## **SNAP CODE:**

030312 040614

SOURCE ACTIVITY TITLE:	<b>PROCESSES WITH CONTACT</b>
	Lime
	Lime (decarbonizing)
NOSE CODE:	104.01.02
NFR CODE:	1 A 2 f
	2 A 2

#### **1 ACTIVITIES INCLUDED**

This chapter includes information on atmospheric emissions during lime work operations. Lime (CaO) is the high-temperature product of the calcination of limestone. The production occurs in vertical and rotary kilns fired by coal, oil or natural gas. Calcium limestone contains between 97 and 98 % of calcium carbonate on a dry basis. The rest includes magnesium carbonate, aluminium oxide, iron oxide and silica. However, some limestones contain as much as 35 to 45 % magnesium carbonate and are classified as dolomite.

## 2 CONTRIBUTIONS TO TOTAL EMISSIONS

Atmospheric emissions in the lime manufacturing industry include particulate emissions from the mining, handling, crushing, screening, and calcining of the limestone and emissions of air pollutants generated during fuel combustion in kilns. These emissions are not very significant on global or even regional scale. However, lime works can be an important emission source of air pollutants on a local scale.

Source-activity	SNAP-code	Contribution to total emissions [%]							
		SO <sub>2</sub>	NO <sub>x</sub>	NMVOC	$CH_4$	CO	CO <sub>2</sub>	$N_2O$	$\mathrm{NH}_3$
Lime	030312	0.1	0.2	0	0	0.3	0.3	-	-

#### Table 1: Contribution to total emissions of the CORINAIR90 inventory (28 countries)

0 = emissions are reported, but the exact value is below the rounding limit (0.1 per cent)

- = no emissions are reported

# **3 GENERAL**

## 3.1 Description

Two major types of processes can be considered within the lime work operations: quarrying, crushing, and size grading of minerals and then combustion of fuels in lime kilns. Limestone quarries are usually developed in a number of benches or lifts. For primary blasting of the limestone, holes are made by drills operated by compressed air (Parker, 1978). The excavated limestone is transferred for crushing and grinding. There are several types of crushing and grinding machines to produce limestone of sizes suitable for several designs of kilns.

During the kiln operations the limestone reaches temperatures as high as 900° C, and carbon dioxide is driven off limestone to leave so-called quicklime. The quicklime descends through the cooling zone and is discharged at the base of the kiln. Obviously, various air pollutants are generated during combustion of fuels in the kiln. At present two major types of kilns are in use: vertical and rotary kilns.

The vertical kilns, because of larger size of charge material, lower air velocities, and less agitation emit lower amounts of particles but higher amounts of sulfur dioxide and carbon monoxide. However, in recent years there have been important developments in the design and use of rotary kilns. They require a more carefully classified and smaller size of limestone than for the vertical kilns.

Hydrated lime is made by adding water to crushed or ground quicklime and thoroughly mixing the quicklime and the water.

Milk of lime can be produced either by slaking quicklime with an excess of water or by mixing hydrated lime with water.

# **3.2** Definitions

Lime: - the high-temperature product of the calcination of limestone.

# 3.3 Emissions

Pollutants released are sulphur oxides  $(SO_x)$ , nitrogen oxides  $(NO_x)$ , volatile organic compounds (non-methane VOC and methane  $(CH_4)$ ), carbon monoxide (CO), carbon dioxide  $(CO_2)$ , and nitrous oxide  $(N_2O)$ . According to CORINAIR90 the main relevant pollutants are  $SO_2$ ,  $NO_x$ , CO and CO<sub>2</sub> (see also table 1).

Sulphur dioxide emissions are influenced by several factors, including the sulphur content of the fuel, the sulphur content and mineralogical form (metal sulphide like pyrite, or sulphates like gypsum) of the stone feed, the quality of lime being produced, and the type of kiln. Due to variations in these factors, plant-specific  $SO_2$  emission factors are likely to vary significantly from the average emission factors presented here. The dominant source of sulphur emissions is the kiln's fuel, particularly coal and petroleum derived coke, where the levels of sulphur may be as high as 5 % by weight. The amount of sulphur present will vary widely according to the nature of the deposits used. During the calcining operation, sulphide and sulphates are decomposed to yield sulphur dioxide. On combustion of the fuel, the

sulphur compounds present in the fuel are oxidised to sulphur dioxide, and pass through the burning zone of the kiln with the exhaust gases (EPA, 1995; HSMO, 1992).

When sulphur containing fuels are burnt, for practical purposes sulphur in the kiln exhaust may be assumed to be emitted as sulphur dioxide, although there is usually some sulphur trioxide formed. In the case of lime manufacture in shaft kilns, much of the sulphur recombines with the burnt lime and the emissions of sulphur dioxide are subsequently reduced. In the case of rotary and rotating hearth kilns, combinations of process design and combustion conditions can be selected to ensure that most of the sulphur is expelled as sulphur dioxide in the kiln gases (HSMO, 1992).

The oxides of nitrogen are produced through the reaction of the nitrogen and oxygen in the air and through the oxidation of the nitrogen compounds contained in the fuel. There is a significant increase in the amount of oxides of nitrogen (mainly nitric oxide) which is formed at temperatures above 1,400 °C. The formation of nitric oxide is also a function of the excess air. When operating near to stoichiometric conditions in the kiln, there is localised generation of carbon monoxide. This acts as a reducing agent so that any nitric oxide which may be present is converted to nitrogen. Some oxides of nitrogen are also formed in electrostatic precipitators (HSMO, 1992).

Carbon dioxide and carbon monoxide are formed as main products of the combustion process. Carbon monoxide is formed by the incomplete combustion of carbonaceous fuels and even with good combustion control small amounts of carbon monoxide will be present in combustion gases.

## 3.4 Controls

Emissions of sulphur oxide can be reduced by using low sulphur fuels and by limiting the sulphur contents of the fuel and raw materials. Sulphur dioxide emissions may be further reduced if the polluting equipment is fitted to desulphurise the exhaust gases (e.g. by using a wet process) (EPA, 1995; HMSO, 1992).

The design of kiln and combustion conditions may be selected to ensure that most of the sulphur is retained in the burnt lime. In most circumstances, especially in shaft kilns, only a small fraction of the sulphur dioxide generated within the kiln (whether originating from the raw materials or from the fuel) is released to atmosphere, since it is mainly incorporated into the lime by chemical combination (HSMO, 1992).

The following techniques can be reasonably applied to reduce oxides of nitrogen discharges to the atmosphere:

- the use of low-NO<sub>x</sub>-burners where practicable, the principle of which is the avoidance of localised hot spots, and
- the use of very finely pulverised coal so that complete combustion can be achieved with low excess air.

Modern lime works are equipped with electrostatic precipitators that remove at least 98 % of the particulate matter from exhaust gases. Other control devices are also used including multiple cyclones, wet scrubbers, and baghouses.

## 4 SIMPLER METHODOLOGY

Application of emission factors with appropriate activity statistics can be regarded as a simpler methodology for estimation of emissions from lime work operations. However, it should be admitted that the chemical composition of fuel used in kilns is one of the factors affecting the amount of these emissions.

## 5 DETAILED METHODOLOGY

In this case, different emission factors for different types of kilns should be used. An account of the effect of emission controls should be considered. The different emission factors will have to be evaluated through measurements at representative sites.

## 6 **RELEVANT ACTIVITY STATISTICS**

Information on the production of lime is available from the UN statistical yearbooks (e.g. UN, 1994). This information is satisfactory to estimate emissions with the use of the simpler estimation methodology. However, in most cases, no information is available from the statistical yearbooks on the quantities of lime produced in vertical and rotary kilns. Therefore, the application of detailed estimation methodology is much more complicated.

# 7 POINT SOURCE CRITERIA

Lime works should be regarded as point sources if plant specific data are available.

## 8 EMISSION FACTORS, QUALITY CODES AND REFERENCES

Limited information is available on emission factors for various air pollutants emitted from lime works. Old data from the U.S. Environmental Protection Agency (U.S. EPA, 1973) are available for primary and secondary crushing and calcining in both vertical and rotary kilns. Very recently a collection of emission factors was performed for World Health Organization (Economopoulos, 1993). The results of this work are presented in table 2.

Operation	Total suspended particles	so <sub>2</sub>	NO <sub>X</sub>	СО
Coal Storage and Processing (If Coal is used as fuel)				
Coal Storage				
Open Piles	0.5			
Semi-Enclosed Piles	0.25			
Compartments	0.1			
Silos	0.1			
Coal Crushing and Screening				
Uncontrolled	0.18			
Fabric Filter	0.002			
Coal Grinding				
(Semi) Direct Fired System	0.0			
Indirect Fired System				
Uncontrolled	10.0			
Fabric Filter	0.1			
Raw Material Storage	0.16			
	0.10			
Crushing & Screening				
Uncontrolled	1.5			
Fabric Filter	0.0005			
Crushed Material Storage				
Open Piles	1.0			
Semi-Enclosed Piles	0.5			
Compartments	0.2			
Silos	0.2			
Raw Material Conveying				
Uncontrolled	1.2			
Fabric Filter	0.01			
Raw Material Calcining				
Vertical Shaft Kiln				
Uncontrolled	3.0	0.9S	0.1	2.0
Cyclone	1.0	0.9S	0.1	2.0
Multicyclones	0.75	0.9S	0.1	2.0
Vertical Double Inclined Kilns				
Uncontrolled	10.5	0.9S	0.1	2.0
Cyclone	3.6	0.9S	0.1	2.0
Multicyclones	2.6	0.9S	0.1	2.0
Parallel Flow/Counterflow Regenerative Kilns				
Uncontrolled	8.0	0.9S	0.1	2.0
Cyclone	2.8	0.9S	0.1	2.0
Multicyclones	2.0	0.9S	0.1	2.0
Annular Kilns				
Uncontrolled	12.0	0.9S	0.1	2.0
Cyclone	4.2	0.9S	0.1	2.0
Multicyclones	3.0	0.9S	0.1	2.0

# Table 2: Emission factors for selected air pollutants emitted during lime production, in kg/tonne of lime produced, after Economopoulos (1993)

Operation	Total suspended particles	SO <sub>2</sub>	NO <sub>X</sub>	CO
Rotary Short Kiln/Air Suspension Preheater	-			
Uncontrolled	40.0	0.36S	1.5	1.0
Cyclone	14.0	0.36S	1.5	1.0
Multicyclones	9.0	0.36S	1.5	1.0
ESP	0.6	0.36S	1.5	1.0
Fabric Filter	0.2	0.36S	1.5	1.0
Rotary Long Kiln				
Uncontrolled	140.0	0.36S	1.5	1.0
Cyclone	49.0	0.36S	1.5	1.0
Multicyclones	35.0	0.36S	1.5	1.0
ESP	2.0	0.36S	1.5	1.0
Fabric Filter	0.4	0.36S	1.5	1.0
Calcimatic Kiln				
Uncontrolled	25.0	0.9S	0.1	1.0
Cyclone	8.7	0.9S	0.1	1.0
Multicyclones	6.2	0.9S	0.1	1.0
Lime Cooling				
Grate Cooler				
Uncontrolled	20.0			
Cyclone	4.0			
Multicyclones	2.0			
Fabric Filters	0.1			
Planetary, Rotary, or Vertical Shaft Coolers	0.0			
Lime Packaging/Shipping	0.12			
Lime Hydration				
Uncontrolled	35.0			
Scrubber	0.04			

"S" is the sulfur percent in the fuel.

Table 3 contains fuel related emission factors for lime works based on CORINAIR90 data in [g/GJ]. Technique related emission factors, mostly given in other units (e.g. g/Mg product), are listed in footnotes. In the case of using production statistics the specific energy consumption (e.g. GJ/Mg product) has to be taken into account, which is process and country specific. Within CORINAIR90 a range for the specific energy consumption of 3 up to 4.7 GJ/Mg product has been reported.

					8.1.1.1.1	Emission					
	Type of fu	uel		NAPFUE	$SO_{2}^{(3)}$	NO <sub>x</sub> <sup>4)</sup>	NMVOC <sup>5)</sup>	$CH_{4}^{6)}$	CO <sup>7)</sup>	$CO_2$	$N_2O$
				code	[g/GJ]	[g/GJ]	[g/GJ]	[g/GJ]	[g/GJ]	[kg/GJ]	[g/GJ]
s	coal	Hc	steam	102	33-786 <sup>1)</sup>	150-340 <sup>1)</sup>	$15-40^{1}$	0.3-15 <sup>1)</sup>	$10-6000^{1)}$	92-98 <sup>1)</sup>	$4-14^{1}$
s	coal	Нс	brown coal/lignite	105	25 <sup>1)</sup> , 80 <sup>2)</sup>	$140^{1}$ , $300^{2}$	15 <sup>1)2)</sup>	15 <sup>1)2)</sup>	$100^{1}, 15^{2}$	$113^{1},$ $100^{2}$	3.5 <sup>1)</sup> , 3 <sup>2</sup>
s	coal	Hc	briquettes	106	$11^{1)}$	$140^{1}$	15 <sup>1)</sup>	15 <sup>1)</sup>	$6000^{1)}$	95-981)	3.5 <sup>1)</sup>
s	coke	Hc	coke oven	107	25-400 <sup>1)</sup>	40-300 <sup>1)</sup>	0.5-15 <sup>1)</sup>	$0.5 - 15^{1}$	70-6000 <sup>1)</sup>	45-200 <sup>1)</sup>	$4-12^{1}$
s	coke	Bc	coke oven	108	$650^{1)}$	220 <sup>1)</sup>	5 <sup>1)</sup>	15 <sup>1)</sup>	90 <sup>1)</sup>	86 <sup>1)</sup>	3 <sup>1)</sup>
s	coke		petroleum	110	275 <sup>1)</sup>	300 <sup>1)</sup>	$1.5^{1)}$	1.51)	70-75 <sup>1)</sup>	97-99 <sup>1)</sup>	$10-14^{1)}$
					$120-2,852^{2}$	$200-300^{2}$	$1.5 - 112^{2}$	$1.5 - 15^{2}$	10-133 <sup>2)</sup>	95-105 <sup>2)</sup>	3-14 <sup>2)</sup>
s	biomass		wood	111	5.2 <sup>1)</sup>	103-200 <sup>1)</sup>	48-50 <sup>1)</sup>	30-32 <sup>1)</sup>	1430- 6772 <sup>1)</sup>	92 <sup>1)</sup>	4-14 <sup>1)</sup>
s	waste		industrial	116	5.2 <sup>1)</sup>	115 <sup>1)</sup>	48 <sup>1)</sup>	32 <sup>1)</sup>	$1430^{1}$ , $15^{2}$	83 <sup>1)</sup> 76-92 <sup>2)</sup>	4 <sup>1)</sup> 6-14 <sup>2)</sup>
1	oil		residual	203	$47-1,470^{1}$ $94-1,712^{2}$	$100-310^{1}$ $170-215^{2}$	3-4 <sup>1)</sup> 3-46 <sup>2)</sup>	3-8 <sup>1)</sup> 1-3 <sup>2)</sup>	12-6000 <sup>1)</sup> 7-94 <sup>2)</sup>	73-78 <sup>1)</sup> 75-78 <sup>2)</sup>	$2-14^{1}$ 2.5-14 <sup>2</sup>
1	oil		gas	204	$85-305^{1)}$ $26^{2)}$	$70-310^{1}$ $313^{2}$	$1.5 - 2.5^{1}$	$1-8^{1}$	$10-20^{1}$ , $76^{2}$	72-74 <sup>1)</sup>	$2.0^{-11}$
g	gas		natural	301	$0.1-8^{1)}$ $0.9^{2)}$	50-1111 <sup>1)</sup> 14-100 <sup>2)</sup>	$2.5-10^{1)}$ $2.5^{2)}$	0.4-41)	20-6000 <sup>1)</sup> 13-17 <sup>2)</sup>	55-56 <sup>1)</sup> 53 <sup>2)</sup>	$\frac{1-3.7^{1)}}{1.5^{2)}}$
g	gas		coke oven	304	15 <sup>2)</sup>	83 <sup>2)</sup>			84 <sup>2)</sup>		
g	gas		blast furnace	305	63 <sup>2)</sup>	286 <sup>2)</sup>		2.5 <sup>3)</sup>	286 <sup>2)</sup>		
g	gas		coke oven and blast furnace gas	306	328 <sup>2)</sup>	250 <sup>2)</sup>	0.8 <sup>2)</sup>	0.8 <sup>3)</sup>	15 <sup>2)</sup>	205 <sup>2)</sup>	3 <sup>2)</sup>

#### Table 3:Emission factors for lime works<sup>8)</sup>

<sup>1)</sup> CORINAIR90 data, area sources

<sup>2)</sup> CORINAIR90 data, point sources

	CORINA	in yo uata, poi	int sources	
3)	SO <sub>x</sub> :	4,100	g/Mg product	Calcining, vertical kiln (EPA, 1990)
		2,550	g/Mg product	Calcining, rotary kiln (EPA, 1990)
		4,100	g/Mg product	multiple hearth calciner (EPA, 1990)
4)	NO <sub>x</sub> :	1,500	g/Mg product	General (Bouscaren, 1992)
		1,400	g/Mg product	Calcining: vertical kiln, rotary kiln and multiple hearth calciner
		1,111	g/GJ	Cement/lime industry, kilns: natural gas (IPCC, 1995)
		527	g/GJ	Cement/lime industry, kilns: oil (IPCC, 1995)
		527	g/GJ	Cement/lime industry, kilns: coal (IPCC, 1995)
5)	VOC:	10	g/Mg product	Calcining,: vertical kiln (EPA, 1990)
		30	g/Mg product	Calcining: rotary kiln (EPA, 1990)
		10	g/Mg product	Calcining: multiple hearth calciner (EPA, 1990)
6)	CH <sub>4</sub> :	1.1	g/GJ	Cement/lime industry, kilns: natural gas (IPCC, 1995)
		1.0	g/GJ	Cement/lime industry, kilns: oil (IPCC, 1995)
		1.0	g/GJ	Cement/lime industry, kilns: coal (IPCC, 1995)
7)	CO:	83	g/GJ	Cement/lime industry, kilns: natural gas (IPCC, 1995)
		79	g/GJ	Cement/lime industry, kilns: oil (IPCC, 1995)
		79	g/GJ	Cement/lime industry, kilns: coal (IPCC, 1995)
8)				

<sup>8)</sup> It is assumed, that emission factors cited within the table are related to combustion sources in lime works. Footnotes may also include emission factors for other process emissions (e.g. calcination).

### **9** SPECIES PROFILES

Not applicable.

## **10 UNCERTAINTY ESTIMATES**

It is difficult to assess current uncertainties of emission estimates for lime works operations. The difficulty results from a lack of emission measurements in these plants and thus the uncertainty of emission factors based on limited information.

Improvement of emission factors is necessary in order to obtain more accurate emission estimates for lime works operations. This improvement should focus on preparing individual emission factors for different types of kiln operations. In this way, a detailed methodology for emission estimates can be applied. Obviously, it will be necessary to obtain relevant statistical data.

The fuel specific emission factors provided in Table 3 are related to point sources and area sources without specification. CORINAIR90 data can only be used in order to give a range of emission factors with respect to point and area sources. Further work should be invested to develop emission factors, which include technical or fuel dependent explanations concerning emission factor ranges.

## 12 SPATIAL DISAGGREGATION CRITERIA FOR AREA SOURCES

National emission estimates can be disaggregated on the basis of production, population or employment statistics.

## **13 TEMPORAL DISAGGREGATION CRITERIA**

The production process in lime works is continuous.

# 14 ADDITIONAL COMMENTS

## **15 SUPPLEMENTARY DOCUMENTS**

Parker A. (1978) Lime works. In: Industrial Air Pollution Handbook, A. Parker (ed.), Mc Graw-Hill Book Comp. Ltd., London.

# 16 VERIFICATION PROCEDURES

Estimated emission factors could be best verified by measurements at respective plants.

## **17 REFERENCES**

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Economopoulos A.P. (1993) Assessment of sources of air, water, and land pollution. A quide to rapid source inventory techniques and their use in formulating environmental control strategies. Part one: rapid inventory techniques in environmental pollution. World Health Organization, Rept. WHO/PEP/GETNET/93.1-A, Geneva.

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## **18 BIBLIOGRAPHY**

#### **19 RELEASE VERSION, DATE AND SOURCE**

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