

FATE OF CHLORINE COMPOUND IN COMBUSTION OF ALTERNATIVE FUELS

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ABSTRACT

Most of natural materials contain traces of chlorine and it enters also to the combustion process. Chlorine products of combustions are usually inorganic hydrogen chloride vapors and chloride salts, nevertheless smaller amount of organic chlorine compounds are formed. Simpler of these organic compounds can act as greenhouse and ozone depleting gases; more complex compounds are directly dangerous for their mutagenity or extreme toxicity like so called dioxines. Non-fossil natural materials and fuels derived of them can contain more chlorine than common coal. From the published research studies is evident that the formation of organochlorine compounds is limited to the temperature range 300-800 °C. At the higher temperatures, these compounds are destroyed. In the stage of flue gas cooling some chlorine may be by a "de novo" synthesis introduced to the organic form. Well-controlled combustion of alternative fuels need not contribute to the increase of amount of emissions of dangerous chlorine compounds. In our research were moreover studied the fuels with lower chlorine content. The experimental tests of the emissions from large-scale industrial fluid bed boiler indicated that substitution of large percentage of coal by alternative fuels had no significant effect.

KEYWORDS: chlorine, dioxin, combustion, alternative fuel

INTRODUCTION

Demand to reduce the greenhouse gas production turns the attention to the substitution of fossil fuels by waste wood and agricultural residua, that were in past composted or not treated anyhow. Various solid wastes from biorefineries of food, pulp and paper production, textile fiber industries, organic sludge from wastewater treatment can be employed as well. High percentage of combustibles is also contained in solid mixed communal wastes and there are similar problems with employment of the related energy.

More and more effects of combustion to the environment have been systematically monitored recently. First, the attention was paid to the smoke and flue ash. The smoke is no more considered as a symbol of prosperity. Next contaminants under examination were sulfur dioxide and nitrogen oxides known as cause of acid rain. Today, carbon dioxide and of other essentially inert components like volatile organic compounds and nitrous oxide, that can affect the ozone layer and contribute to the greenhouse effect are monitored. More attention is paid to the minor components like compounds of heavy metals and halogens, chlorine in particular.

The chlorine compounds belong to the toxics, carcinogenics, ozone depleting species. Therefore,

prudence is necessary, when introducing them to the combustion process. In this paper, we are studying the problem of chlorine during combustion of biomass and other alternative fuels in industrial boilers. All lignocellulose materials – derived from wood, bark, straw, rice hulls, baggase, etc. contain some chlorine. Lowest percentage is 0.1 % of Cl in dry matter of construction (cellulose) and storage (starch) parts, the specialized cells contain up to 1 % Cl, higher percentage can be detected in plants from saline soils. During the biomass combustion, this chlorine enters number of chemical reactions producing problematic compounds. As the amount of chlorine fed can hardly be limited, it is necessary to control the process to minimalize the non-demanded reactions.

CHLORINE COMPOUNDS IN THE ENVIRONMENT

The chlorine compounds on the Earth occur mostly as chemically stable and non-dangerous chlorides, either dissolved in oceans or stored in crystal form underground. However, low concentration chlorine is scattered everywhere and it is irreplaceable for any living organism. Also a natural chemical transformation of chlorine compounds and their movement is significant. To compare, the complete industrial production of chlorine is about 40

millions tons yearly. One medium size volcano eruption may evolve nearly one billion tons of hydrogen chloride. Production of highly reactive elementary chlorine by photochemical reactions of chlorides at the sea level is estimated to 800 millions tons per year.

Chlorine from the biological materials is released during slow decomposition, during natural fires and during controlled combustion, preferably as inorganic chloride compounds. In any case, small fraction of organo-chlorine compounds is formed, like methyl chloride (0.5 million tons/year), chloroform (0.7 million tons/year) and compounds of the toxic group of dioxins PCDD/F (170 kg/year).

Industrial employment of chlorine was oriented in 19. century to the production of bleaching powder, calcium hypochlorite, for bleaching of textiles and paper and for disinfections. Water chlorination in towns started around 1900. Short episode with elementary chlorine and organo-chlorine compounds as war gases lead to the development of efficient pesticides known as DDT, HCH, PCP, etc. Chlorinated hydrocarbons became used as solvents, chloroprene resin and a wide scale of pharmaceuticals was developed. Polychlorinated biphenyls (PCB), now forbidden as toxics, had been excellent transformer oils. Chemical stability and simple liquefying of chlor-fluorinated hydrocarbons (freons) was employed in refrigerators and in sprays. An interesting effect of halogenated hydrocarbons is fire inhibition and their use as fire retardants and fire extinguishing liquids. An important consumption of chlorine is in manufacture of PVC, which is a still very popular plastic with a wide application.

Fast development at the beginning of the 20th century was accompanied with a low level of discipline at manufacture, transport, storage and application of chemicals, and little attention was paid to the industrial emissions.

One important turning point is dated 1976, when in Italian locality Seveso in a carelessly abandoned reactor for production of 2,4,5-trichlorophenole (intermediate for disinfectants) started uncontrolled spontaneous reaction and the aerosol cloud containing (Bluemler, 2005) 0.2 to 5 kg of polychlorinated dioxins escaped. Large residential area was evacuated and next 4 years were spent by the place decontamination. This accident initiated development of so called EC Seveso II Directive (EC, 1996), internationally accepted rules for prevention of industrial accidents and limiting of their eventual consequences. It results increasing safety of chemical industry processes and also medialization of even banal cases of breakdown and spill.

"DIOXINS"

In the focus of our interest is a group of persistent chlorinated compounds derived from dibenzodioxins and dibenzofurans. Only 17 of the total number 210 of these compounds; just these

containing chlorine at least in positions 2,3,7,8 are categorized as toxics. Common acronym for these polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzo-p-furans (PCDF) is PCDD/F, however the simple term "dioxins" is frequently used in unqualified slang.

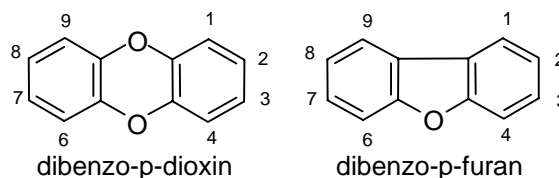


Fig. 1 Formulas of basic compounds and numbering of position of eventual chlorine atoms in PCDD/F

The most dangerous is 2,3,7,8 tetrachloro-dibenzo-p-dioxine. It is a solid material (melting point 259 °C) practically insoluble in water; it can be dissolved in organic solvents and in fat. Its lethal dose differs for various animals, the extremes are 0.6 µg/kg for guinea pigs (Schwetz et al., 1973) and 5000 µg/kg for hamsters (Henck et al., 1981) Data for other tested animals (mink 4, rats 10-4000, chicken 20, monkey 70 µg/kg) are inside this interval. It is formed in traces during decomposition of any organic matter in presence of chlorine compounds. It is formed naturally during the wood and savanna fires mostly as a component of ash. Aerosols distribute PCDD/F throughout land and resulting natural background in soils is about $20 \cdot 10^{-12}$ g per gram of dry matter. The PCDD/F compounds are also produced by slow decomposition of biomass in composts. Due to the development of organo-chlorine chemical industry and extensive application of chlorinated agro-chemicals, it is possible to trace enormous content of persistent chlorinated compounds in sediments from the period 1930-1960. Since 1960, the concentration of androgenic chlorine compounds in environment steadily and significantly decreases (Yake, 2005), (Verta et al., 2004). Toxicity of all PCDD/F is summarized by the toxicity equivalent I-TEQ, calculated as a sum of actual content of particular derivate multiplied by the factor I-TEF. I-TEF is equal to unity for the most toxic 2,3,7,8-CDD and the other coefficients are calculated from the lethal dose for laboratory animals. The factors are considerably smaller than one, e.g. for the 1,2,3,4,6,7,8,9-derivate it makes only 0.001.

Very complex literature review and analysis of the chemistry of PCDD/F, their formation and effects can be found in documents of U.S. Environmental Protection Agency presented recently (EPA, 2005). This set of papers is declared as a draft, which cannot be quoted yet. Nevertheless, it represents several thousands of pages of valuable information with more than 1200 references.

Anything like a safe limit of PCDD/F in food has not been declared. Present level 1 pg/(kg day) in European industrial countries is considered to be acceptable. Lethal poisoning of humans by dioxins is unknown; in fatal cases dioxins represent at most a minor component besides other evidently toxic compound. There are only two well-documented cases of serious acute poisoning of humans by dioxins. In the recent case, Ukrainian politician Yushenko accumulated 1000 μg I-TEQ in his body (for comparison it corresponds to the consumption of 150 tons of meat from a bad locality containing 6 pg/kg).

Release of chlor-organic compounds, containing significant amount of dioxins, taking place in Seveso, caused solely acute burns of skin and mucous membranes, comparable with very low exposition of war gases of yperit type. Chronic effects like immune suppression, birth defects, hormonal imbalance, increasing cancer incidence etc. were proved for laboratory animals. However evaluation of the data for less than 500 people exposed to dioxins in Seveso is insufficient to discriminate any statistically significant long-term effects. Other investigation of human exposure concerns Vietnam, where defoliants Agent Orange were applied for 10 years in large extent (70 thousands tons of chlorinated dioxins, mostly not belonging to the compounds listed as toxics; nevertheless, the release of minor impurities could make 300 kg I-TEQ that time). Even here, the correlation of the health effects to the dioxin exposition is not statistically significant, when taking also in account the war stress, bad regimen and other synergic effects. Some intermediates of these defoliants were paradoxically purchased in communist Czechoslovakia (mainly from Chemko Strážske, and Spolana Neratovice). With respect to the low technical level and to the secrecy measure, we can only roughly estimate that more than 80 persons in the Spolana chlorophenol plant suffered chronically or acute poisoning by dioxins that time.

One result of activities related to the Seveso Directive is inventory of sources, emissions and imissions of PCDD/F. Reduction of PCDD/F emissions became an important criterion of technical culture of industrial processes, without respect to the discussions how the given technologies are important for the environment.

ANTHROPOGENIC SOURCES OF PCDD/F

Toxic PCDD/F have not been anytime purposely industrially produced and their minute laboratory preparation is limited to the production of analytical standards.

Unintentionally, PCDD/F are formed during thermal treatment and combustion anytime, when tar or soot and hydrogen chloride is released in presence of oxygen. In industrial countries, 75 % of anthropogenic emissions originate in following four sources:

- incineration of mixed waste,
- agglomeration of feed for metallurgy plants,
- local furnaces (stoves, boilers, fireplaces, open fires),
- hospital incinerators.

Surprisingly, neither thermal power stations, nor large dangerous waste incinerators are listed. One reason is that production of PCDD/F depends mainly on the thermal regime of the process, composition of the fuel being less important. The emissions of dioxins from chemical plants during regular operation are also less significant in the total balance.

PCDD/F EMISSIONS FROM THE COMBUSTION PROCESSES

PCDD/F can come to the emission by three ways:

1. In a simple case, dioxins are present in the fuel. It concerns waste incinerators; in particular the incinerators for liquidation of dangerous waste material with high chlorine content. However, 99.99 % conversion of dioxins destruction is reached in 1 s at 980 °C; in this region the reaction speed ten times multiplies for every 80 K temperature increase (Shaub and Tsang, 1983).
2. In temperature range 300-800 °C pyrolysis takes place in organic compounds producing aromatic hydrocarbons and chlorinated aromatics in presence of chlorine compounds. Later also more complex compounds PCDD/F are synthesized unintentionally.
3. As mentioned at high enough temperature, all organic compounds are broken to small simple molecules. Nevertheless, in the stage of flue gas cooling, number of synthetic reactions takes place and PCDD/F are formed by the mechanism called "de novo". When alkali metals are captured by sulfur dioxide or by amphoteric oxides, there remains volatile hydrogen chloride. It is oxidized by the Deacon reaction with oxygen at 300 °C to extremely aggressive elementary chlorine. And at the same temperature are usually present some hydrocarbons that can be attacked. About 1.5 % of chlorine enters chloromethane and chloroform. Polyaromatic hydrocarbons (PAH) of tar are also chlorinated and form chlorbenzene and number of precursors of PCDD/F synthesis. Important catalysts are copper compounds. De novo synthesis depends on
 - the residence time at the temperature 300-800 °C (important measure for prevention of dioxin formation is fast cooling of flue gas),
 - presence of flue ash (the reactions run well on its surface),
 - presence of metal compounds as catalysts (copper in particular),

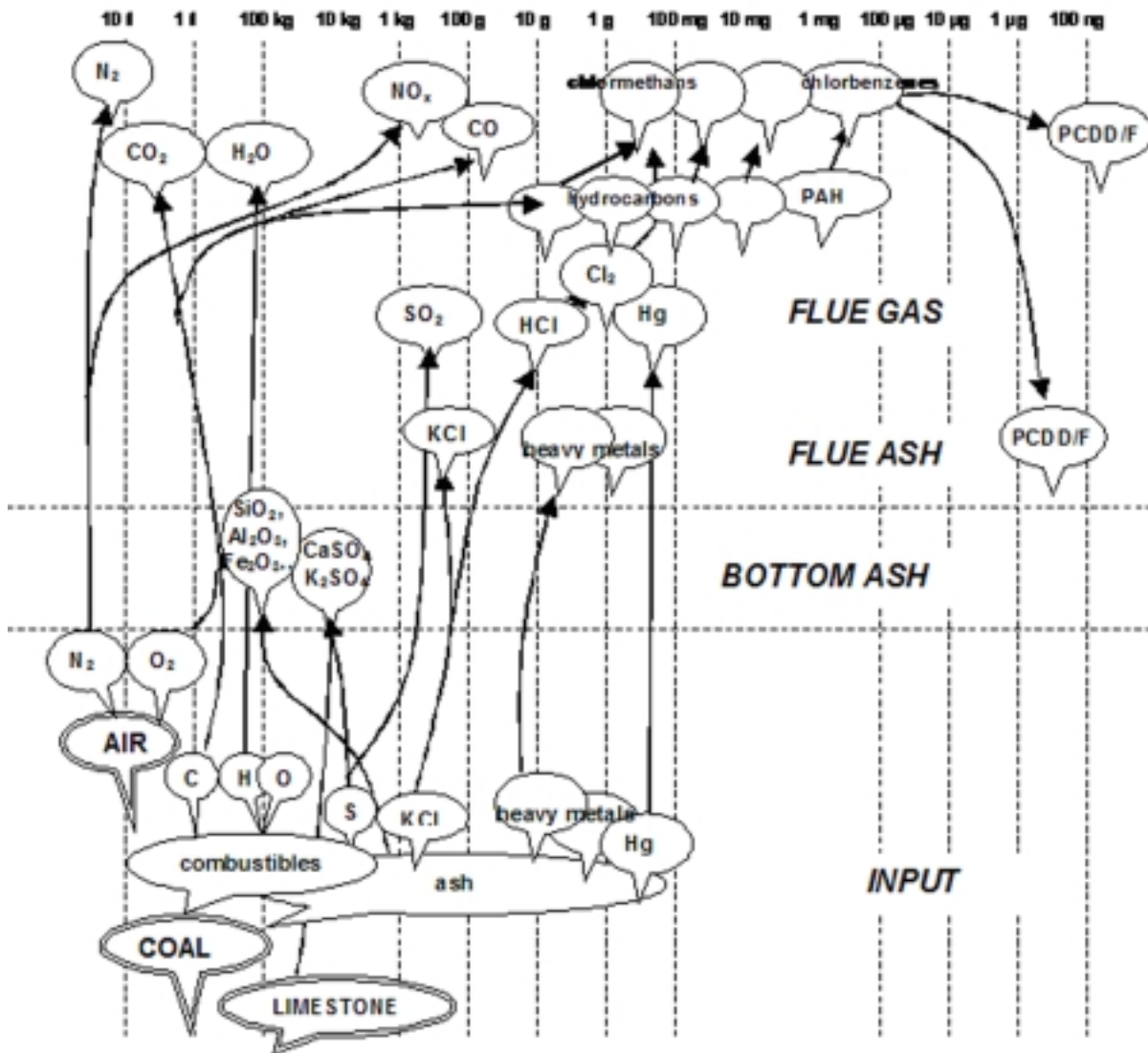


Fig. 2 Estimate of quantitative amount of particular components for combustion of 1000 kg coal in a fluid bed boiler with dry desulfurization

- content of soot and inorganic chlorides in flue ash (they catalyze the formation of chlorinated PAH),
- presence of oxygen (it releases elementary chlorine from chlorides).

These principles are mostly qualitative. With respect to the small content of dioxins, their complicated and expensive analyses, and to synergic effect of a great number of compounds, changing their composition in combustion processes, there have not been completed related thermodynamics data yet. Important fact is that concentration of chlorine in fuel is not considered to be essential. 10-100 µg I-TEQ is formed by controlled combustion of 1000 kg of coal or biomass. This amount of fuel contains usually more

than 1 kg of chlorine (0.1 %), which is comparatively so much that it can hardly affect the equilibrium.

Typical path of controlled combustion intermediates and products is presented in Fig. 2. The balance is based on 1000 kg of coal, which is one-minute consumption of medium-size industrial boiler.

MAIN SOURCES OF DIOXINS

1. **Local residential furnaces** like stoves, boilers, fireplaces and open fires represent an extended number of small, distributed sources. Their main disadvantage is uncontrolled regime and frequent operation out of the optimum conditions (application of improper or non-uniform fuel, wrong control of air supply, start-up and shut-

down period, extremely slow or fast fuel loading, etc.) Essential feature of the combustion in small local furnaces is moderate temperature. Just the problematic range 300-800 °C, where PCDD/F are formed and not destroyed is usual. Flue gases are not treated, lot of flue ash is dispersed and large amount of dangerous chemicals is emitted to the environment. It is reason why the leading areas in the world balance of chlorine emissions are China, India, Africa and Latin America. During the regular combustion of 1000 kg of dry wood, the stoves emissions are 1-3 µg I-TEQ, for fireplaces and open air fires it is up to 30 µg I-TEQ/ton. During combustion of fuel with high chlorine content like waste wood treated with chlorine containing insecticides and fungicides the production of dioxins increases and 500 µg I-TEQ/ton. Common backyard burning of apparently inert waste material from household and gardening is significant source of PCDD/F in developed countries. It was estimated that bonfires and fireworks celebrating the Guy Fawkes Day every November released about 14 % of 1-year dioxins emissions in Britain. Destruction of PVC insulation from copper wires by uncontrolled combustion is reprehensible, though it can be safely done in industrial technologies.

2. Due to non-uniformity of feed and its lower calorific capacity in *waste incinerators*, there is usually a significant of temperature oscillation and a higher probability to operate in below 800°C. Chlorine is usually present in the feed and large amount of fly ash containing number of metallic elements is present. The most of PCDD/F either from feed, or from low temperature incineration, or produced de novo is captured as a solid part of fly ash. In the well-controlled waste incinerators, like in the industrial coal fire boilers, all fuel is subjected to such a high temperature that any chlorinated organic compounds are decomposed and de novo synthesis is suppressed by fast cooling of flue gas. Measurements (Lahl et al., 1991) were carried out in a municipal waste incinerator where 90 µg I-TEQ/ton was fed, the related emissions contained 9 µg in bed ash, 0.9 µg in flue ash and 0.5 µg in gas stake emissions. Some advanced technologies recommend to remove in a second step the PCDD/F adsorbed on the flue ash by baking and to liquidate them separately.
3. *Iron ore sintering plants* are forming granules from iron ore and steelmaking dust by heating with coke dust. Nonferrous metals, including copper in form volatile chlorides are present in recycled dust. Comparatively slow heating and cooling with a long residence in the undesirable temperature range is essential for synthesis of organochlorine compounds. The most of PCDD/F condense on released as a airborne particles. Part

of the dust is dumped as a dangerous material, the other part is returned to the steelmaking process. Anyhow, vast amount of aerosol is emitted. The iron ore sinter plants are major sources of airborne PCDD/F emissions (Rappe, 1992; Lexen et al., 1993; Lahl, 1993 and 1994).

4. Another important class of PCDD/F emissions are *medical waste incinerators*. They should manage in number of localities heterogeneous microbiologically contaminated material. It is done in comparatively small facilities with simple (if any) treatment of flue gas. Emissions up to 5000 µg TEQ/t are reported. Though high percentage of PVC in hospital waste is usually suspected, this level of emissions goes evidently on account of bad control of combustion in outdated kind of furnaces.

Any numbers concerning the concentration of PCDD/F and their inventory should be taken critically. Even the highest concentrations are so small that it requires special analytical tools. Price of one analytical test is charged in hundreds of US\$. Moreover, there is a serious problem of sampling. Scatter of the data is considerable, which is frequently misused to declare biased conclusions by opposing camps of "chlorophiles" and "ecologists".

Polychlorinated dioxin-like compounds stays vapor at elevated temperatures only. The significant part of these compounds rapidly settles on any solid surfaces of aerosols, ash and equipment walls, later in the environment on plant leaves, soil and water surfaces. Later path of dioxins and their very slow decomposition cannot be simply traced. Moreover, the imission data interfere with a background originated in former accidental forest and savanna fires.

ENERGY FROM BIOMASS AND OTHER ALTERNATIVE FUELS

Energy from biomass and other alternative fuels is on issue in last decades. Massive support of related activities comes even from US government, without respect to its quite reserved approach to the commitment to reduce emissions of carbon dioxide. US Department of Energy (DOE, 2001) is proposing to substitute 15 % of coal by biomass in power stations up to 400 MW. 11 large scale facilities just operate in USA. The most of them use powder burners, single plant in Tacoma (Hannan and Rottler, 2005) has a fluid bed boilers 2×25MW. 5 facilities are reported in Europe, the most significant are straw power stations in Denmark.

Different granulometry classes of the size and shape of fuel particles may destabilize the fluid bed, formation of plugs and short circuits can be obtained namely when the particles are non-uniformly distributed (Kostamo, 1999) Respective oscillation of temperature can provoke formation of polyaromatic hydrocarbons (PAH), and persistent organic pollutants (POP) including chlorine compounds up to PCDD/F.

Table 1 Mass, energy and chlorine flow in the combustion process

Run:		1	2	3
<u>Material balance</u>				
coal	kg/h	30000	35000	26700
wood and bark chips	kg/h	-	19800	15200
sewage sludge	kg/h	-	-	15200
refuse-derived-fuel	kg/h	-	-	1000
limestone	kg/h	3490	4320	3240
bottom ash	kg/h	3670	4770	3710
fly ash	kg/h	5510	7180	5560
flue gas	Nm ³ /h	167000	242000	247000
<u>Energy of fuel</u>				
coal	MW	123	139	107
organic fuels	MW	-	31	46
total	MW	123	170	153
<u>Temperature</u>				
fluid bed	°C	880	850	830
residence time	s	4	4	4
cooling time	s	4	4	4
stack	°C	160	160	160
<u>Chlorine balance</u>				
coal	kg/h	15.5	10.6	8.3
wood and bark chips	kg/h	-	4.4	3.4
sewage sludge	kg/h	-	-	0.3
refuse-derived-fuel	kg/h	-	-	0.1
limestone	kg/h	1.4	3.5	3.1
bottom ash	kg/h	5.8	6.3	4.2
fly ash	kg/h	6.4	7.2	5.4
flue gas	kg/h	4.7	6.3	5.5
<u>Copper input</u>				
total	kg/h	0.6	0.9	1.0
<u>PCDD/F</u>				
flue gas	µg/h	1.7	2.9	3.7

Even minor amount of transition metals compounds strongly affect composition and structure of bottom ash and flue ash.

Thinner ash particles from biomass more easily deposits on the walls and heat transfer surfaces. In presence of alkali metals they may form hard glassy layers. Important prerequisite of large-scale use of alternative fuels is just a successful solution of the problems of crusts and corrosion (Sami et al., 2001).

To investigate these potential risks, the effect of addition of several alternative fuels to coal was studied experimentally in an industrial fluid bed combustor.

EXPERIMENTAL

The experiments have been carried out in 175 MW fluid bed boiler K11 in the paper mill Franschach Štětí. The equipment is described in details in other papers of this journal issue.

The boiler was designed for lignite; the supply comes from North Bohemian Brown Coal District

(Most Basin). As alternative fuel, following materials have been tested:

- wood chips with bark from pulp plant,
- paper mill sewage sludge,
- refuse-derived fuel containing chopped paper, textile and plastics from municipal waste.

As shown in Table 1., the applied alternative fuels do not bring into the balance any essential input streams of chlorine. Wood and bark chips contain 200 ppm Cl, the sewage sludge 20 ppm Cl, and the applied refuse-derived fuel 130 ppm. The more important is content 300-520 ppm Cl in the lignite. Surprising fact is comparatively large content of Cl in the limestone used for desulfuration.

Analysis of composition of particulate streams proved that:

- chlorine content in alternative fuel was lower than in coal of the same mass and even the same thermal content

- content of copper and other heavy metals in alternative fuel was considerably lower than in coal itself,
- content of alkali metals in alternative fuel was also lower than in coal.

With respect to the above facts, the alternative fuel applied does not bring any problems in its chemical composition. Potential problem may occur in the effects to the temperature regime in the fluid bed, caused by non-uniformity and lower thermal content of the fuel.

Basic data on the chlorine streams and temperatures are presented in Table 1. Evidently, distribution of chlorine to the emissions – bottom ash, flue ash and flue gas in stack - has not been changed significantly. It can be assumed that the chemical speciation of the stream has not vary as well. Presented data on PCDD/F supports this statement.

CONCLUSION

Low emission of dioxins is a criterion of technological excellence of the combustion and downstream processing of flue gas. It is a well-known fact, that content of PCDD/F depends primarily on the uniformity of combustion and temperature regime in the bed and in the way of flue gas cooling and ash separation. Content of chlorine within the limits (0.1-1 kg Cl per 1000 kg of fuel) has a minor effect. The most of the chlorine is retained in ash as environmentally friendly or at least inert inorganic compounds, less than 0.1 % of chlorine input is emitted in flue gas as volatile organic compounds. Content of toxic polychlorinated dibenzo-dioxins and dibenzo-furans is seven decadic orders lower, i.e. few hundreds nanograms per ton of fuel. Even the large power plants using low grade coal containing serious amount of chlorine are not classified as a main source of PCDD/F.

In this work, these assumptions were checked for the fluid bed boiler 175 MW with dry desulfuration during combustion of alternative fuel. There are two potential reasons for worsening the emissions for alternative fuel. First, it may be increasing input of chlorine with fuel. It was not our case. Second, there may be lower and oscillating temperature. In our fluid bed the temperature level was kept above 800 °C even with the alternative fuel. Therefore there was no reason to find any adverse effect to the emission of chlorine compounds and their speciation. In particular, it has been proved by determination of low toxicity equivalent I-TEQ of PCDD/F in flue gas for all our fuel combinations. A hypotheses that the slight variation of dioxin production can be correlated with the copper content in fuel seems to be plausible, but it should be checked using more extended experimental material. With lower level of alkali metals in alternative fuel, the incrustation of ash on walls is not on issue; this may be problem when combusting straw or reed.

The large-scale experiments proved the feasibility of addition of large percentage, up to 50 %, of alternative organic fuels, namely wood and bark chips, paper mill sewage sludge, and chopped paper, textile and plastic particles, to the fluid bed boiler as a substitute for lignite. From the viewpoint of chlorine derived compounds in emissions, the co-firing of lignite with the alternative fuels under investigation is a good choice.

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