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German Notes on BAT for the production of

Large Volume Solid Inorganic Chemicals

Sodium Silicate

Final report

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1 General Informations

Sodium silicates are mostly used for the production of detergents. Moreover, they are needed in big volumes as basic product for the manufacture of silicic acid as additives for rubbers and plastics and cracking catalysts for the petro-chemical industry. They are also used for the synthesis of zeoliths, kieselgels and brines, for glues, as binding agent for aqueous painting colours, for ore flotations, in ceramic, cement and foundry industries, as flocculator for water treatment and for the chemical solidification of soils.

The required volumes will probably increase importantly in the next years, because the tyre production demands bigger quantities of sodium silicate. The use of sodium silicate for tyre production reduces the resistance to roll friction by 5 %, which leads to a lower fuel consumption of cars and trucks.

Potassium water-glass solutions are mostly used for the production of covers for welding electrodes, as binding agent for fluorescent material in picture tubes, for the impregnation of bricks and walls and as binding agent for scours. Another important application field is the paper recycling. In „deinking“, liquid water-glass is used for stabilizing the pH-value of water-glass.

The most important German suppliers of sodium silicates are summarized in **table 1**.

Table 1: Producers and capacities in Germany

Supplier	**Product category**	**Plant capacity**
PQ Germany GmbH & Co. Wurzen	Solid glas / solution	Capacity in Germany ca. 350 000 t (SiO_2)
Cognis Deutschland GmbH, Düsseldorf	Solid glas / solution	
Woellner Werke GmbH & Co., Ludwigshafen	Solid glas / solution	
Van Baerle GmbH & Co. Gernsheim	Solution	

These capacity refers to the production volume of solid glass. One part is sold directly and one part as liquid glass after being dissolved. Some of the smaller suppliers of liquid glass do not manufacture any solid glass themselves due to the economical considerations, but buy the solid glass from abroad. The evaluation of environmental effects the specific conditions at the production side have to be considered. These suppliers of solutions, however, are not relevant under German environmental aspects and consequently do not figure in table 1.

2 Chemical and Physical Basis

2.1 Chemical Reactions

Sodium silicate is produced by melting very pure quartz sand and sodium carbonate (soda), in most cases by means of a furnace at temperatures of 1.300 – 1.500 °C. The following equations demonstrate the stoichiometry of the process reactions:

$$(1) \quad 2\ SiO_2 + Na_2CO_3 \longrightarrow Na_2O \bullet 2\ SiO_2 + CO_2$$

$$(2) \quad 4\ SiO_2 + Na_2CO_3 \longrightarrow Na_2O \bullet 4\ SiO_2 + CO_2$$

As shown in the above mentioned equations, different ratios between the soda and the sand volume are possible. Due to the different properties of the products, they can be used for various applications.

A general distinction is made between solid silicates and liquid silicate solutions. Silicates are solid glasses, which are produced by solidification of the melt of soda and sand. Glasses soluted in water are called liquid glasses. Important technical sodium silicates have a molecular ratio of 2 – 4 Mol SiO_2 and 1 Mol Na_2O. Most commercial products are concentrated water-glass solutions, which are produced by the help of solid silicates with a mole ratio of about 3,3. In case of a mole ratio between 2 – 2,5 water-glasses are directly produced by melting sand and sodium-bicarbonate lye under pressure (Hydrothermal procedure).

There are also sodium silicates with a mole ratio of 1 Mol SiO_2 and 1 – 1.5 Mol Na_2O. These products are less important and are offered as water-free crystals or as hydrates. Silicates are usually classified according to their raw materials (potassium hydroxide or sodium-bicarbonate, sulphate or carbonate) or to their quotient wt % of SiO_2 / wt % of Me_2O. More interesting than the weight ratio is the mole ratio, which is obtained by multiplying the weight ratio of sodium silicate by 1,032. The ratio SiO_2 / Na_2O is decisive for the properties of the different sodium silicates.

2.2 Different Qualities of Sodium Silicates

2.2.1 Sodium Silicates with $SiO_2/Na_2O \geqq 2$

2.2.1.1 Non-aqueous Silicates (Solid Glasses)

Non-aqueous silicates are transparent pieces of glass. Their shapes depend on the kind of receptacle, in which they are solidified. Their colour can be blue to green in different shades due to Fe^{2+}-ions respectively yellow to brown in different shades due to Fe^{3+}-ions.
Solid glas are produced on the basis of pure sand. Metals oxids, with the exception of ferrous oxide, are not relevant for the colour of liquid glases.
Usually commercial sodium silicate glasses are not any stoichiometric compounds. They have often an average molecular ratio of SiO_2 / Na_2O, which assures a stable solution. **Table 2** shows commercial sodium silicate glasses with a molecular ratio of $SiO_2/Na_2O \geqq 2$.

Table 2: Typical Commercial Sodium Silicate Solid Glasses with a Mole Ratio of $SiO_2/Na_2O \geqq 2$

Quality	wt % Na_2O	wt % SiO_2	wt / mol ratio	
High silicate containing Natronglas	20	80	3,8 – 4,0	3,9 – 4,1
”neutral Natronglas”	23	77	3,3 – 3,4	3,4 – 3,5
”alkaline Natronglas	33	67	2,0 – 2,1	2,1 – 2,2

Sodium silicates with a molecular ratio of $SiO_2/Na_2O \geqq 3$ are hardly affected by water at an ambient temperature. Sodium silicates with a molecular ratio of $SiO_2/Na_2O = 2$

are hygroscopic to a certain extent and stick together in case of humid storage. They can already be solved at a temperature around the boiling-point. In order to accelerate the dissolving process, a temperature of 150 - 160 °C is often is used.

2.2.1.2 Water-glass Solutions with a Mole Ratio of $SiO_2/Na_2O \geqq 2$

Solutions of the above sodium silicates are colourless, transparent and more or less viscous. The viscosity increases with the concentration and, under an unchanged concentration of silicic acid, with the mole ratio of SiO_2/Na_2O . After passing the point of critical concentration, the viscosity increases significantly with further concentration. For each relation exists a maximum concentration. After having passed this maximum concentration, the solution becomes too viscous or instable for technical handling.

Table 3 gives information concerning the physical composition of commercial water-glass solutions.

Table 3: Physical Data of Commercial Sodium Silicate Solutions

Quality	Density kg/m^3 at 20°C	wt % SiO_2	wt % Na_2O	wt % water-glass	Ratio wt/mol		Viscosity at 20°C mPa s	pH at 20°C
HK 30	1255-1270	21,8-23,2	5,6-6,0	27,4-29,2	3,70-3,90	3,82-4,02	10 - 30	10,8
water-glass 37/40 (Germany)	1345-1355	26,6-27,0	7,8-8,2	34,4-35,2	3,30-3,40	3,40-3,51	50 - 100	11,4
water-glass (USÁ)	1390-1400	28,4-29,6	8,5-9,3	36,9-38,9	3,20-3,40	3,30-3,40	~ 200	11,2
58/60	1690-1710	36,0-37,0	17,8-18,4	53,8-55,4	2,06-2,12	2,06-2,12	~ 60000	12,2

All water-glass solutions show alkaline reactions (pH > 10,6). Dilution reduces the pH-value, for example a dilution of the 37/40 quality of water-glass to a solution of 1 wt % causes a reduction of the pH-value from 11,4 to 10,7. The liquid sodium silicate 37/40 with a wt % of 3,35 is the most important water-glass product in Germany, in the USA it is the liquid water-glass with a wt % of 3,25.

2.2.2 Sodium Silicates with a Mole Ratio of $SiO_2/Na_2O \leqq 1$

These products are divided into non-aqueous sodium silicates and sodium silicates containing crystal water. The non-aqueous sodium silicate Na_2SiO_3, the only technically important quality of this kind of product, is manufactured with sand, soda and a mole ratio of 1:1. Sodium-metasilicate is a product, which is crystallizes easily and can be dissolved in water without problems.
There are several technically important sodium silicates containing crystal water in the range of the products with a mole ratio of $SiO_2/Na_2O \leqq 1$, for example hydrates of the acid metasilicate $Na_2H_2SiO_4 \bullet x\ H_2O$ with x = 4, 5, 7, 8. In Germany the product is used with 4 and 8 crystal waters.
These sodium silicates containing crystal water are manufactured by mixing either water-glasses with sodium-hydroxide or sodium-metasilicate with water, adding the required quantity of crystal water and crystallizing them with the help of inonculant crystals.

3 Production Procedures

3.1 General Basis

The basic production process of sodium silicate is the following:

$$\text{sand + soda} \xrightarrow{\text{melting}} \text{solid sodium silicate (glass)}$$

Solid glases are cheap commodities and the import and export is not an economical procedure, inspite of the relatively favourable energy costs, because of the high transport costs.
The production of solid glasses in Germany requires lots of energy, mostly natural gas or heavy heating oil. The use of heavy heating oil results in emissions of sulfuroxids because of the sulfur content of the fuel (< 1 % S). The emissions can be reduced by flue gas reduction methods.

Compared the melting process the energy demand and the environmental emissions of the soluting process are much lower. There are some plants in Germany producing liquid water-glasses, whoses production procedures require less energy. Solid sodium silicate is e.g. imported from Poland and converted into liquid water-glass by adding water:

$$\text{solid sodium silicate + water} \xrightarrow{150\text{-}160°C} \text{liquid water-glass}$$

In the following, the whole manufacturing procedure from the raw material to the product (liquid water-glass) is described. A distinction, however, is made between the use of a revolving hearth furnace and a tank furnace for the melting process, because it determines the required process procedures, the energy demand and the emission volume.

In most cases, quartz sand is used as silicic acid component. It should be pure and washed, containing few iron and clay, size of granulation: between 0,1 and 0,5 mm. Generally the quartz-sand is to 99,7 % pure. Other components (0,3 %) are iron, calcium, aluminium, magnesium, copper, titanium and some trace elements.

For the production of most pure sodium silicates, often for scientific purposes, the very clean and dispersed silicic acid (f.e. Aerosil) is recommended. Sodium oxide is added as carbonate or hydroxide. The higher the required purity of the final product, the purer the raw material and additional components should be.

Generally can be said, that the technique of tank furnaces is used in most cases. In Germany there is only one producer, who is using this process technique, which covers < 15 % of the whole german product capacity.

The required temperature of the furnace is determined by the desired compound quality , i.e. the relation of the components. **Figure 1** shows the melting diagram of the system SiO_2/Na_2O as a function of the wt % of SiO_2. It demonstrates, that for the production of sodium silicate with a molecular ratio of > 3, temperatures above 1.300 °C are required. This diagram, however, presupposes ideal operating conditions, e.g. ideal compound relations.

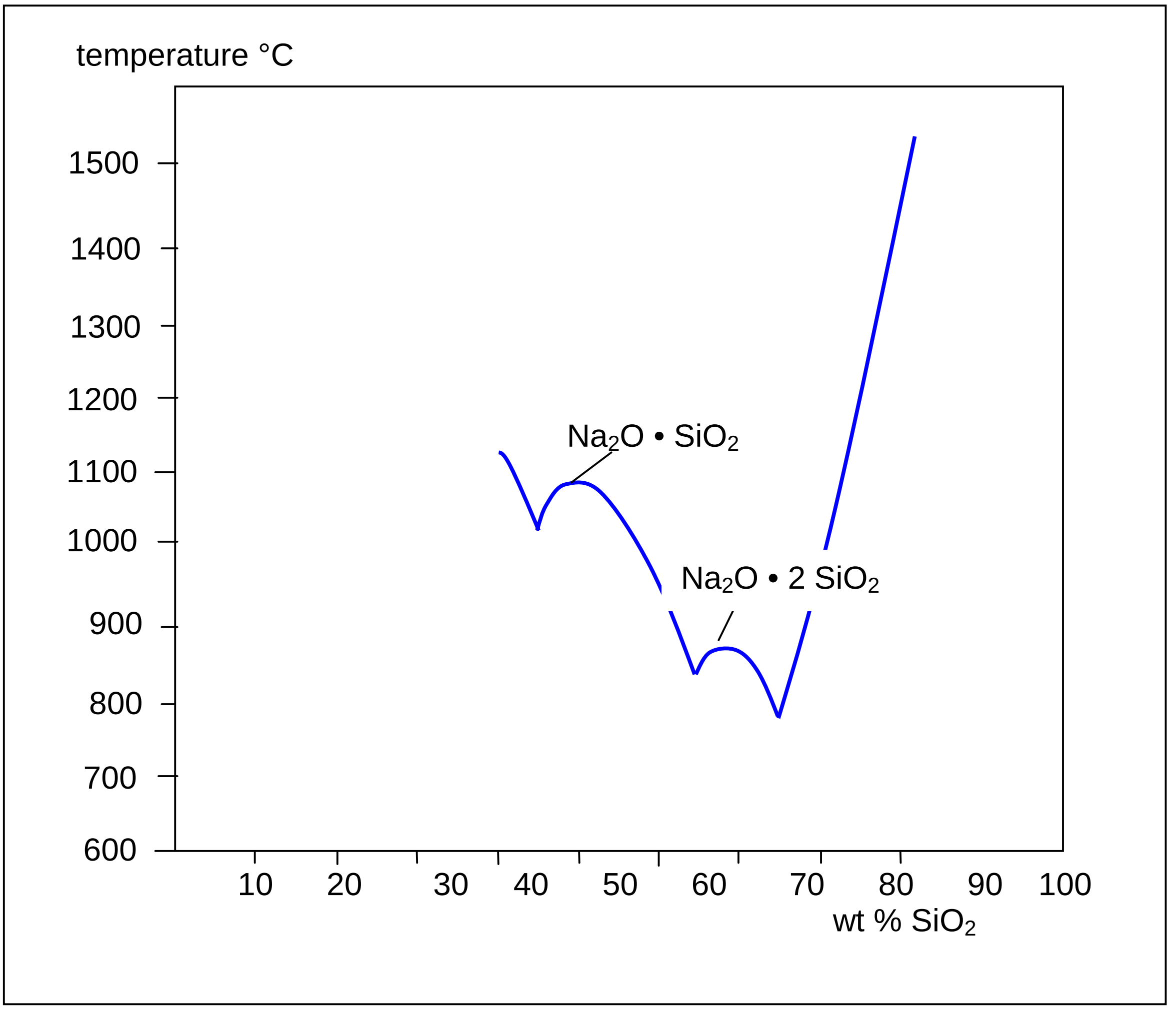

Figure 1: Melting Diagram of the System SiO_2/Na_2O

3.2 Manufacture of Sodium Silicate in a Tank Furnace

3.2.1 Production Procedure

The technique used in most production sides in Germany is the tank furnaces for melting the different substances. The working principles of a tank furnace are demonstrated in **figure 2**.

Soda and sand are led into a tank and are heated from the top by means of a burner (heated with gas or heating oil). Due to the stream of exhaust air, the flame of the burner forms the shape of a „U“ above the melt. The main difference of a tank furnace in comparison to a revolving hearth furnace is that inside the furnace the melt

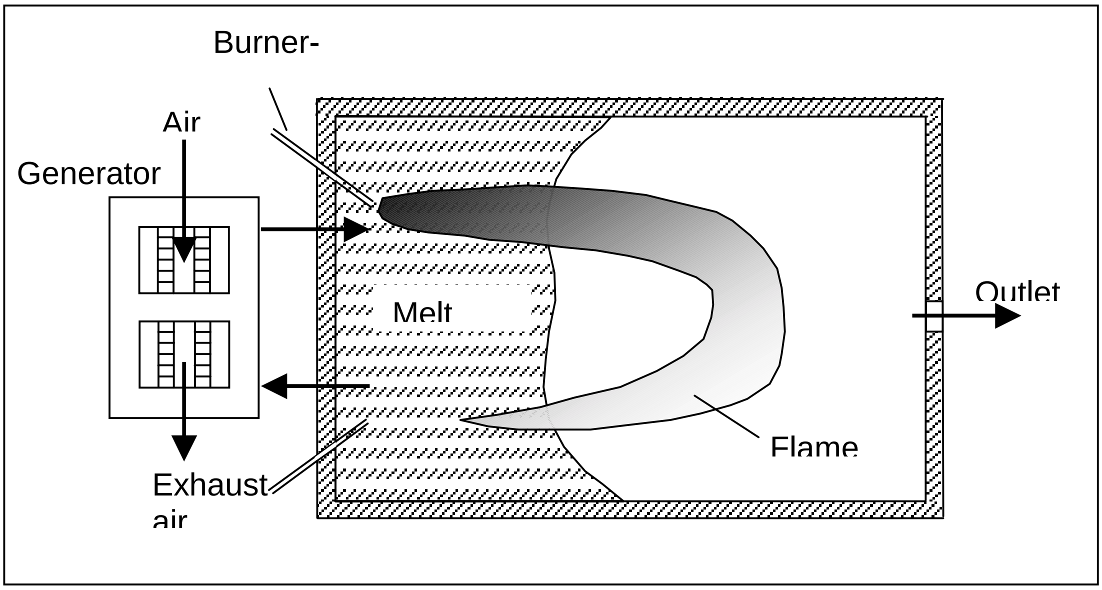

Figure 2: Working Principle of a Tank Furnace

is led to the outlet only by the help of a difference in the density of the initial substances sand / soda and the density of the melt. The elements are not mixed (like by the rotation in a revolving hearth furnace). Consequently, the retention time in a tank furnace (generally between 12 – 18 hours, sometimes even up to 36 hours) is much longer than in a revolving hearth furnace. The melting temperature is 1.300 – 1.400 °C.

Due to longer retention times and higher melting temperatures the substances are melted better than in a revolving hearth furnace. Consequently, the content of residual sand granes in the solid sodium silicate product is much lower in case of the tank furnace. The complete block-scheme of the production procedures with a tank furnace is shown in **figure 3**.

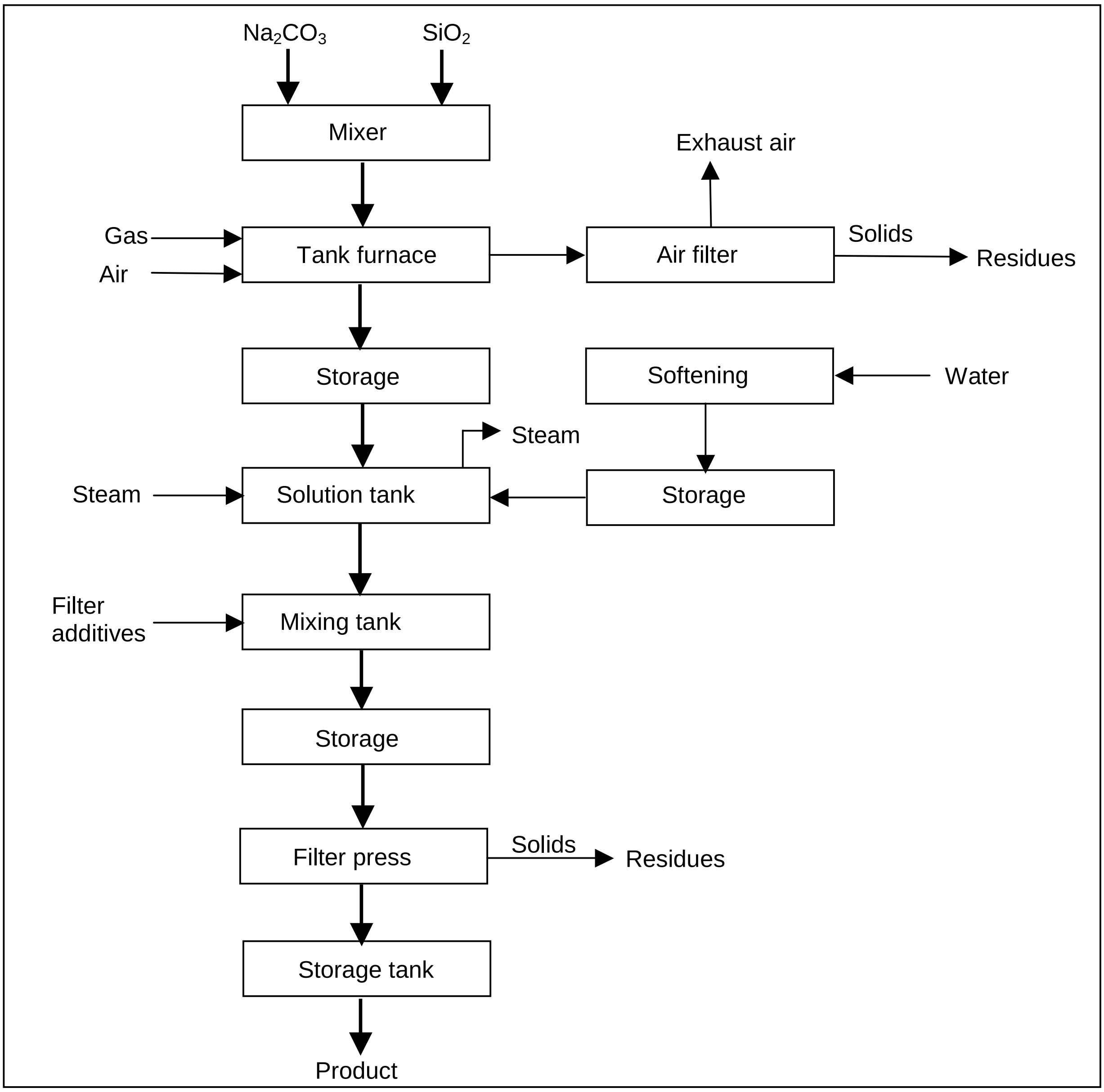

Figure 3: Block-scheme of the Sodium Silicate Production with a Tank Furnace including solution process and filtration

The components are led by a mixing system into the tank furnace, where they are melted. Before being discharged into the atmosphere, the exhaust air is filtered by a filter. In one installation a fabric filter with a sorption step before is installed. Emission concentration below 1 mg/m^3 can be reached. The filtered dust is recycled.

The melt coming out of the tank furnace is fed to forming rollers, where it solidifies very quickly. After an intermediate storage the solid water-glass is put into a solution tank, where water and steam are added. The liquid water-glass is filtered by the help of filter additives and then pumped into storage tanks. The filter cake is recycled.

3.2.2 Energy Consumption

As an alternative to the heat recovery in a recuperator, the combustion air may be preheated, as shown in **figure 4**, by the alternating use of various flues. The hot fume flows out via a brick flue, which is heated by the hot fume. After a certain time another brick flue is used as outlet. The warm flue is now filled with inflowing cold air, which is heated by the warm bricks. A continous operation is reached by regular changes of the flues. The counter-stream principle of substances and exhaust air cannot be used in case of a tank furnace.

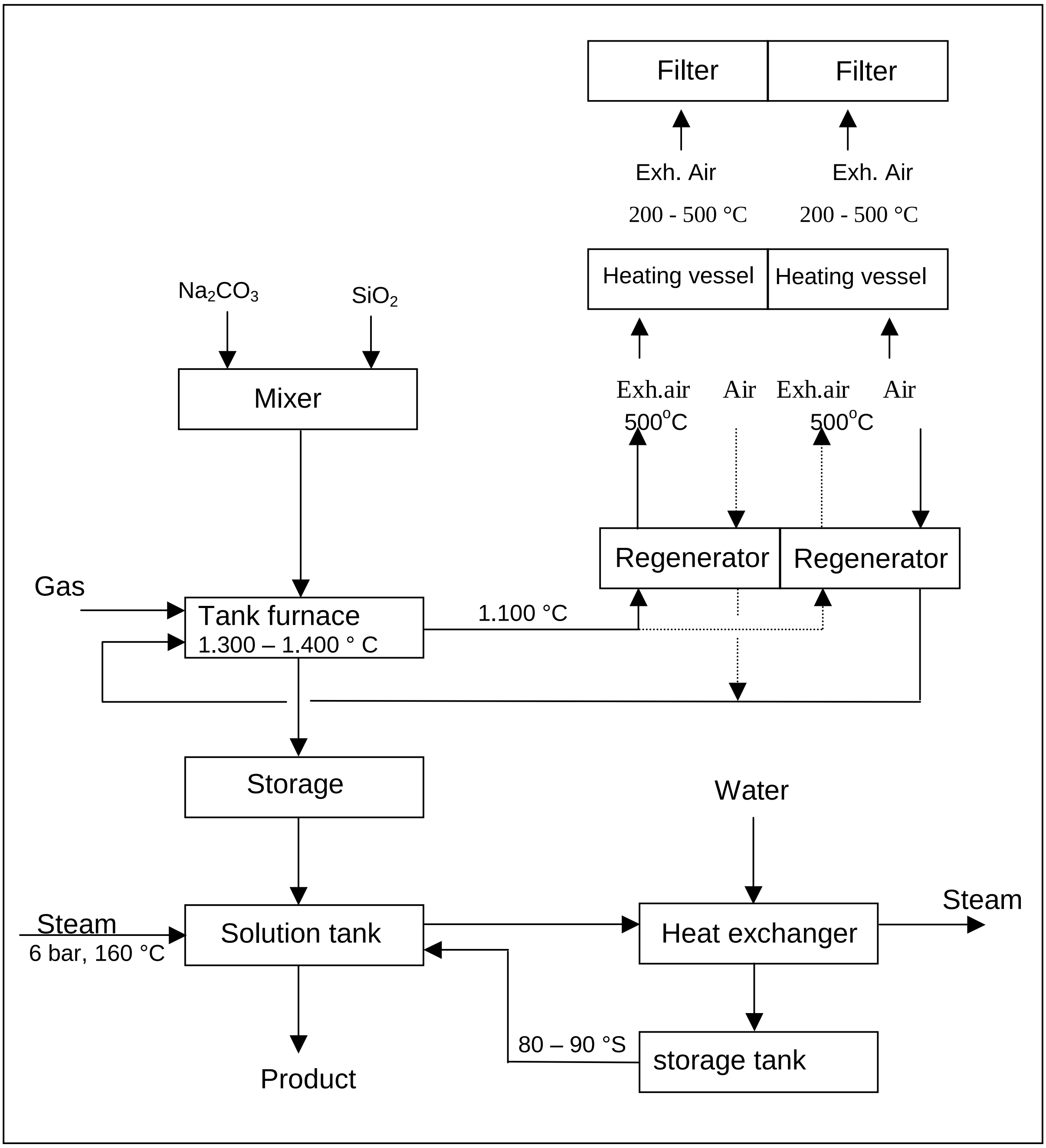

Figure 4: Heat Recovery by Regenerators

Under similar molecular ratios (3,3 – 3,45) the specific energy demand may be similar like in the hearth furnace. In consideration of secondary energy production with a heating vessel the whole energy balance of the tank furnace may be almost as high as for the hearth furnace. The secific energy demand is max. 0,1 t steam/t liquid water glas.

3.2.3. Emissions

Figure 5 shows the different emission sources and their specific loads:

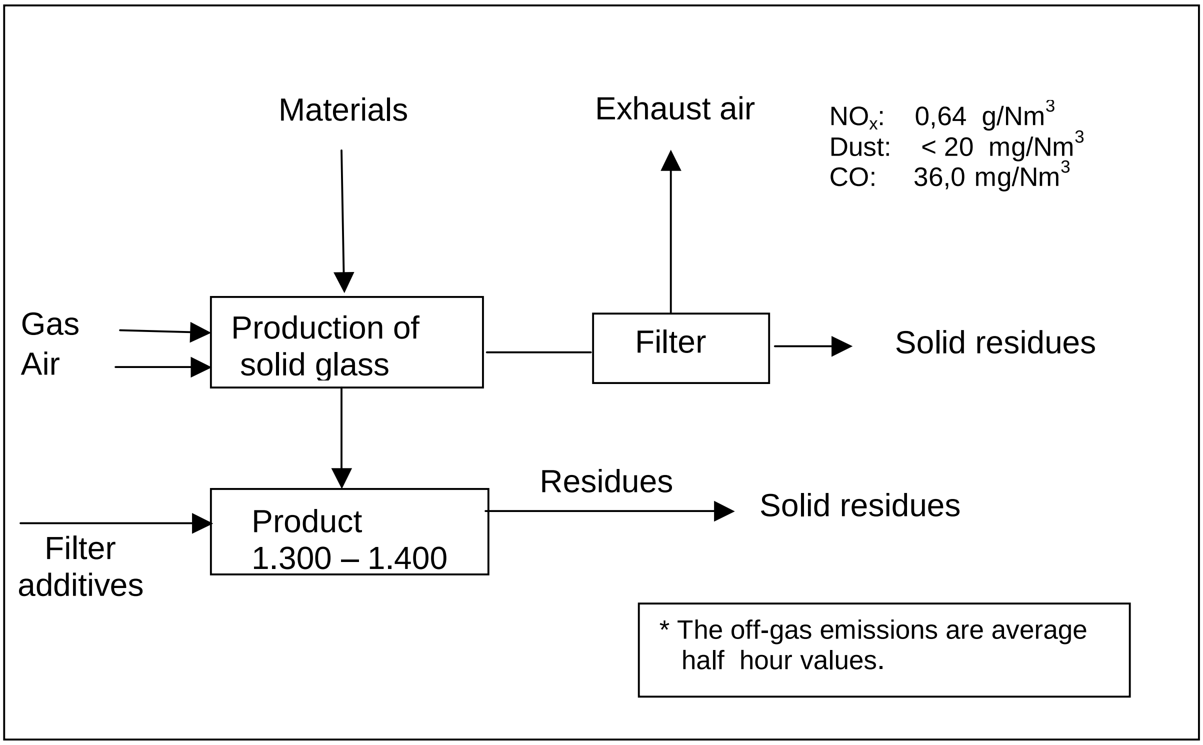

Figure 5: Emissions of the Sodium Silicate Production with a Revolving Hearth Furnace

3.2.3.1. Emissions into the Air

Table 4 shows the concentrations of exhaust air of the analysed plant. The results are indicated as emission volume in relation to the volume in a normal state (273 K, 1.013 hPa) in mg/m^3 and g/m^3 after deduction of the water steam. The obtained results relate to an oxygen content in the exhaust air of 8 %.

The emissions of sulfur dioxide depent strongly on the fuel. The emissions of natural gas are very low. In the case of heavy heating oil (< 1% S) sulfur dioxide emissions should be reduced by secondary measures.

Table 4: Composition of the Exhaust Air of a specific production side Working with tank furnaces

Parameter		Max. average ½ hour value
Carbon monoxide	mg/m^3	36,0
Nitrogenoxide	g/m^3	0,64
Sulfuroxide (depending on the fuel)	g/m^3	0,1
Emission of dust	mg/m^3	< 20
Anorganic chlorine compounds as gas, chlorine hydrogen	mg/m^3	2,0
Fluor and fluor compounds as gas or steam, fluor hydrogen	mg/m^3	0,4

Tabelle 5: Emission concentrations in waste gas from another producer, who is working on the basis of a tank furnace and heavy oil.

Parameter	**Concentrations (average ½ hour values)**
Dust	0,14 mg/Nm^3
Nitrogenoxide	406 mg/Nm^3
Carbonmonoxide	< 4 mg/Nm^3 (maximum average ½ hour value), under the measurable limit in most cases
Sulfurdioxide	364 mg/Nm^3
Chlorine hydrogen	3,8 mg/Nm^3
Fluorin hydrogen	1,07 mg/Nm^3

Basing on dry waste gas under normal conditions, Oxygen content 8 Vol.- %

The main difference between a revolving hearth furnace and a tank furnace is the concentration of NO_x in the exhaust air. More nitrogen is converted to NO_x in a tank furnace due to higher operating temperatures.

3.2.3.2 Waste Water

In the analysed case the filter cake or parts of it are not recycled. Consequently, in this sodium silicate production, there are not any washing processes and no waste water emissions.

3.2.3.3 Residues

The amount of residues is very low. The amount of filter additives is about 0,3 – 0,4 kg/t liquid water-glass.

3.3 Manufacture of Sodium Silicate in a Revolving Hearth Furnace

3.3.1 Production Procedure

The revolving hearth furnace is used only at one production side in Germany.
The different production procedures of solid sodium silicate respectively liquid water-glass may be divided as follows:

- Type of melting furnace,
- kind of energy recovery and
- wash process (for liquid water-glass).

Figure 6 shows the block-scheme of the production procedure in the only German plant, where sodium silicate with a molecular ratio of 3,45 is produced. Sand and soda are transported by a worm conveyor from two bunkers into a mixer. The humidity of the analysed sand is 5 – 6 %. In order to assure stable compound relations, the humidity is controlled regularly. Even a light modification of the molecular ratio may provoke important changes in the required product quality.
Then the compound is transmitted to a revolving hearth furnace and melted at a temperature of 1.100 - 1.200 °C. The heat is generated by a gas burner in counter-current to the inlet of the compound. The retention time of the compound in the furnace is about 5 hours. By continous rotation the compound respectively the melt is slowly transmitted to the deapest point of the furnace. There it leaves the furnace as

a viscous paste and is led on a conveyor. **Figure 7** shows the working principle of a revolving hearth furnace.

The paste solidifies very quickly on the conveyor and looks like glass. The still flexible paste is formed by a drum, installed on top of the conveyor. This is the manufacture procedure of solid sodium silicate.

In the analysed company the solid sodium silicate is led into a storage tank and then filled into an autoclave, where it is dissolved in water. First the tanks are filled with gas. Then softened water is added. During the rotation the tanks are under pressure with the help of hot steam (160°C, 8 bar). After the dissolving process, the liquid is filled into a mixer. Under the addition of filter additives, like kieselghur or perlit, the pollutants are separated from the product in a membrane filter press. The obtained end-product, transparent and with a solids content of about 36 %, is finally filled into storage tanks. The filter cake consists of unsolved sand, traces of iron oxide, calcium, aluminium, filter additives and traces of dust from the off-gas treatment.

The filter cake is washed, in order to purify the water-glass. So it can be avoided that it solidifies too quickly, which would impede the recovery. The filter cake is recycled to 80 % and is remelted together with sand and soda. 20 % of the filter cake are separated from the recycling process and is reused, for instance, in building industry. The purified water-glass is recycled back into the tank and filtered again. One part of it is discharged as waste water.

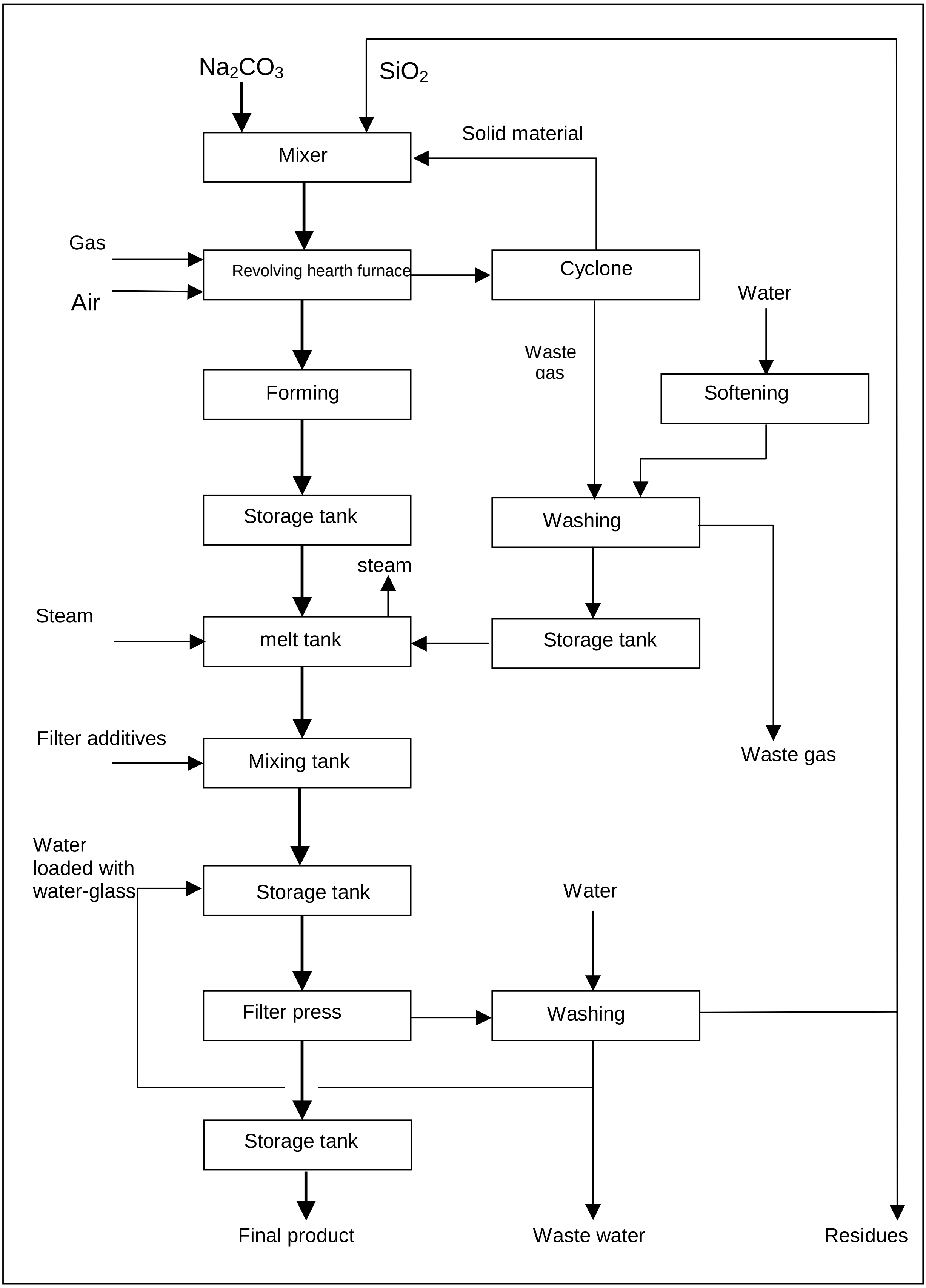

Figure 6: Production Procedure of Sodium Silicate in a Revolving Heart Furnace including soluting process and filtration

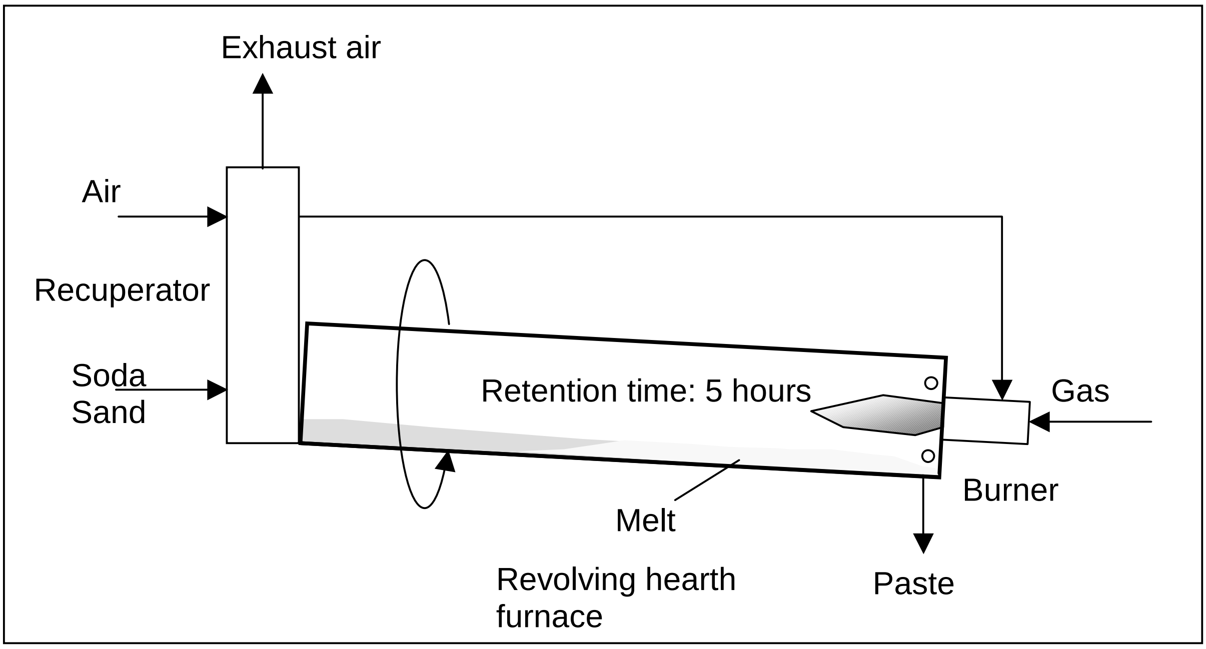

Figure 7: Working Principle of a Revolving Hearth Furnace

Energy Consumption

3.3.2.1 Energy Consumption of the Solid Water-glass Production

The energy cost is importantly determined by the energy demand. In most cases the energy demand of the sodium silicate production depends on the following:

1. Kind and efficiency of the energy recovery
2. Retention time in the reactor

Figure 8 shows the system of heat recovery and energy demand in the analysed plant .

counter-stream principle: For obtaining an maximum energy recovery, the hot waste gas heats the incoming material as far as possible. Therefore sand 7and soda have to be led in counter-stream to the outflowing exhaust air. The furnace is in rotation and consequently the compound is heated to a very high melting temperature (above 1.100 °C). Meanwhile the exhaust air leaves the furnace with about 600 °C.

This demonstrates the intense heat exchange between the incoming material and the exhaust gas.

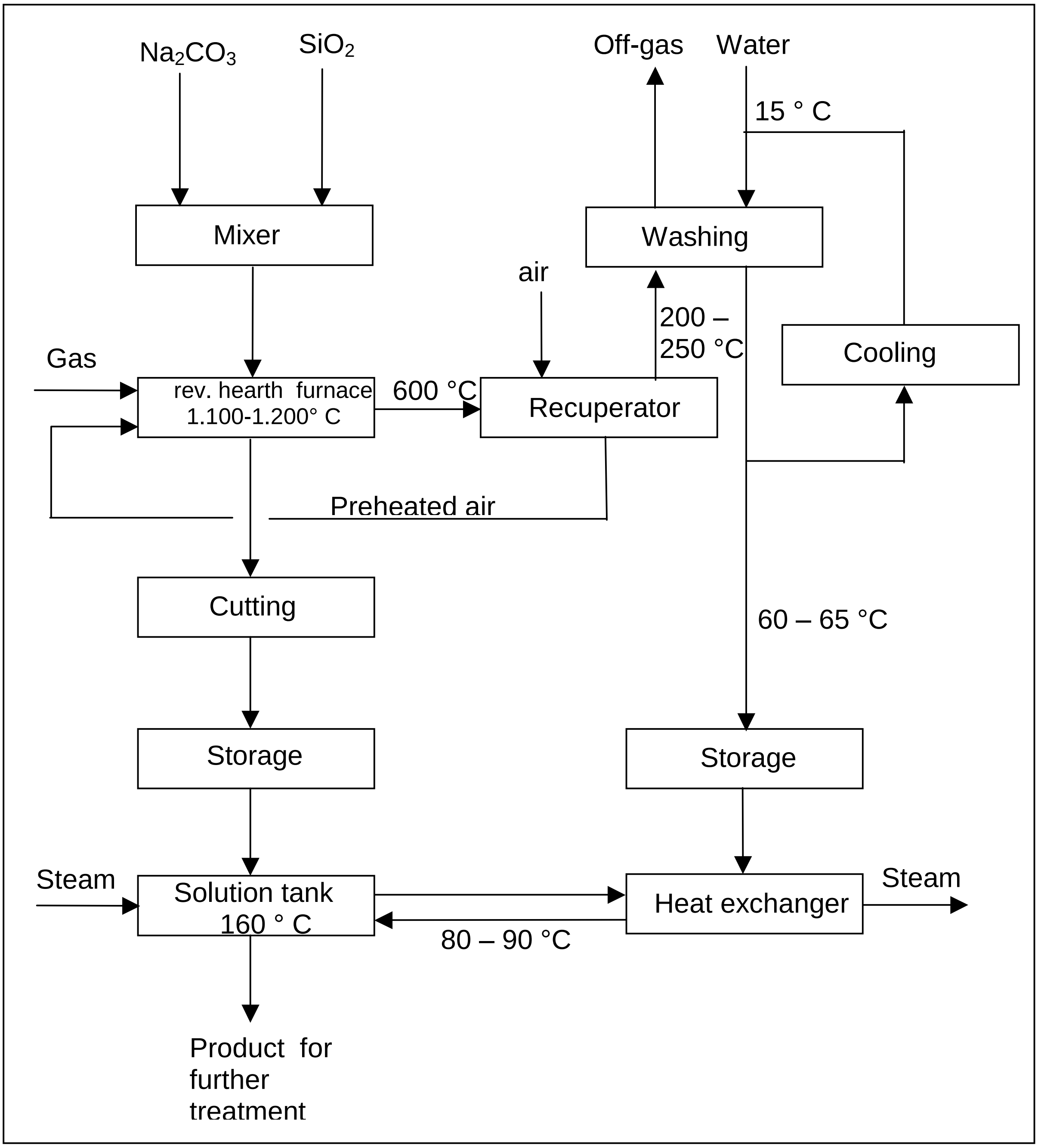

Figure 8: Principle of Heat Recovery and Energy Demands

Recuperator for the preheating of the air	The remaining heat of the exhaust air is used for preheating the incoming air of the combustion process. Therefore the exhaust air of the furnace is led into a recuperator, where it is cooled down from from 600 °C to 200 – 250 °C. At the same time inflowing air is heated to 350 – 400 °C for combustion.

Retention time	Another very important factor determinating the energy cost is the retention time of the compound in the reactor. In the analysed plant the average retention time is about 5 hours. The flow velocity of the charge, however, depends on the velocity of the rotation, which can be modified easily.

The above mentioned factors determine the specific consumption of natural gas of 120 Nm^3/t for the solid sodium silicate production. (1 Nm^3 natural gas = 33 000 kJ)

3.3.2.2 Energy Consumption of Liquid Water-glass Production

Besides the energy demand for the melting of the different materials, steam is required for the solution of the solid sodium silicate. In the present case steam of 8 bar and at a temperature of 160 °C is used. The specific steam demand is 0,1 t per t of liquid water-glass. The kind of steam depends on the dissolving velocity.

3.3.2 Emissions

The production procedures cause different emissions (waste water, exhaust air and residues). The various emission sources and their specific loads are summarized in **figure 9** and are explained in the following.

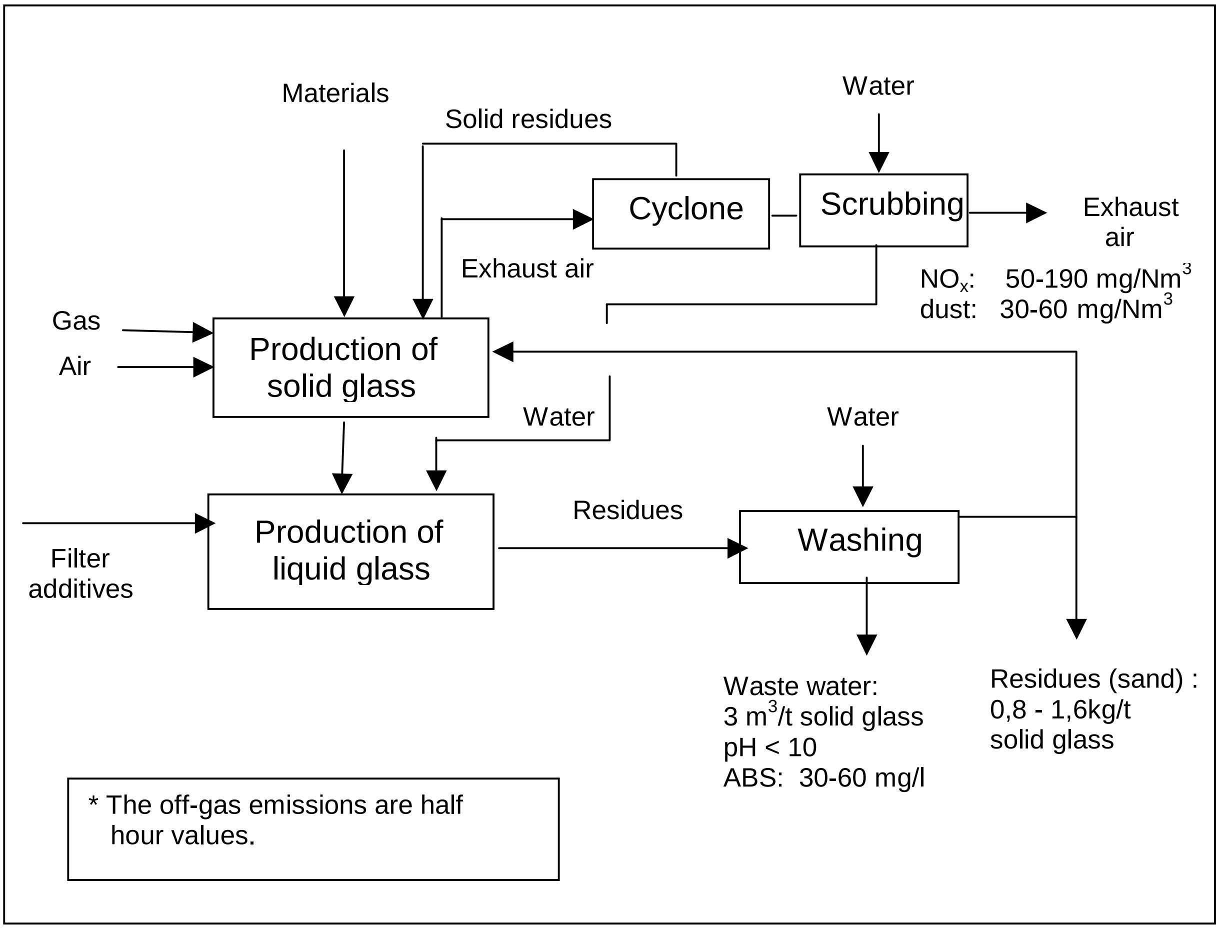

Figure 9: Emissions caused by the Sodium Silicate Production in a Revolving Hearth Furnace including solution process and filtration

3.3.3.1 Emissions of Exhaust Air

The composition of the exhaust air depends on the chemical reactions and the conditions of the combustion process. As shown in equation 1 and 2, carbon-dioxide (CO_2) is generated by the reaction of soda and quartz-sand. CO_2 is also caused by the combustion of gas and air.

Table 6 shows specific emission rates and concentrations. The results refer to the emission volumes in a normal state (273 K, 1.013 hPa) and are indicated in mg/m^3 and g/m^3 after deduction of the water steam. They relate to an oxygen content in the off-gas of 8 %.

Table 6: Emissions and concentrations of Exhaust Air

Parameter	Specifique freight per ton of water-glass	Concentration
Carbon dioxide from combustion of gas from the reaction	238 kg 165 kg	
Nitrogen oxide	0,075 – 0,32 kg	< 200 mg/Nm^3
Dust	45 – 85 g	< 50 mg/Nm^3

* The stated concentrations in table 5 are average half hour values, which are based on several measurements.

3.3.3.2 Waste Water

The emission of waste water or residues depends on the desired product qualities of the water-glass and the necessity to filter the liquid water-glass. Due to steadily increasing product quality requirements, the filtration of the liquid water-glass may become obligatory in the future.
In the analysed case emissions of waste water are caused by the softening process and the washing process of the filter cake. The waste water is alkaline with a pH-value $\leqq$ 10. The concentration of settleable solids oscillates between 30 – 60 mg/l. There are, however, no or only traces of organic elements and heavy metals in the waste water. The waste water volume is between 0 and 3 m^3/t water-glass in the analysed case.

3.3.3.3 Residues

The quartz-sand does not react to 100 % with the sodium-carbonate in the revolving hearth furnace, about 1 % per ton water-glass are residues. Other residues from the off-gas treatment are less important. By filtration of the liquid water-glass, the residues are separated from the product. ½ - 1 kg filter additives per ton liquid water-glass have to be added.
In the analysed case 0,8 – 1,6 kg residues per ton solid sodium silicate are caused by the production procedures, i.e. 20 % of the total filter cake volume.