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Project on Environmentally Sound Management and Disposal of POPs Waste in China

## Technical and Managerial Requirements for POPs Waste Co-processing in Cement Kilns

(Final version)

Client: Foreign Economic Cooperation Office of Ministry of Environmental Protection

Implementation Institution: Chinese Research Academy of Environmental Sciences

June, 2011

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## 1. Overview

On November 11 of 2004, *Stockholm Convention on Persistent Organic Pollutants* (hereafter referred to as the Convention) formally entered into effect in China. According to Article 6 in the Convention, all contracting parties shall adopt necessary administrative and legislative measures to reduce or eliminate the discharge from storage and wastes. According to the Convention, all contracting parties including China must compile and implement national implementation plan for the Convention as soon as possible, adopt effective actions and measures, and perform all obligations required to eliminate, reduce and control POPs.

On April 14 of 2007, State Council approved *National Implementation Plan for the Stockholm Convention on Persistent Organic Pollutants of PRC* (hereafter referred to as National Implementation Plan). In National Implementation Plan, it preliminarily estimates that the amount of pesticide POPs wastes is about 4000~6000t, including 2600-4500t DDT wastes and 1500t HCB, chlordane and mirex wastes. In production field, pesticide POPs wastes with confirmed location and quantity is about 2228~2458t. In agricultural circulation field, the quantity of confirmed DDT is 14t; in health field, the quantity of known DDT is 11t. From 2006 to 2008, Department of Pollution Prevention and Control of Ministry of Environmental Protection organized National Persistent Organic Pollutants Survey to update the POPs wastes and it confirmed that there were over 2000t wastes in production field and 11,000t in circulation field. As shown by the survey, POPs wastes are stored in open air or by simple enclosures, which not only have polluted surrounding water bodies and soils, but threaten the health of residents nearby.

To perform the obligations of Convention and fulfill POPs waste management and disposal requirements in National Implementation Plan, Leading Group Office of Foreign Economic Cooperation Office of Ministry of Environmental Protection starts Project on *Environmentally Sound Management and Disposal of Pesticide POPs Wastes and Fly Ash Rich in Dioxin in China* together with United Nations Industrial

Development Organization (UNIDO). The Project supports the environmentally sound management and disposal of waste pesticide POPs.

After analyzing the generation and distribution characters of POPs wastes, the capacity of existing disposal facilities in China and the characters of hazardous wastes co-processing in cement kilns, it selects cement kiln co-processing as one of the main methods to disposal POPs wastes.

## 2. Compiling Objectives and Applicable Scope

To assess and select enterprises co-processing POPs wastes in cement kilns, standardize the process of cement kiln co-processing POPs wastes, prevent environmental pollution and accidents during co-processing POPs wastes, promote the management of POPs wastes and safe disposal, and on the base of existing research results and practices both at home and abroad, it compiles this Requirements after experimental study and engineering demonstration.

The Requirements put forward technical and management conditions that enterprises co-processing POPs wastes in cement kilns shall fulfill, including facility selection, equipment transformation and construction, operating and pollution control, etc. It is applicable for environment authorities to assess, screen and supervise enterprises co-processing POPs wastes in cement kilns. Besides, it can instruct cement enterprises carrying out POPs wastes sound disposal in cement kilns.

#### 3. Cited Normative Documents

Following articles are references of the Requirements and thus they also serve as part of the Requirements. For undated references, the latest edition of the normative document referred to apply in the Requirements.

Standard for Pollution Control on Hazardous Waste Storage (GB18597)

Technical Specifications for Centralized Incineration Facility Construction on Hazardous Waste (HJ/T176)

Graphical Signs for Environmental Protection -- Solid Waste Storage (Disposal) Site (GB15562.2)

General Rules for Storage of Chemical Dangerous Articles (GB15603)

Identification Standards for Hazardous Wastes - Identification for Corrosivity (GB5085.1)

Identification Standards for Hazardous Wastes - Screening Test for Acute Toxicity (GB5085.2)

 $\label{lem:condition} Identification \ Standards \ for \ Hazardous \ Wastes \ - \ Identification \ for \ Extraction \\ Toxicity \ (GB5085.3)$ 

Identification Standards for Hazardous Wastes - Identification for Ignitability (GB5085.4)

Identification Standards for Hazardous Wastes - Identification for Reactivity (GB5085.5)

Identification Standards for Hazardous Wastes - Identification for Toxic Substance Content (GB5085.6)

Identification Standards for Hazardous Wastes - General Specifications (GB 5085.7)

Technical Specifications on Identification for Hazardous Waste (HJ/T298)

Technical Specifications on Sampling and Sample Preparation from Industry Solid Waste (HJ/T20)

Regulations for Safety Management of Dangerous Chemicals (No.344, People's

Republic of China State Council Decree)

Measures for the Preventing and Control of Environmental Pollution by Obsolete Dangerous Chemicals

Common Portland Cement (GB175)

Specification and Test Procedures for Continuous Emission Monitoring Systems of Flue Gas Emitted from Stationary Sources (on Trial) (HJ/T76)

The Determination of Particulates and Sampling Methods of Gaseous Pollutants Emitted from Exhaust Gas of Stationary Source (GB/T16157)

Technical Specifications for emission monitoring of stationary source (HJ/T 397)

Guidelines for Operation Record and Report for Hazardous Waste Unit (Announcement of Ministry of Environmental Protection, No 55 of 2009)

#### 4. Terms and Definitions

The Requirements adopt some special terms, which are used in cement industry and hazardous waste management, and thus ambiguities may be aroused among cross-industry technicians and management staff. To make sure the scientificity and accuracy, the terms therein are interpreted briefly.

## (1) New dry-process rotary kiln

Rotary kiln equipped with suspension preheater and precalciner at kiln inlet.

## (2) Shaft kiln

Cement kiln with a non-rotary vertical kiln for burning clinkers.

## (3) Compound Operation

Compound operation means that the flue gas of the cement kiln is introduced into the raw mill to help drying the raw materials with the remaining heat of the flue gas and finally the flue gas from the raw mill and the kiln go through the same dust control device.

#### (4) Kiln dust

Dust collected from the flue gas of cement kiln.

## (5) Co-processing in cement kilns

Co-processing means that feeding wastes into cement kilns to achieve sound disposal for wastes base on regular cement production process.

## (6) Destruction and removal efficiency (DRE)

DRE is the percentage of a characteristic organic compound which is destructed in total feeding quantity of that characteristic organic compound. The quantity of that characteristic organic compound destructed equals to the quantity of that characteristic organic compound feeding into the kiln minus the quantity of that characteristic compound remaining in the flue gas emission. DRE should be

calculated according to this equation:

$$DRE = \frac{W_{in} - W_g}{W_{in}} \times 100\%$$

where: Win is the quantity of the total input of that characteristic organic compound in a time unit, kg/h;

Wg is the quantity of the total output of that characteristic compound in the flue gas emission in a time unit, kg/h.

## (7) Principal Organic Hazardous Constituent (POHC)

POHC means a characteristic organic constituent that is difficult to destruct and can be fed into cement kilns during testing the DRE of organic compounds in cement kilns.

## (8) Feeding Amount (FM)

FM means the feeding quantity of a certain element or component during co-processing when producing a unit quantity of clinker or cement. (Unit: mg/kg-clinker or mg/kg-clinker)

## (9) Feeding rate (FR)

FR means the feeding quantity of a certain element or component during co-processing in a time unit. (Unit: mg/h)

#### (10) Pretreatment

Pretreatment means the earlier-stage treatment of wastes prior to co-processing for complying with the requirements of co-processing in cement kilns, including drying, crushing, filtering, neutralizing, stirring, blending, reconstituting, etc.

#### (11) Hazardous waste

Hazardous wastes are the wastes which are listed in the National Catalogue of Hazardous Wastes or identified to have hazardous characteristics with the identification standards and procedures which are specified by national authorities.

## (12) POPs

Persistent organic pollutants (POPs) are organic compounds that are resistant to environmental degradation and toxic and bioaccumulative, including aldrin, chlordane, dieldrin, endrin, heptachlor, HCB, mirex, toxaphene, polychlorinated biphenyls, DDT, polychlorinated dibenzo-p-dioxins, polychlorinated dibenzofurans.

## (13) POPs waste

Refer to waste made up of POPs, or containing POPs, or polluted by POPs.

## 5. Requirements of POPs Co-processing Facilities

#### 5.1 Cement kiln

## 5.1.1 Type and capacity of cement kiln

Cement production lines that meet following requirements can be used for POPs waste co-processing

- (1) New dry-process rotary kiln
- (2) The production capacity of clinker shall be  $\geq 1000 t/day$ . It prefers the production capacity of clinker  $\geq 2000 t/day$ .

## 5.1.2 Necessary functions of cement kiln

Cement kiln co-processing POPs waste shall have following functions:

- (1) Be able to run in the compound operation mode.
- (2) Install online monitoring devices on key locations to monitor the incineration parameters in kiln, such as temperature, pressure and atmosphere, guarantee the stable operation of kiln, including: the temperature and pressure of gas at kiln outlet; temperature of kiln surface; temperature, pressure and  $O_2$  concentration of gas at kiln inlet; temperature, pressure and  $O_2$  concentration of gas at precalciner or lowest cyclone exit; temperature, pressure,  $O_2$  and CO concentration of gas at top cyclone exit.
- (3) The dust removal device shall guarantee that the dust concentration in flue gas is less than 40 mg/Nm<sup>3</sup> (the concentration converted as 11% of O<sub>2</sub> concentration under standard condition). It shall give priority to bag filter. Continuous emission monitoring system shall be equipped to monitor the concentration of dust, NOx and SO<sub>2</sub> in the flue gas. The continuous emission monitoring system shall meet the requirements of Specification and Test Procedures for Continuous Emission Monitoring Systems of Flue Gas Emitted from Stationary Sources (on Trial) (HJ/T76)

and shall be connected with local monitoring center to guarantee that the pollutant emissions meet the standard.

- (4) Be equipped with cooling device that can reduce the temperature of flue gas from  $300\text{-}400^{\circ}\text{C}$  to under  $250^{\circ}\text{C}$ .
- (5) Be equipped with kiln dust returning device that can return the dust collected by flue gas treatment devices, including dust removal devices, to raw material feeding system.

## 5.1.3 Requirements on cement kiln location

The location of cement production facilities used for POPs waste co-processing shall meet the requirements below:

- (1) The distance to residents nearby shall meet the need of environmental protection according to environment impact assessment conclusion approved by local environmental protection authorities.
- (2) The transportation route of POPs waste shall not pass environmental sensitive area, e.g. residential area, business center, school, hospital, etc.

## **5.2.** Waste feeding facility

## 5.2.1 Basic requirements

POPs waste feeding facility shall meet the basic conditions below:

- (1) The feedway and feeding mouth of POPs wastes shall be sealed, and the feeding mouth shall have the function of anti-backfire.
- (2) Install automatic metering device for the feeding rate of POPs wastes to realize quantitative feeding.
- (3) The design of POPs waste feeding facilities, such as aperture, feeding angle, boxhole, pressure, etc, shall keep the feeding smooth and prevent blocking.
  - (4) For corrosive POPs wastes, anti-corrosion materials on feeding and convey

devices shall be adopted.

#### 5.2.2 Feeding points

The feeding of POPs waste shall consider following three options (as shown in Fig.2), main burner, kiln head cover and flu gas chamber at kiln inlet. It shall select different points according to the characters of POPs wastes. The characters of POPs wastes fed from different points are shown in chapter 7 of the Requirements.

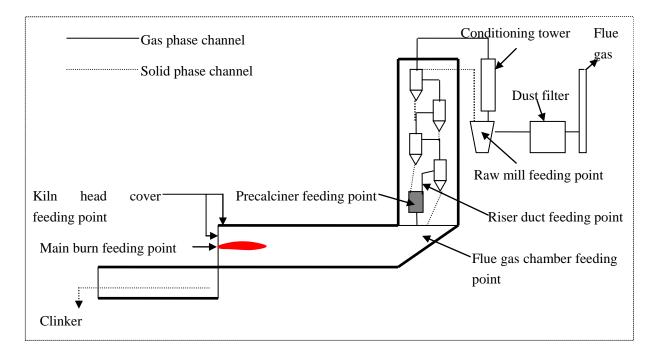


Fig. 2 Feedings points in cement kiln for POPs waste

## 5.2.3 Special requirements for feeding facilities at different points

The feeding points is different for different POPs waste, and the feeding facility at different points shall meet the requirements below:

- (1) Feeding facility at main burner shall adopt multichannel burner equipped with pump or pneumatic convey devices.
- (2) Feeding facility at kiln head cover shall be equipped with pump convey device and the feeding mouth shall be opened at proper location on the kiln head cover.
- (3) Feeding facility at flu gas chamber shall be equipped with electronic automatic or gravity dumping double-layer control door; for bulk solid waste, it shall

adopt leakproof mechanical convey device.

## **5.3.** Waste storage facility

Before POPs wastes co-processing, cement enterprise shall reduce the storage time of POPs waste as possible to reduce the storage risk. The storage or temporary storage of POPs waste in cement plan shall meet the requirements below:

- (1) In cement enterprise of co-processing POPs waste, it shall construct necessary storage facility according to the character and quantity of POPs waste. The facilities shall be constructed separately to prevent POPs waste mixing with raw materials, fuel and products.
- (2) The distance between storage facility for POPs waste and cement kiln, precalciner and preheater shall be no less than 20m.
- (3) The design, safety protection and pollution prevention of storage facility for POPs waste shall meet relevant requirements in Standard for Pollution Control on Hazardous Waste Storage (GB18597), Technical Specifications for Centralized Incineration Facility Construction on Hazardous Waste (HJ/T176) and General Rules for Storage of Chemical Dangerous Articles (GB15603).
- (4) In POPs waste storage area, there shall be distinct safety warning and evacuation route.
- (5) The storage facility for POPs waste shall meet the requirements of fire control. Inside the storage facility, there shall be distinct sign of prohibiting smoke and lighting fire, there shall be fire alarm device and extinguishing medium corresponding to the characters, storage and unloading conditions of POPs waste, the electronic devices shall be grounded and equipped with antistatic device, there shall be intact anti-explosion device.
- (6) There shall be emergent human shower facility within and near the storage area, and the usage shall be marked.

## 5.4. Waste pretreatment facility

There is need of special pretreatment facilities for POPs waste co-processing.

If POPs wastes are pretreated with mixing, stirring and blending, relevant facilities shall meet the requirements below:

- (1) POPs waste pretreatment facilities shall be good in leakproofness and separated from the operators; the pretreatment facilities for powder or volatile POPs waste shall be placed indoor, there shall be special VOC and dust discharge ducts, which can be induced to air through air filter or induced to high temperature of cement kiln.
- (2) POPs waste pretreatment facilities shall adopt proper materials according the property of POPs waste to prevent corrosion and react with the wastes.
- (3) In POPs waste pretreatment area, there shall be distinct safety warning and evacuation route.
- (4) In pretreatment area, there shall be distinct sign of prohibiting smoke and fire, fire prevention and anti-explosion unit, anti-explosion communication unit; electronic device shall be grounded and equipped with antistatic device. For mixing and stirring pretreatment cabins of inflammable POPs wastes, nitrogen filling device shall be adopted preferablly to prevent fire, explosion accidents.
- (5) The distance between POPs waste pretreatment facilities and cement kiln, precalciner and preheater shall be no less than 20m.
- (6) There shall be emergent human shower facility within and near the pretreatment area, and the usage shall be marked.

## 5.5. Waste transportation facility in plant

Cement enterprise shall reduce the transportation and transfer of POPs waste in plant as possible. For necessary POPs waste transportation, the facilities shall meet the requirements below:

- (1) POPs waste entrance and exit, transfer and transportation route shall be away from office and living facilities.
- (2) POPs waste transportation equipments shall be good in leakproofness to prevent leakage, overflow and scattering
- (3) POPs waste transportation facilities in plant shall post safety alarms on distinct place as regulated.

## 5.6. Analytical chemistry lab

Enterprises co-processing POPs wastes shall add necessary waste analytical instruments on the base of cement production analytical lab, and the analytical lab shall be able to perform following tests:

- (1) Regular cement production analysis and test;
- (2) Sample collection and preparation capacity, tools and instruments used to carry out sample analysis for POPs waste before and after entering the plant according to Technical Specifications on Sampling and Sample Preparation from Industry Solid Waste (HJ/T20).
- (3) Capacity and instruments used for compatibility test. Generally, compatibility test needs mixing device (turbine mixing device, magnetic mixing device, low speed mixing device, etc.), thermometer, viscometer, pressure gauge, pH meter, appropriate utensils, reactant gas collector, etc.
  - (4) Analysis and test of the content of Cl in POPs waste.

## 6. Requirements of POPs wastes for co-processing in cement kilns

If POPs waste meets the requirements below or meets the requirements after pretreatment, it can be co-processed in cement kilns.

## 6.1. Cl content

The content of Cl in POPs wastes shall not impact the cement production and the quality of cement quality. With no special measures, such as bypass system, the content of Cl in feeding materials (i.e. POPs waste, fuel and raw materials) shall be no more than 0.04%, that is:

$$\frac{C_w \times m_w + C_f \times m_f + C_r \times m_r}{m_w + m_f + m_r} \le 0.04\%$$

where:  $C_w$ ,  $C_f$  and  $C_r$  are the content of Cl in POPs waste, regular fuel and regular raw materials, respectively, %;

 $m_w$ ,  $m_f$  and  $m_r$  are the feeding rate of POPs waste, regular fuel and regular raw materials, respectively, kg/h.

## **6.2. Physical properties**

The physical properties (granularity, hardness, viscosity, etc) of POPs waste fed into cement kilns shall meet the technical requirements of transportation and feeding facilities.

## 7. Requirements of POPs Co-processing Operation

## 7.1. Waste pre-qualification before entering co-processing plant

## (1) Sampling and analysis

Before co-processing cement enterprise signs co-processing contract and POPs wastes transported to co-processing cement enterprise, it shall collect samples from POPs waste for co-processing and analyze its properties, and then carry out acceptance assessment based on the analytical results.

Before sampling and property analysis of POPs waste for co-processing, it shall investigate the generation of POPs waste and make analytical plan based on the investigation. After sampling, it shall test the content of Cl and all items required by safety of transportation, storage and co-processing, safety of cement production, standards of flue gas emission and quality of cement production. The properties of wastes confirmed by both parties shall be listed in contract.

Co-processing enterprise shall try to appoint professionals to collect samples at POPs waste origins, sampling frequency and method shall refer to the requirements in Technical Specifications on Sampling and Sample Preparation from Industry Solid Waste (HJ/T20) and Technical Specifications on Identification for Hazardous Waste (HJ/T298). The samples shall be representative and consider the impact of waste generation process. If the sampling and/or analysis is completed by waste generation unit, apart from the analytical results of above parameters, relevant information, such as sampling location, sample quantity, sample number and waste quantity, sampling method and working condition during sampling (regular condition, halt condition, maintenance condition, etc) shall be also provided. The sample label shall be clear and complete, the hazardous property and safe operation information of waste shall be specified, and waste generation and production process information shall be provided. The information of waste generation, sampling, sample delivery, sample analysis, etc (person-in-charge, operation procedure, etc) shall also be recorded

Generally, waste analysis parameters include:

- ① Physical property: volume weight, dimension, physical composition;
- ② Chemical property: pH, flash point;
- ③ Industrial analysis: ash content, volatile content, moisture content, fixed carbon, lower heat value;
- 4 Inorganic component analysis: content of C, H, O and N in wastes of high heat value, content of CaO, SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub> in incineration ash
- ⑤ Harmful element and substance analysis: content of Cl, S, Mg, alkali metals (K, Na) and heavy metal (Cd, Hg, Tl, etc), POPs content
  - ⑥ Property analysis (corrosion, reactivity and inflammability), compatibility.

For samples collected before entering the plant, backup samples shall be preserved and the backup samples shall be stored after confirmed by both parties for the convenience of accident and dispute investigation in future. In case the property of backup sample changes during storage, it shall be replaced and the property of backup sample shall be same with that of co-processing waste.

## (2) Acceptance assessment

After sample testing and analysis, it shall judge whether POPs wastes can enter the plant for co-processing with following steps:

- ①Confirm whether the POPs wastes to be received comply with the waste category regulated by the operating permit, and whether the POPs wastes comply with relevant state and local laws and regulations;
- ②Aimed at the potential risk to human health and environmental safety during POPs waste transportation, unloading, storage and co-processing, confirm whether the protection equipments and management measures for those risks prepared by co-processing enterprise are in place, and whether operators shall safely handling the wastes.

3Assess the potential impact of POPs waste to cement kiln flue gas emission, cement product quality and the stability of cement production, and confirm whether the existing facilities of co-processing enterprise are capable of co-processing POPs waste to be received;

4)Assess the cost and benefits of co-processing POPs waste to be received; carry out economic analysis.

Through above analysis and assessment, confirm whether POPs waste to be received can be co-processed. If the POPs wastes to be received pass acceptance assessment, co-processing cement enterprise can sign co-processing contract with waste generation unit and start the transportation.

For different batches of POPs wastes generated with same production technology by the same unit, on the premise of not changing production parameter, it can only sample and analyze the first batch and the analysis of other batches can be performed when they make co-processing plan after entering the co-processing plant.

## 7.2. Waste reception and analysis

- (1) Waste inspection when entering the plant
- 1)Inspection items

When receiving POPs waste, co-processing cement enterprise shall check the waste transfer manifest first and carry out all following inspections:

a Check whether the label of POPs waste meets the requirements; the labeled contents must comply with the hazardous waste transfer manifest the and the contract.

b Through the appearance of waste, preliminarily determine whether the wastes comply with the waste category regulated in transfer manifest and the contract.

c Examine whether the packaging of POPs waste can meet the requirements; there shall be no damage and leakage.

d Weight the POPs waste received and it shall comply with waste transfer manifest and the contract.

POPs waste can access the plant only after all above inspections are completed, and confirming the waste meets the stipulations of the transfer manifest and co-processing contracts, and all technical requirements.

## 2 Treatment procedures for waste failing to meet the requirements

After all inspections above, if the waste tobe received are different from wastes in transfer manifest or co-processing contract, or the package of waste is damaged or leaked, the waste generation unit, transportation unit and transportation chief shall be contacted immediately and carry out site investigation together. Besides, local environmental protection authority shall be informed timely.

In case the co-processing enterprise can carry out co-processing with existing conditions and can guarantee waste co-processing does not impact the production safety and environmental protection, with the approval of local environmental protection authority, co-processing can be carried out regularly after property analysis.

In case the co-processing enterprise cannot co-process those wastes, local environmental protection authority shall be informed immediately and return the wastes received to original generation unit or professional disposal unit appointed by relevant authority. Local safe production authority and public security department shall be informed if necessary.

In case it fails to identify the property of wastes, the wastes received will be regarded as unknown waste, local environmental protection authority and solid waste management responsibilities units shall be informed immediately, and if necessary, local safe production authority and public security department shall be informed if necessary. If the unknown wastes are not explosive and inflammable by confirmation, sampling and analysis with regular method can be performed, and after the waste properties are confirmed, co-processing with regular procedure and requirements can be carried out. If the unknown wastes may be explosive and inflammable or it cannot

identify whether the unknown wastes are not explosive and inflammable, the unknown wastes shall be delivered to professional units appointed by local authorities for inspection and disposal. Before the property is identified, unknown wastes shall be stored separately to prevent uncontrolled reaction with other wastes. To reduce storage risks, the storage time of unknown wastes shall be no more than one week and if it fails to identify the property within one week, unknown wastes shall be delivered to professional units appointed by local authorities for inspection and disposal.

## (2) Waste inspection after entering the plant

After POPs wastes entering the plant, specific sampling and analysis shall be performed timely to judge whether the waste properties comply with that in contract, which can provide most direct and reliable basis for co-processing plan.

Sampling, analysis procedures and requirements after entering the plant include:

- ① After entering the plant, POPs wastes shall be unloaded and stored temporarily in appointed location, and carry out sampling immediately.
- ② Sampling method shall refer to the requirements in Technical Specifications on Sampling and Sample Preparation from Industry Solid Waste (HJ/T20) and Technical Specifications on Identification for Hazardous Waste (HJ/T298), make sure that the samples collected are representative.
- ③ The analytical items after entering the plant shall adopt items similar to that before entering the plant.
- ④ Compare the analytical results with the results before entering the plant and the contents of co-processing contract, and then confirm whether the wastes can be accepted. If POPs wastes comply with the requirements, the co-processing plan shall be made based on the analytical results. If the analytical results after entering the plant do not comply with waste property in the contract, the treatment procedures in chapter 7.2 of the Requirements shall be referred to.
  - ⑤ POPs waste shall be labeled after analysis, mainly including waste number,

waste name, main harmful components, safe operation requirements, waste generation unit, incoming date, etc.

## (3) Make co-processing plan

The POPs waste co-processing plan shall be made based on the analytical results after entering the plant The plan shall cover POPs waste temporary storage, transportation and co-processing technical process and parameters, safety risk and corresponding safe operation regulations.

Attentions shall be paid to the following key points when making co-processing plan:

- ① Classify the POPs wastes according to their property; during the mixed storage or feeding of different POPs wastes, there shall be no abrupt temperature increasing, no explosion, no combustion and no harmful gas generated.
- ② During storage, transportation and incineration in kiln, POPs wastes shall no corrode or damage the contact materials.
- ③ The content of Cl in POPs waste shall meet the requirements in chapter 6 to prevent impacting cement production and cement quality.

## (4) Compatibility test

In case the problems above cannot be confirmed through regular analysis and test, compatibility test shall be carried out to identify whether the POPs wastes received can be co-processed in cement enterprise. Generally compatibility test includes following procedures:

- ① Proportionally mix the sample of POPs waste with that of the POPs waste planning to be transported, stored or co-processed together
- ② Contact or mix the sample of POPs waste with containers that is planned to be used.
  - 3 The mixing or contacting sample shall represent worst working conditions,

e.g. highest concentration of effective components, largest contact area, etc.

- ④ Identify the chemical reactions and phenomenon during mixing or contacting, such as gas, odor, precipitation, layering, dissolution, condensation, polymerization, calorification, etc.
- ⑤ Fully consider the difference of experiments and actual operation. If the waste quantity in actual operation is far more than that of the experiments, there might be more violent reaction, more gases and more heat. Thus, it shall consider the amplification effect between actual operation and experimental test results.
- © Record the chemical reactions and phenomenon in compatibility test, such as temperature increase, gas generation, pressure increase, viscosity change, precipitation and layering, odor generation, material dissolution, etc.

#### (5) Records

The inspection and testing results of POPs waste shall be recorded and put in files together with co-processing plan. The keeping time of inspection, testing results and co-processing plan shall be no less than 3 years.

Generally the recorded and backup POPs waste information include waste incoming date, details of waste generation unit, analysis before, when and after entering the plant, packaging information, transportation information, storage, co-processing plan, operation risks and safe operation requirements.. The analytical sample of POPs waste shall also be preserved and stored for future assessment and review.

#### 7.3. Waste storage

Before co-processing POPs wastes, cement enterprise shall reduce the storage time of POPs waste as possible and reduce the storage risks.

The storage or temporary storage of POPs wastes in cement plant shall meet the requirements below:

- (1) The storage operation and management shall meet the requirements in Standard for Pollution Control on Hazardous Waste Storage (GB18597) and Technical Specifications for Centralized Incineration Facility Construction on Hazardous Waste (HJ/T176).
- (2) POPs wastes shall be separated from regular raw materials, fuels and products in cement plant, and adopting the same storage facility is prohibited. Incompatible POPs wastes shall not be mixed or stored together.
- (3) POPs wastes shall be stored in cool and dry places, prohibit storing in open air and near acid wastes
- (4) In storage area of liquid POPs wastes, there shall be sufficient absorptive materials, such as sand and waste cloth, to prevent liquid POPs waste flowing outside in case of leakage. All wastes generated by clearing POPs waste leakage, including liquid from POPs waste storage area, washing solution, absorptive materials, etc shall be treated as hazardous waste, which can be incinerated in high temperature zone of cement kiln.
- (5) Staff working in POPs waste storage facilities shall be trained and start working after qualifying. The training includes categories, physical and chemical properties, toxicity of POPs wastes, accident prevention and emergency treatment measures of POPs waste leakage, fire and other accidents, POPs personal protection measures, POPs poisoning emergency treatment.

## 7.4. Waste pretreatment

The pretreatments of POPs waste before feeding into the kiln shall be reduced and simplified.

Pretreatments of POPs wastes mainly include mixing, stirring and blending to regulate the convey properties or contents of harmful substances. The unpacking, bottle opening and crushing shall be avoided. Before the mixing, stirring and blending of POPs wastes, the blending proportion shall be calculated according to the heat

value, moisture content, components (esp. concentration of harmful elements), pH and viscosity, and POPs wastes shall be mixed based on the calculated proportion. Compatibility test shall be performed for different POPs wastes to avoid chemical reaction, fire, explosion and other accidents.

The pretreatment of powder or volatile POPs wastes shall be in closed room and the negative pressure shall be maintained; waste gas containing dust or volatile organics shall be collected through special pipeline to high temperature zone of cement kiln or to the air after treated in adsorption facility and bag filter; spraying devices can be adopted to increase the humidity of working space; the concentration of volatile organics in closed space shall be below explosion limit and alarm detector for combustible gas shall be installed in operation space; to guarantee the safety of low flash point, high volatility POPs wastes during mixing, nitrogen can be filled into mixing cabin to reduce the oxygen concentration below 6%-8%.

All the residues and byproducts of pretreatment, such as POPs waste packaging, wastewater, waste active carbon from air purification facility, shall be treated as hazardous wastes and can be incinerated in high temperature zone of cement kiln.

The requirements of anti-leakage, accident treatment and personnel qualification in pretreatment zone are the same as in storage zone.

## 7.5. Waste transportation in plant

Cement enterprise shall reduce POPs waste transportation and transfer in plant as possible. If POPs waste transfer cannot be avoided, the requirements below shall be met:

- (1) When POPs wastes are transported in plant, necessary measurers to prevent POPs waste floating, scattering, overflow and leakage shall be adopted.
- (2) When POPs wastes are transported with vehicles, it shall drive along special route. Transporting incompatible POPs wastes with same vehicle is prohibited. Vehicles transporting POPs wastes shall be washed regularly and the wastewater shall

be treated as liquid POPs wastes.

- (3) All wastes generated by POPs waste convey facilities management and maintenance shall be treated as POPs waste.
- (4) Personnel loading and unloading POPs wastes shall receive necessary training and shall operate according to relevant regulations. Operating personnel shall wear corresponding articles based o the property of POPs wastes.

## 7.6. Waste feeding

## 7.6.1 Basic requirements of POPs waste feeding

During the feeding of POPs wastes, it shall make sure the stability of cement kiln system. The feeding of POPs wastes shall keep closed to prevent leakage, floating and gas evolution and to prevent air leakage into the kiln.

## 7.6.2 Selection of POPs waste feeding point

It shall select proper feeding point according to the property of POPs waste.

- (1) Feeding point of liquid POPs waste
- ① Liquid POPs waste in bulk

The best feeding point for liquid POPs waste in bulk with high heat value is main burner;

The best feeding point for liquid POPs waste in bulk with high moisture content is klin head cover.

## ② Liquid POPs waste in bottle

The best feeding point for liquid POPs waste in bottle is flue gas chamber at kiln inlet.

- (2) Feeding point of solid POPs waste
- (1) Solid POPs waste in bulk

The best feeding point for powder POPs waste in bulk is main burner;

The best feeding point for lump solid POPs waste in bulk is flu gas chamber at kiln inlet.

## ② Solid POPs waste in bottle or in bag

The best feeding point for solid POPs waste in bottle or in bag is flu gas chamber at kiln inlet.

## 7.6.3 Technical requirements of POPs waste feeding

#### (1) Main burner

- ① To prevent blocking the burn nozzle, there shall be no precipitate in the liquid wastes fed by pump
- ② Power wastes fed pneumatically shall be sprayed into the kiln from the multichannel burner. If the ash content in wastes is high, it shall spray a longer distance to reach the solid-phase reaction zone to guarantee sufficient reaction time between wastes and materials in kiln.

#### (2) Kiln head cover

Liquid wastes fed from kiln head cover shall be conveyed by pump and sprayed into the kiln.

## (3) Flue gas chamber at kiln inlet

Lump waste in bulk shall adopt closed mechanical convey and be put into the kiln through double-layer control door. POPs waste in bottle or bag fed from flue gas chamber at kiln inlet can be put into the kiln manually through double-layer control door together with the packaging.

### 7.6.4 Heat value and moisture control

For POPs wastes with high heat value (low heat value larger than 3MJ/kg), it shall consider the impact of its heat value on the heat distribution in kiln when

deciding its feeding rate. If the heat value of POPs wastes is lower than 80% (fed from kiln outlet) or 45% (fed from kiln inlet) of regular fuel, it shall reduce the mass ratio of POPs waste and regular fuel and the deviation between the mass weighted heat value of POPs waste and regular fuel and the heat value of the regular fuel shall be no more than  $\pm 20\%$  (fed from kiln outlet) or  $\pm 55\%$  (fed from kiln inlet); If the heat value of POPs wastes is higher than 120% (fed from kiln outlet) or 155% (fed from kiln inlet) of regular fuel, it shall reduce the power of fan at kiln inlet to avoid temperature and pressure fluctuation in kiln. The mass weighted heat value of POPs waste and regular fuel is calculated with following equation:

$$Q_t = \frac{Q_w \times m_w + Q_f \times m_f}{m_w + m_f}$$

where:  $Q_t$  is the mass weighted heat value of POPs waste and regular fuel, MJ/kg;

 $Q_w$  is the heat value of POPs waste, MJ/kg;

 $m_w$  is the feeding rate of POPs waste, kg/h;

 $Q_f$  is the heat value of regular fuel, MJ/kg;

 $m_f$  is the feeding rate of regular fuel, kg/h.

For POPs wastes containing higher water, it shall reduce the feeding rate to reduce the impact on temperature and pressure in kiln and to prevent the excessive increase of heat consumption. When fed from the kiln outlet, the maximum water feeding amount is 0.013kg/kg-clinker; when fed from kiln inlet, the maximum water feeding amount is 0.11kg/kg-clinker; multiply the value by the clinker output in unit time, and the maximum feeding rate of water will be obtained; the water feeding amount and feeding rate at kiln outlet or inlet can be calculated with following equation:

$$FM_{water} = \frac{C_w \times m_w + C_f \times m_f}{m_{cli}}$$

$$FR_{water} = FM_{water} \times m_{cli} = C_w \times m_w + C_f \times m_f$$

where:  $FM_{water}$  is the feeding amount of water at kiln inlet or outlet, kg/kg-clinker;

 $C_w$  is the water content of POPs wastes fed from kiln head or end, %;  $m_w$  is the feeding rate of POPs wastes fed from kiln head or end, kg/h;  $m_{cli}$  is the clinker output in unit time, kg/h

 $FR_{water}$  is the feeding rate of water, kg/h.

## 7.6.5 Determination of maximum POPs waste feeding rate

Based on the above-mentioned formulas as well as harmful substances (mainly Cl) in POPs wastes, regular raw materials and fuel, maximum allowable feeding rate of POPs wastes can be calculated respectively. In case the maximum allowable feeding rate of POPs wastes is different calculated by harmful substances, water content and heat value, it shall adopt the minimum value as maximum allowable feeding rate of POPs wastes. For POPs wastes of higher ash content (the content of CaO, SiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub> and Al<sub>2</sub>O<sub>3</sub> is larger than 40%), lime saturation factor (KH), silica rate (n) and aluminum rate (p) shall be calculated when determing its feeding rate, and make sure that the three parameters above meet the objective value of enterprise and the cement product can meet the delivery requirements. When POPs waste of higher ash content fed from the kiln inlet, it shall also consider the impact of POPs waste without preheating and precalcinating on the material incineration inside, make sure the kiln current meet the objective value of enterprise and guarantee the quality of clinkers.

## 8. Requirements of Terminal Pollution Control of POPs Waste Co-processing

## 8.1. Kiln dust discharge and bypass control

Generally, kiln dust generated by POPs waste co-processing will not be discharged but recycled with raw materials for clinker production. But to avoid the excessive accumulation of Cl in cement kiln, cement enterprises co-processing POPs wastes can discharge part of the kiln dust gathered by dust collector out of the recycling system of cement kiln, or use the bypass at bottom of preheater.

The dust discharged from recycling system of cement kiln and collected by bypass system cannot be used again in clinker production but can be added into cement mill directly. It shall strictly control the addition proportion to make sure the content of Cl, alkali and S meet the requirements in Common Portland Cement (GB175)

If discharging outside of the dust is needed, before discharging, they shall be identified according to the Identification Standards for Hazardous Wastes(GB5085-1.7). If they are identified as hazardous wastes, they shall be managed as hazardous wastes; the usual way is landfill after the pretreatment of stabilization, or recovering the resources like alkali metal chlorides in them. If they are identified as non-hazardous wastes, they shall be managed as normal solid wastes.

#### 8.2. Flue gas emission control

#### 8.2.1 Emission limit

- (1) Flue gas emitted from cement kiln co-processing POPs waste shall meet the requirements in Table 1.
  - (2) The DRE of POHC in POPs waste shall be 99.9999%.

Table 1 Emission limit for flue gas emitted from cement kiln co-processing POPs

waste				
No.	Pollutants	Emission Level Limit (1)(2)		

		(mg/Nm³)
1	Dust	40
2	SO <sub>2</sub>	200
3	NOx (calculated as NO <sub>2</sub> )	800
4	HF	1
5	HCl	10
6	TOC	10 <sup>(3)</sup>
7	Hg and its compounds(calculated as Hg)	0.05
8	Cd, Pb, As, Tl and their compounds(calculated as Cd+Pb+As+Tl)	1.0
9	Be, Cr, Sn, Sb, Cu, Mn, Ni, V, Co and	0.5
	their compounds(calculated as	
	Be+Cr+Sn+Sb+Cu+Mn+Ni+V+Co)	
10	Dioxins (ng TEQ/Nm <sup>3</sup> )	0.1 ng TEQ/Nm <sup>3</sup>

(1) The emission values of the pollutants must be calculated according to this equation (10% O2):

$$c = \frac{10}{21 - O_s} \times c_s$$

Where: c is the emission concentration of the pollutants in the flue gas calculated on standard condition and 11% of O2 concentration (mg/m3);

Os is the oxygen concentration in the flue gas (%);

cs is the emission concentration of the pollutants in the flue gas measured on standard conditions(mg/m3).

- (2) For continuous emission monitoring items (dust, SO2, NOx, HCl), the figures are 24 hourly average values; for non-continuous emission monitoring items (HF, heavy metals, dioxins), the figures are the average values over the sample period.
- (3) The limit value of TOC means the increased value of TOC when co-processing hazardous wastes compared with normal cement production.

## 8.2.2 Supervision and monitoring

- (1) Permanent sampling hole on the exhaust funnel of cement kiln shall be installed according to The Determination of Particulates and Sampling Methods of Gaseous Pollutants Emitted from Exhaust Gas of Stationary Source (GB/T 16157).
  - (2) Continuous emission monitoring system for articulate matters, NOx and SO<sub>2</sub>

in flue gas shall be adopted, the continuous emission monitoring system shall meet the requirements in Specification and Test Procedures for Continuous Emission Monitoring Systems of Flue Gas Emitted from Stationary Sources (on Trial) (HJ/T76) and shall be interconnected with local monitoring center; continuous emission monitoring system shall be approved by environmental protection authorities above county-level, and the monitoring data within effective period is effective; the 24h average value shall be adopted as the basis of continuous monitoring check.

- (3) The heavy metals (Hg, Tl, Cd, Pb, As, Be, Cr, Sn, Sb, Cu, Mn, Ni, V, and their compounds), HCl, HF and TOC in flue gas shall apply periodical monitoring. The frequency of self-monitoring of co-processing enterprise for heavy metals and HF shall be at least once each year, the frequency of self-monitoring of co-processing enterprise for HCl and TOC shall be at least four times each year; the supervisory monitoring frequency, sampling and analysis shall be based on Technical Specifications for emission monitoring of stationary source (HJ/T397).
- (4) Dioxins (PCDD/PCDF) shall apply periodical monitoring and the monitoring frequency shall be at least once each year.

## 9. Requirements of POPs Wastes Co-processing Facility Performance Test (Trial Burn)

## 9.1. Purpose of performance test

Before POPs waste co-processing, cement enterprise shall carry out performance test for co-processing facilities (exclusive temporary co-processing) and it can obtain POPs waste co-processing qualification after the testing result is qualified. The purpose of performance test is to test and assessment the pollution control level of cement kiln co-processing POPs wastes, mainly organic compound destruction capacity and pollutant emission control effect.

## 9.2. Procedures and requirements of performance test

Performance test is made up of blank test without feeding wastes and trial burn test fed with POHC.

#### (1) Blank test

The working conditions of blank test are the same as normal production, and the compound operation mode shall be applied.

The blank test shall be conducted after one-day normal operation of the cement kiln without waste feeding.

To calculate the feeding rate of Cl or the maximum allowable content of Cl in POPs waste, the content of Cl in raw materials and fuel shall be tested.

#### (2) Trial burn test

In trial burn test, the design working condition of co-processing POPs waste and compound operation mode shall be applied. POPs wastes shall be fed according to the designed maximum feeding rate of POPs wastes and the lasting time shall be no less than 24h.

In trial burn test, the POPs in POPs wastes shall be selected as POHC to test its DRE.

The feeding rate of POHC shall meet the requirements following:

$$FR_{tr} \ge DL_{tr} \times V_{g} \times 10^{-6}$$

where:  $FR_{tr}$  is the feeding rate of POHC, kg/h;

 $DL_{tr}$  is the detection limit of analytical instruments adopted in trial burn test to that POHC, ng/Nm<sup>3</sup>;

 $V_g$  is the flue gas volume generated in unit time in trial burn test, Nm<sup>3</sup>/h;

If the POPs content in waste fed fails to meet the lowest requirements of POHC feeding rate, the POHC chemicals can be added to meet the trial burn requirements. Optional of additional POHC includes sulfur hexafluoride (F6), dichlorobenzene, trichlorobenzene, tetrachlorobenzene and methyl chloride.

In trial burn test, POPs wastes containing POHC shall be fed both at kiln inlet and outlet, and test the DRE respectively. If only one of above two feeding points is selected in test, feeding POPs wastes from the point not tested in actual co-processing Is prohibited.

The sampling of flue gas shall start 4 hours after the stable feeding of POPs wastes containing POHC.

## 9.3. Judgement basis to qulifying the results of performance test

- (1) In both blank test and trial burn test, the flue gas emission shall meet the requirements in Table 1.
- (2) The DRE of POHC shall be no less than 99.9999%. DRE is calculated with POHC concentration in flue gas, flue gas volume flow in unit time and POHC feeding rate with following equation:

$$DRE_{tr} = (1 - \frac{C_{tr} \times V_g}{FR_{tr} \times 10^{12}}) \times 100\%$$

where:  $DRE_{tr}$  is the DRE of POHC, %;

 $C_{tr}$  is the concentration of POHC in flue gas, ng/Nm<sup>3</sup>;

 $V_g$  is the flue gas volume flow in unit time, Nm<sup>3</sup>/h;

FRtr is the feeding rate of POHC, kg/h.

## 9.4. Frequency of performance test

Performance test to POPs waste co-processing facilities shall be carried out periodically and the frequency shall be at least once every two years. The procedure of performance test shall be same as the first performance test.

## 10. Requirements of Personnel and System

## 10.1. Professional technical manning

- (1) 1 professional with senior title or above of cement technology, mainly specializing in cement processing equipment selection and cement processing setup.
- (2) 1 professional with middle title or above of chemical and chemical engineering, mainly specializing in hazardous chemical property and safe processing.
- (3) 3 professionals with middle title or above of environmental science and engineering, mainly specializing in treatment, disposal and management of solid waste, environment monitoring and pollution control, etc.
- (4) Special safety management personnel who must obtained relevant certificates from governmental authorities.

## 10.2. Personnel training system

Aimed at the characters of cement kiln co-processing technology, POPs waste co-processing enterprise shall establish corresponding training system and the training targets are management personnel, technical personnel and operating personnel. Different training targets shall receive different training.

The major contents of training are POPs waste management, hazardous chemical management, cement kiln co-processing technology, cement production management technology, onsite safety protection and personnel protection

## 10.3. Safety management system

- (1) Cement enterprise engaged in POPs waste co-processing shall observe relevant occupation health, safe production standards and regulations.
- (2) Cement enterprise engaged in POPs waste co-processing shall observe relevant laws and regulations on hazardous chemicals, including Regulations for Safety Management of Dangerous Chemicals and Measures for the Preventing and Control of Environmental Pollution by Obsolete Dangerous Chemicals, prevent safety accident caused by improper operation and management of POPs wastes.
- (3) Cement enterprise engaged in POPs waste co-processing shall establish corresponding management system according their characters. Aimed at the safety problems in POPs waste collection, storage, transportation and co-processing, build POPs waste co-processing safety system, fire control management system, poisonous materials management system, co-processing accident management system, etc.

## 10.4. Personnel health management system

- (1) Establish labor protection system for personnel engaged in POPs waste operation; comply with the requirements of labor safety and health, labor protection in Technical Specifications for Centralized Incineration Facility Construction on Hazardous Waste (HJ/T176).
  - (2) POPs waste co-processing enterprise shall establish periodical physical

examination system for personnel engaged in POPs waste operation; specify the frequency and contents of physical examination before, after and on post, and the physical examination shall be organized periodically.

(3) Establish health files for personnel engaged in POPs waste operation;

## 10.5. Emergency management system

- (1) POPs waste co-processing enterprise must establish emergency management system.
- (2) The emergency management system mainly include organizational system for emergency management, compiling emergency response program, emergency management training, emergency drilling, emergency logistics, emergency disposal, emergency rescue agreement, etc.

## 10.6. Operation record system

Cement enterprise co-processing POPs waste shall establish records for hazardous waste operation according to Guidelines for Operation Record and Report for Hazardous Waste Unit. Besides, it shall record the contents below:

- (1) Records for facility performance test, including: basic information of co-processing facilities, such as kiln type, capacity, type of flue gas cooling device, type of duct collector; POHC selected in performance test, the feeding rate and point; DRE of POHC in performance test, flue gas pollutant emission concentration and basic information of cement production, such as temperature of kiln inlet and outlet, oxygen concentration, raw mill operation conditions, flue gas cooling device and main dust collector working conditions.
- (2) Record of co-processing operation: apart from the regulations in Guidelines for Operation Record and Report for Hazardous Waste Unit, also includes category, quantity of POPs waste under pretreatment and co-processing each day; cleaning and sterilizing record of vehicle transporting POPs waste; operating parameters of

pretreatment facilities; harmful elements (mainly Cl) feeding rate, waste feeding rate, and feeding points, etc; record of bypass system and kiln dust disposal; production accidents and facility maintenance record.

## 11. Technical Requirements of Temporary Co-processing of POPs Waste

## 11.1 Definition and scope of temporary co-processing

Temporary co-processing of POPs waste refers to the co-processing which the amount of POPs waste is small and the time is no more than one month.

The technical requirements herein are applicable for temporary co-processing of POPs waste with co-processing time less than one month.

## 11.2 Requirements of temporary co-processing facility

- (1) The feeding rate of POPs waste can adopt manual measurement and automatic metering device is not required.
- (2) Other requirements of temporary co-processing facility of POPs waste are the same as Chapter 5 herein.

# 11.3 Requirements of performance test (trial burn) of temporary co-processing facility of POPs wastes

- (1) The performance test of temporary co-processing fatality of POPs waste may not restrict minimum feeding rate, POHC can adopt POPs contained in POPs waste and it can feed according to the designed maximum feeding rate of POPs waste and the content of POPs.
- (2) If POPs wastes to be co-processed is few and the co-processing lasts no more than 1 week, co-processing can be carried out directly without performance test.
- (3) Other requirements on performance test of temporary co-processing fatality of POPs waste are the same as in Chapter 9 herein.

## 11.4 Personnel qualification for temporary co-processing

- (1) The requirements of 3 professionals with middle title or above of environmental science and engineering can reduce to 1.
- (2) Other requirements on personnel qualification for temporary co-processing are the same as in Chapter 10 herein

## 11.5 Other requirements of temporary co-processing

Other requirements of temporary co-processing are the same as regular POPs waste co-processing and there is no special requirement, it shall refer to the technical requirements of corresponding chapters.