

Making the most out of your metals

Philipp Verbnik and Philipp Hübner, VDM Metals Group, Germany, reveal how the advantages of nickel alloys and the cost benefits of stainless steels can be combined to better mitigate corrosion in phosphoric acid production.

Stainless steels and nickel alloys play a crucial role in fertilizer production, particularly in the wet process for producing phosphoric acid, which is responsible for 98% of global production. Novel alloys combine the advantages of corrosion-resistant nickel-based alloys with the cost benefits of classic stainless steels.

The wet process for the production of phosphoric acid is a chemical process in which phosphate rock is treated with sulfuric acid to produce phosphoric acid and calcium sulfate (gypsum). The process includes reaction, filtration, and concentration steps, whereby the final product, the raw phosphoric acid, is often used as a starting material for a wide variety of phosphate fertilizers or for further processing.

The conditions in the wet process for the production of phosphoric acid are extremely corrosive, with oxidising and reducing acidic environments. In addition, many processes take place at elevated temperatures. The raw materials contain halide impurities (chloride and fluoride), which can lead to localised corrosion and pitting, even at low concentrations of only a few hundred ppm.

Alloy selection

With many differences in feedstock and impurities, as well as process differences and various methods of fluorine controlling, metallic constituents, and precipitates, the right material selection for components such as tubes, valves, and vessels plays a crucial role in terms of plant reliability and safety.

AISI 316 L stainless steel can be considered as workhorse material in phosphoric acid production, mostly for applications below 65 - 82 °C (150 - 180 °F). It is routinely used to store and transport phosphoric acid, or in the first evaporator stage, for example. When it comes to more severe corrosive conditions, such as in agitators, mixers, or pumps, AISI 316 L components typically corrode after only a few months of operation. In particular, chloride contamination requires more highly alloyed stainless and nickel-rich alloys for many applications.

When classic stainless steels reach their limits, higher alloyed 6-Mo stainless steels or nickel-based alloys are essential, as they offer higher corrosion resistance to these aggressive conditions. They also offer thermal stability and resistance to mechanical stress, which ensures a long service life and reliability of the systems; and minimises unplanned process interruptions.

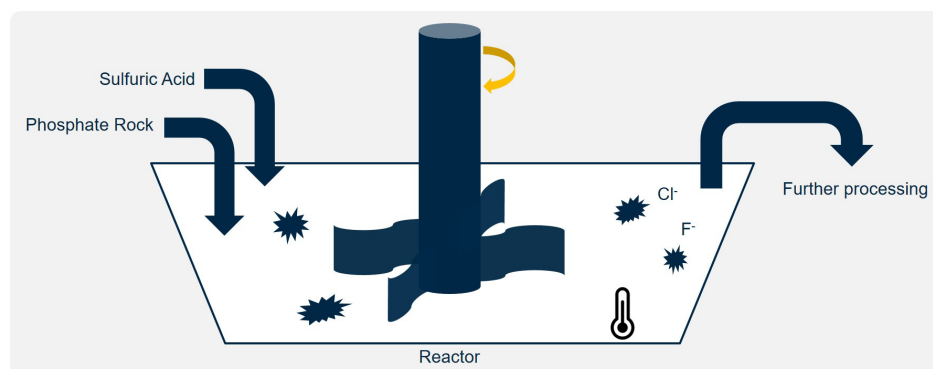


Figure 1. Schematic drawing of the initial mixing step of phosphate rock and sulfuric acid at elevated temperatures.

Table 1. Typical chemical analysis of special stainless steels and nickel alloys used in phosphoric acid production

Alloy	UNS number	Ni	Cr	Mo	Fe	Others
AISI 316 L	S31603	12%	17.5%	2.5%	67%	Mn, N
Alloy 926	N08926	25%	20%	6.5%	48%	Cu, N
Alloy 28	N08028	31%	27%	3.5%	38%	Cu, N
Alloy 31®	N08031	31%	27%	6.5%	35%	Cu, N
Alloy 31 Plus®	N08034	34%	26.5%	6.5%	32%	Cu, N
Alloy 59	N06059	59%	23%	16%	1.3%	Cu, Mn, Al, Co

However, the selection of materials used in the components is based on both technical and cost considerations. The costs in turn depend on the chemical composition of the individual alloy.

Stainless steels, such as AISI 316 L, are based on iron and contain a comparatively low proportion of higher-grade alloying elements such as nickel and chromium. Classic 6-Mo stainless steels are high-alloyed, austenitic stainless steels that contain around 6% molybdenum and are known for their improved corrosion resistance. Their elevated contents of chromium, nickel, and molybdenum, give them excellent resistance to pitting, crevice corrosion, and general corrosion, especially in aggressive chloride-containing environments. The so-called pitting resistance equivalent number (PREN), which indicates resistance to pitting, is particularly high for these materials, making them ideal for applications in environments with high chloride content. A higher PREN value indicates better resistance to pitting corrosion.

The PREN can be calculated using the following formula:

$$\text{PREN} = \% \text{Cr} + 3.3 \times \% \text{Mo} + 30 \times \% \text{N}$$

Abbreviations: Cr = chromium, Mo = molybdenum, N = nitrogen

So-called C-type nickel-based alloys such as Alloy 59 or Alloy 2120 MoN contain nickel as the main alloying element; they generally have excellent corrosion resistance against oxidising and reducing media. They also have higher PREN values owed to the high amounts of beneficial

elements in terms of corrosion resistance such as chromium, molybdenum, and in some cases, even nitrogen.

However, there is a niche between 6-Mo stainless steels and C-type nickel-based alloys. The materials to be found here combine the advantages of corrosion-resistant nickel alloys with the cost benefits of classic stainless steels.

VDM Alloy 31 Plus® is a recent successor to the 6-Mo stainless steels and was developed to meet the challenges of the chemical process industry (CPI), particularly with regard to the manufacture of primary products and fertilizers. The material has improved thermal stability and stabilises the austenitic microstructure. It forms a Cr₂O₃ passive layer and increases resistance in reducing media and against localised corrosion.

Compared to its predecessor VDM Alloy 31®, VDM Alloy 31 Plus has a 3% higher nickel content by weight (34% by weight in total).

Table 2. Pitting resistance equivalent number (PREN) of different nickel alloys and special stainless steels

Alloy	UNS number	PREN
AISI 316 L	S31603	27
Alloy 28	N08926	39
Alloy 926	N08028	43
Alloy 31	N08031	54
Alloy 31 Plus	N08034	54
Alloy 59	N06059	76
Alloy 2120	N06058	86



Figure 2. Crystalliser manufactured using VDM Alloy 31 Plus. The manufacturing process took place at ZIEMEX.

This results in a higher capacity for alloying elements, such as chromium and molybdenum, and makes the material more thermally stable and easier to process. The elements of the alloy interact perfectly:

- Nickel enhances the thermal stability and stabilises the austenitic microstructure.
- Chromium enables the formation of a Cr_2O_3 passive layer.
- Molybdenum increases resistance in reducing media and to localised corrosion.

One aim when developing the material was to make it easier to process. The solution temperature of the sigma-phase was lowered to 1140 - 1160 °C for VDM Alloy 31 Plus, compared to 1160 - 1180 °C for VDM Alloy 31.

The critical pitting corrosion temperature (CPT) for both alloys in the 'Green Death' solution is 60 °C, and the PREN value is approximately 54.

The new alloy has a homogeneous austenitic microstructure. The mechanical properties include a minimum tensile strength (R_m) of 650 MPa, a minimum yield strength ($R_{p0.2}$) of 280 MPa, and a minimum elongation at break (A) of 40 % (ASTM B 625-21).

The corrosion resistance of the alloy is comparable to that of Alloy 31 and much improved on Alloy 926 in many test media, including sulfuric acid, nitric acid (Huey test), hydrochloric acid, and phosphoric acid with added chloride.

Also, in terms of localised corrosion, the new alloy has proven to be at least equally resistant as Alloy 625 when tested according to ASTM G48 Method C and D, while also being a more economical choice. Both alloys show a critical pitting temperature of > 85 °C, which marks the upper limit of the testing solution. In terms of critical crevice temperature, Alloy 31 Plus exhibited signs of crevice corrosion at 60 °C during testing. According to the literature, this is significantly higher than for Alloy 625.

Applications and production

The material is particularly suitable for applications in wet phosphoric acid production, which are characterised by highly corrosive conditions, halide impurities (Cl-, F-), and elevated temperatures.

VDM Alloy 31 Plus is used for seamless or longitudinally welded tubes and other semi-finished products in the chemical process industry. These tubes can be used for heat exchangers, condensers, piping, injection systems, and instrumentation, among other things.

The alloy offers a cost-effective alternative to nickel-based alloys and has excellent corrosion resistance in halide media. It is also weldable and approved for various welding applications.

Application examples include various components for the phosphoric acid and salt industries, such as agitators and crystallisers. The material can also be used as a hot-rolled cladding component.

Conclusion

The conditions in the wet process for the production of phosphoric acid are extremely corrosive, with oxidising and reducing acidic environments. In addition, many processes take place at elevated temperatures. When classic stainless steels reach their limits, higher alloyed 6-Mo stainless steels or nickel-based alloys are needed to handle higher loads of chloride contamination, for example.

High-alloyed special stainless steels that fill the gap between the two material groups such as VDM Alloy 31 and VDM Alloy 31 Plus offer good corrosion resistance in phosphoric acid and sulfuric acid, good ductility and processing characteristics (annealing, welding etc.), combined with cost efficiency. Standard applications include service media with sulfuric acid, phosphoric acid production, and seawater applications. **WF**

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