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für Mensch und Umwelt

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German Notes on BAT for the production of

Large Volume Solid Inorganic Chemicals

Sodium Perborate

Final report

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1 General Information

The manufacture of sodium perborate takes place as tetrahydrate at first, which is converted in a second process to monohydrate by means of dehydration. Both compounds, the tetrahydrate as well as the monohydrate can be used for the production of detergents. The monohydrate is also used for the manufacture of dishwashing detergents.

The only manufacturer of sodium perborate in Germany is the company Degussa-Hüls in Rheinfelden, which produces sodium perborate already since 1907. In the last years, the production procedure has slightly been modified. The approved production capacity amounts to 144.000 t/a. At present, the sodium perborate production is a full-continuous shift operation.

Table 1: Sodium Perborate Manufacturer and Production Capacity in Germany

Company	Location	Capacity
Degussa-Hüls AG	Rheinfelden	144.000 t/a

2 Manufacture of Sodium Perborate

2.1 Chemical Bases

2.1.1 Sodium Perborate Tetrahydrate

Sodium perborate tetrahydrate is produced in a two-step process: first the formation of sodium metaborate from borax pentahydrate and sodium hydroxide, then the reaction of metaborate with H_2O_2 forming sodium perborate according to the **reaction equations (1) and (2):**

(1) $Na_2B_4O_7 * 5\ H_2O + 2\ H_2O + 2\ NaOH \longrightarrow 4\ NaBO_2 + 8\ H_2O$

Borax pentahydrate — Sodium hydroxide — Sodium metaborate

(2) $NaBO_2 + H_2O_2 + 3\ H_2O \longrightarrow NaBO_2 * H_2O_2 * 3\ H_2O$

Sodium metaborate — H_2O_2 — Sodium perborate tetrahydrate

2.1.2 Sodium Perborate Monohydrate

The dehydration of the sodium perborate tetrahydrate formed according to equation (2) and the generation of sodium perborate monohydrate takes place following **reaction equation (3):**

(3) $NaBO_2 * H_2O_2 * 3\ H_2O \longrightarrow NaBO_2 * H_2O_2 + 3\ H_2O$

Sodium perborate tetrahydrate — Sodium perborate monohydrate

2.2 Production Procedure

2.2.1 Manufacture of Sodium Perborate Tetrahydrate

The production procedure of perborate tetrahydrate of Degussa-Hüls AG in Rheinfelden is shown as a block-scheme in **figure 1**. The raw material boron (as borax pentahydrate) is led from the silo into the solution receptacle. Under the addition of sodium hydroxide it is continously dissolved in the recovered mother liquor of the perborate manufacture and a sodium metaborate solution is generated (see reaction equation 1). Afterwards the metaborate solution is cleaned by filtration. Due to the high quality of the raw material presently used, the volume of filtration residues is relatively small in this process step. If required, sodium hydroxide can again be added, in order to increase the conversion rate.

Then the sodium metaborate solution is cooled in a vacuum cooler to a temperature of approximately 30 °. In the subsequent vacuum crystallizer it is converted into sodium perborate by the addition of a hydrogen peroxide solution of approximately 40 % at reaction temperatures between 20 and 30 °C (see reaction equation 2). For the stabilization of the solution a magnesium sulfate solution is added. The vacuum required for the vacuum cooler and the crystallizer is generated in a three-step vacuum installation, consisting of vacuum pumps, steam jets and a condenser.

The precipitated sodium perborate tetrahydrate is separated in centrifuges. The mother liquor is collected in receptacles, recycled back into the solution receptacle and reused mainly for the manufacture of the metaborate solution. A partial stream of the mother liquor is reused for the off-gas scrubbers. The separated sodium

perborate with a residual moisture of approximately 4 - 6 % is collected in salt tanks and afterwards dried in a rotatory tube. Before being discharged into the atmosphere, the off-gas from the dryer is led across a scrubber driven with the mother liquor .
The dry sodium perborate is cooled down in a fluidized bed cooler, driven with filtered, cooled air , then sieved and finally stored in silos. The off-gas from the cooler is cleaned by an off-gas scrubber.

2.2.2 Sodium Perborate Monohydrate

The manufacture of sodium perborate monohydrate on the basis of sodium perborate tetrahydrate is shown as a block-scheme in **figure 2**. The tetrahydrate is continuously led from the storage tanks onto the flowing bed dryer and is dehydrated over several drying zones at temperatures between 60 and 95 °C to sodium perborate monohydrate (see reaction equation 3).

The warm air required for the dehydration is generated in air heaters. Afterwards the warm product is cooled in flowing bed coolers down to approximately 25 °C. The required cool air is generated in a water cooler.

The dehydration and the cooling of the product are partially performed with dry air, that is dried and cooled itself in a dehydration installation by the addition of Silicagel. The cold for the air cooler is generated by a compressor, where cold water is cooled to approximately 5 °C. The further cooling is executed with the help of water.

The dust-containing off-gas from the flowing bed dryers and coolers is sucked by fans and is fed into the wet washer equipped with a droplet separator. Another droplet separator is installed inside the off-gas pipe. The cleaned off-gas is discharged into the atmosphere. The used mother liquor is continuously recycled back into the process of the tetrahydrate manufacture.

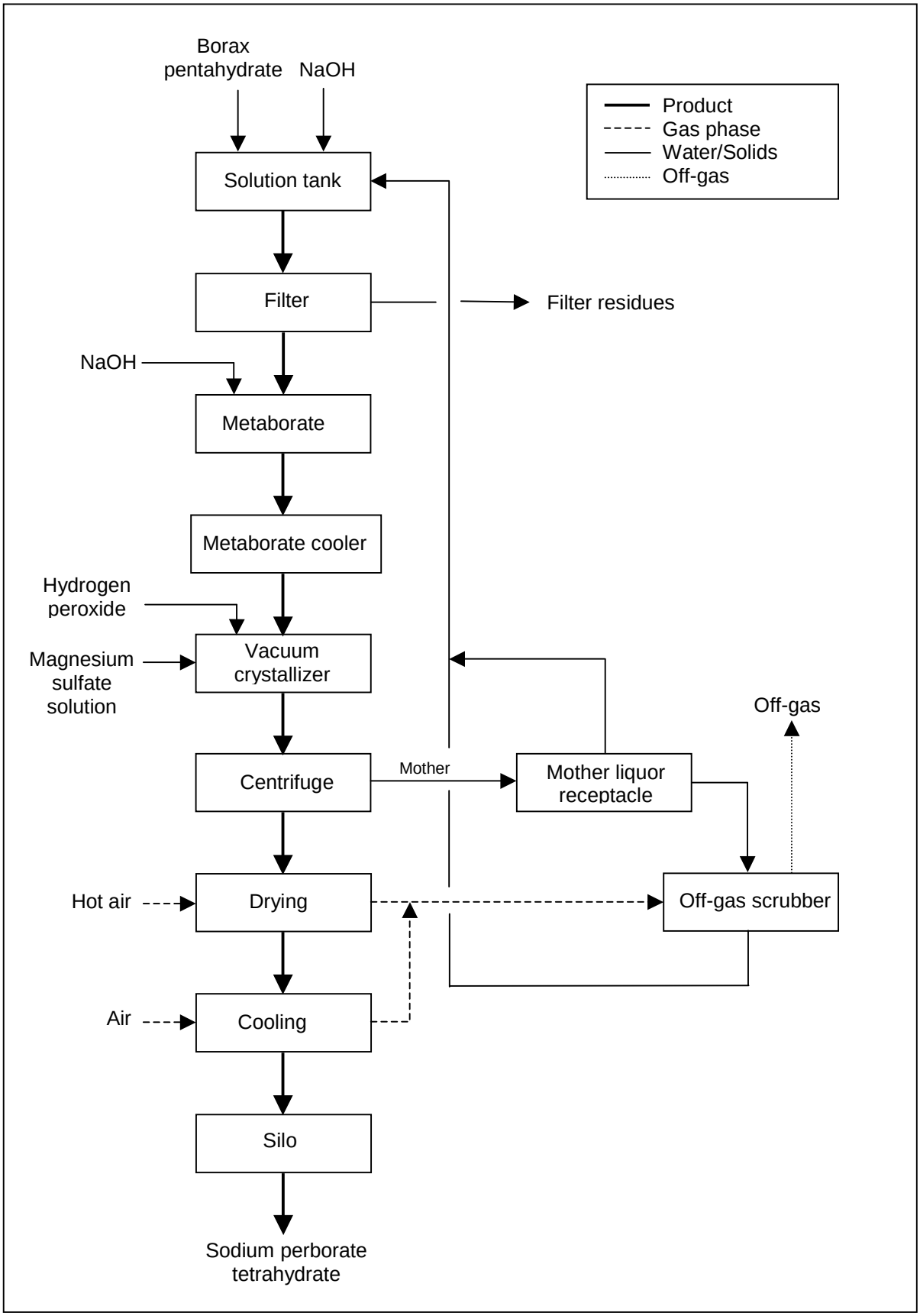

Figure 1: Block-scheme of the Sodium Perborate Tetrahydrate Production

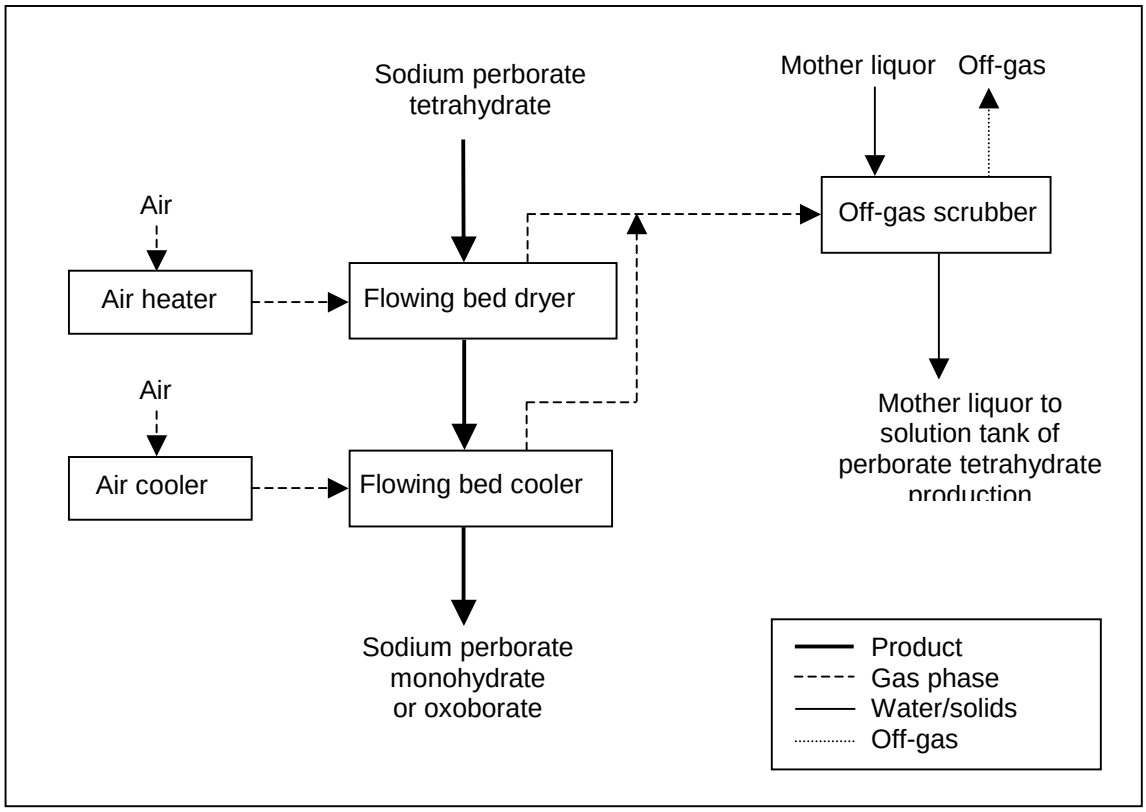

Figure 2: Block-scheme of the Manufacture of Sodium Perborate Monohydrate or Oxoborate

2.2.3 Emissions Data

2.2.3.1 Off-gas Emissions

The main emission sources of the sodium perborate production are the following:

1. Loading and Unloading Operations at the Borax Silo

   The dust-shaped borax contained in the off-gas is separated by a filter.

2. Cleaning of Conveyors and Perborate Silos

   The dust-shaped sodium perborate in the off-gas from suction units is separated by filters.

3. Drying and Cooling of Tetrahydrate and Monohydrate

The dust and droplets containing off-gas is treated by jet washers equipped with droplet separators and driven with the recycled mother liquor from the tetrahydrate manufacture. The cleaned off-gas is discharged into the atmosphere

The dust emission concentrations as well as the total dust emissions are shown in **table 2**. The emission sources, the concentrations and the off-gas volumes are presented again in **figure 3**. The stated values refer to an average utilization factor of the plant.

Table 2: Concentrations and Loads of Dust Emissions

	Parameter	
	[mg/m³]*	[kg/a]
Content of borax in the flue gas	3	
Loading and unloading operations at the borax silo (Dust)	5 – 10	200 – 300
Cleaning (suction) of conveyors, perborate silos (Dust)	1 - 5	10 – 15
Drying and cooling of tetrahydrate and monohydrate (Dust)	5 – 20	5.000 – 15.000

*The stated concentrations are average half-hour-values.

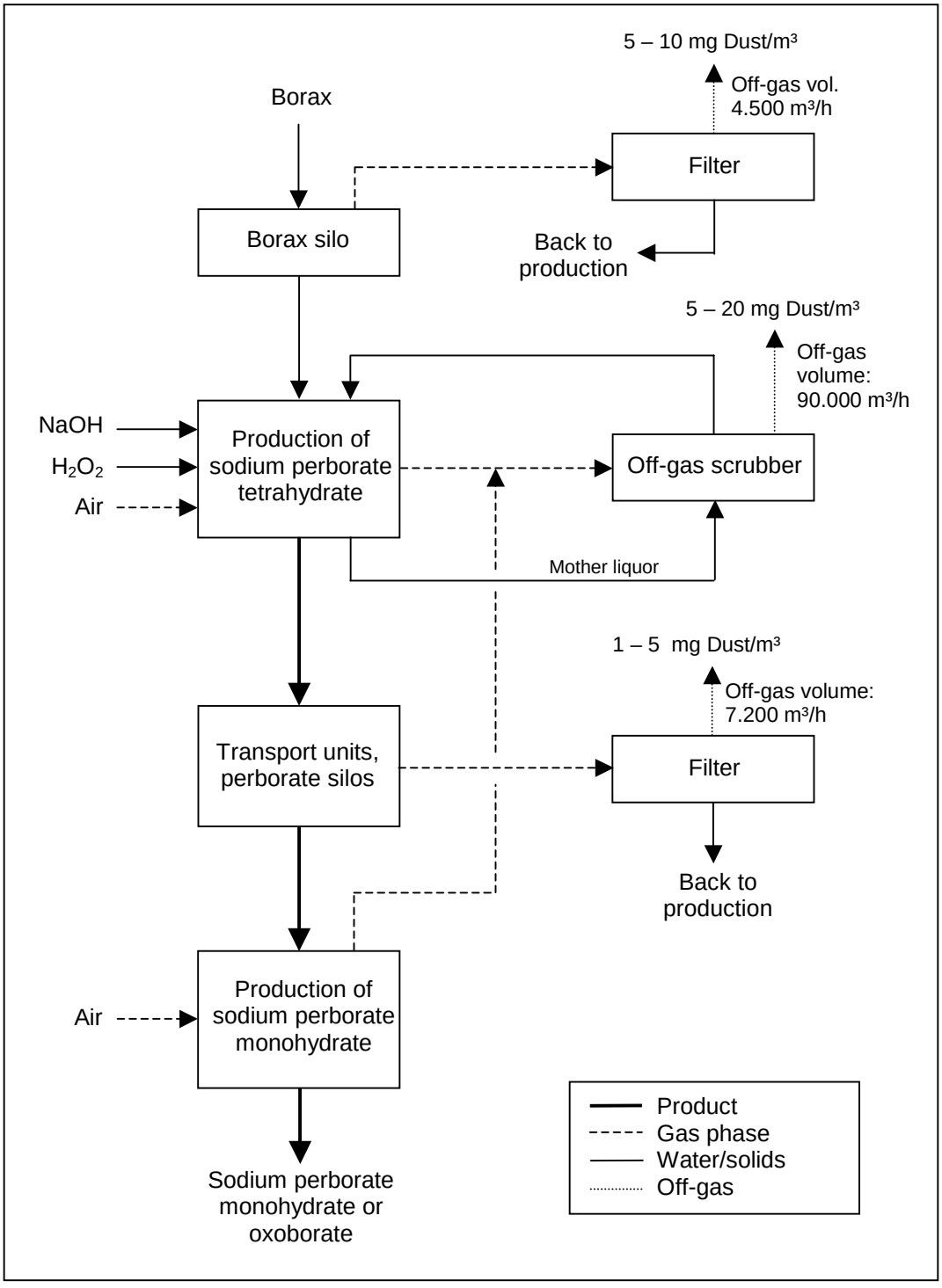

Figure 3: Emission Sources, Concentrations and Off-gas Volumes

2.2.3.2 Waste Water

The sodium perborate production by the procedure described above causes four different sources of waste water depending on the individual conditions :

1. Excess Mother Liquor

Excess mother liquor only occurs, if the water balance of the production procedure is not equalized, which mainly depends on the raw material (borax pentahydrate, borax decahydrate, polution degree of the boron raw material, water content of the hydrogen peroxide solution). Water is separated from the process cycle by vacuum crystallization.

Excess mother liquor mainly contains unconverted material as well as pollutants brought into the process by this material, e.g. soluable elements of clay minerals, compounds of the minerals from the raw material or traces of organic substances.

Degussa-Hüls Rheinfelden does not generate any excess mother liquor at present.

2. Waste Water from the Off-gas Scrubbers of the Product Dryers

Depending on the different conditions (water balance), the waste water from the off-gas scrubbers may be recycled back into the process and be reused for the mother liquor. It contains anorganic boron compounds (perborate is decomposed in an aqueous solution to sodium borate, oxygen and water).

At present, Degussa-Hüls Rheinfelden completely recycles the sewages from the off-gas scrubbers back into the production process.

3. Waste Water from the Vacuum Generation (Cooling Water)

The water-ring vacuum pumps as well as the injection coolers of the vacuum crystallization are driven with cooling water. The separated water contains low loads of soluted compounds.

4. Rinse and Cleaning Waters

In the waste water treatment plant of Degussa-Hüls Rheinfelden the rinse and cleaning waters are treated concerning the pH-value and their load of solids. They accrue in short, but irregular intervals.

The specific boron freights in the waste water from 1994 - 1999 are summarized in **table 3**. The decrease of the boron loads during the last years is mainly due to the fact, that the mother liquor is not cleaned any more by filtration and that higher concentrated wash waters are recycled back into the process. The consequence, however, is a minor purity of the final product.

Table 3: Specific Boron Freight in Relation to Perborate Tetrahydrate (g/t)

Year	Specific boron freight in relation to perborate tetrahydrate (g/t)
1994	47
1995	56
1996	49
1997	24
1998	17
1999	13

2.2.3.3 Residues

The filtration of the sodium metaborate solution causes filter residues, whose volume depends decisively on the quality of the sodium borax. The borax quality presently used at Degussa-Hüls is so high that residues can almost completely be avoided.