ACAP Project «Reduction/Elimination of dioxin and furan emissions in the Russian Federation with Focus on the Arctic and Northern Regions Impacting the Arctic»

Phase II report

Centre for international projects

Moscow, 2008
ACAP Project «Reduction/Elimination of dioxin and furan emissions in the Russian Federation with Focus on the Arctic and Northern Regions Impacting the Arctic»

Phase II Report
Preface

The Project "Reduction/Elimination of Emissions of Dioxins and Furans in the Russian Federation with focus on the Arctic and northern regions impacting the Arctic" was implemented within the framework of the Arctic Council Action Plan (ACAP) by the Centre for International Projects in 2003 and 2004.

The Project aims to implement the Programme on identification and quantification of emissions of dioxins and furans with the purpose to reduce the formation and emission of these pollutants.

**Donor countries:** Sweden (SWE EPA), USA (US EPA) and Norway (SFT).

**Participants in Russia:** The Centre for International Projects, CIP, (attached to the Ministry of Natural Resources) coordinating role for Russian activities, the Ministry of Industry and Energy, the Ministry of Health and the Federal Environmental, Industrial and Nuclear Supervision Service (Rostechnadzor).

In addition also the Research Engineering Centre “Syntez”, Cleaner Production and Sustainable Development Centre in cooperation with TEKNA (the Norwegian Society of Chartered Technical and Scientific Professionals) and Russian Research Centre of Emergencies of the Ministry of Social Development of the Russian Federation are partners in the project.

This project is performed under the Arctic Council, through its “Arctic Contaminants Action Program”, ACAP. The Arctic Council is an intergovernmental forum for cooperation, coordination and interaction between Arctic states, indigenous communities and industrial facilities.

**Overall objectives**
Achieve reductions in the formation and emission of dioxins and furans in the Arctic and in areas affecting the Arctic.
Support Russian authorities and enterprises to reduce the emission of POPs from other parts of Russia to the Arctic.
Facilitate the development of dioxin and furan inventories in Russia.
Gain new information on sources of dioxins and furans and the magnitude of their releases.
Identify recommendations on adequate measures and techniques (based on BAT and BEP) for reduction/elimination of dioxins/furans emissions.
These activities are steps to facilitate the implementation of the UN ECE LRTAP POPs Protocol and the Stockholm Convention on POPs in the Russian Federation.

**Phase I – Finalised**
Translation of UNEP Chemicals’ Standardized Toolkit into Russian.
Production and distribution of a dioxins/furans Fact Sheet.
Analytical hands-on training programme for sampling and analysis of flue gas.
Inventories of emissions to air based on UNEP Toolkit estimations at the investigated facilities.

**Phase II – Ongoing**
A feasibility study of measures:
Analysis of dioxins in gas, liquid and solid wastes.
Implementation of training programmes for operation personal at individual industries.
Development of recommendations of measures.
Phase III – Start late 2007
Implementation of demonstration projects commensurate with financial resources. Funding of environmentally sound investments at individual enterprises will be discussed with national and international financial institutions.

The emissions of dioxins and furans from major sources in Archangelsk and Murmansk Oblasts and the Komi Republic were estimated within the framework of Phase I, forming the base for implementation of Phase 2. The emissions from the sources were estimated from data on production and raw materials consumption multiplied with so-called emission factors for dioxins/furans formed per unit of end product produced or unit raw materials consumed.

The largest sources of dioxin and furans identified in the region during Phase I were:
- Murmansk Solid Waste Incineration Plant (Murmansk Oblast);
- Koryazhma Pulp and Paper Plant in Kotlas (Arkhangelsk Oblast);
- Vorkutinskiy Cement Plant in Vorkuta (the Komi Republic).

The report: "Assessment of some major sources of dioxins/furans in Archangelsk and Murmansk regions and Republic of Komi" on results of the activities implemented in the framework of the Phase 1 was made.

Policy making authorities on central level:
- The Ministry of Nature Resources
- The Federal Service for Industrial, Environmental and Nuclear Supervision (Rostekhnadzor)
- The Ministry of Health

Enterprises and implementing supervision authorities on regional level:

In Murmansk Oblast
- Rostekhnadzor in M.O.;
- Committee of Nature Resources and Nature Protection of the M.O. Adm.;
- Top Managers and engineers at the Murmansk Solid Waste Incineration Plant

In Arkhangelsk Oblast
- Rostekhnadzor in A.O.;
- Committee of Nature Resources and Nature Protection of the A.O. Adm.;
- Top Managers and engineers at the Koryazhma Pulp and Paper Plant in Kotlas.

In Komi Republic
- Rostekhnadzor in Komi Rep.;
- Ministry of Environmental Protection of the Komi Rep.
- Top Managers and engineers at the Syktyvkar Timber Mill;
- Top Managers and engineers at the Vorkutinskiy Cement Plant in Vorkuta.
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Abbreviations

‘C
13C12-PCDD/F
2,3,7,8-TCDD
ADt
BAT
CJSC
ECF
FC
GC/MS
I-TEF
I-TEQ
Kotlas PPP
MBP SFC
NA
ND
Nm3
OJSC
PCDD
PCDF
PPS
PUF
PVC
QA / QC
QCA
rpm
SRB
TCE
UNEP
PPP

Units

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>‘C</td>
<td>Degrees Celsius</td>
</tr>
<tr>
<td>13C12-PCDD/F</td>
<td>Isotopic labelled standards (^{13}C_{12}) of PCDD and PCDF</td>
</tr>
<tr>
<td>2,3,7,8-TCDD</td>
<td>2,3,7,8 Tetrachlorodibenzo-p-dioxin</td>
</tr>
<tr>
<td>ADt</td>
<td>Air-Dried ton</td>
</tr>
<tr>
<td>BAT</td>
<td>Best Available Techniques/Technologies</td>
</tr>
<tr>
<td>CJSC</td>
<td>Closed Joint-Stock Society</td>
</tr>
<tr>
<td>ECF</td>
<td>Elemental Chlorine Free (bleaching)</td>
</tr>
<tr>
<td>FC</td>
<td>Forest Complex</td>
</tr>
<tr>
<td>GC/MS</td>
<td>Gas Chromatography-Mass Spectrometry</td>
</tr>
<tr>
<td>I-TEF</td>
<td>International Toxicity Equivalency Factor</td>
</tr>
<tr>
<td>I-TEQ</td>
<td>International Toxic Equivalent</td>
</tr>
<tr>
<td>Kotlas PPP</td>
<td>“Kotlas Pulp-and-Paper Plant” Public Corporation</td>
</tr>
<tr>
<td>Ltd.</td>
<td>Company with Limited Responsibility</td>
</tr>
<tr>
<td>MBP SFC</td>
<td>“Mondi Business Paper Syktyvkar Forest Complex” Public Corporation</td>
</tr>
<tr>
<td>NA</td>
<td>Not Applicable or Not Analysed</td>
</tr>
<tr>
<td>ND</td>
<td>No Data available or Not Detected</td>
</tr>
<tr>
<td>Nm3</td>
<td>standard (normal) (m^3), gas volume at normal atmospheric pressure and 25°C</td>
</tr>
<tr>
<td>OJSC</td>
<td>Open Joint-Stock Society</td>
</tr>
<tr>
<td>PCDD</td>
<td>Polychlorinated dibenzo-p-dioxins</td>
</tr>
<tr>
<td>PCDF</td>
<td>Polychlorinated dibenzofurans</td>
</tr>
<tr>
<td>PPP</td>
<td>Pulp and Paper Plant</td>
</tr>
<tr>
<td>PUF</td>
<td>solid adsorbent (foamed polyurethane)</td>
</tr>
<tr>
<td>PVC</td>
<td>Production of Viscose Cellulose</td>
</tr>
<tr>
<td>QA / QC</td>
<td>Quality Assurance and Control</td>
</tr>
<tr>
<td>QCA</td>
<td>Quantitative Chemical Analysis</td>
</tr>
<tr>
<td>rpm</td>
<td>rotations per minute</td>
</tr>
<tr>
<td>SRB</td>
<td>Soda Regenerating Boiler</td>
</tr>
<tr>
<td>TCE</td>
<td>Ton Coal Equivalent, corresponds to 1 ton of standard fuel with combustion value of 7 Gcal</td>
</tr>
<tr>
<td>UNEP</td>
<td>United Nations Environment Programme</td>
</tr>
<tr>
<td>PPP</td>
<td>Pulp and Paper Plant</td>
</tr>
<tr>
<td>ПНД Ф</td>
<td>Chemical Analysis Standard in Russia</td>
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<table>
<thead>
<tr>
<th>Unit</th>
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<tbody>
<tr>
<td>t</td>
<td>(10^6) g</td>
</tr>
<tr>
<td>kg</td>
<td>(10^3) g</td>
</tr>
<tr>
<td>g</td>
<td>(10^0) g</td>
</tr>
<tr>
<td>mg</td>
<td>(10^{-3}) g</td>
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<tr>
<td>μg</td>
<td>(10^{-6}) g</td>
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<td>(10^{-9}) g</td>
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<td>(10^{-12}) g</td>
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<td>l</td>
<td>(10^0) l</td>
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<td>(10^{-6}) l</td>
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<tr>
<td>Gcal</td>
<td>(10^9) calories</td>
</tr>
<tr>
<td>MJ</td>
<td>(10^6) Joule</td>
</tr>
<tr>
<td>TJ</td>
<td>(10^{12}) Joules</td>
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2. Introduction

In the framework of the Phase I of the Project at first the estimated inventory of the polychlorinated dibenzo-\(p\)-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) releases (for short “dioxins” and “furans” or just “dioxins”) from the main sources of Arkhangelsk and Murmansk oblasts and the Republic of Komi was implemented. Then analysis of gas releases for dioxins was carried out at the most significant objects (Annex A). After that the experimental dioxin emission factors were found.

The Phase II of the Project was intended as the more thorough and detailed study of factors affecting the dioxins generation. This work is planned for implementation at the “Kotlas Pulp-and-Paper Plant” Public Corporation (Kotlas PPP) and Vorkuta Cement Plant (at the present time “Vorkutacement”).

The report «Revisit of the list of environmental «hot spots» in the Russian part of the Barents region: proposals for environmentally significant investment projects» of 2003, developed according to the request of the High-Level Kirkenes Meeting of the Barents Euro-Arctic Council, which is orientated to the countries of the Arctic region for the co-ordinated activity to address the issues of environmental character and selection of optimal ways to their solution at the concrete enterprises.

The above enterprises are considered in this report as the objects where it is necessary to implement the activities that provide elimination or reduction of their adverse impact of the environment of the region.

In particular, the Kotlas PPP is the biggest air polluter in Arkhangelsk oblast and is the most powerful source of pollution with sewage. At the same time the Vorkuta Cement Plant in the Republic of Komi is reported as the serious air polluter, and with the dust amongst all.

Phase II of the present ACAP Project is in the common course of the joint activity of the countries of the Barents region, NEFCO and AMAP to address environmental problems of the region, and at the same time significantly to extend and deepen it with regards to pollution with persistent organic pollutants, and in particular dioxins and furans.

Collection and analysis of different technical information on two enterprises selected for the study: Vorkuta Cement Plant and Kotlas PPP was carried out at the first stage. The technologies of production used at these enterprises, raw materials used, data on contaminants releases, and products were considered above all.

Then analysis and assessment of controlled parameters of processes that can initiate generation of dioxins was carried out. For the cement production the dioxins generation depends on such main factor, as the temperature of dust collector from the cement kiln.

There are several sources of dioxins at pulp and paper plants. This most important are related to pulp bleaching with chlorine gas. Another significant source of dioxin emission is the incineration of timber wastes. Incineration of used liquor – the pulping waste – generates less significant emission of dioxins.

Data on assessment of technologies applied at the enterprises, selection of the most efficient technologies and development of recommendations to reduce the dioxin releases at the Vorkuta Cement Plant and Kotlas PPP are provided in the report. Also the present report provides the technical and economic assessment of arrangements related to the reduction/elimination of dioxin/furan releases at the Kotlas PPP and the Vorkuta Cement Plant.
3. **Determination and assessment of factors impacting on formation of dioxins/furans at the Vorkuta cement plant**

As the question of use of recommendations of the best available techniques (BAT) is the key for the present project it is useful to state their main requirements in details (For “Revised draft Guidelines on best available techniques and provisional guidance on best environmental practices relevant to Article 5 and Annex C of the Stockholm Convention on persistent organic pollutants” (10).

### 3.1.1. The technology of cement production

Cement plants as a rule are located at the extraction sites of the raw material for cement manufacturing.

The cement manufacturing includes two stages: the first - obtaining of clinker, and the second – clinker powdering with admixing of a gypsum or other additives to it. The extraction of raw materials (limestone) is preceded to the manufacturing process. Then the crushing of this material to pieces of 10 cm in diameter is following. After this the limestone is drying and then the process of grinding and mixing if it with other components is following too. Further this raw mixture is firmed. This is the way to obtain a clinker.

The next stage is composed of several steps either. This includes: crushing of clinker, drying of mineral additives, crushing of gypsum stone, grinding of clinker with gypsum and active mineral additives. It should be considered however that the raw material is not always the same and its physical and technical characteristics (such as firmness, humidity etc.) vary. Each raw type has is own way of manufacturing. There are three ways of manufacturing in the cement industry, which are grounded on the different technological methods of raw material preparation: wet, dry and combined.

Wet method of manufacturing is used for producing of the cement from chalk (carbonate component), mud (silicate component) and iron containing additives (converter slam, ferriferous product, sulphur wastes). Mud humidity should not be over 20%, and the chalk humidity – 29%. This method is called wet because crushing of the raw mixture is carrying out in the aqueous media, and the output is the batch as the aqueous suspension – slam with humidity 30-50%. Further, slam is progressing to the kiln for firming, which diameter is 7 m and length – 200 m and more. Carbon acids are emitted from the raw during firming. After this the clinker balls that are generating as the output from the kiln, are pounded to fine powder, which is a cement finally.

Dry method is when raw materials are dried before or during the grinding. And the raw batch is released as fine-pounded dry powder.

Combined method, following its name, is supposing the utilization of both the dry and the wet methods. Combined method has two varieties. The first proposes that the raw mixture is producing through the wet method as a slam, than it is dehydrated at filters to humidity of 16-18% and progress for firming as the semidry mass. The second option is absolutely opposite to the first one: firstly the dry method is applied to make the raw mix, and than it is granulated through admixing of 10-14% of water, the granule size is 10-15 mm, and it is forwarding for firming. The specified equipment and strictly regulated sequence of operations is applied.
General principles

The basic chemistry of the cement manufacturing process begins with the decomposition of calcium carbonate (CaCO$_3$) at about 900° C to leave calcium oxide (CaO, lime) and liberate gaseous carbon dioxide (CO$_2$); this process is known as calcination. This is followed by the clinkering process in which the calcium oxide reacts at high temperature (typically 1,400°–1,500° C) with silica, alumina and ferrous oxide to form the silicates, aluminates and ferrites of calcium that comprise the Portland clinker. This clinker is then ground together with gypsum and other additives to produce cement.

Figure 1 identifies the principal processes and system boundaries of cement production.

Figure 1. Process identification and system boundaries of cement production

Emission control

Modern cement kilns are equipped with either electrostatic precipitators or fabric filters, or both, for particulate matter control. In some cases, the flue gases are cooled prior to the dry air pollution control device. Acid gas pollution control devices have not been used at cement kilns as the raw materials are highly alkaline and provide a significant degree of acid gas control, although there are a number of kilns equipped with wet scrubbers, if the sulphur content of the raw meal is high.

Operation with conventional fuels

Conventional fuels used in cement plants are fossil fuels such as coal, lignite, fuel oil or natural gas. These fuels can be used singly or in combination, in which case a minimum quality (in terms of heating value, heavy metal or sulphur content) must be ensured. Some of the fossil fuels (e.g. coal) are ground in mills before they are injected. For smooth kiln operation, the production of a homogeneous clinker and complete combustion, some important criteria have to be considered for conditioning of the fuels. The oxidation of the fuel constituents occurs more quickly when the fuels are well mixed and the specific surface is larger. In the case of liquid fuel, injection has to be as smooth as possible. In the case of solid fuels, thorough mixing with other fuels used at the same time is required. This is not necessarily required as long as the material is homogenous and highly uniform.

A cement plant consumes 3,000 to 6,500 MJ (electricity and transport not included) per
ton of clinker produced, depending on the raw materials and the process used. Most cement kilns today use coal and petroleum coke as primary fuels, and to a lesser extent natural gas and fuel oil. As well as providing energy, some of these fuels burn to leave fuel ash containing silica and alumina compounds (and other trace elements). These combine with the raw materials in the kiln, contributing to the structure of the clinker and forming part of the final product. Energy use typically accounts for 30–40% of the production costs. The different types of fuels, in decreasing order of importance, are:
- Pulverized coal and petroleum coke (pet coke);
- (Heavy) fuel oil;
- Natural gas.

Potential feed points for supplying fuel to the kiln system are via:
- The main burner at the rotary kiln outlet end;
- A feed chute at the transition chamber at the rotary kiln inlet end (for lump fuel);
- Secondary burners to the riser duct;
- Pre-calciner burners to the pre-calciner;
- A feed chute to the pre-calciner/pre-heater (for lump fuel);
- A mid-kiln valve in the case of long wet and dry kilns (for lump fuel).

Depending on operational conditions – explicitly in the case of improper operation of the installation – significant emissions of polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF) can occur. In proper operation the release of PCDD/PCDF should be well below 0.1 ng I-TEQ/ m³.

**Examples of waste and alternative fuels**

The substitution of fossil fuels with alternatives is a well-developed practice in a number of countries. Some countries have been using wastes as alternative fuels for almost 30 years, and some national governments actively promote this approach, provided that stringent requirements with regard to input, process and emission control are met. However, some stakeholders and other jurisdictions have viewed the practice in the same light as incineration. In the countries where this practice is well established, consideration has been given to the types of materials best suited to use in cement kilns, which may include:
- Used tyres;
- Meat, bone meal and animal fat;
- Plastics;
- Impregnated sawdust;
- Wood, paper, cardboard, packaging waste;
- Sludge (paper fibre, sewage);
- Agricultural and organic waste;
- Shale, oil shales;
- Coal slurries;
- Distillation residues;
- Fine fractions of coal or coke/anodes/chemical cokes;
- Waste oils, oiled water;
- Spent solvents.

It is important to control waste parameters (e.g. heat value, water content, ash content, content of chlorine, content of heavy metals).
Negative waste list

Co-processing should only be applied if not just one but all tangible preconditions and requirements of environmental, health and safety, socio-economic and operational criteria are fulfilled. As a consequence not all waste materials are suitable for co-processing. The following is a list of waste not recommended for co-processing in cement plants:

• Nuclear waste;
• Electronic waste;
• Explosives;
• Mineral acids;
• Asbestos-containing waste;
• High-concentration cyanide waste;
• Infectious medical waste;
• Chemical or biological weapons destined for destruction;
• Entire batteries;
• Unssorted municipal garbage and other waste of unknown composition.

The list outlined above is not an exhaustive list. In general, wastes with a low heat value and a very high heavy metal content are not suitable for being inserted into a cement kiln. Municipal solid waste should not be co-incinerated in cement kilns due to its unpredictable composition and its characteristics. Furthermore, individual companies may exclude additional materials, depending on local circumstances.

Considerations for selection of wastes

The selection of wastes is a complex process and is influenced by many factors, such as kiln operation, the nature of the waste itself, the general impact on the environment, the desired clinker quality and the probability of the formation and release of chemicals listed in Annex C of the Stockholm Convention and other releases into the environment. The operator should develop a fuels evaluation and acceptance procedure. Based on this procedure an assessment is carried out of the effect of the fuel on plant emissions and the potential need for new equipment or procedures to ensure that there is no negative impact on the environment. The variables that should be considered when selecting fuels and raw materials include:

**Kiln operation**

• Chlorine, sulphur, and alkali content: These may build up in the kiln system, leading to accumulation, clogging and unstable operation; excess in chlorine or alkali may produce cement kiln dust or bypass dust (and may require installation of a bypass), which must be removed, recycled or disposed of responsibly;
• Water content: High water content may reduce the productivity and efficiency of the kiln system;
• Heat value (fuel): The heat value is the key parameter for the energy provided to the process;
• Ash content: The ash content affects the chemical composition of the cement and may require an adjustment of the composition of the raw materials mix;
• Additional factors are relevant, such as treatment capacity and volume of waste gas;
• Stability of operation (e.g. CO peaks) and the state (liquid, solid), preparation (shredded, milled) and homogeneity of the waste.

**Clinker and cement quality**

• Phosphate content: This influences setting time;
• Chlorine, sulphur, and alkali content: These affect overall product quality;
• Thallium and chromium: in relation to cement kiln dust and cement quality and possible allergic reactions in sensitive users.
Atmospheric pollutant emissions other than chemicals listed in Stockholm convention

• High sulphur contents in raw materials and inserted fuels and wastes: These may result in the release of SO2;

• Control of exhaust: Where an alkali bypass system is installed, appropriate control of the exhaust to atmosphere also needs to be provided on the bypass exhaust similar to that mandated for the main exhaust stack;

• Chlorides in raw materials or fuels: These may combine with alkalis also present in the feed to form fine particulate matter composed of chlorides of those alkalis, which can be difficult to control; in some cases chlorides have combined with ammonia present in the limestone feed to produce highly visible detached plumes of fine particulate composed mainly of ammonium chloride;

• Metals in fuel or raw material: Raw materials and fuels will always contain metals in varying concentrations. The behaviour of these metals in the burning process is dependent on their volatility. Non-volatile metal compounds remain within the process and exit the kiln as part of the cement clinker composition. Semi-volatile metal compounds are partly taken into the gas phase at sintering temperatures to condense on the raw material in cooler parts of the kiln system. This leads to a cyclic effect within the kiln system (internal cycles) which builds up to the point where an equilibrium is established and maintained between input and output via the cement clinker. Volatile metal compounds condense on raw material particles at lower temperatures and potentially form internal or external cycles, if not emitted with the flue gas of the kiln. Thallium and mercury and their compounds are particularly easily volatilised and to a lesser extent so are cadmium, lead, selenium and their compounds.

• The metal concentration in cement kiln dust depends on the feedstock and recirculation in the kiln system. In particular, the use of coal and waste fuels may increase the input of metals into the process. Dust control devices can only capture the particle-bound fraction of heavy metals. The retention rate for the gaseous fraction of volatile metals such as mercury is low. Such inputs into the kiln system should therefore be limited. This needs to be taken into account as soon as wastes containing volatile heavy metals such as mercury, lead or cadmium are co-incinerated. Wood treated with copper, chromium, arsenic etc. also requires special consideration with regard to the efficiency of the flue gas cleaning system.

• The choice of fuels can also affect greenhouse gas emissions. For example, substituting fossil fuels by biomass results in a decrease of net CO2 emissions;

• Wastes may influence NOx emissions, depending on their composition and water content.

Raw materials and product

The main environmental issues associated with cement production are emissions to air, energy use, and soil and groundwater contamination from the handling and storage of waste cement kiln dust. Wastewater discharges are usually limited to surface run-off and cooling water and generally do not contribute substantially to water pollution.

Primary process outputs of cement production are:

• Product: Clinker, which is ground and then mixed with other ingredients to produce cement;

• Kiln exhaust gas: Typical kiln exhaust gas volumes range between 1,700 and 2,500 m$^3$/Mg of clinker (cubic metres per metric ton of clinker; reference conditions 101.3 kPa, 273 K, dry gas basis) for all types of kilns. Suspension pre-heater and pre-calciner kiln systems normally have exhaust gas volumes around 2,000 m$^3$/Mg of clinker (dry gas, 101.3 kPa, 273 K);

• Recycling cement kiln dust (collected in the air pollution control equipment;

• Cement kiln dust (collected in the air pollution control equipment;

• Recycling cement kiln dust to the kiln generally results in a gradual increase in the alkali content of generated dust, which may lead to damage to kiln linings, produce inferior cement and increase both stack particle emissions and the amount of cement kiln dust that must be disposed of and the resulting air emissions due to its handling and disposal. In Europe cement kiln dust is usually circulated back to the kiln feed material or added directly to the product cement The
build up of alkalis in the kiln system may be avoided by either removal of the collected kiln dust or by using an alkali bypass system. For pre-heater and pre-calciner kilns, this is sometimes accomplished by alkali bypass systems at the pre-heater tower that removes alkalis from the kiln system;

- Alkali bypass exhaust gas: At facilities equipped with an alkali bypass, the alkali bypass gases can be released either from a separate exhaust stack or from the main kiln stack.

Energy use

The cement industry is an energy-intensive industry where energy typically accounts for 30–40% of operating costs (i.e., excluding capital costs). A cement plant consumes 3,000 to 6,500 MJ of fuel per ton of clinker produced. This large range of energy demand covers all kinds of cement kilns. The theoretical energy use for the burning process (involving chemical reactions) is about 1,700 to 1,800 MJ per ton of clinker. The actual fuel energy use for different kiln systems is in the following ranges (MJ per ton of clinker):

- 3,000–3,800 for dry process, multistage cyclone pre-heater and pre-calciner kilns;
- 3,100–4,200 for dry process rotary kilns equipped with cyclone pre-heaters;
- 3,300–4,500 for semi-dry/semi-wet processes (Lepol kiln);
- Up to 5,000 for dry process long kilns;
- 5,000–6,000 for wet process long kilns;
- 3,100 to > 6,500 for shaft kilns and for special cements.

The electricity demand is about 90–130 kWh per ton of cement.

Formation of PCDD/PCDF

Any chlorine input in the presence of organic material may potentially cause the formation of PCDD and PCDF in heat (combustion) processes. PCDD/PCDF can be formed by the de novo synthesis mechanism in or after the pre-heater and in the air pollution control device if chlorine and hydrocarbon precursors are available in sufficient quantities in the temperature range 200º C to 450º C. A graph of the temperature profile for gases and materials and their typical residence times in each stage of a clinker kiln with cyclonic pre-heater and pre-calciner is shown in Figure 2.

Figure 2. Temperature profile and typical residence time stages of clinker kiln with cyclonic pre-heater and pre-calciner Source: Fabrellas et al. 2004.
Studies on emissions of PCDD/PCDF into air

A comprehensive survey of PCDD/PCDF emissions from cement kilns in developed and developing countries is given in (Karstensen 2006). The data represents more than 2200 measurements in kilns with and without the firing of a wide range of waste materials and covering the period from early 1990’s until recently. Table 1 summarizes the results of the PCDD/PCDF measurements; some examples are described in more detail hereunder.

<table>
<thead>
<tr>
<th>Country or company</th>
<th>Use of alternative fuel and raw materials</th>
<th>Concentration, in ng I-TEQ/m³, of PCDD/PCDF *</th>
<th>Number of measurements</th>
<th>Emission factor μg I-TEQ/ton cement *</th>
</tr>
</thead>
<tbody>
<tr>
<td>Australia</td>
<td>Yes</td>
<td>0.001–0.07</td>
<td>55</td>
<td>0.0032–0.216</td>
</tr>
<tr>
<td>Belgium</td>
<td>Yes</td>
<td>&lt; 0.1</td>
<td>23</td>
<td></td>
</tr>
<tr>
<td>Canada</td>
<td>Yes</td>
<td>0.0054–0.057</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>Chile</td>
<td>Yes</td>
<td>0.0030–0.0194</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Colombia</td>
<td>Yes</td>
<td>0.00023–0.0031</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Denmark</td>
<td>Yes</td>
<td>&lt; 0.0006–0.0027</td>
<td>?</td>
<td></td>
</tr>
<tr>
<td>Egypt</td>
<td>Yes</td>
<td>&lt; 0.001</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Europe</td>
<td>Yes</td>
<td>&lt; 0.001–0.163</td>
<td>230</td>
<td>&lt; 0.001–5</td>
</tr>
<tr>
<td>Germany 1989–1996</td>
<td>Yes</td>
<td>0.02</td>
<td>&gt; 150</td>
<td></td>
</tr>
<tr>
<td>Germany 2001</td>
<td>Yes</td>
<td>&lt; 0.065</td>
<td>106</td>
<td></td>
</tr>
<tr>
<td>Holcim 2001</td>
<td>Yes</td>
<td>0.0001–0.2395</td>
<td>71</td>
<td>0.104 (clinker)</td>
</tr>
<tr>
<td>Holcim 2002</td>
<td>Yes</td>
<td>0.0001–0.292</td>
<td>82</td>
<td>0.073 (clinker)</td>
</tr>
<tr>
<td>Holcim 2003</td>
<td>Yes</td>
<td>0.0003–0.169</td>
<td>91</td>
<td>0.058 (clinker)</td>
</tr>
<tr>
<td>Heidelberg</td>
<td>Yes</td>
<td>0.0003–0.44</td>
<td>&gt; 170</td>
<td></td>
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<tr>
<td>Japan</td>
<td>Yes</td>
<td>0–0.126</td>
<td>164</td>
<td></td>
</tr>
<tr>
<td>Lafarge</td>
<td>Yes</td>
<td>0.003–0.231</td>
<td>64</td>
<td></td>
</tr>
<tr>
<td>Mexico</td>
<td>Yes</td>
<td>0.0005–0.024</td>
<td>3</td>
<td></td>
</tr>
<tr>
<td>Norway</td>
<td>Yes</td>
<td>0.02–0.13</td>
<td>&gt; 20</td>
<td>0.04–0.40</td>
</tr>
<tr>
<td>Philippines</td>
<td>Yes</td>
<td>0.0059–0.013</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Poland</td>
<td>Yes</td>
<td>0.009–0.0819</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td>Portugal</td>
<td>Yes</td>
<td>0.0006–0.0009</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>RMC</td>
<td>Yes</td>
<td>0.0014–0.0688</td>
<td>13</td>
<td></td>
</tr>
<tr>
<td>Siam Cement Co.</td>
<td>Yes</td>
<td>0.0006–0.022</td>
<td>4</td>
<td></td>
</tr>
<tr>
<td>South Africa</td>
<td>Yes</td>
<td>0.00053–0.001</td>
<td>2</td>
<td></td>
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<tr>
<td>Spain</td>
<td>Yes</td>
<td>0.00695</td>
<td>89</td>
<td>0.014464</td>
</tr>
<tr>
<td>Spain Cemex</td>
<td>Yes</td>
<td>0.0013–0.016</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Spain Cimpor</td>
<td>Yes</td>
<td>0.00039–0.039</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>Taiheiyo</td>
<td>Yes</td>
<td>0.011</td>
<td>67</td>
<td></td>
</tr>
<tr>
<td>Thailand</td>
<td>Yes</td>
<td>0.0001–0.018</td>
<td>12</td>
<td>0.00024–0.0045</td>
</tr>
<tr>
<td>UK</td>
<td>Yes</td>
<td>0.012–0.423</td>
<td>14</td>
<td>&lt; 0.025–1.2</td>
</tr>
<tr>
<td>Uniland</td>
<td>Yes</td>
<td>0.002–0.006</td>
<td>2</td>
<td>0.005–0.011</td>
</tr>
<tr>
<td>USAb</td>
<td>Yes</td>
<td>0.004– ~ 50</td>
<td>~ 750</td>
<td>&lt; 0.216–16.7</td>
</tr>
<tr>
<td>Venezuela</td>
<td>Yes</td>
<td>0.0001–0.007</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Vietnam</td>
<td>Yes</td>
<td>0.0095–0.014</td>
<td>3</td>
<td></td>
</tr>
</tbody>
</table>

a. The numbers are either given as a range or as the mean value, and refer to 10 or 11% O₂, depending on national regulations.
b. The high numbers from the United States relate to measurements obtained in the 1990s; the number of measurements is approximate. Source: Karstensen 2006b.
In a recent survey performed by Cembureau, PCDD and PCDF measurements from 110 cement kilns in 10 countries were presented. The countries covered by the survey were Czech Republic, Denmark, France, Germany, Hungary, Italy, the Netherlands, Norway, Spain and the United Kingdom. The average concentration, taking into account all of the data in this dataset, was 0.016 ng I-TEQ/ m³. The range between the lowest and highest concentrations measured was < 0.001 to 0.163 ng I-TEQ/ m³ (Karstensen 2006b). All measurements were expressed corrected to standard conditions (dry gas, 273 K, 101.3 kPa and 10% O₂).

**Study on releases of PCDD/PCDF through solids**

Since the data for stack emissions from cement kilns indicate that well-designed, well-operated facilities can achieve very low exhaust gas concentrations of PCDD/PCDF, it can also be expected that such facilities will have low levels in cement kiln dust recovered from the air pollution control system. The same factors that contribute to low levels remaining in the exhaust to atmosphere argue for low concentrations in the collected solid material. The two main solid materials produced in cement production are cement clinker from the cooler and dust materials trapped in the air pollution control devices.

New analyses of solid materials have been gathered from cement companies participating in the Cement Sustainability Initiative (CSI) (Karstensen 2006b). Eight CSI companies reported the PCDD/PCDF concentration in cement clinker dust in 2005. Ninety samples showed an average value of 6.7 ng I-TEQ/kg, seemingly strongly influenced by a few high-level samples. The highest concentration reported was 96 ng I-TEQ/kg. Eight CSI companies reported the PCDD/PCDF concentration in 57 clinker samples in 2005. The average value of all samples was 1.24 ng I-TEQ/kg. The clinker samples came from wet and dry suspension pre-heater kilns. The highest concentration reported was 13 ng I-TEQ/kg.

Two CSI companies reported the PCDD/PCDF concentration in 11 kiln feed samples in 2005, consisting of raw meal, pellets, and slurry and raw material components. The average value of these samples was 1.4 ng I-TEQ/kg. The kiln feed samples came from wet and dry suspension pre-heater kilns. The highest concentration reported was 7.1 ng I-TEQ/kg.

### 3.1.2. Best available techniques and best environmental practices

#### Primary measures and process optimization

**Process optimization**

- Ensure rapid cooling of exhaust gases to a temperature lower than 200° C.
- Characterize the parameters that correspond to good operation and use these as a basis to improve other operational performance.;
- Manage the kiln process to achieve and maintain stable operating conditions, i.e. by optimizing process control (including implementing computer-based automatic control systems) and using modern, gravimetric solid fuel feed systems;
- Minimize fuel energy use by employing pre-heating and pre-calcination to the extent possible considering the existing kiln system configuration; and use of modern clinker coolers, enabling maximum heat recovery from the exhaust gas.

**Input controls**

- Consistent long-term supply of a main or alternative fuel is required in order to maintain stable conditions during operation;
- Substances entering the kiln should be carefully selected and controlled; specifications should be set based on product/process or emission considerations and monitored;
- Waste-derived fuel should never be used during start-up and shutdown.
- The feeding of raw mix containing waste with organic compounds that could act as precursor should be avoided;
• Halogenated waste should be fed through the main burner.
• Waste feed containing organic compounds that could act as precursor should not be fed as part of the raw mix;
• Waste-derived fuel should never be used during start-up and shutdown.

**Process modification**

The off-gas dust (also known as cement kiln dust) must be managed carefully. In many cases it may be fed back into the kiln to the extent that it can be demonstrated to be practicable and to avoid excessive emissions of volatile metals and alkali salts. Where this recycle stream can be maximized it will reduce issues related to disposal of the dust. Dust that cannot be recycled must be managed in a manner demonstrated to be safe. Depending upon the level of contaminants of concern (e.g. heavy metals, persistent organic pollutants), this material can in some cases be considered hazardous waste and may then require the special handling and disposal measures mandated by such a determination.

Control of chemicals listed in Annex C: Indirect measures for control of such chemicals are an important element of an integrated emission control strategy.

**Summary of primary measures**

In general, the primary measures mentioned above are sufficient to achieve an emission level below 0.1 ng I-TEQ/N m³ in flue gases for new and existing installations. Where all of these options do not lead to performance down to 0.1 ng I-TEQ/Nm³, secondary measures may be considered:

- *Activated carbon injection;*
- *Activated carbon filter;*
- *Selective catalytic reduction;*
- *Activated carbon injection, an emerging technology.*

**3.1.3. Main methods of production of Portland cement**

Production of the portland cement usually consists of the following operations:
- extraction of raw materials;
- preparation of raw mix consisting of ragging, milling and its homogenization;
- firming of raw mix;
- milling of the firmed product (clinker) to fine powder.

Lime and silica as well as aluminium oxide and iron oxide as the flux are the main components for the portland cement production. Other oxides always exist in geological materials as admixtures in small quantities [5].

There are two main methods of production – wet and dry methods. In case of the wet method the raw mix is milled with water. The obtained a sour-cream like liquid – slam – contains 32-45% of water. In case of the dry method the raw materials are preliminary dried and then they are jointly milled. The obtained fine powder is named as a raw meal.

In case of the wet method the raw mix is composed of only solid materials - lime-stone, marl and argillaceous slates, they are grinding without water, and then they are milled with water admixing.

The kiln is the heart of the cement production. It consists of the cylindrical iron body faced with refractory material, slightly horizontally tilted and rotating at a speed of 1-3 rev/min. Raw material is loaded at the top and is gradually forwarding towards the bottom-end facing the stream of incandescent gases. The difference between the rotary kilns for cement production and the classic rotary kilns used for incineration is that the raw materials and emitting gases are
counter-flowing what leads to careful mixing, generation of high temperatures (over 1400°C at the hot end where a clinkering takes place) and continuous dwelling time in the installation (5-7 seconds). As a result of such conditions all organic pollutants brought with fuel are destroyed in a primary furnace.

The raw material is forwarding with controlled speed from the top. When the loading reaches the high temperature organic materials are incinerated, sulphates are decayed, chlorides and alkaline salts partially evaporated.

Application of the wet process when the milled raw flour is mixing with water and is loading to firming furnace as the cement paste results in power consumption that exceed for 40% the power consumption of the dry process.

The clinker is chilled at last step. As the hot clinker leaves the bottom end of the furnace, it is quickly chilled with atmospheric air in a clinker refrigerator, for example, on a moving lattice with fans below it blowing the cold air through the clinker.

Coal, oil, gas or oil coke are common types of fuel. Such fuel as pounce, oil or gas is injected from the bottom end with hot air heated through gating above clinker in a cooler. The various combustible wastes alongside with fossil fuel are applied in a number of cases. These wastes could include: used oils, and solvents, some industrial wastes, and in some cases hazardous wastes. The bigger part of them is incinerated in a combustion (hot) end of the furnace. Tyres are frequently used, which could be placed in the furnace in some distance from its hot end integrally or milled.

Fettling has two functions. Firstly, it protects the body from hot gases, which could destroy or fuse the steel. Secondly, it serves as the media to transfer the heat between hot gases and raw material for loading.

In the centre of furnace Ca and Mg carbonates are decayed to CO₂ and CaO, and MgO. About third of loading is lost during the incineration. In a hot zone 20-30% of loading turns to a liquid. Transit time of loading through the furnace depends on the length and the rotation speed and could make 2 through 4 hours.

CaCO₃ decays at 894°C. Clay begins decaying at 980°C with generation of γ-Al₂O₃ and 3Al₂O₃·2SiO₂. Interaction between CaO and SiO₂ becomes visible at 1100°C and rapid at 1370°C with generation of C₃S.

Clinker drips from the bottom end of the furnace to a braking circuit, which unloads it to a stack or other form of the cooler where its temperature is rapidly reduced. There are various forms of coolers, through which the combustion air is gated.

Cold clinker is grinned and atomized with gypsum and other additives in drum-type ball mills and then it is transported to reinforced concrete cylindrical reservoir – so called cement silo[6].
3.1.4. Analysis and assessment of controlled factors that define formation of dioxins at the Vorkuta Cement

Data of study of PCDD and PCDF Releases in Cement Kilns

The main appropriation of cement kilns is production of clinker. Incineration of wastes in these kilns is aimed at energy production and replacement of fossil fuels. In some cases hazardous wastes are disposed in cement furnaces [10].

The inspection data of several kilns in the USA has demonstrated that PCDD and PCDF emissions during operation of their devices for control of air pollution within the range of temperatures 200-230°C are reaching 1.76 ng I-TEQ/nm³. Other studies in the USA have also demonstrated that some kilns provide bigger emissions during the incineration of hazardous wastes.

Investigations both in the USA and in Germany have revealed doubtless correlation between the concentration of PCDD emissions and temperature in the system electrostatic precipitator - smoke stack. During tests at one of the US plants the temperature in electrostatic precipitator varied between 255 and 400°C. The highest release of PCDD was at 400°C and it decreased in 50 times at 255°C. The similar correlation was observed at all other inspected plants. There was no correlation observed between the temperature and PCDD release at the input to electrostatic precipitator at temperatures below 250°C. These data are in agreement with known mechanisms of PCDD generation in municipal wastes incineration systems [10].

More detailed studies have demonstrated that the main regulatory factor (in terms of fine incineration) is the temperature of dust-collecting devices in air cleaning system. It is obvious that plants with low-temperature electrostatic precipitators provide well controlled emissions, with or without waste as fuel [10].

Therefore, optimization of technological process consists in a rapid chilling of kiln gases to temperatures below 200°C. During unloading of clinker the critical range of temperatures is usually passed quickly enough.

Cement production

It is considered that the raw material could substantially affect on the emissions and the high level of organics in raw material is connected to increased emissions of PCDD/PCDF. It should be noted that higher levels of emissions were registered in the USA, where the cement kilns with wet process were used, while for the European cement kilns (mainly in Germany and Switzerland) where dry process was used, measurements have indicated lower emissions (over 150 measurements). At the same time emitting gases from the cement kilns with the dry process could not be rapidly chilled and therefore they enter the system of kiln gases treatment relatively hot (> 300°C). However there was no data on increased PCDD/PCDF concentrations for the kilns provided with electro filters from the European enterprises [2].

The low values identified at the majority of the European enterprises were confirmed during the implementation of the dioxin sampling program and their analysis in Thailand, where PCDD/PCDF samples for two rotary firming kilns at the modern and finely controlled cement plant were selected and analysed. Samplings were selected from two firming kilns during their normal work (full loading, mix of lignite and oil coke as the primary and secondary fuel) with incidental incineration of (a) the used tires and (b) industrial wastes including used oils [2].

Firming kilns are usually provided with the equipment for reduction of solid particles emissions and catching of these particles which could be used as finished cement. The pollution
control system could represent a simple dust collector (cyclone), electrostatic precipitators or textile filters. Other equipment could be applied at some enterprises to address the pollution, for example, gas scrubbers.

The below classes of emission factors (Table 2) [2] were developed. As it is evident from the Table there is no emission factor for releases to residuals. In a typical case the dust generated at cement plants is re-submitted to firming kilns with the raw material.

**Emission factors for cement production**

<table>
<thead>
<tr>
<th>Classification</th>
<th>Emission factors – µg I-TEQ/t of cement</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Air</td>
</tr>
<tr>
<td>1. Pit kilns</td>
<td>5.0</td>
</tr>
<tr>
<td>2. Older firming kilns, working on wet process, electro filters, temperature &gt;300°C</td>
<td>5.0</td>
</tr>
<tr>
<td>3. Rotary kilns, electro filters, textile filters, temperature 200-300°C</td>
<td>0.6</td>
</tr>
<tr>
<td>4. Firming kilns, working on wet process, electro filters, textile filters, temperature &lt;200°C</td>
<td>0.05</td>
</tr>
<tr>
<td>Firming kilns, working on wet process, heater / calcinator, temperature &lt;200°C</td>
<td>ND</td>
</tr>
</tbody>
</table>

ND – not determined (no data)
NA – not applicable (not essential)

**Entry into the air**

The PCDD/PCDF emissions into air correlated with unit of product will depend on PCDD/PCDF concentration in kiln gas and gas amount generated per unit of product. The greater volume of kiln gases per unit of product is generated in the kilns with wet process, than in kilns where dry process (4000 m³ per ton against 2500 m³ per ton) is applied.

Measurements conducted in Germany at 16 cement clinker kilns for the past ten years demonstrated that average concentrations are about 0.02 ng I-TEQ/m³ [2].

Very low concentrations of PCDD/PCDF were detected during sampling in Thailand at the cement plant operating on dry process.

As the result, emission factors were on the average 0.02 and 0.001 µg I-TEQ/t of clinker at normal mode, and 0.005 and 0.003 µg I-TEQ/t of clinker with incidental incineration of alternative fuel/wastes. Therefore, all results of the study were considerably lower than the guide value 0.1 ng I-TEQ/m³. The results demonstrated that addition of tires and/or liquid hazardous wastes did not affect on resulting emissions, taking into account the fact that the dry process used at the cement firming kiln was conducted in accordance with the modern technologies and the arrangement of the production at the enterprise was very good [2].

According to other data [11] the cement production could play an essential role in emissions of dioxins during the incineration of hazardous wastes in cement kilns. Thus, during
the dioxin inventory in the USA the emission factor was accepted as 0.29 µg I-TEQ/t of clinker for the production of cement without incineration of wastes is. Emissions of dioxins dramatically raised during incineration of hazardous wastes in cement kilns: the emission factor was determined to be 24.34 µg I-TEQ/t of clinker.

Even more significant emission factors during incineration of nontoxic and especially toxic wastes are provided in the work [12].

Emission factors during production of cement in Krasnoyarsk coincide almost precisely with the data for the cement kilns incinerating nontoxic wastes in Germany. It could be connected with the fact that the “Cement” company in Krasnoyarsk incinerates nontoxic wastes or uses coal as fuel, what, in opinion of authors [13], provides more considerable emissions of dioxins than application of black oil or gas as fuel.

Probably the value of dioxin emissions is affected by the amount and composition of wastes added to fuel, as well as compliance with technological parameters of the process. It is obvious that these parameters should be under control.

It seems that the temperature of the dust-collecting equipment influences on PCDD/PCDF concentrations in kiln gases during wet process. Temperatures over 300°C increase the probability of detection of the increased emissions. Possibly, it is connected with the high content of organic substance in raw material, as well as with use of some types of wastes under inappropriate conditions.

The average factor of emission 5 µg I-TEQ/t of product (clinker) is applied for kilns with temperature in dust collectors over 300°C. The average emission factor 0.6 µg I-TEQ/t of the product is applicable where the temperature of dust collector is between 200 and 300°C. And the emission factor 0.05 µg I-TEQ/t of the product is used in cases when the temperature of dust collector is supported below 200°C.

**Entry into the water**
Discharges to the water are not expected [2].

**Entry into the soil**
Some residuals could be stored on the ground, and the cases of application of cement kiln dust for increasing of alkalinity and admixing to lime were reported [2].

**Entry into the products**
Insignificant entry to finished cement is expected as the product is exposed to the very high temperatures [2].

**Entry into the residuals**
It should be noted that the dust collected by the system of the air pollution control, usually by electrostatic precipitators or cyclones, generally consists of raw material loaded to the firming kiln (at the end of the secondary heating). The remain of dust consists of emissions from this firming kiln passed the hot area. Usually the dust from electrostatic precipitators/cyclones repeatedly returns to the kiln.

The main residue subject for the disposal is the dust of cement kilns (DCK) caught by the pollution control systems. The average productivity 0.4 million tons of DCK per 13.5 million tons of clinker/cement production [2], i.e. approximately 30 kg of DCK per ton of clinker, is taken for the primary assessment of PCDD/PCDF entry to DCK.
There is no enough data for all firming kilns to conduct the exact assessment of PCDD/PCDF levels. According to reports the range of concentrations is very wide - 0.001-30 ng I-TEQ/kg for kilns in the Great Britain and 1 - 40 ng I-TEQ/kg for the studies implemented in Germany. Tests in the USA demonstrated that on the average the kilns incinerated hazardous wastes provide higher levels (35 ng I-TEQ/kg) than kilns not incinerated them (0.03 ng I-TEQ/kg) [2].

For the primary assessment of entry to DCK it is suggested to apply three classes of emission factors, which are provided in the Table 2. These sizes are approximate.

3.2.1. Background information on the “Vorkuta Cement Plant”

The Vorkuta Cement Plant was put into operation in 1950 as a one of baseline objects of building sector in the north of the European part of the country. Product output was up to 430 000 tons of cement and 110 000 cubic meters of crushed rock annually after the reconstruction, but decline in the industrial production in Russia in 90s of the past century resulted in the “Vorkuta Cement Plant” bankruptcy in 2002 [3].

At first major investors, in particular the “Stern-cement” company, were interested in the plant, but after studying of economic situation they refused from purchasing of this enterprise. The challenge on liquidation of the unique cement plant in the Republic of Komi was raised. The plant administration, maintaining the enterprise with difficulties, was searching for the investor for over half a year and it was found.

The Vorkuta company “Driver” purchased the production complex and the “Vorkuta Cement Plant” commenced its work in February 2003. The majority of employees of the former legal entity - “Vorkuta Cement Plant” JSC – was transferred to the new enterprise.

In 2003-2004 the production and shipment was 180 000 tons of cement.

In the framework of the Phase I of the Project the Russian Scientific Research Centre of Emergencies of the Ministry of Health of the Russian Federation has carried out the measurements of dioxin releases at the Vorkuta Cement Plant in July 2004. And already in October 2004 the plant operation was suspended.

According to the information from the Internet the plant was intended to re-commence the cement production in later May 2006 and in 2-3 years to recover its full capacity. In fact the cement production achieved the significant amount (about 10 000 t/month) only by September-October 2006.
Alongside with the reduction of costs for the last one and a half year the work towards the perspective was conducted intensely at the plant. Aimed at the smooth provision of consumers with the production the founders, regardless of expenses, decided to open three large storage terminals in different areas of the Republic. The owners of the plant invested funds in purchase of idle capacities in Syktyvkar where the “Vorkuta Cement Warehouse” started its operations for cement reception and storage in 2004. The warehouses premises of this first base allow to ship there up to 6 000 tons of cement. The second base was opened in Usinsk and the third - in Pechora. The plant already makes a shipment of production there at full speed [4].

The cement is packed to paper sacks of 50 kg weight and to soft containers of MKP-1 type (big bag) of weight up to 1 ton. The later meets the specificity of the Far North: delivery of such containers from the plant to the place of construction is performed via air transport – helicopters.

3.2.2. Characteristic of production and nomenclature of products:

Characteristics of production:
- Capacity: up to 450 000 tons of cement annually
- Fuel Type: coal
- Method of production: wet
- Raw materials: lime-stone (Vorkutinskoe deposit), argillaceous slate (Vorkutinskoe deposit)
- Corrective additives: cinders
- Active mineral additives: ashes of heat and power station, burnt rock (gob piles of Vorkuta mines)
- Basic equipment: 3 processing lines for firming with productivity up to 17 tons/hour, 3 coal and 4 raw mills, 2 cement mills of total productivity 42 tons/hour.
The Vorkuta Cement Plant includes the following main objects:
1. Clampshell-type raw material warehouse
2. Section for coal milling.
4. Section for milling of raw materials and cement.
5. Kiln unit.
6. Clinker transportation gallery to the warehouse.
7. Clampshell-type warehouse for clinker and additives.
8. Cement silo with uploading to motor transport and railroad.
9. Laboratory.
10. Utility facilities.

**Nomenclature of products:**
- Portland cement with mineral additives PC 400-D20
- Portland cement with mineral additives PC 500-D5 and D20.
  
  Cement composition: clinker – 80%
  
  ash – 15%
  
  gypsum – 5%
- Cement of special brands, Portland cement PC500 D0.
  
  Cement composition: clinker – 95%
  
  gypsum – 5%
- Portland cement clinker

At the present time the works on manufacturing and installation of rather powerful equipment for preparation of the coal slam to provide the operation of two kilns are carried out and release of inert dust and mineral powder for road construction of the Republic of Komi is planned.

### 3.2.3. Cement Production at the Vorkuta Cement Plant

The cement production process at the Vorkuta Cement Plant is the following. Normal raw slam is generated through joint milling of limestone and clay slate in a raw four-chamber mill for wet milling of Ø 2.2 x 13 meters with size. Mill productivity is 25-30 tons per hour. After wet milling of solid raw materials the raw mix is pumped to vertical adjusting slam-tanks. The finished raw slam is pumped to horizontal slurry tanks. There is a feeder for continuous slam loading to the furnace above the slurry tanks. Surplus of slam is dumped back to the slam tanks.

Slam hashing is performed with compressed air serially over all tanks. Slurry tanks are operating in a regime of kiln unit – three shifts round the clock.

The dusty solid fuel of the Vorkuta coal strip mine with combustion heat of 6350-6700 kcal/kg or 26600-28000 kJ/kg, accordingly, is used to firm the cement clinker.

There are 3 coal mills (Ø 2.2 x 3.3 meters) equipped at the first step with a closed cycle air through separator (Ø of 2500 mm), and with precipitating cyclone (Ø of 1800 mm) at the second installed at the plant.

There are 3 rotary furnaces for clinker firming at the plant:
- One furnace with Ø 3.6 x 3.0 x 82 meters - productivity 11.2 ton/hour;
- Two furnaces with Ø 3.6 x 88.6 meters - productivity 17 ton/hour.
The complete furnace set includes a cooler, fuel incineration devices, fan and means for dust-cleaning of emitting furnace gases.

All kilns are equipped with exhausters trade mark D–20.0 with capacity of 215 thousand m³/hour, and pressure of 300 mm of water column (~ 3000 Pa).

The obtained clinker is dumped via lift gallery on band conveyor to the clamshell warehouse through the aspirating shaft. De-dusting of clinker dump is carried out with bag filter of SMC 40.3 type.

To store the normative stocks of clinker, gypsum and ashes a closed clamshell-type warehouse with clamshell-type crane is envisaged; gypsum and ashes are delivered to the warehouse with motor transport.

2 cement mills (Ø 3.0 x 14 meters) operating in open cycle are installed at the plant for clinker grinding. Cement mills has 3 purification steps for de-dusting of emitting air. At the first step the reduction of dust content is provided by aspirating mines and dust-collecting chambers. Cyclones of CN type with diameter 800 mm are installed at the second step, and bag filters of FHCN type - 360 and 270 with diameter 800 mm - at the third step. There are exhausters VVSM/2U with productivity 33 thousand m³/hour, and pressure 270 mm of water column (~ 2700 Pa).

The installed and operated for 56 years equipment provides a project capacity of cement release. However it is necessary to note that the process does not meet the modern norms and approaches to systems of emitting gases purification.

The cement production generally consists of the following stages (Fig. 3):
- Extraction and preparation of raw mix consisting of grinding, milling and its homogenization;
- Preparation of fuel and mineral additives, which consists in ragging and drying;
- Firming of raw mix in the cement kiln
- Treatment of kiln gas from cement dust and chilling;
- Grinding of clinker and obtained cement to the fine powder.

![Diagram of cement production](image)

**Figure 3.** Diagram of cement production.
4. Determination and Assessment of Factors effecting on generation of dioxins and furans at the Kotlas PPP

4.1.1. Best available techniques (10)

In the mid-1980s the discovery of dioxins and furans in effluents from pulp mills using chlorine and hypochlorite in their bleaching sequences prompted extensive research into how to reduce or eliminate their formation. The intense international research showed that the principal mechanism for formation of 2,3,7,8-TCDD and 2,3,7,8-TCDF is the chlorination of the precursor compounds dibenzodioxin and dibenzofuran present in the unbleached pulp via aromatic electrophilic substitution. The formation of 2,3,7,8-TCDF will be reduced by increasing chlorine dioxide substitution. The use of molecular chlorine in bleaching has been largely replaced by chlorine dioxide (ECF, elemental chlorine-free) and other oxygen-based chemicals such as molecular oxygen, peroxide and ozone (TCF, totally chlorine-free). Over 80% of all chemical pulp comes from the kraft process.

Raw materials

Wood and the main non-wood materials used in papermaking represent a complex mixture of the same substances – cellulose (40–45%), hemicelluloses (25–35%), lignin (20–30%) and extractives (2–15%). Most ligno-cellulosic and cellulosic materials of fibrous structure may be processed into various grades of papers and paperboard.

Technology and final product

Pulping and bleaching technology must be matched with the quality and characteristics of the pulp and paper grades to be produced. No single pulping or bleaching process can produce pulp suitable for all uses. For instance, newsprint is a high-volume product of moderate strength, opacity and printability, and it has a relatively short life. Therefore, a high yield of pulp at the expense of maximum achievable strength and brightness can be manufactured from the raw materials, and there is a lower bleaching requirement due to the natural brightness of the pulps. On the other hand, packaging papers need strength if they are to be usable: here it is necessary to accept a lower yield via a different manufacturing route in order to obtain this strength, but once again the bleaching requirement may be low.

Pulping methods applied

The main processes involved in making pulp and paper products are raw material handling and preparation, storage (and preservation for non-woods), wood debarking, chipping and agricultural residue cleaning, de-knotting, pulping, pulp processing and bleaching if required and, finally, paper or paperboard manufacturing. The manufacture of pulp utilizes mechanical, thermo-mechanical, chemo-mechanical and chemical methods.

The main chemical, semi-chemical and chemo-mechanical pulping techniques are as follows:

- Sulphate (kraft) uses a mixture of sodium hydroxide and sodium sulphide under alkaline conditions to dissolve the lignin from wood and most non-wood fibres (chemical method);
- Sulphite: Acid bisulphite, bisulphite, alkaline and neutral sulphite methods (Ca, Mg, NH, Na); different bases, including anthraquinone, under a range of pH, to dissolve the lignin; most wood fibres (chemical and semi-chemical methods);
- Lime, lime-soda: In particular, non-wood fibres;
- Cold soda uses sodium hydroxide pre-treatment at ambient temperatures, alone or with sodium carbonate: In particular, hardwood and non-wood fibres (semi-chemical);
- Soda anthraquinone (AQ): Sodium hydroxide alone or with sodium carbonate and a catalyst anthraquinone; hardwood and non-wood fibres (chemical, similar to kraft but without sulphur), reduced odour;
• Organic methods: Wood and non-wood applications, some proven at mill scale but only one process is available commercially.

The kraft or sulphate process is the dominating pulping process worldwide, constituting 84% of the world’s chemical pulp production and 63% of total chemical and mechanical pulp production.

**The kraft (sulphate) pulping process**
The kraft process uses a sodium-based alkaline pulping solution consisting of sodium sulphide (Na₂S) and sodium hydroxide (NaOH). The fibres are liberated in the cooking plant by dissolving the lignin and part of the hemicellulose in the cooking chemical solution (white liquor). Used cooking liquor (black liquor) is recovered to generate white liquor for the first pulping step. At mills with chemical recovery, most of the dissolved wood substances are combusted, and the wastewater mainly contains the organics in condensates and, at bleached mills, the substances dissolved during bleaching and the residues of the bleaching chemicals. Many small mills do not recover the liquor.

**Lime and soda processes**
These are processes that use simple alkaline cooking liquors in a similar process to kraft pulping but without the use of sulphur compounds. At mills with no chemical recovery, all the dissolved wood substances and pulping and bleaching chemicals remain in the wastewater, apart from the volatiles incidentally released to the atmosphere. The delignification ability is inadequate for producing wood based pulps with low yield and high brightness.

**Sulphite pulping processes**
The sulphite pulping process is based on aqueous sulphur dioxide and a base – calcium, sodium, magnesium or ammonium. This method is losing its importance and only 10% of the world’s pulp is produced with this method. Compared to kraft pulps, sulphite pulps are relatively bright and are also relatively easy to bleach with oxygen-based chemicals, such as peroxides.

**Solvent-based processes**
Solvent-based pulping processes can be used for both wood and non-wood raw materials. These organosolv pulping processes use the following solvents, amongst others: formic acid, peroxyformic acid, acetic acid, ethanol, methanol and acetone. Some solvent-based cooking methods are better suited for hardwood (e.g. Alcell) and some for both hardwood and softwood raw materials (e.g. NAEM, Organocell, Acetocell, Formacell and ASAM). However, none of these suggested techniques has been proven to be feasible in commercial operation, and the pilot production lines have been shut down.

**Bleaching**
Bleaching after pulping is a chemical process applied to pulps in order to increase their brightness. To reach the required brightness level, bleaching should be performed by removing the residual lignin of chemical pulps (de-lignifying or lignin-removing bleaching). All lignin cannot be removed selectively enough in a single bleaching stage, but pulp is usually bleached in three to six stages. The first two stages primarily release and extract lignin, and the subsequent stages remove the lignin residues and finish the product. These bleaching sequences are applied to maximize the bleaching effect of each component. Water is used to perform intermediate washes to remove extracted waste from the pulp. The commonly applied chemical treatments in bleaching, and their abbreviated designations, are shown in Table 3.
Table 3

Commonly applied chemical treatments in bleaching

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorination</td>
<td>C</td>
<td>Reaction with elemental chlorine in acidic medium</td>
</tr>
<tr>
<td>Alkaline extraction</td>
<td>E</td>
<td>Dissolution of reaction products with NaOH</td>
</tr>
<tr>
<td>Hypochlorite</td>
<td>H</td>
<td>Reaction with hypochlorite in alkaline medium</td>
</tr>
<tr>
<td>Chlorine dioxide</td>
<td>D</td>
<td>Reaction with chlorine dioxide (ClO₂)</td>
</tr>
<tr>
<td>Chlorine and chlorine dioxide</td>
<td>CD</td>
<td>Chlorine dioxide is added in chlorine stage</td>
</tr>
<tr>
<td>Oxygen</td>
<td>O</td>
<td>Reaction with molecular oxygen at high pressure in alkaline medium</td>
</tr>
<tr>
<td>Extraction with oxygen</td>
<td>EO</td>
<td>Alkaline extraction with oxygen</td>
</tr>
<tr>
<td>Peroxide</td>
<td>P</td>
<td>Reaction with hydrogen peroxide (H₂O₂) in alkaline medium</td>
</tr>
<tr>
<td>Chelating</td>
<td>Q</td>
<td>Reaction with chelating agent EDTA or DTPA in acidic medium for removal of metals</td>
</tr>
<tr>
<td>Ozone</td>
<td>Z</td>
<td>Ozone using gaseous ozone (O₃)</td>
</tr>
</tbody>
</table>

If molecular chlorine and hypochlorite are excluded, the term applied for the bleaching sequence is chlorine dioxide bleaching or elemental chlorine-free (ECF) bleaching. If the sequence only uses oxygen-based chemicals, such as oxygen, ozone, alkaline or acidic peroxide, the terms oxygen chemical bleaching or totally chlorine-free (TCF) bleaching can be used. For softwood kraft pulps, a number of bleach sequences utilizing four to six stages are commonly used to achieve full-bleach brightness (level 89–91%). Bleaching sequences (full brightness) like CEHDED and CEDED were in operation in the 1960s and 1970s. Sequences more typical of modern mills are OD(EOP)D, OD(EOP)DP, Q(PO)DD, Q(PO)(DQ)(PO) and (Z(EO))DD (full brightness).

With an oxygen delignification stage or reinforced extraction stage, the bleaching sequences could be as follows: O(D+C)(EO)D; O(CD)EDED; and O(D)(EO)DED. Hardwoods are easier to bleach due to their lower lignin content. Furthermore, less bleaching effort is required for sulphite pulps due to their lower pre-bleach brightness.

**Bleaching with elemental chlorine and hypochlorous acid**

Elemental chlorine and hypochlorous acid are electrophilic bleaching chemical agents that react with all unsaturated structures, namely lignin structures; with polysaccharide degradation products, such as hexenuronic acid; and with extractive structures that contain carbon-carbon double bonds. These electrophilic bleaching agents are able to react with different unsubstituted aromatic carbon atoms in lignin to:

a. Chlorinate (when the carbon is not bonded with an oxygen atom); or
b. Chlorinate and depolymerize (via displacement of an α-hydroxyl group); or
c. Merely depolymerize without chlorination (via hydroxylation).

These chlorination or depolymerization reactions make lignin alkaline soluble, and it can be removed from pulp in the alkaline bleaching stages of the bleaching sequence.

**Formation of 2,3,7,8-TCDD/TCDF**

Formation of dioxins occurs mainly in the C-stage via the reaction of chlorine with the precursors dibenzo-\(p\)-dioxin (DBD) and the unchlorinated dibenzofuran (DBF). When these precursors are chlorinated, the key reaction is electrophilic aromatic substitution. The rate of this reaction will depend both on the concentration of the precursor and the concentration of chlorine.
The chlorination of non-aromatic structures, such as hexenuronic acid, does not lead to the formation of polychlorinated aromatic degradation products.

The unchlorinated dioxin precursors are prevalent in certain mineral oils, which are part of some defoamer formulations used in the pulp and paper industry and are the major source of precursors. Wood itself may act as the source of dioxin precursor. Compression wood in particular contains higher concentrations of precursors than normal wood. The compression of wood also entails higher levels of coumaryl-type lignin, which may be a source of DBD- and DBF-like precursors.

**Elimination mechanisms for 2,3,7,8-TCDD/TCDF**

Preventing the formation of 2,3,7,8-TCDD and 2,3,7,8-TCDF in the bleaching can be achieved mainly by using totally chlorine-free bleaching method and virtual elimination can be achieved by decreasing the amount of chlorine used in the first bleaching stage. This can be accomplished by reducing the atomic chlorine multiple by improving washing prior to chlorination, by using an oxygen and peroxide-reinforced extraction stage, and by increasing ClO₂ substitution. The formation of 2,3,7,8-TCDF and 2,3,7,8-TCDD will be reduced by increasing ClO₂. When the ClO₂ substitution level is higher than 85%, 2,3,7,8-TCDF and 2,3,7,8-TCDD can be virtually eliminated.

Elemental chlorine can be completely replaced by ClO₂ (elemental chlorine-free bleaching). In this process ClO₂ is usually the main bleaching agent. The elemental chlorine can be replaced with ClO₂ in the first bleaching stage because the ClO₂ per chlorine atom has fivefold oxidation power compared with chlorine and it has practically the same selective lignin removal properties. Reinforcing the alkaline extraction stages in bleaching with oxygen and/or hydrogen peroxide results in an enhanced oxidizing bleaching effect, which reduces the residual lignin content of the pulp before the final ClO₂ bleaching stages. Increasing the degree of ClO₂ substitution decreases the formation of chlorinated organic substances and eliminates the formation of dioxins and furans. The increased substitution of chlorine by ClO₂ generally requires modifications in the bleaching process and also expansion of the on-site chlorine dioxide plant.

The elemental chlorine-free bleaching process is different for softwood and hardwood, and in existing mills the possibilities of the concept are tied to the current bleaching process. Generally, to reach a certain brightness target hardwood requires fewer chemicals than softwood, which usually means that the number of bleaching stages can be reduced. Over the years the dosage of chlorine dioxide has decreased in hardwood bleaching by one-third as it has been substituted by oxygen-based chemicals.

Elemental chlorine-free pulp (kraft pulp) bleached with ClO₂ holds the predominant position within the industry, accounting for roughly three-quarters of the bleached pulp produced worldwide.

**Best available techniques for production of pulp using elemental chlorine**

**Primary measures**

The principal best available techniques for minimizing or eliminating the formation of 2,3,7,8-TCDD/TCDF in wood and non-wood bleaching processes are as follows:

- Reduction of the application of elemental chlorine by decreasing the multiple or increasing the substitution of ClO₂ for molecular chlorine;
- Elimination of elemental chlorine by replacing it with ClO₂ (elemental chlorine-free bleaching) or with chlorine-free chemicals;
• Utilization of DBD- and DBF-free defoamers;
• Effective brownstock washing to enable the reduction of chlorine multiple;
• Maximization of knot and dirt removal to enable the reduction of chlorine multiple;
• Elimination of the pulping of furnish contaminated with polychlorinated phenols.

Secondary measures
The following general measures are suggested:
• Substitution: The identification and substitution of potentially harmful substances with less harmful alternatives;
• Investment planning/cycles;
• Training, education and motivation of personnel;
• Process control monitoring and optimization;
• Adequate maintenance;
• Environmental management system;
• Development of environmental monitoring and standard monitoring protocols, including release monitoring for new facilities.

Alternatives
Totally chlorine-free bleaching for kraft pulp
The totally chlorine-free (TCF) process developed rapidly in the 1990s but has gradually lost its attraction because of its weaknesses in fibre characteristics, lower pulp yield and higher energy consumption. The elemental chlorine-free (ECF) process has taken over as the leading bleaching method. Some TCF processes have started to lose their shares in the market and a number of TCF mills are converting to ECF pulp production. The operating costs of TCF pulping are usually higher than those of ECF pulping due to the higher chemical costs required to reach the same level of pulp brightness. TCF bleaching is a bleaching process carried out without any chlorine-containing chemicals. In this process, hydrogen peroxide together with ozone or peracetic acid are the most commonly used chemicals. Ozone has become the most common complement to peroxide in TCF bleaching sequences. The main purpose of using ozone is to provide more delignification power.

<table>
<thead>
<tr>
<th>Softwood</th>
<th>Hardwood</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q(OP)(ZQ)(PO)</td>
<td>Q(OP)(ZQ)(PO)</td>
</tr>
<tr>
<td>Q(EOP)Q(PO)</td>
<td>Q(EOP)Q(PO)</td>
</tr>
<tr>
<td>Q(OP)ZQ(PO)</td>
<td>Q(OP)ZQ(PO)</td>
</tr>
</tbody>
</table>

Notes:
Q = Acid stage where chelating agent EDTA or DTPA has been used for removal of metals.
EP = Extraction stage using NaOH with subsequent addition of H₂O₂ solution as a reinforcing agent.
EOP = Alkaline extraction bleaching stage using sodium hydroxide with subsequent addition of oxygen and hydrogen peroxide solution as a reinforcing agent.
EO = Extraction stage using NaOH with subsequent addition of gaseous oxygen as a reinforcing agent.
P = Alkaline stage with H₂O₂ as liquid.
Z = Ozone bleaching using gaseous O₃.
PO = Pressurized peroxide bleaching.

TCF kraft and sulphite pulp accounts for less than 5% of production and is primarily produced in Northern and Central Europe.
4.1.2. Technologies of pulp production

The technological scheme of production of pulp from wood includes: raw bucking, bark removal, wood chopping and sorting, pulping in leach, removal of used leach, refinement, drying and cutting of end product. The basic methods for pulping are: sulphate (generally), sulphonate, alkaline, nitrate; moreover, combined methods (sodium-sulphonate and sodium-sulphonate-sulphate) as well as oxygen-alkaline delignification of timber are used [8].

The sulphate method allows to process timber of any species through its pulping for 5-7 hours at 165-170°C and under pressure of 0.6-0.8 MPa in leach containing 9-10% of NaOH.

The sulphite method is applicable mostly for softwood, which pulping is carried out in leach containing 5-10% of general SO₂ and 0.8-1.3% of SO₂ in compounds (as hydrosulphites of Na, Ca, Mg, NH₄ or their mixtures) for 5-12 hours at 130-155°C and under pressure of 0.5-0.8 MPa.

Pulping with the above methods is carried out at periodically or continuously operating devices of 60-170 m³ volumes equipped with the heating systems and compulsory circulation systems of leaches and other reagents.

After pulping mechanical admixtures are removed from the pulp and it is additionally chemically refined – with bleaching and alkali treatment. Bleaching is implemented with oxidizers (C12, ClO₂, NaClO, O₂ of air in alkaline condition, etc.). Alkali treatment is carried out via processing of pulping with 0.5-2% or 4-10% of water solutions of NaOH for several hours at temperatures from 15-25 through 95-135°C.

The cellulose pulp is bleaching and refining, which usually consists of 3-6 stages for a sulphite pulp and 5-8 stages for pre-hydrolised craft-pulp with sluicing before each stage [5].

4.1.3. Analysis and assessment of factors under control that determine generation of dioxins at PPP

The process of pulp production is the main source that affects the environment in pulp and paper industry. Generally the process of production of paper and pasteboard consists of three stages: pulp production, pulp processing and paper/pasteboard production [2].

Releases of PCDD and PCDF by the pulp-and-paper plants may occur in the following ways:
- Emissions into air during incineration of lignin and black liquor for energy production;
- Emissions into air during incineration of timber or bark for energy production;
- Emissions with water from the process (modern enterprises on production of pulp operate with no sewage waters);
- Emissions into residue, generated during pulp production, which could be used at the fields, incinerated or disposed;
- Emissions into the products (pulp, paper) that enter the market as commercial value.

Pulping

a) Sulphite process

This process with application of pulping acid is based on use of water sulphur dioxide (SO₂) and the alkalis of: calcium, sodium, magnesium or ammonium. Its significance decreased in the course of time and at the present time not more than 10% of pulp is produced globally using this method. Sulphite process requires a high-quality fibre and produced products are of small tensile strength. The most frequent use is for soft timber.

b) Kraft or sulphate process

This process with application of pulping liquor is the prevailing pulping process worldwide
(80% of world's pulp production). It is applicable to all types of timber/fibres and provides pulp of a big tensile strength. The sodium-containing pulping liquor consisting of sodium sulphide (Na$_2$S) and sodium hydroxide (NaOH) in a 10% solution is used in the Kraft-process. The not reacted chemical substances (black liquor) are regenerated with formation of white liquor for use at the first stage of pulp cooking.

**Bleaching**
To increase the pulp whiteness degree the pulp is treated with the chemical process of bleaching after the pulping. To achieve a required level of whiteness the bleaching should be carried out through removal of residual lignin (delignification, or bleaching with removal of lignin) from the chemically obtained pulp. It is impossible to selectively remove all lignin at one stage of bleaching, therefore pulp is usually bleached at three-six stages. The lignin is derived and extracted at the first two stages, and at the subsequent steps – the residual lignin is disposed and an end-product is obtained. Such a consecutive bleaching results in the maximum bleaching effect for each component. Water is used for intermediate scavenging of extracted wastes from the pulp [10].

The Table 4 provides methods of chemical processing usually applied for bleaching and their indications [10].

**Table 4**

<table>
<thead>
<tr>
<th>Processing</th>
<th>Description</th>
<th>Designation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlorinating</td>
<td>Reaction with elementary chlorine in acid media</td>
<td>C</td>
</tr>
<tr>
<td>Alkaline extraction</td>
<td>Dissolution of reaction products in NaOH</td>
<td>E</td>
</tr>
<tr>
<td>Hypochlorite</td>
<td>Reaction with hypochlorite in alkaline media</td>
<td>H</td>
</tr>
<tr>
<td>Chlorine dioxide</td>
<td>Reaction with chlorine dioxide (ClO$_2$)</td>
<td>D</td>
</tr>
<tr>
<td>Chlorine and chlorine dioxide</td>
<td>Chlorine dioxide is added at the chlorinating stage</td>
<td>CD</td>
</tr>
<tr>
<td>Oxygen</td>
<td>Reaction with molecular oxygen under high pressure in alkaline condition</td>
<td>O</td>
</tr>
<tr>
<td>Extraction with oxygen</td>
<td>Alkaline extraction with oxygen</td>
<td>EO</td>
</tr>
</tbody>
</table>

The sequence of bleaching operations in which chemical the reagents on the chlorine basis are used is called “chlorine bleaching”. In case if molecular chlorine and hypochlorite are excluded from the process the terms “chlorine dioxide bleaching” or “bleaching without elementary chlorine” are used. If only oxygen-containing chemical agents, such as oxygen, ozone, alkaline or acidulous peroxide are used in the specified sequence it is possible to use terms “oxygen bleaching” or “bleaching completely without chlorine”.

The four-six bleaching steps sequence is usually used for the pulps produced from coniferous timber according to the Kraft process what allows to achieve the complete whiteness (whiteness degree of 89-91%). Such sequences as CEHDED and CEDED that provide the complete whiteness were applied in 60s and 70s. For the modern plants the sequences (D+C) (E+O) DED; (D+C) (E+O) D; and D (E+O) DD are more typical (complete whiteness) [10].
Bleaching with elementary chlorine and hypochlorous acid
Elementary chlorine and hypochlorous acid represents the electrophilic bleaching chemical agents, which react with non-saturated structures, namely with lignin structures; polysaccharide decay products, and extracting structures containing twin carbon-carbon bounds.

These chlorination and depolymerization reactions make lignin soluble in alkalis, therefore lignin could be scavenged from the pulp at the alkaline bleaching stages part of the bleaching operations sequence [10].

Bleaching of the Kraft pulp completely without chlorine
Complete chlorineless bleaching (CCB) – is the process performed without any chlorine containing chemical reagents. This process is rapidly developed, although its application usually requires several modifications of the pulping process [10].

The most frequently used chemical agents in this process are hydrogen peroxide with ozone or peracetic acid. Ozone became the most usual addition to peroxide in the complete chlorineless bleaching operations sequence. The overall objective of the ozone use is to provide more powerful delignification.

Systems of regeneration of chemical substances
The Kraft-process of chemical regeneration did not experience significant changes since 1884. Residual black liquor is concentrated through evaporation to concentrated black liquor, which incinerated in the regeneration boiler (disposing boiler) with energy production, and the chemical substances participated in the process are removed from the mix in a liquid form. To cover the energy expenditures of the enterprise the regeneration boilers could be supplied with boilers working on fossil fuel or timber wastes (milled timber fuel). Emissions of such boilers could contain PCDD and PCDF [2].

The Guidelines [2] adheres to the standard approach and provides the data for pulp in tons at air drying (Air Dry tons, ADt), what corresponds to one ton of pulp of 90% of dryness and 900 kg of completely dry cellulose. The processed paper with dryness of 94-96% as a rule is the basis for paper.

For the pulp-and-paper industry the emission factors in accordance with the Tables 5-7 should be selected. [2].

Table 5

<table>
<thead>
<tr>
<th>Classification</th>
<th>Emission factor</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Air, µg I-TEQ/ADt</td>
</tr>
<tr>
<td>1. Boilers for black liquor</td>
<td>0.07</td>
</tr>
<tr>
<td>2. Boilers incinerating silt or biomass/bark</td>
<td>0.2</td>
</tr>
</tbody>
</table>

NA – not applicable (not essential)

Annual discharges with sewage and silts generated during pulp and paper manufacturing (residuals) could be calculated through multiplication of concentration in outflow (in pg I-TEQ/l) or concentration in silt (in µg I-TEQ/t of dry substance) and annual discharge or volume of production accordingly. In the tables provided to simplify the assessment of discharges the characteristic values in µg I-TEQ/ADt are provided along with characteristic concentrations in outflows and solid
residues – they could be used if values for mass flow are unknown. The PCDD/PCDF concentrations for various classes are provided in the Table 6 [2].

Table 6
Emission factors for outflows and silts in the pulp and paper industry

<table>
<thead>
<tr>
<th>Classification</th>
<th>Emission factor – µg I-TEQ/ADt</th>
<th>pg I-TEQ /l</th>
<th>µg I-TEQ /ADt</th>
<th>µg TE /t in silt</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Kraft-process, old technology (Cl₂)</td>
<td>4.5</td>
<td>70</td>
<td>4.5</td>
<td>100</td>
</tr>
<tr>
<td>2. Combined technology (BFWC, but Cl₂ is partially at the first stage)</td>
<td>1.0</td>
<td>15</td>
<td>1.5</td>
<td>30</td>
</tr>
<tr>
<td>3. Kraft-process, modern technology (ClO₂)</td>
<td>0.06</td>
<td>2</td>
<td>0.2</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 7
Emission factors for the pulp and paper products

<table>
<thead>
<tr>
<th>Classification</th>
<th>Emission factors – µg I-TEQ/t of product</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Kraft-pulp and paper from primary fibre, bleaching by free chlorine</td>
<td>8</td>
</tr>
<tr>
<td>2. Combined technology (BFWC, but Cl₂ is partially at the first stage)</td>
<td>3</td>
</tr>
<tr>
<td>3. Sulphite paper, old technology (free chlorine)</td>
<td>1</td>
</tr>
<tr>
<td>4. Kraft-paper, new technology (ClO₂, BFWC), unbleached paper</td>
<td>0.5</td>
</tr>
<tr>
<td>5. Sulphite paper, new technology (ClO₂, BFWC)</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Emissions into the air

The main emissions into air from the pulp and paper enterprises occur as a result of the energy production but not as a result of the production process.

Pulp and paper plants incinerate lignin generated during pulping for the energy production used directly at the enterprises. Moreover, wastes, woodchips, bark, etc. could be incinerated at boilers. The average volumes amount to 6000-9000 m³/t of pulp and concentrations are about 0.41 ng I-TEQ/m³ (range is 0.036-1.4 ng I-TEQ/m³) both for the sulphite cellulose manufacturing enterprises and the Kraft-pulp producing enterprises [2].

The boilers functioning on the Kraft-pulp liquor are used in pulp and paper industry for incineration of concentrated black liquor. The majority of them are equipped with simple devices to clean gases, for example, cyclones, wet scrubbers or electrostatic precipitators.

The Guidelines [2] affirms that the setup emission factor for timber incineration at the pulp plants will be the same as for timber incineration in energy sector, and the setup emission factor of loaded material is proposed as 0.2 µg I-TEQ/t.
**Discharge into the water**

The pulp and paper industry is one of the largest water consumers. The sulphite process pulp production enterprises are discharging more sewage than those using the Kraft-process. The modern bleaching enterprise discharges 15-20 m$^3$ of water per ton of air-dry pulp (15-20 m$^3$/t ADt) [2].

In 1988 in the USA the typical pulp and paper plant used 60-64 m$^3$ of water per ton of pulp; in the European Union countries the water consumption amounts to 15-100 m$^3$/t. Water consumption could be reduced by increase of water recycle within the enterprise. Usually outflows amount to 20-40 m$^3$ per ton of pulp. The value of 30 m$^3$ of water per ton of produced pulp is used in the Guidelines [2].

Concentrations in outflows vary from 3 pg I-TEQ/l through 210 pg I-TEQ/l with the median of 73 pg I-TEQ/l provided in [2]. The setup emission factor for the bleached Kraft-pulp amounts to 4.5 µg I-TEQ/t of pulp when apply the old bleaching processes. As an alternative option it is possible to use multiplication of the value of concentration in sewage and total amount of annual sewage discharge for calculation of annual entry.

Replacement Cl$_2$ with ClO$_2$ at the first bleaching stage drastically reduces the generation of dioxins and furans (lower than limit of detection of 0.3-0.9 pg/l).

With the conservative approach the setup emission factor for discharges of the modern pulp plants that use chlorine dioxide will be established as 60 ng I-TEQ/t of the bleached pulp. This emission factor would be applied only in case of the direct sewage discharge into the environment. If there is the silt generation dioxins will be cached in it and sewage discharging from the treatment facilities will contain insignificant concentrations of PCDD/PCDF.

**Entry into the products**

The pulp and paper industry production could by polluted with PCDD and PCDF. The pollution degree depends on the technology used for bleaching. It was reported on high concentrations of PCDD/PCDF when applying bleaching methods with elementary chlorine. Application of modern technologies leads to reduced concentrations in products. Replacement of Cl$_2$ with ClO$_2$ resulted in the reduction of dioxin and furan concentrations to levels beyond the detection limit. However, total PCDD/PCDF lack in sewage and products of enterprises applying technology without elementary chlorine depends on the clearance of ClO$_2$. The probability of PCDD/PCDF generation is increased as a result of increased pollution with ClO$_2$ (i.e. high amount of elementary chlorine admixture).

Concentrations in the pulp could be ranged from 0.6 ng I-TEQ/kg of pulp up to 200 ng I-TEQ/kg of bleached pulp [2]. Median concentration calculated for “the old technology” amounted to 9 ng I-TEQ/kg of the bleached Kraft-pulp. The setup emission factor is equal to 10 µg I-TEQ/t of the bleached Kraft-pulp.

Concentrations of PCDD/PCDF in the bleached Kraft-paper produced with application of free chlorine and the relevant setup emission factors are 5 µg I-TEQ/t for the make-up tissues, shopping bags and other consumer papers, and 2 µg I-TEQ/t for filter and newsprint papers from primary fibbers. In case when the chlorine dioxide or chlorineless bleaching applies the emission factor would be 0.5 µg I-TEQ/t.

The emission factor for unbleached paper is 0.5 µg I-TEQ/t.
**Entry into the residues**

The main residues related to the emissions of dioxins that are emitting from the pulp-and-paper enterprises are silts generated during the sewage waters treatment. The output of silt amounts from 14 through 140 kg per ton of pulp [2]. According to the data provided by the European Union 30-60 kg of organic wastes fall per ton of the bleached Kraft-pulp and additionally 40-70 kg of inorganic wastes fall per ton of pulp. 20-60 kg of the dry solid residues are generated during the unbleached pulp production. For the calculation of the emission factor it is assumed that 50 kg of silt (dry substance) are generated as the result of the production of one ton of pulp.

Concentrations in silts of the pulp production with old bleaching technologies vary from 2 ng I-TEQ/kg of dry substance to 370 ng I-TEQ/kg of dry substance with a median of 93 ng I-TEQ/kg of silt. The emission factor for silt in the production of the bleached Kraft-pulp is 4.5 µg I-TEQ/t of bleached Kraft-pulp. As the alternative for determination of annual PCDD/PCDF emission the multiplication of concentration in silt of 100 ng M-I-TEQ/kg of silt and total amount of silt disposed annually could be used.

Concentrations in silts generated in the sewage treatment systems of the enterprises that use regular delignification were not practically different from those using delignification with oxygen.

During assessment of average value of 4 ng I-TEQ/kg of dry substance the setup emission factor for silts generated as a result of the pulp production with new technology will be 0.2 µg I-TEQ/t of pulp.

The same emission factor is applied in the present Guidelines for the boilers functioning on timber/bark, which is applied for incineration of timber. According to the data [2] the emission factor for the boilers operating on bark is 48 µg I-TEQ/t of ash.

**4.2.1. Kotlas PPP – background information**

Kotlas PPP (Arkhangelsk region, city of Koryazhma) – is the largest timber-chemical complex in Europe.

The share of Kotlas PPP amounts to 19% of total domestic pulp, 9% of paper and 22% of carton produced in Russia [7].

In 1953 the USSR Council of Ministers adopted the project and the general plan of construction of the Kotlas PPP, and in 1961 the plant pulped its first tone and occupied strongly the leading position in the sector. Being the largest manufacturer of various pulp and paper products the plant not only increases volumes of production but, while improving the technological processes, permanently works towards increasing the quality of manufacturing products including their environmental indicators. The plant is among the first enterprises in Russia that applied chlorineless pulp bleaching. The environmentally friendly products manufactured with such a technology are of great demand both in Russia and abroad.
For nine months of 2006 the volume of pulping has increased for 22.6 thousand tons in comparison with nine months of 2005, and amounted to 772.3 thousand tons at the Kotlas PPP. Since the year beginning some 203.7 thousand tons of paper were produced. Volumes of production of this type of product increased to 5.5%, or for 10.6 thousand tons. Release of pasteboard has increased for 13 thousand tons, and made 246.5 thousand tons. In 2005 volumes of pulping at the Kotlas PPP, which is the part of the “Ilim Pulp” corporation have exceeded 1 million tons (for 47.6 thousand tons higher than in 2004).

Kotlas PPP joined the “Ilim Pulp” in 1994. The corporation consolidated about 93% of the plant stock capital. Introduction of a new technology of bleaching of pulp without chlorine (the total cost of the project – US$ 15 million) has moved the plant to the rank of the elite Russian pulp-and-paper manufacturers and has significantly strengthened its position at the international market.

Priority directions of environmental activity of “Ilim Pulp” are introduction of a low-waste production technology and efficiency increase of treatment facilities operation, what would allow to drastically reducing dumping and emissions of contaminants to the environment, including organochlorine compounds. Aimed at this for the first time in the post reform Russia the modern scheme of bleaching of sulphate pulp from hardwoods timber with the oxygen-alkaline processing stage was introduced at the Kotlas PPP in 2000.
Kotlas PPP production building.

About 65% of production of the plant is exported to Europe, the Middle East and the North America.

The plant includes:
- 6 manufactures;
- 9 independent units;
- 3 power stations.
The plant occupies 600 ha.

Products of the plant include:
- sulphated bleached hardwood pulp
- viscose pulp
- pasteboard for plane layers of corrugated flute
- paper for corrugating
- offset paper for printing
- bag paper
- paper sacks
- wallpaper
- timber-chemical and biochemical processing products

Designed capacity – 938 thousand tons of cooking pulp and 255 thousand tons of pasteboard annually.
4.2.2. Pulp production at the Kotlas PPP

The greatest volume of production made by the plant falls on pulp. Cooking of pulp – is a complicated chemical process. During this process not only cellulose is evolved from timber, but the physical and chemical properties necessary for its further use are provided simultaneously [9].

In order to obtain the high quality semi-product the pulp is exposed to two major technological processes - bleaching and drying. The multistage schemes of bleaching are applied at the plant. The pulp is processed with oxidizers (chlorine, sodium hypochlorite, chlorine dioxide) and caustic soda. Processes of pulp bleaching are improved constantly; introduction of oxygen-alkaline processing at separate technological sites allows reducing chlorine-containing products utilization at the plant.

The Kotlas PPP releases the following types of pulp: sulphate bleached pulp derived from hardwood timber, and viscose pulp (soluble sulphite). Viscose pulp is designed for further chemical processing into viscose silk and for production of sanitary products and paper.

Final stage of manufacturing process.

Production of printing papers is arranged at the technological streams consisting of cooking, bleaching and paper workshops and completely equipped with domestic equipment. Papermaking machines compose its basic part. Their working speed amounts up to 450 meters per minute. Edging width of paper is 4.20 m.

The technological lines for production of sack paper and bags from are functioning at the plant along with manufacturing of pasteboard and flute paper from which packing boxes are producing.

Both closed and opened sacks used for many quick products are released at the 8 flow lines.

One more type of the commercial output produced at the plant is compressed fibreboards (CFB) widely used for various finishing works. Woodchips from lumber wastes of mixed wood species are used for its production.

CFB are produced according to the typical technological scheme of the Swedish company “Defibrator”. Board’s thickness is 3.2 mm.

The plant aligned a release of wide assortment of the public goods, production of which is based on processing of wastes from leading industries.
Some groups might be fetched out among this type of products: fair goods (notepads, notebooks, consumer paper, etc.); photo m³ albums and file folders; paper bags and sacks; sanitary-hygienic products.

4.2.3. Production of goods from wastes of main industries

Wastes that are generated as a result of basic technological processes carried out at the plant might find a useful application.

In this manner nutrient yeast and technical methyl carbinol results from biochemical processing of sulphite liquors that are the wastes of pulp cooking.

Thus, the feed yeast and technical ethyl alcohol are originating after the biochemical processing of sulphite liquors, which are wastes from the pulp cooking.

One more product of sulphite liquors processing are technical lignosulphonates used as binding substance at pig-iron, steel and nonferrous castings, in manufacture refractory goods and cements.

In case of sulphate method of pulp cooking the soap by-product separated from its leaches is processed into lipoid acids, tall oil and rosin.

The organic part of used sulphate leaches jointly with wastes of wood processing to woodchips allows to produce the thermal and electric power through incineration at soda-regeneration and bark (for a wood bark) boilers for the needs of the plant.

Used leaches (of coniferous and deciduous species) are incinerated in small square furnaces with lateral length of ~6 m. There are 6 furnaces. Soda regeneration boilers SRK-5 adjoin to furnaces. The alkali solution is sprayed through atomizers, and there is nothing for incineration beyond. Timber wastes and bark are incinerated separately in regular shaft kilns with obtaining of steam and cleaning from ashes at wet scrubbers.

There is a sodium sulphate at the SRK-5 floor. Fans are installed at the output from SRK. There are big electric filters to collect volatilizing sodium sulphate. The steam boiler with the turbine at the SRK output provides production with the electric power.

4.2.4. Cleaner Production Antidioxin Programme. Results Kotlas PPP

The Programme was performed at Kotlas PPM in accordance with Cleaner Production methodology in September 2006 through February 2007.

We are very grateful to Mr. Robert Dyer, ACAP Chairman, who wrote a supportive letter to Mr. Zakhar Smushkin, Chairman of the Board of Ilim Pulp Corporation, owner of the JSC Kotlas PPM.

The company employs chlorine pulp bleaching and chlorine disinfection of pure drinking water. The mill uses pure water in debarking and wood processing. The treatment facilities are very old (started up in 1969) and employ a single-stage sewage treatment technology.

Due to the fact that most of dioxin environmental emissions are released by pulp and paper mills together with wastewater, including the Kotlas PPM, the major goal of this Programme, along with reduction in pure (chlorinated) water consumption at all production stages, was to reduce the amount of liquid waste produced by primary facilities and decrease the pollution content of wastewater as discharged from the treatment facilities.
There were representatives from the Kotlas PPM facilities participating in the Programme, such as White Papers business line, Power Engineering business line, production support management, Pulp business line, Paperboard business line, Wood Chemistry business line, and Environmental Department.

Every Cleaner Production Programme attendee developed a series of projects aimed at production efficiency improvement and environmental enhancement at the same time. Many of the projects developed have already been implemented or are being implemented now. Complete project data are given in the table below.
### Cleaner Production Programme Results

| 1. Number of programme attendees certified | 12 |
| 2. Measures developed, including those of Groups A, B, and C | 48 |
| 3. Total economic efficiency | USD 5,955,000 per year |
| 4. Investments | USD 7,595,000 |

### Yearly Environmental Efficiency

<table>
<thead>
<tr>
<th>Description of Activities</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduction in filtered water consumption (,000 m³)</td>
<td>10,943</td>
</tr>
<tr>
<td>Reduction in pure/chlorinated water consumption (,000 m³)</td>
<td>1,706</td>
</tr>
<tr>
<td>Effluent reduction (.000 m³)</td>
<td>10,755</td>
</tr>
<tr>
<td>Energy saved (.000 kWh)</td>
<td>2,148</td>
</tr>
<tr>
<td>Heat saved (.000 kWh)</td>
<td>227,400</td>
</tr>
<tr>
<td>Solid waste reduction (t)</td>
<td>283,876</td>
</tr>
<tr>
<td>Reduction of biological oxygen demand (BOD) (t)</td>
<td>21,025</td>
</tr>
<tr>
<td>Reduction of suspended solids (t)</td>
<td>146,400</td>
</tr>
<tr>
<td>Compressed air saved (.000 m³)</td>
<td>137,970</td>
</tr>
<tr>
<td>Wood saved (m³)</td>
<td>4,800</td>
</tr>
<tr>
<td>Pulp saved (t)</td>
<td>10,352</td>
</tr>
<tr>
<td>Sulphuric acid saved (t)</td>
<td>99</td>
</tr>
<tr>
<td>Sodium sulphate saved (t)</td>
<td>160</td>
</tr>
</tbody>
</table>

4) cellulose productivity on Kotlas pulp-and paper plant by data of 2001 was equal 842000 t. By data of 2006 the cellulose productivity of plant has been increased to 1 026 329 t (~ 22%). Such increase in capacity due to fulfilling of various actions and expansion of "bottlenecks" is usual practice of the enterprises when their production is in demand.
<table>
<thead>
<tr>
<th>Group A measures (no investments)</th>
<th>21</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total economic efficiency</td>
<td>USD 332,600</td>
</tr>
<tr>
<td>Number of measures implemented</td>
<td>12</td>
</tr>
<tr>
<td>Economic efficiency of the measures implemented</td>
<td>USD 117,500</td>
</tr>
<tr>
<td>Time of implementation</td>
<td>2006 through 2007</td>
</tr>
<tr>
<td>Reduction in filtered water consumption (m³)</td>
<td>621,400</td>
</tr>
<tr>
<td>Reduction in pure/chlorinated water consumption (m³)</td>
<td>121,000</td>
</tr>
<tr>
<td>Effluent reduction (m³)</td>
<td>837,000</td>
</tr>
<tr>
<td>Heat saved (,000 kWh)</td>
<td>25,400</td>
</tr>
<tr>
<td>Solid waste reduction (t)</td>
<td>76</td>
</tr>
<tr>
<td>Compressed air saved (.000 m³)</td>
<td>59,130</td>
</tr>
<tr>
<td>Reduction in filtered water consumption (m³)</td>
<td>113,700</td>
</tr>
<tr>
<td>Effluent reduction (m³)</td>
<td>85,200</td>
</tr>
<tr>
<td>Heat saved (,000 kWh)</td>
<td>3,170</td>
</tr>
<tr>
<td>Solid waste reduction (t)</td>
<td>76</td>
</tr>
<tr>
<td>Compressed air saved (.000 m³)</td>
<td>59,130</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Group B measures (investments required)</th>
<th>20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total economic efficiency</td>
<td>USD 828,000</td>
</tr>
<tr>
<td>Investments</td>
<td>USD 806,000</td>
</tr>
<tr>
<td>Average payback period</td>
<td>0.97 yr</td>
</tr>
<tr>
<td>Economic efficiency of the measures implemented</td>
<td>USD 298,000</td>
</tr>
<tr>
<td>Investments</td>
<td>USD 302,000</td>
</tr>
<tr>
<td>Average payback period</td>
<td>1.01 yr</td>
</tr>
<tr>
<td>Number of measures implemented</td>
<td>8</td>
</tr>
<tr>
<td>Reduction in filtered water consumption (m³)</td>
<td>2,064</td>
</tr>
<tr>
<td>Reduction in pure/chlorinated water consumption (m³)</td>
<td>1,585</td>
</tr>
<tr>
<td>Effluent reduction (m³)</td>
<td>1,660</td>
</tr>
<tr>
<td>Energy saved (kWh)</td>
<td>308,400</td>
</tr>
<tr>
<td>Heat saved (,000 kWh)</td>
<td>202,000</td>
</tr>
<tr>
<td>Solid waste reduction (t)</td>
<td>133,800</td>
</tr>
<tr>
<td>BOD reduction (t)</td>
<td>18,275</td>
</tr>
<tr>
<td>Compressed air saved (.000 m³)</td>
<td>78,840</td>
</tr>
<tr>
<td>Pulp saved (t)</td>
<td>102</td>
</tr>
<tr>
<td>Sulphuric acid saved (t)</td>
<td>99</td>
</tr>
<tr>
<td>Sodium sulphate saved (t)</td>
<td>160</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Group C measures (investments required)</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduction in filtered water consumption (.000 m³)</td>
<td>8,258</td>
</tr>
<tr>
<td></td>
<td></td>
</tr>
<tr>
<td>--------------------------------</td>
<td>----------------</td>
</tr>
<tr>
<td><strong>Total economic efficiency</strong></td>
<td>USD 4,794,400</td>
</tr>
<tr>
<td><strong>Investments</strong></td>
<td>USD 6,789,000</td>
</tr>
<tr>
<td><strong>Total payback period</strong></td>
<td>1.42 yr</td>
</tr>
</tbody>
</table>

- Effluent reduction (,000 m³) 8,258
- Energy saved (,000 kWh) 1,840
- Solid waste reduction (t) 150,000
- BOD reduction (t) 2,750
- Reduction of suspended matters (t) 2,240
- Wood saved (m³) 4,800
- Pulp saved (t) 10,250

*All savings marked red refer to minimization of dioxin emission into environment.*
The following projects can be given as examples of measures aimed at reduction of dioxin emissions:

**White Papers business line**

Project: Fibre Saving Filter Installation

A new filter is planned to be installed to recover pulp fibres from the wastewater and return the pulp trapped into production.

The project implementation is expected to result in the environmental benefits, as follows:

- Reduced fibre consumption 318 tpy
- Reduced filler consumption 256 tpy
- Reduced filtered water consumption 888,000 m$^3$
- Reduced effluent 888,000 m$^3$

The project implementation will save 318 tons of fibre which contains a lot of dioxins after bleaching and 888,000 cubic meters of waste water, which carries dioxins as well.

To implement the project the mill needs investments amounting to USD 700,000. Yearly net economic saving will come to USD 313,000. Payback period for the project is 2.2 yr.

**Pulp business line**

Project: Zero warm water discharge into sewage system after cooling of yeast-growing apparatus.

Planned to be connected is the existing warm water collecting and cooling tank, being currently out of use, after yeast-growing apparatus 6 and its further re-use for cooling.

The project implementation is expected to result in the environmental benefits, as follows:

- Reduced pure water consumption 248,000 m$^3$
- Effluent reduction 248,000 m$^3$

After implementation of the project the effluent, which carries dioxin, will be cut.

The measure does not require investments, can be implemented out of the shop funds for preventative maintenance and can return a benefit of USD 16,120, if implemented. Planned to be implemented in 2008.

**Production support management**

Project: Reduced warm water consumption in spruce wood debarking department

Water supply control valves (4 pcs.) are offered to be installed on each barker and a water meter on the central pipeline.

The project implementation is expected to result in the environmental benefits, as follows:

- Reduced pure water consumption 490,000 m$^3$
- Effluent reduction 490,000 m$^3$

After implementation of the project the effluent, which carries dioxin, will be cut.

To implement the project the mill needs investments in the amount of USD 34,800. Yearly net economic saving will come to USD 49,000. Payback period for the project is 0.71 yr. Planned to be implemented in 2008.

Project: Flocculant supply to primary sedimentation tanks of the 1st and 2nd treatment stages

Flocculant is proposed to be supplied to the primary sedimentation tanks for more effective sedimentation of organic substances contained in industrial effluent, reduced load upon biological treatment facilities and higher quality of effluent treatment.

The project implementation is expected to result in the environmental benefits, as follows:

- BOD reduction at outfall on the River Vychegda 316 t
• Energy consumption 4,390,000 kWh

After implementation of the project the BOD (biologically destroyable organics) will be reduced and dioxin, mixed with other organic compounds, will be cut.

To implement the project the mill needs investments in the amount of USD 62,000. Yearly net economic saving will come to USD 89,300. Payback period for the project is 0.7 yr. The project is being implemented.

**Paperboard business line**

Project: Collecting liquor from loading lines of digesters 1 and 2. The liquor is offered to be collected with a pump installed, to be used in production, with lower water and sodium sulphate consumption.

The project implementation is expected to result in the environmental benefits, as follows:

- Reduced pure water consumption 273,000 m³
- Effluent reduction 273,000 m³
- Reduction in sodium sulphate consumption 160 t

After implementation of the project the effluent, which carries dioxin, will be cut.

To implement the project the mill needs investments in the amount of USD 18,000. Yearly net economic saving will come to USD 42,000. Payback period for the project is 0.43 yr. The project is to be implemented in 2008.

**Wood Chemistry business line**

Project: Flushing sulphate soap with neutralised acid water.

Raw sulphate soap is contaminated with different impurities and contains a great amount of black liquor. This increases the sulphuric acid flowrate needed to decompose sulphate soap and deteriorates the tall oil produced. The sulphate soap has been proposed to be flushed with a neutralised acid water solution. It has been offered to install a new collecting tank for the neutralised acid water to be pumped into an agitator located at an early process stage.

The project implementation is expected to result in the environmental benefits, as follows:

- Acid water discharge reduction 30,940 m³
- Reduced sulphuric acid requirement 33 t
- Tall oil production increase 372 t

After implementation of the project the acid water discharge will be cut which will cause consequent reduction of chlorinated water consumption for acid water treatment before the treatment facilities. And decrease in chlorinated water consumption directly corresponds to decrease of effluent and, hence, decrease in dioxin amount, forming at purification station and leaving the treatment facilities.

To implement the project the mill needs investments in the amount of USD 37,800. Yearly net economic saving will come to USD 44,000. Payback period for the project is 0.9 yr.
5. Technical and economical assessment of actions on decrease of dioxin’s emissions

5.1. Technical and economical assessment of actions on decrease of dioxin’s emissions on the Vorkuta cement plant including a choice of the most ecologically effective technologies

Generation of dioxins could take place only at the stage of firming of raw mixture in the cement kiln and at the stage of purification of kiln gases from cement dust and chilling.

According to the observations [2,10] the most efficient method of drastic reduction of dioxin releases at the cement plant is rapid chilling of kiln gases to the temperatures below 200°C. The critical range of temperatures is usually passed quite rapidly during the production of clinker.

Considering the lack of installations for treatment of emitting from the cement kiln gases from dust and harmful gas admixtures at the Vorkuta cement plant to levels of environmental safety, the two-stage treatment including the rapid dry (small time of contact) dust cleaning and then the wet cleaning at temperatures guaranteed to be below 200°C is suggested. In our opinion this will allow implementation of task on reduction of dioxin emissions and simultaneous improvement of the environmental characteristic of the cement production due to the drastic reduction of dust emissions.

Dry dust cleaning is carried out in the device with the Opposite Swirling Flows - OSF device (Fig. 4), where the principle of inertial cleaning of gas streams from solid particles is incorporated.

![Figure 4](image_url)

Figure 4. Scheme of installation for inertial dust-and-gas cleaning from solid particles.

The dusty gas stream is loaded for cleaning trough two beans placed one at above (secondary stream) and another at the bottom of the device (primary stream). The body of the
device is cylindrical with ratio of diameter to height as 1:2.5. The primary stream of air is twisted by whirler installed at axis of the device in its bottom part. Solid particles are rejected by inertial forces to lateral surface of the device. The secondary stream is twisted by coaxial whirler. Solid particles slip upon the lateral surface of the body to a bottom of the device, where they are unloaded by sluice feeder.

OSF devices are highly effective for catching the dust from industrial dusty gases at the cement industry productions.

Productivity on dusty gas could be up to 140 thousand m³/hour.

The dusty gases temperature loaded to the device could reach 600-700°C and is limited with thermal resistance of the body material.

Operation of OSF device does not require special service and additional equipment, reliability of its operation is always provided.

Dimensions of OSF device for maximal productivity of 140 thousand m³/hour are: diameter - 2600 mm, height - 14000 mm. With the wall thickness 10 mm the device weighs 12000 kg. Carbonaceous steel is usually used as a material for its manufacturing. In this case cost of OSF device with the maximal productivity would be 700 thousand roubles. With the equipment for dust removal the total cost will be ~ 1 million roubles.

The gases are inside of the OSF device for ~ 0.5 sec. Such a small time of contact at relatively high temperature reduces to a minimum the possibility of secondary synthesis of dioxins. According to Methodical Guidelines [2] the highest factor of dioxin emissions 5.0 µg I-TEQ/t of cement are recommended for firming kilns with the wet process at temperature of absorbed gases over 300°C.

The fabric filters and reduction of temperature of absorbed gases to 200-300°C are reduced the dioxin emission factor to 0.6 µg I-TEQ/t of cement. Further reduction of temperature of absorbed gases to less than 200°C is decreased the emission factor to 0.05 µg I-TEQ/t of cement.

The device for wet dust-and-gas cleaning (DPC) provides simultaneous cleaning from dust and harmful gas admixtures to the environmentally safe levels corresponding to the requirements of domestic and international standards. Quality of cleaning is achieved through effective implementation of absorption and chemisorption processes and transfer of harmful substances to neutral solutions safe for the natural environment.

The device provides dust-and-gas cleaning of gas streams in modular construction with a unit capacity from 1 to 200 thousand m³/hour with irrigation by liquid up to 0.2 l per 1 m³ of treated gas. Energy consumption would be 0.5 kW per 1 thousand m³/hour of treated gas stream.

Hydraulic resistance of one step of contact (one-stage absorber) corresponds to 70-120 mm of the water column.

The content of installation of dust and gas cleaning includes an absorber, reservoir, the centrifugal pump, fan, metal structures, set of stopping and regulating equipment and pipe shells (Fig. 5).
Figure 5. Scheme of installation for dust and gas cleaning with active hydrodynamic interaction zone.

Material for the equipment included into the installation depends on aggression of the media. Installations made of both the stainless steel and the carbonaceous steel are produced.

Location of installations is possible both inside the industrial premises and outside. In a later case the external surface of the main technological equipment and gas flues is isolated.

The process of dust and gas cleaning does not require manual or automatic controls and is supplied with blocking devices only.

Dimensions of the device for wet dust and gas cleaning with productivity for gas 150 thousand m$^3$/hour: diameter - 6500 mm, height - 10750 mm. With wall thickness of 12 mm the device weighs 33500 kg. The cost of the device made of carbonaceous steel will be ~ 2 million roubles, and the cost of all installation amounts to ~ 2.5 million roubles.

The gases are inside the DPC device for 6 sec. The secondary generation of dioxins practically does not occur at temperature below 150°C.

The technical and economic assessment of installation of the system for dust and gas cleaning is presented below.

Assessment of capital investments on introduction of measurements directed to reduction of dioxin releases at the Vorkuta cement plant
Initial data for assessment of capital investments:

1. There are 3 kilns used at the plant with the following capacity:
   - 1st kiln – 11.2 t/hour
   - 2nd kiln – 17.0 t/hour
   - 3rd kiln – 17.0 t/hour

2. Volume of gas releases from kilns in terms that 9440 nm$^3$ of gas is released per 1 t of cement, is accordingly:
   - 1st kiln – 105 728 nm$^3$/hour
   - 2nd kiln – 160 480 nm$^3$/hour
   - 3rd kiln – 160 480 t/hour

3. Diagram for each kiln considering the gas releases and abilities of technological equipment

![Diagram of installation of systems for dust and gas cleaning in the cement kilns at the Vorkuta Cement Plant.](image)

**Figure 6.** Diagram of installation of systems for dust and gas cleaning in the cement kilns at the Vorkuta Cement Plant.

**Calculation of cost of main and secondary equipment as well as design and installation works**

**1st kiln**

Basic equipment:
- OSF device with productivity 110 000 nm$^3$/hour – 600 thousand roubles
- Device for wet dust and gas cleaning (DPC) with productivity 110 000 nm$^3$/hour – 1600 thousand roubles.

Auxiliary equipment:

Schemes of installation for inertial dust and gas cleaning from solid particles (OSF) and installation for dust and gas cleaning with an active hydrodynamic zone of interaction (DPC) are
simple enough, and basically consist of main OSF and DPC devices, which operation does not require special additional equipment. In this case auxiliary equipment consists of the device for dust removal, exhausters, container and centrifugal pump. The cost of auxiliary equipment is determined in terms of percentage from the cost of the basic equipment. As a rule, its cost is within 30%-60% of the basic equipment cost. In our case it is advisable to accept 30% of cost of the basic equipment what will be 660 thousand roubles.

2nd kiln

Basic equipment:
- OSF advice with productivity 80 000 nm³/hour – 440.0 thousand roubles
  Quantity - 2. Total – 880000 roubles
- Device for wet dust and gas cleaning (DPC) with productivity 160 000 nm²/hour – 2300 thousand roubles.
Total cost of basic equipment – 3180000 roubles

Auxiliary equipment

Cost of auxiliary equipment for the 2nd kiln is determined as 30% of the cost of the basic equipment, as in case of the 1st kiln, what would be 950 thousand roubles.

3rd kiln

Cost of the basic and auxiliary equipment for the 3rd kiln is estimated similarly to the equipment for the 2nd kiln and is as follows:
- Basic equipment – 3180.0 thousand roubles.
- Auxiliary equipment – 950.0 thousand roubles.

Calculation of cost of design and installation works

Cost estimation for design and installation works is determined in terms of percentage of cost of basic and auxiliary equipment. This value is within 25%-100% depending on cost of the implemented scheme.

Taking into account the simplicity of two-stage installation for dust and gas cleaning (OSF and DPC) it is advisable to determine the cost of design and installation works at a rate of 25% of the cost of basic and auxiliary equipment for all 3 kilns what will be:

<table>
<thead>
<tr>
<th></th>
<th>Cost of all equipment</th>
<th>Design and installation works</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st kiln</td>
<td>– 2860.0 thousand roubles</td>
<td>715.0 thousand roubles</td>
</tr>
<tr>
<td>2nd kiln</td>
<td>– 4130.0 thousand roubles</td>
<td>1035.0 thousand roubles</td>
</tr>
<tr>
<td>3rd kiln</td>
<td>– 4130.0 thousand roubles</td>
<td>1035.0 thousand roubles</td>
</tr>
</tbody>
</table>

Assessment capital investments

The assessment of capital investments in view of the proposed arrangements is determined for both each furnace and the whole complex. The estimations are provided in the Table 8 below.

Table 8
<table>
<thead>
<tr>
<th>№</th>
<th>Name of item</th>
<th>Cost of all equipment, thousand roubles</th>
<th>Cost of design and installation works, thousand roubles</th>
<th>Total, thousand roubles</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>1st kiln</td>
<td>2860.0</td>
<td>715.0</td>
<td>3575.0</td>
</tr>
<tr>
<td>2.</td>
<td>2nd kiln</td>
<td>4130.0</td>
<td>1035.0</td>
<td>5165.0</td>
</tr>
<tr>
<td>3.</td>
<td>3rd kiln</td>
<td>4130.0</td>
<td>1035.0</td>
<td>5165.0</td>
</tr>
<tr>
<td></td>
<td><strong>Total:</strong></td>
<td><strong>11120.0</strong></td>
<td><strong>2785.0</strong></td>
<td><strong>13905.0</strong></td>
</tr>
</tbody>
</table>

Some 13 905 000 roubles are necessary to implement the proposed arrangements at the Vorkuta cement plant aimed at the reduction of dioxin releases to parameters set forth in the normatives.

Possibly at first it is advisable to install two-stage dust and gas cleaning at one firming kiln, and then at two others.

It should be noticed that the data in the report [1] on gas releases volume per 1 t of cement, 9440 nm³, accepted as the basis for calculations of productivity of installations for dust and gas cleaning was found as higher than those in the Guidelines [2] recommended for calculation, 4000 nm³/t of cement. This will be corrected later in Moscow (CIP).

It is possible, that the value of gas emissions will be less than 9440 nm³/t during the plant development and achievement of the full capacity. It could be found that it would be enough to install one OSF device with productivity 140000 nm³/hour or less per each kiln instead of 2 twin devices at the cement kilns № 2 and № 3. This will be corrected later in Moscow (CIP).

As at the present time the dioxin emissions are ~ 0.6 g I-TEQ per annum during production of 110 thousand tons of cement per annum, so at full production capacity of 360 thousand tons of cement per annum the dioxin emissions will be 1.9 g I-TEQ/year. It is expected that with introduction of the two-stage system (dry and wet) of dust and gas cleaning dioxin emissions will be reduced from 5.2 µg I-TEQ/t of cement [1] (0.55 ng I-TEQ/nm³) ~ to 0.5-0.6 µg I-TEQ/t of cement (0.06 ng I-TEQ/nm³) and will step on to the following lower level according to the classification [2]. Moreover, emissions of a huge amount of cement dust, which could be returned in production, are eliminated. The estimation of environmental effect in monetary terms for dioxin emissions is not yet developed due to the lack of corresponding normatives.

The dioxin emission factor will be 0.94 µg I-TEQ/t of cement when the European norms for the content of dioxins in gas emissions not over 0.1 ng I-TEQ/nm³ and volume of gas emissions 9440 nm³ per 1 ton of cement will be achieved. These values are higher than those supposed to be achieved after the introduction of recommended arrangements - 0.6 µg I-TEQ/t of cement, i.e. the required norm for content of dioxins. The dioxin emission factor per 1 ton of cement would be reduced as of volume of gas emissions per 1 ton of cement would decreased.

The communication of A.V. Lomako, General Director of “Vorkutacement”, related to the interest of the enterprise in the introduction of two-step system for dust and gas cleaning.

Other methods could be also applied for removal of dioxins from absorbed gases. Thus, treatment of absorbed gases with filters contained activated charcoal is characterized by high efficiency of removal of trace quantity of pollutants (> 90%). However, among the cement plant in Europe the filter with activated charcoal is installed only at Ziggentale (Switzerland) at kiln with productivity of 2000 tons of clinker per day [10]. Measurements demonstrated its high efficiency with respect to PCDD and PCDF. Application of such an additional method of treatment could be considered after obtaining of experimental data on efficiency of the proposed arrangements.
5.2. Technical and economic assessment of arrangements to reduce the dioxin releases at the Kotlas PPP, including the selection of the most environmentally sufficient technologies

Production of paper consists in the following main stages (Fig. 7):
- Preparation of timber raw, which includes roughing of bark, bucking and milling of timber to chips;
- Incineration of bark and timber wastes;
- Pulping to separate cellulose fibres from lignin;
- Regeneration of cooking liquor composed of sodium sulphide and sodium hydroxide in sulphate or Kraft-process (80% of global pulp production);
- Bleaching of pulp with molecular chlorine, chlorine dioxide, hypochlorite, as well as with ozone or peroxide;
- Sewage waters treatment;
- Pulp drying and manufacturing of paper.

**Figure 7. Diagram of paper products manufacturing**

Dioxins are generated at two high-temperature processes of incineration of:
- bark and timber wastes in bark boilers;
- black liquor in soda regeneration boilers.

Moreover, considerable generation of dioxins takes place during bleaching of pulp with molecular chlorine.

Dioxin releases to the biosphere during the technological process of pulp production are taken place through the following ways:
- Emission of dioxins into sewage waters;
- Emission into wastes – into silt residues;
- Emission into products – pulp, paper;
- Emission into air – during incineration of black liquor;
- Emission into air – during incineration of timber wastes, bark, silts.

In line with the recommendations [2] the emission factor for sewages in the pulp-and-paper industry with old technology of chlorine bleaching is 4.5 µg I-TEQ/ADt (ton of air dried pulp). In the modern technology of bleaching with chlorine dioxide the emission factor of 0.06 µg I-TEQ/ADt is recommended.

According to the report [14] only 29694 tons of sulphate coniferous pulp of the total amount
350195 (~8.5%) were bleached with elementary chlorine at the Kotlas PPP for production of printing paper. Some 146580 tons of sulphite viscose coniferous pulp were also bleached with elementary chlorine. So the total amount of pulp bleached with chlorine is 176274 tons.

It is possible to assess the total annual emission of dioxins from the pulp bleaching stages at the Kotlas PPP: \( 4.5 \times 176274/1000000 = 0.79 \text{ g TE} \) using the emission factor recommended in [2] and being aware of the total amount of bleached pulp.

At the same time within the framework of this work the analyses of sewage waters of the flux collector from bark disposal where water from the chlorinating stage I (bleaching with chlorine) is discharged, were carried out. As the average of two analyses the content of dioxins is 3.56 pg I-TEQ/l, what is lower than norms 20 pg I-TEQ/l established for drinking water, ground and surface waters, and water off take sites.

There are no dioxins detected in other sewage including those from the bleaching and drying productions, and production of sulphate bleached pulp (thru ECF method) are not detected.

The share of the flux collector from bark disposal is 20% [14] or 28400 thousand m³ for total amount of biologically purified sewage waters of 142046 thousand m³ at the Kotlas PPP. Then the annual emissions from the molecular chlorine bleaching stage will be \( 28'400'000'000 \times 3.56 \times 10^{-12} = 0.1 \text{ g} \). It is rather less than the value of 0.79 g obtained according to the emission factor recommended in [2].

There are 369576 tons of pulp bleached with chlorine dioxide at the Kotlas PPP. Considering the above provided emission factor for this type of bleaching of 0.06 µg I-TEQ/Adt the total emissions of dioxins of this production stage are 0.022 g TE what represents relatively small value.

High-temperature processes (over 200°C) in the oxygen media and with chlorine-containing products or incomplete incineration of natural organic material containing carbon and chlorine also result in the generation of PCDD and PCDF.

The incineration of black liquor in black-liquor boilers (BLB) aimed at the regeneration of alkali and sulphur for reuse during pulping with simultaneous utilization of released heat for evaporation of the liquor's moisture during the evaporation and for generation of steam is envisaged in the technological cycle of the sulphate pulp production. Hence, black-liquor boilers in the pulp plants system perform the technological and energy functions.

In line with the technological regulation the incineration process is arranged based on the principle of torch fuel-bed firing of liquor supply of which is provided through the specialized atomizers as the dispersed jets. The air necessary for the incineration is entered the furnace chamber at three levels: through the nozzles of primary, secondary and tertiary blowing. The zonal circuit of blasting air supply to the furnace with amplified bottom blasting (up to 90% in sum) in terms of incineration of highly concentrated liquor provides development of enough high temperature in regenerative zone (up to 1100°C). Maintenance of excess air behind the heating at the level of 1.10-1.15 provides full combustion of liquor.

Kiln gases generated during the incineration of liquor consistently pass safety festoon, steam overheater, convection (boiler) bank, economizers, electro filters and are released into the atmosphere through smoke stack by exhausters.

According to report [15] 0.062 g TE of dioxins were released out per 551 thousand tons of pulp of general cooking in three black-liquor boilers (BLB), i.e. the emission factor is 0.11 µg I-TEQ/t of pulp.
In our work for the phase 1 [1] based on the Methodical Guidelines of 2001 [16] the emission factor was established as 0.5 µg I-TEQ/t of pulp what corresponds to content of dioxins in gas emissions of 0.06 ng I-TEQ/t, i.e. less than normatively admissible 0.1 ng I-TEQ/nm$^3$. Content of dioxins experimentally discovered during this work was rather less - 0.0072 ng I-TEQ/nm$^3$ at average, and accordingly the emission factor of dioxins appeared as lower than the recommended, namely 0.06 µg I-TEQ/t of pulp.

Emissions of dioxins from 5 BLBs of the Kotlas PPP per the total pulp production in 2006 of 1026329 tons with the emission factor of dioxins as 0.06 µg I-TEQ/t of pulp made 0.06 g. It seems that there is no need in any arrangements, as the content of dioxins in gas emissions from BLBs does not exceed the norm.

Finally, incineration of bark and timber wastes is one more source of dioxin emissions at the Kotlas PPP. This stage does not directly relate to the pulp production and serves for the energy production necessary for the plant.

During the incineration of the timber wastes (chips) and especially of the bark, the PCDD/PCDF emission factor is rather high in comparison with the black liquor incineration. There is data provided for 0.4 through 5.4 µg I-TEQ/t of timber [2].

There are 5 so-called bark boiler-facilities (2 boilers of Tampella-Karlson type and 3 KM-75 boilers) in the boiler workshop at the Kotlas PPP.

The total amount of bark incinerated will be 1026329 × 0.771 m$^3$/year × 0.22 m$^3$ = ~ 174000 t/year if the value of incinerated bark – 0.771 dense m$^3$ per ton of total pulp cooking and average density of wet bark of 220 kg/dense m$^3$. If the emission factor of 0.4 µg I-TEQ/t of bark from the Guidelines of 2001 [16] the total emissions would be insignificant - 0.07 g I-TEQ. According to the Guidelines of 2005 [2] the total emissions will increase to 0.205 g if the emission factor will be 0.2 µg I-TEQ/t of pulp.

The average content of dioxins in gas emissions experimentally found under this work is 0.41 ng I-TEQ/nm$^3$ for 4 bark boilers. Total gas emission from 5 boilers is 606000 nm$^3$/hour [14]. Then emissions of dioxins would be 606000 × 0.41/1000 = 248 µg/hour. Total capacity of bark boilers is composed from 3 boilers with 26 t/hour and 2 boilers with 13 t/hour (Tables 9,10) and is 104 t/hour.

Knowing the total amount of incinerated bark (174000 t/year) and the total capacity of boilers (104 t/hour) we could find amount of working hours of boilers per annum - 1670 hours. Thus, regular load of bark boilers is significantly lower than the annual capacity what is reflected in regime maps (Tables 10 and 11). On the basis of the hour emission of dioxins from all 5 boilers (248 µg) and their work time (1670 hours) we could find the annual emission of dioxins at this stage - 0.41g.

Hence, excess of norms for content of dioxins in gas emissions was discovered only during the incineration of bark and timber wastes - 0.41 ng I-TEQ/nm$^3$ instead of admissible 0.1 ng I-TEQ/nm$^3$. From the point of view of annual amount of dioxin emissions the emissions from incineration of bark and timber wastes - 0.41g are at the first place also.

At the same time during this work at the Syktyvkar FIC there were the analyses made of kiln gases at the output of the bark boilers №№ 1 and 2, which indicated the average content of dioxins as 0.022 ng/nm$^3$, i.e. lower than the norm.

Possibly, it is related to some technology infringements at the Kotlas PPP as the gas line at the BLB and bark boilers output has the regular set of elements: steam overheaters, steam boiler,
economizers and filters at both the Syktyvkar Wood Complex and the Kotlas PPP. The circuit scheme of kiln gases flow at the output from the black liquor boilers is provided at Fig. 8.

The presence of undesired contaminants in incinerated timber wastes could be the other negative factor. However according to the data of Kotlas PPP the common salt and antiseptic - sodium pentachlorophenol were out of the incinerated raw material during implementation of analyses.

As a result from the point of view of the activities necessity to reduce dioxins emissions the incineration a bark and timber wastes are the first place.

**Figure 8** Principle scheme of kiln gases movement in soda-regeneration boilers gas-path during the black liquor incineration.
### Table 9

**REGIME MAP**

(up to 13 t/hour for bark)

<table>
<thead>
<tr>
<th>№</th>
<th>Indicator</th>
<th>Measuring unit</th>
<th>Loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Steam-generating capacity</td>
<td>t/hour</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>25</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>Pressure of overheated steam</td>
<td>kgf/cm²</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>39</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>39</td>
</tr>
<tr>
<td>3</td>
<td>Pressure in boiler drum</td>
<td>kgf/cm²</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>40</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>40</td>
</tr>
<tr>
<td>4</td>
<td>Temperature of overheated steam</td>
<td>°C</td>
<td>430-440</td>
</tr>
<tr>
<td>5</td>
<td>Temperature of boiler feed water</td>
<td>°C</td>
<td>135-145</td>
</tr>
<tr>
<td>6</td>
<td>Pressure of air after air-heater</td>
<td>kgf/cm²</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>25</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>30</td>
</tr>
<tr>
<td>7</td>
<td>Pressure of air under grid</td>
<td>kgf/cm²</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>25</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>30</td>
</tr>
<tr>
<td>8</td>
<td>Temperature of cold air</td>
<td>°C</td>
<td>25 + 5</td>
</tr>
<tr>
<td>9</td>
<td>Temperature of hot air</td>
<td>°C</td>
<td>250 + 10</td>
</tr>
<tr>
<td>10</td>
<td>Pressure of gas on burners 1/2</td>
<td>kgf/cm²</td>
<td>0.06/0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.006/0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.06/0</td>
</tr>
<tr>
<td>11</td>
<td>3/4</td>
<td>&quot;-&quot;</td>
<td>0/0</td>
</tr>
<tr>
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<td></td>
<td></td>
<td>0.6/0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0/0</td>
</tr>
<tr>
<td>12</td>
<td>Pressure of air on burners 3/4</td>
<td>kgf/cm²</td>
<td>20/0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>20/0</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>20/0</td>
</tr>
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<td>13</td>
<td>3/4</td>
<td>&quot;-&quot;</td>
<td>0/0</td>
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<td></td>
<td></td>
<td>20/0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0/0</td>
</tr>
<tr>
<td>14</td>
<td>Temperature of gases after FWE</td>
<td>°C</td>
<td>290 + 10</td>
</tr>
<tr>
<td>15</td>
<td>Temperature of emitting gases beyond BCC</td>
<td>°C</td>
<td>200 + 10</td>
</tr>
<tr>
<td>16</td>
<td>Exhaustion before ash collector</td>
<td>kgf/cm²</td>
<td>135 + 5</td>
</tr>
<tr>
<td>17</td>
<td>Exhaustion in the burner</td>
<td>mm of water column</td>
<td>0 - 2</td>
</tr>
<tr>
<td>18</td>
<td>Content of oxygen in kiln gases after s/s</td>
<td>%</td>
<td>8 - 12.5</td>
</tr>
<tr>
<td>19</td>
<td>CO Content in emitting gases</td>
<td>mg/nm³</td>
<td>not more 500</td>
</tr>
<tr>
<td>20</td>
<td>Content of NOx</td>
<td>mg/nm³</td>
<td>not more 120</td>
</tr>
<tr>
<td>21</td>
<td>Dustiness after BCC</td>
<td>g/nm³</td>
<td>not more 0.5</td>
</tr>
</tbody>
</table>

Note: utilization of gas is recommended only to support the steam parameters and at excess of bark wetness for more than 60% (in this case incineration time is increased).
### Table 10

**REGIME MAP**

of boiler-facility KM-75 st. № 7, KTC - 1. EPS fuel – bark + natural gas.

(up to 26 t/hour on bark)

<table>
<thead>
<tr>
<th>№</th>
<th>Indicator</th>
<th>Designation</th>
<th>Measuring unit</th>
<th>LOADING</th>
<th>30%</th>
<th>45%</th>
<th>55%</th>
<th>65%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Steam-generating capacity</td>
<td>Dss</td>
<td>t/hour</td>
<td></td>
<td>25</td>
<td>35</td>
<td>40</td>
<td>55</td>
</tr>
<tr>
<td>2</td>
<td>Pressure of steam in boiler drum</td>
<td>Pd</td>
<td>kgf/cm²</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>up to 43</td>
</tr>
<tr>
<td>3</td>
<td>Pressure of overheated steam</td>
<td>Pss</td>
<td>kgf/cm²</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>39</td>
</tr>
<tr>
<td>4</td>
<td>Temperature of boiler feed water</td>
<td>Tbф</td>
<td>°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>140</td>
</tr>
<tr>
<td>5</td>
<td>Temperature of overheated steam</td>
<td>Tсs</td>
<td>°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>430</td>
</tr>
<tr>
<td>6</td>
<td>Air pressure before OSF</td>
<td>Pah</td>
<td>kg/m²</td>
<td></td>
<td>130</td>
<td>150</td>
<td>150</td>
<td>190</td>
</tr>
<tr>
<td>7</td>
<td>Air pressure after OSF</td>
<td>Pah</td>
<td>kg/m²</td>
<td></td>
<td>90</td>
<td>100</td>
<td>130</td>
<td>130</td>
</tr>
<tr>
<td>8</td>
<td>Air-heater resistance</td>
<td>Pah</td>
<td>kg/m²</td>
<td></td>
<td>40</td>
<td>50</td>
<td>50</td>
<td>40</td>
</tr>
<tr>
<td>9</td>
<td>Cold air temperature</td>
<td>Tсг</td>
<td>°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>35</td>
</tr>
<tr>
<td>10</td>
<td>Air temperature after II stage</td>
<td>Thа</td>
<td>°C</td>
<td></td>
<td>330</td>
<td>330</td>
<td>350</td>
<td>360</td>
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<tr>
<td>11</td>
<td>Air temperature after I stage</td>
<td>Th</td>
<td>°C</td>
<td></td>
<td>240</td>
<td>235</td>
<td>210</td>
<td>210</td>
</tr>
<tr>
<td>12</td>
<td>Consumption of natural gas</td>
<td>Bг</td>
<td>nm³/hour</td>
<td></td>
<td>2790</td>
<td>1400</td>
<td>2400</td>
<td>550</td>
</tr>
<tr>
<td>13</td>
<td>Gas pressure after regulator</td>
<td>P</td>
<td>kg/cm²</td>
<td></td>
<td>0.19</td>
<td>0.1</td>
<td>0.18</td>
<td>0.08</td>
</tr>
<tr>
<td></td>
<td>Air pressure against burners:</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>Left bottom</td>
<td>P</td>
<td>kg/m²</td>
<td></td>
<td>0.15</td>
<td>0.08</td>
<td>0.12</td>
<td>0.06</td>
</tr>
<tr>
<td>15</td>
<td>Right bottom</td>
<td>P</td>
<td>kg/m²</td>
<td></td>
<td>0.15</td>
<td>0.08</td>
<td>0.14</td>
<td>0.12</td>
</tr>
<tr>
<td>16</td>
<td>Air pressure over chain grating zones, zone II</td>
<td>P</td>
<td>kg/m²</td>
<td></td>
<td>20</td>
<td>30</td>
<td>30</td>
<td>20</td>
</tr>
<tr>
<td>17</td>
<td>Air pressure over chain grating zones, zone III</td>
<td>P</td>
<td>kg/m²</td>
<td></td>
<td>15</td>
<td>20</td>
<td>20</td>
<td>10</td>
</tr>
<tr>
<td>18</td>
<td>Air pressure against burners, left bottom</td>
<td>P</td>
<td>kg/m²</td>
<td></td>
<td>30</td>
<td>20</td>
<td>20</td>
<td>30</td>
</tr>
<tr>
<td>19</td>
<td>Air pressure against burners, right bottom</td>
<td>P</td>
<td>kg/m²</td>
<td></td>
<td>30</td>
<td>20</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>20</td>
<td>Exhaustion in burner</td>
<td>Sr</td>
<td>kg/m²</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>2</td>
</tr>
<tr>
<td>21</td>
<td>Temperature of kiln gases beyond steam overheater</td>
<td>V</td>
<td>°C</td>
<td></td>
<td>440</td>
<td>460</td>
<td>500</td>
<td>480</td>
</tr>
<tr>
<td>22</td>
<td>Temperature of emitting gases</td>
<td>V</td>
<td>°C</td>
<td></td>
<td>260</td>
<td>280</td>
<td>285</td>
<td>290</td>
</tr>
<tr>
<td>23</td>
<td>Exhaustion before AC</td>
<td>Sac</td>
<td>kg/m³</td>
<td></td>
<td>270</td>
<td>280</td>
<td>290</td>
<td>290</td>
</tr>
<tr>
<td>24</td>
<td>Oxygen content beyond steam overheater</td>
<td>O2</td>
<td>%</td>
<td></td>
<td></td>
<td></td>
<td>12</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>CO content beyond steam super heater, not exceed</td>
<td>CO</td>
<td>mg/nm³</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>not exceed 500</td>
</tr>
<tr>
<td>26</td>
<td>NOx content beyond steam overheater, not exceed</td>
<td>NOx</td>
<td>mg/Nm³</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>not exceed 120</td>
</tr>
<tr>
<td>27</td>
<td>Dustiness after PGI</td>
<td>Z</td>
<td>g/Nm³</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>not exceed 0.370</td>
</tr>
</tbody>
</table>

Note: gas utilization is recommended to support steam parameters and at bark wetness excess over 60% only (in this case fuel incineration time is increased).

With regards to the volume of dioxin emissions into the environment the second place is occupied by bleaching with molecular chlorine. For dramatic emission reduction during bleaching measures are well known - replacement of chlorine with chlorine dioxide. For incineration of bark and timber wastes it might be several reasons and for identification of the main reason a special study
is required. Moreover, significant funding would be required for the replacement of main devices of wastes treatment facility.

Therefore designing of the facility for purification of gas emissions according to the required norm of 0.1 ng I-TEQ/Nm$^3$ (~ 4 times) is expedient to reduce the dioxin releases.

Reconstruction of the bark boiler with replacement of cyclones with electro filters of 60 million roubles cost, according to the data [17] will provide reduction of the suspended substances releases into the atmosphere for 770 tons per annum, but apparently will be of insignificant effect on dioxin emissions. At the same time the degree the suspended substances removal with cyclone (80%) is rather lower comparing with electrofilter (99%).

The drastic quenching of incineration gases is necessary to avoid the re-synthesis of dioxins during the gradual reduction of temperature (from 650 to 150°C). However this contradicts with one of the purposes of the incineration facility: energy production for the enterprise operation. Aimed at this the incineration gases are passing the steam overheaters, steam boilers, economizers and providing the heat for steam generation (fig. 8). We would reduce steam generation through the temperature range decreasing used for the steam generation.

In this case the main control elements for reduction of dioxins emissions is implementation of effective incineration process in accordance with recommendations of BAT: temperature, dwelling time, turbulence, and surplus of oxygen [18].

Application of incineration kilns in "boiling bed" would promote the reduction of dioxins emissions at the stage of bark and timber wastes incineration according to the data in [19]. Replacement of the old mazut-burning boiler with the boiler in the "boiling bed" allowed economizing of 25000 tons of mazut annually at the “Segezhskiy PPP”. The total cost of work package for new boiler installation has exceeded 200 million roubles.

According to [20] the more efficient option for timber wastes and bark processing at PPP is gas-generating installations, installations of timber wastes processing to carbon materials and fuel briquettes. But all these arrangements are cost-expensive.

Recently the catalytic decomposition of dioxins is considered as an effective method. to provide this it is necessary to install a bag filter with a ceramic nozzle the “Medison”company. The cost of the filter with productivity of 5000 m$^3$/hour is ~ 1 million roubles. However it would require installation of 120 bag filters to obtain the full capacity.

Installation of filters with activated charcoal (AC) would be a less expensive arrangement. Taking into account that dioxins are compounds with big molecular weight, their adsorption with the activated charcoal should be of high effectiveness. The content of dioxins in gas emissions are insignificant and therefore replacement of the activated charcoal will be not frequent, and the used charcoal can be incinerated with bark and timber wastes.
Assessment of capital investments related to introduction of arrangements to reduce the dioxin releases at the Kotlas PPP

1. Two bark boilers with productivity of 70000 Nm$^3$/hour and with discharge temperature 160$^\circ$C.

1.1. To decrease temperature of absorbed gases to 50$^\circ$ we should heat the water for boilers in radiator from 20$^\circ$ to 80$^\circ$C.
Radiator surface - 1000 m$^2$
Cost of radiator - 1.4 million roubles.

1.2. Rectangular adsorber 4 x 5 m is installed for adsorption of dioxins.
AC layer height is 1 m. Charcoal amount is 20 m$^3$. Weight is 9 t. Cost of AC – 1.35 million roubles.
Coal type is SC40. Germany. Cost is 150 roubles/kg.
Validity of charcoal is about 10 years.
Cost of device is 380 thousand roubles.

1.3. Total cost of one installation is ~ 1.8 million roubles, and of two installations - ~ 3.6 million roubles. Cost of charcoal is 2.7 million roubles.

2. Two bark boilers with productivity of 148000 Nm$^3$/hour and with discharge temperature - 135$^\circ$C.

2.1. Radiator with surface of 2000 m$^2$ will be required to reduce the temperature of absorbed gases to 50$^\circ$.
Cost is 2.7 million roubles.

2.2. Adsorber with dimensions of 6 x 7 m. AC layer height = 1 m.
Amount of charcoal is 42 m$^3$. Weight is 18.9 t. Cost of AC – 2.8 million roubles.
Cost of device is 750 thousand roubles.

2.3. Total cost of one installation is 3.45 million roubles, and of two installations – 6.9 million roubles.
Cost of charcoal is 5.6 million roubles.

3. Two bark boilers with productivity of 170 Nm$^3$/hour and with discharge temperature - 115$^\circ$.

3.1. Radiator with surface of 2150 m$^2$ will be required to reduce the temperature of absorbed gases to 50$^\circ$.
Cost - 2. 9 million roubles.

3.2. Adsorber with dimensions of 6 x 8 m. AC layer height = 1 m.
Amount of charcoal is 48 m$^3$. Weight is 21.6 tons. Cost of AC – 3.2 million roubles.
Cost of device is 800 thousand roubles.

3.3. Total cost of one installation is 3.7 million roubles, total cost of coal – 3.2 million roubles.

4. Total cost of all five installations

4.1. Total cost of equipment – 14.2 million roubles.
4.2. Total cost of coal – 11.5 million roubles.
Total capital investments

<table>
<thead>
<tr>
<th>Cost of equipment</th>
<th>– 14.2 million roubles.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Design and installation works</td>
<td>– 10.0 million roubles.</td>
</tr>
<tr>
<td>Total</td>
<td>– 24.2 million roubles.</td>
</tr>
<tr>
<td>Project implementation</td>
<td>– 11.5 million roubles.</td>
</tr>
<tr>
<td>Grand Total</td>
<td>– 35.7 million roubles.</td>
</tr>
</tbody>
</table>

It is expedient to test the installation for purification of gas releases from dioxins with AC at the one of bark boilers firstly.

To estimate the cost of arrangements related to the replacement of the chlorine bleaching stage with the chlorine dioxide bleaching stage it is possible to use the data of the environmental report [17] and the reference [18]. According to this data 715 million roubles were spent on the replacement of the bleaching process with molecular chlorine of approximately 200 thousand tons of pulp to achieve the BAT norms on organochlorine compounds release and increase of environmental safety of bleached products and its competitiveness at the world market.

Hence, considerable capital investments are required for the introduction of the chlorineless pulp bleaching. At the Kotlas PPP 176274 tons of pulp are bleached with chlorine [14]. Preliminary, 600-700 million roubles might be required for the introduction of the chlorineless bleaching.
Calculation and assessment of dioxin emissions before the arrangements to decrease the dioxin emissions at the Vorkuta Cement Plant and the Kotlas Pulp-and-Paper Plant according to analytical measurements of the Institute of Biological and Chemical Safety and the UNEP Guidelines

Calculation of emission factors and dioxin emissions before the activities related to their decrease at the Vorkuta Cement Plant and the Kotlas Pulp-and-Paper Plant (PPP) was carried out according to the analytical measurements [22, 23] and recommendations of the UNEP Methodological Guidelines [2,16]. The experimental and estimated data obtained is summarized in the Table 11.

Analytical measurements carried out in 2004 were collected and considered in the report [22]. The experimental emission factors were calculated and experimental total values of annual dioxin emissions were determined on the basis of these data [22]. The emission factors from the recommended by the UNEP Guidelines [16] of 2001 were selected and estimated total values of annual dioxins emissions were found in the same report on the basis of the technology analysis.

Analytical measurements of dioxin contents in the emissions, carried out in 2007, were summarized in the report [23].

Analyses of gas emissions from the cement kilns at the Vorkuta Cement Plant were not carried out in this study due to the rejection of the administration of the enterprise. At the same time studies were expanded at the Kotlas PPP as the analysis of gas emissions from 4 bark boilers and sewage analysis including from the chlorine bleaching workshop. Moreover, the analyses of gas emissions from two bark boilers and sewage waters, including from the chlorine dioxide bleaching workshop were carried out at the Syktyvkar Timber Industry Combine (Syktyvkar TIC).

The new UNEP Methodological Guidelines was issued in 2005 during this period, where some emission factors were specified. For instance, the dioxin emission factor in gas emissions of soda regeneration boilers is reduced from 0.5 through 0.07 µg I-TEQ/t of cellulose, what corresponds to both domestic [23] and foreign [2] experimental data. Thus, the emission factor that we obtained [23] is 0.037 µg I-TEQ/t of cellulose. This is more than 100 times lower than the of dioxin emission factor from the sodium regeneration boilers obtained in [22]. Apparently, there were some kinds of infringements in the mode of incineration during the sampling period any as because there were no sodium chloride and sodium pentachlorinephenolate in the incinerated raw according to the Kotlas PPP data [22].

At the same time the dioxin emission factor of incineration of bark and timber waste recommended in [16] - 0.07 µg I-TEQ/t of cellulose was found as reduced. Therefore in the 2005 edition of the Guidelines [2] this factor was amplified up to 0.2 µg I-TEQ/t. At the Kotlas PPP we obtained the emission factor 2 times higher than the recommended one in [2] - 0.4 µg I-TEQ/t of cellulose, and at the Syktyvkar TIC, vice versa, is 10 times lower.

The experimental dioxin emission factor in sewage of the chlorine bleaching unit at the Kotlas PPP as 0.57 µg I-TEQ/t of cellulose [23] was almost 8 times lower than the recommended in the Guidelines [2,16].

The experimental dioxin emission factor in the chlorine dioxide bleaching workshop' sewage (modern ECF technology) at the Syktvykar TIC was obtained as 3 times lower (0.02 µg I-TEQ/t of cellulose) than the recommended in the new UNEP Guidelines [2] - 0.06 µg I-TEQ/t of cellulose.

The ideal concurrence of dioxin emission factors into kiln gases from the cement kilns provided in the Guidelines [16] - 5 µg I-TEQ/t of cement and the one obtained experimentally - 5.2 µg I-TEQ/t of cement.
Table 11.

<table>
<thead>
<tr>
<th>Enterprises</th>
<th>Source of dioxin emissions</th>
<th>Data of dioxin content analyses</th>
<th>Experimental emission factors, µg I-TEQ/t of a product</th>
<th>The UNEP Guidelines emission factors, µg I-TEQ /t of a product</th>
<th>Dioxin emissions, mg I-TEQ/year</th>
</tr>
</thead>
<tbody>
<tr>
<td>The Kotlas Pulp-and Paper Plant</td>
<td>Kiln gases from soda regeneration boilers</td>
<td>0.83 ngI-TEQ/Nm³</td>
<td>0.0075 ng I-TEQ/Nm³</td>
<td>4.1</td>
<td>0.037</td>
</tr>
<tr>
<td></td>
<td>Kiln gases from bark boilers</td>
<td>0.41 ng I-TEQ/Nm³</td>
<td></td>
<td>0.4</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>Sewage from the chlorine bleaching unit</td>
<td>3.56 pg I-TEQ/L</td>
<td></td>
<td>0.57</td>
<td>4.5</td>
</tr>
<tr>
<td>The Vorkuta Cement Plant</td>
<td>Kiln gases from Cement kilns</td>
<td>0.55 ng I-TEQ/Nm³</td>
<td></td>
<td>5.2</td>
<td>5.0</td>
</tr>
<tr>
<td>The Syktyvkar TIC</td>
<td>Kiln gases from bark boilers</td>
<td>0.022 ng I-TEQ/Nm³</td>
<td></td>
<td>0.02</td>
<td>0.07</td>
</tr>
<tr>
<td></td>
<td>Sewage from the chlorine dioxide bleaching</td>
<td>0.80 pg I-TEQ/L</td>
<td></td>
<td>0.02</td>
<td>0.06</td>
</tr>
</tbody>
</table>
7. Study of dioxin releases from selected industrial sources of Arkhangelsk region and THE republic of Komi

Results on emission of dioxins of the enterprises located at the territory of Murmansk and Arkhangelsk regions and the Republic of Komi were obtained in the framework of the Phase 1. The obtained experimental data on dioxin emissions at the Murmansk Incineration Plant, the Vorkuta Heat and Power Station and the Vorkuta Cement Plant were well coordinated with the data provided in the UNEP Methodological Guidelines. At the same time, the experimental emission factor at the Kotlas PPP was rather higher than the recommended in the Guidelines, what is probably connected with technology of PPP wastes incineration or non-compliance with processing method. Taking into account the above as well as lack of opportunity to carry out sampling of gas emissions at the Vorkuta Cement Plant due to the prohibition by new owners of the plant, it was excluded from the list of survey objects.

Hence the present work is devoted firstly to the detailed study of dioxin emissions at the Kotlas PPP with extension of number of objects to study, and secondly to study the similar objects also at the dioxin hazard enterprise - Mondi Business Paper (MBP), located in the city of Syktyvkar, the Republic of Komi.

Data on samples

Dioxins from the enterprises, selected for the study, generally enter the environment as the releases into atmospheric air from heat energy plants for utilization of liquor, bark and timber wastes as well as sewage waters from the production. Therefore all operating bark boilers and sodoregenerating boilers (SRB) were selected to measure the dioxins in gas releases of Kotlas PPP and MBP.

Data on samples of kiln gases sampled from April 2 to 28, 2007 is provided in the Table 12.

<table>
<thead>
<tr>
<th>REGION</th>
<th>ENTERPRISE</th>
<th>FUEL</th>
<th>QCA Protocol №</th>
</tr>
</thead>
<tbody>
<tr>
<td>REPUBLIC</td>
<td>arkhangelsk</td>
<td></td>
<td></td>
</tr>
<tr>
<td>OF KOMI</td>
<td>MBP</td>
<td>Bark boiler № 1</td>
<td>14 CIPD/07</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Bark boiler № 2</td>
<td>13 CIPD/07</td>
</tr>
<tr>
<td></td>
<td>Kotlas PPP</td>
<td>Alkali liquor</td>
<td>21 CIPD/07</td>
</tr>
<tr>
<td></td>
<td>SRB №1</td>
<td></td>
<td>16 CIPD/07</td>
</tr>
<tr>
<td></td>
<td>SRB №5</td>
<td></td>
<td>18 CIPD/07</td>
</tr>
<tr>
<td></td>
<td>SRB №6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The data on sewage waters sampled from February 20 to April 21, 2007 is provided in the Table 13.

<table>
<thead>
<tr>
<th>ENTERPRISE</th>
<th>DATE OF SAMPLING</th>
<th>CHARACTERISTICS OF SEWAGE WATERS</th>
<th>QCA PROTOCOL №</th>
</tr>
</thead>
<tbody>
<tr>
<td>MBP</td>
<td>20.02.2007</td>
<td>Total water flux from bleaching unit</td>
<td>06 CIPD/07</td>
</tr>
<tr>
<td>″</td>
<td>5.04.2007</td>
<td>Total water flux from bleaching unit</td>
<td>07 CIPD/07</td>
</tr>
<tr>
<td>″</td>
<td>20.02.2007</td>
<td>Discharge chamber</td>
<td>05CIPD/07</td>
</tr>
<tr>
<td>″</td>
<td>5.04.2007</td>
<td>Discharge chamber</td>
<td>08 CIPD/07</td>
</tr>
<tr>
<td>Kotlas PPP</td>
<td>20.02.2007</td>
<td>Gravity canal (discharge to river)</td>
<td>04CIPD/07</td>
</tr>
<tr>
<td>″</td>
<td>21.04.2007</td>
<td>Gravity canal (discharge to river)</td>
<td>09 CIPD/07</td>
</tr>
<tr>
<td>″</td>
<td>20.02.2007</td>
<td>Bark flow. Flow of timber-preparation units, water from stage I of chlorination during PVC (chlorine bleaching)</td>
<td>03 CIPD/07</td>
</tr>
<tr>
<td>″</td>
<td>21.04.2007</td>
<td>Bark flow. Flow of timber-preparation units, water from stage I of chlorination during PVC (chlorine bleaching)</td>
<td>10 CIPD/07</td>
</tr>
<tr>
<td>″</td>
<td>20.02.2007</td>
<td>Bleaching and drying production of pulp, printing paper, total flow of production of sulphate bleached pulp</td>
<td>01 CIPD/07</td>
</tr>
<tr>
<td>″</td>
<td>21.04.2007</td>
<td>Bleaching and drying production of pulp, printing paper, total flow of production of sulphate bleached pulp</td>
<td>12 CIPD/07</td>
</tr>
<tr>
<td>″</td>
<td>20.02.2007</td>
<td>Flux from paperboard and paper production; sulphite-and-alcohol unit; acidulous canalization of production of viscose cellulose</td>
<td>02 CIPD/07</td>
</tr>
<tr>
<td>″</td>
<td>21.04.2007</td>
<td>Flux from paperboard and paper production; sulphite-and-alcohol unit; acidulous canalization of production of viscose cellulose</td>
<td>11 CIPD/07</td>
</tr>
</tbody>
</table>
Method of determination

Essence of method

Method and ПНД Ф 13.3.10-97, and EN 1948-1 (26) are based on collecting in a isokinetic regime of PCDD/F from gaseous releases into the atmosphere by special sampling device providing capture of PCDD/F both adsorbed on particles and in the gas phase. Collecting is providing by the filters and solid or liquid adsorbents. Before the sampling procedure an isotopic labelled $^{13}\text{C}_{12}$ PCDD/F is added to them to provide control of collecting efficiency.

After collecting the samples are transferred to the laboratory where labelled $^{13}\text{C}_{12}$ PCDD/F (other set of congeners) are added again.

Further the extraction of PCDD/F from filters and adsorbents by organic solvent is conducted. Then the extract is cleaned from accompanying compounds that hinder the determination, and is concentrated to small volume and is analyzed thru a high-efficiency capillary gas chromatography and mass spectrometry (GC/MS). The isotopic labelled $^{13}\text{C}_{12}$ PCDD/F (third set) is added before introduction of the device in injector for control of operation of GC/MS.

Identification of 2,3,7,8 PCDD/F is implemented according to retention time and correlation of areas of chromatographic peaks of identified components and isotopic labelled $^{13}\text{C}_{12}$ PCDD/F in registered ionic chromatograms.

Concentrations of PCDD/F are determined by areas of the relevant peaks by the method of internal standard.

Sampling procedure

Collecting of blank sample and the sampling train leak checked were conducted before each sampling. Leak check procedure was executed after sampling too.

In this work the "Cooled Probe Method" was applied during sampling of the flue gases in accordance with EN 1948 -1. Samples of the flue gases were sampling from straight part of the duct in isokinetic regime. Before sampling the standard solution of isotopic labelled $^{13}\text{C}_{12}$ PCDD/F was added to the condensate flask (Table 14). Total amount of solution of standards – 100 microlitre (acetone containing 4% of tridecane).

Table 14
Composition of the standard solution of isotopic labelled $^{13}\text{C}_{12}$ PCDD/F added before sampling to the condensate flask.

<table>
<thead>
<tr>
<th>Added congeners</th>
<th>Quantity, pg</th>
</tr>
</thead>
<tbody>
<tr>
<td>$^{13}\text{C}_{12}$-1,2,3,7,8-PeCDF</td>
<td>1000</td>
</tr>
<tr>
<td>$^{13}\text{C}_{12}$-1,2,3,7,8,9-HeCDF</td>
<td>1000</td>
</tr>
<tr>
<td>$^{13}\text{C}_{12}$-1,2,3,4,7,8,9- HpCDF</td>
<td>2000</td>
</tr>
</tbody>
</table>

The preliminary measurement of speed of smoke gas flow and its humidity was carried out to provide the condition of isokinetic sampling. The temperature of the collected gas was decreased below 20°C using the titan probe cooled with water. The condensate and most of
particles were caught in the condensate flask. The bubbler with organic solvent (ethylene glycol) and solid adsorbent (polyurethane foam, PUF) was used to collect the gaseous PCDD/F. The filter was placed in front of the adsorbent to increase the efficiency of aerosol particles collection. Sampling time at different objects varied from 4 to 6 hours. After the sampling all parts of sampling device were carefully packed, marked and submitted to laboratory for the analysis. The aluminium foil was used as a packing material.

New probes were used for further samplings.

**Flue gas volume calculation**

Volume of flue gas sampling using gas meter was calculated according to the following equation (24):

\[
V_{\text{meter}} = U_{\text{end}} - U_{\text{beginning}} \quad \text{equation (24),}
\]

\(V_{\text{meter}}\) – volume of sample measured
\(U_{\text{end}}\) – volume meter indication after sampling
\(U_{\text{beginning}}\) – volume meter indication before sampling

Value of the measured flue gas volume was corrected in accordance with standard conditions for temperature, pressure and initial humidity regime and oxygen content in line with equation (25):

\[
V_{n-\text{reset}} = V_{\text{meter}} \cdot \frac{T_{\text{stat}}}{T_{\text{atmos}}} \left( \frac{P_{\text{atmos}} + P_{\text{stat}} - P_{\text{H2O}}}{p_{n}} \right) \cdot \left( \frac{21 - O_{\text{measur}}}{21 - O_{\text{norm}}} \right) \quad \text{equation (25)}
\]

\(V_{n-\text{reset}}\) – measured volume in standard and reset conditions
\(T_{n}\) – standard temperature (273.15 K)
\(T_{\text{meter}}\) – temperature of sample in the gas meter
\(P_{\text{atmos}}\) – atmosphere pressure
\(P_{\text{stat}}\) – difference between static pressure in crosscut of pipe and barometer indication
\(P_{\text{H2O}}\) – water steam partial pressure
\(p_{n}\) – normal atmospheric pressure (101.325 kPa)
\(O_{\text{measur}}\) – concentration of oxygen in the chimney
\(O_{\text{norm}}\) – normative oxygen concentration (11%)

**Extraction and cleaning of samples**

- Extraction of sample.
  Isotopic labelled \(^{13}\text{C}_{12}\) 2,3,7,8 - chlorine-substituted PCDD/F were added to the condensate and the adsorbent surface (PUF) before extraction. The condensate was extracted by dichloromethane to 20 ml four times. PUF was extracted within 8 hours by toluene in the Soxhlet apparatus. Extracts were combined, dried and carefully evaporated for further cleaning.

- Cleaning of sample.
  Cleaning of samples from interfering organic compounds different in their chemical properties from PCDD/F was implemented by liquid chromatography on multilayer column. Modified silicogel was used as the filling.

  Interfering substances with small difference in polarity or structure comparing with
PCDD/F were removed using the column liquid chromatography on aluminium oxide with different activity rate.

**Identification and quantitative determination**

Cleaned extract was evaporated and $^{13}\text{C}_2\text{-1,2,3,4-TCDD}$, $^{13}\text{C}_2\text{-1,2,3,7,8,9- HxCDD}$ mixtures were added as an internal standard before the instrumental analysis. Operation of GC/MS system was tested through introducing a solvent or blank sample (blank) into the chromatograph injector, and general device sensitivity, noise, “memory” effect availability and artefacts were assessed. The analysis was implemented in two stages, as there are no capillary columns able to divide all congeners at the present time. Firstly a non-polar column DB-5 (60m x 0.32mm x 0.25μm) was applied, and then the same sample was analyzed on a polar column DB-DIOXIN (30m x 0.32mm x 0.20μm).

Analysis was implemented according to the temperature programme matched during the preliminary tests in order to provide separation of determined PCDD/F from other isomers to the best degree. Efficiency of chromatographic system separation before each series was experimentally confirmed through introducing of PCDD/F isomer standard mixture to GC/MS.

After the analysis peaks in the area of retention time corresponding to output of 2,3,7,8-displaced PCDD/F and internal standards were registered on the mass-chromatograms with the assistance of the data processing system. The ratio of areas of chromatographic peaks at mass-chromatograms of isotopic ions registered for each identified compound and internal standard and matching it with theoretical value provided in the methods was conducted. This ratio should be within the limits of ±15% of theoretical value, for example for TCDD – from 0.65 thru 0.89 (theoretical correlation is 0.77). In case there are chromatographic peaks in the indicated area of retention time but the correlation of squares of peaks is outside these limits, so positive identification through these peaks of PCDD and PCDF in this test could not be observed, and additional analysis (at the chromatographic column with other stationary phase, ionization by negative ions and with application of tandem mass spectrometry) or reanalysis after additional cleaning at the column with activated charcoal and aluminium oxide is required. Also in case if the retention time of this component coincided with the retention time of relevant isotopic labelled internal standard (differed from it for not more than 1 s/scan) or differed from the retention time measured for standard sample for not more than 0.01% and correlation of squares of peaks is within the indicated limits, this component in this sample was considered as identified.

Quantitative measurement of PCDD/F concentrations was carried out on squares of the relevant peaks according to the internal standard method in line with ПНД Φ 13.3.10-97 method.

**Equipment and materials**

In this work the equipment and materials were used in accordance with ПНД Φ 13.3.10-97 and EN 1948-1 (cooled probe method).

**Equipment**

The device provided by the Swedish party to hold the training workshop was used for sampling. Moreover, the following devices were used: gas volume meter measurements, integrated detector of temperature, flux rate, humidity, pressure and oxygen (Testo 350), inspected by Rostechregulirovanie bodies, as well as flow activator (diaphragm pump).
The Hewlett-Packard, Agilent Technology, USA, GC/MS HP 5988A and HP 5973, were used for analysis in regimes of electron impact and chemical ionization with registration of negative ions (in case of low concentrations of measured PCDD/F to increase the measurement sensitivity). Fused silica columns of 50-60 m length—with fixed non-polar phase Rtx-Rxi 5MS and polar phase DB-DIOXIN that provide the best separation degree were applied for analyses.

**Materials**

Materials recommended in EN 1948-1 were used for sampling. Materials for samples extraction and cleaning were used in accordance with ПНД Ф 13.3.10-97.

The WELLINGTON Lab. PCDD and PCDF calibration standards provided with metrological characteristics were used for calibration, identification, quantitative determination, and to provide control and quality. List of standards used during sampling and analysis of samples is provided in the Table 15.

<table>
<thead>
<tr>
<th>Name of standard sample</th>
<th>Directory №</th>
<th>Composition of standard sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard for GC/MS calibration</td>
<td>NK-ST-A</td>
<td>17 non-labelled PCDDs/PCDFs</td>
</tr>
<tr>
<td>Standard-imitator</td>
<td>EPA – 8280IS</td>
<td>$^{13}$C$_{12}$-2,3,7,8-TCDD 5 ng/µL</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^{13}$C$_{12}$-2,3,7,8-TCDF 5 ng/µL</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^{13}$C$_{12}$-1,2,3,6,7,8-HxCDD 5 ng/µL</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^{13}$C$_{12}$-1,2,3,4,6,7,8-HpCDF 10 ng/µL</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^{13}$C$_{12}$ -OCDD 10 ng/µL</td>
</tr>
<tr>
<td>Internal standard</td>
<td>EPA – 8280RS</td>
<td>$^{13}$C$_{12}$ -1,2,3,4-TCDD 5 ng/µL</td>
</tr>
<tr>
<td>Standard for sampling</td>
<td>EN 1948SS</td>
<td>$^{13}$C$_{12}$ -1,2,3,7,8-PeCDF 200 pg/µL</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^{13}$C$_{12}$ -1,2,3,7,8,9-HxCDF 200 pg/µL</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^{13}$C$_{12}$ -1,2,3,4,7,8,9-HpCDF 400 pg/µL</td>
</tr>
<tr>
<td>Standards for checking of chromatographic system efficiency</td>
<td>5TCDD</td>
<td>DB-5 test mix:</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1,2,3,4-TCDD 0.5 µg/ml</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1,2,3,7-TCDD &amp; 1,2,3,8-TCDD 0.5 µg/ml</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2,3,7,8-TCDD 1.0 µg/ml</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1,2,3,9-TCD 1.0 µg/ml</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^{13}$C$_{12}$ -1,2,3,4-TCDD 0.5 µg/ml</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^{13}$C$_{12}$-2,3,7,8-TCDD 0.5 µg/ml</td>
</tr>
<tr>
<td></td>
<td>225TCDF</td>
<td>DB-225 test mix:</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1,3,6,8-TCDF 1.0 µg/ml</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2,3,4,7-TCDF 1.0 µg/ml</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2,3,7,8-TCDF 2.0 µg/ml</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$^{13}$C$_{12}$-2,3,7,8-TCDF 0.5 µg/ml</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1,2,3,9-TCD 1.3 µg/ml</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1,2,8,9-TCD 1.2 µg/ml</td>
</tr>
</tbody>
</table>
Quality assurance and quality control (QA/QC).

Verification of experimental data obtained

The specific attention was paid to provide QA/QC during sampling of flue gases, preparation of samples for analysis and analysis of samples at GC/MS.

Providing of QA/QC during sampling

The following procedures that provide QA/QC in accordance with EN 1948-1 were implemented during sampling of gas releases:
- a new titanic probe (prepared in the laboratory) was used for each sampling;
- glassware was prepared for sampling in the laboratory according to the described in EN 1948-1 method, transporting it to the sampling site in aluminium foil;
- prepared in the laboratory adsorption module consisting of polyurethane adsorbent, fibreglass filter and additional urethane foam adsorbent was also transported to the sampling site in aluminium foil;
- during the preparation and assembling of sampling device all breaches, through which the pollution could take place, were closed until the assembling or commencement of sampling;
- pressure test took place before and after each sampling procedure;
- parameters of flue gas were checked in regular intervals to coordinate flow rate of collecting gas to provide isokinetic conditions;
- blank sample was collected before each sampling;
- to control the sampling procedure, $^{13}$C$_{12}$ labelled PCDD/F in tridecane solution was added before sampling to the flask for condensate collection.

Providing of QA/QC during preparation of samples

The following procedures providing QA/QC in accordance with ПНД Ф 13.3.10-97 were implemented during preparation of samples to analysis:
- Glassware for extraction, cleaning and concentrating of sample was prepared according to the method described in ПНД Ф 13.3.10-97 that guarantees high cleanness degree. After preparation it was stored in aluminium foil before use;
- in the laboratory before the extraction to control the procedure of sample preparation for analysis the solutions of isotopic labelled $^{13}$C$_{12}$ PCDD/F in tridecane were added to the retort for condensate collecting and to PUF;
- samples delivered to the laboratory were combined into series that passed all stages of sample preparation simultaneously. Blank samples (blank) were introduced to each series, analysis results of which (along with results of analysis of blank sampling) testified about compliance with QA/QC.

Providing of QA/QC during GC/MS analysis

The following procedures providing QA/QC in accordance with ПНД Ф 13.3.10-97 were implemented during GC/MS analysis:
- functioning of GC/MS system was checked thru introducing a solvent and/or blank sample (blank) to the injector of chromatograph; general instrument sensitivity, noise, “memory” effects and artefacts availability were assessed;
efficiency of separation of chromatographic system was confirmed thru introducing the relevant standard mixture of PCDD/F congeners (5TCDD for capillary column DB-5 and 225TCDF for column DB-DIOXIN) before each series;

criteria of ПНД Ф 13.3.10-97 were used during identification of ion chromatographic peaks. For example, correlation of isotopic ions of each referred to PCDD/F peak should be differed from the theoretical one for not more than ±15% (for TCDD – from 0.65 through 0.89 for theoretical value equal to 0.77).

Results

Complete results of studies finalized as the protocols of quantitative chemical analysis (QCA) adopted by Rostechregulirovanie are provided as the Annex. Summary results are provided in the Tables 16 and 17.

Table 16

Summary results of studies of PCDD/F content in flue gases of tested enterprises.

<table>
<thead>
<tr>
<th>REGION</th>
<th>ENTERPRISE - OBJECT</th>
<th>FUEL</th>
<th>RESULTS ng I-TEQ/Nm³, O₂ =11%</th>
</tr>
</thead>
<tbody>
<tr>
<td>ARKHANGELSK</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OBLAST</td>
<td>Kotlas PPP</td>
<td>Alkali liquor</td>
<td>0.007</td>
</tr>
<tr>
<td></td>
<td>SRB № 1</td>
<td>&quot;</td>
<td>0.008</td>
</tr>
<tr>
<td></td>
<td>SRB № 6</td>
<td>&quot;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Bark boiler №1</td>
<td>Bark, timber wastes</td>
<td>0.518</td>
</tr>
<tr>
<td></td>
<td>Bark boiler №2</td>
<td>&quot;</td>
<td>0.458</td>
</tr>
<tr>
<td></td>
<td>Bark boiler №7</td>
<td>&quot;</td>
<td>0.302</td>
</tr>
<tr>
<td></td>
<td>Bark boiler №8</td>
<td></td>
<td>0.369</td>
</tr>
<tr>
<td>REPUBLIC</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>OF KOMI</td>
<td>MBP</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Bark boiler №1</td>
<td>&quot;</td>
<td>0.020</td>
</tr>
<tr>
<td></td>
<td>Bark boiler №2</td>
<td>&quot;</td>
<td>0.024</td>
</tr>
</tbody>
</table>

Results are provided to bulk concentration of oxygen (O₂) equal to 11% and expressed in toxic equivalents corresponding to the International Equivalents System of I-TEQ. Values of used toxicity coefficients are provided in the protocols of QCA in the Annex.
Table 17
Summary results of study of PCDD/F content in sewage waters of tested enterprises.

<table>
<thead>
<tr>
<th>ENTERPRISE</th>
<th>DATE OF SAMPLING</th>
<th>CHARACTERISTICS OF SEWAGE WATERS</th>
<th>RESULTS pg I-TEQ/l</th>
</tr>
</thead>
<tbody>
<tr>
<td>MBP</td>
<td>20.02.2007</td>
<td>Total amount of water flux from bleaching unit</td>
<td>0.967</td>
</tr>
<tr>
<td></td>
<td>5.04.2007</td>
<td>Total amount of water flux from bleaching unit</td>
<td>0.637</td>
</tr>
<tr>
<td></td>
<td>20.02.2007</td>
<td>Discharge chamber</td>
<td>N.D.</td>
</tr>
<tr>
<td></td>
<td>5.04.2007</td>
<td>Discharge chamber</td>
<td>N.D.</td>
</tr>
<tr>
<td>Kotlas PPP</td>
<td>20.02.2007</td>
<td>Gravity canal (discharge to river)</td>
<td>N.D.</td>
</tr>
<tr>
<td></td>
<td>5.04.2007</td>
<td>Gravity canal (discharge to river)</td>
<td>N.D.</td>
</tr>
<tr>
<td></td>
<td>20.02.2007</td>
<td>Bark flow. Flux from timber-preparation units, water from stage I of PVC chlorination (chlorine bleaching)</td>
<td>3.62</td>
</tr>
<tr>
<td></td>
<td>5.04.2007</td>
<td>Bark flow. Flux from timber-preparation units, water from stage I of PVC chlorination (chlorine bleaching)</td>
<td>3.50</td>
</tr>
<tr>
<td></td>
<td>20.02.2007</td>
<td>Bleaching and drying production of pulp, printing papers, total flux of sulphate bleached pulp production</td>
<td>N.D.</td>
</tr>
<tr>
<td></td>
<td>5.04.2007</td>
<td>Bleaching and drying production of pulp, printing papers, total flux of sulphate bleached pulp production</td>
<td>N.D.</td>
</tr>
<tr>
<td></td>
<td>20.02.2007</td>
<td>Flux from pulp-and-paper production, sulphite-and-alcohol unit, acidulous canalization of viscose pulp production</td>
<td>N.D.</td>
</tr>
<tr>
<td></td>
<td>5.04.2007</td>
<td>Flux from pulp-and-paper production, sulphite-and-alcohol unit, acidulous canalization of viscose pulp production</td>
<td>N.D.</td>
</tr>
</tbody>
</table>

As a result of work the experimental data on PCDD/F content in releases and discharges of enterprises located at the territory of Arkhangelsk oblast and the Republic of Komi, the most significant for their potential impact on pollution of the Arctic ecosystems of the North of Russia with dioxins and furans was obtained.

Russian standard ПНД Ф 13.3.10-97 and European standard EN 1948-1 admitted for application by the Federal Agency on Technical Regulation and Metrology of the Russian Federation was used during the measurements and obtaining of experimental data.

Accordingly, the experimental data really reflecting the content of PCDD/F, which adjusts the data provided in (24), was obtained during the work implemented. Generally, the
content of PCDD/F in releases of the tested enterprises Kotlas PPP and MBP is within the limits of PCDD/F concentrations provided in (24). Protocols of quantitative and chemical analysis of PCDD and PCDF (ANNEX B).
8. The additional information concerning efficiency of proposed actions on reduction of dioxin emissions

I. The Vorkuta cement plant

The general capacity of manufacture:
One kiln - 11.2 t/h · 8000 h = 89600 t/year
Two kilns - 17 t/h · 8000 h = 136000 x 2 = 272000 t/year
Totally 361600 t/year ≈ 360000 t/year

In 2006 it was produced 110000 t of cement.
Reduction of dioxins emissions from 5.2 µg I-TEQ/t to 0.55 µg I-TEQ/t, i.e. on 4.65 µg I-TEQ/t. In case of full capacity of 360000 t/year reduction of emissions will be 1 674 000 µg I-TEQ/YEAR.

Expenses for carrying out of actions on decrease of dioxin emissions per all capacity are estimated in 13 905 000 rbl (or 375 810 Euro, 1 Euro = 37 rbl).
Specific expenses are equal 13 905 000/1 674 000 = 8.3 rbl/µg I-TEQ of dioxins (or 0.224 Euro/µg I-TEQ of dioxins).

II. The Kotlas pulp-and-paper plant

1) Gas emissions of 5 bark burning kilns contain 410000 µg I-TEQ/YEAR of dioxins. Possible reduction of dioxin emissions from 0.41 ng I-TEQ/Nm³ to 0.022 ng I-TEQ/Nm³ (according to Syktyvkar Timber Mill) will be 0.388 ng I-TEQ/Nm³ or 388000 µg I-TEQ/YEAR. The total installed cost of equipment for gas clearing emissions will be 35 700 000 rbl (or 964 865 Euro). Then specific expenses will be equal 92 rbl/µg I-TEQ of dioxins (or ~ 2.5 Euro/µg I-TEQ of dioxins).

2) The dioxin emissions from a bleaching stage by the molecular chlorine, which was estimated by quantity of the bleached cellulose 176274 t/year and the known emission factor of 4.5 µg I-TEQ/t, has reached 790000 µg I-TEQ/YEAR. The dioxin emissions from a bleaching stage by molecular chlorine has appeared considerably below 100000 µg I-TEQ/YEAR according to results of analyses of effluent sewage.

At replacement of chlorine by chlorine dioxide the emission factor will decrease to 0.06 µg I-TEQ/t and the dioxin emission will decrease up to ~ 10000 µg I-TEQ/YEAR. Then emission reduction will be equal 90000 µg I-TEQ/YEAR.

For input in action of chlorine dioxide bleaching it is roughly required up to 650 million rbl (or 17 567 567 Euro). Specific expenses will become 650 000 000/90000 ≈ 7200 rbl/µg I-TEQ of dioxins (or ~ 195 Euro/µg I-TEQ of dioxins).

3) experimentally it was found that dioxin content in emissions of soda regeneration kilns will be equal 0.0072 ng I-TEQ/Nm³, i.e. considerably below the admissible specification 0.1 ng I-TEQ/Nm³. Therefore carrying out of any actions for decrease of emissions was not planned. The dioxin emissions from five kilns were equal 60 000 µg I-TEQ on the general cellulose productivity in 2006.

Professor Yu. Treger
9. PROPOSALS concerning plants which are expedient for choosing as pilot for Phase 111 of the Project

In connection with preparation of the Project for Phase III it is necessary to solve a complex of legal, financial, economic, technical and other questions concerning the technology improvements. Thus, the enterprise choice should be principal and be of high priority. During the fulfilment of the Project for Phase III it should be developed requirements to the typical enterprises of this branch of the industry for subsequent use of the experience received within the limits of the project at the similar enterprises.

After a final choice of the enterprise it should be carried out the technical and economic calculations, prepared the business plan and the feasibility study on investments (FSI).

The sequence of actions should be the following:

- coordination of the planned actions list with the enterprise;
- preparation of initial data for feasibility study;
- coordination of business plan and FSI with local authorities;
- development of the design and budget documentations;
- equipment order and manufacturing;
- construction and assembling of installations;
- start-up and putting into operation of installations.

Conciliation procedures at all levels include contacts to local governing bodies, including environmental bodies. The account of the public opinion (or the non governmental organizations) is also a necessary element.

It is expedient for the enterprises:
- to make environment impact assessment (EIA);
- to carry out ecological audit.

Thus at the certain stage it will be necessary to train the technical personnel of the enterprise for operating on the new equipment.

Naturally, the numerous quantities of questions in this general plan concerning search of means, manufacturers of the equipment, etc. are not considered and should be formulated in details while preparing the design proposal.

By our opinion the Vorkuta cement plant and the Kotlas PPP can be offered as pilot plants on which should be realized recommendations formulated within the limits of a phase II.

Vorkuta Cement Plant

Thus it is proposed the two-stage (dry and wet) installation for dust capturing and clearing of gas emissions of three cement kilns on the Vorkuta cement plant.

First, it is expedient to carry out the installation for dust capturing and clearing of gas emissions on one of these kilns. The preliminary designs have shown, that it is possible to reduce of dioxin’s emissions from 5.2 µg I-TEQ/t to 0.55 µg I-TEQ/t, i.e. on 4.65 µg I-TEQ/t. In case of full capacity of the Vorkuta cement plan- 360000 t/year reduction of emissions will be 1 674 000 µg I-TEQ/YEAR.

Expenses for carrying out of actions on decrease of dioxin emissions per all capacity of
the Vorkuta cement plant are estimated in \textbf{13\,905\,000} rbl (or \textbf{375\,810} Euro, \textbf{1 Euro} = \textbf{37.00} rbl).

\textbf{The Kotlas PPP}

It is recommended to install of carbon absorbers before the emission of absorption gases from burning of a bark and a wood waste on the Kotlas PPP. It is expedient initially to carry out the adsorber installation on one of five so-called "bark" kilns, and then on all the subsequent. According to additional calculations the total installed cost on equipment for gas clearing emissions will be \textbf{35\,700\,000} rbl (or \textbf{964\,865} Euro).

The replacement of chlorine by chlorine dioxide will decrease the emission factor up to \textbf{0.06} µg I-TEQ/t and will decrease dioxin emissions up to \textbf{10000} µg I-TEQ/YEAR. Then emission reduction for Kotlas PPP will be equal \textbf{90000} µg I-TEQ/YEAR.

For input in action of chlorine dioxide bleaching it is roughly required up to \textbf{650} million rbl (or \textbf{17\,567\,567} Euro).

If our proposals on the Vorkuta cement plant has already coordinated with its administration, but our proposals for Kotlas PPP before their inclusion in a phase III are not coordinated with its management till to day.
Summary

In the framework of the Phase I of the Project the estimated inventory of the polychlorinated dibenzo-\(p\)-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) releases (for short “dioxins” and “furans” or just “dioxins”) from the main sources of Arkhangelsk and Murmansk oblasts and the Republic of Komi was implemented. Then analysis of gas releases for dioxins was carried out at the most significant objects. After that the experimental dioxin emission factors were found. (table 1a).

The Phase II of the Project was intended as the more thorough and detailed study of factors affecting the dioxins generation. This work was planned for implementation at the “Kotlas Pulp-and-Paper Plant” Public Corporation (Kotlas PPP) and Vorkuta Cement Plant (at the present time “Vorkutacement”).

The above enterprises are considered in this report as the objects where it is necessary to implement the activities that provide elimination or reduction of their adverse impact of the environment of the region.

In particular, the Kotlas PPP is the biggest air polluter in Arkhangelsk oblast and is the most powerful source of pollution with sewage. The Vorkuta Cement Plant in the Republic of Komi is reported as the serious air polluter, and with the dust amongst all.

Phase II of the present ACAP Project is in the common course of the joint activity of the countries of the Barents region, NEFCO and AMAP to address environmental problems of the region, and at the same time significantly to extend and deepen it with regards to pollution with persistent organic pollutants, and in particular dioxins and furans.

Collection and analysis of different technical information on two enterprises selected for the study: Vorkuta Cement Plant and Kotlas PPP was carried out at the first stage. The technologies of production used at these enterprises, raw materials used, data on contaminants releases, and products were considered above all.

Then analysis and assessment of controlled parameters of processes that can initiate generation of dioxins was carried out.

Such main factor, as the temperature of dust collector from the cement kiln impacting on the dioxins generation in the cement production.

There are several sources of dioxins at pulp and paper plants. This most important are related to pulp bleaching with chlorine gas. Another significant source of dioxin emission is the incineration of timber wastes. Incineration of used liquor – the pulping waste – generates less significant emission of dioxins.

Data on assessment of technologies applied at the enterprises, selection of the most efficient technologies and development of recommendations to reduce the dioxin releases at the Vorkuta Cement Plant and Kotlas PPP are provided here. Also the present summary provides the technical and economic assessment of arrangements related to the reduction/elimination of dioxin/furan releases at the Kotlas PPP and the Vorkuta Cement Plant.
Table 1a.
Calculation and assessment of dioxin emissions according to analytical measurements and the UNEP Guidelines of 2005.

<table>
<thead>
<tr>
<th>Enterprises</th>
<th>Source of dioxin emissions</th>
<th>Data of dioxin content analyses</th>
<th>Experimental emission factors, µg I-TEQ/t of a product</th>
<th>The UNEP Guidelines emission factors, µg I-TEQ/t of a product</th>
<th>Dioxin emissions, mg I-TEQ/year</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>The Kotlas Pulp- and Paper Plant</td>
<td>Kiln gases from soda regeneration boilers</td>
<td>0.83 ngI-TEQ/Nm³</td>
<td>0.0075 ng I-TEQ/Nm³</td>
<td>4.1</td>
<td>0.037</td>
</tr>
<tr>
<td></td>
<td>Kiln gases from bark boilers</td>
<td>0.41 ng I-TEQ/Nm³</td>
<td>0.4</td>
<td>0.2</td>
<td>410</td>
</tr>
<tr>
<td>The Vorkuta Cement Plant</td>
<td>Kiln gases from Cement kilns</td>
<td>0.55 ng I-TEQ/Nm³</td>
<td>5.2</td>
<td>5.0</td>
<td>570</td>
</tr>
</tbody>
</table>
Cement Production at the Vorkuta Cement Plant

The cement production generally consists of the following stages:
- Extraction and preparation of raw mix consisting of grinding, milling and its homogenization;
- Preparation of fuel and mineral additives, which consists in ragging and drying;
- Firming of raw mix in the cement kiln
- Treatment of kiln gas from cement dust and chilling;
- Grinding of clinker and obtained cement to the fine powder.

The cement production process at the Vorkuta Cement Plant is the following. Normal raw slam is generated through joint milling of limestone and clay slate in a raw four-chamber mill for wet milling. Mill productivity is 25-30 tons per hour. After wet milling of solid raw materials the raw mix is pumped to vertical adjusting slam-tanks. The finished raw slam is pumped to horizontal slurry tanks. There is a feeder for continuous slam loading to the furnace above the slurry tanks. Surplus of slam is dumped back to the slam tanks.

Slam hashing is performed with compressed air serially over all tanks. Slurry tanks are operating in a regime of kiln unit – three shifts round the clock.

There are 3 rotary furnaces for clinker firming at the plant:
- One furnace with $\Omega \times 3.6 \times 3.0 \times 82$ meters - productivity 11.2 ton/hour;
- Two furnaces with $\Omega \times 3.6 \times 88.6$ meters - productivity 17 ton/hour.

The complete furnace set includes a cooler, fuel incineration devices, fan and means for dust-cleaning of emitting furnace gases.

All kilns are equipped with exhausters. The obtained clinker is dumped via lift gallery on band conveyor to the clamp-shell warehouse through the aspirating shaft. De-dusting of clinker dump is carried out with bag filter.

2 cement mills operating in open cycle are installed at the plant for clinker grinding. Cement mills has 3 purification steps for de-dusting of emitting air. At the first step the reduction of dust content is provided by aspirating mines and dust-collecting chambers. Cyclones of CN type with diameter 800 mm are installed at the second step, and bag filters.

The installed and operated for 56 years equipment provides a project capacity of cement release. However it is necessary to note that the process does not meet the modern norms and approaches to systems of emitting gases purification.

**Characteristics of production:**
- Capacity: up to 450 000 tons of cement annually
- Fuel Type: coal
- Method of production: wet
- Raw materials: lime-stone (Vorkutinskoe deposit), argillaceous slate (Vorkutinskoe deposit)
- Active mineral additives: ashes of heat and power station, burnt rock (gob piles of Vorkuta mines)
- Basic equipment: 1 processing line for firming with productivity up to 11.2 tons/hour and 2 processing lines for firming with productivity up to 17 tons/hour, 3 coal and 4 raw mills, 2 cement mills of total productivity 42 tons/hour.
Generation of dioxins could take place at the stage of firming of raw mixture in the cement kiln and at the stage of purification of kiln gases from cement dust and chilling.

According to the observations the most efficient method of drastic reduction of dioxin releases at the cement plant is rapid chilling of kiln gases to the temperatures below 200°C. The critical range of temperatures is usually passed quite rapidly during the production of clinker.

Considering the lack of installations for treatment of emitting from the cement kiln gases from dust and harmful gas admixtures at the Vorkuta cement plant to levels of environmental safety, the two-stage treatment including the rapid dry (small time of contact) dust cleaning and then the wet cleaning at temperatures guaranteed to be below 200°C is suggested. In our opinion this will allow implementation of task on reduction of dioxin emissions and simultaneous improvement of the environmental characteristic of the cement production due to the drastic reduction of dust emissions.

**Dry dust cleaning** is carried out in the device with the Opposite Swirling Flows - OSF device, where the principle of inertial cleaning of gas streams from solid particles is incorporated.

OSF devices are highly effective for catching the dust from industrial dusty gases at the cement industry productions.

Productivity on dusty gas could be up to 140 thousand m³/hour.

The dusty gases temperature loaded to the device could reach 600-700°C and is limited with thermal resistance of the body material.

Operation of OSF device does not require special service and additional equipment, reliability of its operation is always provided.

The gases are inside of the OSF device for ~ 0.5 sec. Such a small time of contact at relatively high temperature reduces to a minimum the possibility of secondary synthesis of dioxins.

The fabric filters and reduction of temperature of absorbed gases to 200-300°C are reduced the dioxin emission factor to 0.6 µg TE/t of cement. Further reduction of temperature of absorbed gases to less than 200°C is decreased the emission factor to 0.05 µg TE/t of cement.

**The device for wet dust-and-gas cleaning** (DPC) provides simultaneous cleaning from dust and harmful gas admixtures to the environmentally safe levels corresponding to the requirements of domestic and international standards. Quality of cleaning is achieved through effective implementation of absorption and chemisorption processes and transfer of harmful substances to neutral solutions safe for the natural environment.

The content of installation of dust and gas cleaning includes an absorber, reservoir, the centrifugal pump, fan, metal structures, set of stopping and regulating equipment and pipe shells.

Material for the equipment included into the installation depends on aggression of the media. Installations made of both the stainless steel and the carbonaceous steel are produced.

Location of installations is possible both inside the industrial premises and outside. In a later case the external surface of the main technological equipment and gas flues is isolated.
The process of dust and gas cleaning does not require manual or automatic controls and is supplied with blocking devices only.

As at the present time the dioxin emissions are ~ 0.6 g TE per annum during production of 110 thousand tons of cement per annum, so at full production capacity of 360 thousand tons of cement per annum the dioxin emissions will be 1.9 g TE/year. It is expected that with introduction of the two-stage system (dry and wet) of dust and gas cleaning dioxin emissions will be reduced from 5.2 µg TE/t of cement (0.55 ng TE/nm³) ~ to 0.5-0.6 µg TE/t of cement (0.06 ng TE/nm³) and will step on to the following lower level according to the classification. Moreover, emissions of a huge amount of cement dust, which could be returned in production, are eliminated.

Approximately 14 million roubles (≈ US$ 560 thousand) are necessary to implement the proposed arrangements at the Vorkuta cement plant aimed at the reduction of dioxin releases to parameters set forth in the normative.

At first it is advisable to install two-stage dust and gas cleaning at one firming kiln (≈US$ 140 thousand), and then at two others.

**Pulp Production at the Kotlas Pulp and Paper Plant**

Production of paper consists in the following main stages:

- Preparation of timber raw, which includes roughing of bark, bucking and milling of timber to chips;
- Incineration of bark and timber wastes;
- Pulping to separate cellulose fibres from lignin;
- Regeneration of cooking liquor composed of sodium sulphide and sodium hydroxide in sulphate or Kraft-process (80% of global pulp production);
- Bleaching of pulp with molecular chlorine, chlorine dioxide, hypochlorite, as well as with ozone or peroxide;
- Sewage waters treatment;
- Pulp drying and manufacturing of paper.

Dioxins are generated at two high-temperature processes of incineration of:
- bark and timber wastes in bark boilers;
- black liquor in soda regeneration boilers.

Moreover, considerable generation of dioxins takes place during bleaching of pulp with molecular chlorine.

“Kotlas Pulp and Paper Plant” – KPPP (Arkhangelsk region, city of Koryazhma) – is the largest timber-chemical complex in Europe.

The share of KPPP amounts to 19% of total domestic pulp, 9% of paper and 22% of carton produced in Russia.

In 2005 volumes of pulping at the “Kotlas PPP”, which is the part of the “Ilim Pulp” corporation have exceeded 1 million tons (for 47,6 thousand tons higher than in 2004).

Introduction of a new technology of bleaching of pulp without chlorine (the total cost of the project – US$ 15 million) has moved the plant to the rank of the elite Russian pulp-and-paper manufacturers and has significantly strengthened its position at the international market.
Priority directions of environmental activity of “Ilim Pulp” are introduction of a low-waste production technology and efficiency increase of treatment facilities operation, what would allow to drastically reduce dumping and emissions of contaminants to the environment, including organochlorine compounds.

About 65% of production of the plant is exported to Europe, the Middle East and the North America.

The plant includes:
- 6 manufactures;
- 9 independent units;
- 3 power stations.

The plant occupies 600 ha.

Products of the plant include:
- sulphated bleached hardwood pulp
- viscose pulp
- pasteboard for plane layers of corrugated flute
- paper for corrugating
- offset paper for printing
- bag paper
- paper sacks
- wallpaper
- timber-chemical and biochemical processing products

Designed capacity – 938 thousand tons of cooking pulp and 255 thousand tons of pasteboard annually.

The greatest volume of production made by the plant falls on pulp. Cooking of pulp – is a complicated chemical process. During this process not only cellulose is evolved from timber, but the physical and chemical properties necessary for its further use are provided simultaneously.

In order to obtain the high quality semi-product the pulp is exposed to two major technological processes - bleaching and. The multistage schemes of bleaching are applied at the plant. The pulp is processed with oxidizers (chlorine, sodium hypochlorite, chlorine dioxide) and caustic soda. Processes of pulp bleaching are improved constantly; introduction of oxygen-alkaline processing at separate technological sites allows to reduce chlorine-containing products utilization at the plant.

The total amount of pulp bleached with chlorine is 176274 tons at the Kotlas PPP.

There are 369576 tons of pulp bleached with chlorine dioxide at the Kotlas PPP (the report of 2007).

Content of dioxins experimentally discovered during this work was less than normatively admissible 0.1 ng TE/nm$^3$ - 0.0072 ng TE/nm$^3$ at average, and accordingly the emission factor of dioxins appeared low - namely 0.06 µg TE/t of pulp.

Incineration of bark and timber wastes is one more source of dioxin emissions at the Kotlas PPP. This stage does not directly relate to the pulp production and serves for the energy production necessary for the plant.
During the incineration of the timber wastes (chips) and especially of the bark, the PCDD/PCDF emission factor is rather high in comparison with the black liquor incineration.

There are 5 so-called bark boiler-facilities in the boiler workshop at the Kotlas PPP.

The average content of dioxins in gas emissions experimentally found under this work is 0.41 ng TE/nm³ for 4 bark boilers.

The annual emission of dioxins at this stage - 0.41 g.

As a result from the point of view of the activities necessity to reduce dioxins emissions the incineration a bark and timber wastes are the first place.

With regards to the volume of dioxin emissions into the environment the second place is occupied by bleaching with molecular chlorine. At the same time if the arrangements for drastic emission reduction during bleaching are well known – replacement of chlorine with chlorine dioxide, so there might be several reasons for incineration of bark and timber wastes and a special study is required for identification of the main reason. Moreover, significant funding would be required for the replacement of main devices of wastes treatment facility.

Therefore designing of the facility for purification of gas emissions according to the required norm of 0.1 ng TE/nm³ (~ 4 times) is expedient to reduce the dioxin releases.

Recently the catalytic decomposition of dioxins is considered as an effective method. to provide this it is necessary to install a bag filter with a ceramic nozzle the “Medison” company. The cost of the filter with productivity of 5000 m³/hour is ~ 1 million roubles. However it would require installation of 120 bag filters to obtain the full capacity.

Installation of filters with activated charcoal (AC) would be a less expensive arrangement. Taking into account that dioxins are compounds with big molecular weight, their adsorption with the activated charcoal should be of high effectiveness. The content of dioxins in gas emissions are insignificant and therefore replacement of the activated charcoal will be not frequent, and the used charcoal can be incinerated with bark and timber wastes.

**Estimated total capital investments**

<table>
<thead>
<tr>
<th>Description</th>
<th>Cost</th>
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</thead>
<tbody>
<tr>
<td>Cost of equipment</td>
<td>14.2 million roubles.</td>
</tr>
<tr>
<td>Design and installation works</td>
<td>10.0 million roubles.</td>
</tr>
<tr>
<td>Total</td>
<td>24.2 million roubles.</td>
</tr>
<tr>
<td>Project implementation</td>
<td>11.5 million roubles.</td>
</tr>
<tr>
<td><strong>Grand Total</strong></td>
<td><strong>35.7 million roubles (≈ US$ 1.5 million)</strong></td>
</tr>
</tbody>
</table>

Firstly it is expedient to test the installation for purification of gas releases from dioxins with AC at the one of bark boilers which will require ≈ US$ 300 thousands.

Considerable capital investments are required for the introduction of the chlorineless pulp bleaching. At the Kotlas PPP 176274 tons of pulp are bleached with chlorine. Preliminary, 600-700 million roubles (US$ 24-28 million) might be required for the introduction of the chlorineless bleaching.

**Literature**
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26. EN 1948-1, European standard on sampling of kiln gases for measurement of PCDD/PCDF content
