



CHLORINE IN SOLID FUELS FIRED IN PULVERIZED COAL BOILERS – SOURCES, FORMS, REACTIONS AND CONSEQUENCES: A LITERATURE REVIEW

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EXECUTIVE SUMMARY

Because Foster Wheeler NA is supplying and supporting pulverized fuel (PF) boilers producing steam with higher temperatures and pressures, increasing emphasis must be given to potential sources of corrosion and deposition. Further, because Foster Wheeler NA is developing projects involving cofiring of biomass fuels (e.g., wood waste, agricultural materials) with coals from a variety of sources, again corrosion and deposition must be thoroughly investigated. Chlorine frequently is identified as a significant source of corrosion and deposition, both from coal and from biomass, and in PF boilers. Given the pressures to advance to higher steam pressures and temperatures, an investigation of the consequences of chlorine was undertaken. This investigation was designed to highlight the potential for corrosion risks associated with once through units and advanced cycles.

This research took the form of a detailed literature investigation to evaluate chlorine in solid fuels: coals of various ranks and origins, biomass fuels of a variety of types, petroleum cokes, and blends of the above. The investigation focused upon an extensive literature review for papers, book chapters, and other documents dating back largely to 1991. The issues addressed focused upon deposition—slagging and fouling—and corrosion. Issues such as mercury control facilitation, or HCl emissions, are not considered in this review. It is recognized that chlorine can facilitate mercury capture by influencing the oxidation state of mercury (see, for example, Pavlish et. al., [1]; Senior et. al., [2]; Senior, Sadler, and Sarofim, [3]). This, however, is outside the focus of this analysis. Municipal solid waste, and its derivatives, are also not included in this review.

Issues with municipal waste tend to focus on formation of polychlorinated dioxins and furans (see, for example, Everaert [4]), again outside the considerations of this review. The focus is strictly corrosion and deposition.

To address the deposition and corrosion issues, this review evaluates the following considerations: concentrations of chlorine in available solid fuels including various coals and biomass fuels, forms of chlorine in those fuels, and reactions—including reactivities—of chlorine in such fuels. The assessment includes consideration of alkali metals and alkali earth elements as they react with, and to, the chlorine and other elements (e.g., sulfur) in the fuel and in the gaseous products of combustion. The assessment also includes other factors of combustion: e.g., combustion conditions including excess O₂ and combustion temperatures. It also considers analyses conducted at all levels: theoretical calculations, bench scale laboratory data and experiments, pilot plant experiments, and full scale plant experience. Case studies and plant surveys form a significant consideration in this review.

The result of this investigation focus upon the concentrations of chlorine acceptable in coals burned exclusively, in coals burned with biomass, and in biomass cofired with coal. Values are posited based upon type of fuel and combustion technology. Values are also posited based upon both first principles and field experience.

INTRODUCTION

Chlorine, a minor constituent in virtually all coals and all biofuels, contributes to a number of combustion phenomena depending upon concentration. This constituent is also prominent in such opportunity fuels as municipal solid waste and combustible hazardous wastes. Corrosion and deposition are primary concerns; the occurrence and extent of these phenomena depends significantly upon the concentration of chlorine in the fuel, the form of the chlorine in the fuel, and other combustion considerations (see, for example, Stringer and Banerjee, [5]; Vassilev, Eskenazy, and Vassileva, [6]; Yudovich and Ketris, [7]; Baxter et. al. [8,9]). The use of chlorine to oxidize mercury, facilitating its capture and control, is a benefit of this halogen (see Cao et. al., [10]; Cao et. al., [11]; Liu et. al. [12]) not reviewed extensively in this assessment.. Formation and control of polychlorinated dioxins and furans (PCDD, PCDF) is yet another combustion issue associated with chlorine in fuels (see, for example, Liu, Pan, and Riley, [13]). Chlorine, as HCl, can also be a significant contributor to low temperature corrosion in such areas as flues, precipitators, baghouses, and other post-air heater equipment. Deposition and corrosion are the focus of this review. Mercury capture, a pollution control issue, remains outside the scope of this review. Because sulfur clearly suppresses, if not eliminates, formation of PCDD's and PCDF's (Liu, Pan, and Riley, [13]), and because this issue is focused upon municipal and hazardous waste incineration, it—too—remains outside the scope of this review. Low temperature post-air heater corrosion as condensed phase HCl is also outside the scope of this review, since the focus is on the boiler.

Fuels of interest include the various ranks and deposits of coal where environments during the coalification process clearly influence chlorine concentrations in the fossil

fuels. Interest is both in US coals and in off-shore coals (where environments and coalification processes differ significantly from US and North American coals). Fuels of interest also include woody and herbaceous biomass—both of which are proposed either for firing as an exclusive fuel or, more commonly, as a supplementary fuel to coal in utility boilers (see Baxter et. al. [8,9]; Bryers [14]; Dayton et. al. [15]; Frandsen [16]). Crude oil can contain varying concentrations of chlorine; however the refining process typically removes the volatile material before petroleum coke is created. Consequently, while chlorine exists in some petroleum coke samples, it is not commonly a significant constituent in this class of fuels.

Given this framework, this review considers deposition in the following sequence: 1) the concentration of chlorine in fuels; 2) the form of chlorine in the fuels, with focus on chemistry and chemical structure; 3) reactions of chlorine based upon thermodynamic data and laboratory experiments; and 4) experience of large plants with high chlorine fuels. Coals and biofuels are treated separately initially; reactions and experience with cofiring biomass and coal are then dealt with.

SOURCES AND CONCENTRATIONS OF CHLORINE IN SELECTED SOLID FUELS

Chlorine, which exists in varying concentrations in solid fuels, is among the most volatile of the trace elements (Clarke and Sloss, [17]), as is shown in Figure 1. Its volatility, and reactivity, is central to the issues at hand.

Chlorine Concentrations in US Coals

Table 1 summarizes the concentrations of chlorine by province, and by selected region, in the US. The US Geological Survey data, the basis for this table, shows that the maximum chlorine concentration in any US coal is 8760 parts per million by weight (ppmw) or 0.88% in the coal—from the Fire Clay Rider coal bed in Kentucky (Bragg, Finkelman, and Tewalt, [18]). This coal is a Central Appalachian coal of the Hyden formation in the Licking River District (Greenberger, Fiscor, Guzzino, and Sljivar, [19]). The Appalachian Region, followed by the Interior Province (the Illinois Basin and associated deposits), contains the coals with the highest concentrations of chlorine (Bragg, Finkelman, and Tewalt, [18]).

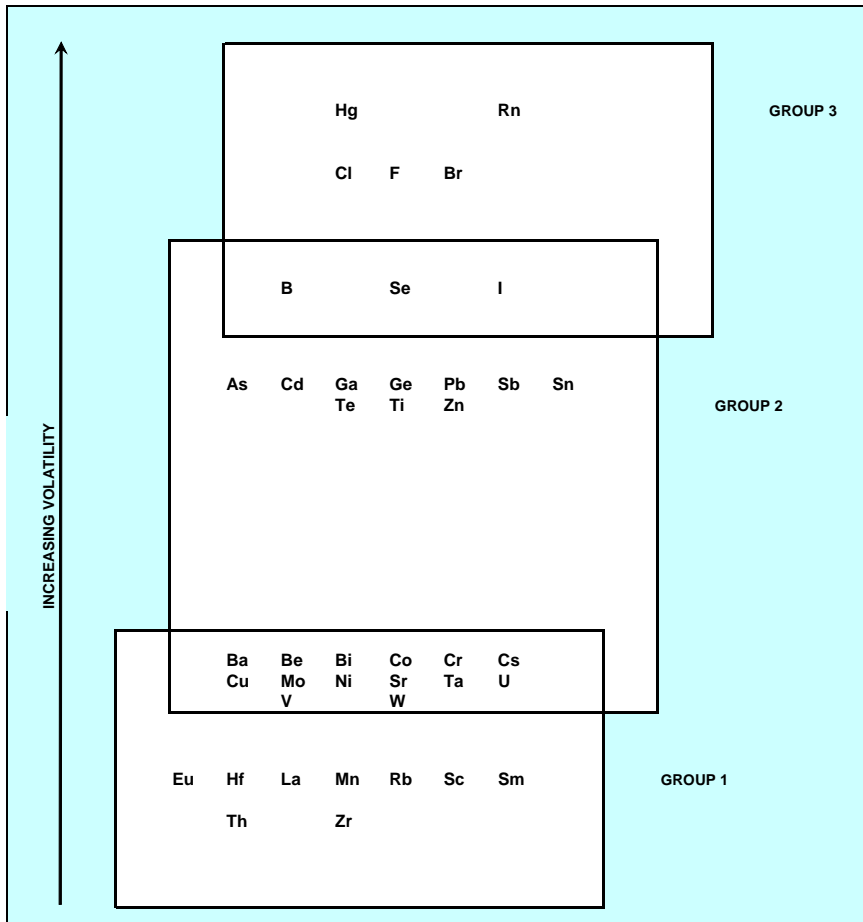


Figure 1. Volatility of Trace Elements Found in Coals and Solid Fuels (from Clarke and Sloss, [17]).

What becomes apparent from Table 1 is the fact that chlorine concentration is, to a significant extent, a function of coal age and rank. The higher concentrations exist in the bituminous coal fields—particularly the Appalachian and Interior Province coal fields. Highest chlorine concentrations exist in coal fields around southern West Virginia and Kentucky; in the Central Appalachian coal fields the mean chlorine concentrations are 1503 ppm in the New River Formation, 1408 ppm in the Kanawha Formation, and 1097 ppm in the Allegheny Formation. The New River and Kanawha formations are in southern West Virginia while the Allegheny Formation is in Pennsylvania.

Interior Province coals also can contain significant concentrations of chlorine. Chou [20] documents the fact that at least half of the Illinois coal reserves which can be mined economically have chlorine concentrations >3000 ppm; many have chlorine concentrations approaching or exceeding 5000 ppm. One coal deposit in the Herrin coal field (Illinois #6 coal) has a chlorine concentration of 7700 ppm. Several deposits in the Springfield coal field (Illinois #5 coal) have chlorine concentrations between 5500 and 6500 ppm.

Table 1. Concentrations of Chlorine in US Coals by Province or Selected Region (values in ppm of the coal on an oven dry coal)

Province/Region	Arithmetic Mean	Maximum	Standard Deviation
Eastern	730	8760	680
Interior	540	3000	600
Pacific Coast	180	560	120
Alaska	150	4900	470
Rocky Mountain	150	3400	300
Gulf	120	900	110
Northern Great Plains	100	1370	100
Appalachian	730	8760	680
Green River	180	3400	420
Powder River	100	1370	120
Uinta	170	2100	230
Texas Lignite	120	900	110
Fort Union	90	350	50
Pennsylvania	160	360	90

Source: Bragg, Finkelman, and Tewalt, [18]

Note that the younger, western, coals have significantly lower concentrations of chlorine. In particular, note that the most economically significant deposits—Powder River Basin, Green River, Uinta, Northern Great Plains, and Texas Lignite all have arithmetic mean values <200 ppm, and several including PRB and NGP have arithmetic mean values of 100 ppm chlorine. The highest concentrations are in the Appalachian coals, followed by the Interior Province/Illinois Basin Coals.

A more detailed set of studies was made, as shown in Tables 2 and 3. These evaluated eastern Bituminous coals and western coals based upon the USGS database (see Bragg et. al. [21]). The USGS database does not include chlorine data for Interior Province (Illinois Basin) coals. Such coals are well known for high chlorine concentrations.

Notice that the Appalachian coals can contain significant concentrations of chlorine—particularly the Central Appalachian coals. Some of the coals from Alabama, Kentucky, Ohio, and West Virginia may be difficult to manage in a boiler with particular attention to deposition and corrosion. Note, also, that the western coals do not contain high concentrations of chlorine. This holds for the western bituminous coals, the subbituminous coals, and the lignites. Rarely do these coals exhibit significant concentrations of chlorine.

Table 2. Chlorine Content of Selected Eastern Bituminous Coals

State	Coal Region	Avg Btu/lb	Avg Cl (ppm)	Max Cl (ppm)	2 nd Max Cl (ppm)*
Alabama	Southern Appalachian - Cahaba	13,500	369	1,500	1,200
Alabama	Southern Appalachian - Warrior	12,628	283	3,300	2,900
Georgia	Southern Appalachian	13,587	872	1,600	1,500
Kentucky	Central Appalachian	12,779	1148	8,800	4,300
Maryland	Northern Appalachian - Castleman	12,824	800	1,100	1,100
Ohio	Northern Appalachian	11,948	730	3,300	2,500
Pennsylvania	Northern Appalachian/Main	12,729	956	2,600	2,400
Virginia	Central Appalachian	13,613	502	2,200	2,000
West Virginia	Central Appalachian	13,398	1262	8,200	2,500
West Virginia	Northern Appalachian	13,064	949	1,600	1,500

*Note: In order to ensure that the maximum Chlorine content was not an outlier, the second highest chlorine content in the population of coal samples was also reported.
Source: Bragg et. al [21]

Table 3. Chlorine Content of Selected Western Coals

State	Coal Region	Coal Type	Avg Btu/lb	Avg Cl (ppm)	Max Cl (ppm)	2 nd Max Cl (ppm)*
Alaska	Beluga	Subbit	8,064	100	100	n/a
Alaska	Nenana	Subbit	7,782	70	n/a	n/a
Colorado	Green River	Bit	10,367	129	1,000	550
Colorado	Uinta	Bit	70,918	100	200	100
Montana	Fort Union	Lignite	6,379	77	200	100
Montana	PRB	Subbit	8,195	88	400	300
North Dakota	Fort Union	Lignite	6,248	110	350	300
Utah	Uinta	Bit	10,358	101	300	200
Wyoming	Hanna Basin	Subbit	9,079	75	140	100
Wyoming	Rock Springs	Subbit	9,325	149	1,200	400
Wyoming	PRB – Powder River	Subbit	8,877	73	100	90
Wyoming	PRB - Sheridan	Subbit	8,367	79	100	93

*Note: In order to ensure that the maximum Chlorine content was not an outlier, the second highest chlorine content in the population of coal samples was also reported
Source: Bragg et. al. [21]

Forms of Chlorine in US Coals

The behavior of chlorine in combustion systems depends, to a significant extent, not only on the concentration of chlorine but also the forms of that chlorine. For US coals, the Appalachian and Illinois Basin coals are of most interest due to their higher concentrations of chlorine. In these coals, chlorine is found mostly in the vitrinite, and less so in other macerals; in other coals, particularly younger coals, the chlorine is more evenly distributed among macerals (Yudovich and Ketris, [7]). Vassilev, Eskenazy, and Vassileva [6] also report the high concentration of chlorine, evenly distributed, in the vitrinite; they also report significantly lower levels of chlorine in the exinite and inertinite macerals.

The Yudovich and Ketris [7] review highlights chlorine in several forms: chlorine in saline coals (e.g., as NaCl), true organic chlorine (Cl_{org}) covalently bonded in the coal macromolecule, and as organically associated chlorine in the form of anion chlorine-adsorbed on the coal organic surface in pores, and being surrounded by pore moisture. The Vassilev, Eskenazy, and Vassileva [6] research also identifies chlorine in both inorganic and organic forms. It identifies the mineral and inorganic forms as halite (NaCl), sylvite (KCl), calcium chloride ($CaCl_2$) magnesium chloride ($MgCl_2$), and ferric chloride ($FeCl_3$). Other chlorine bearing minerals identified by Vassilev and co-workers include chlorapatite ($Ca(PO_4)_3(Cl,F,OH)$) and sodalite ($Na_8(AlSiO_4)_6Cl_2$).

Research reviewed by Sheth et. al. [22] identifies a number of forms of chlorine postulated for US coals. These include inorganic salts, organic chlorides, ion exchangeable chlorides, and chloride ions adsorbed on the pore walls of the coal structure. These researchers conclude that chloride anions adsorbed on the pore walls are probably the dominant form of chlorine in coal. Initial research by Huggins and Huffman [23] was based upon the potential that chlorine could occur in three major forms: inorganic chlorides, organochlorine compounds, and chloride ions in brines and other sources of water associated with coals. One form of chlorine routinely postulated to occur is NaCl crystals deposited from “salty water.” The research by Huggins and Huffman [23] into Pocahontas #3 coal, Illinois #6 coal, and Pittsburgh seam coal utilized X-ray absorption fine structure (XAFS) spectroscopy and X-ray absorption near-edge structure (XANES) techniques. Using these analytical methods, Huggins and Huffman [23] concluded that, with the exception of low chlorine concentrations in Beulah Lignite, chlorine is present largely in a single form, as chloride anions in moisture contained within the coal macerals; a secondary form—as NaCl crystals—also can exist but in minor concentrations. The chlorine content in Beulah Lignite was postulated to be organochlorine. Raask [24] also considers the issue of whether inorganic sodium chloride crystals exist within the coal.

Studies of Illinois Basin coals show chlorine ions to be adsorbed on the inner surface of micropores (Chou, [20] as cited by Peltola, [25]), and that the chlorine anions are anchored on the surfaces of micropores by organic ionic complexes such as quaternary amine groups and alkali carboxyl complexes (Huggins and Huffman, [26] as cited by Peltola, [25]).

The chlorine in lignite—as organochlorine—is not surprising. As will be discussed in a subsequent section, chlorine in the biomass fuels is part of the nutrient cycle (see Baxter et. al., [27]; Baxter et. al., [28]; Dunaway et. al. [29]) and is intimately associated with the structure and composition of the material.

Given the compositional characteristics of the chlorine in US coals, its high reactivity is expected. Baxter [30], reporting chemical fractionation data, shows that 25% of the chlorine in coal is water soluble, and the remaining 75% is ion exchangeable (soluble in ammonium acetate) regardless of rank or location of deposit. Both water soluble and ion exchangeable materials are highly mobile, available, and reactive. None of the chlorine in US coals is reported to remain in the residual material (Baxter, [30]).

Chlorine Concentrations in Off-Shore Coals

Most coals from countries other than the US contain <1000 ppmw chlorine (Spears, [31]) although some regions and nations have coals exhibiting significantly higher concentrations of this halogen. Data are readily available for coals from the United Kingdom, Japan, Bulgaria, and other nations.

The most detailed and complete studies of chlorine in coal have been performed concerning coals of Great Britain (see, for example, Latham, Meadowcroft, and Pinder,[32]; Raask, [24]; Spears, [31]). British coals, as a whole, contain higher concentrations of chlorine than US coals; on average Spears' samples indicated that the average chlorine concentration is 0.44% with high levels exceeding 1% (Spears, [31]). Lagtham, Meadowcroft, and Pinder [32] put the average chlorine concentration in British steam coal at 0.25%, with some seams exhibiting >0.8% chlorine. Chlorine in these coals can be found as organic compounds, as crystalline and amorphous inorganic constituents, in fluid constituents, and as discrete minerals (Spears, [31]). The dominant source of chlorine appears to be the inherent moisture in the coal. Oakley, Minchener, and Hodges [33] state that the initial source of chlorine in British coals was probably seawater entering the deposits during the later stages of coalification, however the chlorine exists largely independently of Na. Again the chlorine is reported to be largely found in inherent moisture in the coal, in the form of anions that may be adsorbed on the coal pore structure.

Vassilev, Eskenazy, and Vassileva [6] studied coals from 34 deposits and identified chlorine concentrations. Representative concentrations are shown in Table 4.

Table 4. Chlorine Concentrations in Some World-wide Coals

Country	Coal	Chlorine Concentration in Coal (ppm)	Chlorine Concentration in Coal Ash(ppm)
Bulgaria	Maritza West	150	290
	Sofia	80	290
	Elhovo	90	210
	Maritza East	200	500
	Bobov Dol	360	1150
	Balkan	150	390
Australia	Ebenezer	370	2910
	Wambo	360	2950
	Blair Athol	440	3930
	Lithgow	480	2250
	Moura	710	6890
USA	Usibelli (Alaska)	90	970
	Black Thunder	200	3190
	Illinois	750	6470
Japan	Taiheiyo	1090	4700
	Akabira	110	220
	Sunagawa	200	660
	Takashima	230	2800
Canada	Coal Valley	140	1370
	Fording River	280	2720
South Africa	Ermelo	260	2430
China	Datong	210	1590
Ukraine	Donbass	500	3420

Source: Vassilev, Eskenazy, and Vassileva [6]

Like all coals, the off-shore fuels show two trends: 1) chlorine concentrations tend to increase with increasing coal age and rank, and 2) the dominant sources of chlorine appears to be in the following: as organic compounds, as impurity components in the crystalline and amorphous inorganic constituents, in fluid constituents, and as discrete minerals. Vassilev, Eskenazy, and Vassileva [6] have identified that significant concentrations of chlorine may be anions in solutions in the inherent moisture of coal structures. Chlorine enrichment in coal may result from favorable coal-forming vegetation (e.g. angiosperms, algae), marine influence (seawater), arid and stable conditions, and volcanic activity. The region of the world, local vegetation conditions, and coalification processes can influence chlorine concentrations in coal. As such the chlorine in all world-wide coals, like the chlorine in North American coals, is readily available, mobile, and reactive.

Of the off-shore coals, the most significant finding concerning the form of chlorine is that it occurs as halite crystals (NaCl) in the brown coal from Germany (see Peltola, [25]). In coal from the Buna deposits of Germany, the halite crystals are found in veins in the

cracks of coal (Peltola, [25]). Otherwise the general description of the form of chlorine in US coals holds for those off-shore coals studied.

Chlorine Concentrations in Biomass Fuels

Chlorine concentrations in the biomass fuels, unlike the chlorine concentrations in coals, are associated with the nutrient cycle and the living portion of the biomass material. Korbee et. al. [34] identifies chlorine as a micronutrient. It plays a catalytic role in the photosynthetic and enzymatic processes and in related plant growth processes. Baxter et. al. ([27], [28]) and other researchers also have identified chlorine as part of the nutrient cycle and, therefore, a significant issue with biomass fuels.

Table 5 identifies typical chlorine concentrations in a range of biomass fuels. Note that, with the exception of wood fuels and a few other biomass forms, the chlorine concentrations are significantly higher in plant materials than in various deposits of coal.

Table 5. Typical Chlorine Concentrations in Biomass Materials Used as Fuel

Biomass	Cl Concentration (% in dry fuel)	Cl Concentration (lb/10 ⁶ Btu)	Typical Moisture Content (%)
Alfalfa stems	0.50	0.623	15
Wheat straw	0.23	0.298	15
Rice hulls	0.12	0.176	20
Rice straw	0.58	0.894	10
Switchgrass	0.19	0.245	10
Switchgrass (2) - WI	0.03	0.0425	11
Bagasse	0.03	0.037	---
Willow wood	0.01	0.012	40
Hybrid poplar	0.01	0.012	40
Softwood sawdust	0.052	0.062	42
Right of way trimmings	0.01	0.027	45
Short rotation poplar	0.01	0.024	45
Almond shells	0.01	0.012	15
Almond hulls	0.02	0.025	30
Olive Pits	0.04	0.043	20
Demolition wood	0.05	0.063	8
Urban wood waste	0.06	0.072	15
Corn stover (1)	0.22	0.282	10
Corn stover (2)	0.72	0.923	10
Corn stover (3)	0.23	0.297	10

Sources: Jenkins et. al., [35]; Miller et. al., [36]; Cunningham, [37]; Tillman, [38]; Tillman, [39]; Robinson et. al [40,41,42]

It becomes readily apparent that the chlorine concentration in field crop materials is, by and large, significantly higher than the chlorine concentration in woody crops. This results from its incorporation into the growth cycle. The exceptions appear to be nut

shells, pits, and switchgrass. The chlorine concentration in the latter is heavily influenced by time of harvest and field storage practices that encourage leaching of the chlorine from the fuel by rain and snow. Field crop concentrations of chlorine may well be influenced by fertilization practices as well as annual growth/harvest cycles.

Like the chlorine in coal, all of the chlorine in biomass is readily available and reactive (see Baxter et. al., [27]; Jenkins et. al., [35]; Dayton [15]; Robinson et. al. [40,41,42]). Further, much of the alkalinity is also readily available and reactive (see Robinson, Junker, and Baxter, [43]). Other fuels such as refuse-derived fuel (RDF) and mixed municipal solid waste also contain concentrations of chlorine. For the waste-based fuels, polyvinyl chloride plastics are a critical source of this material see Su, S., W. Orndorff, W. Xie, W. Pan, J. Riley, K. Anderson, and S. Smith, [44]. Hazardous wastes incinerated for waste management purposes also contain significant concentrations of chlorine.

CHLORINE-BASED CORROSION MECHANISMS

Numerous corrosion mechanisms exist with chlorine in solid fuels. These have been well documented in the literature. These mechanisms have been elucidated for biomass, biomass cofiring, and coal; additionally low temperature corrosion occurs as a consequence of condensation reactions. While low temperature corrosion is not of direct interest to boiler vendors, it is of significance to the client base—to the owners and operators of the fleet of solid fuel-fired boilers.

High Temperature Corrosion Mechanisms

Chlorine is among the most volatile elements in coal; for every 0.1% chlorine in coal, HCl and other chlorine species concentrations in flue gas are typically 80 ppm (Doane, Campbell, and Abbott, [45]). It is the fate of chlorine, and the consequences of chlorine, that is of significance here. Numerous authors have proposed key corrosion mechanisms applicable to PF boilers (see, for example, Bakker et. al. [46]; Chou et. al. [47, 48]; Davis et. al. [49]; McNallan [50]; Monroe et. al. [51]; Takeda [52])

The most commonly identified corrosion mechanism when firing biomass—alone or in the presence of coal—concerns the reactions of chlorine with alkali metals: potassium and sodium. Chlorides form the most stable alkali-bearing species in the gas phase: KCl and NaCl (see, for example, Baxter et. al., [27]; Jenkins et. al., [35]; Nielson et. al., [53]). Of these potassium chloride is the most significant with biomass fuels. Because chlorides are the most stable gaseous species, the initial combustion processes result in the formation alkali chlorides (see Nielson et. al., [53]). These deposit on pendant tubes and other heat transfer surfaces as a highly aggressive, corrosive, materials. The deposits can generate liquid phase corrosion, a highly aggressive mechanism. Corrosion rates for condensed phase deposits are known to be among the most aggressive (Nielson et. al., [53]) with low melting point eutectics such as potassium-iron-chromium compounds. Figure 2 depicts the formation of gaseous chlorine species in combustion processes while Figure 3 shows the thermodynamic forces favoring the initial production of alkali

chlorides, represented by KCl. Figure 3 is based upon research investigating the fate of alkali metals in combustion systems.

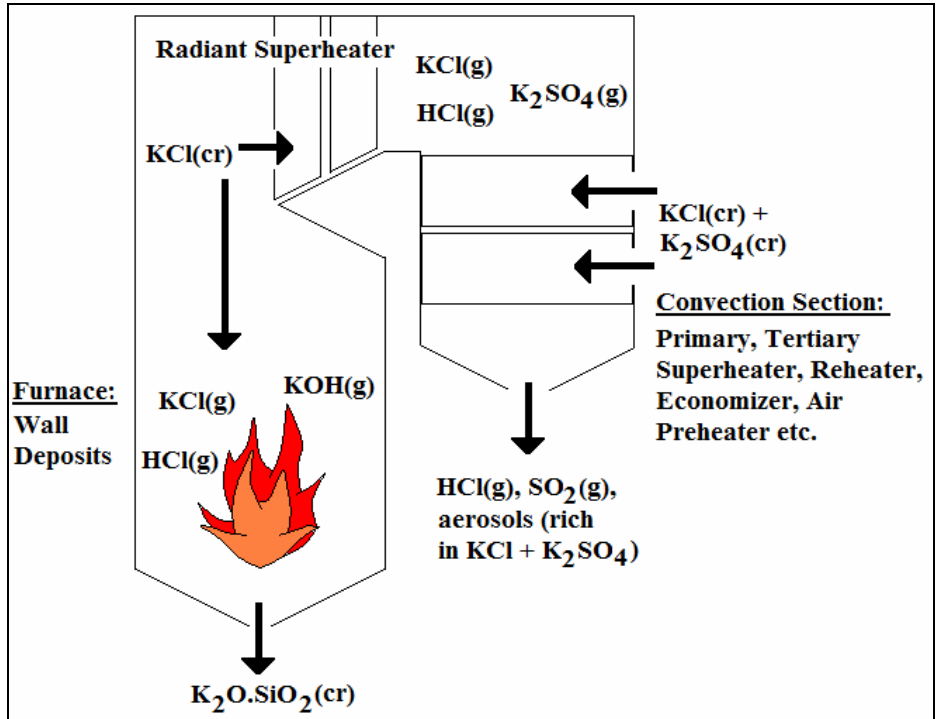


Figure 2. Formation of chlorine-laden gases and alkali gases during combustion processes (source: Nielson et. al., [53]).

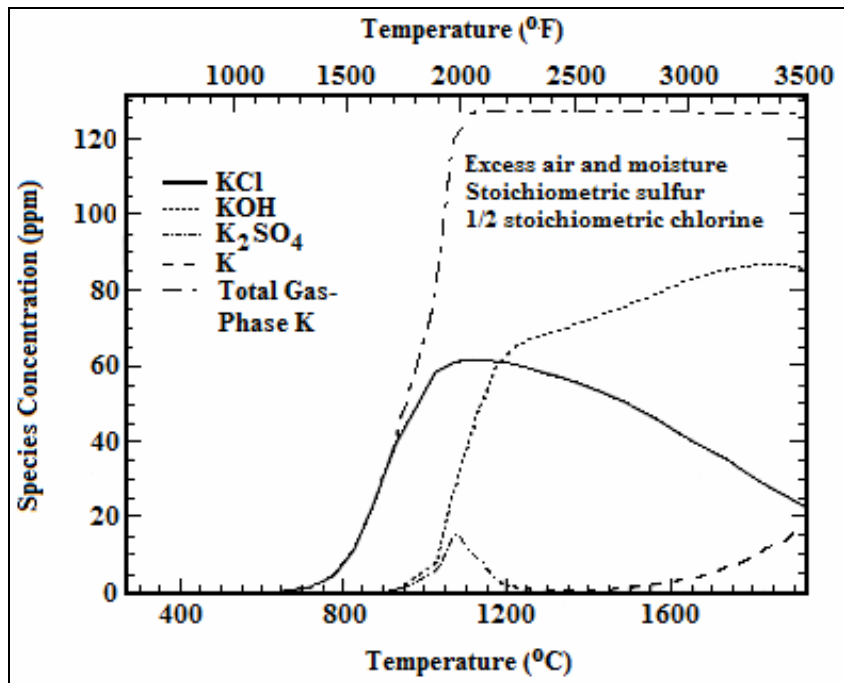


Figure 3. Equilibrium Concentrations of Potassium Species as a Function of Temperature Under Typical Biomass Combustion Conditions (Baxter et. al., [27]).

Thermodynamic calculations can also be made to assess the favored chlorine products as a function of temperature, and as a function of a combustion environment with excess alkali metal or with a paucity of alkali metal. Figure 4 depicts the trade-off between HCl and alkali chloride products as a function of temperature, assuming a combustion environment with a stoichiometric oxygen ratio of 1.2, and with a coal containing 1.6% sulfur. Figures 5 – 7 show the equilibrium products with fuels having sufficient available alkali metal to form alkali chlorides, and with fuels starved for available sodium and potassium. These calculations, made using the NASA combustion code—CET-89 (see, for example, Gordon et. al., [54]; Gordon and McBride, [55])—clearly show that the initial chlorine products that are thermodynamically favored are alkali chlorides if sufficient alkali metals are in the system and if fuel particle temperatures exceed 1900°F. Below particle temperatures of 1900°F, HCl is the favored product regardless of the availability of alkali metals. What becomes interesting from the thermodynamic calculations, also, is the fact that the alkali chloride products are formed first; sulfation reactions follow. The initial products of combustion showed relatively little alkali sulfates despite the surplus of sulfur in the system. The sulfation reaction—displacing the chlorine with sulfur in the alkali compound—is well known and well understood. It clearly follows the formation of initial products of combustion.

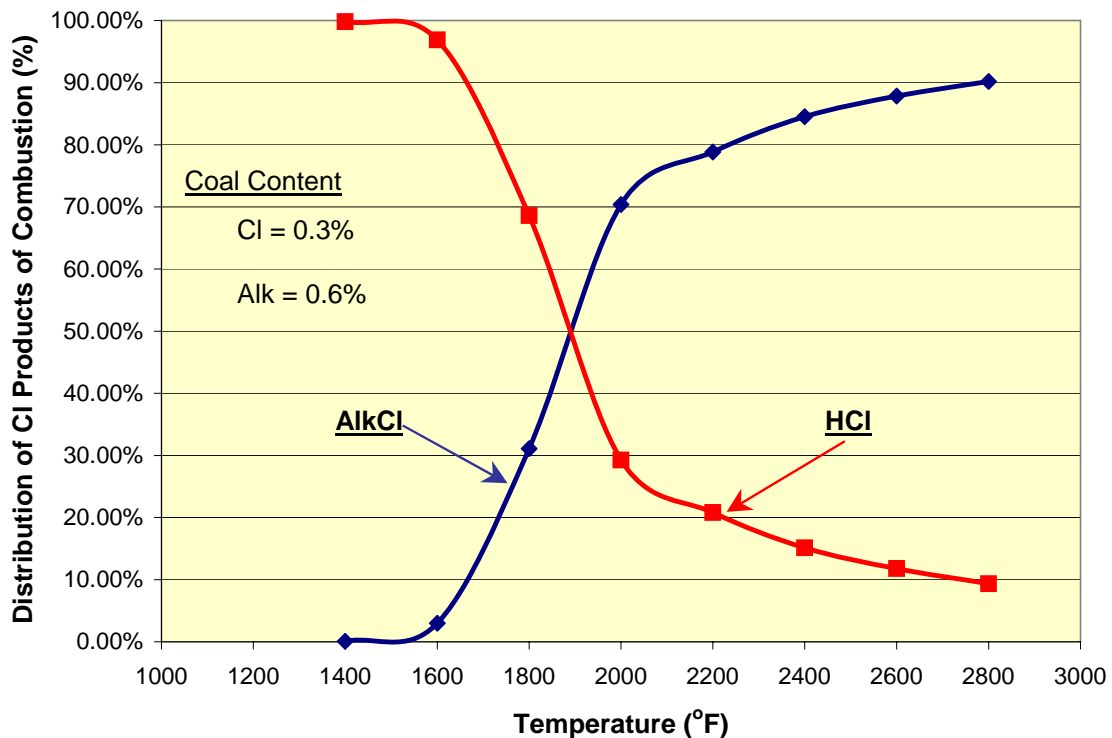


Figure 4. Formation of Chlorine-based Products of Combustion as a Function of Temperature Given Sufficient Available Alkali Metals to Promote Reactions.

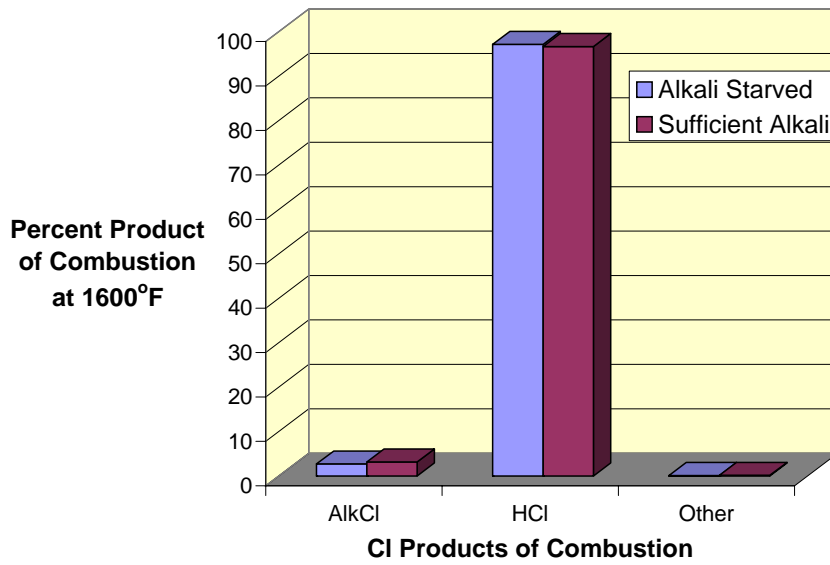


Figure 5. Distribution of Chlorine-based Products of Combustion at Equilibrium with Particle Temperatures of 1600°F.

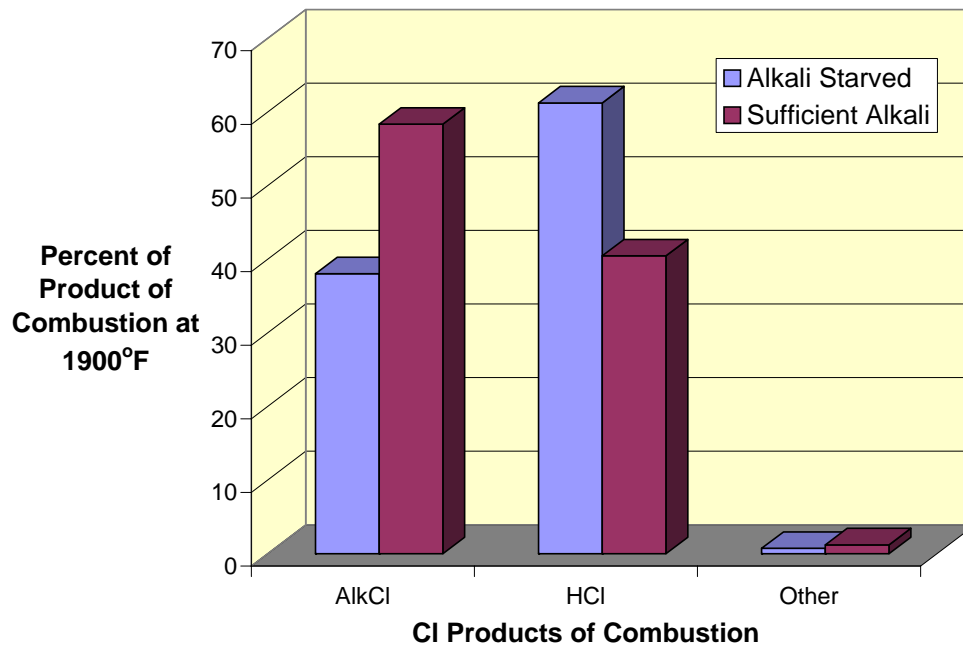


Figure 6. Distribution of Chlorine-based Products of Combustion at Equilibrium with Particle Temperatures of 1900°F.

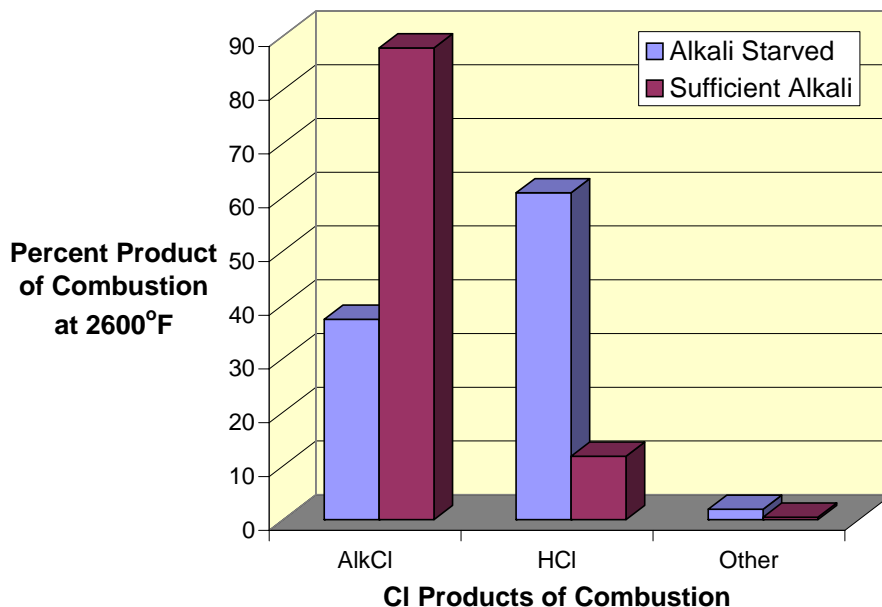


Figure 7. Distribution of Chlorine-based Products of Combustion at Equilibrium with Particle Temperatures of 2600°F.

The alkali chloride corrosion is particularly aggressive in the liquid phase (Lokare et. al., [56]). These reactions take place far more rapidly than the same reactions with solid phase alkali chlorides. While KCl has a relatively high melting temperature, it reacts with iron in the tubes to form low temperature eutectics as shown below (from Lokare et. al., [57]):

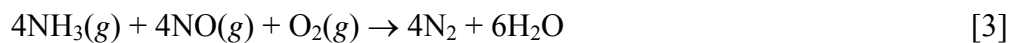
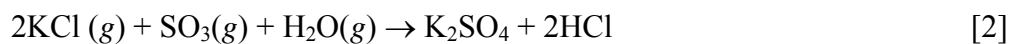
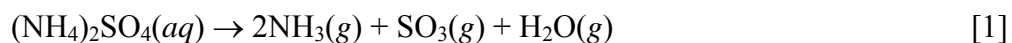
<u>Molten Phase</u>	<u>Melting Temperature (or eutectic), °F</u>
KCl	1425
FeCl ₂	1250
FeCl ₃	570
KCl-FeCl ₂	645 – 740
KCl-FeCl ₃	400 - 430

Similar melting temperatures can be found for sodium-based compounds and eutectics. Given the low melting temperatures of the eutectics, and given conventional boiler tube temperatures, local liquid deposits can form. Subsequent to formation of liquid deposits, and at elevated temperatures, the chlorine compounds readily evaporate and give way to gas-phase corrosion. The most aggressive corrosion—liquid phase corrosion—occurs in a narrow temperature band.

A refinement of this mechanism has been proposed by Frandsen et. al. [58]. This mechanism is based upon the concept that gaseous chlorine attaches where iron and chromium in the boiler tube react with gaseous chlorine to form volatile metal chlorides. The high partial pressure of chlorine close to the metal has been ascribed as the result of in-deposit sulfation of KCl to K₂SO₄. The refinement proposed by Frandsen et. al. [58] is that KCl forms a melt with K₂SO₄ and various iron compounds, and that the sulfation reaction proceeds rapidly in this melt. This refinement provides an explanation of the shift in corrosion behavior as a function of temperature. When the metal temperature (of the boiler tube) exceeds the lowest melting point in the KCl/K₂SO₄/iron compounds system, the sulfation of the KCl proceeds rapidly generating the high partial pressure of Cl₂/HCl and results in accelerated oxidation and corrosion of the metal tubes (see, also, Nielsen, Frandsen, and Dam-Johansen, [59]).

The formation of alkali chlorides, followed by sulfation of the alkali chlorides, are reactions that are well known for biomass fuels (see, for example, Baxter et. al., [60]; Frandsen et. al., [58]; Lokare et. al., [56]; Lokare et. al., [57]). Equally well known is the set of reactions between KCl and sulfur—particularly as SO₃. Under oxidizing conditions the sulfur displaces the chlorine in a sulfation reaction, producing alkali sulfates and HCl. The alkali sulfates, while far from inert, are much less corrosive than the alkali chlorides. Skog et. al. [61], for example, use mass gain as a function of time to measure corrosion rates. Within 24 hrs they document a mass gain of 1.2 mg/cm² with 304L at 600°C (1110°F) when subjected to KCl. At the same time the mass gain when subjected to K₂SO₄ was an order of magnitude less. The mass gain when subjected to K₂CO₃ was about 0.7 mg/cm² in 24 hrs at 600°C (Skog et. al., [61]). Figure 2, shown previously, depicts the entire process in a typical boiler (from Nielson et. al., [53]).

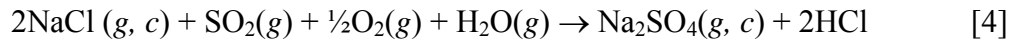
Because this reaction is well recognized and well proven, Vattenfall AB has developed and patented an additive—ChlorOut—consisting of an aqueous solution of ammonium sulfate to manage chlorine-induced corrosion (see Bronstrom et. al., [62]). The reactions associated with this process are as follows:



The process reportedly achieves both sulfation of the potassium [Rxn-2] and NO_x reduction [Rxn-3] with the latter using the conventional SNCR reaction (Bronstrom et. al., [62]). Rxn-2 is the basic process described above as well. Using sulfation to control corrosion, however, assumes that the HCl formed in Rxn-2 evolves *away* from the metal tube surface and exits into the gas stream. Interestingly, prior work to recover potassium-based seeding in the magnetohydrodynamics (MHD) cycle shows that the ammonium may also play a favorable role in chlorine management (Sheth et. al., [22]). The ChlorOut additive does show some potential in this arena; more trials are necessary to completely prove the product.

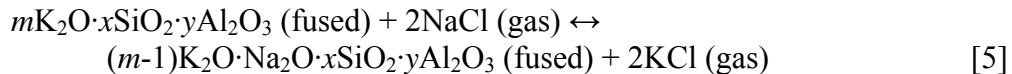
With respect to the injection of sulfur additives such as ChlorOut, the experience of SO₃ injection for particulate conditioning to enhance the performance of electrostatic precipitators is instructive. SO₃ injection works—up to a point. Beyond certain injection concentrations, the added SO₃ does no good. It does not condense effectively on the flyash particles and does not penetrate completely to where it satisfies the conditioning need. Past a certain concentration, the SO₃ passes through the system without causing the desired reactions. There is a window of success depending upon concentrations of all reactants, and temperatures at both the injection point and the flyash interaction point. (Nordstrand, [63]). The limits to SO₃ injection associated with flyash conditioning for precipitator performance merit careful consideration when sulfur injection for chlorine management is attempted; the processes are different but analogous.

The process of sulfation can also be depicted for sodium-based fuels as well (Iisa and Lu, [64]):



In the gas phase, Rxn-2 and Rxn-4 proceed rapidly, with rates limited by the availability of SO₃. In the condensed phase, however, the sulfation reactions proceed more slowly (Iisa and Lu, [64]). Driving these reactions, particularly the critical Rxn-2 or Rxn-4, depends upon the S/Cl molar ratio, and requires a significant excess of sulfur. The intensity of corrosion is more dependent upon available alkali than available chlorine; the chlorine not reacting with potassium or sodium can be expected to form hydrogen chloride.

The influence of chlorine on available alkali—particularly potassium—is more significant than simply reaction with highly reactive alkali. Conn [65], performing research on fouling at one installation in Canada firing a high chlorine coal, identified that the chlorine can mobilize potassium from limestone and from clays, increasing the concentration of alkali metals in the combustion system. One mechanism that may be responsible for this phenomenon, identified by Conn, is the exchange reaction with vapor phase sodium chloride previously identified by Raask [24]:



The mechanism identified in Rxn-5 has been shown to be prevalent with British coals, where chlorine is present as sodium chloride. The installation in question is located in Nova Scotia, by the ocean; it has fired coals mined from under the ocean. Yet another mechanism for mobilizing potassium—particularly from biomass fuels—is the reaction of HCl with aluminosilicates (see Baxter et. al., [27]). Again the chlorine plays a significant role in increasing the potassium content of the gaseous products of combustion—ultimately resulting in deposits. These deposits may then react with available SO₂ or SO₃ to form alkali sulfates, depending upon the availability of sulfur in the system.

Figure 8, from Baxter et. al. [60] and from Lokare et. al. [56], shows that increasing the available sulfur/chlorine molar ratio to high values reduces the corrosion potential to a low state. While the thermodynamic equilibrium for the sulfation reaction and the formation of alkali sulfates from alkali chlorides is favorable when the lb-moles of sulfur exceed the lb moles of alkali chlorides, kinetics and transport phenomena require a very high molar ratio to eliminate chlorine from the system and reduce the corrosivity of the deposit (Lokare et. al., [56]). As the chlorine content in the fuel increases, the sulfur content must also increase significantly. This ratio, however, is normally very high for coals; consequently chlorine is frequently not observed in corrosion deposits; alkali sulfates are frequently found, however. This supports the research of Skog et. al. [61].

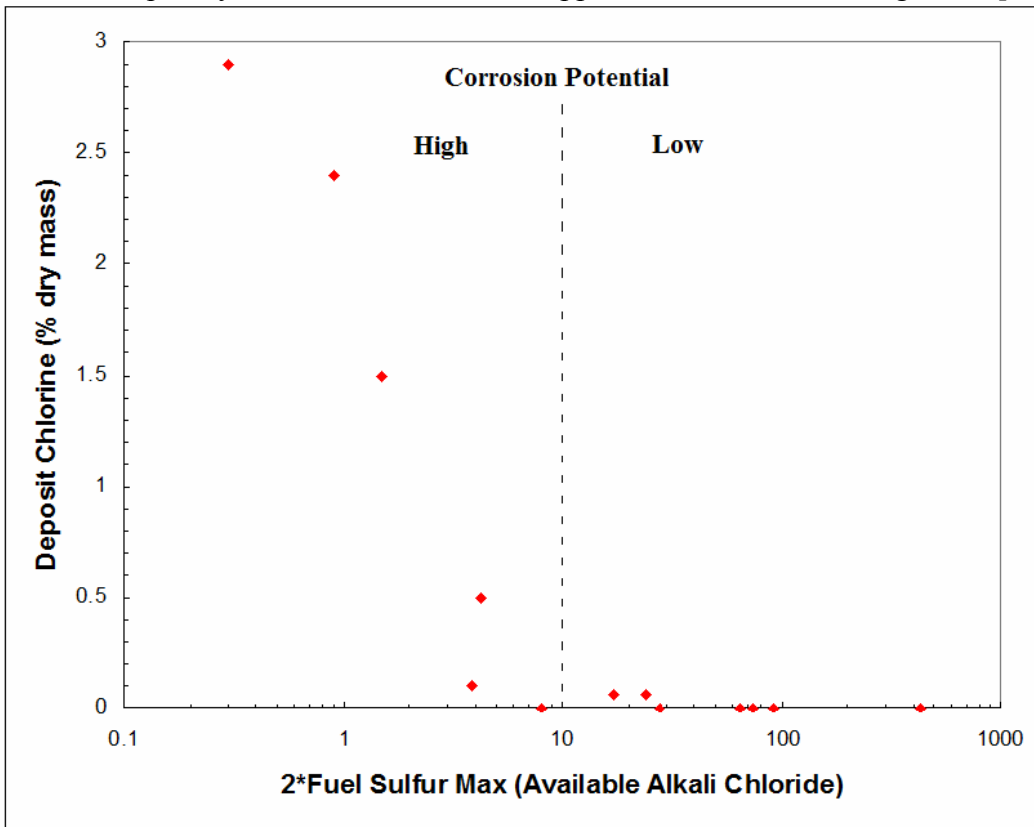
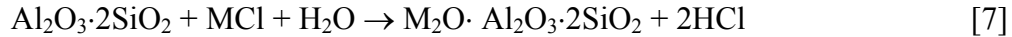


Figure 8. Influence of Available Sulfur on Chlorine Content in Deposits and Corrosion Potential (from Lokare et. al., [56])

The mechanisms described above have been developed with respect to biomass and biomass cofiring applications. However, given the nature of low rank coals—lignites and many subbituminous coals—it is not unexpected that these mechanisms can apply to such solid fuels as well. While these are low chlorine fuels, it is common for such PRB subbituminous coals to be blended with higher Btu/high chlorine bituminous coals from the Appalachian or Interior Province coal fields. There are few low rank coals with high potassium contents sufficient to be concerned either with the deposition mechanism or the use of sulfation to manage that mechanism.

The liberation of chlorine from alkali chlorides can proceed by other mechanisms as well. Aho and Ferrer [65] show that aluminum silicates release water at 750 – 1100°F and form an amorphous mixture called meta-kaolinite as shown in Rxn [6]. The meta-kaolinite then reacts with the alkali chlorides to release HCl as shown in Rxn [7].



Where M represents either potassium (K) or sodium (Na). This release of HCl in the gas phase, while not benign, produces far less aggressive corrosion than the alkali chloride deposits (Aho and Ferrer, [65]; Aho and Silvennoinen, [66]).

Other high temperature chlorine-based corrosion mechanisms also exist; some based upon the very reactions shown above. Daniel [67] states that high chloride and alkali concentrations existing simultaneously—in an environment with low sulfur concentrations—will form stable deposits that cause very high corrosion rates as indicated above. This is common to biomass and waste firing, not coal firing.

The alternative high temperature mechanisms involve either HCl or Cl₂. Significantly, the HCl either generated directly or formed by Rxn-2 can then cause high temperature corrosion by reacting with the iron in the boiler tube according to the following reactions (from Stanko, [68]):



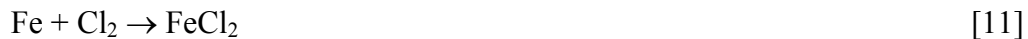
Or



In the presence of O₂ (from excess O₂ in the gaseous combustion products) Cl₂ can be formed by the following reaction:



The Cl₂ can then react directly with the boiler tube according to the following reactions:



And



In the presence of excess O₂, necessary in combustion systems, the FeCl_x compounds can then be converted to oxide form as shown below. In the process, the chlorine is regenerated to continue the attack in a self-sustaining manner (Stanko, [68]):



And



Given Rxn-2 and Rxn-4, when the gases generated pass inward towards the metal tube surface, Rxn-8 – Rxn-14 can proceed as a consequence of sulfation reactions.

In the presence of excess oxygen—in typical combustion settings—these corrosion mechanisms are considered to be active oxidation processes. In the absence of chlorine, or alkali chlorides, boiler tubes form a thin oxide layer that resists subsequent oxidation and corrosion. Oxygen can not penetrate through the oxide layer to the metal below. Chlorine, however, can penetrate the oxide layer, driving reactions [8] through [14]. The metal chlorides diffuse back towards the bulk gaseous combustion products due to the tube metal temperatures driving evaporation, resulting in tube wastage. The metal chlorides subsequently form metal oxides that weaken the scale layer. The chlorine attack develops a loose scale that readily sloughs off, exposing the metal below to continuous chlorine and oxygen attack. Cl_2 has the ability to diffuse through the oxide layer and form metal chlorides (see Rxn-11 and Rxn-12). Alternatively HCl penetrates through the oxide layer and drives Rxn-9 and Rxn-10. The metal chlorides, in the vapor phase, diffuse through the oxide layer and react with oxygen creating metal oxides and regenerating chlorine gas (Nielson et. al., [53]). The result is metal wastage. Again, however, the alkali chlorides discussed previously—particularly the molten alkali chlorides—are considered to be the most aggressive agents for corrosion and deposition if allowed to persist as deposits on heat transfer surfaces.

Such mechanisms include the Deacon reaction and the subsequent formation of SO_3 and HCl as shown below (from Liu, Pan, and Riley, [13]):



Rxn [16] is known as the Deacon Reaction and it is most favored, in the forward direction, at 1110°F (600°C). It is the initial driver in promoting sulfur capture by use of chlorine. Interactions between HCl and SO_2 (see, also, Xie et. al., [69]; Liu, Pan, and Riley, [13]; Furimsky and Zheng, [70]) highlight the fact that HCl can promote sulfur capture.

Low Temperature Mechanisms

In addition to high temperature mechanisms, owners of power plants must be concerned regarding low temperature corrosion mechanisms. These are largely the result of condensation of HCl in the presence of moisture in the flue gas. Figure 9 presents the

dew point of HCl as a function of temperature, H₂O concentration in the gaseous combustion products, and HCl concentration. Note that condensation of HCl to liquid hydrochloric acid occurs at temperatures of about 105 – 140°F. Areas where this is known to attack include expansion joints, air heater seals with significant in-leakage, and precipitators or baghouses where air in-leakage creates sub-dewpoint conditions. This is experienced at many power plants across the US.

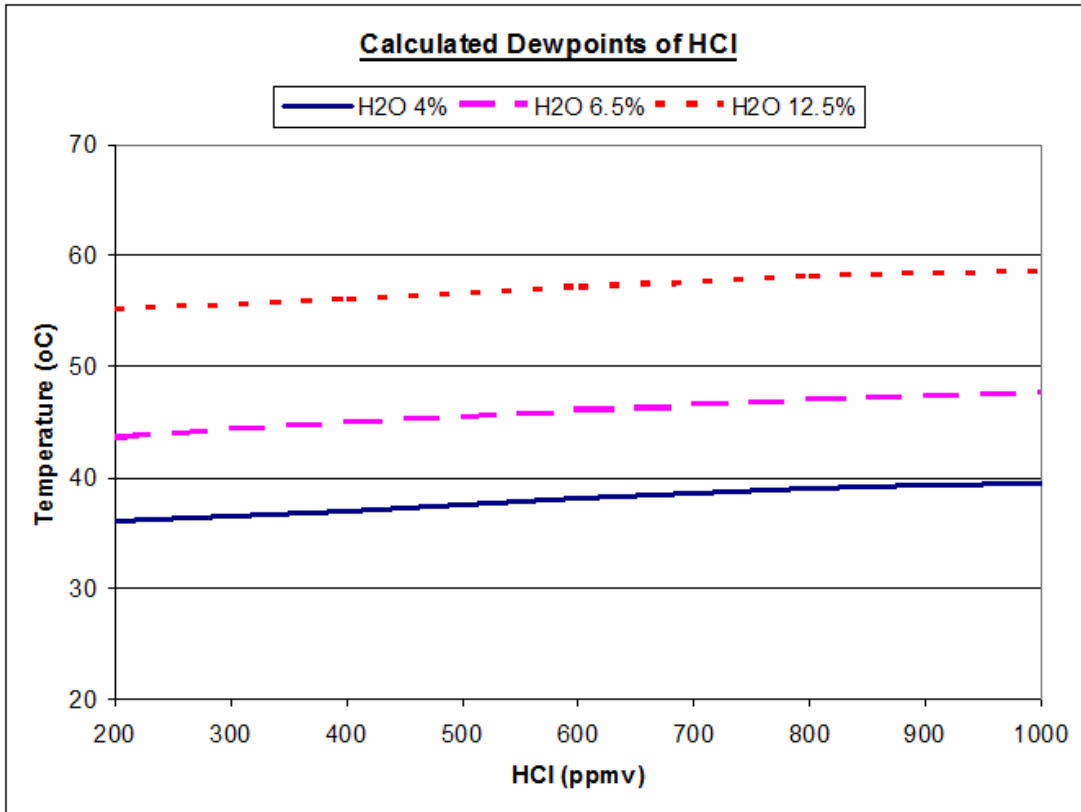


Figure 9. HCl Dewpoint as a Function of HCl and H₂O Concentrations in Gaseous Products of Combustion (Huijbregts and Leferink, [71]).

Conclusion Regarding Mechanisms

The most aggressive high temperature corrosion results from the formation of alkali chloride deposits on superheater tubes; this mechanism can be mitigated by the presence of sulfur, particularly in the form of SO₃ and also in the form of SO₂ with excess oxygen available. The sulfur displaces the chlorine in the alkali chloride (NaCl or KCl), reducing the corrosivity of the deposit. HCl and Cl₂ attack can also proceed in combustion systems. The mechanisms involved are active oxidation mechanisms. These are aggressive, but less so than the alkali chloride mechanisms. Low temperature corrosion—while not of concern to the boiler—occurs when air in-leakage causes sub-dewpoint conditions. This is more common than would be desirable within the power generating fleet.

EXPERIENCE WITH CHLORINE CORROSION IN PF BOILERS

The literature contains some information concerning examples of chlorine corrosion studies on full-scale and pilot-scale pulverized fuel installations. Several studies of the potential for chlorine-based corrosion were conducted in the 1990's (see, for example, Wright, Mehta, and Ho, [72]; Chou et. al., [20]; Doane, Campbell, and Abbott, [45]; Latham, Meadowcroft, and Pinder, [32]); these studies focused upon surveys of boilers, with an attempt to convert operator experiences into an overall picture. Most were performed at boilers firing Illinois Basin coals, the fossil fuels in the US with very high chlorine levels. Cao et. al. [11] also reported on results of testing in a 100 MW_e pulverized coal boiler. Other studies have been conducted on British coals.

Wright, Mehta, and Ho [72] reported on a survey taken by the Electric Power Research Institute concerning the experience utilities and boiler operators firing Illinois basin coal. Some 23 utilities and one independent boiler operator were contacted. Sixteen organizations with 55 boilers had experience with deep mined Illinois basin coal with chlorine concentrations exceeding 0.25%. All types of boilers—wall-fired and tangentially fired pulverized coal boilers, and cyclone boilers were included in the survey. Major suppliers of these boilers included Foster Wheeler, Babcock & Wilcox, Combustion Engineering, and Riley Stoker. Seven of these burned high chlorine coal (0.3 – 0.39% Chlorine or 0.37 lb/10⁶ Btu in the coal) as the sole fuel. The sulfur contents of the fuels burned ranged from 0.23 to 3.5 lb/10⁶ Btu while the alkali metal contents ranged from 0.04 to 0.50 lb/10⁶ Btu. The conclusions of this study included the following:

- Reportedly the operators of these boilers did not find systematic increases in maintenance problems of the combustion system that could directly attribute to the use of high chlorine content coal.
- Furnace wall corrosion problems for the units surveyed were virtually always attributed to the sulfur in the coal, and particularly H₂S formation with low-NO_x firing practices.
- Superheater and reheater corrosion problems were reported. For some units, molten salt corrosion of the leading tubes of the secondary superheater was reported. In one case the corrosion was blamed on high potassium content (0.24% K₂O in the coal) and moderate chlorine content in the coal. This is consistent with the dominant corrosion mechanism discussed previously.
- Reheater corrosion was attributed to chlorine in one case—in a front wall, down-shot firing boiler generating 2625 psi/1050°F steam. The surfaces of the tubes, made from 304H stainless, were rough and exhibited fine cracking. Little deposit remained on the reheater tubes. Alternatives to chlorine-induced corrosion included the potential for this area to

experience constant reducing conditions; however the description is consistent with chlorine-based corrosion.

- Cold end corrosion issues resulting from HCl in liquid phase did exist with some units.

Wright, Mehta, and Ho [72] indicated that data in Great Britain do show significant high temperature corrosion as a consequence of chlorine, a conclusion reached also by numerous other researchers (see, for example, Raask, [24]; Latham, Meadowcroft, and Pinder, [32]).

A second major survey study was reported on by Doane, Campbell, and Abbott [45]. Their report states: “More than 1.3 billion tons of Illinois Basin steam coal was burned by utilities in the past two decades. . . . Yet with all this experience there is no evidence of accelerated corrosion resulting from the chlorine content of Illinois Basin coals.

This study considered a number of power plants shown in Table 6. The data shown in Table 6 reflect conditions as of 1994, when the work was published.

Table 6. Utility Power Plants Surveyed by Doane, Campbell, and Abbott [35]

Plant	Total Coal Supply (10 ³ t/y)	Deep Mined Illinois Basin Coal		Avg Cl Concentration
		% of total	(10 ³ t/y)	Wt % in coal
Union Electric - Meramac	671	91	612	0.37
Sikeston Municipal - Sikeston	521	90	471	0.22
Illinois Power – Wood River	649	88	571	0.44
Gulf Power Co. - Crist	1891	59	1116	0.22
Electric Energy Inc. - Joppa	2516	47	1171	0.37
Union Electric - Sioux	2000	44	877	0.26
WEPCO – Oak Creek	2189	44	970	0.31
Georgia Power Co. - Wansley	4464	41	1829	0.31
Seminole Electric Coop - Seminole	2578	40	1025	---
PSI Energy - Gibson	7012	38	2693	---
TVA - Johnsonville	2584	36	935	0.31
Union Electric - Labadie	5134	30	1545	---
Gulf Power Co. - Smith	773	30	232	0.22

Source: [45]

The survey found no evidence of a relationship between furnace wall corrosion rates and coal chlorine content. Cao et. al. [11] also found no evidence of chlorine-induced corrosion firing a variety of coals in a 100 MW_e boiler.

Regarding superheater and reheater fouling and corrosion, the paper stated:

“There is a consensus among corrosion engineers that the cause of high-temperature SH/RH corrosion is accumulation of Na₂SO₄ and K₂SO₄ at the base of fouling deposits, which react to form aggressive molten alkali-iron sulfates at metal temperatures greater than 550°C (1020 °F). Chloride is not detected in these deposits.

The conditions described are consistent with the alkali chloride – alkali sulfide mechanism described previously. Consequently, while these researchers concluded that elevated chlorine levels in the coal were not responsible for corrosion, the detailed discussion in the paper leaves room for debate on this issue.

The influence of elevated levels of chlorine on corrosion in biomass cofiring settings was studied extensively in the Studstrup Power Station Unit #1 demonstration of ELSAM/MIDKRAFT (see Wieck-Hansen, Overgaard and Larsen, [73]; Andersen et. al., [74]; Hansen et. al., [75]; Friberg et. al. [76]).

Studstrup Power Station Unit #1 was a 150 MW_e pulverized coal boiler (since demolished) converted to cofiring straw with coal; the cofiring demonstration occurred from January 2006 through February 2008. The boiler was equipped with 12 burners—four on each row. The middle row of burners was modified to accept straw in cofiring

applications, with the straw supplying up to 20% of the thermal input to the unit. Typical fuel analyses for two types of coal burned at the plant, and straw burned at the plant, are shown in Table 7. The coals burned were Columbian (#1) and US-high volatile bituminous (#2) coals while the straw was produced locally (Andersen et. al., [74]).

Table 7. Representative Fuel Characteristics for Coals and Straw Burned at Studstrup Power Station Unit #1

Parameter	Fuel		
	Coal #1	Coal #2	Straw
Total Coal Analysis			
% Carbon (dry)	68.5	64.2	46.1
% Hydrogen (dry)	4.2	4.4	6.0
% Nitrogen (dry)	1.48	1.50	0.58
% Sulfur (dry)	1.01	2.20	0.12
% Chlorine (dry)	0.023	0.25	0.55
% Moisture	10.5	11.4	12.4
% Ash	13.8	8.6	6.8
Lower Heating Value (Btu/lb)	10,300	11,020	7,360
Alkali Metal in Coal			
K (% in coal, dry)	0.06	0.07	1.5
Na (% in coal, dry)	0.018	---	0.02
Ash Elemental Analysis			
SiO ₂	59.7	50.0	34.0
Al ₂ O ₃	19.2	20.0	0.94
TiO ₂	0.75	0.89	0.06
Fe ₂ O ₃	8.1	14.7	0.65
CaO	2.05	3.3	7.3
MgO	1.76	0.9	2.0
Na ₂ O	0.63	1.05	0.85
K ₂ O	2.15	2.0	29.8
SO ₃	1.98	3.4	4.74
P ₂ O ₅	0.18	0.23	2.83

Source: (Weick-Hansen, Overgaard, and Larsen, [73])

Note that the concentration of chlorine in the straw is particularly high, as is the concentration of potassium oxide in the straw ash. Further, like all biomass fuels, the alkalinity in the straw ash can be considered as highly available when measured by chemical fractionation. Over 80% of the potassium is soluble either in water or in ammonium acetate (Robinson, Junker, and Baxter, [43]).

Because high temperature chlorine corrosion was expected, specific temperature - controlled corrosion probes were employed to simulate relevant steam temperatures. These probes were located in the convective pass of Studstrup Power Plant Unit #1, and exposed for 3000 hrs. Test tubes were also built into the superheaters of the unit.

The results of this program indicated that little if any corrosion could be attributed to chlorine, particularly at 10% cofiring. At 10% cofiring the corrosion was comparable to a low corrosivity coal. At 20% cofiring the corrosion rate increased by a factor of 2 – 3, elevating the rate to that of the upper limit of low corrosivity coals. The conclusion, however was as follows (Weick-Hansen, Overgaard, and Larsen, [73]):

- Test results indicated that no chlorine corrosion occurs and chlorine was not detected in the corrosion samples
- Co-firing of 10% straw in the boiler with steam temperature of 540°C (1004°F) showed that there are not corrosion related problems
- Test results did not show considerable corrosion risks when co-firing 10% straw in boilers with higher steam temperatures up to 580°C (1076°F). However, the corrosion rate is very sensitive to temperature and chemistry.

Co-firing of 20% straw with coal increased the corrosion in the superheaters of plants with steam temperatures up to 540°C. Even with the increase, the corrosion rates were still low.

The deposition studies carried out by Andersen (see Andersen et. al., [74]) provide additional insights into the fate of chlorine from both the coal and the biomass. This work documents the following:

- Approximately $96 \pm 4\%$ of chlorine leaves the boiler with the flue gas as HCl. Small quantities of chlorine are observed in the ash, particularly in the bottom ash; it is speculated that this is contributed by the unburned straw.
- Very small quantities of chlorine are retained in the deposits supporting the observation that chlorine leaves the boiler as gaseous HCl with the flue gas.
- Experiments have shown that the majority of the chlorine (>98%) recovered in mass balance closures found in the flue gas was presumably HCl. At higher temperatures, chlorine (g) and KCl (g) are also thermodynamically stable (<2%).
- Co-combustion results are similar to the combustion of coals alone with HCl(g) as the major species; at higher temperatures, chlorine(g) and KCl (g) constitute less than 2% of the total chlorine in the system.

The behavior of K and Cl from the cofired straw in the ash formation was governed by ash behavior of the coal species. Calculation of the thermodynamically stable ash species as a function of the straw cofiring percentage documented that the first major change for K is observed between 55 and 60% straw share, where KCl (cr,l) is observed at low temperatures. $K_2O \cdot SiO_2$ (cr,l), which is the major K-species in straw cofiring combustion apart from KCl, is not a stable phase until between 75 and 80% straw share. On the basis of these results, coal-straw co-firing could be manageable at

straw shares as high as 50-60% in PF boilers with regard to the deposits formed, assuming perfect mixing.

- In conclusion, the practically manageable percentage of co-firing with straw is 20% straw – this conclusion is based mainly on deposition trials; provided good mixing and the deposit behavior observed, higher straw shares might be possible.

The conclusions by Andersen based upon the most extensive corrosion testing of cofiring agricultural biofuels with coal in PF boilers are favorable, particularly considering the fact that the chlorine concentration in the straw was 0.55% and the concentration of K_2O in the ash product was 29.8%. The overall conclusion between the work of Weick-Hansen and Andersen is that 20% straw cofiring in a PC boiler is governed by the behavior of the coal, and that it can be accomplished with some increase in corrosion potential. At 10% straw cofiring, the impact of the chlorine in the fuel is negligible. At 20% straw cofiring, the corrosion level, while increased, is still low.

The experience reported to date is reasonably favorable, although it has to be viewed from several perspectives: fuel (including coal) availability, chlorine content(%, $LB/10^6$ Btu), active alkali availability, available sulfur to manage the chlorine through the sulfation reaction, ash content, ash chemistry, and firing method are among those variables.

Further, it should be noted that resolving chlorine corrosion does not inherently resolve sulfur corrosion; There are many other mechanisms (e.g. sulfur caused corrosion that also come into play during the corrosion management). Addressing chlorine addresses just one combustion mechanism. There are many others to take its place. For example, related experience has been reported by Montgomery and Larsen [77], and by Sander et. al. [78] and Skrifvars et. al. [79]. Much of this research has also been converted into computer models [80, 81] including models of deposition rates (see, for example, [82] and the research by Westberg, Bystrom, and Leckner [83]).

CONCLUSIONS

Chlorine is an increasing problem in the PF combustion of all solid fuels including the various ranks of coal and the biofuels. Mechanisms for chlorine induced corrosion focus on the release of chlorine during pyrolysis with alkali metals (e.g., KCl, NaCl) and the subsequent attack of superheater tubes and other surfaces with these chlorides in molten state. High temperature corrosion also can involve active oxidation—a self perpetuating corrosion mechanism. The alkali chloride mechanism can be managed by driving sulfation reactions, substituting sulfur for chlorine and forming the K_2SO_4 and Na_2SO_4 materials by substitution reactions.

Experience has shown that chlorine corrosion does occur for high chlorine solid fuels; however the severity of this corrosion may be overstated. When cofiring biomass fuels with coal, high concentrations of chlorine even in the presence of reactive alkali materials

do not always result in excessive chlorine-induced corrosion. However the potential remains.

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