HAYNES INTERNATIONAL, INC.

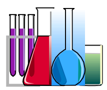
GUIDE TO CORROSION-RESISTANT NICKEL ALLOYS

1020 West Park Avenue
P.O. Box 9013
Kokomo, Indiana 46904-9013 USA

H-2114B

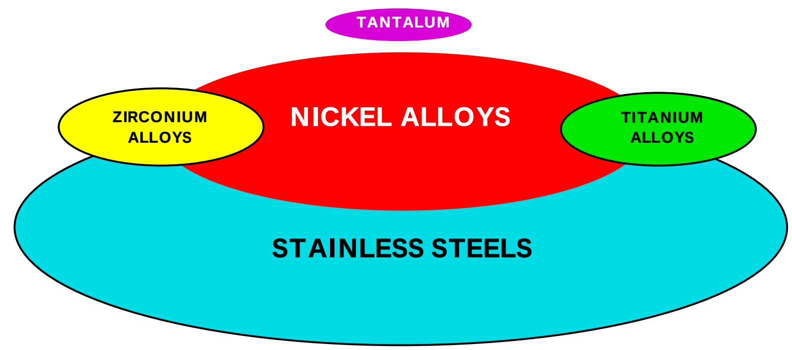
Table of Contents

CORROSION-RESISTANT NICKEL ALLOYS



- The purpose of this information is to introduce and categorize the corrosion-resistant nickel alloys. The attributes of each alloy will be discussed, in relation to other metallic materials, and a simplified selection guide provided.

CORROSION-RESISTANT ALLOYS HIERARCHY



- In a corrosion sense, the nickel alloys fall between the stainless steels and the exotic materials, such as tantalum. They are commonly used in aggressive inorganic acids and chloride-bearing environments, where many of the stainless steels are prone to stress-corrosion cracking, pitting, and crevice attack. Also, commercially pure nickel is the material of choice for service in sodium and potassium hydroxides (the so-called "caustic" chemicals).
- Within the same performance band as the corrosion-resistant nickel alloys lie the zirconium and titanium alloys. However, these so-called "reactive metal" alloys have more specific uses and are intolerant of certain ionic species, such as fluorides.

CORROSION-RESISTANT NICKEL ALLOYS
Main Attributes

- Most possess high resistance to chloride-induced stress corrosion cracking
- Many resist aggressive reducing acids, such as hydrochloric, hydrofluoric, and low-to-medium concentrations of sulfuric
- Some withstand both strong reducing acids and strong oxidizing acids
- Many exhibit high resistance to the alkalis
- Some have high resistance to localized attack (pitting and crevice corrosion)
- All are ductile and easily formed, and welded

- The main attributes of the nickel alloys are shown here. In essence, nickel alloys are available to resist most forms of corrosion. Some are extremely versatile and possess resistance to both oxidizing and reducing acids, alkalis, stress corrosion cracking, pitting, and crevice attack.
- With regard to the manufacture of industrial components, the nickel alloys are easy to work with, being very ductile, formable, and weldable.

CORROSION-RESISTANT NICKEL ALLOYS
Main Groups & Uses

- Ni — for ALKALIS
- Ni-Cu — for REDUCING ACIDS
- Ni-Mo — for REDUCING ACIDS
- Ni-Fe-Cr — for OXIDIZING ACIDS
- Ni-Cr-Si — for SUPER-OXID. ACIDS
- Ni-Cr-Mo — for ALKALIS & ALL ACIDS

- There are six, main nickel alloy groups, namely pure nickel (for caustic service), nickel-copper and nickel-molybdenum (for reducing acids), nickel-iron-chromium (for oxidizing acids), nickel-chromium-silicon (for the so-called super-oxidizing acids, such as concentrated sulfuric), and nickel-chromium-molybdenum (the group which contains the most versatile alloys).
- The terms reducing and oxidizing refer to the nature of the reaction at cathodic sites during corrosion. Reducing solutions, such as hydrochloric acid, generally induce hydrogen evolution at cathodic sites. Oxidizing solutions, such as nitric acid, induce cathodic reactions with higher potentials.

CORROSION-RESISTANT NICKEL ALLOYS
Main Alloying Elements

- CHROMIUM - enhances passivation
- COPPER - enhances nobility
- MOLYBDENUM & TUNGSTEN - enhance nobility and solid solution strength
- IRON - influences passivation
- SILICON - forms pseudo-passive films in super-oxidizing media
- NIOBIUM (COLUMBIUM) & TANTALUM - increase solid solution strength

- The role of chromium in the corrosion-resistant nickel alloys is the same as that in the stainless steels; in the presence of oxygen, it enhances the formation of passive films. These passive films impede the corrosion process. Iron, if added to the nickel alloys, also influences the formation of passive films.
- Copper, molybdenum, and tungsten enhance the nobility of nickel under active corrosion conditions. In addition, due to their large atomic sizes, molybdenum and tungsten are significant strengtheners of the nickel alloys. Niobium is also an effective strengthener.
- At high corrosion potentials, alloys which rely upon chromium for protection enter the so-called transpassive state, where chromium-rich passive films cannot be maintained. Silicon provides extended protection under such conditions, by encouraging the formation of more stable, pseudo-passive, silicon oxide films.

CORROSION-RESISTANT NICKEL ALLOYS
Metallurgy

- Most are single phase (face-centered cubic)
- Many are over-alloyed and reliant upon annealing and quenching to "freeze-in" the high temperature structure
- Phase transformations are possible with these over-alloyed materials during elevated temperature excursions (e.g. during welding)

- Most of the corrosion-resistant nickel alloys have a single atomic structure. In common with the austenitic stainless steels, this is face-centered cubic.
- To optimize their performance, designers of the nickel alloys have taken advantage of the fact that greater quantities of elements such as chromium and molybdenum are soluble in this face-centered cubic structure at temperatures in excess of about 1000°C than at lower temperatures. These elements can be maintained within this single structure (or phase) if the materials are water quenched. Thus, solution annealing (to dissolve any unwanted second phases) and water quenching (to "freeze-in" the high temperature structure) are used with these alloys.
- Second phases are possible within the nickel alloys, if they are subjected to elevated temperature excursions, for example during welding. The kinetics of second phase formation are critically dependent on the amount of over-alloying and the content of minor elements, such as carbon and silicon. In the wrought alloys, these elements are kept as low as possible through special melting techniques. In casting materials, to provide fluidity during pouring, higher silicon conents are usually necessary.

CORROSION-RESISTANT NICKEL ALLOYS
Metallurgy
Attributes of Nickel As Base Element

- Unique electrochemical properties
- Ability to form passive films
- Compatibility with other elements

- Because nickel is close to the hydrogen potential on the redox scale, nickel does not easily liberate hydrogen during corrosion.
- Nickel has the ability to form a passive film and thereby has good corrosion rates in this condition. The presence of an oxidizer will passivate nickel, but the passive state is easily destroyed.
- Nickel has a solubility for chromium and molybdenum that allows for more than 30% of each element in solid solution at elevated temperatures. Iron will only dissolve 12% chromium before the structure becomes two phase.

CORROSION-RESISTANT NICKEL ALLOYS
Common Compositions (wt.%)

Group	Alloy	Ni	Cu	Mo	Fe	Cr	Ti	W	V	Si	Nb+ Ta
Ni	200	99*	-	-	-	-	-	-	-	-	-
Ni-Cu	400	Bal.	31.5	-	-	-	-	-	-	-	-
Ni-Mo *HASTELLOY® B-TYPES*	B-2	Bal.	-	28	-	-	-	-	-	-	-
Ni-Fe-Cr *HASTELLOY G-TYPES*	825	Bal.	2.2	3	30	21.5	0.9	-	-	-	-
Ni-Cr-Si *HASTELLOY D-TYPES*	D-205™	Bal.	2	2.5	6	20	-	-	-	5	-
Ni-Cr-Mo *HASTELLOY C-TYPES*	C-276	Bal.	-	16	5	16	-	4	0.4°	-	-

* MINIMUM
° MAXIMUM

- This chart gives the compositions of several families of nickel alloys that are commercially used. There are distinct performance differences between and within the groups.
- With regard to the HASTELLOY® alloys, the B-types fall within the nickel-molybdenum group, the C-types are nickel-chromium-molybdenum alloys, the D-types are nickel-chromium-silicon alloys, and although they contain higher molybdenum levels than alloy 825, the G-types fall within the nickel-iron-chromium category.

WROUGHT Ni-Cu ALLOY COMPOSITIONS (wt.%)

Alloy	Ni	Cu	Others
400	Bal.	31.5	-
K500	Bal.	29.5	Al 2.8, Ti 0.5

- The alloy of major commercial importance in this group is alloy 400. This alloy finds significant use in seawater corrosion environments and hydrofluoric acid environments.
- Alloy K-500 is a precipitation hardening grade that provides higher strength for shafting and bolting.

WROUGHT Ni-Mo ALLOY COMPOSITIONS (wt.%)

Alloy	Ni	Cr	Mo	Fe	Others
B	Bal.	1*	28	5	V 0.30*
B-2	Bal.	1*	28	2*	-
B-3®	Bal.	1.5	28.5	1.5	-

* MAXIMUM
\+ MINIMUM

- All alloys in this group are used primarily in strongly reducing environments.
- In 1974, B-2 alloy replaced alloy B to offer resistance to heat-affected zone corrosion.
- In 1992, B-3 alloy was introduced to provide a composition that offered the same corrosion resistance with improved fabricability and thermal stability.

WROUGHT Ni-Fe-Cr-Mo ALLOY COMPOSITIONS (wt.%)

Alloy	Ni	Cr	Mo	W	Fe	Others
825	Bal.	21.5	3	-	30	Cu:2.2 Ti:0.9
G	Bal.	22	6.5	-	20	Nb+Ta:2 Cu:2
G-3	Bal.	22	7.0	-	20	Nb+Ta:0.5* Cu:2
G-30®	Bal.	30	5.5	2.5	15	Nb:0.8 Cu:2*

* MAXIMUM

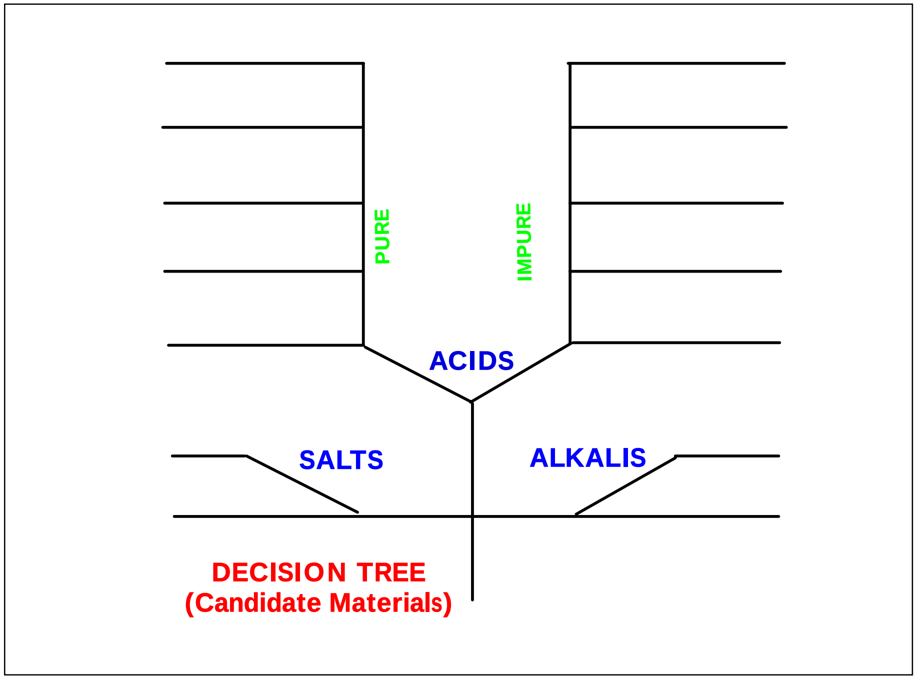
- Several commercial alloys are close in composition to alloy 825. Nickel is a deliberate addition to impart resistance to stress corrosion cracking, while iron is the balance element.
- In the HASTELLOY G alloy series, nickel is the base element with the other elements being balanced to provide the best localized corrosion resistance.
- The variation in molybdenum from 3 to 7% has significant influence on corrosion resistance in reducing acids.

WROUGHT Ni-Cr-Mo ALLOY COMPOSITIONS (wt.%)

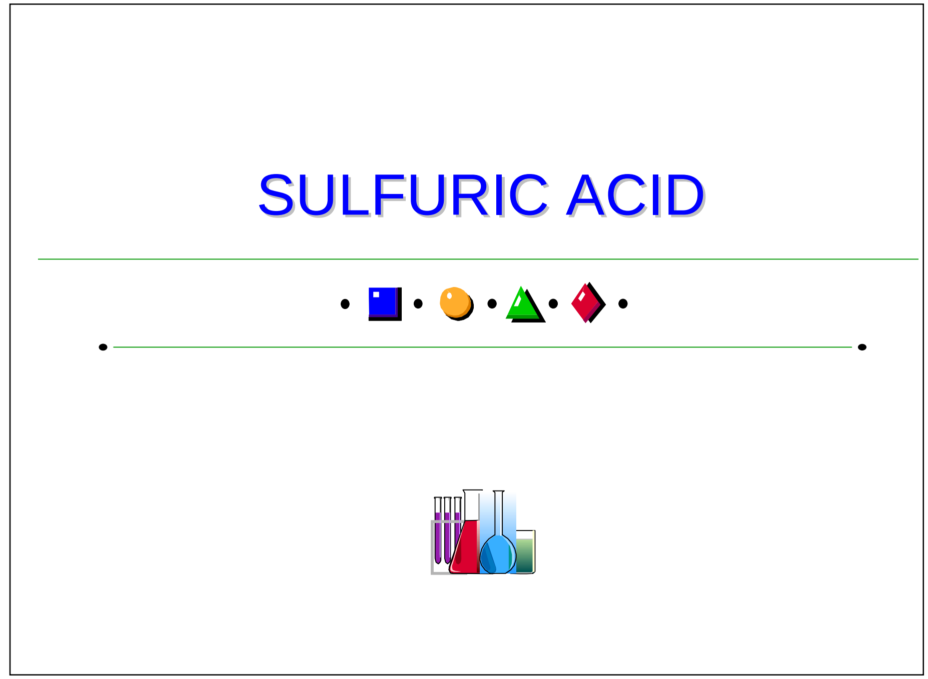
Alloy	Ni	Cr	Mo	W	Fe	Others
625	Bal.	21	9	-	5*	Nb+Ta:3.7
C-4	Bal.	16	16	-	3*	Ti:0.7*
C-22®	Bal.	22	13	3	3	V:0:35*
C-276	Bal.	16	16	4	5	V:0:35*
C-2000®	Bal.	23	16	-	3*	Cu:1.6
59	Bal.	23	16	-	-	-
686	Bal.	21	16	3.7	-	Ti:.25*

* MAXIMUM

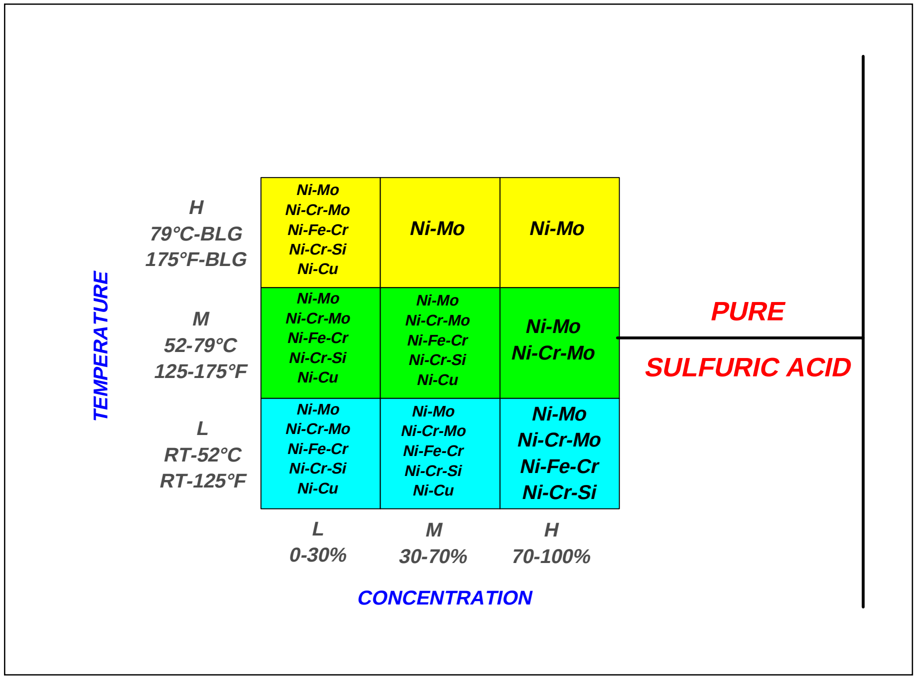
- The compositions of the currently available, wrought, nickel-chromium-molybdenum alloys are shown here. Several casting compositions are also available.
- From this table, it is evident that the chromium content of these alloys range from 16 to 23 wt.%, molybdenum ranges from 9-16%, and that tungsten, iron, and copper are optional additions. The effects of these variations are significant; in particular, the high chromium alloys exhibit much higher resistance to the oxidizing acids, such as nitric, while the higher molybdenum alloys have better resistance to reducing environments.

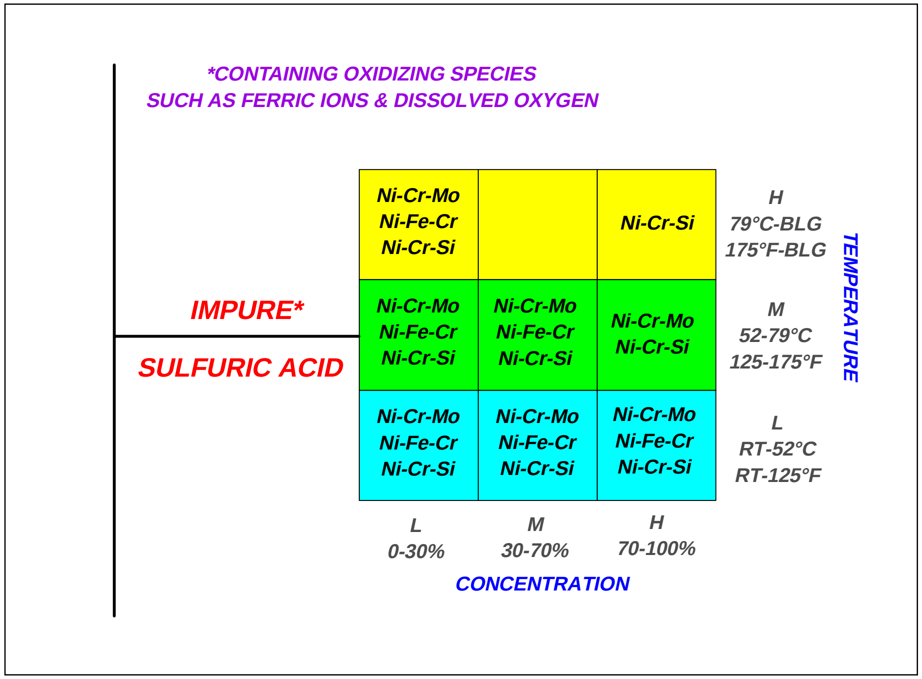


- We shall now consider the corrosion-resistant nickel alloys from a user's standpoint. Typically, users have chemical mixtures and, possibly, aggressive residuals, to deal with. However, with some knowledge of the effects of the residuals, candidate materials can usually be selected for test based on their performance in the most aggressive constituents. In many cases, the most aggressive constituents and residuals are inorganic chemicals upon which this package is focused.
- In making decisions about candidate materials, it is useful to consider a diagram such as this. In this package, many branches of this decision tree will be considered, and details about the likely performance of the nickel alloys, by group, will be given. Supporting data will also be provided, with some references to alternate materials, such as the stainless steels and reactive metal alloys.
- The most important aspect of this simplified diagram is the division between pure and impure acids. For some nickel alloy groups, residuals of an oxidizing nature, such as ferric compounds, cannot be tolerated.



- The first chemical of concern is sulfuric acid. Sulfuric is one of the most important industrial chemicals. It is used in the manufacture of fertilizers, detergents, plastics, synthetic fibers, and pigments. It is also used as a catalyst in the petroleum industry.

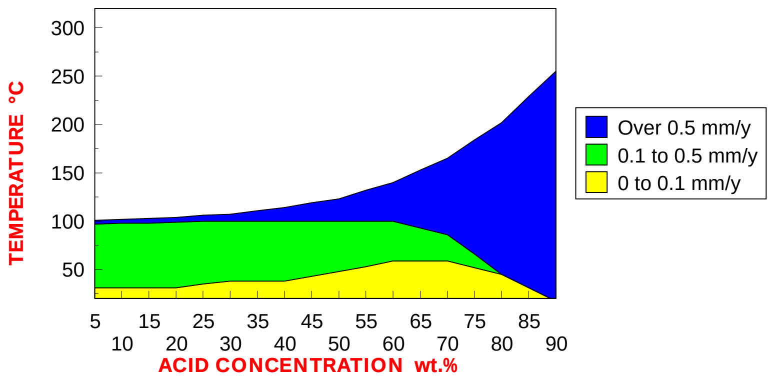




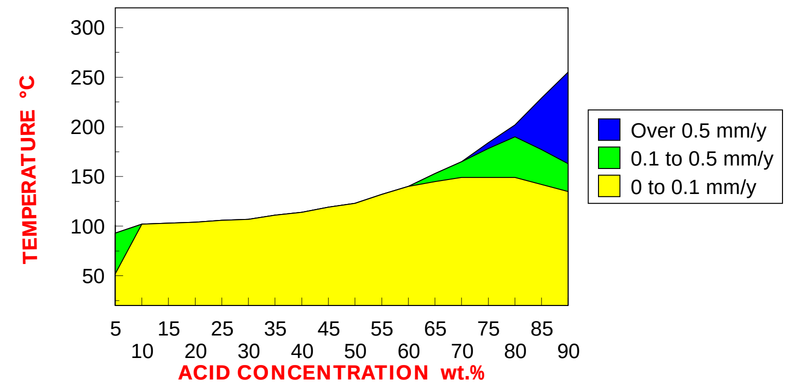
- For each of the acid branches of the decision tree, nine concentration/ temperature segments are used. The low, medium, and high temperature ranges extend from room temperature to the boiling points. In most cases, the low, medium, and high concentration ranges go from zero to the maximum concentration that is stable at the boiling point.
- Since boiling points change with concentration, the upper boxes cover varying temperature ranges. For example, in the case of sulfuric acid, boiling points increase dramatically at the medium and high concentrations. Thus, the temperature range of the upper right-hand segment is very large.
- The purpose of this chart is to provide users with a guide to the alloy groups which might work within particular concentration/temperature segments. The selections are based on evidence that alloys from the chosen groups exhibit rates of 0.5 mm/y or less over significant concentration and temperature ranges, within those segments.
- The important revelations of this chart are the excellent corrosion resistance of the nickel-molybdenum alloys in pure sulfuric acid (which is available in concentrations up to 96 wt.%), the good resistance of the nickel-chromium-molybdenum alloys, and the usefulness of several groups at lower concentrations and temperatures.

- Consider now the corresponding branch on the impure side of the decision tree. It should be noted that the nickel-molybdenum and nickel-copper alloys have been removed from the chart. This is because alloys from these groups are intolerant to oxidizing residuals, such as ferric ions and dissolved oxygen.
- Since D-205™ alloy provides exceptional resistance to concentrated, commercial sulfuric acid, the nickel-chromium-silicon group has been added to the upper right-hand boxes. Its resistance is highest in the 90 to 99 wt.% concentration range, where there is an inverse relationship between corrosion rate and concentration.

ISO-CORROSION DIAGRAM FOR ALLOY 400 IN SULFURIC ACID



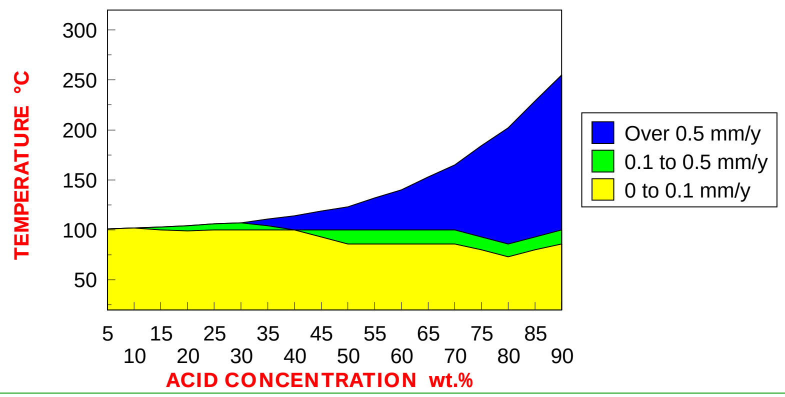
ISO-CORROSION DIAGRAM FOR B-3® ALLOY IN SULFURIC ACID



- To support the selections on the decision tree, and to provide details of performance within individual segments, several iso-corrosion diagrams are presented in this package. These diagrams were constructed mathematically from numerous data points, and each one defines, for a given alloy and solution, the "very safe", "moderately safe", and "unsafe" concentration/temperature regimes. These correspond to the corrosion rate ranges 0 - 0.1 mm/y, 0.1 - 0.5 mm/y, and over 0.5 mm/y. For those more familiar with mils (0.001 in) per year, 0.1 mm/y equals 4 mpy, and 0.5 mm/y equals 20 mpy.
- This is the iso-corrosion diagram for the nickel-copper alloy 400. It defines precisely the limits of use in pure sulfuric acid (in the concentration range 10 to 90 wt.%, and up to the boiling points). These extend to about 100°C at low and medium concentrations but, at high concentrations, the alloy is severely temperature limited.

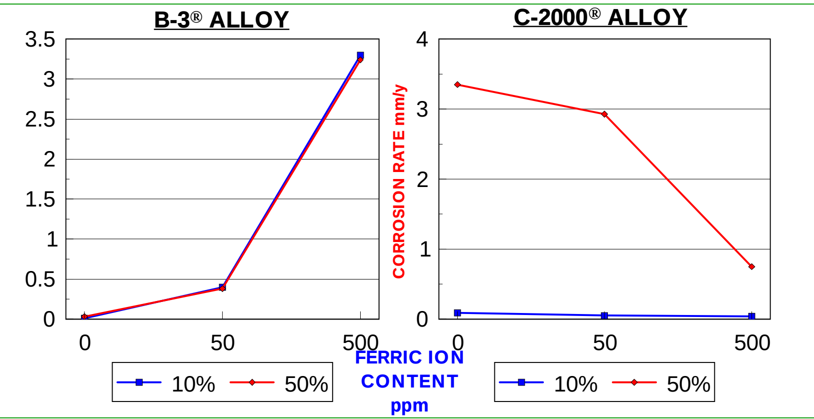
- This is the iso-corrosion diagram for B-3® alloy, one of the nickel-molybdenum alloys. It exhibits a large, "very safe" regime in pure sulfuric acid.

ISO-CORROSION DIAGRAM FOR C-2000® ALLOY IN SULFURIC ACID



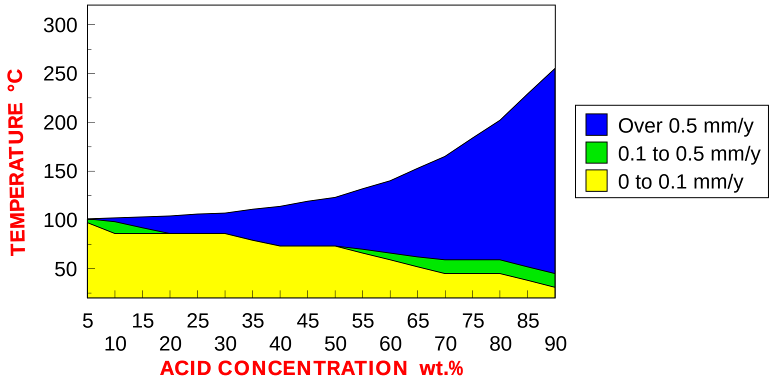
- Here is the iso-corrosion diagram for C-2000® alloy, one of the nickel-chromium-molybdenum materials, in pure sulfuric acid. It is safe for use up to about 100°C, with a dip at concentrations around 80 wt.%.

INFLUENCE OF FERRIC IONS IN BOILING SULFURIC ACID



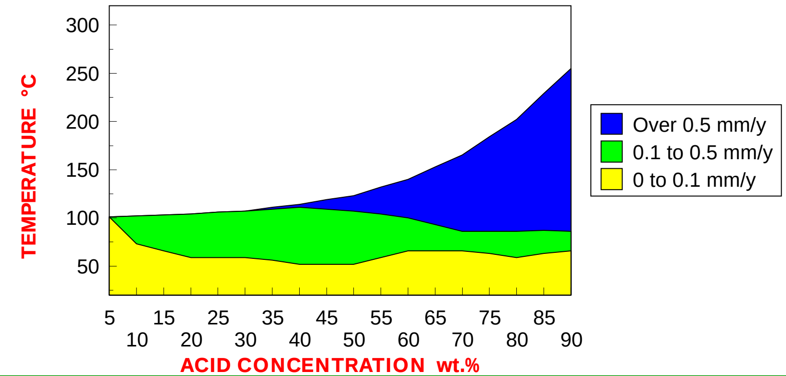
- Having shown the iso-corrosion diagrams for B-3® and C-2000® alloys in sulfuric acid, it is important to indicate how strongly certain impurities or residuals can influence the corrosion process.
- Here are the effects of adding ferric ions (in the form of ferric sulfate) to 10 wt.% and 50 wt.% boiling sulfuric acid. Even at 50 parts per million, the effects are very pronounced, increasing the rates for B-3 alloy by more than an order of magnitude.
- In the case of the nickel-chromium-molybdenum alloys, the addition of ferric ions is very beneficial.

ISO-CORROSION DIAGRAM FOR ALLOY 625 IN SULFURIC ACID



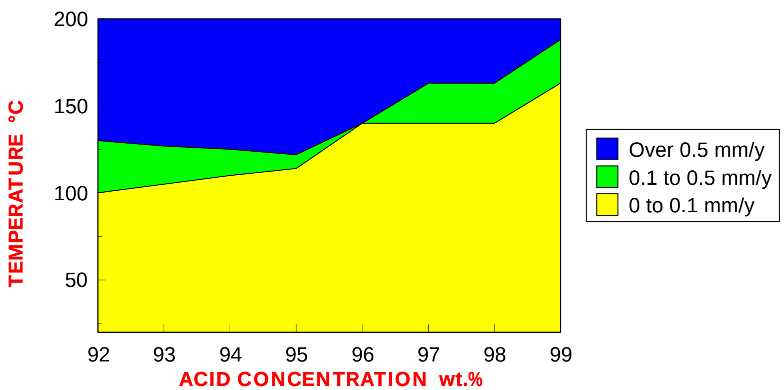
- Here is the iso-corrosion diagram for alloy 625 from the nickel-chromium-molybdenum group indicating a significantly smaller useful range than C-2000® alloy in sulfuric acid.

ISO-CORROSION DIAGRAM FOR D-205™ ALLOY IN SULFURIC ACID



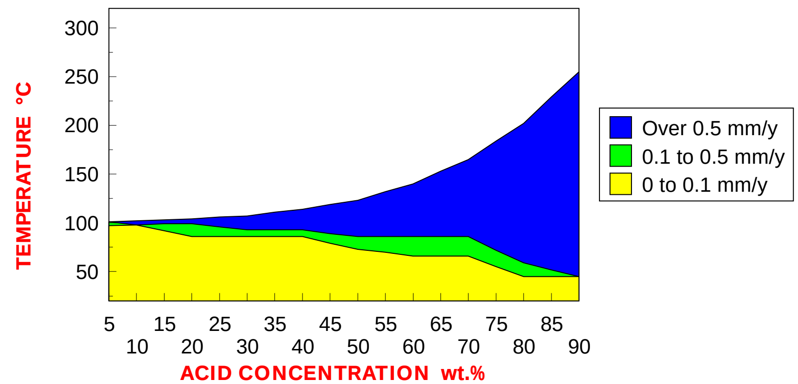
- In that it features a wide, "moderately safe" regime at low and medium concentrations, the nickel-chromium-silicon D-205™ alloy diagram for pure sulfuric is different from that of the nickel-chromium-molybdenum alloys.

ISO-CORROSION DIAGRAM FOR D-205™ ALLOY IN CONCENTRATED COMMERCIAL SULFURIC ACID



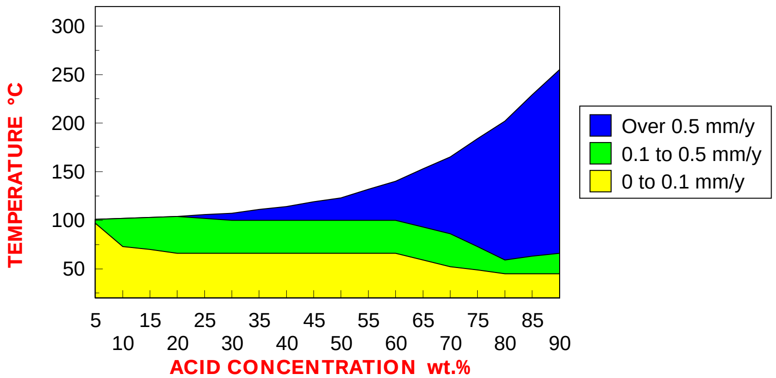
- The main use of D-205™ alloy is in impure, concentrated, commercial sulfuric acid.
- Even though it is only a small portion of an iso-corrosion diagram, and does not extend to the boiling points, this chart, which was compiled using numerous data in the concentration range 92 to 99 wt.%, shows the limits of use of D-205 alloy in commercial sulfuric acid. It is notable that the higher the concentration, within this range, the greater the temperature capability of D-205 alloy.

ISO-CORROSION DIAGRAM FOR G-30® ALLOY IN SULFURIC ACID

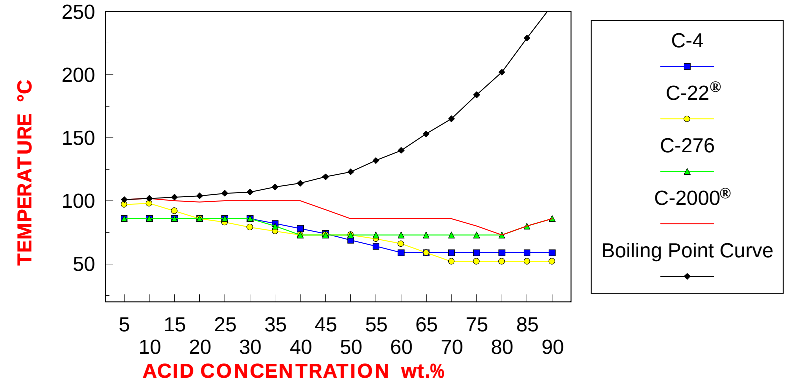


- The iso-corrosion diagram for G-30® alloy, one of the nickel-iron-chromium materials, in pure sulfuric acid indicates very good resistance up to a concentration of 70 wt.%, then decreasing resistance as a function of temperature.

ISO-CORROSION DIAGRAM FOR ALLOY 825 IN SULFURIC ACID



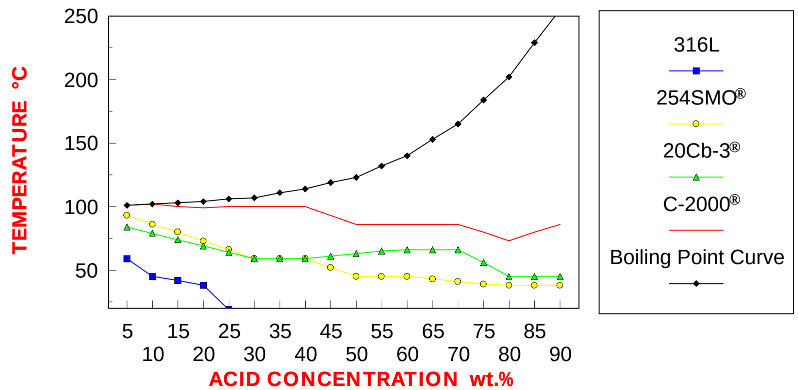
COMPARISON OF 0.1 mm/y LINES FOR Ni-Cr-Mo ALLOYS IN SULFURIC ACID



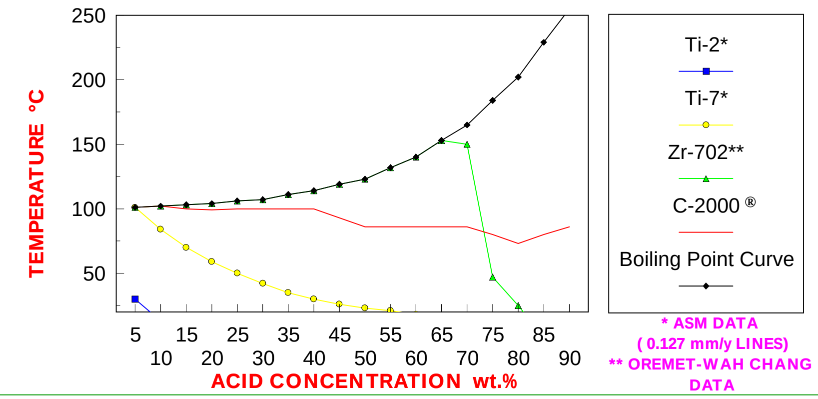
- Alloy 825, like C-2000® alloy, can be safely used in pure sulfuric acid, at low and moderate concentrations, up to about 100°C. However, compared with the nickel-chromium-molybdenum alloy it exhibits a wider "moderately safe" range.

- The purpose of this chart is to provide information on some of the other nickel-chromium-molybdenum alloys in sulfuric acid and to indicate the sort of performance differences that can exist between alloys within the same group. To do this, the 0.1 mm/y lines, i.e. the boundaries between the "very safe" and "moderately safe" regimes, have been plotted for C-4, C-22®, C-276, and C-2000® alloys. Since the nickel-chromium-molybdenum alloys have narrow "moderately safe" regimes, these 0.1 mm/y lines effectively delineate the useful ranges of these alloys.
- From this chart, it is evident that, over a wide concentration range, C-2000 alloy can be used to significantly higher temperatures.

COMPARISON OF 0.1 mm/y LINES FOR STAINLESS STEELS & C-2000® ALLOY IN SULFURIC ACID



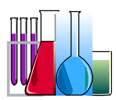
COMPARISON OF 0.1 mm/y LINES FOR REACTIVE METAL ALLOYS & C-2000® ALLOY IN SULFURIC ACID

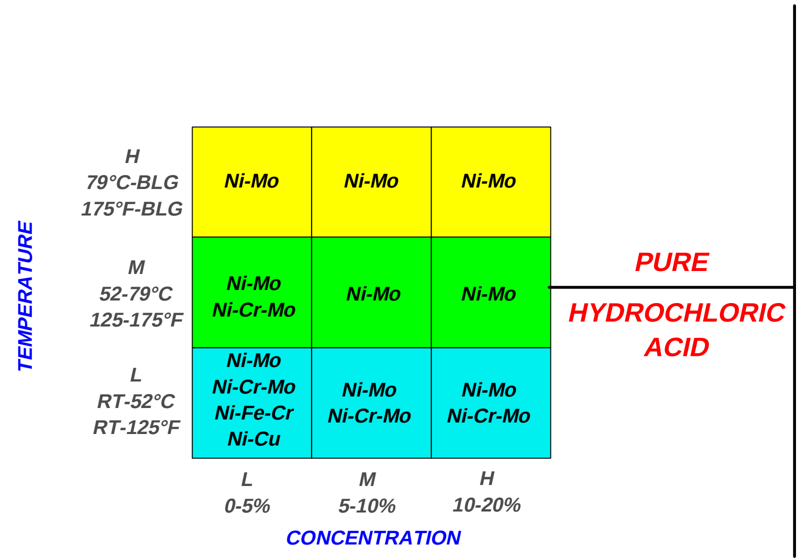


- For perspective, this chart compares the performance of C-2000® alloy with three popular, austenitic stainless steels, namely 316L, 254SMO (of the "6 Moly" variety), and 20Cb-3 alloys. 20Cb-3 alloy is a derivative of alloy 20 which was designed specifically for sulfuric acid service.
- As can be seen, alloy 316L exhibits relatively poor resistance to sulfuric acid, whereas, 254SMO and 20Cb-3 alloys are able to withstand sulfuric acid to moderate temperatures over a wide concentration range.

- For further perspective, this chart compares the performance of C-2000® alloy with three reactive metal alloys, namely, titanium grades 2 and 7 and the zirconium alloy Zr-702.
- The data for titanium grades 2 and 7 were taken from an ASM handbook which gave the 0.127 mm/y lines, rather than the 0.1 mm/y lines.
- Study of this chart reveals several important facts. First, commercially pure titanium, that is grade 2, is unsuitable for service in sulfuric acid. Second, grade 7 (which contains just a small quantity of palladium) possesses useful resistance to very dilute sulfuric. Third, the zirconium alloys are very resistant to low and moderate concentrations of sulfuric acid, but are unsuitable for high concentrations.

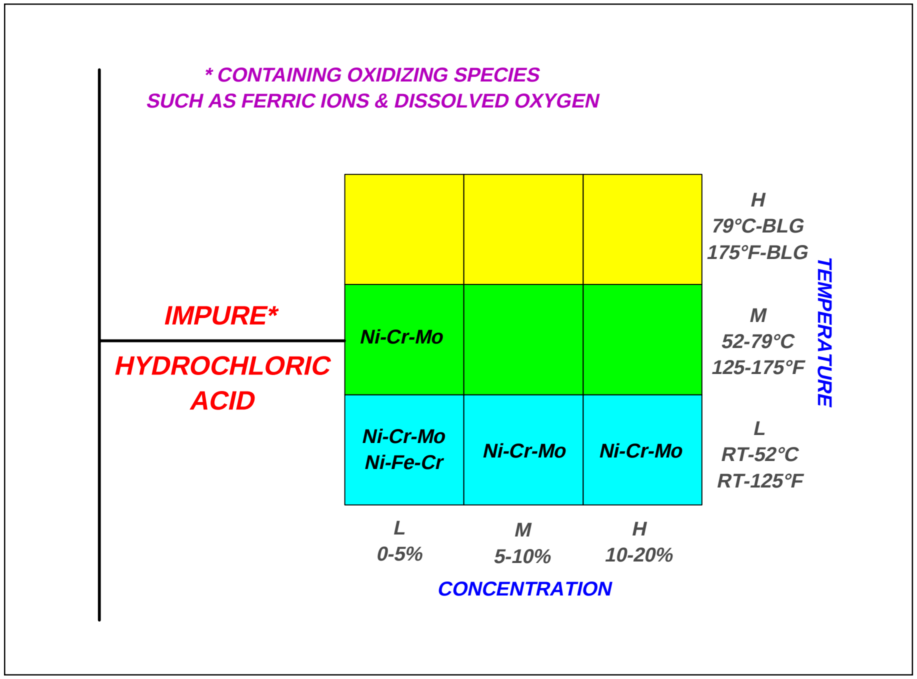
HYDROCHLORIC ACID



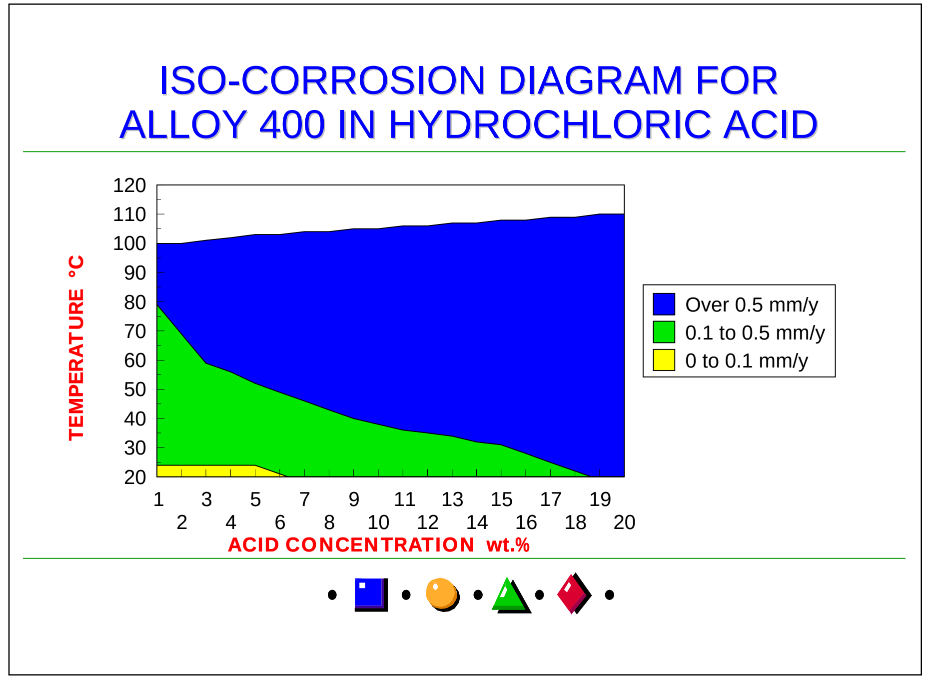


- Hydrochloric acid pervades the chemical processing industries both as a feedstock and by-product. It is extremely corrosive to most metals and alloys.
- As will be shown, many nickel alloys have useful resistance to hydrochloric acid, although in most cases there are strong concentration and temperature dependencies.
- Resistance to hydrochloric acid is also the key to good pitting and crevice corrosion resistance in chloride-bearing environments, since the progression of these phenomena involves the local formation of hydrochloric acid.

- Here is the decision tree branch for pure hydrochloric acid. Only alloys from the nickel-molybdenum group are suitable for service at the higher temperatures and concentrations. However, alloys from other groups, notably the nickel-chromium-molybdenum materials, can also be used within certain concentration and temperature ranges.
- The chart deals with concentrations up to 20 wt.%, the maximum that can be sustained in a boiling solution. Higher concentrations are possible, but these are generally unstable.

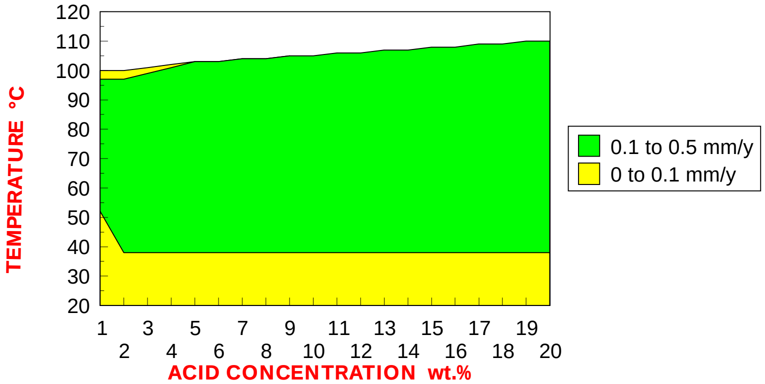


- The corresponding branch on the impure side of the tree indicates that the choices are even more limited in the presence of oxidizing species, unless these are abundant enough to cause passivation of the chromium-bearing alloys.



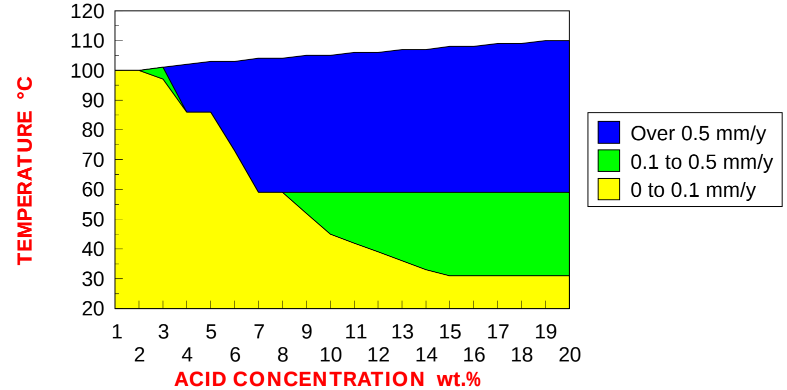
- Consider now the behavior of individual alloys in pure hydrochloric acid.
- This chart indicates that alloy 400 has a very limited range of usefulness in hydrochloric acid.
- In fact, corrosion rates of less than 0.1 mm/y are only exhibited by alloy 400 at room temperature, or just above, and at concentrations below 7 wt.%.

ISO-CORROSION DIAGRAM FOR B-3® ALLOY IN HYDROCHLORIC ACID

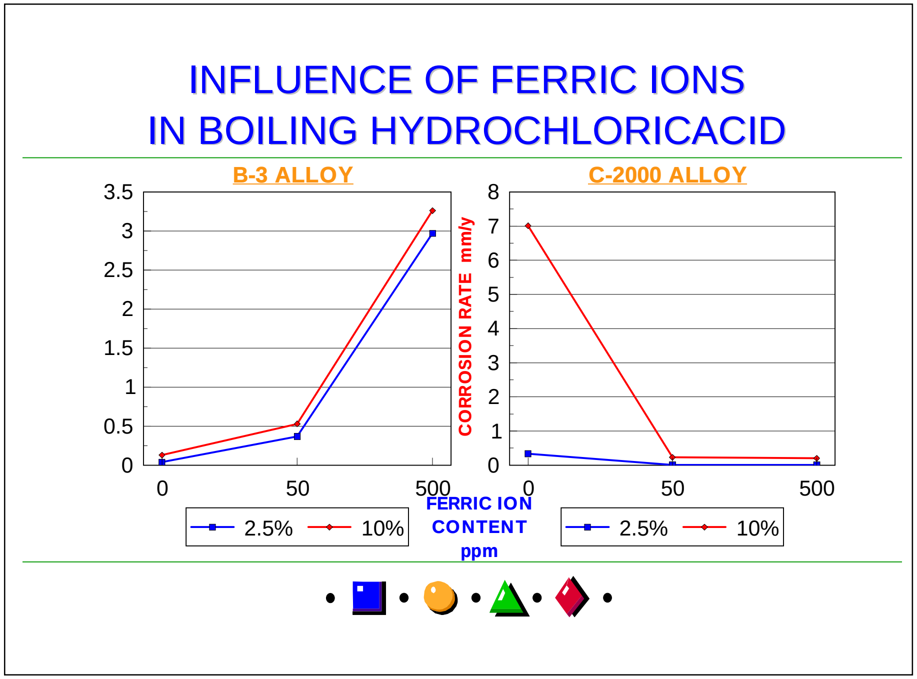


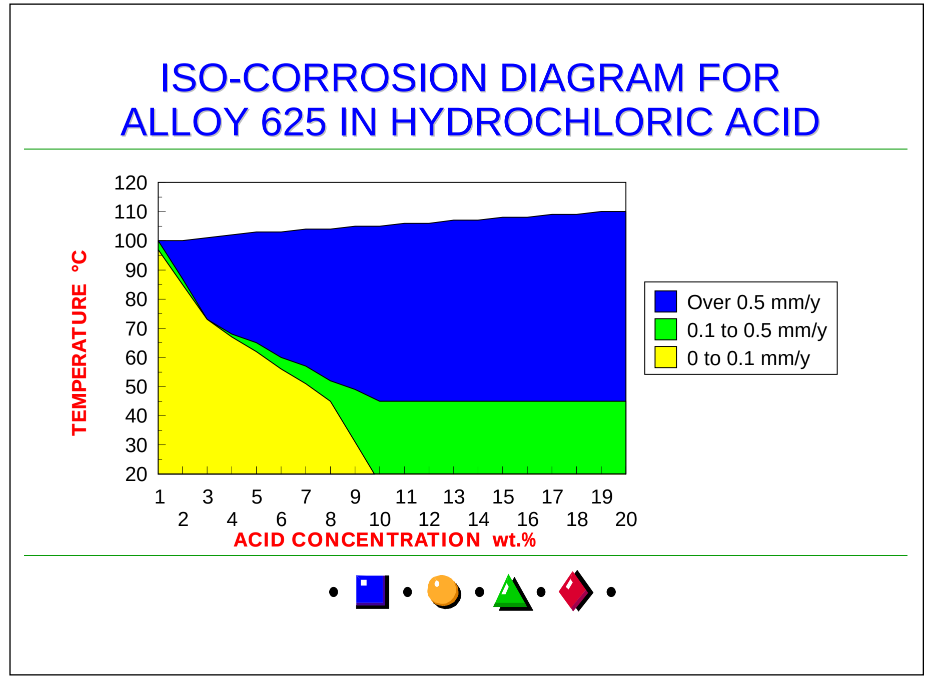
- Above is the iso-corrosion diagram for B-3® alloy. It is note-worthy that while the nickel-molybdenum materials are able to withstand all concentrations of hydrochloric acid, up to the boiling points, the rates of attack generally fall in the "moder-ate" category, that is 0.1 to 0.5 mm/y.

ISO-CORROSION DIAGRAM FOR C-2000® ALLOY IN HYDROCHLORIC ACID



- The nickel-chromium-molybdenum alloys exhibit strong concentration and temperature dependencies in hydrochloric acid. In dilute hydrochloric acid, they exhibit larger "very safe" regimes than the nickel-molybdenum alloys, but as the concentration increases they become severely temperature limited.
- Above is the hydrochloric acid iso-corrosion diagram for C-2000® alloy.

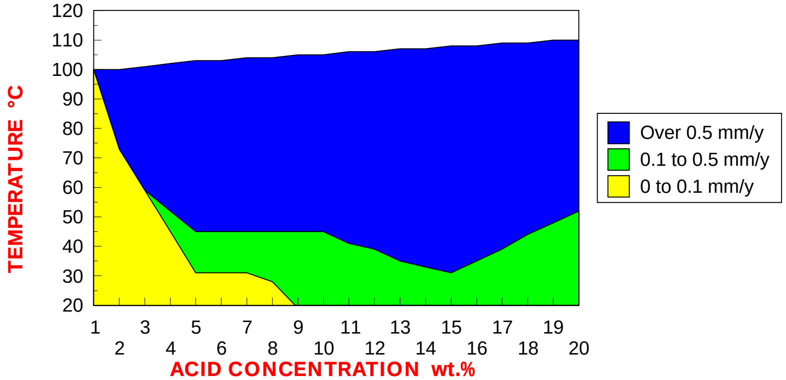




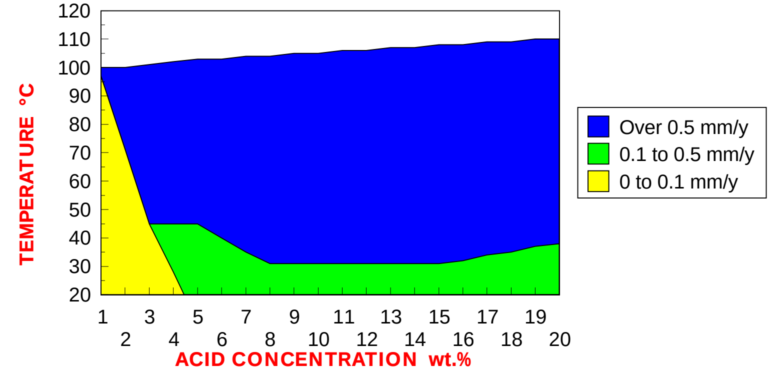
- The above chart considers the effects of impurities or residuals on the performance of B-3® and C-2000® alloys in hydrochloric acid. By adding ferric ions (in the form of ferric chloride) to boiling 2.5 wt.% acid and boiling 10 wt.% acid, the effects mirror those seen in sulfuric acid, except the ferric ions appear to be even more beneficial in the case of C-2000 alloy.

- This is the iso-corrosion diagram for alloy 625 from the nickel-chromium-molybdenum category indicating reasonable resistance to dilute hydrochloric acid, but no "very safe" regime beyond a concentration of 9 wt.%.

ISO-CORROSION DIAGRAM FOR G-30® ALLOY IN HYDROCHLORIC ACID

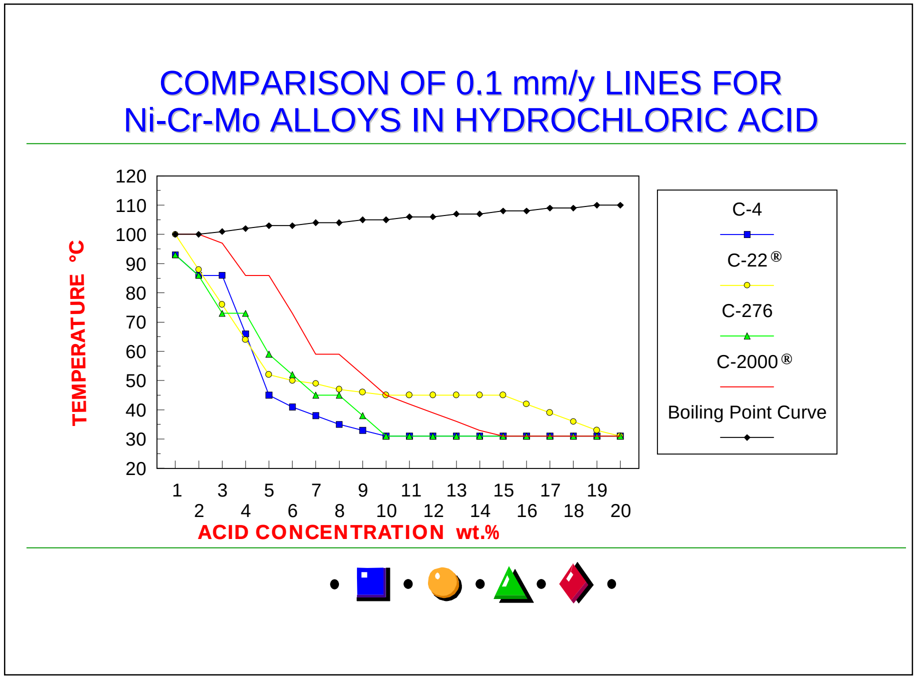


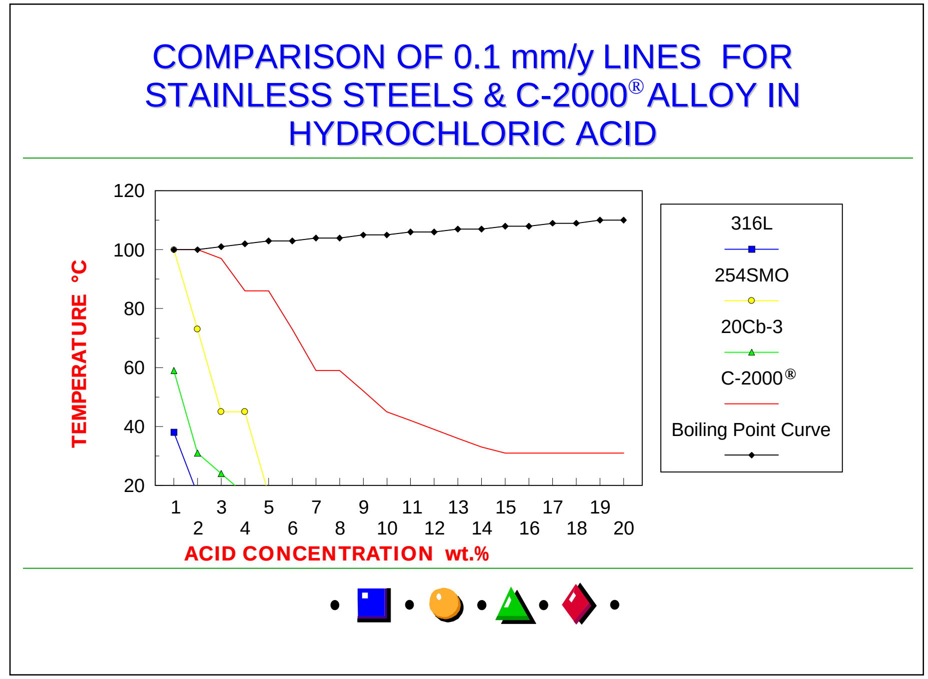
ISO-CORROSION DIAGRAM FOR ALLOY 825 IN HYDROCHLORIC ACID



- Above is the iso-corrosion diagram for G-30® alloy, from the nickel-iron-chromium group. As compared with the nickel-chromium-molybdenum alloys, G-30 alloy exhibits a much smaller "very safe" regime and a much larger "unsafe" one.

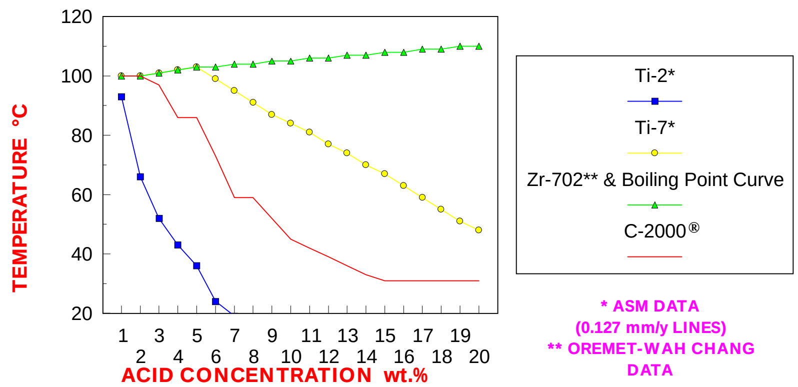
- With a lower molybdenum content than G-30® alloy, alloy 825 (which is also from the nickel-iron-chromium-molybdenum group) has an even smaller useful range in hydrochloric acid.





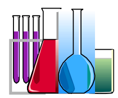
- As with sulfuric acid, comparative charts using the 0.1 mm/y boundary lines from the iso-corrosion diagrams have been created.
- Above, is the first of these comparative charts which shows the advantages of C-2000® alloy at lower concentrations and of C-22® alloy at higher concentrations.
- The second comparative chart, which includes the three common types of austenitic stainless steel, indicates how poorly the stainless steels are in hydrochloric acid relative to the nickel-chromium-molybdenum alloys.

COMPARISON OF 0.1 mm/y LINES FOR REACTIVE METAL ALLOYS & C-2000® ALLOY IN HYDROCHLORIC ACID

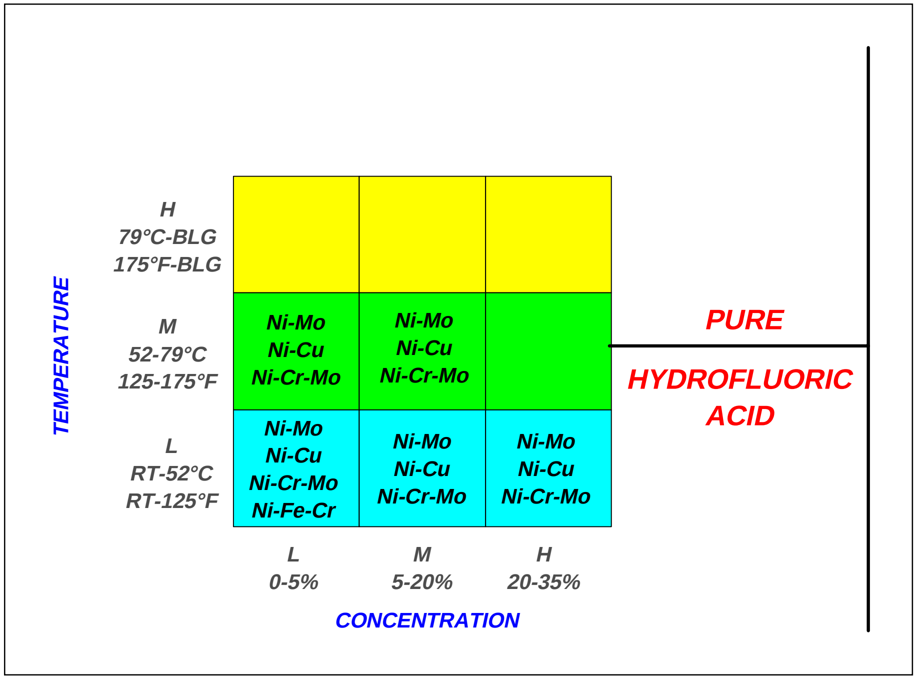


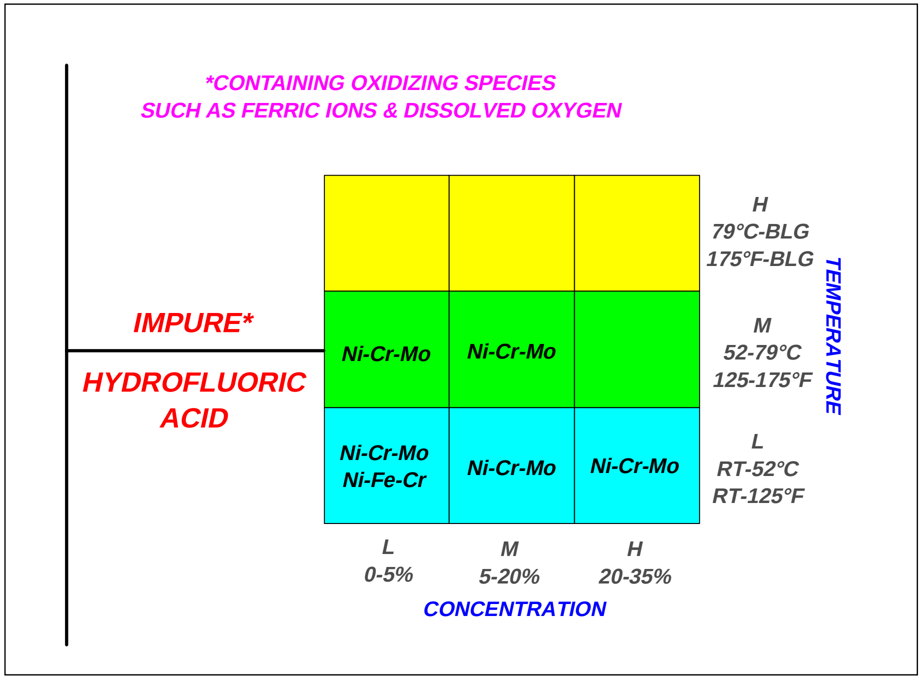
- Some of the reactive metal alloys, in particular the zirconium materials, exhibit high resistance to hydrochloric acid. In fact, according to data from Oremet-Wah Chang, a zirconium alloy supplier, the "very safe" regime for alloy Zr-702 extends well beyond the boiling points for all concentrations of hydrochloric acid. The only limitation of the zirconium alloys is that they are intolerant of residuals such as fluoride ions, ferric chloride, and cupric chloride.

HYDROFLUORIC ACID



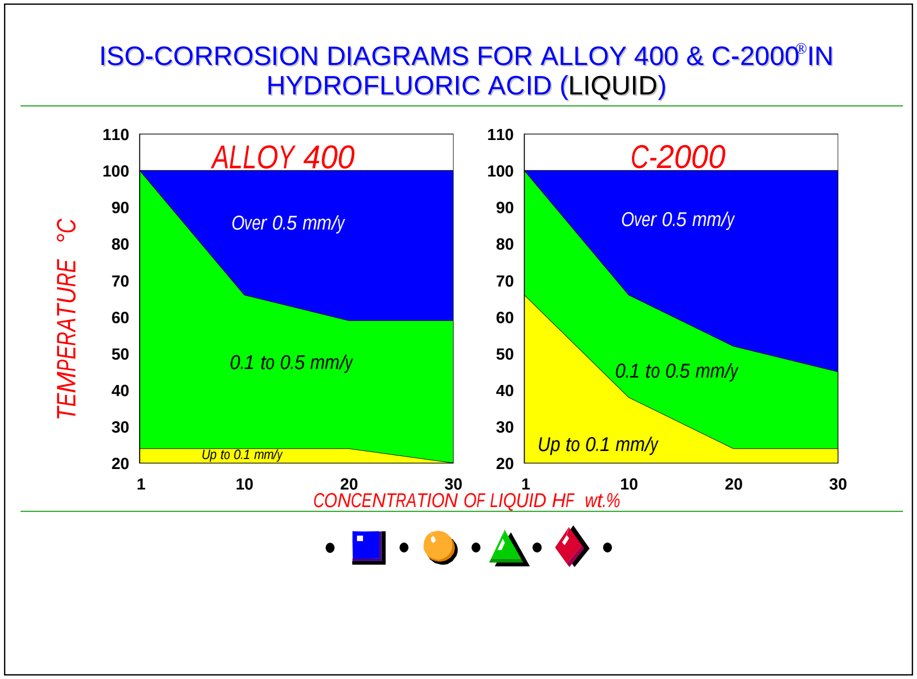
- The next segment deals with hydrofluoric acid which has become very important within the organic chemical and plastics industries.
- Hydrofluoric acid is an extremely aggressive chemical which readily attacks the reactive metal alloys. Fortunately, the nickel alloys provide reasonable resistance to this acid, possibly through the growth of protective, pseudo-passive, nickel fluoride films.

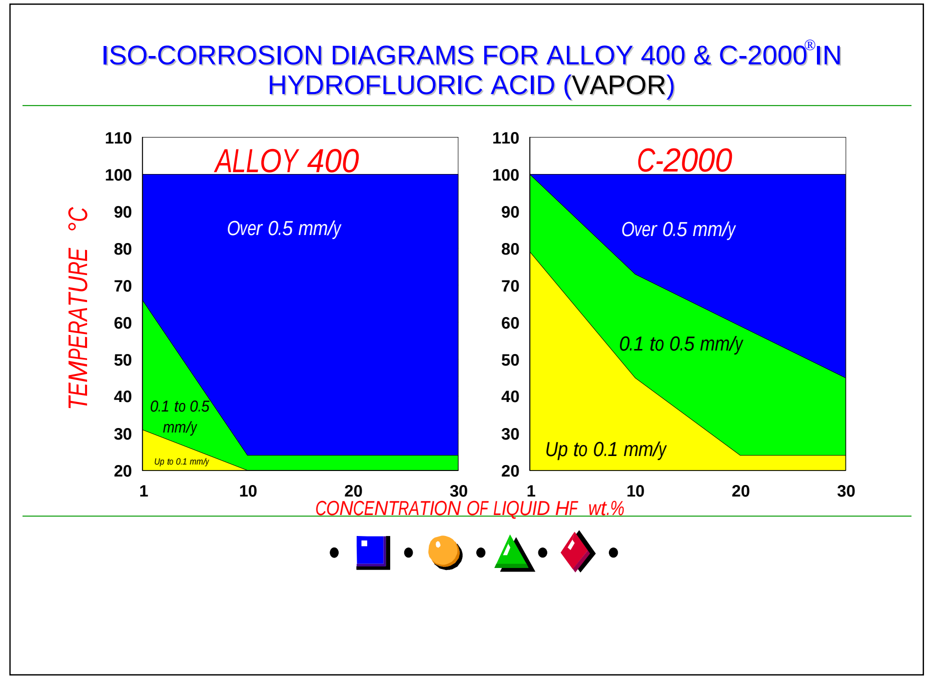




- Looking at the pure hydrofluoric acid branch of the decision tree, it is evident that the nickel-molybdenum, nickel-copper, and nickel-chromium-molybdenum alloys are all suitable for use in hydrofluoric over reasonable concentration and temperature ranges.
- The maximum concentration used in this chart is 35 wt.%. This is the highest concentration that can be maintained as a boiling solution.

- The presence of oxidizing species in hydrofluoric acid essentially limits the choice of materials to the nickel-chromium-molybdenum alloys.

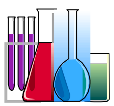




- The characteristics of two of the best nickel alloys for liquid hydrofluoric acid service are compared in these iso-corrosion diagrams. From these charts, it is evident that even the best alloys exhibit moderate corrosion rates over large concentration and temperature regimes.
- It is worthy of note that the performance of the nickel-copper alloys is only weakly influenced by the acid concentration.

- This comparison of the same two alloys placed above liquid hydrofluoric acid (in the vapor space) indicates that problems exist with some nickel alloy groups in the presence of oxygen. For example, the nickel-copper alloys exhibit much higher corrosion rates in the vapor space. Fortunately, oxygen does not appear to be detrimental to the performance of C-2000 alloy in hydrofluoric acid.
- It is also known that hydrofluoric acid can cause stress corrosion cracking of the nickel alloys, so attempts should be made to minimize applied and residual stresses in nickel alloy components subjected to hydrofluoric acid.

HYDROBROMIC ACID



TEMPERATURE	L 0-5%	M 5-20%	H 20-40%
H 79°C-BLG 175°F-BLG	Ni-Mo Ni-Cr-Mo	Ni-Mo	Ni-Mo
M 52-79°C 125-175°F	Ni-Mo Ni-Cr-Mo	Ni-Mo Ni-Cr-Mo	Ni-Mo Ni-Cr-Mo
L RT-52°C RT-125°F	Ni-Mo Ni-Cr-Mo	Ni-Mo Ni-Cr-Mo	Ni-Mo Ni-Cr-Mo

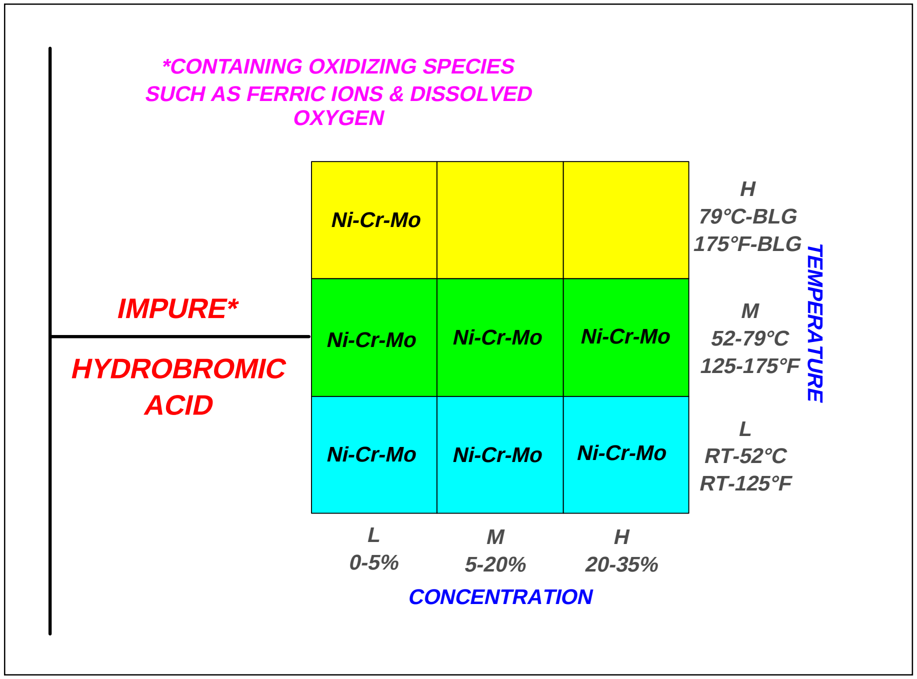
CONCENTRATION

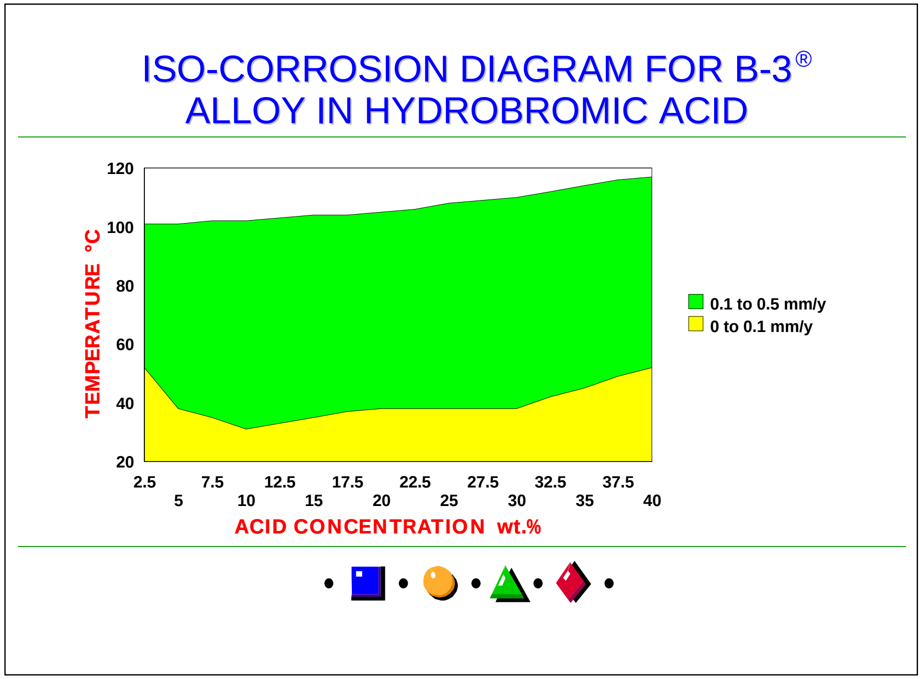
PURE

HYDROBROMIC ACID

- Hydrobromic is the third most important halogen acid, behind hydrochloric and hydrofluoric. It is becoming increasingly important as brominated compounds become more widely used.

- Looking at the pure hydrobromic acid branch of the decision tree, both the nickel-molybdenum and nickel-chromium-molybdenum alloys are useful over wide ranges of concentration and temperature. A maximum concentration of 40 wt.% has been used, since that is about the maximum that can be sustained in a boiling solution.

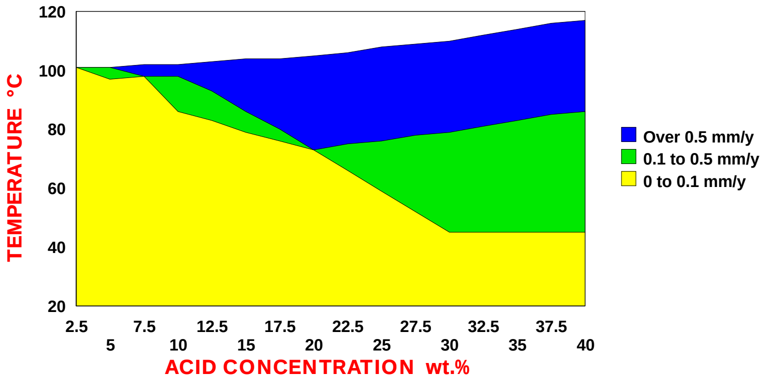




- In the presence of oxidizing species, the nickel-chromium-molybdenum alloys are the most appropriate choice in hydrobromic acid, although they are unsuitable at high temperatures, at concentrations in excess of 5 wt.%.

- Above is the iso-corrosion diagram for B-3® alloy in hydrobromic acid, illustrating that the performance of the nickel-molybdenum alloys in hydrobromic is similar to that in hydrochloric. It is noteworthy that, although B-3 alloy can be used at all temperatures up to the boiling point, in the concentration range 0 to 40 wt.%, moderate corrosion rates are experienced above approximately 40°C.

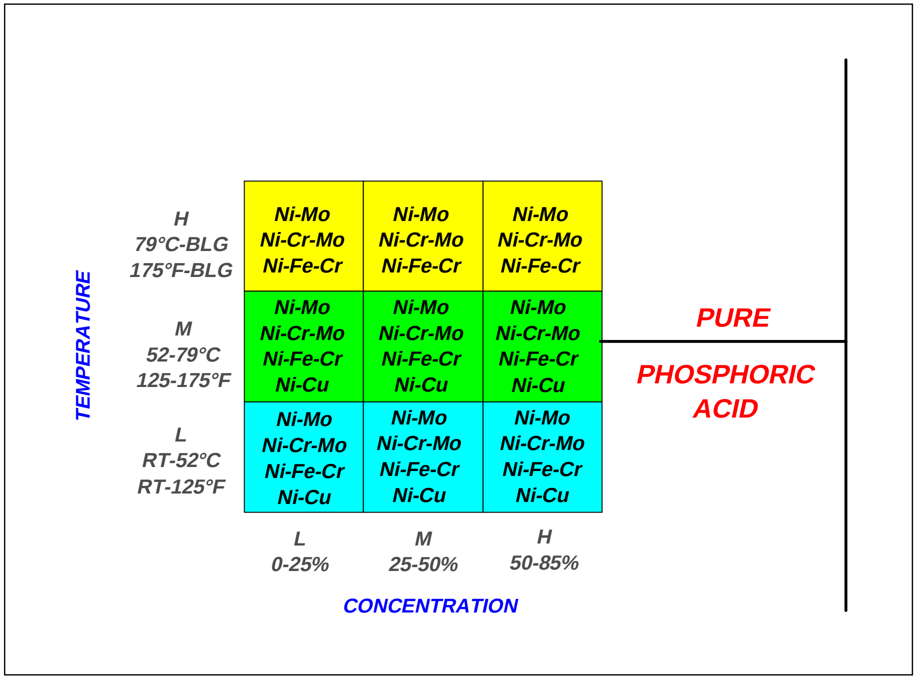
ISO-CORROSION DIAGRAM FOR C-2000® ALLOY IN HYDROBROMIC ACID



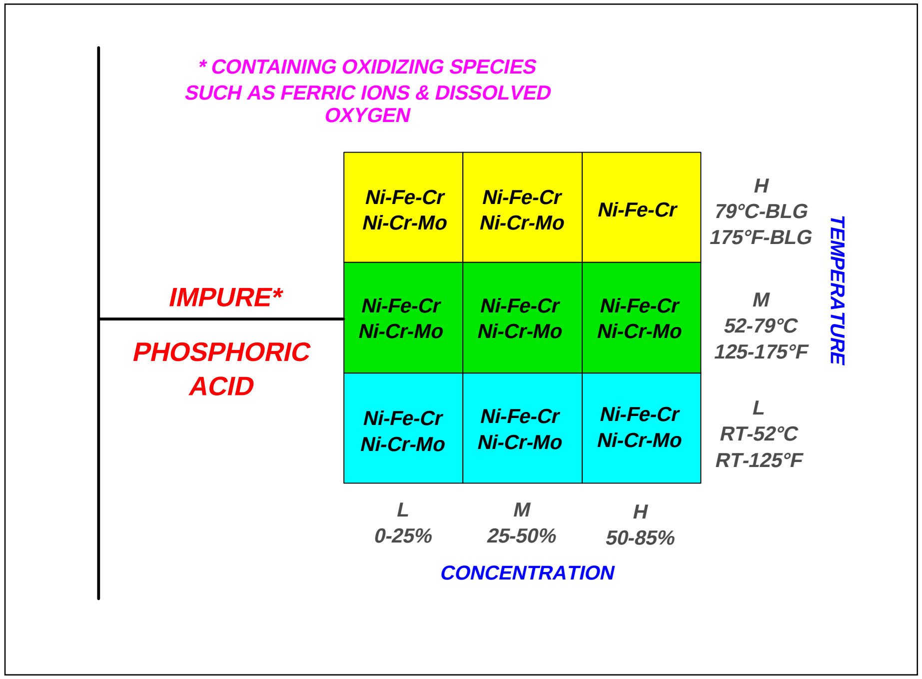
- The iso-corrosion diagram for C-2000® alloy in hydrobromic acid indicates a very large "very safe" regime, up to a concentration of 20 wt. %, and a wide "moderately safe" regime at higher concentrations. These data suggest the hydrobromic acid is not as aggressive to the nickel-chromium-molybdenum alloys as hydrochloric acid.

PHOSPHORIC ACID

- Two distinctly different types of phosphoric acid are encountered in industry. The pure (reagent grade) acid is made from elemental phosphorus, derived from phosphate rock. This is oxidized, then reacted with water.
- On the other hand, the type of phosphoric acid widely used in the agrichemical industries is made by reacting phosphate rock with sulfuric acid. It also contains several impurities, notably sulfuric acid, silica, chloride and fluoride ions, and ferric ions, which markedly affect the oxidizing potential of the acid. The levels of these impurities vary depending on the source of the rock and different batches of this so-called "wet process" acid can vary considerably in their corrosivity.

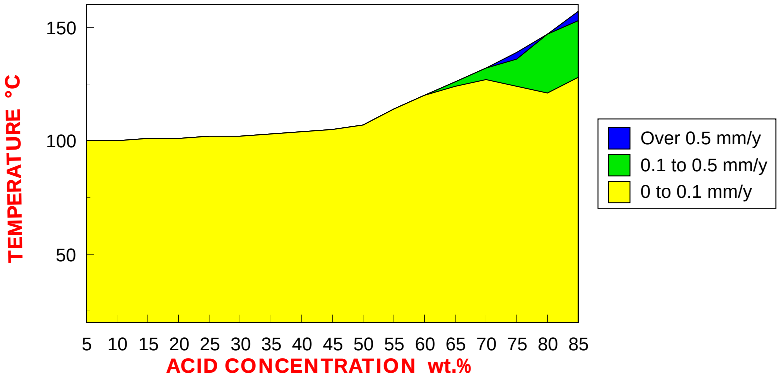


▶ Here is the pure phosphoric branch of the decision tree. As can be seen, the alloy choices are plentiful, even at high concentrations and temperatures.



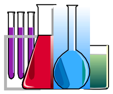
▶ On the impure side, the choices are fewer. However, the nickel-iron-chromium materials, in particular those with high chromium contents, such as G-30® alloy, possess outstand-ing resistance to "wet process" phosphoric acid.

ISO-CORROSION DIAGRAM FOR C-2000® ALLOY IN PHOSPHORIC ACID

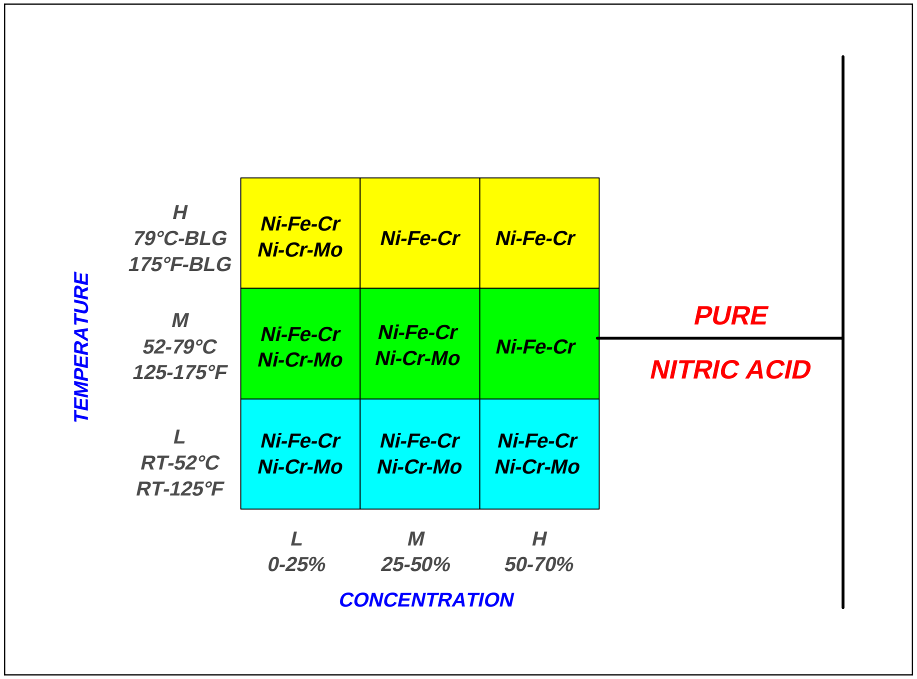


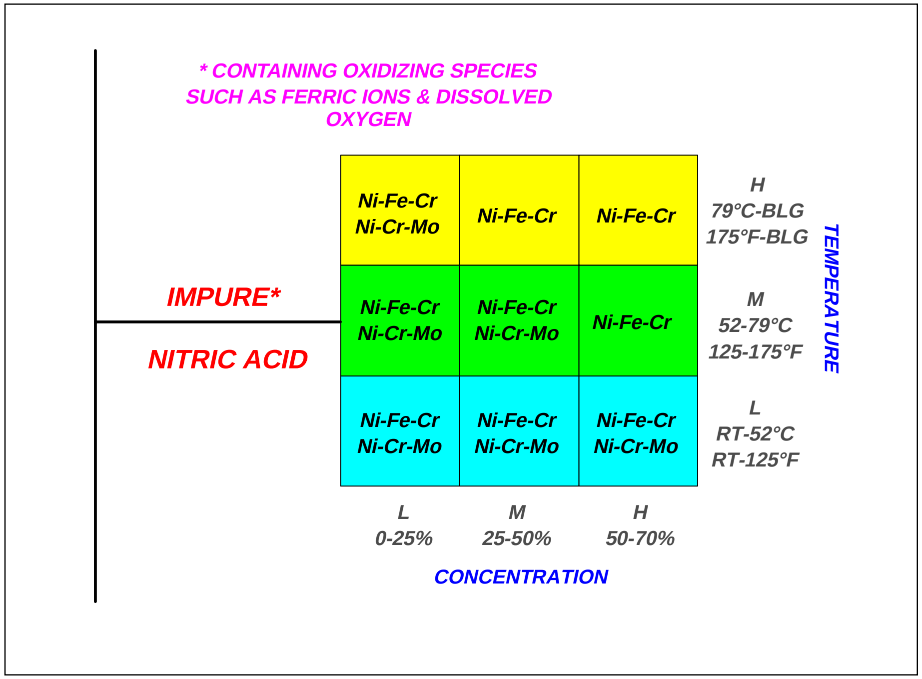
- C-2000® alloy has been tested extensively in pure phosphoric acid. The resulting iso-corrosion diagram, featuring a large "very safe" regime, is shown here.

NITRIC ACID



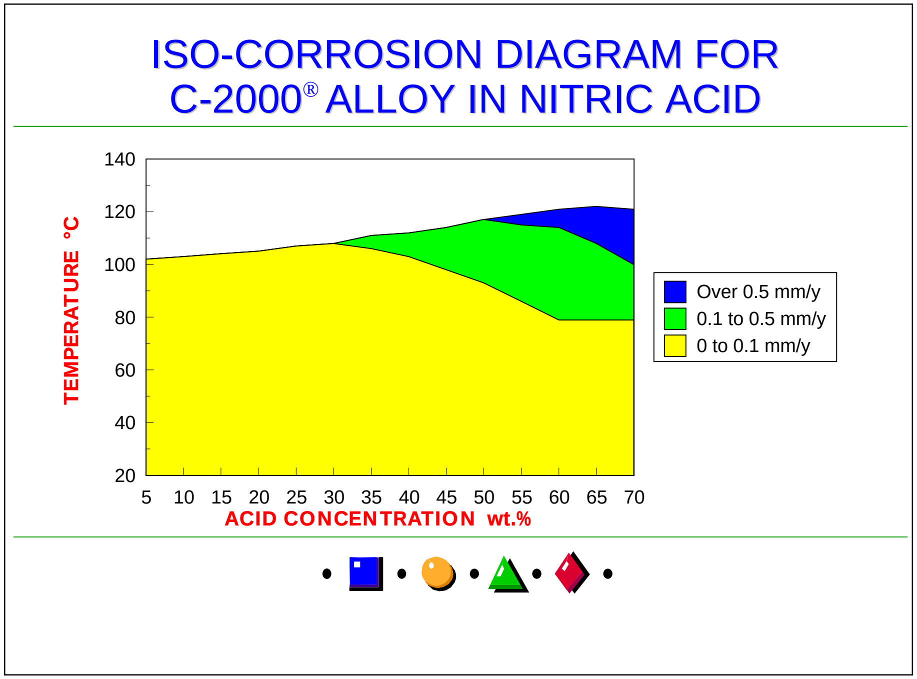
- Nitric is a strong, oxidizing acid. Since it readily provides passivation, therefore, chromium is an extremely beneficial alloying element in nitric acid solutions.
- In general terms, the stainless steels are more resistant to nitric acid than the chromium-bearing nickel alloys. However, there are occasions when nickel alloys are preferred, for example in heat exchangers (where the stainless steels might not possess sufficient pitting resistance on the cooling water side), in multiple-purpose chemical systems (where a batch process involving nitric acid might be followed by another involving a different acid), and in acid mixtures (where the second acid is corrosive to the stainless steels).

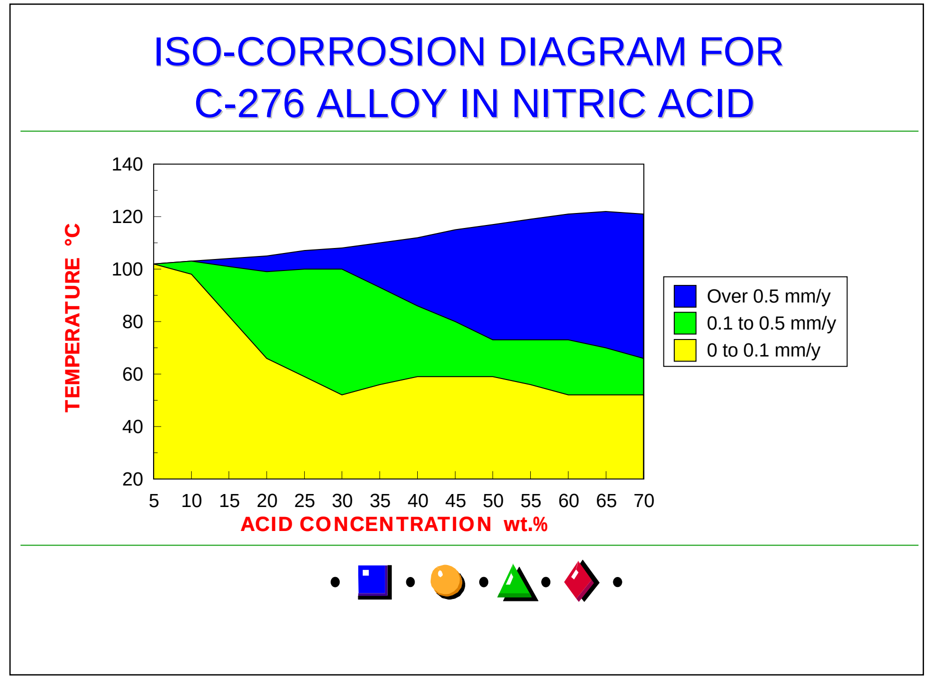




- In the case of nitric acid, the pure and impure branches of the decision tree are identical, and the only suitable materials are the nickel-iron-chromium and nickel-chromium-molybde-num alloys. Above is the pure branch.

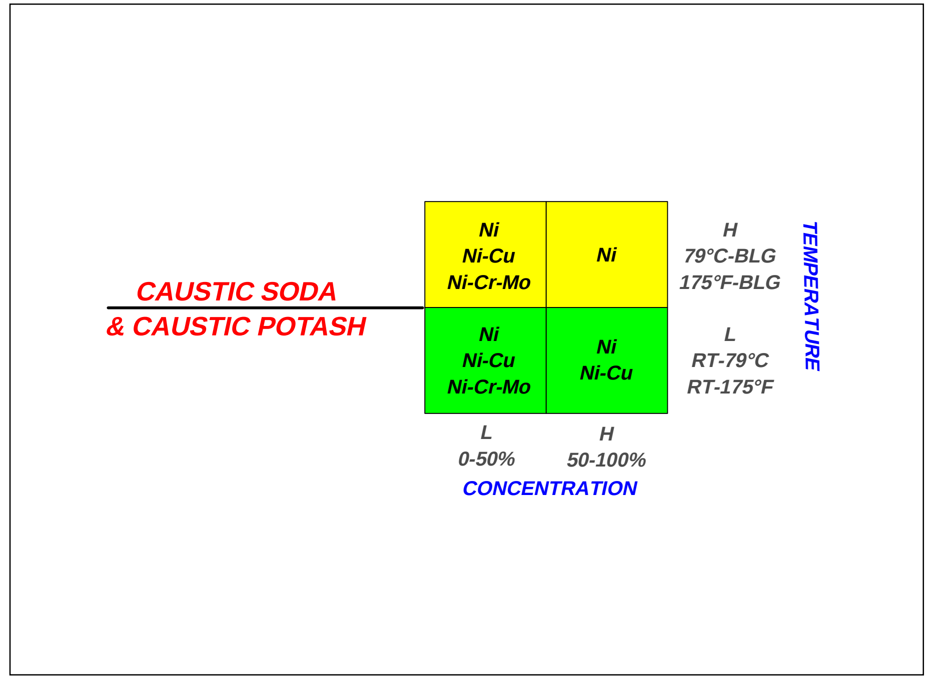
- Here is the impure branch, showing the same candidate materials.





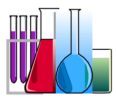
- As with phosphoric acid, enough data have been generated for C-2000® alloy to construct the iso-corrosion diagram. As can be seen, C-2000 alloy can be used very safely in nitric acid over wide ranges of concentration and temperature.

- This chart for C-276 alloy is included to indicate the strong effect of chromium content on the performance of the nickel-chromium-molybdenum alloys in nitric acid. With only 16 wt.% chromium, C-276 alloy possesses a much smaller useful range than C-2000® alloy, with a chromium content of 23 wt.%.



- This segment concerns the alkalis, in particular sodium hydroxide and potassium hydroxide, otherwise known as caustic soda and caustic potash, respectively.
- Nickel 200 alloy is pre-eminent among the material choices for elevated temperature caustic soda. It exhibits corrosion rates of less than 0.025 mm/y in boiling solutions up to a concentration of about 50 wt.% and is very resistant to caustic stress cracking, to which the highly-alloyed nickel alloys are susceptible at high temperatures. Commercially pure nickel is also outstanding in caustic potash.
- Using two concentration ranges and two temperature ranges, this simplified diagram has been used to indicate the choices of material in caustic soda and potash. As well as nickel itself, the nickel-copper alloys and the nickel-chromium-molybdenum alloys have useful resistance to these commonly used alkalis.
- In ammonium hydroxide, another industrially important alkali, commercially pure nickel and the nickel-copper alloys are not recommended, whereas most other nickel alloys resist all concentrations of ammonium hydroxide up to the boiling points.

SALTS



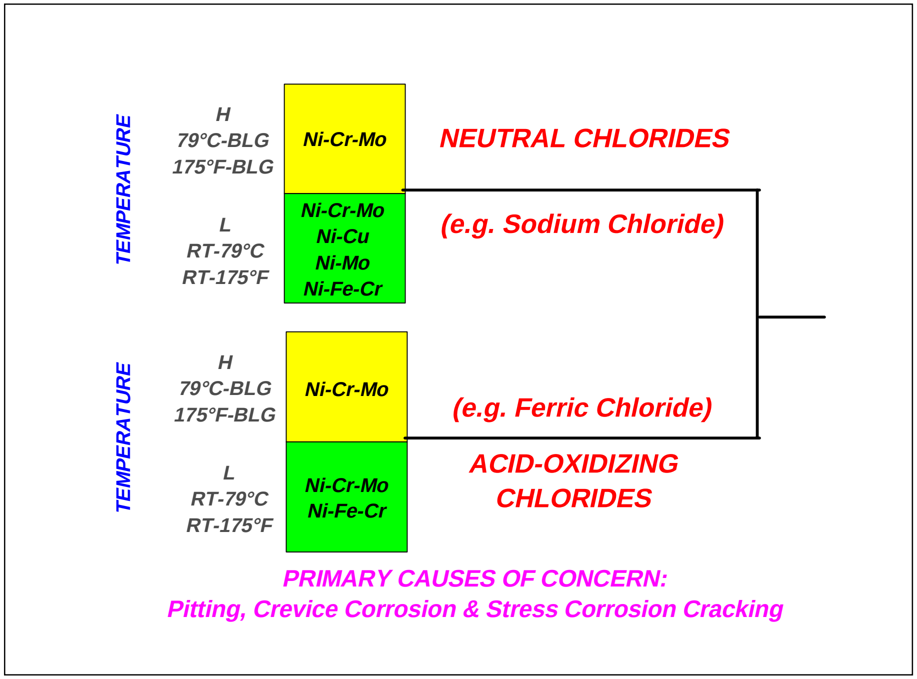
▶ The final segment of this package deals with corrosive salts. Again, the focus will be the inorganic salts, in particular those with a halogen component.

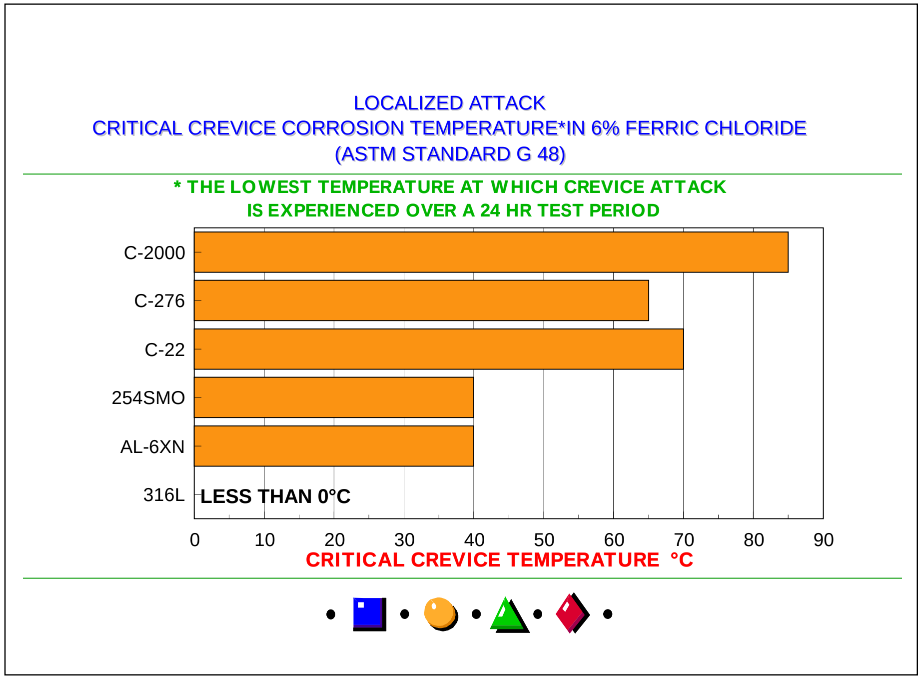
CLASSIFICATION OF SALTS BY CORROSION CHARACTERISTICS

CHARACTERISTIC pH	HALIDE	NON-HALIDE
Neutral	Sodium Chloride Potassium Chloride	Sodium Sulfate Potassium Sulfate
Neutral & Alkaline-Oxidizing	Sodium Hypochlorite Calcium Hypochlorite	Sodium Nitrate Sodium Nitrite Potassium Permanganate
Acid	Magnesium Chloride Potassium Fluoride	Potassium Bisulfate Ammonium Sulfate Aluminum Sulfate
Acid-Oxidizing	Cupric, Ferric, Mercuric, Stannic Chloride	Cupric, Ferric, Mercuric Nitrate or Sulfate
Alkaline	-	Sodium & Potassium Phosphates, Carbonates

▶ This chart, which was taken from the literature of Special Metals, is a classification of the inorganic salts based on pH.

▶ The most commonly encountered corrosive salts are the neutral and acid-oxidizing chlorides. They are a problem, not because they induce highly uniform corrosion rates, but because they induce other forms of corrosion, such as pitting, crevice attack, and stress corrosion cracking. Sodium chloride is, of course, prevalent in the cooling waters used at shoreline sites.





- In regard to the neutral and acid-oxidizing chlorides on the decision tree, concentration has been de-emphasized and temerature has been used as the differentiaing factor in the choice of candidate materials.
- As can be seen, only the nickel-chromium-molybdenum alloys have been selected for high temperatures, and the chromium-free alloys have been omitted from the acid-oxidizing branch.
- In support of these selections, and to provide perspective, here are the lowest temperatures at which crevice attack is experienced (over a 24 hr test period) in 6% ferric chloride, for three of the nickel-chromium-molybdenum alloys and three stainless steels (AL-6XN® alloy being another 6 wt.% molybdenum, austenitic material).
- Note the effectiveness of molybdenum in the austenitic stainless steels (both AL-6XN and 254SMO® alloys contain 6% molybdenum, as opposed to 2.5% in the case of alloy 316L). Also note the outstanding resistance of the nickel-chromium-molybdenum alloys to this form of attack.

TIME TO CRACKING OF U-BEND SAMPLES IN BOILING 45% MAGNESIUM CHLORIDE
(ASTM STANDARD G 36)

ALLOY	TIME TO CRACKING
316L Stainless Steel	2 hr
AL-6XN®	24 hr
254SMO®	24 hr
C-22®	No Cracking after 1008 hr
C-276	No Cracking after 1008 hr
C-2000®	No Cracking after 1008 hr

- As indicated by these test results the nickel-chromium-molybdenum alloys also possess outstanding resistance to stress corrosion cracking, relative to the stainless steels. Even after the maximum test time of six weeks, none of the nickel-chromium-molybdenum alloys cracked in this boiling acid chloride.

SUMMARY

- Most corrosion-resistant nickel alloys possess high resistance to chloride-induced stress corrosion cracking, and many exhibit high resistance to localized attack
- Many resist the aggressive reducing acids, and some also resist oxidizing acids
- They can be classified into 6 main groups
- Group members can have significantly different performance characteristics
- A guide has been provided for candidate materials in specific acids, alkalis, and salts

- In summary, there are nickel alloys available for nearly every corrosion situation. Some are extremely versatile and ideal for chloride-bearing process streams where pitting, crevice attack, and stress corrosion cracking are of concern.
- To simplify selection, this package groups the nickel alloys according to their main alloying elements, and a guide to alloy performance in many of the aggressive inorganic chemicals has been provided.
- With regard to alternate materials, the nickel alloys fall in a higher performance band than the (austenitic and duplex) stainless steels. They are generally more resistant to reducing acids and they withstand the forms of attack induced by chlorides. Relative to the titanium and zirconium alloys, which fall within the same performance band, they are much more tolerant of certain chemicals, in particular fluoride ions.

HASTELLOY® Family of Corrosion-Resistant Alloys

HASTELLOY B-2 alloy (N10665)	69Ni[a]-28Mo-2Fe*-1Co*-1Cr*-1Mn*-0.1Si*-0.01C* Superior resistance to hydrochloric acid, aluminum chloride catalysts, and other strongly reducing chemicals.
HASTELLOY B-3® alloy (N10675)	65Ni[b]-28.5Mo-1.5Cr-1.5Fe-3Co*-3Mn*-3W*-0.5Al*-0.2Ti*-0.1Si*-0.01C* Same excellent resistance to hydrochloric acid and other strongly reducing chemicals as B-2 alloy, but with significantly better thermal stability, fabricability, and stress corrosion cracking resistance.
HASTELLOY C-4 alloy (N06455)	65Ni[a]-16Cr-16Mo-0.7Ti-3Fe*-2Co*-1Mn*-0.08Si*-0.01C* High-temperature stability in the 1200-1900°F (650-1040°C) range as evidenced by good ductility and corrosion resistance. Virtually the same corrosion resistance as alloy C-276.
HASTELLOY C-22® alloy (N06022)	56Ni[a]-22Cr-13Mo-3Fe-3W-2.5Co*-0.5Mn*-0.35V*-0.08Si*-0.01C* Better overall corrosion resistance in oxidizing corrosives than C-4, C-276, and 625 alloys. Outstanding resistance to localized corrosion and excellent resistance to stress corrosion cracking. Best alloy to use as universal weld filler metal to resist corrosion of weldments.
HASTELLOY C-276 alloy (N10276)	57Ni[a]-16Cr-16Mo-5Fe-4W-2.5Co*-1Mn*-0.35V*-0.08Si*-0.01C* Versatile, corrosion resistant alloy. Very good resistance to reducing and mildly oxidizing corrosives. Excellent stress corrosion cracking resistance with very good resistance to localized attack.
HASTELLOY C-2000® alloy (N06200)	59Ni[a]-23Cr-16Mo-1.6Cu-0.08Si*-0.01C* Most versatile, corrosion resistant alloy with excellent resistance to uniform corrosion in oxidizing or re-ducing environments. Excellent resistance to stress corrosion cracking and superior resistance to localized corrosion as compared to C-276 alloy.
HASTELLOY D-205™ alloy	65Ni[a]-20Cr-6Fe-5Si-2.5Mo-2Cu-0.03C* Outstanding resistance to hot concentrated sulfuric acid and other highly concentrated oxidizing acid media.
HASTELLOY G-30® alloy (N06030)	43Ni[a]-30Cr-15Fe-5.5Mo-2.5W-5Co*-2Cu*-1.5Cb*-1.5Mn*-1Si*-0.03C* Many advantages over other metallic and non-metallic materials in handling phosphoric acid, sulfuric acid, nitric acid, fluoride environments, and oxidizing acid mixtures.
HASTELLOY N alloy (N10003)	71Ni[a]-16Mo-7Cr-5Fe*-1Si*-0.8Mn*-0.5W*-0.5(Al+Ti)*-0.35Cu*-0.2Co*-0.08C* Good resistance to aging and embrittlement plus good fabricability. Excellent resistance to hot fluoride salts in the temperature range of 1300°F to 1600°F (705°C-870°C).

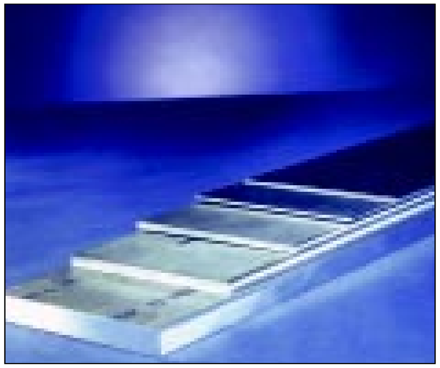
Corrosion-Wear Resistant Alloy

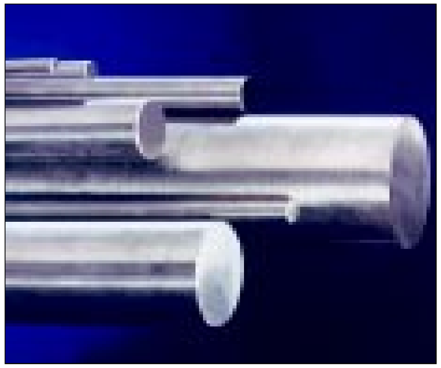
ULTIMET® alloy (R31233)	54Co[a]-26Cr-9Ni-5Mo-3Fe-2W-0.8Mn-0.3Si-0.08N-0.06C High yield-strength alloy with excellent resistance to pitting corrosion and general corrosion, especially in oxidizing acids, plus exceptional wear resistance (cavitation erosion, galling, and abrasion).

[a] As balance * Maximum

Properties Data:

The data and information in this publication are based on work conducted principally by Haynes International, Inc. and occasionally supplemented by information from the open literature, and are believed to be reliable. However, Haynes International does not make any warranty or assume any legal liability or responsibility for its accuracy, completeness, or usefulness, nor does Haynes International, Inc. represent that its use would not infringe upon private rights. Any suggestions as to uses and applications for specific alloys are opinions only and Haynes International, Inc. makes no warranty of results to be obtained in any particular situation. For specific concentrations of elements present in a particular product and a discussion of the potential health effects thereof, refer to the Material Safety Data Sheet supplied by Haynes International, Inc.





For More Information Contact:

North American Service Centers

Midwest Service Center
1020 W. Park Avenue
P.O. Box 9013
Kokomo, Indiana 46904-9013
Tel: 765-456-6012
800-354-0806
Fax: 765-456-6905

Eastern Service Center
430 Hayden Station Road
Windsor, Connecticut
06095
Tel: 860-688-7771
800-426-1963
Fax: 860-688-5550

Southern Service Center
The Northwood Industrial Park
12241 FM 529
Houston, Texas 77041
Tel: 713-937-7597
800-231-4548
Fax: 713-937-4596

Western Service Center
Stadium Plaza
1520 South Sinclair Street
Anaheim, California 92806
Tel: 714-978-1775
800-531-0285
Fax: 714-978-1743

Tubular Products
3786 Second Street
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