

**Lynas Advanced Materials Project:
Study on Potential Dioxin & Furan
Emissions**



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LYNAS MALAYSIA SDN BHD
LYNAS ADVANCED MATERIALS PROJECT
STUDY ON POTENTIAL DIOXIN AND FURAN EMISSIONS

Lynas Advanced Materials Project

Study on Potential Dioxin and Furan Emissions

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SYNOPSIS

WorleyParsons were requested to study the potential for the development of Furans and Dioxins from the Lynas Malaysia Advanced Materials Plant. This report summarizes the findings of the study.

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PROJECT 4219298-300-EN-RP-003-0C – LYNAS ADVANCED MATERIALS PROJECT

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1. EXECUTIVE SUMMARY

This document was developed to assist Lynas Malaysia Sdn Bhd (Lynas) in understanding the potential for dioxin and furan formation from their proposed Advanced Materials Plant in the Gebeng Industrial Estate, Pahang, Malaysia.

Dioxins and Furans are two of the persistent organic pollutants (POPs) emanating from industrial processes and their emission must be regulated to protect the environment. Estimating the rate of emissions from industrial facilities relies on process information and raw material inputs provided by the client and others and is based on the methodology developed by the United Nations Environment Program (UNEP) following the Stockholm Convention on POPs. UNEP first developed a standardized tool kit for identifying and quantifying dioxin and furan releases in 2003. WorleyParsons have used a later revision of this toolkit, released by UNEP in February 2005.

This document uses the quantitative method recommended by UNEP to determine the potential yield of Poly Chloro Di-Benzo Dioxins (PCDDs) and Poly Chloro Di-Benzo Furans (PCDFs) during the cracking and separation process at the proposed plant. These substances only form in a narrow window of process conditions and their formation requires raw materials and conditions generally not found in a lanthanide cracking plant, such as free chlorine, poor combustion conditions resulting in free (uncombusted) hydrocarbons and a certain temperature range.

As we experienced difficulties obtaining source data for other lanthanide processing facilities, conservative yield estimates based on industry data from related industries, such as cement manufacturing, were used. It is recognized that these facilities typically operate at substantially higher temperatures than the proposed Advanced Materials Plant using inferior fuels, resulting in the conservative estimates for dioxin and furan formation.

Therefore, the quantitative emissions calculated are generally based on the 'worst-case' data that was available and sourced, which in some cases may be skewed towards unfavourable process conditions, such as combustion of waste oils and possibly chlorinated feed stocks. These conditions do not occur in the proposed process for the plant and in general, the requirements for dioxins and furans to form are not present. Nevertheless, the estimated emission values, whilst based on conservative assumptions, are extremely low compared to other industries where conditions for their formation are more favourable.



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2. INTRODUCTION

Lynas Malaysia Sdn Bhd (Lynas) intends to construct and operate an Advanced Materials Plant within the Gebeng Industrial Estate in Pahang, Malaysia. The company has engaged Worley Parsons to undertake a brief study on the potential for the development of dioxins and furans from the operation of the plant.

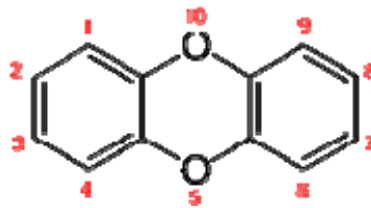
For the purpose of quantifying the potential emissions of dioxins and furans, WP adopted the methodology developed by the United Nations Environment Program (UNEP) for Persistent Organic Pollutants (POPs). The UNEP first developed a Standardized Tool Kit for Identification and Quantification of Dioxin and Furan Releases in 2003. The tool kit was subsequently revised to the current edition dated February, 2005. The toolkit examines various processes that are known to contribute to the production of dioxins and furans and provides a methodology for developing a quantitative estimate of these emissions from the various chemical processes identified. This report uses process data and plant information provided by Lynas in conjunction with the methodology outlined in the tool kit to estimate PCDD and PCDF emissions from the plant.



3. PERSISTENT ORGANIC POLLUTANTS (POPS)

3.1 Dioxins

Dioxin is the common name for a group of compounds classified as polychlorinated dibenzodioxins (PCDDs). The general formula for PCDDs is $(C_{12}H_{(8-n)}Cl_nO_2)$ where 'n' has a value between 1 and 8, corresponding with the number of chlorine atoms. PCDDs which are members of the family of halogenated organic compounds, have been shown to bioaccumulate in humans and wildlife due to their lipophilic properties, and are known teratogens, mutagens, and suspected human carcinogens.



Chemical Structure of Dioxins

Dioxins are produced in small concentrations when organic material is burned in the presence of chlorine, whether the chlorine is present as gaseous chlorine or as organochlorine compounds. The presence of chloride ions alone does not favor dioxin formation unless conditions exist to chemically convert chloride to chlorine. Dioxins have historically been associated with inefficient combustion and chlorine based industrial processes. More recently, and according to current US EPA data, the major sources which account for nearly 80% of dioxin emissions are:

- Coal fired utilities
- Metal smelting
- Diesel trucks
- Land application of sewage sludge
- Burning creosote or PCP treated wood
- Trash burn barrels



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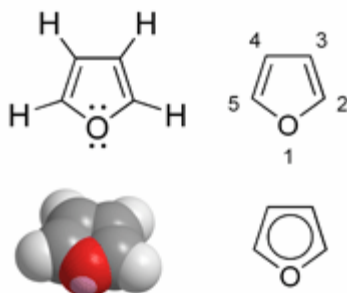
Dioxins can form in the atmosphere as exhaust gases from incineration cool through a temperature window between 600 – 200°C. The most common approach to eliminate or reduce dioxins forming through this process is through rapid (30 millisecond) quenching of the exhaust gases during the 400°C window. Incinerator emissions of dioxins have been reduced by over 90% as a result of new emissions control requirements. As a result, incineration is now a very minor contributor to dioxin emissions.

3.2 Furans

Furan is the common name for a group of compounds classified as polychlorinated dibenzofurans (PCDFs) with a general formula of $(C_{12}H_{(8-n)}Cl_nO)$ where n is a number between 1 and 8 and corresponds to the number of chlorine atoms. The compound is a colorless, flammable, highly volatile liquid with a boiling point close to room temperature. It is toxic and may be carcinogenic. Furans are typically derived by the thermal decomposition of pentose, containing cellulosic solids, especially pine wood.

Synthesis and isolation

- Furan can be obtained from Furfural by oxidation and decarboxylation of the resulting furan-2-carboxylic acid, the Furfural being derived by destructive distillation of corn cobs in the presence of sulfuric acid.
- The traditional furan organic synthesis used in laboratory conditions is the Feist-Benary synthesis.
- Another synthesis method for furan production is the reaction of 1,4-diketones with phosphorus pentoxide (P_2O_5) in the Paal-Knorr Synthesis.



Chemical Structure of Furan



4. TYPICAL SOURCES OF PCDDS AND PCDFS

PCDD and PCDF releases arise from four sources. The following are the primary processes that contribute to PCDD and PCDF emissions.

- Chemical production processes – examples include the production of chlorinated phenols and the oxychlorination of mixed feeds to produce certain chlorinated solvents. Another is the now outmoded production of pulp and paper using elemental chlorine for chemical bleaching.
- Thermal and combustion processes – including incineration of wastes, and also when chlorine is present during the combustion of solid and liquid fuels and the thermal processing of metals.
- Biogenic processes – including the use of pentachlorophenol which was once widely used as a wood preservative.
- Reservoir sources – such as historic dumps of contaminated waste, soils and sediments, which have accumulated PCDDs/PCDFs over extended periods.



5. REGULATORY FRAMEWORK

Federal Regulations

Malaysian Environmental Quality (Dioxin and Furan) Regulations 2004

These regulations apply to the following four types of facilities:

- municipal solid waste incinerator;
- scheduled waste incinerator;
- pulp or paper industry sludge incinerator; and
- sewage sludge incinerator.

The regulations apply to new facilities installed on or after 1 May 2004. The maximum concentration limit for air emission of Dioxin and Furans is 0.1 ng/Nm³ TEQ

For existing facilities (already installed/purchased/acquired/under construction on or prior to 1 May 2004) the compliance date is between 1 May 2004 and 30 April 2007. The maximum concentration limit must comply with the air emission limit for Dioxin and Furan emissions as prescribed in the license under Section 18 of Environmental Quality Act 1974 or the approved conditions stated in the environmental impact assessment report.

Since May 1, 2007, the concentration limit for air emission of Dioxin and Furan is 0.1 ng/Nm³ TEQ.

[Source: International POPs elimination project – Country situation report – Malaysia Aug – 2005]

International Treaties

Minimization or elimination of the formation and releases of PCDDs/PCDFs is requirements under the Stockholm Convention on POPs. To achieve this goal, parties to this convention are required to implement best available techniques (BAT) and best environmental practices (BEP). An Expert Group under the administration of UNEP has been established to provide guidelines and guidance for BAT and BEP. Final guidelines and guidance will be adopted by parties to the Convention when they subsequently meet.



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6. UNEP TOOLKIT METHODOLOGY

The UNEP Toolkit is a methodology designed to help countries estimate the amount of emissions of PCDD/PCDF during the development stages of their own emissions inventories. The Toolkit also guides countries to processes of enhancing and refining these inventories.

Key elements of the Toolkit include:

1. A methodology for identifying the main industrial and non-industrial processes which release PCDD and PCDF to air, water and land and a screening process to identify the most important ones.
2. Guidance on gathering information on relevant processes which will help with grouping of releases into similar categories to assist with applying relevant processes.
3. A database of emission factors which can be used as default data for each classification group.
4. Guidance with assembly and presentation of an inventory using default emission factors and country specific data.

The primary goal for the use of the Toolkit is to establish a national PCDD/PCDF inventory. This is done by:

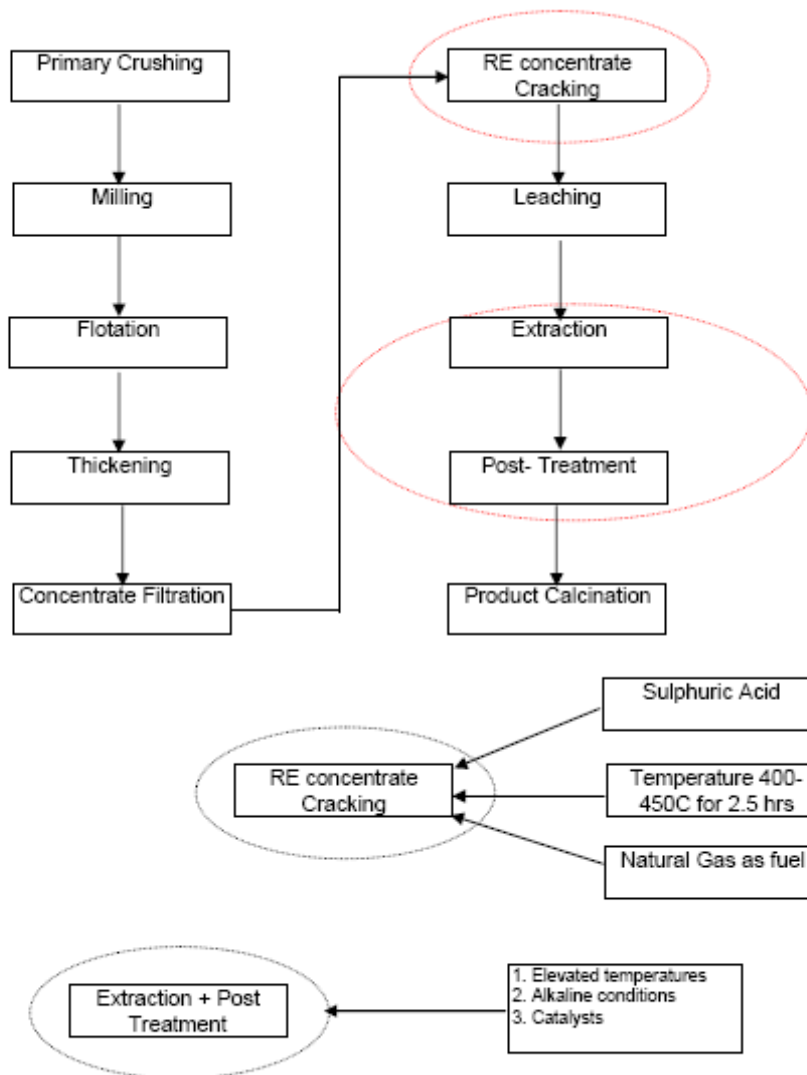
1. Apply a Screening Matrix to identify Main Source Categories.
2. Check subcategories to identify existing activities and sources in the country.
3. Gather detailed information on the processes and classify processes into similar groups by applying the Standard Questionnaire.
4. Quantify identified sources with default/measured emission factors.
5. Apply the approach nation-wide to establish a full inventory and report results using guidance given in the standard format

The UNEP Toolkit methodology is generally designed to quantify the PCDDs and PCDFs nationwide; therefore, for this project the Toolkit was used to identify the major process that contribute to PCDDs and PCDFs emissions from the Advanced Materials Plant, and to quantify their emissions based on emissions from similar processes that are closely related to lanthanide ore extraction.



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7. PROCESS DESCRIPTION





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7.1 Main Phases

Lanthanide Concentrate Cracking

The lanthanide concentrate produced by the concentrator plant (located in Australia) is transported to the lanthanide concentrate feeder. This concentrate is further fed into the feeder of the cracking workshop through a belt conveyor. The weighed concentrate is fed into concentrate acid mixers where 98% sulphuric acid is added. This mixture further flows into rotary kilns that are fuelled by natural gas for intensive roasting at 400-450°C for 2.5 hrs.

The roasted concentrate from the kiln is crushed by roller crushers before the concentrate enters the 5-stage continuous leaching tanks.

Extraction and Post Treatment

The extraction process involves the use of mixer settlers where the organic and aqueous phases flow conversely. During the aqueous phase diluted sulphuric acid and hydrochloric acid are used to scrub the lanthanide of impurities. The organic phase involves the use of six different organic materials for extraction. These include:

- P₂₀₄, D₂HEPA/HDEHP, C₁₆H₃₅O₄P
- P₅₀₇, HEH[EHP]PA
- N₂₃₅, Iso Octylamine
- Isooctyl alcohol, C₃(C₂H₅)C₅H₁₀OH
- Naphthenic acid
- Kerosene

During the post treatment stage various lanthanide products are produced after coming in contact with sodium carbonate solution. This stage also involves the use of hydrochloric acid to wash out aluminium. The various lanthanide products produced in this stage are:

- LCPN Carbonate
- SEG-HRE Carbonate
- Lanthanum Chloride
- Lanthanum Carbonate, LaCe Carbonate, Cerium Carbonate
- Dydimium Oxide

The PCDDs and PCDFs from these processes are relatively negligible. See section 8 for the quantification of PCDDs and PCDFs generated from the processes at the facility.



7.2 Conditions for Dioxins and Furans to Form

7.2.1 Introduction

PCDDs and PCDFs are formed as unintentional by-products in certain processes and activities. Besides being formed as unintentional by-products of manufacturing or disposal processes, PCDDs/PCDFs may also be introduced into processes as contaminants in raw materials. Consequently, PCDDs/PCDFs can occur even where PCDDs/PCDFs are not formed in the process under consideration. PCDDs/PCDFs formation routes can be divided into two broad categories: (a) formation in thermal processes and (b) formation in industrial-chemical processes, as outlined in the following sections.

General Conditions

Conditions conducive for the formation of dioxin and furans in conventional incinerators include:

- in-complete or inefficient combustion caused by poor circulation of air inside the incineration chamber;
- formation of 'colder areas' within the incineration chamber; and
- in-coming waste streams that contain chlorinated plastics and hydrocarbons.

Process Specific Conditions

The rotary kilns proposed by Lynas for the facility differs from conventional incinerators in the following manner:

- the incoming gas stream is counter flowed to the general direction of particle travel resulting in thorough mixing of the entrained gas stream;
- the walls of the kilns will be insulated with refractory brick which is maintained at an elevated temperature eliminating 'cold spots' where inefficient combustion and anoxic or chemically 'reducing' conditions can predominate; and
- the elevated temperatures and oxygen abundant conditions favour the destruction of any entrained organic carbon which may in other circumstances result in PCDD and PCDF formation.



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7.2.2 Formation of PCDDs/PCDFs in Thermal Processes

PCDDs/PCDFs are formed in trace quantities in combustion processes when carbon, oxygen, hydrogen and chlorine are present in a temperature range between 200°C and 650°C. Formation occurs via two primary mechanisms:

1. the so-called *de novo* synthesis in which PCDDs/PCDFs are formed from non extractable carbon (C) structures that are basically dissimilar to the final product (PCDDs/PCDFs); and
2. precursor formation/reactions *via* aryl structures derived from either incomplete aromatic oxidation or cyclization of hydrocarbon fragments.

Factors that influence the formation of PCDDs and PCDFs in thermal processes include the following.

- **Combustion Technology:** PCDDs/PCDFs formation can occur either in poor combustion or in poorly managed post-combustion chambers and air pollution control devices.
- **Temperature:** Temperatures between 200°C and 650°C in the post-combustion zone or air pollution control devices have been reported to be conducive for the formation of PCDDs and PCDFs. The range of greatest formation is generally in the range of 200°C to 450°C, with a maximum at approximately 300°C.
- **Metals:** Copper, iron, zinc, aluminium, chromium, and manganese are known to catalyse PCDDs/PCDFs formation.
- **Chlorine:** Chlorine must be present in organic, inorganic or elemental form. Its presence in fly ash or in the elemental form in the gas phase may be especially important.
- **Sulphur and Nitrogen:** Sulphur- and nitrogen-containing chemicals inhibit the formation of PCDDs/PCDFs but may give rise to other by-products.

7.2.3 Formation of PCDDs/PCDFs in Industrial-Chemical Processes

In chemical manufacturing processes, as with thermal processes, carbon, hydrogen, oxygen, and chlorine are required and the generation of PCDDs and PCDFs is favoured if one or several of the conditions below apply:

- elevated temperatures (>150 °C);
- alkaline conditions (especially during purification);
- metal catalysis; or
- ultraviolet (UV) radiation or substances that generate radicals.



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In the manufacture of chlorine-containing chemicals, the following processes have been identified as sources of PCDDs and PCDFs with a decreasing probability of generating PCDDs/PCDFs (from first to last):

- chlorinated phenols and their derivatives;
- chlorinated aromatics and their derivatives;
- chlorinated aliphatic chemicals; and
- chlorinated catalysts and inorganic chemicals.

7.2.4 Applicability to Advanced Materials Plant

It is possible that the processes at the plant could potentially contribute to minor emissions of PCDDs and PCDFs. The majority would emanate from the rotary kiln cracking chamber under unfavourable combustion conditions and an excess of carbon. The following section quantifies the yield and emission factors for the cracking process based on the UNEP Toolkit.



8. ESTIMATE OF YIELD/PRODUCTION OF PCDDS, PCDFS

8.1 Overview

The estimation of the PCDDs and PCDFs was based on the methodology outlined in the recommended methods of the UNEP Standardized Toolkit for the Identification and Quantification of Dioxin and Furan Releases (February 2005). The study examined the potential for PCDDs and PCDFs to arise from air emissions from the plant operations which were identified as the most relevant for the purposes of this study.

The calculation of the annual Toxic Equivalent (TEQ) as per the UNEP Toolkit methodology and the estimation of dioxin and furan concentrations in the emissions from the plant (i.e. scrubber exit gas) was conducted to enable comparison to Malaysian regulations. Currently, the permissible limit for dioxin and furan in air emissions for new facilities in Malaysia is 0.1 ng/Nm³ TEQ.

Step 1: Identification of products/waste streams associated with the lanthanide processing industry

Gaseous products/waste streams associated

1. Natural gas
2. Air/natural air
3. Waste gas

Liquid products/waste streams associated

1. 98% H₂SO₄ (sulphuric acid)
2. Primary leaching slurry
3. Washing water
4. Primary leachate
5. Neutralized slurry
6. Neutralized leachate
7. Water leaching liquor
8. Process water
9. Acidified residue slurry



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10. Acidified residue filtrate

11. Reclaiming water

Solids products/waste streams associated

1. Feed concentrate
2. Cracked product
3. Primary leaching residue
4. MgO (Magnesium oxide for neutralization)
5. Neutralized residue

Step 2: Identification of the likely primary contributors for PCDDs and PCDFs (natural gas, H₂SO₄, other processes taking place in rotary kiln)

Step 3: Process classification and quantification, where the worst case quantitative yield estimates were derived.

The plausible contributors of minor quantities of PCDDs and PCDFs during the rotary kiln cracking stage are the chloride content of the lanthanide concentrate coupled with H₂SO₄ and natural gas. The gaseous discharge temperature of the kiln is maintained at less than 300°C although it is understood the solid, calcined product achieves temperatures up to a maximum of 450°C.

8.2 Primary Sources

The emission values for the primary sources of PCDD and PCDF formation at the plant (natural gas, chloride content of concentrate coupled with H₂SO₄), are calculated in the following sections.

Natural Gas

Natural gas is used for heat production in the rotary kiln cracking phase. Therefore, PCDDs and PCDFs emissions may be generated during this phase. The emission factors used in this study were taken based on the *power and heat generation using natural gas (p.201 Table 82: Emission Factors for Category 3 Power and Heat Generation; UNEP 2005 Toolkit)*. The emission factor of 0.5 µg TEQ/TJ for air emissions was used.

Formula: Source strength = (Emission Factor (air)) * (Activity Rate/year)
Calculation: (0.5 µg TEQ/TJ) * (8656 TJ/year)

→ **0.0043 g TEQ/year** (for a single rotary kiln)



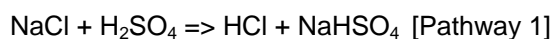
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→ 0.0086 g TEQ/year (for the two rotary kilns proposed for the facility)

Chloride Content of Lanthanide Concentrate Coupled with H₂SO₄

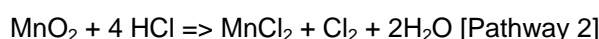
For the production of PCDDs and PCDFs the presence of chlorine gas is required. Although there is no chlorine gas directly present in the plant process, the circumstances under which PCDDs and PCDFs could be generated because of the presence of chloride ions (salts or non-metallic chloride) from the lanthanide concentrate ore were reviewed.

Chloride ions present in the lanthanide concentrate could potentially react with sulphuric acid to form hydrogen chloride gas or aqueous hydrochloric acid. The chloride salts can be NaCl, CaCl₂, MgCl₂ or others and the reaction would be as follows:



HCl as a result of this reaction could react with oxygen, if present in surplus, to produce gaseous chlorine. However, a review of available literature shows that a catalyst is required for the reaction to proceed. As no catalyst is available within the process, the reaction does not go ahead and the potential for the formation of PCDDs and PCDFs is unlikely.

The other source considered for the production of chlorine gas is the presence of manganese dioxide (MnO₂) in the lanthanide concentrate. It may react with hot hydrogen chloride gas (from Pathway 1) as follows.



For the production of chlorine gas via this process route, both manganese dioxide and a minimum concentration of gaseous HCl are required. This is considered unlikely, since HCl is highly reactive with the abundant alkaline earth minerals present in the lanthanide concentrate. However, after considering the possible presence of such chlorine emissions in the presence of H₂SO₄ an emission factor of 50µg TEQ/T (*P.76 table 25: Emission Factors for Copper Industry- Well Controlled, UNEP 2005*) was chosen. Since H₂SO₄ is used in the acid concentrate mixing process, it is assumed that any PCDDs and PCDFs generated will form during the rotary kiln cracking process. The total H₂SO₄ used at the plant is 56,240 t/year for the initial design case (IDC).

In the absence of PDDs and PCDFs emission data in the Toolkit for lanthanide facilities, similar emissions to the production of copper metal were assumed (chosen as a worst case scenario due to the presence of high temperatures and sulphuric acid in the rotary kiln process in the copper industry) to derive an emission factor of 50µg TEQ/t (based on the use of H₂SO₄).

Formula: Source strength = (Emission Factor (air)) * (Activity Rate/year)
Calculation: (50µg TEQ/TJ) * (56,240 t/year)



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→ 2.812 g TEQ/year (for a single rotary kiln)

8.3 Other Sources

For other potential sources besides the cracking process (as above), such as extraction and post-treatment processes, the emission factor used was taken from the cement industry (*p.109 Table 41: Emission Factors for Cement Production; UNEP 2005 Toolkit*). Since the kiln operates at a bed temperature > 300°C (at 450°C) the emission factor of 5 µg TEQ/T (air) was considered appropriate.

The total mass rate of the concentrate produced = 32,680 tonnes/annum.

Formula: Source strength = (Emission Factor (air)) * (Activity rate/year)
Calculation: (5 µg TEQ/t) * (32,680 t/year)

→ 0.1634 g TEQ/year

8.4 Results

Combining the calculations from all sources, the potential formation of dioxins and furans from the facility is **2.984 g TEQ/year**.



9. CONCLUSION

Rotary kilns of the cement industry and incinerators widely used throughout Asia differ in terms of their combustion conditions. Kiln feed and rotary kiln exhaust gases are conveyed in counter-flow and mixed thoroughly. Thus, temperature distribution and residence time in rotary kilns afford particularly favourable conditions for organic compounds, introduced either via fuels or derived from them, to be completely destroyed. For that reason, only very low concentrations of polychlorinated dibenzo-p-dioxins and dibenzofurans (colloquially dioxins and furans) can be found in the exhaust gas from cement rotary kilns. The exception to this is where chlorinated hydrocarbons have been used intermittently as fuel sources. This is now extremely rare.

Lynas propose to undertake combustion using counter-current air flow under which conditions the formation of dioxins and furans are not favourable.

Form this it is concluded that dioxins and furans will only be released when conditions arise which include the presence of chlorine gas, coupled with unspent or inefficiently combusted natural gas fuel. These reactants are unlikely to occur in the processes examined for the reasons outlined above. The addition of chloride containing materials to the lanthanide cracking stage is specifically discouraged since this provides the only mechanism for dioxins to form in the presence of a reductant and incompletely combusted gas or other hydrocarbons. Current levels are considered too low to provide the required conditions. It is concluded that the use of best available technologies (BAT) for air and water/residue treatment, as proposed for the Lynas project, will ensure that emissions of PCDDs and PCDFs will be non-existent or, at the most, insignificant.



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10. LIMITATIONS

This report has been compiled on the basis of a necessarily limited amount of information supplied to WorleyParsons by Lynas. Furthermore, the emission factors as contained within the UNEP Toolkit were considered to be the most relevant to this study in the absence of more concise information.

Calculations shown in this report have been carried out with the intention of reflecting conservative levels. However, WorleyParsons does not accept any responsibility for any on-site modifications implemented on either raw materials or process streams subsequent to the preparation of this report.