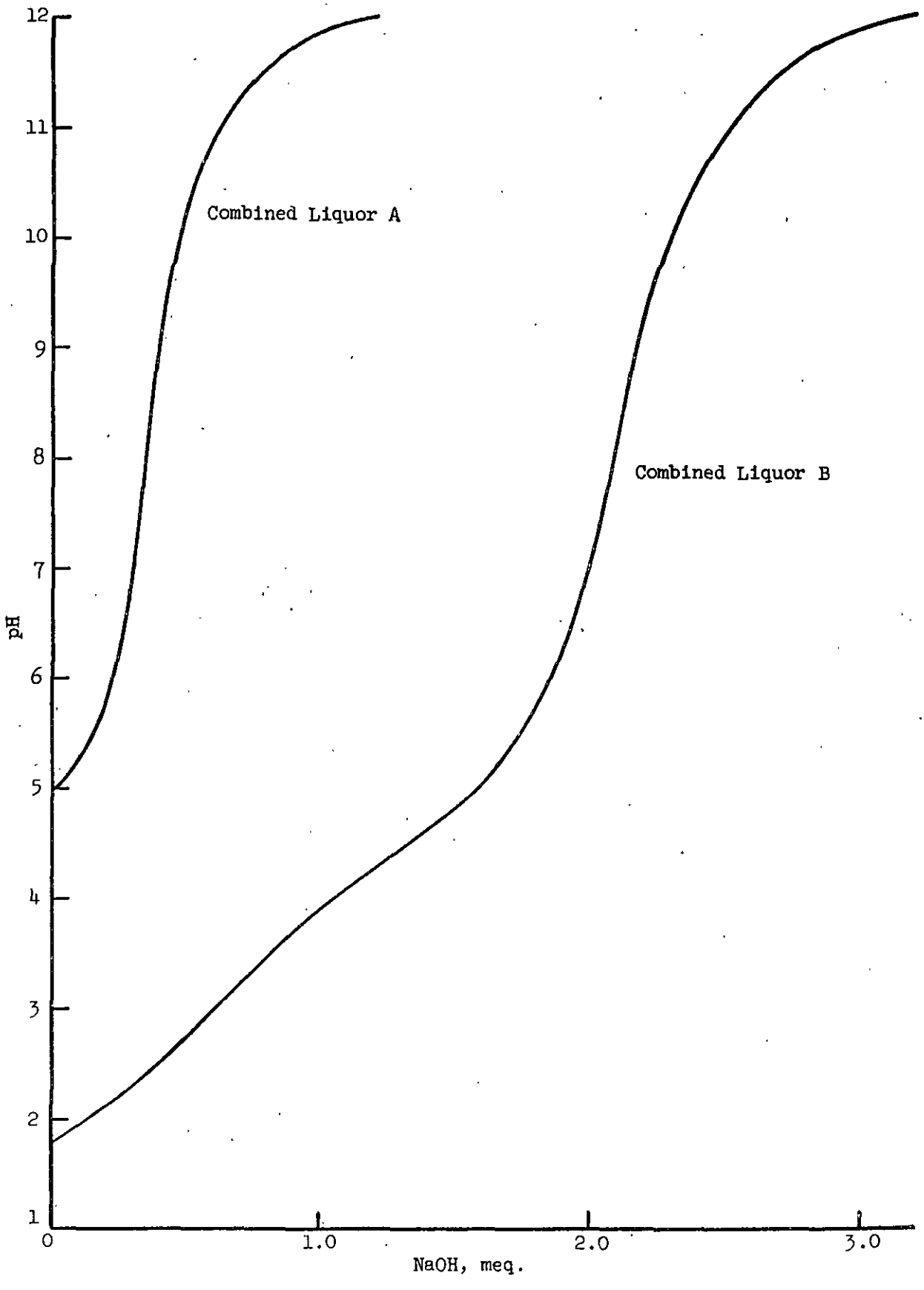


Figure 1. Neutralization Curves for Liquors A and B

A noticeable feature of these spent liquors is their extreme dilution. It must be pointed out that these dilutions were a consequence of a deliberate decision to carry out the pulping in such a manner as to obtain quantitatively the liquor from each pulping stage. They should not be considered typical of actual holopulp spent liquor concentrations. It was felt that these would be perfectly adequate for the purposes of this work and would, in fact, constitute a sort of worst case. Thus it should be emphasized that the results of the work to be reported on evaporation and combustion are valid and are applicable to the real case.

EVAPORATION OF SPENT LIQUORS

OBJECTIVES

The basic objective in all of the work on evaporation was to determine the extent to which pollution problems might exist in holopulp liquor evaporation and to see if there were any characteristics of holopulp liquors which would cause difficulties in evaporation. No attempt was made to gather design data such as liquor viscosity data or boiling-point-rise data.

The experiments consisted, in general, in carrying out the evaporation and in collecting and analyzing the condensate. Noncondensable gases were also collected and tested for odor. Major emphasis was placed on analysis for chlorine in the condensate since it was felt that chlorine emissions would constitute the most troublesome problems. The pH at which the evaporation was carried out was a major variable in the program.

APPARATUS AND PROCEDURES

Portions of the spent liquors were adjusted to different pH values by the addition of NaOH solution. The original and adjusted samples are identified as AC5, AC6, AC7, AC8, AC9.1, AC10, BC1.8, BC3, BC4.1, BC5, BC6, BC7, BC8, and BC9.35, where "A" or "B" represents the batch number, "C" indicates a combined spent liquor from all stages, and the numeral shows the various pH values after adjustment with NaOH, if any. AC5 and BC1.8 are the identifications of the original liquors.

Two pieces of equipment were used in the evaporation studies. Initial studies were done in a rotary vacuum evaporator (a Büchi Rotavapor evaporator). This was operated at a vacuum of 30 inches of mercury with the water bath temperature ranging from 30 to 45°C. This apparatus was suitable for collecting condensate and concentrated liquor, but because of the need for continuous evacuation,

noncondensable gases could not be collected. Because of the high vacuums employed, evaporation took place at quite low temperatures. Studies carried out on this apparatus are referred to as "low-temperature evaporation" (LTE) studies. In order to carry out evaporation studies at higher temperatures, an all-glass steam-heated side-arm evaporator of a type commonly used in the laboratory was employed. By carefully adjusting the applied vacuum, evaporations could be carried out at different boiling temperatures. Such experiments were referred to as "high-temperature evaporation" (HTE) runs.

The condensates were analyzed for total chlorine content as well as the conventional BOD and COD tests. Total chlorine was determined by a chromic acid digestion method, which is described in detail in Appendix I. Condensates were also analyzed for chloride content by the Volhard method. The total sodium content of condensates, concentrates, and original liquors was determined with a flame electrophotometer.

A special method was used to collect noncondensable gases. A flask was filled with spent liquor and heated with all gases passing through a tube into inverted flasks immersed in a water bath. The procedure was similar to methods used for obtaining oxygen, hydrogen, etc. in elementary chemistry laboratories.

RESULTS

Low-Temperature Evaporation

Low-temperature evaporations were carried out at pH 5, 6, 7, 8, 9.1, and 10 for Liquor A and at pH 1.8, 3, 4.1, 5, 6, 7, 8, 9.35, and 10 for Liquor B. A summary of the results of this work is given in Tables IV and V for Liquors A and B, respectively.

TABLE IV

LOW-TEMPERATURE EVAPORATION DATA ON LIQUOR A

Sample	AC5	AC6	AC7	AC8	AC9.1	AC10
Original pH	5.0	6.0	7.0	8.0	9.1	10.0
Concentrate pH	5.2	5.9	6.7	7.1	7.4	8.0
Condensate pH	3.6	4.4	7.1	7.2	6.7	9.0
Concentrate solids, %	27.4	20.3	25.0	27.1	26.8	25.8
Original total sodium, %	0.116	0.127	0.130	0.133	0.135	0.139
Concentrate total sodium, %	3.28	2.83	3.34	3.64	3.60	3.57
Condensate total sodium, %	0	0	0	0	trace	trace
Original total chlorine, %	0.121	--	--	--	--	--
Concentrate total chlorine, %	3.90	--	--	3.75	--	--
Condensate total chlorine, %	0.0005	0	0.0003	0.0002	0.0001	0.0003
Condensate chloride	Trace in some, but unmeasurable					
Condensate BOD_5, mg./liter	346	227	256	256	278	272
Condensate BOD_5, lb./ton pulp	68.1	44.7	50.4	50.4	54.7	53.6
Condensate COD, mg./liter	487	307	346	360	351	378
Condensate COD, lb./ton pulp	95.9	60.5	68.1	70.9	69.1	74.4

TABLE V

LOW-TEMPERATURE EVAPORATION DATA ON LIQUOR B

Sample	BC1.8	BC3	BC4.1	BC5	BC6	BC7	BC8	BC9.4	BC10
Original pH	1.8	3.0	4.1	5.0	6.0	7.0	8.0	9.35	10.0
Original solids, %	1.07	--	--	--	--	--	--	--	--
Concentrate solids, %	10.9	12.6	19.8	22.7	22.2	20.8	20.8	21.2	27.4
Original total chlorine, %	0.232	--	--	--	--	--	--	--	--
Concentrate total chlorine, %	3.23	--	--	--	--	--	--	--	--
Condensate total chlorine, %	0.0002	0.0005	0.0011	0.0004	0.0004	0.0001	0.0001	0.0003	--
Condensate chloride	0	0	0	0	0	0	0	0	0

The dominant feature of these data is that the chlorine stays in the spent liquor during evaporation and is not volatilized. Concentrations of total chlorine in the condensate are never more than a few p.p.m. This is true regardless of pH and Cl/Na ratio in the range covered. Thus, these data establish that the chlorine compounds which exist in holopulp spent liquors are not volatile. Only about 0.1% of the chlorine which was present in the liquor was found in the condensate.

Material balances were carried out for the experiments on AC5 and AC8 as shown below.

LTE of AC5

Materials in:

(1)	AC5 spent liquor (sp. gr. = 1.00195 at 70°F.), g. =	1473
(2)	Chlorine, g. = 1473(1.22)/(1.00195)(1000) =	1.79
(3)	Sodium, g. = 1473(0.00116) =	1.71

Materials out:

(1)	Condensate (sp. gr. = 0.9964), g. =	1363
(2)	Concentrate, g. (sp. gr. = 1.1169) =	52.1
(3)	Chlorine, g. = 1363(0.00000499) + 52.1(38.8)/(1.1169)(1000) =	1.80
(4)	Sodium, g. = 52.1(0.0328) =	1.71

Balances:

(1)	Total materials loss, g. = 1473 - (1363 + 52.1) =		57.9
	or	3.93%	
(2)	Chlorine loss, g. = 1.79 - 1.80 =		-0.01
	or	-0.6%	
	(This gain of chlorine must be due to analytical error.)		
(3)	Sodium loss, g. = 1.71 - 1.71 =		0.00
	or	0%.	

LTE of AC8

Materials in:

(1) 1500 ml. of AC5 liquor (sp. gr. = 1.00195), 0.314 g. of NaOH pellets, and 31.28 ml. of 0.1044N NaOH solution (estimated sp. gr. = 1.0)

1500(1.00195) + 31.28(1.0) + 0.314, g. = 1534

(2) Chlorine in, g. = 1500(1.22)/(1.00195)(1000) = 1.

(3) Sodium in, g. = 1500(1.00195)(0.00116) + 0.314(23/40) + 31.28(0.1044)(0.04) = 2.

Materials out:

(1) Condensate (sp. gr. = 0.9997), g. = 1464

(2) Concentrate (sp. gr. = 1.1137), g. = 55.9

(3) Chlorine, g. = 1464(0.00000181) + 55.9(37.2)/(1.1137)(1000) = 1.8

(4) Sodium, g. = 55.9(0.0364) = 2.0

Balances:

(1) Total material loss, g. = 1534 - (1464 + 55.9) = 14.1
or 0.9%

(2) Sodium, g. = 2.05 - 2.04 = 0.0
or 0.5%.

These balances show good internal agreement in the data and also indicate that the loss of chlorine compounds with noncondensable gases is negligible.

The condensates obtained from these experiments were clear and colorless, and did not have any appreciable odor. Lack of a significant odor is also characteristic of the spent liquor. That the condensates do contain organic material is obvious from the relatively high values of BOD and COD. The condensate from Experiment AC5 was given to the Analytical Chemistry Group for analysis by gas chromatography. About 1 to 1.5 g./liter of methanol was found. No other components were found in amounts sufficient for identification. There were no ether-soluble materials.

High-Temperature Evaporation

The data from the low-temperature evaporation showed that chlorine compounds were not volatile under the evaporation conditions used. However, it was felt that the results would be on a firmer basis if it could be established that evaporation temperature did not have an effect. Thus, a series of experiments at different boiling temperatures were carried out. Evaporation of AC liquors was carried out at temperatures of 48, 58.5, 68.5, 78, 87, and 99°C. Condensates were collected and analyzed for total chlorine and chloride. The results are given in Table VI. It can be seen that there is measurable chloride in the condensate and that the total chlorine in the condensate is higher than in the low-temperature evaporation runs. There is no obvious correlation between increased total chlorine and increasing temperature. It is quite possible that the higher total chlorine values reflect increased entrainment with this method of evaporation. The liquor is heated in a side-arm and tends to geyser. This method of evaporation would tend to give more entrainment than the thin film evaporation in the rotary device. In any event, the amounts of total chlorine are quite low and the basic conclusion that the chlorine compounds are nonvolatile holds true for the temperature range covered.

TABLE VI

CHLORIDE AND TOTAL CHLORINE IN CONDENSATES OF HTE OF AC SPENT LIQUORS

Run	Evaporation Temp., °C.	pH	Chloride %	Chloride p.p.m.	Total Chlorine %	Total Chlorine p.p.m.
HTE-1	48	3.90	0.0000922	1	0.000922	9
HTE-2	58.5	3.83	0.000118	1	0.00118	12
HTE-3	68.5	3.80	0.0000693	1	0.00146	15
HTE-4	78	3.65	0[a]	0	0.000451	5
HTE-5	87	3.76	0.000239	2	0.00239	24
HTE-6	99	3.70	0.0000855	1	0.00140	14

[a] Negative calculated value.

Noncondensable Gases

Several flasks of noncondensable gases were collected. The gases were odorless and colorless. There did not appear to be any significant amounts of chlorine compounds in them. This corroborates the evidence of negligible loss of chlorine as noncondensable gases shown by material balance on the low-temperature evaporation work.

General Observations

All indications are that there should be no difficulties in evaporating holopulp spent liquors. No serious foaming problems were encountered and there was no observable tendency toward solids precipitation. Evaporation was very easily carried out at all conditions examined.

Summary

It is believed that the experimental evidence strongly indicates that there are no major difficulties in evaporating holopulp spent liquors. Chlorine

compounds were definitely shown to be nonvolatile over the range of conditions tested. Noncondensable gases were odorless and contained negligible amounts of chlorine compounds. There is no apparent reason to fear chlorine emissions in either condensate or noncondensable gases. On a commercial scale, the major source of chlorine compounds in condensate would be through entrainment. This can be minimized by proper design of the evaporators. The lack of foaming tendency should aid in minimizing entrainment. Thus, it may be concluded that there should be no serious emission problems with chlorine compounds in the evaporation of holopulp spent liquors.

The BOD and COD loadings in the condensate are real and significant and could well constitute an effluent treatment problem. The BOD content can be reduced somewhat by evaporating under more alkaline conditions, but not to the extent that the problem is eliminated. The amount of BOD appears to be intermediate between that from sulfite pulping and kraft pulping of hardwoods. It appears that a significant portion of the organic content of the condensate is methanol. The BOD problem requires further study as to means of control. It is, at least, a problem with which the industry is familiar and is not unique to holopulp.

COMBUSTION OF SPENT LIQUOR

Combustion of holopulp spent liquor has occupied the major attention of this program. This work has been directed toward three major objectives: definition of combustion products, determination of potential air emission problems, and specification of a method which could be employed in commercial-scale combustion. In order to reach conclusions, many different facets of the problem were investigate

Thermodynamic equilibrium calculations were carried out on the sodium-chlorine-carbon-hydrogen-oxygen system to establish expected combustion products and potential emission species. Small batch and semicontinuous combustion experiments were carried out under both oxidizing and reducing conditions to confirm the equilibrium predictions and determine the effects of nonequilibrium pyrolysis and therma decomposition. In addition, heating values for the spent liquors were determined, and the melting points of various mixtures of sodium chloride and sodium carbonate were measured. Finally, a series of runs were made on a bench-scale fluidized bed combustion unit to evaluate fluidized bed burning as a possible method for holopulp spent liquors.

THERMODYNAMIC EQUILIBRIUM CALCULATIONS

The purpose of the thermodynamic equilibrium calculations is to establish a base line for understanding the combustion of holopulp spent liquors. Equilibrium calculations determine the relative proportions of various species which would be present if equilibrium existed. They serve to establish expected combustion products and indicate which compounds may be dismissed from consideration. Such calculations have been a great aid in understanding the combustion behavior of conventional pulping liquors and are the logical starting point for studying the combustion of holopulp spent liquor.

Thermodynamic Data

Combustion of holopulp liquors involves the elements sodium, chlorine, carbon, hydrogen, and oxygen. The source of the thermodynamic data used in these calculations is the JANAF Tables. All relevant chlorine and sodium compounds for which JANAF data existed were included in the calculations. This included all major compounds and many minor ones. A listing of the species considered in these calculations is shown in Table VII. All species are gases unless otherwise noted.

TABLE VII

SPECIES CONSIDERED IN THERMODYNAMIC CALCULATIONS

Carbon compounds:	C(s) CO, CO_2, Na_2CO_3(s/l), $COCl_2$, ClCN, CCl, CCl_2, CCl_3, CCl_4, $CHCl_3$, CH_2Cl_2, CH_3Cl.
Hydrogen compounds:	H_2, H_2O, HCl, HOCl, $CHCl_3$, CH_2Cl_2, CH_3Cl, NaH, NaOH(s/l).
Chlorine compounds:	HCl, Cl_2, Cl, ClO, Cl_2O, HOCl, $COCl_2$, ClCN, CCl, CCl_2, CCl_3, CCl_4, $CHCl_3$, CH_2Cl_2, CH_3Cl, NaCl(s/l), NaCl, Na_2Cl_2.
Sodium compounds:	NaCl(s/l), NaCl, Na_2Cl_2, NaH, Na, Na_2, Na_2CO_3(s/l), Na_2O(s/l), NaOH(s/l).
Oxygen compounds:	O_2, CO, CO_2, H_2O, ClO, Cl_2O, HOCl, $COCl_2$, Na_2CO_3(s/l), Na_2O(s/l), NaOH(s/l).

The data which are needed to carry out the calculations are the standard free energy of formation of all of the species involved. These data were taken from the JANAF Tables and are shown in Table VIII. It must be borne in mind that these data on standard free energies of formation cannot be used as such in determining what compounds will be present in significant quantities. Simply because a compound has a negative free energy of formation does not mean it will be present when all competing reactions are accounted for. It becomes necessary to examine the equilibrium constants for reactions involving these species.

TABLE VIII

STANDARD FREE ENERGIES OF FORMATION

Species	ΔG^o, kcal./mole				
	800°K 980°F.	1000°K 1340°F.	1200°K 1700°F.	1400°K 2060°F.	1600°K 2420°F.
C(s)	0	0	0	0	0
CO	-43.612	-47.859	-52.049	-56.189	-60.284
CO_2	-94.556	-94.628	-94.681	-94.716	-94.739
H	0	0	0	0	0
H_2O	-48.646	-46.040	-43.371	-40.663	-37.927
HCl	-23.774	-24.093	-24.390	-24.675	-24.950
Cl_2	0	0	0	0	0
Cl	18.347	15.547	12.713	9.853	6.975
HOCl	-13.358	-11.004	-8.623	-6.226	-3.818
ClO	21.758	21.123	20.482	19.835	19.186
Cl_2O	29.488	32.332	35.165	37.986	40.801
$COCl_2$	-43.630	-41.437	-39.252	-37.074	-34.897
ClCN	27.519	26.268	25.018	23.771	22.529
CCl	111.136	105.890	100.680	95.506	90.366
CCl_2	67.695	65.875	64.085	62.326	60.593
CCl_3	43.204	45.147	47.072	48.987	50.891
CCl_4	0.585	6.899	13.135	19.307	25.434
$CHCl_3$	-3.721	1.653	7.002	12.324	17.613
CH_2Cl_2	-4.326	0.577	5.505	10.434	15.350
CH_3Cl	-3.966	0.857	5.749	10.669	15.592
NaCl(s/l)	-80.516	-76.200	-72.385	-65.734	-59.271
Na_2CO_3(s/l)	-216.445	-203.925	-191.547	-173.627	-156.248
Na_2O(s/l)	-73.277	-66.780	-59.704	-47.579	-35.816
NaOH(s/l)	-73.662	-67.745	-61.587	-52.138	-42.886
NaH	17.612	15.125	13.165	14.726	16.279
Na	7.593	3.529	0	0	0
Na_2	11.545	7.285	4.119	8.030	11.955
NaCl	-54.627	-56.906	-58.632	-56.819	-54.995
Na_2Cl_2	-132.713	-131.248	-128.748	-119.219	-109.714
O^o	0	0	0	0	0

Note: All species are gaseous unless otherwise indicated. For NaCl(s/l), Na_2CO_3(s/l), and Na_2O(s/l) the data are for the solid phase at 800°K and 1000°K, and for the liquid phase at the higher temperatures. For NaOH(s/l) the data are for the liquid phase at all temperatures.

Examination of Table VIII shows that 30 species are included. Thus a minimum of 25 reactions along with the elemental balances on Na, Cl, C, H, and O are needed to specify the system. The minor complication due to nitrogen in ClCN can be ignored since adding nitrogen as a species would simply require adding a nitrogen balance. If the minimum number of reactions is used, each must be independent of the others (no reaction can be obtained as a linear combination of the other reactions). Such an independent set of 25 reactions, along with the 5 elemental balances, uniquely determines the composition of the system. The reactions themselves are not unique, but the solution given by an independent set is unique.

Equilibrium constants for the reaction are determined by $\Sigma\Delta G^{o}_{reaction} = -2.303\underline{RT}\ \log_{10}\underline{K}$. Calculated values of the equilibrium constants for an independent set of reactions is shown in Table IX. The standard free energy change of the reactions is found from the standard free energy of formation data in Table VIII. The fourth reaction is written in two forms: 4a and 4b. The latter is more convenient to use when there is no solid or liquid NaCl present. The number of independent reactions is still 25 since 4b is a linear combination of 4a and 24. The equilibrium constants so calculated are for gas partial pressures in atmospheres.

Procedure

The solution to the problem at any given temperature is found by obtaining the set of partial pressures of the species which fit both the equilibrium relations and the material balances. This is not necessarily straightforward since the equilibrium relations involve powers and the material balances are additive relations. Some simplification is used to keep the effort within reasonable bounds. This is achieved by using the equilibrium constants to indicate which compounds may be

TABLE IX

EQUILIBRIUM CONSTANTS FOR AN INDEPENDENT SET OF REACTIONS AS A FUNCTION OF TEMPERATURE

$\log_{10} \underline{K} = -(\Sigma\Delta\underline{G}^{o}_{prod} - \Sigma\Delta\underline{G}^{o}_{react})/2.303\underline{RT}$

Reactions	800°K 980°F.	1000°K 1340°F.	1200°K 1700°F.	1400°K 2060°F.	1600°K 2420°F.
1. $CO + \frac{1}{2}O_2 \rightarrow CO_2$	13.916	10.220	7.764	6.014	4.706
2. $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$	13.288	10.061	7.898	6.347	5.180
3. $C + \frac{1}{2}O_2 \rightarrow CO$	11.913	10.459	9.478	8.771	8.234
4a. $2NaCl(s/l) + H_2O + CO_2 \rightarrow Na_2CO_3(s/l) + 2HCl$	-10.992	-8.950	-7.739	-6.848	-6.154
4b. $NaCl + \frac{1}{2}H_2O + \frac{1}{2}CO_2 \rightarrow \frac{1}{2}Na_2CO_3(s/l) + HCl$	1.576	-0.259	-1.365	-2.032	-2.493
5. $2HCl + \frac{1}{2}O_2 \rightarrow H_2O + Cl_2$	0.300	-0.469	-0.985	-1.356	-1.635
6. $Na_2O(s/l) + CO_2 \rightarrow Na_2CO_3(s/l)$	13.279	9.291	6.767	4.891	3.509
7. $Na_2CO_3(s/l) + H_2O \rightarrow CO_2 + 2NaOH(s/l)$	-6.340	-4.337	-3.107	-2.388	-1.866
8. $HCl + \frac{1}{2}O_2 \rightarrow HOCl$	-2.845	-2.860	-2.871	-2.880	-2.886
9. $CO + Cl_2 \rightarrow COCl_2$	0.005	-1.403	-2.330	-2.984	-3.467
10. $Cl_2 \rightarrow 2Cl$	-10.023	-6.795	-4.630	-3.076	-1.906
11. $\frac{1}{2}Cl_2 + \frac{1}{2}O_2 \rightarrow ClO$	-5.943	-4.616	-3.730	-3.006	-2.620
12. $Cl_2 + \frac{1}{2}O_2 \rightarrow Cl_2O$	-8.055	-7.065	-6.404	-5.929	-5.573
13. $CO_2 + \frac{1}{2}Cl_2 \rightarrow CCl + O_2$	-56.187	-43.819	-35.576	-29.692	-25.282
14. $CO_2 + \frac{1}{2}Cl_2 + \frac{1}{2}N_2 \rightarrow ClCN + O_2$	-33.347	-26.419	-21.798	-18.495	-16.017
15. $CO_2 + Cl_2 \rightarrow CCl_2 + O_2$	-44.321	-35.074	-28.912	-24.513	-21.215
16. $CO_2 + \frac{3}{2}Cl_2 \rightarrow CCl_3 + O_2$	-37.631	-30.545	-25.814	-22.431	-19.890
17. $CO_2 + 2Cl_2 \rightarrow CCl_4 + O_2$	-25.989	-22.187	-19.634	-17.798	-16.413
18. $CO + 3HCl \rightarrow CHCl_3 + H_2O$	-30.379	-26.615	-24.078	-22.249	-20.862
19. $CO_2 + 2HCl \rightarrow CH_2Cl_2 + O_2$	-37.636	-31.335	-27.128	-24.116	-21.851
20. $CO + HCl + 2H_2 \rightarrow CH_3Cl + H_2O$	-17.324	-15.911	-14.967	-14.288	-13.771
21. $Na + \frac{1}{2}H_2 \rightarrow NaH$	-2.737	-2.534	-2.397	-2.299	-2.223
22. $NaCl \rightarrow Na + Cl$	-22.008	-16.605	-12.992	-10.407	-8.464
23. $Na_2 \rightarrow 2Na$	-0.995	0.050	0.750	1.253	1.633
24. $NaCl(s/l) \rightarrow NaCl$	-7.072	-4.216	-2.505	-1.392	-0.584
25. $2NaCl \rightarrow Na_2Cl_2$	6.408	3.810	2.091	0.871	-0.038

neglected in the material balance. This assumption is then checked before considering the solution complete.

Simple considerations serve to eliminate $Na_2O(s/l)$ and $NaOH(s/l)$. Reaction (6) indicates that Na_2O can exist only if the partial pressure of CO_2 is less than $10^{-13.279}$ at 800°K and $10^{-3.509}$ at 1600°K. At the lower temperatures, $\underline{P}_{CO_2}$ never gets that small, and at the higher temperatures Na_2CO_3 breaks down first. Similarly, Reaction (7) shows that $\log \underline{P}_{CO_2} - \log \underline{P}_{H_2O} = -6.340$ to -1.866 over the temperature range. Thus, the dissociation pressure of NaOH is given by $\log \underline{P}_{H_2O} = \log \underline{P}_{CO_2} + 6.340$ to 1.866 over the range. This is higher than the prevailing vapor pressure of water, and hence NaOH will not exist.

The assumption is made that the concentration of HOCl, COCl, ClCN, ClO, Cl_2O, CCl, CCl_2, CCl_3, CCl_4, $CHCl_3$, CH_2Cl_2, and CH_3Cl are negligible. This greatly reduces the number of species which must be considered in the material balance. The assumption is easily checked at the end. With this assumption, the species considered are:

Carbon:	$C(s)$, CO, CO_2, $Na_2CO_3(s/l)$
Hydrogen:	H_2O, H_2, HCl, NaH
Oxygen:	O_2, CO, CO_2, H_2O, $Na_2CO_3(s/l)$
Sodium:	$NaCl(s/l)$, $Na_2CO_3(s/l)$, NaCl, Na_2Cl_2, Na, Na_2, NaH
Chlorine:	HCl, Cl_2, Cl, $NaCl(s/l)$, NaCl), Na_2Cl_2.

In order to set up a material balance, it is necessary to define the composition of the spent liquor. The exact composition used does not critically influence the results except that defining sodium in excess of chlorine (or vice versa) is critical. The composition chosen for these calculations was a dry liquor with the following elemental analysis:

Cl:	17.3 weight %	=	5.0 mole %
Na:	15.7 weight %	=	7.0 mole %
C:	35.1 weight %	=	30.0 mole %
H:	3.9 weight %	=	40.0 mole %
O:	28.0 weight %	=	18.0 mole %.

These elemental compositions may then be used to quantify the material balance. Bauer and Dorland, in an early paper applying thermodynamic concepts to combustion of kraft black liquor, made the assumption that

$$P_{CO} + P_{CO_2} = 0.15 \quad \text{and} \quad P_{H_2O} + P_{H_2} = 0.10 .$$

This same condition can be applied to the present case with the specified elemental analysis to yield the following equations:

Carbon: $P_{CO} + P_{CO_2} + P_{C(s)} + P_{Na_2CO_3(s/l)} = 0.15$

Hydrogen: $2P_{H_2O} + 2P_{H_2} + P_{HCl} + P_{NaH} = 0.20$

Chlorine: $P_{HCl} + 2P_{Cl_2} + P_{Cl} + P_{NaCl(s/l)} + P_{NaCl} + 2P_{Na_2Cl_2} = 0.025$

Sodium: $P_{NaCl(s/l)} + 2P_{Na_2CO_3(s/l)} + P_{NaCl} + 2P_{Na_2Cl_2} + P_{Na} + 2P_{Na_2} + P_{NaH} = 0.035$

Oxygen: $2P_{O_2} + P_{CO} + 2P_{CO_2} + P_{H_2O} + 3P_{Na_2CO_3(s/l)} = 0.09 + \text{added}$

where the P's constitute the partial pressure of each species in atmospheres. Two points should be made clear about this expression of the material balance: First, partial pressures are used to describe the solid or liquid phase present even though they are not in the gas phase. This is merely a convenience in handling the material balance and implies nothing about these materials actually being gases.

It represents what the partial pressure of that material would be if all vaporized and thus relates quantitatively to the amount of solid or liquid phase present. The second point is that the material balances assume no accumulations of solids or liquids within the system. For each element entering the system, another leaves. The only exception is oxygen, where oxygen for combustion is added.

In carrying out the equilibrium calculations, it was assumed that the activities of all solid and liquid phases were unity. Then the amounts of solids or liquids present do not enter into the equilibrium relations (only the material balance) and reactions involving solid or liquid phases determine only gas compositions or whether or not the condensed phase exists. The oxygen partial pressure was used as an independent variable in the calculations, with the amount of oxygen added determined by an oxygen balance. This greatly simplifies the calculations.

A short description of the calculation procedure follows for a given temperature:

1. Select P_{O_2}.

2. Calculate $P_{Na_2CO_3(s/l)}$ assuming all chlorine as NaCl(s/l) and excess sodium as $Na_2CO_3(s/l)$.

3. Use carbon balance and Reactions (1) and (3) to determine P_{CO_2}, P_{CO}, and $P_{C(s)}$.

4. Use hydrogen balance and Reaction (2) to get P_{H_2} and P_{H_2O}. Make initial assumption that P_{HCl} and P_{NaH} are negligible.

5. Use Reactions (4a), (5), and (10) to get P_{HCl}, P_{Cl_2}, and P_{Cl}.

6. Use Reactions (24) and (25) to get P_{NaCl} and $P_{Na_2Cl_2}$.

7. Use chlorine material balance to calculate $P_{NaCl(s/l)}$.

8. If $P_{NaCl(s/l)}$ is positive, go to step 10.

9. If $P_{NaCl(s/l)}$ is negative, set it equal to zero and use Reactions (4b), (5), (10), (25), and the chlorine material balance to get P_{NaCl}, $P_{Na_2Cl_2}$, P_{HCl}, P_{Cl_2}, and P_{Cl}.

10. Use Reactions (21), (22), and (23) to get P_{NaH}, P_{Na}, and P_{Na_2}.

11. Use sodium balance to get $P_{Na_2CO_3(s/l)}$. If positive, go to 15. If negative, set $P_{Na_2CO_3(s/l)} = 0$ and go to 12.

12. If $P_{Na_2CO_3(s/l)}$ is zero but $P_{NaCl(s/l)}$ is not, use the following procedure:

    Use Reactions (24) and (25) to get P_{NaCl} and $P_{Na_2Cl_2}$. Combine the sodium and chlorine material balances to get

    $$\text{sodium - chlorine} = P_{Na} + 2P_{Na_2} + P_{NaH} - P_{HCl} - 2P_{Cl_2} - P_{Cl}.$$

    Use Reactions (5) and (10) to express P_{HCl} and P_{Cl_2} in terms of P_{Cl} and Reactions (21) and (23) to express P_{NaH} and P_{Na_2} in terms of P_{Na}. Use Reaction (22) to relate P_{Na} to P_{Cl} and solve.

13. Use chlorine balance to determine $P_{NaCl(s/l)}$. If it is positive, go to 15. If negative, set it equal to zero.

14. This procedure is used if neither $Na_2CO_3(s/l)$ or $NaCl(s/l)$ is present. The approach is similar to step 12 except that P_{NaCl} and $P_{Na_2Cl_2}$ are not fixed if there is no $NaCl(s/l)$. This makes it necessary to use the chlorine balance to determine P_{NaCl}. The three resulting equations are solved by trial and error.

15. The carbon and hydrogen balances are checked and the procedure is iterated from step 3 if necessary.

16. The concentrations of the minor constituents are calculated from the appropriate equilibrium relations.

17. The oxygen balance is used to calculate the amount added. If it is positive, P_{O_2} is incremented and the procedure repeated from the beginning. If oxygen added is negative, the calculation is terminated.

The above procedure was programmed for an IBM 360 computer and calculations carried out at the five temperature levels shown in Tables VIII and IX. The results of these calculations are presented below.

Results

The results of thermodynamic equilibrium calculations are shown in Tables X-XIV. At each temperature, partial pressures (in atm.) of each gaseous species are given for an oxidizing condition, a mild reducing condition, and a strong reducing condition. For solid or liquid phases, the data are presented as percents of the stoichiometric amounts. Stoichiometric amounts are defined on the basis that all chloride is present as NaCl(s/l), the remaining sodium as Na_2CO_3(s/l), and all carbon not used for Na_2CO_3(s/l) available for combustion. The amount of oxygen added is also expressed as a percent of the stoichiometric amount. Stoichiometric oxygen is based on CO_2, H_2O, NaCl(s/l), and Na_2CO_3(s/l) as the only combustion products.

TABLE X

EQUILIBRIUM PARTIAL PRESSURES (atm.) AT 800°K (980°F.)

Species	Oxidizing	Mild Reducing	Strong Reducing
O_2 added	163.5%	93.9%	39.3%
CO_2	0.145	0.140	6.75×10^{-2}
CO	5.6×10^{-16}	5.36×10^{-3}	2.59×10^{-2}
C(s)	-	-	35.7%
H_2O	0.100	8.60×10^{-2}	3.80×10^{-2}
H_2	1.6×10^{-14}	1.40×10^{-2}	6.20×10^{-2}
HCl	3.8×10^{-7}	3.5×10^{-7}	1.6×10^{-7}
Cl_2	9.3×10^{-13}	9.0×10^{-24}	4.3×10^{-26}
Cl	9.4×10^{-12}	9.2×10^{-18}	2.0×10^{-18}
NaCl(g)	8.5×10^{-8}	8.5×10^{-8}	8.5×10^{-8}
Na_2Cl_2	1.8×10^{-8}	1.8×10^{-8}	1.8×10^{-8}
NaCl(s/l)	100%	100%	100%
Na_2CO_3(s/l)	100%	100%	100%
Na	9×10^{-19}	9×10^{-13}	4×10^{-12}
Na_2	8×10^{-38}	8×10^{-24}	2×10^{-22}
NaH	2×10^{-28}	2×10^{-16}	2×10^{-15}
HOCl	2×10^{-10}	2×10^{-22}	7×10^{-24}
$COCl_2$	5×10^{-27}	5×10^{-27}	1×10^{-27}
ClO	3×10^{-13}	3×10^{-31}	7×10^{-33}
Cl_2O	3×10^{-21}	3×10^{-48}	1×10^{-47}
CCl	9×10^{-63}	9×10^{-48}	9×10^{-44}
CCl_2	6×10^{-57}	6×10^{-48}	1×10^{-44}
CCl_3	3×10^{-58}	3×10^{-50}	1×10^{-49}
CCl_4	1×10^{-60}	1×10^{-60}	1×10^{-61}
ClCN	5×10^{-40}	5×10^{-22}	5×10^{-21}
$CHCl_3$	1×10^{-63}	1×10^{-51}	1×10^{-51}
CH_2Cl_2	5×10^{-61}	4×10^{-37}	4×10^{-26}
CH_3Cl	3×10^{-64}	2×10^{-29}	2×10^{-27}

TABLE XI

EQUILIBRIUM PARTIAL PRESSURES (atm.) AT 1000°K (1340°F.)

Species	Oxidizing	Mild Reducing	Strong Reducing
O_2 added	163.5%	85.8%	9.2%
CO_2	0.145	0.122	4.78×10^{-3}
CO	2.8×10^{-11}	2.32×10^{-8}	9.10×10^{-2}
C(s)	-	-	34%
H_2O	0.100	7.84×10^{-2}	3.51×10^{-3}
H_2	2.8×10^{-11}	2.16×10^{-2}	9.65×10^{-8}
HCl	4.0×10^{-6}	3.3×10^{-6}	1.4×10^{-7}
Cl_2	1.8×10^{-11}	1.5×10^{-20}	5.8×10^{-24}
Cl	1.7×10^{-9}	4.9×10^{-13}	9.6×10^{-16}
NaCl(g)	6.1×10^{-5}	6.1×10^{-5}	6.1×10^{-5}
Na_2Cl_2	2.4×10^{-5}	2.4×10^{-5}	2.4×10^{-5}
NaCl(s/l)	99.6%	99.6%	99.7%
Na_2CO_3(s/l)	100%	100%	100%
Na	9×10^{-13}	3.1×10^{-8}	1.6×10^{-6}
Na_2	7×10^{-35}	9×10^{-16}	2×10^{-12}
NaH	1×10^{-20}	1×10^{-11}	1×10^{-8}
HOCl	2×10^{-9}	1×10^{-18}	6×10^{-22}
$COCl_2$	2×10^{-23}	1×10^{-23}	2×10^{-26}
ClO	3×10^{-11}	9×10^{-25}	2×10^{-28}
Cl_2O	5×10^{-19}	4×10^{-37}	2×10^{-42}
CCl	9×10^{-50}	2×10^{-36}	2×10^{-35}
CCl_2	2×10^{-46}	2×10^{-37}	2×10^{-38}
CCl_3	3×10^{-47}	6×10^{-43}	2×10^{-45}
CCl_4	3×10^{-44}	2×10^{-44}	1×10^{-48}
ClCN	2×10^{-32}	5×10^{-20}	4×10^{-18}
$CHCl_3$	4×10^{-53}	3×10^{-44}	2×10^{-46}
CH_2Cl_2	1×10^{-42}	6×10^{-25}	4×10^{-25}
CH_3Cl	1×10^{-52}	6×10^{-26}	4×10^{-24}

TABLE XII

EQUILIBRIUM PARTIAL PRESSURES (atm.) AT 1200°K (1700°F.)

Species	Oxidizing	Mild Reducing	Strong Reducing
O_2 added	163.5%	74.7%	1.4%
CO_2	0.145	9.39×10^{-2}	1.75×10^{-4}
CO	7.9×10^{-9}	5.11×10^{-8}	9.51×10^{-2}
C(s)	-	-	37.8%
H_2O	0.100	7.14×10^{-2}	2.49×10^{-4}
H_2	4.0×10^{-9}	2.86×10^{-2}	9.97×10^{-2}
HCl	1.6×10^{-8}	1.1×10^{-5}	5.8×10^{-8}
Cl_2	8.7×10^{-11}	6×10^{-18}	4×10^{-23}
Cl	4.5×10^{-6}	1×10^{-11}	3×10^{-14}
NaCl(g)	3.13×10^{-3}	3.13×10^{-3}	3.13×10^{-3}
Na_2Cl_2	1.21×10^{-3}	1.21×10^{-3}	1.21×10^{-3}
NaCl(s/l)	77.8%	77.8%	77.8%
Na_2CO_3(s/l)	100.2%	99.8%	-
Na	7.1×10^{-9}	2.8×10^{-8}	9.95×10^{-3}
Na_2	9×10^{-18}	1.4×10^{-10}	1.76×10^{-5}
NaH	1.8×10^{-18}	1.9×10^{-8}	1.26×10^{-5}
HOCl	7×10^{-8}	5×10^{-18}	2×10^{-21}
$COCl_2$	3×10^{-21}	1×10^{-21}	2×10^{-26}
ClO	5×10^{-10}	1×10^{-20}	4×10^{-26}
Cl_2O	1×10^{-17}	7×10^{-32}	6×10^{-40}
CCl	4×10^{-41}	6×10^{-31}	3×10^{-30}
CCl_2	2×10^{-39}	6×10^{-33}	9×10^{-38}
CCl_3	2×10^{-41}	2×10^{-38}	8×10^{-43}
CCl_4	3×10^{-40}	7×10^{-41}	8×10^{-48}
ClCN	2×10^{-27}	3×10^{-17}	2×10^{-18}
$CHCl_3$	3×10^{-46}	8×10^{-40}	6×10^{-44}
CH_2Cl_2	3×10^{-37}	9×10^{-24}	4×10^{-28}
CH_3Cl	2×10^{-44}	7×10^{-24}	2×10^{-23}

TABLE XIII

EQUILIBRIUM PARTIAL PRESSURES (atm.) AT 1400°K (2060°F.)

Species	Oxidizing	Mild Reducing	Strong Reducing
O_2 added	163.5%	84.8%	19.1%
CO_2	0.145	0.111	4.90×10^{-5}
CO	4.4×10^{-7}	3.40×10^{-2}	0.145
C(s)	-	-	-
H_2O	0.100	8.75×10^{-2}	7.0×10^{-5}
H_2	1.4×10^{-7}	1.25×10^{-2}	0.100
HCl	2.2×10^{-5}	1.8×10^{-5}	5.9×10^{-6}
Cl_2	6.6×10^{-11}	5×10^{-16}	7×10^{-18}
Cl	2.4×10^{-7}	6.5×10^{-10}	8×10^{-11}
NaCl(g)	1.94×10^{-2}	1.94×10^{-2}	1.94×10^{-2}
Na_2Cl_2	2.79×10^{-3}	2.79×10^{-3}	2.80×10^{-3}
NaCl(s/l)	-	-	-
Na_2CO_3(s/l)	100.2%	88.5%	-
Na	3.2×10^{-6}	1.17×10^{-3}	9.98×10^{-3}
Na_2	6×10^{-13}	7.6×10^{-8}	5.6×10^{-6}
NaH	6×10^{-12}	6.6×10^{-7}	1.6×10^{-5}
HOCl	9×10^{-9}	7×10^{-14}	2×10^{-18}
$COCl_2$	3×10^{-20}	2×10^{-20}	1×10^{-21}
ClO	2.5×10^{-8}	7×10^{-17}	8×10^{-22}
Cl_2O	2×10^{-17}	2×10^{-27}	3×10^{-33}
CCl	3×10^{-36}	2×10^{-30}	1×10^{-27}
CCl_3	3×10^{-38}	5×10^{-36}	3×10^{-34}
CCl_4	1×10^{-38}	4×10^{-39}	4×10^{-38}
ClCN	3×10^{-24}	7×10^{-17}	3×10^{-13}
$CHCl_3$	3×10^{-42}	1×10^{-37}	2×10^{-35}
CH_2Cl_2	5×10^{-34}	3×10^{-24}	1×10^{-20}
CH_3Cl	1×10^{-38}	6×10^{-24}	6×10^{-18}

TABLE XIV

EQUILIBRIUM PARTIAL PRESSURES (atm.) AT 1600°K (2420°F.)

Species	Oxidation	Mild Reducing	Strong Reducing
O_2 added	163.5%	74.5%	19.1%
CO_2	0.145	9.23×10^{-2}	2.41×10^{-5}
CO	9.0×10^{-6}	5.74×10^{-2}	0.150
C(s)	-	-	-
H_2O	0.100	8.27×10^{-2}	4.78×10^{-5}
H_2	2.1×10^{-6}	1.73×10^{-2}	9.99×10^{-2}
HCl	9.3×10^{-6}	2.48×10^{-5}	5.93×10^{-5}
Cl_2	6.3×10^{-12}	5×10^{-15}	5×10^{-15}
Cl	2.8×10^{-7}	8.2×10^{-9}	8.2×10^{-9}
NaCl(g)	2.39×10^{-2}	2.39×10^{-2}	2.39×10^{-2}
Na_2Cl_2	5.25×10^{-4}	5.25×10^{-4}	5.23×10^{-4}
NaCl(s/l)	-	-	-
Na_2CO_3(s/l)	97.1%	-	-
Na	2.94×10^{-4}	1.00×10^{-2}	1.00×10^{-2}
Na_2	2.0×10^{-9}	2.33×10^{-6}	2.34×10^{-6}
NaH	2.6×10^{-9}	7.88×10^{-6}	1.90×10^{-5}
HOCl	3.8×10^{-9}	1×10^{-12}	2×10^{-16}
$COCl_2$	2×10^{-20}	1×10^{-19}	3×10^{-19}
ClO	1.9×10^{-9}	6×10^{-15}	6×10^{-19}
Cl_2O	5×10^{-18}	5×10^{-28}	5×10^{-29}
CCl	2×10^{-31}	4×10^{-35}	9×10^{-31}
CCl_2	6×10^{-33}	3×10^{-28}	8×10^{-24}
CCl_3	3×10^{-37}	5×10^{-34}	1×10^{-29}
CCl_4	2×10^{-39}	1×10^{-37}	3×10^{-33}
ClCN	3×10^{-22}	5×10^{-16}	1×10^{-11}
$CHCl_3$	1×10^{-40}	1×10^{-35}	9×10^{-31}
CH_2Cl_2	2×10^{-32}	8×10^{-24}	1×10^{-18}
CH_3Cl	6×10^{-35}	9×10^{-23}	3×10^{-17}

The equilibrium calculations show that under oxidizing conditions the combustion products are mainly CO_2, H_2O, NaCl, and Na_2CO_3 at all temperatures. Under reducing conditions, CO, H_2, and possibly elemental carbon are present and there is some tendency for Na_2CO_3 to decompose, particularly at the higher temperatures. If equilibrium conditions are approached, there should not be too great a difficulty with chlorine-containing gases. If an arbitrary limit of 10^{-8} atm. is used to indicate insignificant species, Cl_2, HOCl, COCl, ClO, Cl_2O, CCl, CCl_2, CCl_3, CCl_4, ClCN, $CHCl_3$, CH_2Cl_2, and CH_3Cl can all be dismissed from consideration. Using this criterion, the only chlorine compounds of significance are HCl, Cl, NaCl(g), Na_2Cl_2, and NaCl(s/l).

By far the bulk of the chlorine is present as sodium chloride in some form or other. At lower temperatures, it exists mainly as the solid or liquid phase. At the higher temperatures, sodium chloride vapor and its dimer predominate. Other than the various forms of sodium chloride, the major chlorine compound is HCl. Monatomic chlorine, Cl, is present only as high as 0.3 p.p.m. and then only at the highest temperature levels.

Equilibrium levels of HCl appear to be high enough to constitute a potential emission problem. Concentrations range from about 0.4 p.p.m. at 800°K to 22 p.p.m. at 1400°K. The general trend is for the HCl concentration to increase with temperature and to decrease with reducing conditions, although the data at 1600°K go in the opposite direction. Oxidizing or reducing conditions have only a slight effect until very strong reducing conditions such as in a pyrolysis or destructive distillation are reached.

Considering all of the data as a whole, it appears that there are no significant advantages to operation under reducing conditions. Thus, it is expected that oxidizing conditions would be used for holopulp spent liquor combustion. From

the standpoint of temperature, the most favorable distribution of combustion product is obtained at the lowest temperature, and gradually deteriorates as the temperature is raised. Thus, thermodynamics suggests that the combustion be carried out under oxidizing conditions and at the lowest temperature at which combustion is feasible. The combustion products will be CO_2, H_2O, Na_2CO_3, and NaCl. At higher temperature levels, a significant amount of the NaCl would be in volatile forms. If equilibriu exists, the only potential air emission problem is with HCl. Concentrations would be expected to range from about 0.5 p.p.m. to about 25 p.p.m. over the temperature range covered. The level would increase with temperature up to 1400°K (2060°F.). From a thermodynamic standpoint, the recovery process appears soundly based and the emission levels controllable.

SMALL BATCH COMBUSTION

Although the equilibrium analysis indicated that sodium chloride and sodium carbonate would be the combustion products, and a preliminary experiment some years back also indicated this, it was thought advisable to obtain experimental confirmation. This was done by carrying out duplicate batch combustions in a muffle furnace for two different liquors.

Concentrated spent liquor samples of AC5 and AC8 were weighed in tared crucibles. These crucibles containing the samples were put into a muffle furnace equipped with automatic temperature control. The temperature was brought up slowly so that spattering of samples was avoided. The temperature was maintained at 1000°F. for 10 hours. The crucibles were cooled and weighed and the residues dissolved in distilled water. The liquid samples were analyzed for sodium with a spectrophotometer, for chloride by the Volhard volumetric method, and for sodium carbonate by titration with hydrochloric acid. During the titration, the pH at each addition of

0.20 ml. of hydrochloric acid was measured with a pH meter. The titration data are shown in Table XV and presented graphically in Fig. 2 and 3.

The titration curves are exactly the type of curve one would obtain in titrating sodium carbonate solutions with hydrochloric acid. The pH of sodium bicarbonate, the half-neutralized stage of Na_2CO_3, is 8.3. The amount of hydrochloric acid theoretically required to arrive at this half stage is exactly one half of the total quantity required, as can be seen from these equations:

$$Na_2CO_3 + HCl \rightarrow NaCl + NaHCO_3$$

$$NaHCO_3 + HCl \rightarrow NaCl + CO_2 + H_2O \ .$$

In this study, for the AC5 runs the two inflection points can easily be read at pH values of 8.3 and 4.2, respectively.

The amounts of 0.1N HCl consumed are 2.60 and 5.20 ml., respectively. These agree perfectly with what theoretically should happen when Na_2CO_3 is titrated. For the AC8 runs, the amounts of HCl used corresponding to the two inflection points are 3.62 and 7.23 ml.

In addition to this reasoning, the analyses of total sodium and total chlorine indicated also that the combustion products were primarily NaCl and Na_2CO_3. For Run 1 of AC5 concentrated liquor, the sodium and chlorine balances are as follows:

Concentrated AC5 liquor (4.9486 g.) containing 3.28% Na and 38.8 g./liter chlorine were combusted. Therefore,

Chlorine in = (4.9586/1.1169)(38.8/1000) =	0.1726 g.
Sodium in = 4.9586(3.280/100) =	0.1626 g.
Solid combustion product =	0.4114 g.
Total chloride found =	0.1765 g.

TABLE XV

NEUTRALIZATION DATA OF AC5 AND AC8 COMBUSTION RESIDUES

HCl Added, ml.	pH			
	AC5		AC8	
	Titration 1	Titration 2	Titration 1	Titration 2
0.0	10.99	11.01	11.05	11.05
0.2	10.88	10.91	10.97	10.97
0.4	10.78	10.80	10.89	10.89
0.6	10.69	10.71	10.82	10.82
0.8	10.58	10.61	10.75	10.75
1.0	10.48	10.49	10.66	10.67
1.2	10.35	10.35	10.58	10.59
1.4	10.22	10.24	10.51	10.51
1.6	10.10	10.11	10.41	10.42
1.8	9.96	9.97	10.31	10.32
2.0	9.79	9.79	10.24	10.25
2.2	9.56	9.55	10.14	10.13
2.4	9.16	9.24	10.04	10.04
2.6	8.32	8.27	9.93	9.93
2.8	7.55	7.55	9.79	9.79
3.0	7.19	7.21	9.63	9.63
3.2	6.98	7.00	9.42	9.40
3.4	6.77	6.79	9.13	9.05
3.6	6.59	6.57	8.42	8.29
3.8	6.45	6.40	7.69	7.69
4.0	6.30	6.25	7.36	7.35
4.2	6.12	6.09	7.14	7.13
4.4	5.95	5.92	7.0	6.98
4.6	5.75	5.72	6.85	6.82
4.8	5.52	5.49	6.72	6.69
5.0	5.14	5.10	6.59	6.57
5.2	4.15	4.09	6.48	6.46
5.4	3.52	3.51	6.38	6.35
5.6	3.27	3.23	6.26	6.25
5.8	3.05	3.05	6.15	6.15
6.0	2.94	2.95	6.04	6.03
6.2	2.83	2.85	5.93	5.90
6.4	2.75	2.77	5.79	5.77
6.6	2.69	2.70	5.63	5.61
6.8	2.62	2.63	5.43	5.39

TABLE XV (CONTD.)

NEUTRALIZATION DATA OF AC5 AND AC8 COMBUSTION RESIDUES

HCl Added, ml.	pH			
	AC5		AC8	
	Titration 1	Titration 2	Titration 1	Titration 2
7.0	2.58	2.58	5.13	5.09
7.2	2.52	2.52	4.47	4.39
7.4	2.49	2.50	3.72	3.77
7.6	2.45	--	3.40	3.42
7.8	--	--	3.21	3.22
8.0	--	--	3.05	3.09
8.2	--	--	2.97	3.00
8.4	--	--	2.87	2.90
8.6	--	--	2.81	2.83
8.8	--	--	2.72	2.76
9.0	--	--	2.69	2.72
9.2	--	--	2.64	2.66
9.4	--	--	2.59	2.62
9.6	--	--	--	2.58
9.8	--	--	--	2.54

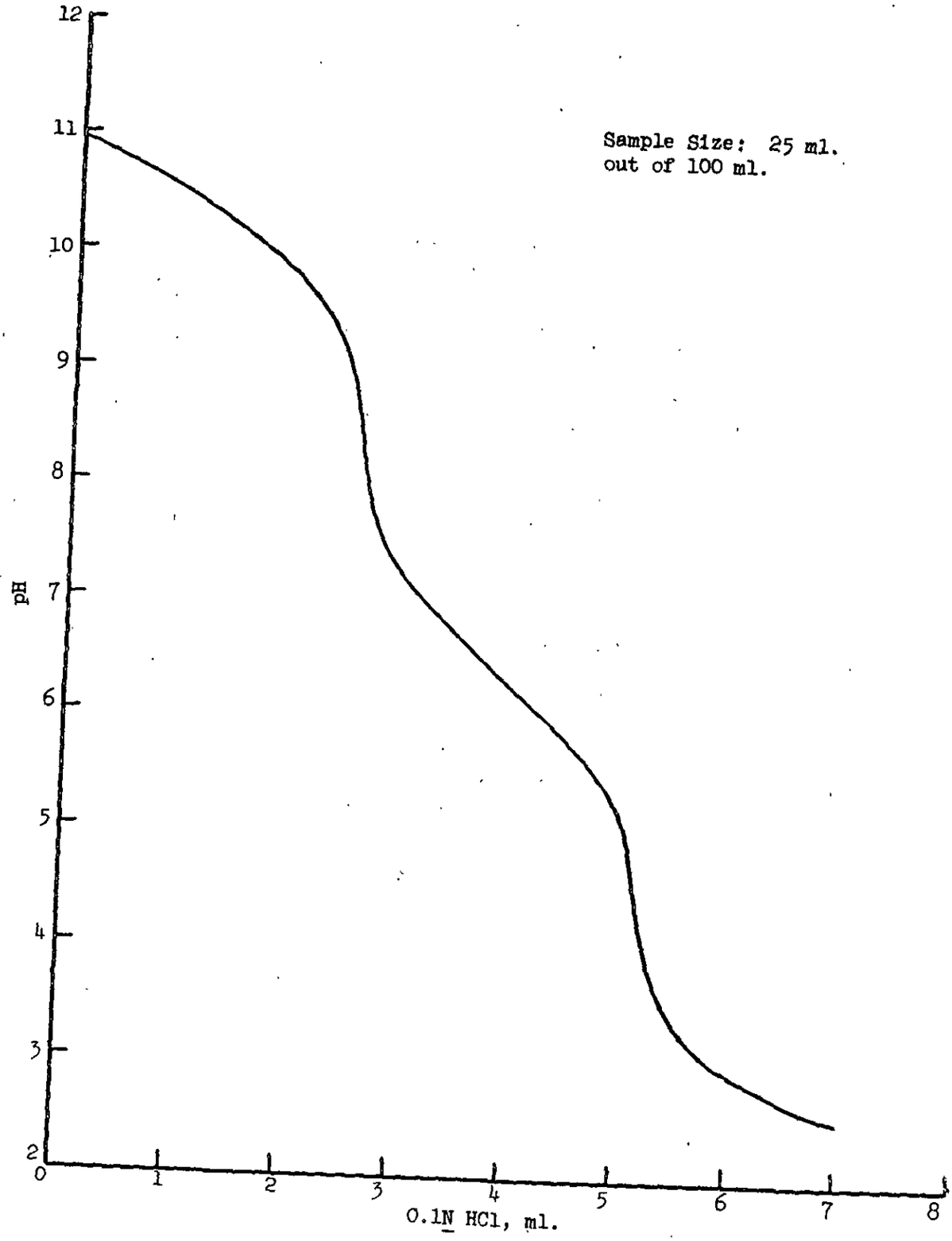


Figure 2. Titration of Combustion Products of AC5 Concentrated Liquors

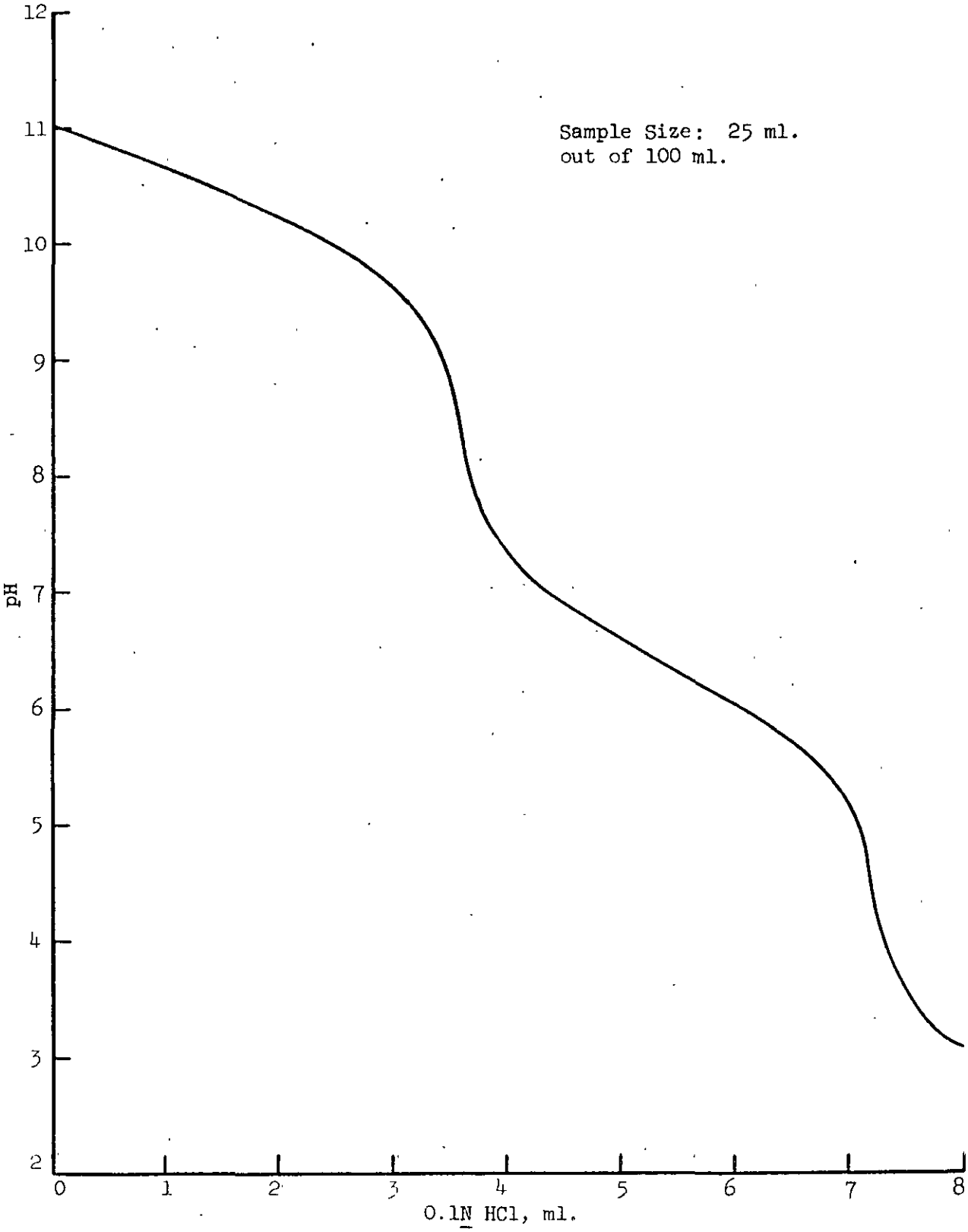


Figure 3. Titration of Combustion Products of AC8 Concentrated Liquors

Total sodium found =	0.1574 g
Total Na_2CO_3 found = 5.20(0.1)(53)(100)/(25)(1000) =	0.1102 g
Total NaCl found = 0.1765(58.46)/35.46 =	0.2901 g
NaCl + Na_2CO_3 =	0.4003 g
Predicted NaCl =	0.2846 g
Predicted Na_2CO_3 =	0.1167 g

The results for duplicate runs on the AC5 and AC8 liquors are shown in Table XVI. The top grouping gives the inputs based on analysis of the spent liquc The amounts found in the combustion products are shown in the middle grouping. Th bottom group is the amounts of Na_2CO_3 and NaCl predicted from the elemental inputs.

TABLE XVI

RESULTS OF OPEN COMBUSTION ON AC5 AND AC8 CONCENTRATED LIQUORS

	AC5		AC8	
	1	2	1	2
Concentrated liquor, g.	4.9586	5.0000	5.0035	5.0010
Total sodium, %	3.28	32.8	3.64	3.64
Total chlorine, %	3.48	3.48	3.34	3.34
Initial sodium, g.	0.1626	0.1640	0.1821	0.1820
Initial chlorine, g.	0.1726	0.1737	0.1671	0.1670
Solid combustion prod., g.	0.4114	0.4156	0.4394	0.4390
Total sodium found, g.	0.1574	0.1606	0.1716	0.1688
Total chloride found, g.	0.1765	0.1778	0.1674	0.1674
Total Na_2CO_3 found, g.	0.1102	0.1102	0.1526	0.1526
Total NaCl found, g.	0.2901	0.2931	0.2760	0.2760
NaCl + Na_2CO_3, g.	0.4003	0.4033	0.4286	0.4286
Predicted NaCl, g.	0.2846	0.2864	0.2755	0.2753
Predicted Na_2CO_3, g.	0.1167	0.1183	0.1699	0.1698

The numbers in Table XVI were obtained in the following manner. The amount of spent liquor used was determined by weighing. Percentages of sodium and chlorine in the concentrated liquor were determined by analysis. Inputs of sodium and chlorine were calculated by multiplying the amount of spent liquor by the weight fractions of sodium and chlorine. After combustion, the crucibles were weighed to determine the total amount of ash remaining. The ash was then dissolved in a known amount of water. Sodium by flame photometry, chloride by Volhard analysis, and sodium carbonate by titration were run on these solutions. The total sodium and chloride found is based on these measurements. Total Na_2CO_3 found is based on the titration. Total NaCl found is calculated from the chloride content by multiplying by the molecular weight ratio. The predicted values are calculated from the elemental input by assuming all chloride converted to NaCl and the excess sodium converted to Na_2CO_3.

The data in Table XVI conclusively demonstrate that NaCl and Na_2CO_3 are the combustion products when holopulp spent liquors are burned. The greatest uncertainty in these data lies in the determinations of the sodium and chlorine content in the starting spent liquor. The material balances close within the accuracy of the input data. These results are in complete agreement with the equilibrium predictions at this temperature level and thus support the use of equilibrium calculations to predict performance. Of particular importance is the fact that the data indicate quantitative recovery of chlorine as sodium chloride.

SMALL SEMICONTINUOUS COMBUSTION

The data from the batch combustion experiments established NaCl and Na_2CO_3 as the primary combustion products. However, it was not possible to conclude from these data that there would not be air emission problems due to small amounts of chlorine compounds. The accuracy of the data was insufficient to permit precise

determination of losses by material balance. The basic difficulty in determining emissions in the batch experiments was that the combustion was carried out in open crucibles and the gaseous products could not be collected for direct analysis. In order to overcome this difficulty, semicontinuous combustion experiments were carried out in a closed vessel with controlled air supply and collection of the combustion gases.

Runs Under Oxidizing Conditions

Spent liquors were dried in a vacuum oven at 60°C. The dried samples were then pulverized in a mortar. Samples were weighed out of this stock and sealed in pyrex glass vials, each of which was provided with a gas inlet and a gas outlet. The vials were heated slowly to 1100°F. and maintained at this temperature for a selected time. During the entire heating process, air was passed through the vial to aid the combustion and carry away the gaseous combustion products. The gases were scrubbed with an aqueous sodium hydroxide-hydrogen peroxide solution. The scrubbed gas was then led through a potassium iodide solution scrubber so that the presence of any unabsorbed chlorine gas could be detected. It was found that a slow heating at a temperature from 250 to 500°F. was highly desirable; otherwise, smoky gaseous combustion products would evolve and cause a yellowish color in the scrubbers. Even though this yellowish color did not represent the presence of iodine in the KI scrubber, it definitely indicated a heating process which was increased too rapidly. For the 0.3-g. sample, 12 minutes were allowed between 250 and 500°F.

Preliminary runs were made with Liquors AC5 and BC1.8 to establish this analytical procedure. The control samples were analyzed for chlorine according to the chromic acid digestion method. The results are tabulated in Table XVII.

TABLE XVII

PRELIMINARY RESULTS ON LOW-TEMPERATURE COMBUSTION

	BC1.8		AC5	
	1	2	1	2
Sample weight, g.	0.4623	0.4714	0.3982	0.2729
Chlorine found by chromic acid digestion[a]	0.1073	0.1092	0.0613	0.0435
Combustion time, hr.	4	4	4	4
Chlorine found in NaOH-H_2O_2 scrubber, g.	0.0058	0.0007	0[b]	0[b]
Chlorine found in KI scrubber, g.	0.0000	0.0004	0.0000	0.0000
Chlorine in ash, g.	0.1062	0.1088	0.0586	0.0422
Total chlorine found, g.	0.1120	0.1099	0.0586	0.0422
Total recovery, %	104.3	100.6	95.6	97.0
Volatile chlorine loss, %	5.4	1.0	0.	0.

[a] For BC1.8 samples, this is based on the 0.232% total chlorine found in the original weak spent liquor.

For AC5 samples, it is based on an average of 14.69% total chlorine determined on two samples taken from the same batch of dried, ground AC5 liquor solids.

[b] Actual calculated value is negative.

Some comments on these results and the procedure appear to be in order. The NaOH-H_2O_2 scrubber was designed to retain all NaCl, HCl, and Cl_2 coming over as a chloride solution. Any chlorine present should react with peroxide to yield chloride. The analysis of this scrubber solution was for chloride ion by the Volhard method. The second scrubber, which contained KI, was intended as a trap for any chlorine which passed through the first scrubber. It would detect any

compounds which liberate I_2 from KI. Thus, the measurement on the $NaOH-H_2O_2$ scrubber is specific to chlorine compounds, while that on the KI scrubber is not. This should be borne in mind in interpreting the results.

The order of the scrubbing solutions for the data in Table XVII was as follows: The $NaOH-H_2O_2$ scrubber was first in line for BCl.8-1 and AC5-2. The order was reversed for BCl.8-2 and AC5-1. A relatively large volatile loss was found in BCl.8-1, all in the $NaOH-H_2O_2$ scrubber. Reversing the scrubbers gave a small amount of chlorine in each scrubber. This would indicate that the great bulk of the loss occurred as NaCl and HCl. These would be absorbed in the KI solution without liberating I_2 and would be undetected in Run 2. Very little of the chlorine loss is seen as occurring as Cl_2 gas. The indication of no chlorine loss for the AC5 runs is somewhat suspect.

A run in triplicate was made on the dried solids from AC5 spent liquor, with very slow heating between 300 and 500°F. The solutions in the $NaOH-H_2O_2$ scrubber remained nearly colorless, indicating a minimum of smoky products were evolved. The order of the scrubbing solutions was first $NaOH-H_2O_2$ and then the KI. This order was used in the remainder of the work. The results of this experiment are shown in Table XVIII. Two additional series of runs were made with AC5 liquor solids. The purpose of the first series was to determine if combustion time had any effect on volatile losses. The second series examined the effect of sample size. The results of these runs are presented in Table XIX.

TABLE XVIII

LOW-TEMPERATURE COMBUSTION RESULTS ON AC5

Sample	AC5 1	AC5 2	AC5 3
Weight, g.	0.2988	0.2842	0.3098
Chloride ($NaOH-H_2O_2$ scrubber), g.	0.0006379	0.0006425	0.0006034
Chlorine in terms of chloride (KI scrubber), g.	0	0	0
Total chloride in ash, g.	0.04511	0.04250	0.04675
Total chloride found, g.	0.04574	0.04314	0.04735
Total chloride in control sample (chromic acid digestion), g.	0.04618	0.04393	0.04788
Combustion time, hr.	4	4	4
Total recovery, hr.	99.1	98.2	98.9
Volatile chlorine loss, %	1.36	1.46	1.26

TABLE XIX

LOW-TEMPERATURE COMBUSTION OF SPENT LIQUOR IN AIR

A. Time Effect

Sample	1	2	3	4
Combustion time, hr.	1	2	3	5
Weight of sample, g.	0.3029	0.2997	0.3134	0.3110
Chlorine in $NaOH-H_2O_2$, g.	0.000660	0.000638	0.000705	0.000420
Chlorine in KI, g.	0	0	0	0
Chlorine in ash, g.	0.04877	0.04685	0.04781	0.04878
Total chlorine found, g.	0.04943	0.04749	0.04851	0.04920
Total chlorine by chromic acid digestion for same amount of sample, g.	0.04830	0.04780	0.04998	0.04960
Total recovery, %	102.4	99.4	97.1	99.2
Volatile chlorine loss, %	1.35	1.33	1.41	0.85

B. Sample Size Effect

Sample	5	6	7
Combustion time, hr.	4	4	4
Sample weight, g.	0.5983	1.2031	2.4064
Chlorine in $NaOH-H_2O_2$, g.	0.000839	0.000631	0.001055
Chlorine in KI, g.	0.001715	0.001225	0.001225
Chlorine in ash, g.	0.09506	0.1884	0.3733
Total chlorine found, g.	0.09761	0.1903	0.3756
Total chlorine by chromic acid digestion for same amount of sample, g.	0.09448	0.1859	0.3717
Total recovery, %	103.3	102.4	101.0
Volatile chlorine loss, scrubber 1, %	0.89	0.34	0.28
Volatile chlorine loss, scrubber 2, %	1.82	0.66	0.33

The results of the run in triplicate indicate a fairly consistent loss of chlorine as volatiles of about 1.35%. The series of runs in which time was a variable did not show any appreciable trends in chlorine loss with time, although the five-hour run gave a lower loss. The runs with larger sample sizes do show a trend of decreasing volatile loss with increasing sample size. They are also the only runs in which a significant amount of iodine was liberated in the KI scrubber. It should be noted that smoke was produced in the run of Sample 5 at about 400°F., probably because the heating period at 250-500°F. was not extended enough for the nearly double-size sample. As a consequence, the low-temperature period for Samples 6 and 7 was lengthened in proportion to the sample size; however, smoke was never completely eliminated. It is quite possible that the liberation of I_2 in the KI scrubber was due to organic compounds other than chlorine compounds. One indication of this is the fact that total chlorine recovery exceeded 100% for Samples 5, 6, and 7, while for the smaller sample runs, 6 out of 7 gave total chlorine recoveries of less than 100%. The fact that sample size influenced the volatile chlorine loss is a little puzzling. If the chlorine loss is based on the amount of chloride found in the $NaOH-H_2O_2$ scrubber, the percentage volatile chlorine loss drops from 1.35 to 0.89 to 0.34 to 0.28 on successive doublings of the sample size. A possible interpretation of this is that a significant portion of the loss occurs as carryover as the liquor begins to decompose and is affected mainly by exposed surface rather than total amount of sample. The formation of "smoke" also appears to play a role.

Runs Under Reducing Conditions

In addition to the runs carried out in the presence of air, a series of runs were made in an inert atmosphere to study the decomposition behavior in a reducing atmosphere. The procedure was similar to the previous runs except that

nitrogen from a commercial gas cylinder was used instead of air. In these experiments 50 minutes were allowed to heat the sample from 250 to 500°F. The smoking problem was completely eliminated. The elimination of smoke was definitely associated with the long heating period and not the inert atmosphere. A single run with a 30-minute heating period did give off some smoke. The results of these experiments are presented in Table XX. The amounts of volatile chlorine driven off are of the same order of magnitude as for the case when oxidizing conditions were used. The high value for Sample 4 is believed due to a smoky condition. The apparent decreasing trend with increasing combustion time is inexplicable.

Summary

In general, the results of all of the experiments showed a volatile chlorine loss of about 1% during combustion. Almost all of this loss occurred as HCl and NaCl. The loss of chlorine in volatiles was unaffected by the use of either oxidizing or reducing conditions. These findings would seem to correlate quite well with the equilibrium calculations. There was evidence of a smoke-forming condition in the temperature range 250-500°F. The amount of smoke formed appeared to relate to the rate of heating in this temperature range. There are indications that a significant portion of the chlorine loss is associated with this smoky stage. It may be necessary to take this feature into account in designing a commercial-sized furnace.

TABLE XX

LOW-TEMPERATURE PYROLYSIS OF SPENT LIQUORS IN N_2 ATMOSPHERE

Time Effect

Sample	1	2	3
Weight of sample, g.	0.3034	0.3646	0.3744
Time, hr.	1.5	2.5	5
Chlorine in $NaOH-H_2O_2$, g.	0.000462	0.000204	0.000109
Chlorine in KI, g.	0	0	0
Chlorine in ash, g.	0.03351	0.03985	0.03906
Total chlorine found, g.	0.03397	0.04005	0.03917
Total chlorine by chromic acid digestion for same amount of sample (dry proportion), g.	0.03218	0.03867	0.03971
Total recovery, %	105.5	103.6	98.6
Volatile chlorine loss, %	1.43	0.53	0.27

Sample Size Effect

Sample	4	5	6
Weight of sample, g.	0.3068	0.4767	0.5959
Time, hr.	2	2	2
Chlorine in $NaOH-H_2O_2$, g.	0.000987	0.0000629	0.000177
Chlorine in KI, g.	0	0	0
Chlorine in ash, g.	0.03318	0.05098	0.06073
Total chlorine found, g.	0.03417	0.05104	0.06091
Total chlorine by chromic acid digestion for same amount of sample (dry proportion), g.	0.03254	0.05056	0.06321
Total recovery, %	105.1	101.0	96.4
Volatile chlorine loss, %	3.0	0.12	0.28

HEATING VALUES OF LIQUORS

Heating values on the original A and B liquors (AC5 and BC1.8) were determined with a Parr oxygen bomb calorimeter. Triplicate determinations were carried out on each liquor at about 50% solids. A single run on an ovendry sample of each liquor was also carried out. The results are shown in Table XXI.

TABLE XXI

HEAT OF COMBUSTION OF SPENT LIQUORS

Spent Liquor	B.t.u./lb. o.d. solids
AC5	5830
	6010
	5530
	5184[a]
BC1.8	4810
	4620
	4490
	4581[a]

[a] Ovendry samples.

The average value for the triplicate determinations on the AC5 liquor is 5790 B.t.u./lb. dry solids, and for the BC1.8 liquor, 4630 B.t.u./lb. dry solids. The direct measurement on dry solids checked quite well for Liquor B but was about 600 B.t.u./lb. low for Liquor A. This could be due to incomplete combustion if the powder blew out of the pan during ignition. The heating values of the holopulp liquors are lower than heating values of kraft liquor. This is not unexpected for a high-yield pulping process employing oxidation. The lower value for Liquor B is probably due to three causes. The relatively large amount of chlorine used in the oxidation step could have led to greater oxidation of the soluble material. The

second cause was the loss of some of the oxidation-stage liquor in the collection process. The third reason is a higher inorganic content in the liquor. It appears that heating values of holopulp liquors will be similar to those of NSSC liquors.

MELTING POINTS OF Na_2CO_3-NaCl MIXTURES

One of the critical elements in the selection of a method of combustion of holopulp liquor is the melting point of the Na_2CO_3-NaCl mixture produced. Melting points of such mixtures were determined according to ASTM Method D 271-48. A mixture of C.P. grade anhydrous sodium carbonate powder and C.P. grade chloride crystals was melted in a small stainless steel crucible in an electric muffle furnace. After cooling, the fused mixture was pulverized into powder form in a porcelain mortar. The powdery mixture was moistened with a solution of dextrin (ca. 10%) and worked into a plastic mass with a spatula. The plastic material was then molded into triangular cones 3/4 in. in height with a quarter-inch equilateral base. One side of the cone was perpendicular to the base. The cones were then dried in a vacuum oven at 60°C. The dry cones were mounted in a base composed of equal parts by weight of kaolin and alumina. The base was about 1/8 in. thick. The cones, which were mounted on the base, were put into the electric muffle furnace and the temperature was slowly raised to 400°F. and maintained there for 20 minutes. Then heating was resumed with a rate of temperature rise of 5-10°C. per minute. When the cone had melted and spread out, the temperature was recorded as the melting point of the mixture. The melting points of Na_2CO_3-NaCl mixtures in various weight proportions were determined. The results are shown in Table XXII and graphically presented in Fig. 4.

TABLE XXII

MELTING POINTS OF Na_2CO_3-NaCl MIXTURES

Na_2CO_3-NaCl Weight Ratio		Number of Determinations
100-0	1520	1
90-10	1500, 1500, 1500	3
85-15	1470, 1460, 1480	3
80-20	1460-1500, 1450, 1440	3
75-25	1400, 1410, 1400	3
70-30	1310, 1280, 1310	3
65-35	1190, 1190, 1190	3
60-40	1180, 1190, 1180, 1180, 1210, 1200, 1180, 1190	8
55-45	1200, 1190, 1200	3
50-50	1280, 1250, 1280	3
45-55	1440, 1440, 1440	3
40-60	1420, 1410, 1430, 1470, 1470, 1400, 1450	7
20-80	1450, 1460, 1460, 1460, 1460, 1440	6
0-100	1460	1

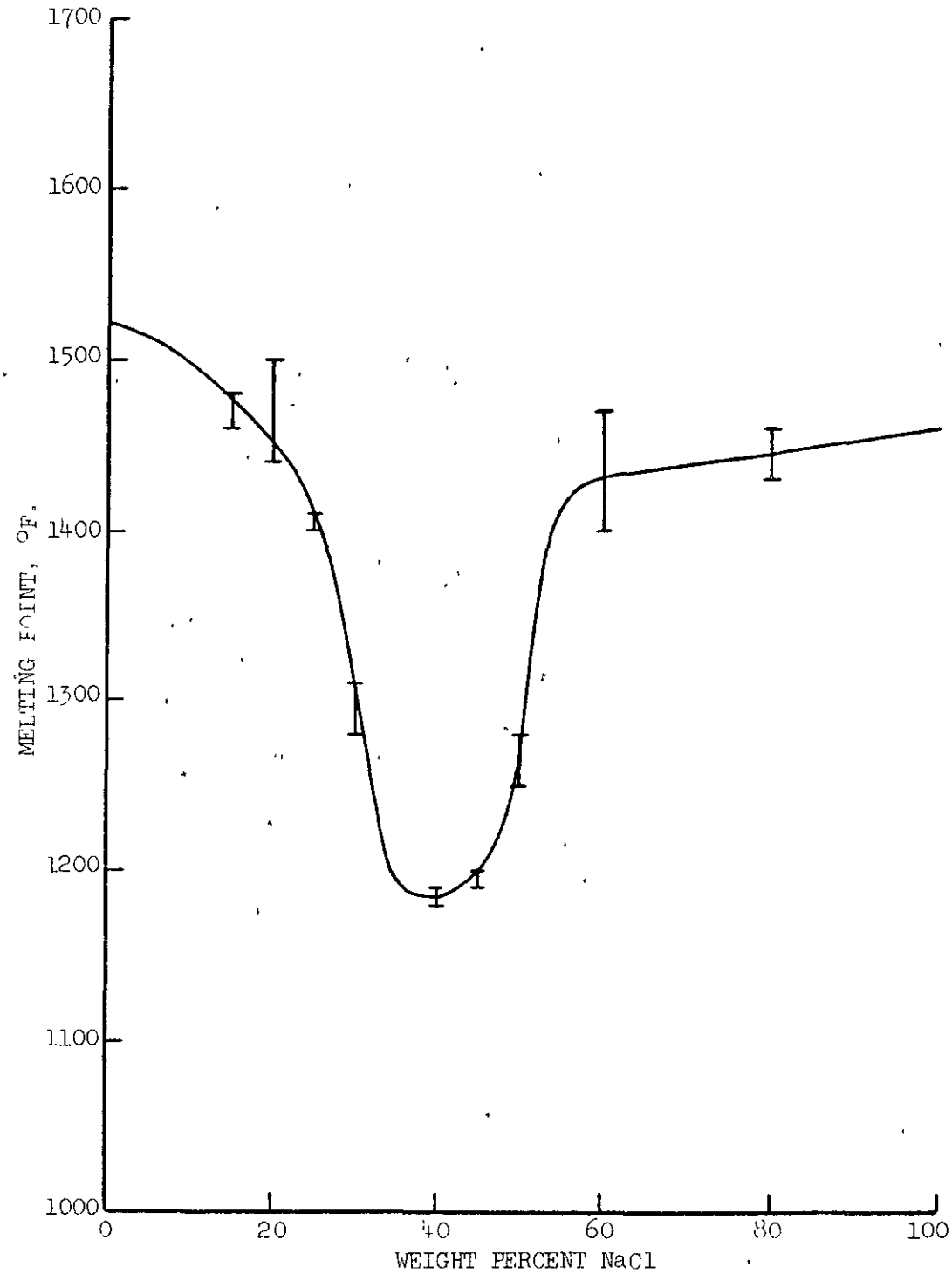


Figure 4. Melting Points of Na_2CO_3-NaCl Mixtures

It is evident that there is a region of intermediate composition in which the melting point is significantly lower than the melting point of either pure compound. Between 35 and 45% NaCl, the melting point is below 1200°F. This could have a significant effect on the type of combustion system employed, particularly the possible use of fluidized bed combustion. In fluidized bed combustion of NSSC liquor, the minimum combustion temperature is around 1300-1320°F. The melting point would have to be some distance above this. If an arbitrary melting point of 1400°F. is taken to set the limit to fluidized bed combustion, it would be limited to NaCl contents below 25% or above 55%. For the types of pulping conditions currently used, the composition of recovered inorganic is about 70% NaCl. Thus, fluidized bed combustion may be a feasible technique.

BENCH-SCALE FLUIDIZED BED STUDIES

On the basis of equilibrium calculations and preliminary laboratory experiments, it became apparent that the most advantageous method of combustion from the standpoint of emissions and product recovery was at low temperatures. Particular advantages were attainable if the combustion could be carried out at temperatures below the melting point of the recovered sodium chloride/sodium carbonate mixture. Fluidized bed combustion appeared to be the most promising approach to low-temperature combustion because of the long holding times of material within the reactor and the large amount of gas-solid contact which could be attained. It was recognized that the main limitation to low-temperature combustion was the combustion rate and the carbon removal efficiencies which could be obtained. It was decided that the potential advantage justified the risks and so a program to study low-temperature fluidized bed combustion of holopulp spent liquor was initiated.

Apparatus

A bench-scale fluidized bed combustion unit was used to study the feasibility of this method of combustion. The unit consists of five major pieces: a preheat burner and firebox, the fluidized bed, a direct-contact scrubber for cooling hot gases, a vacuum pump, and a liquor supply system. A schematic diagram of the system is shown in Fig. 5. The particular experimental system used had a pronounced effect on the course of the work and it is worth considering the various parts in some detail.

The heart of the unit is the fluidized bed itself. This is basically a mild steel pipe, 5 feet long and 6 inches i.d. with provisions made for thermocouples, pressure taps, and liquor feed. The bed itself under most conditions was sand. An orifice plate is used at the bottom of the pipe to contain the bed. No expanded freeboard section was provided. Initially, the orifice plate was simply a drilled plate covered with a screen. With this configuration, the system was subject to pronounced flow oscillations which could not be controlled by measures downstream of the bed. It was necessary to restrict the flow of gases entering the bed to maintain stability. A modified orifice plate was designed to achieve this restriction. A detail of this orifice plate is shown in Fig. 6. Since the number and size of the holes in this arrangement was fixed, the pressure drop over the orifice plate was a function of the flow rate and temperature of the gases, and not separately controllable. The bed was designed for semicontinuous operation only. No provisions were made for removal of bed material during operation. The bed area was insulated to minimize heat losses.

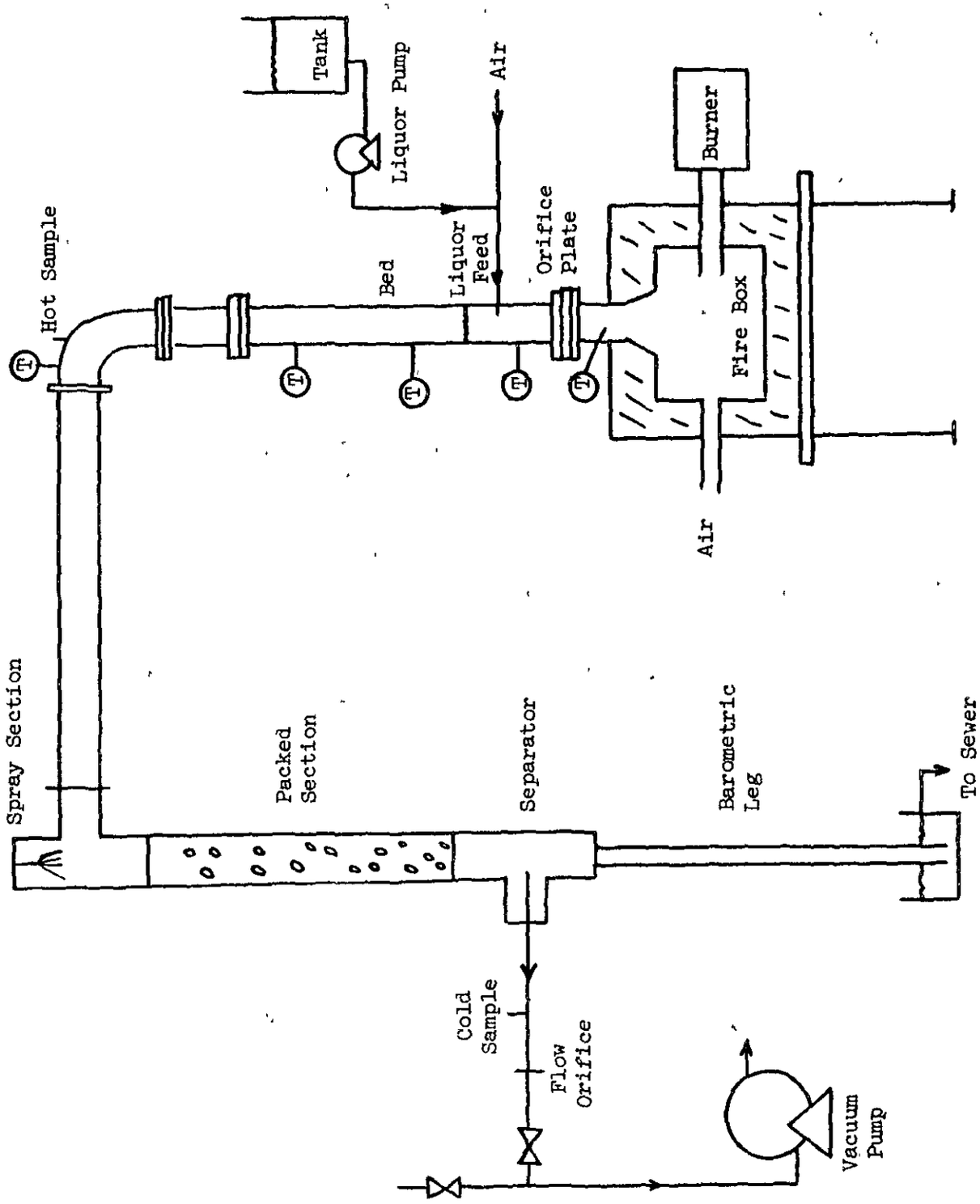
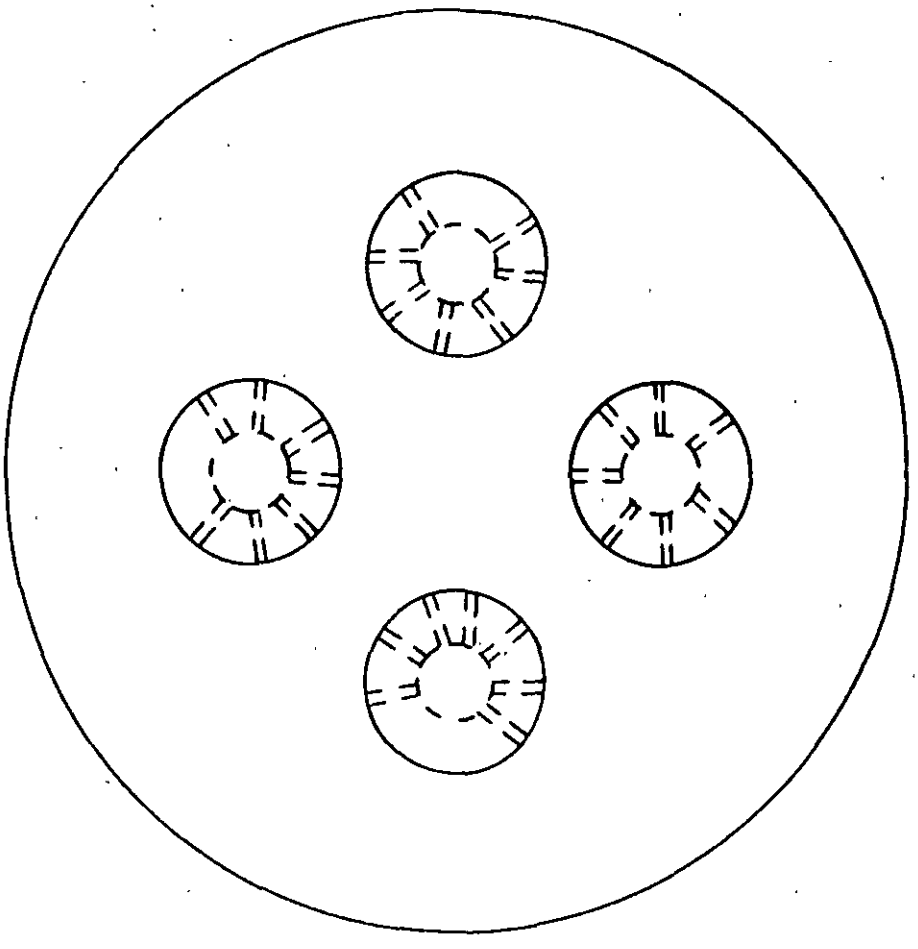


Figure 5. Schematic of Fluidized Bed System



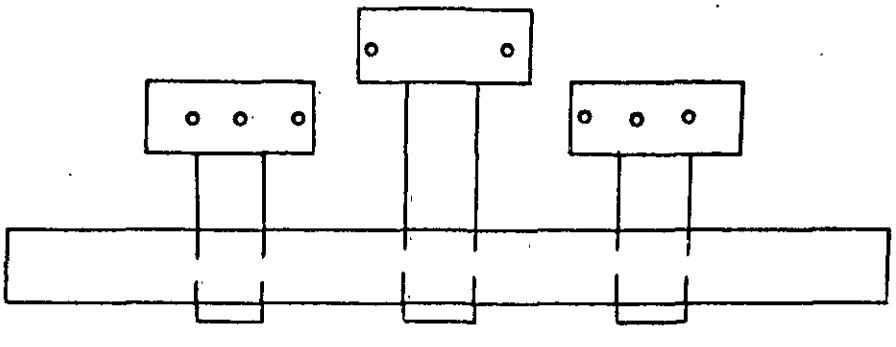


Figure 6. Schematic of Orifice Plate

A natural gas burner and a refractory-lined firebox were used to preheat the air entering the fluidized bed. Direct firing of natural gas was chosen as the method of heating for reasons of simplicity. It was also decided that the preheater should be designed for atmospheric pressure operation in order to use a simple burner and avoid high-pressure gas. This meant that the remainder of the system operated under a vacuum. The firebox is a cylindrical vessel 30 inches high and 30 inches in diameter with a refractory lining 5 inches thick on top, bottom, and sides. A 4-inch pipe to house the burner and a 3-inch pipe for air intake are located 90° apart on the sides of the firebox. A 6-inch pipe comes out of the top of the firebox. The fluid bed unit sits directly on this pipe. The burner is equipped with 3 different sized nozzles and is also partly throttleable. The heat input from the burner can be controlled from about 50,000 B.t.u./hr. to 200,000 B.t.u./hr.

At the top of the fluidized bed is a 6-inch elbow connected to a 6-inch diameter flue which conducts the hot gases to the scrubber-cooler. The scrubber-cooler consists of a spray chamber and a packed section. The packed section is about 5 ft. high and is packed with 1-inch Raschig rings. Cooling water passes downward in concurrent flow through the tower. The water is removed by a barometric leg and the gas is passed through an orifice and flow control valve to a Nash vacuum pump. The height of the barometric leg is about 5 feet and this sets the maximum pressure drop obtainable across the inlet restriction, the bed itself, and the packed tower.

The liquor supply system consisted of a tank containing a steam coil, a pump, control valves and a rotameter, a feed line and a liquor injection probe. The steam coil was used to preheat the liquor and control its temperature. In the initial design, the liquor was fed in at the top of the elbow above the fluidized bed. This proved unsatisfactory as the liquor tended to dry out and char on the walls above the bed. The next step was to modify one of the pressure taps along

the side of the bed to permit insertion of the feedline and inject the liquor directly into the bed. This worked much better, but there was still a tendency for the liquor to char up in the vicinity of the feed probe. Another problem with injecting liquor directly into the bed was a tendency for the liquor to char up inside the feedline and plug it because of overheating. In order to prevent feedline plugging, it was necessary to feed liquor at a higher rate than desired. This aggravated bed plugging problems as char formed faster than it was burned off. The next step was to introduce the liquor into a mixing tee and then force the liquor into the bed as a spray in a small air stream. This gave good distribution in the bed, but was still subject to plugging within the feedline at low liquor rates. In the current design of the feed probe, the feedline is surrounded by a cooling water jacket except at the point where it injects into the bed. A piston pump is used to pump the liquor into a mixing tee and it is blown into the bed with air. A schematic diagram of this system is shown in Fig. 7.

Procedures

The system is made ready for operation by putting in the bed material and bolting the unit together. For most runs, the bed was silica sand of about 20 mesh. Normally, the static bed height was about 12 to 14 inches. Flow of air through the unit is obtained by starting the vacuum pump and adjusting the flow control valves. After the desired flow rate has been established, the natural gas burner is turned on to bring the system up to the desired operating temperature. Normally, about a two-hour warm-up period is needed to achieve steady state. Immediately after the burner is turned on, the pressure drop over the orifice plate restriction rises rapidly as the gas temperature increases. If the rise becomes excessive, total flow must be reduced to permit the cooling water to flow out of the barometric leg at the base of the cooling tower. Once the system steadies out at the desired operating temperature, liquor injection into the bed can begin. The natural gas

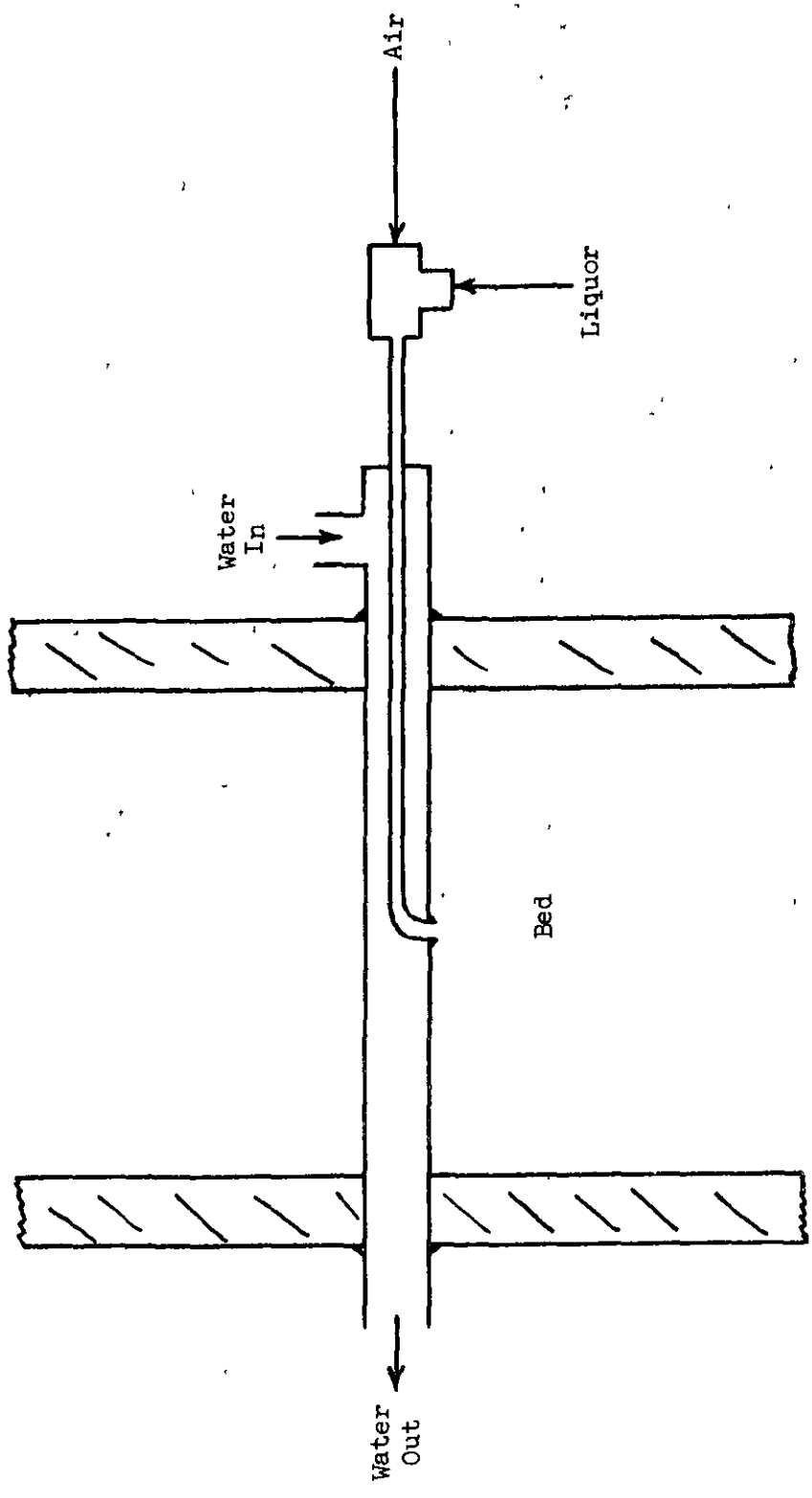


Figure 7. Schematic of Current Feed Device

burner can be adjusted to maintain the desired temperature. Runs with liquor were continued until either a sufficiently long steady-state operating period was obtained or until operating problems forced a shutdown. The latter case was the more frequent. Once the system was shut down, it was allowed to cool and then opened up for inspection.

Measurements which were taken during a run included the following. Gas temperatures were monitored continuously at five points: leaving the firebox just ahead of the orifice plate, one foot above the bottom of the bed, halfway up the 5-foot section, one foot below the top of the 5-foot section, and at the top of the 6-inch elbow. The pressure distribution over the 5-foot section was monitored with a bank of six manometers with the taps evenly spaced along the length. Pressure was also measured in the gas line just downstream of the cooling tower and ahead of the flow orifice. This measurement was needed to apply a pressure correction to the orifice reading. Flow rate of flue gas was measured with an orifice just downstream of the cooling tower. It was also measured with a velometer at the discharge of the vacuum pump. The flow rate of the natural gas was measured with an integrating dry gas meter. The liquor flow was determined by a rotameter. The rotameter was calibrated with the liquor being fired immediately before and after a run. The amount of liquor fired could also be determined by the level change in the tank. Liquor temperature was continuously monitored. The temperature of the water leaving the cooling tower was also measured. Samples could be taken for analysis as needed. Provisions were made for taking gas samples at two locations. "Hot" samples were taken at the top of the elbow above the bed. The samples were pulled through a coil immersed in water in order to cool the gas. Cold samples were taken at a tap between the cooling tower and the flow orifice. Orsat analyses and tests for chloride content were run on these samples.

The data taken were sufficient to allow material and energy balances to be carried out for the runs. Three different approaches to determining carbon removal efficiencies can be used. One method is to use material balances in conjunction with the Orsat analyses and the carbon-hydrogen content of the liquor. A second is through a heat balance using the heating value of the liquor. The third is to determine the residual carbon content of the bed. Each of these methods has its difficulties and all three methods were used to some extent in evaluating completeness of combustion.

Experimental Program

Because of the limited amount of holopulp spent liquor available and because of the expected difficulties in obtaining good data, it was decided that shakedown runs and preliminary experiments should be performed with synthetically prepared liquors rather than actual spent liquor. The initial plan involved the use of sand as bed material for the following series of runs.

1. Sucrose solutions: These runs would be used to check out the liquor feed system, assess the ability to make the necessary material and energy balances, and determine the capacity of the system.

2. Sucrose solutions containing NaOH, Na_2CO_3, and sodium acetate: These runs would be used to determine the effect of the presence of a residual inorganic ash, verify the formation of sodium carbonate, and determine the extent to which inorganics suppressed the combustion behavior.

3. Sucrose solutions containing sodium and chloride: This would involve the liquor from Step 2 plus the addition of NaCl and organic chlorine compounds. It would permit an evaluation of the effect of $NaCl/Na_2CO_3$ mixtures on combustion performance, check out procedures for measuring chlorine emissions, and assess the chlorine emission problem.

4. Actual holopulp spent liquor: This would determine if the liquor could be burned at low temperature and what emission problems occurred.

As the work proceeded and problems developed, this program had to be abandoned. Major difficulties arose from liquor feeding problems and the fact that sodium carbonate reacted with the sand at the combustion temperature to form clinkers. The program then shifted to using sucrose-sodium chloride mixtures to solve system problems and the use of rock salt beds instead of sand. This work progressed far enough to define the conditions needed to burn the spent liquor. A new feed system was put in to permit burning spent liquor, but the first two attempts have been unsuccessful.

Results

The bulk of the work has involved solving experimental difficulties, and the results to date are inconclusive with respect to the objectives of the program. Most of the problems with the loop have been solved. The remaining difficulty rests with the ability to feed liquor continuously at the low flow rates compatible with the capacity of the system at the low temperatures used. It was hoped that the water-cooled feed probe would overcome this problem, but two attempts to use it to burn holopulp spent liquor were unsuccessful as the line plugged within five minutes. Work is continuing, and a separate report covering the bench-scale combustion work in detail will be written shortly.

COMBUSTION SUMMARY

The thermodynamics of the combustion of holopulp spent liquor are favorable. They indicate a nearly quantitative conversion of sodium and chloride in the spent liquor to sodium chloride and sodium carbonate. The only significant volatile chlorine compounds are HCl and NaCl vapor. These should not cause any major problems in commercial-scale combustion as both could be scrubbed from the flue gas by

spent liquor. Laboratory combustion experiments confirmed the thermodynamic predictions. Sodium chloride and sodium carbonate are the combustion products. The volatile chlorine loss in laboratory experiments ran about 1%. This consisted mainly of HCl or NaCl. Heating value determinations indicated that heating values are 15 to 25% below kraft values and are in the range of NSSC liquors. The heating value is high enough to support combustion without auxiliary fuel if the furnace is so designed. Melting points of $NaCl-Na_2CO_3$ mixtures range from 1500 to 1200°F. Low melting points may eliminate fluidized bed combustion in the range between 20% NaCl and 60% NaCl. Bench-scale fluidized bed combustion studies have bogged down in system problems. Conclusive results have not yet been obtained.

OTHER WORK ON RECOVERY

Two other aspects of the recovery problem were investigated. One was the possibility of separating sodium carbonate from sodium chloride by crystallization techniques. If a separation could be achieved, the carbonate could be causticized with lime while the sodium chloride would be electrolyzed. The second aspect was the influence of sodium chloride on causticization. If it can be established that a reasonable separation of NaCl and Na_2CO_3 can be achieved and that the presence of some NaCl does not unduly influence causticization, an option is provided to the use of HCl to convert all Na_2CO_3 to NaCl for electrolytic regeneration. In this case, the most economic solution to a given situation could be employed.

SEPARATION OF NaCl AND Na_2CO_3

The separation of NaCl and Na_2CO_3 depends primarily on the equilibria in the system sodium chloride-sodium carbonate-water. Table XXIII shows such data given by Freeth (1).

These data indicate that there are real possibilities for achieving a separation of sodium chloride from sodium carbonate. Under the pulping conditions currently employed, the ratio of NaCl to Na_2CO_3 is about 3 to 1. Looking at the solubility data, at 30°C. the composition of a saturated solution with both solid phases present is 17.7 g./100 g. Na_2CO_3 and 15.0 g./100 g. NaCl. Thus, the ratio of NaCl to Na_2CO_3 in solution is 0.85. Thus, the way is open to remove the bulk of the NaCl from the mixture. If the amount of water added is just enough to solubilize the Na_2CO_3 or leave a small amount behind, 71% of the NaCl would remain in the solid phase and could be separated out. This could be done in principle by leaching the solid recovered material or by concentrating a solution of the recovered material. The supernatant liquor would contain nearly all of the carbonate plus salt at an 0.85-to-1 ratio. Carbonate could be removed from the liquor by co[illegible]

TABLE XXIII

EQUILIBRIA IN THE SYSTEM SODIUM CARBONATE-SODIUM CHLORIDE-WATER

Temp., °C.	Satd. Soln., g./100 g. Na_2CO_3	Satd. Soln., g./100 g. NaCl	Solid Phase
0	6.6	0.0	$Na_2CO_3 \cdot 10H_2O$
0	4.3	4.5	$Na_2CO_3 \cdot 10H_2O$
0	3.7	8.2	$Na_2CO_3 \cdot 10H_2O$
0	3.1	12.3	$Na_2CO_3 \cdot 10H_2O$
0	2.9	15.6	$Na_2CO_3 \cdot 10H_2O$
0	2.8	20.4	$Na_2CO_3 \cdot 10H_2O$
0	0.0	26.3	NaCl
15	14.0	0.0	$Na_2CO_3 \cdot 10H_2O$
15	9.9	9.9	$Na_2CO_3 \cdot 10H_2O$
15	8.7	14.7	$Na_2CO_3 \cdot 10H_2O$
15	9.2	20.2	$Na_2CO_3 \cdot 10H_2O + NaCl$
15	3.5	24.0	NaCl
15	0.0	26.3	NaCl
20	17.6	0.0	$Na_2CO_3 \cdot 10H_2O$
20	15.5	4.0	$Na_2CO_3 \cdot 10H_2O$
20	14.1	7.7	$Na_2CO_3 \cdot 10H_2O$
20	12.9	12.8	$Na_2CO_3 \cdot 10H_2O$
20	13.5	17.4	$Na_2CO_3 \cdot 10H_2O + NaCl$
20	6.9	22.0	NaCl
20	9.5	20.3	NaCl
20	11.5	18.9	NaCl
20	0.0	26.4	NaCl
25	22.7	0.0	$Na_2CO_3 \cdot 10H_2O$
25	19.6	5.6	$Na_2CO_3 \cdot 10H_2O$
25	18.8	10.8	$Na_2CO_3 \cdot 10H_2O$
25	19.0	11.8	$Na_2CO_3 \cdot 10H_2O + Na_2CO_3 \cdot 7H_2O$
25	18.4	13.0	$Na_2CO_3 \cdot 7H_2O$
25	17.3	15.5	$Na_2CO_3 \cdot 7H_2O + NaCl$
25	7.9	21.3	NaCl
25	0.0	26.4	NaCl
30	28.5	0.0	$Na_2CO_3 \cdot 10H_2O$
30	27.0	3.7	$Na_2CO_3 \cdot 10H_2O$
30	26.9	3.9	$Na_2CO_3 \cdot 10H_2O + Na_2CO_3 \cdot 7H_2O$
30	26.6	4.2	$Na_2CO_3 \cdot 7H_2O$
30	24.6	7.2	$Na_2CO_3 \cdot 7H_2O$
30	22.7	9.3	$Na_2CO_3 \cdot 7H_2O$
30	22.5	10.2	$Na_2CO_3 \cdot 7H_2O + Na_2CO_3 \cdot H_2O$
30	21.9	10.4	$Na_2CO_3 \cdot H_2O$
30	20.5	11.1	$Na_2CO_3 \cdot H_2O$
30	21.2	12.9	$Na_2CO_3 \cdot 7H_2O + NaCl$
30	17.7	15.0	$Na_2CO_3 \cdot H_2O + NaCl$
30	5.0	22.7	NaCl
30	0.0	26.5	NaCl

TABLE XXIII (CONTD.)

EQUILIBRIA IN THE SYSTEM SODIUM CARBONATE-SODIUM CHLORIDE-WATER

Temp., °C.	Satd. Soln., g./100 g. Na_2CO_3	NaCl	Solid Phase
35	32.9	0.0	$Na_2CO_3 \cdot 7H_2O$
35	31.5	2.0	$Na_2CO_3 \cdot 7H_2O$
35	31.0	2.5	$Na_2CO_3 \cdot 7H_2O + Na_2CO_3 \cdot H_2O$
35	30.2	2.9	$Na_2CO_3 \cdot H_2O$
35	25.5	7.1	$Na_2CO_3 \cdot H_2O$
35	16.8	16.1	$Na_2CO_3 \cdot H_2O + NaCl$
35	7.4	21.7	NaCl
35	4.0	24.0	NaCl
40	32.2	0.0	$Na_2CO_3 \cdot 7H_2O$
40	28.2	3.9	$Na_2CO_3 \cdot 7H_2O$
40	24.4	7.3	$Na_2CO_3 \cdot 7H_2O + Na_2CO_3 \cdot H_2O$
40	20.7	11.1	$Na_2CO_3 \cdot H_2O$
40	17.6	14.6	$Na_2CO_3 \cdot H_2O$
40	15.0	17.4	$Na_2CO_3 \cdot H_2O + NaCl$
40	10.3	20.2	NaCl
40	3.6	24.2	NaCl
60	31.8	0.0	$Na_2CO_3 \cdot H_2O$
60	24.0	7.2	$Na_2CO_3 \cdot H_2O$
60	20.2	10.9	$Na_2CO_3 \cdot H_2O$
60	16.6	14.5	$Na_2CO_3 \cdot H_2O$
60	13.9	17.8	$Na_2CO_3 \cdot H_2O + NaCl$

At 0°C., the carbonate solubility would only be about 2.8 or 2.9 g./100 g. Thus, about 85% of the Na_2CO_3 could be removed for separate treatment. The salt solution containing the small amount of carbonate could be combined with the separated salt and sent to the electrolytic cells. If greater degrees of separation or higher purity is desired, multistage operation could be used.

CAUSTICIZATION OF NaCl AND Na_2CO_3 MIXTURES

It has been demonstrated that the combustion of the spent liquor yields a mixture of sodium carbonate and sodium chloride. It has also been demonstrated that the separation of NaCl and Na_2CO_3 may leave a solution containing a mixture of

Na_2CO_3 and NaCl. Information on the causticization of sodium carbonate in the presence of sodium chloride is therefore very useful. Without the presence of sodium chloride, the reaction between sodium carbonate and calcium hydroxide depends on the low-solubility product of Ca^{++} and CO_2^{--} ions, forming calcium carbonate.

$$Na_2CO_3 + Ca(OH)_2 \rightarrow 2NaOH + \downarrow CaCO_3 \ .$$

As the above reaction proceeds, the concentration of NaOH increases; thus the concentration of $Ca(OH)_2$ is no more soluble than the $CaCO_3$ in the solution and an equilibrium is reached. Thus, the conversion of Na_2CO_3 to NaOH cannot proceed to completion, and in the solution both $CaCO_3$ and $Ca(OH)_2$ exist in small amounts. The percentage of conversion, which is defined as the percentage of hydroxides of the total alkalinity, in practice is usually slightly higher than 90%. A series of runs were made with fixed quantities of Na_2CO_3 solution and $Ca(OH)_2$ solution. NaCl was added before causticization and the amounts added in the runs were 0, 20, 40, 50, 60, and 80% by weight of the total amounts of Na_2CO_3 and NaCl, respectively. The mixture of Na_2CO_3-NaCl solution and the $Ca(OH)_2$ solution was heated to 185-195°F., maintained at this temperature for one-half hour with constant stirring, and allowed to settle. The supernatant solution together with the washings of the precipitates was titrated with 0.1N sulfuric acid, following the "two-indicator" method for determination of Na_2CO_3 and total alkali. The results are shown in Table XXIV.

From these results it can be concluded that the presence of NaCl in various portions from zero to 80% bears no appreciable effect on the conversion of $NaCO_3$ to NaOH by $Ca(OH)_2$ causticization.

After the causticization, the dilute caustic solution can be concentrated to 46-49°Bé. corresponding to a specific gravity of 1.47-1.51 for the removal of Na_2CO_3 and NaCl (2). The solubilities of NaCl and Na_2CO_3 in aqueous sodium hydroxide solution are shown in Table XXV (1).

TABLE XXIV

CAUSTICIZATION DATA

Run	NaCl Added, g.	Na_2CO_3 Found, g. Sample 1	Na_2CO_3 Found, g. Sample 2	Percent Conversion Sample 1	Percent Conversion Sample 2
1	0.0	3.66	--	93.7	--
2	20.0	4.07	4.60	93.2	92.3
3	53.3	4.08	4.38	93.8	93.3
4	80.0	4.17	3.95	93.5	93.9
5	120.0	3.61	3.91	94.1	93.6
6	320.0	4.57	4.96	93.3	92.7

TABLE XXV

EQUILIBRIA IN THE SYSTEM SODIUM CARBONATE-SODIUM HYDROXIDE-SODIUM CHLORIDE-WATER AT VARIOUS TEMPERATURES

Temp., °C.	Saturated Solution, g./100 g. Na_2CO_3	NaOH	NaCl	Solid Phase
0	2.4	8.4	17.3	$Na_2CO_3 \cdot 10H_2O + NaCl$
0	2.4	14.3	12.7	$Na_2CO_3 \cdot 10H_2O + NaCl$
0	2.8	16.0	11.2	$Na_2CO_3 \cdot 10H_2O + NaCl + Na_2CO_3 \cdot 7H_2O$
0	2.9	20.5	4.2	$Na_2CO_3 \cdot 10H_2O + Na_2CO_3 \cdot 7H_2O$
0	2.9	19.9	8.5	$Na_2CO_3 \cdot H_2O + Na_2CO_3 \cdot 7H_2O + NaCl$
0	3.4	22.1	4.2	$Na_2CO_3 \cdot H_2O + Na_2CO_3 \cdot 7H_2O + NaCl$
0	2.2	25.1	6.9	$Na_2CO_3 \cdot H_2O + NaCl$
0	1.9	23.0	6.5	$Na_2CO_3 \cdot H_2O + NaCl$
0	1.2	25.8	5.6	$Na_2CO_3 \cdot H_2O + NaCl$
0	0.6	29.2	4.3	$Na_2CO_3 \cdot H_2O + NaCl$
15	9.2	1.5	19.4	$Na_2CO_3 \cdot 10H_2O + NaCl$
15	8.4	5.8	16.2	$Na_2CO_3 \cdot 10H_2O + NaCl$
15	8.7	7.2	14.9	$Na_2CO_3 \cdot 10H_2O + NaCl + Na_2CO_3 \cdot 7H_2O$
15	7.9	10.4	10.5	$Na_2CO_3 \cdot 10H_2O + Na_2CO_3 \cdot 7H_2O$
15	8.7	15.6	2.4	$Na_2CO_3 \cdot 10H_2O + Na_2CO_3 \cdot 7H_2O$
15	7.5	10.6	12.7	$NaCl + Na_2CO_3 \cdot 7H_2O$
15	7.2	12.5	11.7	$NaCl + Na_2CO_3 \cdot 7H_2O + Na_2CO_3 \cdot H_2O$
15	8.2	13.6	9.6	$Na_2CO_3 \cdot 7H_2O + Na_2CO_3 \cdot H_2O$
15	7.9	17.7	3.1	$Na_2CO_3 \cdot 7H_2O + Na_2CO_3 \cdot H_2O$
15	1.9	23.1	7.4	$NaCl + Na_2CO_3 \cdot H_2O$
15	0.2	46.2	0.9	$NaCl + Na_2CO_3 \cdot H_2O$
20	12.8	1.7	16.9	$Na_2CO_3 \cdot 10H_2O + Na_2CO_3 \cdot 7H_2O + NaCl$
20	11.6	9.5	6.9	$Na_2CO_3 \cdot 10H_2O + Na_2CO_3 \cdot 7H_2O + NaCl$
20	12.0	3.6	15.9	$NaCl + Na_2CO_3 \cdot 7H_2O$
20	9.6	8.5	13.4	$NaCl + Na_2CO_3 \cdot 7H_2O$
20	9.6	9.7	12.4	$NaCl + Na_2CO_3 \cdot 7H_2O + Na_2CO_3 \cdot 7H_2O$

TABLE XXV (CONTD.)

EQUILIBRIA IN THE SYSTEM SODIUM CARBONATE-SODIUM HYDROXIDE-SODIUM CHLORIDE-WATER AT VARIOUS TEMPERATURES

Temp., °C.	Saturated Solution, g./100 g. Na_2CO_3	NaOH	NaCl	Solid Phase
20	10.1	12.4	7.5	$Na_2CO_3 \cdot H_2O + Na_2CO_3 \cdot 7H_2O$
20	10.6	15.5	1.9	$Na_2CO_3 \cdot H_2O + Na_2CO_3 \cdot 7H_2O$
20	7.0	12.3	11.9	$Na_2CO_3 \cdot H_2O + NaCl$
20	1.2	25.1	6.6	$Na_2CO_3 \cdot H_2O + NaCl$
20	1.7	46.7	0.9	$Na_2CO_3 \cdot H_2O + NaCl$
25	18.1	1.7	8.6	$Na_2CO_3 \cdot 10H_2O + Na_2CO_3 \cdot 7H_2O$
25	18.3	6.3	3.3	$Na_2CO_3 \cdot 10H_2O + Na_2CO_3 \cdot 7H_2O$
25	15.9	1.7	15.0	$NaCl + Na_2CO_3 \cdot 7H_2O$
25	14.9	8.6	6.4	$Na_2CO_3 \cdot H_2O + Na_2CO_3 \cdot 7H_2O$
25	15.2	11.0	3.2	$Na_2CO_3 \cdot H_2O + Na_2CO_3 \cdot 7H_2O$
25	13.5	4.4	14.1	$Na_2CO_3 \cdot H_2O + Na_2CO_3 \cdot 7H_2O + NaCl$
25	9.1	8.9	13.5	$Na_2CO_3 \cdot H_2O + NaCl$
25	3.1	18.5	9.9	$Na_2CO_3 \cdot H_2O + NaCl$
25	0.3	41.5	1.5	$Na_2CO_3 \cdot H_2O + NaCl$
25	0.3	44.0	1.3	$Na_2CO_3 \cdot H_2O + NaCl$
25	0.5	45.7	1.1	$Na_2CO_3 \cdot H_2O + NaCl + Na_2CO_3$
25	0.2	49.9	1.0	$NaCl + Na_2CO_3$
30	26.7	2.2	1.2	$Na_2CO_3 \cdot 10H_2O + Na_2CO_3 \cdot 7H_2O$
30	23.1	1.5	7.6	$Na_2CO_3 \cdot H_2O + Na_2CO_3 \cdot 7H_2O$
30	22.4	5.2	2.9	$Na_2CO_3 \cdot H_2O + Na_2CO_3 \cdot 7H_2O$
30	6.0	12.4	12.5	$Na_2CO_3 \cdot H_2O + NaCl$
30	0.2	34.6	3.0	$Na_2CO_3 \cdot H_2O + NaCl$
30	0.2	41.8	1.5	$Na_2CO_3 \cdot H_2O + NaCl + Na_2CO_3$
30	0.2	51.3	1.0	$Na_2CO_3 + NaCl$
35	11.0	5.4	15.3	$Na_2CO_3 \cdot H_2O + NaCl$
35	4.6	14.7	11.8	$Na_2CO_3 \cdot H_2O + NaCl$
35	1.4	24.9	7.0	$Na_2CO_3 \cdot H_2O + NaCl$
35	0.3	40.8	1.8	$Na_2CO_3 \cdot H_2O + NaCl + Na_2CO_3$
35	1.0	49.0	1.2	$Na_2CO_3 + NaCl$
45	9.2	6.1	16.7	$Na_2CO_3 \cdot H_2O + NaCl$
45	2.9	18.1	10.8	$Na_2CO_3 \cdot H_2O + NaCl$
45	0.4	33.4	3.8	$Na_2CO_3 \cdot H_2O + NaCl$
45	0.3	37.2	2.7	$Na_2CO_3 \cdot H_2O + NaCl + Na_2CO_3$
45	0.3	38.8	2.4	$Na_2CO_3 + NaCl$
45	0.2	40.4	2.1	$Na_2CO_3 + NaCl$
45	0.5	54.1	1.3	$Na_2CO_3 + NaCl$
60	5.8	9.4	15.8	$Na_2CO_3 \cdot H_2O + NaCl$
60	2.6	18.1	11.3	$Na_2CO_3 \cdot H_2O + NaCl$
60	1.7	22.3	8.4	$Na_2CO_3 \cdot H_2O + NaCl$
60	0.5	33.2	4.3	$Na_2CO_3 \cdot H_2O + NaCl + Na_2CO_3$
60	0.2	52.6	1.7	$Na_2CO_3 + NaCl$

SUMMARY

These data show that the possibility of separating Na_2CO_3 from the NaCl for separate causticization is feasible. This is a promising development because it would eliminate the need to operate electrochemical cells to produce HCl for converting Na_2CO_3 to NaCl. This is bound to have a favorable effect on process economics.

There are several possibilities for achieving the separation. Probably the simplest approach would involve a controlled leaching of the solid recovered material to solubilize the carbonate and leave the bulk of the salt as a solid phase. The carbonate solution so obtained, containing about 0.85 g. NaCl/g. Na_2CO_3, could then be causticized. This salt could be dropped by concentrating the resultant caustic solution. This is especially attractive since a caustic evaporator is already a part of the system if diaphragm cells are used. This approach would be favored if fluidized bed combustion is used since the NaCl and Na_2CO_3 would be recovered in solid form.

A second approach could be used if the NaCl and Na_2CO_3 are recovered as molten smelt and a dissolving tank is used. The separation of the bulk of the NaCl could then be achieved by concentrating the solution and cooling to 30°C. The solution remaining could then be separately causticized. In either of these two approaches, the bulk of the carbonate can be removed by cooling to around 0°C. for causticizing in a nearly salt-free condition.

A more elegant (and complex) system involving several stages and recirculation of liquors could be used to achieve a nearly complete separation of NaCl and Na_2CO_3 if desired. At present, this does not appear necessary.

STATUS OF ClO_2 TECHNOLOGY

At the time that Progress Report Eleven was written, there were some doubts about the technical feasibility of the Chemech process for ClO_2 generation. These doubts were due in the main to a lack of information about details of the Chemech process. A meeting was held with Chemech in June, 1970, to resolve the uncertainties.

A major concern was the type of diluent gas used in the ClO_2 generator. Chemech's patent (Can. pat. 782,574) implied that hydrogen gas was used as the diluent. We were concerned about the safety aspects of a hydrogen-chlorine dioxide mixture. In discussions with Chemech, it was confirmed that they do not use hydrogen as the diluent gas (although they say they ran some tests using hydrogen without explosions). They can use either water vapor or air as the diluent for ClO_2. Water vapor is preferred. Thus, there do not appear to be any inherent safety problems in the Chemech process.

A second question concerned the physical form of the feed to the ClO_2 generator, specifically, whether gaseous HCl or aqueous hydrochloric acid is used. Chemech indicated that the generator could be operated with either gaseous HCl or aqueous hydrochloric acid. They prefer hydrochloric acid because of increased operating flexibility, but can go either way. Use of hydrochloric acid entails a greater steam consumption for the generator. With 33% hydrochloric acid, 3.7 lb. of steam per lb. of ClO_2 are needed. The ability of the system to operate either way is important from the standpoint of integration of the ClO_2 generation step into the rest of the regeneration system. Aqueous hydrochloric acid provides a means of storage and can serve to decouple the ClO_2 generator from the rest of the recovery system. On the other hand, the system can be set up to use gaseous HCl directly, thus saving some steam costs. This flexibility eliminates the need for a chlorine liquefication system.

The temperature in the generator can range up to 110°C., which is the boiling point of the generator solution. The temperature of the gas stream leaving the generator would be governed by the generator temperature and might be expected to range up to 200°F. With water vapor as the diluent gas, the concentration of ClO_2 in the generator gas is about 6-7% ClO_2 by volume. Control of the efficiency of the generator is dependent on the ratio of reactants, temperature, and pH. They are willing to flatly guarantee an efficiency of 90% and are quite confident of the ability to achieve 95% efficiency. There are two aspects to the problem of generator efficiency. Since the efficiency is based on the percentage of chlorate converted to ClO_2, the lower the efficiency, the more chlorate is needed per lb. of ClO_2 and the power usage is increased. Lowering the generator efficiency also causes a significant increase in the amount of chlorine produced in the generator. The relevant reactions are:

$$NaClO_3 + 2\ HCl = ClO_2 + \tfrac{1}{2}Cl_2 + NaCl + H_2O\ , \quad \text{and}$$

$$NaClO_3 + 6HCl = 3Cl_2 + NaCl + 3H_2O\ .$$

At 100% generator efficiency, there is 0.5 mole of Cl_2 per mole of ClO_2. At 95% efficiency, this becomes 0.66 mole of Cl_2/mole of ClO_2, and at 90% efficiency, 0.83 mole of Cl_2/mole of ClO_2. Since the chlorine may be separated from chlorine dioxide by virtue of its limited solubility and recycled, this latter problem may not be serious. Control of generator efficiency would become critical if the gas from the generator were used directly on the wood in the oxidation step. The feasibility of pulping by this method has yet to be demonstrated.

The technology of chlorate production was also discussed with Chemech. The most significant advance has been the development of metal electrodes. These electrodes are a titanium substrate with a noble metal (e.g., platinum-iridium) surface. The metal electrodes are much thinner than graphite electrodes and permit a constant electrode gap. They also require less power at a given current density.

Normal design is at a higher current density than with graphite electrodes in order to provide a more compact cell and to minimize capital costs. Metal electrodes provide much greater design flexibility.

The remaining uncertainty regarding the Chemech process rests with the fact that it has not been put into commercial practice. The process has been piloted, and to our knowledge there are no technical limitations. However, commercial use of the process would certainly increase the confidence in it. There appear to be two major reasons why the process has not been put to commercial use: First, Chemech has concentrated its effort on chlorate technology and the development of metal electrodes. Secondly, the dominant use of ClO_2 today is in bleaching kraft pulp where sulfur-containing generator by-products are not as serious a problem. At the present time, we are confident that the Chemech process could be used in holopulp recovery.

Holopulp recovery is not necessarily tied to the Chemech process for ClO_2 generation. It does require a ClO_2 generation process not based on sulfuric acid. Of the existing processes, the Day-Kesting process is the only one meeting that criterion, and the Chemech version appears to be the most advanced. Events of the past year have not significantly changed this picture.

CONCLUSIONS

The work of the past year has confirmed the validity of recovery concepts hich had been presented earlier. A recovery process based on evaporation and urning of the liquor to produce sodium chloride and sodium carbonate, causticization f the carbonate, electrolytic processing of the chloride, and Day-Kesting ClO_2 roduction appears workable. The process should be essentially closed with a inimum of pollution problems. There should be no significant odor problems. It s believed that the basis for a recovery system has been firmly established. What emains to be done is to solve the detailed engineering problems needed to bring the ystem into commercial reality.

VAPORATION

The work on evaporation has established that the chlorine compounds are ot volatile under evaporating conditions. Negligible amounts of chlorine were ound in the condensates. This finding held true over the pH range from 1.8 to 11. oncondensable gases are odorless and contain negligible amounts of chlorine com- ounds. There should be no pollution problem associated with the presence of alorine in the evaporation step. The evaporation of holopulp spent liquor is not ntirely pollution free. There is a significant BOD load in the condensate. This n be only partly reduced by evaporating under alkaline conditions. This could fect the ability to recycle condensates and could require treatment facilities. e liquor behaves reasonably well during evaporation. There is no strong foaming ndency, nor is there evidence of precipitation. These findings are restricted to quors produced from hardwoods under pulping conditions which give an excess of dium over chlorine.

COMBUSTION

Thermodynamic calculations showed that sodium chloride and sodium carbonate are the combustion products from holopulp spent liquor. They indicated that the only significant volatile forms of chlorine under combustion conditions are hydrogen chloride and sodium chloride vapor. These predictions were confirmed by laboratory combustion experiments. Calorimetric determinations gave heating values in the range of NSSC liquors. The heating value of holopulp spent liquors should be adequate to support combustion without the need for an auxiliary fuel. Bench-scale experiments to determine the feasibility of fluidized bed combustion have been inconclusive. They are continuing.

The amounts of HCl and NaCl vapor produced during combustion are probably too great to permit their direct discharge to the atmosphere. This should cause no great difficulty since they are both readily soluble in water and could be scrubbed from the flue gas. The spent liquor itself could be used for this purpose. A direct-contact evaporator scrubber is very attractive for combustion of holopulp liquor. Such a direct-contact evaporator would not act as an emission source for this system because volatile gases are not released during acidification (at least down to pH 1.8). The device would, instead, minimize emissions by scrubbing HCl and NaCl from the flue gas.

There are valid reasons for using direct-contact evaporation as the sole heat recovery process in holopulp liquor combustion. In the first place, the heating values of holopulp liquors are significantly lower than kraft so that there is less heat available to be recovered. A second problem lies with the corrosive nature of the flue gases and the volatility of NaCl. It could be very difficult to maintain clean heating surfaces and heat recovery equipment could be very expensive to install. A third factor is associated with the desirability of low combustion

temperatures to minimize volatile chlorine compounds. This would also reduce the potential for recovering heat as steam. A final consideration is that the holopulp process as a whole requires much more steam than could be obtained from the heating value of the spent liquor. Auxiliary power boilers would be needed in any event. Thus, the thrust of the design of the liquor furnace might well be toward simplicity, low capital cost, reliable operation, and low emissions. Use of the liquor heating value for direct-contact evaporation also reduces the investment in multieffect evaporators.

At the present time, there are two concepts of holopulp liquor combustion which appear most attractive. Each of these uses a direct-contact evaporator-scrubber as the sole heat recovery device. One is based on recovering the NaCl and Na_2CO_3 in solid form, while the other recovers the material as a molten smelt. Each of these is discussed below.

Fluidized bed combustion appears to be the most attractive method for carrying out the combustion below the melting point of the recovered NaCl-Na_2CO_3 mixture. Such devices are currently operating successfully in the industry on SSC spent liquors. The major question mark about fluidized bed combustion is whether or not the melting point is high enough to permit combustion at efficiencies approaching 100%. Melting points of NaCl-Na_2CO_3 mixtures have been determined in the laboratory. There is a definite region between about 25% NaCl and 60% NaCl where the melting point would be too low for fluidized bed combustion. However, NaCl content above 70% (which is the range expected under current pulping conditions), the melting point approaches that of pure NaCl. Thus, fluidized bed combustion could well be feasible. Attempts to demonstrate this with a bench-scale system have not yet been successful. The system has been in operation for about three months and is still in the shakedown stage. Work is continuing.

The second concept would involve carrying out the combustion at temperatures sufficiently higher than the melting point so that smelt flows freely from the system. This would likely be at about 1600-1700°F. The furnace itself would be completely refractory lined to minimize heat losses and maintain stable combustion. There would be no need to maintain reducing conditions in the furnace, and the air supply could be adjusted accordingly. It may be anticipated that a char bed would exist in the furnace and that a substantial portion of the combustion would take place there. Smelt could be removed in the conventional manner. Flue gases would be conducted directly to the contact evaporator-scrubber. Such a system would seem to have a minimum of problems due to corrosion and salt deposits.

SEPARATION OF NaCl AND Na_2CO_3

Solubility data on the NaCl-Na_2CO_3 system indicate that a separation of salt and carbonate can be achieved with a relatively simple system. Experiments showed that the presence of substantial amounts of salt did not affect the causticizing reaction. The net result is that it appears feasible to causticize the recovered carbonate directly and eliminate the step of using hydrochloric acid to convert Na_2CO_3 to NaCl for electrolysis. The simplest approach would involve leaching the carbonate from the recovered material, causticizing the solution so obtained, and sending the chloride-rich caustic solution to the caustic evaporator in the chlor-alkali loop.

ClO_2 TECHNOLOGY

There appear to be no technical problems to ClO_2 generation. The Chemech process remains the most applicable process for holopulp recovery. There are no reservations regarding its feasibility other than the fact that it has not been put into commercial operation.

ACKNOWLEDGMENT

A project of this magnitude could not be carried out without the assistance of a great many people. Particular mention should be made of Messrs. D. Sachs, O. Kuehl, H. Grady, and C. Piette for their help in setting up the equipment and running experiments. Special thanks go to Mrs. E. A. Cary for typing the manuscript.

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APPENDIX I

DETERMINATION OF TOTAL CHLORINE

The procedure adopted in this study for the chlorine determination is based primarily on the Thompson and Oakdale (4, 5) method. The apparatus is shown in Fig. 8. The samples, either liquid or finely pulverized, were put into the reaction flask and potassium dichromate crystals were added. Concentrated sulfuric acid was than added, drop by drop, through the funnel. The mixture was heated to boiling and the chlorine in the sample was expelled as chlorine gas, which was reduced to the chloride form and absorbed by the $NaOH-H_2O_2$ mixture in the absorption column. The $NaOH-H_2O_2$ solution was analyzed for Cl^- by the Volhard method. For a 250-ml. sample of concentrated spent liquor, 13 g. of potassium dichromate, 30 ml. of concentrated sulfuric acid, 60 ml. of 0.25N sodium hydroxide solution, and 30 ml. of 30% hydrogen peroxide were used. The addition of a couple of pieces of pumice stone in the flash was found helpful.

Samples of sodium chloride solution of different chlorine concentrations were digested, and the total amounts of chlorine in the $NaOH-H_2O_2$ were determined. These runs were used to test the method. The results are shown in Table XXVI.

The arithmetic average of the percentage of detection for all the runs is 96.9%. The resulting points are random and indicate no significant pattern or trend between the percentage of detection and the chlorine concentration of the sample, which ranges from a few parts per million to ca. 15 grams per liter.

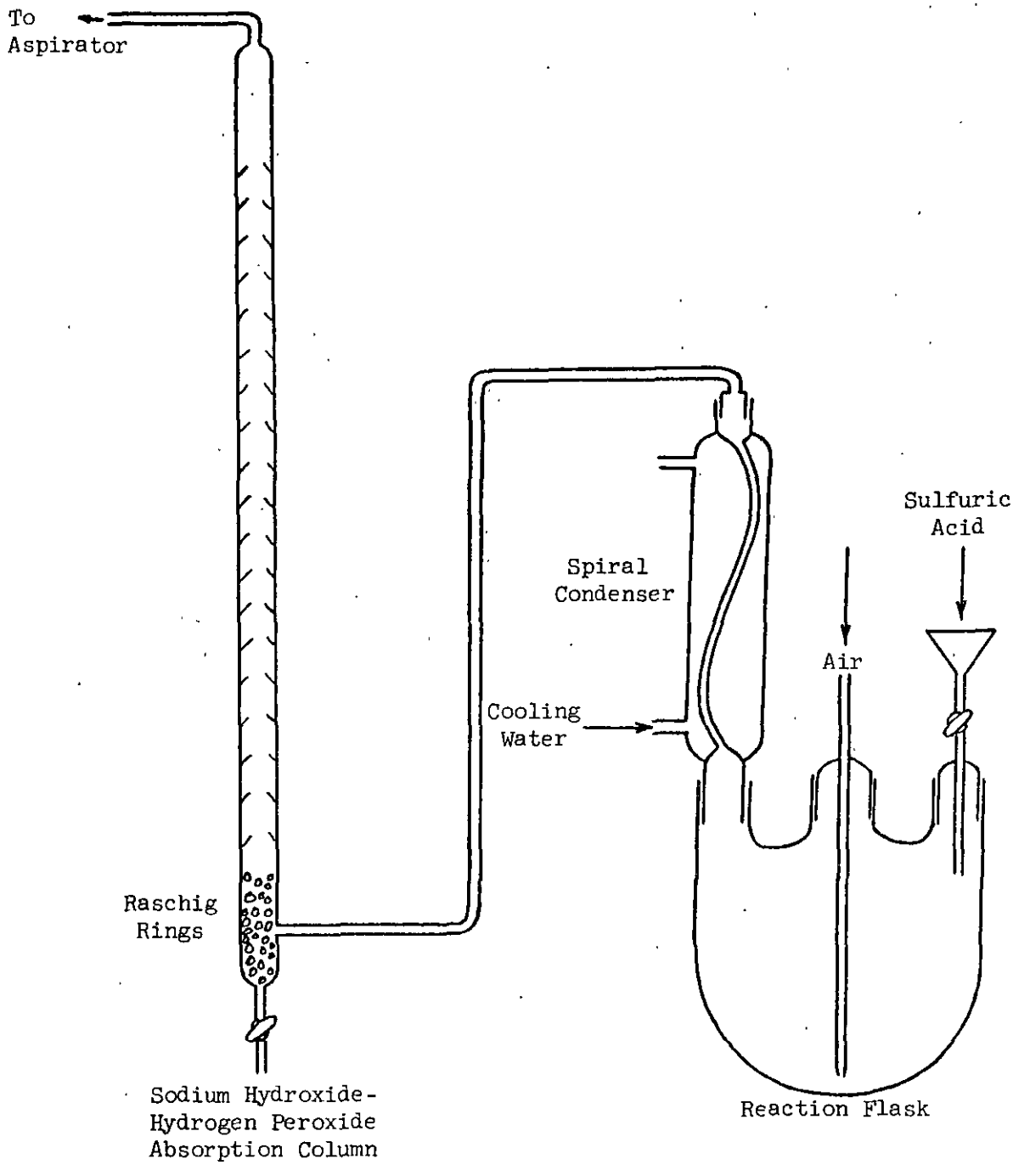

Figure 8. Assembly for Chromic Acid Digestion of Samples

TABLE XXVI

TOTAL CHLORINE CONTENT IN KNOWN SAMPLES BY THE THOMPSON-OAKDALE METHOD

Sodium Chloride	Total Chlorine In, g.	Total Chlorine Detected, g.	Total Chlorine in Scrubber Solution, g./liter	Recovery, %
5 ml. of 0.102N	0.01821	0.01771	0.3641	97.3
20 ml. of 0.1027N	0.07283	0.07110	14.57	97.6
5 ml. of 0.002054N	0.0003641	0.0003249	0.003641	89.3[a]
5 ml. of 0.002054N	0.0003641	0.0003650	0.003641	100.3
50 ml. of 0.002054N	0.003641	0.003494	0.03641	96.0
5 ml. of 0.02054N	0.003641	0.003585	0.03641	98.4
10 ml. of 0.02054N	0.007283	0.007105	0.1457	97.6
25 ml. of 0.02054N	0.01821	0.01835	0.7283	100.8
50 ml. of 0.02054N	0.03641	0.03448	3.641	94.7

[a] Sulfuric acid was added too fast accidentally.