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# Material selection and recent case histories with nickel alloys

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## Abstract

Materials of construction for the chemical process industry (CPI) must resist uniform corrosion and have sufficient resistance to localized corrosion such as pitting, crevice corrosion and stress corrosion cracking. Corrosion data from the literature and corrosion tables are not sufficient for material selection for chemical plants. Simulated corrosion testing in the laboratory, testing in pilot or reference plant is necessary for validation. Which standard tests are helpful and how to use and interpret their results is another aspect to consider.

In addition, further aspects like mechanical stability, fabricability, safety, testing, cost efficiency, etc. have to be considered in the process of material selection so that at the end the material properties match the requested material requirements in the best way.

Over the past 50 years, improvements in alloy metallurgy, melting technology, and thermo-mechanical processing, along with a better fundamental understanding of the role of various alloying elements have led to many different nickel alloys which are available for use in severe corrosive environments of the chemical process industry. On the other hand new chemical processes, more stringent environmental regulations, higher temperatures and pressures, more corrosive catalysts, multipurpose use and flexibility to handle different feed stock and upset conditions pose new challenges in the material selection process requiring the right approach.

The aim of this paper is to review the main aspects of the material selection for the process industry and present different examples to illustrate the material selection process.

Keywords: nickel alloys, material selection, material properties, corrosion, corrosion tests

## Introduction

Material selection consists basically of selecting the materials with properties that best fit the profile requested for a particular application or process.

The criteria for material selection in the process industry have to be defined according to the chemical substances to be handled and treated. This can be very ambitious and is - in most cases - not limited to aspects of corrosion resistance under specific service conditions and mechanical properties. Safety in the working place can be a dominant aspect. Therefore, safety is mentioned in central position in **Fig. 1.** Economy can include quite a bundle of cost factors such as availability of different product forms, availability of fabricators, necessity of heat treatments, weldability and manifold additional points. The process and product requirements may refer to different aspects like catalytical reactions and consequent interaction with the catalysts, limitation of metals content e.g. in final product, discoloration by corrosion products and others.

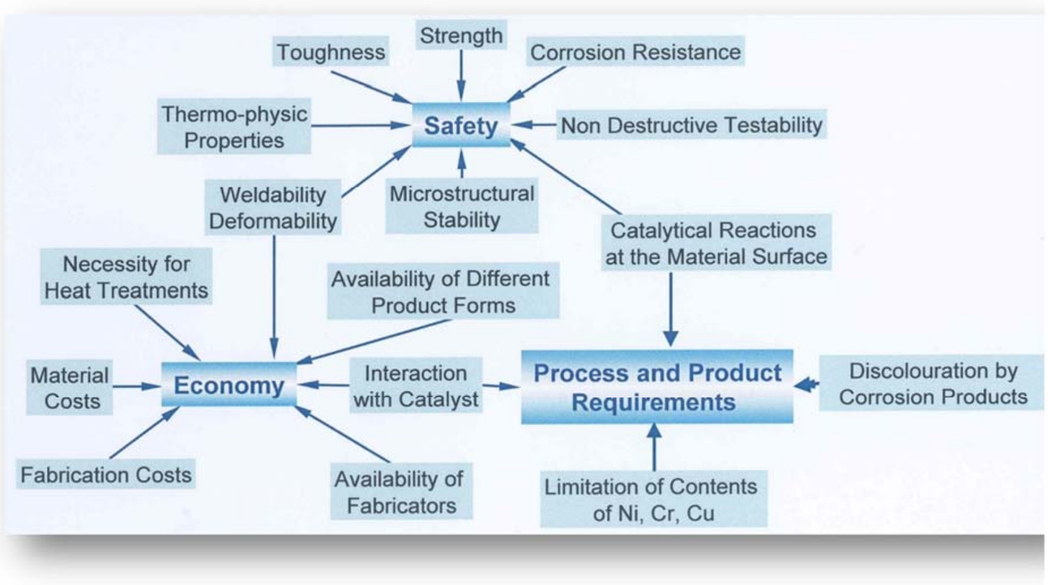


**Fig. 1:** Criteria for material selection in the process industry (from J. Korkhaus, ACHEMA 2006 [1]).

Both technical and economic aspects deserve special attention in material selection. To address the corrosion resistance aspect the service conditions must be well defined in regard to raw materials, intermediate substances, final products, contaminants, flow conditions, temperature and pressure. The mechanical properties, such as strength and ductility, must fit into the required profile of properties and are of immediate importance for the possibility of shaping of the materials. The material behaviour during forming, hot and cold working, machining, welding, heat treatment, etc. must also be considered. An important aspect is to ensure that the good corrosion and mechanical properties of the materials prevail after fabrication. Finally, there is the complex of cost efficiency which includes all investment costs (material, manufacturing and installation) as much as the life-cycle costs (maintenance and lost revenue during shutdowns)**.**

Sometimes overlooked is the reliability of available information on the corrosion resistance of the materials which one would like to make use of. The reliability of information is best with references from identical or similar plants and from simulated corrosion testing. Standard corrosion tests reflect the corrosion behaviour in these tests only, not in real plants. Corrosion data from literature and corrosion tables are not sufficient for material selection for chemical plants. They may provide a first direction of which materials or material groups could be of interest and should be further evaluated.

Important requirements for corrosion resistance in the chemical process industry are:

- Corrosion rate below a maximum allowable value, in many cases such as < 0.1 mm/a
- No localized corrosion such as pitting, crevice and stress corrosion cracking allowed
- Particular specifications e.g. metal ion concentration below a maximum allowable value in the production of high purity chemicals.

Nickel and nickel alloys have very useful resistance to a wide variety of aqueous corrosive environments typically encountered in the chemical process industry and energy technology. Nickel by itself is a versatile corrosion resistant metal. More importantly, its metallurgical compatibility over a considerable composition range with a number of other metals as alloying elements has become the basis for many binary, ternary, and other complex nickel alloy systems, having very unique and specific corrosion resistant behavior for handling corrosive environments. Thus, although unalloyed metallic nickel has its merits as material of construction in the chemical process industry, it is mainly used as base-material of nickel alloys that can behave very different when compared to nickel.

A survey on the role of the alloying elements is presented in **Table 1.** As the survey suggests, after nickel as base material the main alloying element is chromium, which is necessary for a stable passive surface layer, upon which the corrosion resistance depends. After chromium, molybdenum is the most important alloying element by increasing the resistance to general corrosive attack in reducing media. Together with chromium it is of paramount importance for pitting and crevice corrosion resistance. Tungsten and nitrogen also contribute to improve the resistance to localized corrosion, however to a less extend.

However, such a survey is good for first considerations only, since the corrosive behaviour of the materials or alloys depends on the chemical composition of the alloy but also on the alloy's microstructural features, on the chemical nature of the environment, and the nature of the alloy / environment interface. Corrosion is always a result of an interaction of the material and the surrounding corrosive medium including the service conditions as temperature, pressure and flow velocity. All this will lead to a very variable picture. Comprehensive reports on nickel alloys, its development, aqueous corrosion behaviour and applications can be found in [2, 3, 4, 5].

**Table 1**: The role of the alloying elements in nickel alloys

| Element | Main Features | Wet Corrosion Resistance |
|---|---|---|
| Ni | metallurgical compatibility, thermal stability, weldability | acids, mild reducing, alkalis, stress corrosion cracking |
| Cr | forms protective oxide | oxidizing media, uniform and localized corrosion resistance (pitting and crevice) |
| Mo | stabilizes the effect of chromium | reducing media, uniform and localized corrosion resistance (pitting and crevice) together with chromium |
| Fe | reduces the cost | not beneficial |
| W | similar to Mo, but less effective | beneficial for local corrosion resistance, detrimental to thermal stability |
| N | austenite stabilizer, strength | effective for local corrosion resistance (pitting) |
| Cu | raises strength | can be helpful in reducing media: $H_2SO_4$ alkalis, brines, seawater (Ni-Cu alloys) |
| Nb, Ti | tie up carbon: carbide former, and raise strength by Al, Ti, Nb - precipitation hardening | can be useful to fight intergranular corrosion |

## Selected nickel alloys for the chemical process industry

**Unalloyed nickel** is the starting point for a multitude of metallic materials being based on nickel as one of their main alloy constituents. Unalloyed nickel which is traditionally referred to as “pure nickel” is an important material of construction for the chemical process industry, too.

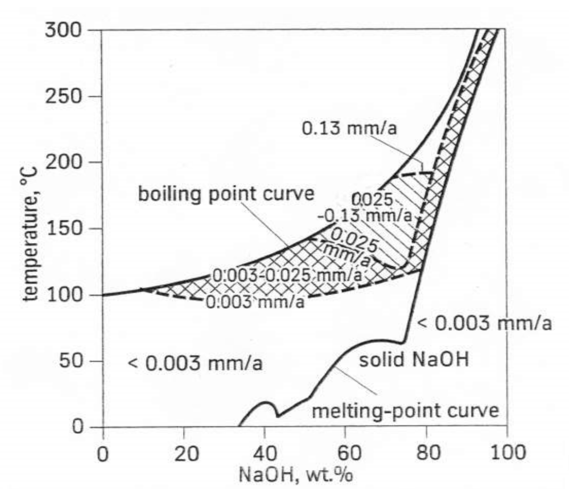


**Fig. 2:** Corrosion resistance of unalloyed nickel (UNS N02200) in sodium hydroxide as a function of concentration and temperature (from W. Z. Friend, 1980 [6])

As shown in **Fig. 2** nickel is outstandingly resistant to alkalis such as sodium hydroxide, even at high concentrations and temperatures. For this reason it is used in chemical process equipment for the production and processing of caustic soda. An example is shown in **Fig. 3**.

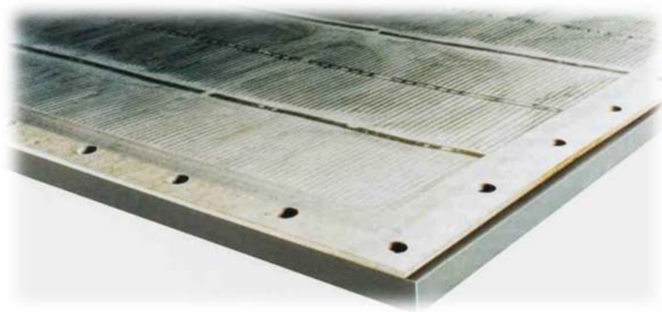

**Fig. 3:** Nickel cathode from the membrane cell process

**Nickel-chromium alloys**

Nickel and nickel alloys are alloyed with chromium to improve their resistance to strongly oxidizing media. Substances of this kind include nitric acid, chromic acid, phosphoric acid, highly concentrated sulfuric acid and some acidic solutions containing oxidizing salts, with the exception of chlorides. In this case, corrosion resistance increases approximately in proportion to the chromium content, provided that it is more than approx. 12 wt.%. In the case of aerated acidic solutions, especially at elevated temperatures, chromium contents of more than 18 % are preferable. Since nickel-chromium alloys require the presence of further alloying elements in order for them to be universally suitable for wet-corrosion service, they are few in number and their use tends to be limited to special cases. The most important nickel chromium alloys for wet corrosive engineering applications are alloy UNS N06600 and alloy UNS N06690. Owing to their high nickel content, UNS N06600 and UNS N06690 can be considered for corrosive attack by hot alkaline solutions if they contain oxidants; examples are chlorates from diaphragm cells or sulfur compounds. The high chromium content makes it particularly suitable for the handling and storage of strongly oxidizing media, as in reprocessing of nuclear fuels. The material exhibits outstanding resistance to intercrystalline corrosion and to attack by fluoride-contaminated hot nitric acid, as well as to caustic cracking, for example in oxygen-containing sodium hydroxide solutions. Alloy UNS N06690 is also widely used for steam generator equipment of nuclear pressurized water reactors. It is required in this application due to its resistance to stress corrosion cracking.

## Nickel-molybdenum alloys

Another field of application of nickel is in form of nickel-molybdenum alloys, e.g. alloy UNS N10665, for special use under highly reducing conditions, such as in boiling hydrochloric acid or in the acetic acid production. As comes out from **Fig. 4** alloying nickel and nickel alloys with molybdenum improves their corrosion resistance in reducing media and a molybdenum content of about 28 % provides an optimum corrosion resistance. In addition, a controlled composition with 1.7 % Fe and 0.7 % Cr is essential to avoid cracking during fabrication and stress corrosion cracking in service. The presence of oxidants has to be avoided since it strongly increases the corrosion rate.

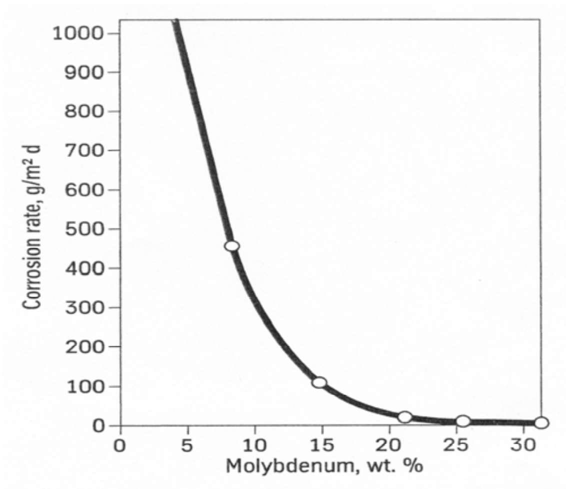


**Fig. 4:** Corrosion rate of binary nickel-molybdenum alloys in boiling 10 % hydrochloric acid as function of the molybdenum content (from K. E. Volk, 1970 [7])

In the Monsanto process acetic acid is produced by a catalytic reaction of methanol and carbon monoxide at 180 - 200 °C and a pressure of about 15 bar. Rhodium activated with iodine is used as catalyst. Within the reactor, flash tank, scrubber and columns the conditions are highly reducing due to the presence of hydroiodic acid and acetic acid. The nickel-molybdenum alloy UNS N10665 is frequently used under these conditions and **Fig. 5** shows a particular example.

**Fig. 5:** Equipment for acetic acid production as example of application of the nickel-molybdenum alloy UNS N010665.

## Nickel-chromium-molybdenum alloys

The nickel-chromium-molybdenum alloys comprise a range of alloys with differing corrosion properties, but have in common that they are highly corrosion resistant both in reducing as well as in oxidizing media due to the simultaneous alloying with chromium and molybdenum. Some important ones are listed in **Table 2**.

**Table 2:** Typical chemical alloying constituents of nickel-chromium-molybdenum alloys *) PREN = %Cr + 3.3 %Mo + 30 %N

| UNS | Composition, wt.-% | | | | | | PREN* |
|---|---|---|---|---|---|---|---|
| | Ni | Cr | Mo | Fe | W | N | |
| N10276 | 57 | 16 | 16 | 6 | 4 | | 69 |
| N06455 | 66 | 16 | 16 | 1 | | | 69 |
| N06022 | 56 | 22 | 13 | 4 | 3 | | 65 |
| N06059 | 59 | 23 | 16 | 1 | | | 76 |
| N06058 | 59 | 21 | 19 | <1 | | 0.075 | 86 |

**Table 2** shows the principal alloying constituents of the nickel-chromium-molybdenum alloys only. Minor constituents are not mentioned though they may be of some importance as e.g. carbon and silicon. The first of these alloys to be invented in the 1930s was the forerunner of alloy UNS N10276, named alloy C at this time. However, when it became clear that it was necessary to reduce both the carbon and the silicon content of such materials to very low levels, the UNS N10276 alloy type emerged in the 1950s. The designation "C-type alloys" remained as a popular description for the alloys mentioned in **Table 2** and related variants. It is worth mentioning that a prerequisite for successful manufacturing was the introduction of today's metallurgical processes like AOD and VOD which allow the manufacturing of high-chromium/extra-low carbon grades on a large scale.

Alloy UNS N06455 is a variant of alloy UNS N10276 which differs from the later material in the absence of tungsten as an alloying element and greatly reduced iron content. Consequently the alloy is less resistant in predominantly reducing media, but is much less prone to precipitation and much easier to work, with the result that on its commercial launch in the 1970s, it rapidly gained acceptance in the chemical industry, particularly in Europe. With alloy UNS N06022, a nickel-chromium-molybdenum alloy was brought onto the market in the mid-1980s which owing to the increased chromium content has better corrosion resistance than the alloys UNS N06455 and UNS N10276 in oxidizing media. However, owing to the reduced molybdenum content of only 13%, the effect of which can only be partly compensated for by the tungsten addition, it is inferior to alloy UNS N10276 in strongly reducing media and in conditions of extreme crevice corrosion attack.

The most recent members of this alloy group are alloy UNS N06059 and alloy UNS N06058. Alloy UNS N06059 has found a large number of applications rather immediately after its introduction to the market in many areas of chemical process technology, in multi-purpose equipment e.g. in the production of fine and specialty chemicals, in marine technology, as well as in environmental engineering. It has a very universal corrosion resistance arising from its balanced composition: high contents of nickel (59%), chromium (23%) and molybdenum (16%) without addition of other elements like tungsten or copper and very low iron level.

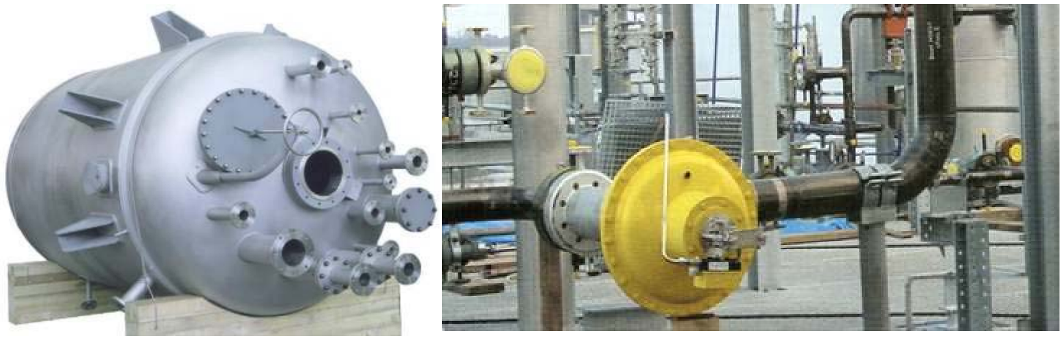

**Fig. 6:** Application of alloy UNS N06059 as material of construction for: (left side) reactor for the production of catalysts and (right side) piping for a HP-technology melamine plant.

**Fig. 6** shows examples of the application of this nickel-chromium-molybdenum alloy in the chemical process industry. In addition, these alloys have experienced a true story of success in sulphuric acid applications, namely in flue gas desulphurization by the wet route.

The newest member of the alloy C family group is alloy UNS N06058. As shown in **Table 2**, this alloy excels by a very high molybdenum content close to 19 wt.-%. In addition, it is the first nickel-chromium-molybdenum alloy to be alloyed with nitrogen. The high chromium and molybdenum contents together with the alloying with nitrogen result in a pitting resistance equivalent number (PREN) of about 86, surpassing all nickel-chromium-molybdenum alloys in use so far. Preferred applications are in flue gas desulphurization, sulphuric acid, hydrochloric acid, acid mixtures even when contaminated with chlorides and geothermal technologies. A first report on the main properties of alloy UNS N06058 has been given in 2013 [8]. Alloy UNS N06058 possesses good fabricability including weldability. It can be used as an over-alloyed filler metal for welding of the other Ni-Cr-Mo alloys of the C-type family.

As a result of the specific combination of its alloying constituents the new alloy is featuring an excellent balanced corrosion resistance in oxidizing as well as in reducing environments. **Fig. 7** and **Fig. 8** demonstrate that the new alloy is less dependent on variations in the oxidizing conditions and on the presence of chlorides than the traditional alloy UNS N10276. As shown in **Fig. 7** additions of $Fe^{3+}$ up to 3 x $10^{-3}$ mol/l to a 50 % acetic acid + 40 % formic acid + 5 % sulphuric acid solution at 95 °C have a smaller impact on the corrosion rate of alloy UNS N06058, but result in a significant increase of the corrosion rate of alloy UNS N10267. In these tests the influence of aeration of the 50 % acetic acid + 40 % formic acid + 5 % sulphuric acid solution at 95 °C was negligible whereas a de-aeration by purging with nitrogen caused a distinct overall reduction of the corrosion rates. In general the new material is characterised by superior resistance to general corrosion in acids and acidic mixtures even when contaminated with chlorides as well as to localised corrosion in regard to all other C-type alloys.

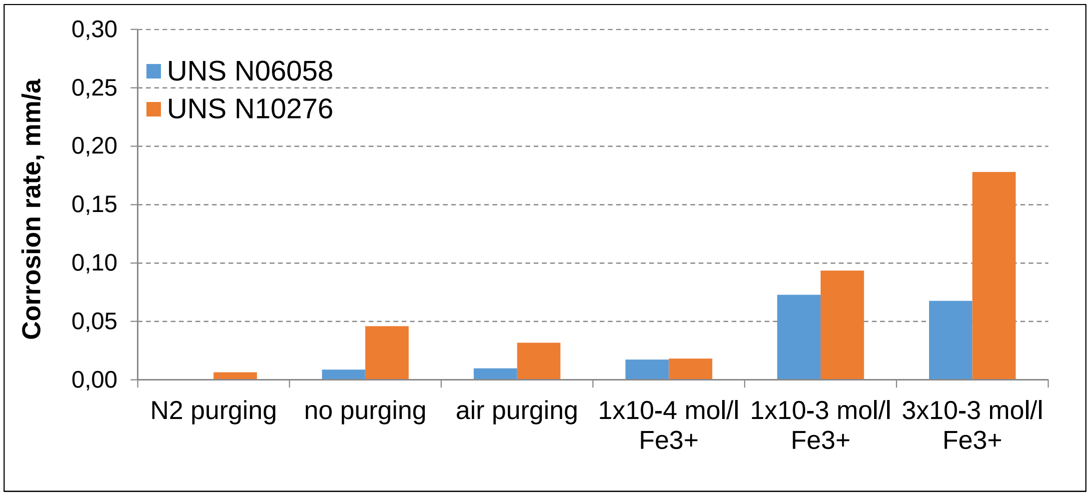


**Fig. 7:** Corrosion rate (mm/a) of alloy UNS N06058 test samples in 50 % acetic acid + 40 % formic acid +5 % sulphuric acid at 95 °C under different oxidizing conditions in comparison to alloy UNS N10276. Testing period for immersion 24 hrs.

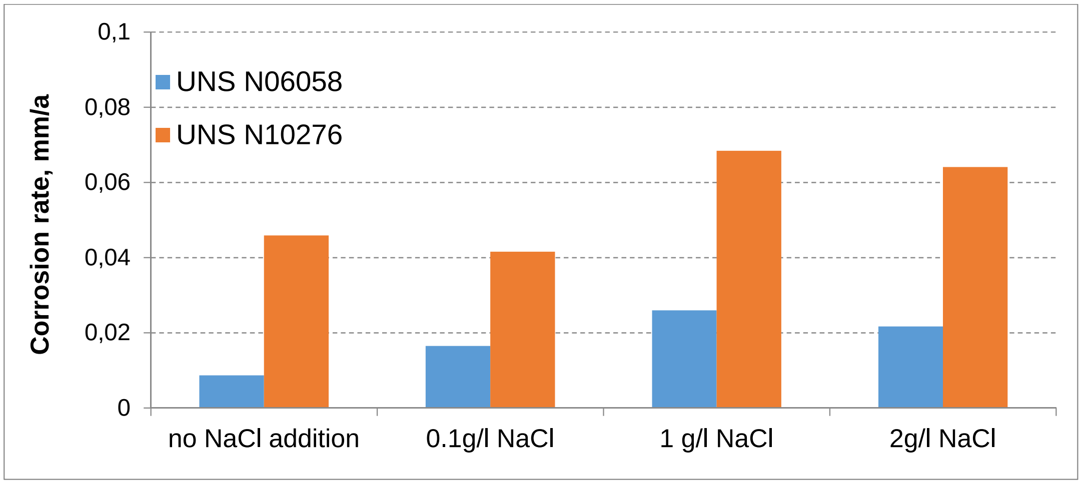


**Fig. 8:** Corrosion rate (mm/a) of alloy UNS N06058 test samples in 50 % acetic acid + 40 % formic acid + 5 % sulphuric acid at 95 % without and with different additions of chlorides in form of NaCl in comparison to alloy UNS N10276. Testing period for immersion 24 hrs.

**Fig. 8** shows additions of sodium chloride up to 2 g/l to the 50 % acetic acid + 40 % formic acid + 5 % sulphuric acid solution at 95 °C to cause an increase of the corrosion rate up to 0.07 mm/a in case of alloy UNS N10276 whereas the corrosion rate of the new alloy UNS N06058 is still below 0.05 mm/a. More details on these investigations are given in [9].

**Fig. 9** shows alloy UNS N06058 in use as material of construction for interesting areas of application like flue gas desulfurization (FGD) and severely corrosive chemical processes.

**Fig. 9**: Application of alloy UNS N06058 as material of construction for: (left side) heat recovery systems for indirect heat transfer in a FGD plant and (right side) plate heat exchangers for hydrochloric acid in a chemical plant (equipment manufactured by ZIEMEX).

### Nickel-chromium-iron-molybdenum-copper alloys

Whereas alloys UNS N06059 and UNS N06058 have shown their versatility to resist changing wet corrosive conditions, there may arise conditions where alloys which display a composition that is closer to special stainless steels are advantageous. That is why the development of alloy UNS N08031 has become a success. It is a 31Ni-27Cr-6.5Mo-1.2Cu-0.2N alloy which is combining the advantages of high-chromium alloyed materials, that is the high resistance to corrosive attack by oxidizing media, with a molybdenum content of more than 6 %. The nickel content is comparatively low. This way it was possible to create a highly corrosion resistant material in using only small amounts of expensive alloying elements. It is readily weldable without the risk of intercrystalline corrosion. Alloy UNS N08031 has given outstanding performance under particular aggressive conditions of phosphoric acid production and chemical processes involving sulfuric acid. **Fig. 10** shows its application for chemicals transportation and in flue gas desulphurization units.

**Fig. 10:** Application of alloy UNS N08031 as material of construction for: (left side) road truck for the transport of waste acids and solvents, mainly waste sulphuric acid (Lobbe, Germany) and (right side) quencher spray system after 10 years in service in a flue gas scrubber.

The successful and widespread use of alloy UNS N08031 resulted in the need to make it easier to handle since the original alloy is requiring a solution annealing treatment at about 1180 °C followed by fast cooling that is not easy to perform in every place of manufacturing. This requirement was met by a recent adaptation of alloy composition resulting in a new alloy UNS N08034. This alloy can be solution annealed at 1140 **-** 1170 °C that is much more convenient in manufacturing. The nominal chemical composition of alloy UNS N08034 is shown in **Table 3** in comparison with the precursor alloy UNS N08031. The alloy modification facilitates manufacturing of large components in particular in roll bond cladding as in shaping and heat treating of large dished vessel heads. Thus, alloy UNS N08034 can be technically hot roll bonded using conventional methods and equipment allowing a more economical use in chemical and environmental applications, e.g. for large vessels, tube sheets, etc. [10].

**Table 3:** Nominal composition of alloy UNS N08034 in comparison to alloy UNS N08031

| UNS | Ni | Cr | Fe | Mo | Mn | Cu | N |
|---|---|---|---|---|---|---|---|
| N08034 | 34 | 27 | Bal. | 6.5 | 2 | 1.2 | 0.2 |
| N08031 | 31 | 27 | Bal. | 6.5 | 1.5 | 1.2 | 0.2 |

The increased thermal stability of alloy UNS N08034 is shown **Fig. 11** in terms of the Charpy impact energy on ISO V-notch samples as function of the heat treatment at intermediate temperatures. As is evident from this diagram, alloy UNS N08034 allows much longer heat treatment times than alloy UNS N08031 before the Charpy impact data are lowered to a value of 50 Joule [4].

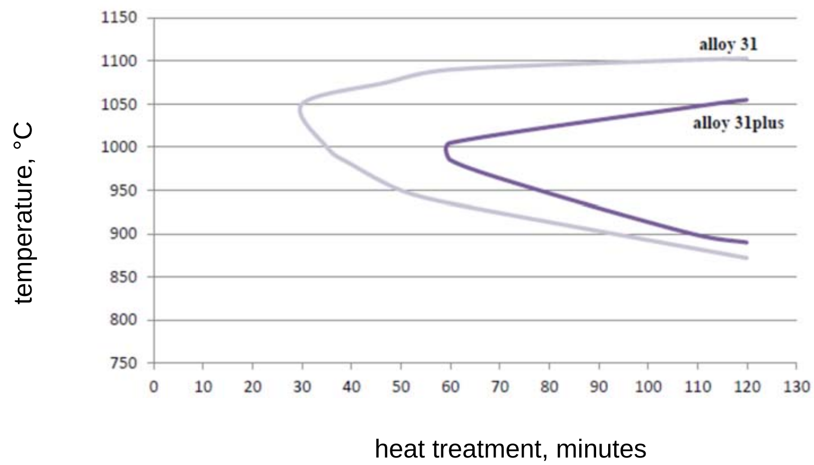


**Fig. 11:** Diagram representing the lines where the ISO V-notch impact strength decreases from initially more than 250J to a value of 50J as a function of the heat treatment temperature and time for alloy UNS N08034 and alloy UNS N08031.
Testing done at - 60 °C.

**Fig. 12** shows an example of application for the new alloy UNS N08034.

**Figure 12:** Example of application of alloy UNS N08034 for evaporators in the salt industry. Equipment manufactured by ZIEMEX.

## Role of alloying elements vs. corrosive conditions

In case of the application of nickel alloys in the chemical process industry the most favourable corrosion behaviour is obtained when the principal alloying constituents of the nickel materials fit to the corrosive conditions of the surrounding corrosive media. Examples are to be seen in **Fig. 13**. This diagram shows the corrosion rate of the alloy UNS N08031 (in the diagram designated Alloy 31), alloy UNS N06059 (in the diagram designated Alloy 59) and alloy UNS N10665 (in the diagram designated Alloy B-2) if immersed in a 50 % $CH_3COOH$ + 40 % HCOOH + 5 % $H_2SO_4$ + 5 % $H_2O$ solution under various oxidizing conditions. Obviously the alloy UNS N08031 needs oxidizing conditions in order to become corrosion resistant whereas alloy UNS N10665 develops its corrosion resistance when the conditions are suffiently reducing. Only alloy UNS N06059 displays a remarkable corrosion resistance as much under the reducing conditions as under the oxidizing conditions of this test.

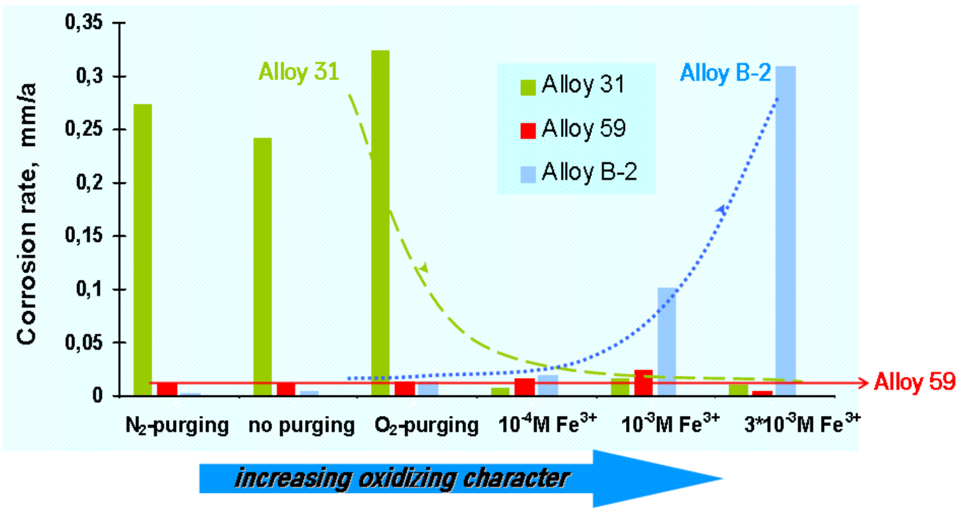


**Fig. 13:** Corrosion behaviour of a nickel-chromium-molybdenum alloy (alloy 59), a nickel-chromium-iron-molybdenum-copper alloy (alloy 31) and a nickel-molybdenum alloy (alloy B-2) in an aquous solution with increasing oxidizing character

## Conclusions

1) Nickel is an important material of construction in the chemical process industry.

2) Metallic unalloyed nickel as e.g. UNS N02200 is outstandingly resistant to alkalis.

3) Metallic nickel serves as carrier for alloying elements the most prominent of which are chromium and molybdenum. When added in a reasonable manner and in suitable amounts these alloying elements are rendering the nickel alloys corrosion resistant vs. reducing media (nickel-molybdenum alloys, e.g. UNS N10665), oxidizing media (nickel-chromium alloys) or both (nickel-chromium-molybdenum alloys, e.g. UNS N06059 and UNS N06058).

4) New nickel alloys aiming at improved or more versatile corrosion resistance like UNS N06058 or aiming at improved fabricability like UNS N08034 have been developed recently.

5) Knowledge of all corrosion relevant data, qualified fabrication with the right parameters and individual, project related materials selection in co-operation with the materials supplier are essential to get as economically as much as technically optimised solutions.

6) With the right high performance alloys as e.g. UNS N06058 and UNS N08034 nearly all corrosion problems can be solved.

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