MULTI-NUTRIENT FERTILISERS PRODUCTION

1 GENERAL INFORMATION

Mineral fertilisers contain one or more of the primary nutrients (macronutrients) such as nitrogen, phosphorus or potassium as salts or in form of urea. The primary nutrients N, P, K are required by plants in large or moderate amounts. Depending on the formulation mineral fertilisers also contain other nutrients required by plants to a minor degree, such as Ca, Mg, and S. Trace elements required in small quantities (micronutrients) are B, Cu, Fe, Mn, Mo, Zn. Fertilisers can be classified as follows in terms of their major nutrient contents (IFA 2016):

- Single-nutrient or straight fertilisers generally contain only one mayor (primary) nutrient.
- Multi-nutrient fertilisers (MN-fertilisers) or compound fertilisers contain two or more major nutrients. The term complex fertiliser refers to a compound fertiliser formed by mixing ingredients that react chemically.

Table 1: Main mineral fertiliser types with regard to their primary nutrient composition. (IFA 2016)

Common names	**nutrient composition as % of product**				
	N	**P_2O_5**	**K_2O**	**S**	**MgO**
Nitrogen fertilizers					
Ammonia	82	0	0	0	0
Ammonium sulphate	21	0	0	23	0
Ammonium nitrate	33 – 34.5	0	0	0	0
Calcium ammonium nitrate	20.4 – 27	0	0	0	0
Urea	45 – 46	0	0	0	0
Phosphate fertilizers					
Single superphosphate	0	16 – 20	0	12	0
Triple superphosphate	0	46	0	0	0
Diammonium phosphate	18	46	0	0	0
Monoammonium phosphate	11	52	0	0	0
Ground rock phosphate	0	20 – 40	0	0	0
Potash fertilizers					
Muriate of potash (potassium chloride)	0	0	60	0	0
Sulphate of potash	0	0	50	18	0
Sulphate of potash magnesia	0	0	22 – 30	17 – 22	10 – 11
Magnesium fertilizers					
Kieserite	0	0	0	20 – 22	25 – 27
Epsom salt	0	0	0	12 – 13	15 – 16
Complex fertilizers					
NPK fertilizers	5 – 25	5 – 25	5 – 25	*	*
NP fertilizers	15 – 25	15 – 25	0	*	0
NK fertilizers	13 – 25	0	15 – 46	*	0
PK fertilizers	0	7 – 30	10 – 30	*	*

** some with S and/or Mg and/or micronutrients*

Solid fertilisers are the most important group of fertilisers in Europe. Solid fertilisers include granular, prilled, and compacted products. Granular fertilisers are composed of spheroid particles, usually 1.5 – 5 mm in diameter, and are formed by any of a number of granulation processes. Prilled fertilisers are of nearly spherical form and made by the solidification of freefalling droplets. (UMWELTBUNDESAMT 2002)

The thereafter described reference fertiliser plant is located at an industrial park in lower Austria. The location is connected to the railway network and has a shipment point for loading and unloading of ships.

The installation produces fertilisers mostly starting from phosphate rock and sulphuric acid. Raw material is mainly delivered by ship on the River Danube. Sulphuric acid is obtained from a sulphuric acid plant on site.

The reference plant operates installations for the production of single and triple superphosphate, compound fertilisers (PK and NPK produced by the mixed acid route) and hyperproducts (phosphate rock for direct application). The combined production capacity reaches approx. 200,000 to 250,000 tons per year.

2 INDUSTRIAL PROCESSES USED

2.1 Production of Single Superphosphate (SSP)

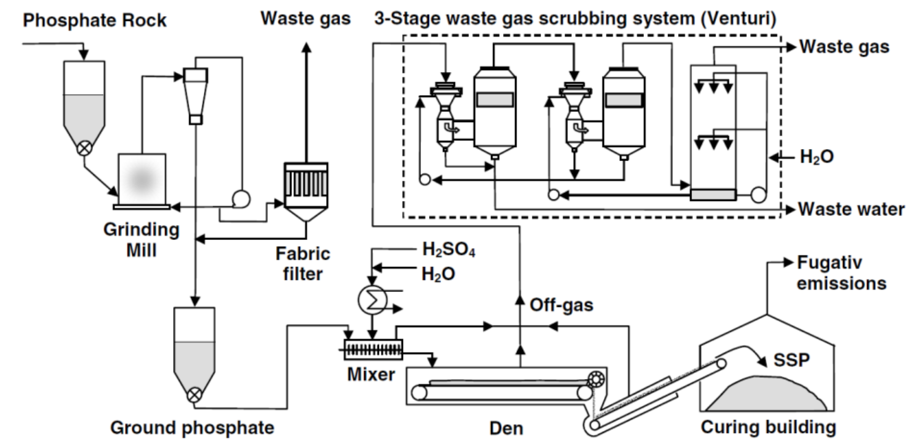
Single superphosphate (SSP) is manufactured by treating phosphate rock with sulphuric acid. Figure 1 presents a simplified block diagram of the production of single superphosphate in a so-called Broadfield den.

$$Ca_5F(PO_4)_3 + 5\ H_2SO_4 \rightarrow 3\ H_3PO_4 + 5\ CaSO_4 + HF$$

$$Ca_5F(PO_4)_3 + 7\ H_3PO_4 \rightarrow 5\ Ca(H_2PO_4)_2 + HF$$

After a mixing time of 1 – 3 minutes, the reaction mass is discharged from the mixer onto a continuously moving enclosed conveyor, the so-called den, which has a slow moving circulating floor. The mass is held in the enclosed area for a residence time of about 20 – 40 minutes, thereby moving to the end of the den. The solidified mass is broken up by a cutter and transferred by an enclosed conveyer to a storage pile for “curing” at least for 1 week, in order to complete the reaction. The reference plant uses single superphosphate as a main raw material for the production of MN-fertilisers (see also 2.1). Waste gases containing dust and considerable amounts of HF and SiF_4 arise from the digestion of phosphate rock in sulphuric acid. Waste gases are treated by wet scrubbing (see also 3.1). The resulting waste water is recycled into the production process. (see also 3.2). (UMWELTBUNDESAMT 2002)

Production of single superphosphate in a den



Source: UMWELTBUNDESAMT (2002)

umweltbundesamt

Figure 1: Schematic diagram of the production of single superphosphate in a den.

2.2 Production of Multi-Nutrient (MN) Fertilisers by the Mixed Acid Route

There are several processes for the production of multi-nutrient fertiliser using to the mixed acid route. As regards the phosphate content, starting materials might be:

- Phosphoric acid;
- Single superphosphate or triple superphosphate (digestion of phosphate rock with H_2SO_4);
- Nitrophosphoric acid (digestion of phosphate rock with HNO_3).

Figure 2 presents a simplified schematic diagram of the production process of MN-fertiliser used by the reference installation. The production process starts from single and triple superphosphate and uses a rotary granulation drum in combination with a pipe reactor. (UMWELTBUNDESAMT 2002)

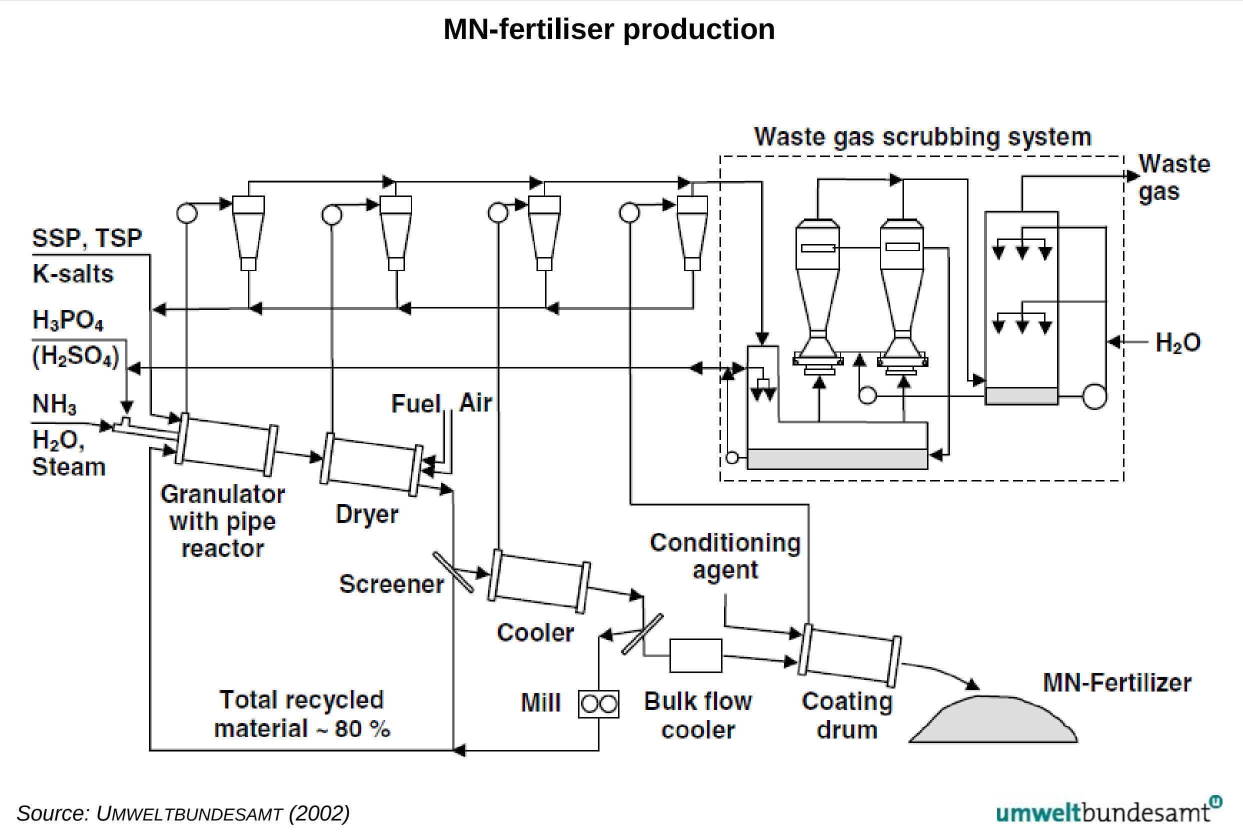


Figure 2: Schematic diagram of MN-fertiliser production (NPK and PK) in a rotary granulation drum with a pipe reactor (NPK) starting from single or triple superphosphate.

3 CURRENT EMISSIOIN AND COSNUMPTION LEVELS

3.1 Air

Single superphosphate

Dust emissions arise from grinding of the phosphate rock. Emissions of dust, HF and SiF_4 arise from the digestion of phosphate rock in sulphuric or phosphate acid. SiF4 is formed by the reaction of HF with SiO_2.

$$4\,HF + SiO_2 \rightarrow SiF_4 + 2\,H_2O$$

Phosphate rock contains 2 – 5 % fluorine. 10 – 30 % of fluorine is rapidly evolved as silicon tetrafluoride during acidulation with H_2SO_4. The production of triple superphosphate (acidulation with H_3PO_4) evolves less silicon tetrafluoride than at the production of single superphosphate.

The grinding mill for disintegration of phosphate rock is equipped with a fabric filter. In order to reduce air emissions from digestion of phosphate rock with sulphuric or phosphate acid a three stage scrubbing system is used. The first and second stages are Venturi scrubbers, the third stage is a conventional scrubber.

Multi-nutrient fertilisers (mixed acid route)

Main pollutants from the production of MN-fertilisers by the mixed acid route are dust, NH_3 and HF. When PK-fertilisers are produced, HCl is released from chloride salts during granulation or drying operations.

There are several emission sources from the production processes.

Off gases are released from the production of SSP in the den and are abated with a three stage wet scrubber under alkaline conditions.

Waste gases from granulation drum and the pipe reactor as well as from the subsequent operations drying, cooling, screening and crushing for the production of MN fertilisers are de-dusted with cyclones, combined and treated together. The waste gas is scrubbed in a 3 stage scrubbing system consisting of the following steps.

- A first stage for pre-moistening of the waste gas,
- two parallel Venturi scrubbers and
- a conventional scrubber.

For scrubbing, fresh water and effluent from periodical cleaning of the plant is used. (UMWELTBUNDESAMT 2002)

Dust emissions from the mill and the silo are abated by bag filters.

Table 2 presents emissions to air from production at the reference fertiliser plant.

A scrubber of installation 2 was exchanged in 2016, since it was too old to meet the requirements.

Table 2: Emissions to air from different installations at the reference plant (Source: Operator information)

All values in mg/Nm³	Dust		HCl		HF		NH_3	
Emission limit value	50		30		5		20	
Year of measurement	2013	2016	2013	2016	2013	2016	2013	2016
Installation 1 [1)] den	6.6	< 0.5	6.8	7.1	< 0.6	< 0.3		
	6.2	0.8	6.6	4.3	< 0.6	< 0.3		
	4.9	0.5	6.4	6.7	< 0.6	< 0.3		
		< 0.5		6.4		< 0.3		
		< 0.5		6.8		< 0.3		
		< 0.5		7.4		< 0.3		
Installation 2 [2)] Granulation	36		1.3	< 1	< 0.6	< 0.3		
	29		1.8	< 1	< 0.6	< 0.3		
	14		1.8	< 1	< 0.6	< 0.3		
Installation 3 [3)] Granulation	1.7	< 0.5	1.1	< 1	2.7	< 0.3	3.3	0.3
	1.4	< 0.5	1.2	< 1	2.8	< 0.3	3.4	0.9
	2.7	< 0.5	1.2	< 1	2.7	< 0.3	2.5	1.2
Installation 4 Mill	2.4	< 0.5						
	6.4	< 0.5						
	3.1	< 0.5						
Installation 5 raw material silo	0.8	0.7						
	0.8	0.7						
	1.0	< 0.5						

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

[1)] waste gas stream approx. 22,000 Nm^3/h

[2)] waste gas stream approx. 65,000 Nm^3/h

[3)] waste gas stream approx. 220,000 Nm^3/h

3.2 Water

Wastewater is in general reused in the production process. Due to incompatibilities between two consecutive batches, the waste water cannot be recycled into the product and has to be discharged. Emission values as well as emission limit values are displayed in

As far as possible, the granulation plant is operated alternatingly under acidic (PK-fertiliser) and alkaline conditions (NPK-fertiliser). Effluent generated from periodically cleaning the plant with water is collected in a reservoir and used for waste gas scrubbing within the next production period.

Table 3: Summary of water consumption and wastewater treatment (Source: NUA-Umweltanalytik GmbH, 14.10.2015 & NUA-Umweltanalytik GmbH, 15.04.2016)

Consumption and treatment of water	
Type of wastewater discharge	Wastewater gets indirectly discharged via the communal WWTP.
Ordinance	Wastewater from the fertilizer production is regulated by the Ordinance on inorganic fertilizer (2/8/6/3/5 anorganische Düngemittel, Anlage B). Cooling water (partial stream 1) and condensates (partial stream 6) are not regulated by the Ordinance on inorganic fertilizer. Emission limit values are determined by permit.
Internal treatment of wastewater from the process	• Partial stream 1 (digestion plant): No pre-treatment • Partial stream 3 (process water neutralisation): Neutralisation • Partial stream 6 (condensate heating station coating tanks): No pre-treatment

Table 4: Emission values from external-monitoring (EM) 2015, 2016, ELVs permit and Ordinance (2/8/6/3/5 Anorganische Düngemittel, Anlage B) (Source: NUA-Umweltanalytik GmbH, 14.10.2015 & NUA-Umweltanalytik GmbH, 15.04.2016)

Parameter	Unit	EM[1] 2015	EM[1] 2016	ELV Permit	ELV Ordinance	Method
Partial stream 1						
Q	m³/d	1200	1200			
T	°C	17.2	9.9	30		ÖNORM M 6616
pH		7.3	5.7[2]	6.0 – 8.5		DIN 38404-5; EN ISO 10523
Partial stream 3						
Q	m³/d	5	5			
T	°C	17.7	8.3	30	35	ÖNORM M 6616
ph		7.3	7.1	6.0 – 8.5	6.0 – 9.5	DIN 38404-5; EN ISO 10523
Settleable substances	ml/l	< 0.3	< 0.3	0.3		ÖNORM M 6271
COD	mg/l	< 15	< 15			ÖNORM M 6265
COD load	kg/d	< 0.075	< 0.075	117		calculated

[1] External-monitring

[2] No exceedance because of „4 out of 5“ rule – The parameter pH is complying if the spot sample of a day does not deviate more than 0.5 units from the permitted pH-value („4 out of 5“ rule) (Ordinance on inorganic fertilizer production; §4(3) Z2, 2/8/6/3/5 Anorganische Düngemittel)

Parameter	Unit	EM[3] 2015	EM[1] 2016	ELV Permit	ELV Ordinance	Method
COD specific load	kg/t			0.6	0.6	calculated
NH_4-N	mg/l	3.6	1.2			EN ISO 11732
NH_4-N load	kg/d	0.018	0.006	180		calculated
NH_4-N specific load	kg/t			2	2	calculated
Nitrite	mg/l	0.024	0.033			EN ISO 13395
Nitrate	mg/l	3.70	5.20			EN ISO 13395
Total N	mg/l	6.90	17.00			EN 25663
Total N load	kg/d	0.035	0.085	180.00		calculated
–Total P	mg/l	0.60	1.70			EN ISO 6878
Total P load	kg/d	0.003	0.009	117.00		calculated
Total P specific load	kg/t			0.60	0.60	calculated
Cadmium	mg/l	<0.010	<0.010			EN ISO 17294-2
Cadmium load	g/d	<0.05		19.50		calculated
Cadmium specific load	g/t			0.10	0.10	calculated
Mercury	mg/l	<0.00010	<0.00010			EN ISO 12846
Mercury load	g/d	<0.0005		3.90		calculated
Mercury specific load	g/t			0.02	0.02	calculated
Zinc	mg/l	<0.010	0.038			EN ISO 17294-2
Zinc load	g/d	<0.05	0.19	390.00		calculated
Zinc specific load	g/t			2.00	2.00	calculated
Fluoride	mg/l	0.10	0.60			ÖNORM M 6607; ISO 10359-1
Fluoride load	kg/d	0.0005	0.003	585.00		calculated
Fluoride specific load	kg/t			3.00	3.00	calculated
Partial stream 6						
Q	m^3/d	0.10	0.1			
T	°C	16.30	10	30		ÖNORM M 6616
pH		7.50	7	6.0 – 8.5		DIN 38404-5; EN ISO 10523

3.3 Waste

Production waste is reused as much as possible. Solid waste (e.g. dust, particles too big or small) is recycled into the granulation process; oversized particles after milling. Scrubber liquor is recycled into the production process too. When the scrubbers have to be cleaned, the scrubber liquor is stored in a tank and afterwards reused. If it is not possible to reuse the water, it is neutralized with CaO and released.

3.4 Energy

Required energy for the production is mainly supplied by a biomass plant. According to the permit the plant is fuelled only with untreated wood and has a rated heat output of 9 MW.

[3] External-monitring

The emission limit values (13% O_2, standard conditions, dry as half hourly averages) according to the permits are:

CO: 100 mg/Nm^3

NO_x: 250 mg/Nm^3

dust: 50 mg/Nm^3

unburnt hydrocarbons: 50 mg/Nm^3

NH_3: 20 mg/Nm^3

HF: 5 mg/Nm^3

HCl: 30 mg/Nm^3

The emission limit values have to be monitored yearly.

4 REFERENCES

SCHERER, H. W.; MENGEL, K., DITTMAR, H.; DRACH, M.; VOSSKAMP, R.; TRENKEL, M. E.; GUTSER, R; STEFFENS, G.; CZIKKELY, V.; NIEDERMAIER, T.; HÄHNDEL, R.; PRÜN H.; ULLRICH, K. H.; MÜHLFELD, H.; WERNER, W.; GÜNTER, K.; KUHLMANN, F.; STEINHAUSER, H.; BRÄNDLEIN, W.; KUMMER, K. F. (2000): Fertilisers. Ullmann´s Encyclopedia of Industrial Chemistry, Wiley-VCH Verlag GmbH, Weinheim, Germany, Revised 2000.

IFA – International Fertiliser Industry Association (2016): Glossary of Fertiliser Terms; http://www.fertilizer.org/En/Knowledge_Resources/About_Fertilizers/About_Fertilizers_Home_Page.aspx?WebsiteKey=411e9724-4bda-422f-abfc-8152ed74f306&New_ContentCollectionOrganizerCommon=3#New_ContentCollectionOrganizerCommon.

UMWELTBUNDESAMT (2002): Wiesenberger, H.: State-of-the-art for the production of fertilisers with regard to the IPPC-directive. Monographien, Bd. M-105. Umweltbundesamt, Wien.

NUA-UMWELTANALYTIK GMBH 2015: Prüfbericht KW-15915-1/2-2015 vom 14.10.2015.

NUA-UMWELTANALYTIK GMBH 2016: Prüfbericht KW-15915-1/3-2016 vom 15.04.2016.