Schmidt + Clemens

Märker® Alloy 31

FIELDS OF APPLICATION

Shutoff and Fluid Control Devices, Feed Pumps and Agitators in Inorganic and Organic Chemistry Plants well as in the Pharmaceutical Industry

These plants mainly process aqueous solutions because they are easy to transport and to measure out. In the majority of cases aqueous solutions of inorganic substances are solutions of salts containing chlorides, fluorides, sulfites or sulfates.

Highly alloyed special stainless steels such as "Märker Alloy 31" are employed in these plants, when ever there is the challenge of high concentrations or high temperature ranges, i.e. where standard stainless steel does not provide adequate resistance and the use of nickel base alloys is not yet justified.

A measure for the employment is the "Pitting Resistance Equivalent", defined with the formula:

PRE_N = % Cr + 3.3 x % Mo + 30 x % N

Examples:	W. Nr.	PRE_N
Märker Alloy 31	1.4562	53
Alloy 625	2.4856	51
Alloy 926	1.4529	47
Alloy 28	1.4563	39

Märker Alloy 31 therefore is the most economic solution due to its low nickel content und therefore low material cost combined with excellent resistance against oxidizing and reducing media.

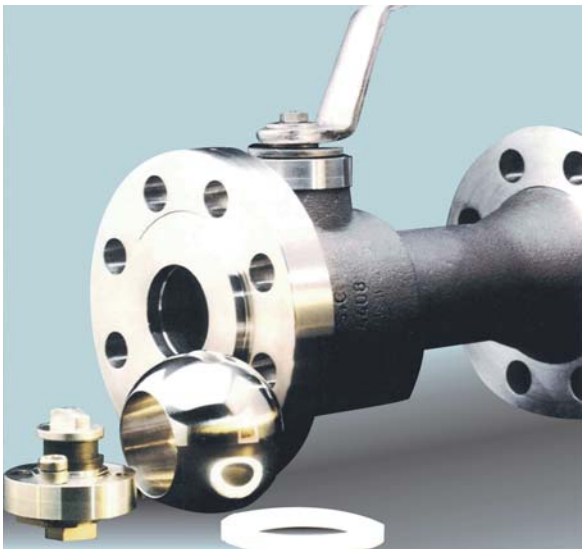
For apparatus and tubular systems semi finished products out of Nicrofer 3127hMo are available as plate, bar and seamless or longitudinally welded tubes from the portfolio of ThyssenKrupp VDM.
Particularly the parts of pumps and valves in contact with the chemicals cannot be made – or only with tremendous effort – from forgings.

Therefore Schmidt + Clemens obtained the license for the production of castings out of Alloy 31.

S+C is capable of producing single pieces as well as batches of conventional or precision castings, supplied as cast or machined following the instructions from the component manufacturer.

Pump casings

Valve bodies, conventional casting or shell moulding



Ball valve, casing by shell moulding, ball machined from centricast tube

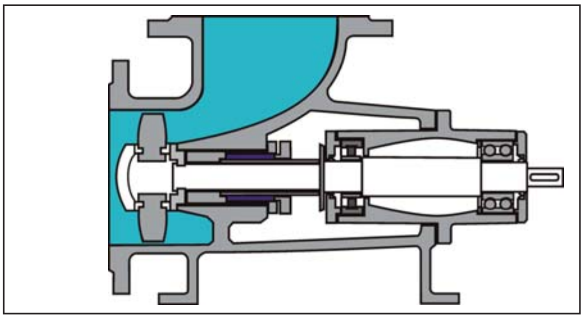
Decomposition of Phosphate Minerals for the Fertilizer Industry

Phosphoric acid (H_3PO_4 resp. P_2O_5) are essen-tial starting products for the production of fertilizers like Ammonium-Phosphate and NPK fertilizer. The production starts with the decomposition of phosphate minerals (Apatit) with sulfuric acid.
Byproducts are gypsum ($CaSO_4$ $*2H_2O$) and hydrofluosilicic acid (H_2SiF_6). Apatit minerals are primarily found in northern Africa (Morocco) and South America.

Depending on the composition of the phosphate minerals, strong impurities like chlorides and fluorides are released during the production of phosphoric acid. The corrosiveness is even further increased by the presence of sulfuric acid.

Already during transportation of the minerals and water slurry out of ground, strong erosion-corrosion takes place in the pipes as the hard mineral particles remove the protective oxide layer of the materials used.
Therefore these pipes, as well as the first stage of the plant in which the minerals are mixed with sulfuric acid, need materials, highly alloyed with chromium and molybdenum.
Especially the agitators in these reactors are subject of severe erosion-corrosion combined with strong abrasion.
Trials with samples, attached to the agitator propellers, exposed to this media have shown the superiority of Alloy 31 compared to Alloy 28 and the so far used alloy 904L = 1.4539.

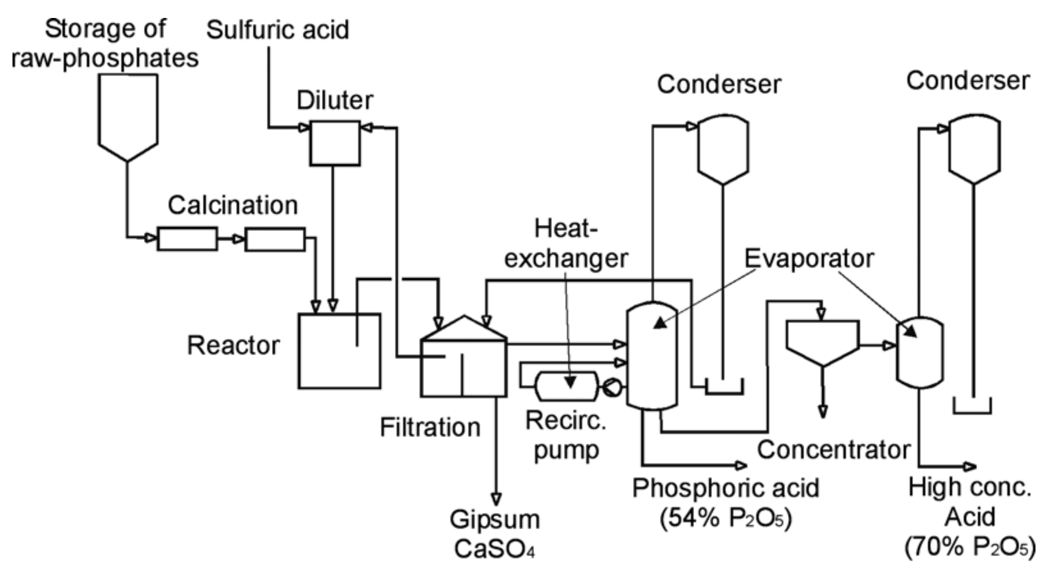
Also in the thickener tanks and the mixers of a plant, using the Nissan-Process (28 % P_2O_5, 350 ppm chlorides, 1.5 % fluorides, 400 ppm sulfites, 3 % free sulfuric acid and 34% solids at 95 °C) alloy 31 has replaced alloy 904L.
The same changes have been made to the pipes behind the re-concentration part of the plant with 54% P_2O_5 at 80 °C.
In a sulfuric acid cooler a cast material with 30% chromium was replaced by Alloy 31. The pipe carries 98.5 % H_2SO_4 and is cooled from outside with seawater. Defects were detected on the outside of the pipe due to pitting- and crevice-corrosion caused by the seawater.



Typical Re-Circulation Pump

In another plant the rubber-lined hood of a re-concentration plant was replaced by Alloy 31. despite weekly flushing with cold water, acid concentrations of 28 to 54 % at temperatures between 90 and 100 °C and mineral deposits form strongly corrosive conditions.
Increasing impurities of the minerals and higher temperatures of the decomposition process require highly corrosion resistant materials.

The cast material Märker Alloy 31 presents an outstanding addition to of the well established Alloy 31 for semi-finished parts in the production of phosphoric acid.

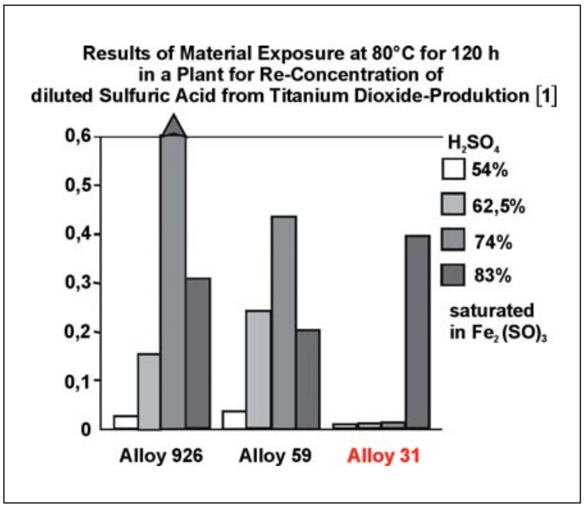


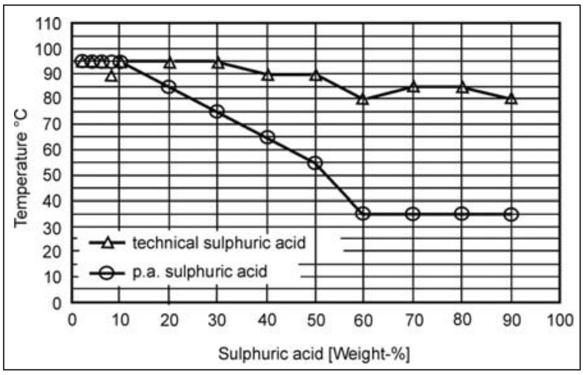
Flow-diagram of Phosphoric Acid Production

Re-Concentration of diluted Sulfuric Acid e.g. from Titanium Dioxide Plants

The diluted sulfuric acid, byproduct in the production of titanium dioxide TiO_2 by the sulfuric acid routing was immersed in the open sea up to 1986. Apart from the environmental damages, the loss of the acid was so expensive that processes for the recovery of the sulfuric acid became economically viable.
The diluted acid with about 20 to 28 % strength now is re-concentrated in several steps in heat exchangers by cross-flowing steam from the TiO_2 production or by vacuum, up to concentrations of 80 to 85 % and re-used in the process.

Recent trials have shown that Alloy 31 can be used in technical applications with sulfuric acid in a wide range of concentrations and temperatures, due to oxidants like Fe+ being present in the acid. Due to the high content of chromium and molybdenum the alloy remains in the passive stage. [2]





Iso-corrosion diagram for Nicrofer 3127hMo in aerated technical and p.a. sulfuric acid. The areas below the iso-corrosion-lines correspond to a material loss < 0.1 mm/a.

This material behavior allows replacement of the components normally made out of plastic materials or lined with plastics with solid castings out of Märker Alloy 31 in many areas of the plants.

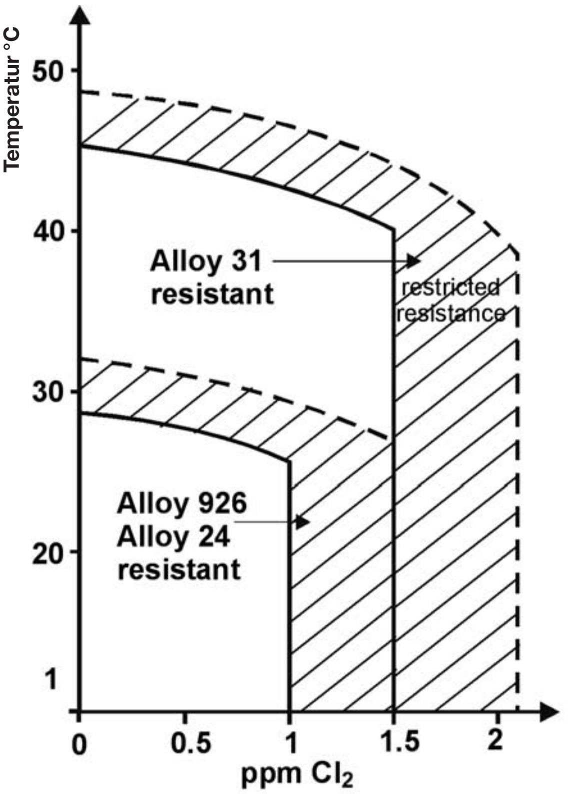
Sulfuric Acid Re-Concentration Plant [1]

Maritime Technology, Components for Piping Systems

More than 70 % of the earth's surface is covered by seawater. The salt content of the seawater varies between 8 g/kg in the Baltic Sea and 42 g/kg in the Persian Golf.

The exceptional resistance of Alloy 31 against pitting- and crevice-corrosion in chloride containing media results from the high content of chromium and molybdenum.
The material also proved its capability against sea- and brackish water in piping systems on ships or offshore platforms as well as in off-shore oil and gas production plants, near-seashore chemical plants and power stations.
The piping systems contain numerous parts like flanges, supports, valves and pumps for which so far only forged material with this analysis was available, out of which such parts can only be produced with enormous effort.

With the equivalent cast material Märker Alloy 31 the option becomes available of castings for complex housings and internals of pumps and valves.



Guideline for the Selection of Flange Materials in chlorinated Seawater
(hatched areas show restricted resistance)

Particularly critical is the application of metallic materials in cooling circuits which are injected with chlorine to avoid the growth of marine organisms.

Lower alloyed special stainless steels like 1.4529 or 254 SMO and also duplex stainless steels fail beyond the addition of 0.5 ppm chlorine and 27 °C, or 1 ppm and 25 °C, particularly by crevice corrosion in flange connections.
Alloy 31 however is resistant up to 1.5 ppm chlorine and 40 °C which is very important in tropical seas with higher water temperatures.

Formerly, piping systems in ships were made from CuNi-alloys or NiCu alloy 400. These materials however are very limited in operating pressure and flow velocity, but avoid maritime fouling due to their copper content.

For the new requirements in shipbuilding and offshore technology special steels had to be developed which allow higher pressures and flow velocities with reduced wall thickness as the weight load above sea level is a major factor for the design of the submerged parts of these designs.

Alloy 31 is the most prominent material of these steels.

The tests to obtain the temperature limits were made in North-Sea and Baltic Sea water with test racks, combined from flanged tube sections out of different materials.

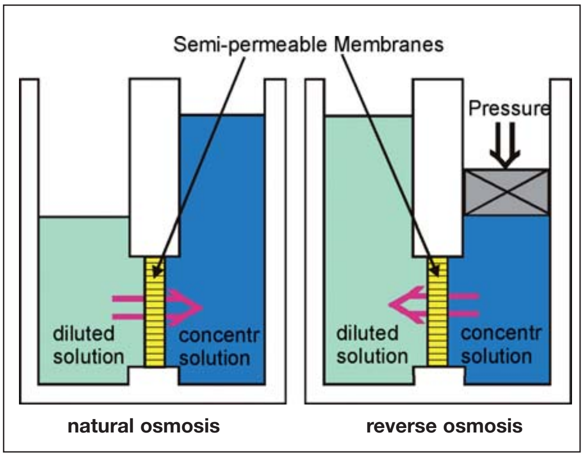
Seawater Desalination

The first seawater desalination plants were built in the Persian Gulf as so called Multi-Flash plants, using the waste heat from power stations.
The seawater in these plants is heated by low pressure steam and evaporated in huge heat exchangers. The pure water is collected as condensate.
The piping systems for the seawater and the shells of the vessels are made from alloy 400 (2.4360), which is corrosion resistant in seawater up to 130°C and prevents from algae growth.
Alternatively titanium is used with chlorination.

On offshore facilities for production of oil and gas and in most desert areas of this world no waste heat from power stations is available. Therefore, another technology had to be applied which was made available by the development of large semi-permeable membranes for the **R**eversed **O**smosis (RO) process.
In this technology the seawater is forced by 20 to 40 bar pressure into the intermediate layers of the spirally wound membranes through which the desalinated water (permeate) is separated into the center pipe. The pressure is needed to overcome the natural osmotic pressure difference between the salty seawater and the pure water as well as the pressure loss in the membrane.

In numerous trials materials have been tested, from standard stainless steel through 6-Mo special stainless steels, up to nickel-base-alloys.

Depending on the salt content and the temperature of the seawater, today, with increasing corrosivity, Super-Duplex, alloy 926, 254 SMO and alloy 31 are used for the piping systems.
When the seawater is chlorinated against algae growth, now in pumps and valves in which the salt concentration increases in crevices and cavities the cast version of alloy 31 = Märker Alloy 31 can be used, and consequently the lifetime of these parts increased.

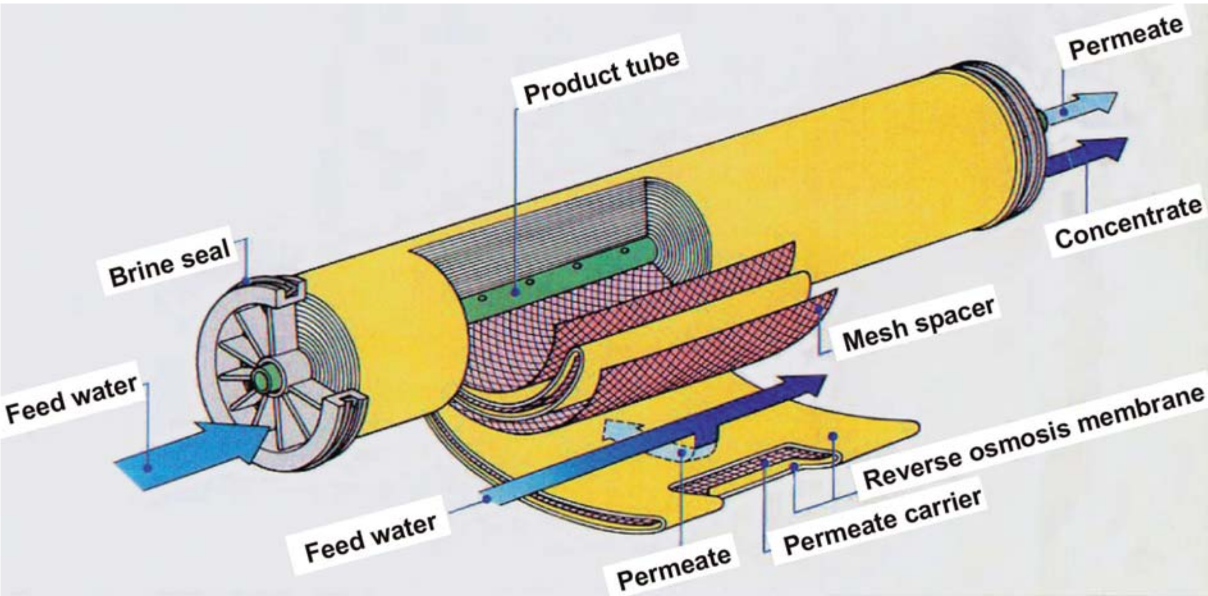


Principle of reverse osmosis (RO)

The concentrated brine from the RO units is returned to the sea by low pressure plastic pipes.

In the south of Spain, spray irrigation has lowered the groundwater level so much that seawater is permeating into the watertable.
The water from deep wells therefore became salty and has to be treated by reverse osmosis.

Large RO plant



RO membrane built-up

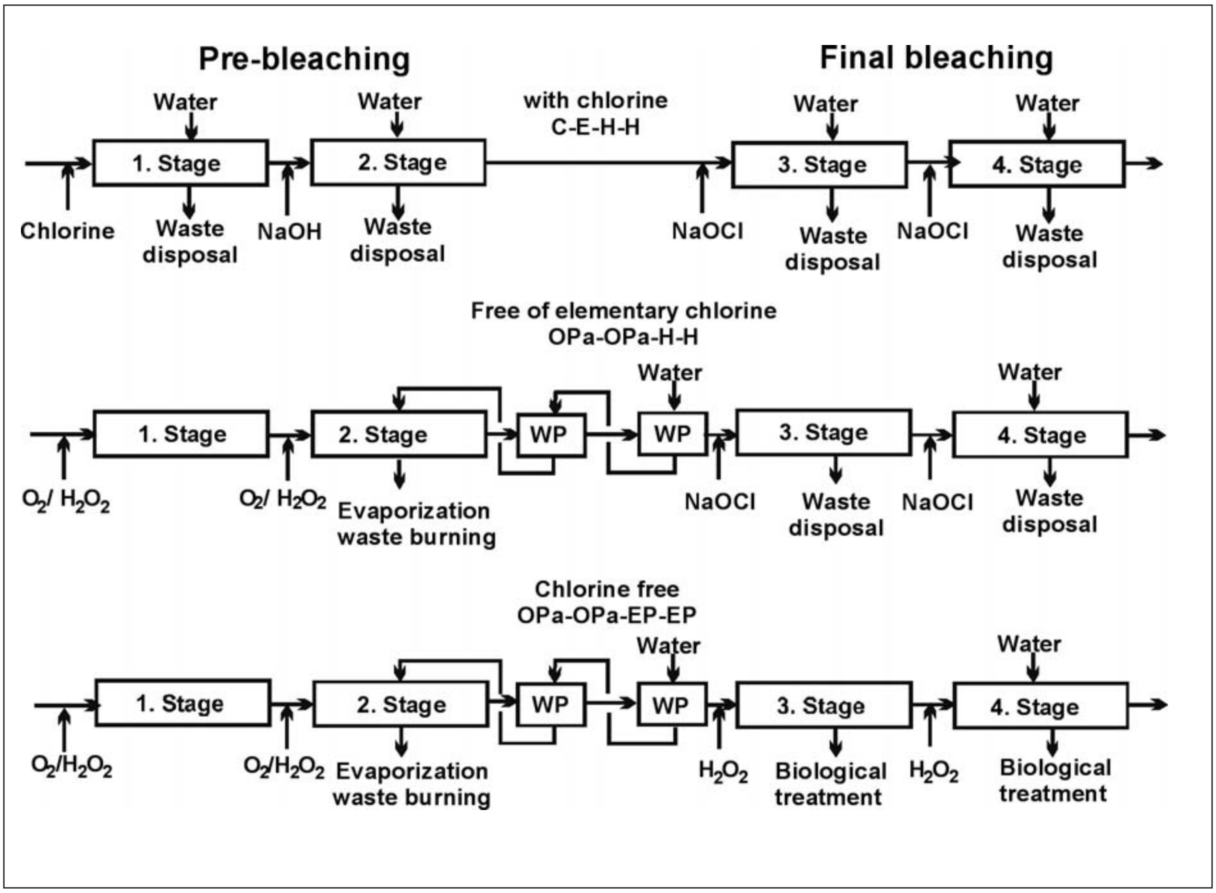
Pulp and Paper Production

Paper is made from pulp and water. Pulp is mainly made from wood or recycled paper.
Wood consists of cellulose, hemi-cellulose and lignin. Cellulose and hemi-cellulose form the fibers which are glued together by the lignin. Two different commercial-scale pulping procedures are applied: digestion with either Na_2S and NaOH (sulfate procedure) or with $Mg(HSO_3)_2$ (sulfite procedure). [7,8]
Exceptionally the organosolv procedure is applied in which the digestion happens by acetic acid.

Paper becomes white only by bleaching, otherwise it is more or less a brown color from the lignin. Bleaching of cellulose acts to destroy the remaining lignin. In Europe bleaching is made environmental acceptable by oxygen or hydrogen-peroxide and ozone (TCF = Total Chlorine Free).

A Scandinavian paper-mill has qualified Alloy 31 for these also very corrosive procedures. [1]
Outside Europe however, even now bleaching with elemental chlorine or chlorine-dioxide (ECF = Elemental Chlorine Free) is applied.
Elemental chlorine causes the most corrosive conditions and the highest environmental load. Chlorine dioxide is somewhat environmental friendly.
Particularly in Canada, USA and Indonesia, the large cellulose productions still use the chlorine route.

Commercial grades of stainless steels fail in these very sour solutions at 70 °C due to pitting-, crevice- and stress-corrosion cracking.
Alloy 31 has proven to be superior to other Molybdenum containing stainless steels like Alloy 926 and 254 SMO.



Development of bleaching technologies

Viscose Fibers, Rayon

Viscose fibers are basically cellulose produced industrially by the viscose-process.

The cellulose from the viscose production contains less remaining parts of lignin and hemi-cellulose and therefore has a higher reactivity with caustic (NaOH) and carbon bi-sulfite (CS_2).

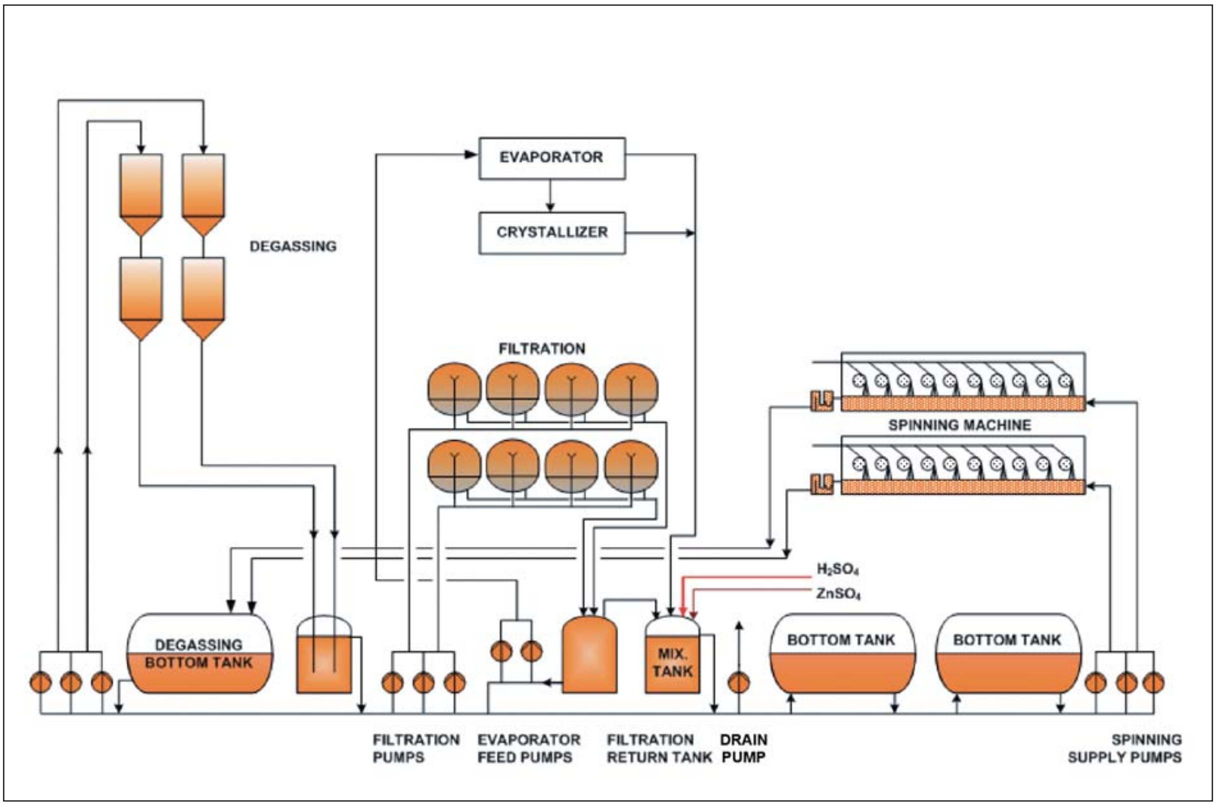
The reaction with these two chemicals produces a “viscous” pulp which is ejected through fine nozzles into an spinning bath composed from diluted sulfuric acid (H_2SO_4) with sodium sulfate (Na_2SO_4) and zinc sulfate ($ZnSO_4$).

The resulting products, apart from the viscose fibers, are again caustic and carbon bi-sulfite but also sodium sulfate and sulfur hydride (H_2S).

The viscose fibers (Rayon) are subsequently washed and bleached.

The spinning bath for the production of the fibers is very corrosive and therefore very demanding on the materials used.

Because its high resistance against diluted sulfuric acid, Alloy 31 is an ideal candidate for applications in the pulp and paper industry.



Flow diagram of a spinning bath recovery plant (by Lenzing)

Production of Salt in Salt-Mines

Industrially mined rock salt has to be purified prior to its use, particularly from heavy metal ions.
In general the purification operates by a chemical precipitation, a so called hydroxide precipitation in which caustic soda is added continuously to the brine.
Alloy 31 has a Pitting Resistance Equivalent of 53 (PRE = % CR + 3.3 % Mo + 30% N) due to its high content of chromium and molybdenum and forms the top of the austenitic special stainless steels.
It performs perfectly in the production of highly purified NaCl.

This high alloyed special stainless steel is resistant against all kinds of corrosion, including pitting-, crevice- and stress-corrosion cracking.

Huge amounts of plate out of Alloy 31 have been used for tanks, mixer-preheater, storage tanks and pipes in a seven stage re-crystallizing plant of a German salt mine.
The piping system naturally also needs pumps and valves for which now the cast version Märker Alloy 31 can be used.

Pickling Plants

Pickling tanks in the metal transforming industry are increasingly made from Alloy 31.
The pickling liquids, composed from 5 % nitric acid, 5 % fluoric acid and 5 % sulfuric acid operate at temperatures of 60 to 65 °C.
Casing out of Märker Alloy 31 are now also available for pumps and valves in such plants.

In continuously operating pickling plants for strip, deflecting bars, so far made from aluminium bronze could now be replaced by centrifugally cast tubes out of Märker Alloy 31. [1]

Color Anodization

This surface treatment of e.g. aluminium is made in baths, composed from mixtures of phosphoric and sulfuric acids.
For the tank of such a bath with 70 % H_3PO_4 and 9% H_2SO_4 at 110 °C, Alloy 31 was used.
All connected pumps and valves therefore can be made out of the corresponding cast material Märker Alloy 31 [1]

Literature Sources used

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2. Materials and Corrosion 55 (2004) 671-675: The influence of oxidants on the corrosion resistance of Nicrofer 3127hMo in low and medium concentrated sulfuric acid.

3. Corrosion 95, Paper No. 279, Alloy 31, a new 6 Moly Stainless Steel with improved corrosion Resistance in Seawater.

4. VDM Report No. 20, 1992, Corrosion resistant materials for use in desalination plants In particular for reverse Osmosis (RO) plants.

5. U. Heubner et. al. : Nickel Base Alloys and high alloyed stainless steels Expert Verlag Band 53, ISBN 3-3169-1011-4

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