

German Notes on BAT for the production of

Large Volume Solid Inorganic Chemicals

Soda

Final report

Institut für Umwelttechnik und Management
an der Universität Witten/Herdecke gGmbH
Alfred-Herrhausen-Str. 44
58455 Witten

1 General Information

The annual world production of sodium carbonate (soda) amounted to approximately 31,5 million tons in 1993. The main share is synthetic soda. Nowadays it is only manufactured by means of the Solvay technology, which – as it uses NH_3 as auxiliary material – is also called „ammonia soda process“. Approximately 35 % of the world production is natural soda, mainly manufactured in the USA.

It is increasingly difficult to sell soda produced in Germany, since soda for instance from White Russia or the Ukraine is offered much cheaper on the market due to lower labour cost and overheads. Also in Turkey, two new soda plants have been built, which sell their products mainly on the Balkans. As consequence of the difficult market conditions, Matthes & Weber GmbH, Duisburg, gave up its soda production end of 1999, so that now soda is produced in Germany only by two companies at three locations. Table shows the production capacities of the plants in **table 1**:

Table 1: Soda Manufacturers and Production Capacities

| Company | Location | Capacity |
|------------------------------|-----------|-----------------|
| Solvay Soda Deutschland GmbH | Rheinberg | 605.000 t/a |
| | Bernburg | ca. 500.000 t/a |
| Sodawerke Staßfurt GmbH | Staßfurt | ca. 400.000 t/a |

Besides the soda production by means of the Solvay technology, soda is manufactured at the BASF in Ludwigshafen as a by-product of the caprolactam production. As this kind of production is a special proceeding, it is only shortly described in the framework of this report.

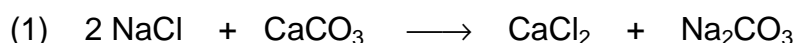
The predominant share of soda is required in the glass industry, where it is used as raw material for the decomposition of sand. Another main share of soda is used in the chemical industry for the production of chemicals. In the detergent and soap industry, soda is used for the manufacture of detergents and for the saponification of grease. Also the paper and cellulose industry uses soda for the digestion, the neutralization, the cleaning and the leaching as well as for the recycling of

wastepaper. Smaller quantities of soda are required in almost every production branch. Soda is the chemical product, which is used for the most different purposes.

2 Production of Sodium Carbonate

2.1 Chemical Bases

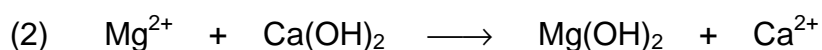
The technical manufacture of soda with the Solvay Technique is effected by the conversion of sodium chloride (salt) and calcium carbonate (lime stone) according to the following reaction equation:



Besides soda the Solvay technique also causes CaCl_2 as a by-product. The total process can be divided into the following reaction steps:

Brine Cleaning

- Precipitation of magnesium hydroxide and calcium carbonate by the addition of lime milk and soda solution into the brine:



Manufacture of the Product

- Precipitation of the relatively heavy-soluble bicarbonate (NaHCO_3) by the addition of carbonic acid into a salt solution saturated with ammonia :

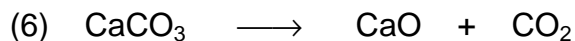


- Thermic decomposition of the bicarbonate:



Lime Milk Preparation

- Manufacture of caustic lime:

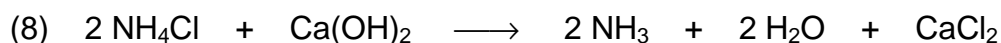


- Manufacture of lime milk :



NH₃-Recovery

- Recovery of the ammonia by distillation of the ammonium chloride containing mother liquor with lime milk:



2.2 General Bases of the Production Process

For the manufacture of one ton of soda by means of the Solvay technique 1,5 t salt, approximately 80 m³ water, 1,2 t limestone and 0,1 – 0,5 t coke are required. The raw material sodium chloride is mined in solid form (stone-salt) and then dissolved to brine or it is already won as saturated salt solution by salting-out mines. The saturation of the brine is necessary for an optimal Na⁺ yield. The technical solution should perform a maximum conversion of Na⁺ and NH₃, which means that a maximum quantity of Na⁺ should be available in the precipitated NaHCO₃ and of NH₃ as dissolved NH₄Cl in the liquid phase.

2.3 Soda Production by means of the Solvay Technique

2.3.1 Production Process

Figure 1 shows a simplified block scheme of the soda production by means of the Solvay technique. It gives a survey regarding the production procedure and works out relevant emission sources in connection with **figure 2**.

The brine is first led to a cleaning step, since inorganic by-materials may cause difficulties in the production process and lead to a lower quality of the final product. Mainly calcium and magnesium ions can generate carbonates during the ammonia absorption, which causes incrustations in the installations and the tubes. The cleaning is normally effected by means of the lime-soda-procedure (lime milk and soda solution are added into the brine). In this process the Mg^{2+} -ion is precipitated to hydroxide and the Ca^{2+} -ion to carbonate, according to reaction equation 2 and 3. The effluents discharged by this process are loaded with solids.

Then the cleaned brine is led into several gas scrubbers in countercurrent to the off-gases from the absorption, the carbonisation, the filtration and the calcination. The brine recovers the ammonia and a part of the carbon dioxide contained in the off-gases.

The main absorption of the brine with ammonia takes place in the subsequent absorption step under the addition of a part of the required carbon dioxide (approximately 20 %).

NH_3 -losses during the process are compensated by the help of the ammonia water receptacle. The off-gas from the absorption is led across the gas scrubber run with the brine and is then added to the exhaust gas from the calcination. The ammonia concentration of the brine amounts now to approximately 85 – 90 kg NH_3/m^3 . Because the reactions running during the absorption are strongly exothermic, the absorption columns are equipped with coolers.

Afterwards the ammoniacal brine is oversaturated with carbon dioxide from the lime-kiln as well as from the calcination led in countercurrent and sodium bicarbonate is precipitated (see reaction equation 4). Also the carbonization is an exothermic process, so that the cast-iron precipitation columns are equipped with tube coolers in the lower part. The ideal temperature of the brine in the outlet of the carbonization column lies between 25 °C and 30 °C. Lower temperatures can cause precipitations of salt or ammonium hydrogen carbonate, whereas higher temperatures hinder the complete precipitation of the formed bicarbonate. The off-gas from the carbonization is washed with brine in a countercurrent and afterwards discharged into the atmosphere.

As the installations of the precipitation columns including the cool tubes crust within few days due to the precipitated bicarbonate, they must be rinsed. This is effected by the help of fresh ammoniacal brine under the addition of few carbonic acid gas,

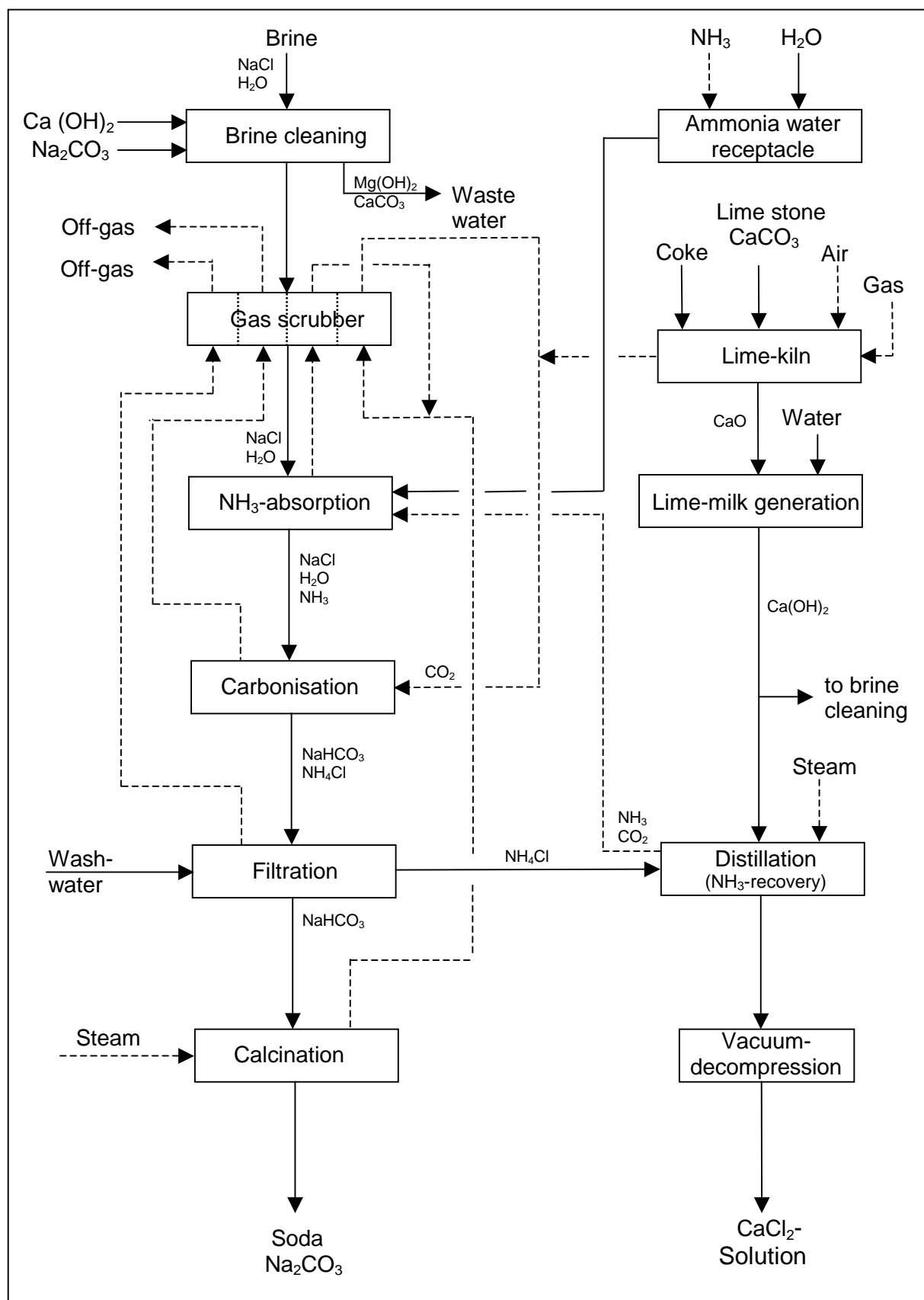


Figure 1: Soda Production by means of the Solvay Technique

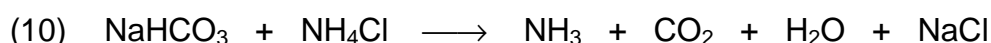
through which the incrustations are dissolved again. The precarbonized rinse brine is then led onto parallel precipitation columns, which are less crusted.

Afterwards the precipitated bicarbonate is filtered from the mother liquor by means of vacuum filters or centrifuges. Mother liquor still contained in the bicarbonate is washed off by the use of condensates from the production or by softened wash water. The wash water volume fluctuates between 0,3 and 1 m³/t soda according to the grain size of the bicarbonate. The off-gas from the filtration is washed in countercurrent with fresh brine and then discharged into the atmosphere.

The filtered raw bicarbonate is approximately composed as follows:

| | |
|----------------------------------|--------|
| NaHCO ₃ | 75,6 % |
| Na ₂ CO ₃ | 6,9 % |
| NH ₄ HCO ₃ | 3,4 % |
| NaCl + NH ₄ Cl | 0,4 % |
| H ₂ O | 13,7 % |

The residual humidity of the raw bicarbonate influences the energy demand of the subsequent thermic decomposition to soda (calcination). The calcination generates carbon dioxide and steam (see reaction equation 5). Besides the main reaction, i.e. the generation of soda, the calcination also leads to the following parallel reactions, which generate ammonia as well as sodium chloride:



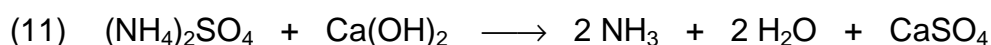
In this side reaction, soda is polluted with sodium chloride.

From one ton of crude bicarbonate approximately 520 - 560 kg of soda are generated by calcination. The decomposition takes place above 100 °C. For ensuring a complete reaction, temperatures > 170 °C are used. The off-gas sucked from the steam heated rotatory drums contain, besides CO₂, NH₃ and H₂O, also larger quantities of dust (soda and bicarbonate), which is separated from the gas by filtration. Before being used in the carbonisation this gas is cooled and cleaned from NH₃ by the help of fresh brine.

The product withdrawn from the calcination is either directly packed as "easy soda" with a pour weight of 0,6 - 0,7 t/m³ or it is changed to a monohydrate and then into "heavy soda" with a pour weight of 1,05 t/m³ by means of hydration and subsequent dehydration. The manufacture of soda briquettes is also possible by the addition of sodium silicate (water glass).

The residual ammonia in the filter lye in form of carbonate, hydrogen carbonate, sulfate and chloride is recovered by distillation and is led back to the NH₃-absorption. Consequently ammonia represents a pure support material. Merely inevitable losses are supplemented by concentrated aqueous NH₃-solutions (25 %), from the ammonia receptacle.

(NH₄)₂CO₃ and NH₄HCO₃ are completely decomposed already at temperatures of 85 - 90 °C and the entire carbon dioxide and a small part of the ammonia is separated from the solution. For the separation of ammonia from NH₄Cl, however, a chemical reaction with lime milk is necessary (see reaction equation 8). The addition of lime milk simultaneously leads to the separation of ammonia bound as sulfate:



The carbon dioxide required for the carbonisation and the lime milk required for the NH₃-recovery are generated by burning the limestone (see reaction equations 6 and 7).

Before being fed into the CO₂-compressors, which take the off-gas from the furnace and lead it into the carbonisation, the hot and dust-loaded gas is cooled and cleaned in direct exchange with water. At Staßfurt, there is another dry treatment for the separation of dust before the washing step.

In order to obtain a highly concentrated CO₂-gas, the excess of air and the consumption of coke should be as small as possible, even if a part of the CaCO₃ remains unburned. Besides coke, also natural gas is used as fuel.

The caustic lime leaving the furnace is changed in horizontal trick drums under the addition of used cooling water to a most concentrated suspension of lime milk. The

lime milk is then used for the destillative recovery of the ammonia as well as for the brine cleaning (see reaction equation 2).¹⁾

The limestone volume depends on the quantity of caustic lime required for the ammonia recovery. On this occasion an excess of carbonic acid is generated, that is either discharged into the atmosphere or handed over to other consumers.

The residual ammonia is separated from the solution with low-pressure steam and is cooled down with the filter lye in an heat exchanger. The residual lye of the ammonia recovery (final lye) mainly contains calcium chloride besides sodium chloride and unconverted lime components and is discharged as waste water.

2.3.2 Emission Data and Energy Consumption

2.3.2.1 Exhaust Air Emissions

At the example of Rheinberg, **figure 2** shows the essential emission sources, the off-gas cleaning procedures as well as the concentrations emitted into the atmosphere. The values analysed on this occasion are half hour values, which were taken many times in the course of the year in individual cases.

In **table 1** the specific emission values per ton product are displayed.

¹⁾ Matthes & Weber, who closed its production at the end of the year 1999, did not generate lime milk for the ammonia recovery, but led CaO directly to the NH₃-distillation (dry lime process).

Figure 2: Emission Sources and Concentrations at Rheinberg

Table 1: Specific Emissions at Rheinberg

| Emitted material | Physical state | spec. emission value [g/t Product] |
|-------------------------------------|----------------|---------------------------------------|
| SO ₂ | gas | 0,3 |
| NO ₂ | gas | 193 |
| NH ₃ | gas | 58 |
| CO | gas | 3.635 |
| Ca(OH) ₂ | dust | 1,2 |
| CaO | dust | 6,5 |
| CaCO ₃ | dust | 2,9 |
| Na ₂ CO ₃ | dust | 2,3 |
| coke (from coal) | dust | 0,4 |
| dust (undivided rest) | dust | 0,8 |
| total dust (Σ of all dust material) | dust | 14 |

The present off-gas emission data are based on the emission declaration of Solvay for the year 1996 according to the 11th Directive of the BImSchV (German Emission Directive). The present concentrations are average values taken from different measurements and systems. Basis of the data are :

- average half-hour-measurements of external analysis institutes
- average concentrations from on-line measurements
- internal company measurements and calculations

2.3.2.2 Waste Water

The soda manufacture essentially causes the following three waste water sources :

1. Waste water from the brine cleaning
2. Wash water from the off-gas treatment (lime oven)
3. Final lye from the NH₃-distillation

At Rheinberg these three effluents are discharged together directly into the recipient. The proceeding is similar to Matthes & Weber. The data for both plants are summarized in **table 2**:

Tabelle 2: Comparison of the Effluents from the Soda Production of Solvay Soda Germany, Rheinberg, and Matthes & Weber, Duisburg

| | Solvay Soda Deutschland, Rheinberg | | | | Matthes & Weber, Duisburg | |
|--------------------|---------------------------------------|------------------------|--------------------------------|---------------------------|---------------------------|-----------------------------|
| | Control values | | Values 1999 | | Values 1999 | |
| | Average value: appr. 8,7 m³/t Product | | | | appr. 7 m³/t Product | |
| | Conc. [mg/l] | Freight [g/t Prod.] | Conc. [mg/l] | Freight [g/t Prod.] | Conc. [mg/l] | Freight [g/t Prod.] |
| pH | | | 9,5 – 11,3 | | | |
| CSB | 70 | 700 | < 15 – 70 | 120 – 510 | 21 | |
| NH ₄ -N | (70) | 0,9 | 4,3 – 73 | 40 – 600 | 2 – 7 | 10 – 80 |
| NO ₂ -N | | | 0,11 – 0,62 | | | |
| P | 10 | | 5,8 – 8,5 | | 3 – 9 | |
| Ca | | | 37 – 51,4 [g/l] | | 30 - 54 [g/l] | |
| Cd | 0,03 | 0,3 | < 0,011 - 0,034 | 0 - 0,31 | 0,016 - 0,024 | 0,18 - 0,2 |
| Cl | | 1,2x10 ⁶ | 86 – 115 [g/l] | (0,7 - 1)x10 ⁶ | 72 - 132 [g/l] | (0,7 – 1,2)x10 ⁶ |
| Cr | 0,5 | 5 | 0,09 – 0,18 | 0,8 – 1,8 | 0,05 - 0,2 | 0,55 - 1,48 |
| Cu | 0,6 | 6 | 0,11 – 0,32 | 0,9 – 2,4 | 0,12 - 0,25 | 1,1 - 2,1 |
| Hg | 2x10 ⁻³ | 0,02 | (<0,2 - 0,72)x10 ⁻³ | 0,002 – 0,005 | 0 | 0 |
| Ni | 0,5 | 5 | 0,07 – 0,22 | 0,6 – 1,8 | 0,04 - 0,22 | 0,4 - 1,8 |
| Pb | 1,5 | 15 | 0,34 – 1,13 | 2,9 – 9,6 | 0,28 - 4,5 | 2,17 - 44,74 |
| G _D | | | um 32 | | | |
| G _F | 32 | | < 32 – 48 | | < 40 | |
| G _L | | | 4 – 8 | | | |
| resi- dues | | | 6 – 14 g/l | 54 - 126 [kg/t] | 10 - 31 [g/l] | 77 – 140 [kg/t] |

The present waste water data are measuring results of the official examinations for the year 1999. In the case of Solvay Rheinberg: 21 measurements, in the case of

Matthes & Weber: 8 measurements. Basis is the qualified spot check. In table 2 the minimum and maximum values are summarized.

As the analysis shows, the effluents from both plants are very similar with the exception of the ammonium content. Matthes & Weber, however, reached lower outflow concentrations (1). Matthes & Weber explained that these values were due to the reduced water consumption (dry lime process), the optimized consumption of operating materials (lime and steam) and to an especially careful control of the NH_3 -distillation.¹⁾

While the solid materials from the brine cleaning are mainly composed by precipitation products, the solid materials of the final lye are essentially caused by pollutants in the used lime and the coke used for the burning. Furthermore, the operating manner of the lime-kiln plays an important role. A local overheat, for example, causes a so-called „dead caustic lime“, which is not converted and is a residual solid material in the final lye. The solids are extremely fine and generally settle down very slowly.

In order to limit the content of solids, both companies used lime with a CaCO_3 -content of over 95 % (Wülfrather Kalk). This is a way to decrease the share of undesired by-materials. Bernburg and Staßfurt, on the other hand, dispose of own limestone mines. This limestone has a CaCO_3 -content of about 85 percent, which leads to 400 - 500 kg filterable solids per ton product in the untreated waste water. As such an important load of solids cannot be discharged into the comparatively small recipients (Bode and Saale), so-called industrial sedimentation basins have been installed in Staßfurt and Bernburg (see **figure 3**).

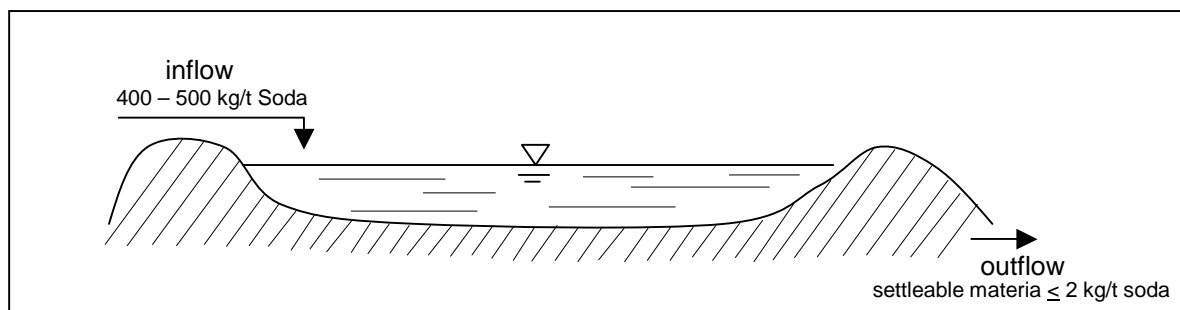


Figure 3: Scheme of the Sedimentation Basins in Bernburg and Staßfurt

¹⁾ Matthes & Weber gave up the production at the end of the year 1999, but the standards of this production site should be mentioned in this report.

They mainly consist of huge basins, in which the effluents are filled. The waste water penetrates the sludge and leaves the basin at the bottom. The basin is equipped with a water-impermeable ground layer. The content of the whole basin is a thixotrope mass, that starts to harden only after the filling process of the basin is finished. By means of these sedimentation basins, the content of settleable solids has been decreased to under 2 kg/t product. All other waste water parameters are, in comparison to the waste water concentration in Rheinberg, without significance (like for example the load of heavy metals) or on the same level ($\text{NH}_4\text{-N}$, Cl, CSB). The fish toxicity is $G_F \leq 32$.

While in Bernburg all three part streams are treated together in the industrial sedimentation basins, in Staßfurt the wash water is discharged from the lime-kiln directly into the recipient. In order to decrease the loads of the wash water in Staßfurt, a dry dust removal has been installed before the off-gas scrubber. The concentration of the filterable solids in the wash water of the lime-kiln off-gas washer is under 80 mg/l. The COD-concentration is under 30 mg/l. These concentrations also consider the preload of the water, which is either weakly loaded cooling water or water from the outlet of the clarifier. The waste water volume amounts to a maximum of 3.800 m³/d.

2.3.2.3 Residues

The separation of the solids from the industrial waste water in Bernburg and Staßfurt causes sludge heavily loaded with chlorides, which is deposited in sedimentation basins as described above .

2.3.2.4 Energy

The reactions of the NH_3 -absorption and the carbonisation are strongly exothermic. According to literature statements approximately 1,84 GJ/t soda leave the NH_3 -absorption und 1,42 GJ/t soda are emitted by the carbonisation process.

This energy is recovered to produce steam, which partially covers the demand of the calcination. The calcination of the crude bicarbonate including the drying of the filter-moist product requires altogether a heat volume of approximately 3,7 GJ per ton soda.

For the distillation to the NH_3 -recovery low-pressure steam is necessary. In Rheinberg the final lye is led at boil temperature into a vacuum decompression as energy recovery.

2.4 Soda Production by Means of Special Proceedings

The BASF in Ludwigshafen produces marketable soda as by-product of the Caprolactam production with a special proceeding. Caprolactam is mostly used for the production of Nylon 6, which is a basic material for fibers with diverse applications, like for example in the textile industry and for technical purposes.

In a special plant the effluents from the synthetization, loaded with organic sodium salts, and carboxylic acid solutions from the different processes are converted to water-free soda. The residues are fed into a combustion chamber, where sodium contained in organics is converted to soda and the organic substances are burned.

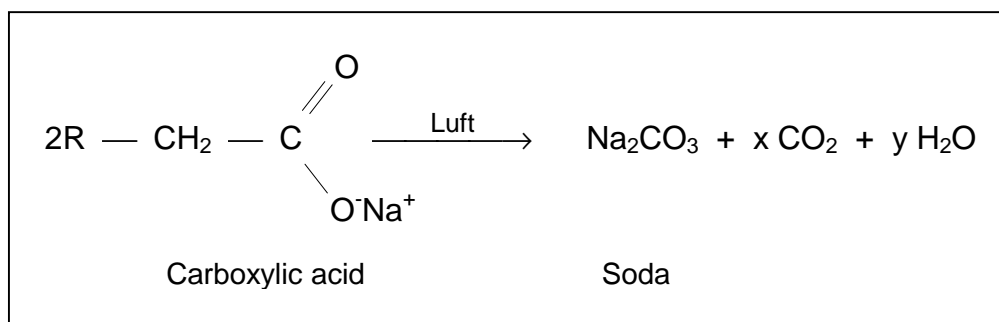


Figure 4: Soda Manufacture by Combustion of Production Residues

The obtained soda in the kettle is partly molten and partly ash. The fumes loaded with soda dust are cleaned by an electro-filter. Solid and liquid soda are dissolved and afterwards converted by means of crystallization and calcination into marketable soda with high purity.

Moreover, the exhaust heat kettle generates high pressure steam, which is fed into the energy system of the plant and is also available as energy for other productions.