

# Chlorine Issues with Biomass Cofiring in Pulverized Coal Boilers: Sources, Reactions, and Consequences – A Literature Review

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## **ABSTRACT**

An extensive literature review (see Tillman, Duong, and Miller, 2009[1] of well over 100 literature sources has been performed concerning the sources, reactions, and consequences of chlorine in solid fuels; particular attention in this review has been given to biomass cofiring with various US and world-wide coals. Among the issues addressed is the fact that some coals (e.g., Interior Province coals, Central Appalachian coals) can supply significant concentrations of chlorine to the fuel mix while the biofuels can supply alkali metals (e.g., sodium, potassium) and alkali earth elements to the fuel mix. Several major mechanisms are reviewed including formation of alkali-chlorides (with subsequent reactions), active oxidation, and formation of HCl for low temperature corrosion around air seals and leaking expansion joints. This paper reviews many of the major mechanisms and consequences, and provides assessments of potentially useful and potentially harmful combinations of biomass and coal in the power generation industry.

## **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, [2]; Vassilev, Eskenazy, and Vassileva, [3]; Yudovich and Ketris, [4]; Baxter et. al. [5 - 7]). 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.

## **SOURCES AND CONCENTRATIONS OF CHLORINE IN SOLID FUELS**

Chlorine, which exists in varying concentrations in solid fuels, is among the most volatile of the trace elements (Clarke and Sloss, [8]). 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, [9]). This coal is a Central Appalachian coal of the Hyden formation in the Licking River District (Greenberger, Fiscor, Guzzino, and Sljivar, [10]). The Appalachian Region, followed by the Interior Province

(the Illinois Basin and associated deposits), contains the coals with the highest concentrations of chlorine [9]). Table 2 provides more detail on some eastern US coal deposits.

Tables 1 and 2 demonstrate that chlorine concentration is, to a significant extent, a function of coal age and rank. 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 [11] 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)*

<b>Province/Region</b>	<b>Arithmetic Mean</b>	<b>Maximum</b>	<b>Standard Deviation</b>
Interior	540	3,000	600
Pacific Coast	180	560	120
Alaska	150	4,900	470
Rocky Mountain	150	3,400	300
Gulf	120	900	110
Northern Great Plains	100	1,370	100
Appalachian	730	8,760	680
Green River	180	3,400	420
Powder River	100	1,370	120
Uinta	170	2,100	230
Texas Lignite	120	900	110
Fort Union	90	350	50
Pennsylvania	160	360	90

Source: [9]

*Table 2. Chlorine Content of Selected Eastern Bituminous Coals (As Received Basis)*

<b>State</b>	<b>Coal Region</b>	<b>Avg Btu/lb</b>	<b>Avg Cl (ppm)</b>	<b>Max Cl (ppm)</b>
Alabama	Southern Appalachian - Cahaba	13,500	369	1,500
Alabama	Southern Appalachian - Warrior	12,628	283	3,300
Georgia	Southern Appalachian	13,587	872	1,600
Kentucky	Central Appalachian	12,779	1,148	8,800
Ohio	Northern Appalachian	11,948	730	3,300
Pennsylvania	Northern Appalachian/Main	12,729	956	2,600
Virginia	Central Appalachian	13,613	502	2,200
West Virginia	Central Appalachian	13,398	1,262	8,200
West Virginia	Northern Appalachian	13,064	949	1,600

\*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: [9]

## **Forms of Chlorine in US Coals**

The behavior of chlorine in combustion systems depends on both the concentration of chlorine and the forms of that chlorine. Maceral analysis provides the initial basis for such an evaluation. In the eastern and Midwestern bituminous 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 [4].

The Yudovich and Ketris [4] review highlights chlorine in several forms: chlorine in saline coals (e.g., as NaCl), true organic chlorine ( $\text{Cl}_{\text{org}}$ ) covalently bonded in the coal macromolecule, and as organically associated chlorine in the form of anion chlorine- sorbed on the coal organic surface in pores, and being surrounded by pore moisture. The Vassilev, Eskenazy, and Vassileva [3] research also identifies chlorine in both inorganic and organic forms. It identifies the mineral and inorganic forms as halite (NaCl), sylvite (KCl), calcium chloride ( $\text{CaCl}_2$ ), magnesium chloride ( $\text{MgCl}_2$ ), and ferric chloride ( $\text{FeCl}_3$ ). Other chlorine bearing minerals identified by Vassilev and co-workers include chlorapatite ( $\text{Ca}(\text{PO}_4)_3(\text{Cl},\text{F},\text{OH})$ ) and sodalite ( $\text{Na}_8(\text{AlSiO}_4)_6\text{Cl}_2$ ).

Research reviewed by Sheth et. al. [12] 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. The research by Huggins and Huffman [13] 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. Huggins and Huffman [13] 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.

Studies of Illinois Basin coals show chlorine ions to be adsorbed on the inner surface of micropores, [11] 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, [13] as cited by Peltola, [14]).

## **Chlorine Concentrations in Biomass Fuels**

Chlorine concentrations in the biomass fuels are associated with the nutrient cycle and the living portion of the biomass material and is intimately associated with the structure and composition of the material [5 - 7]. Korbee et. al. [15] 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. ([5 - 7]) and other researchers also have identified chlorine as part of the nutrient cycle and, therefore, a significant issue with biomass fuels.

Table 3 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.

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.

*Table 3. Typical Chlorine Concentrations in Biomass Materials Used as Fuel*

Biomass	Cl Concentration (% in dry fuel)	Cl Concentration (lb/10 <sup>6</sup> 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., [16]; Miller et. al., [17]; Tillman, [18]; Tillman, [19]

Like the chlorine in coal, all of the chlorine in biomass is readily available and reactive (see Baxter et. al., [5 - 7]; Jenkins et. al., [16]; Dayton [20]; Robinson et. al. [21]). Further, much of the alkalinity is also readily available and reactive (see Robinson, Junker, and Baxter, [21]).

### **CHLORINE-BASED CORROSION MECHANISMS**

Numerous corrosion mechanisms exist with chlorine in solid fuels. These mechanisms have been elucidated for biomass, biomass cofiring, and coal; additionally low temperature corrosion occurs as a consequence of condensation reactions, largely around air in-leakage sources and in low temperature equipment.

#### **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 [22]. Numerous authors have proposed key corrosion mechanisms applicable to pulverized fuel (PF) boilers (see, for example, Bakker et. al. [23]; Chou et. al. [24]; McNallan [25]; Monroe et. al. [26]; Takeda [27])

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., [6]; Jenkins et. al., [16]; Nielsen et. al., [28]). 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 [28]. 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 [28] with low melting point eutectics such as potassium-iron-chromium compounds. Baxter et. al. [5 - 7], shows that the thermodynamic forces favoring the initial production of alkali chlorides (e.g., KCl).

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 1 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. These calculations, made using the NASA combustion code—CET-89—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.

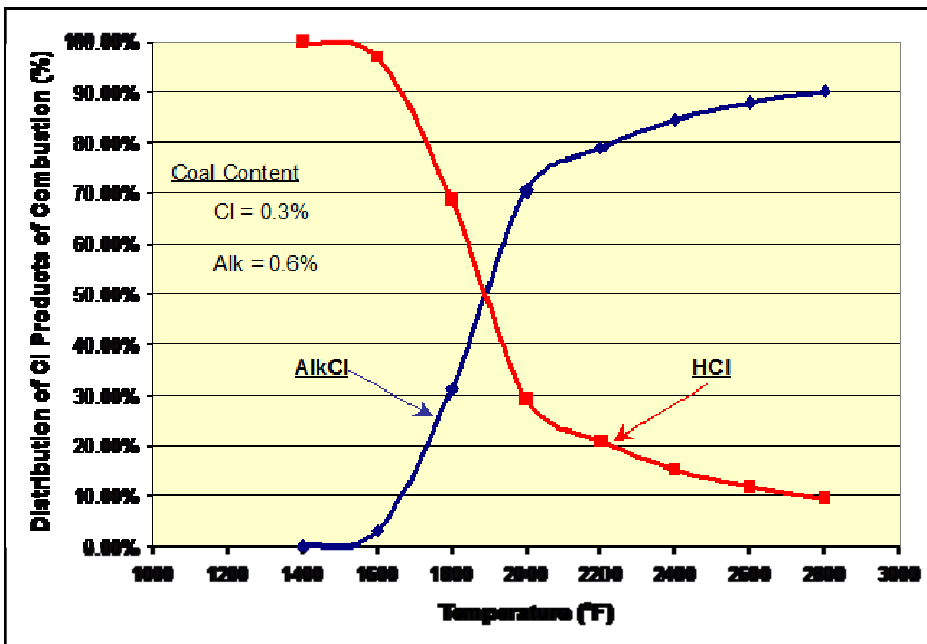


Figure 1. Thermodynamic calculations showing formation of chlorine products of combustion as a function of temperature, given sufficient availability of alkali metals to promote alkali-chlorine reactions.

The alkali chloride corrosion is particularly aggressive in the liquid phase (Lokare et. al., [29]). 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., [30]):

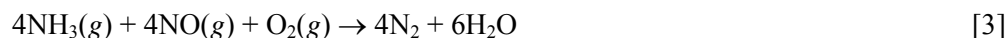
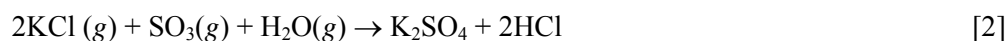
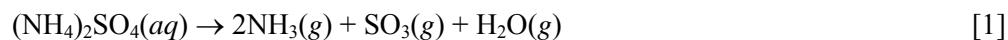
<u>Molten Phase</u>	<u>Melting Temperature (or eutectic), °F</u>
KCl	1425
FeCl <sub>2</sub>	1250
FeCl <sub>3</sub>	570
KCl-FeCl <sub>2</sub>	645 – 740
KCl-FeCl <sub>3</sub>	400 - 430

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. [31]. 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 K<sub>2</sub>SO<sub>4</sub>. The refinement proposed by Frandsen et. al. [31] is that KCl forms a melt with K<sub>2</sub>SO<sub>4</sub> 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/K<sub>2</sub>SO<sub>4</sub>/iron compounds system, the sulfation of the KCl proceeds rapidly generating the high partial pressure of Cl<sub>2</sub>/HCl and results in accelerated oxidation and corrosion of the metal tubes.

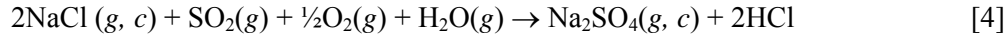
The formation of alkali chlorides, followed by sulfation of the alkali chlorides, are reactions that are well known for biomass fuels (see, for example, Baxter et. al., [32]; Frandsen et. al., [31]; Lokare et. al., [29]; Lokare et. al., [30]). Equally well known is the set of reactions between KCl and sulfur—particularly as SO<sub>3</sub>. 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. [33], 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/cm<sup>2</sup> with 304L at 600°C (1110°F) when subjected to KCl. At the same time the mass gain when subjected to K<sub>2</sub>SO<sub>4</sub> was an order of magnitude less.

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., [34]). The reactions associated with this process are as follows:



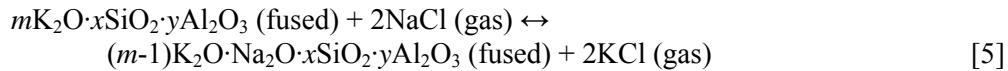
The process reportedly achieves both sulfation of the potassium [Rxn-2] and NO<sub>x</sub> reduction [Rxn-3] with the latter using the conventional SNCR reaction [34]. Rxn-2 is the basic process described above as well. Using sulfation to control corrosion, however, assumes that the HCl formed in Rxn-2 evolves *away* from the metal tube surface and exits into the gas stream.

The process of sulfation can also be depicted for sodium-based fuels as well (Iisa and Lu, [35]):



In the gas phase, Rxn-2 and Rxn-4 proceed rapidly, with rates limited by the availability of  $\text{SO}_3$ . In the condensed phase, however, the sulfation reactions proceed more slowly [35]. 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.

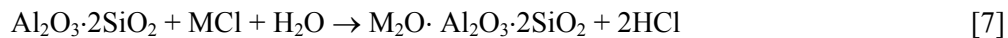
The influence of chlorine on available alkali—particularly potassium—is more significant than simply reaction with highly reactive alkali. One mechanism that may be responsible for this phenomenon is the exchange reaction with vapor phase sodium chloride identified by Raask [36]:



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  $\text{SO}_2$  or  $\text{SO}_3$  to form alkali sulfates, depending upon the availability of sulfur in the system.

Baxter et. al. [32] and Lokare et. al. [29], show 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 [29]. As the chlorine content in the fuel increases, the sulfur content must also increase significantly.

The liberation of chlorine from alkali chlorides can proceed by other mechanisms as well. Aho and Ferrer [37] 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 [37]. Other high temperature chlorine-based corrosion mechanisms also exist; some based upon the reactions shown above. Daniel [38] 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 firing, not coal firing.

The alternative high temperature mechanisms involve either HCl or Cl<sub>2</sub>. 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 active oxidation reactions [39]:



Or



In the presence of O<sub>2</sub> (from excess O<sub>2</sub> in the gaseous combustion products) Cl<sub>2</sub> can be formed by the following reaction:



The Cl<sub>2</sub> can then react directly with the boiler tube according to the following reactions:



And



In the presence of excess O<sub>2</sub>, necessary in combustion systems, the FeCl<sub>x</sub> 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 [39]:



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<sub>2</sub> 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 (Nielsen et. al., [28]). 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<sub>3</sub> and HCl as shown below:





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<sub>2</sub> (see, also, Xie et. al., [40]) highlight that HCl can promote sulfur capture.

### **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 SO<sub>3</sub> and also in the form of SO<sub>2</sub> with excess oxygen available. The sulfur displaces the chlorine in the alkali chloride (NaCl or KCl), reducing the corrosivity of the deposit. HCl and Cl<sub>2</sub> 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 COFIRING**

Many pulverized coal/biomass cofiring experiments were conducted in the USA and Europe in the late 1990's and early 2000's. These included firing switchgrass at Blount St. Station of Madison Gas & Electric, Plant Gadsden and Plant Hammond of Southern Company, Ottumwa Generating Station of Alliant Energy, Kingston and Colbert Fossil Plants of TVA, Greenidge Station of NYSEG, Seward and Shawville Generating Stations of GPU Genco, and Albright Generating Station of Allegheny Energy. Chlorine-based corrosion was not noted in any of these cofiring demonstrations (see, for example, Tillman [19]).

The influence of elevated levels of chlorine on corrosion in biomass cofiring settings was studied explicitly at the Studstrup Power Station Unit #1 demonstration of ELSAM/MIDKRAFT (see Wieck-Hansen, Overgaard and Larsen, [41]; Andersen et. al., [42]; Hansen et. al., [43]).

Studstrup Power Station Unit #1 was a 150 MW<sub>e</sub> 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, 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 [43]. 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 [21].

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.

**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 <sub>2</sub>	59.7	50.0	34.0
Al <sub>2</sub> O <sub>3</sub>	19.2	20.0	0.94
TiO <sub>2</sub>	0.75	0.89	0.06
Fe <sub>2</sub> O <sub>3</sub>	8.1	14.7	0.65
CaO	2.05	3.3	7.3
MgO	1.76	0.9	2.0
Na <sub>2</sub> O	0.63	1.05	0.85
K <sub>2</sub> O	2.15	2.0	29.8
SO <sub>3</sub>	1.98	3.4	4.74
P <sub>2</sub> O <sub>5</sub>	0.18	0.23	2.83

Source: Weick-Hansen, Overgaard, and Larsen [41]

The deposition studies carried out by Andersen [42] provide additional insights into the fate of chlorine from both the coal and the biomass. This work documents the following:

- About 96% of the chlorine leaves the boiler in flue gas, largely as HCl
- Very little chlorine is retained in the ash, and then most commonly in bottom ash
- Very little chlorine is retained in deposits on boiler surfaces
- The dominant chlorine species is HCl(g) however at higher temperatures Cl<sub>2</sub>(g) and KCl are thermodynamically stable and may also exist.

## CONCLUSION

Chlorine is a common minor element in all solid fuels, existing in varying concentrations; chlorine, a participant in the photosynthesis process, exists in varying concentrations in biomass as well. It is more prevalent in agricultural materials. Mechanisms for chlorine release, and chlorine reactions are well defined. When biomass is cofired with coal in PC boilers, corrosion effects are not common; sulfation of deposits with sulfur from coal may well be the agent minimizing chlorine corrosion in PC cofiring applications. Sulfation may result in the high concentration of HCl in the final products of combustion in such applications.

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