

DESTRUCTION OF ODS/HFC IN CEMENT KILNS

Technical Protocol

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The growing refrigeration and air conditioning sector significantly contributes to greenhouse gas emissions and substances contained in old equipment, foams, or other products not yet released into the atmosphere. ODS Banks must be comprehensively addressed to seize climate actions preventing ozone layer depletion and global warming. Thus, all outdated or end-of-life refrigerants, including foams, must be managed environmentally sound; countries must avert the accumulation of so-called ODS and HFC banks, and the international community needs to implement resilient and adaptive infrastructures to address this challenge.

UNIDO commissions this technical protocol as a partner in the GIZ initiative within the "Climate and Ozone Protection Alliance for HFC and ODS Banks Management (COPA)" framework. The protocol has been prepared by Mr. Yunrui Zhou, COPA-Project Manager, and Ms. Veronica Villacis, international consultant of UNIDO, with the support of Mary Najjuma.

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PROLOGUE

This guide has the intention to provide the National Ozone Units (NOUs) and Environmental Authorities with the principal elements and considerations for implementing a Burning Protocol for the Destruction of ODS and HFC, starting from the identification of ODS Banks coming from obsolete or damaged refrigeration and air conditioning (RAC) equipment to the refrigerant gas collection, transporting, and safe destruction in cement kilns.

The management of electric and electronic waste (Waste Electrical and Electronic Equipment, WEEE) from RAC equipment will also need the correct disposal of plastics, metals, batteries, and electronic pieces; however, those elements are not part of the scope of this protocol, but the burning protocol of ODS/HFC and its corresponding burning trail in processes of high temperature, over 1200°C. The safe destruction of ODS/HFCs considers not only effectively eliminating the ozone-depleting substances, part of the mission of the Montreal Protocol, but also avoiding damages in the kiln and preventing the generation of hazardous byproducts during the exhaust gases such as dioxins and furans (unintentional persistent organic pollutants-UPOPs), controlled under the Stockholm Convention.

Most of the countries in the world are signatories of both the Montreal Protocol and the Stockholm Convention, and the objectives of these two international instruments convey looking for the environmentally sound management of WEEE from RAC. Therefore, the objective of this protocol is to ensure the environmentally responsible handling of ODS/HFCs and UPOPs, emphasizing the urgent need for the global community to tackle ODS Banks effectively and to establish straightforward, actionable guidelines. These guidelines are also designed to encourage Cement Producers to set up the necessary facilities for the safe disposal of ODS/HFCs, tailored specifically to the unique operational demands of clinker production, including its associated infrastructure, monitoring systems, and laboratory analysis capabilities.

1. INTRODUCTION

The Montreal Protocol aims to protect the stratospheric ozone layer by regulating the production and consumption of ozone-depleting substances (ODS), such as Chlorofluorocarbons and Hydrochlorofluorocarbons (CFCs, HCFCs), which are considered hazardous substances by the local regulation of most countries and become ODS banks after electric refrigeration and air conditioning (RAC) devices are obsolete or disposed of.

Refrigerators and air conditioners play a dominant role in developed and developing countries, but the management discrepancy between countries with strong regulations and those without them is enormous. ODS banks need to face a sound regulatory framework applicable in each country, most of them referring to certified e-waste managers who have received training and have the capacity to dismantle the equipment and recover the refrigerant gases to contribute to ultimately eliminating ODS safely. Addressing certified e-waste managers could ensure best practices for tackling effects of hazardous elements of RAC appliances such as CFCs, HCFCs, HFCs, ammonia solution containing chromium-VI, blowing agents, mercury (rarely found inside household refrigerators and air conditioners, but often present behind the lamp on the top cover of chest freezers or switches of old equipment), printed circuit board components (containing lead, cadmium, hexavalent chromium), polychlorinated biphenyl (PCB) in capacitors, and polybrominated biphenyl (PBB) and polybrominated diphenyl ether (PBDE) in plastics as flame retardants. In this instance, we need to promote not only the protection of the ozone layer but also the prevention of the release of toxic substances, the strengthening of economic benefits from the resale of valuable materials, and the introduction of circular economy concepts. Therefore, the need for certified managers is imperative; they are crucial in reaching the safe destruction of ODS banks.

CFCs and HCFCs have an ozone-depleting potential but also a high or moderate level of greenhouse effect. Thus, several technologies have been outlined as suitable for destroying CFCs/HCFCs. One that seems to present more advantages because of the use of already installed high-temperature processes

and facilities is a "cement Kiln." This technology has been recognized as one of the approved technologies for destruction of ODS by the Meeting of Parties to the Montreal Protocol in 2023 (Decision XXXV/5), as recommended by the Technology and Economic Assessment Panel's Medical and Chemical Technical Options Committee (TEAP TOC).

On the other hand, HFCs have been used as replacement substances for ODS. The current global problem is that although HFCs have been used as replacement products because they do not impact the ozone layer, they have been identified as potent greenhouse gases that contribute significantly to climate change. For this reason, the member countries of the Montreal Protocol at their 28th Meeting in Kigali, Rwanda, in October 2016, adopted the Amendment of Kigali, which included HFCs in the list of substances that must be regulated and whose consumption must be reduced and contaminated/non-reclaimable HFC destroyed.

Consequently, CFCs, HCFCs, and HFCs can share a common destruction facility. A rotary clinker production cement kiln reacts in its burning zone, where the raw meal achieves temperatures of up to 1450°C [1], known as the clinkering temperature. This high temperature ensures the destruction of CFCs/HCFCs/HFCs if some specific considerations are undertaken and controlled during the process. The non-observance of technical standards for CFCs/HCFCs/HFCs destruction could generate more environmental impacts instead of preventing them.

Deviations during the CFCs/HCFCs/HFCs destruction process might also implicate high economic maintenance costs because the system recirculates dust and gas containing chlorine. In addition, avoiding dioxin formation in exhaust gases is one of the most critical concerns. For this reason, operational control in dosing, monitoring, sampling, oxygen providing, and temperature control is essential to recognize internal reactions of chlorine inside the kiln and, simultaneously, avoid dioxin formation [2] [3].

Therefore, the next section will refer to the primary considerations of chlorine technical control, evaluating the implications of environmental safety expected in cement kilns by controlling internal technical measures during the process.

2. TECHNICAL CONCEPTUALIZATION OF THE DESTRUCTION TECHNOLOGY: CEMENT KILNS

The cement kilns have many intrinsic features that make them ideal for hazardous waste treatment, such as high temperatures, long residence time, a good supply of oxygen during and after combustion, good turbulence and mixing conditions, thermal inertia, dry scrubbing of the exit gas, fixation of the traces of heavy metals in the clinker structure, and no generation of byproducts such as slag, ashes or liquid residues [2].

As can be seen in [Figure 1 \[1\]](#), cement production involves heating, calcination, and clinkering of ground and blended raw materials [3]. The first step is the preparation of raw materials, followed by pyro-processing, which covers the thermal treatment necessary to obtain the cement clinker. It involves preheating raw materials, calcination, clinker reaction, and clinker cooling [2] [1]. The preheater region of a cement kiln has a temperature gradient ranging from approximately 250 to 850°C with high particles and gas retention time in this area of about 25 seconds [2]. Besides, the main burner flame area can reach a temperature of 1450°C in clinker and about 2000°C in the gas flow [3].

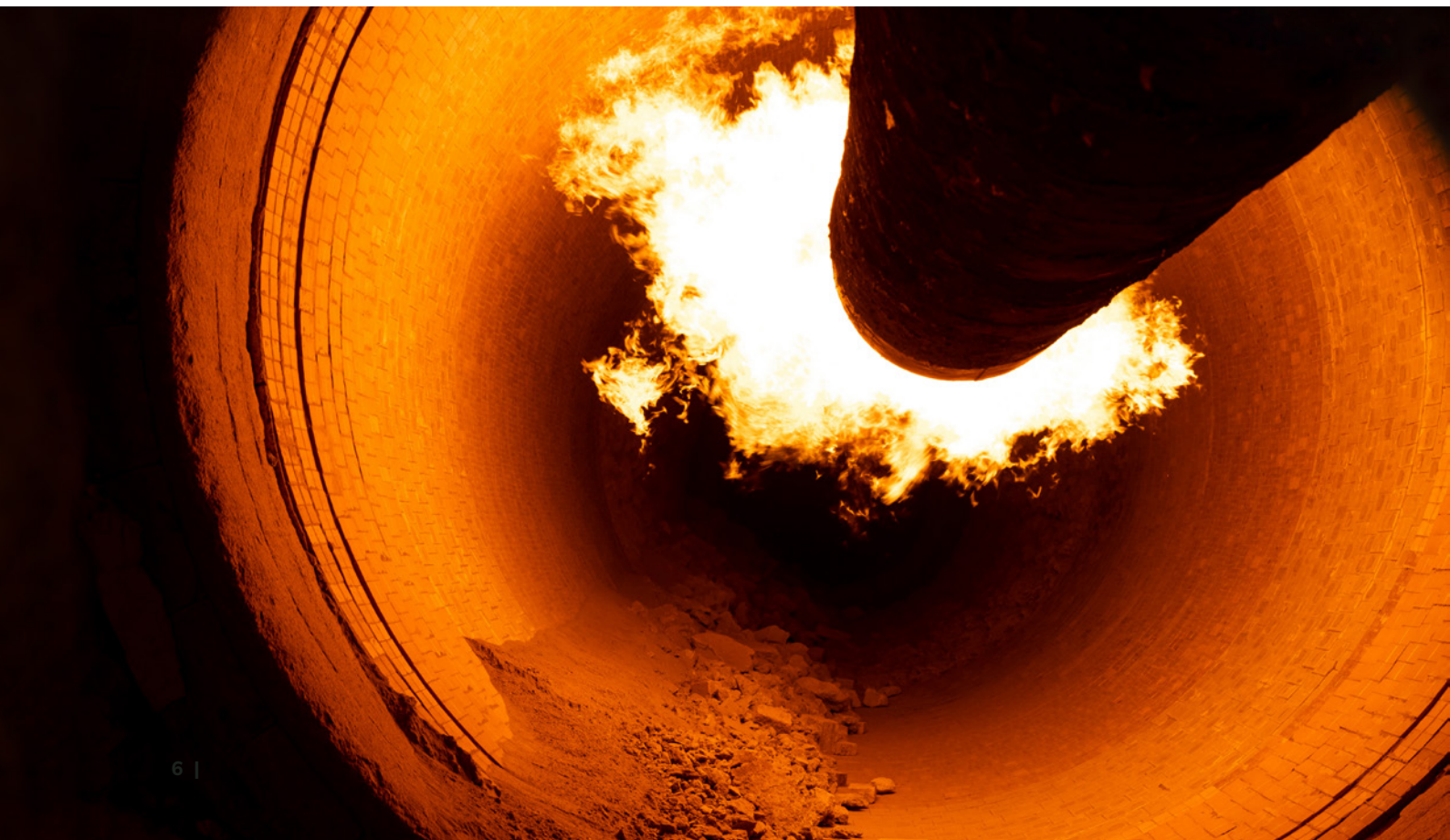
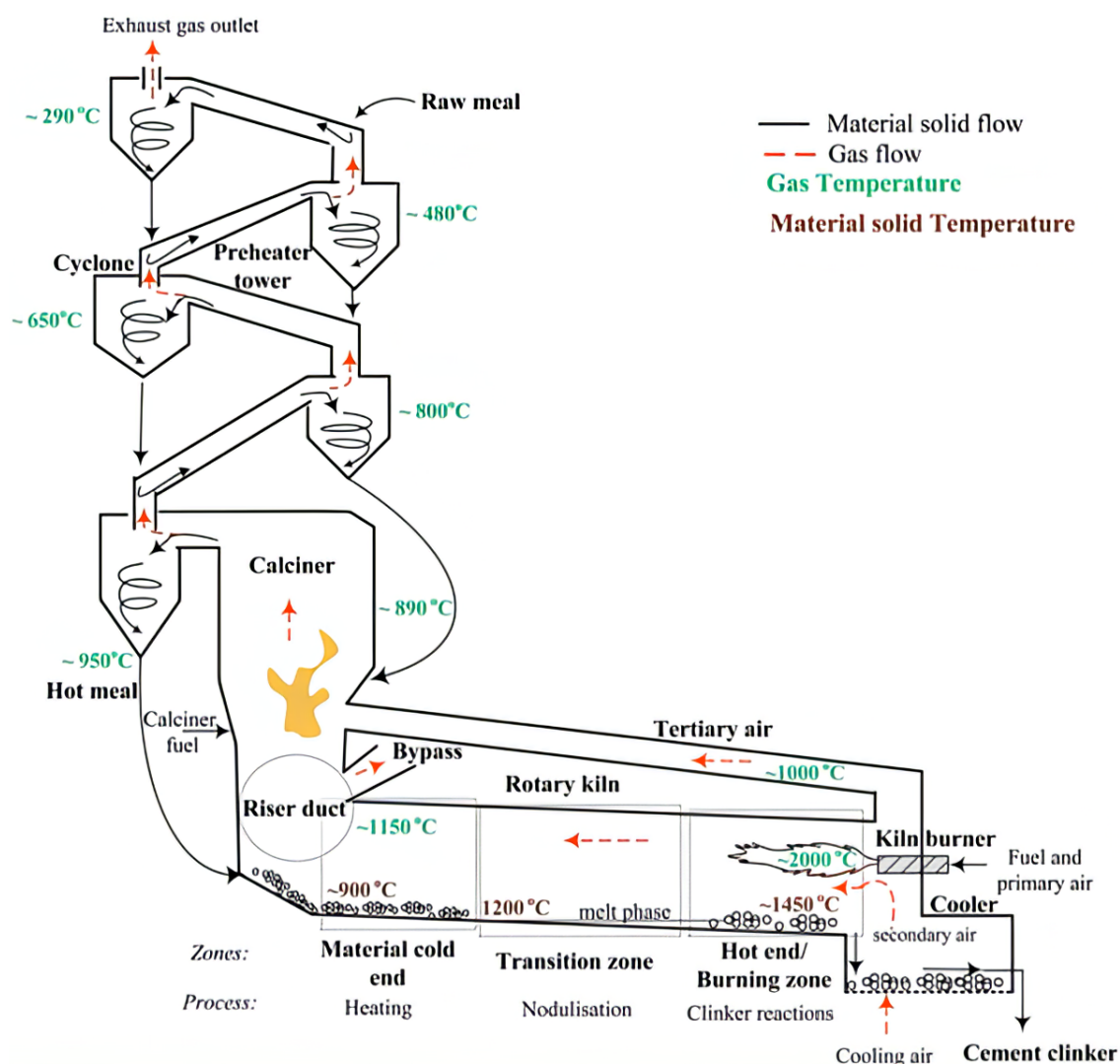


Figure 1. Chemistry of chlorinated substances inside Cement Kilns - Schematic of a typical modern kiln system and their parts, inspired by FLSmidth [1]



Avoidance of dioxin formation in the exhaust gas of the kiln is linked to two considerations: first, the chemical and physical characteristics of the CFCs/HFCs/HFCs gas considered for destruction, and second, the flow of CFCs/HFCs/HFCs being fed through the main burner to a flame of 1200°C (never during kiln start-ups, kiln shutdowns or major upsets) [4]. Some compounds normally administrated through the main burner (as fuels, raw material, or, in this case, ODS/HFCs) containing Sulphur (S), Chlorine (Cl), Sodium (Na), and Potassium (K) are

evaporated when they are exposed to high temperatures, and may subsequently condense in cooler parts of the plant. In these parts, compounds change phases from gas to liquid, liquid to solid, and solid to gas in a cyclic, almost endless pattern depending on the concentration. Condensation caused especially by recirculation of S and Cl generates difficulties in kiln operation because it forms material buildups, material rings, and, in the future, shell corrosion, affecting the process stability and operation [1].

Chlorine inside the kiln reacts primarily with alkali metals, forming potassium chloride (KCl) or sodium chloride (NaCl), typically in the gas phase. Chlorine evaporates with a factor range of 0.900-0.996 (99.6%) in the burning zone of the kiln and condenses (in a factor range of 0.004%) in the cooler parts of the system. The residual chlorine in the system forms chlorellestadite (liquid). Conversely, the contact of residual chlorine with calcium forms calcium chloride (CaCl_2) (solid/liquid), leading to the deposit of buildups and coating formation on the non-moving parts of the kiln. Therefore, buildup formation on cyclone walls, obstruction of pipes, decreased clinker output, and demand for buildup removal are consequences of high internal circulation of inorganic elements, which may reduce the kiln production, cause higher heat consumption, and generate expensive kiln/plant stops [1].

The presence of chlorine in the system can also lead to dioxin formation, which is a carcinogenic substance related to the effects from air pollution. Most of the dioxins would get destroyed in the cement kiln at temperatures over 1200 °C. Still, the exposition of chlorinated substances to different temperatures all over the cement production system may cause the formation of dioxins and the release of gas containing exceeding the legal limit in exhaust gas emissions (0.1 ng I-TEQ/m³) [2]. In other words, polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF), all known as dioxins and furans, can be unintentionally formed and released from cement kilns if CFCs/HCFs/HFCs are exposed to lower temperatures in the range of 250-400°C and mixed with the exhaust dust without a previous oxidative breakdown of macromolecular structures at 1200°C [2]. Ideally, the destruction efficiency of dioxins can be over 99.0% at over 850°C; for this reason, Cement Kiln Dust (CKD) is usually re-introduced back to the system and fed again with raw material.

Thus, a chlorine and dioxins control solution can be installing a bypass system at the gas extraction point at the kiln side of the riser duct. The bypass system involves extracting a portion of kiln exhaust gases, cooling the extracted exhaust gases, and

separating the dust [1]. At this position, the kiln gases have a low dust concentration and high gaseous concentration of Cl, which is quenched by air to initiate condensation of the chlorides and facilitate the subsequent separation of chlorides from the gas, in an electrostatic precipitator or a baghouse filter. Approximately 90% of the chlorine can be removed by extracting 5% of kiln exhaust gas, although no more than 15% of the alkali or sulfur can be removed [1]. The bypass installation requires extra expenses and increases heat and material losses, inferring higher specific heat consumption per ton of clinker of removed kiln inlet gas.

In summary, understanding the chemistry of chlorinated substances inside the kilns is a matter of critical importance. The destruction of CFCs/HCFs/HFCs in cement kilns requires not only information about the physical and chemical properties of the CFC/HCF/HFC but strict control of

- 1) appropriate flow fed through the main burner,
- 2) chemical reactions inside the kiln,
- 3) mass balance of S, Cl, F, KCl, NaCl, CaCl_2 , and chlorellestadite in the system,
- 4) temperature monitoring and
- 5) exhaust gas and dust control.

Also, the input of chlorinated substances in cement production must be controlled carefully to comply with product quality, avoid operational problems, and prevent cost increases. The installation of a gas extraction bypass system could be a good solution to prevent exhaust gas emissions containing dioxins. In consequence, controlling technical actions and chemical reactions during the destruction of existing stocks of (CFCs/HCFs/HFCs) in cement kilns will prevent the generation of environmental liabilities, preventing at the same time ozone depletion and climate change simultaneously.

As a consequence of the precedent technical statements of the technology, these guidelines will provide general recommendations for the recovery of refrigerant gases, the destruction facilities analysis, and the trial burn of CFCs/HCFs/HFCs in Cement Kilns, developed under the considerations presented below.

3. RECOVERY OF REFRIGERANT GASES

CFCs/HCFCs/HFCs have been released into the atmosphere over time through leakage and venting unless recovered and adequately treated. While the Montreal Protocol does not control emissions from ODS banks, many countries have voluntary or regulatory requirements to reduce emissions of ODS at the end of the RAC equipment's useful life. Thus, reclaim or destruction is crucial after equipment containing ODS is recovered and collected. Nonetheless, there are other problems related to the absence of a proper policy framework for ODS/HFC banks. Obtaining permits/ licenses to operate and handle these hazardous substances is often a challenge because in many countries ODS/HFC reclamation is not a regulated activity, or a very new task for the authority. Instead, these reclamation projects are completely new activities in some countries, causing delays in the response of environmental authorities and in the acquisition of permits and authorizations [20].

Since ODS are widely replaced by HFCs with high GWP, ODS banks are projected to decline over time, but the HFC banks will increase, demanding the safe destruction not only of ODS but also of HFC that could not be reclaimed. ODS and HFCs should be recovered from equipment by a properly trained technician using appropriate equipment to minimize refrigerant loss during evacuation. In some countries, the recovery equipment used for evacuating small appliances must also be certified.

Once obsolete RAC equipment is collected, it is important to consider that refrigerator heat exchangers should be oriented in the same direction and appliances should be upright, not resting on their cooling coils during transport. Refrigerators and air conditioners should be handled carefully when loading or unloading vehicles to avoid being dropped which can lead to damage and leakages. When the devices arrive at the WEEE management companies or certified technicians for dismantling, the devices should preferably be sorted according to the type of refrigerant contained, which will facilitate subsequent processing, especially in countries where refrigerant

reclaim is available. Also, tracking the type of refrigerant will be a high-value datum, not only for promoting the reclaiming process but also for dosing the refrigerant in systems of high-temperature destruction and when assessing the CO₂e emissions avoided by the destruction of each type of refrigerant due to their indistinct value of global warming potential.

Many guidelines are available for disassembling refrigerators and air conditioners; hence, the following detail summarizes the main elements and considerations applicable to best practices on RAC equipment.

Main equipment, tools, and materials:

- Refrigerant gas recovery machine and puncture elements, hoses, valves, and pressure gauges
- Weighing scale
- Gas identifier
- Recovery cylinders
- Personal protection equipment

Technicians involved:

- Refrigeration and air conditioning technician with knowledge of gas recovery.
 - Basic technician knowledge, i.e., connecting and disconnecting hoses and valves to and from the recovery machine pressure measuring equipment.
 - Add or remove refrigerant.
- Mechanical vapor compression, open-drive compressors, operation of refrigeration and air conditioning systems.
- Identification of refrigerant gases.
- Parallel processes:
- Storage and management of recovered gases and transportation of cylinders to qualified managers (as appropriate upon each country's legislation).

Measures in the process:

- Gas identification.
- Installation of gas recovery machine elements and connections.
- Cylinder vacuum requirement assurance.
- The recovery equipment must recover 90% of the refrigerant when the compressor is operating and 80% when the compressor is not operating.
- To avoid losses, the residual refrigerant ("heel") of the cylinder being emptied should be pumped out and all hoses should be fully evacuated following transfer.
- Use personal protective equipment such as glasses with side shields, gloves, safety shoes, and helmets.
- Use of piercing pliers for gas identification and recovery connection. Opening stopcocks, purges, pressure control, and weight control of extracted gas.
- All hoses must have closure devices located within 30 cm of the connection point and the system in service to minimize the introduction of non-condensable gases into the recovery equipment during connection and the release of refrigerant during disconnection [6].
- The equipment must separate the lubricant from the recovered refrigerant and accurately indicate the amount of refrigerant removed from the system during the processing of 30 ml units [6].
- The refrigerant should be pumped out, and all hoses should be fully evacuated following transfer to avoid losses of the residual refrigerant from emptying the cylinder.
- Transfer equipment should be well maintained, and dry-break coupling should be used for hose connections.

Specific requirements

- Refrigerant Gas Identifier Calibration Certificate
- Scale Calibration Certificate
- Certification of operating technicians
- Certification of Holders of gas recovery and recycling equipment
- Labeling for refillable and non-refillable cylinders.

Particular Regulations/Guidelines or certifications for review:

- Recovery and recycling equipment for use in small applications must be tested under EPA Appendix C or under requirements based upon the ARI 740 test protocol (i.e., Appendices B and B1 to 40 CFR 82 subpart F).
- National RAC technicians' certifications (as applicable in each country's legislation) -reference: EPA Approved Certification Organization - Section 608 of the Clean Air Act technicians.
- AHRI GUIDELINE Q 2010 Edition, January 1, 2010. Recovery & Proper Recycling of Refrigerant Cylinders. Published By: Air-Conditioning, Heating and Refrigeration Institute (AHRI)
- AHRI GUIDELINE Q 2016. Guideline for Content Recovery & Proper Recycling of Refrigerant Cylinders. Published By: Air-Conditioning, Heating and Refrigeration Institute (AHRI)
- Deutsche Gesellschaft für Internationale Zusammenarbeit (GIZ) GmbH, Management and Destruction of Existing Ozone Depleting Substances Banks- Guideline on the Manual Dismantling of Refrigerators and Air Conditioners.

4. STORAGE AND TRANSPORTATION OF RECOVERED GASES

Pressure vessels and ISO tanks should be used instead of cylinders, when possible, to avoid shipping many smaller containers of ODS, which leads to inventory and recordkeeping complications, damage or loss during shipment, and additional transport expenses. Thus, ODS recovered from appliances are often transferred to recovery cylinders of about 14 to 22 liters (L) (about 14 to 23 kilograms (kg)). ODS recovered from bulk and industrial stocks, recovered in larger quantities, are generally stored in large containers, such as pressure vessels ranging in size

from 950 to 1,890 L (holding between 1,000 and 2,000 kg of refrigerant). It is estimated that 1 to 3 percent of the gas is typically lost during transfer from small cylinders to bulk storage [15].

Temporary storage should be kept to a minimum, and all cylinders should be stored in a safe indoor area with leak monitoring procedures, using installed automated leak detection equipment or manual leak monitoring procedures.

Materials/Equipment

- Weighing scale
- Gas identifier
- Personal protection equipment
- ODS recovery cylinders

Parallel processes

- Certification of adequate recovery and conditions for final disposal

Measures in the process

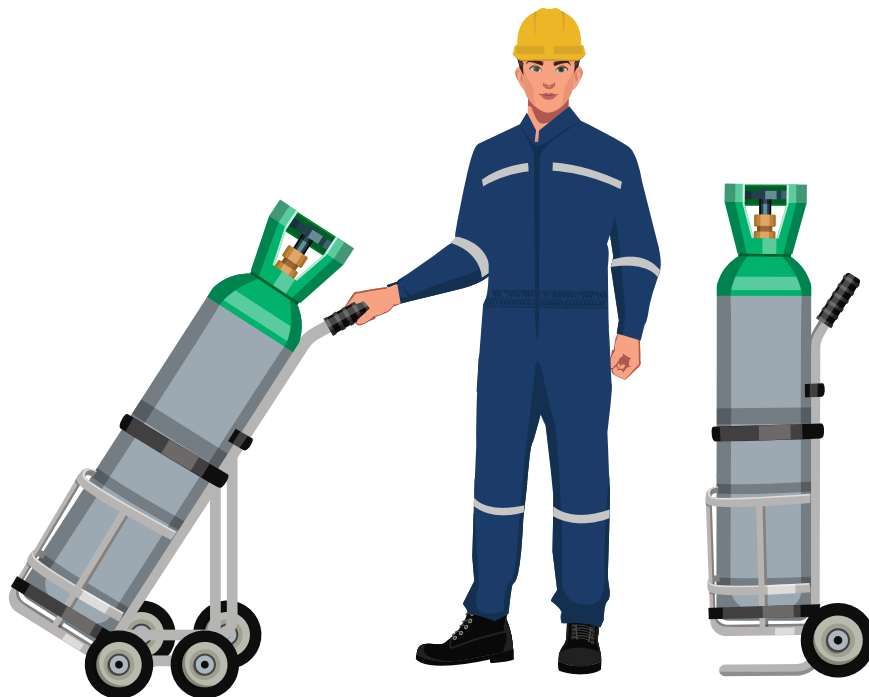
- Use personal protective equipment such as glasses with side shields, gloves, safety shoes, and helmets when lifting and handling cylinders.
- Avoid and prevent contact of coolant with skin.
- Be aware that inhalation of high concentrations of refrigerant gas vapor can be harmful and cause cardiac irregularities, unconsciousness, or death. Therefore, these processes should not be carried out in low areas without ventilation.
- Heat of fire can build pressure in the cylinder and cause it to rupture. No part of a cylinder should be subjected to a temperature higher than 52°C (125°F).
- Use only cylinders designed and marked for refrigerant recovery service. Do not reuse cylinders used for virgin refrigerant services.
- Ensure the cylinder is charged only with the refrigerant for which it is designed.
- Do not mix different refrigerant gases in the same cylinder unless destruction has been selected as the final disposal option.

Specific requirements

- Identify the gas you are handling and its possible reactions.
- Evaluate gas properties such as molecular weight, gas phase, liquid phase, solid phase, melting point, latent heat of fusion/vaporization, density, boiling point, critical point of temperature, pressure, and density, triple point of temperature and pressure, compressibility factor, heat capacity at constant pressure and constant volume, viscosity, and thermal conductivity.
- Most of the Fact Data Sheets of ODS describe higher risks, such as significant danger if ODS decomposes when heated, releasing toxicity, potential flammability, regularly slightly ethereal smell, and other risks depending on the substance.
- Labeling cylinders, the safety identification must be located in a visible place.
- The cylinder valve must meet the standards for cylinder valves.
- The pressure relief device must meet the appropriate standard.
- The cylinder test date must be marked, which preferably must not be more than five years from the date of manufacture of the cylinder.

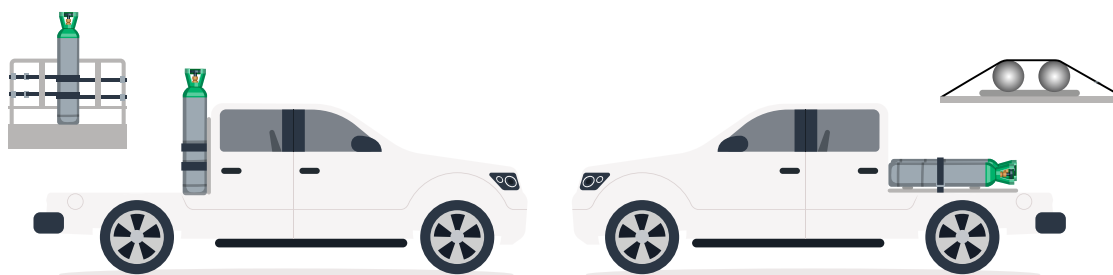
- Cylinders should be stored in an upright position; if cylinders have been placed lying down, at least place the cylinder upright and wait 30 minutes before using. The cylinders can be secured to the wall with the help of a chain or cable that does not damage or scratch the marks or labels on the cylinder. For safety, gas storage places must be outdoors and protected from sunlight. Indoor storage can be done if the place has appropriate ventilation [7].
- Make sure the valves are completely closed, and maintain valve protection devices such as caps when the cylinder is not in use. The storage location should be dry, without exposure to mechanical or physical damage, heat, or electrical circuits, and away from areas of frequent foot traffic. Empty and full tanks must be stored in areas identified for each of them. Objects should not be stored above the tanks, nor should the cylinders block stairs, exits, or pedestrian or vehicular passages [7].
- Ensure inventory is updated every time a cylinder enters or leaves.
- Any person who handles the cylinders must receive initial gas storage and transportation training using personal protective footwear, glasses, and appropriate gloves.
- When moving the cylinders, avoid rolling or dragging them, and ensure the appropriate handling mechanism, such as a cylinder cart or manual forklift designed for this purpose. Large cylinders must be handled using mechanical assistance (as seen in the following figure) [7].

Figure 2. Mechanical handling devices for cylinders.



- Do not use and report cylinders that show damage or corrosion. Do not use or transport the gas if the gas label cannot be identified.
- Gas recovery cylinders will require the use of appropriate vehicles, which have the respective permits following the requirements of the local environmental authorities.
- In the case of transporting cylinders, only vehicles with an open box or a rear canopy device that is separated from the body of the vehicle should be used. Ideally, cylinders should be transported standing and firmly secured. If the cylinders are transported lying down, adequate support devices must be provided to prevent them from rolling (as shown in the following figure) [7].
- Once arrive at their destination, the cylinders must be unloaded immediately and placed in a safe place following safe storage regulations.
- Cylinders should not be transported in any passenger compartment [8].

Figure 3. Correct transport requirements for transporting gas cylinders on the back of a utility vehicle



- Semi-trailer or coupled trucks must consider: the box of these motor vehicles will preferably be covered with wood (the floor and the sides) and open so that the cylinders receive good ventilation, the side faces of the box must have a height that allows the cylinders to be covered up to at least two-thirds of its total height. The box must be equipped with ropes to secure the cylinders and reduce friction, shaking, and any other harmful effects. The electrical installations attached to the box or the elements on which it rests must be perfectly insulated. The vehicle must be provided with two exterior rear-view mirrors and an audible rear-view signal. Additionally, it must be provided with a hand truck to transport the cylinder and a rubber cushion so that the cylinder falls on it when it is taken off the vehicle. Handcarts should use rubber wheels or other cushioning material.
 - Every vehicle must have appropriate safety devices and be in perfect mechanical condition.
- Associated certifications**
- Refrigerant gas transport permit granted by local environmental authorities (as appropriate).
 - Please consider used ODS should be classified with the proper waste code, and shipments should be clearly labeled. If done correctly, fugitive emissions from ODS transport can be considered negligible. When transferring ODS from pressurized storage into an unpressurized shipping container, there is a risk of loss through vent holes, which are used to equalize the pressure as the shipping container is filled. Thus, a closed-loop transfer system with dry-break couplings should be used instead. Using these two technologies can assume a loss of between 0.0004 percent and 0.05 percent [15]. This leak rate is a substantial reduction from the 5 percent loss experienced without using a closed loop system or dry-break couplings [15]. Each country will have specific waste codes used to classify hazardous wastes, including ODS.

5. ODS DESTRUCTION FACILITIES IN CEMENT KILNS

5.1. EVALUATION OF ODS DESTRUCTION FACILITIES

A destruction and removal efficiency (DRE) of 99.99 percent for concentrated sources of ODS and 95 percent for dilute sources of ODS (i.e., foams¹) is recommended by the Technology & Economic Assessment Panel (TEAP), along with other emissions limits (mainly national regulations) and the use of a Montreal Protocol approved destruction technology. DRE is a measure of the efficiency of destroying, degrading, or removing a chemical in a treatment device (including its air pollution control system) before being emitted to the atmosphere via the stack. DRE is calculated by feeding a measured chemical mass into the system and dividing it by the mass of that chemical that escapes in the exhaust stream; the percentage that has not been emitted is the DRE.

The DRE can be used to estimate the ODS emitted through exhaust gases. For example, an ODS destruction technology with a DRE of 99.99 percent results in 0.01 percent of ODS emissions.

Because of the relatively volatile nature of ODS and, except for foams, they are generally introduced as relatively clean fluids. Therefore one would not expect a very significant difference between DRE and DE (destruction efficiency). For these reasons this update of ODS destruction technologies uses DRE as the measure of destruction efficiency. For the purposes of screening destruction technologies, the minimum acceptable DRE is [16]:

- 95% for foams; and,
- 99.99% for concentrated sources

$$\text{Destruction and removal efficiency (\%)} = \frac{\text{ODS fed in the system} - \text{ODS in the exhaust gas}}{\text{ODS fed in the system}} \times \text{GWP}$$

Since different ODS have different ODP, consideration should be given to taking into account the ODP of each type of ODS present in the stack gas in calculating the DRE. An appropriate definition that takes into account the differences in ODP is: DRE of an ODS is determined by subtracting from the number of moles of the ODS fed into a destruction system during a specific period of time, the total number of moles of all types of ODS that are released in stack gases, weighted by their ODP relative to that of the feed ODS, and expressing that difference as a percentage of the number of moles of the ODS fed into the system [16].

1 Only small amounts of HFCs have been used in foam production since 2002 (FTOC, 2015). These appliances are only now reaching the waste stream. They are recovered and treated the same way as (H)CFCs [18].

The quantity destroyed (DRE/DE) should be measured, calculated, and documented [18]. Thus, destruction facilities such as Cement Kilns where ODS destruction is carried out have a technology approved by the Parties to the Montreal Protocol and are required to observe the following conditions:

Materials/Equipment

- Continuous combustion gas monitoring system. Total particle meter in rotary kiln combustion gases, clinker cooling, and clinker grinding, nitrogen oxides meter in rotary kiln combustion gases, sulfur dioxide meter in rotary kiln combustion gases.
- Data Logging System².
- Thermal imaging camera.
- Temperature gauge in the main burner and pre-calciner.
- Personal protective equipment (helmet, gloves, high-top steel-toed shoes, protective glasses, hearing protection), including devices for working at height (safety harness, lifeline anchoring devices).
- Gas detector
- Generate a chemical compatibility analysis of the ODS cylinders and those related to other gases that could be stored in the same facility.
- In the storage location, the plant manager must maintain a record of gas inventory, storage capacity, entry rate, maximum occupancy capacity, type of cylinders and capacities, identification of the type of gas, and registration of movements in and out of the storage area.
- The following guidelines are considered in the handling and storage of refrigerant gas cylinders:
 - Secure the cylinder in a vertical position
 - Never store cylinders where they may be in contact with water or near direct heat sources, radiators, or coolers.
 - Do not place obstacles in front of the cylinders or objects on them.
 - Secure the cylinders in a vertical position with a lock or chain.
 - Always connect the primary regulation valve directly or through a high-pressure hose.
 - Always keep cylinders away from heat sources.
 - Always check the cylinder labeling before use and ensure the correct gas mixture (correct substance) will be destroyed.
 - Never touch a frozen cylinder; freezing usually indicates a rapid gas release.
 - Never try to unscrew the valve fittings from the cylinder.
 - Using a forklift to move the cylinders will reduce the risk of accidents and save time.

Technicians Involved

- Cement production technical staff
- Technical personnel with experience in refrigerant management
- Mechanical personnel qualified in handling pressure systems. With practical and technical training in the handling of cylinders and filling of high-pressure gases (the profile could include technicians/technologists in mechanics or industrial maintenance or electromechanics, with training in dimensional, physical, and non-destructive testing)
- Parallel Processes/Plant conditions
- Adequate refrigerant gas reception storage area conditions comply with the conditions of the previous section. In addition, cylinders must be located as close to the destruction facilities in the plant as possible. The receiving area must consider sufficient temporary storage and handling capacity at least two times the daily co-processing capacity.

2 Consider that the data from fixed source measurements must be recorded in mg/Nm³ (milligrams per cubic meter of combustion gas under normal conditions), 760 mmHg pressure and temperature of zero degrees Celsius (0°C), on a dry basis and corrected salt 10% oxygen (O₂) [11].

- risk matrix and an analysis of occupational risks that include designing the lift, identifying risks and areas of restriction, selecting competent personnel, specifying the minimum number of people required to drive the lifting operation, selecting the loading and lifting equipment to be used, communicate the lifting requirements and dangers, apply procedures for changing the lifting plan, emergencies, contingencies, and recovery.
- The specific working conditions must include evaluation parameters of climate, visibility, noise, communicators, ground stability, inclinations, heights, facilities involved, and access. Establishing controls includes communicating operations with all relevant personnel.
 - It must be remembered that charges are controlled according to the complexity of the risk. The plant manager must approve routine and non-routine loads and lifts and must test at least ten specific questions:
 1. They are all knowledgeable and understand the loading and lifting to be carried out.
 2. They had a quick safety chat before starting tasks.
 3. A pre-inspection of the loading equipment has been carried out (recorded inspection).
 4. All safety devices are working
 5. All people are qualified and competent for their activities.
 6. Everyone knows the leading and freight manager.
 7. The loading plan, including the precautions, has been understood by everyone.
 8. They know all the load and speed limits and maximum environmental conditions, such as wind associated with the load.
 9. The loading/hoisting area is clear to avoid damage due to falls or swinging loads. No personnel should be allowed to stand under the load.
 10. The signs and methods of signaling and communication are clear and agreed upon by all.
 - The plant manager will only receive refrigerant gases for destruction from transporters with an environmental license or national registration for the entry of hazardous waste.
 - The cement company must align the recommendations with its own procedure for loading, unloading, and storing the ODS/HFCs to be processed, and in addition to the considerations above for loading/lifting and handling cylinders, it may take into account the following guidelines for External visual inspection [10]:
 - Verification of valve operation: observe if the cover is fixed or removable (remove it carefully), and identify and record the cylinder contents: legend on the cylinder, valve type, cylinder color, and identification label. The identification label must indicate the gas contained in the cylinder, the indication of risks, precautions for use, and the name of the refrigerant gas.
 - The gas must be emptied safely, verify that the valve is clean and free of grease or oil, open the valve slowly, attach a pressure measuring manometer and a flow meter, and verify the maximum flow to evacuation in the pre-storage system or feeding in destruction facilities.
 - If no pressure is detected when opening the valve, it should be checked to see if it is clogged. In no case should the escape of refrigerant gases to be destroyed be allowed unless it is absolutely essential, for which the valve must be slowly loosened until small leaks are obtained through its thread, and the way of capture or transfer must be verified.
 - The cylinders must be subjected to leak tests, inspection, and label placement if none exists during the inspection.
 - Cylinders, upon receipt, must be free of dents and protrusions on the cylinder wall, indentations, cuts and marks caused by sharp or sharp objects, cylinder deformations, corrosion, electric welding or torch marks, and contamination such as dirt, grease, oils. If any cylinders present these failures, they will be returned for special inspection.
 - In the event that a cylinder is rejected, the refrigerant gas must be recovered, and the cylinder must subsequently be disabled to render it inoperable so that it is impossible to reuse.

- Once the unloading and reception of cylinders have been carried out, as well as the correct internal manual transport, it must be considered that the cylinder location area must be on a single level, with a smooth horizontal floor, without obstructing communication with drains or sewers. The cylinder maneuvering area must be at least 6 m wide. The area must be signposted and allow operation only to personnel qualified for the activity. Ventilation must be extensive and permanent so that the accumulation of gases is impossible. The cylinders must be stored under a roof (not translucent) to prevent them from suffering excessive temperature increases, physical damage, or the action of the environment.

Measures in the Process

- For the facility evaluation estimate, it is important to carry out survey and verification of the following:

A1. Existence of incinerator-type Suspension Preheater

A2. Gas outlet treatment system for ash and dust

A2.1. Anti ash or dust device/filter or dust collector

A2.2. Acid gas treatment devices such as cleaning tower

A2.3. A gas cooling system

A3. Check if the gas passage facilities involve water (as per each cement kiln technology). If applicable, identify that the effluents have removed suspended solids, which could also imply the removal of dioxins from the aqueous effluent.

A3.1. Existence of an effluent discharge treatment system to comply with fluoride and hydrogen ion concentration standards.

A4. The system must have national standards for particulate matter concentrations and toxic substances (HCl, HF) (gas emissions and water if applicable). Work environment legislation for occupational health and industrial safety due to emissions.

A5. Amount of Chlorine in raw materials and fuel. Detail of current quality of chlorine in clinker and chlorine tolerance limits with safety factor.

A6. The facilities have an electric dust collector and a feedback system for dust collected in the calcination process.

With points A1 to A6, a global plan of the treatment area will be generated, including the process equipment, temperature diagram, flow of operations, and points where emissions into the atmosphere, discharges of contaminated water (if any), waste byproducts, or pollutants are generated.

The general plan will be accompanied by a description of the Clinker manufacturing process, a description of the kiln of the selected plant, dimensions, type of kiln, type of burner, existing equipment, temperature gradient, type of co-processing materials, type of fuel, and recognition of previous blockages/accumulations due to moisture content in waste or fuel, ash content, and estimation of exhaust gas flow rate.

Note: Co-processing in cement kilns is a good option for waste management. It uses the optimal mix of used materials such as plastics, wood, tires, liquids, process sludge and packaging to create an alternative fuel. However, co-processing is frequently confused with waste incineration, but co-processing recovers 100% of the calorific value of the waste and recycles the minerals they contain generating an environmentally safe integration of waste generated by an industry or known source as an input to another production process.

In co-processing, the alternative fuel residual provides the energy necessary for the clinker manufacturing process (a raw material for cement). Some of the minerals contained in the waste, such as calcium, aluminum, and iron oxides, are also recycled

or reincorporated into the final product.

Co-processing in cement kilns occurs at a higher temperature, longer residence time, and does not leave additional ash.

Co-processing for waste management was approved and recommended by the United Nations Program (UNEP) in the Basel Convention. The Multilateral Agreement on the Environment (MEA), adopted on March 22, 1989. The objective is to protect the environment and human health from the harmful effects caused by the generation, handling and disposal of hazardous waste.

A7. Monitoring of dioxins and furans will be carried out.

The monitoring base will be carried out according to:

- US EPA METHOD 23—DETERMINATION OF POLYCHLORINATED DIBENZO-P-DIOXINS AND POLYCHLORINATED DIBENZOFURANS FROM STATIONARY SOURCES
- US EPA METHOD 26—DETERMINATION OF HYDROGEN HALIDE AND HALOGEN EMISSIONS FROM STATIONARY SOURCES NON-ISOKINETIC METHOD
- BS EN 1948-1:2006. STATIONARY SOURCE EMISSIONS. DETERMINATION OF THE MASS CONCENTRATION OF PCDDS/PCDFS AND DIOXIN-LIKE PCBS. SAMPLING OF PCDDS/PCDFS
- BS EN 1948-2:2006. STATIONARY SOURCE EMISSIONS. DETERMINATION OF THE MASS CONCENTRATION OF PCDDS/PCDFS AND DIOXIN-LIKE PCBS. EXTRACTION AND CLEAN-UP OF PCDDS/PCDFS

A8. Location of temperatures from 200 to 400°C in the system with special emphasis on locating 300°C

For this detail, internal sensors or thermal imaging cameras can be used. System temperature profiles must be generated.

Specific Requirements

- Past monitoring records. Historical analysis of CO, particles, O₂, and output flow.
- Calculation of emission flow rate within the system.
- Verification of the bypass system for the gas process, installed to reduce the concentration of chlorine in the oven; the bypass system involves the extraction of a portion of the gases exiting the oven, cooling them, and separating the dust. The bypass begins at the gas extraction point which is located on the furnace side of the highest duct. In this position, the furnace gases have a low dust concentration and high chlorine gas concentrations. The extracted furnace gases containing Cl and dust are inactivated by air to initiate chloride condensation and facilitate subsequent separation of chlorides from the gas. This separation occurs in an electrostatic precipitator or bag filter; the typical bypass rate is up to 15% for chlorine. Installing a bypass requires additional capital investment and increases heat and material losses. Removing hot gas through the bypass generates a greater specific heat consumption of between 6-12 M.J./ton Clinker per percentage of gas removal entering the kiln [1].
- For purposes of screening destruction technologies, the maximum concentration of dioxins and furans in the stack gas from destruction technologies is 0.5 ng-ITEQ/Nm³ for foams and 0.2 ng-ITEQ/Nm³ for concentrated sources. These criteria were determined to represent a reasonable compromise between more stringent standards already in place in some industrialized countries [for example, the Canada-Wide Standard of 0.08 ng/m³ (ITEQ)], and the situation in developing countries where standards may be less stringent or non-existent. Although a previous standard of 1.0 ng/m³ (ITEQ) had been suggested in the UNEP 1992 report, advances in technology in recent years and the level of concern for emissions of these highly toxic substances justified a significantly more stringent level [16].
- The following table presents the DRE and emission limits recommended by the TEAP for concentrated and diluted ODS [16].

Table 1 Technical Performance Qualifications for ODS Destruction

Technical Performance Qualifications for ODS Destruction ³			
Efficiency/Emission	Diluted Sources	Concentrated Sources	EU Standards [18]
DRE (%)	95	99.99	
PCDD + PCDFs (ng/m ³)	0.5	0.2	0.1
HCl/Cl ₂ (mg/m ³)	100	100	10
HF(mg/m ³)	5	5	1
HBr/Br ₂ (mg/m ³)	5	5	
Particulate Matter(mg/m ³)	50	50	10
CO (mg/m ³)	100	100	50

Emission limits are consistent with the Selected technical performance standards (emission concentrations: dry, 0 °C, 101.3 kPa) of the European Parliament and Council, 2000 [18].

Associated Certifications

- US EPA METHOD 26—DETERMINATION OF HYDROGEN HALIDE AND HALOGEN EMISSIONS FROM STATIONARY SOURCES NON-ISOKINETIC METHOD
- US EPA METHOD 23—DETERMINATION OF POLYCHLORINATED DIBENZO-P-DIOXINS AND POLYCHLORINATED DIBENZOFURANS FROM STATIONARY SOURCES

3 Emission limits are expressed as mass per dry cubic meter of exhaust gas at 0°C and 101.3 kPa corrected to 11 percent O₂.

5.2. OPERATION CONTROL CONDITIONS FOR DESTRUCTION OF ODS

Since most ODS have negligible fuel value and a high halogen content (associated with corrosion and air emissions), fuel blending for coprocessing in cement kilns does not typically accept large quantities of ODS for blending with other waste-derived fuel. Thus, being completely aware of chlorine and sulfur sources is important in the clinkering process. Worldwide, after the initial methodologies and trials in cement kilns, destruction potential has been increasing into feasible and large dosing of ODS in cement kilns. Some CFC/HCFC/HFC dosing references vary from 10 kg/hour to 200 kg/hour, depending on

the type of refrigerant gas. These conditions will rely on the kiln size, operational steadiness, fuel type, coprocessing allowance, maintenance, and regular operational conditions. However, the recovery of ODS/HFCs takes a lot of effort in developing countries, so taking more time to safely destroy the gases in the cement kilns at low dosing rates has more environmental and operational benefits than risking high destruction dosing rates in the kiln. For the environmental authorities, the lower the dosage rate, the less environmental risk the process of ODS destruction represents.

Materials

- Continuous combustion gas monitoring system.
- Total particle meter in rotary kiln combustion gases, clinker cooling and clinker grinding/milling, nitrogen oxides meter in rotary kiln combustion gases, sulfur dioxide meter in rotary kiln combustion gases.
- Data Logging System⁴.
- Refrigerant gas injection system.
- Temperature gauge on the main burner and pre-calciner.
- Personal protective equipment (helmet, gloves, high-top steel-toed shoes, protective glasses, hearing protection), including devices for working at height (safety harness, lifeline anchoring devices).
- Photographic camera.

Technicians Involved

- Cement production technical staff
- Technical personnel with experience in refrigerant management
- Mechanical personnel qualified in handling pressure systems. With practical and technical training in the handling of cylinders and filling of high-pressure gases (the profile could include

technicians/technologists in mechanics or industrial maintenance or electromechanics, with training in dimensional, physical, and non-destructive testing)

Parallel Processes

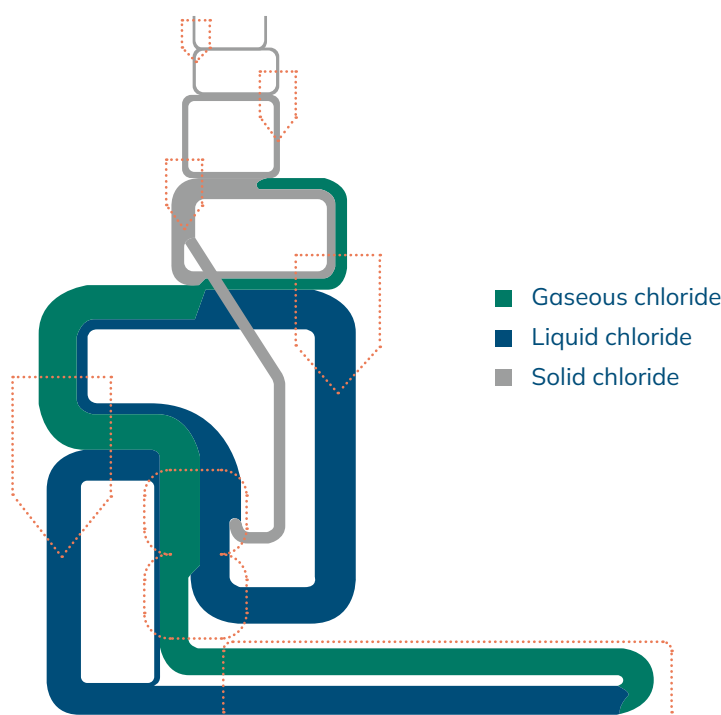
- Fuel homogeneity control, especially when parallel coprocessing of other materials or substances/alternative fuel residual.
- CFC/HCFC/HFC feed calculation considers product reception capacity (especially clinker) and treatment of halides in the gas emissions system. Chlorine existing in the system and possible contribution from fuels must also be considered. Consider an increase in concentration of 10ppm or less in clinker.
- Calculation of dosage influence on Clinker quality, emissions, and facilities.
- Calculation of HCl and HF concentration in output emissions. Estimated measurements of the CFC/HCFC/HFC concentration in the final exhaust gas should be 1 ppm or less.

4 Consider that the data from fixed source measurements must be recorded in mg/Nm³ (milligrams per cubic meter of combustion gas under normal conditions, 760 mmHg pressure and temperature of zero degrees Celsius (0°C), on a dry basis and corrected to 10% oxygen (O₂)) [11]

Measures in the Process

- The temperature in the main burner will be greater than 1450°C in the material and greater than 1800°C flame temperature.
- The retention time in the main burner should be greater than 12-15 seconds at a temperature greater than 1200°C and greater than 5 to 6 seconds at a temperature greater than 1800°C.
- The retention time and temperature in the pre-calciner will be more than 2 to 6 seconds at more than 800°C. If the hazardous waste fed to the kiln contains more than 1 percent halogenated organic substances (expressed as chlorine), the temperature must be maintained at 1100°C for at least two seconds [12].
- Describe the management of waste until destruction, including the development of the process through reaction kinetics and material balance, indicating the byproducts obtained as a result of the treatment and the contribution of clinker.
- For this, it is important to take samples from the cement production raw material, which must be analyzed [13]: Mg, Al, Si, K, Ca, Fe, Cl.
- At this point, the reaction affinity between volatile materials must be considered:
 - 1) chlorine reacts primarily with alkali metals, forming KCl or NaCl typically in the gas phase; residual chlorine combines with calcium, forming CaCl_2 (s/l). However, the chlorine input is rarely greater than the alkali input.
 - 2) excess alkali reacts with sulfur, forming K_2SO_4 and/or Na_2SO_4 ; the residual alkali combines with CO_2 , forming K_2CO_3 and Na_2CO_3 , or with humidity, forming NaOH and KOH, the alkali can also be embedded in the Clinker minerals.
 - 3) excess sulfur, present as SO_2 and/or SO_3 in the gas, will react with CaO(s) forming $\text{CaSO}_4\text{(s)}$.
- The volatility of the materials is described using the evaporation factor for each component varying from 1 to 0, where 1 means that all volatile materials evaporate at high temperature (but without necessarily escaping to the atmosphere) and 0 means that no materials evaporate.

Figure 4. Sankey diagram for chlorine circulation in a modern calciner kiln, showing the gaseous, liquid, and solid chloride flows. (Adapted from Jons et al.) [1]



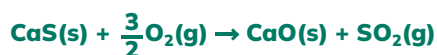
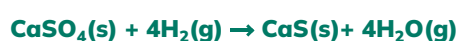
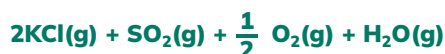
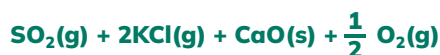
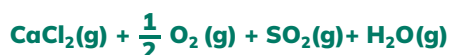
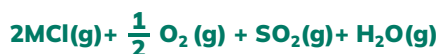
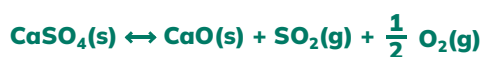
- The following reactions and calculations refer specifically to CFCs since this molecule has a higher chlorine concentration than HCFCs (HFCs have no chlorine in their composition but fluorine), explicitly considering the difference between the ozone depletion power that the substances have

when comparing them, i.e., destroying CFCs safely will definitely destroy HCFCs/HFCs safely too. However, both F and Cl form strong acids in contact with water and require emission control measures [18].

Stabilization reactions [1]:



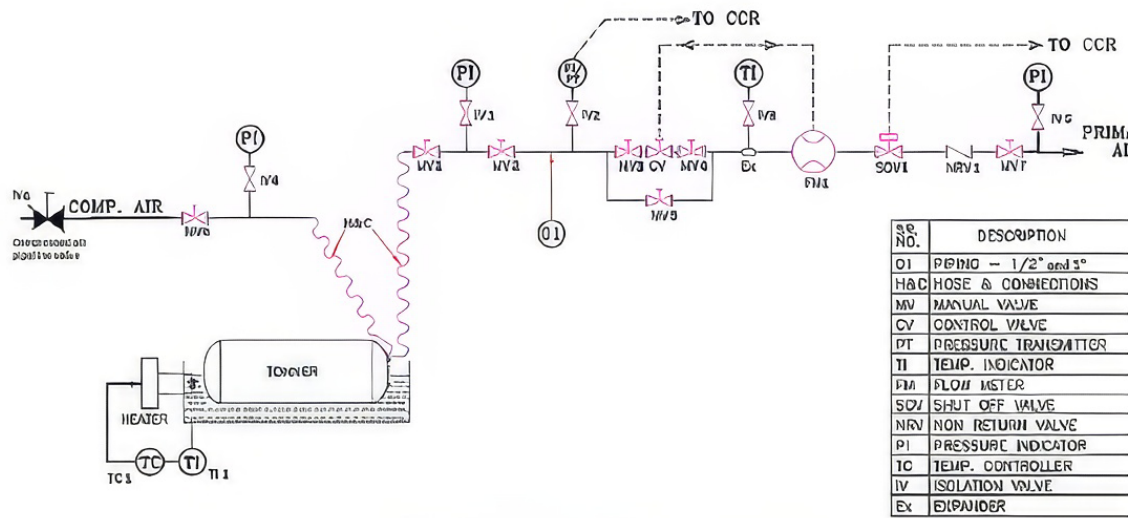
or



- In addition to understanding the chemistry of the process involved, the relationship and technical specifications of the equipment, instruments, and machinery used to destroy polluting gases must be presented. The feeding point in the kiln must be supported and clear [3], in the specific

case of the cement company, and validated with the appropriate technical personnel. In the bibliographic reference found, it has been verified that the entry point through the primary air is viable, as demonstrated by the experience in India and Ecuador.

Figure 5. CFC Feeding System- India [3]



CFC feeding system (tonner is the steel cylinder with CFCs).

- CFC-12 does not require heat or a thermal bath since the boiling point is -29.8°C ; however, everything will depend on the gas outlet pressure and the system's constant dosage controls; specific boiling point conditions must be analyzed for HCFCs/HFCs. The gas must be pumped from the cylinder to the valve train, pressure and temperature gauges with valve and gas flow control, shutoff valves, and finally to a non-return valve. However, thermal jackets for cylinders can be used if the pressure system varies.
- A flexible hose can connect the cylinders with gas flowing through ducts connected to the inlet connector to the primary air blower towards the main burner. Power lines will be provided with heat lining and insulation to prevent condensation. Compressed air can be used to evacuate the system, ensuring that no CFCs/HCFCs/HFCs are left behind. The feeding system must be calibrated appropriately.
- Detail all the equipment's operation and maintenance systems, the safety measures implemented, and prevention of contamination in air, water, and soil. For this, the following minimum security measures will be applied [3]:
 - The CFC/HCFC/HFC should only be fed into the burner flame during normal operating conditions, not during the start-up of the furnace, shutdowns, or major disruptions.
 - The process must be executed in compound mode operation; the exit gas is directed through the crude mill and under identical process conditions every day.
 - All personnel involved must be trained prior to the test.
 - Combustion air flow interruptions must be controlled
 - Pressure control in the burning zone
 - Control of scab/encrustation formation
 - Physical-chemical criteria (limit values dioxins and furans) to be met for feeding CFCs/HCFCs/HFCs [2].

- In the destruction campaigns to be applied, the monitoring and control of the following operating conditions will manage:
 - Raw flour (ton/h)
 - Fuel (ton/hour)
 - AFR (waste material with combustion potential) as secondary fuel (ton/h)
 - Clinker production (ton/h)
 - Cement kiln dust (ton/h)
 - Dust reintroduction rate (%)
 - Chimney gas flow (m³/h)
 - Burning temperatures (°C)
 - Gas outlet temperature (°C)
- To verify sensor locations, the temperature gradients to be monitored must be provided for the preheater systems, gas flow, and system stages.
- Once the dioxin and furan monitoring results are available, a mass balance of the cement production system must be carried out, considering as inputs raw materials, raw flour, co-processing material, total emissions, net emissions with factors broadcast, and as outputs to exhaust gas flows, collected dust and clinker.
- The turbulence and influence factors of primary and secondary air on the formation of the flame and gas-burning area at the appropriate temperature with adequate retention time must be estimated.
- It should be noted that the preheater cyclone system (4 to 6 stages), with or without pre-calciner but without dust extraction or bypass, would be possible to tolerate a chlorine input of 300 g per ton of clinker. If the dust from the filters is not recycled back into the process but rather extracted, the chlorine tolerance could increase to 300 to 400 grams per ton of clinker if the kiln is equipped with a bypass, which extracts part of the hot kiln gases at the kiln inlet, this would allow an additional chlorine input of 100 grams per ton of clinker for each percentage of bypass rate, for example 8% bypass, 800 grams per ton of clinker would be the limit (applicable for a 5-10% bypass rate). The maximum amount of chlorine allowed in

cement quality standards is 1000 grams of chlorine per ton of cement; this limit is also identical for all types of kilns. [3]

- Test protocols (Trial burn) must be carried out to demonstrate 99.9999% destruction and removal efficiency of CFC/HCFC/HFC and will be carried out with nationally or internationally accredited laboratories.
- Cement companies must annually submit to the competent Environmental Authority a report on monitoring the minimum parameters for the destruction of CFCs/HCFCs/HFCs such as CO, particles, HCL, HF, Dioxins and Furans, and also submit the declaration corresponding to the waste disposal process carried out.

Specific Requirements

- It is necessary to operate the system in such a way as to ensure the successful destruction of CFCs/HCFCs/HFCs and the safe control of atmospheric emissions. For this purpose, the combustion conditions should be managed as follows:
 - Combustion temperature: 850°C – 1200°C or higher.
 - Retention time of refrigerant gas in the combustion temperature range: 2 seconds or more.
 - Carbon monoxide (CO) concentrations at the exhaust gas outlet (corresponding to an oxide concentration value of 12%): 100 ppm or less
- It is necessary to operate the facility in the same manner as ordinary cement production in order to ensure the successful destruction of ODS/HFCs and the safe control of atmospheric emissions.
- Considering that the calcination temperature and gas retention time requirements in ordinary cement kiln operation are generally more favorable for the destruction of ODS/HFCs than in rotary kilns for waste incineration, ODS/HFCs are considered to be destroyed with certainty.
- Manual treatment of chlorine compounds requires operational control conditions such as:

- Maintain the kiln temperature at the combustion chamber exit at 800°C or higher.
- Maintain the concentration of oxides at the gas outlet at 6% or higher.
- Maintain the CO concentration at the gas outlet, which is calculated as a value corresponding to 12% of the oxide concentration at 100 ppm or lower.
- This interpretation provides recommendations for combustion temperatures in the combustion chamber, gas retention time in the following temperature range, and combustion conditions:
 - It is preferable to obtain a removal efficiency of 99.99% or higher by installing an afterburner room that ensures a gas retention time of 2 seconds or more at 900°C or higher to decompose and oxidize chlorine carbon compounds in the gas sufficiently.
- Maintain the oxygen concentration in the combustion exhaust gas at 6% or higher and maintain the carbon monoxide concentration in the exhaust gas, which is calculated as a 4-hour average value of the corresponding concentration values of 12% oxides at 100 pm or less to decompose and oxidize the chlorine compounds in the gas sufficiently.
- In general, reaching 850°C or higher for 2 seconds or more during incineration would control the generation of dioxins.

5.3. GAS DOSAGE CONDITIONS FOR DESTRUCTION OF ODS

The dosage will be carried out following current legislation in each country and based on each kiln's operational conditions. In the case of doubts or uncertainty regarding the dosage, a dosage of 10 – 15 kg/hour can guarantee a cement kiln's correct destruction and non-operational impact. A destruction rate of 10 kg/hour is approximately the refrigerant gas of around 50⁵ domestic refrigerators, though rates of gas recovery in some developing countries do not pass from 50 equipment per day per recovery facility.

Materials

- CFC/HCFC/HFC cylinders
- Pipelines
- Hoses and connections
- Manual valves
- Valve control
- Pressure transmitter
- Temperature indicator
- Mass flow meter
- Shutoff valve
- Non-return valve
- Pressure indicator
- Isolation valve
- Expander

Technicians involved

- Refrigeration and air conditioning technician with knowledge of gas recovery and gas pressure systems.

5 This value may vary depending on the age of the appliance, the condition of the engine, the internal contamination of the evaporator, the contamination of the entire system, the size and model of the appliance

- Basic knowledge of the technician [5]:
 - Connect and disconnect hoses and valves of pressure equipment
 - Mechanical vapor compression, open-drive compressors, operation of refrigeration and air conditioning systems
 - Identification of refrigerant gases
- Knowledge of the injection system under normal operating conditions of the cement plant.

Parallel Processes

- Measurement of exhaust gases, clinker analysis, and concentrations of chlorine and fluorine in the system
- Identify raw material characteristics
- Identify alternative fuels used and their reactions
- Power control systems in operation and aligned to operation control systems
- Adequate, stable physical infrastructure and safety standards

Measures in the Process

- Definition of safe dosage in the chlorine condition control system and equipment.
- Location of CFC/HCFC/HFC dosing point closest to the burner, under normal operating conditions, and ensuring sufficient combustion temperature and retention time.
- Feeding equipment with oil filter, mass flow meter, and other devices for adequate feeding. Assurance of pressure supply to equalize the latent heat of CFC/HCFC/HFC gas.
- Type of CFC/HCFC/HFC delivery cylinders. Type of latent heat of gas.
- Future feeding sequence for destruction of CFCs/HCFCs/HFCs in the kiln.
- Identification of power connections and prevention of CFC/HCFC/HFC gas leaks from the system.
- Identification of detection limits of gas and Clinker monitoring equipment.
- Contrast detection limits with permissible limits.

Specific Requirements

- Generation of injection design, flow rates, and controlled dosage.
- Laboratory measurement of gaseous emissions to identify HCl, HF, Dioxins and furans, fluorides, particles, and CO. Additional to the monitoring of hydrogen ions in the water effluent (if applicable).
- Demonstrate 99.9999% destruction and removal efficiency [12].

Associated Certifications

- Calibration of online monitoring equipment. Calibration of laboratory monitoring equipment and laboratory accreditation certification

Particular Regulations

- The standards established and recommended by the UNEP Ad-hoc Technical Advisory Committee on emission gases in ODS destruction technologies are considered particular regulations.

Table 2. Exhaust Gas Standards recommended by the UNEP Ad-hoc Technical Advisory Committee on ODS Destruction Technologies

PCDD/PCDF	<1.0 mg-TEQ/Nm ³
HCl	<100 mg/Nm ³
HF	<5 mg/Nm ³
HBr/Br ²	<5 mg/Nm ³
Particulates	<50 mg/Nm ³
CO	<100 mg/Nm ³

Source: <https://digitallibrary.un.org/search?f1=author&as=1&sf=title&so=a&rm=&m1=e&p1=UNEP.+Ad+Hoc+Technical+Advisory+Committee+on+ODS+Destruction+Technologies&ln=es> [17]

5.4. MONITORING PROTOCOL

The CFC/HCFC/HFC destruction monitoring protocol will follow the national guidelines and protocols existing specifically for controlling Dioxins, Furans, CO, Particles, Hydrochloric Acid, and Hydrofluoric Acid (if not available, international references can be considered), plus the following considerations:

- Dosing is carried out only under normal operating conditions of production, loading, and fuel consumption.
- Blank evaluation (which corresponds to the system's operation without CFC/HCFC/HFC load but under normal co-processing conditions load).
- Evaluation with 100% co-processing load and 10-15kg/hour CFC/HCFC/HFC load.
- Chimney analysis in three runs per element and under corrected isokinetic conditions. Sampling tests are to be defined with the laboratory's available equipment's capture capacity under the trial conditions.
- Use of main monitoring methods:
 - US EPA METHOD 23—DETERMINATION OF POLYCHLORINATED DIBENZO-P-DIOXINS AND POLYCHLORINATED DIBENZOFURANS FROM STATIONARY SOURCES
 - BS EN 1948-1:2006. STATIONARY SOURCE EMISSIONS. DETERMINATION OF THE MASS CONCENTRATION OF PCDDs/PCDFs AND DIOXIN-LIKE PCBS. SAMPLING OF PCDDs/PCDFs
 - BS EN 1948-2:2006. STATIONARY SOURCE EMISSIONS. DETERMINATION OF THE MASS CONCENTRATION OF PCDDs/PCDFs AND DIOXIN-LIKE PCBS. EXTRACTION AND CLEAN-UP OF PCDDs/PCDFs
 - METHOD 26 A – DETERMINATION OF HYDROGEN HALIDE AND HALOGEN EMISSIONS FROM STATIONARY SOURCES ISOKINETIC METHOD. HCL (CAS No. 7647-01-0), HF (CAS No. 7664-39-3), CL₂ (7882-50-5)
 - US EPA METHOD 23—DETERMINATION OF POLYCHLORINATED DIBENZO-P-DIOXINS AND POLYCHLORINATED DIBENZOFURANS FROM STATIONARY SOURCES
- Use the gas verifier to ensure correlation with the physical-chemical description of ODS and % purity identified.
- The dosage, in accordance with the Japanese guide (1999) [19] for the Destruction of CFCs, as well as for safety factors, should not exceed 10

- Kg/hour of CFC-12 feeding into the system for safe destruction. Experiences in Ecuador (2015) demonstrated a safe destruction dosage at 15 kg/hour of CFC/HCF, and even higher dosage rates have been tested in recent years in Mexico.
- The consideration of surrogates or water does not apply since the feeding system has humidity filters, and the % of oxygen is evaluated with the % of oxygen for adequate combustion that allows reaching the conditions of 1500°C in the main burner for the destruction of ODS/HFCs.
 - The HF parameter will be evaluated under the same EPA method 26 A, so compatibility is accepted to support monitoring under the same protocol.
 - The type of emissions expected according to UNEP standards correspond to:

Table 3. Recommended limits for gas emissions in cement kilns

Parameter	Recommended limit
PCDD/PCDF	< 1 ng-TEQ/Nm ³
HCL	< 100 mg/Nm ³
HF	< 5 mg/Nm ³
Particles	< 50 mg/Nm ³
CO	< 100 mg/Nm ³

- As shown in the previous stabilization reactions, in the case of the destruction of CFCs (also applicable for HCFCs/HFCs), chlorine reacts primarily with alkali metals, forming KCl or NaCl typically in the gas phase; the residual chlorine combines with calcium, forming CaCl₂ (s/l); however, the chlorine input is rarely greater than alkali input. Excess alkali reacts with sulfur, forming K₂SO₄ and/or Na₂SO₄; the residual alkali combines with CO₂, forming K₂CO₃ and Na₂CO₃, or with moisture, forming NaOH and KOH, the alkali can also be embedded in the Clinker minerals. Excess sulfur, present as SO₂ and/or SO₃ in the gas, will react with CaO(s), forming CaSO₄(s). In the case of CFC-12, no effluents result from the treatment (similar condition prevented for HCFC/HFC).
- The affected concentrations will be verified according to Clinker quality standards, so no solid or liquid effluents or by-products require subsequent treatment. The emissions system is controlled with the same dust and concentration controls in the outlet gas effluent.
- To carry out the destruction test, a blank sample must be taken, and the hazardous waste could be loaded at a dosage rate of up to 15 kg/hour.
- Given the particularities of the CFC/HCF/HFC destruction systems, the target corresponds to normal co-processing conditions of the cement plant and the loading amount is designed at 100% of the maximum dosage established in the test of 15kg/hour, and with a dosage under normal conditions of 10- 15 kg/hour.
- The ODS destruction schedule will be applied under the chlorine concentration controls registered by the cement company, operating under co-processing conditions or with loading without co-processing.
- One of the most important considerations is the calculation of the retention time for which, according to the Japanese guide [19], the following formula will be used:

$$\text{Gas retention time (sec)} = \frac{\text{Furnance volume [m}^3\text{]} \times 3,600}{\text{Wet exhaust gas amount [Nm}^3\text{/hr]} \times (273.15 + \text{furnance temperature [}^\circ\text{C]})/273.15}$$

- The test reports will be prepared by a laboratory accredited locally or internationally, or at least with the corresponding method validations.
- The report of test results and monitoring protocols will consider:
 - An executive summary of the testing protocol carried out in which the real times of each of the activities carried out will be indicated, including the description of those stoppages and eventualities that may have occurred during them, as well as the actions implemented to restore them.
 - Present documents accrediting the parameters and methods.
 - Submit the executive summary of the testing laboratory that performed the sampling and analysis that includes:
 - Copy of the methods used for sampling and analysis of the protocol components.
 - Chain of custody sheets
- Results of the characterization of hazardous waste before treatment, including the interpretation of chromatograms.
- Results of the characterization of the effluents resulting from the thermal treatment, including the interpretation of the chromatograms.
- Results of gas sampling for each of the runs, including the interpretation of the chromatograms.
- Present the development of the calculation of the destruction efficiency of the system based on the results obtained (by the laboratory).
- Present the summary of the emissions values detected for each of the runs.
- The material balance applicable for ODS destruction will be presented. In the case of energy balance, it does not apply because the gas does not have a calorific value.

Table 4. Material Balance applicable for ODS destruction registry form

Material balance							
Parameter / Number of system streams	←	↑	→	↓	°	±	"
W (kg or ton)							
Q (lo m ³)							
Pressure (atm or kg/cm ²)							
Temperature (°C)							
% HCL							
% CaCl ₂							
% Cl ₂							
% NaCl							
Physical state S/L/G							
% excess O ₂							

This form is only a template that can be used for the registry of material balance.

The following on-site checklist developed using EPA criteria, could be used for the monitoring protocol, to ensure testing is performed under standardized guidelines. The objective is for the operator and/or observer to have a general working knowledge of the test applicable to methods: EPA 1, 2, 3, 4, 5, 23, 26A, and Instrumental Methods 3A-O₂/CO₂, 6C-SO₂, 7E-NO_x and 10-CO;

Before sampling, the following activities should be considered:

- Internally review the list of quality assurance activities, prior to the Test.
- Review standards applicable to the source (permit, NSPS, NESHAP, etc.).
- Read and become familiar with the EPA protocol.
- Review any previous test reports.
- Read the performance standards/test methods listed in the testing protocol.
- Review checklists. If you have questions, please review additional information on the EMC website (<https://www.epa.gov/emc>).
- The trial coordinator must have full knowledge of the performance of the personnel and the test)

The sampling laboratory must have at least the following documentation:

- Calibration certificates for equipment and measuring instruments
- Daily check sheets
- Certificate of Analysis of gas cylinders
- Field data sheets
- Recovery data sheets, and
- Chains of custody (when applicable).

Table 5. Check items prior to the air emissions sampling of dioxins, furans and bromine from the combustion of the destruction of electronic waste

EVIDENCE CHECK	MAX ERROR EMITTED (emp)	Method Reference and article
Leak test at 76 mm H ₂ O before testing on the pitot tube- hoses-manometer	±2.5 mm H ₂ O	EPA 2 No. 8.1
Geometric verification of Pitot alignment specifications in the X, Y, Z planes	$\delta: \leq 10^\circ$ $\beta: \leq 5^\circ$ $Z: \leq 3.2$ $W: \leq 0.8$ $Pa/Da: 1.05 \text{ to } 1.5$	EPA 2 Number: 10.1 Number: 6.1
Distance between pitot and temperature sensor tip	5cm	EPA 2 Number: 10.1
Yc Coefficient Verification Regarding Y (Calibration coefficient of the gas meter)	$0.97Y < Y_c < 1.03Y$ based on AH@)	EPA5 Number: 9.2.1.2

Leak Test between 130 to 180 mm H ₂ O in the section between the suction pump and volume counter	0.57 bpm either 4% of the average sampling rate, whichever is less. (before and after the test)	EPA 5 Number: 16.2.2.1.2 Number: 8.4.1
Sampling Train Leak Check 15 in Hg to filter holder 1 in Hg Complete train including probe	-	EPA 5 Number: 8.4.1
Temperature checks of the thermocouples of the sampling train: filter, probe, chimney gas temperature, gas meter temp., condenser outlet gas temp., XAD2 Trap	≤20°C	EPA 5 Number: 8.5.6
Field scale verifications with a standard weight	Resolution ≤ 0.5g Value ≤ emp scale	EPA 5 Number: 10.7
Verification of nozzle diameter and integrity	The difference between the values: minimum and maximum ≤ 0.1 mm	EPA 5 Number: 10.1
SAMPLING REQUIREMENTS	CRITERION	Reference Method
Cyclonic flow verification	Compensation angle ∂ rotation ≤ 20°	EPA 1 NUM: 11.4.2
Level and Wax the manometers before, in between and after completing sampling	Regarding the horizontal plane Regarding Zero	EPA 2 No. 8.2 Number: 10.1.3.3 EPA 1 Number: 11.5.3.2.1
Calibration of dry gas meter, thermocouples, nozzle, critical orifice devices, scales, thermocouples, barometer, length gauge, clinometer	Parameters and emp, according to the manufacturer or the validation criteria and objectives	EPA 5 Number: 10.3 to 10.8
Constitution of the Isokinetic train materials (nozzle, heated probe, particle filter, Impactors)	Quartz, Borosilicate, pyrex or glass, Titanium	EPA 23: Number: 6.1.1to 6.1.10
Particle Filters Characteristics Visual inspection	Fiberglass Integral and without perforations	EPA 5 No. 7.1.1 No. 8.1.2
Inspection of: nozzles	Conical leading edge with angle ≤30	EPA 5 Number: 6.1.1.1
Have the necessary amount of: Silica gel, acetone, ice, distilled water, and materials	According to the quantities recommended in the method	EPA 5 Number: 7.1 EPA 23 7.1.1 to 7.1.6
Water characteristics	Deionized or distilled	EPA 5 Number: 7.1.3 Ç

Adverse weather conditions: Rain, extreme solar radiation	Ensure the correct performance of sampling with the protection of the entire train.	IMPLIED IN THE METHODS
Location of sampling ports	≥ 0.5 diameters before last disturbance ≥ 2 diameters after penultimate disturbance	EPA 1 Number: 11.1.1
Determination of the number of points (centroids)	Based on the location of the sampling ports	EPA 1 Number: 11.2
Location of sampling points	According to the geometry and diameter of the chimney	EPA 1 Number: 11.3
Probe length	$\geq 50\%$ duct diameter (to complement sampling on the opposite side)	EPA 1 Number: 11.2
Mark the centroid sampling points on the probe	Based on the Method EPA 1 Num: 11.3 Depending on the diameter of the chimney	EPA 1 Number: 6.1.1
Filters are encoded and pre-weighted	Internal coding and use of analytical balance	EPA 5 Number: 8.7.6.1
Avoid filter contamination in storage and sampling	Supported on glass or Teflon	EPA 5 Number: 6.1.1.5 EPA 23 6.1.3
Use of sealing grease in connections between nozzle and last bubbler	Do not use	EPA 23 Number: 6.1
Nozzle size selection	It must cover the operating ranges of differential pressure and chimney temperature to guarantee Isokineticism. Sample suction ≥ 55 lpm	EPA 5 Number: 8.2.2
Pitot and sampling probe position in the chimney	It is attached perpendicularly to the duct to travel through the centroid points.	EPA 5 Number: 6.1.1.3
Isokineticism (IC)	$90\% \geq CI \leq 110\%$ of the true value	EPA 5 Number: 12.11.3 8.5
The annular space between the probe and the sampling port is sealed during sampling	With thread or other mechanism that prevents the entry of pirate air	IMPLIED IN THE METHODS
Filter Temperature during sampling	$120 \pm 14^\circ\text{C}$	EPA 23 Number: 8.1.5.1

Recirculation trap	Running throughout sampling	EPA 23 Number: 8.1.35
Gas temperature at the entrance of the XAD2 resin	$\leq 20^{\circ}\text{C}$	EPA 5 Number: 8.1.5.2
Probe temperature during sampling	$120 \pm 14^{\circ}\text{C}$	EPA 5 Number: 6.1.1.2
Temperature at the outlet of the bubblers	$\leq 20^{\circ}\text{C}$	EPA 5 Number: 6.1.1.8
Storage temperature of the Filter with the recovered sample and other containers	In cooler $\leq 20^{\circ}\text{C}$ Protected from sunlight with aluminum foil	EPA 23 Number: 8.2.4
If a filter and filter holder change is required during sampling due to excess pressure drop	Perform leak test	EPA 5 Number: 8.5.7 8.4.3
Total volume and Sampling time	$\geq 2.5 \text{ m}^3$ of gas $\geq 2 \text{ min}$ / centroid point	EPA 23 Number: 8.1.2.1 8.1.2.2
Inspection of the nozzle and Pitot before and after the test	Integer and free of breaks or fissures,	EPA 2 Number: 10.1 Number: 6.1
Determination Dry Molecular Weight	Gas analysis Equipment contrasted with NIST traceable standard gases	EPA 2 Number: 8.6
Oxygen Analysis (O_2)		EPA 3 EPA 3A EPA 7E, NUM 6.2.4 CTM 34
Seal nozzle and exposed sampling train sections	With: glass lids sealed with aluminum foil and Teflon tape	EPA 23 Number: 6.2.1
Immediately after sampling Seal and cover the resin trap	With: glass lids, Teflon tape and aluminum foil (to protect from light and prevent dioxin destruction)	
After finishing the sampling proceed with the leak test	-	Numerals already indicated

Source: Project PREAL Costa Rica, with the collaboration of Ambigest, UNIDO 2024.

6. ADDITIONAL NOTES FOR FOAMS

Foams can use CFCs/HCFCs/HFCs/HFOs as blowing agent during their manufacturing. The mentioned substances have also chlorine and fluorine in their composition, but furthermore, foams, as a thermoset plastic group, are multifunction polymer materials with a wide-ranging of applications in rigid foams, flexible foams, coatings, and elastomers. Thus, regarding the application of the foam, foams could also be related to flame retardants (FR), which are applied mostly to rigid foam as additives to reduce flammability levels, although reactive flame retardants can also be used. The use of flame retardants and the type of flame retardants used highly depend on the region and country [21].

The main FR reported to be used in polyurethane foams could be halogen-containing, non-halogen organo-phosphorous, or other non-halogen FRs. According to the amended POP Regulation No. 2019/2021 in the EU, landfilling these rigid polyurethane PUR wastes will no longer be allowed if the wastes show higher contents than 0.1% PBDEs. Therefore, all facilities dealing with end-of-life PUR foam must observe the general BAT/BEP considerations, where cement kilns are increasingly used in waste management schemes in industrial and developing countries [21].

Foams are not the best alternative fuel, given their high volume and low mass; however, they do have a certain calorific value that can be used to guarantee their safe destruction at high temperatures and co-processing in cement kilns. Alternative co-processing fuels are always fed into the high-temperature combustion zones of the Clinker production system. Experimental studies on the destruction of plastic resins in cement kilns have addressed the thermal decomposition of pure brominated FR (BFR) and/or BFR-loaded polymers in oxidative and pyrolytic environments, generally in the temperature range of 280 to 900°C [22]. In addition to FR, in the case of

foams, the thermoforming cells contain encapsulated blowing agents (potentially SAOs/HFC), so crushing the material could release the gas contained in the cells. For this reason, it is expected that the foams can be fed into the cement kiln in larger pieces by the precalciner as long as the feeding point is evaluated by the technical staff of the cement plant according to the physical and chemical characteristics of the material to be destroyed, and usually within the AFR stream that is injected for regular co-processing.

Under test standards, which are still under development, in the UNIDO's PREAL Project regarding the environmentally sound management of plastics with BFR from electrical and electronic equipment, the feeding of 75 kg/hour of plastics (including foams) with concentrations of PBDE of the order of 1,200 ppm for destruction tests in cement kilns has been considered, estimating that the test at 75 kg/hour will validate the feed rate for regular processes of 45 kg/hour, also considering that the maximum limit of Br in the feed of the furnace concerning the total AFR must be less than 0.015%.

Thus, if we feed any brominated compound contained in the foams (PBDE or other), this same chemical parameter must be analyzed in the atmospheric emissions released by the chimney. The following table explains the main parameters to monitor in the case of feeding plastic waste with the presence of Bromine into a cement kiln.

Table 6. Monitoring of Substances in Chimney Emissions, in the case of feeding plastic waste with brominated flame retardants [24] [27]

Substance/Group	Reason	Sampling	measurement method
PBDEs/BFR	Major pollutant	Stockholm Convention sampling method	chromatographic techniques coupled with a mass spectrometer/ electron capture detector (ECD)
PXDD/F	Potentially hazardous products formed	Stockholm Convention Sampling Method	chromatographic techniques coupled with a mass spectrometer
HBr/Br ₂	Emissions may appear	International Standard IEC 62321 Ed.1	gas chromatography
Brominated volatile organic compounds (Br-VOCs, methanobromide)	Br-VOCs are powerful substances that deplete the ozone layer		
Sb (antimony)	Br plastics contain significant amounts of antimony	Stockholm Convention Sampling Method	mass spectroscopy

Table 7. Monitoring of Substances in Clinker & Hot flour [25] [26]

Substance/Group	Reason	Sampling	measurement method
PBDEs	Main pollutant	Stockholm Convention Sampling Method	chromatographic techniques coupled with a mass spectrometer/ electron capture detector (ECD)
PXDD/F	Potentially hazardous product formed	Stockholm Convention Sampling Method	chromatographic techniques coupled with a mass spectrometer
Br total (3)	Br mass balance	International Standard IEC 62321 Ed.1	chromatographic techniques coupled with a mass spectrometer
Sb (antimony)	Antimony may be beneficial or may need careful handling to have consistent cement quality	Stockholm Convention Sampling Method	mass spectroscopy

Table 8. Monitoring of substances in raw meal feed [23]

Substance/Group	Reason	Sampling	measurement method
Br total (3)	Br mass balance	International Standard IEC 62321 Ed.1	Chromatographic techniques coupled with a mass spectrometer

In this way, if joint destruction of ODS and foams (that have an ODS/HFC as a foaming agent in addition to brominated compounds as a flame retardant) is carried out, the atmospheric emissions of chlorinated and brominated dioxins and furans must always be measured, as well as hydrochloric acid, hydrobromic acid, and the respective substances to be destroyed, such as in this case SAOs/HFC/PBDEs or another

specific compound to be determined in the characteristics of foam to be fed into the oven (e.g., PBDEs).

To calculate the destruction and removal efficiency, the same formula established above for the DRE calculation of ODS/HFC can be used, replacing the ODS with the particular brominated compound fed into the furnace within the foam plastic waste.

$$\text{Destruction and removal efficiency (\%)} = \frac{\text{BFR fed in the system} - \text{BFR in the exhaust gas}}{\text{BFR fed in the system}} \times 100$$

The analytical method for measuring brominated dioxins and furans is the same as for measuring the chlorinated type.

In the case of including plastic waste in co-processing in parallel to the destruction of ODS/HFCs, it is necessary to report the information collected before and during the test, at least the following:

- Characteristics of polyurethane foams and AFR mixtures usually used for co-processing
- Result of mass coupled gas chromatography analysis on the type of substance applied in the foams as a flame retardant.
- Physical and chemical analysis of fuels, raw materials, and clinker.
- Records of process parameters monitored during the test.
- Amount of waste consumed, cement produced, and use of conventional and alternative fuel.

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Other sources of information:

General BAT BEP guidance relevant to recovery processes in cement kilns is available in:

- Basel Convention technical guidelines on the environmentally sound co-processing of hazardous wastes in cement kilns [<http://www.basel.int/Implementation/TechnicalMatters/DevelopmentofTechnicalGuidelines/TechnicalGuidelines/tabid/8025/Default.aspx>]
- Stockholm Convention BAT/BEP guidelines: V.B Cement kilns firing hazardous waste [<http://chm.pops.int/Implementation/BATBEP/BATBEPGuidelinesArticle5/tabid/187/Default.aspx>]
- EU CLM BREF [https://eippcb.jrc.ec.europa.eu/sites/default/files/2019-11/CLM_Published_def_0.pdf]

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