

Hydrochloric acid emissions from kraft recovery furnaces

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ABSTRACT: Hydrochloric acid emissions from kraft recovery furnace testing involved ten noncontact and four direct-contact furnaces. For NDCE furnaces, stack HCl concentrations correlated well with corresponding stack SO₂ concentrations. This was not true for direct-contact furnaces. Liquor chloride content and stack oxygen content did not affect the level of HCl emissions. On average, only 1.6% of the as-fired liquor chloride converted to HCl. The remainder stayed in the smelt or in the precipitated ash. The paper contains calculated chloride material balances around the furnaces.

KEYWORDS: Emission, hydrochloric acid, kraft mills, materials balance, recovery furnaces, sulfur dioxide, test methods, variables.

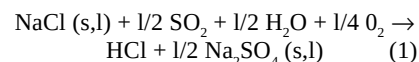
Over the years, mills have worked to reduce recovery furnace particulate emissions and liquor losses. This has caused the concentration of chlorides in various liquors to trend upwards which, in turn, has caused occasional problems with plugging of flue gas passages in kraft recovery furnaces. A small fraction of the chlorides present in the liquor burned in a kraft recovery furnace can convert to hydrochloric acid. This then escapes into the atmosphere with the flue gases. This paper presents the results of tests conducted to characterize kraft recovery furnace hydrochloric acid emissions and

to investigate the factors that play a role in its formation and release. It also presents the results of preliminary material balances to determine the inputs, outputs, and internal flows of chloride in a mill liquor cycle. The study includes 14 furnaces at eight kraft mills—ten noncontact (NDCE) and four direct-contact (DCE). Another publication provides the detailed results (1).

HCl formation in kraft recovery furnaces

The published literature lacks detailed information on the mecha-

nisms of HCl formation in kraft recovery furnaces. Using laboratory simulation experiments, some authors have reported that HCl may form from the reactions in the gas phase between inorganic chlorides present in fume particles (liquid or solid) and SO₂, O₂, and water vapor (2–4). Equation 1 gives this reaction:



One would expect a similar reaction between KCl and SO₂ to occur. Henriksson and Warnqvist (3) studied the kinetics of the above reaction in a laboratory reactor. They proposed for the range of 500–800°C that the rate of HCl formation was proportional to the one-half power of SO₂ and O₂ concentrations and was independent of the H₂O vapor concentration. The results of the actual experiments, however, showed an unexpected influence of mass transfer resistance. The most likely cause was the experimental apparatus (3). Boonsongsup *et al.* (4) conducted a study that included the kinetics of SO₂ capture by NaCl and subsequent release of HCl in a fixed-bed reactor. They showed that the order of the NaCl and SO₂ reaction decreased from 0.67 at the lowest SO₂ concentrations (0.3%) to 0.16 at the highest SO₂ concentrations (1.1%). Because of this gas concentration effect, the authors concluded that SO₂ participated in the rate limiting step of the reaction. Experiments to observe the O₂ and H₂O

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I. Summary of hydrochloric acid emissions from kraft recovery furnaces

Mill code	No. of tests	Furnace type	BLS	Stack flue gas concentrations:				Stack HCl:	
			fired avg. % Cl	Range ppm HCl @ 8% O ₂	Avg. ppm HCl @ 8% O ₂	Range ppm SO ₂ @ 8% O ₂	Avg. ppm SO ₂ @ 8% O ₂	Range lb per ton BLS	Avg. lb per ton BLS
AA1	4	NDCE	0.43	38–48	44.0	113–352	224	0.57–0.72	0.66
AA9	3	DCE (CS)	0.36	3.5–7.3	5.9	48–82	60	0.06–0.13	0.10
BB3	4	DCE (CS)	1.35	25–33	30.2	114–117	116	0.39–0.52	0.47
BB4	3	NDCE	1.29	0.3–0.9	0.5	0.4–0.5	0.5	0.00–0.02	0.01
CC2	6	NDCE	0.45	23–56	36.2	222–326	273	0.30–0.72	0.47
CC3	6	NDCE	0.44	40–56	48.4	219–418	322	0.60–0.84	0.72
DD	3	NDCE	1.05	0.4–1.1	0.8	0.0–0.3	0.1	0.01–0.02	0.01
EE6	2	DCE (CY)	1.04	17–23	19.9	66–67	67	0.26–0.35	0.30
EE7	3	DCE (CS)	1.09	7–9	8.1	11–15	13	0.12–0.15	0.14
FF2	3	NDCE	1.06	0.5–7.6	4.3	0.0–17	7	0.01–0.08	0.05
FF3	3	NDCE	0.96	0.1–0.3	0.2	ND	ND	0.002	0.002
FF4	3	NDCE	1.10	0.1	0.1	ND	ND	0.0008	0.0008
GG	4	NDCE	0.61	12–31	24.1	9–49	30	0.23–0.61	0.47
HH	3	NDCE	0.63	34–52	40.8	46–88	62	0.43–0.65	0.51
AVG			0.85		18.8		84		0.28
MAX			1.35		56.0	418			0.84
MIN			0.36		0.1		ND		0.0008
#			14		14		14		14

CS = cascade DCE
CY = cyclone DCE
Mill CC furnaces fired an 80:20 Kraft:NSSC liquor
ND = not determined

vapor concentration effects showed the reaction rate was independent of both concentrations. These authors also found that between 400–600°C the SO₂ and NaCl reaction rate was very slow. Based on the low activation energy obtained for the reaction rate, Boonsongsup *et al.* (4) proposed an HCl formation mechanism in which the adsorption rate of SO₂ (g) governed the rate of reaction. Using a Langmuir form of isotherm for the adsorption process, they expressed the rate of formation of HCl according to Eq. 2:

$$r_{\text{HCl}} = K_1 \left(P_{\text{SO}_2} \right) / \left[1 + K_2 \left(P_{\text{SO}_2} \right) \right] \quad (2)$$

The authors found agreement between the observed rate data and the proposed form of the above rate equation (4). Based on the kinetic data for the SO₂ and NaCl reaction and an evaluation of previously published data on the sulfation of Na₂CO₃, Boonsongsup *et al.* (4) concluded that the SO₂ capture reactions with NaCl and Na₂CO₃ were not fast enough to account for any significant SO₂ capture at conditions prevailing in the boiler and generator banks. This conclusion implies that nearly all the sulfation of fume

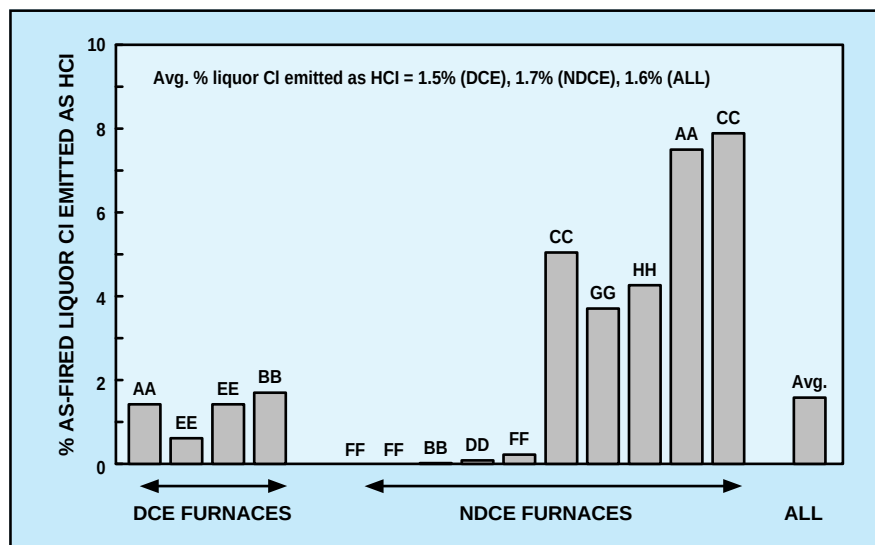
particles or vaporized sodium species in recovery furnaces occurs as reactions in the gas phase in the lower furnace and superheater regions or before the particles solidify. Note that these authors did not investigate the SO₂ and NaCl reaction above the melting point of NaCl. In that region, the mechanisms of reaction may very well be different. The authors concluded, however, that the reactions were fast enough to account for sulfation of deposits in the upper furnace and depletion of chlorides as HCl from these deposits. Bishop (5) reported while burning high chlorine coal in a laboratory combustor that NaCl occurred in the initial deposits

II. Correlation coefficients between stack HCl and other variables for NDCE furnaces

Model	$Y = ax_1 + b$	$Y = ax_2 + b$	$Y = ax_3 + b$	$Y = ax_4 + b$	$Y = ax_5 + b$
r^2	0.946	0.559	0.175	0.521	0.004
Model	$Y = ax_1 + b$	$Y = ax_1 + bx_2 + c$	$Y = ax_1 + bx_2 + cx_3 + d$	$Y = ax_1 + bx_2 + cx_3 + dx_4 + e$	$Y = ax_1 + bx_2 + cx_3 + dx_4 + ex_5 + f$
r^2	0.946	0.952	0.961	0.961	0.962

Y = ppm HCl at stack O_2
 x_1 = ppm SO_2 at stack O_2
 x_2 = % Cl in as-fired BLS
 x_3 = % stack O_2
 x_4 = % Cl in precipitated ash
 x_5 = furnace load ratio
 N = number of data points = 22
 All data correspond to stack SO_2 between 0 ppm and 100 ppm

1. Percentage of as-fired liquor chloride emitted as HCl



on a simulated superheater tube. After four hours, however, there was complete elimination of the NaCl.

Results of tests for HCl emissions

Table I provides a summary of the test results for the 14 kraft recovery furnaces considered in this study. Detailed descriptions of the furnaces tested, measurement methods used, samples analyzed, etc., are available elsewhere (1). The table also shows concurrent emissions of SO_2 . HCl emissions ranged widely—0.1–56 ppm. The average was approximately 19 ppm at 8% O_2 . In units of lb/ton of

black liquor solids (BLS) as-fired, the range was 0–0.84 and averaged 0.28. The conversion from ppm to lb/ton BLS used measured or estimated stack flow rates and measured BLS firing rates. Depending on the use of diaphragm grade or rayon grade caustic for white liquor makeup, the average chloride input to the eight mill liquor cycles in this study was approximately 0.31 lb/ton and 0.60 lb/ton BLS, respectively.

The chloride content of as-fired BLS ranged from 0.36% to 1.35% with an average of approximately 0.85%. **Figure 1** is a bar graph showing the fraction of chloride present in as-fired BLS emitted to the atmo-

sphere as HCl. The fraction of as-fired BLS chloride released to the atmosphere is very small. It averages approximately 1.6% for all 14 furnaces. The gaseous purge of chlorides from the liquor cycle as HCl is therefore very small. One would also expect other purges such as from the white or green liquors to be small owing to the high solubility of chlorides in alkaline liquors. This explains why kraft liquor chlorides undergo a high degree of recycling within the mill. Conversely, one would expect the accumulation or depletion of chlorides in the kraft liquor cycle to occur over a relatively long time.

Impact of process variables on HCl formation

This work investigated the impacts of stack SO_2 concentration, as-fired BLS chloride content, stack O_2 content, chloride concentration in precipitated ash, and furnace load on recovery furnace HCl emissions. The only variable that had a definite impact on NDCE furnace HCl emissions was the concentration of SO_2 in the stack gas (1). For example, **Table II** presents the coefficients of correlation obtained for a simple linear regression analysis between NDCE furnace stack HCl concentrations and the five variables. For the 22 data points for which data on all five variables were available, the SO_2 and

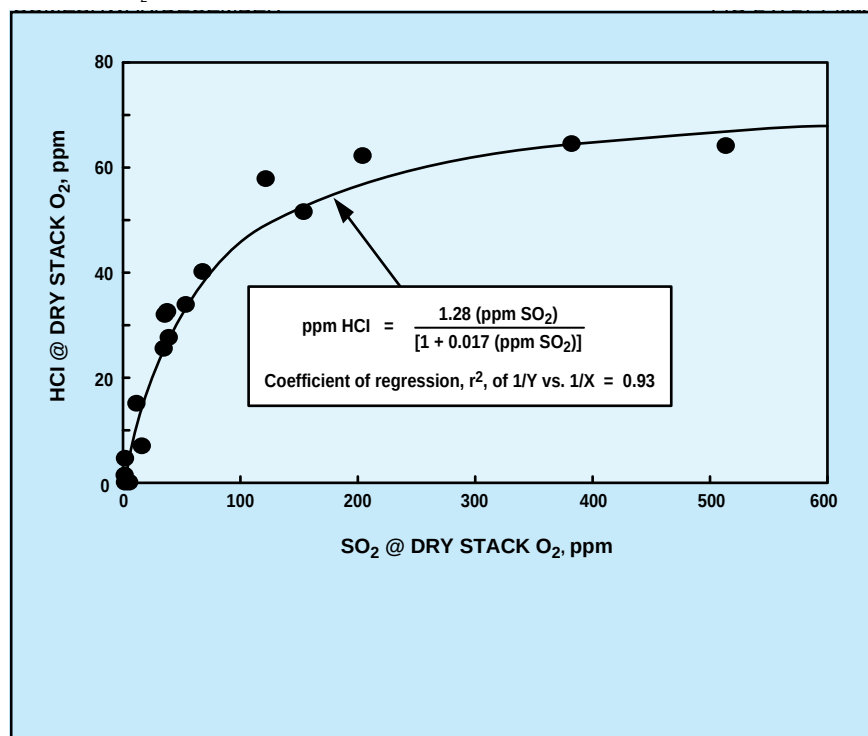
Atmospheric Emissions

HCl correlation is very strong. The correlations of HCl with percentage of chloride in the as-fired liquor and with percentage chloride in the precipitator ash are moderately strong. While the r^2 for HCl vs. SO_2 is approximately 0.946, the inclusion of the other four variables improves this r^2 only marginally to 0.962. For furnaces with DCE, none of the variables had any clear impact. The limited data suggest that stack HCl concentrations at comparable stack SO_2 levels would be far less for DCE than for NDCE furnaces.

Relationship between stack HCl and SO_2

For NDCE furnaces, relationships of linear, power law, and Langmuir form of isotherm between stack HCl and stack SO_2 were investigated. The Langmuir isotherm relationship of Eq. 2 gave the best representation (1). **Figure 2** shows this graphically. In developing the HCl and SO_2 relationship shown in this figure, the data only includes stack SO_2 emissions above 25 ppm. This selection was primarily due to the finding that the relative percentage error for HCl measurement at low stack SO_2 concentrations was quite large. Inclusion of these low SO_2 data points therefore might have an undue impact on the nature of the HCl and SO_2 relationship (1). The choice of 25 ppm as a selection point was entirely arbitrary, however. For 0–100 ppm SO_2 , stack HCl concentrations rise sharply with corresponding SO_2 concentrations. For stack SO_2 exceeding approximately 300 ppm, the rise in corresponding HCl levels is very small. All concentrations are in dry stack O_2 , i.e., stack concentration of O_2 on a dry basis. Data corresponding to the two cross recovery furnaces (kraft and neutral sulfite semichemical) tested at Mill CC showed considerable scatter. These therefore were not components in the development of the HCl and SO_2 relationship for straight kraft NDCE furnaces.

2. HCl vs. SO_2 for NDCE kraft recovery furnaces



3. HCl vs. SO_2 for four DCE kraft recovery furnaces (one cyclone and three cascade)

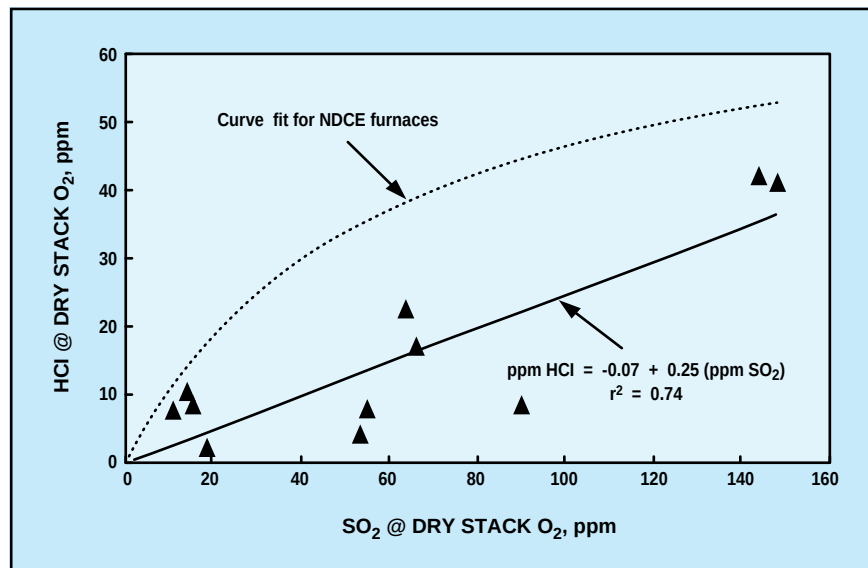
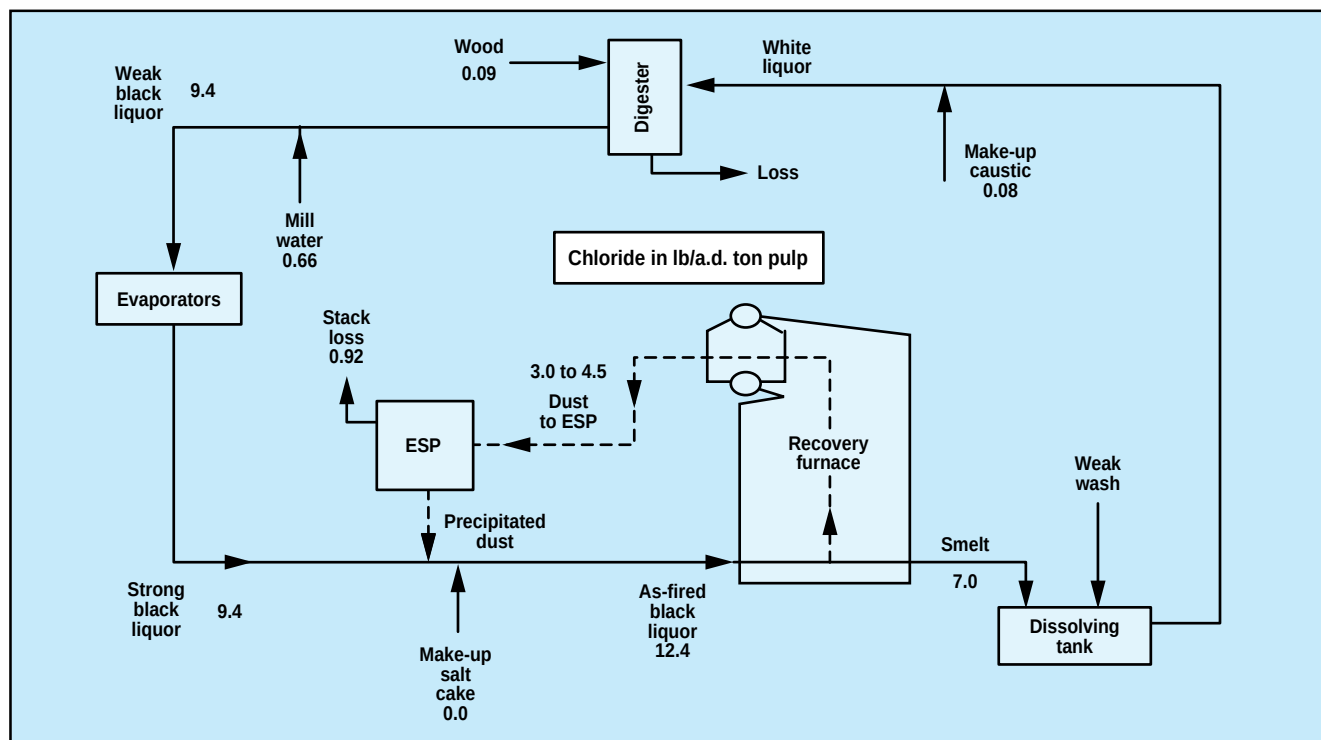


Figure 3 presents a linear regression curve fit between stack HCl and SO_2 concentrations for the four kraft recovery furnaces with DCE tested in this study. For 0–150 ppm SO_2 , the slope of this fit is less than half the slope of the curve fit for NDCE furnaces shown in Fig. 3. This is consistent with the fact that any aque-

ous solution and certainly the alkaline black liquor in the DCE will absorb the more reactive HCl with greater efficiency from the flue gases than SO_2 . The HCl and SO_2 emission data for DCE furnaces in Fig. 3 do exhibit a linear relationship. Note, however, that HCl and SO_2 emission data corresponding to other DCE

4. Example chloride flows in mill liquor cycle for Mill AA NDCE furnace



furnaces tested by mill contractors and available to these authors do not support this trend (1). Factors such as the type of DCE—cyclone vs. cascade—that determine the efficiency of contact of liquor and flue gas in the DCE and alkalinity of strong liquor would complicate the relationship between HCl and SO₂ after a DCE. The data nevertheless suggest for a wide range of corresponding SO₂ emissions that the HCl emissions for furnaces with DCE are significantly less than for NDCE furnaces.

Results of chloride material balances

Analyses for Cl⁻, SO₄⁼, Na⁺, and K⁺ concentrations in black liquors as-fired, green liquors, recycled ESP ashes, black liquors after concentrator or after multiple effect evaporators, and white liquors were carried out. Material balances using these analyses were conducted around the furnace and salt cake mix tank for 13 of the 14 furnaces tested (1). **Figure 4** presents the results of the

material balance calculations for chloride flows around the NDCE furnace at one of the furnaces (Mill AA). **Tables III and IV** provide the results of these calculations for the remaining 13 furnaces. The chloride inputs to the liquor cycle included the wood-pulped, makeup caustic, fresh-water makeup, and salt cake makeup. Chloride and sulfate analyses of liquors, ash, and caustic were done using a modified version of a TAPPI method (6). The chloride content of wood was determined using an oxygen bomb and ion chromatography. Sodium and sulfate analyses of liquors and ashes were obtained using ion selective electrodes.

Table III shows the four chloride inputs and one chloride output (stack) for the liquor cycles corresponding to the 14 furnaces tested. While the chloride input was 0.52–1.56 lb/a.d. ton of pulp, the chloride outputs were quite random at 0–1.14 lb/a.d. ton of pulp. The ratio of output to input of chlorides for the 14 cases ranged from 0–219%. The average was approximately 62% for the eight mills.

Table IV provides the chloride contents in the internal streams within a kraft liquor cycle. The flow streams include strong virgin liquors, as-fired strong liquors, smelt or green liquor, and recycled dust from the collection devices. The range in the estimates for recycled dust is because the results came either from a material balance around the salt cake mix tank or from a balance around the recovery furnace (1). The range is also an indicator of the closure of the balance. Table IV shows that the chloride content in pounds per a.d. ton of pulp in the liquors is much larger than the chloride emitted through the stack. The ratio of virgin strong liquor chloride content to chloride content in stack HCl emissions ranges from 10 to as high as 18,000.

Implications on furnace operations

The relationship between emissions of SO₂ and HCl from kraft recovery furnaces poses a unique problem for

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III. Chloride inputs and outputs in 14 kraft liquor cycles

Mill code	Furnace		Input to liquor cycle:				Total input*	Output:	
			Wood chip	Makeup caustic	Salt cake	Mill water		Cl in stack	Output as
	No.	Type	Cl, lb/ a.d. ton pulp	Cl, lb/ a.d. ton pulp	Cl, lb/ a.d. ton pulp	Cl, lb/ a.d. ton pulp	Cl, lb/ a.d. ton pulp	as HCl, lb/ a.d. ton pulp	% of input
AA	1	NDCE	0.09	0.08	0.00	0.66	0.83	0.92	111%
AA	9	DCE	0.09	0.08	0.00	0.66	0.83	0.14	17%
BB	3	DCE	0.17	0.47	0.01	NA	1.05	0.62	59%
BB	4	NDCE	0.17	0.47	0.01	NA	1.05	0.01	1%
CC	2	NDCE	0.10	0.01	0.01	NA	0.52	0.74	143%
CC	3	NDCE	0.10	0.01	0.01	NA	0.52	1.14	219%
DD	4	NDCE	0.13	0.04	0.01	NA	0.58	0.01	2%
EE	6	DCE	0.14	0.82	0.00	0.60	1.56	0.47	30%
EE	7	DCE	0.14	0.82	0.00	0.60	1.56	0.22	14%
FF	2	NDCE	0.15	0.61	0.00	0.33	1.09	0.08	7%
FF	3	NDCE	0.15	0.61	0.00	0.33	1.09	0.00	0%
FF	4	NDCE	0.15	0.61	0.00	0.33	1.09	0.00	0%
GG	10	NDCE	0.26	0.40	0.04	0.28	0.98	0.85	86%
HH	3	NDCE	0.21	0.40	0.00	0.12	0.73	0.80	110%
Average for 8 mills			0.16	0.35	0.01	0.40	0.92	0.46	62.2%
* For mills BB, CC, and DD, the Cl content in mill water makeup was assumed equal to the average of the other five mills, viz; 0.40 lb/ a.d. ton pulp									

recovery furnace operators. One possible answer to controlling emissions of HCl is to incorporate strategies that minimize the emissions of SO₂. These could include firing of liquors with lower sulfidities or higher solids content, modifying combustion air firing patterns in a way that increases lower furnace temperatures, etc. NCASI asked paper industry personnel familiar with recovery furnace operations to comment on the adoption of these strategies for HCl emission control. The answers identified some potential problems:

- Increased NO_x emissions due to higher temperatures in the lower furnace
- An increase of chlorides in the liquor cycle to a point where detrimental effects such as fouling and plugging occur in the economizer and superheater areas due to the lower melting ashes

- Inability of older furnaces to withstand higher temperatures in the lower furnace without suffering increased risk of corrosion of the lower tube walls and smelt spouts
- Decreased particulate capture efficiencies in electrostatic precipitators due to increased sodium carbonate content
- Increased scaling problems in multiple-effect evaporators due to a buildup in chlorides.

Some mills may also have a limitation on the extent to which liquor sulfidities could be lowered (based on the pulp quality desired) or lower furnace temperatures raised (based on inherent furnace design limitations). In any case, a lowering of HCl emissions will invariably lead to an increase in liquor chloride contents. Alternative strategies for avoiding the increase of chlorides in the liquor include the following:

- Disposing of part of the precipitator catch

- Reducing the input of chloride by switching to diaphragm grade vs. rayon grade caustic for white liquor makeup
- Pursuing technologies for separating chlorides from the precipitated ash.

All these options have significant concomitant cost factors associated with them, however, that would also be site specific.

Summary and conclusions

This work covered the testing of 14 kraft recovery furnaces for HCl emissions to characterize these emissions and understand the major factors that affect them. Stack HCl concentrations correlated only with corresponding SO₂ concentrations. For NDCE kraft recovery furnaces with stack SO₂ concentrations ranging from 0 to 500 ppm, the following relationship provided the best fit:

$$(\text{ppm HCl}) = 1.28 (\text{ppm SO}_2) / [1 + 0.017 (\text{ppm SO}_2)] \quad (3)$$

IV. Internal chloride flows in 14 kraft mill cycles

Mill code	Furnace		Cl in stack as HCl, lb a.d. ton pulp	Internal chloride flows				Chloride accumulation ratio**
	No.	Type		BLIQ as-fired Cl, lb/ a.d. ton pulp	Strong BLIQ Cl, lb/ a.d. ton pulp	Smelt or GLIQ Cl, lb/ a.d. ton pulp	Recycled dust* Cl, lb/ a.d. ton pulp	
AA	1	NDCE	0.92	12.4	9.4	7.0	3.0–4.5	10
AA	9	DCE	0.14	10.4	6.5	6.6	3.7–3.9	45
BB	3	DCE	0.62	36.4	24.9	26.0	9.8–11.5	40
BB	4	NDCE	0.01	47.5	23.4	32.1	15.4–24.1	1623
CC	2	NDCE	0.74	14.7	11.4	9.9	3.3–4.1	15
CC	3	NDCE	1.14	14.4	11.4	9.2	3.0–4.0	10
DD	4	NDCE	0.01	30.9	19.1	24.7	6.2–11.9	1330
EE	6	DCE	0.47	33.3	25.1	23.9	8.2–8.9	54
EE	7	DCE	0.22	34.8	22.3	25.9	8.8–12.5	102
FF	2	NDCE	0.08	34.7	21.5	27.1	7.5–13.1	272
FF	3	NDCE	0.00	31.2	23.0	26.3	4.9–8.2	7315
FF	4	NDCE	0.00	35.8	23.7	25.1	10.8–12.2	17962
GG	10	NDCE	0.85	22.7	15.5	20.5	1.4–7.1	18
HH	3	NDCE	0.80	20.4	18.8	16.5	1.6–3.0	23
Average of 8 mills			0.48	26.2	17.9	19.8	6.6–8.8	

* Cl in recycled ash obtained using balance over salt cake mix tank and over recovery furnace
 ** Defined as the ratio of Cl in strong virgin black liquor to Cl in stack emissions
 BLIQ = black liquor
 GLIQ = green liquor

In Eq. 3, all concentrations are at dry stack O₂. The relationship between (1/ppm HCl) and (1/ppm SO₂) is linear. The coefficient of correlation, r², between (1/ppm HCl) and (1/ppm SO₂) was 0.93. Parameters other than stack SO₂—as-fired liquor chloride content, stack O₂ concentration, and chloride concentration in the precipitated dust—had statistically insignificant effects on HCl emissions. The relationship between stack HCl and stack SO₂ for DCE furnaces was less direct because of absorption of HCl and SO₂ in the

DCE. The data obtained in this study, however, did show that for comparable levels of SO₂ in the stack the stack HCl concentrations for DCE furnaces were always much lower than for NDCE furnaces. Using the measured concentrations of HCl in stack gases, a very small amount of the chloride present in the as-fired black liquor solids (1.6% on average) resulted in HCl emissions. The remainder underwent capture in the precipitated dust or retention in the smelt. 

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