Chlorine Balance at Brown Coal Combustion and Flue Gas Desulfurization

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Abstract

Our paper deals with the balance of chlorine in coal combustion and flue gas desulfurization based on measurement results acquired at two different boilers of the CEZ thermal power plant in Melnik, Czech Republic. In bottom ash and electrostatic ash 30–35% of chlorine remains and more than 60% chlorine enters flue gas desulfurization. Almost all chlorine in flue gas entering flue gas desulfurization is removed from 90% in limestone scrubbers. Only up to 8% of chlorine content leaving the scrubbers is emitted to ambient air.

Keywords: chlorine in coal, pulverized coal combustion, chlorine in fly ash, chlorine in clinker, flue gas desulfurization, chlorine metal corrosion

Introduction

The world average Cl contents in coal for hard and brown coals are, respectively, 340±40 and 120±20 ppm [1]. Aside from "normal" coals with average Cl contents, there are saline coals enriched in Cl up to 1%, for instance some Austrian and German deposits. The modes of Cl occurrence in coal are varied. Among them are inorganic salt like Na and other chlorides, as well as chlorine-bearing silicates, sulphides and chlorides in pore moisture. Organic associated Cl seems to predominate in coal. It may consist of two different types. One minor site may be as covalent bounded in coal as organic macromolecules [1]. The major part of organic Cl is represented by "semi-organic" Cl, as anion Cl⁻ adsorbed on coal organic surface in pores and surrounded by pore moisture. These are HCl complexes bonded with bases, such as quaternary nitrogen. F is presented in coal in mineral forms prevalent as mineral fluorite [2]. Other halogens in coal are not reported in mentioned papers [1, 2].

Flue gas arising from coal combustion usually includes small amounts of halogen elements – chlorine (Cl) in the form of Cl_2 and HCl and F as HF. Their amounts in flue gas depend on their contents in a fuel. The content can differ according to geological conditions at which the fuel was formed [3, 9]. Flue gas enters desulfurization with HCl concentration 3-15 mg·m⁻³. No elemental chorine (Cl_2) in flue gas during our experiment was detected.

For example, German and Austrian coal, particularly coal deposited in an area of the salt basin (e.g. Hambach), include relatively high amounts of chlorine, while fluorine content is in some cases low [4]. On the other side most Czech brown coal deposits include small amounts of chlorine, but fluorine content is relatively higher. This holds true especially for brown coal from the Nastup mine in the Chomutov region [5].

Implementation of contemporary generation of flue gas desulfurization processes proved negative chlorine influence on applied installations and on chemical reactions of desulfurization processes [12, 13], such as the wet limestone-gypsum process. This is the most used flue gas desulfurization process for large coal combustion plants. First generation of the installations employed water scrubbers in

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order to cool flue gas to the temperature of sulfur dioxide absorption. These scrubbers were placed before absorbers with lime or limestone. Almost all chlorides (Cl⁻) and fluorides (F⁻) were separated at pre-washing. Mentioned halogens were removed in Venturi scrubbers by water before flue gas entering desulfurization limestone scrubbers.

Contemporary installations do not employ flue gas pre-washing by water. Heat is partly removed from flue gas in heat exchangers that are consequently used to heat cooled desulfurized flue gas before scattering by stacks. Another portion of flue gas heat is removed directly in absorber cooling to 60ºC by limestone slurry [7, 17]. At the same time a prevailing portion of chlorine and fluorine enters the desulfurization process, where it can cause undesirable corrosion problems, particularly in scrubber metal lining. On the other side, fluorine reacts with aluminium oxide to form complex ion AlF_6^{3-} that causes hard deposits in scrubbers as a result of limestone blinding. Al^{3+} in suspension comes from leaching fly ash.

A dangerous range of chlorine concentrations (more than 40-50 mg·l⁻¹) with the pattern of special lining materials used in the Melnik Power Plant (Stainless steel 316 L and Ni-Cr alloys) was studied in laboratory [6].

Chlorine impacts on Desulfurization Processes

A high amount of chlorides (Cl⁻) in absorption suspension causes corrosion of metallic materials, including Ni-Cr-Mo alloys, so-called point (pitting) corrosion [12, 15]. Chlorides contained in suspension can inhibit the desulfurization process itself. For the reason given above it is necessary to keep their concentration on an acceptable level (<50g·l⁻¹). The extent of corrosion depends on the content of chlorine in coal that predominantly passes as HCl to flue gas at combustion. Nevertheless, all chlorine ions can develop serious corrosion. Process water can bring considerable amounts of chlorides into desulfurization as well.

There must be sufficient concentration of aggressive anions and oxidation agents in order to emerge point corrosion and at the same time corrosion potential must be higher than critical potential for initiation of point corrosion. Critical potential measured against to Cl^-/Ag^+ electrode is specific for each metal material. Point corrosion occurs particularly in solutions containing chlorine, bromine, fluorine, iodine and their salts. Ions of these halogens penetrate easily through protective passive film and then a local anodic dissolution in active state follows promptly penetrating into depth [6, 13, 14]. As a consequence of suitable impact of these factors, point corrosion can quickly cause complete perforation, even on a relatively thick plate or a tube.

Local damage of passive film can preferentially occur in points where a surface is not continuous and it is affected by physical and chemical heterogeneity. It occurs in points of material defects emerged on surface in places of non-metallic inclusions. Micro cracks are formed by dissolution of non-metallic inclusions or metal surrounding inclusions. Hydrolysis of dissolving metal

ions and concentration of chloride ions proceed in micro cracks. Significant acidification of solution and local corrosion in an active state are consequences of the facts [6, 14].

It is obvious from the reasons mentioned above, that it is necessary to keep content of chlorides in suspension on a level not exceeding 50 g·l⁻¹ Cl⁻ at which undesirable impacts do not occur, particularly corrosion. Most often it is realized by a partial discharging of absorption liquid after discharging $CaSO_4·2H_2O$ to a water treatment plant or to wastewater disposal, together with $CaSO_4·2H_2O$ and fly ash in the form of a stabilizer. Wastewater disposal (containing chloride compounds apart from the others) by its evaporating together with fly ash separation is the other possibility. In this case wastewater containing chlorides is supplied to a boiler between economizer and an air heater. Fly ash containing absorbed chlorine is separated in boiler electrostatic separators. It is comprehensible that if the separated fly ash has to be used in building industry, the content of chlorides in fly ash must be limited to 0.1% mass [7, 10].

Chlorides separated from flue gas in an absorber are discharged with suspension into the separation of formed $CaSO_4·2H_2O$ and their content can be constraining for using such regulator as cement setting at a production of plaster building materials [8]. If $CaSO_4·2H_2O$ (so-called energy-plaster) produced at desulfurization process is subsequently processed to building materials, the chloride content is required to be lower than 0.1% by weight. The same value is required for processing fly ash from lignite combustion. Greater content of chlorine is unfavourable to stability of building material.

Chlorine Behaviour at Coal Combustion and Flue Gas Desulfurization

Chlorine behaviour at coal combustion and flue gas desulfurization was studied in a power plant Melnik, joint-stock company CEZ. The power plant consists of three boilers [11, 15]. Boiler K11 has 500 MW_e of installed power capacity; boilers K9 and K10 have 110 MW_e each. Counter-current absorbers without filling are used for desulfurization. Highly alloyed materials and alloys of Ni-Cr-Mo types protect an absorption area from corrosion impacts [12].

The corrosive attack of chlorine to metal plating of absorber is a serious problem. The lifetime of metal plating can reach 10 to 15 years; nevertheless, in the case of high chloride concentrations in scrubber liqueur must be replaced during two or three years. To avoid this problem it is necessary to keep Cl⁻ concentration limestone slurry in the mentioned narrow range (40-50 mg·l⁻¹), removing part of wastewater to the outside of the power plant area through the wastewater treatment plant.

Power plant Melnik fires two classes of coal: from Bilina and Most Czech deposits. Quality parameters of fired coal and chlorine content are shown in Tables 1 and 2.

Table 1. Balance of chlorine at coal combustion in boiler K 9.
Boiler output: 108 MW$_e$, steam output 343 t·h^{-1}
Heat-specific consumption on kWh = 11.4663 MJ
Coal parameters: W^r = 37.60%, A^r = 21.25, S^r =1.30%, Q^r = 10.55 MJ·kg^{-1} (power plant data); Cl^r = 14.61 g·t^{-1}
(analysis of the University of Chemical Technology)

Parameter	Inputs			Outputs		
	Quantity [t·h^{-1}]	Cl content [g·t^{-1}]	Cl mass flow [g·h^{-1}]	Quantity [t·h^{-1}]	Cl content [g·t^{-1}]	Cl mass flow, [g·h^{-1}]
Coal (as received)	117.38	14.61	1714.92	-	-	-
Ash in coal (as received)	24.943	-	-	-	-	-
Fly ash (82% of ash content)	-	-	-	20.45	27.39	559.20
Clinker (15% of ash content)	-	-	-	3.74	13.94	52.14
Flue gas[1]	-	-	-	451,555	2.27	1,025.03
Boiler input, total	-	-	1,714.92	-	-	-
Boiler outputs, total	-	-	-	-	-	1,636.37
Difference in balance towards input	-	-	-	-	-	-78.55
% Of difference towards input	-	-	-	-	-	-4.6

[1]Flue gas: quantity in m³·h^{-1}, chlorides concentration in mg·m^{-3} (always 273 K, 101.32 kPa, dry), recalculated to content 6% O$_2$; stated mass flow of chlorides in flue gas is an input to balance of flue gas desulfurization in Table 3.

Process measurements were performed in order to prove chlorine behaviour at processes of coal combustion and desulfurization. Measurements were performed at forced boiler outputs, the closest to a nominal power capacity (Tables 1 and 2).

Method of Measurements

For analyses we used the following analytical procedures:
1. CSN ISO 10780: Stationary Source of Emission. Measuring Speed and Flow Rate of Gas in Pipe.
2. EN 1911. Stationary Source of Emissions, parts 1, 2 and 3. Manual Methods of Determination of HCl and Cl$_2$ by Ionic Chromatography.

Data concerning quality of coal was overtaken from records of power plant laboratory.

Data concerning quantities of coal combusted, output of the boilers and flue gas composition of the boilers K9 and K10 was overtaken from certificated monitoring of the power plant.

Chlorine Balance at Coal Combustion

According to performed measurements and analyzes, chlorine content in fired coal was low (in comparison to some sorts of Austrian and German coal) and ranged from 14.6 to 16.2 g·t^{-1} of chlorine. Table 1 shows that from total chlorine mass flow supplied to boiler K9 in coal (1714.92 g·t^{-1}) approximately 3% of chlorine remains in clinker in a form of chlorides, approximately 33% of chlorine remains

in fly ash separated in electric separator and approximately 60% of chlorine was exhausted with flue gas into desulfurization. Balance error was 4.6%.

Similar results for boiler K10 were achieved (Table 2). From total chlorine mass flow supplied to boiler in coal (1560.41 g·h^{-1}) approximately 3% of chlorine also remains in clinker in a form of chlorides, approximately 17% of chlorine was removed with fly ash and approximately 60% of chlorine was exhausted with flue gas. Balance error 19.6% is higher in comparison to 4.6% (see boiler K9) and can be explained to some changes in boiler output during measurement.

Chlorine Balance at Flue Gas Desulfurization

Chlorine balance at desulfurization process was calculated as a difference between inputs and outputs. Individual balances are shown in Table 3 (boiler K9) and Table 4 (boiler K10).

Inputs were balanced as follows: chlorides in process water supplied to a drop separator, chlorides in process water for heat exchanger spraying, chlorides supplied to the process with CaCO$_3$ and content of chlorides in flue gas entering desulfurization.

Outputs from desulfurization were concentrated on mass flows in produced gypsum, in wastewater discharged to water treatment plant and in desulfurized flue gas. Outputs from water treatment plant were related to removal of chlorides in treated water and sludge. When outputs from desulfurization were compared to inputs, good balance was

Table 2. Balance of chlorine at coal combustion in boiler K 10.
Boiler output: 98 MW, steam output 312 t·h^{-1}
Heat-specific consumption on kWh = 11.4663 MJ
Coal parameters: W^r = 36.64%, A^r = 18.31%, S^r = 0.46%, Q^r = 11.67 MJ·kg^{-1},
(power plant data); Cl^r = 16.15 g·t^{-1} (analysis of the University of Chemical Technology)

Parameter	Inputs			Outputs		
	Quantity [t·h^{-1}]	Cl content [g·t^{-1}]	Quantity [t·h^{-1}]	Cl content [g·t^{-1}]	Quantity [t·h^{-1}]	Cl content [g·t^{-1}]
Coal (as received)	96.62	16.15	1,560.41	-	-	-
Ash in coal (as received)	17.63	-	-	-	-	-
Fly ash (82% of ash content)	-	-	-	14.45	18.71	270.40
Clinker (15% of ash content)	-	-	-	2.645	17.36	45.91
Flue gas[1]	-	-	-	443,700	2.112	937.00
Boiler input, total	-	-	1,560.41	-	-	-
Boiler outputs, total	-	-	-	-	-	1,253.31
Difference in balance towards input	-	-	-	-	-	-307.1
% Of difference towards input	-	-	-	-	-	-19.6

[1] flue gas: quantity in m^3·h^{-1}, chlorides concentration in mg·m^{-3} (always 273 K, 101.32 kPa, dry), recalculated to content 6% O$_2$; stated mass flow of chlorides in flue gas is an input to balance of flue gas desulfurization in Table 4.

Table 3. Chloride mass flows in desulfurization process at plant No. 9.

Technological flows	Inputs			Technological flows	Outputs		
	Quantity [m^3·h^{-1}]	Chlorides concentration [mg·l^{-1}]	Chlorides mass flow [g·h^{-1}]		Quantity [m^3·h^{-1}]	Chlorides concentration [mg·l^{-1}]	Chlorides mass flow [g·h^{-1}]
In water to water traps	15.59	26.11	407.29	In produced gypsum[2]	0.00	0.00	0.00
In water to REGAVO	1.00	26.11	26.11	In water to WTP	5.00	401.68	2,008.40
In suspension	14.70	45.23	664.88	In desulfurized flue gas[1]	447 s700	0.40	178.63
In flue gas[1]	451,550	2.27	1,025.03	Total			2,187.03
Total			2,123.31	In water from WTP[3]	5.0	415.71	2,078.55
				Difference			
				(Inputs - outputs):			-63.72
				2,123.31 – 2,187.03			–2.9%

[1] flue gas quantity in m^3·h^{-1}, chlorides concentration in mg·m^{-3} (always 273 K, 101.32 kPa, dry), recalculated to content 6% O$_2$;
[2] gypsum was not dewatered during measurement;
[3] estimated value only.

achieved for both measured boilers. From total amount of chlorides entering desulfurization (example K10, Table 4) 75% of chlorides were removed in treated wastewater, 13.2% in waste sludge (output from water treatment plant 88% in total), 5.71% by weight in desulfurized flue gas and 5.9% in gypsum washed by water in centrifuges. The balance of boiler K9 desulfurization plant is similar (Table 3), but centrifuges were out of operation in this plant due to starting the desulfurization plant. Entire extract from desulfurization plants behind hydro-cyclones was discharged to water treatment plant during measurement.

Measurements performed in mentioned desulfurization plant of both boilers proved that approximately the same amount of chlorides in process water (26 mg·l^{-1} Cl$^-$ from treatment plant in power plant) enters desulfurization process as in the case of flue gas.

However, it is notable that chlorides are supplied to the system in limestone as well. Limestone from Certovy schody quarry includes 1.2 g·t^{-1} of chlorine according to performed analyzes. Experiments proved that its participation on inputs of desulfurization process amounts to 0.1-0.3 percents Cl$^-$ at a total balance only.

Table 4. Chloride mass flows in desulfurization process at plant No.10.

Technological flows	Inputs			Technological flows	Outputs		
	Quantity [m³·h⁻¹]	Chlorides concentration [mg·l⁻¹]	Chlorides mass flow [g·h⁻¹]		Quantity [m³·h⁻¹]	Chlorides concentration [mg·l⁻¹]	Chlorides mass flow [g·h⁻¹]
In water to water traps	16.55	25.41	420.53	In produced gypsum[2]	2.24 (t·h⁻¹)	54.49 (g·t⁻¹)	122.06
In water to REGAVO	1.00	25.41	25.41	In water to WTP	5.00	363.39	1,816.95
In suspension	13.09	45.81	599.65				
In flue gas[1]	443,700	2.112	937.00	In desulfurized flue gas[1]	443,700	0.265	117.58
Total			1,982.59	Total			2,056.59
				In water from WTP[3]	5.00	308.99	1,544.95
				Removed with sludge[4]			272.00
				Difference			
				(Inputs - outputs):			+74.00
				1,982.59 – 2,056.59			3.60%

[1] flue gas quantity in m³·h⁻¹, chlorides concentration in mg·m⁻³ (always 273 K, 101.32 kPa, dry), recalculated to content 6% O_2;
[2] quantity of $CaSO_4 \cdot 2H_2O$ with 4% of surface moisture in tons per hour - calculated from absorbed SO_2 (90.5% of S content in coal);
[3] estimated value only;
[4] not measured; only difference between chlorides mass flows downstream and upstream to water treatment plant (WTP); estimated value.

Conclusions

Chlorine predominantly passes to flue gas (approximately 60%) and about one third is contained in fly ash removed in electrostatic precipitators (30-35%) at combustion of brown coal from Bilina and Most deposits in pulverized coal boilers as measured at boilers K9 and K10 in power plant Melnik. Identically, 3% by weight from total chlorine amount in fired coal were determined in bottom ash from both boilers.

Almost all chlorides after boilers (approximately 90%) are washed in limestone suspension at flue gas desulfurization process in absorbers. Gypsum formed in the desulfurization process is washed in centrifuges and part of water is led to chemical wastewater treatment plant. Flue gas after scrubbers contains 6-8% of total chlorine amount in flue gas entering absorber according to performed measurements.

In the case of measurement on boiler K9 gypsum dewatering in centrifuges was not applied. All chlorides retained in an absorber were discharged to a wastewater treatment plant.

In the case of boiler K10 gypsum dewatering in centrifuges and subsequent washing were applied. Treated water contains 83% of chlorides and treatment plant sludge contains approximately 17% of chlorides from total amount of chlorides entering the water treatment plant.

An interesting finding is that the amount of chlorides entering desulfurization in flue gas from coal combustion is generally the same as in the case of chlorides in process water. On the other side, contribution content of chlorine in limestone from the Certovy schody deposit is negligible.

Acknowledgements

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