

**BEST AVAILABLE TECHNIQUES GUIDANCE DOCUMENT ON  
NON-METALLIC (MINERAL) INDUSTRY**

## **FOREWORD**

Best Available Techniques Economically Achievable (BAT) document had been prepared as a guidance notes for the nine (9) major industries in Malaysia and to support the implementation of the new Environmental Quality (Clean Air) Regulations 20xx. These documents were prepared based on the latest state-of-the-art technologies, internationally accepted limit values but had been adjusted and tailored to local requirements.

BAT is defined as the effective methods in preventing pollution and, where generally that is not practicable, to reduce emissions from industrial activities and their impact on the environment. This definition implies that BAT not only covers the technology used but also the way in which the installation is operated, to ensure a high level of environmental protection. Implementations of BAT in any specific industrial sectors are under economically and technically viable condition.

It is hope that the technical contents of these documents will prove beneficial to the industries in their endeavour to comply with the environmental regulations and standards through more cost-efficient means. In the identification of BAT, emphasis is placed on pollution prevention techniques rather than end-of-pipe treatment. These documents will be reviewed and updated from time to time.

These documents have been prepared in consultations with the University of Malaya Consultancy Unit (UPUM), Malaysia German Technical Cooperation (GTZ) and the relevant industries/stakeholders. The Department of Environment wishes to record appreciation to representatives of the relevant industrial sectors, government agencies and individuals for their invaluable input.

**DATO' HALIMAH HASSAN**

Director General

Department the Environment, Malaysia

## TABLE OF CONTENTS

<b>LIST OF TABLES</b>	<b>v</b>
<b>LIST OF FIGURES</b>	<b>v</b>
<b>LIST OF ABBREVIATIONS</b>	<b>vi</b>
<b>1.0 PREFACE</b>	<b>1</b>
1.1 Status of This Document	1
1.2 Definition of BAT	1
1.3 Objective of This Document	3
1.4 Information Sources	3
1.5 How to Use This Document	4
<b>2.0 OVERVIEW OF NON METALLIC (MINERAL) INDUSTRY</b>	<b>5</b>
<b>3.0 PROCESS DESCRIPTIONS</b>	<b>7</b>
3.1 Cement Plants	7
3.2 Lime Production Plants	10
3.3 Glass Production Plants	<b>13</b>
<b>4.0 PROCESS OPTIMIZATION</b>	<b>21</b>
<b>5.0 SOURCES OF AIR POLLUTION</b>	<b>21</b>
5.1 Cement	21
5.2 Lime	23
5.3 Glass	<b>24</b>
<b>6.0. EMISSION CONTROL OPTIONS</b>	<b>26</b>
6.1 Cement Productions	26
6.2 Lime Productions	29
6.3 Glass Productions	<b>31</b>
<b>7.0 RECOMMENDED PRACTICE AND EMISSION VALUES</b>	<b>32</b>
7.1 Cement	32
7.2 Lime	33
7.3 Glass	34

<b>8.0</b>	<b>EMISSION MONITORING AND REPORTING</b>	<b>34</b>
8.1	Cement Plants	34
8.2	Lime Plants	35
8.3	Glass Plants	35
	<b>REFERENCES</b>	<b>36</b>

## LIST OF TABLES

Table 1:	Important Glass Making Raw Material	16
Table 2:	Elements That Can Be Added to Obtain Specific Glass Color	17
Table 3:	Typical Container Glass Composition	18
Table 4:	Summary of Emissions to Atmosphere Arising from Melting Activities	25
Table 5:	Recommended Emission Limits for Cement Plant more than 30 Ton/ Hour	33
Table 6:	Recommended Emission Limits for Lime Producing Plant	33
Table 7:	Recommended Emission Limits for Glass Producing Plant	34

## LIST OF FIGURES

Figure 1:	Approved investments in the non-metallic mineral products industry by sub-sector, 2012 (RM mil)	6
Figure 2:	Schematic of Dry Cement Production Process	8
Figure 3:	Overview of Lime Manufacturing Process	11
Figure 4:	Press and Blow Forming	20

## LIST OF ABBREVIATIONS

BAT	-	Best Available Techniques
BREF	-	Best Available Technique Reference
CaCo <sub>3</sub>	-	Calcium Carbonate
CAR	-	Clean Air Regulation Document
CO	-	Carbon Monoxide
DOE	-	Department of Environment
IPPC	-	Integrated Pollution Prevention and Control
mg/Nm <sup>3</sup>	-	milligram per cubic meter at standard temperature (273K) and pressure (1atm)
NO <sub>x</sub>	-	Nitrogen Oxide
PAH	-	Polycyclic Aromatic Hydrocarbon
PCB	-	Polychlorinated biphenyl
PCDD/F	-	Polychlorinated dibenzo-p-dioxin furan
RAC	-	Regenerative Activated Carbon
ROK	-	Run of Kiln
SCR	-	Selective Catalytic Reduction
SNCR	-	Selective Non-Catalytic Reduction
SO <sub>x</sub>	-	Sulphur Dioxide

## **1.0 PREFACE**

### **1.1 Status of This Document**

This document forms a part of a series presenting the guidance notes for selected industries in Malaysia (list given at the end of this preface) to apply best available techniques economically achievable (BAT), associated monitoring and developments in them. This series is published by the Department of Environment (DOE) in accordance to the Environmental Quality (Clean Air) Regulations 2014 (CAR 2014).

### **1.2 Definition of BAT**

In order for the user of this document to understand the legal context of this document, the interpretation on the definition of BAT is taken from Regulation 2 – Interpretation of CAR 2014 and described as below:

“Best Available Techniques Economically Achievable” means the effective methods in preventing pollution and, where that is not practicable, generally to reduce emissions in the air from the industrial activities and their impact on the environment as a whole. In this regard:

“Techniques” includes both the technology used and the way in which the facility is designed, built, maintained, operated and decommissioned;

“Available Techniques” means those techniques that are accessible to the occupier and that are developed on a scale that allows implementation in the relevant industrial sector, under economically and technically viable conditions, taking into consideration the costs and advantages; and

“Best” means effective in achieving a high general level of protection of the environment as a whole;

On the basis of this assessment, techniques, and as far as possible emission and consumption levels associated with the use of BAT, are presented in this document that are considered to be appropriate to the sector as a whole and in

many cases reflect current performance of some installations within the sector. Where emission or consumption levels “associated with best available techniques” are presented, this is to be understood to mean those levels representing the environmental performance that could be expected as a result of the application, of the techniques described, taking into account the balance of costs and advantages inherent within the definition of BAT. However, they are neither emission nor consumption limit values and should not be understood as such.

In some cases it may be technically possible to achieve better emission or consumption levels but due to the costs involved or cross media considerations, they are not considered to be appropriate as BAT for the sector as a whole. However, such levels may be considered to be justified in more specific cases where there are special driving forces.

The emission and consumption levels associated with the use of BAT have to be seen together with any specified reference conditions (e.g. averaging periods).

The concept of “levels associated with BAT” described above is to be distinguished from the term “achievable level” used elsewhere in this document. Where a level is described as “achievable” using a particular technique or combination of techniques, this should be understood to mean that the level may be expected to be achieved over a substantial period of time in a well maintained and operated installation or process using those techniques.

The actual cost of applying a technique will depend strongly on the specific situation such as taxes, fees, and the technical characteristics of the installation concerned. It is not possible to evaluate such site-specific economic viability of techniques drawn from observations on existing installations.

The purpose of CAR 2014 is to achieve prevention and control of pollution arising from activities listed in its First Schedule and Second Schedule. More specifically, it provides for a notification system for certain categories of



industrial installations to conduct an integrated and comprehensive view of the pollution and consumption potential of their installation. The overall aim is to ensure a high level of protection of the environment as a whole based on appropriate preventative measures through the application of BAT.

### **1.3 Objective of This Document**

The 'emission minimization principle' as cited in CAR 2014 requires that the goal of emission abatement is to achieve minimum emissions as a result of applying current BAT. Hence this guideline document is meant to provide the reference information for the permitting authorities to take into account when determining permit conditions. This document should serve as valuable input to achieve better environmental performance.

### **1.4 Information Sources**

The information is mainly based on the European IPPC BREF document where the assessment was achieved through an iterative process involving the following steps:

- identification of the key environmental issues for the sector
- examination of the techniques most relevant to address those key issues;
- identification of the best environmental performance levels, on the basis of the available data world-wide;
- examination of the conditions under which these performance levels were achieved; such as costs, cross-media effects, main driving forces involved in Implementation of these techniques;
- selection of the BAT and the associate emission and/or consumption levels for this sector

## **1.5 How to Use This Document**

It is intended that the general BAT in this document could be used to judge the current performance of an existing installation or to judge a proposal for a new installation and thereby assist in the determination of appropriate BAT based conditions for that installation. It is foreseen that new installations could be designed to perform at or even better than the general BAT levels presented here. It is also considered that many existing installations could reasonably be expected, over time, to move towards the general "BAT" levels or perform better. This reference document does not set legally binding standards, but they are meant to give information for the guidance of industry, the relevant government bodies and the public on achievable emission and consumption levels when using specified techniques.

The structure of the guideline document is as follows:

An overview of each particular sector in the Malaysian context is firstly covered briefly followed by process description, process optimization, sources of pollution, emission control options, recommended practices and emission values and finally emission monitoring and reporting. More often than not, trade-off judgements between different types of environmental impacts and specific site condition are the influencing factors.

Another important point to note is that BAT change over time and this guidance document needs to be reviewed and updated as appropriate.

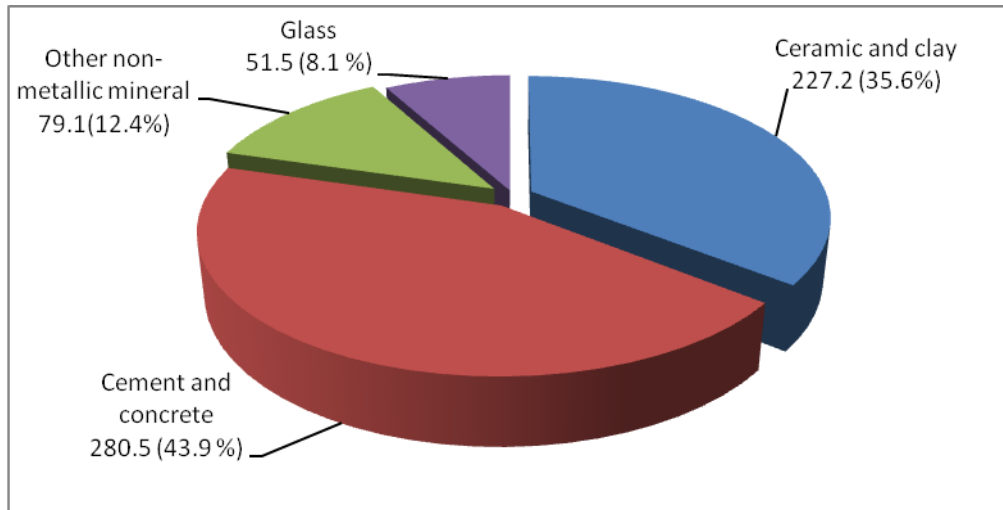
## **2.0 OVERVIEW OF NON-METALLIC (MINERAL) INDUSTRY**

The non-metallic mineral industry consists of ceramic and clay based products, cement and concrete products, glass products, and other non-metallic (mineral) products such as quicklime, barite, marble and granite. In 2012, the industry was the 14th largest export earner, with total exports of RM5.8 billion that contributed approximately 1.2 per cent to total exports of manufactured goods. Malaysia imported non-metallic mineral products amounting to RM5.3 billion for the same period. Major exports included glass and glassware (RM2.3 billion), mineral products (RM1.4 billion) and lime, cement and fabricated construction materials (RM935.6 million). The major export destinations were Singapore, Japan and Indonesia.

A total of 22 non-metallic mineral projects were approved in 2012 with total investments of RM638.3 million. Of the 22 projects approved, three projects (RM51.5 million) were for glass products, six projects (RM280.5 million) for cement and concrete products, 11 projects (RM227.2 million) for the manufacture of ceramic and clay products and two projects (RM79.1 million) for other non-metallic minerals. Three major projects were approved in 2012, the largest of which was a new Malaysian-Taiwanese joint venture project with investments of RM145 million to produce ground granulated blast-furnace slag. The product can be considered recycled material and significantly reduces energy consumption and greenhouse gas emission in the production of concrete raw materials. About 90 per cent of the production will be supplied domestically.

The second comprises a wholly foreign-owned project with investments of RM77.6 million to manufacture carbon fibre and graphite parts and components for machinery and equipment. This development, which is expected to generate 138 job opportunities with 20 per cent of them comprising skilled and technical positions, will see 80 per cent of its production exported to Japan. The third is a Malaysian-Singapore joint venture project with investments of RM71 million to produce and supply high calcium high re-activity industrial lime products such as hydrated lime, quicklime, calcium carbonate powder and lime slurry to

diverse industries. About 95 per cent of the production will be supplied to the domestic market.



**Figure 1 : Approved investments in the non-metallic mineral products industry by sub-sector, 2012 (RM mil)**

The advanced ceramics sub-sector, which comprises parts and components for application in electronics, aerospace, medical and other high technology industries, is a potential growth area in the non-metallic mineral product industry. This is attributed to Malaysia's status as one of the world's leading producers of electrical & electronic (E&E) components. In 2012, the E&E industry exported RM231.2 billion worth of output, comprising mostly semiconductors and components using advanced ceramics as raw material. High technology advancements in the E&E, aerospace and life sciences industries will provide vast opportunities for the application of advanced ceramics. These factors could enhance Malaysia's position as a preferred location for the manufacture of advanced ceramics products (Malaysia Investment Performance Report, 2012).

### 3.0 PROCESS DESCRIPTIONS

#### 3.1 Cement Plants

The basic chemistry of the cement manufacturing process involve the decomposition of calcium carbonate ( $\text{CaCO}_3$ ) at about 900 °C to obtain calcium dioxide (CaO) and liberated gaseous carbon dioxide ( $\text{CO}_2$ ), this process is known as calcinations. This is followed by the clinkering process in which the calcium oxide reacts at high temperature (typically 1400-1500 °C) with silica, alumina, and ferrous oxide to form the silicates, aluminates, and ferrites of calcium which comprise the clinker.

There are **main** process routes for the manufacture of cement.

- a. Dry process- The raw materials are ground and dried to raw meal in the form of a flowable powder and fed to the pre-heater or pre-calciner kiln or to a long dry kiln. A typical schematic of a dry process is shown in **Figure 2**.
- b. Semi-dry process-dry raw meal is palletized with water and fed into a grate pre-heater before the kiln or to a long kiln equipped with crosses.
- c. Semi-wet process- The slurry is first dewatered in filter presses. The filter cake is extruded into pellets and fed either to a grate pre-heater or directly to a filter cake drier for raw meal production.
- d. Wet process- The raw materials are ground in water to form a pumpable slurry. The slurry is either fed directly into the kiln or first to slurry drier.

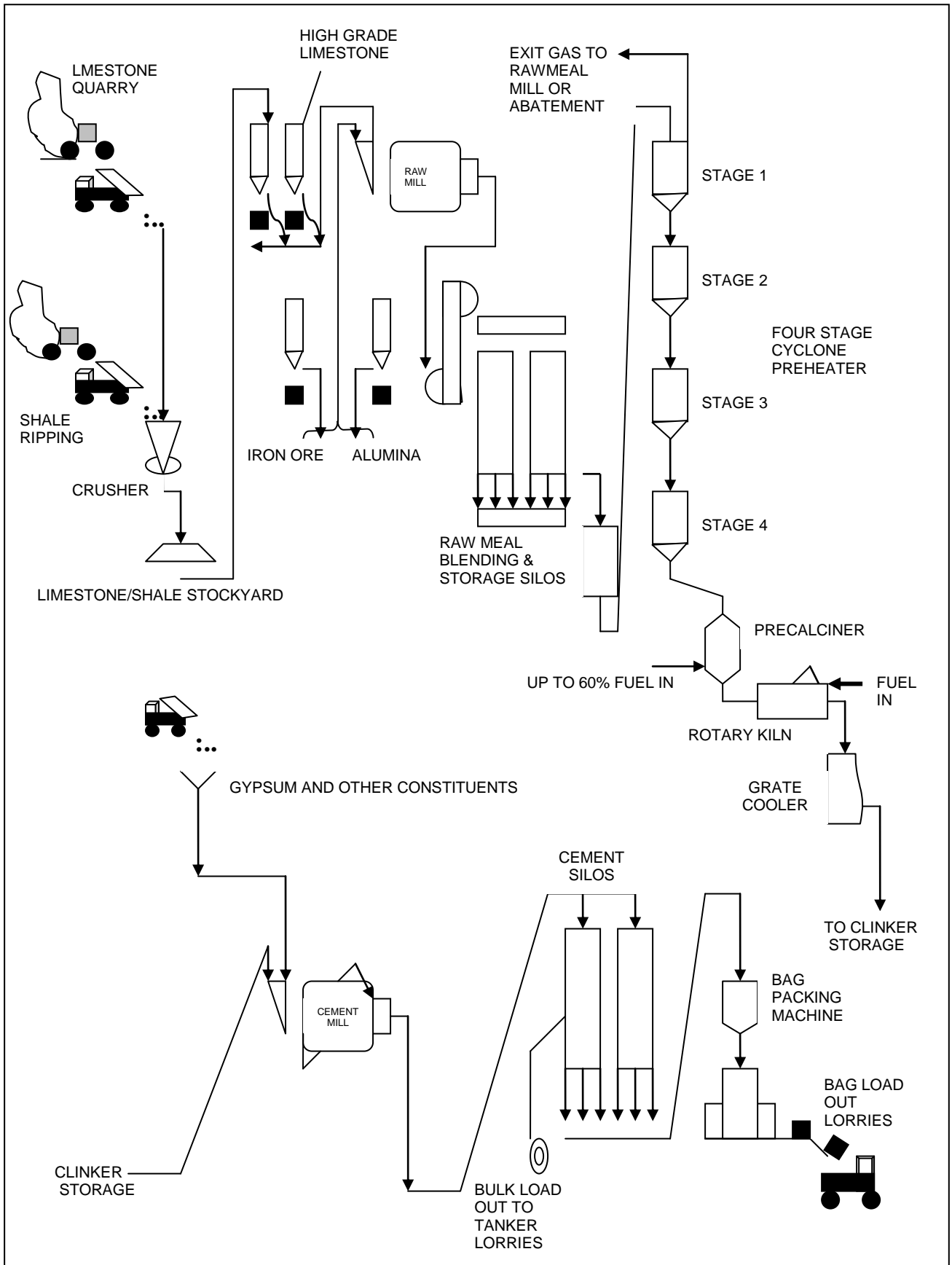


Figure 2: Schematic of Dry Cement Production Process

All processes the sub-processes mentioned above have the following sub-processes in common:

### **3.1.1 Raw Material-Storage and Preparation**

Preparation of the raw material is of great importance to the subsequent kiln system both in getting the chemistry of the raw feed right and in ensuring that the feed is sufficiently fine. This is achieved by controlling the feed into the raw grinding plant. The raw materials, in controlled proportions, are ground and mixed together to form a homogeneous blend with the required chemical composition.

Cement plants are currently substituting natural raw materials with alternative raw materials (ARM's). These ARMs can include industrial sludge, slag, ash and foundry sand to replace the major oxides required for the production clinker.

### **3.1.2 Fuel, Storage and Preparation**

Various fuel including fossil fuels such as coal, pet coke, fuel oil, natural gas etc, and waste fuels can be used to provide the heat required for the process. Examples of waste fuels included used tyres, sewage sludge, spent solvents, spent oil and biomass can be used to substitute fossil fuels in cement plants which leads to reduction of CO<sub>2</sub> emission from fossil fuel combustion plants.

### **3.1.3 Clinker Burning**

This part of the process is the most important in terms of emission potential and of product quality and cost. In clinker burning, the raw meal (or raw meal slurry in the wet process) is fed to the rotary kiln system where it is dried, pre-heated, calcined and sintered to produce cement clinker. The clinker is cooled with air and then stored. In the clinker burning process it is essential to maintain kiln charge temperatures of between 1400 to 1500 °C and gas temperatures of about 2000 °C. Also, the clinker needs to be burned under oxidizing conditions.

Therefore, an excess of air is required in the sintering zone of a cement clinker kiln.

#### **3.1.4 Cement Grinding and Storage**

Clinker and other cement components are stored in silos or in closed sheds. Portland cement is produced by intergrinding cement clinker and sulphates such as gypsum and anhydrite. In blended cements (composite cements) there are other constituents, such as granulated blast furnace slag, natural or artificial pozzolanas, limestone, or inert fillers. These will be interground with the clinker or may need to be dried and ground separately.

#### **3.1.5 Packing and Dispatch**

Cement is transferred from the silos either direct into bulk road or rail (or ship) tankers, or to a bag packing station.

### **3.2 Lime Production Plants**

The lime making process consists of the burning of calcium and/or magnesium carbonates at a temperature between 900 and 1500 °C, which is sufficiently high to liberate carbon dioxide, and to obtain CaO. The calcium oxide product from the kiln is generally crushed, milled and/or screened before being conveyed to silo storage. From the silo, the burned lime is either delivered to the end user for use in the form of quicklime, or transferred to a hydrating plant where it is reacted with water to produce hydrated or slaked lime. Lime production processes are illustrated in **Figure 3**.



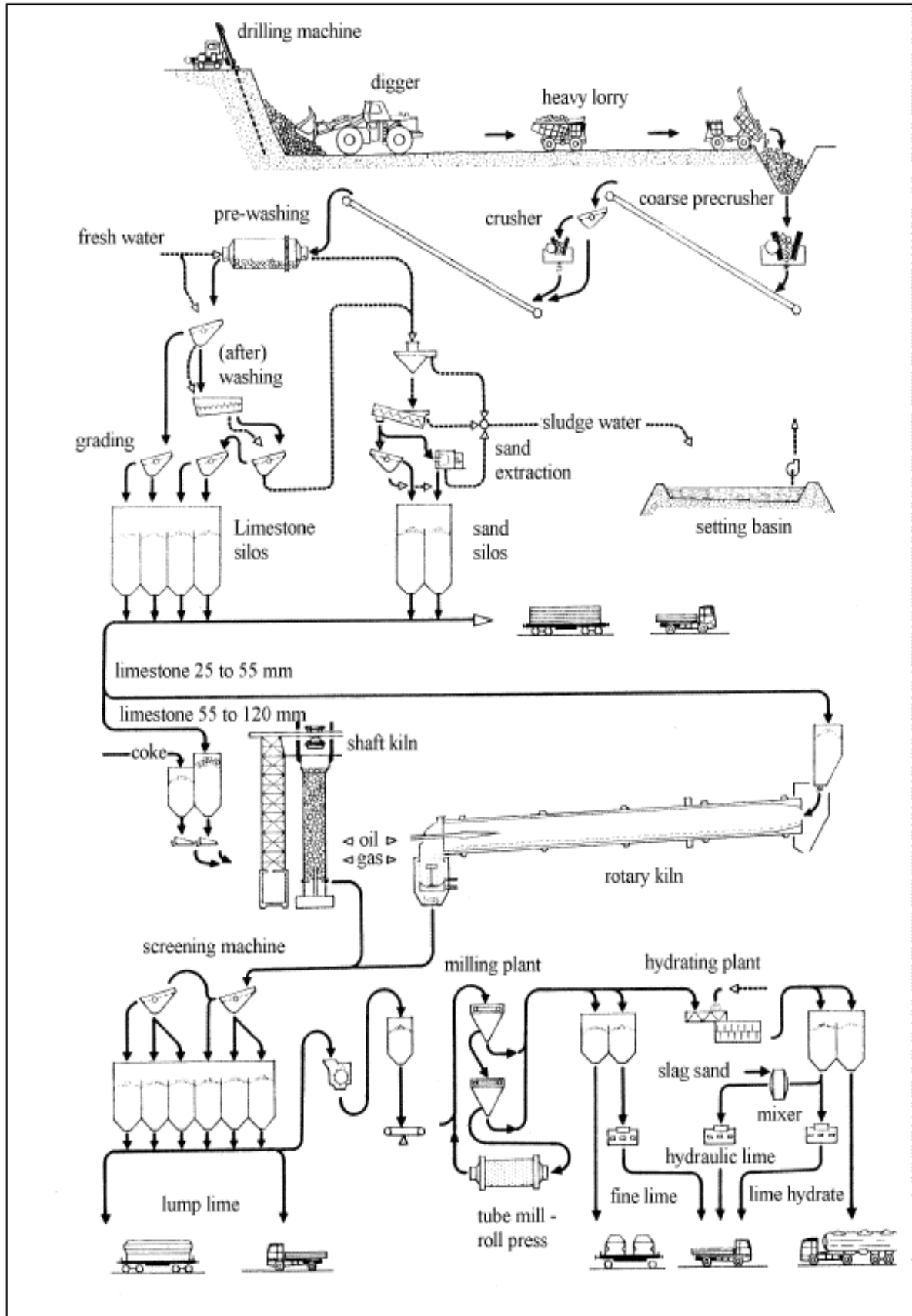


Figure 3: Overview of Lime Manufacturing Process

### **3.2.1 Mining of Limestone**

The main raw material for lime production is limestone. A typical mining process includes:

- Removal of the overburden (i.e., the soil, clay and loose rock overlying the deposit).
- Blasting of rock.
- Loading and transportation of the blasted rock to the crushing and screening plant.

### **3.2.2 Limestone Preparation and Storage**

Limestone is crushed to the appropriate size range, which is normally 5 to 200 mm depending upon the kiln used. Crushed stone from the primary crushers is transported via conveyors to vibrating screens, where large pieces are separated and recycled while those passing through are used as kiln charge, or may be fed into the secondary crushers located further down the process line.

### **3.2.3 Fuels, Storage and Preparation**

In lime burning, the fuel provides the necessary energy to calcine the lime. It also interacts with the process, and the combustion products react with the quicklime. Many different fuels are used in lime kilns.

### **3.2.4 Calcining of Limestone**

The lime burning process typically involves:

- providing sufficient heat at above 900 °C to heat the limestone and to cause decarbonation, and

- holding the quicklime for the requisite time at a sufficiently high temperature (typically in the range 1200 to 1300 °C to adjust reactivity).

### **3.2.5 Quicklime processing**

The objective of processing run-of-kiln (ROK) quicklime is to produce a number of grades with the particle sizes and qualities required by the various market segments. A number of unit processes are used, including screening, crushing, pulverizing, grinding, air-classifying and conveying.

### **3.2.6 Production of Slaked lime**

Slaked lime includes hydrated lime (dry calcium hydroxide powder), milk of lime and lime putty (dispersions of calcium hydroxide particles in water). The hydration of lime involves the addition of water in a hydrator ( $\text{CaO} + \text{H}_2\text{O} \rightarrow (\text{Ca}(\text{OH})_2)$ ).

### **3.2.7 Storage and Handling**

Quicklime is preferably stored in dry conditions, free from draughts to limit air slaking. Great care is exercised to ensure that water is excluded from the lime, as hydration liberates heat and causes expansion, both of which could be dangerous. Air pressure discharge vehicles are able to blow directly into the storage bunker, which is fitted with a filter to remove dust from the conveying air. The filter should be weatherproof and watertight. Hydrated lime absorbs carbon dioxide from the atmosphere, forming calcium carbonate and water. Therefore, it is best stored in dry draft-free conditions.

### **3.3 Glass Production Plants**

#### **3.3.1 Characteristics of Glass**

The term glass does not have a convenient simple definition. In its broadest sense glass is a collective term for an unlimited number of materials of different compositions in a glassy state. Glasses are structurally similar to liquids, but at ambient temperatures they react to the impact of force with elastic deformation and so must also be considered to behave as solids. The use of the term glass is generally restricted to inorganic substances and not used in connection with organic materials such as transparent plastics.

#### **3.3.2 Broad Classification of Glass Types**

The most widely used classification of glass type is by chemical composition, which gives rise to four main groupings: soda lime glass, lead crystal and crystal glass, borosilicate glass and special glasses. The first three of these categories account for over 95% of all glass produced. The thousands of special glass formulations produced mainly in small amounts account for the remaining 5%. With very few exceptions most glasses are silicate based, the main component of which is silicon dioxide ( $\text{SiO}_2$ ).

##### **3.3.2.1 Soda-lime Glasses**

Soda-lime glass is used for bottles, jars, everyday tableware and window glass. A typical soda-lime glass is composed of 71 – 75 % silicon dioxide ( $\text{SiO}_2$  derived mainly from sand), 12 – 16 % sodium oxide ('soda'  $\text{Na}_2\text{O}$  from soda ash –  $\text{Na}_2\text{CO}_3$ ), 10 – 15 % calcium oxide ('lime'  $\text{CaO}$  from limestone –  $\text{CaCO}_3$ ) and low levels of other components designed to impart specific properties to the glass.

### **3.3.2.2 Lead Crystal and Crystal Glass**

Lead oxide can be used to replace much of the calcium oxide in the batch to give a glass known popularly as lead crystal. A typical composition is 54 – 65 %  $\text{SiO}_2$ , 25 – 30 %  $\text{PbO}$  (lead oxide), 13 – 15 %  $\text{Na}_2\text{O}$  or  $\text{K}_2\text{O}$ , plus other various minor components. This type of formulation, with lead oxide content over 24 %, gives glass with a high density and refractive index, thus excellent brilliance and sonority, as well as excellent workability allowing a wide variety of shapes and decorations. Typical products are high quality drinking glasses, decanters, bowls and decorative items.

### **3.3.2.4 Borosilicate Glasses**

Borosilicate glasses contain boron trioxide ( $\text{B}_2\text{O}_3$ ) and a higher percentage of silicon dioxide. A typical composition is 70 - 80 %  $\text{SiO}_2$ , 7 - 15 %  $\text{B}_2\text{O}_3$ , 4 - 8 %  $\text{Na}_2\text{O}$  or  $\text{K}_2\text{O}$ , and 2 - 7 %  $\text{Al}_2\text{O}_3$  (aluminium oxide). Glasses with this composition show a high resistance to chemical corrosion and temperature change (low thermal expansion coefficient). Applications include chemical process components, laboratory equipment, pharmaceutical containers, lighting, cookware, and oven doors and hobs. Many of the borosilicate formulations are for low volume technical applications and are considered to fall into the special glass category. A further application of borosilicate glass is the production of glass fiber, both continuous filaments and glass wool insulation.

### **3.3.2.5 Special Glasses**

This is an extremely diverse grouping, which covers the specialized low volume, high value products, the compositions of which vary very widely depending on the required properties of the products. Some of the applications include: specialist borosilicate products; optical glass, glass for electro technology and electronics; cathode ray tubes; fused silica items; glass seals; X-ray tubes; glass solders; sintered glass; electrodes; and glass ceramics.

### 3.3.3 Typical Glass Products

There are many types of glass products available (flat, container, continuous filament, domestic glass, special glass, mineral wool, ceramic fiber and frits). In Malaysia largest glass production is the container glass type. The sector covers the production of glass packaging i.e. bottles and jars. The main environmental problem associated with container glass production is that it is a high temperature, energy intensive process. This results in the emission of products of combustion and the high temperature oxidation of atmospheric nitrogen; i.e. sulphur dioxide, carbon dioxide, and oxides of nitrogen. Furnace emissions also contain dust (arising from the volatilization and subsequent condensation of volatile batch materials) and traces of chlorides, fluorides and metals present as impurities in the raw materials.

### 3.3.4 Raw Materials for Glass Making

**Glass forming materials:**

Silica sand, process cullet, post consumer cullet

**Intermediate and modifying materials:**

Soda ash ( $\text{Na}_2\text{CO}_3$ ), limestone ( $\text{CaCO}_3$ ), dolomite ( $\text{CaCO}_3.\text{MgCO}_3$ ), feldspar, nepheline syenite, potassium carbonate, fluorspar, alumina, zinc oxide, lead oxide, barium carbonate, basalt, anhydrous sodium sulphate, calcium sulphate and gypsum, barium sulphate, sodium nitrate, potassium nitrate, boron containing materials (e.g. borax, colemanite, boric acid), antimony oxide, arsenic trioxide, blast furnace slag (mixed calcium, aluminium, magnesium silicate and iron sulphide)

**Colouring/Decolouring agents:**

Iron chromite ( $\text{Fe}_2\text{O}_3.\text{Cr}_2\text{O}_3$ ), iron oxide ( $\text{Fe}_2\text{O}_3$ ), cobalt oxide, selenium/zinc selenite

**Table 1: Important Glass Making Raw Materials**

Sand is the most important raw material for glass making, being the principal source of  $\text{SiO}_2$ . It is a common raw material but most deposits are not of sufficient purity for glass making. The melting point of sand is too high for economic melting and a fluxing agent, usually sodium oxide, is needed to reduce the melting temperature.

---

Soda ash ( $\text{Na}_2\text{CO}_3$ ) is the main source of the fluxing agent sodium oxide ( $\text{Na}_2\text{O}$ ). During melting the sodium oxide becomes part of the melt and the carbon dioxide is released. Sodium sulphate is added as a refining and oxidizing agent and is a secondary source of sodium oxide. Other metal oxides are added to the glass to reinforce the structural network to improve the hardness and chemical resistance. Calcium oxide ( $\text{CaO}$ ) has this effect and is added to the glass as calcium carbonate ( $\text{CaCO}_3$ ) in the form of limestone or chalk. It can also be added as dolomite, which contains both calcium carbonate and magnesium carbonate ( $\text{MgCO}_3$ ).

Aluminium oxide ( $\text{Al}_2\text{O}_3$ ) is added to improve chemical resistance and to increase viscosity at lower temperatures. It is usually added as nepheline syenite ( $\text{Na}_2\text{O} \cdot \text{K}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot \text{SiO}_2$ ), feldspar, or alumina, but is also present in blast furnace slag and feldspatic sand.

Lead oxides ( $\text{PbO}$  and  $\text{Pb}_3\text{O}_4$ ) are used to improve the sonority and to increase the refractive index of the glass to give better brilliance in products such as lead crystal. Barium oxide (derived from barium carbonate), zinc oxide, or potassium oxide may be used as alternatives to lead oxide, but they produce lower levels of density and brilliance than those associated with lead crystal. There is also a penalty in the workability of handmade glass.

Boron trioxide ( $\text{B}_2\text{O}_3$ ) is essential in some products, particularly special glass (borosilicate glasses) and in glass fibers (glass wool and continuous filaments). The most important effect is the reduction of the glass expansion coefficient, but in fibers it also changes viscosity and liquidity to aid fiberisation, and confers resistance to attack by water. **Table 2** shows some of the elements used to impart colour to the glass. The colouring materials can be added either in the main batch or into the canal following the furnace (in the form of coloured frit).

**Table 2: Elements That Can Be Added to Obtain Specific Glass Color**

Element	Ion	Colour
Copper	(Cu <sup>2+</sup> )	Light blue
Chromium	(Cr <sup>3+</sup> )	Green
	(Cr <sup>6+</sup> )	Yellow
Manganese	(Mn <sup>3+</sup> )	Violet
Iron	(Fe <sup>3+</sup> )	Yellowish-brown
	(Fe <sup>2+</sup> )	Bluish-green
Cobalt	(Co <sup>2+</sup> )	Intense blue, in borate glasses, pink
	(Co <sup>3+</sup> )	Green
Nickel	(Ni <sup>2+</sup> )	Greyish-brown, yellow, green, blue to violet, depending on the glass matrix.
Vanadium	(V <sup>3+</sup> )	Green in silicate glass; brown in borate glass
Titanium	(Ti <sup>3+</sup> )	Violet (melting under reducing conditions).
Neodymium	(Nd <sup>3+</sup> )	Reddish-violet
Selenium	(Se <sup>0</sup> )	Pink (also Se <sup>2+</sup> , Se <sup>4+</sup> , and Se <sup>6+</sup> , depending on glass type)
Praseodymium	(Pr <sup>3+</sup> )	Light green

### 3.3.5 Glass Melting

Melting, the combination of the individual raw materials at high temperature to form a molten glass is the central phase in the production of glass. There are numerous ways to melt glass depending on the desired product, its end use, the scale of operation, and the prevailing commercial factors. The glass formulation, raw materials, melting technique, fuel choice and furnace size will all depend on these factors.

### 3.3.6 Container Glass Making

Typical container glass composition is given in **Table 3** below:



**Table 3: Typical Container Glass Composition**

Component	Percentage
Silicon Oxide (SiO <sub>2</sub> )	71 – 73
Sodium Oxide (Na <sub>2</sub> O)	12 - 14
Calcium Oxide (CaO)	9 – 12
Magnesium Oxide (MgO)	0.2 – 3.5
Aluminium Oxide (Al <sub>2</sub> O <sub>3</sub> )	1 – 3
Potassium Oxide (K <sub>2</sub> O)	0.3 – 1.5
Sulphur trioxide (SO <sub>3</sub> )	0.05 – 0.3
Colour modifiers etc.	Traces

Glass containers are produced in a two stage moulding process by using pressing and blowing techniques. There are five essential stages in automatic bottle production.

- a. Obtaining a piece of molten glass (gob) at the correct weight and temperature.
- b. Forming the primary shape in a first mould (blank mould) by pressure from compressed air or a metal plunger.
- c. Transferring the primary shape (parison) into the final mould (finish mould).
- d. Completing the shaping process by blowing the container with compressed air to the shape of the final mould.
- e. Removing the finished product for post forming processes.

Simplified diagrams of the two main forming processes are shown in **Figure 4**.

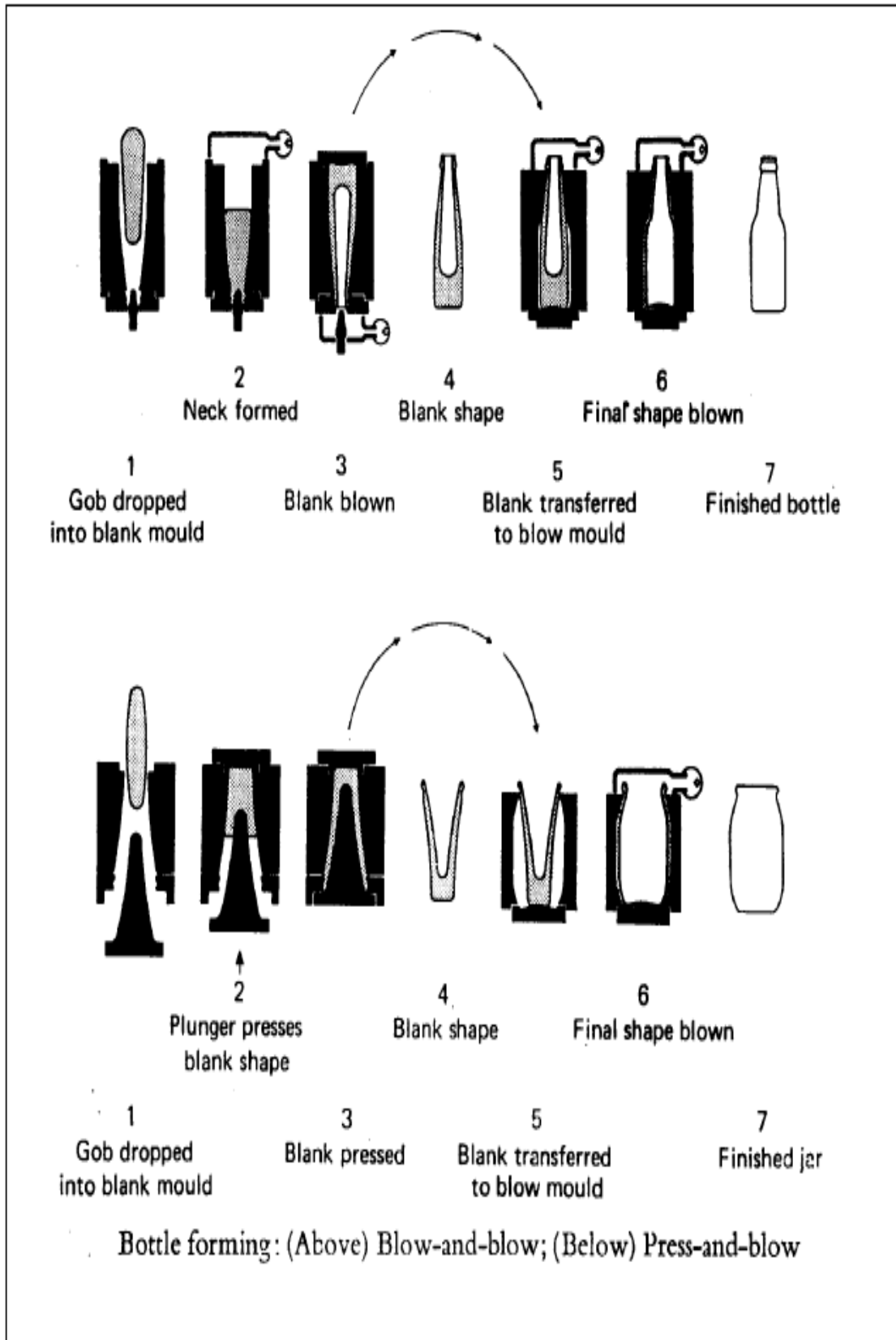


Figure 4: Press and Blow Forming

## **4.0 PROCESS OPTIMIZATION**

Process optimization aspect for cement, lime and glass production are largely dependent on raw materials, methods of production, size of plant and types of products. Some of the optimization steps are incorporated in emission control options and recommended practices and emission values section of this document.

## **5.0 SOURCES OF AIR POLLUTION EMISSIONS**

### **5.1 Cement**

#### **5.1.1 NO<sub>x</sub>**

NO and NO<sub>2</sub> are the dominant nitrogen oxides in cement kiln exhaust gases (NO >90% of the nitrogen oxides). There are two main sources for production of NO<sub>x</sub>:

- Thermal NO<sub>x</sub>: part of the nitrogen in the combustion air reacts with oxygen to form various oxides of nitrogen.
- Fuel NO<sub>x</sub>: nitrogen containing compounds, chemically bound in the fuel, react with oxygen in the air to form various oxides of nitrogen

#### **5.1.2 SO<sub>x</sub>**

When raw materials containing organic sulphur or pyrite (FeS) are used, the emissions of SO<sub>2</sub> can occur. Normally SO<sub>2</sub> is the main (99%) sulphur compound to be released in cement plants. It is also possible to produce SO<sub>3</sub> and in some cases H<sub>2</sub>S.

In a dry process kiln, sulphur introduced in the kiln system by the fuels is recaptured in the preheated tower via the formation of alkalis and sulphates by the partly pre calcined material.

### **5.1.3 Dust**

Traditionally the emission of dust, particularly from kiln main stacks, has been the main environmental concern in relation to cement manufacture. The point sources of dusts are kilns, raw mills, and clinker coolers, cement mills and coal mills.

### **5.1.4 CO<sub>x</sub>**

CO<sub>2</sub> emission in cement plant approximately 60% originates in the calcining process and the remaining 40% is related to fuel combustion. The emission of CO is related to the content of organic matter in the raw material, but may also result from poor combustion

### **5.1.5 Volatile Organic Compound (VOC's)**

Emissions of volatile organic compounds (VOC's) can occur in the primary steps of the process (pre-heater, pre-calciner), when organic matter that is present in the raw materials is volatilized as the feed is heated.

### **5.1.6 Polychlorinated Dibenzodioxins (PCDDs) and Polychlorinated Dibenzofurans (PCDFs)**

Formation of polychlorinated dibenzodioxins (PCDD's) and polychlorinated dibenzofurans (PCDF's) can result from combination of formation mechanisms, combustion conditions, kiln process design, feed characteristic and the type and operation of pollution control equipment. However, the main factors affecting PCDD/F emission are:

- Hydrocarbons;

- Chlorides;
- Catalyst;
- Appropriate temperature window (between 200<sup>0</sup>C and 450<sup>0</sup>C with maximum at 300<sup>0</sup>C-325<sup>0</sup>C); and
- A long retention time in appropriate temperature window.

### **5.1.7 Metal and Their Components**

The concentrations vary widely from one location to another depending on the type of raw materials. Metal compounds are classified based on the volatilities of the metals and their salts. Non volatile includes Ba, Be, Cr, As, Ni, V, Al, Ti, Ca, Fe, Mn, Cu and Ag. Semi volatile metal and compound includes Sb, Cd, Pb, Se, Zn, K and Na. Volatile metal compounds commonly found in cement plants are Hg and Tl.

## **5.2 Lime**

### **5.2.1 NO<sub>x</sub>**

NO<sub>x</sub> is commonly produces in lime producing plant and the emission concentration is largely dependent on type of kiln type used.

### **5.2.2 SO<sub>x</sub>**

In lime production plant, part of the sulphur in the fuel and limestone is expelled as sulphur dioxide in the exhaust gases.

### **5.2.3 Dust**

Dust is mainly generated in limestone calcination, lime hydrating and grinding processes. Dust is also generated in other subsidiary operations which include crushing, screening, conveying, slaking, storage and discharge.

#### **5.2.4 CO<sub>x</sub>**

The dissociation of limestone produces up to 0.75 tones of carbon dioxide (CO<sub>2</sub>) per tones of quicklime, depending on the composition of the limestone and the degree of calcination. CO is also normally produced due to incomplete combustion. Some limestone contain carbon, which can lead to higher CO emissions from the lime burning process

#### **5.2.5 Volatile Organic Carbon (VOC)**

Emissions of volatile organic compounds (VOC's) may occur for short periods during start-up. If the limestone contains a significant amount of organic matter, volatile organic compounds can be emitted continuously.

#### **5.2.6 Polychlorinated dibenzodioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs)**

Raw materials or fuels that contain chlorides may potentially cause the formation of polychlorinated dibenzodioxins (PCDD) and polychlorinated dibenzofurans (PCDF) in the heat (combustion) process of the lime kiln.

#### **5.2.7 Metals**

Little data is available concerning metal emissions. The high purity of most limestone used for the production of calcium and dolomitic limes means metal emissions are normally low.

### **5.3 Glass**

In general, glass making involves the melting of a significant mass of materials such as metal oxides, carbonates, sulphates and nitrates. On melting these substances decompose and release gases such as carbon dioxide, water vapor, and oxides of sulphur and nitrogen. The furnaces encountered within the Glass Industry, and within each sector, vary considerably in size, throughput,

melting technique, design, age, raw materials utilized, and the abatement techniques applied. Therefore, there is considerable variation in the pollutant gas and particles emissions. The main emissions arising from melting activities within the Glass Industry are summarized in **Table 4**.

**Table 4: Summary of Emissions to Atmosphere Arising From Melting Activities**

Emission	Source
Particulate matter	Condensation of volatile batch components. Carry over of fine material in the batch. Product of combustion of some fossil fuels.
NO <sub>x</sub>	Thermal NO <sub>x</sub> due to high melter temperatures. Decomposition of nitrogen compounds in the batch materials and oxidation of nitrogen contained in fuels.
SO <sub>x</sub>	Sulphur in fuel. Decomposition of sulphur compounds in the batch materials. Oxidation of hydrogen sulphide in hot blast cupola operations.
Chlorides /HCl	Present as an impurity in some raw materials. NaCl used as a raw material in some special glasses.
Fluorides/HF	Present as a minor impurity in some raw materials. Added as a raw material in the production to provide certain properties.
Heavy Metals (V, Ni, Cr, Se, Pb, Co, Sb, As, Cd)	Present as minor impurities in some raw materials, post consumer cullet, and fuels. Used in some special glass formulations. Selenium is used as a colourant (bronze glass), or as a decolorizing agent in some clear glasses.
CO <sub>2</sub>	Combustion product. Emitted after decomposition of carbonates in the batch materials (e.g. soda ash, limestone)
CO	Product of incomplete combustion.
H <sub>2</sub> S	Formed from raw material or fuel sulphur.

## **6.0 EMISSION CONTROL OPTION**

### **6.1 Cement Production**

#### **6.1.1 Process Selection**

The selected process has a major impact on the energy use and air emissions from the manufacture of cement clinker. For new plants and major upgrades the best available technique for the production of cement clinker is considered to be a dry process kiln with multi-stage preheating and precalcination. The associated BAT heat balance value ranges from 3000 - 3600 MJ/tonne clinker.

#### **6.1.2 General Primary Measures**

The best available techniques for the manufacturing of cement include the following general primary measures:

- A smooth and stable kiln process, operating close to the process parameter set points, is beneficial for all kiln emissions as well as the energy use. This can be obtained by applying:
  - Process control optimization, including computer-based automatic control systems.
  - The use of modern, gravimetric solid fuel feed systems.
- Minimizing fuel energy use by means of:
  - Preheating and precalcination to the extent possible, considering the existing kiln system configuration.
  - The use of modern clinker coolers enabling maximum heat recovery.
  - Heat recovery from waste gas.
  - Fossil fuel



- Minimizing electrical energy use by means of:
  - Power management systems.
  - Grinding equipment and other electricity based equipment with high energy efficiency.
  
- Careful selection and control of substances entering the kiln can reduce emissions.
  - When practicable selection of raw materials and fuels with low contents of pyrite sulphur, volatile organic compounds and volatile heavy metal
  - Apply quality assurance systems to characterize the waste and to analyze any waste that is to be used as raw material or fuel.

### **6.1.3 Reduction of NO<sub>x</sub>**

The best available techniques for reducing NO<sub>x</sub> emissions are the combination of the above described general primary measures and:

- Process Optimization
- Flame Cooling : 500 – 1000mg/ m<sup>3</sup> NO<sub>x</sub>
- Low NO<sub>x</sub> burner: 500- 1000 mg/m<sup>3</sup> NO<sub>x</sub>
- Stage combustion : 500-1000 mg/m<sup>3</sup> NO<sub>x</sub>
- Selective Non- catalytic Reduction (SNCR) : 200-500 mg/m<sup>3</sup> NO<sub>x</sub>
- Selective Catalytic Reduction (SCR) : 200 – 500 mg/m<sup>3</sup> NO<sub>x</sub>

The BAT emission level associated with the use is considered to be in the range 200-500 mg NO<sub>x</sub>/m<sup>3</sup> expressed as NO<sub>2</sub> on a daily average basis. There was also a view that selective catalytic reduction (SCR) is BAT with an associated emission level of 100-200 mg NO<sub>x</sub>/m<sup>3</sup> (as NO<sub>2</sub>), based upon SCR being regarded as an available and economically viable technique. Emission levels given are expressed on a daily average basis and standard conditions of 273 K, 101.3 kPa, 10% oxygen and dry gas.

#### 6.1.4 Reduction of SO<sub>x</sub>

The best available techniques for reducing SO<sub>x</sub> emissions are the combination of the above described general primary measures and:

- For initial emission levels not higher than about 1200 mg SO<sub>2</sub>/m<sup>3</sup>, use absorbent
- For initial emission levels higher than about 1200 mg SO<sub>2</sub>/m<sup>3</sup> use wet scrubber and dry scrubber.

The BAT emission level associated with the use of these techniques is in the range 200-400 mg/m<sup>3</sup> expressed as SO<sub>2</sub> on a daily average basis.

A wet scrubber can achieve a level of less than 200 mg SO<sub>2</sub>/m<sup>3</sup>, irrespective of initial concentration. The SO<sub>2</sub> reduction achieved with dry scrubbing is up to 90% that corresponds to a clean gas content of 300 mg SO<sub>2</sub>/m<sup>3</sup> when the initial SO<sub>2</sub> concentration is 3000 mg /m<sup>3</sup>. A wet scrubber can be fitted to all kilns, and a dry scrubber can be fitted to all dry kilns.

#### 6.1.5 Reduction of Dust

The best available techniques for reducing dust emissions are the combination of the above described general primary measures and:

- Minimization/prevention of dust emissions from fugitive sources
- Efficient removal of particulate matter from point sources by application of:
  - Electrostatic precipitators with fast measuring and control equipment
  - Fabric filters with multiple compartments and 'burst bag detectors'

The BAT emission level associated with these techniques is 20-30 mg dust/m<sup>3</sup> on a daily average basis. This emission level can be achieved with new or

upgraded electrostatic precipitators and/or fabric filters at the various types of installations in the cement industry.

### **6.1.6 Controlling Volatile Component and Metal Emissions**

Material control is the most significant method. If material choice cannot be avoided, adsorption using activated carbon can be considered.

## **6.2 Lime Production**

Emission levels given below are expressed on a daily average basis and standard conditions of 273 K, 101.3 kPa, 10% oxygen and dry gas, except for hydrating plants for which conditions are as emitted.

### **6.2.1 General Primary Measures**

Best available techniques for the manufacturing of lime include the following general primary measures:

- A smooth and stable kiln process, operating close to the process parameter set points, is beneficial for all kiln emissions as well as the energy use. This can be obtained by applying process control optimization.
- Minimizing fuel energy use by means of heat recovery from exhaust gases.
- Minimizing electrical energy use by means of utilization of mills and other electricity based equipment with high energy efficiency.
- Minimizing limestone consumption by means of kiln selection to make optimum use of quarried limestone and specific quarrying and well-directed use of limestone (quality, grain size).
- Careful selection and control of substances entering the kiln can reduce/avoid emissions. Example is selection of fuels with low contents of sulphur (rotary kilns in particular), nitrogen and chlorine.

### **6.2.2 Dust Reduction**

Best available techniques for reducing dust emissions are the combination of the above described general primary measures and:

- Minimization/prevention of dust emissions from fugitive sources.
- Efficient removal of particulate matter from point sources by application of :
  - Fabric filters with multiple compartments and 'burst bag detectors'
  - Electrostatic precipitators
  - Wet scrubbers

The BAT emission level associated with these techniques is 50 mg/m<sup>3</sup>. This emission level can be achieved by fabric filters and/or electrostatic precipitators and/or wet scrubbers at the various types of installations in the lime industry.

### **6.2.3 Controlling NO<sub>x</sub> Emission**

Emission can be controlled by selecting appropriate material and use of low NO<sub>x</sub> burners.

### **6.2.4 Controlling SO<sub>x</sub> Emission**

SO<sub>2</sub> emission can be controlled by proper selection of fuel.

### **6.2.5 Fugitive Dust Abatement**

The methods used for cement plants as described above can be used for fugitive dust abatement in a lime producing plants.

## **6.3 Glass Production**

### **6.3.1 Dust**

In general in this sector, BAT for dust is considered to be the use of an electrostatic precipitator or bag filter operating, where appropriate, in conjunction with a dry or semi-dry acid gas scrubbing system. The BAT emission level associated with these techniques is 5 – 30 mg/Nm<sup>3</sup> which generally equates to less than 0.1 kg/tonne of glass melted. Values in the lower part of the range given would generally be expected for bag filter systems. In some cases, the application of BAT for metals emissions may result in lower emission levels for dust.

### **6.3.2 NO<sub>x</sub>**

The main techniques (or combinations thereof) likely to represent BAT in this sector are primary measures (combustion modifications), 3R/Reburning (for regenerative furnaces), oxyfuel firing, SNCR or SCR. It is considered that the emission level for oxides of nitrogen (expressed as NO<sub>2</sub>) associated with the techniques that will generally constitute BAT is 500 – 700 mg/Nm<sup>3</sup> which generally equates to 0.5 – 1.1 kg/tonne of glass melted.

### **6.3.3 SO<sub>x</sub>**

For the emission levels given below the use of secondary abatement for dust is assumed, with dry or semi-dry acid gas scrubbing where appropriate.

Therefore in general in this sector, the emission levels associated with BAT for oxides of sulphur (expressed as SO<sub>2</sub>) are considered to be:

- For natural gas firing 200 – 500 mg/Nm<sup>3</sup> which generally equates to 0.3 to 0.75 kg/tonne of glass melted.

- For oil firing 500 – 1200 mg/Nm<sup>3</sup> which generally equates to 0.75 to 1.8 kg/tonne of glass melted.
- For natural gas firing up to 800 mg/Nm<sup>3</sup> which generally equates to 1.2 kg/tonne of glass melted
- For oil firing up to 1500 mg/Nm<sup>3</sup> which generally equates to 2.25 kg/tonne of glass melted

#### 6.3.4 Other Emissions from Melting

In general in this sector, BAT is considered to be raw material selection to minimize emissions, combined with acid gas scrubbing, where appropriate. Acid gas scrubbing may not always be necessary either to protect the abatement equipment or to achieve the figures given above for SO<sub>x</sub>. Where this is the case, acid gas scrubbing is considered to constitute BAT if the levels identified below cannot be achieved by primary measures. The emission levels associated with BAT for the pollutants specified below are considered to be:

- Chlorides (expressed as HCl) <30 mg/Nm<sup>3</sup>
- Fluorides (expressed as HF) <5 mg/Nm<sup>3</sup>
- Metals (Group 1 + 2) <5 mg/Nm<sup>3</sup>
- Metals (Group 1) <1 mg/Nm<sup>3</sup>

## 7.0. RECOMMENDED EMISSION VALUES

### 7.1 Cement

For cement industry the **Table 5** below list the recommend emission limits for plants with 30 ton clinker per hour.

**Table 5: Recommended Emission Limits for Cement Plant more than 30 Ton/Hour.**

<b>Pollutant</b>	<b>Limit</b>	<b>Measurement</b>
SO <sub>2</sub> (mg/Nm <sup>3</sup> )	400	Daily average
NO <sub>x</sub> (mg/Nm <sup>3</sup> )	500	Daily average
PCDD/F (ng TEQ/Nm <sup>3</sup> )	0.1	Daily average
Dust (mg/Nm <sup>3</sup> )	50	Daily average
TOC(mg/Nm <sup>3</sup> )	75	Half hourly
HCl (mg/Nm <sup>3</sup> )	30	Half hourly
HF (mg/Nm <sup>3</sup> )	5	Half hourly
NH <sub>3</sub> (mg/Nm <sup>3</sup> )	150	Half hourly
CO (mg/Nm <sup>3</sup> )	1000	Half hourly
Hg (mg/Nm <sup>3</sup> )	0.05	Half hourly
Total Cd, Tl, Hg (mg/Nm <sup>3</sup> )	0.2	Half hourly
Total Se, Te, AS, Co, Ni (mg/Nm <sup>3</sup> )	1.0	Half hourly
Total Sb, Pb, Cr, Cu, Mn, V, Sn (mg/Nm <sup>3</sup> )	5.0	Half hourly

Note: Reference condition at 273 K, 101.3 kPa, dry gas and 10% O<sub>2</sub>.

## 7.2 Lime

**Table 6** below list the recommended emission limits for lime producing plants.

**Table 6: Recommended Emission Limits for Lime Producing Plant**

<b>Pollutant</b>	<b>Limit</b>	<b>Measurement</b>
SO <sub>2</sub> (mg/Nm <sup>3</sup> )	400	Daily average
NO <sub>x</sub> (mg/Nm <sup>3</sup> )	500	Daily average
Dust (mg/Nm <sup>3</sup> )	50	Daily Average
HCl (mg/Nm <sup>3</sup> )	30	Half Hourly

Note: Reference condition at 273 K, 101.3 kPa , dry gas and 10% O<sub>2</sub>.

### 7.3 Glass

The abatement technology for dust, NO<sub>x</sub>, SO<sub>x</sub> and acid gases are similar to the one used for cement and lime plants. The recommended emission limits for glass plants are given in **Table 7**.

**Table 7: Recommended Emission Limits for Glass Producing Plant**

Pollutant	Limit (mg/Nm <sup>3</sup> )
Particulate matter	<20
NO <sub>x</sub>	500 -700
SO <sub>x</sub>	800
Chlorides /HCl	< 30
Fluorides/HF	<5
CO	< 200
H <sub>2</sub> S	<5
Metal (V, Ni, Cr, Se, Pb, Co, Sb, As, Cd)	<5
Ammonia	30-60
VOC	10-50

## 8.0. EMISSION MONITORING AND REPORTING

### 8.1 Cement Plants

- a. To control kiln process, continuous measurements are recommended for pressure, temperature, oxygen content, NO<sub>x</sub>, CO and SO<sub>2</sub>.
- b. To accurately quantify the emissions, continuous measurements are recommended for exhaust volume, humidity, temperature, dust, O<sub>2</sub>, NO<sub>x</sub>, SO<sub>2</sub> and CO
- c. Regular periodical monitoring is appropriate to carry out for metals and their compounds, TOC, HCl, HF, NH<sub>3</sub>, and PCDD/F's.



- d. Measurements benzene, toluene, xylene, polyaromatic hydrocarbons and other organic pollutants (for example chlorobenzenes, PCB (polychlorinated biphenyls) substances may be required occasionally under special operating conditions:

## **8.2 Lime Plants**

1.5 Regular periodical monitoring is appropriate to carry out for metals and their compounds, NO<sub>x</sub>, SO<sub>2</sub>, CO, TOC, HCl, HF, NH<sub>3</sub>, and PCDD/F's.

1.6 Measurements benzene, toluene, xylene, polyaromatic hydrocarbons and other organic pollutants (for example chlorobenzenes, PCB (polychlorinated biphenyls) substances may be required occasionally under special operating conditions:

## **8.3 Glass**

Majority of the air emission occurs at the melting section. Therefore in this section periodical monitoring is required for dust, CO, NO<sub>x</sub>, SO<sub>x</sub>, HF, HCl, boron compounds, H<sub>2</sub>S and heavy metals is required. In material handling and downstream activities sections, dust, VOC, formaldehyde and ammonia need to be monitored on a periodical manner.

## REFERENCES

1. European Integrated Pollution Prevention and Control Bureau (EIPPCB), (2013). Best Available Techniques (BAT) Reference Document for the Production of Cement, Lime and Magnesium Oxide. Joint Research Centre, Institute of Prospective Technological Studies, EIPPCB
2. European Integrated Pollution Prevention and Control Bureau (EIPPCB), (August 2007). Best Available Techniques (BAT) Reference Document in the Ceramic Manufacturing Industry. Joint Research Centre, Institute of Prospective Technological Studies, EIPPCB
3. European Integrated Pollution Prevention and Control Bureau (EIPPCB), (2013). Best Available Techniques (BAT) Reference Document for the Manufacture of Glass. Joint Research Centre, Institute of Prospective Technological Studies, EIPPCB