

EVOLVING STANDARD TEST METHODS FOR VAPOR INHIBITING ABILITY (VIA) FOR CORROSION PROTECTION

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ABSTRACT

The paper provides technical and historical perspective considered in creating the recently published NACE standard test method TM0208-2008¹ for rapid qualitative evaluation to determine the presence of Vapor Inhibiting Ability (VIA) for corrosion protection of ferrous metal surfaces (VIA-F). The standard includes improvements in repeatability of outcomes and criteria for judging and reporting outcomes. An optional test method is included to judge possible confounding of the VIA effect with partial water absorption (desiccant) effects of some Volatile Corrosion Inhibitor (VCI) materials. The paper also provides considerations for creating one or more test methods to determine VIA with non-ferrous metals (VIA-NF), including consideration of “witness” metal specimens, atmospheric contaminants and appropriate rapid qualitative test methods for them.

Keywords: atmosphere, corrosion, inhibitor, volatile, vapor, test method, ferrous, non-ferrous, VCI, VPI, VPCI

INTRODUCTION

Volatile corrosion inhibitors (VCI), also called vapor-transported corrosion inhibitors or vapor-phase corrosion inhibitors (also VPI and VPCI) are chemical substances that act to reduce corrosion by a combination of (1) volatilization from a VCI material or vapor transport in the presence of solvent vapors, usually water vapor, (2) diffusion within the atmosphere of an enclosed environment, and (3) condensation onto and chemical action with metal surfaces in the space, including absorption, dissolution, and hydrophobic effects.

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This paper provides technical perspective on existing and planned NACE standards for test methods of rapid qualitative evaluation of the presence of vapor-inhibiting ability (VIA) of VCI materials. Several years work of a NACE Task Group resulted in recently published standard TM0208-2008¹ for determining VIA for corrosion protection of representative ferrous metal surfaces (VIA-F). The method defined in the new standard is of limited scope, using only test specimens of 1010 carbon-steel (UNS G10100) to represent the class of carbon and low alloy steels which readily corrode in the presence of atmospheric humidity to form of visible corrosion product (“rust”).

A general consideration for additional new VIA test methods for protection of non-ferrous metals (VIA-NF) is a preference, if possible, to emulate the relatively quick accelerated VIA-F test method, typically taking a day or a few days, with relatively inexpensive and simple apparatus that may be easily duplicated for multiple tests, and for which a competent laboratory should be able to achieve reasonable and reproducible results in distinguishing between VCI materials that have VIA properties from those that do not. Other properties of VCI materials unrelated to corrosion remain outside the scope of a VIA standard, e.g., specific application requirements for flammability or flame retardancy, other types of safety and health hazard assessment, stability under ultraviolet and solar radiation, and other factors.

Thousands of inhibitor chemicals are known. One handbook² contains more than 3800 materials that may be used as inhibitors. Other publications list compounds and compositions that are identified as inhibitors under various conditions with various metals. The number of possible inhibitors is considerably higher than the number of such listed chemical compounds, since: (1) inhibitors may be used singly and in synergistic combinations, (2) properties may vary in media, e.g., solvents (water, oil, alcohol), coatings, plastics and paper, (3) compositions and concentration of inhibitors may vary in effect over wide ranges, and (4) environment and application conditions also vary widely and influence efficacy of inhibitors. The selection of corrosion inhibitors to fit specific requirements, such as VCI materials to protect various metal components, is reflected in the proliferation of test methods for corrosion effectiveness and service-life with various metals, considerations for cost and time of testing, and other considerations. Accelerated laboratory test methods like the VIA concept are generally favored for use in screening and initial evaluation of materials, thereby reducing the number of compounds, compositions and products that must be tested more specifically and thoroughly in the other laboratory and actual usage conditions.

Corrosion mechanisms of non-ferrous metals and even of most stainless and high strength alloy steels are not represented in the VIA-F test method. Improved repeatability of test results also comes with the limitation that metal specimens have only freshly polished and cleaned surfaces. Therefore, the VIA-F test results are limited by providing only a quick screen of basic VCI performance for clean carbon steels. Effects of corrosive contaminants and other conditions in actual field experiences may have substantial accelerating effects that must be tested by other means. However, the VIA-F standard does provide useful improvements and clarification from the basis of similar precursor standards and non-standard practices that have been widely used by manufacturers and users.

The work of recent years on the VIA-F standard is expected to be of value in developing a new standard for VIA test methods for non-ferrous metals (VIA-NF). Standard VIA-NF tests do not currently exist and necessarily require agreement on the few representative non-ferrous metals, given the variety of corrosion reactions in this broad class of materials, ranging from uniform and non-uniform tarnish as well as localized pitting and cracking. Further, this variety in forms of corrosion result from varying responses to atmospheric conditions, such as relatively slow effects in the presence of warm humidity alone to more rapid and diverse effects in the presence of small concentrations of atmospheric or surface contaminants, particularly chloride salts or acid gases.

Considerations for VIA test methods are that the results should be readily obtained by qualitative visual evaluation, typically against inspection criteria for degree and pattern of corrosion, e.g., uniformity or degree of “spots”, general color of patina or tarnish, etc. Materials that perform well in this test should exhibit the combined effect of: (1) vapor transport without contact between the VCI sample and the test surface of the metal specimen, (2) corrosion inhibition on the surface of the metal specimen, and (3) exposure to static humid warm air, generally including water condensation and/or added acid gas or other accelerants of specific corrosion processes.

A critical element of VIA test methods is that there must be vapor transport by diffusion from the VCI source across a gap to a metal specimen, always in the presence of high humidity. However, VIA test methods as well as other tests and practical uses of VCI materials do not distinguish whether the transported vapor is solely the result of evaporation from a VCI source having adequate vapor pressure, a commonly limited and incorrect assumption, or if VCI materials that have low or essentially no vapor pressure are effective by assisted transport in combination with solvent vapors, such as water vapor. Assisted vapor transport may be inferred, for example, in the case of sodium nitrite, an important and widely used VCI having extremely low vapor pressure and high solubility. In fact, the combination of high VCI efficacy and low vapor pressure led to first patent and fundamental innovation of VCI incorporated into plastic materials³.

The following considerations may also be useful to guide development of VIA-NF test methods toward the objective of a validated NACE standard that may become widely useful.

1. “Witness” metals representative in their corrosion reactions and usage of a wide range of industrial and military applications
2. Atmospheric environments that appropriately accelerate corrosion for the selected “witness” metals
3. Procedures from which VIA test concepts may evolve, including sample preparation, grading or pass/fail criteria for the selected “witness” metals in the selected test atmospheres.

CONSIDERATIONS for VIA-NF TEST METHODS

Representative “Witness” Metals

A practical consideration for relatively quick and manageable tests of VIA-NF is to select a few representative metals as “witness” specimens, perhaps no more than three. These should be widely used and represent a larger class of related metals and their alloys, and for which corrosion protection has high value. Divergent suggestions were considered for a possible single first choice during initial discussions of the NACE task group. Table 1 is a summary of responses to a simple poll in early 2009 when NACE Task Group members were asked to provide their top 3 selections of “witness” metals in rank order, considering also markets served and economic importance.⁴

Additional perspective may be gained from the metals with highest relative abundance: aluminum (about 8%) and iron (about 5%). Both have a wide range of alloys and levels of purity for use in a wide range of applications, and each has distinctive corrosion reactions. The next most abundant metals (from 4% to 2%) are: calcium, sodium, potassium and magnesium, followed by titanium (about 0.6%), manganese (about 0.1%). Farther down the list are chromium, copper and nickel, all an order of magnitude less abundant, and even rarer are zinc and tin.

An alternative perspective may be relative market value of commodity metals, as roughly summarized in Table 2. Relative valuations suggest consideration of copper and its alloys, followed by titanium and nickel. Even stainless steels are vulnerable to staining from corrosion reactions in special atmospheric conditions, such as tropical ocean air. Chromium, copper, nickel, zinc and tin are also used as protective coatings, so that the resulting materials, and parts made from them, have several orders of magnitude higher relative value.

In summary, it is recommended that initial choices for “witness” metals for initial standardization of VIA-NF test methods are first copper, then aluminum alloys, e.g., 6061 and/or 7075, followed by zinc and zinc coating on steel.

Representative Atmospheric Environments for Accelerated Corrosion

Another practical consideration is the selection of appropriate atmospheric conditions that lend themselves to meaningful acceleration of corrosion for the selected “witness” metals, that are easily reproduced and controlled, and that represent appropriate classes of indoor and outdoor environments in which VCI materials may be used.

Corrosion reactions are strongly accelerated by temperature, and practical applications of VCI materials may experience up to about 55°C (130°F), e.g., inside enclosures that are exposed to direct tropical or desert sunlight. Corrosion rates are generally highest near saturating humidity, 100% RH.

Typical atmospheric components are nitrogen and oxygen molecules, comprising concentrations of about 78% and 21%. The remaining portion, about 1%, contains all other components. Depending on local conditions, primary corrosive contaminants other than oxygen are water vapor, chlorides from proximity to sea water, and “acid gases”, such as those listed below and summarized in Table 3 and Figure 1.

- Hydrogen sulfide (H_2S), e.g., released from anaerobic bacterial processes, decay of plant and animal protean, waste water and petrochemical processes, natural gas emissions
- Sulfur dioxide (SO_2), e.g., released from fossil fuel combustion
- Carbon dioxide (CO_2) and various nitrogen oxides, released from combustion in air, from nitrogen bearing fuels, and from some agricultural processes)

The pH of the condensed moisture layer on metals in which VCI action must perform is nearly neutral (6-8) in most atmospheric conditions. This may be reduced to perhaps 4 in the presence of acidic contaminants.

Accelerated test methods are likely to be selected from among choices of: elevated temperature, constant or cyclic humidity, contaminant concentrations relevant to typical corrosion reactions of the metal species, and expected applications of the VCI material. For ferrous metals, it is sufficient to use warm humidity conditions to accelerate the formation of oxides and hydroxides, corrosion products that are seen as “rust”. For various non-ferrous metals, the use of warm humidity alone may not provide adequate acceleration to achieve results in days or even a few weeks. The accelerating effects of acid-gas or chloride salt spray or fog may meet the preference for a quick test while making the results applicable to a small subset of possible uses of a VCI material.

Contaminants listed in Table 3, in combination with elevated temperature and humidity, are candidates for environmental conditions for VIA tests of some “witness” metals. However, VIA performance obtained with aggressive contaminants may not correlate with field performance in more

benign conditions. VIA performance ratings obtained with additions of acid-gas or chloride salt accelerants must be clearly labeled as such and their suitability for a wider range of less aggressive atmospheric conditions noted.

Corrosion Mechanisms of Metals in Test Environments

Accelerating test environments should match mechanisms of corrosion that occur in typical applications of the “witness” NF metals. For the recommended witness metals, copper and aluminum alloys, the basic corrosion mechanisms in aqueous solutions may be described with the simplifying schematic in Figure 2. The speed of the corrosion reactions will vary depending on the temperature and concentration of accelerating contaminants, of which a simple measure is the pH. In most cases, the corrosion rate increases with increasing temperature and decreasing pH or increasing acidity. The relationship between corrosion rate and the pH may be a useful means of accelerating and specifying a VIA test method.

The following broad statements are made from personal perspective to suggest that VIA test methods may be divided into the following four groups of potential “witness” metals and their corrosion mechanisms. Alloys may exhibit combinations of properties and corrosion reaction that relate to the component metals. Corrosion rates for these metals are substantially accelerated in acidic environments as the pH is reduced.

- Carbon steel and iron have corrosion products that are oxides and hydroxides that are porous and unstable in humid conditions. Suitable accelerating environments are elevated temperature and relative humidity, as is done in the VIA-F test. Corrosion rates may be substantially accelerated with increasing concentrations of chloride ions.
- Zinc and Magnesium also have relatively low corrosion resistance in humid conditions, except that corrosion rates are reduced as oxides accumulate. Corrosion rates may be substantially accelerated with increasing concentrations of chloride ions. Test environments can be similar to carbon steel.
- Copper, silver, nickel, chromium and tin have relatively higher corrosion resistance in humidity alone, but generally low corrosion resistance in acid-gas environments. Suitable accelerating VIA test conditions are low concentrations of hydrogen sulfide and/or sulfur dioxide. However, these contaminants may interact to neutralize some VCI materials which are otherwise effective in relatively neutral pH conditions. As mentioned above, the preference for an accelerated test may make results applicable to a subset of possible uses of a VCI material.
- Aluminum and titanium have protective but porous oxides that are unstable in environments with pH below about 5, such as low concentrations of acid gas, or alkaline conditions above about 9.

Compatibility

VIA testing for corrosion protection may also be used to evaluate possible incompatibility of some VCI with some non-ferrous metals. For example, the VIA-F test method includes a separate test to assure that protection of ferrous metal does not cause corrosion or staining of copper. In general, it may be that testing of candidate VCI samples with each VIA-F and VIA-NF test may be a basis for rating relative compatibility as well as corrosion protection.

Sample Preparation

The outcome of a VIA test with a specific type of metal and test atmospheric may depend whether specimens are prepared by surface abrasion and/or polishing, followed by cleaning in alcohol, solvent or reactive solution, or by cleaning alone without abrasion or polishing. Another cleaning method for silver and copper is to use a commercial tarnish remover followed by deionized water rinse. The specimens are then maintained clean and dry until sealed into the test jar.

Apparatus, Conditioning, Inspection Criteria

It is desirable, if possible, to have the simplicity of a “jar” apparatus for VIA-NF tests similar to that specified for the VIA-F test method. Whether the accelerating test atmosphere can be simply condensing humidity, as in the VIA-F test method, or whether quick results require acceleration with acid gas or chloride salt atmospheric contaminants, is to be determined for each “witness” metal and range of VCI applications.

It is good practice to allow for a period of conditioning, typically up to 24 hours, before introduction of elevated temperature and any chemical accelerants. This allows initial transport of VCI to the metal specimen and inhibitor reactions, similarly to what is done in the VIA-F test standard.

Inspection criteria will necessarily include changes in color and texture, such as visible pitting, compared to reference diagrams or photographs.

“Jar” Test Method with Temperature, Humidity and Galvanic Effects

An attempt was made to create a VCI test method that used five dissimilar and electrically interconnected metals with warm humidity.⁵ The results were stated to be inconclusive, perhaps confounded by galvanic effects. The interconnected metal panels were: carbon steel, stainless steel, zinc coated (galvanized) steel, brass and aluminum. This method has evidently not gained further interest and usage.

“Jar” Test Methods with Acid Gases

The above summary of corrosion mechanisms of several metals includes perspective that warm humidity alone may not provide sufficient acceleration of corrosion to achieve results in days. Accelerating effects of acid-gas or chloride salt spray or fog may meet the preference for a quick test, but this may also reduce the relevance of test outcomes to a subset of possible uses of tested VCI material. Ultimately, any rapid test to screen for VCI performance must consider the likely applications and be compared with longer-term field experiences.

Acid-gas contaminants may be combined or used individually. The tests may be operated in steady conditions or cyclic temperature and humidity. For example, the following highly aggressive test environments are cited in a related paper in this symposium for evaluation of sealed plastic bags for physical and chemical barrier effects in addition to VIA-NF effects.⁶

Acid-gas concentrations created by the methods described below are several orders of magnitude greater than those listed in Table 3 and Figure 1 for unusually high industrial and city environments, shown in the perspective of Figure 1 as “VIA modified H₂S & SO₂“

Jar Test with High Concentration of Hydrogen Sulfide. Hydrogen sulfide is generated in the test jars by adding a small beaker containing a 0.2% solution of ammonium sulfide. The reaction in humid air may be characterized as follows.



A related test method is mentioned in a previous NACE paper⁷ in which the concentrated H₂S is created in the presence of warm wet humidity by the reaction with ferrous sulfide (FeS) and hydrochloric acid (HCl).

Jar Test with High Concentration of Sulfur Dioxide. A small beaker of dilute sodium thiosulphate (also called sodium hyposulfite, Na₂S₂O₃) is placed into a jar that also contains a small amount of water in the bottom. Dilute sulfuric acid is added to this jar at the moment it is sealed, releasing sulfur dioxide with byproducts of sodium sulfate and precipitated sulfur. A similar test method is mentioned in a patents^{8,9} and a previously cited paper⁷, all which mention an optional second small beaker to maintain about 95% RH by the combination of 1% solutions of sodium sulfate and ammonium chloride.

CONCLUSIONS & RECOMMENDATIONS

The paper offers considerations for creating one or more test methods to determine VIA with non-ferrous metals (VIA-NF). VIA-NF test methods should be relatively quick accelerated tests, typically taking a day or a few days, performed with relatively inexpensive “jar” apparatus that may be easily replicated, and “witness” metal test specimens from the following group of non-ferrous metals: first copper, then aluminum alloys, e.g., 6061 and/or 7075, followed by zinc and zinc coating on steel. The latter may be suitable for a test method similar to that for VIA-F, as described in the published NACE standard TM0208-2008.

The accelerating VIA test atmosphere for copper may low concentration of acid gas, hydrogen sulfide perhaps combined with sulfur dioxide, since the relatively high corrosion resistance of copper in warm and high humidity alone does not provide results in days. Accelerated VIA tests with that use relatively pure aluminum specimens will require relatively low or high pH to achieve timely results, and these conditions may not represent most applications of VCI use. Further consideration must be given to use of alloys where accelerating by means of acid-gas or chlorides may result in pitting attack of alloying components that, again, may not be representative of general usage in VCI enclosures. An accelerated VIA test of zinc or zinc plated (“galvanized”) steel may consider either the warm humid conditions of the VIA-F test method unless additional acceleration is preferred by small additions of chloride or acid gas contaminants.

In general, VIA performance obtained with aggressive contaminants may not correlate with field experience in more benign conditions. VIA performance ratings obtained with additions of acid-gas or chloride salt accelerants should be clearly identified, and suitability of the tested VCI materials for a wider range of less aggressive atmospheric conditions noted. A related caveat for interpreting the outcome of VIA tests in general is that the effects of corrosive contaminants and other conditions in actual field experiences may have substantial accelerating effects that are not predicted by a VIA test method, and that therefore must be tested by other means.

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TABLE 1
**PROPOSED “WITNESS” METALS FOR VIA-NF LISTED AS
RANK 1 or 2 IN A POLL of TG MEMBERS**

Proposed “witness” metal	Total of votes as 1 or 2
Copper	8
Copper alloy	3
Aluminum alloy *	3
Aluminum	2
Zinc **	1
Silver	1

* Alloys 6061 and 7075 were noted in poll responses without other detail

** Zinc as galvanized coating on steel was noted without other detail

TABLE 2
**APPROXIMATE RELATIVE MARKET VALUE FOR METALS
RELATIVE TO CARBON STEEL, BASED ON TYPICAL RANGE OF
COMMODITY PRICES IN THE RECENT DECADE**

Metals	Relative Cost per unit	
	Volume	Weight
Carbon steels	1	1
Alloy steels	~ 1.3 - 2	~ 1.3 - 2
Aluminum & alloys	~ 1.3 - 2	~ 2.5 - 4
Magnesium & alloys	~ 1.7 - 2	~ 6 - 8
Zinc & alloys	~ 3 - 5	~ 3 - 5
Stainless steels	~ 7 - 10	~ 7 - 10
Copper, brasses, bronzes	~ 8 - 16	~ 8 - 16
Titanium & alloys	~ 15 - 20	~ 20 - 30
Nickel & alloys	~ 30 - 40	~ 20 - 35

TABLE 3
**EXAMPLES OF RELATIVELY EXTREME LOCAL ATMOSPHERIC CONCENTRATIONS
OF CORROSIVE CONTAMINANTS NEAR INDICATED TYPICAL SOURCES**

Locations	Concentration of atmospheric contaminant, $\mu\text{g}/\text{m}^3$			
	Cl ⁻	SO ₂	H ₂ S	NOx
Countryside	~ 0.3	~ 0.04	~ 0.07	~ 0.1
Industries	~ 1	0.5 - 2	~ 0.2	
Water Treatment	~ 100		Occup limits 15	
Large City	~ 1	0.5 - 2	~ 0.05	0.3 - 2
Seaside & Sea	10 to 30	~ 0.2		

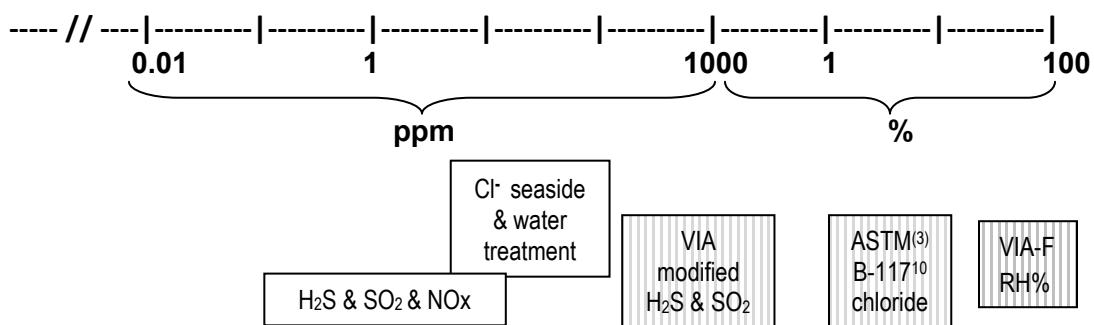


FIGURE 1. Simplified perspective of approximate concentrations of corrosive atmospheric contaminants in extreme local conditions. Scale is logarithm of concentration; cross-hatched boxes are examples of standard and non-standard accelerating conditions that are used in some VCI evaluations.

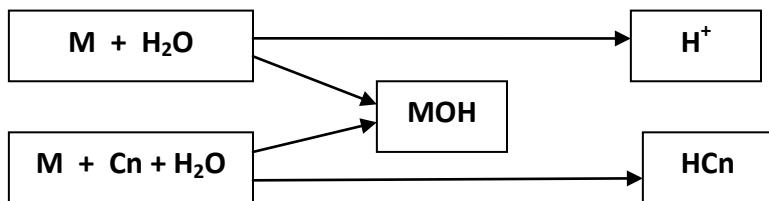


FIGURE 2. Simplified schematic of corrosion reactions between metals (M), water (H_2O), and contaminant ions (Cn), without showing all intermediate combinations.

⁽³⁾ ASTM International (ASTM), 100 Barr Harbor Dr., West Conshohocken, PA 19428-2959

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