International POPs Elimination Project

Fostering Active and Efficient Civil Society Participation in Preparation for Implementation of the Stockholm Convention

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Cement kilns in Belarus

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About the International POPs Elimination Project

On May 1, 2004, the International POPs Elimination Network (IPEN http://www.ipen.org) began a global NGO project called the International POPs Elimination Project (IPEP) in partnership with the United Nations Industrial Development Organization (UNIDO) and the United Nations Environment Program (UNEP). The Global Environment Facility (GEF) provided core funding for the project.

IPEP has three principal objectives:

- Encourage and enable NGOs in 40 developing and transitional countries to engage in activities that provide concrete and immediate contributions to country efforts in preparing for the implementation of the Stockholm Convention;
- Enhance the skills and knowledge of NGOs to help build their capacity as effective stakeholders in the Convention implementation process;
- Help establish regional and national NGO coordination and capacity in all regions of the world in support of longer term efforts to achieve chemical safety.

IPEP will support preparation of reports on country situation, hotspots, policy briefs, and regional activities. Three principal types of activities will be supported by IPEP: participation in the National Implementation Plan, training and awareness workshops, and public information and awareness campaigns.

For more information, please see http://www.ipen.org

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Situation with cement kilns in Belarus

Maryna Karavai

Cement Manufacturing

Process technological characteristics of clinker production

The manufacturing method and engineering procedure includes three main stages. *The initial production step* in Portland cement manufacturing is raw materials acquisition. Calcium, the element of highest concentration in Portland cement, is obtained from a variety of calcareous raw materials, including limestone, chalk, marl, sea shells, aragonite, and an impure limestone known as "natural cement rock". Other elements included in the raw mix are silicon, aluminum, and iron. These materials are obtained from ores and minerals such as sand, shale, clay, and iron ore. Again, these materials are obtained most commonly from open-pit quarries or mines, but they may be dredged or excavated from underwater deposits.

Either gypsum or natural anhydrite, both of which are forms of calcium sulfate, is introduced to the process during the finish grinding operations described below. The Portland cement manufacturing industry is relying increasingly on replacing virgin materials with waste materials or byproducts from other manufacturing operations, to the extent that such replacement can be implemented without adversely affecting plant operations, product quality or the environment. Materials that have been used include fly ash, mill scale, and metal smelting slags.

The second step in Portland cement manufacture is preparing the raw mix, or kiln feed, for the pyroprocessing operation. Raw material preparation includes a variety of blending and sizing operations that are designed to provide a feed with appropriate chemical and physical properties. The raw material processing operations differ somewhat for wet and dry processes, as described below.

Cement raw materials are received with an initial moisture content varying from 1 to more than 50 percent. If the facility uses dry process kilns, this moisture is usually reduced to less than 1 percent before or during grinding. Drying alone can be accomplished in impact dryers, drum dryers, paddle-equipped rapid dryers, air separators, or autogenous mills. However, drying can also be accomplished during grinding in ball-and-tube mills or roller mills. While thermal energy for drying can be supplied by exhaust gases from separate, direct-fired coal, oil, or gas burners, the most efficient and widely used source of heat for drying is the hot exit gases from the pyroprocessing system. Materials transport associated with dry raw milling systems can be accomplished by a variety of mechanisms, including screw conveyors, belt conveyors, drag conveyors, bucket elevators, air slide conveyors, and pneumatic conveying systems. The dry raw mix is pneumatically blended and stored in specially constructed silos until it is fed to the pyroprocessing system.

In the wet process, water is added to the raw mill during the grinding of the raw materials in ball or tube mills, thereby producing a pumpable slurry, or slip, of approximately 65 percent solids.

The slurry is agitated, blended, and stored in various kinds and sizes of cylindrical tanks or slurrybasins until it is fed to the pyroprocessing system.

The pyroprocessing system transforms the raw mix into clinkers, which are gray, glass-hard, spherically shaped nodules that range from 0.32 to 5.1 centimeters (cm) (0.125 to 2.0 inches [in.]) in diameter. The chemical reactions and physical processes that constitute the transformation are quite complex.

Five different processes are used in the Portland cement industry to accomplish the pyroprocessing step: the wet process, the dry process (long dry process), the semidry process, the dry process with a preheater, and the dry process with a preheater/precalciner.

The wet process

Conventional wet process kilns are the oldest type of rotary kilns to produce clinker. Wet kiln feed (raw slurry) typically contains 28 to 43 % of water which is added to the raw mill (slurry drums, wash mills and/or tube mills). Batch blending and homogenisation is achieved in special slurry silos or slurry basins where compressed air is introduced and the slurry is continuously stirred.

The slurry is pumped into the rotary kiln where the water has to be evaporated in the drying zone at the kiln inlet. The drying zone is designed with chains and crosses to facilitate the heat exchange between the kiln feed and the combustion gases. After having passed the drying zone, the raw material moves down the kiln to be calcined and burnt to clinker in the sintering zone.

Conventional wet kiln technology has high heat consumption and produces large volumes of combustion gases and water vapour. Wet rotary kilns may reach a total length of up to 240 m compared to short dry kilns of 55 to 65 meter length (without the preheater section).

In modern wet kiln systems, the raw slurry is fed to a slurry drier where the water is evaporated prior to the dried raw meal entering a cyclone preheater/precalciner kiln. Modern wet kiln systems have a far lower specific heat consumption compared to conventional wet kilns.

Wet process and long dry process pyroprocessing systems consist solely of the simple rotary kiln. Usually, a system of chains is provided at the feed end of the kiln in the drying or preheats zones to improve heat transfer from the hot gases to the solid materials. As the kiln rotates, the chains are raised and exposed to the hot gases. Further kiln rotation causes the hot chains to fall into the cooler materials at the bottom of the kiln, thereby transferring the heat to the load.

The fuels most commonly used in Belarus are natural gas purchased from Russian Federation, which may be supplemented by other fuels such as mazut M100 (heavy fuel oil).

The dry process

Dry raw meal is fed to a cyclone preheater or precalciner kiln or, in some cases, to a long dry kiln with internal chain preheater. For dry and semi-dry kiln systems, raw meal is prepared by drying and grinding of the raw material components in tube mills or vertical roller mills, making use of the hot kiln exhaust gases or cooler exhaust air for drying. Prior to being fed to the kiln, the raw meal is homogenised and/or blended either in batch type or in continuously operating homogenising silo systems.

In suspension preheater kilns, the raw meal is fed to the top of a series of cyclones passing down in stepwise counter-current flow with hot exhaust gases from the rotary kiln thus providing intimate contact and efficient heat exchange between solid particles and hot gas. The cyclones thereby serve as separators between solids and gas.

Prior to entering the rotary kiln, the raw meal is heated up to a temperature of approximately 810-830 °C where the calcination (i.e. the release of CO_2 from the carbonates) is already about 30 % complete. The exhaust gases leave the preheater at a temperature of 300-360 °C and are further utilised for raw material drying in the raw mill. Four-stage preheater kilns are susceptible to blockages and build-ups caused by excessive input of elements such as sulfur, chlorides or alkalis which are easily volatilised in the kiln system. This input has to be carefully controlled. Excessive input may require the installation of a system which allows part of the rotary kiln gases to bypass the preheater. Thereby part of the volatile compounds are extracted together with the gas.

A bypass system extracts a portion (typically 5-15 %) of the kiln gases from the riser pipe between the kiln and preheater. This gas has a high dust burden. It is cooled with air, volatile compounds are condensed onto the particulates and the gas then passes through a dust filter. Modern suspension preheater kilns usually have 4 cyclone stages with a maximum capacity limited to approximately 4000 ton pr day (t/d). In some cases, 2- stage cyclone preheaters or 1-stage preheaters supported by internal chain heat exchangers are still in operation.

In some cases, the raw meal is fed directly to a long dry kiln without external preheater. A system of chains in the inlet part of the rotary kiln provides the heat exchange between the hot combustion gases from the hot zone of the kiln and the kiln feed. Long dry kilns have high heat consumption and high dust cycles requiring separate dedusting cyclones.

Fuels

The main fossil fuels (“primary” fuels) in the cement industry are coal, petcoke, heavy oil, and – to a lesser extent – natural gas. Alternative “fuels” are sometimes derived from industrial waste sources such as tyres, waste oil, plastics, solvents etc. The chemical components of the ash of solid fuels combine with the raw materials and will be fully incorporated in the clinker produced. Thus, the chemical composition and levels of contamination of the ash has to be considered in the raw mix design.

Cement manufacturing in Belarus

According to statistics cement production in Belarus comes to an average of 1.47 million tons per year. According to the data of the Ministry of Statistics of the Republic of Belarus the production volume has increased by 9 percent in 2005 as compared with 2004.

Cement is manufactured by three main plants in Belarus. The cement manufacturing is carried out by three processes mainly: the wet process, the dry process (long dry process) and the semi-dry process. There are also five small cement manufacturing enterprises which operate on the occasional basis.

The most commonly used technology is the wet process: 80.6% of cement is produced with the application of the wet process. The heavy fuel consumption is a major disadvantage of the wet process.

Approximately 19.4 % of cement is produced with the application of the dry process. The average temperatures for the combustion process are: 1450ºC for the material and approximately 2000 ºC for the gas flow. The average gas flow speed is 15-30 m/sec.

The main primary goods are carbonate rocks (limestone, chalk, lime marl), clay materials (loam, adobe, loess) and ferriferous primary goods (sulfur waste, iron ore). Other ingredients (20-40%) such as industrial wastes (blast-furnace slag, fuel ashes, nepheline tailings) are also added.

Main fossil fuels (“primary” fuels) in the Belarusian cement industry conversion to standard coal % are mazut – 27.5, natural gas – 54.7, coal – 16.9, shale oil – 0.9. According to the information of the Scientific Research Institute of the Problems of Utilization of Natural Resources and Ecology of National Academy of Sciences of the Republic of Belarus the municipal waste, hazardous waste tires, waste oil, plastics, solvents are not used as substitute fuels in Belarus. But according to the chief engineer of one of the cement plants the main reason for not using waste as a fuel for cement kilns is that the system of supplying with the separated waste fractions is not developed in the republic. However, the waste, especially the household waste is rated as a potential fuel for the cement kilns together with tyres.

Besides that there testimonies that in 2000 the JSC “Krasnoselskstroymateryaly” and the Grodno interkolkhoz enterprise on cement manufacturing in the frame of joint Belarusian-Danish project on utilization of the obsolete pesticides were recommended as suitable for combustion of the cumulative obsolete pesticides. The current status of these plans is unclear but need to be subject to a full public consultation exercise if they are to be progressed further.

The possible future use of municipal, industrial and pesticide wastes as potential “fuels” for cement manufacturing causes significant concerns. It is especially important from the standpoint of the rising gas prices for Belarus.

The list of cement manufactures

Industrial union “Krichevcementshifer”

The planned production capacity is 1.2 million tons per year. The range of products includes five descriptions of goods: Portland cement with mineral addition M400, Portland blast-furnace (slag) cement (amer. type IS cement) M400, portland-pozzolan(a) cement (amer. type IP cement) M400, sand Portland cement M400, Portland cement for asbestos-cement products M400, Portland cement for asbestos-cement products M500.

The plant operates 4 rotary kilns, but since 1993 only 2 of them operate. The clinker and adding grinding is accomplished in four-pipe two-cell mills, operating on the open cycle. The enterprise uses the wet process method.

The main fuel is residual fuel oil with an average impurity content of sulfur around 1.98%.

The rotary kilns are equipped with the powder-gas treating machine, which include the cyclones of different types and electrostatic precipitators with a claimed efficiency of 89.8% according to the data of the Scientific Research Institute of the Problems of Utilization of Natural Resources and Ecology of National Academy of Sciences of the Republic of Belarus. It is assumed that this average does not include periods of electrostatic precipitator carbon monoxide 'trips' during which the filter is turned off to protect the equipment. Releases of particulates, and almost certainly also of POPs, can be extremely high during these outages which can occur at frequent intervals in some kilns. According to the maximum permissible emission volume the enterprise emits to the atmosphere approximately 18320 tonnes of polluting substances per year according to the official statistics of the Ministry of Natural Resources and Environment of Belarus for 1996.

JSC "Krasnoselskstroymateryaly"

The plant is situated in the western part of Belarus near the Krasnoselskij town in the Grodnenskaya oblast. The enterprise was put into operation in 1990.

The planned production capacity is 840 thousands tons per year. The amount of cement produced in 1996 was 389 thousands tons. The range of products includes different types of Portland cement (with additions, without additions, rapid-hardening cement - type III cement, non-contracting [nonshrinking] cement), portland-pozzolan(a) cement (amer. type IP cement) M400 and other.

The enterprise uses the wet process method. The chalk and loam are used from the local sources, pyrite drosses are imported from Cherepovec (Russian Federation) and Mariypl (Ukraine), tripoli powder from Briansk (Russian Federation), gypsum rock from Nikolaev (Ukraine), lignosulphate from Kaliningrad (Russian Federation).

The main fuel is natural gas imported from Russian Federation. The reserve fuel is mazut from the Novopolotsk or Mozyr oil-refining enterprises.

The plant operates 4 rotary kilns from 6 equipped. The clinker and adding grinding is accomplished in five-pipe two-cell mills, operating on the open cycle.

According to the maximum permissible emission volume the enterprise emits to the atmosphere approximately 9868 tons of (unspecified) pollutant substances per year. The emission to the atmosphere is realized through the 60 m long chimneys.

Industrial unitary enterprise "Belarusian Cement Plant"

The plant is situated in the eastern part of Belarus near the Kostjukovichi city in the Mogilevskaja oblast. The enterprise was put into operation in 1996. It is appointed with the equipment purchased in Russian Federation and is used for the dry production process.

Rotary kiln is appointed with the calcining oven and triple-stage cyclone trap. The planned production capacity is 9000 of cement clinker a day. The enterprise is not at full-load.

The main fuel is heavy residual fuel oil with an average impurity content of sulfur around 4% and natural gas imported from Russian Federation.

Dioxin and POPs emissions from cement production in Belarus

The assessment of emissions on the cement production enterprises is currently fulfilled only for the dust emissions by the calculated method and instrumental measurement.

Measurements of dioxin emission to air from the cement kilns have never been performed in Belarus and so the emissions of dioxins and of other POPs releases are difficult to predict.

The general releases of POPs from the production of cement are to air from the exhaust gases, i.e. the kiln, the clinker cooler and any bypass system. There may also be releases of POPs from dusts captured in the various APCDs (generally called CKD, or cement kiln dust) depending on how the CKDs are managed. Release of POPs through the product, i.e. clinker and cement is supposed to be low but this depends upon, for example, the levels of contamination of CKD and whether it is added to the product.

Sources of dioxins in cement manufacturing

The discussion of how dioxins are formed has been long and involved but with respect to cement kilns, no definitive set of mechanisms has been demonstrated to account for dioxin emissions. It is understood and generally accepted that there is a relationship between dioxin emissions and temperature. But what temperature ranges and at what location in the process is a matter of some debate.

PCDD/Fs can result from a combination of formations mechanisms depending on kiln and process design, combustions conditions, feed characteristics, and type and operation of air pollution control device (APCD) equipment. PCDD/F formation mechanisms have been studied since the late 1970s when PCDD/Fs were found in municipal waste combustor emissions. Lustenhouwer advanced three theories to explain the presence of PCDD/Fs (Lustenhouwer et al, 1980). The theories may now be described as:

1. If there are traces of PCDD/Fs in the fuel or raw materials, trace amounts can survive and be emitted; This cannot, however, explain the additional dioxin formation at different stages in the process.

2. PCDD/F formation from gas-phase precursors which are chemically similar to PCDD/Fs, such as chloroaromatics, via:

a. Homogeneous gas-gas phase reactions, or;

b. Heterogeneous gas-solid phase condensation reactions between gas phase precursors and a catalytic particle surface.

3. De novo synthesis of PCDD/Fs from carbon sources that is chemically quite different from the dioxin and furan ring structures. De novo synthesis involves heterogeneous, surface-catalyzed reactions between carbonaceous particulate and an organic or inorganic chlorine donor.

Less significant reaction pathways that have been proposed include gas phase reactions, uncatalysed surface reactions and emission of residual dioxin from contaminated feedstock.

From the above it is likely that 2(b) and 3 are the most important mechanisms for dioxin formation. Experimental evidence suggests that dioxin formation reactions occur within a temperature range of approximately 200 °C to 450 °C or wider, with maximum formation occurring near 350 °C. These critical temperatures occur where the combustion gases have cooled in flue ducts, heat exchangers, air pollution control equipment or the stack. Operating air pollution control device, for example, within this range been shown to generate high levels of dioxins and should be avoided. This is an important step which can substantially limit dioxin formation in cement kilns.

Cement kilns firing hazardous wastes are listed in the Stockholm Convention as a potential source category for the formation and release of dioxins. Even kilns not burning hazardous wastes have been linked to high dioxin releases (ENDS, 2005). The addition of extra pre-cursors through the use of waste as either fuel or as alternative raw materials increases the risk of dioxin and POPs formation by “De novo” and pre-cursor synthesis. As it is known that cement kilns can be very significant sources of dioxin - with emission concentrations of 50 ng TEQ /m^3 or higher which, together large volumes of exhaust gases, result in large mass emissions (see, for example, Chadbourne, 1997: ENDS, 2005). Consequently great care must be taken when changes are made which can increase dioxin and other POPs emissions.

Conclusions

According to statistics the cement production in Belarus come to an average of 1.47 million tons per year. Cement is manufactured by three main plants in Belarus. The cement manufacturing is carried out by three processes mainly: the wet process, the dry process (long dry process) and the semi-dry process. The main fuel is natural gas which would normally imply that there should be no large emissions of POPs.

However dioxin production in cement kilns is linked to a range of variables including type of furnace or kiln; the inputs to the kilns: the operating conditions; and the type, efficiency and operating conditions of the air pollution control devices. It is therefore not possible to be confident that emissions in Belarus will be low – particularly as no measurements of dioxin emissions to air from cement kilns have ever been performed (or, if they have, the data has not been put into the public domain).

It is strongly recommended that:

1) Measurements should be performed in order to evaluate the actual dioxin and other POPs emissions from cement kilns.
2) Before any wastes are used in cement kilns – either for fuel as alternative raw materials – there should be a full and transparent public consultation process.

Appendix 1: Background information

Chemical terminology

The dioxin family of compounds falls into two major categories, the polychlorinated dibenzo-p-dioxins (PCDD) and the polychlorinated dibenzofurans (PCDF). For purposes of discussion in this paper, these groups will be collectively referred to as dioxins. There are 75 individual PCDD compounds and 135 PCDF compounds, which are classified into groups depending on the number of chlorine atoms in the molecule. The position and the number of chlorine atoms influence the chemical and potentially harmful properties of the individual compounds. The compound 2,3,7,8-TCDD (tetrachlorodibenzo-p-dioxin) is considered to be the most harmful member of the dioxin family and those compounds which have at least four chlorine atoms substituted at the 2, 3, 7, and 8 positions are considered to have “dioxin-like” effects. Of the 210 dioxin compounds, only 17 are substituted in these positions and are considered potentially harmful to humans.

These dioxin-like compounds are found in complex mixtures. For risk assessment purposes, procedures to describe the cumulative harmful effects of these mixtures as a single result have been developed. Thus, the generally accepted method of reporting dioxin results is in terms of an international toxic equivalent quantity (I-TEQ).

Exposures and health effects

Dioxins are ubiquitous in soil, sediments and air. These compounds are the unintentional by-products of a range of natural and man-made combustion processes. The relative amounts of dioxin compounds produced depend on the type of production or combustion process and vary widely.

Dioxins are poorly soluble in water, are not very volatile and adsorb strongly to particles and surfaces. The most harmful compounds are stable in the environment and accumulate in the fatty tissues of animals and humans. Exposure to dioxin in sufficient doses is associated with a number of ailments and illnesses, such as an increased risk of severe skin lesions, altered liver function and lipid metabolism, depression of the immune system, and endocrine and nervous system abnormalities. It can also cause cancers of the liver and other organs in animals.

In 1997, the International Agency for Research on Cancer (IARC) classified the most harmful form of dioxin as carcinogenic to humans. All other forms of dioxins were classified as non-carcinogenic to humans. In normal circumstances it would be expected that more than 90% of the daily intake of dioxins results from eating food, primarily, meat, dairy products and fish.

Appendix 2:

http://www.brcirt.bas-net.by/smb/firm.php?id=7438&first=1
Industrial Union “Krichevcementshifer”

http://www.100best.ru/100bsite/show.phtml?t=352&blockid=1&rid=10&aid=7469&type=3&nom=4&rn=93&lang=
Industrial Unitary Enterprise “Belarusian Cement Plant”

http://www.ais.by/component/option,com_jbd/Itemid,238/task,detail/catid,22/navstart,0/mode,0/id,298/search,/
JSC “Krasnoselskstroymateryaly”

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