HUGO PETERSEN
Verfahrenstechnischer Anlagenbau

SO2^{RICH}
Intelligent SO$_2$-Recovery
for Environmental Quality Control

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The company

HUGO PETERSEN GmbH located in Wiesbaden, origins from the renowned engineering company Hugo Petersen, founded in 1906, in Berlin. HUGO PETERSEN is part of the Chemieanlagenbau Chemnitz (CAC) group and as such, can provide full support and security for the development and implementation of small to large scale installations.

Initially, using the expertise gained in the classical production of sulphuric acid, from off-gases generated in the refining of metallurgical ores, the company HUGO PETERSEN specialized in the field of manufacture of sulphuric acid, hydrochloric acid and gas cleaning.

Figure 1:
Hugo Petersen 1906

HUGO PETERSEN has more than 110 years of experience in the design and operation of sulphuric acid plants and their equipment. Today, HUGO PETERSEN offers a vast range of technology, to this industry. The design, whilst incorporating HUGO PETERSEN's extensive experience, has been developed and optimised through a comprehensive research program, conducted using HUGO PETERSEN´S own pilot plant facilities. This, together with its 50 years know-how in the design and operation of Gas Cleaning Equipment and Plants processes, offers further advantages, through the experience from both worlds.

Hence, the SO2^{RICH}-Technology is favoured, for sulphuric acid and gas cleaning needs.

About 50 well trained process technologists and engineers, contribute their knowledge and expertise, in the fields of mechanical and electronic engineering, as well as material science, to their design work.

Accurate Planning - the basis for our work

The scope of the tender, for a custom designed plant, is solely defined by the task, operating requirements and the requirements of our customer.

The thorough evaluation of the ecological and economic factors, ensures the best plant specific solution. Proven technology, combined with HUGO PETERSEN´s site specific developments, leads to the construction of a plant suitable for the respective application.

HUGO PETERSEN has installed more than 400 turnkey plants and plant components for the manufacture of sulphuric acid, oleum and SO$_2$/SO$_3$.

Every plant is unique and all plant components have to be finely adjusted. Hence, it is of great advantage, when a single company designs all components.

As plant designer and constructor, we assume the full responsibility for the reliability and performance of our plant design. Individual fabrication and selection of the right materials are a matter of course, as well as the timely supply, erection and commissioning of the plant.

Qualified personnel supervise the erection of our plants, down to the last detail, prepare the final documentation and provide long-term post-implementation support to our clients.

SO2^{RICH} – Upgrade SO$_2$ to a Valuable Product

The SO2^{RICH}-Process is an absorptive-regenerative technology, used in the elimination of SO$_2$ from off-gases, by concentrating the SO$_2$ for up-cycling as:

- SO$_2$-liquid
- Elemental sulphur
- Concentrated sulphuric acid
- Chlorosulphonic acid
- or any other sulphur containing product

The production of liquid SO$_2$ is technically considered, a very economical way of upgrading, as the investment costs are reasonable and a product with food-grade quality, is produced for use in the food and paper industries.

The absorption media is a buffered sodium hydroxide solution.

The development of the SO2^{RICH}-Process is closely linked to the Norwegian institute, SINTEF:

The so called CITRATE_Process was developed in 1967, by Prof. Olav Erga from SINTEF, at the NTH Trondheim (Norway).

The first pilot plant went on stream, in 1976, at Boliden Metall AB in Skelleftehamn.

In 1980, EPRI (Electric Power Research Institute) sponsored another pilot plant, downstream from a coal-fired power plant, run by TVA (Tennessee Valley Authority), for flue-gas desulphurisation.

From 1983 till 1986, HUGO PETERSEN was the licensee for the above-mentioned SINTEF process. During this time, the experience and knowledge gained from the pilot studies, was adapted and transferred into an upgraded, industrial process technology. HP, was even the initiator for research into more effective buffer systems, like the phosphate buffered system.

The use of steam-compression, eliminates the need for fresh steam and consequently provides a more attractive OPEX. The evaporation heat, for the stripping-steam, can be generated through heat-recovery, from the process.

The use of state of the art-materials has helped to reduce investment costs, significantly.

Physical-Chemical Basics

The following description focuses on, the demonstration of the SO₂-Equilibrium in the gas-and liquid phase, for the absorption and the desorption of SO₂.
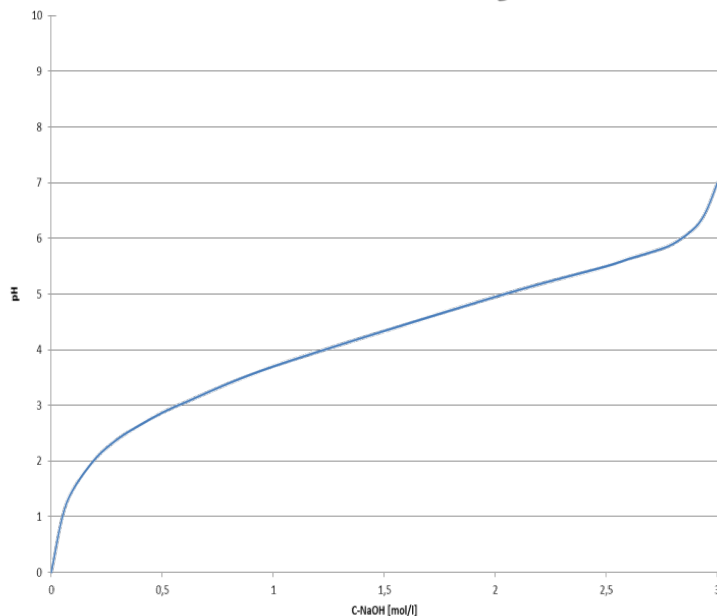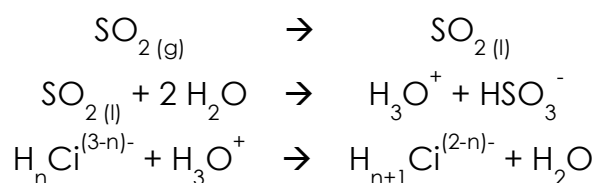

Figure 2: Buffer curve for a one-molar citric acid solution of a polyvalent buffered system (Buffer curve for 1.0 mol / l H₃Ci at 40 °C).

Citric acid, being a tri-carbonic acid, has a strong buffer effect and a nearly linear buffer curve with a slow incline, over a wide pH-range.

Adipic Acid, being a di-carbonic acid is, on the contrary, a much stronger buffer, but has a shorter linear range. Another interesting buffer, is phosphoric acid, which being a tri-proton inorganic acid, behaves similarly, but at a higher pH.

The selection of the corresponding buffer system, depends on the very different conditions experienced, during the elimination of SO₂ from off-gases or process gases.

During SO₂-absorption with a citric acid-buffered system, the following reactions occur:

$$SO_{2\,(g)} \rightarrow SO_{2\,(l)}$$

$$SO_{2\,(l)} + 2\,H_2O \rightarrow H_3O^+ + HSO_3^-$$

$$H_n Ci^{(3-n)-} + H_3O^+ \rightarrow H_{n+1} Ci^{(2-n)-} + H_2O$$

as n = 0, 1 und 2

These reactions are very rapid and reversible, which simplifies the design of the absorber and the stripper.

From equilibrium measurements, the following dependencies for the SO$_2$ partial pressure were determined, which very well reflect the measured equilibrium values.

$$P_{SO_2} = C_{HSO_3^-} * 10^{\left[a - \frac{b}{T} - \left(pH_S - \frac{1}{\beta_0} * \frac{C_{HSO_3^-}}{C_{H3Ci}} \right) \right]}$$

Components of the formula are:

- a: coefficient
- b: coefficient
- T: absolute temperature
- pH$_S$:   pH of solution without SO$_2$
- β_0: buffer capacity $\dfrac{dC_{NaOH}}{dC_{H_3Ci}}$ per 1 mol/l H$_3$Ci
- $C_{HSO_3^-}^0$: total concentration kmol/m³

A similar relationship can also be derived for the adipic acid buffered system. Let us now turn back to the possibilities offered by such a buffered system, for plant design and optimization.

The outstanding advantage of a buffered absorption / desorption process is the great flexibility, which makes it possible to adapt the design, to a wide variety of gas compositions. Exhibited in the following graphs; Figure 3 shows equilibrium curves with the same concentration of SO$_2$, in the liquid. It can be seen that as the concentration of citric acid increases, the equilibrium curves are flatter, which allows a higher specific loading of the liquid with SO$_2$, or, in other words, allows for a smaller liquid circulation in the absorption / desorption system.
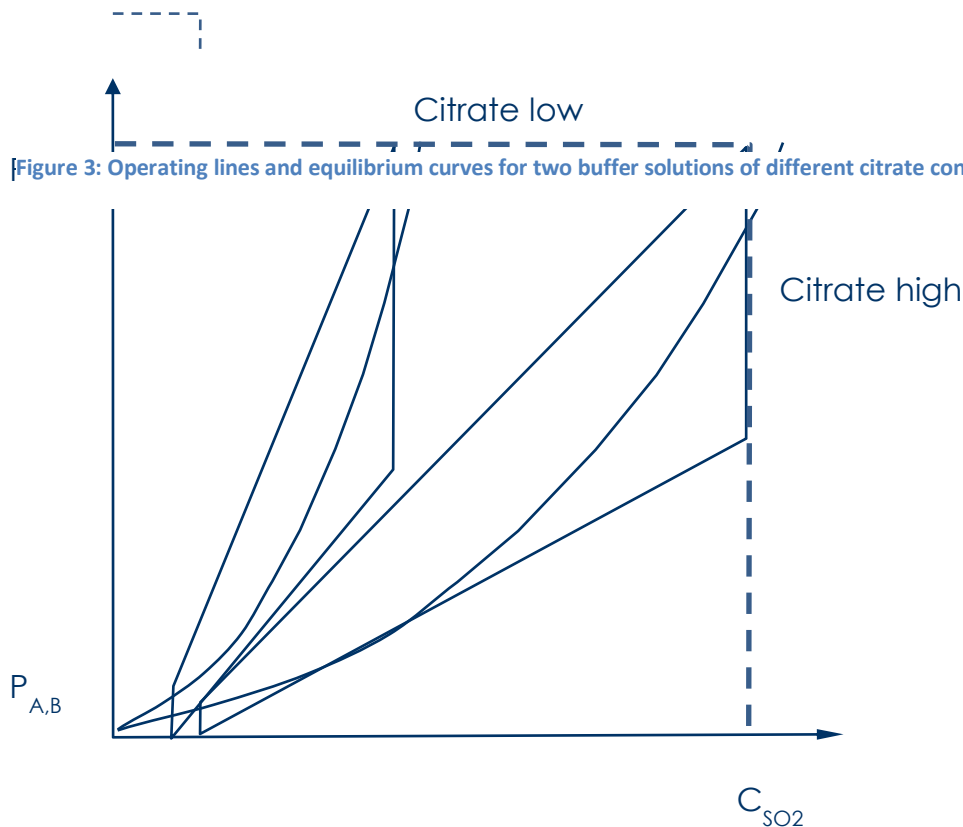
Figure 3: Operating lines and equilibrium curves for two buffer solutions of different citrate concentrations.

With consideration to operational costs, the lowest possible strip-vapour requirement is, of course, to be striven for. The steam consumption is calculated by the SO_2 content of the vapours at the outlet of the desorption column.

Tests carried out have shown, provided that the SO_2 loadings of the liquid and absorption temperatures, remain the same, that the steam requirement is practically independent of the system pressure in the desorber. However, a change of the absorption temperature has a great influence on the steam required.

For example, for low-concentration gases, a stripping steam reduction of half, is possible, when the absorption temperature is lowered from 55 °C. to 42 °C.

Absorption systems buffered by adipic acid versus citric acid, show a reduction of 20% of the steam consumption by the former, if the scrubbing solution is acidified directly before the desorption, with injected free adipic acid and re-crystallisation of the acid occurs, before entry into the absorber.
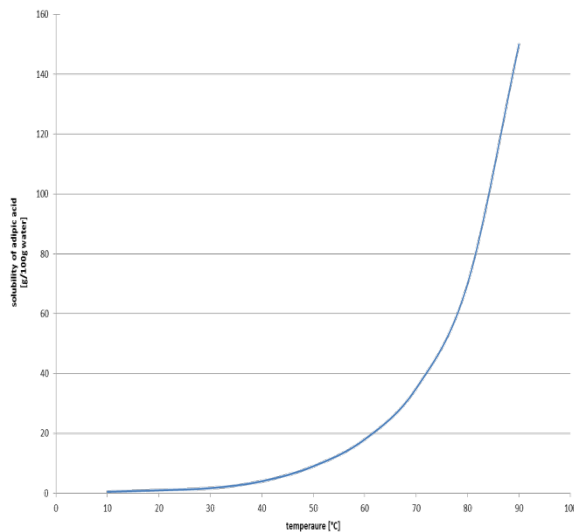
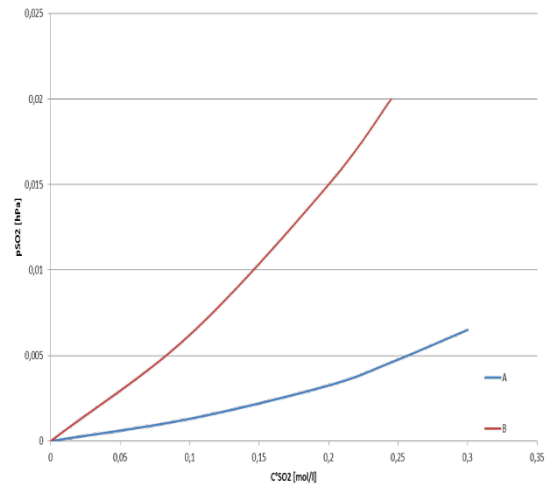**Figure 4:Solubility of Adipic acid in water (Kirk-Othmer)**

Figure 5: Equilibrium Curves with $P_{SO2}=f(C°_{SO3})$ bei 70°C
Curve A: 1 mo1/1 H_2Ad + 1 mol/l NaOH
Curve B : 2.5 mo1/1 H_2Ad + 1 mol/l NaOH

Figure 4, shows the solubility of adipic acid in water, depending on the temperature. Figure 5, shows the advantages of the before-mentioned acidifying procedure at equilibrium of 70 °C, for various buffer compositions. Due to the gained increase in the SO_2 partial pressure in the desorber, the stripping steam requirement is greatly reduced.

Buffered process systems versus unbuffered sodium hydroxide solution

The chemistry of the sodium hydroxide process is well known as the 'Wellman-Lord-Process'. SO_2 is absorbed to form sodium hydrogen sulphite, in a sodium sulphite solution. The solution is thermally regenerated by converting bisulphite to sodium sulphite and extracting a SO_2 water vapor mixture overhead. The process is used for SO_2 recovery in Claus plants, sulphuric acid plants, as well as, in power stations. Its characteristic property is that the specific steam requirement, is barely dependent on the absorber temperature and the SO_2 partial pressure, in the raw gas. An important aspect is the high SO_2 losses due to the enormous SO_2 oxidation to sulphate. It can be seen from the literature   that 7-8 t_{steam} / t_{SO2} must be expected when a 2-stage vacuum crystallizer is used. For each ton of SO_2 absorbed, more than 2 tonnes of sodium sulphite must be crystallized and 6-9% oxidation losses, have to be considered.
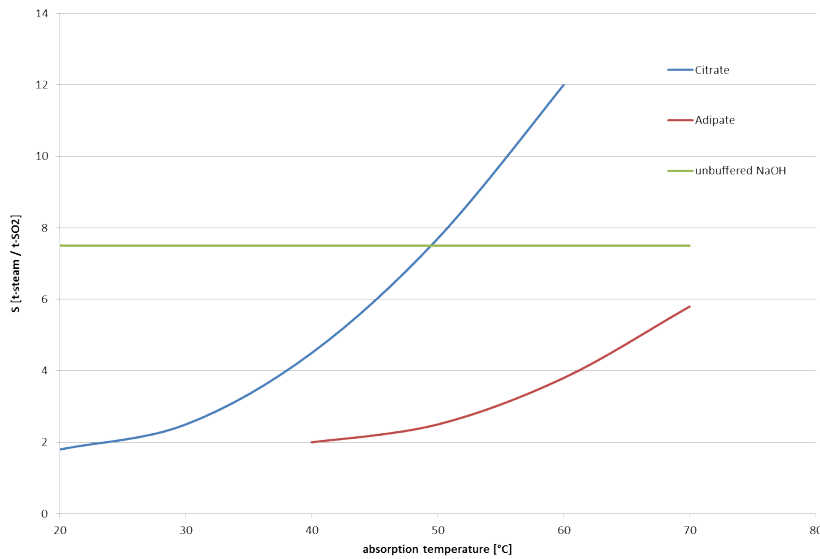
Figure 6: Comparison of the citrate and adipate process versus the unbuffered sodium hydroxide solution with respect to the required stripping vapour

In Figure 6, the sodium hydroxide process is compared with the citrate or adipate process. The absorption temperature T_A is plotted on the abscissa and the specific steam requirement S on the ordinate. The diagram applies to raw gases with

- approx. 1.4 vol.% SO$_2$.
- C = the crystallized adipic acid amount / t_{SO2} (0.5-1.0 mol H$_3$Ad / t SO$_2$),
- a crystallization temperature of 30 °C.

It can be seen from the diagram, that the citrate system operates with a lower steam requirement than the unbuffered sodium hydroxide process, up to an absorption temperature of 50 °C.

If the latter is operated with a 1-stage vacuum evaporation, the citrate process can be carried out up to an absorption temperature of 60 °C with lower steam consumption. The adipate process has advantages at an absorption temperature between 45 and 70 °C.

The **oxidation losses** for the citrate system are based on pilot tests, over an extended period of time and are estimated to be **about 1%**.

Process Description

The following explanations can be followed in the SO2^{RICH} Process scheme (see below) with regard to the process using a citrate-buffered sodium hydroxide solution.

Gas Cooling and Pre-Washing

The raw gas is cooled down (by a recuperative heat exchanger (W1), the waste heat being used for the reheating of the cleaned gas after the SO$_2$ absorption.

In the scrubber (K1), the gas is cooled down to the absorption temperature, and pollutants such as

Dust,

Heavy metals,

SO$_3$,

HF and HCl

are eliminated from the gases.

The concentrations of the pollutants, in the circulating washing solution, are kept constant, by discharging a partial stream, since the pollutants accumulate in the liquid.

This small wastewater stream is first freed of dissolved SO$_2$, in air, in a degasser (K2) and can then be fed to a waste water treatment or evaporation. The SO$_2$ exhaust gases from K1 and K2 are supplied to the SO$_2$ absorption via the blower (W 1)

SO$_2$ Absorption and Desorption

The absorption solution, used in the absorber (K3), is either buffered with citric, adipic or phosphoric acid. The buffer and composition selected, depends on the operational and environmental circumstances.

Taking into account local conditions and by using the appropriate buffer substances, it is possible to greatly reduce the steam requirement for the desorption of the SO$_2$, from the circulated solution. The absorber (K3) is designed as a column with a structured packing, where gas and liquid are fed to one another in a counter-current, the gas leaves the column via a droplet separator and is reheated in the heat exchanger already mentioned before.

The scrubbing solution, charged with SO$_2$, is heated in a special recuperative heat exchanger (W2) nearly to the desorption temperature. The exchanged heat quantity is used to cool the desorbed solution back to the absorber.

The temperature of the liquid to be stripped, must be raised by further 5 K, using a steam-operated heat exchanger (W3). In the desorber (K4), the solution is freed from SO$_2$, by stripping steam, fed in a counter-current.

The SO$_2$-freed solution is cooled, as already noted, in W2 and refed for absorption in K3.

Despite the low oxidation rate of about 1% of the absorbed SO$_2$, the solution enriches with sodium sulphate. For this reason, a partial stream of this solution must be discharged and fed to the sodium sulphate elimination. Here, the sulphate is partially crystallized as Glauber Salt (Na$_2$SO$_4$ × 10 H$_2$O).

The mother liquor is supplied to the citric acid feed tank (B2). The chemical losses are covered by B1 and B2. In order to reduce drastically the cost of stripping-steam-generation, the SO$_2$-laden steam is compressed in a vapour compressor (V2) and the largest part of the water is condensed in a reboiler (W4). With the heat generated in W4, the stripping-steam is generated without additional fresh-steam. The gas and liquid phases are separated from one another in a condensate separation tank (B3). The effluent gases from B3 are condensed in a condenser (W5) operated by cooling water.

The gas and liquid are separated in a further condensation separator vessel (B4). The two condensate streams of B3 and B4 are combined, expanded and collected in the separation tank (B5). As a result, the SO$_2$ is widely desorbed, thus the condensate can be reused again as stripping steam via the reboiler (W4) in the stripper (K4). The SO$_2$ gas flowing out from (B5) is fed to the desorber (K4) in the head.
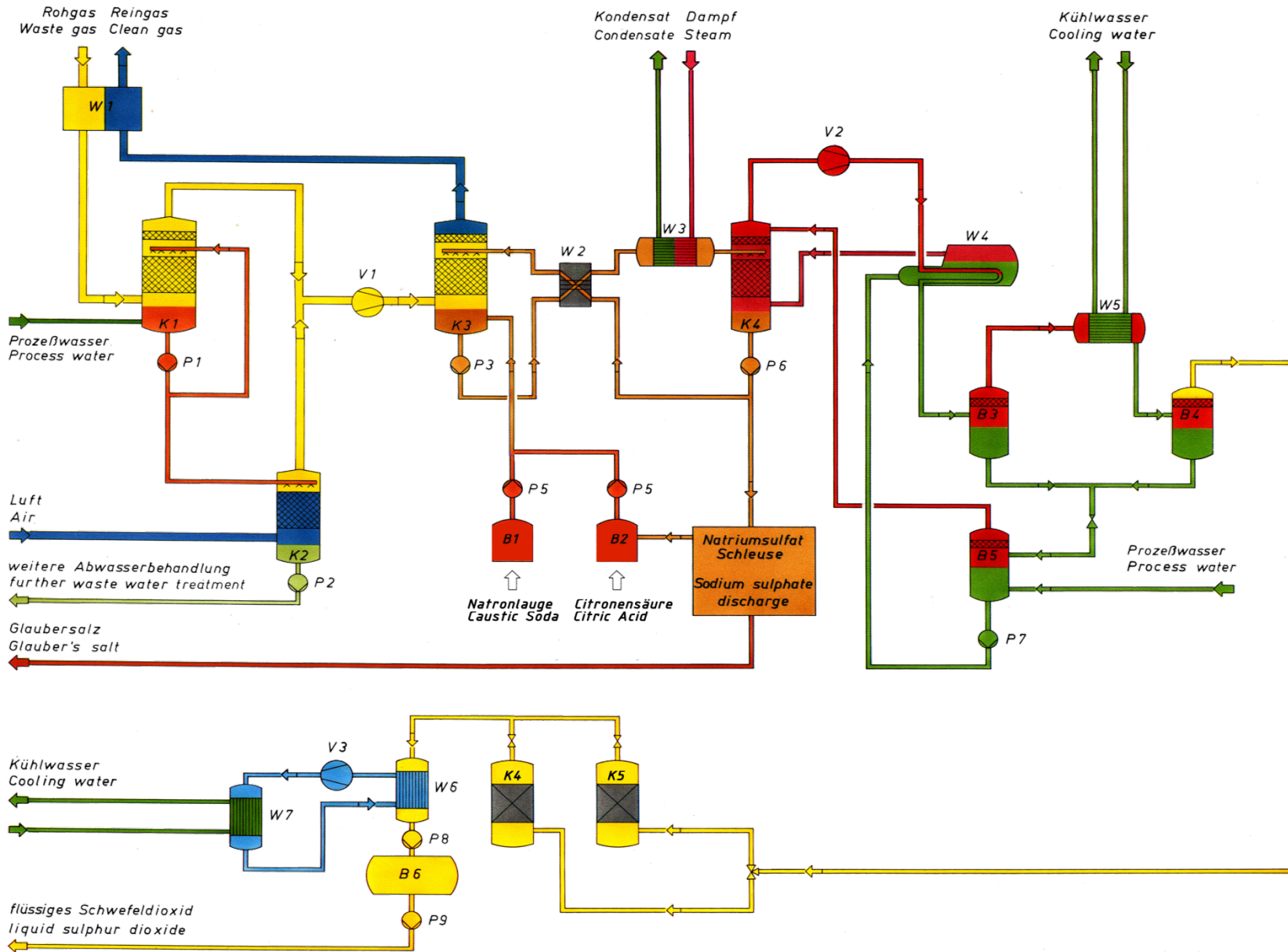
The SO$_2$ rich gas from B4 is dried in the adsorbers (K5 and K6), thus it can be condensed in an SO$_2$-liquification plant (W6, W7, V3).

The SO$_2$ is stored in the pressure storage tank (B6).

The water removed, through the drying of the gases, is fed to the vessel (B5) as fresh process water.

The cooling capacity necessary for the liquefaction of the SO$_2$ is generated by a liquefier, which is operated with refrigerant. The refrigerant evaporates in the condenser (W6), which is subsequently compressed in the compressor (V3). The refrigerant is condensed in the condenser (W7), whereupon it can again be used for SO$_2$ liquefaction.

SO2^{RICH} Process Scheme

Rohgas   Reingas
Waste gas Clean gas

Kondensat Dampf
Condensate Steam

Kühlwasser
Cooling water

V 2

W 1

W 3

W 4

V 1

W 2

W 5

K 1

K 3

K 4

B 3

B 4

Prozeßwasser
Process water

P 1

P 3

P 6

B 5

Luft
Air

P 5

P 5

Natriumsulfat
Schleuse

Sodium sulphate
discharge

P 7

K 2

B 1

B 2

Prozeßwasser
Process water

weitere Abwasserbehandlung
further waste water treatment

P 2

Natronlauge
Caustic Soda

Citronensäure
Citric Acid

Glaubersalz
Glauber's salt

Kühlwasser
Cooling water

V 3

W 6

K 4

K 5

W 7

P 8

B 6

flüssiges Schwefeldioxid
liquid sulphur dioxide

P 9

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