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INDUSTRIAL EXPERIENCE ON THE CAUSTIC CRACKING OF STAINLESS STEELS AND NICKEL ALLOYS - A REVIEW

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ABSTRACT

Caustic environments are present in several industries, from nuclear power generation to the fabrication of alkalis and alumina. The most common material of construction is carbon steel but its application is limited to a maximum temperature of approximately 80°C. The use of Nickel (Ni) alloys is recommended at higher temperatures. Commercially pure Ni is the most resistant material for caustic applications both from the general corrosion and the stress corrosion cracking (SCC) perspectives. Nickel rich alloys also offer a good performance. The most important alloying elements are Ni and chromium (Cr). Molybdenum (Mo) is not a beneficial alloying element and it dissolves preferentially from the alloy in presence of caustic environments. Austenitic stainless steels such as type 304 and 316 seem less resistant to caustic conditions than even plain carbon steel. Experimental evidence shows that the most likely mechanism for SCC is anodic dissolution.

Keywords: Environmentally Assisted Cracking, Nickel Alloys, Stainless Steels, Caustic Cracking

INTRODUCTION

Environmentally Assisted Cracking (EAC) is a general term that includes events such as stress corrosion cracking (SCC), hydrogen embrittlement (HE), sulfide stress cracking (SSC), liquid metal embrittlement (LME), corrosion fatigue (CF), etc. EAC refers to a phenomenon by which a normally ductile metal looses its toughness (e.g. elongation to rupture) when it is subjected to mechanical tensile stresses in presence of a specific corroding environment. For EAC to occur, three affecting factors must prevail simultaneously. These are: (1) Mechanical tensile stresses, (2) A susceptible metal microstructure and (3) A specific aggressive environment. If any of these three factors is removed, EAC will not occur. This is the method that many design engineers use to mitigate the occurrence of EAC, for example, by eliminating residual stresses in a component or, by limiting the application of the component to certain non-aggressive chemicals (environment). The term environment not only includes the chemical composition of the solution in contact with the component but also other variables such as temperature and the redox potential in the system.

CORROSION PROPERTIES OF STAINLESS STEELS AND NICKEL ALLOYS

Stainless steels and nickel alloys, the same as other alloys, may suffer two main types of corrosion, uniform corrosion and localized corrosion. Uniform corrosion may happen under reducing conditions in the active region of potentials and also under oxidizing conditions in the form of a slow passive dissolution. Localized corrosion such as pitting and crevice corrosion generally occurs under oxidizing conditions. Stress corrosion cracking (SCC) or environmentally induced cracking could occur at any electrochemical potential range. In many alloy systems, SCC is also associated to specific potential windows, for example, in the anodic region above a critical potential of in the cathodic region, also below a threshold potential.

Stainless steels and nickel (Ni) alloys are extensively used in chemical process and other industries where aggressive environments could be found. These alloys resist to aggressive solutions mainly by the presence of passive films, which slow down the rate of corrosion. For example, in nitric acid (HNO_3), alloys with a high content of chromium (Cr) (e.g. N06030) are the recommended alloys since chromium oxide (Cr_2O_3) is stable in oxidizing acidic conditions. In reducing conditions, such as hot hydrochloric acid (HCl) solutions, a recommended alloy should contain an important proportion of molybdenum (Mo). In hot HCl solution, Cr_2O_3 is not stable. [1]

In general, individual nickel alloys can be more resistant to general and localized corrosion than stainless steels, basically because nickel can dissolve a larger amount of alloying elements than iron (Fe) and therefore nickel alloys can be tailored to more specific applications. This is particular true in the case of hot HCl in which a large amount of Mo is needed. Nickel alloys of the B family which contain up to 28% Mo are the recommended alloys for HCl. Stainless steels can contain only a maximum of 6-7% Mo. The same can be said relating resistance to localized corrosion such as pitting corrosion and crevice corrosion in chloride (Cl^-) containing environments. The beneficial elements protecting against localized corrosion induced by chloride ions are Cr and Mo. The factor of protection is called the pitting resistance equivalent (PRE) and is generally defined as $PRE = Cr + 3.3\ Mo$ where the element symbols represent the weight percent of the element in the alloy. Nitrogen (N) and tungsten (W) are also a beneficial elements against localized corrosion and a modified factor can be defined as $PREN = Cr + 3.3\ (Mo + 0.5\ W) + 16\ N$. The higher the PRE the more resistant the alloy to chloride promoted localized corrosion. The maximum PRE that can be reached with austenitic wrought stainless steels is approximately 45 (e.g. in N08367) but with wrought nickel alloys, the high PRE factors can be in the order of 76 (e.g. N06059).

In general nickel alloys are more resistant than stainless steels to EAC. Austenitic stainless steels (such as S30400) suffer SCC in presence of hot aqueous solutions containing chloride ions. Since chloride ions are ubiquitous in most industrial applications, the use of stainless steels components containing sometimes only minimal residual stresses is seriously limited because of the chloride cracking. On the other hand, nickel alloys (such as C-276) are to all intents and purposes immune to SCC in presence of hot chloride solutions and therefore an excellent alternative to replace the troubled austenitic stainless steels. Nickel alloys may be prone to EAC in other environments such as hot caustic and hot wet hydrofluoric acid. [2,3] In other environments such as hot caustic solutions, both stainless steels and nickel alloys are prone to EAC (Table 1).

THE FAMILIES OF STAINLESS STEELS AND NICKEL ALLOYS

Stainless Steels (SS) are solid solutions of the element iron (Fe). The alloying with Cr makes them stainless, by the development of a Cr_2O_3 film on the surface. Commercial stainless steels can generally divided in four large groups: (1) Martensitic and Ferritic, (2) Austenitic and (3) Superaustenitic and (4) Duplex (Table 2). [4-7] The content of Cr in the stainless steels varies from approximately 12% in the martensitic to approximately 30% in some ferritic. Some austenitic steels contain Mo, Copper (Cu), N and other elements for enhanced corrosion performance (Table 2). Mo and N are added for resistance to localized corrosion such as pitting and crevice corrosion. Cu is generally added to offer protection in sulfuric acid (H_2SO_4) and hydrofluoric acid (HF). The microstructure of ferritic steels is body centered cubic (bcc) and of the austenitic is face centered cubic (fcc). The duplex stainless have both microstructures, approximately 50% of each one. Age hardenable steels have second phases for extra strength. The ductility of the stainless steels can vary from less than 5% for the martensitic to approximately 40% for the austenitic. The strength (UTS) can vary from less than 500 MPa for some ferritic and austenitic to more than 1000 MPa for the martensitic and age hardenable.

Nickel-based alloys are solid solutions based in the element nickel (Ni). There are two large groups of the commercial Ni-based alloys. One group was designed to withstand high temperature and dry or gaseous corrosion while the other is mainly dedicated to low temperature (aqueous) applications. Nickel based alloys used for low temperature aqueous or condensed systems are generally known as corrosion resistant alloys (CRA) and nickel alloys used for high temperature applications are known as heat resistant alloys (HRA) or high temperature alloys (HTA). The practical industrial boundary between high and low temperature nickel alloys is in the order of 500°C (or approximately 1000°F). There are five basic families of corrosion resistant Ni alloys (Table 2): (1) Commercially pure Ni, (2) Ni-Copper (Cu) alloys, (3) Ni-Mo Alloys, (4) Ni-Cr-Mo Alloys and (5) Ni-Cr-Fe Alloys. Even though Ni-based alloys in general contain a large proportion (sometimes up to 50%) of other alloying elements, nickel alloys still maintain the face centered cubic lattice (fcc) or austenitic microstructure from the Ni base element. As a consequence of the austenitic structure, nickel based alloys have excellent ductility, malleability and formability. Nickel alloys are also readily weldable.

CAUSTIC ENVIRONMENTS IN THE INDUSTRY

Caustic or strongly alkaline environments are rather common in the industry. They refer usually to highly concentrated solutions of sodium hydroxide (NaOH) or caustic soda, potassium hydroxide (KOH) or caustic potash and calcium hydroxide ($Ca(OH)_2$) or caustic lime. [8] High temperature caustic environments containing sometimes over 50% of alkalis are found in many industries including the fabrication of alkalis, oil refineries, pulp and paper and the process of alumina. [8]

In the Bayer process of producing alumina, bauxite is dissolved with hot caustic soda to produce sodium aluminate. [9] This mixture may also contain other species such as carbonate (CO_3^{2-}), sulfide (S^{2-}) and sulfate (SO_4^{2-}).

Gibbsite: $Al(OH)_3 + Na^+ + OH^- \;=====\; Al(OH)_4^- + Na^+$
Böhmite and Diaspore: $AlO(OH) + Na^+ + OH^- + H_2O \;=====\; Al(OH)_4^- + Na^+$

In the Bayer process the NaOH concentration is generally 10-15% and the temperatures can range from 140°C to 240°C, depending on the chemical composition of the mineral bauxite. The pressure can as high as 35 atmospheres. If the bauxite is monohydrate, which is more difficult to dissolve, the NaOH concentration could be as high as 30%, the temperature 300°C and the pressure 150 atm. [9]

The term chlor-alkali refers to the two chemicals (chlorine and an alkali), which are simultaneously produced as a result of the electrolysis of a saltwater. [10] There are 3 types of electrolytic processes used in the production of chlorine: (1) the diaphragm cell process, (2) the mercury cell process, and (3) the membrane cell process. In each process, a salt solution is electrolyzed by the action of direct electric current that converts chloride ions to elemental chlorine. The overall process reaction is

$$2\ NaCl + 2\ H_2O\ \ ===== \ \ Cl_2 + H_2 + 2\ NaOH$$

In all 3 methods, the chlorine (Cl_2) is produced at the positive electrode (anode) and the caustic soda (NaOH) and hydrogen (H_2) are produced, directly or indirectly, at the negative electrode (cathode). The 3 processes differ in the method by which the anode products are kept separate from the cathode products. For example, in the mercury cell process, sodium is amalgamed with mercury in the cathode. The amalgam is then washed with water to produce NaOH. The NaOH slurry product generally has a concentration of 30% and a temperature just above 100°C. The NaOH product can be concentrated further to 50% through the purging with steam in a vacuum evaporator.

Sodium hydroxide electrolytes are used in petroleum refining to remove hydrogen sulfide (H_2S) gas and mercaptans from many hydrocarbon streams. The resulting sulfide-laden waste stream is called spent-sulfidic caustic. [11,12] In the refining industry low molecular weight mercaptans are solubilized and therefore in caustic soda (NaOH), during the treating feedstocks such as natural gases and refinery gases.

$$RSH + NaOH\ \ ====== \ \ NaSR + H_2O$$

Extraction equilibrium is favored by lower molecular weight mercaptans and lower temperatures. The rich caustic containing the extracted mercaptans in the form of sodium mercaptides, is regenerated as shown in the equation given below:

$$4\ NaSR + O_2 + 2\ H_2O\ \ ====== \ \ 2\ RSSR + 4\ NaOH$$

For example, in ethylene production, ethane, propane or naphtha gas is cracked in a furnace, forming carbon dioxide (CO_2) and hydrogen sulfide (H_2S) byproducts. A caustic scrubbing tower removes these byproducts, which are absorbed out of the gas phase and into the caustic solution. Over time, the caustic material becomes spent. Refineries generate three types of spent caustic materials – sulfidic, naphthenic and cresylic. The three are often mixed together before disposal. Sulfidic spent caustic comes from caustic washing liquid propane gas for sulfur removal and can be treated much like ethylene spent caustic. Naphthenic spent caustic results from the treatment of diesel and jet fuels for sulfur and naphthenic acid removal. Cresylic spent caustic comes from the treatment of gasoline for sulfur and cresylic acid removal. Crude caustic can contain approximately 2% hydroxide at a temperature of 260°C.

The pulp and paper industry is the largest consumer of caustic soda worldwide. Uses include the de-inking of waste paper and water treatment, as well as the raw material in the pulping and bleaching treatments of wood (cellulose). In the Kraft pulping process a caustic soda solution is pumped to large chambers where it is mixed with wood chips under heat and pressure. The caustic attacks the lignin to release the cellulose and in the process it is converted to sodium carbonate (Na_2CO_3).

Caustic soda is also frequently used in the saponification or conversion of fat, tallow and vegetable oils in the soap manufacturing process. The largest use of caustic soda in detergents is in the manufacture of anionic surfactants. In the chemical process industry (CPI) caustic soda is a basic ingredient as an intermediate and as a reactant in processes that produce solvents, plastics, synthetic fabrics, adhesives, coatings, herbicides, dyes, inks, pharmaceuticals, and many other industrial products. Caustic soda is in addition used for the neutralization of low pH waste streams and the scrubbing of acidic components of flue gases.

MATERIALS FOR HANDLING CAUSTIC SOLUTIONS IN THE INDUSTRY

The most common material to handle caustic environments is carbon steel if the contamination by iron can be tolerated. Carbon steels suffer high corrosion rates at temperatures above 80°C and caustic cracking maybe expected. [8] Ni containing carbon steels may be used for a wider and more aggressive ranges of caustic applications. The caustic cracking of carbon steels may be mitigated by stress relieving after fabrication. [8] The use of carbon steels or mild steels is recommended for applications up to 50% NaOH and temperatures as high as 66°C. [13] In spite of the cracking problems, carbon steel is the preferred material for alumina processing vessels such as digesters, decomposers and precipitators. [14] Slow strain rate tests (SSRT) were carried out using A516 carbon steel in pure 2.25 M NaOH and in several other caustic solutions containing impurities such as carbonate, aluminate, silicate and sulfate at 100°C. It was shown that the presence of impurities such as aluminate increases the cracking susceptibility of the carbon steel by making the passive film less protective. [14-15] SSRT was performed at several strain rates using mild steel specimens in presence of 4.65 M NaOH + 1.9 M Al_2O_3 at 90°C and 150°C. [16] Cracking was found in this caustic solution only at 150°C at the low strain rate of 0.12 and 0.24 x 10^{-6} s^{-1} was used. When EAC occurred the brittle fracture was intergranular. At 90°C, at all the investigated strain rates, the fracture was mechanical. At 150°C and at 0.4 x 10^{-6} s^{-1} and higher strain rates the fracture was also mechanical (no environmental impact). [16]

Stainless steels such as austenitic types 304 (S30400) and 316 (S31600) seem even less reliable than carbon steel for caustic service. The application limits for the austenitic SS are 50% caustic and 70°C to 90°C. [8,13] The 300 series of SS also suffer caustic cracking at temperatures above 100°C. [8,13] The cracking susceptibility of either 304 or 316 SS is the same and sensitization does not seem to play a role. [13] Likely applications of stainless steels for caustic service include piping, valves, pumps and equipment. Problems rarely occur when the NaOH concentration is limited to 10-20%. [17]

NACE International prepared the Standard Recommended Practice RP0403-2003 for avoiding caustic stress corrosion cracking of carbon steel refinery steel and piping. [18] This recommendation includes the Caustic Soda Service Chart. This chart allows non-stress relieved carbon steel to be used for caustic service up to 140°F (60°C) for NaOH concentrations up to 30% (Area A in the Chart). Stress-relieved carbon steel is recommended to be used in conditions delineated by Area B. The maximum temperature for Area B is approximately 230°F (110°C) at 20% NaOH and decreases to approximately 170°F (~80°C) at 50% NaOH. In the Area C, for temperatures higher than 110°C, only nickel alloys are recommended for all concentration of caustic soda. [18]

The best metallic material overall to handle caustic solutions at all concentration and temperatures is Ni-200 (N02200) (Table 2). Ni-200 can be used even in molten anhydrous NaOH at temperatures as high as 538°C (1000°F). Figure 1 shows the general corrosion rate by weight loss of several alloys of interest. [1,19] The higher the Ni content the lower the corrosion rate. Ni-200 may be still slightly susceptible to caustic cracking but mainly at temperatures higher than 300°C. [8] Others consider Ni-200 practically immune to caustic cracking. [13] Other high nickel alloys such as Alloy 600 (N06600) can also be used to handle hot caustic environments but after prolonged service it will also develop cracks. [8] Other Ni alloys such as C-276 or B-2 may not be recommended since they suffer dealloying by the preferential dissolution of Mo.

LABORATORY TESTING FOR ENVIRONMENTAL CRACKING OF STAINLESS STEELS AND NICKEL ALLOYS

The environmental cracking susceptibility of Alloys 800 (N08800), 600 (N06600) and 690 (N06690) (Table 2) in caustic solutions was studied in some detail over the last thirty years due to the application of these nickel alloys as tubing materials for the steam generators in nuclear power plants. [20,21] In the secondary side of the steam generator caustic solutions may develop, at temperatures in the vicinity of 300°C. In general in hot high purity water (primary side) at approximately 300°C, Alloy 690 is more resistant to environmentally assisted cracking than Alloy 600. Welded C-ring specimens of Alloy 690 exposed to primary water at 348°C were free from cracking. However, other C-ring specimens exposed to 10% NaOH at 348°C suffered intergranular cracking. [22] When cracking occurs, more cracks were found in the base metal than in the weld seam. [22] In caustic solutions at high temperatures (>250°C) Alloy 690 seems to be more susceptible to cracking than Alloy 600. [21] Alloy 600 contains approximately 14% more Ni than Alloy 690, which could provide the additional resistance to cracking in caustic environments. Thermally treated (TT) Alloy 690 (which contains carbides at the grain boundaries) is more resistant to cracking than mill-annealed (MA) Alloy 690. [21] When TT Alloy 690 tends to suffer cracking, the mode of attack is transgranular rather than intergranular as in the MA condition. [23]

The presence of inhibitors (such as TiO_2 and CeB_6) seem to decrease the susceptibility of Alloy 600 to cracking even in aggressive conditions such as 40% NaOH at 315°C. [21,23-24] The inhibition of cracking is also related to a decrease in the anodic corrosion current. The presence of other species in solution such as lead oxide (PbO) and sodium tiosulfate ($Na_2S_2O_3$) seem to be detrimental, that is, the accelerate the occurrence of cracking. [21] The caustic cracking of Alloy 600 is also influenced by the temperature and the applied stress. [21, 25]

Caustic cracking of Alloys 800, 600 and 690 is also strongly dependent on applied potential. [21,23,26-28] The maximum susceptibility for cracking seems to occur at approximately 200 mV more positive than the corrosion potential (E_{corr}) in deaerated conditions. [21] It has been suggested that the transition between the region of potentials in which Alloy 600 is susceptible to cracking to a region in which Alloy 600 is not susceptible to cracking is related to the type of oxide film formed on the metal surface. [26] In a 10% NaOH solution at 315°C cracking occurred in Alloy 600 only when p-type films were found but when n-type films formed, the alloy did not suffer cracking.

Rondelli et al. did a methodical study of the variables affecting caustic cracking of both Ni alloys and stainless steels. [29-31] Most of their tests were carried out in solutions that can be found in the production of alumina. Rondelli et al. performed slow strain rate tests of specimens made of austenitic and duplex stainless steels 200 g/L NaOH + 10 g/L NaCl at 200-250°C. [29] They reported that duplex stainless steels are more resistant to caustic cracking than austenitic stainless steels. [29] Mo was a detrimental alloying element for caustic cracking. [29] They also reported that a small amount of Ni in the steel may be detrimental but when the amount of Ni reached near 30% the resistance of the steels to cracking greatly increased. [29] This finding is very similar to the behavior of austenitic stainless steels in magnesiumchloride ($MgCl_2$) solutions (Copson curve). [32] Rondelli et al. also performed slow strain rate tests of Type 316 SS, 904L and a duplex SS in a solution of 300 g/L NaOH at 200°C and in a similar solution containing also 20 g/L sodium sulfide ($Na_2S.9H_2O$). [30] They reported that sulfide increases the cracking susceptibility of the metals mainly because it increases their anodic dissolution current. [30] The susceptibility to cracking of S31600 was practically the same as for N08904 (Table 2), that is, an increase of Ni content from 12% in S31600 to 25% in N08904 did not produce an increase in caustic cracking resistance, suggesting that a minimum of 30% Ni may be necessary to mitigate EAC in caustic environments. [30] In a more recent paper, Rondelli and Vicentini published results from the SSRT of several alloys in 300 g/L NaOH solution at 200°C. [31] The studied alloys included: 904L, 825, 28 and 33 (Table 2). The order of increased resistance to cracking was N08904 < N08825 < N08028 < R20033. The most resistant alloy of the four tested to caustic cracking was Alloy 33 (R20033) and the authors suggested that it was due to its high content in Cr. [31] It is also likely that Mo, Fe and other alloys also played a role in the cracking behavior of these alloys. When sulfide was present in the caustic solution, even Alloy 33 suffered cracking. [31]

Caustic cracking of stainless steels is generally transgranular and caustic cracking of Ni alloys is generally intergranular. But both type of cracking can happen in both alloys. For example, the cracking of alloys 600 and 690 can be changed from intergranular in the mill-annealed condition to transgranular in the thermally treated condition.

DEALLOYING OF STAINLESS STEELS AND NICKEL ALLOYS

Stainless steels and nickel alloys suffer dealloying in hot caustic solutions. Alloying elements such as Mo and Cr dissolve preferentially, leaving behind a layer rich in Ni. [33-36] Anodic polarization of pure Fe, Ni and Cr specimens in argon deaerated 50% NaOH at 130°C shows that Fe and Cr would dissolve preferentially from a stainless material, while Ni would remain. [33] Foils of Type 316 SS were exposed to several concentrations of caustic soda up to 50% NaOH and at 140°C for 20 h to 40 h. After 20-h exposure Deakin et al. reported the existence of a dealloyed layer, which was rich in Ni and poor in Cr and Fe. [34] Coupons of several nickel alloys were exposed to 50% NaOH solutions at 107°C for 720 h. [35] After the exposure time, the coupons were weighed and also cross-sectioned to determine the depth of dealloying attack if any. The alloys included N02200, N06600, N10276, N06022, N06200 and N10675 (Table 2). Electrolyte solutions included pure NaOH and 50% caustic soda contaminated with oxidizing species such as 500 ppm ferric ions (Fe^{3+}), 1% sodium hypochlorite (NaOCl) and 1% sodium chlorate ($NaClO_3$). [35] Figure 2 shows the general corrosion rate of the six tested Nickel alloys in the four electrolytes. [35] The lowest corrosion rate corresponded to Ni-200 and the highest corrosion rate to N10675 (Ni-Mo Alloy). In general alloys containing large amount of Mo suffered high corrosion rates. Figure 3 shows the internal penetration of the sectioned coupons. The internal penetration varied from alloy to alloy. For Ni-200 the internal penetration was surface roughening. For Alloy 600 the internal penetration was surface roughening, cracks, fissures and intergranular attack. For C-276 and Alloy 22 the internal penetration was dealloying and some intergranular attack. For Alloy 2000 the internal penetration was also dealloying, intergranular attack and some roughening. For Ni-Mo (N10675) the internal penetration was dealloying. Results show that dealloying mainly occurred to alloys that had a high proportion of Mo. [35] Figure 4 shows the mode of attack in C-276. The outermost right layer is pure Ni and it was formed by re-precipitation of previously dissolved Ni. The second layer from the right is pure Ni leftover by the dealloying of Cr, Mo and W from the alloy matrix. In another series of tests, N10675, N06200 (Table 2) and the new Alloy 35 (59Ni-33Cr-8Mo) were tested side by side in 50% NaOH for 720 h. [36] The depth of internal attack (dealloying) increased as the temperature increased for N010675 and N06200. For N10675 dealloying started at 66°C but for N06200 dealloying only started at 79°C. Alloy 35 did not show attack in these caustic tests. [36] It is apparent again that Mo is the most likely element to suffer dealloying. Significant amounts of Cr seem to be beneficial for caustic service.

MECHANISM FOR CAUSTIC CRACKING

The evidence reported in the literature suggests that anodic dissolution is the most likely mechanism for the cracking of stainless steels and nickel alloys in caustic environments. Cracking seems to occur only in a particular window of potentials just above the open circuit potential in deaerated conditions. That is, EAC occurs when an active peak seems to exist in a potential-current curve. [26,33] The band of potential for EAC seems to be only in the order 200 mV wide. Furthermore, electrochemical measurements show that when a chemical species is added to the caustic environment and the dissolution peak increases in the active region of potentials, the susceptibility to cracking of the alloy also increases. [27,30] Likewise, if this species decreases the anodic peak in the active region, cracking susceptibility decreases (inhibition). [23,24] Baek et al. [28] showed that the SCC parameter (P_{SCC}) proposed by Fang and Staehle [37] is applicable to the behavior of Alloy 600 in 10% NaOH at 315°C. This parameter (P_{SCC}) is obtained by dividing the values of current from a fast potential scanning (1200 mV/min) by the values of current from a slow potential scanning (20 mV/min). High values of PSCC should show areas of susceptibility for caustic cracking. Baek et al. showed that the highest value of P_{SCC} was at 0.2 V where the SCC rate was the highest. [28]

Hydrogen effect was also proposed as a mechanism for EAC. [30] Even though several effects seem to direct us to hydrogen, it is unlikely that the hydrogen effect would be important considering that the environment is highly corrosive and that the stability of the oxide films on the surface are highly important for the corrosion resistance of the alloys. That is, it is difficult to accept an “internal” mechanism like hydrogen when there is plenty of “activity” at the metal solution interface. Another mechanism that has been suggested to explain the cracking of stainless steels and nickel alloys in caustic solutions is dealloying. [34] As it was mentioned before, dealloying does occur in certain alloys; however, it appears that it is not the presence of the dealloyed layer the one that induces cleavage in non-attacked base metal. Cracking susceptibility seems to be too close associated behavior to the anodic peak dissolution process to be ignored. Therefore, the preferential dissolution of a specific element seems to be the cause of cracking rather than the dealloyed layer left behind. Thirty year old evidence, based on the dissolution and cracking pattern of several engineering stainless alloys, showed that in deaerated caustic solutions Ni is the beneficial alloying element and that in mildly oxidizing conditions such as aerated caustic solutions both Ni and Cr play a protective role. [38]

SUMMARY

1. Caustic environments are found in many industries from nuclear power generation to the production of alkalis and alumina.

2. In the production of alkalis and alumina, carbon steel is the most ubiquitous alloy. Some pumps and valves may be made of nickel alloys.

3. Austenitic stainless steels such as type 304 and 316 seem to offer a poorer resistance than plain carbon steel. For protection a content of Ni higher than 30% may be needed.

4. Commercially pure Ni is the most resistant material to both general corrosion and to environmentally assisted cracking (EAC) or stress corrosion cracking (SCC).

5. Under mild oxidizing conditions both Ni and Cr are important alloying elements. Mo is a detrimental alloying element. Alloys containing an important amount of Mo (such as C-276) would suffer dealloying especially under mildly oxidizing conditions.

6. The occurrence of SCC seems to be associated to the presence of an anodic peak in the active region of potentials. Anodic dissolution seems to be the governing mechanism for caustic cracking.

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DISCLAIMER

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TABLE 1

ENVIRONMENTS THAT MAY CAUSE ENVIRONMENTALLY ASSISTED CRACKING OF STAINLESS STEELS AND NICKEL ALLOYS

Alloys	Environments that May Cause Cracking
Stainless Steels	Hot Chloride, Hot Caustic, etc.
Nickel Alloys *	Hot Caustic, Wet Hydrofluoric Acid, etc.
*A more detailed list is available in Reference 3	

TABLE 2

APPROXIMATE CHEMICAL COMPOSITION AND TYPICAL MECHANICAL PROPERTIES OF STAINLESS STEELS AND NICKEL ALLOYS

Alloy	**UNS**	**Approximate Composition**	**YS 0.2% (MPa)**	**UTS (MPa)**	**ETF (%)**
		Stainless Steels			
410[A]	S41000	86Fe-12Cr-1Mn-1Si-0.10C	965	1241	15
440C[A]	S44004	80Fe-17Cr-1Mn-1Si-1C	1896	1965	2
17-4 PH [B]	S17400	74Fe-16Cr-4Ni-4Cu-1Mn-1Si-0.3Nb	1275	1378	14
430	S43000	83Fe-17Cr-0.12C	205	450	22
Sea-Cure	S44660	67Fe-27.5Cr-3.4Mo-1.7Ni-0.4Ti-0.02C	450	585	18
AL 29-4C	S44735	66Fe-29Cr-4Mo-1Ni-0.03C	415	550	18
304	S30400	72Fe-19Cr-9Ni-0.08C	205	515	40
316	S31600	71Fe-17Cr-12Ni-2.5Mo-0.03C	205	515	40
AL-6XN	N08367	46Fe-21Cr-24Ni-6.5Mo-2Mn-0.22N-0.03C	310	655	30
254 SMO	S31254	55Fe-20Cr-18Ni-6.3Mo-1Mn-0.2N-0.02C	310	655	35
20Cb-3	N08020	37Fe-20Cr-35Ni-2.5Mo-2Mn-3.5Cu-0.07C	241	551	30
28	N08028	34Fe-27Cr-32Ni-3.5Mo-2.5Mn-1Cu-0.03C	215	500	40
904L	N08904	46Fe-21Cr-25Ni-4.5Mo-2Mn-1.5Cu-0.1N-0.02C	215	490	35
2205	S31803	69Fe-22Cr-5.5Ni-3Mo-0.14N-0.03C	450	620	25
255	S32550	64Fe-25Cr-6Ni-3.3Mo-2Cu-0.2N-0.04C	550	760	15
2507	S32750	69Fe-25Cr-7Ni-4Mo-0.28N-0.03C	550	795	15

TABLE 2 - CONTINUED

Nickel Alloys

200	N02200	99Ni-0.2Mn-0.2Fe	190	450	50
400	N04400	67Ni-31.5 Cu-1.2Fe	270	540	43
B-2	N10665	72Ni-28Mo	407	902	61
B-3	N10675	68.5Ni-28.5Mo-1.5Cr-1.5Fe-	400	885	58
B-4	N10629	65Ni-28Mo-4Fe-1Cr-0.3Al	340	755	40
600	N06600	76Ni-15.5Cr-8Fe	275	640	45
690	N06690	62Ni-29Cr-9Fe	334	690	50
800	N08800	45Fe-33Ni-21Cr-0.4Ti			
825	N08825	43Ni-21Cr-30Fe-3Mo-2.2Cu-1Ti	338	662	45
G-30	N06030	44Ni-30Cr-15Fe-5Mo-2Cu-2.5W-4Co	317	689	64
33	R20033	31Ni-33Cr-32Fe-1.6Mo-0.6Cu-0.4N	380	720	40
C-276	N10276	59Ni-16Cr-16Mo-4W-5Fe	347	741	67
C-4	N06455	65Ni-16Cr-16Mo	335	805	63
625	N06625	62Ni-21Cr-9Mo-3.7Nb	535	930	45
22	N06022	59Ni-22Cr-13Mo-3W-3Fe	365	772	62
2000	N06200	59Ni-23Cr-16Mo-1.6Cu	345	758	68
59	N06059	59Ni-23Cr-16Mo-1Fe	340	690	40
686	N06686	46Ni-21Cr-16Mo-4W-5Fe	364	722	71
21	N06210	60Ni-19Cr-19Mo-1.8Ta	370	775	64
22HS *	NA	61Ni-21Cr-17Mo	742	1232	50
725HS *	N07725	57Ni-21Cr-8Mo-9Fe- 3.4Nb-1.4Ti	1043	1375	25

Mechanical Properties at ambient temperature YS = Yield Strength, UTS = Ultimate Tensile Strength, ETF = Elongation to Failure, A = Quenched and Tempered, B = Precipitation Hardenable, NA = Not Available, * Age Hardened

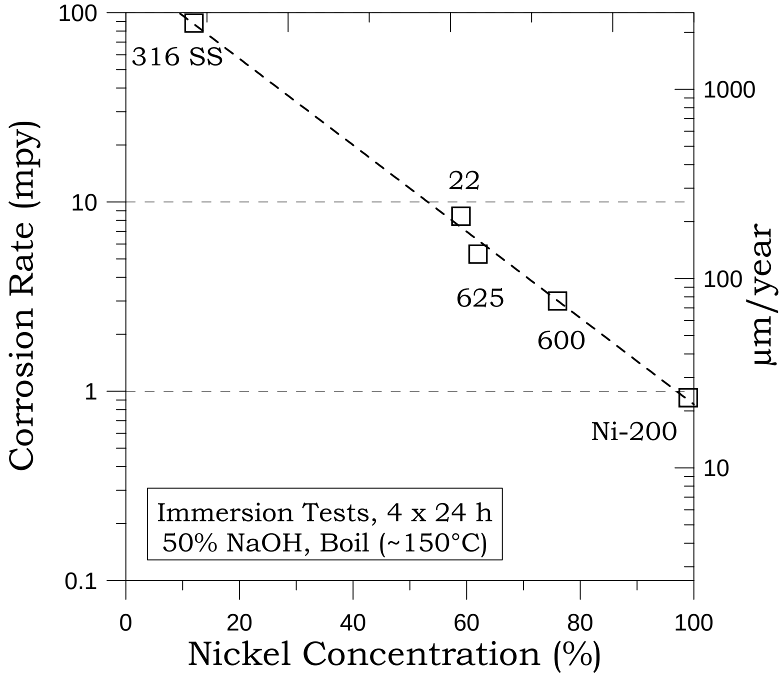


FIGURE 1 – General Corrosion Rate of Nickel Alloys and 316 SS in Boiling 50% NaOH
The higher the Ni content in the alloys the lower the corrosion rate

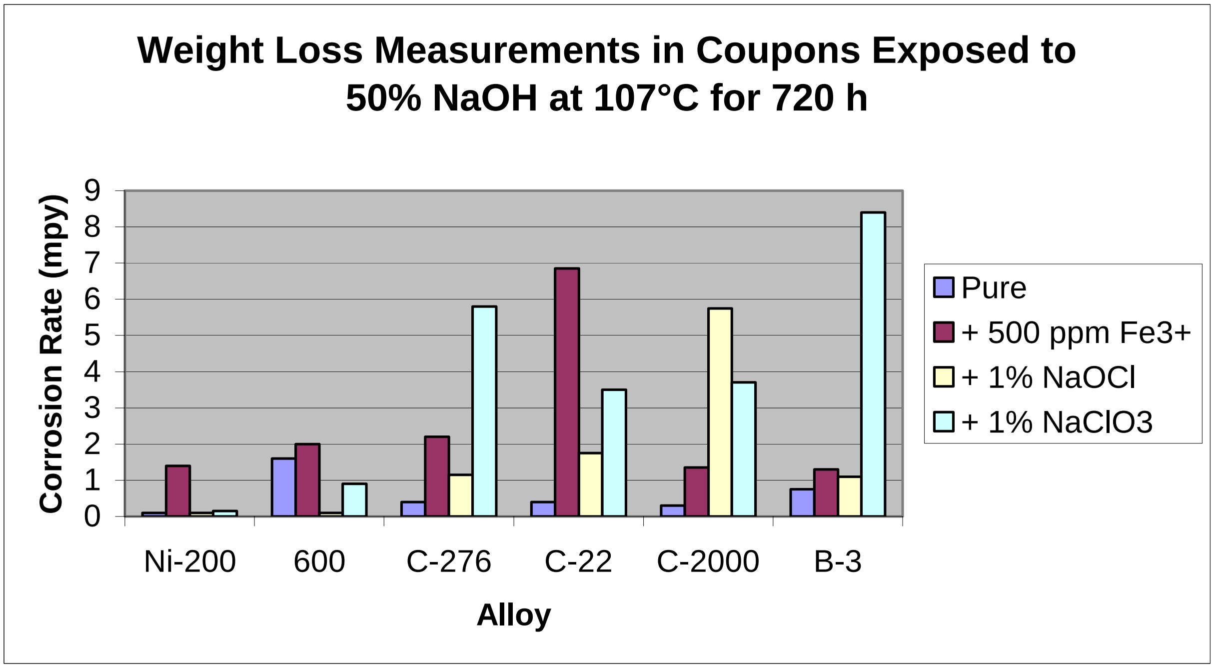


FIGURE 2 – Corrosion Rate by Weight Loss of Ni-Alloys in 50% NaOH
The alloys containing high Mo had the highest corrosion rate in the contaminated electrolytes.

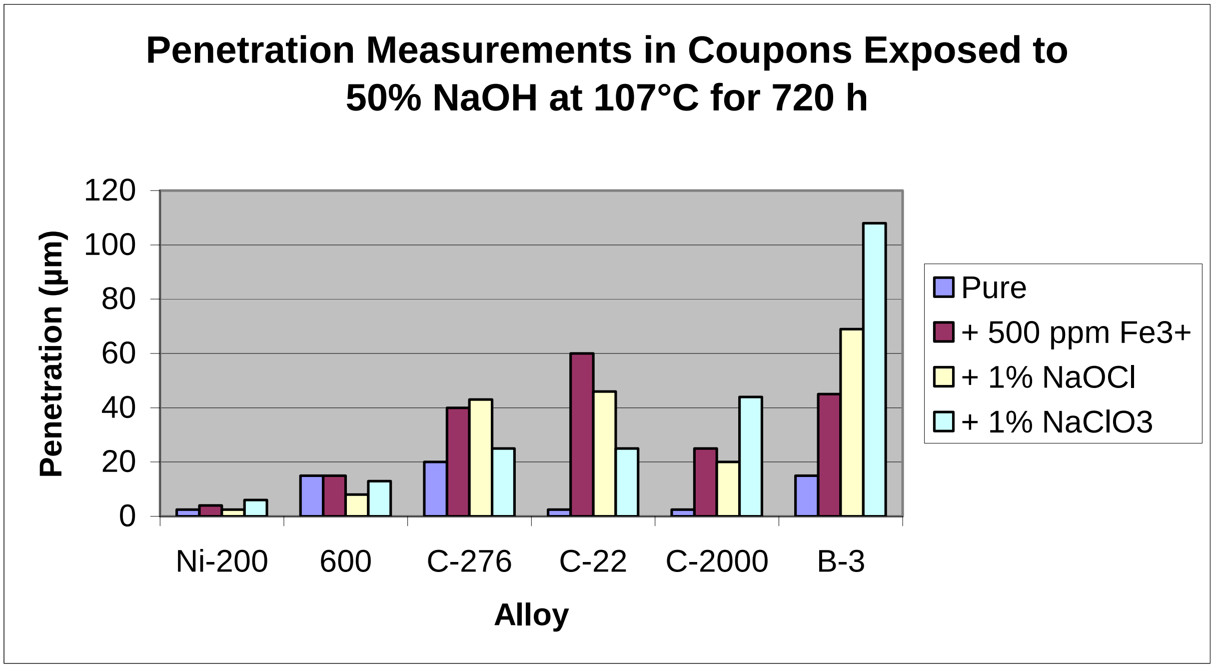
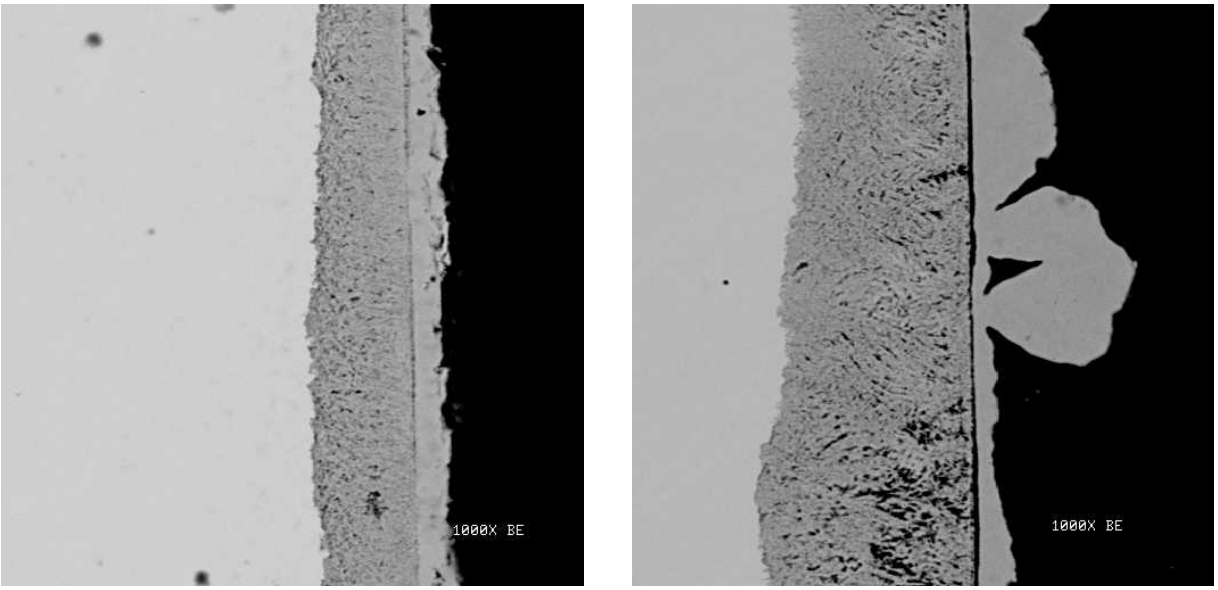


FIGURE 3 – Internal Penetration as Cracks or Dealloyed Layer in Ni-Alloys in 50% NaOH
The alloys containing high Mo had the largest degradation, especially in the contaminated electrolytes.



C-276, 50% NaOH, 107°C, 720 h, X1000

C-276, 50% NaOH + Fe^{3+}, 107°C, 720 h, X1000

FIGURE 4 – Dealloying of C-76 in caustic solutions. The outermost right layer is pure Ni (re-precipitated from the solution) and the second layer is pure Ni as a leftover sponge.