

Section VI.B.3.

Guidance by source category: Annex C, Part III Source Categories

Magnesium production

Coordinated by Mr. Patrick Finlay (Canada)

Guidelines on Best Available Techniques (BAT) for Magnesium Production

List of Contents

List of Contents.....	2
1.0 Process Description.....	2
2.0 Sources of Unintentional POPs.....	5
2.1 Releases to Air.....	5
2.1.1 <i>General Information on Emissions from Magnesium Production</i>	5
2.1.2 <i>Emissions of PCDD and PCDF</i>	5
2.2 Releases to Other Media	6
2.2.2 Water	6
2.2.3 Land	6
3.0 Alternate Processes for Magnesium Production.....	7
4.0 Primary and Secondary Measures.....	9
4.1 Primary Measures.....	9
4.2 Secondary Measures.....	10
5.0 Emerging Research.....	10
6.0 Summary of Measures.....	11
7.0 Achievable Levels	12

MAGNESIUM

1.0 Process Description

There are two major process routes utilized for production of magnesium metal. The first process recovers magnesium chloride from the raw materials and converts it to metal through molten salt electrolysis. The second type of process involves reducing magnesium oxide with ferro-silicon or aluminium at high temperatures. Examples of the two types of processes are described below.

Magnesium can also be recovered and produced from a variety of magnesium containing secondary raw materials (e.g., see reference 1).

1.1 Magnesium production process from magnesium oxide resources¹

The process allows producing magnesium from oxide raw materials: magnesite, brucite, serpentine and other. It is also suitable for magnesium production from raw materials, containing magnesium sulphate or its mixture with chlorides, including sea water. In all the cases chlorine produced by electrolysis is recycled which is used for conversion of magnesium oxide or sulphate into magnesium chloride.

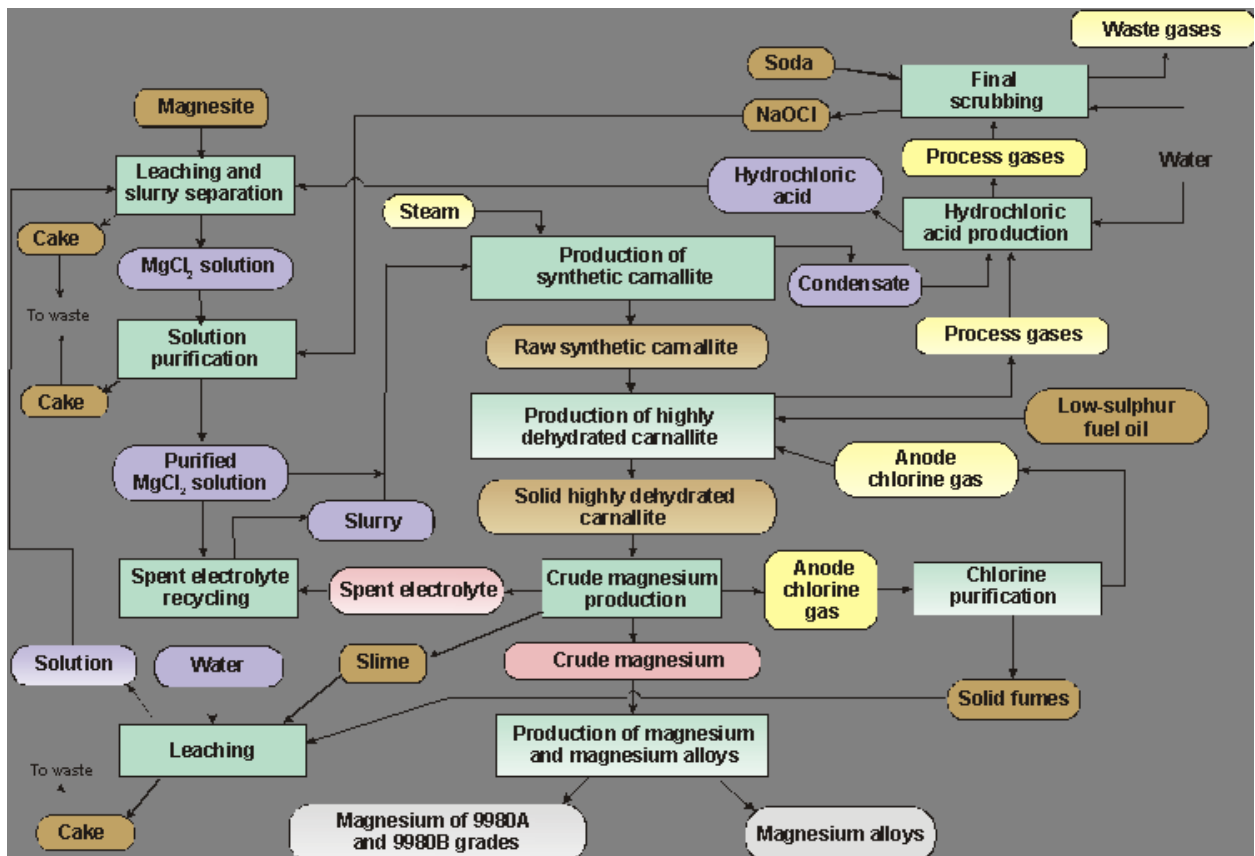
The process consists of the following stages (see flow sheet):

- leaching of raw material by hydrochloric acid and purification of the solution produced
- separation of magnesium chloride product in the form of synthetic carnallite or mixture of chlorides from said solution,
- dehydration of said product in fluidized bed by the stream of hot gases, containing hydrogen chloride, with production of solid dehydrated product, containing not more than 0,3 wt.% of magnesium oxide and water each,
- feeding of said product into electrolyzers or head unit of flow line and its electrolysis with production of magnesium and chlorine.

Chlorine produced by electrolysis is fed into the burners of fluidized bed (FB) furnaces, where it is converted into hydrogen chloride. Waste gases of FB furnaces, containing HCl, are either treated by water to produce hydrochloric acid that is used for raw material leaching, or neutralized by aqueous suspension of magnesium oxide to produce magnesium chloride solution.

Spent electrolyte forming in the course of electrolysis is used for synthetic carnallite production. All the waste products containing chlorine are utilized with the production of neutral oxides. It is a significant advantage of the process from environmental point of view.

¹ http://www.vami.ru/processes/magnesium/sposob_proizvod_magния_is_oksidnogo_siria.htm



©2000 -2002 VAMI® Russian National Aluminium-Magnesium Institute

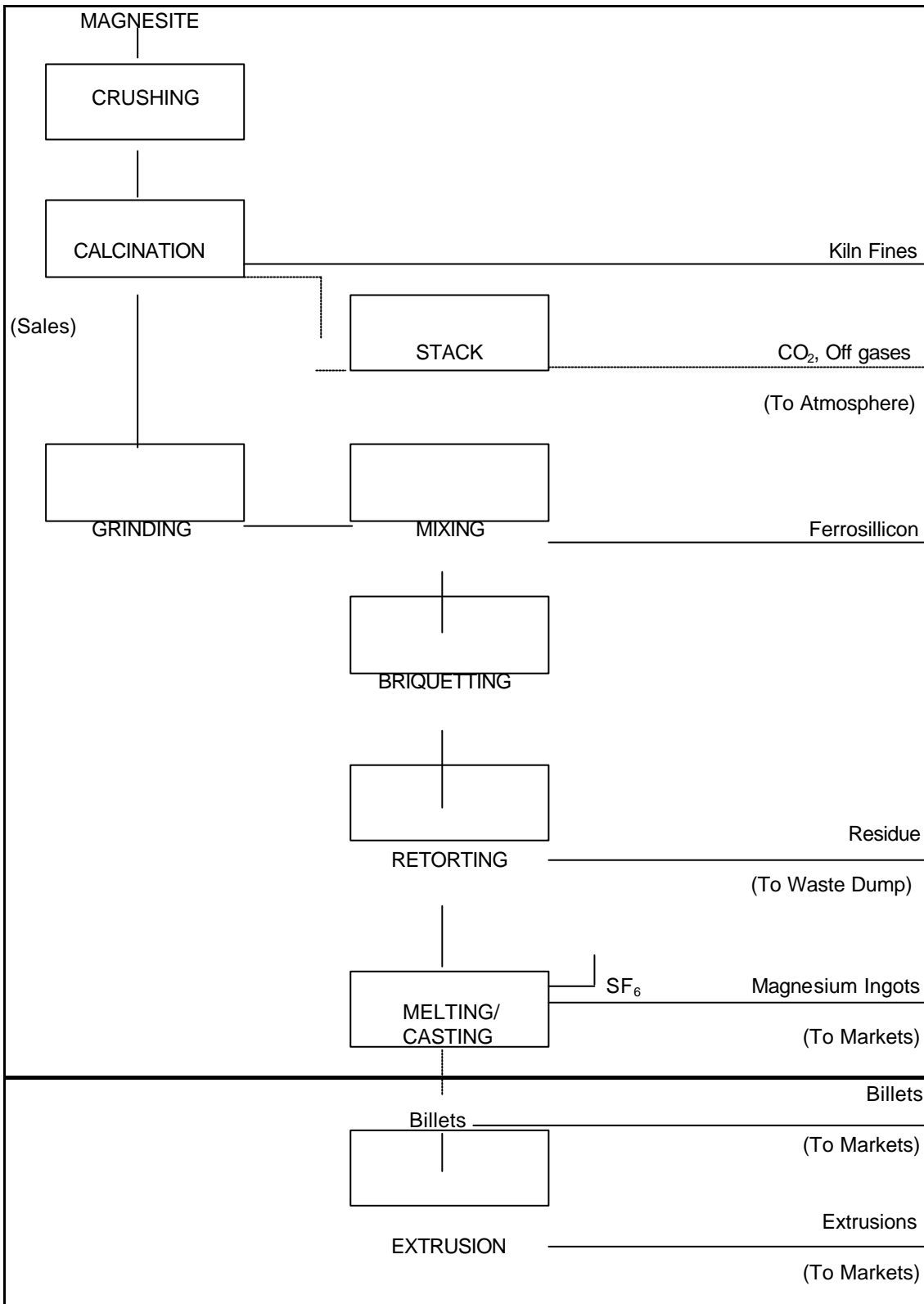
Figure 1: Flow Diagram of Magnesium production process from magnesium oxide resources

1.2 The Pidgeon Process – The thermal reduction process²

In the Pidgeon Process, magnesium is produced from calcined dolomite under vacuum and at high temperatures using silicon as a reducing agent. In the process, the finely crushed dolomite (magnesium/calcium) carbonate is fed to rotary kilns where it is calcined, and where the carbon dioxide is driven off leaving a product of calcined dolomite. The calcined dolomite is then pulverized in a roller mill prior to mixing with finely ground ferrosilicon and fluorspar. The fine calcined dolomite, ferrosilicon, and fluorspar are weighed in batch lots and mixed in a rotary blender. This mixture is then briquetted in briquetting presses.

Briquettes are then conveyed to the reduction furnaces. The reduction operation is a batch process releasing magnesium in vapour form, which condenses in the water cooled section of the retort outside furnace wall. After removal from the furnace, the magnesium “crown” is pressed from the sleeve in a hydraulic press.

² <http://www.norandamagnesium.com/>



Source: Hatch and Associates, Addendum to Primary NonFerrous Smelting and Refining Sector in Canada - Magnesium, October 1995

Figure 2. Process Flow Chart - Timminco Magnesium Plant

The residue from the reduction charge is removed from the retort and sent to a waste dump.

2.0 Sources of Unintentionally Produced POPs

2.1 Emissions to Air

2.1.1 General Information on Emission from Magnesium Production

Magnesium production facilities generate several types of pollutants that include dust, SO₂, NO_x, Cl₂, HCl, and in several cases emission of sulphur hexafluoride (SF₆) throughout the manufacturing process.

Dust and sulphur dioxide are mainly emitted from the calcinations of dolomite and MgO, from pellet drying as well as from chlorination off-gas treatment. The source of nitrogen oxides emissions are dolomite and MgO calcinations and pellet drying. Chlorine and hydrochloric acid are released from electrolysis and chlorination processes, and chlorination off-gas treatment system.

While carbon dioxide is emitted from the whole manufacturing process, the source of sulphur hexafluoride (SF₆) discharges is the cast-house.

2.1.2 Emissions of Dioxins and Furans

According to tests conducted in an electrolytic process of magnesium production plant in Norway, the main process causing the formation of PCDD/PCDF was a furnace converting pellets of MgO and coke to MgCl₂ by heating in a Cl₂ atmosphere at 700-800 °C (Oehme et al. 1989)³.

The purification of MgO using HCl and graphite blades ("chlorination) or electrolysis of MgCl₂ using graphite electrodes are also possible other sources of PCDD/PCDF formation.⁴

Timminco Ltd, in Ontario, Canada, which utilizes the "Thermal Reduction" Pidgeon process technology, reported dioxins and furans release to the air of 0.416 g TEQ/y. (*Dioxins and Furans CWS status report, pg 25*)

³ Integrated Pollution prevention and Control (IPPC), Reference Document on Best Available Techniques in the Non-Ferrous Metal Industries, May 2000

⁴ UNEP- http://www.pops.int/documents/guidance/Toolkit_2003.pdf

Process Type	Source Source	Emissions (ng/Nm ³)	Unit Mass/t (ug/t TEQ)
Electrolytic	From Chlorination of off gas treatment.	0.8	12
	From Chlorination vent gas	0.8	28
	From electrolysis/chlorination		13
Thermal	Reduction, refining and melting	0.08	3
Norsk Hydro Process			<1.0

Table 1: PCDD/PCDF Emissions to Air From Different Magnesium Production Process

Hydro Magnesium Canada (HMC) reported a total of 0.456 g/year⁵ emissions of dioxins and furans to air. Broken down as follows:

Source	g/year
Dissolving	0.001
Dehydration	0.112
Electrolysis	0.277
Foundry	0.025
HCl synthesis	0.0003
Mg remelting	0.050

2.2 Releases to Other Media

2.2.1 Water

The main water pollutants in the magnesium manufacturing process are suspended solids, metal compounds. However chlorinated hydrocarbons and dioxins are also found in wastewater from magnesium electrolysis process (see table 2 below)

⁵ HMC presentation at "Electrolytic Magnesium Industry Bi-national Informative Meeting", Montreal, Dec. 12, 2000 by Jean Laperriere, Environment Chief)

- **Land**

The wet scrubbing process utilized in treatment of gas streams would be expected to generate residues containing PCDD/PCDFs. A water treatment system which includes settling of these residues in a lagoon would then constitute a release to the land⁶

- Releases of PCDD and PCDF to water (IPPC Bref)⁷

Type	ng/Nm³	Unit mass/t of Mg
Electrolytic	100	13
Thermal	0.08	3
Norsk Hydro Process		<0.1

Table 2: Release of PCDD/PCDF to Water From Different Magnesium Production Process

3.0 Alternative Process for Magnesium Production

Although process efficiency and productivity could be the main deriving forces in the advancement and the development of alternative new technologies, it is expected that environmental aspects will be given due consideration. This means elimination or minimization of the formation of pollutants at the source, and the incorporation of effective pollution abatement system should be part of the initial design of the project.

Norsk Hydro has developed and successfully implemented a new technology⁸ Of MgCl₂ Dehydration process in its plant in Canada. Release of pollutants, especially PCDD/PCDF generated from this process are significantly lower than existing processes (see Tables 1 &2)

The plant produces MgCl₂ brine by dissolving magnesite rock in hydrochloric acid. Impurities such as aluminium, iron, manganese etc are removed from the leach

⁶ UNEP PCDD/PCDF Tool Kit, May 2003.

⁷ ibid

⁸ *Integrated Pollution prevention and Control (IPPC), Reference Document on Best Available Techniques in the Non-Ferrous Metal Industries, May 2000.*

liquor by purification. The brine is subjected to evaporation and prilling and drying by fluidised bed technique. This will result in an anhydrous $MgCl_2$ product.

Hydro's electrolysis cells are operated at around 400 kA. The $MgCl_2$ prills are fed continuously from the dehydration plant into the electrolysis cells. This operation produces magnesium metal and chlorine gas. The chlorine gas is reacted with hydrogen to produce hydrochloric acid which is recycled to the magnesite dissolving stage. The molten magnesium is cast under controlled conditions. The final products are pure metal and alloys in the form of ingots and grinding slabs.

Noranda's Magnesium Recovery from Asbestos Tailings.

A new technology in use by Noranda* involves recovery of magnesium from asbestos tailings. The process description is as follows:

* Note: *This plant was shutdown for an indefinite time due to market conditions – April 2003)*

TRANSFORMING SERPENTINE INTO HIGH-GRADE MAGNESIUM⁹

In Noranda's proprietary magnesium process, serpentine undergoes a series of chemical processes and filtration steps to produce a very pure anhydrous magnesium chloride. This is electrolytically reduced in state-of-the-art high efficiency cells into magnesium and chlorine. The chlorine is completely captured and recycled. The company's projections for its environmental performance includes, an emission levels of no more than 0.09 g TEQ of PCDD/Fs to air, using an activated carbon adsorption system.

Feed Preparation

Noranda's magnesium process starts with crysotile serpentine ($3MgO \cdot 2SiO_2 \cdot 2H_2O$), a mining residue containing 23% magnesium. The material is already mined and above ground, adjacent to the plant. Serpentine is crushed, screened, and magnetically separated.

The material is then leached with hydrochloric acid to create magnesium chloride brine, along with a silica and iron residue.

Brine Purification

To purify the magnesium chloride solution, the brine goes through further purification steps to remove major impurities such as boron. The impurities are extracted from the brine by precipitation.

⁹http://my.noranda.com/Noranda/magnesium/Introducing+Noranda+Magnesium/A+Production+Breakthrough/_A+Production+Breakthrough.htm

Fluid Bed Drying

High purity brine is dried to produce granular magnesium chloride. This yields partially dehydrated magnesium chloride ($MgCl_2$). HCl is recycled for use in the Leaching phase.

Melt Chlorinator

The magnesium chloride granules are melted in an electrolyte and treated by a chlorination process involving the injection of gaseous HCl. The acid and water are recovered in the process for use in the Leaching phase.

Electrolytic Cell

Metallic magnesium is produced through electrolysis by sending a strong electrical current through the electrolyte. The chlorine gas that is produced during the electrolysis phase is washed and combined with hydrogen thereby reconverted into acid, which will be reconverted into gas and re-used for the chlorination process.

Casting

The metallic magnesium is tapped and then cast in ingots.

Purification of Emissions

The production facility is equipped with gas scrubbers throughout the process to purify the process and ventilation emissions. The chlorine is completely captured, recycled, and returned to the process. Emissions are washed to extract particles and other contaminants before being released into the atmosphere. The process releases no water effluent to the environment.

4.0 Primary and Secondary Measures.

4.1 Primary Measures

The electrolysis process is of most interest from the PCDD/PCDF point of view because of the presence of carbon and of chlorine in the process and the high temperature conditions.

Primary measures which may assist in reducing the formation and release of the identified substances include eliminating the carbon source, by substituting the graphite by a non-graphite anode, possibly metal anodes. Replacement of graphite anodes by metal anodes took place in the chlorine industry in the beginning of 1970s, and very minor amounts of PCDFs were formed¹⁰.

¹⁰ <http://www.eurochlor.org/PDF>

The new $MgCl_2$ dehydrating process has been found to produce much lower levels of PCDD/PCDF (Tables 1 & 2).

It is expected that in the proposed Cogburn Magnesium Project, in British Columbia, that the STI/VAMI technology will produce less Chlorinated Hydrocarbons (CHC's) than produced at Magnola due to the absence of chlorinators. See Section 5 for additional information.

4.2 Secondary Measures

Measures include:

1. Treatment of effluents using techniques such as nano-filtration and use of specially designed containment for solid residues and effluents.
2. Treatment of off-gases by cleaning of the off-gas from the chlorinators in a series of wet scrubbers and wet electrostatic precipitators before incineration, and using bag filters to clean and remove entrained salts from the magnesium electrolysis process.
3. Use of Activated Carbon: In the Cogburn Magnesium Project, there are two CHC removal systems; both are based on activated carbon removal of CHC's in liquid effluents.

5. Emerging Research

The Cogburn Magnesium Project¹¹

A Cogburn magnesium project in British Columbia is expected to utilize the STI/VAMI electrolytic cell technology for the decomposition of $MgCl_2$ to magnesium metal and chlorine gas. Presently in the magnesium industry, this is done largely in mono-polar diaphragm-less electrolytic cells. The STI/VAMI technology is based on a flow through design in which all the cells in the cell hall are linked together. Each cell is fed individually. The magnesium and electrolyte flow from one cell to the next via a system of enclosed launders. The magnesium is collected at the end of the flow line in a separator cell, and is siphoned out for casting at the cast house. This system is currently utilized at the Dead Sea Magnesium plant in Israel.

¹¹ (http://www.leadermining.com/Binder_No1_Project_Summary.pdf)



15D 9001-24

Leader Mining International - Cogburn Magnesium Feasibility Study
Project Summary Report

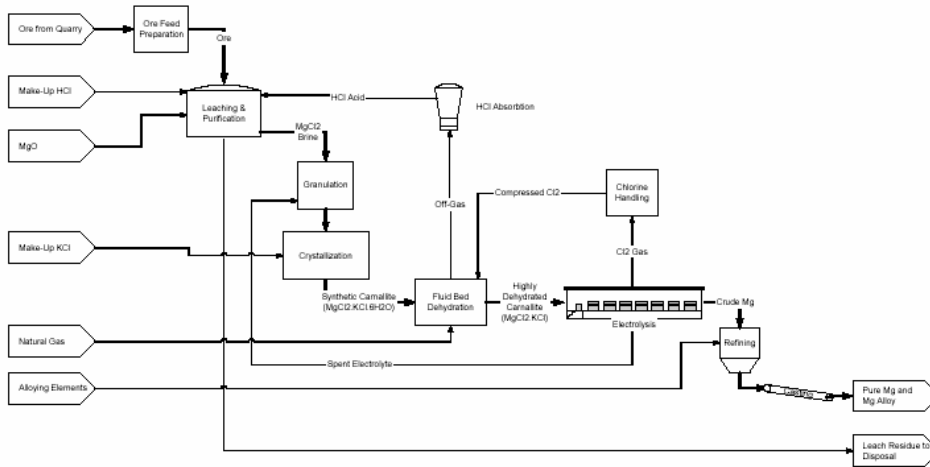


Figure 13. Cogburn Magnesium Production Plant – Simplified process flow diagram

PR56736.011

Rev. 0, Page 49

p:\leader\156736\docs\p56736.011 project summary.doc

PR DOT, 0001

Figure 3: Simplified Flow Diagram: Cogburn Magnesium Plant

5.0 Summary of Measures

The following tables present a summary of the measures discussed in previous sections.

Measures for Magnesium Plants

Measure	Description	Considerations	Other comments
Magnesium Plants-Primary Measures			
Alternate Processes	Priority consideration should be given to alternate processes with less environmental impacts than traditional magnesium manufacturing process.	Examples include: - Norsk Hydro's MgCl ₂ brine Dehydration Process. - Elimination of carbon source-replaces graphite with non-graphite anode.	
Feed Quality	Increasing availability of magnesium scrap and other magnesium containing raw materials would make it attractive for smelters to use it in their process.	Smelter should ensure that only high grade scrap, free of contaminants be used.	
Pre-treatment	The calcinations of dolomite creates	Use of Gas	

Measure	Description	Considerations	Other comments
Techniques	significant amount of dust	Suspension Calciner could reduce it significantly.	

Measure	Description	Considerations	Other comments
Magnesium Plants-Secondary Measures			
Treatment of the off-gases	Off-gases from chlorination furnaces in magnesium plants contain pollutants such as PCDD, PCDF, CHCs, and others.	Use of wet scrubbers and wet electrostatic precipitators remove aerosols, followed by incineration to destroy PCDD/PCDF and other VOCs. Activated carbon is also used to absorb pollutants.	
Treatment of effluent	Wastewater collected from the various parts of the magnesium plant such as the scrubbing effluent from the chlorination stage contain PCDD/PCDF and other CHCs.	Removal of solids by flocculation, sedimentation and filtration. followed by activated carbon injection to remove contaminants.	

6. Achievable Levels

Emission Factors in the Magnesium Industry¹² (UNEP)

PCDD/PCDFs

Classification

Emission factors – ug TEQ/t of Mg

	AIR	Water	Land	Product	Residue
--	-----	-------	------	---------	---------

1. Production using MgO/C thermal Treatment in Cl ₂ no effluent, limited gas treatment.	250	9000	NA	NA	0
2. Production using MgO/C thermal NA treatment.	50	30	NA	NA	
3. Thermal reduction process NA	3	ND	NA	NA	

¹² http://www.pops.int/documents/guidance/Toolkit_2003.pdf

HCBs

Emission factors – (ug/Kg)¹³

	AIR	Water	Land	Process	Volatilized Generated from
Land					
Norsk Hydro, Posgrum	700-3000	-	unknown	unknown	unknown
Norsk Hydro, Beconcour	90-170	2.4	60-120	unknown	unknown
Noranda, Asbestos	300	nil	800-3000	84,000	600-2400

The figure below shows emissions and discharges of dioxins from Norsk Hydro’s magnesium production. The graph for specific values shows grams dioxin per 1000 tonnes magnesium. The reduction in 2002 is mainly due to the closure of the magnesium plant in Porsgrunn¹⁴.

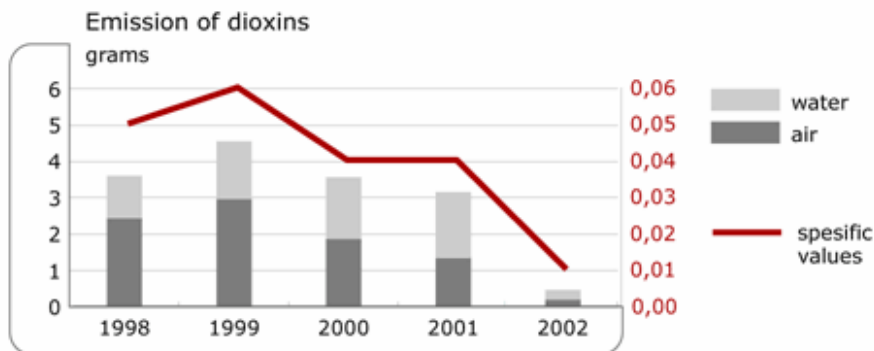


Figure 4: Emissions and Discharges from Norsk Hydro’s Magnesium Production

¹³ Dioxin and Hexachlorobenzene Release from Magnesium Production in North America: Lessons from Noranda’s Magnola Project in Asbestos, Quebec; Mathew J. Bramley, Ph.D., Greenpeace, Canada (June 5, 1998)

¹⁴ profile Nordsk Hydro.htm

