

PRODUCTION OF INORGANIC METAL COMPOUNDS

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LEAD OXIDE PRODUCTION

1 GENERAL INFORMATION

The main present uses of lead oxides are for the manufacture of lead-acid batteries, in additives to glass production and stabilisers for PVC.

The hereafter described reference plant is producing lead based PVC-stabilisers. The European Chemicals Agency (ECHA) has submitted a Restriction Proposal (date of submission 16/12/2016) for lead and its compounds on the placing on the market and use of lead compounds to stabilise PVC. Based on the assessment of the ECHA of the risks to human health or the environment associated the European Commission will restrict the lead compounds for the aforementioned use earliest 2018.

The main applications of lead stabilisers in PVC are the production of pipes, cables and profiles in which the lead content is usually in the range of 0.5 and 2.5 %. In 2007 the consumption of formulated¹ lead stabilisers was 100,000 tonnes in Europe (EU 28). In 2014 the consumption was reduced to 14,000 t/a and for 2015 the target of the European stabilisers producers association was the total substitution of lead based products. The stabilisers are nowadays based on calcium and tin (ESPA 2016).

The member companies of the European Stabiliser Producers Association (ESPA) have committed to carry out risk assessments by 2004 on lead-based stabilisers. Moreover, the industry has developed alternative stabilisers to lead-based systems and envisaged replacing lead-based stabilisers with lead-free stabilisers till the year 2015 (www.vinylplus.eu).

The reference installation under discussion hereafter is producing lead based PVC stabilisers (lead salts and lead soaps as granulates and tablets) as well as lead free products. The production capacity of the reference installation is approx. 40.000 t/a.

2 INDUSTRIAL PROCESSES USED

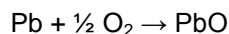
Generally, there are four forms of lead oxide: PbO (litharge), having two forms with different crystal structure, lead dioxide (PbO₂) and Pb₃O₄ (minium). Whereas litharge is the economically dominating lead oxide, the use of minium today is rather small.

In the following, the production process of PbO (litharge), lead solutions and Pb stabilisers is described in a general way.

¹ "Formulated" means that these systems are complete stabiliser/lubricant packages and may also include pigments or fillers as a service to the customer.

3 PRODUCTION OF PBO

The raw material for the production of PbO is lead-billets. These lead-billets are melted and introduced into a stirrer vessel (so-called Barton furnaces). Then, lead (Pb) is oxidised in an exothermic reaction to crude PbO (so-called Bartonoxide) at approx. 450 °C through injection of air according to the formula:



The content of free Pb in the Bartonoxide is usually comprised between 8 and 14%. The Bartonoxide is then precipitated with the help of a pre-filter system (cyclone and fabric filter).

In order to meet the quality demand of less than 1% of free Pb in the PbO, a post-oxidation at ca. 700 °C takes place in a so-called glazing plant. Then, the PbO is milled and transferred into a silo.

3.1 Production of Pb-stabilisers

The main components of Pb-stabilisers are Pb-stearate, Pb-sulfate and Pb-phosphide. Their production is mainly accomplished in a wet chemical way. The fusible Pb-stearin can also be produced by melting processes.

In the wet chemical process, PbO is mixed with acid in the presence of water. The so-produced basic component is dewatered and dried. In the melting process, stearin acid is molten with PbO giving Pb-stearin. Thus, the production of lead-stabilisers in the form of tablets is possible.

Stabilisation compounds are produced through physical mixing. Partially, dust poor compounds are produced by compression.

4 CURRENT EMISSION AND CONSUMPTION LEVELS

4.1 Dust emissions

The production of PbO and Pb-stabilisers causes dust emissions with an important share of lead. At the reference plant dust emissions below 0.05 mg/Nm³ with a total volume flow from all abatement systems of ca. 130,000 m³/h are typical.

In order to minimise fugitive dust emissions at hand-over points and at filling- and packaging machines, these devices are equipped with air extraction systems. Contaminated packaging materials are disposed in closed systems.

The dust emission limit from the production of PbO and Pb-stabilisers at the reference plant is 0.1 mg/Nm³, at one emission point 0.05 mg/Nm³. No specific emission limit is set for lead since the limit of 0.1 mg/Nm³ for dust emissions is already far below the Pb emissions limit from the TA Luft² of 0.5 mg/Nm³.

² TA-Luft is currently under revision. For Pb and its compounds no proposal for changing the emission limit values was made.

Compliance with permitted values is verified yearly by periodic measurements.

The reference plant applies High Efficiency Particulate Air (HEPA) filters after a pre-filter system (cyclone and fabric filter) in the process of PbO- and Pb-stabilisers production. These HEPA filters basically consist of a two-stage cassette-filter with which dust-emission are reduced below 0.05 mg/Nm³. The main advantage of this filter is that it is independent from production, which guarantees highest security without cleaning-peaks at blowing off.

The compliance with the emissions limit values is controlled by

- Differential pressure measurement
- Optical inspection of cassette-filters
- Continuous haze measurement in the stack and alarm system
- Internally and externally emission measurements

Maintenance is carried out according to the revision guidelines including a half yearly revision of all dust abatement systems (e.g. filter cassettes and bags). The Measurement, display and alarm systems are also maintained accordingly.

Table 1: Dust emissions to air. (Source: Operator Information 2016)

Origin	2013	2014	2015	ELV	Max. exhaust air stream
	mg/Nm ³	mg/Nm ³	mg/Nm ³	mg/Nm ³	Nm ³ /h
Source 1	< 0.0119 ^{3) 5)}	< 0.0122 ^{3) 6)}	< 0.0090 ^{3) 7)}	0.1 ²⁰⁾	29,500
Source 2					29,500
Source 3					29,500
Source 4	< 0.0121 ^{3) 8)}	< 0.0101 ^{3) 9)}	< 0.0097 ^{3) 10)}	0.1 ²¹⁾	22,362
Source 5					24,000
Source 6	< 0.0119 ^{3) 11)}	< 0,0117 ^{3) 12)}	< 0.011 ^{3) 13)}	0.1 ²²⁾	48,000
Source 7	< 0.07 ¹⁾ < 0.04 ^{2) 14)}	< 0.10 ¹⁾ < 0.05 ^{2) 15)}	< 0.09 ¹⁾ < 0.05 ²⁾ < 0.05 ^{2) 16)}	0.1 ²³⁾	24,600
Source 8	< 0.09 ¹⁾ < 0.05 ^{1) 17)}	< 0.09 ²⁾ < 0.10 ^{4) 18)}	< 0.05 ²⁾ < 0.09 ¹⁾ < 0.06 ^{2) 19)}	0.1 ²³⁾	8,800

All values are for dry gas at 0 °C, 1,013 mbar. No averaging periods are given in the permits.

Averaging periods: ¹⁾ 30 minutes ²⁾ 1 hour ³⁾ 3 hours ⁴⁾ 50 minutes ⁵⁾ ÖSBS 2013a
⁶⁾ ÖSBS 2014a ⁷⁾ ÖSBS 2015a ⁸⁾ ÖSBS 2013b ⁹⁾ ÖSBS 2014b ¹⁰⁾ ÖSBS 2015b ¹¹⁾ ÖSBS 2013c
¹²⁾ ÖSBS 2014c ¹³⁾ ÖSBS 2015c ¹⁴⁾ ÖSBS 2013d ¹⁵⁾ ÖSBS 2014d ¹⁶⁾ ÖSBS 2015d ¹⁷⁾ ÖSBS 2013e
¹⁸⁾ ÖSBS 2014e ¹⁹⁾ ÖSBS 2015e ²⁰⁾ BH VILLACH 1991 ²¹⁾ BH VILLACH 1994 ²²⁾ BH VILLACH 1993 ²³⁾ BH VILLACH 1992

4.2 Water

Accruing wastewater from the production of PbO is pre-treated (physical-chemical treatment) before being discharged into the public sewer system. Required cooling water is reused in the process. Emission limit values are set by permit. Wastewater emissions from PbO production are regulated by the wastewater ordinance for inorganic chemicals. Table 2 presents a summary of water consumption and wastewater treatment. Table 3 compares emission values evaluated via self-monitoring (2015) with the respective permit and ordinance emission limit values. Table 4 compares emission values evaluated via external-monitoring (2016 & 2015) with the respective permit and ordinance emission limit values.

Table 2: Summary of water consumption and wastewater treatment. (Source: verbal information from 21.03.2016)

Consumption and treatment of water	
Consumption of fresh water	150,000 m ³ /h – 200,000 m ³ /h cooling water (reused in the process)
Type of wastewater discharge	Treated wastewater gets indirectly discharged via the communal WWTP Villach.
Ordinance	Wastewaters from the production of PbO is regulated by the Ordinance on inorganic chemicals (2/8/6/3/15 Anorganische Chemikalien, Anlage A). Emission limit values are determined by permit. External-monitoring has to be performed twice a year.
Internal treatment of wastewater from the process	<ul style="list-style-type: none"> ● Precipitation of lead ● Filtration ● Neutralisation
Short description of the process wastewater treatment	Lead contaminated wastewater from the production process is collected in sealed floor channels. In the in-house wastewater treatment comprises of precipitation of lead as PbCO ₃ via sodium carbonate. After filtration and adjustment of the pH-value with sulphuric acid, the waste water gets discharged into the communal wastewater system and further treated in the communal WWTP Villach.

Table 3: Emission values (self-monitoring), ELV permit and Ordinance (2/8/6/3/15 Anorganische Chemikalien, Anlage A). (Source: Self-monitoring report, 2015; Permit VL5-WA-733/1999, BH Villach, 2007)

Parameter	Unit	Self-monitoring 2015			ELV permit	Ordinance	Number of samples
		Daily min.	Daily max.	Annual average			
Q	m ³ /d	12	230	131.33	230		245
Total P	mg/l	1.5	141	66.07			51
Lead	mg/l	0.1	0.56 ³	0.11	0.5	0.5	243
Lead load	g/d	1.2	33.3	14.44	50		
Aluminium	mg/l	0.15	10.6	1.6			243
Thallium	mg/l	0.03	0.05	0.03			243
Thallium load	g/d	0.36	9.2	0.36	10		243
Cadmium	mg/l	0.01	0.01	0.01	0.1	0.1	26
Cadmium load	g/d	0.12	2.3	1.31	10		245
Zinc	mg/l	0.03	0.07	0.04	2	1	26
Zinc load	g/d	0.36	11.5	4.05	200		245
Arsenic	mg/l	0.03	0.1	0.03		0.1	82
Arsenic load	g/d	0.36	18	4.24	10		245
T	°C					35	
TSS	mg/l					250	
pH						6.5 – 9.5	
Antimony	mg/l					0.3	

³ No exceedance due to „4 out of 5“ rule – the ordinance on wastewater defines an emission value as complying if 4 out of 5 consecutive measurements do not exceed the permitted emission limit value and one measurement does not exceed the permitted emission limit value by more than 50%.

Table 4: Emission values (external-monitoring), ELV permit and Ordinance (2/8/6/3/15 Anorganische Chemikalien, Anlage A). (Source: External-monitoring report 2015 & 2016; Permit VL5-WA-733/1999, BH Villach, 2007)

Parameter	Unit	External-monitoring			ELV permit	Ordinance	Method
		19.05.2016	12.11.2015	27.05.2015			
pH	-	8.4	8.7	8.5		6.5 – 9.5	DIN 38404-4
Lead	mg/l	0.091	0.03	0.09	0.5	0.5	DIN EN ISO 11885
Cadmium	mg/l	< 0.001	< 0.001	< 0.001	0.1	0.1	DIN EN ISO 11885
Zinc	mg/l	0.006	0.008	0.019	2	1	DIN EN ISO 11885

4.3 Waste

At the reference plant, approx. 700 t hazardous and ca. 300 t non-hazardous waste was produced in 2001 (corresponding production of PbO and Pb-stabiliser compounds: ca. 35,000 t/a). Lead-sulphate contaminated packaging material and lead-salts represent the major part of hazardous waste. Non-contaminated wooden waste has the highest share of non-hazardous waste.

4.4 Energy

The oxidation of molten lead in the Barton-furnaces is an exothermic process. Natural gas input is required during start-up and for the complete oxidation of PbO.

5 REFERENCES

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- ÖSBS – Österreichische Staub- (Silikose-) Bekämpfungsstelle (2013a): Prüfbericht Nr. 682/13
- ÖSBS – Österreichische Staub- (Silikose-) Bekämpfungsstelle (2013b): Prüfbericht Nr. 684/13
- ÖSBS – Österreichische Staub- (Silikose-) Bekämpfungsstelle (2013c): Prüfbericht Nr. 685/13
- ÖSBS – Österreichische Staub- (Silikose-) Bekämpfungsstelle (2013d): Prüfbericht Nr. 689/13
- ÖSBS – Österreichische Staub- (Silikose-) Bekämpfungsstelle (2013e): Prüfbericht Nr. 690/13
- ÖSBS – Österreichische Staub- (Silikose-) Bekämpfungsstelle (2014a): Prüfbericht Nr. 725/14
- ÖSBS – Österreichische Staub- (Silikose-) Bekämpfungsstelle (2014b): Prüfbericht Nr. 716/14
- ÖSBS – Österreichische Staub- (Silikose-) Bekämpfungsstelle (2014c): Prüfbericht Nr. 717/14

ÖsBS – Österreichische Staub- (Silikose-) Bekämpfungsstelle (2014d): Prüfbericht
Nr. 721/14

ÖsBS – Österreichische Staub- (Silikose-) Bekämpfungsstelle (2014e): Prüfbericht
Nr. 722/14

ÖsBS – Österreichische Staub- (Silikose-) Bekämpfungsstelle (2015a): Prüfbericht
Nr. 711/15

ÖsBS – Österreichische Staub- (Silikose-) Bekämpfungsstelle (2015b): Prüfbericht
Nr. 713/15

ÖsBS – Österreichische Staub- (Silikose-) Bekämpfungsstelle (2015c): Prüfbericht
Nr. 717/15

ÖsBS – Österreichische Staub- (Silikose-) Bekämpfungsstelle (2015d): Prüfbericht
Nr. 716/15

ÖsBS – Österreichische Staub- (Silikose-) Bekämpfungsstelle (2015e): Prüfbericht
Nr. 721/15

Self-monitoring Report (2015): Self-monitoring of wastewater pre-treatment, 2015

ZINK OXIDE PRODUCTION

6 GENERAL INFORMATION

The reference installation under discussion hereafter produces zinc oxide in different qualities via the indirect process (French process). The installation is covered by the IED Annex I.

Zinc oxide is primarily used in the rubber industry as compounding material. All kinds of sulphur – crosslinked rubbers contain ZnO as it activates the vulcanisation process.

Another major use of zinc oxide is in glass and ceramic products.

Due to the absorption properties of ultraviolet light zinc oxide, it is used in sunscreens. Additionally ZnO is applied in pharmaceuticals and cosmetic products for healing wounds, as a bacteriostat in medical plasters, in baby creams and calamine lotion.

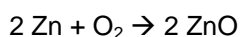
Zinc oxide is furthermore used as pigment and as additive in polymers and paints, mainly to inhibit corrosion and for its opacity.

Zinc is a trace element, is one of the main additives of zinc to fertilisers, animal feed and human vitamin supplements. It is also used in dental cement. Finally zinc oxide acts as a catalyst in alkylation, oxidation, hydrogenation and desulphurisation reactions.

7 PRODUCTION OF ZINK OXIDE

Zinc oxide is produced via the indirect process route. The starting material is zinc metal (primary or secondary with a purity of 92 – 99.995 %) which is melted in a first stage at a directly heated (natural gas) reaction vessel.

The liquefied zinc is subsequently transferred to the vaporiser. The molten metal is vaporised by boiling depending on the sub-process. It can be carried out in an electro thermal furnace, a muffle arch furnace or a retort. The vapour is then oxidised in a combustion chamber with air to zinc oxide:



The product is precipitated in settling chambers, in which the fractionation of the zinc oxide particles takes place according to their size.

The exhaust air stream is cleaned with bag filters after cooling and remaining ZnO collected.

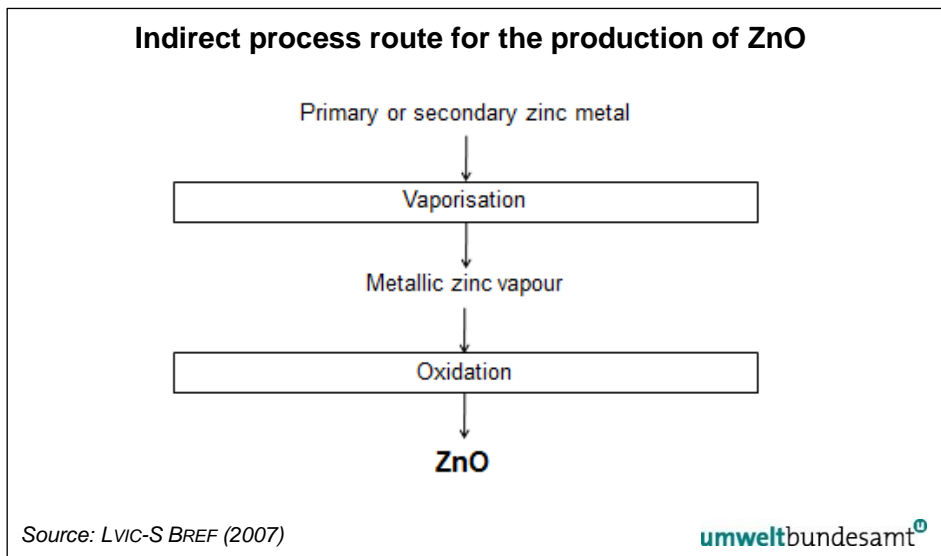


Figure 1:
Indirect process route
for the production of
ZnO. (according to
LVIC-S BREF 2007)

8 CURRENT EMISSION AND CONSUMPTION LEVELS

8.1 Process emissions

At the reference installation 8 bag filters are operated for the abatement of dust (ZnO). The main emission sources are the zinc furnaces, additional the mill is equipped with an abatement system.

The emission limit value for all bag filters is 20 mg/Nm³ at standard conditions (0° C, 1013 mbar and dry exhaust gas). The filter equipment has to be maintained and malfunctioning filter hoses have to be replaced immediately.

The emission limit values must be monitored externally at least every 3 years. The last emission values from 2014 are displayed in Table 5.

The emission values for dust are usually within the range of the emission limit value. For filter 6 one emission value (22.8 mg/Nm³) was above the emission limit value. Filter 4 had emission values of 15.6 mg/Nm³ and 7.3 mg/Nm³. All other emission values from filters abating furnaces and a mill were well below 10 mg/Nm³.

Table 5:
Emission values of the reference plant for the production of ZnO via the indirect process. Emission values represent measurements from 2014. (Source: Operator information 2016)

Filter number	Origin	1 st HA	2 nd HA	mean
		dust, mg/Nm ³	dust, mg/Nm ³	dust, mg/Nm ³
F1	Ball mill	3.99	4.37	4.18
F2	Ash filter	3.15	3.18	3.17
F4	Zinc furnaces	15.6	7.3	11.5
F5	Furnace hood	<0.39	<0.39	<0.39
F6	Zinc furnaces	22.8	16.2	19.5
F7	Zinc furnaces	0.79	0.94	0.87
F8	Zinc furnaces	2.24	1.81	2.03

Emission limit value for all bag filters: 20 mg/Nm³ as half hourly averages at 0 °C, 1013 mbar and dry gas.

All emission values represent half hourly averages at 0 °C; 1,013 hPa and dry gas. Oxygen content as obtained.

8.2 Water

The indirect process route does not have any waste water streams and therefore no emissions to water occur.

Waste water can be obtained when producing zinc oxide produced via the wet chemical process route.

8.3 Waste

Residues from the indirect process are reused in the process. No solid residues are emitted.

Waste from the direct process in the form of a slag is either directed to landfill, or is used in road construction.

9 REFERENCES

BREF LVIC-S (2007): Reference Document on Best Available Techniques for the Manufacture of Large Volume Inorganic Chemicals – Solids and Others industry from August 2007.

All other information was received in personal messages from the operator of the reference installation.

PRECIPITATED CALCIUM CARBONATE PRODUCTION

10 GENERAL INFORMATION

Precipitated calcium carbonate (PCC) and ground calcium carbonate (GCC) have the same chemical formula CaCO_3 . Nevertheless, the formation of these materials diverges as GCC is produced top down, whereas PCC is synthesized bottom up. Due to different production regimes, PCC differs from GCC in, e.g.

- higher purity,
- control of crystal morphology,
- finer crystallites (down to the nanometre range),
- specific surface area,
- and control of agglomeration in the final PCC product.

The properties of PCC can be adjusted to the needs of the customer by the production conditions.

The precipitated calcium carbonate can be subsequently coated for specific applications. At the reference IPPC-installation, no coating is performed within the installation borders.

The main application of PCC is the paper production, as filler material and adsorption agent for printing inks. Smaller amounts are used for the production of paints, adhesives, sealants, inks, plastics, rubber, healthcare and pharmaceuticals.

The hereafter described reference plant is situated next to a cement plant producing quick lime. CO_2 from calcination of limestone is ducted after scrubbing from the cement plant to the PCC plant for the carbonisation step in the calcium carbonate process.

The plant has a capacity of processing approx. 80,000 t/a quicklime to slaked lime and a production capacity of approx. 400,000 t/a slurry.

The reference plant is under the regime of the IED (Annex I, activity 4.2). The final products are transported by trucks and rail to paper mills.

11 INDUSTRIAL PROCESSES USED

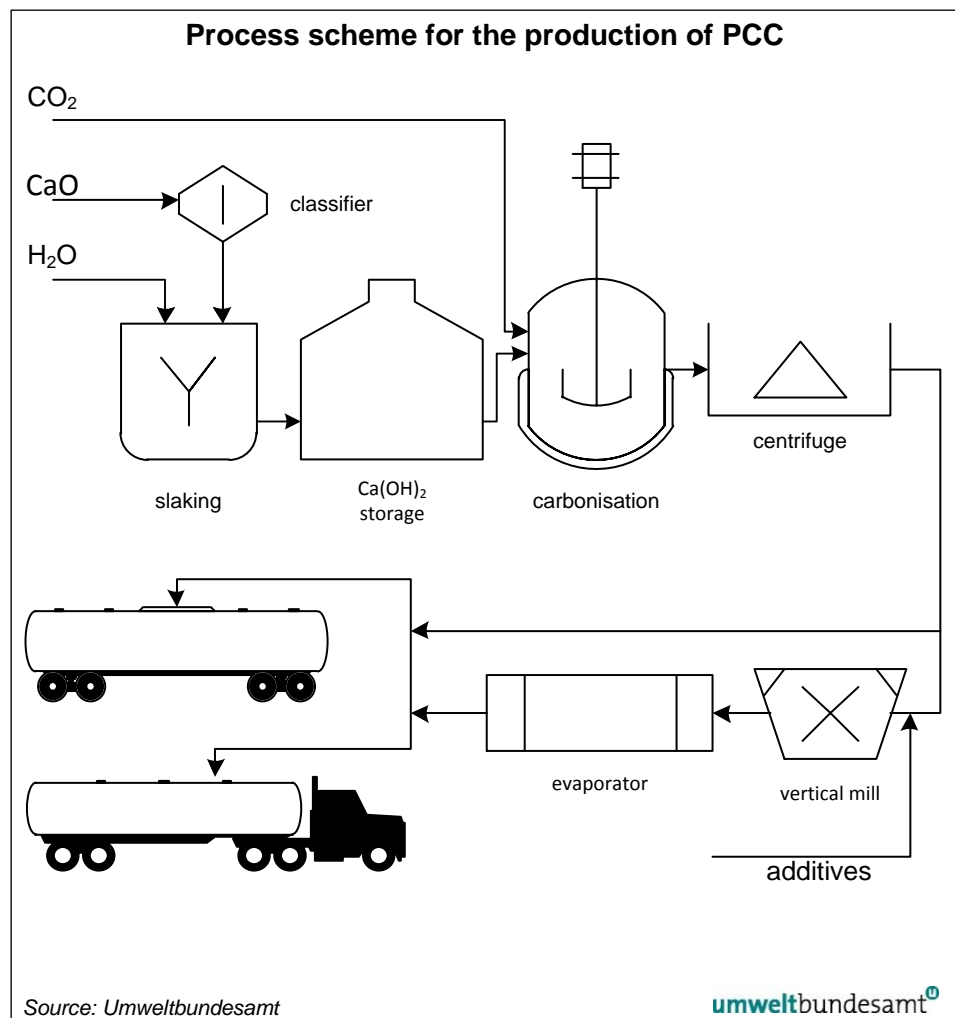
The production of PCC is a multistep process. The first step is slaking of quick lime (CaO). In this continuous slaking process, quick lime reacts in an exothermic process with water to slaked lime (Ca(OH)_2). The milk of lime is stored in tanks, intermediately.

In a batch process scrubbed lime-kiln gas containing mainly carbon dioxide from the neighbouring cement installation is added to the milk of lime. The slaked lime reacts with the carbon dioxide to calcium carbonate, which crystallizes subsequently from the solution. Crystallization is controlled by adjusting:

- temperature (heating or cooling of the slurry may be necessary before carbonation),
- CO₂ concentration and flow rate,
- agitation level,
- composition of hydrated lime slurry
- and presence of additives.

to obtain particles with specific morphology, size, agglomeration rate and surface area.

Figure 2:
Simplified process
scheme for the
production of PCC.



The chemical reactions in these two steps (1, 2) and the overall stoichiometric reaction (3) are:

1. $\text{CaO} + \text{H}_2\text{O} \rightarrow \text{Ca(OH)}_2$
2. $\text{Ca(OH)}_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$
3. $\text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3$

The slurry is thickened by centrifuges and dispersants are added for the final product. Some special products are then deagglomerated using a vertical mill and concentrated to different solid contents by means of an evaporation plant.

A simplified process scheme is shown in Figure 2.

12 CURRENT EMISSION AND CONSUMPTION LEVELS

12.1 Air

No emissions to air arise in the reference plant.

The quicklime is transported fully encapsulated to the slaking container and poured in under the water level.

Additionally, the reference plant is producing solely aqueous PCC slurries, no dry products are made. Therefore, no dust emissions from bagging occur.

12.2 Water

Table 6 presents the treatment of waste water, the corresponding Austrian ordinance and the type of discharge.

Table 6: Summary of water consumption and wastewater treatment (Source: Permit 2/152-1070/11-1999, Land Salzburg, 1999)

Treatment of water	
Type of wastewater discharge	Treated wastewater gets directly discharged into the river Salzach.
Ordinance	Wastewaters from the production of PCC is regulated by the Ordinance on industrial minerals (2/8/8/4 Industrieminerale, Anlage A). Emission limit values are determined by permit.
Internal treatment of wastewater from the process	Precipitation and flocculation Filtration via lamella separator Neutralisation
Short description of the process wastewater treatment	There are two wastewater lines at the installation. Wastewater line I represents the in the process accruing wastewater. Wastewater line II represents cooling and splashing waters.
	<p>Wastewater line I:</p> <p>Process wastewater of PCC production is treated via precipitation (aluminiumhydroxidchlorid), flocculation (anionic hydrosoluble polymers) and filtration. Filtration is carried out via a lamella separator (Lamellenklärer I). Due to the low flow velocity of the water flocculated particles are settling in the lamellas and collected in separate tank. The treated wastewater passes quality control (online-turbidity measurement) before entering a clear water collection tank. If the quality requirements of the treated wastewater are not met, it is sent back into wastewater treatment. If the quality measurements are met the cleared wastewater is either discharged into the river Salzach or used in the production process. The from the wastewater treatment accruing sludge is re-used in the process.</p> <p>Wastewater line II:</p> <p>Cooling and splashing waters are collected in a 70,000 l tank where the pH value is adjusted between 7.5 and 8.5 via CO₂. From the collection tank the wastewater is sent to a lamella separator (Lamellenklärer II) where the flocculated solids are settling and collected. The treated wastewater passes quality control (online-turbidity measurement) before entering a clear water collection tank. The accruing sludge is collected, drained via a chamber filter press and re-used externally (cement plant). The from draining accruing wastewater passes quality control (online-turbidity measurement) before entering a clear water collection tank.</p>

Table 7 presents the emission values of wastewater line I (process wastewater) from external-monitoring, the emission limit values set by permit, defined by appendix A of the ordinance on industrial minerals (2/8/8/4 Industrieminerale, Anlage A) and the applied measuring methods. One exceedance regarding the aluminium concentration in the treated wastewater occurred in the course of the second external-monitoring in 2016.

Table 7: Emission values from external-monitoring 12. – 13.01.2016 (EM1), 04. – 05.10.2016 (EM2), ELVs permit and Ordinance (2/8/8/4 Industriemineralie, Anlage A) (Source: Hydrologische Untersuchungsstelle Salzburg, external-monitoring report, 28.03.2016, Hydrologische Untersuchungsstelle Salzburg, external-monitoring report, 27.10.2016, Permit 2/152-1070/11-1999, Land Salzburg, 1999)

Parameter	Unit	EM1 2016	EM2 2016	ELV Permit	ELV Ordinance	Method
Q	m ³ /d	1,121	1,682	2,000	-	-
T	°C	15-19	20-27	30	30	-
pH		8.22	8.03	6.5 – 9.5	6.5 – 9.5	DIN EN ISO 10523:2012
TSS	mg/l	38	32	100	100	ÖNORM M 6274:1984
TSS load	kg/d	42.6	53.8	200	-	calculated
Al	mg/l	0.669	2.02 ¹⁾	2	2	ÖNORM EN ISO 11885
Al load	kg/d	0.75	3.4	4	-	calculated
COD	mg/l	32	22	75	75	ÖNORM M 6265:1991
COD load	kg/d	35.9	37	150	-	calculated
Sum of hydrocarbons	mg/l	< 0.09	< 0.1	5	5	ÖNORM M 6608:1996
Sum of hydrocarbons load	kg/d	< 0.1	< 0.16	10	-	calculated
Anionic tensides	mg/l	< 0.1	< 0.1	1	-	DIN EN 903:1994
Anionic tensides load	kg/d	< 0.12	< 0.12	2	-	calculated
Non-ionic tensides	mg/l	< 0.1	< 0.1	-	-	DIN 38409-23-2
Non-ionic tensides load	kg/d	< 0.12	< 0.12	-	-	calculated

¹⁾ Ordinance on industrial minerals 2/8/8/4 AEV Industriemineralie, §4.(3)Z1: In case of a measured ELV exceedance of wastewater parameters number 2,3 or 5 to 21 of appendix A to C (includes Al) in the course of an up to 4 times a year conducted external-monitoring, which is not higher than the 1.5-fold ELV, the external-monitoring has to be repeated. If the measured value is below the ELV at the repeat measurement, the parameter is complying. The repeat measurement is not yet available.

12.3 Waste

Hazardous and non-hazardous wastes are generated in the reference plant (Table 8). Hazardous waste consists predominantly of waste oil, oil contaminated materials and common office wastes. Non-hazardous waste consists predominantly of packaging materials (e.g. wood, cardboard, ferrous metals, plastic foils) and municipal waste.

Rejected quicklime (approx. 5%) is returned to the delivering quicklime plant.

Calcium carbonate originating from the waste water treatment is analysed and recycled onsite (PCC production) or externally (cement plant).

Table 8:
Wastes arising the
reference plant. (Source:
Operator information
2017)

Year	Non-hazardous waste [t]	Hazardous waste [t]	Waste water [m ³]
2012	27,965	2,615	474,660
2013	35,420	4,270	417,848
2014	28,250	1,196	416,094
2015	40,166	1,288	408,707
2016	36,603	3,325	548,031

12.4 Energy

Process heat is partly used for heating the plants. Additionally a natural gas heating system (400 kW) is installed.

13 REFERENCES

- Permit 2/152-1070/11-1999, Land Salzburg, 1999: Änderung der Betriebsanlage; Gewerbe-, bau- und wasserrechtliche Genehmigung, 2/152-1070/11-1999, Land Salzburg, 1999
- HYDROLOGISCHE UNTERSUCHUNGSSTELLE SALZBURG (2016a): external-monitoring report, 28.03.2016: Betriebswasseruntersuchung, Prüfbericht, Hydraulische Untersuchungsstelle Salzburg, 28.03.2016
- HYDROLOGISCHE UNTERSUCHUNGSSTELLE SALZBURG (2016b): external-monitoring report, 27.10.2016: Betriebswasseruntersuchung, Prüfbericht, Hydraulische Untersuchungsstelle Salzburg, 27.10.2016
- Permit 2/152-1128/2-1999, Land Salzburg, 1999: Errichtung einer Erdgasheizungsanlage; Gewerbebehördliche Genehmigung, 2/152-1128/2-1999, Land Salzburg, 1999
- Waste management concept 2016, Operator, 2016
- Permit 2/152-923/3-1997, Land Salzburg, 1997: Errichtung einer Betriebsanlage; Gewerbe- und baurechtliche Genehmigung, 2/152-923/3-1997, Land Salzburg, 1997
- Permit 2/152-923/27-1999, Land Salzburg, 1999: Errichtung und Betrieb einer vollautomatischen Kalklöschanlage; Gewerbebehördliche Genehmigung, 2/152-923/27-1999, Land Salzburg, 1999

CALCIUM CHLORIDE PRODUCTION VIA THE ACID-LIME NEUTRALISATION ROUTE

14 GENERAL INFORMATION

The reference installation produces calcium chloride (CaCl_2) solution with variable concentrations in a batch process. CaCl_2 solutions are mainly used for de-icing, high purity solutions are also used in the paper industry.

The reference installation under discussion has a permitted annual capacity of 42,120 t of calcium chloride brine and produces on average 11,000 t per year.. The installation is permitted according to the IED Annex I, activity 4.2.

15 PRODUCTION OF CALZIUMCHLORID

In the acid-lime route for the calcium chloride production high purity lime stone (CaCO_3) is mixed with hydrochloric acid (HCl). HCl and CaCO_3 react to CaCl_2 , carbon dioxide (CO_2) and water (H_2O).

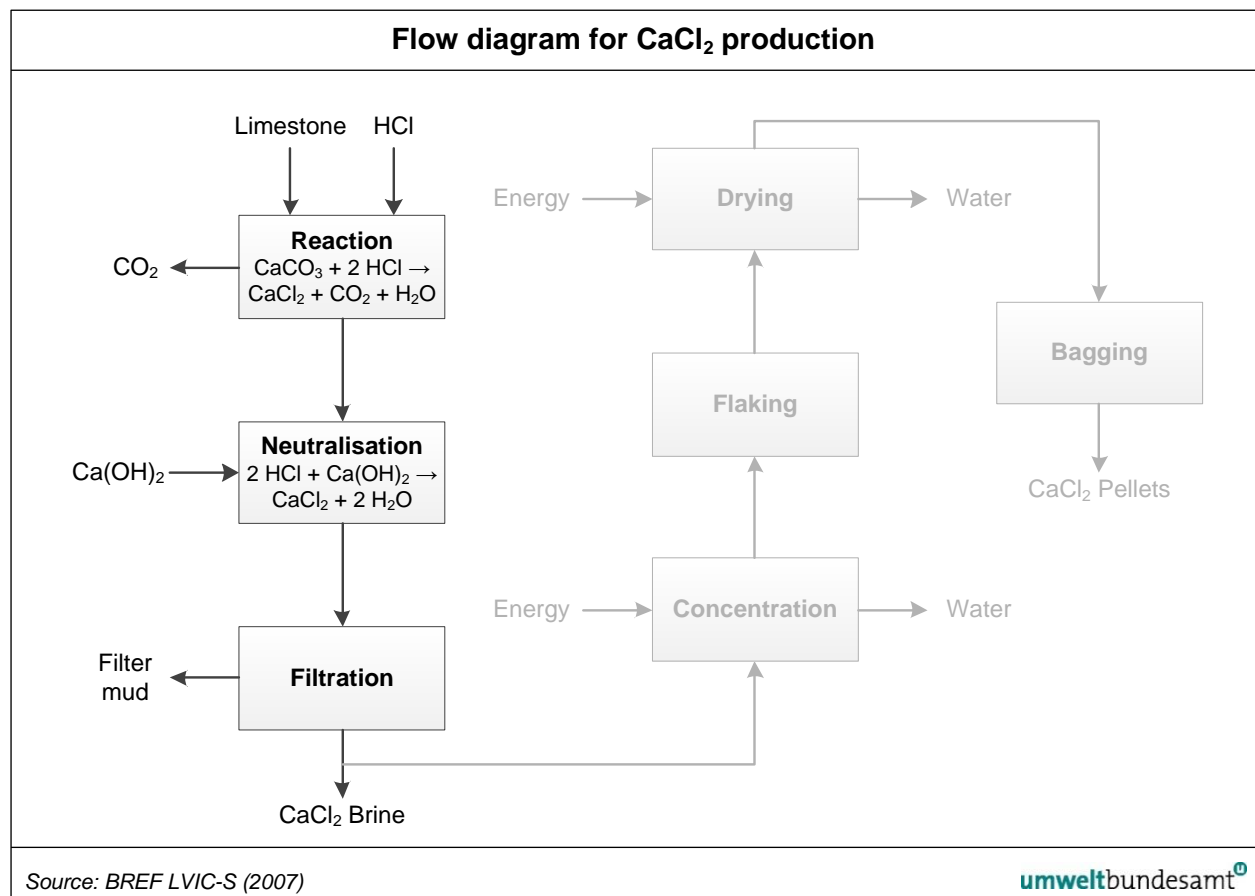


Figure 3: Schematic process flow diagram for CaCl_2 production via the acid-lime neutralisation route according to BREF LVIC-S

In the next step, the pH value is raised by adding milk of lime ($\text{Ca}(\text{OH})_2$). The increased pH value cause the precipitation of impurities from the lime stone such as magnesium or iron salts. Silicates, also impurities from the lime stone, and the precipitated impurities mentioned before are removed by filtration.

Source: *BREF LVIC-S (2007)*

Figure 3 gives an overview of the production process.

The concentration of CaCl_2 in the final aqueous solution is up to 33%. Lower concentrations are diluted on customer request.

The plant has a retention pond in size of at least the largest single container including the areas associated.

16 CURRENT EMISSION AND CONSUMPTION LEVELS

16.1 Process emissions

The exhaust air of the production process of calcium chloride and from the HCl storage tank is washed in an aqueous gas scrubber. The permitted emission limit value for HCl in the released off gas is 30 mg/Nm^3 .

The compliance with the permitted emission limit value had to be verified by one single acceptance test. No periodic measurements to be in compliance with the permit are required.

HCl emissions over the period of one batch including refilling of the HCl storage tank (equals 4 hours and 20 minutes) was measured in 2015 with 7.8 mg/Nm^3 (Source: Operator information 2016).

16.2 Water

No waste water emissions from the process occur. Process water from the aqueous scrubber to abate HCl is reused in the reactor for the production of calcium chloride. HCl is needed for the reaction of limestone to CaCl_2 and CO_2 .

16.3 Waste

The primary source of waste in the production process is the amount of insoluble silicates in the limestone, which are filtered off and disposed.

Hazardous waste produced in the years 2010 to 2014 according to the E-PRTR register is shown in Table 9.

Year	Hazardous waste in tonnes per year
2010	29
2011	32
2012	5
2013	3
2014	13
2010	29
2011	32

*Table 9:
Hazardous waste from
calcium chloride
production according to
E-PRTR register from
2010 – 2014.*

16.4 Energy consumption

In 2014 approx. 16.6 MWh electricity were used for production and approx. 2.2 MWh for non-production (e.g. office). Approx. 30.5 MWh heat were used for the whole site.

17 REFERENCES

BREF LVIC-S (2007): Reference Document on Best Available Techniques for the Manufacture of Large Volume Inorganic Chemicals – Solids and Others industry from August 2007.

All information was received in personal messages from the operator of the reference installation.

METAL SULPHIDES PRODUCTION

18 GENERAL INFORMATION

The reference installation under discussion hereafter produces metals sulphides for tribological adjustments in brake linings, abrasives and lubricants. Furthermore, the products are used in electronics, metallurgy and as polymer additives. The products include a variety of sulphides such as iron, copper, molybdenum, tungsten, zinc, tin, bismuth, chromium, silver and antimony sulphides. Since the use of naturally occurring sulphides without a chemical reaction is not covered by the IED Annex I, the description refers solely to processes where a chemical synthesis is carried out.

The installation is covered by the IED Annex I. The installation is currently negotiating the IED-permit with the local authorities.

19 PRODUCTION OF SULPHIDES

The synthetic sulphides are produced by a closed chemical reaction in a reactor. Some raw materials require a pre-treatment, by e. g. grinding to enhance the surface. The raw materials are fed into a reaction container and the chemical reaction is initiated. The resulting metal sulphides are subsequently milled, homogenised and packaged.

20 CURRENT EMISSION AND CONSUMPTION LEVELS

20.1 Process emissions

The main pollutants in the process used for the synthesis of sulphides are:

- dust
- SO₂

Dust emissions occur due to milling of the final products and the charging of the reaction vessel with raw materials. The exhaust gas from the processes are pre-cleaned in a fabric filter and subsequently collected with other waste gas streams from non-IPPC process units. The combined exhaust gas is finally cleaned by a High Efficiency Particulate Air filter (HEPA). The guaranteed maximum concentration after the central filter device is 2 mg/Nm³.

SO₂ emissions are obtained in the reaction vessels. The exhaust gas from the sulphides synthesis is washed in a 2-stage wet scrubber with lime water resulting in the formation of gypsum. The emission levels and the emission limit values are displayed in Table 5.

Reactor 1 has an emission limit value of 100 mg/Nm³ whereas in reactor 2 an emission limit value of 150 mg/Nm³ is mandatory. SO₂ emissions have to be monitored continuously. The daily averages of both reactors in two representative months range from approximately 45 mg/Nm³ to 80 mg/Nm³.

SO ₂ [mg/Nm ³]		Emission values	Emission limit values
reactor 1 ¹⁾	feb.16	DAmin	100
		MA	
		DAmix	
	mar.16	DAmin	77.5
		MA	
		DAmix	
reactor 2 ²⁾	feb.16	DAmin	150
		MA	
		DAmix	
	mar.16	DAmin	76.8
		MA	
		DAmix	

Table 10:
Emission limit values and emission levels of SO₂ after wet scrubber, continuous monitoring in the reference months February and March 2016.

DA_{min}: minimum daily average within 1 month;

DA_{max}: maximum daily average within 1 month;

MA: monthly average.

¹⁾ dry gas, standard conditions with 3°C, no reference oxygen content (O₂ as obtained).

²⁾ dry gas, standard conditions, no reference oxygen content (O₂ as obtained).

20.2 Waste

Waste occurs due to the SO₂ abatement. Calcium hydroxide is used in the scrubbers to reduce sulphur dioxide resulting in the formation of gypsum. The waste is disposed to a landfill site.

The yearly amount of gypsum in the reference year 2015 was 396 to.

21 REFERENCES

All information was received in personal messages from the operator of the reference installation.