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Sensitization and Corrosion in Stainless Steel Filters

RATIONALE

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1. SCOPE:

This document reviews briefly the subject of woven metal screens. Conditions that can promote damaging corrosion in stainless steel filter screens are discussed and recommendations are listed for minimizing corrosion damage. This is a general document only; for specific applications it is suggested that the reader refer to the technical literature, and selected references listed below.

2. REFERENCES:

2.1 Metal Handbook, Ninth ed., Vols. 3,4,5 and 6, 1980, 1981, 1982 and 1983, American Society for Metals

2.2 Metals Handbook, Eighth ed., Vols. 1,2,3,4,5 and 6. 1961, 1964, 1967, 1970 and 1971. American Society for Metals

2.3 1983 Annual Book of ASTM Standards, Section 3, Vol. 03.02, Metal Corrosion, Erosion and Wear, American Society for Testing & Materials

2.4 Corrosion and Corrosion Control, An Introduction to the Subject, by J.T.N. Atkinson and H. Van Droffelgar, 1982, National Association of Corrosion Engineers

2.5 An Introduction to Metallic Corrosion by Ulick R. Evans, Third ed., 1981 Edward Arnold (publishers) Ltd. and American Society for Metals

2.6 Corrosion and Corrosion Control, An Introduction to Corrosion Science and Engineering, by Herbert H. Uhlic, 1963, John Wiley and Sons

2.7 A Guide to Corrosion Resistance, 304, 316, 317, "20" and Ni-O-Nel, by J.P. Polar, 1961 Climax-Molybdenum Company, a division of American Metal Climax, Inc.

3. TECHNICAL INFORMATION:

3.1 Summary:

The reliability of stainless steel depends on the reliability of the manufacturer in achieving and maintaining proper metallurgical control over procurement and processing. Sensitization and subsequent intergranular corrosion of fine austenitic stainless steel filter mesh is an important problem which is often unrecognized by the filter user. Recognition of this major corrosion problem and other metallurgical deficiencies often found in filters, followed by appropriate action based on a sound understanding of the required technology, is necessary to achieve adequate control.

3.1 (Continued):

Sensitization is caused by an excessive carbon content in the stainless steel, improper heat treatment including sintering or annealing and welding or brazing operations, or both together. Sensitization can be controlled by applying good metallurgical quality control procedures and manufacturing practices and by specifying low carbon alloys such as AISI type 304L or stabilized alloys such as AISI type 347 stainless steel for filter mesh construction. It should be noted that sensitization can occur in as-woven mesh as well as in subsequently annealed or sintered mesh. If proper quality control procedures are utilized and the material is properly processed, either annealed or sintered mesh is equally resistant to corrosion. If proper quality control procedures or processing steps are not observed, either material can be sensitized. Therefore, procurement documents for filters and other structures made from stainless steel wire mesh should stress the quality control requirements rather than limit the use of annealed or sintered mesh. Other causes of metallurgical or corrosion failure, while less common in occurrence and less important in practice, must also be controlled to achieve reliability. These problems are best solved by filter manufacturers and users working together on a common ground of understanding.

3.2 Woven Metal Screen:

Woven metal screens are produced just as the term implies, by weaving metal wire strands into a mesh or screen with dimensionally controlled opening sizes. Screen can be woven from virtually any metal or alloy that can be drawn into ductile wire. However, filter screens are largely woven from stainless steel wire because of cost considerations and the fact that most filter applications are intended for handling mildly corrosive liquids and solutions. Where greater corrosion resistance is required screens can be woven from more corrosion resistant alloys or even the noble metals, if necessary. Filtration of aggressively corrosive media requires that the filter screen material be selected carefully to assure the desired filter life. The filter body may also require special construction and processing, and non-standard cleansing methods.

Stainless steel filter screens are most frequently produced from 300 series stainless steels. Screen wires may be as small as 13 µm (0.0005 in) diameter and as large as 0.8 mm (0.032 in). There is very little use of ferritic, martensitic or precipitation hardenable SS alloys for this application. Both 304 and 316 SS are widely used for filter screen, however 304L, 316L, 347, 348, and 321 SS alloys may be specified for greater resistance to intergranular corrosion.

From a metallurgical standpoint the quality of screen products, although certified to meet certain requirements, may be subject to considerable and sometimes functionally detrimental variation. For this reason, acceptance sampling for evaluation of screen or wire characteristics considered to be important to filter function should be implemented where appropriate by the filter fabricator. Important fabricator quality provisions other than acceptance sampling should also receive attention; for example, clear and unambiguous marking of each batch of screen and wire as to producer, purchase order number, heat number, process lot number, composition and size characteristics is essential to prevent material mix-ups in the fabrication shop. These same recommendations apply to weld filler metal and brazing alloy material where these processes are used in filter fabrication. Control of ancillary heating operations is also important.

3.2 (Continued):

Generally, filter screens are fabricated from stainless steel wire in the fully annealed or dead soft condition. The screen weaving process necessarily introduces various levels of cold work into the screen wires, depending on the controls and inherent consistency of the weaving process. Filter screens are mostly used in the as-woven condition unless annealing is specified in the purchase order; therefore the wire alloy characteristics are modified from the as-woven condition only by additional forming, welding or brazing cycles that occur as a result of filter fabrication. Without attention to the effects that the various manufacturing operations may have on the corrosion resistance of the alloy from which the screen is produced, the assembled filters may exhibit wide variations in effective service life.

It is recommended that stainless steel filter screens be passivated after weaving by screen manufacturers. Passivation of the 300 series stainless steels is basically accomplished in room temperature nitric acid solutions of 50% concentration sometimes with sodium dichromate added. Special rinses may also be used after passivation. The major purposes of passivation are twofold; first the solutions are designed to dissolve free iron resulting from contact with steel tools or grinding dust from the wetted surfaces. Second, these same solutions are intended to create a blemish free continuous oxide film or passive layer on all wetted surfaces. Even when perfectly accomplished, however, passivation will not provide resistance against destructive corrosive attack in appropriate corroding media. Passivation will minimize rust and stain formation in alloys that are not "sensitized"; it does not help much in “sensitized" areas.

3.3 Corrosion of Stainless Steels:

The 300 series stainless steels can be very resistant to corrosive attack, but they are certainly not immune to corrosion. A mechanism termed "sensitization" is responsible in most instances of intergranular corrosion in these alloys. Whether sensitized or unsensitized, pitting attack and stress corrosion cracking may also be serious, structurally degrading corrosion modes in filter screens. Crevice corrosion and corrosion fatigue may also occur, however the extent to which any of these corrosion mechanisms are responsible for reduced life or outright failure of filter screens is not known. Much has been written in the technical literature on the causes and prevention of corrosion in stainless steels and is not the intent of this report to repeat this. A brief discussion is provided below on this principle mechanisms of corrosion, for continuity in this document:

3.3.1 Intergranular Corrosion: This type of corrosive attack is generally confined to grain boundaries. It occurs most severely in metal that has been “sensitized”. “Sensitization” is best explained as depletion of chromium at grain boundaries, below the nominal 12% Cr required to attain passivity. This occurs when the carbon dissolved in and normally distributed uniformly in the steel combines with chromium at temperature to form chromium carbides in the regions where carbon diffuses most readily at the grain boundaries. Chromium depletion by this mechanism (carbide precipitation) happens as a result of excessive exposure time at temperatures in the range from 400 °C (750 °F) to as high as 870 °C (1600 °F), the severity of sensitization depends largely on average carbon content, time in the sensitizing range, exposure temperature and alloy composition. The time-temperature relationship for intergranular attack due to sensitization in one alloy is drawn in Figure 1. This characteristic “C” curve shape is typical for 300 series stainless steels.

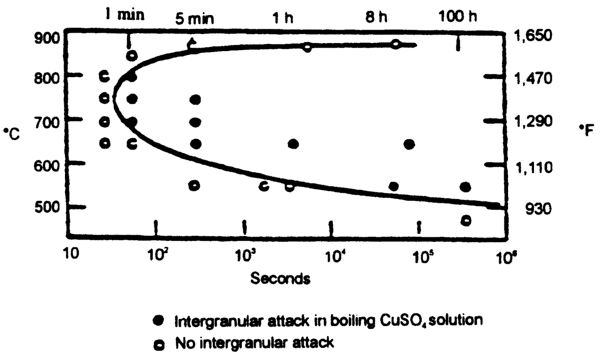

FIGURE 1 - Effect of Time and Temperature on Sensitization of 18.2% Cr, 11.0% Ni, 0.05% C, 0.05% N Stainless Steel

3.3.1 (Continued):

In addition to carbide precipitation, other detrimental intermetallic compounds (sigma phase and chi phase) may also form in 316, 321, 347 and 348 alloys and in welds, in the sensitizing temperature range. Carbide precipitation causes only minor increases in strength and hardness, while sigma (and chi) phase can cause significant reductions in ductility that can initiate premature failure.

Sensitizing can be caused by welding, furnace brazing, heat treatment and/or improper mill processing of these alloys. Sensitizing can occur in any stainless steel, but significant reductions in resistance to intergranular corrosion in most media can be prevented by the use of 304L, 316L, 321, 347 and 348 alloys.

This is because 304L and 316L are held to carbon contents at or below 0.03% by weight, by specification, which significantly reduces carbide precipitation effects compared to the 0.08% carbon maximum allowed in standard 304. Alloys 321, 347 and 348 are stabilized grades with titanium (321) or Niobium (columbium) (347, 348) added to act as carbon getters; these elements minimize chromium depletion by the preferential formation of titanium/columbium carbides. In fact, any of these steels can be sensitized, but the severity of intergranular attack is much reduced from that in standard grades of stainless steel for most corrosive media. Also, proper heat treatment can virtually eliminate sensitizing effects. A series of standard tests for evaluating resistance to intergranular corrosion in stainless steels are covered by ASTM Specification A262.

3.3.2 Pitting Corrosion: Because stainless steel filters are passive for almost all fluids for which they are normally used, any localized corrosion, under circumstances that prevent restoration of passivity, may cause rapid penetration at the point of initiation. This occurs because an active-passive electrolytic cell is formed between the large cathodic (passive) area and the small anodic area under attack; any surrounding oxygen serves as a depolarizer, and pitting proceeds.

Solutions containing ionic or free chlorides are especially detrimental because they promote formation of active-passive electrolytic cells. Acid chlorides in their higher-valence state (such as cupric chloride and ferric chloride) are particularly severe, but any chloride ion in appreciable concentration is a possible source of trouble. Solutions of other halide salts and of some sulfates may cause pitting.

Pitting attack can be greatly reduced in many corrosive media by using molybdenum bearing grades of stainless steel (316 and 316L). However, when conditions for pitting do exist, the pits can be as deep in these alloys as in the molybdenum-free grades.

3.3.3 Stress Corrosion: Stress corrosion is the nucleation and propagation of cracks, typically transgranular, but in some instances intergranular, in tensile stressed metal when immersed in or in contact with one of the active corroding media. As-welded areas (without stress relieving heat treatments), as-cold-formed parts, those with residual stresses, and parts that experience sustained service loads are subject to stress corrosion attack. For most combinations of alloy and corroding media there is a threshold stress below which stress corrosions attack will not occur. For the 300 series stainless steels, the potential for stress corrosion cracking to occur also depends on the chemistry and temperature of the corroding media. An abbreviated tabulation is presented in Table 1 to describe the general requirements for stress corrosion attack of these alloys. Note that there is little recorded data available on threshold stresses for cracking to occur in these alloys, although in general, stresses approaching yield point appear to be a necessary precondition.

3.3.4 Crevice Corrosion: Crevices formed by joints and connections, or at points of contact between metals and nonmetals, are most frequently subject to attack. Similarly, deposits of foreign matter may promote local attack. This is not commonly a problem with filters, however, for long term use of woven wire filters in systems containing oxygenated fluids the possibility exists.

In a crevice, the oxygen supply is limited and cannot repair the passive oxide film, and a so-called "differential concentration cell" appears. Porous substances in the crevice may trap corrosive solutions such as sea-water or moisture condensed from the atmosphere. A crevice stays damp longer than a fully exposed surface. Salts are likely to accumulate in crevices and under deposits, particularly if the area around the crevice is alternately wet and dry. Gasket materials containing sulfur or graphite contribute to this type of corrosion. On the other hand, corrosion will seldom occur if the crevice is sealed completely to prevent the intrusion of moisture.

TABLE 1

Active Media	Solution Concentration	Threshold Temperature	Nature of Cracking Observed
Aqueous Chloride Solutions			
Neutral pH	Chloride ion over about 25 ppm with dissolved oxygen present	70 °C (160 °F) and above	In sensitized material-intergranular. Note: little attack in unstressed metal. In nonsensitized material-transgranular.
Acid pH	Chloride ion relatively concentrated with or without dissolved oxygen	70 °C (160 °F) and above	Generally transgranular: occurs in nonsensitized, sensitized and in severely cold worked material.
Alkaline pH	Concentrated OH-with or without dissolved oxygen	Near or above boiling point	Either transgranular or intergranular. No stress level indicated.
Polythionic Acids	Unknown	Hot	In sensitized material - intergranular. In nonsensitized material-transgranular.

3.3.4 (Continued):

If the oxygen concentration decreases below a level necessary to maintain passivity in the anodic area, there is a double electrolytic effect. The difference in oxygen concentration alone will tend to accentuate attack on the anodic area; then the electrolytic potential between the active anode and the passive cathode is quite high, in itself, leading to a further degree of sustained continuous corrosion. There is a tendency for the cathode to become polarized with "plated hydrogen", but because oxygen is immediately available, the hydrogen film is destroyed, permitting attack to proceed, often at an unacceptably high rate. Chlorides and other nonoxygenating salts, being electrolytes that will not contribute to passivity, assist in this type of corrosion, often leading to destructive pitting. Furthermore, the solution within the crevice becomes very acidic (pH of 1.2 has been reported), which adds to the accelerated attack.

3.3.5 Galvanic Corrosion: The factors that influence galvanic corrosion include conductivity of the circuit, potential differences between anode and cathode, polarization, relative areas of cathode and anode, geometrical relationships between dissimilar metal surfaces and contact between metals. Of these, relative areas of anodic and cathodic surfaces have the most pronounced effect on the extent of damage produced by galvanic action, because of small anode and a large cathode result in an increase in current density at the anode with a great consequent increase in the rate of corrosion. Thus, small differences in potential under these conditions may produce extensive corrosion because of increased current density in the anodic areas.

A carbon steel bolt in a stainless steel plate will corrode at a rapid rate because the stainless acts as a large cathode. A stainless bolt in a large carbon steel plate will, in general, cause the carbon steel to corrode at only a slightly increased rate. It is generally considered poor practice to couple an anodic material such as carbon steel to a large cathode of stainless steel for exposure in a nonpassivating electrolyte; in a few instances, it is poor practice to couple carbon steel to stainless steel even if the area of exposed stainless steel is small.

If the solution promotes an active state, a galvanically coupled metal such as copper or bronze will accelerate corrosion of stainless steel, particularly if the area of activated stainless steel is small in comparison with the area of copper or bronze. On the other hand, passivated stainless steels are extremely stable in contact with these metals if the solution sustains the passive state.

3.4 Sensitization:

Where noble passivity is the hallmark of austenitic stainless steels, sensitization is a common cause of their failure. Sensitization is the migration of chromium into the grain boundaries forming harmful chromium carbides, resulting in chromium depletion in the grain boundary envelope. This leaves the grain boundaries susceptible to rapid corrosion. Intergranular corrosion may later cause catastrophic failure under conditions which do not affect normal stainless steel. Only the grain boundaries are corroded, the bulk of the metal matrix being unaffected. Intergranular corrosion may be compared to dissolving the mortar from a brick wall. The resultant collapse of the structure is also similar.

3.4.1 Causes: Sensitization is caused by cooling through or prolonged heating of austenitic stainless steel within the temperature range of 455 to 845 °C (850 to 1550 °F). Within this temperature range complex chromium carbides precipitate along grain boundaries. This results in a lowered available chromium content in the grain boundaries and the elimination of passivation benefits so that intergranular corrosion may later occur. Corrosion is accelerated by a galvanic cell effect between the anodic chromium-poor grain envelope and the cathodic precipitated chromium carbide phase surrounding the grain. Sensitization requires both an appreciable free carbon content, and some time of heating in the critical temperature range. The degree of corrosivity of the external environment determines the degree or extent to which intergranular corrosion will occur under a given alloy carbon content and sensitization heating conditions. For the less severe external environments, sensitized standard austenitic stainless steel, with carbon contents of 0.08% or 0.15% maximum can perform satisfactorily (e.g. 302 or 304 types). But as the environment corrosivity increases, first, sensitized austenitic stainless steels with 0.03% or less

3.4.1 (Continued):

carbon are necessary to alleviate intergranular corrosion (e.g. 302L or 304L) and ultimately titanium or niobium (columbium) stabilized types (e.g., 321 or 347). The temperature range for sensitization also varies with time. At 6 min the temperature range is 645 to 760 °C (1200 to 1400 °F), while at 1000 h it is 455 to 620 °C (850 to 1150 °F).

3.4.2 Processes: The manufacturing processes for austenitic stainless steels which can affect alloy sensitization include the degree of cold work in the mill product and during subsequent forming operations, hot forming, heat treatment, sintering, welding, brazing, surface contamination by carbonaceous material such as forming oils followed by heating and acetylene torch heating. Thus, the basic shapes (e.g., bar, wire, etc.) manufactured at the mill and all phases of subsequent product manufacture must be closely controlled and adequately monitored to prevent austenitic stainless steel sensitization. The carbon content of all incoming stainless steel materials must be check analyzed against the mill certification when possible. Metallographic examination of incoming stainless steel stock for cross-section microstructure freedom from grain boundary carbides is also necessary. Special care must be taken to insure that the product surfaces are clean and free of oil, drawing compounds and any other carbon containing substances prior to any type of heating operation during manufacture to prevent carbon diffusion into the alloy surfaces. Welding processes must minimize heating time in the sensitizing range. Otherwise, annealing after welding is necessary to dissolve precipitated carbides. Heliarc, tungsten inert gas (TIG), or electron beam welding are preferred to open arc or torch welding for reducing contamination and excess heating. Heliarc and TIG welding are performed with a surrounding blanket of insert gas. Electron beam welding is performed in a high vacuum and produces 1/25 or less the heat of an equivalent heliarc or TIG weld. Welding filler alloys must be carefully selected. Niobium (columbium) containing filler alloys are preferred for weld stabilization. Acetylene torches can cause stainless steel surface carburization- hydrogen-oxygen torches do not. Silver (and other alloy) brazing operations which may be performed near the sensitizing range must be critically analyzed, controlled and monitored to prevent galvanic, processing or other problems. Special precautions in designing thin brazed sections and placing of chill blocks are required to avoid damaging heat exposure. Surprisingly enough, short exposure times can be much more damaging than long time heating because thin carbide films which are first formed may agglomerate on continued heating into discontinuous particles which cause less structural damage during corrosion.

3.4.3 Prevention: Stabilization alloys prevent sensitization through the incorporation of niobium (type 347) or titanium (type 321) each of which has a greater affinity than chromium for carbon. Essentially all of the carbon is harmlessly precipitated as niobium or titanium carbides within the grain and chromium carbide formation is prevented. Subsequent sintering or welding operations may then be performed without the risk of sensitization providing normal good practice is observed. Stabilized stainless steel is specified when sensitization and subsequent intergranular corrosion cannot be tolerated. Stabilized bar stock is widely available, but is more difficult to process than nonstabilized or free-machining types and is not required for many applications. Stabilized wire mesh is also available but costs at least twice as much as regular type 304 mesh because it is more difficult to weave in good quality. Delivery is often slow when the finer weaves are imported from Europe.

3.5 Sensitization Testing:

Five standard tests have been developed for detecting susceptibility to intergranular attack in austenitic stainless steels. ASTM A262 presents detailed standard practices for these tests. One is an acid etch test and the other four are acid corrosion tests.

3.5.1 Oxalic Acid Etch Test: The oxalic acid etch test classifies the etch microstructure of austenitic stainless steels. It is a rapid method for identifying by simple etching whether an incoming lot of austenitic stainless steel wire, bar, sheet or other shape is free of susceptibility to intergranular attack associated with chromium carbide precipitates near the grain boundaries. When the etch microstructures are acceptable in the oxalic acid etch test, the lot of stainless steel will be essentially free of intergranular attack by any of the four other standard tests and can be accepted without further testing.

The type of stainless steel for which the oxalic acid etch test is applicable are shown in Table 2. If not in the listing, only an acid corrosion test is applicable. When a lot of stainless steel is non-acceptable by the oxalic acid etch test, one or more of the acid corrosion tests must be performed.

TABLE 2

Test	AISI Type	ACI Type[1]
Ferric sulfate-Sulfuric acid	304, 304L	CF-3, CF-8
	316, 316L	CF-3M, CF-8M
	317, 317L	
Nitric acid	304, 304L	CF-3, CF-8
	309, 310, 348	CF-3, CF-8
	410, 430, 446	
Nitric, Hydrofluoric Acid	316, 316L	------------
	317, 317L	
Copper, copper sulfate, Sulfuric Acid	304, 304L	------------
	316, 316L	
	317, 317L	
	321, 347	

[1] Alloy Casting Institute

For alloys not listed refer to ASTM A262 for the most applicable acid corrosion test.

3.5.2 The Ferric Sulfate - Sulfuric Acid Corrosion Test: The ferric sulfate - sulfuric acid corrosion test has a 120 h duration in a boiling 50% solution which detects susceptibility to intergranular attack associated with chromium carbide precipitates. This test does not detect susceptibility associated with sigma phase or end grain attack in chromium-nickel molybdenum stainless steels (e.g., 316, 316L, 317, 317L) when in nitric acid environments. Nor does the test reveal susceptibility associated with a sigma-like constituent in stabilized stainless steels.

3.5.3 The Nitric Acid Test: The nitric acid test has a 240 h duration in a 65% boiling solution which detects susceptibility to intergranular attack associated with chromium carbide precipitates. It also detects susceptibility to intergranular attack associated with a sigmalike phase precipitate and to end grain attack in all types of stainless steels (certain nitric acid environments only).

3.5.4 The Nitric-Hydrofluoric Acid Corrosion Test: The nitric-hydrofluoric acid corrosion test has a 4 h duration in a 10% nitric, 3% hydrofluoric acid solution at 70 °C (158 °F) which detects only susceptibility to intergranular attack associated with chromium carbide precipitates in molybdenum bearing grades of austenitic stainless steels such as 316, 316L, 317, 317L. It does not detect susceptibility to intergranular attack associated with sigma phase or end grain corrosion.

3.5.5 The Copper-Copper Sulfate-Sulfuric Acid Corrosion Test: The copper-copper sulfate-sulfuric acid corrosion test has a 24 h duration in a boiling solution of 6% copper sulfate, 16% sulfuric acid with the test specimen embedded in metallic copper shot or grindings. It detects susceptibility to intergranular attack associated with chromium-rich carbide precipitates. It does not detect sigma phase or end grain corrosion.

3.5.6 Summary of Acid Corrosion Tests: The ferric sulfate-sulfuric acid corrosion test, the nitric acid corrosion test, and the nitric-hydrofluoric acid test are based on weight loss determinations and, thus, provide a quantitative measure of the relative performance of specimens evaluated. In contrast, the copper-copper sulfate-sulfuric acid test is based on visual examination of bend specimens and, therefore, classifies the specimens only as acceptable or nonacceptable. In most cases either the 24 h copper-copper sulfate-sulfuric acid corrosion test or the 120 h ferric sulfate-sulfuric acid corrosion test, combined with the oxalic acid etch test, will provide the required information in the shortest time.

3.6 Annealing and Sintering:

3.6.1 Austenitic stainless steel wire mesh used for filter construction is often sintered or diffusion bonded. Sintering serves the dual purpose of annealing the mesh wires which have been heavily cold worked during previous drawing and weaving operations and metallurgically bonding each tiny wire to its neighbor at points of contact. Annealing is necessary to relieve stresses and soften the mesh for further forming operations and to regain optimum corrosion resistance by dissolving or "solutioning" previously precipitated carbides and by converting the ferrite formed cold working back into austenite. Sintering is accomplished in a process similar to annealing by holding the mesh for a somewhat longer time at a higher temperature so that diffusion can occur between contacting wire surfaces. Sintering and annealing process details are usually considered to be proprietary and may differ between manufacturers, but common denominators of good metallurgical practice apply to all satisfactory processes.