7.14 Sodium perborate

7.14.1 General information

7.14.1.1 Introduction

Sodium perborate, more correctly sodium peroxoborate, exists in hexahydrate, tetrahydrate and anhydrous forms, of which the most important is the hexahydrate – commercially known as sodium perborate tetrahydrate $Na_2B_2O_4(OH)_4 \cdot 6\ H_2O$ [48, W. Buchner et al, 1989].

Sodium perborate became industrially significant in Germany in 1907, when it was employed in a laundry powder, making obsolete the very laborious process of sun bleaching that had been common up until that time [13, EIPPCB, 2000]. Sodium perborate is the most important bleaching agent used in the solid detergent powders. It is a solid salt available mainly in the tetrahydrate form, although the monohydrate can also be used [6, CEFIC, 2002].

Anhydrous sodium perborate (oxoborate) is not a bleaching agent, but its ability to liberate gaseous oxygen immediately on contact with water makes it suitable for use as a disintegrating agent in the form of a tablet.

The production capacity of sodium perborate in 1992 was 900000 tonnes per year (as the tetrahydrate). Because over 80 % of the world's perborate is consumed in Europe, most of the manufacturers are located there as well [13, EIPPCB, 2000].

Since hydrogen peroxide became available on an industrial scale, the product has been obtained primarily by a continuous crystallisation process.

The boron ore (today, essentially tincal or borax) is first dissolved by a reaction with sodium hydroxide at temperatures of 60 – 90 ºC, leading to a sodium metaborate ($NaBO_2$) solution. [6, CEFIC, 2002], [13, EIPPCB, 2000]. During this step, the hydroxides of heavy metals are precipitated:

$$Na_2B_4O_7 + 2\ NaOH + 7\ H_2O \rightarrow 4\ NaB(OH)_4$$

The metaborate solution, once clarified by e.g. centrifugation, is then put into contact with an aqueous solution of hydrogen peroxide, leading to the precipitation of sodium perborate tetrahydrate crystals ($NaBO_3 \cdot 4\ H_2O$):

$$NaB(OH)_4 + H_2O_2 + H_2O \rightarrow NaBO_3 \cdot 4\ H_2O$$

The crystals are separated from the mother liquor, dried with air at a moderate temperature and shipped. The perborate tetrahydrate crystals can also be sent to an air dryer operated at a higher temperature, where the tetrahydrate is dehydrated into perborate monohydrate ($NaBO_3 \cdot H_2O$), which is also a commercial product. After solid/liquid separation the mother liquor is usually sent back to the metaborate make-up vessel.

Dust emissions to air are essentially from the drying, and to a lesser extent from the handling of solids. Emissions to water include the bleeding of excess mother liquor water from the crystallisation of perborate. The generation of waste is minor with ores like borax, but very noticeable with ores rich in inert materials like tincal [6, CEFIC, 2002].

Sodium perborate monohydrate is obtained by the dehydration of sodium perborate tetrahydrate:

$$NaBO_3 \cdot 4\ H_2O \rightarrow NaBO_3 \cdot H_2O + 3\ H_2O$$

This reaction is usually carried out by continuous contact with warm air in fluid-bed or vibrating-conveyors dryers.

To prevent agglomeration of the product bed, the temperature of feed air is raised from 80 to 160 ºC zone by zone. Before it exits the drying zone, the monohydrate is cooled with cold air.

In turn, anhydrous sodium perborate (oxoborate) is produced by removing all the crystallisation water from either sodium perborate monohydrate or tetrahydrate. Dehydration is performed in fluid-bed equipment at air temperatures of 120 – 160 ºC [13, EIPPCB, 2000].

7.14.1.2 History of production

The first industrial production of sodium perborate in the early years of the 20th century also marks the beginning of production of the so-called 'heavy duty' powder detergents for consumer use [63, CEFIC-PEROXYGENES PERBORATE Sub Group, 2004].

Starting from a wet chemical process with boron concentrates, hydrogen peroxide and sodium hydroxide being used as raw materials, part of the industry soon changed to an electrolytic process because of the limited availability of hydrogen peroxide. In the 1950s when H_2O_2 became sufficiently available from the 'anthraquinone process', all producers of sodium perborate successively turned to the wet chemical process, which, by all relevant parameters (technical, economic and environmental), had clear advantages.

7.14.1.3 Production process

The wet chemical process starts with the formation of a metaborate solution from borax pentahydrate and sodium hydroxide. In a second step, the metaborate solution reacts with hydrogen peroxide to form sodium perborate. The sodium perborate forms crystals which are separated from the mother liquor and dried to the basic end-product of sodium perborate tetrahydrate. Sodium perborate tetrahydrate can be converted by further drying into monohydrate.

7.14.1.4 Uses in industrial sectors

Sodium perborate is used as a bleach component in detergent and dishwashing powders and tablets, as well as in dental cleaners and cosmetics. Based on the draft perborate risk assessment report the usage percentages of sodium perborate are as listed in Table 7.82. These percentages have not changed significantly over the last few years.

Use	Percentage used
Processing (polymerisation aid in polysulphide sealants)	<1
Laundry detergents (heavy duty powders)	approx. 96
Dishwashing agents (automatic dishwashers)	approx. 3
Bleaching agents (denture cleansers, stain removers, buffer salts for textile bleaching)	<1

Table 7.82: Sodium perborate uses in industrial sectors
[63, CEFIC-PEROXYGENES PERBORATE Sub Group, 2004]

7.14.1.5 Production capacity

The production capacity in the European Union including new Member States was close to 400 kt PBS4 for the year 2003.

In 2006, there was one production site in each of the following countries: Austria, Belgium, Germany, Poland, Slovenia and Spain.

As the sodium perborate plants in Rheinfelden, Germany [44, UBA - Germany, 2001], and in Torrelavega, Spain [53, EIPPCB, 2004] have been closed, the example plants refered to in Section 7.14.4 are the sodium perborate plant in Hönningen, Germany and the sodium perborate plant in Althofen, Austria [85, EIPPCB, 2004-2005].

7.14.1.6 Socio-economic aspects

Sodium perborate, having been the bleach component of choice for the detergent industry for decades, is now facing an accelerating downturn in consumption due to the change in formulation trends of the detergent industry.

7.14.2 Industrial processes used

7.14.2.1 Process chemistry

Sodium perborate tetrahydrate is produced in a two step process: first the formation of sodium metaborate from borax pentahydrate and sodium hydroxide followed by the reaction of sodium metaborate with hydrogen peroxide forming sodium perborate according to the reaction equations (1) and (2):

$$(1)\ Na_2B_4O_7 \cdot 5\,H_2O + 2\,NaOH \longrightarrow 4\,NaBO_2 + 6\,H_2O$$

$$(2)\ NaBO_2 + H_2O_2 + 3\,H_2O \longrightarrow NaBO_3 \cdot 4\,H_2O$$

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):

$$(3)\qquad NaBO_3 \cdot 4\,H_2O \longrightarrow NaBO_3 \cdot H_2O + 3\,H_2O \uparrow$$

7.14.2.2 Production process

7.14.2.2.1 Manufacture of sodium perborate tetrahydrate

The typical production process of perborate tetrahydrate is shown in Figure 7.40.

The boron containing raw material borax pentahydrate is fed from the storage silo into the sodium metaborate solution preparation vessel. After the addition of sodium hydroxide, the borax pentahydrate is dissolved in the recovered mother liquor coming from the crystal separation sector, and a concentrated sodium metaborate solution is produced (see reaction equation 1). This process step can be operated continuously or batch wise. If required, sodium hydroxide or borax pentahydrate can again be added, in order to increase the conversion rate.

The metaborate solution can contain a low amount of insolubles which, in some cases, are partially removed by decantation or filtration. In some cases, flocculation aids are used to improve the separation of insolubles. Due to the high quality of the raw material currently used, the volume of filtration residues is close to zero in this process step.

The sodium metaborate solution is brought to a temperature of 30 to 60 ºC by different techniques such as vacuum or indirect cooling with a coolant.

In the subsequent vacuum crystalliser or cooling crystalliser, the sodium metaborate solution is converted into sodium perborate tetrahydrate by the addition of hydrogen peroxide solution of approximately 40 % at reaction temperatures of between 5 and 40 ºC.

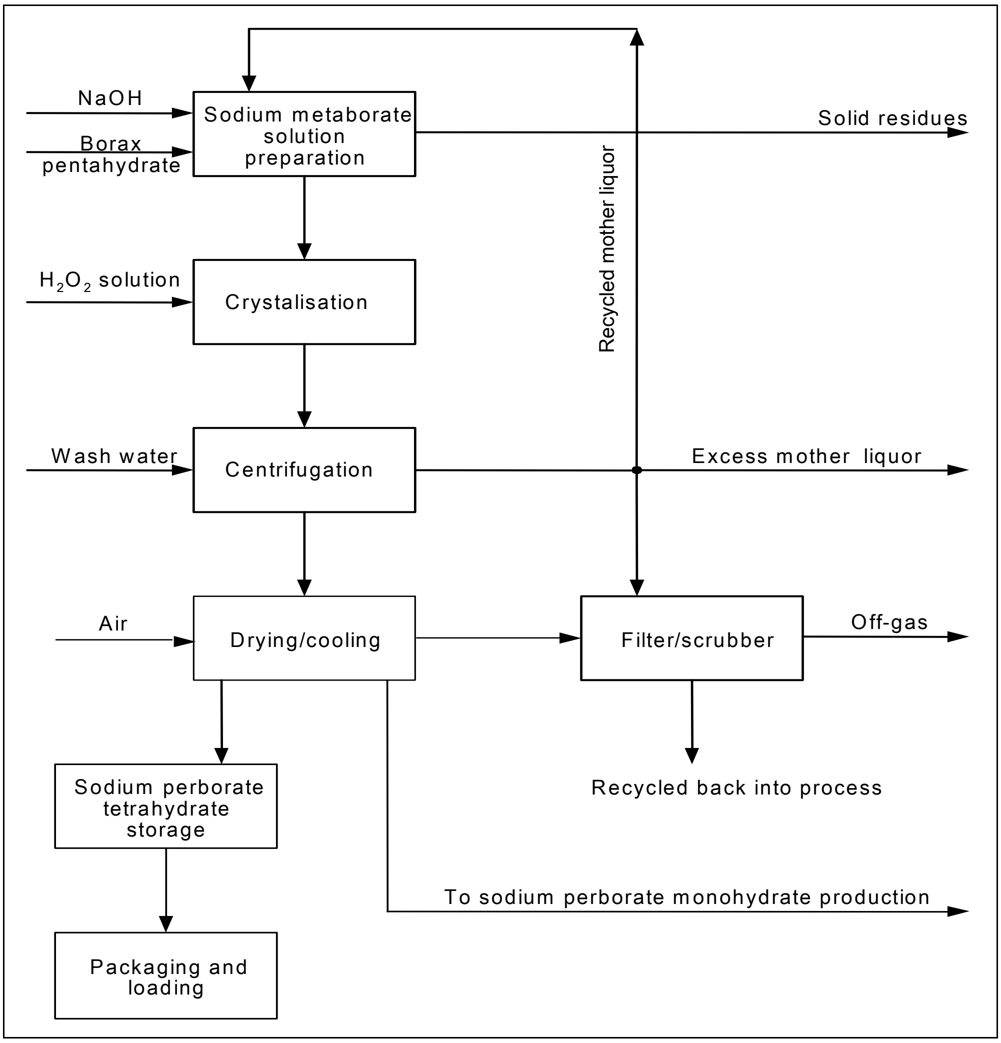

Figure 7.40: Flow diagram showing sodium perborate tetrahydrate production [63, CEFIC-PEROXYGENES PERBORATE Sub Group, 2004]

In addition to the major raw materials, there are a number of miscellaneous auxiliary materials which may be added to the process for their various attributes such as stabilisation of the sodium perborate produced. All of these are expected to have minimal potential environmental impacts.

The vacuum required for the vacuum cooler and the crystalliser is generated in a vacuum installation, consisting of vacuum pumps and/or steam jets and condenser(s). In the case of using the cooling crystallisation technique, different coolants are being applied.

The precipitated sodium perborate tetrahydrate crystals are separated from the mother liquor in centrifuges. The mother liquor is collected in storage vessels and recycled back into the process. Excess mother liquor is discharged into the sewerage system. A partial stream of the mother liquor is used for the off-gas scrubbers for dust abatement in the air coming from the drying and cooling sections.

The separated sodium perborate, with a residual moisture of approximately 4 – 8 %, is transported to the drying section for the removal of residual moisture. The dryers used are of the rotary or the fluid bed type. The drying air can be heated with steam, electrical energy or gas.

Before being discharged into the atmosphere, the off-gas from the dryer is led through a wet scrubber or bag filter. The wet scrubber is operated with the mother liquor which is recycled back into the process. The fines collected from the bag filter are also recycled back into the process.

If required, the dry sodium perborate tetrahydrate is cooled down with filtered cooled air in a fluidised bed cooler. The off-gas from the cooler is cleaned by an off-gas scrubber or bag filter.

If required, the sodium perborate tetrahydrate is sieved to remove fine and coarse particles before being stored.

7.14.2.2.2 Manufacture of sodium perborate monohydrate

The manufacture of sodium perborate monohydrate, on the basis of sodium perborate tetrahydrate, is shown in a flow diagram in Figure 7.41. The sodium perborate tetrahydrate is fed into fluid bed dryers in which the hydration water is removed to form sodium perborate monohydrate (see reaction equation 3).

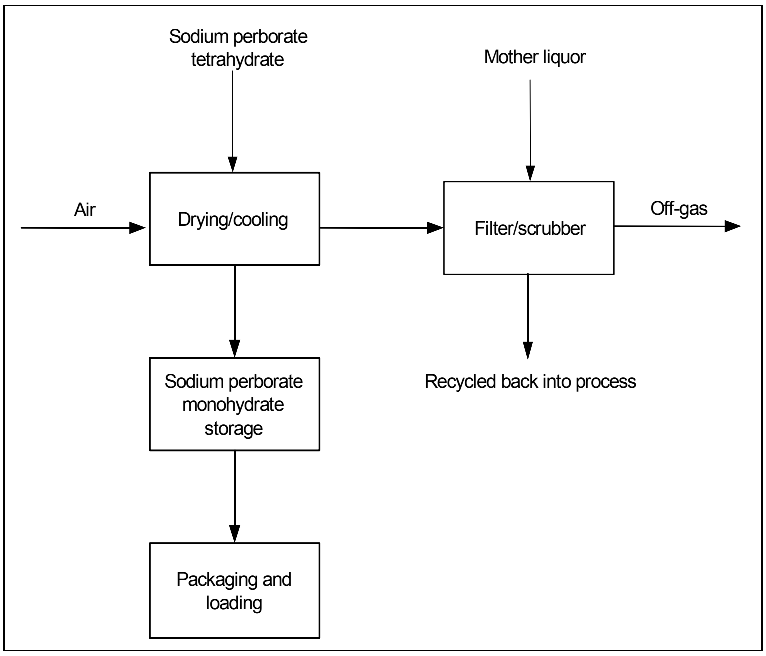

Figure 7.41: Flow diagram showing sodium perborate monohydrate production [63, CEFIC-PEROXYGENES PERBORATE Sub Group, 2004]

This process can be operated continuously or batch wise. The required hot drying air can be generated in air heaters which are heated by steam or gas.

Afterwards the warm product is cooled down to approximately 25 – 35 ºC in fluid bed coolers. The required cool air is generated in a cooler by means of a coolant.

If required, the sodium perborate monohydrate is sieved to remove fine and coarse particles before being stored.

The dust containing off-gas from the sodium perborate monohydrate dryers and coolers is led through wet-scrubbers or bag filters before being discharged to the air. The wet scrubber is operated with mother liquor and the used mother liquor is recycled back to the process. In case a bag filter is used, the collected fines are also recycled back to the process.

7.14.3 Present consumption and emission levels

7.14.3.1 Raw materials

The following list gives the main raw materials used in the production of sodium perborate tetrahydrate/monohydrate:

- borax pentahydrate
- sodium hydroxide
- hydrogen peroxide.

Borax pentahydrate and sodium hydroxide are used for the preparation of sodium metaborate solution. In the crystallisation step, the obtained solution is mixed with hydrogen peroxide to form a suspension of sodium perborate tetrahydrate.

The ore from which borax pentahydrate is produced is excavated primarily in the US and Turkey. The ore is purified and crystallised to obtain the borax pentahydrate which contains a minimum level of impurities.

Sodium hydroxide solution (typically 50 % concentration) is produced by electrolytic processes.

Hydrogen peroxide is produced by the anthraquinone process.

The Table 7.83 shows the consumption of the main raw materials per tonne of sodium perborate tetrahydrate (PBS4):

PBS4	Units	Consumption min/max
Borax pentahydrate (as is)	kg/t PBS4	470/520
Hydrogen peroxide (as 100 % H_2O_2)	kg/t PBS4	220/250
Sodium hydroxide (as 100 % NaOH)	kg/t PBS4	130/150

Table 7.83: Main raw materials used in the production of sodium perborate tetrahydrate [63, CEFIC-PEROXYGENES PERBORATE Sub Group, 2004]

7.14.3.2 Utilities

7.14.3.2.1 Steam

For the production of sodium perborate, steam is an important energy transfer medium and is generated in boilers.

Steam is used to heat up the mother liquor in the preparation of sodium metaborate, in order to boil out crystallisers (to clean the cooling coils), to generate a vacuum and to heat up the air that is used in the drying of sodium perborate tetrahydrate and monohydrate.

7.14.3.2.2 Cooling media

Some steps in the production of sodium perborate tetrahydrate require cooling. Cooling is needed predominantly in the crystallisation process (to remove the heat of the reaction) and, to a lesser degree, to cool the solution of sodium metaborate and the air in the drying/cooling process. Water is normally used as a cooling medium. In a closed cooling system, other cooling media can be used such as a mixture of glycol and water or a brine solution. The closed cooling system requires the use of either cooling towers or cooling aggregates. With open cooling systems, fresh water from different sources is used and then discharged to the sewerage system.

7.14.3.2.3 Electric energy

Electric energy is needed to operate the different process steps such as cooling aggregates, pumps, centrifuges, blowers, heating, etc.

7.14.3.2.4 Natural gas

Natural gas can also be used to heat up the air that is used in the drying of sodium perborate tetrahydrate and monohydrate.

7.14.3.2.5 Total energy consumption

The total energy consumption in the production of sodium perborate tetrahydrate is up to 3.7 GJ/t and in the production of sodium perborate monohydrate up to 9.4 GJ/t PBS4 equivalent.

It should be noted, however [85, EIPPCB, 2004-2005], that these maximum levels of energy consumption are linked to much lower boron emissions than the maximum level of boron emission to water of up to 5 kg B/t sodium perborate tetrahydrate produced, as reported in Section 7.14.3.3.2 below.

A relationship exists between boron emissions to water and energy consumption and, therefore, two alternative options for PBS4 and PBS1 production are available:

- option A (high energy consumption – low boron emission to water). In this option, illustrative for boron emissions of below 0.35 kg B/t PBS4, the plant can be operated for the production of PBS4 with a total energy consumption of less than 3.7 GJ/t PBS4, and for the production of PBS1 with a total energy consumption of less than 9.4 GJ/t PBS4 equivalent
- option B (low energy consumption – high boron emission to water). In this option, illustrative for boron emissions of below 5 kg B/t PBS4, the plant can be operated for the production of PBS4 with a total energy consumption of less than 1.5 GJ/t PBS4 and for the production of PBS1 with a total energy consumption of less than 4 GJ/t PBS4 equivalent.

Thus, when starting from the boron ore, and assuming boron emissions to water as in the options analysed above, the overall energy consumption in the production of sodium perborate tetrahydrate can be within the range of <1.5 – 3.7 GJ/t PBS4, and when followed by the production of sodium perborate monohydrate, within a range of <4.0 – 9.4 GJ/t PBS4 equivalent. The lower ends in these ranges relate to higher boron emissions to water (<5 kg B/t PBS4) and the higher ends relate to lower boron emissions to water (<0.35 kg B/t PBS4).

Consequently, it should be also noted, that in the above-mentioned extreme options (boron emissions to water of either <5 kg B/t PBS4 or <0.35 kg B/t PBS4), energy consumption to convert PBS4 to PBS1 is within the range <2.5 – 5.7 GJ/t PBS4 equivalent, which translates to energy consumption within the range <4.0 – 9.1 GJ/t PBS1 product.

Depending on the local situation, a choice can be made between these two alternative options for PBS4 and PBS1 production. Options A and B are extreme ones, and there are several operational possibilities between them.

7.14.3.3 Emissions

7.14.3.3.1 Dust emissions

Dust emissions occur mainly in the process of drying sodium perborate tetrahydrate and monohydrate. The exhaust air from the dryers is cleaned by means of bag filters or wet scrubbers. In this way, the dust content in the air that is discharged into the atmosphere is greatly reduced. In addition, filters or scrubbers are used for dust abatement during conveying, packing and loading.

The level of dust emissions is up to 0.2 kg of dust/t of sodium perborate tetrahydrate (based upon full conversion to sodium perborate monohydrate). However, emissions of dust as low as 0.03 – 0.1 kg of dust/t of sodium perborate tetrahydrate have been reported [44, UBA - Germany, 2001], with the average half hourly values of dust concentrations in the outlet air of 5 – 20 mg/m^3 from drying and cooling of sodium perborate tetrahydrate and monohydrate.

It is reported that in the Austrian plant, applying a combination of cyclones and a scrubber for the production of PBS4, and a combination of cyclones and bag filters for the production of PBS1, sodium perborate dust emissions far below 5 mg/Nm^3 are achieved [85, EIPPCB, 2004-2005].

However, the PBS industry considers that with techniques such as bag filters or wet scrubbers, the achievable dust emission value is below 20 mg/Nm^3 air [85, EIPPCB, 2004-2005].

7.14.3.3.2 Water emissions

The source of water emissions is the excess mother liquor from the centrifugation step and cleaning water. A major part of the mother liquor is recycled while a part of it is neutralised and discharged to the sewerage system. The mother liquor contains small amounts of sodium metaborate.

Cooling water from an open or closed system is discharged together with the neutralised mother liquor.

The emissions of boron to water are up to 5 kg boron/t sodium perborate tetrahydrate produced, however, emissions of boron to water as low as 13 – 17 g/t sodium perborate tetrahydrate have been reported in the sodium perborate plant in Rheinfelden, Germany [44, UBA - Germany, 2001]. As mentioned above, this plant is closed.

It should be also noted, that according to the Austrian Ministerial Order on inorganic chemicals (pertaining also to the example sodium perborate plant in Althofen, Austria), the limit of boron emissions to water is set at 0.35 kg B/t installed capacity calculated as PBS4 [85, EIPPCB, 2004-2005].

7.14.4 Techniques to consider in the determination of BAT

Introduction: Techniques to consider in the determination of BAT – refer to Section 7.1.4

The use of pure raw materials as specified in Section 7.14.3.1 and the techniques described in Section 7.14.4.1 and used in the process steps for dissolution, crystallisation, centrifugation and drying, are the main techniques to consider in the determination of BAT for the production of sodium perborate. The industry has selected and developed the techniques over many years in multiple locations which has resulted in mature processes with similar performances. Further improvements, especially with regard to the environment, are mainly in the fine tuning of the processes and are expected to result in marginal changes of emissions [63, CEFIC-PEROXYGENES PERBORATE Sub Group, 2004].

7.14.4.1 Pure raw materials used for the production of sodium perborate

Description

The type and the purity of the boron raw material used has a major influence on the environmental performance of the production of sodium perborate tetrahydrate (PBS4).

Today, the boron raw material used is borax pentahydrate. The use of borax pentahydrate has, in comparison to other raw materials containing boron (e.g. calcium borates), the advantage of good water solubility, thus avoiding large quantities of by-products, which occur in the breaking down of boron minerals containing calcium.

The industry-wide change to use borax pentahydrate as a boron mineral has reduced the quantity of solid waste originating from the boron mineral to very low levels and has also reduced the use of energy for this process step.

The use of borax pentahydrate, which has a high B_2O_3 content of >46 % and, correspondingly, a low content of crystallisation water, helps to minimise the production of excess mother liquor from the sodium perborate process. In the last few decades, the use of increasingly purer raw materials containing boron with a high active matter content has led to an increasingly reduced environmental impact caused by the perborate production process. Other raw materials, hydrogen peroxide and sodium hydroxide, are of standardised technical grades.

Achieved environmental benefits

The use of pure raw materials, and particularly borax pentahydrate, in the production of sodium perborate helps to reduce the quantity of solid waste coming from the boron mineral, to minimise the amount of mother liquor and to reduce the amount of energy used in the process.

Cross-media effects

There are no reported disadvantages caused by the implementation of this technique.

Operational data

No detailed data submitted. The production of sodium perborate is carried out according to the wet process route in which borax pentahydrate, hydrogen peroxide and sodium hydroxide are the main raw materials used – refer to Table 7.83 and to Figure 7.40.

Applicability

Applicable to the plants producing sodium perborate by the wet process route (PBS4).

Economics

No data submitted.

Driving force for implementation

High material and energy efficiency in the process, leading to the minimisation of the impact of the production of sodium perborate on the environment and to the reduced manufacturing cost.

Example plants

The sodium perborate plant in plant in Hönningen, Germany.
The sodium perborate plant in Althofen, Austria.

Reference literature

[44, UBA - Germany, 2001], [63, CEFIC-PEROXYGENES PERBORATE Sub Group, 2004], [53, EIPPCB, 2004], [48, W. Buchner et al, 1989], [6, CEFIC, 2002].

7.14.4.2 Manufacture of the intermediate product (metaborate solution)

Description
The manufacture of the intermediate product, metaborate solution from borax pentahydrate and sodium hydroxide occurs in the temperature range of 60 – 95 °C, after which it is cooled to 30 - 60 °C. This process step can be operated continuously or batch wise.

In order to set the temperature of the metaborate solution, the heat can either be transferred directly by the use of steam or indirectly using a heat carrier. Carrying out this process step in the lower temperature of approx. 60 °C saves energy.

Achieved environmental benefits
Energy savings in the process, indirectly resulting in the protection of the environment.

Cross-media effects
It is reported that the influence of the reaction temperature on the required reaction time for sodium metaborate production is very limited.

Operational data
By keeping a lower level of the temperatures in the process, the excessive losses of energy are avoided. No detailed data submitted – refer to Table 7.83 and to Figure 7.40.

Applicability
Applicable to the plants producing sodium perborate by the wet process route.

Economics
No data submitted.

Driving force for implementation
Lower energy losses in the process.

Example plants
The sodium perborate plant in plant in Hönningen, Germany.
The sodium perborate plant in Althofen, Austria.

Reference literature
[44, UBA - Germany, 2001], [63, CEFIC-PEROXYGENES PERBORATE Sub Group, 2004], [85, EIPPCB, 2004-2005].

7.14.4.3 Purifying the metaborate solution/waste aspect

Description
The metaborate solution is usually purified before the crystallisation step, i.e. through decanting or through filtration of the insoluble impurities.

The waste quantities resulting from the separation step can be kept to a minimum, if the boron raw material used was selected under the conditions mentioned in section.

Achieved environmental benefits
The use of borax pentahydrate in the production of sodium perborate helps to reduce the quantity of solid waste coming from the boron mineral – refer to Section 7.14.4.1.

Cross-media effects
There are no reported disadvantages caused by the implementation of this technique.

Operational data
No detailed data submitted – refer to Table 7.83 and to Figure 7.40. The purification of the metaborate solution results in better performance of the crystallisation and centrifugation steps, and in the reduction of the volume of the mother liquor produced, and this, in turn, allows for achieving a higher performance of the whole process.

Applicability
Applicable to the plants producing sodium perborate by the wet process route.

Economics
No data submitted.

Driving force for implementation
High material and energy efficiency in the process, leading to the minimisation of the impact of the production of sodium perborate on the environment.

Example plants
The sodium perborate plant in plant in Hönningen, Germany.
The sodium perborate plant in Althofen, Austria.

Reference literature
[44, UBA - Germany, 2001], [63, CEFIC-PEROXYGENES PERBORATE Sub Group, 2004].

7.14.4.4 Crystallisation of perborate tetrahydrate

Description
The reaction of sodium metaborate and hydrogen peroxide, as well as the crystallisation of perborate tetrahydrate, are exothermic, i.e. energy for cooling is required. In practice, in order to remove the heat of crystallisation, either a cooling or a vacuum system is used.

In the first method, an additional cooling system is required to provide cold (e.g. an ammonia cooling system, or a salt brine cooling system).

In the second method, water is removed from the mother liquor by evaporation, thus reducing the quantity of excess mother liquor produced. In this system, steam ejectors are typically used in combination with water condensors, however vacuum systems in which only high efficiency vacuum pumps are used, are also applied in the chemical industry sector.

Achieved environmental benefits
High material efficiency of the PBS4 process is achieved by the decreased volume of excess mother liquor circulating within the process (by water evaporation) and by the reduced borate concentration in the mother liquor (by a lower temperature in the case of cooling crystallisation) – refer to to Figure 7.40, indirectly resulting in the protection of the environment.

Cross-media effects
No information submitted, in particular regarding the possible emissions of PBS4 droplets/mist to water in the barometric condensers used in the vacuum system, however, when liquid ring vacuum pumps operating with water are used in the vacuum system, apart from the process water droplets, no mother liquor droplets leave the pumps.

Operational data
Refer to Table 7.83 and to Figure 7.40.

When a vacuum system is used in the crystallisation step, the evaporation of water from the mother liquor takes place, leading to the reduction of the volume of the mother liquor recirculated in the plant, and this, in turn, allows for achieving a higher performance of the whole PBS4 process.

The energy requirement for the operation of the cooling system has been estimated at 0.2 GJ/t PBS4, while the energy consumption for the vacuum crystallisation at 0.05 GJ/t PBS4. This is a small part of the total energy requirement which can reach 3.7 GJ/t in the production of sodium perborate tetrahydrate and 9.4 GJ/t in the production of sodium perborate monohydrate. Additionally, crystallisation at lower temperatures also results in a product with improved attrition resistance.

Applicability
To a varying degree, applicable to the plants producing sodium perborate by the wet process route, depending on the cooling system used in the crystallisation step (PBS4 crystallisation by cooling vs. PBS4 crystallisation by evaporation).

Economics
No data submitted.

Driving force for implementation
High material efficiency of the PBS4 plant.

Example plants
The sodium perborate plant in plant in Hönningen, Germany.
The sodium perborate plant in Althofen, Austria.

Reference literature
[44, UBA - Germany, 2001], [63, CEFIC-PEROXYGENES PERBORATE Sub Group, 2004], [85, EIPPCB, 2004-2005].

7.14.4.5 Separation of the crystals from the mother liquor

Description
For energy saving reasons, it is especially advantageous to achieve a low surface moisture in the centrifuge wet cake which is obtained after the separation of the mother liquor. A low moisture content of the wet cake reduces the energy input for the final drying step. In order to achieve this, discontinuous centrifuges or multiple step continuous centrifuges are used for the separation of the crystallised perborate tetrahydrate today. Depending on the crystal structure of the product and the type of centrifuge used, it is possible to reach residual moistures of 3 – 10 % in the centrifuged wet cake.

Achieved environmental benefits
Energy savings in the process, in particular in the subsequent drying section, indirectly and directly resulting in the protection of the environment.

Cross-media effects
No information submitted, in particular with regard to using one of the mutually excluding options in the crystallisation system, for the size and the structure of PBS4 crystals obtained.

Operational data
No detailed data submitted. The lower the moisture in the wet PBS4 cake, the less energy required for its drying in the subsequent drying section.

Applicability
To a varying degree, applicable to the plants producing sodium perborate by the wet process route, also depending on the cooling sytsem used in the crystallisation step (PBS4 crystallisation by cooling vs. PBS4 crystallisation by evaporation).

Economics
No data submitted.

Driving force for implementation
High energy efficiency of the PBS4 plant.

Example plants
The sodium perborate plant in plant in Hönningen, Germany.
The sodium perborate plant in Althofen, Austria.

Reference literature
[44, UBA - Germany, 2001], [63, CEFIC-PEROXYGENES PERBORATE Sub Group, 2004].

7.14.4.6 Drying sodium perborate and the purification of the exhaust air

Description
To dry the sodium perborate products, i.e. sodium perborate tetrahydrate (PBS4) and sodium perborate monohydrate (PBS1), both rotary or fluidised bed dryers are used. In particular, for drying PBS1, fluid bed dryers are more suitable. In both cases, large quantities of drying air are required, which, before being released into the environment, have to be scrubbed or filtered to remove dust particles. Both techniques allow the complete return of the separated dust to the process.

Achieved environmental benefits
Complex dedusting of the air used for drying the sodium perborate products (PBS4 and PBS1), has a direct positive impact on the environment.

Cross-media effects
There are no reported disadvantages caused by the implementation of this technique.

Operational data
The sodium perborate monohydrate product (PBS1) is preferred in some applications where a lesser amount of crystallisation water in the product is required. PBS1 is produced using PBS4 as a raw material. The major unit operation in the PBS1 process is the drying/cooling step of the final product. For the illustration of the PBS4 process and the PBS1 process, refer to Figure 7.40 and Figure 7.41 respectively.

The exhaust air from the dryers is cleaned by means of bag filters or wet scrubbers. In addition, filters or scrubbers are used for dust abatement during conveying, packing and loading. The PBS4 or PBS1 dust is recycled back to the process. If a wet scrubbing system is used, the mother liquor, which is a scrubbing medium, is also returned back to the process. The level of dust emission is up to 0.2 kg of dust/t of sodium perborate tetrahydrate (based upon full conversion to sodium perborate monohydrate). However, emissions of dust as low as 0.03 - 0.1 kg of dust/t of sodium perborate tetrahydrate have been reported, with the average half hourly values of dust concentrations in the outlet air of 5 – 20 mg/m^3 from drying and cooling of sodium perborate tetrahydrate and monohydrate. It is reported that in the Austrian plant, applying a combination of cyclones and a scrubber for the production of PBS4, and a combination of cyclones and bag filters for the production of PBS1, sodium perborate dust emissions far below 5 mg/Nm^3 are achieved.

However, the PBS industry considers that with techniques such as bag filters or wet scrubbers, the achievable dust emission value is below 20 mg/Nm^3 air.

Applicability
Applicable to the plants producing both PBS4 and PBS1, and using either the rotary or the fluid bed dryers.

Economics
No data submitted.

Driving force for implementation
The protection of the environment and energy efficiency in the drying operations.

Example plants
The sodium perborate plant in plant in Hönningen, Germany.
The sodium perborate plant in Althofen, Austria.

Reference literature
[44, UBA - Germany, 2001], [63, CEFIC-PEROXYGENES PERBORATE Sub Group, 2004], [85, EIPPCB, 2004-2005].

7.14.4.7 Optimum water balance in the process/minimum waste water

Description
The perborate process is an almost closed loop process, i.e. with little waste water being generated. The quantity of water introduced into the process (with raw materials or as cleaning water) is not much greater than the quantity, which is removed from the process with the product (as crystallisation water) or through evaporation. On the basis of the above objectives, it is advantageous to add raw materials in a concentrated form or as concentrated solutions and to limit the introduction of water into the process as much as possible.

Also, as illustrated in Section 7.14.3.2.5 above, a relation exists between boron emissions to water and energy consumption and, therefore, two alternative options for PBS4 and PBS1 production are available: option A – high energy consumption and lower boron emission to water, and option B – low energy consumption and higher boron emission to water.

Depending on the local situation, a choice can be made between the two alternative options for PBS4 and PBS1 production.

Achieved environmental benefits
Substantially reduces the amount of waste waters generated in the production of PBS4, and in the case of a higher consumption of energy, boron emissions to water can also be substantially reduced.

Cross-media effects
There are no reported disadvantages caused by the implementation of this technique. However, the consumption of a higher amount of energy results in associated emissions of SO_X, NO_X and dust.

Operational data
The source of water emissions is the excess mother liquor from the centrifugation step and cleaning water. The use of vacuum crystallisation, or any other means applied to eliminate water from the process, reduces the amount of excess mother liquor. A major part of the mother liquor is recycled, while a part of it is neutralised and discharged to the sewerage system. The mother liquor contains small amounts of sodium metaborate.

The emissions of boron to water are up to 5 kg boron/t sodium perborate tetrahydrate produced, however, emissions of boron to water as low as 13 – 17 g/t sodium perborate tetrahydrate have been reported. It should be also noted, that according to the Austrian Ministerial Order on inorganic chemicals (pertaining also to the example sodium perborate plant in Althofen, Austria), the limit of boron emissions to water is set at 0.35 kg B/t installed capacity calculated as PBS4.

In the case of cooling crystallisation, the amount of excess mother liquor is higher than in the case of vacuum crystallisation. In the case of cooling crystallisation, the concentration of borate (expressed as B) in the excess mother liquor is reduced, as the crystallisation is carried out at lower temperatures of 5 to 10 ºC, thus making it possible to decrease the emission of boron to less than 5 kg/t sodium perborate tetrahydrate produced. In turn, as illustrated in Section 7.14.3.2.5 above, two alternative options for PBS4 and PBS1 production are available: high energy consumption with lower boron emissions to water, and low energy consumption with higher boron emissions to water.

Applicability
This technique is applicable to the plants producing sodium perborate.

Economics
No data submitted.

Driving force for implementation
High material and energy efficiency in the process, leading to the minimisation of the impact of the production of sodium perborate on the environment.

Example plants
The sodium perborate plant in plant in Hönningen, Germany.
The sodium perborate plant in Althofen, Austria.

Reference literature
[44, UBA - Germany, 2001], [63, CEFIC-PEROXYGENES PERBORATE Sub Group, 2004], [85, EIPPCB, 2004-2005].

7.14.5 Best Available Techniques for the manufacture of sodium perborate

For general information on understanding a BAT section and its contents, see Section 7.1.5.

Sodium perborate is currently produced in the EU by the wet chemical process in which the boron ore is reacted with sodium hydroxide to yield sodium metaborate solution which is then reacted with hydrogen peroxide to obtain sodium perborate tetrahydrate $NaBO_3 \cdot 4\ H_2O$ (PBS4). The other product of lesser importance is sodium perborate monohydrate $NaBO_3 \cdot H_2O$ (PBS1) obtained by drying sodium perborate tetrahydrate (PBS4).

The use of the pure raw materials and techniques developed in multiple locations resulted in mature processes with similar performance and represent BAT for the production of sodium perborate.

For the production of sodium perborate tetrahydrate, BAT is to:

1. Reduce the amount of discharged solid waste to land by using a high purity, high boron content raw material, preferably borax pentahydrate in the range of 470 - 520 kg borax pentahydrate (of at least 46 % B_2O_3 content) per tonne of sodium perborate tetrahydrate (PBS4) produced (see Sections 7.14.3.1 and 7.14.4.1).

2. Save energy in the manufacture of sodium metaborate solution by carrying out the process at the lower level end of temperatures in the operational range of 60 – 95 ºC (see Section 7.14.4.2).

3. Minimise emissions of boron compounds to water to the level below 0.35 – 5 kg B per tonne of sodium perborate tetrahydrate (PBS4) produced, by purifying the sodium metaborate solution, reducing the amount of excess mother liquor and optimising water balance in the process – see Sections 7.14.3.2.5, 7.14.3.3.2, 7.14.4.3 and 7.14.4.7.

   Note:
   Low emissions of boron to water (13 – 17 g B/tonne PBS4) have been reported – see Sections 7.14.3.3.2 and 7.14.4.7. However, the lower the boron emissions to water, the higher the total energy consumption in the process – refer to Section 7.14.3.2.5.

4. Reduce the concentration or the volume of the mother liquor originating from the crystallisation of sodium perborate tetrahydrate (PBS4) by using either a cooling system or a vacuum evaporation system to improve overall material and energy efficiency of the process (see Sections 7.14.3.3.2, 7.14.4.4 and 7.14.4.7).

5. Reduce residual moisture in the wet cake to 3 – 10 % by using an efficient centrifugation system fit to the characteristics of the PBS4 crystals to save energy in the subsequent PBS4 drying stage (see Sections 7.14.2.2.1 and 7.14.4.5).

6. Maintain the overall energy usage in the process within the range of 1.5 – 3.7 GJ per tonne of sodium perborate tetrahydrate (PBS4) produced by optimising process parameters, in particular in the wet process stage and in the PBS4 drying stage (see Section 7.14.3.2.5, and Sections 7.14.4.1 through to 7.14.4.7).

   Note:
   The lower the total energy consumption in the process, the higher the boron emissions to water and vice versa – refer to Section 7.14.3.2.5 and 7.14.4.7.

7. Reduce dust emissions to air from drying and cooling sodium perborate tetrahydrate (PBS4) to below 5 – 20 mg/Nm^3 of the outlet air by using bag filters or wet scrubbers, as appropriate. Wet scrubbers operate at the upper end of the range (see Sections 7.14.3.3.1 and 7.14.4.6).

For the production of sodium perborate monohydrate, BAT is to:

1. Maintain the overall energy usage in the process within the range of 4.0 – 9.4 GJ/t PBS4 equivalent for one tonne of sodium perborate monohydrate (PBS1) produced (when starting from the boron ore) or within the range of 2.5 – 5.7 GJ/t PBS4 equivalent for one tonne of PBS1 produced (when starting from the PBS4), by optimising process parameters, in particular in the sodium perborate monohydrate (PBS1) fluid-bed drying stage – see Sections 7.14.3.2.5, 7.14.4.6 and 7.14.4.7.

   Note:
   The energy consumption to convert PBS4 to PBS1 is within the range 2.5 – 5.7 GJ/t PBS4 equivalent, which translates to energy consumption within the range 4.0 – 9.1 GJ/t PBS1 product.

2. Reduce dust emissions to air from the steps of drying and cooling sodium perborate monohydrate (PBS1) to below 5 – 20 mg/Nm^3 of the outlet air by using bag filters or wet scrubbers, as appropriate. Wet scrubbers operate in the upper end of the range (see Sections 7.14.3.3.1 and 7.14.4.6).

In the early 1990s, driven by performance and environmental considerations, the industry intensified the efforts to increase the stability of sodium percarbonate (especially by means of coating techniques) to make it also suitable for use in detergent and cleanser applications.

In 2004, a transition period started in which sodium percarbonate was continuously gaining a market share from sodium perborate. Substantial production capacities were installed in various European countries [57, CEFIC-PEROXYGENES, 2004].

7.15.1.3 Production processes

There are two main processes used to produce sodium percarbonate, the ‘crystallisation’ process and the ‘spray-granulation’ process, both of which use sodium carbonate and hydrogen peroxide as the raw materials [57, CEFIC-PEROXYGENES, 2004]. These are described in more detail in Section 7.15.2. For most applications, the basic sodium percarbonate resulting from either process has to go through a second production step, the ‘coating’ process, to achieve the required stability.

7.15.1.4 Uses in industrial sectors

Sodium percarbonate is used as a bleach component in detergent powders, dishwashing powders and tablets as well as in dental cleansers and cosmetics.

The estimated usage percentages for the year 2003 are given in Table 7.84.

Use	Percentage used
Laundry detergents (heavy duty powders), bleach boosters, stain removers	>90
Dishwashing agents (automatic dishwashing powders)	>5
Bleaching agents (denture cleansers, cosmetics)	<1

Table 7.84: Sodium percarbonate usage for the year 2003
[57, CEFIC-PEROXYGENES, 2004]

7.15.1.5 Production capacity

The production capacity in the European Union (including the capacities of new Member States) was close to 500 kt in the year 2003.

In 2006, there was one production site in each of the following countries: Austria, Belgium, Germany, Poland, Slovenia and Spain. The most characteristic example sodium percarbonate plants are the plant in Hönningen, Germany, the plant in Treibach-Althofen, Austria, and the plant in Bussi, Italy.

7.15.1.6 Socio-economic aspects

Sodium percarbonate is considered to be an outstanding environmentally-friendly bleach component for heavy duty powder detergents and dishwashing agents for consumer use.

7.15.2 Industrial processes used

7.15.2.1 Process chemistry

Sodium percarbonate is produced by reacting sodium carbonate with hydrogen peroxide to form the additional product sodium carbonate perhydrate according to the reaction equation:

$$2\ Na_2CO_3 + 3\ H_2O_2 \quad \rightarrow \quad 2\ Na_2CO_3 \cdot 3\ H_2O_2$$

Depending on the application, sodium percarbonate can be optionally coated with auxiliary agents to improve the stability of the product.

7.15.2.2 Production processes

In this section two main technologies for the production of sodium percarbonate: the crystallisation process and the spray-granulation process are described as state-of-the-art processes [57, CEFIC-PEROXYGENES, 2004].

Although the processes are environmentally comparable, they are fundamentally different in the technology used to produce basic sodium percarbonate. For this reason, the production processes used for either route are described separately in the following sections.

The coating process of sodium percarbonate does not depend on the way the basic sodium percarbonate is produced and has, therefore, been described in a separate section.

7.15.2.2.1 The crystallisation process

This process is the classical wet chemical method where a solution of sodium carbonate is put into a reaction with hydrogen peroxide to form crystals of sodium carbonate perhydrate which are separated from the mother liquor by centrifugation [57, CEFIC-PEROXYGENES, 2004].

The typical production process of sodium percarbonate by the crystallisation process is shown in a flow diagram in Figure 7.42.

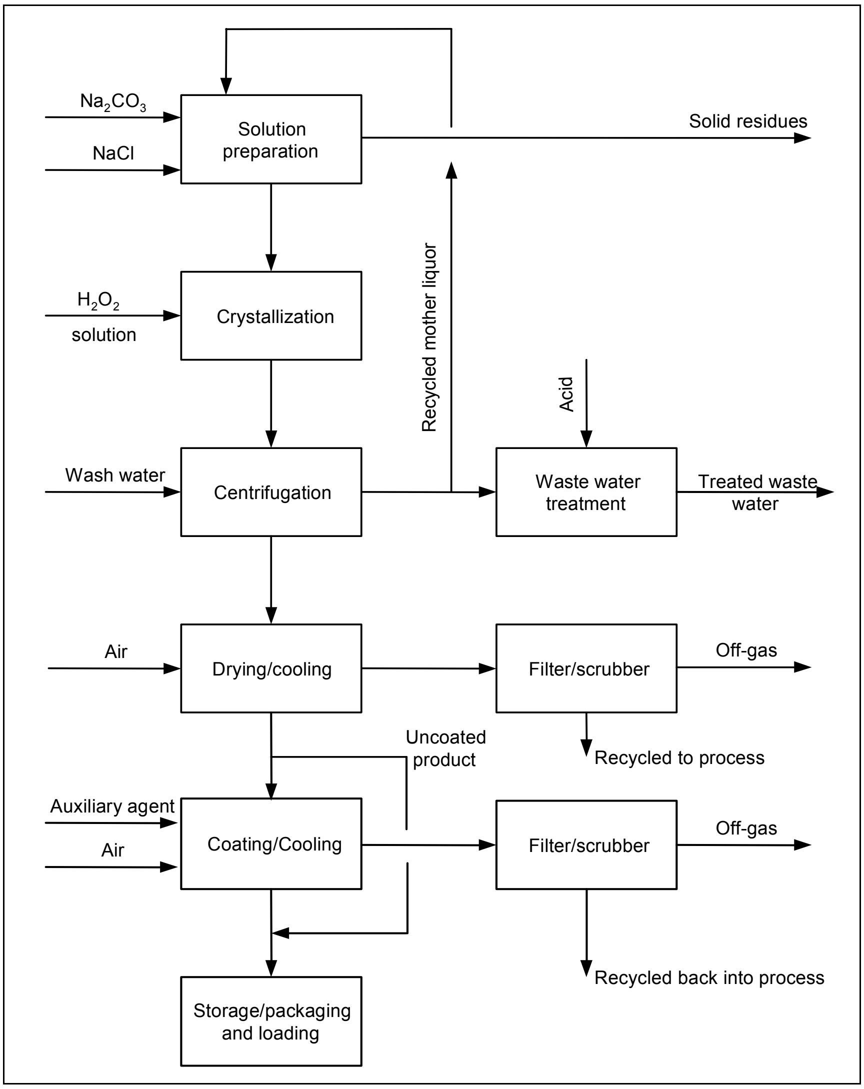

Figure 7.42: Sodium percarbonate production by the crystalisation process [57, CEFIC-PEROXYGENES, 2004]

The first step of this process is the solution preparation in which sodium carbonate and salt (sodium chloride or other sodium salts) are added to the recycled mother liquor coming from the crystal separation step. This process step can be operated continuously or batch wise. The carbonate/salt solution can contain a low amount of insolubles, which, in some cases, are partially removed by decantation or filtration. In some cases, flocculation aids may be used to improve the separation of the insolubles. Due to the high quality of the sodium carbonate currently used, the volume of filtration residues is very low.

This solution is fed to the crystalliser in which the sodium carbonate is reacted with the hydrogen peroxide solution to form the sodium percarbonate crystals (see the reaction equation). The hydrogen peroxide concentration is typically between 40 and 70 %. The crystalliser has to be cooled to remove the heat of the reaction and to reduce the solubility of the sodium percarbonate.

In addition to the major raw materials, there are a number of miscellaneous auxiliary materials which may be added to the process for their various attributes such as stabilisation of the product sodium percarbonate. All of these are regarded to have minimal environmental impact.

The sodium percarbonate crystals are separated from the mother liquor in centrifuges. The mother liquor is collected in storage vessels and recycled back into the process. Excess mother liquor can be used to remove from the process small amounts of contaminants, present in the raw materials. After treatment, the excess mother liquor is discharged into the sewerage system. The centrifugation step can include a washing step to improve the centrifugability of the sodium percarbonate crystals.

The separated sodium percarbonate crystals have a residual moisture content of approximately 5 – 15 %. This moisture is removed in the drying section. The dryers used are typically of the fluid bed type. The drying air can be heated with steam, gas or electric energy.

Before being discharged into the atmosphere, the off-gas from the dryer is led through a wet scrubber or bag filter. The wet scrubber is operated with the mother liquor which is recycled into the process. The fines collected from the bag filter are also recycled back into the process.

If required, the dry sodium percarbonate is cooled. The off-gas from the cooler is cleaned by an off-gas scrubber or bag filter, and if necessary, the sodium percarbonate is sieved to remove fine and coarse particles before being stored.

7.15.2.2.2 The spray-granulation process

In this process, fine nuclei of sodium carbonate are brought into a hot fluid bed into which hydrogen peroxide and a solution of sodium carbonate are sprayed. By continuous evaporation of water and reaction of the components, the nuclei grow until they reach the required size and they are then removed from the process [57, CEFIC-PEROXYGENES, 2004].

The production of sodium percarbonate by the spray-granulation process is a single-step process according to the reaction equation above. In a fluid bed reactor, a sodium carbonate solution is sprayed with H_2O_2 solution on seed crystals, thus forming sodium percarbonate granules. In a subsequent, optional process step, the percarbonate granules can be coated by special auxiliary materials.

The typical spray-granulation production process is shown in the flow diagram in Figure 7.43.

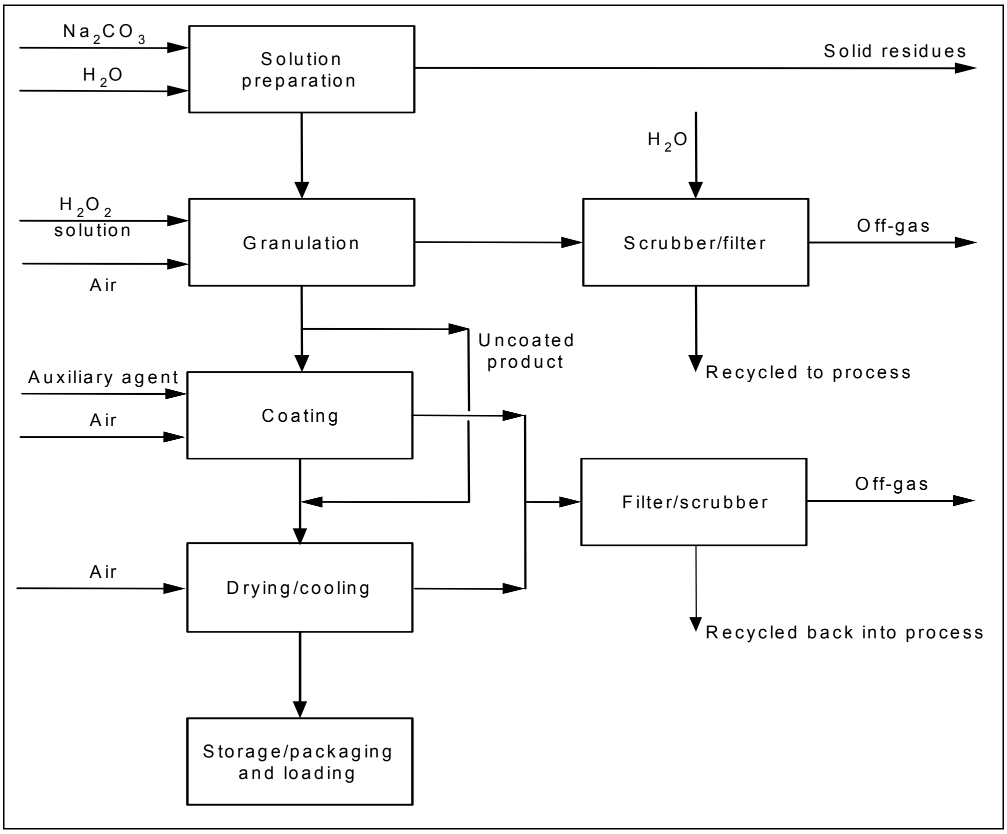

Figure 7.43: Sodium percarbonate production by the spray-granulation process [57, CEFIC-PEROXYGENES, 2004]

The sodium carbonate is fed from the storage silo into the sodium carbonate solution preparation vessel. By adding water, sodium carbonate is dissolved together with recovered material from the scrubber or filter sections. This process step can be operated continuously or batch wise.

Sodium carbonate solution can contain a low amount of insolubles which, in some cases, are partially removed by decantation or filtration. In some cases, flocculation aids may be used to improve the separation of the insolubles. Due to the high quality of the raw material, the volume of the filtration residues is very low.

The preparation of the sodium carbonate solution is an exothermic process. Due to the rise in temperature, there is no need to heat this solution for the subsequent process step.

In a fluid bed granulator, the sodium carbonate solution and a H_2O_2 solution are sprayed simultaneously onto small percarbonate seed crystals which grow to granules of the desired size. The water coming from the raw material solutions is removed by means of hot air. The drying air can be heated with steam, electrical energy or gas.

In addition to the major raw materials, there are a number of miscellaneous auxiliary materials which may be added to the process for their various attributes such as stabilisation of the sodium percarbonate product. All of these are regarded to have minimal environmental impact.

Before being discharged into the atmosphere, the off-gas from the fluid bed granulator is led through a wet scrubber or bag filter. The wet scrubber is operated with water, forming the scrubber solution, which is recycled back into the sodium carbonate solution preparation. The fines from the bag filter are also recycled back into the process.

If required, the dry sodium percarbonate is cooled down. The off-gas from the cooler is cleaned by an off-gas scrubber or bag filter, and if necessary, the sodium percarbonate granules are sieved to remove the fine and the coarse particles which are fed back into the process.

7.15.2.2.3 The coating process

Here, the crystals or granules are sprayed with an aqueous solution of auxiliary agents, and dried in a fluid bed dryer. By the continuous evaporation of water, a layer is built to a certain thickness and thereafter the particles are dried to form the final coated product.

The storage stability of sodium percarbonate is usually improved by the addition of stabilisers in the crystallisation and spray-granulation processes. An additional form of stabilisation consists of coating the sodium percarbonate granules with different auxiliary agents (see flow diagrams in Figure 7.42 and Figure 7.43).

Normally, the coating process takes place in a fluid-bed coater. The drying air can be heated with steam, gas or electric energy.

Before being discharged into the atmosphere, the off-gas from the dryer is led through a wet scrubber or bag filter. The wet scrubber is operated with mother liquor which is recycled back into the process. The fines collected from the bag filter are also recycled back into the process.

If required, the dry coated sodium percarbonate is cooled down. The off-gas from the cooler is cleaned by an off-gas scrubber or bag filter, and if necessary, the coated sodium percarbonate is sieved to remove fine and coarse particles before being stored.

7.15.3 Present consumption and emission levels

7.15.3.1 Raw materials

The following list gives the main raw materials used in the production of sodium percarbonate:

- sodium carbonate
- hydrogen peroxide
- sodium salt (e.g. sodium chloride, sodium sulphate).

Sodium carbonate can be natural soda ash or produced by the Solvay process.

Hydrogen peroxide is produced by the anthraquinone process.

The Table 7.85 shows the consumption of the main raw materials per one tonne of sodium percarbonate. These are comparable for the two processes, except for the consumption of salt, which is only used in the crystallisation process.

The main raw materials of sodium percarbonate	Units	Consumption min/max
Sodium carbonate	kg/t sodium percarbonate final product	573/720
Hydrogen peroxide	kg 100 %/t sodium percarbonate final product	310/485
Salt	kg/t sodium percarbonate final product	29/150

Table 7.85: Consumption of the main raw materials in the production of sodium percarbonate [57, CEFIC-PEROXYGENES, 2004]

7.15.3.2 Utilities

7.15.3.2.1 Thermal media (steam and natural gas)

In the production process of sodium percarbonate, steam and/or natural gas are important energy transfer media. Thermal energy is used to heat up the mother liquor, to boil out reagents from crystallisers and to heat the air used in the spray-granulation process. It is also used in the drying of sodium percarbonate and in the coating process.

7.15.3.2.2 Cooling media

Some steps in the production of sodium percarbonate require cooling. Cooling is needed predominantly in the crystallisation process (to remove the heat of the reaction). Water is normally used as a cooling medium. In a closed cooling system, other cooling media such as a mixture of glycol and water or a brine solution can be used. The closed cooling system requires the use of either cooling towers or cooling equipment. With open cooling systems, fresh water from different sources is used.

7.15.3.2.3 Electric energy

Electric energy is needed to operate machinery for the different process steps such as cooling equipment, pumps, centrifuges, blowers, heating, etc.

7.15.3.2.4 Total energy consumption

The total energy consumption in the production of sodium percarbonate is between 2 GJ/t and 12.6 GJ/t sodium percarbonate final product for the crystallisation process route, and up to 12.6 GJ/t sodium percarbonate final product for the spray-granulation process route.

In the production of sodium percarbonate by the crystallisation route the energy consumption is linked to the emission of sodium salts discharged with excess mother liquor to water and, therefore, can vary in a broad range, between 2 GJ/t and 12.6 GJ/t sodium percarbonate final product [85, EIPPCB, 2004-2005].

In this route, in the case of a low energy consumption in the range of 2 – 4 GJ/t PCS product, the emission of sodium salts is below 80 kg Na/t PCS product, while in the case of a high consumption of energy of up to 12.6 GJ/t PCS product, the emission of sodium salts can be reduced to below 10 kg Na/t PCS product [85, EIPPCB, 2004-2005].

In turn, in the production of sodium percarbonate by the spray-granulation route (an almost water-free process), with the consumption of energy of up to 12.6 GJ/t PCS product, the emission of sodium salts can be maintained at a level below 10 kg Na/t PCS product [85, EIPPCB, 2004-2005].

7.15.3.3 Emissions

7.15.3.3.1 Dust emissions

Dust emissions occur mainly in the spray-granulation, drying and coating sectors of sodium percarbonate production. The exhaust air from the dryers is cleaned by means of bag filters or wet scrubbers. In this way, the dust content in the air that is discharged into the atmosphere is greatly reduced. In addition, filters or scrubbers are used for dust abatement during conveying, packing and loading. The level of dust emission is up to 0.62 kg of dust/t sodium percarbonate final product [57, CEFIC-PEROXYGENES, 2004].

It is reported that in the Austrian plant, when applying bag filters, the sodium percarbonate dust emissions of far below 5 mg/Nm^3 are achieved. In turn, the CEFIC PCS Subgroup considers that with techniques such as bag filters or wet scrubbers, the achievable dust emission value is below 20 mg/Nm^3 air [85, EIPPCB, 2004-2005].

7.15.3.3.2 Water emissions

Water emission sources are the excess mother liquor from the centrifugation step and cleaning water. A major part of mother liquor is recycled while a minor part of it is treated and discharged. The mother liquor contains sodium salts. Cooling water from an open system can also be discharged together with the treated mother liquor. The emission of sodium salts into the water varies up to 80 kg sodium/t sodium percarbonate final product and depends on the process route and the amount of water being added and evaporated in the process [57, CEFIC-PEROXYGENES, 2004].

In the production of sodium percarbonate by the crystallisation route, the emission of sodium salts into water varies in the range <10 – 80 kg Na/t sodium percarbonate product, and depends on the amount of mother liquor directed to the waste water treatment unit, and then discharged to water [85, EIPPCB, 2004-2005]. The lower the excess of mother liquor discharged to water, the lower the emissions of sodium salts to water, but at the same time, the higher the energy required for the evaporation of water from the mother liquor – refer to Section 7.15.3.2.4 above.

In the production of sodium percarbonate by the spray-granulation process route, the emission of sodium salts into the water is below 10 kg Na/t sodium percarbonate product [85, EIPPCB, 2004-2005].

7.15.4 Techniques to consider in the determination of BAT

Introduction: Techniques to consider in the determination of BAT – refer to Section 7.1.4

The use of the pure raw materials as specified in Section 7.15.3.1, as well as the process steps described in Section 7.15.2, for dissolution, crystallisation and centrifugation, granulation, drying and cooling respectively, have been taken into account in analysing techniques to consider in the determination of BAT for the production of sodium percarbonate [57, CEFIC-PEROXYGENES, 2004]. Industry has selected and developed the applied techniques over many years in multiple locations which have resulted in the application of mature processes on an industrial scale. In 2004, more than 90 % of the equipment installed was less than 10 years old which means that the processes reflect up-to-date environmental practices [57, CEFIC-PEROXYGENES, 2004]. Further improvements, especially with regard to the environment, are mainly in the fine tuning of the current processes and are expected to result in marginal changes with regard to emissions.

7.15.4.1 Raw materials used for the production of sodium percarbonate

<u>Description</u>
The purity of the technical sodium carbonate grades has improved over the last few decades and has resulted in very low emissions of solid residues from the solution preparation step. However, sodium carbonate contains very low amounts of insolubles, and sodium carbonate solution can still be purified to improve the stability of the sodium percarbonate produced. A purification step can make use of small amounts of additives which result in precipitates that can be removed by decantation or filtration together with the insolubles present in the sodium carbonate. The waste quantities resulting from the separation step are kept to a minimum as the sodium carbonate used is of high purity.

For hydrogen peroxide, the most important aspect is its concentration which can typically vary between 40 and 70 %. The higher the H_2O_2 concentration, the less water is added to the process, which results in a reduction of excess mother liquor and also a reduced loss of sodium salt with the mother liquor.

Achieved environmental benefits
The use of pure raw materials in the production of sodium percarbonate, in particular purified sodium carbonate solution and concentrated H_2O_2, helps to minimise the amount of mother liquor and to reduce the amount of energy used in the process. The use of pure raw materials also reduces the quantity of solid residues.

Cross-media effects
The production of a high concentration hydrogen peroxide requires more energy. The insolubles, introduced with the raw materials, are removed from the process as solid residues.

Operational data
The production of sodium percarbonate is carried out according to the crystallisation and the spray-granulation process routes in which soda ash and hydrogen peroxide are the main raw materials used – refer to Table 7.85, as well as to Figure 7.42 and Figure 7.43. The insolubles contained in the sodium carbonate solution, sodium chloride, and the recycled mother liquor, are removed from the process by decantation/filtration as solid residues. The concentration of the input H_2O_2 is typically between 40 and 70 %.

Applicability
Applicable to the plants producing sodium percarbonate by the crystallisation and the spray-granulation process routes.

Economics
No data submitted.

Driving force for implementation
High material and energy efficiency in the process, leading to the minimisation of the impact of the production of sodium percarbonate on the environment. Improved stability of the product.

Example plants
The sodium percarbonate plant in Hönningen, Germany.
The sodium percarbonate plant in Bussi, Italy.
The sodium percarbonate plant in Althofen, Austria.

Reference literature
[57, CEFIC-PEROXYGENES, 2004].

7.15.4.2 Energy consumption in the production of sodium percarbonate

Description
In the crystallisation process, the crystalliser is cooled to remove the heat of the reaction and to decrease the temperature to reduce the solubility of the sodium percarbonate. The crystals are then separated in a centrifuge and it is advantageous to achieve low surface moisture in the centrifuge wet cake. A low moisture content of the wet cake reduces the energy input for the sodium percarbonate drying step.

It should be noted, however, that in the crystallisation route, for a low energy consumption in the range of 2 – 4 GJ/t PCS product, the emission of sodium salts is at a higher level of up to 80 kg Na/t PCS product. In order to achieve the level of the emission of sodium salts to water of <10 kg Na/t PCS product, a much higher consumption of energy of up to 12.6 GJ/t PCS product is required.

In the spray-granulation process, water coming from both the sodium carbonate and hydrogen peroxide solutions has to be evaporated in the granulator, which results in a higher use of energy for the granulation and drying steps. The total energy consumption in this process route is up to 12.6 GJ/t PCS product.

Achieved environmental benefits

The crystallisation process route is typically characterised by lower energy requirements and, therefore, by lower direct/indirect impact of combustion products on the environment. In turn, the spray-granulation process, characterised by much higher energy usage, is almost a waste water free process.

Cross-media effects

In the crystallisation process route, in which the centrifugation step is used, a waste water treatment unit is required, so a relationship between energy consumption and emissions of sodium salts to water exists (the lower the energy usage, the higher the emission of sodium salts to water, and vice versa) – refer to Sections 7.15.3.2.4 and 7.15.3.3.2 above.

In the spray-granulation process, depending on the thermal medium used (steam or natural gas), there is an indirect or a direct impact of combustion products on the environment.

Operational data

The production of sodium percarbonate is carried out according to the crystallisation and the spray-granulation process routes – refer to Figure 7.42 and Figure 7.43. Depending on the process used, the total energy consumption in the production of sodium percarbonate is between 2 GJ/t and 12.6 GJ/t sodium percarbonate final product (crystallisation route) or up to 12.6 GJ/t (spray-granulation route) – refer to Sections 7.15.3.2.4 and 7.15.3.3.2 above.

Economics

No data submitted.

Driving force for implementation

High energy efficiency in the process, leading to the minimisation of the impact of the production of sodium percarbonate on the environment.

Example plants

The sodium percarbonate plant in Hönningen, Germany.
The sodium percarbonate plant in Bussi, Italy.
The sodium percarbonate plant in Althofen, Austria.

Reference literature

[57, CEFIC-PEROXYGENES, 2004], [85, EIPPCB, 2004-2005].

7.15.4.3 Purification of the exhaust air

Description

The required drying air has to be scrubbed or filtered to remove dust particles, before being released into the environment. Both techniques allow the return of the separated dust to the process.

Achieved environmental benefits

The dedusting of the air used for drying the sodium percarbonate product has a direct positive impact on the environment, as the outlet air is cleaned and dust is recycled back into the process.

Cross-media effects

There are no reported disadvantages caused by the implementation of this technique.

Operational data

The exhaust air from the dryers is cleaned by means of bag filters or wet scrubbers. In addition, filters or scrubbers are used for dust abatement during conveying, packing and loading. The dust is recycled back to the process. The level of dust emission is up to 0.62 kg of dust/t of sodium percarbonate final product. It is reported that in the Austrian plant, when applying bag filters, sodium percarbonate dust emissions of far below 5 mg/Nm^3 are achieved.

In turn, the CEFIC PCS Subgroup considers that with techniques sich as bag filters or wet scrubbers, the achievable dust emission value is below 20 mg/Nm^3 air.

Applicability
Applicable to the plants producing sodium percarbonate and using fluid bed dryers.

Economics
No data submitted.

Driving force for implementation
The protection of the environment.

Example plants
The sodium percarbonate plant in Hönningen, Germany.
The sodium percarbonate plant in Bussi, Italy.
The sodium percarbonate plant in Althofen, Austria.

Reference literature
[57, CEFIC-PEROXYGENES, 2004], [85, EIPPCB, 2004-2005].

7.15.4.4 Minimisation of waste water discharged from the process

Description
In the crystallisation process, the quantity of excess mother liquor from the centrifugation step depends, amongst others, on the concentration of the hydrogen peroxide and the wash-water used.

The quantity of excess mother liquor and the related sodium salt emission can be reduced by a reduction in the quantity of water introduced into the process or by an increase of the water removed from the process.

Some possibilities are: the use of concentrated hydrogen peroxide solution, the reduction of the wash-water quantity used in the centrifugation step and the evaporation of water from the excess mother liquor. All these methods, however, will result in a higher consumption of energy as more water needs to be evaporated – refer to Sections 7.15.3.2.4 and 7.15.3.3.2 above.

The spray-granulation process generates a low waste water flow, as the excess mother liquor flow is negligible and water is only generated during washing and cleaning.

Achieved environmental benefits
Optimum water balance in the process results in a reduced amount of waste water generated in the production of sodium percarbonate.

Cross-media effects
As the mother liquor can contain relatively high amounts of sodium salts, the discharge of the treated waste water could cause some environmental impact depending on the location of the sodium percarbonate plant.

However, the lower the amount of excess mother liquor discharged from the plant, the higher the consumption of energy – refer to Sections 7.15.3.2.4 and 7.15.3.3.2.

Operational data
It is advantageous to reduce the amount of water added to the process, as this reduces the amount of excess mother liquor or the quantity of water that needs to be evaporated. The emission of sodium salts into the water varies in the range below 10 – 80 kg sodium/t sodium percarbonate final product, and depends on the process route and the amount of water being added and evaporated in the process.

Applicability
This technique is applicable to the plants producing sodium percarbonate, in particular to the plants based on the crystallisation process route.

Economics
No data submitted.

Driving force for implementation
The protection of the environment.

Example plants
The sodium percarbonate plant in Hönningen, Germany.
The sodium percarbonate plant in Bussi, Italy.
The sodium percarbonate plant in Althofen, Austria.

Reference literature
[57, CEFIC-PEROXYGENES, 2004].

7.15.5 Best Available Techniques for the manufacture of sodium percarbonate

For general information on understanding a BAT section and its contents, see Section 7.1.5.

Sodium percarbonate ($Na_2CO_3 \cdot 1.5\ H_2O_2$), obtained by the reaction of sodium carbonate solution with 40 – 70 % hydrogen peroxide solution is currently manufactured in the EU using the wet crystallisation process and by the dry fluidised-bed process.

More than 90 % of the installations are less than 10 years old and use up-to-date environmental practices.

In both process routes, the raw sodium percarbonate product is coated to improve its stability. Accordingly, for each of these process routes, BAT conclusions are drawn separately, as follows.

For the production of sodium percarbonate by the crystallisation route, BAT is to:

1. Reduce emissions of sodium salts to water to <10 – 80 kg Na per tonne of sodium percarbonate product by purifying sodium carbonate solution, using as concentrated as possible (40 – 70 %) hydrogen peroxide solution and adding low amounts of wash-water, which aim to decrease the volume of both the recycled and the excess mother liquor in the process and the resulting discharges to water (see Sections 7.15.2.2.1, 7.15.3.1, 7.15.3.2.4, 7.15.3.3.2, 7.15.4.1 and 7.15.4.4).

   Note:
   The emissions of sodium salts to water depend on the energy consumption in the process; the lower the emission of sodium salts to water, the higher the energy usage.

2. Minimise the consumption of energy in the process within the maximum operational range of 2 – 12.6 GJ per tonne of sodium percarbonate final product, by reducing the volume of both the recycled and the excess mother liquor in the process, and by optimising the operations of crystallisation by cooling, centrifugation (to a moisture content of 5 – 15 %) and subsequent fluid-bed drying (see Sections 7.15.2.2.1, 7.15.3.2.4, 7.15.3.3.2 and 7.15.4.2).

3. Reduce dust emissions to air to below 5 – 20 mg/Nm^3 of the outlet air by using bag filters or wet scrubbers, as appropriate. Wet scrubbers operate at the upper end of the range (see Sections 7.15.3.3.1 and 7.15.4.3).

For the production of sodium percarbonate by the spray-granulation route, BAT is to:

1. Minimise the consumption of energy in the process within the range of 2 – 12.6 GJ per tonne of sodium percarbonate final product by optimising the process parameters. In particular, in the fluid-bed spray-granulation step, the upper end of the range is more likely to be achieved – see Sections 7.15.2.2.2, 7.15.3.2.4 and 7.15.4.2.

   Note:
   The emissions of sodium salts to water in the spray-granulation process can be maintained at the low level of <10 kg Na per tonne of sodium percarbonate product.

2. Reduce dust emissions to air to below 5 – 20 mg/Nm^3 of the outlet air by using bag filters or wet scrubbers, as appropriate. Wet scrubbers operate at the upper end of the range (see Sections 7.15.3.3.1 and 7.15.4.3).