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German Notes on BAT for the production of

Large Volume Solid Inorganic Chemicals

Titanium Dioxide

Final report

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1 General Information

Two different types of processes are used for the production of titanium dioxide in Germany : the sulfate process and the chloride process. In Germany, titanium dioxide is produced at four plants, three of them apply the sulfate process, one of them uses the sulfate as well as the chloride process. **Table 1.1** gives an overview of the titanium dioxide producers in Germany and their production capacities:

Table 1.1: Titanium Dioxide Producers in Germany

Manufacturers	Location	Production capacity	Processes
KRONOS TITAN GmbH & Co.OHG	Leverkusen	30.000 t/a 100.000 t/a	Sulfate process Chloride process
KRONOS TITAN GmbH & Co.OHG	Nordenham	62.000 t/a	Sulfate process
Kerr-McGee Pigments GmbH &Co.KG	Uerdingen	130.000 t/a	Sulfate process
Sachtleben AG	Duisburg	100.000 t/a	Sulfate process

2 Production of Titanium Dioxide in Germany

2.1 Production of Titanium Dioxide by Means of the Sulfate Process

2.1.1 Production Process

The production of titanium dioxide by means of the sulfate process is presented as a block scheme in **figure 2.1.1.1**. At first the raw materials ilmenite or titanium slag are dried to a humidity content of < 0,1%. The drying is necessary in order to avoid a warming-up and a premature reaction during the mixing with sulfuric acid. In ball mills the dried raw materials are ground to an average grain size of approximately 40 µm. The off-gas streams are led over a dust filter.

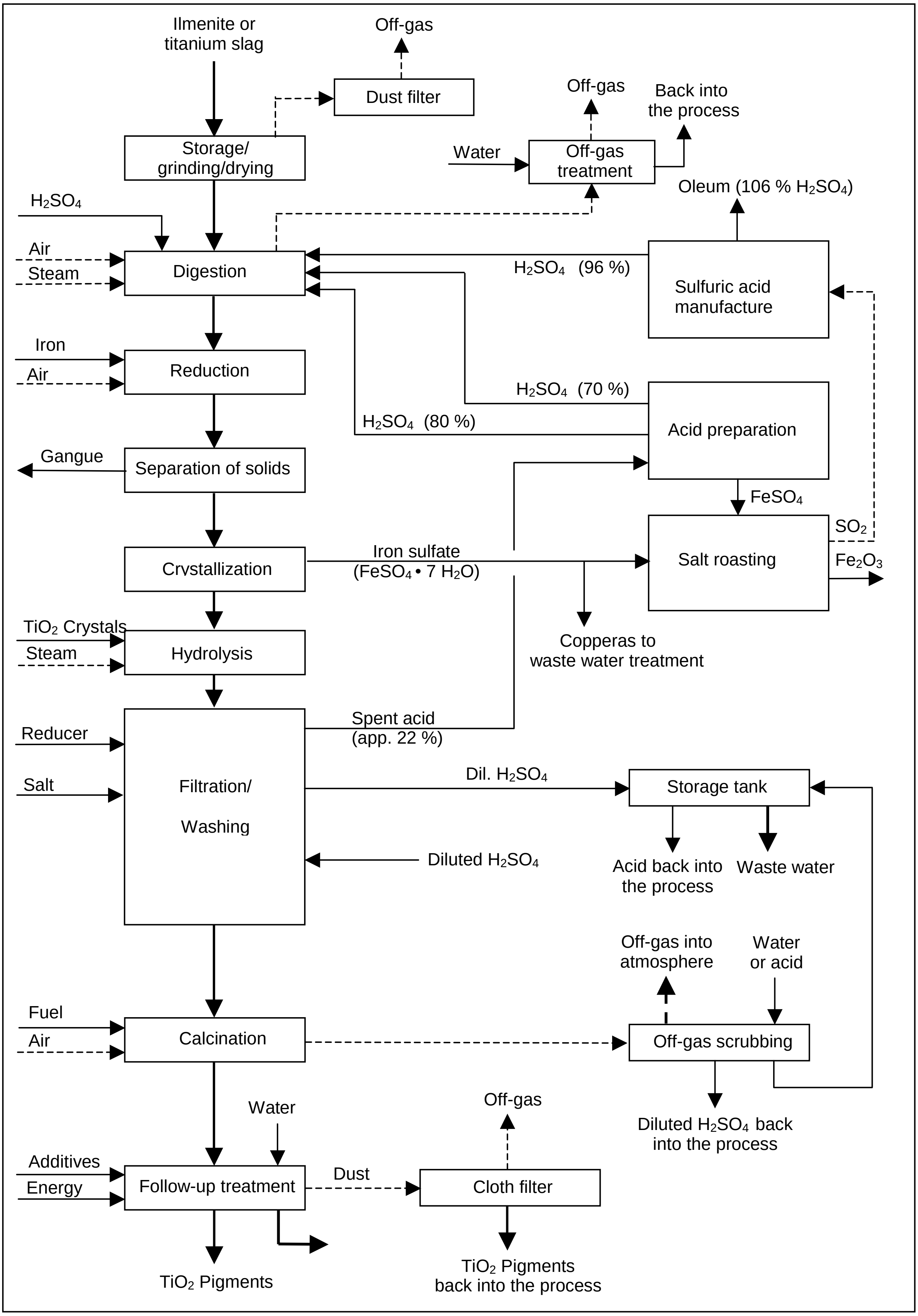


Figure 2.1.1.1: Production of Titanium Dioxide by Means of the Sulfate Process

In the subsequent batch digestion process, the ground titaniferous material is mixed with sulfuric acid. The concentration of the added H_2SO_4 fluctuates between 92 and 106 % depending on the applied preparation process at the location. The reaction in the digestion tank is initiated by the addition of water, H_2SO_4 (<70%) and perhaps steam. The hydration heat of the acid leads at first to a reaction temperature of 50 – 70 °C, which ascends to 170 – 220 ° C by the help of the exothermic formation of sulfate in accordance with equation (1).

$$(1) \qquad FeTiO_3 + 2\ H_2SO_4 \longrightarrow TiOSO_4 + FeSO_4 + 2\ H_2O$$

After achievement of the maximum temperature, the cake has to ripen for 1 – 12 hours depending on the raw material, in order to reach the highest possible yield. The off-gas is treated, before being discharged into the atmosphere.

The cake is dissolved in the digestion tank with cold water or diluted acid, which is recycled from the process. A temperature of < 85 °C has to be kept during this process, in order to avoid a premature hydrolysis. During the dissolving process, the cake must be stirred by blowing in air. The digestion velocity can be increased by blowing in air during the digestion and the ripening process. The TiO_2 concentration of the solution lies between 8 – 12 % (ilmenite decomposition) respectively 13 – 18 % (titan slag decomposition). In order to prevent the precipitation of the Fe^{3+} ions during the hydrolysis, the reduction from Fe^{3+} to Fe^{2+} in case of the ilmenite decomposition is effected by the addition of irons chips or a Ti^{3+} solution.

Afterwards all insoluble solids are separated as far as possible from the solution by a thickener, a vacuum filter or a filter press. The solutions contain 5 – 6 % $FeSO_4$ (in case of slag decomposition) respectively 15 – 20 % $FeSO_4$ after the Fe^{3+}-reduction in case of ilmenite decomposition. In the latter case iron sulfate $FeSO_4 * 7H_2O$ is crystallized out by means of vacuum cooling. Consequently the concentration of $FeSO_4$ in the spent acid is decreased and the TiO_2 concentration of the solution is increased to approximately 25 %. The salt is separated by centrifuging or filtration. The iron sulfate can be reused as copperas in the waste water treatment or it is dehydrated and discharged to the salt roasting plant, where the thermal decomposition to Fe_2O_3 and SO_2 is effected.

In accordance with equation (2), titanium oxide hydrate is selectively precipitated by hydrolysis (at 95 – 110 °C), which takes place in special stirring receptacles under the direct addition of steam. In order to achieve TiO_2-yields of up to 93 – 96 %, special nuclei accelerating the hydrolysis are added respectively generated at the beginning of the hydrolysis.

(2) $TiOSO_4 + 2\ H_2O \longrightarrow TiO(OH)_2 + H_2SO_4$

After the hydrolysis, the liquid phase of the solution contains 20 – 28 % H_2SO_4 and depending on the raw material different quantities of solved sulfates. The hydrate is separated by filtration from the spent acid. In Germany, the spent acid is concentrated to appr. 70 - 80 % H_2SO_4 and reused for the digestion of titanium raw materials. In some other European countries the spent acid is neutralized instead of preparation and recycling with lime milk, which generates gypsum. The third possibility is the utilization of the spent acid for the fertilizer production.

After the separation of the spent acid, the hydrate is washed with water or a weak acid. The residual solid metals (Fe, Cr, Mn, V) in the hydrate are eliminated by the addition of a reducer additive (f.e. Ti3+ solution or aluminum) and acid (leacher). After another filtration and washing with diluted acid, the hydrate contains only few colouring impurities. The filtered acids are collected in a storage tank, from where they can be recycled back into the process again or discharged as waste water.

After washing, the hydrate still contains 5 – 10 % H_2SO_4. For the production of a crystallized (rutile or anatas structure), most pure technical TiO_2, the hydrate is calcined in a revolving hearth furnace (calciner). Depending on the calcination temperature, a relatively coarse titanium dioxide is generated with different contents of rutile.

In order to obtain certain pigment qualities, alkali-metal compounds as well as phosphorus acid as mineralisators (< 1%) are added to the hydrate before the calcination process. Then the hydrate is filtered and led into the furnace. The cake is dehydrated to a content of approximately 40 % TiO_2 (vacuum filter) and 50 % TiO_2 (press filter).

The revolving hearth furnace is heated by oil or gas. Approximately 2/3 of the entire retention time in the furnace of 7 – 20 hours is required for the drying process. From a temperature of approximately 500 °C, sulfur trioxide is separated, which is partially decomposed to SO_2 and O_2. The product reaches maximum temperatures of 800 – 1.100 °C. The exhaust gas must have a temperature of > 300 °C, when leaving the furnace, in order to avoid the condensation of the H_2SO_4 in the duct work. A part of the exhaust gas can be recycled and is led back into the furnace for saving energy. The main quantity, however, has to be treated in the off-gas scrubber.

The obtained clinker is cooled by air and is ground then. As follow-up treatment, additives and water are added, which causes waste water. On this occasion, a dust containing off-gas occurs, which is filtered, in order to separate very small TiO_2 particles, and then discharged into the atmosphere. The residual titanium dioxide is recycled back into the process.

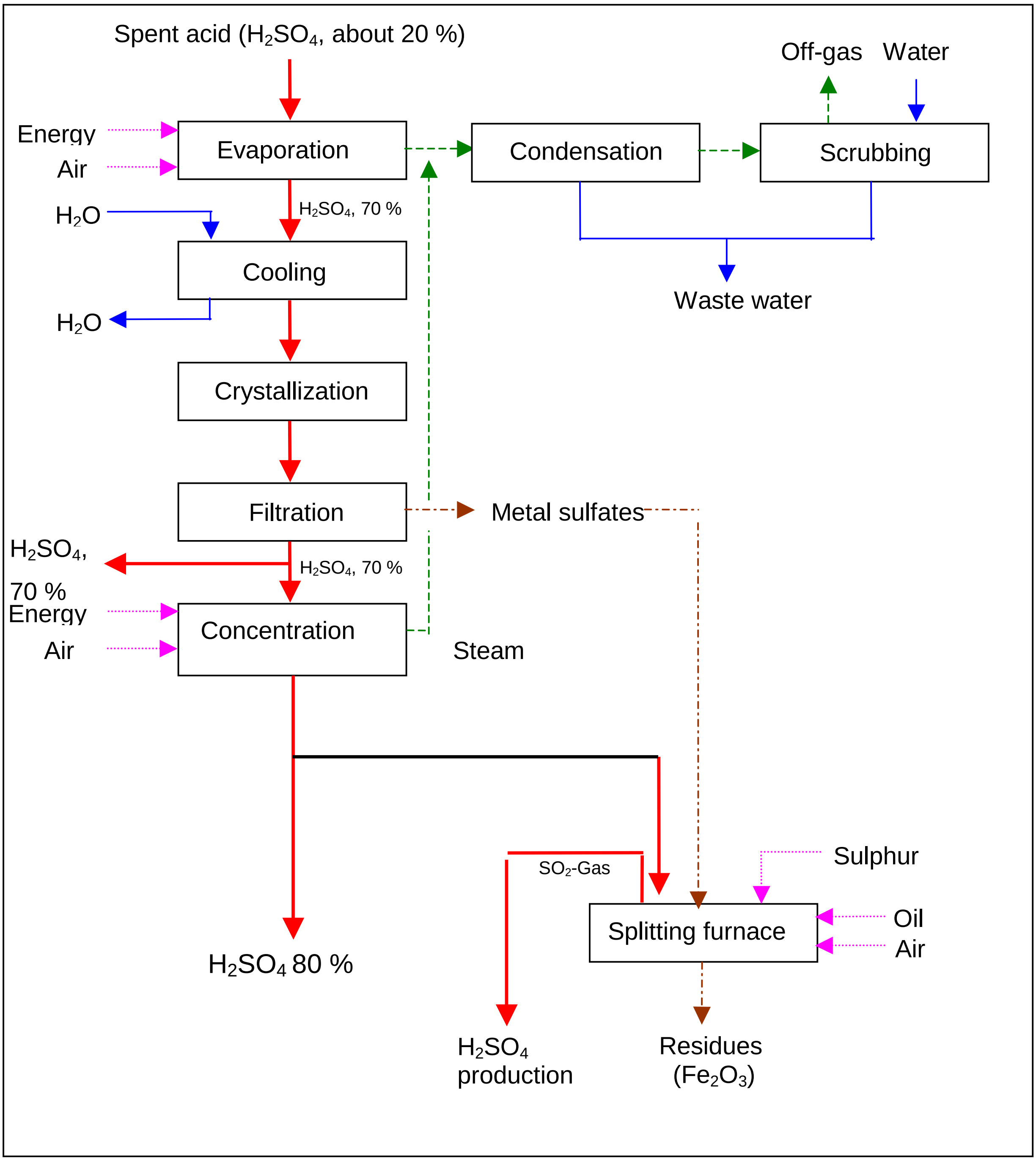
2.1.2 Sulfuric Acid Recovery

The sulfate process requires 2,4 – 3,5 t concentrated H_2SO_4 per ton TiO_2 depending on the used raw material. Sulfuric acid is discharged from the process as sulfate, especially as iron(II) sulfate, or as free sulfuric acid in the spent acid. The total volume of spent acid caused by this process amounts to approximately 6 – 9 t per ton pigment .

The recovery of the sulfuric acid from the used acid is shown in **figure 2.1.2.1.** This procedure is divided into two processes:

1. Recovery of the free acid by evaporation
2. Thermal decomposition of the sulfates and H_2SO_4 production on the basis of sulfur dioxide.

Figure 2.1.2.1: Sulfuric Acid Recovery



The spent acid is concentrated by evaporation to approximately 70 %, where iron sulfate has a minimum solubility. Then the acid is cooled. After crystallization of the salts they are separated from the acid by filtration. The almost salt-free acid can now directly or after a further concentration be recycled for the digestion. Alternatively it can also be used for other chemical processes or be decomposed to SO_2.

The separated sulfates strongly loaded with sulfuric acid are thermally decomposed in flowing bed reactors at temperatures of 800 – 1.000 °C (under the addition of sulfur, coal or oil as fuel) to sulfur dioxide and iron oxide. After cleaning the obtained sulfur dioxide is processed to virgin sulfuric acid. The residual iron oxide can be reused in the cement industry.

The spent acid of KRONOS TITAN is transported from Leverkusen to a sulfuric acid recovery plant of the company Sachtleben. Afterwards the recovered sulfuric acid is reused at KRONOS TITAN as 70 % acid and at Sachtleben and Kerr-McGee as 80% acid.

2.1.3 Emission Data and Energy Consumption

The emissions from the production of titanium dioxide by means of the sulfate process are shown in **figure 2.1.3.1**.

2.1.3.1 Off-gas Emissions

In case of the sulfate process the main emission sources are the following:

1. Off-gas from the storage, grinding and drying of the raw materials
2. Off-gas from the decomposition of the raw materials
3. Off-gas from the calciner
4. Off-gas from the follow-up treatment of the product

The off-gas streams from the storage, the grinding and the drying are purified in a dust filter before being discharged into the atmosphere.

Off-gas from the Decomposition of the Titanium Materials

The procedure for the treatment of the off-gas streams from the decomposition depends on the used raw materials. In case of ilmenite or certain slag/ilmenite-ratios

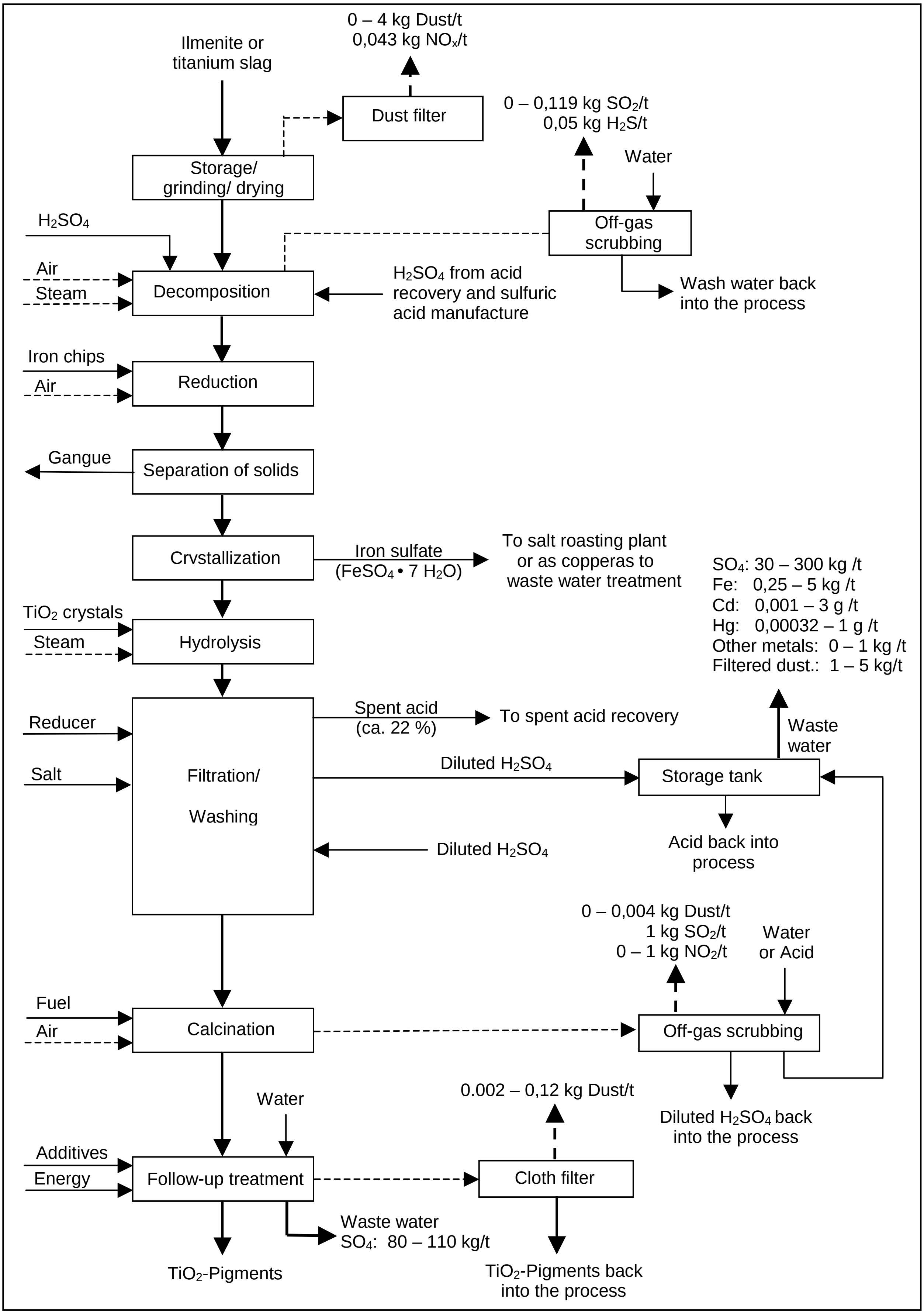


Figure 2.1.3.1 : Emissions from the Sulfate Process

Off-gas from the Storage, the Grinding and the Drying

the SO_2 concentration is so low that an off-gas scrubbing is sufficient, like e.g. at KRONOS TITAN. The acid wash water is recycled back into the process. An alternative to the recycling and recovery is at some plants the neutralization and discharge as waste water.

Another off-gas treatment, which is mainly used in case of higher SO_2 concentrations, is composed by a spray washing, a wet electrical gas scrubbing and further wash chambers. Such an off-gas treatment plant is installed e.g. at Sachtleben, where a significant decrease of the SO_2- and H_2S concentrations in the off-gas could be reached.

Off-gas from the Calciner

Different treatment concepts have also been developed for the off-gas from the calciner. KRONOS TITAN separates e.g. dust by means of a washer. Then the H_2SO_4 dust is eliminated from the off-gas by electro-static gas scrubbing. Afterwards sulfur trioxide and sulfur dioxide are washed out with water or acid. Finally the purified gases, saturated with vapour, are discharged into the atmosphere.

A further possibility for the gas desulfurization is the addition of carbonic adsorbing materials like active carbon or active coke. Sachtleben uses e.g. the sulfacid procedure as treatment for the off-gas from the calcination (see **figure 2.1.3.1.1**).

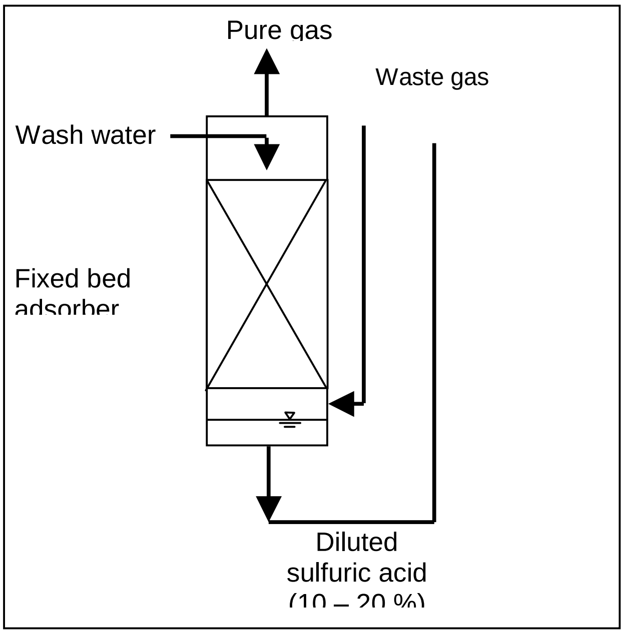


Figure 2.1.3.1.1: Sulfacid Procedure for the Treatment of Off-gases loaded with Sulfur Dioxide

In this case the adsorbing material is continuously regenerated in the fixed bed reactor by spraying water onto the loaded active carbon and by extracting diluted sulfuric acid from the adsorber at the bottom. The quality of the sulfuric acid importantly depends on other substances, which are contained in the off-gas and are in some cases also ad- or absorbed. Therefore this procedure is mainly used for off-gas that contains other substances only to a certain extent. At Kerr-McGee, altogether 7 active carbon reactors are used for the off-gas treatment, in order to keep below the German limit value for off-gas emissions of $< 0,5$ g SO_2/m^3 .

A decrease of the specific off-gas volume from the calcination can be reached by recycling as secondary air. The wash liquors from the off-gas treatment can be recycled into the process. Alternatively, the wash liquors are discharged as waste water after neutralization.

Off-gas from the Follow-up Treatment of the Products

For the purification of the off-gas from the follow-up treatment of the products a cloth filter is generally used for separating fine TiO_2 pigments. The filtered product is recycled into the process. The specific emission freights of all off-gas sources are summarized in **table 2.1.3.1.1.** with minimum, maximum and average values of the single measurements at the 4 production locations.

Table 2.1.3.1.1: Specific Emission Freights of the Sulfate Process

		Min. value [kg/t]	Max. value [kg/t]	Average [kg/t]
Storage/grinding/drying	Dust	< 0,001	0,04	1
	NO_x	< 0,001	0,043	0,043
Decomposition	SO_2	0	0,119	0,03
	H_2S	0	0,005	0,005
Calcination	Dust	<< 0,001	0,004	0,0018
	SO_2	1	1	1
	NO_2	<<0,01	1	0,7
Follow-up treatment	Dust	0,002	0,12	0,047

2.1.3.2 Waste Water

Sewages occur from the storage tanks, which store the filtered acids from the hydrate washing and from the follow-up treatment of the products. The volume of specific process waste water (without cooling water) amounts to approximately 2,5 m^3/t product. **Table 2.1.3.2.1** summarizes the specific emission loads of all German production locations of titanium dioxide.

Table 2.1.3.2.1: Specific Loads of the Process Waste Water

		Min. value [kg/t]	Max. value [kg/t]	Average [kg/t]
Filtration/Washing	SO_4	30	300	122
	Fe	0,25	5	2
	Cd	10^{-6}	0,003	$1,023 * 10^{-3}$
	Hg	$3,2 * 10^{-7}$	0,001	$3,39 * 10^{-4}$
	other met.	-	1	-
	filterable materials	1	5	3
Follow-up treatment	SO_4	80	110	95

2.1.3.3 Residues

Residues occur from the decomposition (gangue residues and neutral residues from the hydrofiltration). In most cases, decomposition residues of ilmenite and titanium slag are not recovered, but are disposed on special waste dumps. The specific residues of all German production locations of titanium dioxide are shown in **table 2.1.3.3.1**.

Table 2.1.3.3.1: Specific Volumes of Residues from the Sulfate Process

	Residue volumes from the decomposition
Min. value [kg/t]	340
Max. value [kg/t]	670
Average [kg/t]	515

2.1.3.4 Energy

The energy demand for the titanium dioxide manufacture by means of the sulfate process is shown in **table 2.1.3.4.1.** (Minimum and maximum values of all German production locations).

Table 2.1.3.4.1: Energy Demand of the Sulfate Process

		TiO_2 manufacture	Follow-up treatment	Acid concentration and filter salt decomposition	Total
Electric energy	GJ/t	1,5 – 2,31	0,6 – 1,46	0,13 – 1,3	
Steam	GJ/t	3,7 – 7,7	6,7 – 10,47	0 – 5,07	
Gas	GJ/t	7,3 – 11,85	2,37 – 4,22	0 – 0,1	
Coal	GJ/t			5,8 – 8,5	
Total energy	GJ/t	12,6 – 20,5	9,9 – 14,3	5,93 – 15,17	32,7 – 40,9

2.2 Production of Titanium Dioxide by Means of the Chloride Process

2.2.1 Production Process

The titanium dioxide production by means of the chloride process is shown in **figure 2.2.1.1**. In contrast to the sulfate process, the chloride process is continuous, where the essential share of the required chlorine necessary for the conversion of the raw materials (chlorination) is discharged during combustion and is recycled back into the process according to equation (3) and (4).

(3) $TiO_2 + 2\ Cl_2 + x\ C \longrightarrow TiCl_4 + y\ CO_2 + z\ CO$ (Chlorination)

(4) $TiCl_4 + O_2 \longrightarrow TiO_2 + 2\ Cl_2$ (Combustion)

The chlorination of the raw materials (slag, rutile, synthetic rutile and in rare cases ilmenite or leucoxene) takes place in a fluidized bed reactor with petrol coke as reducing agent. Equation (3) is also valid for all other metal oxides contained in the raw material.

Petrol coke has an extremely low ash content and only causes a small amount of HCl to be generated (chlorine losses), because it is only slightly loaded with volatile components. Generally, all raw materials should preferably be dry and free from volatile substances, in order to avoid unnecessary chlorine losses by the HCl generation. Altogether the conversion rate is high, since the only losses are dust emissions. Chlorine is converted to 98 – 100 %, the TiO_2 content in the raw material is converted to 90 –100%.

The chlorination temperature is approximately 1.000 °C, a temperature, where most of the generated metal chlorides are gaseous with the exception of Mg and Ca chlorides (which are liquid and are discharged only by vapour as well as by adherance on emitted dust. Therefore the raw materials should not exceed certain limit values of Mg and Ca, in order to avoid a „sticking together “ in the fluidized bed. Certain limit values must also be kept regarding SiO_2, since otherwise the concentration of unchlorinated SiO_2 would increase in the fluidized bed reactor.

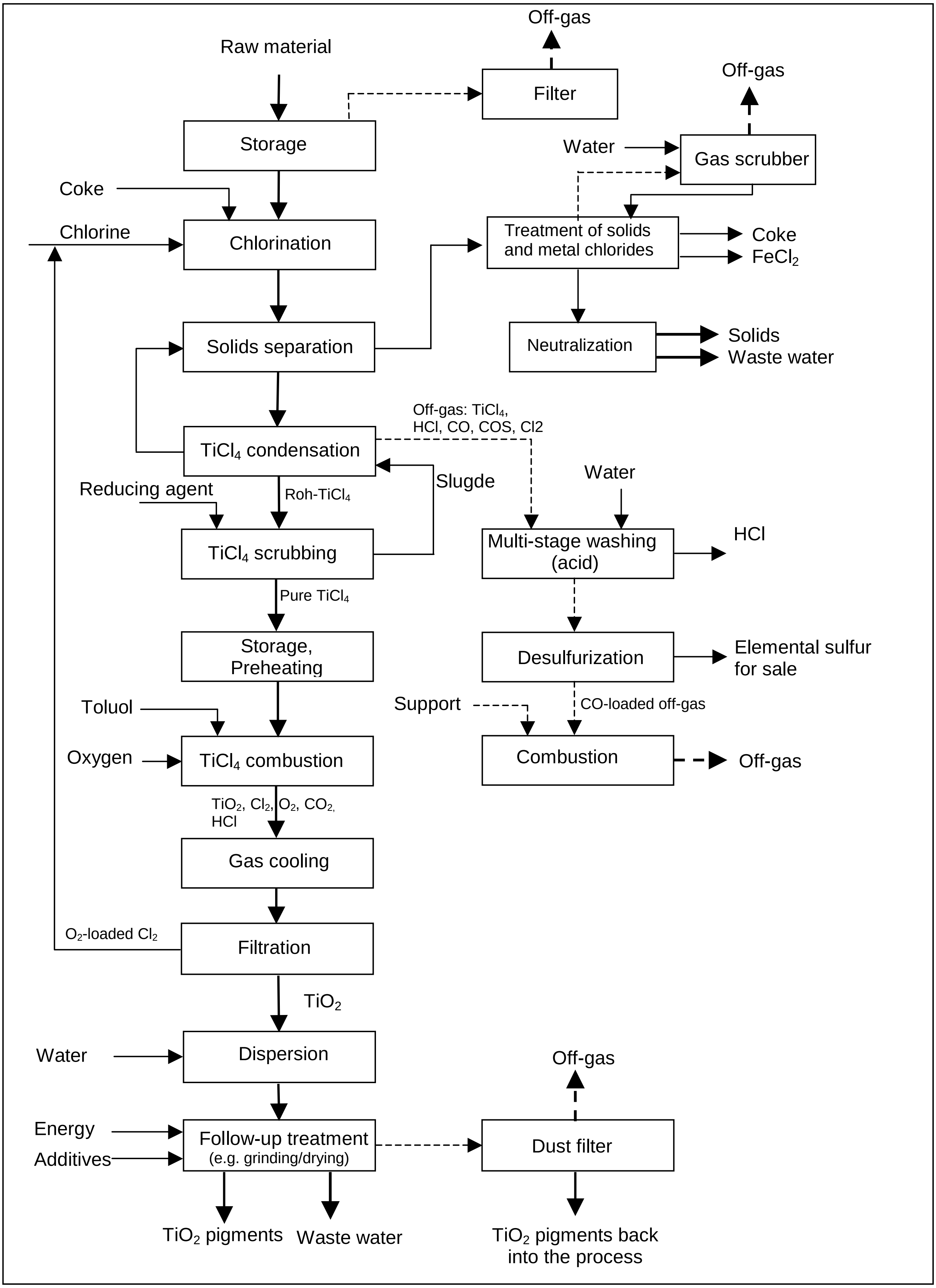


Figure 2.2.1.1: TiO_2 Production by Means of the Chloride Process

Gaseous metal chlorides as well as fine solids (residual TiO_2, SiO_2 and petrol coke) are discharged from the reactor together with the $TiCl_4$ and the residual reaction gases (CO_2, CO, HCl, N_2, COS from the sulfur content of the petrol coke). Afterwards they are cooled by the addition of cold $TiCl_4$ to a temperature barely above the boiling point of $TiCl_4$. The main part of the other metal chlorides condenses to fine dust and can be separated together with the solids from the main gas stream of the reactor. The separated solids are submitted to a treatment and coke and a metal chloride solution are generated. Under the condition that the metal chloride solution predominantly contains Fe (II) by the use of suited chlorination materials, the solution can be used as precipitation agent for the waste water treatment. Otherwise, it has to be neutralized with lime and the solids are discharged on a waste dump.

The off-gas from the treatment of the solids is cleaned in a scrubber before being discharged into the atmosphere. The acid wash water from the scrubber is recycled.

In the next process step, $TiCl_4$ is separated by further cooling (multi-stage condensation to < 0 °C) from the gas stream. The residual off-gas stream (CO_2, CO, HCl, N_2, COS, SI_2 and traces of $TiCl_4$) is treated by a multi-stage scrubber ($TiCl_4$, HCl), by a subsequent desulfurization (COS) and finally by an off-gas combustion, where CO is converted into CO_2. The off-gas from the combustion is discharged into the atmosphere. By means of a suited proceeding a pure chloric acid, which can be sold, is generated in the off-gas scrubbing. The sulphur from the desulfurization can also be sold as a separate product.

The liquid „raw $TiCl_4$ " separated by condensation is led to a distillation under the addition of a reducing agent, in order to precipitate vanadium (vanadium must almost completely be removed, since already a few ppms would lead to a yellow coloring of the pigments).

Then, corresponding to equation (4), the cleaned $TiCl_4$ is burned to TiO_2 (from about 900 °C initial temperature to approximately 2.000 °C max. temperature), under the addition of oxygen. The reaction conditions are controlled, so that the desired particle size distribution of the pigment is achieved.

The hot gas with the suspended TiO_2 particles leaving the burner is indirectly cooled by water and the TiO_2 is separated by fine porosity filters. The gas - now free of TiO_2 (mainly Cl_2 with low quantities O_2) - is recycled directly to the chlorination. Additional fresh chlorine is required to a certain extent, so that just the demand for converting the impurities of the ore (metal chlorides, emitted as dust) and for generating HCl is covered. A high TiO_2 concentration in the raw material is required to minimize chlorine losses.

Then the TiO_2 is suspended in water and is treated further for obtaining the desired pigment qualities, for example by fine grinding, surface treatment, drying, micronizing, packaging. The off-gas streams from the subsequent treatment are purified by a dust filter, before being discharged into the atmosphere: The separated TiO_2 pigments are recycled back into the process. The liquid phase of the subsequent treatment is disposed as waste water.

2.2.2 Emissions and Energy Consumption

The emissions of the titanium dioxide manufacture by the chloride process are shown in **figure 2.2.2.1.**

2.2.2.1. Off-gas Emissions

The main off-gas emission sources of the chloride process are the following:

1. Off-gas from the filling process of the storage
2. Off-gas from the recovery of the metal chlorides
3. Off-gas from the chlorination after cooling of the reaction gases
4. Off-gas from the follow-up treatment of the products

The off-gas streams from the storage are filtered before being discharged into the atmosphere.

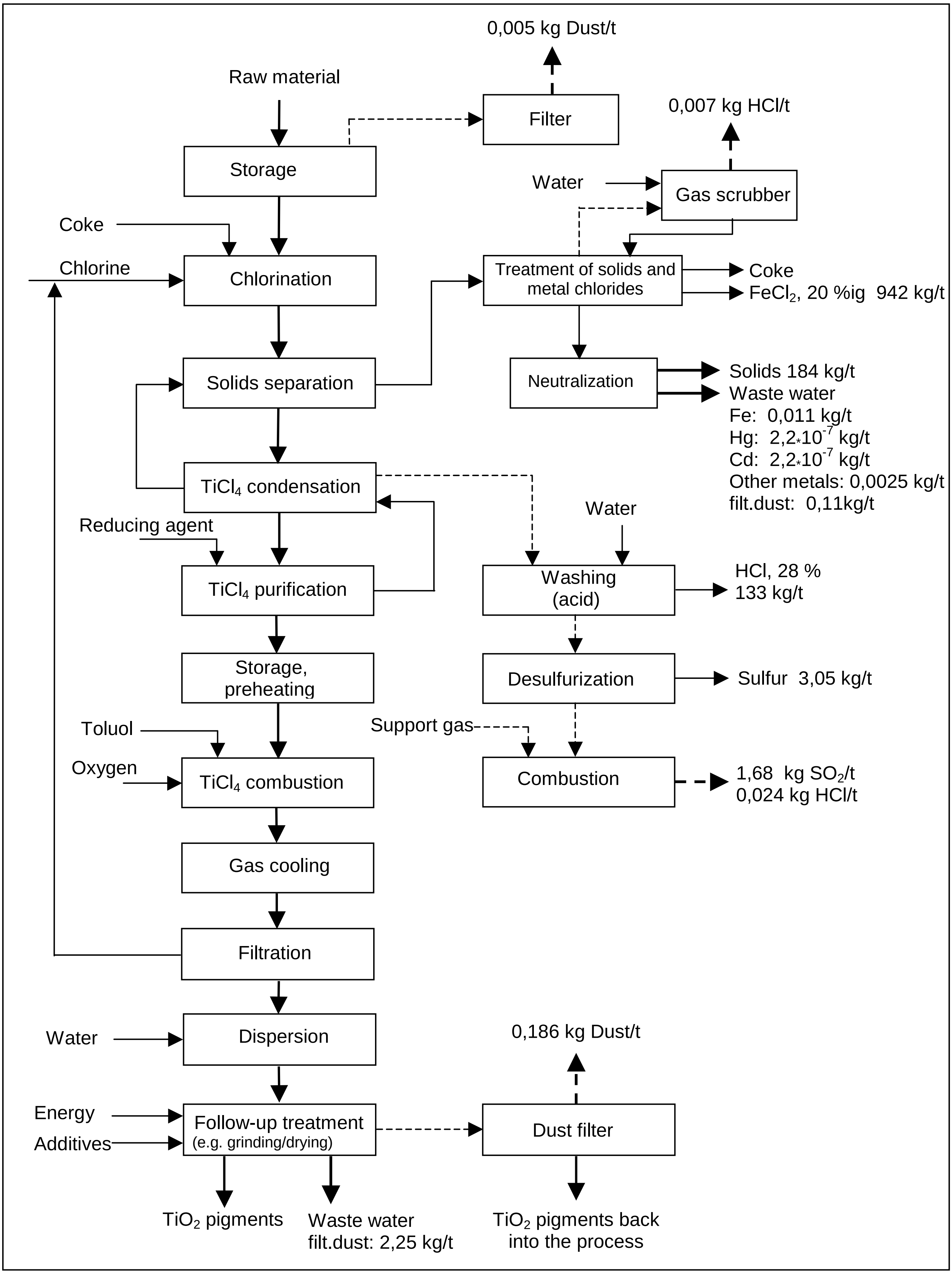


Figure 2.2.2.1.: Emissions from the Chloride Process

The off-gas from the recovery of the metal chlorides are purified by an acid washing step before being discharged into the atmosphere. The occuring wash liquor is recycled back into the process.

The off-gas from the chlorination contains traces of $TiCl_4$, Cl_2, HCl, CO and COS, even after the $TiCl_4$ condensation. $TiCl_4$, Cl_2 and HCl are eliminated by an acid off-gas washing in several steps. The wash liquors are recycled in the process or recovered and partly sold as pure hydrochloric acid (28 %). After separation of the acid substances the off-gas stream is cleaned from COS in a desulfurization process and then led into an off-gas combustion for oxidizing CO.

The off-gas from the follow-up treatment of the products is purified by a dust filter.

The specific emission freights from the different off-gas sources of the location Leverkusen are summarized in **table 2.2.2.1.1.**

Table 2.2.2.1.1.: Specific Emissions of the Chloride Process

Storage	Dust	0,005 kg/t
Solids treatment	HCl	0,007 kg/t
Off-gas treatment	SO_2 HCl	1,68 kg/t 0,024 kg/t
Follow-up treatment	Dust	0,186 kg/t

2.2.2.2. Waste Water

Sources for waste water are the recovery of the separated solids and the follow-up treatment of the products. The specific sewage volume from process water (without cooling water) amounts to 1,7 m^3/t product under the conditions in the analysed year. The spezific waste water loads of Leverkusen are summarized in **table 2.2.2.2.1**

Table 2.2.2.2.1: Spezific Waste Water Loads in the Process Waste Water at the Location Leverkusen

Preparation of the separated solids	Fe	0,011 kg/t
	Hg	$2,2 \ast 10^{-7}$ kg/t
	Cd	$2,2 \ast 10^{-7}$ kg/t
	other met.	0,0025 kg/t
	filt. dust	0,11 kg/t
Follow-up treatment	filt. dust	2,25 kg/t

2.2.2.3 Residues

Residues are caused by the preparation of the separated solids. The specific waste volume amounts to 184 kg per ton of product under the conditions in the analysed year (Chlorination materials).

2.2.2.4 Energy

The energy demand of the titanium dioxide manufacture by the chloride procedure is shown in **table 2.2.2.4.1.** The indicated values are the average of the location Leverkusen.

Table 2.2.2.4.1: Energy Demand of the Chloride Procedure

		TiO_2 manufacture	Follow-up treatment	Sum
Electricity	GJ/t	1,51	0,83	
Steam	GJ/t	1,71	7,68	
Gas	GJ/t	2,86	4,22	
Total energy	**GJ/t**	**6,1**	**12,7**	**18,8**