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*Institute of Paper Science and Technology*  
*Atlanta, Georgia*

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**IPST TECHNICAL PAPER SERIES**



**NUMBER 401**

**TRAPPING OF ORGANICALLY-BOUND CHLORINE DURING  
BURNING OF CONCENTRATES FROM ULTRAFILTRATION  
OF BLEACHED-KRAFT EFFLUENTS**

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**OCTOBER, 1991**

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Ultrafiltration of Bleached-Kraft Effluents

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Submitted for presentation at the  
AIChE Annual Meeting  
November 17–22, 1991  
Los Angeles, California

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# TRAPPING OF ORGANICALLY-BOUND CHLORINE DURING BURNING OF CONCENTRATES FROM ULTRAFILTRATION OF BLEACHED-KRAFT EFFLUENTS

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Prepared for presentation at the 1991 AIChE Annual Meeting,  
November 17-22, 1991, "Amelioration of Chlorination Byproducts" session.

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November 1991

UNPUBLISHED

## ABSTRACT

Data are reported showing the fate of organically-bound chlorine during burning of bleach plant concentrates. The concentrates were produced by ultrafiltration of C/D and E1 effluents from a bleached kraft mill and contained 8-20% (weight percentage of dry solids) total chlorine, a substantial part of which was organic. Upon rapid heating in air at oven temperatures of 600-800 °C, the organic chlorine in both C/D and E1 concentrates was converted to chloride. For the E1 concentrates which contained a molar excess of Na over Cl, the organic chlorine was trapped as NaCl, such that approximately 100% of the total chlorine was accounted for in the unburned residue. This trapping was not observed for C/D concentrates having a molar excess of Cl over Na, showing that chlorine trapping is dependent on the molar ratio of Na/Cl. The rate of chlorine trapping was independent of the mass of chlorinated organics and independent of oxygen concentration in the combustion air. The rate increased with increasing temperature.

## INTRODUCTION

Recent studies have shown that ultrafiltration of effluents from chlorine bleaching of kraft pulps may be a viable treatment technology for reducing the rates of water usage and effluent discharge. Laboratory-scale and pilot-scale studies (1-4) and full-scale applications (5,6) have demonstrated that ultrafiltration will remove color, organic carbon, and chlorinated organic compounds from bleached-kraft effluents. A major technical problem associated with the ultrafiltration process is lack of a generally accepted means for concentrate disposal (7).

One disposal alternative is thermal destruction of the concentrate in a device such as a fluidized bed furnace or a rotary kiln. Such burning raises concerns regarding emissions of HCl and chlorinated organic compounds. Trace levels of such compounds, including polychlorinated dibenzodioxins and dibenzofurans, have been measured in the gas and solid emissions of a wide variety of chlorine-containing waste incineration facilities (8). This has resulted in public awareness and concern related to combustion of chlorine-containing materials.

Previous work on characterizing ultrafiltration concentrates (9,10) has shown that ultrafiltration concentrates of C/D stage and E1 stage effluents contain in the range 10-20% chlorine (weight % of moisture-free concentrate), showing the potential for chlorinated emissions. However, previous work has shown that under both combustion (9) and pyrolysis (11) conditions, the organically-bound chlorine is not emitted from the process as HCl as might be expected, but it is converted quantitatively to alkali chlorides. This phenomenon has

been termed chlorine trapping and was attributed to the molar excess of sodium in the concentrate.

In this paper we attempt to further explain chlorine trapping and provide additional quantitative data on the dependency of chlorine trapping on factors, such as temperature, gas composition, sodium-to-chlorine ratio, and bleach stage.

## EXPERIMENTAL

The concentrates used were produced by ultrafiltration of E1 and C/D stage effluents from a bleached kraft mill. Details of the ultrafiltration process have been reported elsewhere (9). The compositions of the concentrates are shown in Table 1. The molar ratio of sodium to chlorine is 2.3 for the E1 concentrate and 0.36 for the C/D concentrate. The C/D concentrate has a higher level of total chlorine. For the E1 concentrate, over half of the chlorine was found to be organically bound. Organic chlorine was determined by AOX.

Measurements of chlorine trapping were made by exposing samples of concentrates to hot air in a preheated furnace. For each determination, a crucible was charged with a known mass of finely ground solids (approximately 50 mg, particle size less than 70 microns). The crucible with sample was placed in the preheated furnace. The floor of the crucible was a fritted piece which retained the particles and allowed air to flow by natural convection through the sample during heat-up. Particle heating occurred due to convection/conduction from the gas, radiation from the surrounding

furnace walls, and heat release from exothermic reactions. Particle heat-up times were estimated to be approximately 15 seconds.

After the desired burn time had elapsed, the crucible and contents were removed from the furnace and cooled. The residue remaining after the burn was dissolved in a known volume of water, and the AOX concentration determined for this solution was used as a direct measure of the amount of organic chlorine in the residue. Similarly, the chloride concentration was determined for the solution by ion chromatography and used as a direct measure for the amount of inorganic chlorine in the residue. The sum of organic chlorine and inorganic chlorine was considered as the total chlorine.

## RESULTS AND DISCUSSIONS

Results from combustion of E1 concentrate are shown in Figure 1. As seen by the solid bars, the amount of organically-bound chlorine decreased sharply as the samples were heated. At all three temperatures, the disappearance of organic chlorine was mirrored by an increased level of inorganic chlorine such that the total chlorine mass in the unburned residue remained nearly constant. Most of the organic chlorine was not converted to HCl but was trapped in the noncombustible ash as inorganic salts, primarily NaCl.

A similar pattern is seen, for the data at all three temperatures in Figure 1, in that the fraction of total chlorine remaining decreases slightly for short combustion times then increases as the concentration of chlorinated organics disappears. It does not seem possible that total chlorine content of the unburned residue increased with greater combustion time. A probable

explanation for this apparent pattern is variability in AOX analyses. The nature of the organic compounds in the concentrate solids will be changed upon heating and may not give the same response in AOX analysis as the organics in unheated samples.

The combustion time required for complete disappearance of the organic chlorine was approximately 50 seconds at 600 °C, 35 seconds at 700 °C, and 15 seconds at 800 °C. The actual combustion time required for disappearance at these temperatures is somewhat less since the time required for heating the sample particles from room temperature to oven temperature was approximately 15 seconds. It was shown earlier (9) that combustion of these concentrates occurs by rapid pyrolysis and volatiles evolution followed by less rapid oxidation of the remaining char (fixed) carbon. Pyrolysis was shown to be complete in approximately 25 seconds at 800 °C and 85 seconds at 600 °C. Thus, the chlorine trapping shown in Figure 1 occurred completely during the rapid pyrolytic stage of combustion, and the time scale of chlorine trapping is similar to or smaller than the time scale of volatiles evolution.

While it is difficult to determine the precise dependency of chlorine trapping rate on concentration of organic chlorine remaining, it is apparent from the data in Figure 1 that the rate was not strongly dependent on concentration. The rate was not seen to decrease with decreasing concentration. At a given temperature, the rate was approximately constant until the trapping was complete.

Additional evidence that chlorine trapping occurs during pyrolysis has been reported by Sasaki et al. (11). During pyrolysis of chlorinated thiolignin at



while NaCl concentrations increase, until essentially all of the chlorine is accounted for as NaCl.

The equilibrium values shown in Figure 3 were determined using a computer program developed at the NASA Lewis Research Center (12) for calculation of complex chemical equilibrium compositions. These calculations were based on the moles of C, H, O, Na, Cl, and S in the fuel (concentrate), moles of O and N in the oxidizer (air), initial energy state (heats of formation for fuel and oxidizer at 298 K), and pressure as input. For these conditions and mole constraints, the composition of products which yielded the lowest free energy state was determined. Over 50 chlorine-containing species were considered as possible products.

## CONCLUSIONS

During combustion of E1 ultrafiltration concentrates, the chlorine-containing organic compounds are rapidly destroyed; and the chlorine is trapped in the unburned residue. This occurs during the early stage of combustion (devolatilization). Trapping of chlorine does not occur during combustion of C/D concentrates, indicating that a molar excess of sodium over chlorine is essential for trapping to occur. The rate of trapping is at least as rapid as the rate of volatiles evolution during devolatilization. The rate increases with increasing temperature, is not dependent on oxygen concentration, and does not show a strong dependency on the concentration of undestroyed chlorinated organic compounds.

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### ACKNOWLEDGEMENTS

Financial support for this work has been provided by NCASI through 301m research funding, by Weyerhaeuser Company, and by the Member Companies of the Institute of Paper Science and Technology.

**TABLE 1. COMPOSITIONS OF  
ULTRATILTRATION CONCENTRATES**  
(weight %, moisture-free basis)

	<u>C/D Conc.</u>	<u>E1 Conc.</u>
C (total)	32.2	42.4
C (carbonate)	0.00	0.24
H	2.38	3.37
O	31.7	34.8
S	2.91	0.58
N	0.10	0.12
Cl (total)	19.4	7.76
Cl (organic)	4.76	4.31
Na	4.49	11.4
K	0.50	0.41
Other Inorganic	3.16	
TOTAL	96.94	100.8
Na/Cl Molar Ratio	0.36	2.26

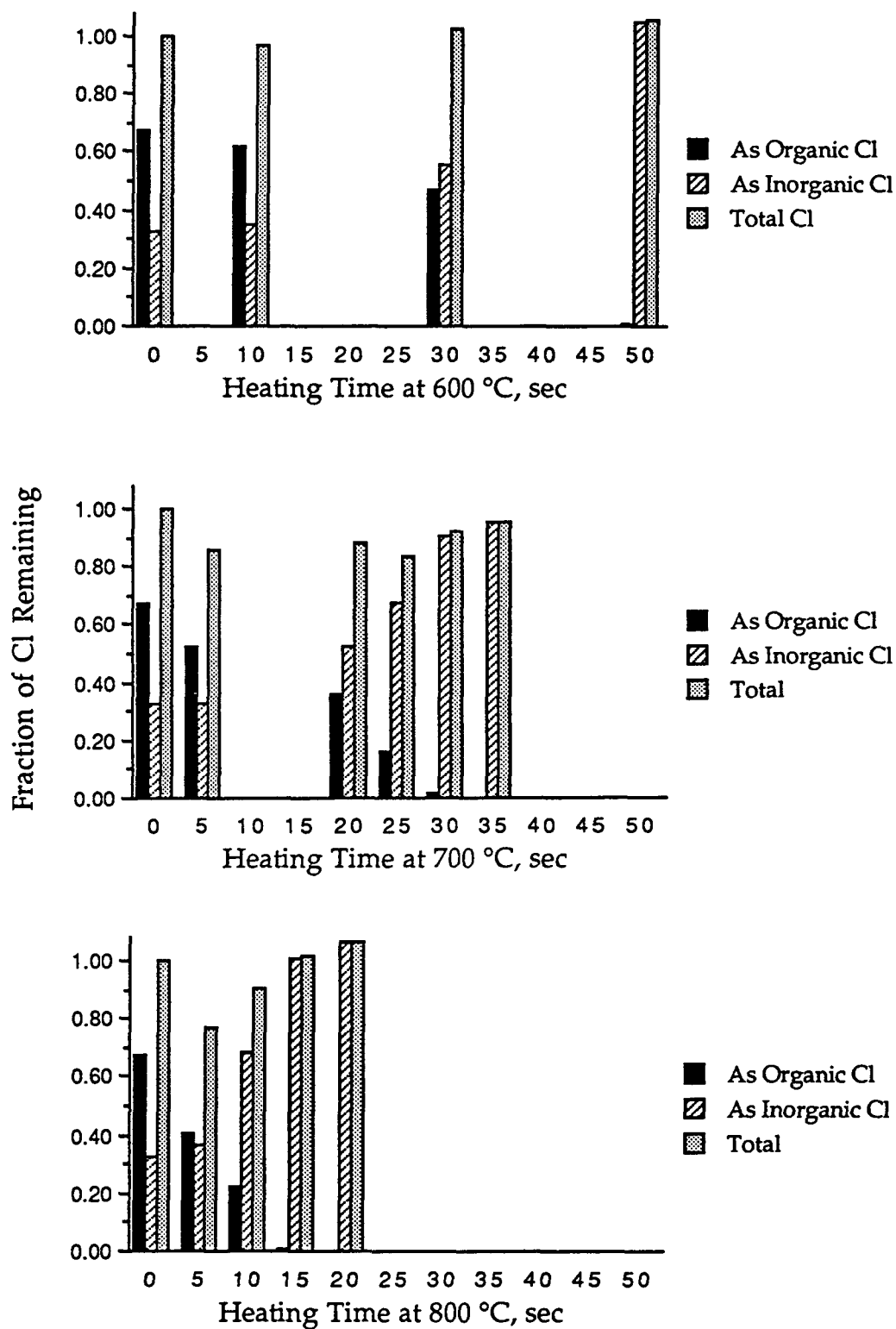


Figure 1. Chlorine trapping during combustion in air of E1 concentrate.

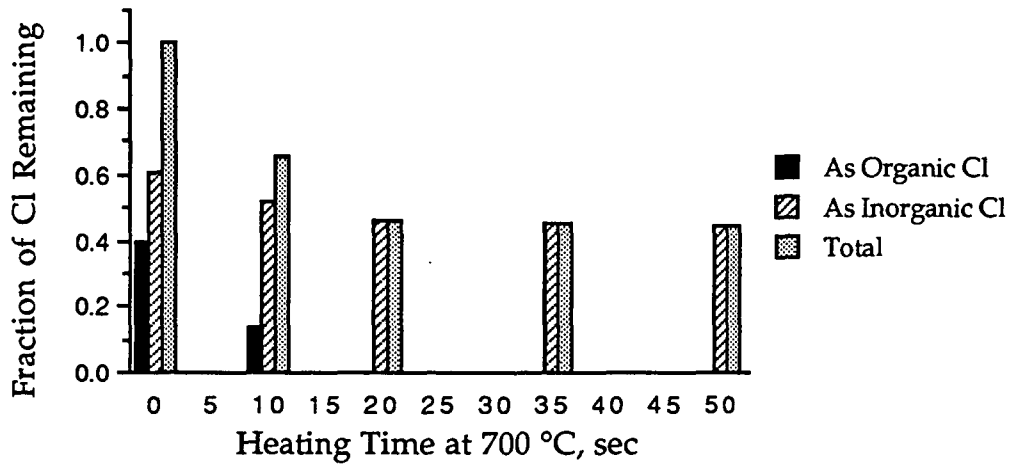


Figure 2. Fate of chlorine during combustion in air of C/D concentrate.

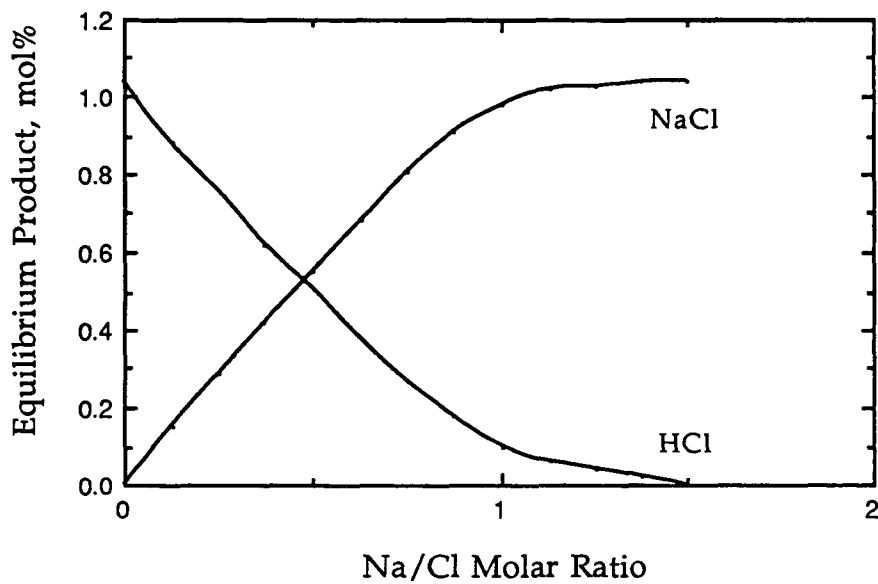


Figure 3. Chemical equilibrium prediction of fate of chlorine.