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Copper Corrosion and Its Relationship to Solar Collectors: A Compendium

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Copper Corrosion and Its Relationship to Solar Collectors: A Compendium

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Abstract

Copper has many fine qualities that make it a useful material. It is highly conductive of both heat and electricity, is ductile and workable, and reasonably resistant to corrosion. Because of these advantages, the solar water heating industry has been using it since the mid-1970s as the material of choice for collectors, the fundamental component of a solar water heating system. In most cases copper has performed flawlessly, but in some situations it has been known to fail. Pitting corrosion is the usual failure mode, but erosion can also occur. In 2000 Sandia National Laboratories and the Copper Development Association were asked to analyze the appearance of pin-hole leaks in solar collector units installed in a housing development in Arizona, and in 2002 Sandia analyzed a pitting corrosion event that destroyed a collector system at Camp Pendleton. This report includes copies of the reports and accounts of these corrosion failures, and provides a bibliography with references to many papers and articles that might be of benefit to the solar community. It consolidates in a single source information that has been accumulated at Sandia relative to copper corrosion, especially as it relates to solar water heaters.

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Copper Corrosion and its Relationship to Solar Collectors: A Compendium

Section 1. Introduction

Copper is one of the oldest metals used by mankind. According to the Copper Development Association (CDA), copper has been in use for nearly 10,000 years and is often referred to as one of the original Metals of Antiquity.

Today, copper is heavily used in its pure state and alloyed with other materials to produce bronze and brass. Copper has many fine qualities that make it a useful material. It is highly conductive of both heat and electricity and it is quite ductile and workable. It is also reasonably resistant to corrosion and is generally non-toxic to humans. It also has a distinctive and pleasing color and luster when polished.

As a result, copper is used for a wide variety of products from electrical wiring, water piping, roof coverings, kitchen utensils, and jewelry. Copper is easily joined using soldering and brazing techniques. Welding of copper is more difficult due to its high thermal conductivity. Inert gas welding methods are typically required for welding applications [1]. Laser welding has shown promise in specialized configurations [2]. It is easily recycled and, in fact, much of the copper in use now has been around for centuries.

As a result of the many advantages of copper, the solar water heating industry has been using it since the mid-1970s as the material of choice for collectors, the fundamental component of a solar water heating system. Depending on the type of collector and how it is configured into a water heating system, different liquids are in direct contact with the copper that is being heated by the sun.

Some collectors operate in a closed loop arrangement where the liquid that flows through the copper collector is captive and is used only as a heat transfer material between the collector and a heat exchanger. Other collectors, such as thermosiphon and integral types, are used to pre-heat domestic water that flows into a conventional water heater. The copper in these systems are therefore exposed to whatever quality of water exists in the locality in which it operates.

Copper has been used in domestic water systems for many years and in the vast majority of cases it has performed flawlessly. In some situations, though, copper has been known to fail. Pitting corrosion is the usual failure mode; however, erosion can also occur under high flow rate conditions or if the water contains a large amount of suspended solids such as silica.

Copper solar collectors have been manufactured for over 30 years with a preponderance of them installed in the sunnier areas of the world. Relative to the overall number of water heating applications, solar water heating systems serve a very small percentage. As a result, any failures of copper in solar collectors would be relatively imperceptible overall. In those limited situations where copper failure in a solar collector might have occurred, its remedy might be a replacement by the installer, probably dismissing the failure as a random manufacturing flaw. Essentially, for most of the history of the solar water heating industry, there are simply not sufficient quantities of solar collectors installed in any location where failures due to corrosion would occur in a quantity to be noticeable.

In the late 1990s well over 100 integral solar collector units were installed in Civano, a new subdivision located in the southeastern part of Tucson, Arizona. In 2000, pin-hole leaks began to appear in some of these collectors. Sandia National Laboratories and the CDA were asked to analyze the situation and make recommendations to the industry. The analysis was done and some summary information was included in some published papers, but the details were not published. The details are provided in this report.

It is important to note that after the initial failure of about a dozen collectors in Civano, few additional failures were recorded. Moreover, the extent of other corrosion-related failures in collectors in other locations still remains unknown.

In 2002 a 6000-ft^2 unglazed copper collector system at Camp Pendleton was attacked by corrosion. This pool heating system, which had been in full-time operation for 10 years previously, was completely destroyed by a pitting corrosion event that occurred over a 72-hour period. Sandia performed an analysis of this failure and uncovered the source of the failure. A formal report was never produced. However, the essential facts and finding of this case are presented in this report.

Since the Civano and Camp Pendleton events, copper corrosion has remained a minor concern to the industry. However, with the signing of Energy Policy Act in 2005, solar systems are heavily encouraged, and with the possibility of collectors being installed in mass, there is more interest in potential failures due to copper corrosion and what preventative measures might be employed.

Over the past seven years, Sandia staff has been steadily collecting information about copper corrosion. This report consolidates the information into a single document for use by the solar hot water and solar pool industry. Copies of the reports and accounts of the Civano and Camp Pendleton failures are included along with other material relating to copper tubing failures in Arizona. A bibliography contains references to many papers and articles that might be of benefit to the solar community. Additionally, on-line resources to provide assistance regarding copper corrosion are noted.

This report does not purport to present a comprehensive dossier about copper corrosion. Rather, it simply puts forth in a single source all of the information that has been accumulated at Sandia relative to copper corrosion, especially as it relates to solar water heaters.

Section 2 contains the materials relative to Civano and Camp Pendleton. Section 3 presents copies of reports and other materials relating to copper corrosion and how it compares to other materials. Section 4 presents a bibliography of reports and other reference materials relating to copper corrosion.

Section 2a. Information Pertaining to the Analysis of the Failures at the Civano Subdivision

In this subsection we present four reports and papers relating to the Civano situation. First is the Sandia report on their analysis of the failures. That is followed by a report of analysis performed by the CDA. Sandia's response to that report follows. Finally, a conference paper that outlines the lessons learned from the Civano experience is included.

Copper Corrosion Analysis of Civano Solar Collectors Conducted by Sandia National Labs

Dave Menicucci and Rod Mahoney
Sandia National Laboratories

August 2002

Background

The Civano Subdivision, a master-planned sustainable community located in eastern Tucson, AZ, is expected to build-out to a total of around 2000 homes, of which around 200 homes have been completed. Currently over 85% of these homes have solar hot water and/or photovoltaic power systems. All future homes will be encouraged to be as energy efficient as possible through the use of state-of-the-art technology, including solar hot water.

In late calendar year 2000 a small number of solar water heating collectors began to fail in the Civano Community due to leakage. The collectors installed at Civano are the integral type, all of which were fabricated from copper and most of which are manufactured by Thermal Conversion Technologies (TCT) in Florida.

In this type of collector system a set of four-inch diameter copper tubes are mounted adjacent to one another in a metal box and is insulated on all sides except the top. The tubes are interconnected serially via ¾" copper piping allowing cold, potable water to enter the bottom tube and travel progressively through all of the tubes, exiting out of the hottest tube located at the top of the collector. The tubes are coated with a black, moderately selective material to increase the absorption of solar radiation. The TCT collector box design is sealed with a double-glazing on the top surface. Each collector produced by TCT is pressure tested to 160 psi to insure the integrity of the product before it leaves the factory.

The collector is mounted on a residential roof with the glazing side facing the sun. Cold water from the street is connected to the bottom of the collector. The outlet of the collector, located at the top, is connected to the inlet of the standard hot water system in the home. During normal system operation the collector tubes are completely full of water and are warmed by the sunlight. Whenever hot water is drawn throughout the home, solar preheated water is taken from the collector and placed into the standard hot water heater. When the solar collector is optimally sized to the load of the home most of the hot water consumed will have been produced by the sun. Since the TCT collector employs a double-glazed design, the collector can produce water temperatures of near 190F to 200F in high solar radiation environments when the loads conditions in the home are low or zero. This maximum temperature condition is referred to as the "wet stagnation temperature".

The TCT design is unique since each tube is fabricated from premium quality sheet copper that is rolled into a tube and then welded along the seam. The copper sheet material used contains ~99.99% copper and is ISO certified. The tube end caps are also made of copper and welded onto the tube ends. The interconnecting tubing, joining each adjacent collector tube pair, is made from a single length of either standard type L or K copper pipe and is formed into a U-shape. The interconnecting pipes are inserted into a drawn fitting in the end caps and are brazed into place. The collector is pressure tested before delivery to the field to assure that it is free of leaks. The thickness of the copper sheet material used to fabricate the tubes is proprietary as well as is the details of the copper welding process.

In response to the first reports of a failure, TCT asked Sandia National Laboratories to investigate the possible causes of the failures. The Civano community later also asked for assistance.

Sandia's Materials Analysis and Corrosion Departments were enlisted to assist in the analysis that was coordinated by A. R. Mahoney, formerly of the Energy Systems Evaluation Department.

Process

Sandia engineers talked with TCT officials on the phone and then met with the Civano representatives to scope out the project and to define the goals and objectives. The main goal was to determine the probable cause of the failures. A secondary goal was to identify any mitigation strategies or other solutions that might prevent further failures in the Civano community service environment.

At the time of the first meeting, four collectors had failed, all due to pinhole leaks in the copper absorber tubes that were evident from external observations. Samples of the failed collector tubes were collected and submitted to Sandia's Corrosion Lab for analysis.

As the analysis proceeded additional TCT collectors have failed, with a total of ten (10) failures as of July, 2002. All of the failed TCT collectors had been in service at least 18 months.

In addition to the TCT collectors, a single, fully operational Sun Earth solar collector was removed from an installation in the Civano community and samples of the collector tubes were sent to Sandia for inspection and analysis. This collector design is also an integral type and is constructed of copper tubes similar to those built by Thermal Conversion Technology.

There are three (3) significant differences between the TCT and Sun Earth designs, however. First, the collector tubes are fabricated from standard, commercially available Drain-Waste-Vent (DWV) four-inch diameter pipe, which has a relatively thick wall to meet its typical designed use in commercial and industrial settings. The copper alloy in DWV tubing (~99.9% copper) is virtually identical to the material used in the TCT collectors, except with a slightly greater amount of impurities. Second, the Sun Earth collector design utilizes a single glazing, rather than double-glazing collector top, which would allow more heat loss through the front surface and should reduce the maximum wet stagnation temperature of the collector. Third, the TCT collectors have slightly thicker insulation in the collector box. This also would inhibit heat loss and increase the wet stagnation temperature.

The final two copper samples were taken from standard Type L cold and hot water supply tubing that was removed from one of the TCT failed units (Lot 16). These parts were also sent to Sandia for analysis.

Finally, the municipal water supply for the Civano area was also sampled and analyzed by both a professional water analysis laboratory in Albuquerque, Assaigai Analytical Labs and the City of Tucson water department. Water samples were also taken within the Civano community that included a sample from before and after the water softener in a single residence.

In preparation for this analysis, information was obtained by consulting expertise from the Copper Development Association (CDA) as well as performing a literature search.

The analyses have been completed and the findings are outlined below.

Analysis and Findings

Based on our understanding of copper corrosion in water service environments, the water sample results indicate that the dissolved constituents in the supply water are in sufficient quantities for the water to be considered mildly aggressive toward copper under normal service conditions. The level of dissolved CO_2, which is a key parameter in determining the potential for a corrosive water condition for copper, was measured at ~10ppm. This value is at the lower end of the range normally considered as an aggressive corrosive condition for copper.

The table below shows the results of the water quality analysis of typical Civano water samples in summary form. The last row shows the criteria level for determining the potential for pit corrosion in copper. If one or more of these constituent levels are within the tolerances noted in row 4 and the CO_2 level is at a level of ~10 ppm or greater, then the water can be considered aggressive in terms of increasing the potential for pitting corrosion in copper. In this sample, the Civano water clearly meets the criteria for the Nitrate/Nitrite ratio and the K (potassium) level. It is near the limit for pH, and Sulfates-to-Chloride ratio. With a CO_2 level of the Civano water estimated at ~10ppm, the water quality measurements indicated that the supply water resides at the lower border of aggressiveness in terms of pitting corrosion potential to copper metals.

Sample #	**Alkalinity (mg/L)**	**Bicar-bonate (mg/L)**	**Carbonate (mg/L)**	**Chloride (mg/L)**	**Nitrate/ Nitrite (mg/L)**	**Ca (mg/L)**	**K (mg/L)**	**Mg (mg/L)**	**pH**	**Silica (mg/L)**	**Sulfate (mg/L)**	**Sulfate-to-Chloride Ratio**	**Bicar-bonate-to-Sulfate Ratio**
softened	129.0	129.0		6.6	1.2	---	1.8	0.1	7.7	13.0	25.6	3.9	5.0
pre-softened	132.0	132.0		6.0	1.2	34.5	1.5	5.5	8.0	13.1	23.4	3.9	5.6
other Civano water	128.0	128.0		5.3	1.1	29.8	1.4	4.3	8.3	12.2	14.8	2.8	8.6
pitting possible				>15	<25		<4		7.0-7.7	>26	>17	>3.0	<1

To the extent of our understanding, the quality of the water meets all acceptable standards for potable water uses.

The results of the Tucson Water Department's water analysis were not made available for inclusion in this report.

The TCT collector samples were visually inspected for evidence of pit corrosion. It was obvious that to the naked eye that pit corrosion had occurred in both the tube wall of the collectors as well as the welded seams. The photo below shows an example of corrosion sites and a pitting site that were visible.

To obtain a better understanding of the corrosion extent and to increase the number of total samples, 32 copper tubes were visually examined from four failed TCT collectors. A summary of the results from these examinations is as follows:

a. Twelve tubes exhibited evidence of numerous sites of pit corrosion, most of which had not fully perforated the tube wall but would probably eventually penetrate the tube wall if the collector had been left in service.

b. Two tubes had wall pit corrosion that fully perforated the wall.

c. One tube showed a leak in the seam weld, probably related to corrosion.

d. Two tubes showed leaks in the end cap weld seam, which was probably related to corrosion.

e. The remaining tubes showed no apparent evidence of pit corrosion.

Eight tubes from the Sun Earth collector were examined. Numerous surface corrosion sites were observed where only minimal pit corrosion was apparent. The photo below shows one of the tubes with areas of visible corrosion.

No areas were found where tube wall perforation appeared to be an immediate concern. However, additional analysis has shown that the corrosion has penetrated into the tube wall at some of the suspected pitting sites. For more details, see Appendix D, "Sun Earth Collector Removed From Civano after ~1yr Exposure," Mahoney, et. al.

The hot and cold water supply tubing was examined. Corrosion products were observed on the interior of both the cold and hot water tubing. The cold water tubing showed numerous, small surface corrosion sites. The hot water supply tube showed a significantly greater amount of corrosion products and possible pitting.

The photos below clearly show the differences in the amount of corrosion on the cold supply tubing and the hot return tubing.

An analysis of some of the potential pitting sites is complete. The results show that the corrosion has begun to penetrate the tube wall.

Conclusions and Recommendations

Based upon both the metal and water samples analyzed, the observed copper corrosion in the solar collectors and the supply/return tubing is probably due to a combination of both mildly aggressive water and higher water temperatures that are typical of solar collectors fabricated from copper. The solar collector operating water temperatures may routinely reach 180F in the Tucson area. Furthermore, there have been reports from on-site engineers of water temperatures in collectors reaching up to 205F. In most domestic environments, conventional water heater temperatures are typically 120F with a maximum of 140F. The copper corrosion rate in these mildly aggressive water conditions is probably increased with increased collector water temperature. Based upon the current limited results however, the magnitude of the copper corrosion rate, as a function of temperature and water quality, cannot be quantified. More detailed studies would be needed to better understand these relationships. It should be noted that these temperatures and water conditions are specific to the corrosion mechanism of copper materials only.

If the rate of corrosion is strongly related to the water temperature, as the data suggest, then it is probable that the TCT collectors, which employ a double glazed design and higher operating temperatures, may experience more rapid corrosion rates than the Sun Earth collectors. Furthermore, if this temperature correlation is valid, then it is likely that a significant percentage of the copper metal in the Civano community that is subjected to the higher water temperature conditions associated with the solar collectors will continue to experience conditions conducive to corrosion.

Based on the information obtained from both the literature and that provided by the CDA, limited data are available for the copper corrosion observed because of the combination of water temperature and water quality service conditions in Civano. The largest body of copper corrosion knowledge exists for cold supply water temperature conditions, i.e., water temperatures below 140F. Limited information is available to quantify the copper corrosion rate under the higher water temperatures normally associated with solar collectors.

Members of both the solar industry and the Solar Ratings and Certification Corporation (SRCC) have expressed the need to better understand the details of the copper corrosion mechanism(s) at Civano. To meet this objective more detailed studies of the interaction between water temperature and water chemistry are needed. Collaboration between Sandia National Laboratories and the CDA is one possible route to obtain the expertise and structure the investigation process needed to determine the best solutions. Coordination with SRCC would also be integrated into the investigation. A limited controlled experiment, directed by Sandia National Laboratories, to investigate the rate of copper corrosion as a function of water quality and water temperature would be needed to enable prediction of tubing and collector lifetimes in service conditions like Civano. However, current resource limitations prohibit any of this analysis at this time.

Since a complete understanding of the details of the corrosion process has yet to be determined, a definitive mitigation strategy has not been formulated. However, if additional investigative and experimental work can be conducted (as suggested above), it may be possible to develop a set of recommendations and cost-effective engineering strategies to either minimize or totally mitigate the copper corrosion conditions and effects observed at Civano.

Copper Corrosion Analysis of Civano Solar Collectors
Conducted by the Copper Development Association

In addition to the analysis provided by Sandia, a member of the solar industry asked the CDA to perform an analysis of the samples of corroded copper samples taken from the Civano solar systems. Sandia personnel supplied the samples along with a copy of the technical analysis. A copy of the report (page 12) is supplied below with permission of Andy Kireta, Jr., of CDA.

CDA
Copper Development Association Inc.

July 8, 2003

Tom Bohner
Sun Systems
15716 North 76th Street
Scottsdale, AZ 85260

RE: Copper Alloy Technical Information

Dear Mr. Bohner,

The enclosed report contains a summary of the findings related to the cause and mechanism of failure of the copper tube specimen you had Sandia Labs provide. The report further contains recommendations on how this type of corrosion and associated failure of the copper alloy tube can be prevented in the future.

As you can see, our conclusions differ significantly from the Sandia report. Essentially they tried to apply principles of Type I (cold water) pitting to a hot water system. Let me also say that the claims of assistance from CDA in their report appears to be nothing more than referencing materials published by CDA.

Should you require any further information or assistance you can contact me at the phone number or address listed on this letterhead.

Best Regards,

COPPER DEVELOPMENT ASSOCIATION INC.

Jim Weflen

Jim Weflen
CDA Western Region Manager

cc: A. G. Kireta, Jr., CDA/NPM (w/o enclosure)

Main Office: 260 Madison Avenue, New York, New York 10016 Tel: (212) 251-7200 Fax: (212) 251-7234 www.copper.org

COPPER TUBE/FITTING SPECIMENS
CIVANO SUBDIVISION
TUCSON, ARIZONA

Background

In May 2003, Mr. Jim Weflen, Regional Manager for the Copper Development Association (CDA) in the western states, submitted eight copper tube/fitting specimens to the CDA office in New York, New York for laboratory examination. They had been removed from solar collector systems used to heat domestic water at residences in Civano Subdivision, Tucson, Arizona when pinhole-type leaks were repaired. Since preliminary examination revealed essentially identical corrosion had taken place in all of the specimens, only two specimens were selected for in-depth investigation. These were:

1. A 12.1-inch length of 4.0-inch diameter (nominal size), 0.032-0.033-inch thick copper tube;[1]
2. A 16.7-inch length of 4.0-inch diameter (nominal size), 0.032-0.033-inch thick copper tube.

According to the information furnished, the solar collector systems had been in service relatively short time periods when the leaks were detected in 2001.

Water distributed at the affected residence is obtained from the City of Tucson Water Department. The source of the water is a well supply. Representative chemical composition data for the water accompanied the request for laboratory examination. These data are included in the Appendix. In reviewing these data, it should be noted that the aluminum, iron and manganese contents of the waters were not reported.

Results

Examination of the outside surfaces of the specimens revealed no significant deterioration by the external environment. Basically, the outside surfaces were covered with a protective tarnish film of reddish-brown cuprous oxide (i.e., cuprite, Cu_2O). In part, the cuprite was overlaid with a black material (i.e., a coating) which had been applied to facilitate the collection of solar energy. The only significant deterioration was a pinhole-type perforation through each of the tube walls. Stereomicroscopic examination indicated that the perforations through the tube walls had initiated on the inside surfaces of the specimens.

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[1] The copper tube had been fabricated using a proprietary technique wherein sheet material is roll formed and welded longitudinally.

The specimens were subsequently sectioned lengthwise in order to examine the inside surfaces.

Examination of the inside surfaces of the specimens confirmed the belief that the perforations through the tube walls had initiated on the watersides. The sites of the perforations through the tube walls were covered with relatively voluminous tubercles of friable, greenish-colored copper corrosion products. The corrosion-induced pits under the tubercles contained porous, reddish-brown cuprous oxide and had diameters which were much larger than those of the perforations through the tube walls. Further, other tubercle covered corrosion-induced pits containing porous cuprous oxide existed on the waterside surfaces. These pits had propagated to various depths into the tube walls. In general, the size of the tubercle reflected the depth and extent of the underlying pit. The larger the tubercle, the deeper and more extensive was the pit.

Energy dispersive spectroscopy (EDS) and microchemical analysis (MCA) revealed that the outer layers of the tubercles associated with the waterside pitting contained major amounts of copper, iron, oxygen and silicon, minor quantities of sulfur, carbonate and calcium, semi-minor amounts of magnesium and chloride and trace quantities of zinc. The tubercles consisted primarily of basic copper carbonate (i.e., malachite, $CuCO_3 \cdot Cu(OH)_2$) and basic copper sulfate (i.e., brochantite, $CuSO_4 \cdot 3Cu(OH)_2$ which was admixed with some deposits from the water. The deposits included hydrated hematite (i.e., iron oxide, rust, Fe_2O_3). Equally important, EDS revealed that major amounts of iron and oxygen existed in the corrosion-induced pits. Hydrated hematite coexisted with the porous cuprous oxide in the pits.

Where localized pitting attack had not taken place on the waterside surfaces, there was no significant deterioration by the hot water conveyed. Basically, the copper in these essentially unaffected areas was covered with a tarnish film of black cupric oxide (i.e., tenorite, CuO). The presence of tenorite on the waterside surfaces was consistent with the report that the water conveyed had been heated to temperatures in excess of about 160°F (e.g., as hot as 205°F). Undoubtedly, heating of the water into this temperature range had facilitated the rate of pitting attack.

Examination of the limited chemistry data for waters at Civano Subdivision (i.e., see Appendix) revealed no obvious reason to believe that the product conveyed was a factor in the pit-initiation process. Once initiated, pitting was most likely facilitated by the natural presence of dissolved oxygen in the water.

Conclusions

Based upon examination of the specimens submitted for laboratory investigation, it can be concluded that the corrosion-induced pits which culminated in pinhole-type perforations through the tube walls had initiated on and propagated from the waterside surfaces. There was no significant deterioration by the external environment.

The primary factor in the pit-initiation process appeared to be the heating of a water containing an appreciable amount of iron or iron oxide(s) which allowed a highly cathodic, iron-containing compound such as hydrated hematite to be deposited on the hot copper surfaces. In turn, pit initiation occurred by microgalvanic attack or oxygen-differential-type, concentration-cell corrosion. The source of the iron-containing constituent which appeared to be primarily responsible for pit initiation could not be established. Possibly, it resulted from the corrosion of ferrous-base materials upstream of the copper tube systems.

The pitting attack was facilitated by heating the water, at least on occasion, to temperatures approaching 205°F. The same condition probably facilitated the deposition of iron oxide(s) from the water.

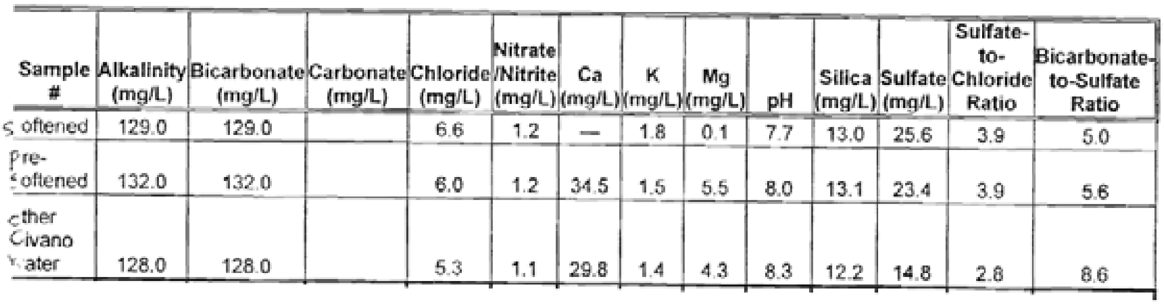
Recommendations

It is recommended that the hot and cold waters at the affected residence be analyzed on six, randomly selected occasions over a three month period for iron/iron oxide and suspended solids.

If potentially deleterious amounts of suspended solids and/or iron oxide(s) presently exist in the water, a qualified water treatment specialist/firm should be retained to establish the most viable and cost effective method for improving the water quality. For example, unacceptable amounts of suspended solids in water can be removed by filtration. It is also known that iron oxide(s) generated by the corrosion of ferrous-base materials can be effectively mitigated by proper water treatment.

Additional information on the role of iron in the hot water pitting of copper is presented in the paper "The Forms of Corrosion in Copper Tube Systems Conveying Domestic Waters." A copy of this paper is included in the Appendix.

JRM/mkk
June 19, 2003



Sample #	Alkalinity (mg/L)	Bicarbonate (mg/L)	Carbonate (mg/L)	Chloride (mg/L)	Nitrate /Nitrite (mg/L)	Ca (mg/L)	K (mg/L)	Mg (mg/L)	pH	Silica (mg/L)	Sulfate (mg/L)	Sulfate-to-Chloride Ratio	Bicarbonate-to-Sulfate Ratio
Softened	129.0	129.0		6.6	1.2	—	1.8	0.1	7.7	13.0	25.6	3.9	5.0
Pre-Softened	132.0	132.0		6.0	1.2	34.5	1.5	5.5	8.0	13.1	23.4	3.9	5.6
Other Civano Water	128.0	128.0		5.3	1.1	29.8	1.4	4.3	8.3	12.2	14.8	2.8	8.6

Chemistry data for water at Civano Subdivision, Tucson, Arizona.
Source: The Sandia National Laboratories report "Copper Corrosion Analysis of Civano Solar Collectors Final Report.

THE FORMS OF CORROSION IN COPPER TUBE SYSTEMS CONVEYING DOMESTIC WATERS

By

J. R. Myers[1]
And
A. G. Kireta, Jr.[2]

Presented at

CDA Copper Symposium 2001 – Plumbing Tube
Sheraton Crystal City Hotel
Arlington, Virginia 22202
25 April 2001

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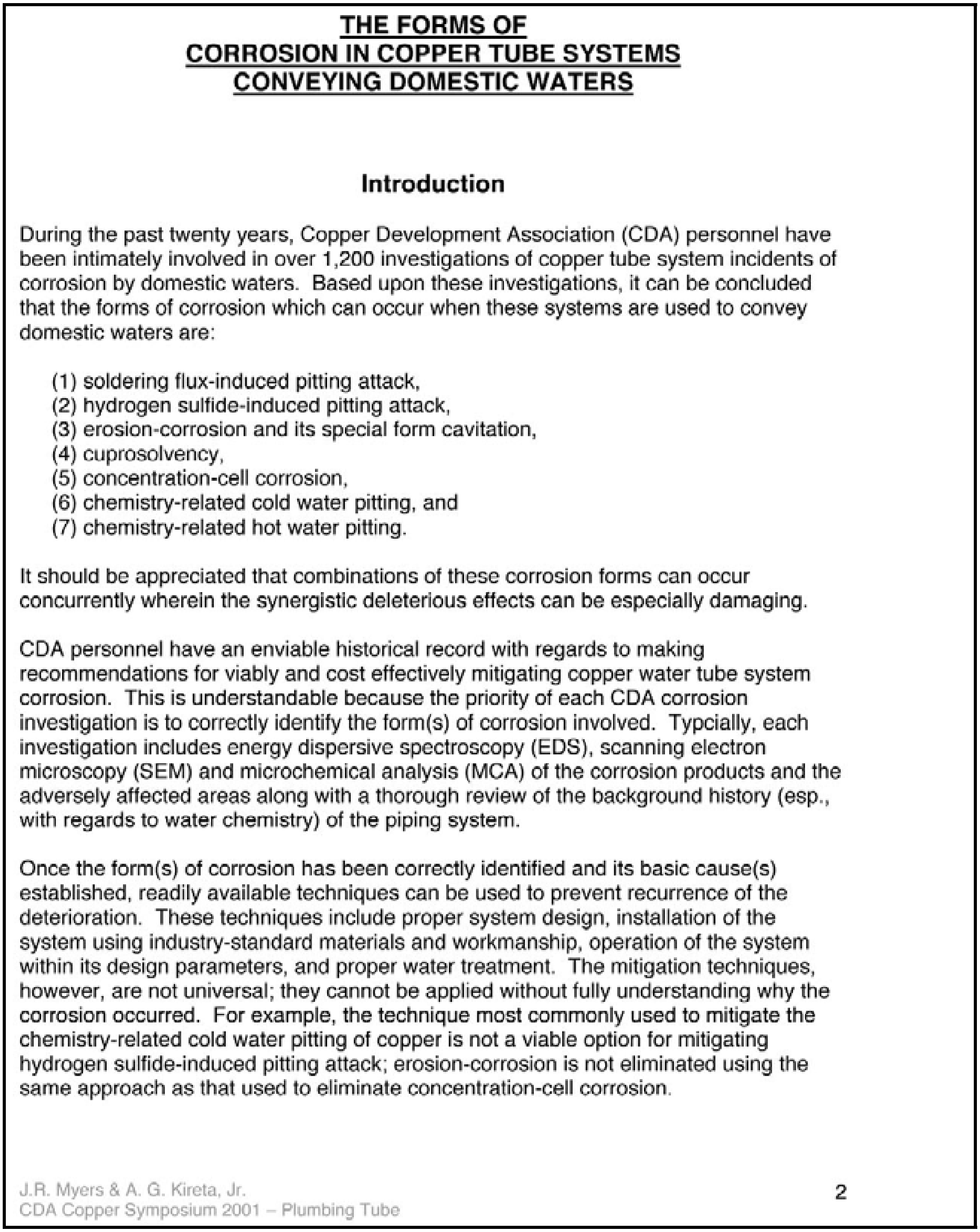

THE FORMS OF CORROSION IN COPPER TUBE SYSTEMS CONVEYING DOMESTIC WATERS

Introduction

During the past twenty years, Copper Development Association (CDA) personnel have been intimately involved in over 1,200 investigations of copper tube system incidents of corrosion by domestic waters. Based upon these investigations, it can be concluded that the forms of corrosion which can occur when these systems are used to convey domestic waters are:

(1) soldering flux-induced pitting attack,
(2) hydrogen sulfide-induced pitting attack,
(3) erosion-corrosion and its special form cavitation,
(4) cuprosolvency,
(5) concentration-cell corrosion,
(6) chemistry-related cold water pitting, and
(7) chemistry-related hot water pitting.

It should be appreciated that combinations of these corrosion forms can occur concurrently wherein the synergistic deleterious effects can be especially damaging.

CDA personnel have an enviable historical record with regards to making recommendations for viably and cost effectively mitigating copper water tube system corrosion. This is understandable because the priority of each CDA corrosion investigation is to correctly identify the form(s) of corrosion involved. Typcially, each investigation includes energy dispersive spectroscopy (EDS), scanning electron microscopy (SEM) and microchemical analysis (MCA) of the corrosion products and the adversely affected areas along with a thorough review of the background history (esp., with regards to water chemistry) of the piping system.

Once the form(s) of corrosion has been correctly identified and its basic cause(s) established, readily available techniques can be used to prevent recurrence of the deterioration. These techniques include proper system design, installation of the system using industry-standard materials and workmanship, operation of the system within its design parameters, and proper water treatment. The mitigation techniques, however, are not universal; they cannot be applied without fully understanding why the corrosion occurred. For example, the technique most commonly used to mitigate the chemistry-related cold water pitting of copper is not a viable option for mitigating hydrogen sulfide-induced pitting attack; erosion-corrosion is not eliminated using the same approach as that used to eliminate concentration-cell corrosion.

With regards to predicting corrosion and the application of corrosion-control techniques for copper tubes and fittings exposed to domestic waters, it must be appreciated that the widely used indices (i.e., the Langelier, Ryznar, saturation, and stability indices) are not applicable. Copper will behave as a noble metal as long as its naturally protective tarnish film of cuprous oxide (Cu_2O) remains intact. It does not require the deposition of calcium carbonate ($CaCO_3$) scale on the waterside surfaces for effective corrosion control.

Soldering Flux-Induced Pitting Attack[1] (1)

Soldering flux-induced pitting attack is almost always associated with the use of an unusually aggressive flux and/or the application of excessive amounts of flux. Once initiated at the flux-activated sites, propagation of the pits is facilitated by the natural presence of dissolved oxygen in the water conveyed. Most often, flux-induced pitting occurs preferentially in cold-water lines; it is also known to occur in infrequently used hot water lines.

Flux-induced pits contain porous, reddish-brown cuprous oxide, with the pits being covered with relatively voluminous, friable tubercles of greenish-colored, copper corrosion products (Figure 1). Typically, the tubercles consist of basic copper carbonate (i.e., malachite) and/or copper chloride(s). The pits are not normally randomly occurring; they tend to occur preferentially along relatively narrow bands that are nearly parallel to the longitudinal axes of the tubes and fittings (i.e., along the "ghosts" of flux runs). Often, the bands/band of pits in these areas are covered with tubercle ridges (e.g., see top tube half-section in Figure 1) rather than distinct, hemispherically shaped, individual tubercles. Flux-induced pits also occur preferentially on the periphery of the sticky, petrolatum-base flux residues/runs, which often exist on the waterside surfaces when the plumbing technician applies excessive flux. When the latter is observed, it is not uncommon to also find globules of solder on the waterside surfaces of the tubes and fittings. Although flux-induced pitting can be expected to occur at or in the near vicinity of soldered connections associated with poor workmanship, cases are known where the pitting occurred over eight feet away from a fitting.

Soldering flux-induced pitting can be confirmed using energy dispersive spectroscopy. Chlorides in major amounts, and sometimes zinc, will be detected in the pits or on the edges of the pits (Figure 2). Copper chloride(s) coexists with the porous cuprous oxide at the pit sites. The latter is understandable because soldering fluxes commonly contain activating chlorides such as ammonium chloride, zinc chloride, tin chloride and/or hydrochloric acid.

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(1) Numbers in parentheses refer to footnotes; numbers without parentheses are references.

Soldering flux-induced pitting can be effectively mitigated by requiring plumbing technicians to use industry-standard materials and workmanship when installing copper tube systems. Fluxes used for soldering copper water tube systems should satisfy the requirements of American Society for Testing and Materials (ASTM) Standard Specification B813[2] and soldered connections must be made in accordance with the guidelines presented in ASTM Standard Practice B828[3] and the CDA Copper Tube Handbook.

Figure 1 – **The soldering flux-induced pits were covered with friable, greenish-colored tubercles of copper corrosion products. The perforations through the tube walls (i.e., see arrows) and most of the pits existed along relatively narrow bands, which were nearly parallel to the longitudinal axes of the tubes (i.e., along the "ghosts" of flux runs).**

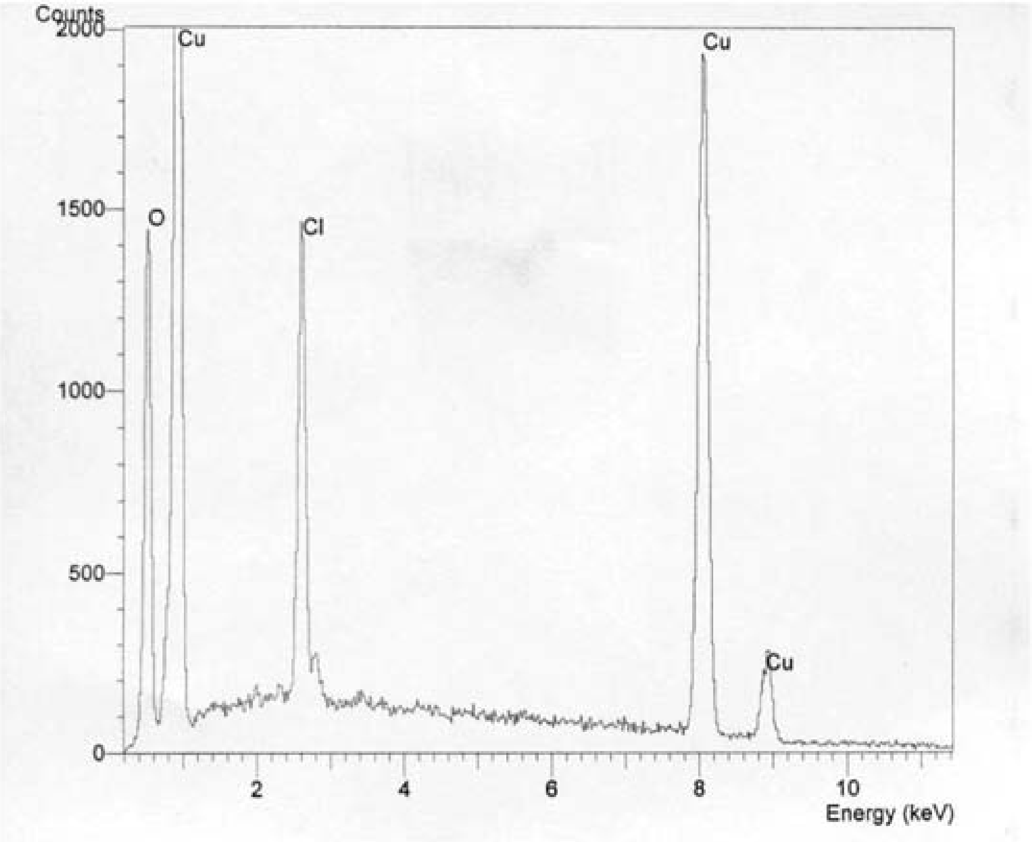


Figure 2 - Energy dispersive spectroscopy normally reveals the presence of major amounts of chloride at the pit sites when the localized attack is soldering flux-induced.

Hydrogen Sulfide-Induced Pitting Attack

Very small quantities of dissolved hydrogen sulfide (H_2S) in water can cause unacceptable pitting of many metallic materials used to convey domestic waters, including copper and many of its alloys. The threshold concentration above which hydrogen sulfide-induced pitting of copper can be expected to occur is not precisely known. It is known that quantities as low as 0.020 milligram per liter (mg/l) have resulted in copper tube and fitting perforations.

Typically, hydrogen sulfide-containing domestic waters are obtained from well supplies. The sulfide is a natural constituent in the well water, resulting from underground, sulfate-reducing-bacteria (SRB) activity and/or general bacteria decomposition. A fairly large number of these well supplies are known to exist in the states of Alabama, Georgia, and Florida. For example, in Florida, the Ocala Aquifer reportedly contains appreciable amounts of sulfide.[4] It is also known that SRB activity exists in many of the mains and lines used to distribute domestic waters.

Hydrogen sulfide-induced pitting is randomly occurring on the waterside surfaces of the copper tubes and fittings (Figure 3). The corrosion-induced pits typically contain porous, dark, reddish-brown to nearly black cuprous oxide; the pits are normally overlaid with friable, greenish-colored tubercles of copper corrosion products. The tubercles most often consist primarily of copper sulfate that is sometimes admixed with some black, copper sulfide(s). Regardless of the tubercle composition, black, loosely adherent and porous layers of copper sulfide(s) are always associated with the pitting attack. The presence of these corrosion products can be readily verified using EDS and MCA.

Hydrogen sulfide can be effectively removed from water supplies at the treatment plant by a number of techniques.[4, 5] For example, it has been successfully accomplished by reducing the pH of the well water followed by aeration in a forced-draft tower(s). Aeration removes the sulfide by the scrubbing action of the air and by oxidation. Lowering the pH of the water greatly reduces the size of the aerating equipment required.

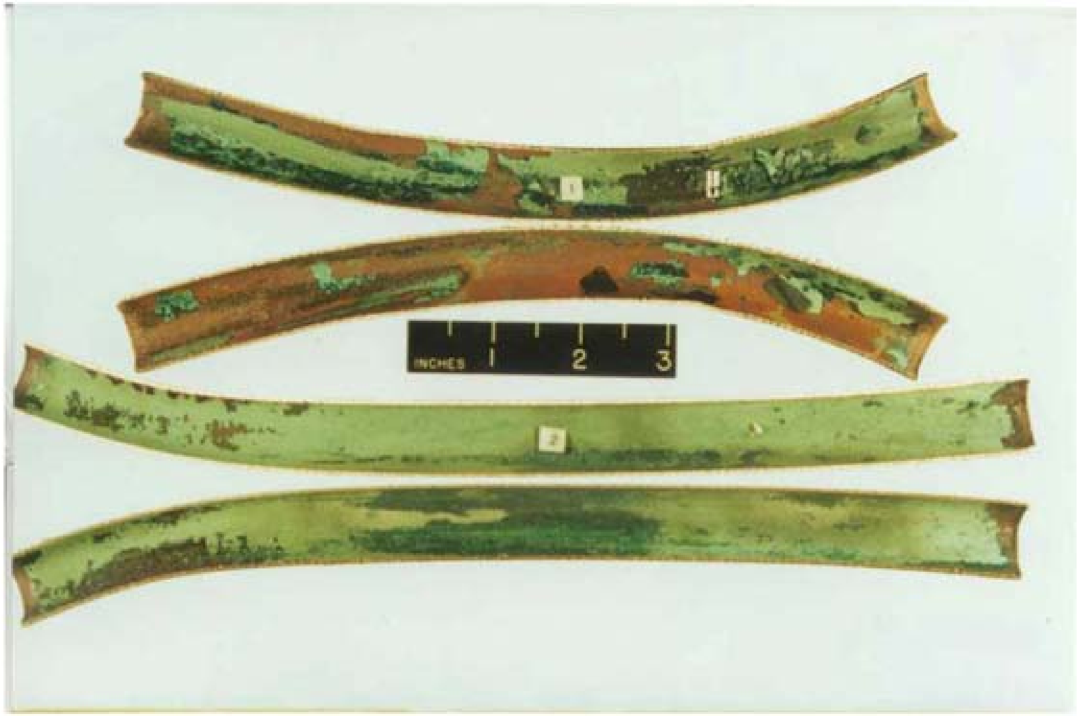


Figure 3 - **Hydrogen sulfide-induced pits are typically overlaid with friable, greenish-colored to blackish tubercles of copper corrosion products. Loosely adherent and porous layers of copper sulfide(s) are associated with the pitting attack (e.g., see upper two tube half-sections where these products had, in part, broken loose).**

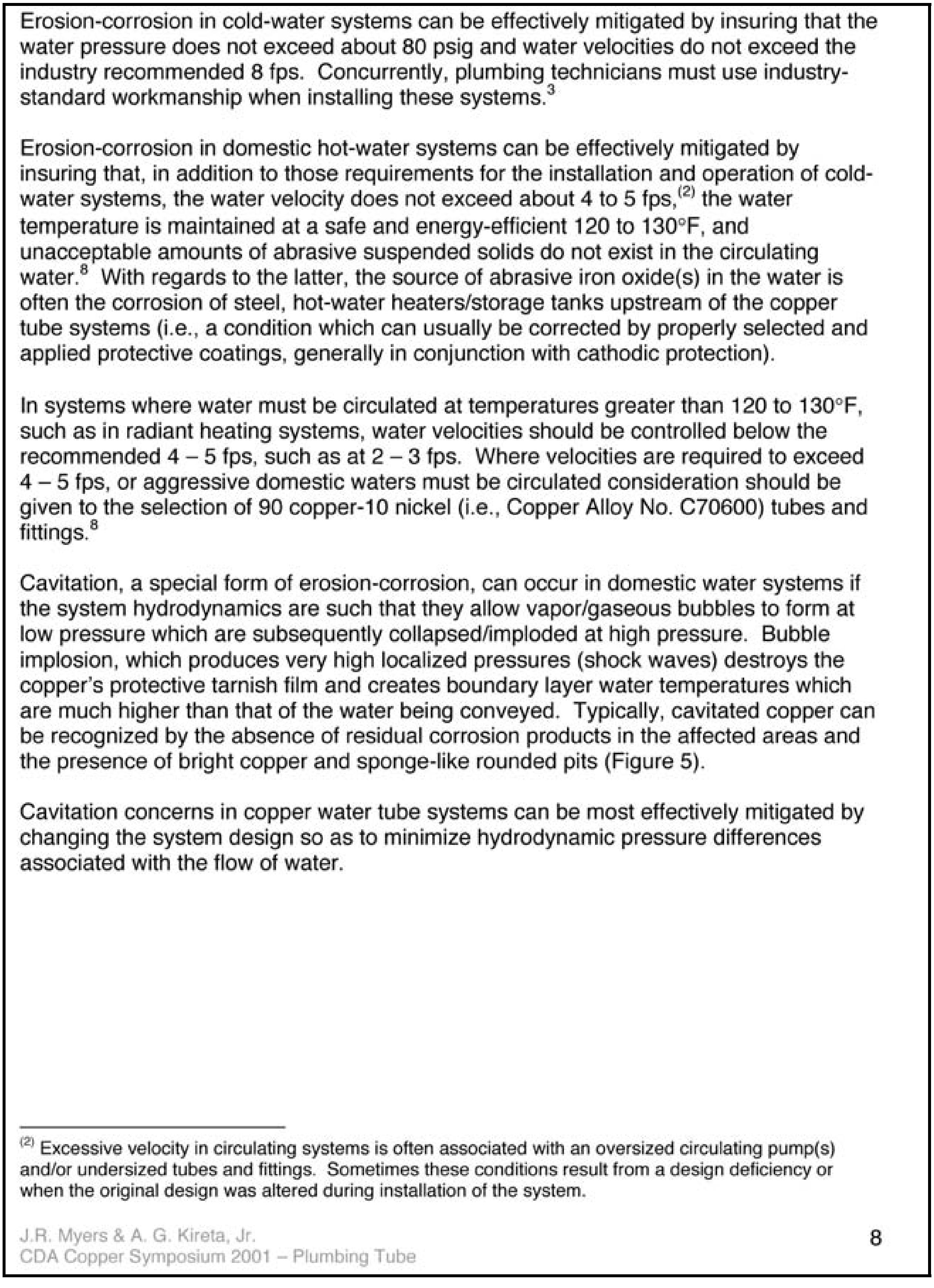
Erosion-Corrosion[6-8]

Erosion-corrosion of copper tubes and fittings (i.e., accelerated attack related to localized, high-velocity/turbulent water inside the tubes and fittings) is normally associated with circulating, domestic hot water systems. Approximately 95% of all erosion-corrosion concerns investigated occurred in circulating, hot water tubes and fittings.

When erosion-corrosion occurs in cold-water lines, the cause is almost always an unusually high water pressure (i.e., a pressure much greater than about 80 pounds per square inch gauge (psig), high water velocity often in excess of 7 – 8 feet per second (fps), and/or poor workmanship when the system was installed. With regards to the latter, erosion-corrosion has been associated with unreamed cut-tube ends, globules of solder on the waterside surfaces, dents in the tubes and fittings, tubes which were not fully inserted into fittings prior to soldering, tubes which were "cocked" in fittings, tubes which were not squarely cut, improperly-installed flared-tube fittings, and other locations where smooth flow had been disrupted and excessive turbulence exists. Of the workmanship-related causes of erosion-corrosion, the most serious and most prevalent is the failure to ream cut-tube ends. These same workmanship-related installation practices also promote and facilitate erosion-corrosion in circulating, hot water systems.

Erosion-corrosion can be readily recognized (Figure 4). The areas of attack are typically grooved and essentially free of residual corrosion products; the affected areas are normally bright and shiny like a new U.S. penny. This is understandable because the erosion phase of the rapidly repetitive, erosion-corrosion process removes the copper oxide(s) films from the copper surfaces. Often, the U-shaped pits in the areas of attack are sufficiently distinct that the direction of former water flow can be determined. When looking down on the surface, the orientation of the attack (i.e., the U-shaped pits) is such that it gives the impression of "horses walking upstream." Lengthwise sections taken through areas of erosion-corrosion will normally reveal undercutting which has the appearance of ocean waves wherein the wave crests face the direction of former water flow.[7]

In circulating, hot water systems, erosion-corrosion is often associated with naturally soft waters or waters which have been softened to a near-zero hardness, especially if the waters contain appreciable amounts of dissolved oxygen and/or dissolved carbon dioxide. Erosion-corrosion is further facilitated by water temperatures greater than about 140°F and flow rates above about 4 to 5 feet per second (fps). Erosion-corrosion can be especially severe at water temperatures greater than about 160°F where black cupric oxide (CuO) forms on the copper tube and fitting surfaces instead of cuprous oxide. Apparently, cupric oxide is much less resistant to erosion-corrosion than cuprous oxide. Cases are also known where the erosion-corrosion process was facilitated by the presence of abrasive suspended solids (e.g., iron oxide and/or sand) in the circulating water. Often, the erosion-corrosion damage is restricted to locations where the water flow makes multiple changes in direction over relatively short distances.



Erosion-corrosion in cold-water systems can be effectively mitigated by insuring that the water pressure does not exceed about 80 psig and water velocities do not exceed the industry recommended 8 fps. Concurrently, plumbing technicians must use industry-standard workmanship when installing these systems.[3]

Erosion-corrosion in domestic hot-water systems can be effectively mitigated by insuring that, in addition to those requirements for the installation and operation of cold-water systems, the water velocity does not exceed about 4 to 5 fps,(2) the water temperature is maintained at a safe and energy-efficient 120 to 130°F, and unacceptable amounts of abrasive suspended solids do not exist in the circulating water.[8] With regards to the latter, the source of abrasive iron oxide(s) in the water is often the corrosion of steel, hot-water heaters/storage tanks upstream of the copper tube systems (i.e., a condition which can usually be corrected by properly selected and applied protective coatings, generally in conjunction with cathodic protection).

In systems where water must be circulated at temperatures greater than 120 to 130°F, such as in radiant heating systems, water velocities should be controlled below the recommended 4 – 5 fps, such as at 2 – 3 fps. Where velocities are required to exceed 4 – 5 fps, or aggressive domestic waters must be circulated consideration should be given to the selection of 90 copper-10 nickel (i.e., Copper Alloy No. C70600) tubes and fittings.[8]

Cavitation, a special form of erosion-corrosion, can occur in domestic water systems if the system hydrodynamics are such that they allow vapor/gaseous bubbles to form at low pressure which are subsequently collapsed/imploded at high pressure. Bubble implosion, which produces very high localized pressures (shock waves) destroys the copper's protective tarnish film and creates boundary layer water temperatures which are much higher than that of the water being conveyed. Typically, cavitated copper can be recognized by the absence of residual corrosion products in the affected areas and the presence of bright copper and sponge-like rounded pits (Figure 5).

Cavitation concerns in copper water tube systems can be most effectively mitigated by changing the system design so as to minimize hydrodynamic pressure differences associated with the flow of water.

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(2) Excessive velocity in circulating systems is often associated with an oversized circulating pump(s) and/or undersized tubes and fittings. Sometimes these conditions result from a design deficiency or when the original design was altered during installation of the system.

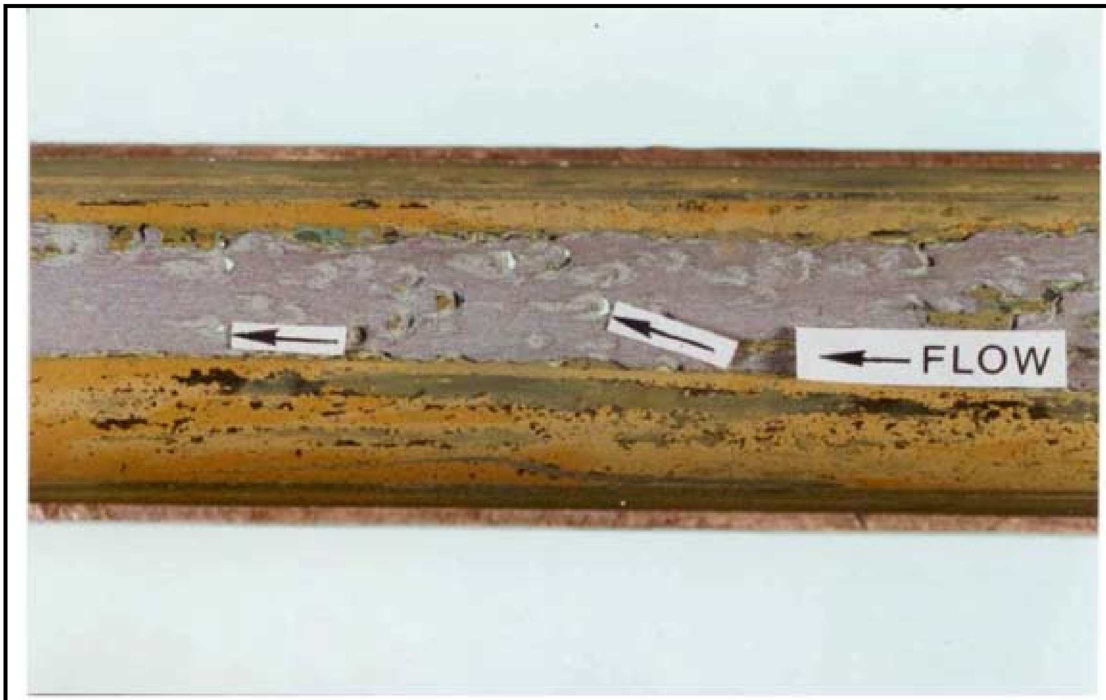


Figure 4 - The U-shaped pits and associated perforations through the tube wall (i.e., see arrows) in the localized, corrosion product free area of erosion-corrosion were sufficiently distinct that the direction of former hot water flow could be determined.

Figure 5 - The perforation through the tube wall (i.e., see arrow) existed in a localized area of severe cavitation. Surface heating by the cavitation process caused the formation of black cupric oxide on the copper where cavitation had not occurred in the cold water line.

Cuprosolvency[9-11]

Cuprosolvency, sometimes referred to as the "blue/green" water concern, describes the slow, general corrosion (i.e., uniform attack) of copper water tubes and fittings by certain domestic waters. The concern with cuprosolvency is that it can result in somewhat elevated copper contents in the water following periods of zero flow (e.g., the first water drawn in the morning may have a higher than normal copper content) and stained plumbing fixtures. Occasionally, it is reported that some "blondes" shampooing in a cuprosolvent water observe that their hair becomes somewhat green. Ironically, cuprosolvent waters and the "green-hair" connection is apparently not a concern for natural blondes. Although a cuprosolvent water can be somewhat annoying, there are no known incidents where it culminated in a perforation through a tube or fitting wall.

Cuprosolvency occurs because the waterside surfaces of the copper tubes and fittings do not form or completely form their naturally protective tarnish film of cuprous oxide. Rather, the copper surfaces develop a thin, loosely-adherent, flocculent-type, layer of bluish to bluish-green colored, copper corrosion products which typically include copper hydroxide (Figure 6).[11] Formed during periods of water stagnation, it is the removal of these products by water flow that creates the cuprosolvency concern.

Cuprosolvent waters typically are very soft (e.g., waters which have been softened to a near-zero hardness); they normally have a pH of less than seven and a low alkalinity. In general, the pHs of these waters are less than neutral because they contain appreciable amounts of dissolved carbon dioxide [9]

The vast majority of bluish/greenish-colored water concerns are self-correcting. Once a sufficient amount of water and its associated dissolved oxygen has flowed through the lines, the concern disappears because the copper, in time, forms its naturally protective tarnish film of cuprous oxide. In persistent situations, cuprosolvency can be corrected by raising the pH of the water to about 8 through additions of chemicals such as sodium hydroxide (NaOH) or calcium hydroxide, $Ca(OH)_2$. Cuprosolvency can often be corrected at individual residences by the installation of neutralizing filters.

Cases are known, however, where the cuprosolvency was soldering flux induced. Instead of developing corrosion-induced pits, the flux causes the slow, nearly uniform dissolution of copper. Water treatment has not been known to be of any significant benefit in mitigating the cuprosolvency concern in these incidents.

Figure 6 - **A loosely adherent, flocculent-type layer of bluish tinted copper corrosion products existed on the waterside surface of the tube. The cuprosolvency was clearly evident to be associated with failure of the copper water tube to completely passivate (e.g., see speckled appearance of the copper tube surface).**

Concentration-Cell Corrosion[12,13]

Although at least five forms of concentration-cell corrosion are known to exist,[13] the form associated with copper, domestic water systems is the oxygen-differential type of attack. It is often referred to as underdeposit corrosion because the deterioration occurs preferentially in the form of pits under deposits, or the thicker layers of deposits, where the oxygen content of the water is low relative to that of the water immediately adjacent to the deposits. In this regard, it should be appreciated that all domestic waters contain dissolved oxygen.

The localized, corrosion process can be especially rapid, for example, when chloride anions migrate to the anodic sites under the deposits and react with metal cations to form metal chlorides, which subsequently hydrolyze to form hydrochloric acid.

The source of the deposits on tubes and fittings is almost always suspended solids in the water conveyed. Often, they consist of iron oxide(s) and/or silica/sand (Figure 7). It is not at all unusual for the source of the iron oxide(s) to be the corrosion of cast-iron/ductile-iron mains used to distribute the water or the galvanized-steel service lines used to connect buildings with the mains. Iron oxide(s) can also result from the oxidation of natural constituents in the water (e.g., iron bicarbonate). The normal cause when the deposits consist primarily of silica/sand is over-pumping a well(s) or a deteriorating concrete or cement-lined water main. Cases are known where the source of the deposits was the post-precipitation of colloids leaving the water treatment plant (e.g., where the coagulation and settling times and/or the filtration process used to clarify turbid water were inadequate).

Once the source of the corrosion-causing deposits is positively identified, suspended solids in water can normally be effectively eliminated. For example, the corrosion of cast-iron/ductile-iron mains and galvanized-steel service lines can be viably and cost-effectively mitigated by proper water treatment,[12] normally by the water purveyor. It is also well established that suspended solids in water can be removed by filtration,[12] either at the treatment plant or the affected building/residence and that improved dwell time at the treatment plant can help eliminate the post-precipitation of suspended solids in the water distribution system.

Figure 7 - **Concentration-cell corrosion in the form of pitting attack had occurred preferentially under the thicker layers of hydrated hematite (Fe_2O_3) and silica (SiO_2) deposits on the waterside surface of the cold water line. The perforation through the tube wall (i.e., see arrow) was covered with a friable tubercle of greenish-colored copper corrosion products.**

Chemistry-Related Cold Water Pitting[9,14-17]

Chemistry-related cold-water pitting of copper tubes and fittings, sometimes referred to as nodular pitting and/or Type 1 pitting, is associated with certain, aggressive well waters or combinations of well and surface supplies. Normally, the pitting only occurs in cold-water lines or infrequently used hot-water lines.

The randomly occurring corrosion-induced pits associated with the pitting attack contain porous, reddish-brown cuprous oxide, with the pits being overlaid with discrete, friable, relatively voluminous tubercles of greenish-colored copper corrosion products (Figure 8). Typically, EDS and MCA reveal that the tubercles consist primarily of basic copper carbonate.[15] EDS will sometimes show that copper chloride(s) coexists with the porous, cuprous oxide in the pits. Where localized pitting has not occurred, there will be no significant deterioration by the water conveyed. Basically, the copper in these essentially unaffected areas will be covered with a protective tarnish film of cuprous oxide which, in general, will be overlaid with a thin layer of greenish-colored deposits from the water (i.e., typically malachite), the source of which is the pitting of copper upstream in the system.

Chemistry-related cold-water pitting can be readily distinguished from flux-induced pitting (i.e., another form of pitting associated with cold-water lines or infrequently used hot-water tubes and fittings) by the randomness of its occurrence. The pitting is not located preferentially along the "ghosts" of flux runs or on the periphery of sticky, petrolatum-base, flux residues.

Waters which are commonly associated with this form of pitting attack normally have a pH in the range of 7.0 to 7.7 and contain more than about 25 mg/l dissolved carbon dioxide along with dissolved oxygen. Often the water will contain more than about 15 mg/l chloride and over 17 mg/l sulfate, with the sulfate-to-chloride ratio often in excess of about 3. Based on better than 100 investigations regarding the chemistry-related cold-water pitting of copper tubes and fittings, there is no reason to believe that any manufacturing-related carbon films or other deleterious films on the copper surfaces are a factor in the pitting attack.[15] This is understandable because chemistry-related cold-water pitting, in those relatively-rare instances when it does occur, can be effectively mitigated by slightly changing the water's chemistry.

The most viable and cost-effective solution to overcoming chemistry-related cold-water pitting in copper domestic water systems is to reduce the dissolved carbon dioxide content of the offending water to a sufficiently-low level.[14-17] Raising a water's pH to about 8 while concurrently reducing its carbon dioxide content to less than about 5 mg/l will successfully mitigate the concern. Environmentally acceptable chemical additions for achieving this objective include caustic soda, lime, and soda ash. These are usually added to the offending water at the treatment plant. For a private residence, the same objective usually can be achieved by the installation of a neutralizing filter.

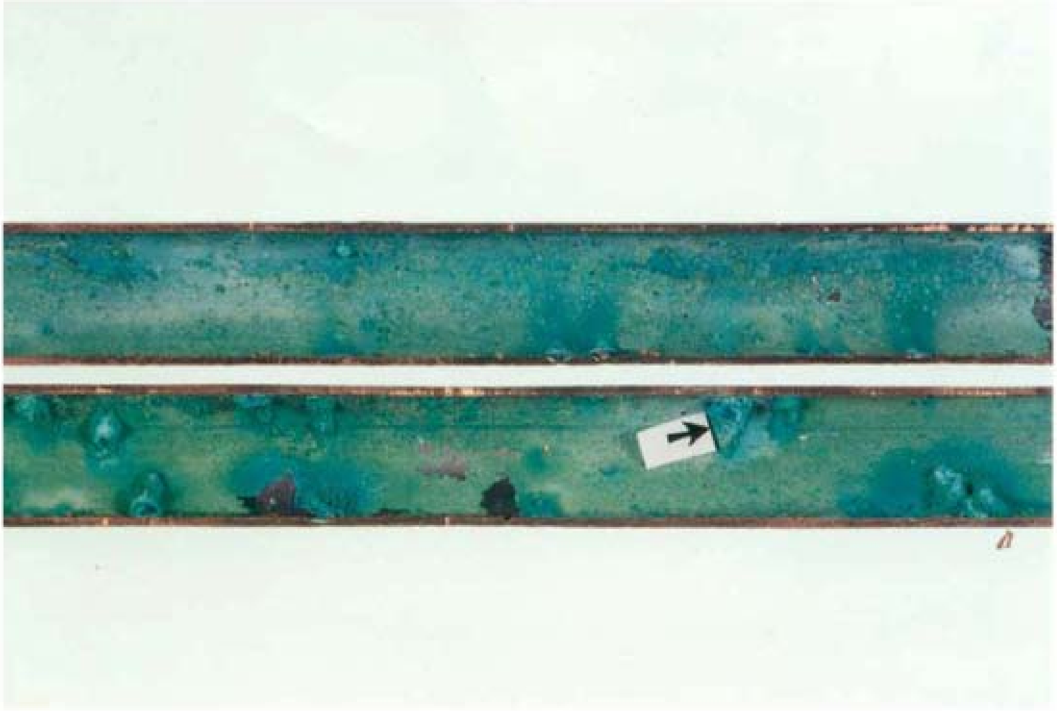


Figure 8 - Randomly-occurring, tubercle-covered corrosion-induced pits (e.g., see arrow where a perforation through the tube wall existed) existed on the waterside surface of the tube which had conveyed a domestic cold water containing appreciable amounts of dissolved carbon dioxide in conjunction with dissolved oxygen.

Chemistry-Related Hot-Water Pitting[18, 19]

Domestic hot waters containing relatively small amounts of iron, manganese, and/or aluminum have been associated with the hot water pitting of copper tubes and fittings. There is also reason to believe that, when the hot water pitting occurs, a silicon-containing constituent could be involved. With regards to the threshold quantities of aluminum, manganese, and iron required to initiate the pitting attack, they are suspected of being as low as, respectively, 0.10,[18] 0.03,[19] and 0.10 mg/l. Generally, hot water pitting associated with the presence of these metals in the water is a concern when the water has been heated to temperatures in excess of about 160°F and black, cupric oxide exists on the hot, copper surfaces.

Typically, the corrosion-induced pits will contain porous, reddish-brown cuprous oxide and be covered with friable, relatively voluminous tubercles of greenish-colored copper corrosion products (Figure 9). EDS and MCA almost always reveal that the tubercles consist primarily of copper sulfate. Often, small amounts of the pit-initiating metal will be detected during EDS of the tubercles. It is unusual for EDS to detect any chloride-containing products in the pits.

Where pitting has not occurred and the copper is covered with a thin layer of cupric oxide, it is common to observe friable, loosely adherent layer of brownish-colored (Figure 10) or brownish-black colored deposits from the water (Figure 9). EDS of these products in the immediate vicinity of the pits will provide the insight required to identify the offending metal(s), which is primarily responsible for the pitting attack. The deposits will contain varying amounts of aluminum, iron, and/or manganese.

Briefly, iron and manganese appear to initiate the pitting attack by the deposition of, respectively, highly cathodic iron oxide (esp., hydrated hematite) and highly cathodic manganese dioxide (MnO_2) on the hot, copper surfaces, especially at locations where temporary defects in the copper oxide layer might exist. Once initiated, the pits will propagate by microgalvanic corrosion and concentration-cell corrosion of the oxygen-differential form. The role of aluminum in the hot-water pitting process (Figure 9) is somewhat less clear because the only investigators on the subject were interested in solving a practical concern, not providing fundamental research.[18] The pitting process could involve the deposition and subsequent hydrolysis of aluminum sulfate to aluminum hydroxide on the hot, copper surfaces which could cause the localized destruction of the copper's passive film.

Regardless of the corrosion mechanisms associated with the copper pitting by waters containing iron, manganese, and/or aluminum, the phenomena is clearly facilitated by heating the waters conveyed to higher-than-necessary temperatures and by the presence of sulfate in the waters.

Hot water pitting by manganese and/or iron-containing waters can often be mitigated by reducing the concentration of these constituents in the waters to acceptable levels at the treatment plant. Iron and manganese-removal systems are available to accomplish this objective. For example, colloidal iron can be removed by coagulation, flocculation and precipitation or filtration. Sometimes the iron content of a water can be sufficiently reduced by, for example, mitigating the corrosion of hot-water heaters/storage tanks, cast-iron/ductile-iron mains, and/or galvanized-steel service lines upstream of the copper tube system. Cases are also known where the hot water pitting was effectively mitigated by reducing the temperature of the water to a safe and energy efficient 120 to 130°F. Properly blended sodium silicate – organic polyphosphate inhibitors added to the water have also been known to mitigate the corrosion concern.

The hot-water pitting associated with the presence of aluminum in the water has been effectively mitigated by raising the pH of the water to about 8.5 while reducing the aluminum content to less than about 0.1 mg/l. Often, the aluminum content of a water, as well as its sulfate content, can be reduced to an acceptable level by simply reducing the amount of aluminum sulfate used for coagulation at the treatment plant and/or insuring adequate coagulation, settling, and filtering of the water before it is distributed. Reducing the temperature of the hot water from 165°F to 130°F has also been known to correct the pitting concern. Recent studies also suggest that the aluminum contents of domestic hot waters can be reduced to acceptable levels by avoiding the use of sacrificial aluminum-alloy anodes in the hot water heaters.

Figure 9 - The pits were covered with friable tubercles of greenish-colored copper corrosion products. Loosely-adherent layers of brownish-colored hydrated hematite deposits covered the black cupric oxide which existed on the waterside surface of the hot water line.

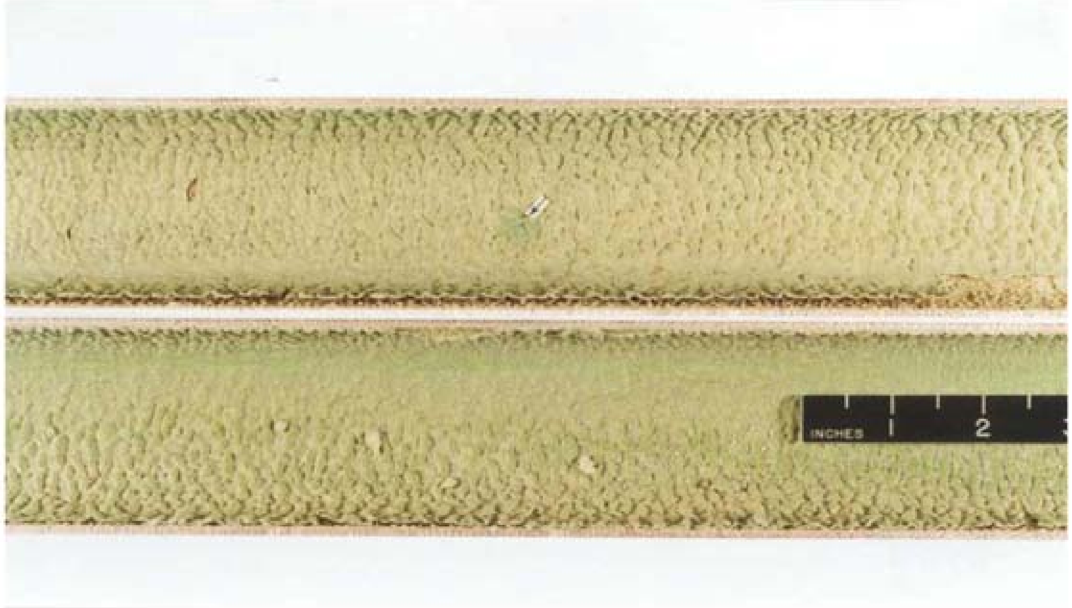
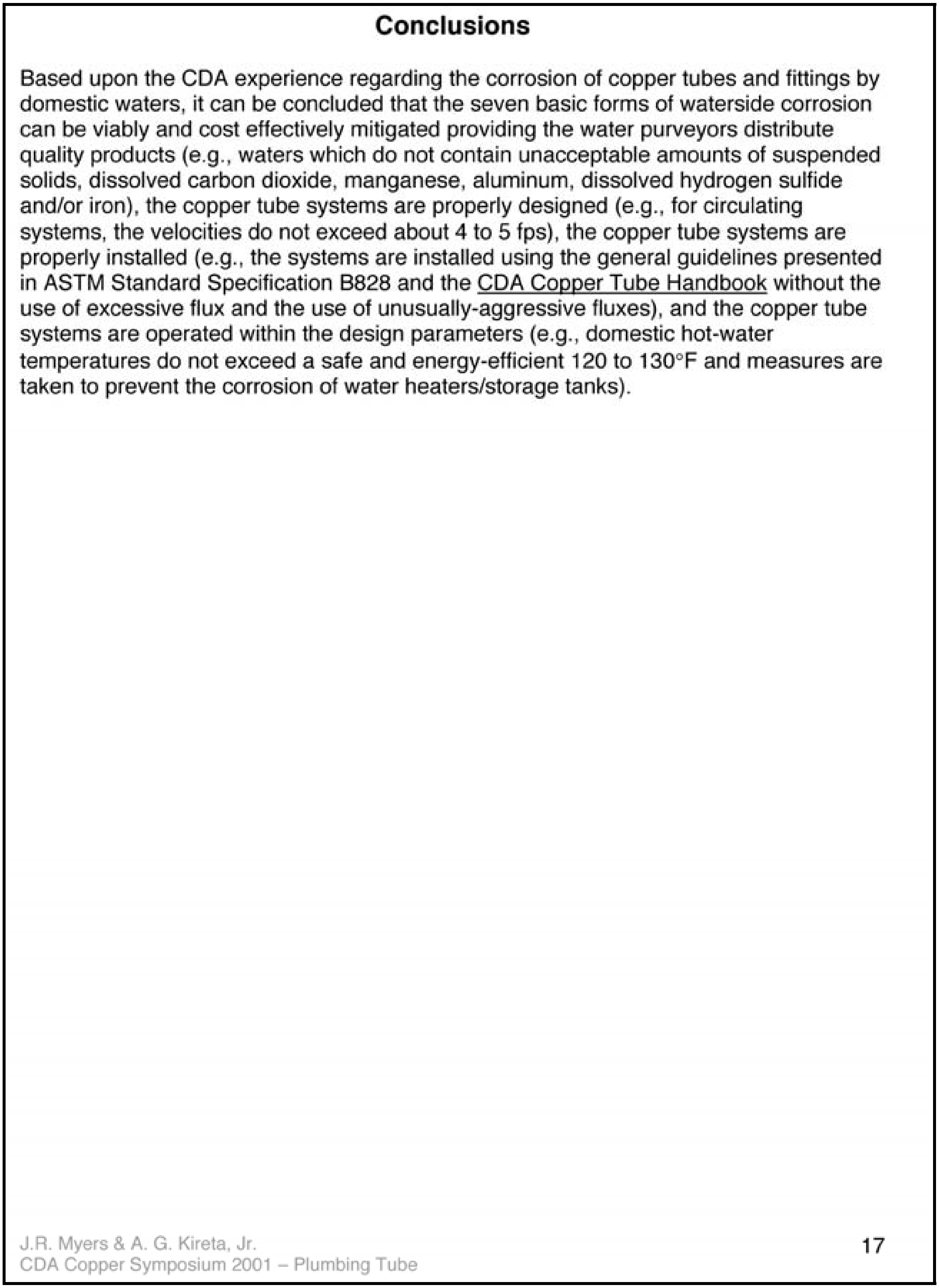


Figure 10 - The perforation through the tube wall (i.e., see arrow) was covered with a friable tubercle of greenish-colored copper corrosion products. In general, the cupric oxide on the copper tube surface was covered with a relatively-thick, loosely-adherent layer of brownish-colored deposits from the hot water conveyed. EDS revealed that the brownish-colored products contained significant amounts of aluminum.



Conclusions

Based upon the CDA experience regarding the corrosion of copper tubes and fittings by domestic waters, it can be concluded that the seven basic forms of waterside corrosion can be viably and cost effectively mitigated providing the water purveyors distribute quality products (e.g., waters which do not contain unacceptable amounts of suspended solids, dissolved carbon dioxide, manganese, aluminum, dissolved hydrogen sulfide and/or iron), the copper tube systems are properly designed (e.g., for circulating systems, the velocities do not exceed about 4 to 5 fps), the copper tube systems are properly installed (e.g., the systems are installed using the general guidelines presented in ASTM Standard Specification B828 and the CDA Copper Tube Handbook without the use of excessive flux and the use of unusually-aggressive fluxes), and the copper tube systems are operated within the design parameters (e.g., domestic hot-water temperatures do not exceed a safe and energy-efficient 120 to 130°F and measures are taken to prevent the corrosion of water heaters/storage tanks).

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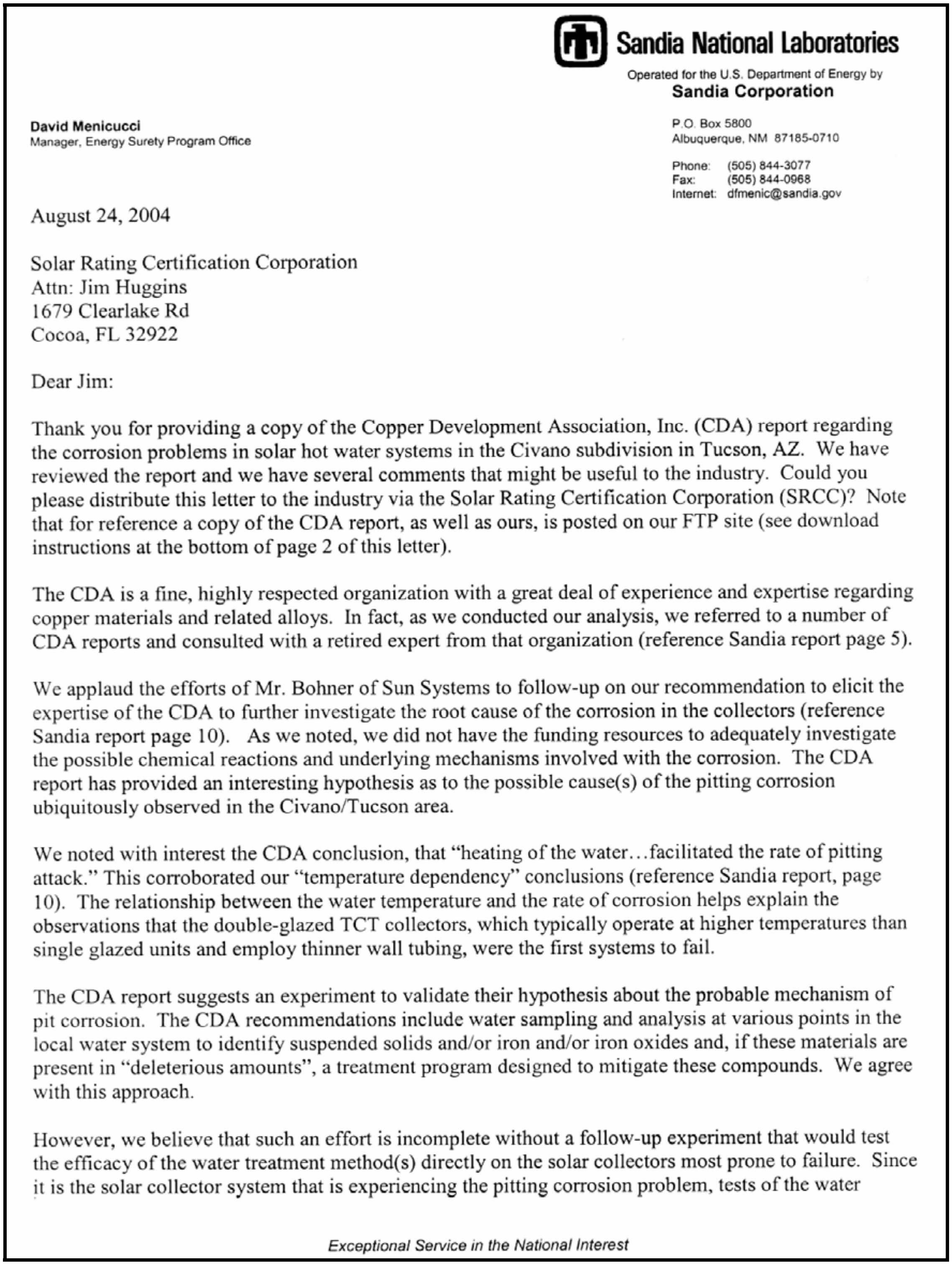
Sandia Response to the Analysis Conducted by the Copper Development Association

In response to the analysis conducted by the CDA, Sandia produced the following document summarizing the situation.



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August 24, 2004

Solar Rating Certification Corporation
Attn: Jim Huggins
1679 Clearlake Rd
Cocoa, FL 32922

Dear Jim:

Thank you for providing a copy of the Copper Development Association, Inc. (CDA) report regarding the corrosion problems in solar hot water systems in the Civano subdivision in Tucson, AZ. We have reviewed the report and we have several comments that might be useful to the industry. Could you please distribute this letter to the industry via the Solar Rating Certification Corporation (SRCC)? Note that for reference a copy of the CDA report, as well as ours, is posted on our FTP site (see download instructions at the bottom of page 2 of this letter).

The CDA is a fine, highly respected organization with a great deal of experience and expertise regarding copper materials and related alloys. In fact, as we conducted our analysis, we referred to a number of CDA reports and consulted with a retired expert from that organization (reference Sandia report page 5).

We applaud the efforts of Mr. Bohner of Sun Systems to follow-up on our recommendation to elicit the expertise of the CDA to further investigate the root cause of the corrosion in the collectors (reference Sandia report page 10). As we noted, we did not have the funding resources to adequately investigate the possible chemical reactions and underlying mechanisms involved with the corrosion. The CDA report has provided an interesting hypothesis as to the possible cause(s) of the pitting corrosion ubiquitously observed in the Civano/Tucson area.

We noted with interest the CDA conclusion, that “heating of the water…facilitated the rate of pitting attack.” This corroborated our “temperature dependency” conclusions (reference Sandia report, page 10). The relationship between the water temperature and the rate of corrosion helps explain the observations that the double-glazed TCT collectors, which typically operate at higher temperatures than single glazed units and employ thinner wall tubing, were the first systems to fail.

The CDA report suggests an experiment to validate their hypothesis about the probable mechanism of pit corrosion. The CDA recommendations include water sampling and analysis at various points in the local water system to identify suspended solids and/or iron and/or iron oxides and, if these materials are present in “deleterious amounts”, a treatment program designed to mitigate these compounds. We agree with this approach.

However, we believe that such an effort is incomplete without a follow-up experiment that would test the efficacy of the water treatment method(s) directly on the solar collectors most prone to failure. Since it is the solar collector system that is experiencing the pitting corrosion problem, tests of the water

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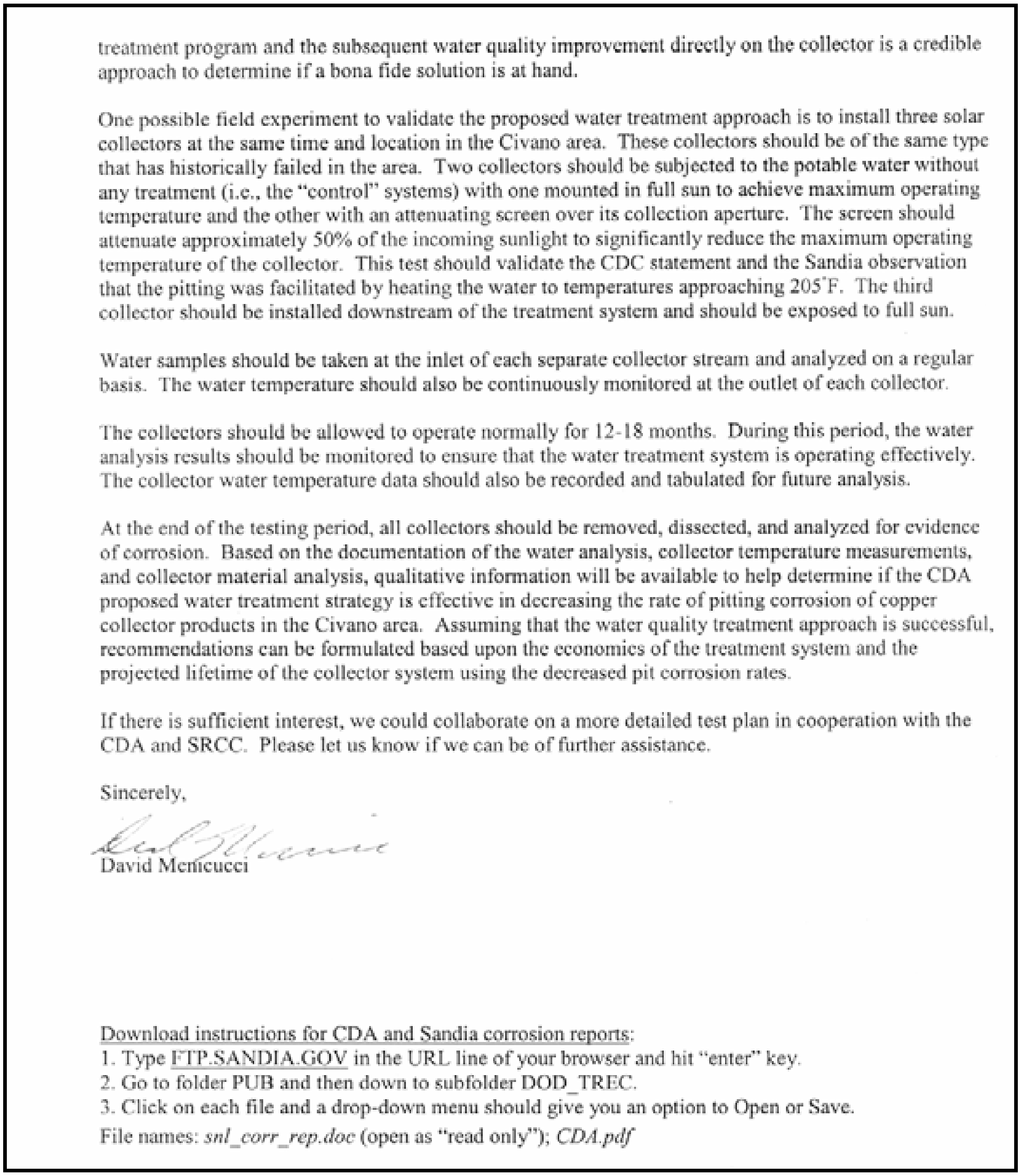

treatment program and the subsequent water quality improvement directly on the collector is a credible approach to determine if a bona fide solution is at hand.

One possible field experiment to validate the proposed water treatment approach is to install three solar collectors at the same time and location in the Civano area. These collectors should be of the same type that has historically failed in the area. Two collectors should be subjected to the potable water without any treatment (i.e., the "control" systems) with one mounted in full sun to achieve maximum operating temperature and the other with an attenuating screen over its collection aperture. The screen should attenuate approximately 50% of the incoming sunlight to significantly reduce the maximum operating temperature of the collector. This test should validate the CDC statement and the Sandia observation that the pitting was facilitated by heating the water to temperatures approaching 205°F. The third collector should be installed downstream of the treatment system and should be exposed to full sun.

Water samples should be taken at the inlet of each separate collector stream and analyzed on a regular basis. The water temperature should also be continuously monitored at the outlet of each collector.

The collectors should be allowed to operate normally for 12-18 months. During this period, the water analysis results should be monitored to ensure that the water treatment system is operating effectively. The collector water temperature data should also be recorded and tabulated for future analysis.

At the end of the testing period, all collectors should be removed, dissected, and analyzed for evidence of corrosion. Based on the documentation of the water analysis, collector temperature measurements, and collector material analysis, qualitative information will be available to help determine if the CDA proposed water treatment strategy is effective in decreasing the rate of pitting corrosion of copper collector products in the Civano area. Assuming that the water quality treatment approach is successful, recommendations can be formulated based upon the economics of the treatment system and the projected lifetime of the collector system using the decreased pit corrosion rates.

If there is sufficient interest, we could collaborate on a more detailed test plan in cooperation with the CDA and SRCC. Please let us know if we can be of further assistance.

Sincerely,

David Menicucci

Download instructions for CDA and Sandia corrosion reports:
1. Type FTP.SANDIA.GOV in the URL line of your browser and hit "enter" key.
2. Go to folder PUB and then down to subfolder DOD_TREC.
3. Click on each file and a drop-down menu should give you an option to Open or Save.
File names: *snl_corr_rep.doc* (open as "read only"); *CDA.pdf*

Lessons Learned from the Civano Experience

The following paper was published in the proceedings of the SOLAR 2003 Annual Conference (page 93). It reflects on the Civano experience and summarizes the lessons learned from it. It is reproduced here with permission of Becky Campbell-Howe, American Solar Energy Association.

LESSONS LEARNED FROM THE COPPER CORROSION EXPERIENCES IN THE CIVANO COMMUNITY, TUCSON, AZ

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Abstract

As solar hot water systems become more common, previously unseen problems are emerging, including pitting corrosion of the copper used in many solar collectors. The lessons learned from these experiences can help improve the reliability of these products.

The Civano Subdivision in Tucson currently has many integral type solar water-heating systems installed on homes (Fig. 1). In late 2000, a few of the systems began to leak. Sandia National Laboratories agreed to investigate the failures and found evidence that the community's water is somewhat corrosive to copper and that the corrosiveness may increase with temperature.

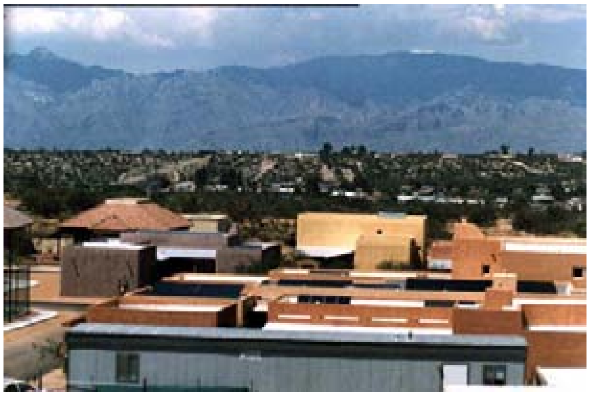

Fig. 1: Aerial Picture of Civano.

Subsequent to the analysis, the community leaders, the solar installer, and the manufacturer disagreed on a process to provide homeowner compensation for the system failures. Most of the liability debate centered on ambiguities within the warranty. Additionally, the installers were not totally versed in the terms of the warranty. The lessons from these experiences are that warranty statements should be enumerated more clearly and that the installer should be fully versed in the details of the warranty.

1. PAPER ORGANIZATION AND AUTHORSHIP

This paper is organized around two themes:
(1) Corroded copper sample analysis and results,
(2) The negotiations regarding compensation for the failures.

The lessons learned from both experiences are documented in the final section of the paper.

The authors from Sandia National Laboratories (SNL) contributed material pertaining to the corrosion analysis. The author from Greater Tucson Coalition for Solar Energy contributed material on the community's reaction to the failures.

2. INTRODUCTION

The Civano Subdivision is a master-planned, sustainable community located in eastern Tucson, Arizona. The project was conceived in the late 1980s and began building in the mid-1990s. By 2002, 286 homes were built in the subdivision. Eventually the subdivision is expected to build a total of about 2000 homes.

Solar technology is a key feature of the homes in this area, with over 95% of the homes having solar hot water and/or photovoltaic power systems. All future homes will be required to install solar hot water systems under a memorandum of understanding with the City of Tucson that supplied an infrastructure loan guarantee.

Two hundred fifty-three of the homes installed at Civano have Integral Collector Storage (ICS) collectors, all of which were fabricated from copper. Of these, 150 were produced by Thermal Conversion Technology and 103 were produced by Sun Earth.

A diagram of the ICS system appears in Fig. 2. Typically, these systems are constructed from a series of 4-inch (10.6-cm) diameter tubes, each connected serially to the adjacent ones using a .75-inch (1.9-cm) pipe.

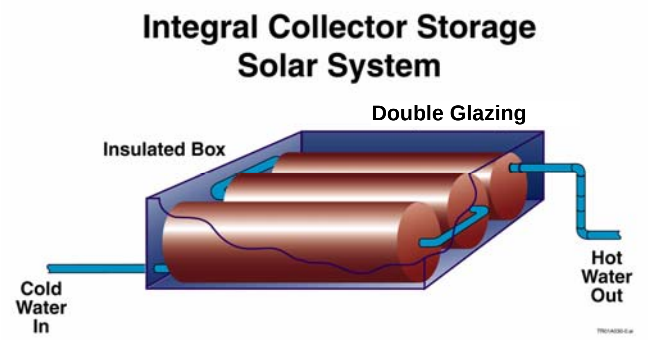

Fig. 2: Diagram of ICS System.

The collector is mounted on a roof with the glazing side facing the sun. Cold water from the street main is connected to the bottom tube of the collector. The collector's outlet, located at the top, is connected to the inlet of the standard hot water system in the home.

During normal system operation, the collector tubes are completely full of water and are warmed by sunlight. Whenever hot water is drawn throughout the home, solar preheated water flows through the collector and into the standard water heater. When the solar collector is optimally sized to the load of the home, most of the hot water consumed will have been produced by the sun.

When the water load in the home is minimal or zero over an extended period and the sun is shining, the water in the tubes achieves a steady-state condition. As such, the solar heat gain through the front glazing equals the heat that is lost through the front, sides, and the back of the box. This is the maximum temperature the system can achieve and is referred to as the "wet stagnation temperature."

3. TCT SYSTEM DESIGN

The TCT design has some notable features. First, each tube is fabricated from premium quality, ISO-certified 99.99% copper sheet material that is rolled into a tube and then tungsten inert gas- (TIG-) welded along the seam.

Second, the collector employs a double-glazed front covering that limits heat loss and allows the collector to produce water temperatures of greater than 180ºF in wet stagnation conditions.

Finally, every collector is pressure tested to 160 psi before delivery to ensure that it is free of leaks.

4. SYSTEM FAILURES AND THE OBJECTIVE OF THE CORROSION STUDY

In late calendar year 2000, some of the TCT collectors began to leak from pinholes that developed in the tube wall. The frequency of failures occurred slowly, with a total of six failures confirmed as of August, 2002.

In response to the first reports of a leakage, TCT and the Civano Community asked Sandia National Laboratories to investigate the possible causes of the failures.

The main goal of the copper material corrosion analysis was to understand the probable cause of the failures. A secondary goal was to identify economical mitigation strategies or other solutions that might prevent or decrease the number of future failures.

5. COLLECTION OF SAMPLES FOR STUDY

Samples of failed collector tubes were submitted for analysis at SNL. All of these tubes had been installed for at least 18 months. However, it was unknown exactly how long each of the collectors were in service.

In addition to the TCT collector samples, a single, fully-operational Sun Earth ICS collector was removed from an installation in Civano and samples of the collector tubes were also sent to SNL for analysis.

Finally, two copper samples were taken from standard Type L tubing used to supply and return water from a leaking ICS system. Fig. 3 shows where the sample tubes were taken. Note that one tube would normally contain hot water (outlet tube) and the other tube would normally contain cold water (inlet tube). These samples were sent to SNL for analysis.

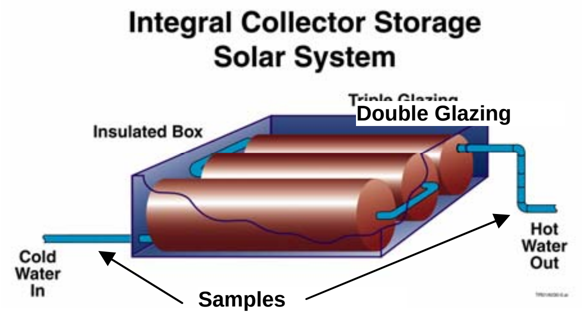

Fig. 3: Diagram of Where the Tube Samples were Taken.

In addition to the copper material samples, water samples were taken, with the assistance of the City of Tucson Water Department, from the municipal water supply for the Civano area. The water analysis was performed by Assaigai Analytical Labs, a certified water analysis laboratory in Albuquerque, NM.

In preparation for this analysis, published information and knowledge concerning copper corrosion process was obtained by consulting a former Copper Development Association (CDA) materials expert, as well as a literature search.

6. DIFFERENCES BETWEEN TCT AND SUNEARTH ICS COLLECTORS

There are three significant differences between the TCT and Sun Earth designs. First, the Sun Earth collector tubes are fabricated from standard, commercially-available Drain-Waste-Vent (DWV) 4-inch (10.6-cm) diameter pipe, which has a relatively thick wall to meet its designed use in commercial and industrial settings. The copper alloy in DWV tubing consists of ~99.9% copper.

Second, the Sun Earth collector utilizes a single glazing, rather than double glazing used by TCT, which should reduce the maximum wet stagnation temperature of the collector.

Third, the TCT collectors have slightly thicker insulation in the collector box, which increases the wet stagnation temperature and slightly improves energy performance.

7. ANALYSIS AND FINDINGS

Based on the limited samples, the water analysis showed that the dissolved constituents in the supply water, including the nitrate/nitrite ratio, potassium level, sulfates/chloride ratio, and dissolved CO_2 (about 10ppm), were sufficiently high to conclude that the water was mildly corrosive toward copper metal.

The TCT collector samples were visually inspected for evidence of pitting corrosion. Fig. 4 shows sites observed on the tube walls.

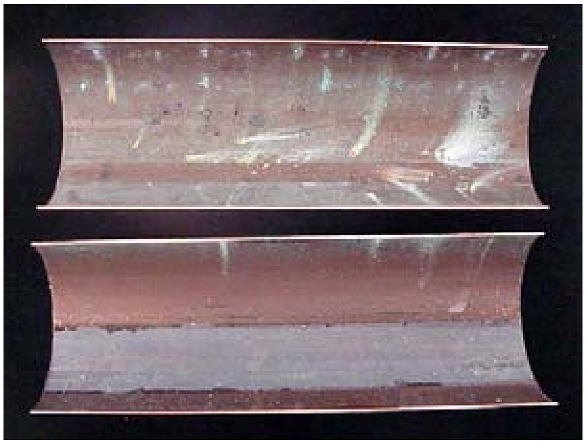

Fig. 4: Photo of Corrosion on the Tube Walls.

Samples of tubes were taken from each of the six failed collectors. A total of 32 tube samples were examined visually. A summary of the observations is as follows.

(1) Twelve tubes sampled exhibited a random distribution of pitting corrosion sites, most of which had not fully perforated the tube wall but probably would have had the collector had been left in service.
(2) Three tubes had wall pit corrosion that fully perforated the wall.
(3) Three tubes had pit corrosion in the seam welds that had perforated the wall. (There was no evidence that the corrosion was due to an improper weld.)
(4) The remaining tubes showed no evidence of pit corrosion.

Fig. 5 shows a close-up view of a corrosion pit site.

Four tubes from the Sun Earth collector were examined. Numerous surface corrosion sites were observed where pit corrosion was apparent. No areas were found where tube wall perforation was imminent. However, additional analysis showed that the corrosion had begun to penetrate the tube wall at some of the pitting sites.

The hot and cold water-supply tubings were examined. Corrosion products were observed on the interior of both the cold and hot water tubing.

The cold water tubing showed numerous, small surface corrosion sites. However, the hot water supply tube showed a significantly greater amount of corrosion products and possible pitting.

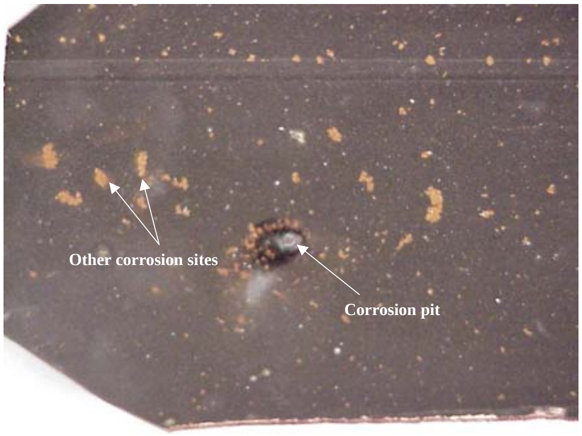

Fig 5: Closeup of Corrosion Pit.

Fig. 6 clearly show the differences in the amount of corrosion on the cold supply tubing and the hot return tubing. An analysis of some potential pitting sites on the hot tube showed that the corrosion had begun to penetrate the tube wall.

Fig. 6: Pictures of Corrosion on Hot and Cold Tubes.

The analysis team considered whether the manufacturing processes could have created conditions that initiated pitting corrosion in the TCT collectors. There are two manufacturing processes where corrosion problems could be induced: tube rolling and seam welding. The team hypothesized that if one or the other process was at fault, there would be a preponderance of pitting corrosion sites in either the tube walls or the seam weld. However, the corrosion sites were randomly distributed over the tube walls and seams, thus failing to support the theory.

The team also considered whether installation techniques could have created the pitting corrosion. However, the team could not theorize how the installation could induce failure, even if the collectors were not installed to the manufacturer's specifications. Therefore, no hypothesis was tested.

8. CONCLUSIONS FROM THE CORROSION ANALYSIS

Conclusions from the analysis are summarized below.

(1) The failures in the TCT collectors were due to copper pitting corrosion in the collector walls.
(2) The water was mildly corrosive to copper, based on current published criteria by the CDA.
(3) Samples from all three copper subsystems showed evidence of pitting corrosion, regardless of design or application.
(4) The pitting corrosion was more pronounced in the samples that were subjected to the highest temperatures, suggesting that the rate of corrosion and/or the corrosion process may be a function of temperature.
(5) If the corrosion rate and/or process are related to temperature, then the TCT collector systems would tend to corrode more quickly than the SunEarth systems because of their higher operating temperatures. Additionally, the walls of the TCT collectors are thinner than the DWV or Type L tubing, which would allow more rapid pitting perforation.
(6) There is no evidence that the pitting process in any of the copper subsystems is related to the manufacturing processes, materials, workmanship, design, or installation.

There are several uncertainties in the analysis.

(1) It is not known whether the water quality in the area has changed over time and is continuing to change. Changing water conditions could affect the rate of pitting corrosion.
(2) ICS collectors with thick walls and lower stagnation temperatures may have a relatively long life in the Civano environment. However, no accurate estimate of the life can be made based on the analysis.
(3) It is not possible to estimate if or how many additional ICS collectors might fail due to pitting corrosion.

The SNL analysis was unable to produce enough information to develop a mitigation strategy. Further study would be needed to better understand the water quality issues and the interaction between the constituents in the water and the copper metal. No funding is available to complete this study.

9. THE NEGOTIATION TO COMPENSATE HOMEOWNERS

Subsequent to the release of the SNL analysis, the homeowners, installer, and the manufacturer began to negotiate a settlement for the failures. There were disagreements regarding whether warranty service was applicable.

The disagreements stemmed from the warrantee document itself, of which there were two versions. One version explicitly excluded warranty service for failures due to “aggressive water.” The other specified a range of pH for the water, outside of which the warranty would not apply.

However, due to incomplete records, it was unclear which warranty applied to each installed system. In addition, the term “aggressive water” was not defined in the warranty and such a term does not have an accepted industry specification. Finally, the details of the warranty were not understood by many of the homeowners or the installer prior to installation.

In the end, the homeowners, installer, and manufacturer agreed on an amicable settlement in lieu of warranty adjustment in which the systems were either repaired or replaced. The exact details of the arrangement were not divulged.

10. SUMMARY OF LESSONS LEARNED

Numerous lessons were learned through this experience and should be carefully reviewed and considered by those contemplating the development of a solar community such as Civano.

In the Civano community, the solar installer and the product were selected without a comprehensive specification for technical performance, warranty, and bonding. One reason is that Civano developed slowly and the solar technologies evolved into the development.

However, many problems can be eliminated by developing a clear set of specifications for the solar product and the installer, developing a solicitation package, and selecting a contractor and solar product based on the specifications. This is not meant to suggest that the procurement must be competitive. However, if it is, it is probably best to select a contractor based on the best value rather than lowest bidder to ensure that the best product is delivered for the price.

Although the manufacturer and the Civano parties eventually settled amicably, ambiguity regarding the warranty created misunderstanding.

From the manufacturer’s perspective, the warranty document should clearly state the conditions under which the warranty will and will not apply. For example, had only one warranty been applied and had it clearly stated that the warranty service was not applicable for corrosion failures, much of the ambiguity would have been eliminated. Furthermore, had such a warranty been made clear to the buyers, they could have purchased the product with full knowledge of the risks, thus eliminating disappointment if the product failed.

Both versions of the warranties are contingent on an installation consistent with the manufacturer’s recommendation. Some installations of failed systems in Civano reportedly did not meet manufacturer’s recommendations for optimal tilt angle and plumbing configuration, which complicated the negotiations.

It is important to ensure that all of the installations meet the manufacturer’s recommendations. If deviations are made to the installation specifications, these changes should be negotiated with the manufacturer prior to installation to avoid disagreements later. This is especially important if local codes require installation details that vary from those of the manufacturer.

All installed solar collectors should meet the local plumbing code. This usually requires a permit be obtained from the local building code official and an inspection of the job at time of completion. It is important to record the time and date of the code enforcer’s inspection and the identification of the approval tag. This will serve as further evidence of proper installation.

Clear records should be kept concerning the installation, including the serial number of the installed unit, the date of installation, the address and owner of the property where the installation took place, and the name and address of the installer. This information is often required to qualify the unit for warranty service.

If the solar system selected for installation is the type where the water will be in direct contact with the collector (such as an ICS), the water quality should be investigated prior to installation. The CDA can provide guidance about how to sample water and how to determine if it might corrode the copper material used in the collector. The experts at CDA can be accessed via their web site at www.copper.org.

If the water is potentially corrosive, some consideration should be given to one of the following actions:

(1) Modify the water quality to make it less corrosive. Typically, the water quality can be altered by a property owner without authorization from authorities after the point of delivery, which is at the water meter.

Water treatment at the subdivision level is more problematic and will often require the cooperation and guidance of the local water authority.

The CDA may provide guidance on how to treat water that is potentially corrosive and whether it is best treated before or after the point of delivery.

(2) Use a solar technology that isolates the collector and components from the water. Typically, closed-loop systems provide this isolation. However, while these systems do offer slightly better energy performance than ICS collectors, there are drawbacks to these systems, including higher initial cost and increased complexity, which could result in more maintenance.

(3) Assess the degree of corrosiveness of the water and choose a product that is likely to withstand the corrosion potential for the life of the application. For example, products that have thicker collector walls, different materials, or internal coatings on the exposed parts might provide additional life to the product. Again, the CDA can provide guidance in this area.

Finally, if such a system is used in a potentially corrosive environment, it may be advantageous to secure an extended warranty against corrosion.

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Section 2b. Information Pertaining to the Analysis of the Failures at the Camp Pendleton Pool

By 1999 unglazed copper collectors had been in use at Marine Corps Base Camp, Pendleton, California, for about 12 years. Camp Pendleton is located about 25 miles north of San Diego. The collectors were used to heat year-round training tanks and summer-only recreational swimming pools. In total, six systems on base used solar heating.

The mechanical system design for all of the pools was very simple. Tapped off of the filtration loop, pool water is pumped directly to the bottom header of the collectors and the warmed water from the upper headers is returned to the filtration loop. The water is subsequently treated with chemicals as needed before flowing back to the pool.

The solar system controls were set so that the pool's fossil-fueled boiler would fire only if the pool temperature reached a critically low value. To prevent the solar system from freezing, which occasionally does occur, the solar pump is energized when the ambient temperature reaches around 35 °F. Essentially, the heat in the pool is used to keep the collectors from freezing in these rare instances.

Over the life of the solar system a number of leaks had occurred in the fin-tubes. There were no analyses of these leaks because they did not occur frequently enough to warrant them and the repairs were quite simple—the leaking fin-tube was cut out of the flow by severing it from the headers and re-sealing the header with plugs that were driven into the short, protruding tube stubs. The disabled fin-tube was left in place for aesthetic purposes. Less than 5% of the fin-tubes had been disabled over the years. This simple system supplied the large majority of the pool's heating load in all but the coldest portion of the winter seasons.

In early 2000 Sandia engineers were called upon to investigate a massive failure of the collectors at one of the pools. Reportedly, leaks suddenly appeared in the collectors over a period of 72 hours during a weekend.

Upon examination of the failures, Sandia engineers immediately identified the source of the failures—pinholes in the copper fin-tubes and headers. Most of the pinholes were rather small, perhaps ≤10 mil. Others were quite large, perhaps ≥1/16 inch. Each pinhole was circular, very much akin to a mechanically drilled hole. The pinholes were randomly distributed over the copper waterways in the collector system and, based on a sample, the Sandia team estimated that over 10,000 pinholes were present in this 6000-ft^2 system.

Samples were returned to Sandia's corrosion lab for analysis. In the interim, the Sandia team interviewed the pool staff, including both civilian and military personnel, regarding the events leading up to the failure. All reported nothing unusual having occurred.

At Sandia's corrosion lab, engineers disassembled the samples and inspected them. They immediately observed that the inside of the tubes were clean, smooth and with a brilliant copper finish. This is unusual because these tubes had been in service for many years and a dark passivation layer typically forms on the copper that has contacted pool water. This very thin passivation layer is the by-product of a small amount of initial corrosion and it typically serves to protect the remaining metal from further corrosion.

They also observed that the pinholes were relatively evenly distributed around the tubes, indicating that the attacking agent was dissolved into the water rather than suspended. Suspended materials might cause more pits on the bottom of the tube as gravity pulls the suspended particle downward during the flow. Micrographs of some of the pinholes indicated clearly that they were caused by pitting corrosion.

The situation presented a conundrum. First, these tubes had been operating for many years at this pool essentially problem-free. Therefore, one would assume that some special event had occurred to stimulate the failures. However, the staff reported no such event.

The Sandia team set forth various possible scenarios to explain the pitting corrosion. The most likely was that the pH of the pool could have changed dramatically to a high value, which might strip the passivation layer from the surface, followed by a very low value, a highly acidic condition that would aggressively attack the copper.

In talking again with the Camp Pendleton pool staff and insisting on more details of the events over the troubled weekend, the team discovered that the pool was “chemically shocked” because they had found fecal matter in it. Chemical shocking of the pool under those conditions is normal and they were adamant that the pool had been shocked numerous times when the collectors were operating. They used sodium hypoclorite to shock the pool followed by muriatic acid to bring the high pH back into the normal region. Both shocking agents are stored at the pool site in high concentrations.

Given that information, it appeared that the shocking incident held promise to explain the failures, but was inconsistent with the fact that the collectors had survived shocking many times before.

During the interviews, one of the Sandia team members observed one of the pool staff pouring sodium hypochlorite directly into the pool. Normally, chemicals are added to the pool with an automatic entraining device that slowly adds the material until the pH is at the desired level. However, in this case the entraining device was not operating so the adjustment would have to be done manually.

After interviewing the staff again, they reported that they did indeed shock the pool manually over the weekend and that this was the <u>only</u> time they had done it. As a result, they poured significantly more sodium hypoclorite into the pool than was needed, thus driving the pH to very high levels. To stabilize the pool, significant quantities of muriatic acid was needed to bring the pH into the right region. However, this too was overdone and the pH of the pool sank to very low levels. More sodium hypoclorite was needed for compensation. Finally, the pool’s pH was stabilized, but not before it had experienced an extreme range of pH conditions.

This report meshed with the observations of the failed tubes and was consistent with Sandia staff's failure hypothesis. The amount of chemicals used in this shocking event, even if they were entrained into the pool by machine, is sufficient to explain the failures.

However, the situation was exacerbated by a report that the chemicals were added to the pool from a 55-gallon drum with their contents spilled directly over the edge and into the scupper area. Unfortunately, the scuppers, which line the edge of the pool, constitute the beginning of the return flow of water from the pool to the treatment area. From the scuppers, the water is filtered and then flows directly to the solar collectors. Consequentially, the very highest concentrations of sodium hypoclorite and muriatic acid were fed into the collectors.

Normally, the chemicals are fed into the pool on the inlet line, which is located in the middle of the pool. Therefore, in normal shocking events the collectors are never subjected to high concentrations of either the acid or base because the pH is carefully controlled by a machine and is well mixed into the pool water by the time it is removed at the scuppers.

As a result, this single event resulted in the complete destruction of the solar system within a 72-hour period. The copper collectors were replaced with polymer collectors and have been operating normally since then. The pool's staff subsequently instituted new procedures for shocking the solar-heated pools, including a requirement to isolate the solar system during the event.

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Section 3. Additional Information Pertaining to Copper Corrosion

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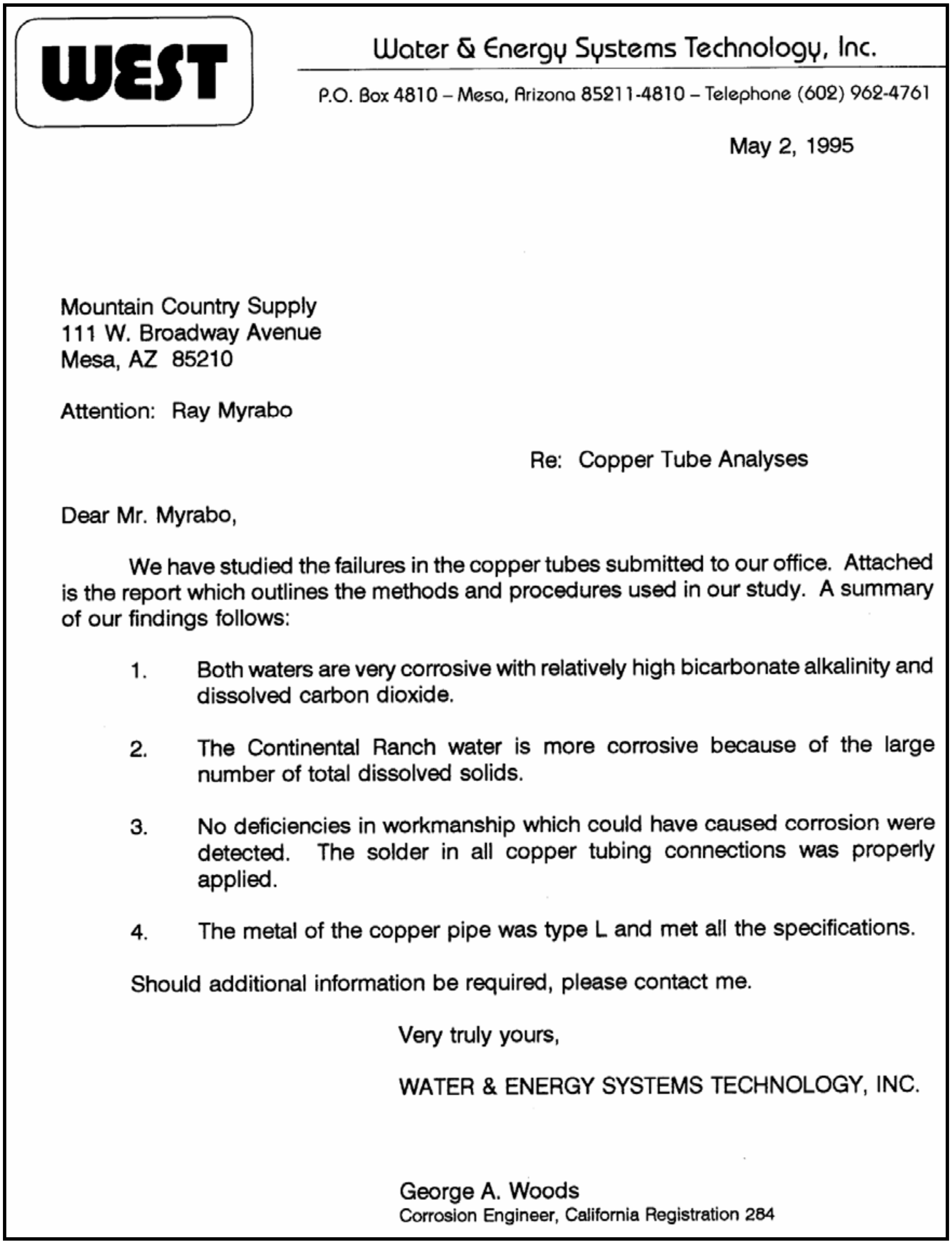


WEST

Water & Energy Systems Technology, Inc.

P.O. Box 4810 – Mesa, Arizona 85211-4810 – Telephone (602) 962-4761

May 2, 1995

Mountain Country Supply
111 W. Broadway Avenue
Mesa, AZ 85210

Attention: Ray Myrabo

Re: Copper Tube Analyses

Dear Mr. Myrabo,

We have studied the failures in the copper tubes submitted to our office. Attached is the report which outlines the methods and procedures used in our study. A summary of our findings follows:

1. Both waters are very corrosive with relatively high bicarbonate alkalinity and dissolved carbon dioxide.
2. The Continental Ranch water is more corrosive because of the large number of total dissolved solids.
3. No deficiencies in workmanship which could have caused corrosion were detected. The solder in all copper tubing connections was properly applied.
4. The metal of the copper pipe was type L and met all the specifications.

Should additional information be required, please contact me.

Very truly yours,

WATER & ENERGY SYSTEMS TECHNOLOGY, INC.

George A. Woods
Corrosion Engineer, California Registration 284

PITTING OF COPPER
IN POTABLE WATER LINES

Introduction

Copper plumbing sections were received by this office. The sections all exhibited corrosion of the copper resulting in leaks. Two building sites were represented; Continental Homes and Saddelbrook. Pipes exhibiting classic areas of corrosion were selected for analyses. Although corrosion to the copper was similar at both sites, the water quality is so different that we will cover the two areas separately.

Continental Ranch

The water analyses for the Continental Ranch area will be considered first. The water analyses will be found in Table A.

Of significance in contribution to corrosion is the high calcium hardness of 300 ppm of calcium as calcium carbonate (120 ppm as the calcium ion). With the high carbonate alkalinity at 220 ppm, and sulfate at 220 ppm, the scale potential exists for this water. The positive 0.4 for Langelier's Index indicates a scale potential.

At the same time the water will be quite corrosive due to the high electrolyte content of the water. The total dissolved solids of 913 ppm will provide the necessary driving force to facilitate corrosion if dirt or deposits are present in the water. Also a significant factor in copper corrosion is the presence of 12 ppm of carbon dioxide. This may be present in the well water as a dissolved gas, or develop as a breakdown from the high concentration of sodium bicarbonate.

$$2NaHCO_3 \rightleftharpoons Na_2CO_3 + CO_2 + H_2O$$

sodium bicarbonate ⇌ sodium carbonate + carbon dioxide + water

The reaction will certainly occur with any heating of the water. In every tube section supplied this office patina or copper carbonate was observed. The physical analyses including x-ray analyses and electron microscope follows.

Sample 1

The tubing was labeled "Waterline leading to the kitchen sink on the hot side". There appeared to be no external corrosion. There was also no indication of corrosion in the area of the silver solder. This would indicate the flux had been appropriately applied and that the plumber doing the work had satisfactorily prepared the connection.

Figure 1 indicates a typical penetration from the exterior side of the pipe. Figure 2 shows the same penetration from the interior of the pipe. There was major nodule development in many places on the interior of the pipe. Nodules are best defined as mounds of corrosion products in localized areas of the pipe. Pits are always found beneath the nodules. In figure 2 the copper is covered first with a red-grey layer, and on top of this a green layer. The Electron Dispersive X-ray Analyses of the module confirmed the presence of copper. Chemical tests confirmed the green material to be copper carbonate. The gray surface deposited directly over the copper metal is copper oxide exhibiting a small amount of copper chloride. The green deposit over the entire surface in addition to being copper carbonate also had a small amount of copper silicate. There were also copper oxide, copper carbonate, and ferric oxide found within the pits.

The absence of significant calcium would indicate the water had been softened.

Sample 2

This sample was labeled as obtained from Continental Ranch, Lot 72, "Pinhole in Copper" A-1. This sample in many respects is similar in failure to sample 1. There was no exterior corrosion of the pipe. The entire surface was totally passivated. There is extensive nodule formation over an oxide coating of copper metal. A significant difference is the presence of major chloride within an under-nodule pit. This is probably a case of better retention of the chloride than in sample 1. Typically, the chloride ion will collect in a differential aeration cell pitting. See Table C which diagrams how this type of pitting will occur.

Although the chloride does assist in the attack of the copper metal, it is usually not the prime cause of the original formation of the pit. Please note the Energy Dispersive X-rays of sample 2.

Sample 3

Sample 3 was obtained from Continental Ranch, 7050 Safflower, and labeled "Waterline leading to ice maker Piece A". The exterior of this pipe was seriously corroded as compared with the other pipes where all of the corrosion was on the interior. Figures 5 and 6 show the extent of external corrosion on the pipe. The figure 6 illustrates in good detail the typical attack site for this sample. Graphically depicted are a rim or raised ridge of green material surrounding a wide pit which includes exposed metal, copper oxide crystals, and a white deposit. The analyses confirms the green rim to be copper carbonate, moderate silicon, and minor amounts of aluminum, potassium, calcium, and iron. The red crystals are copper oxide.

The white material contained silicon, calcium, aluminum, and magnesium, and potassium. The white material is not part of the copper corrosion process but represents portion of the soil in contact with the pipe.

Analyses of the soil had shown all of the elements present including lime, iron, as well as building materials. The soil sample also harbored some sulfate reducing bacteria. Although the bacteria were dormant in the dry soil as received, the spores were present. Upon keeping the soil moist after 72 hours the sulfate reducing bacteria were producing acids of sulfur which lowered the pH and developed some SO_2 gases.

The corrosion on the exterior of the pipe is a result of moisture with sufficient oxygen present. This resulted in differential aeration cells with drastic loss of the copper metal.

Sample 5

Sample 5 was labeled Continental Ranch, 7050 N. Safflower, Piece B, "Waterline has no leak was attached to Piece A".

There was no significant corrosion except over a small area where the tube was cut. The type of corrosion is the same as discussed above. Our analyses confirmed the tube to be Type L copper tube and meeting all requirements of specifications for this schedule tube.

Saddlebrook

The water from Saddlebrook was of low hardness and low solids. The total dissolved solids was measured at 200 ppm. This water is very slightly corrosive and lacks the driving force of the Continental Ranch for aeration type corrosion. However it does contain 6 ppm of carbon dioxide and exhibits some corrosive tendencies. Table B includes a complete analyses of the water.

Sample 4

The analyses of the pipe submitted is labeled Sample 4, "Saddlebrook". The exterior section of pipe had virtually no corrosion. There was some interior corrosion. A yellowish track of deposit exists along one area of the pipe that represents the bottom of a horizontally installed pipe. Within this track there are discrete pits which fit the classic description of under deposit corrosion, or differential oxygen cell corrosion. Figure 7 shows a typical area of the deposit track and small corrosion sites along the deposit.

Of academic interest are two relatively large areas out of the deposit track which show extensive development of large copper oxide crystals. These areas act like typical corrosion sites, but there are no nodules or other obvious mechanisms to provide differential corrosion aeration cells.

These atypical corrosion sites may be associated with physical damage to the pipe from an outside source. Examination shows a physical indentation on the exterior surface. Each corrosion site has the small exterior indentation. The indentation broke the passivating film inside of the pipe and caused irregularities in water flow. Under normal water conditions such dents are not correlated with corrosion sites. With the low solids, carbon dioxide loaded water the corrosion on this site is not unexpected.

Flexible Copper Tubing

Five 1/4 inch flexible copper lines were submitted for examination. All had pin hole leaks. Because of the cold work machining in the manufacture of these lines, stressed areas are induced. The corrosive nature of the water with dissolved oxygen as well as deposits of silt in the valleys inside the tubing has resulted in under deposit corrosion. There already exists a potentiometric difference between the ridge and the valley of the tubing.

Recommendations

The Continental Ranch water is the more corrosive of the two waters. Because of the high electrolyte content influenced by high sulfates and chlorides with dissolved carbon dioxide the water will be aggressive to both copper and iron.

An approved phosphate/zinc product may be fed by the water supply company to all potable water supplying the project. The phosphate level should be maintained between 1 to 2 ppm. This will passivate the copper metal in all homes in the system.

Over-chlorination of the water should also be avoided. Chlorine residuals should be maintained not to exceed 1.5 ppm. The chlorine is quite effective in stripping copper lines of a passivating oxide film.

The Saddlebrook water is of a less corrosive and better quality. The water does have some suspended solids in the form of silt. The silt laydown in pipes contributes to under deposit corrosion. Better filtration at the source of the water will result in less corrosion in the lines.

Because of the better quality water chlorination should be carefully controlled. The carbonate buffering system existing in the Continental Ranch water is reduced in the

Saddelbrook water. The chlorine should not exceed 1 ppm free chlorine.

Flexible copper tubing should be replaced with flexible reinforced plastic tubing. This will eliminate the problem of corrosion inherent in this type of tubing.

Figure 1 - Sample 1

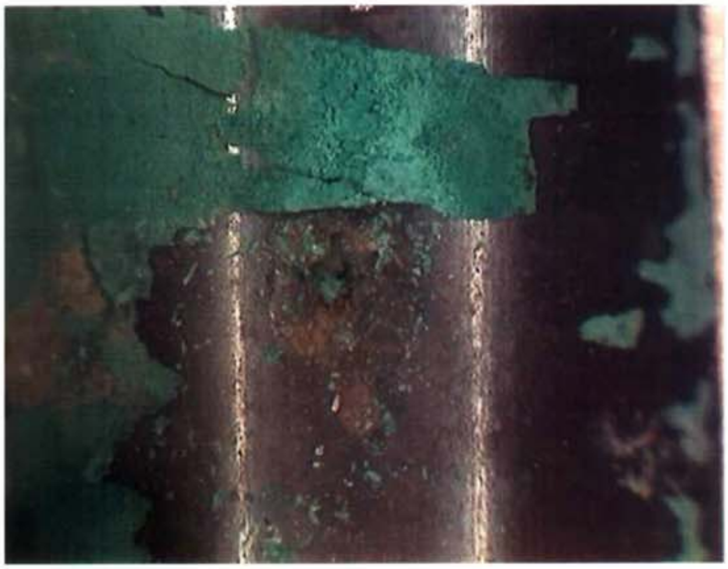


Figure 2 - Sample 1

Figure 3 - Sample 2

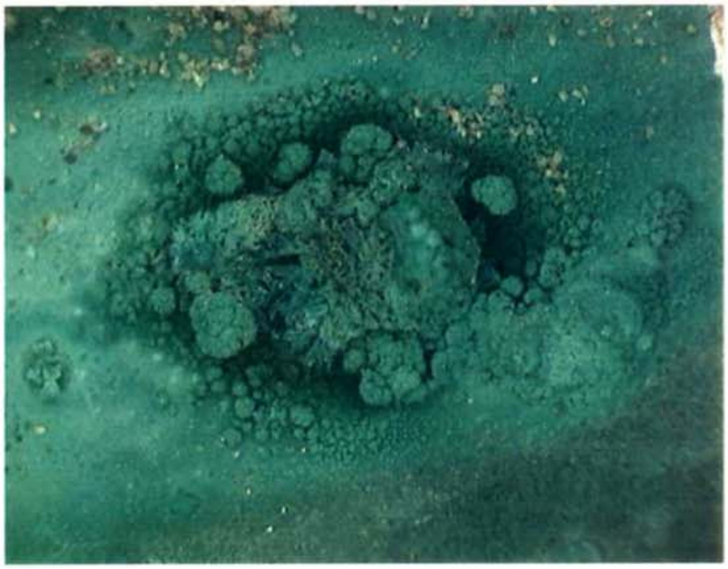


Figure 4 - Sample 2

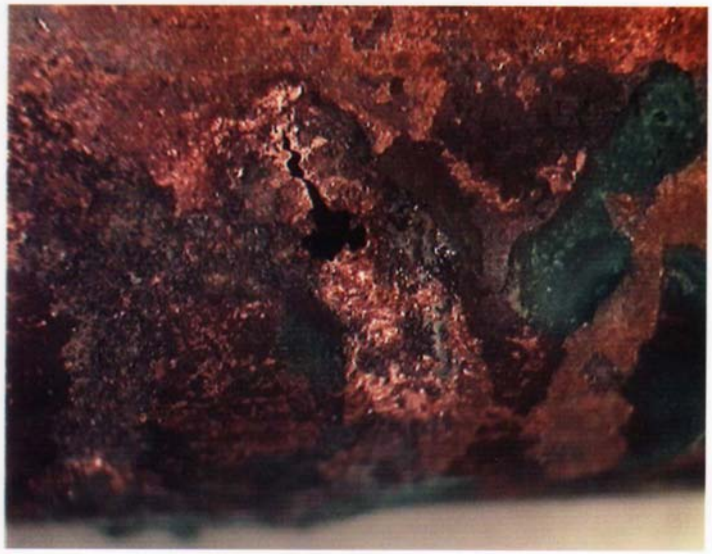


Figure 5 - Sample 3

Figure 6 - Sample 3

Figure 6A - Sample 3

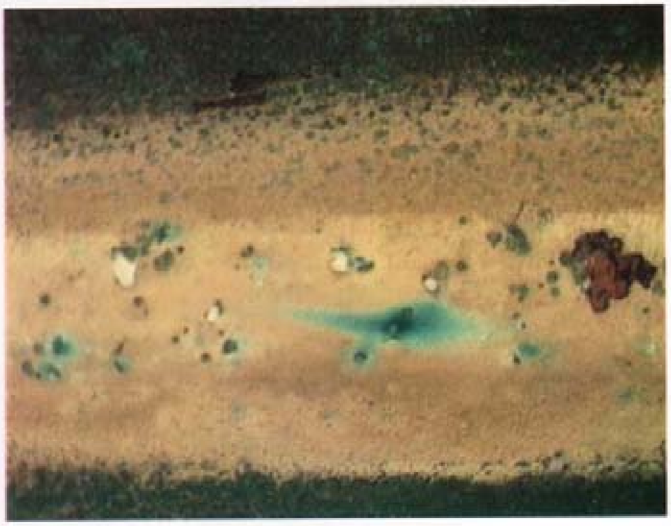
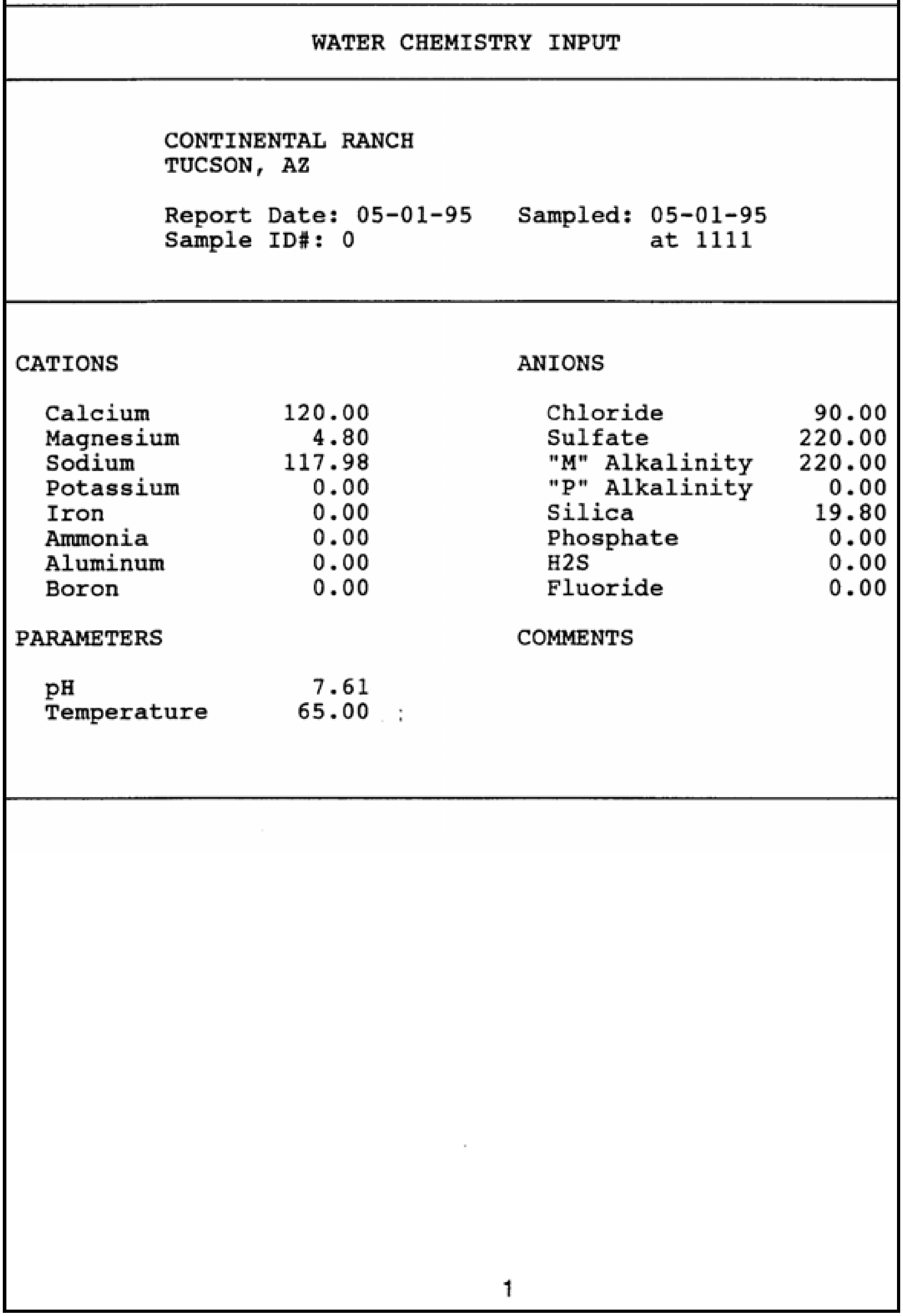


Figure 7 - Sample 4

Table A



```
                    WATER CHEMISTRY INPUT

          CONTINENTAL RANCH
          TUCSON, AZ

          Report Date: 05-01-95   Sampled: 05-01-95
          Sample ID#: 0                    at 1111

CATIONS                         ANIONS

  Calcium            120.00       Chloride             90.00
  Magnesium            4.80       Sulfate             220.00
  Sodium             117.98       "M" Alkalinity      220.00
  Potassium            0.00       "P" Alkalinity        0.00
  Iron                 0.00       Silica               19.80
  Ammonia              0.00       Phosphate             0.00
  Aluminum             0.00       H2S                   0.00
  Boron                0.00       Fluoride              0.00

PARAMETERS                      COMMENTS

  pH                   7.61
  Temperature         65.00
```

1

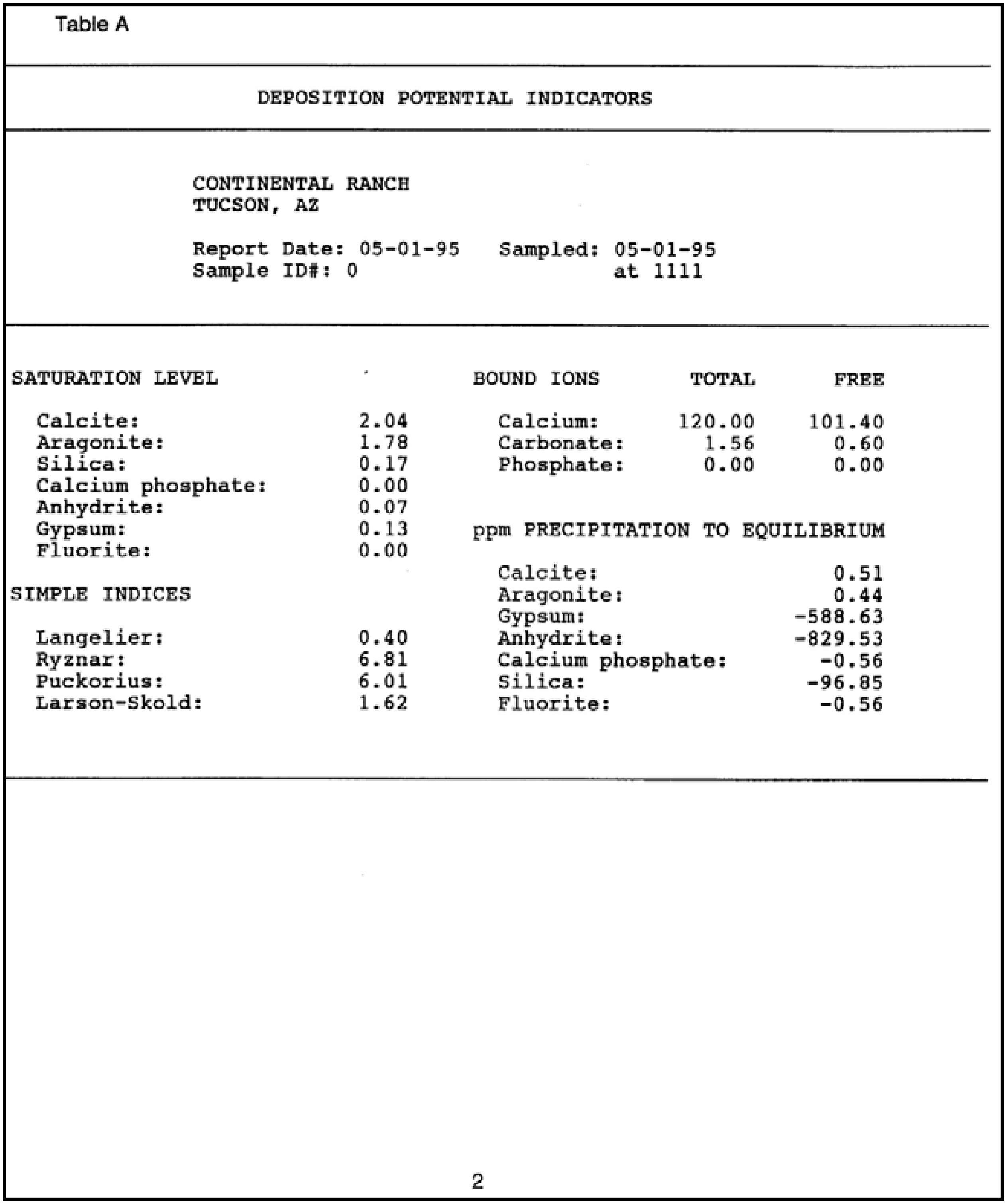
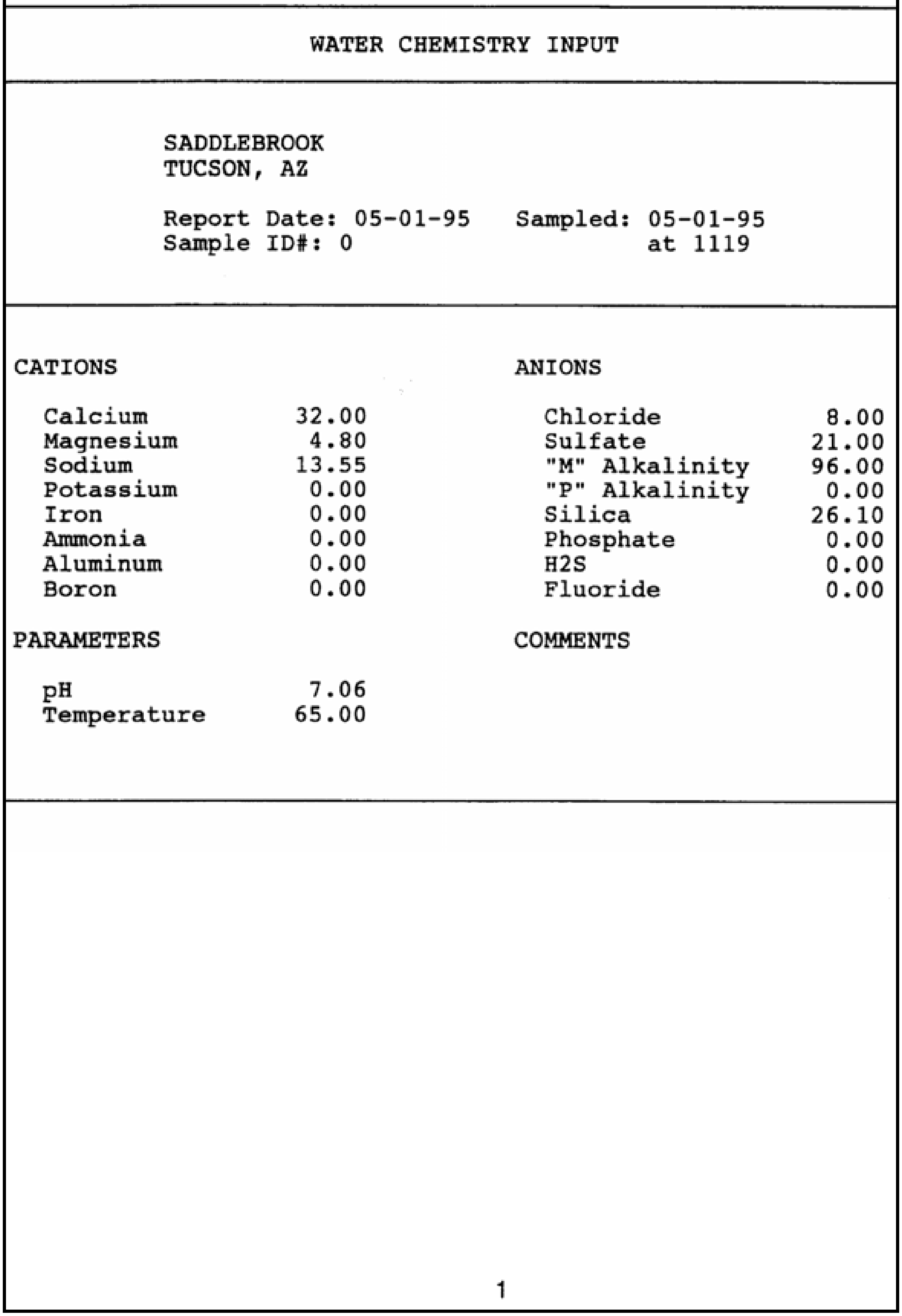


Table A

```
                    DEPOSITION POTENTIAL INDICATORS

               CONTINENTAL RANCH
               TUCSON, AZ

               Report Date: 05-01-95   Sampled: 05-01-95
               Sample ID#: 0                    at 1111

SATURATION LEVEL                        BOUND IONS       TOTAL       FREE

  Calcite:                  2.04          Calcium:      120.00     101.40
  Aragonite:                1.78          Carbonate:      1.56       0.60
  Silica:                   0.17          Phosphate:      0.00       0.00
  Calcium phosphate:        0.00
  Anhydrite:                0.07
  Gypsum:                   0.13        ppm PRECIPITATION TO EQUILIBRIUM
  Fluorite:                 0.00
                                          Calcite:                   0.51
SIMPLE INDICES                            Aragonite:                 0.44
                                          Gypsum:                 -588.63
  Langelier:                0.40          Anhydrite:              -829.53
  Ryznar:                   6.81          Calcium phosphate:        -0.56
  Puckorius:                6.01          Silica:                  -96.85
  Larson-Skold:             1.62          Fluorite:                 -0.56
```

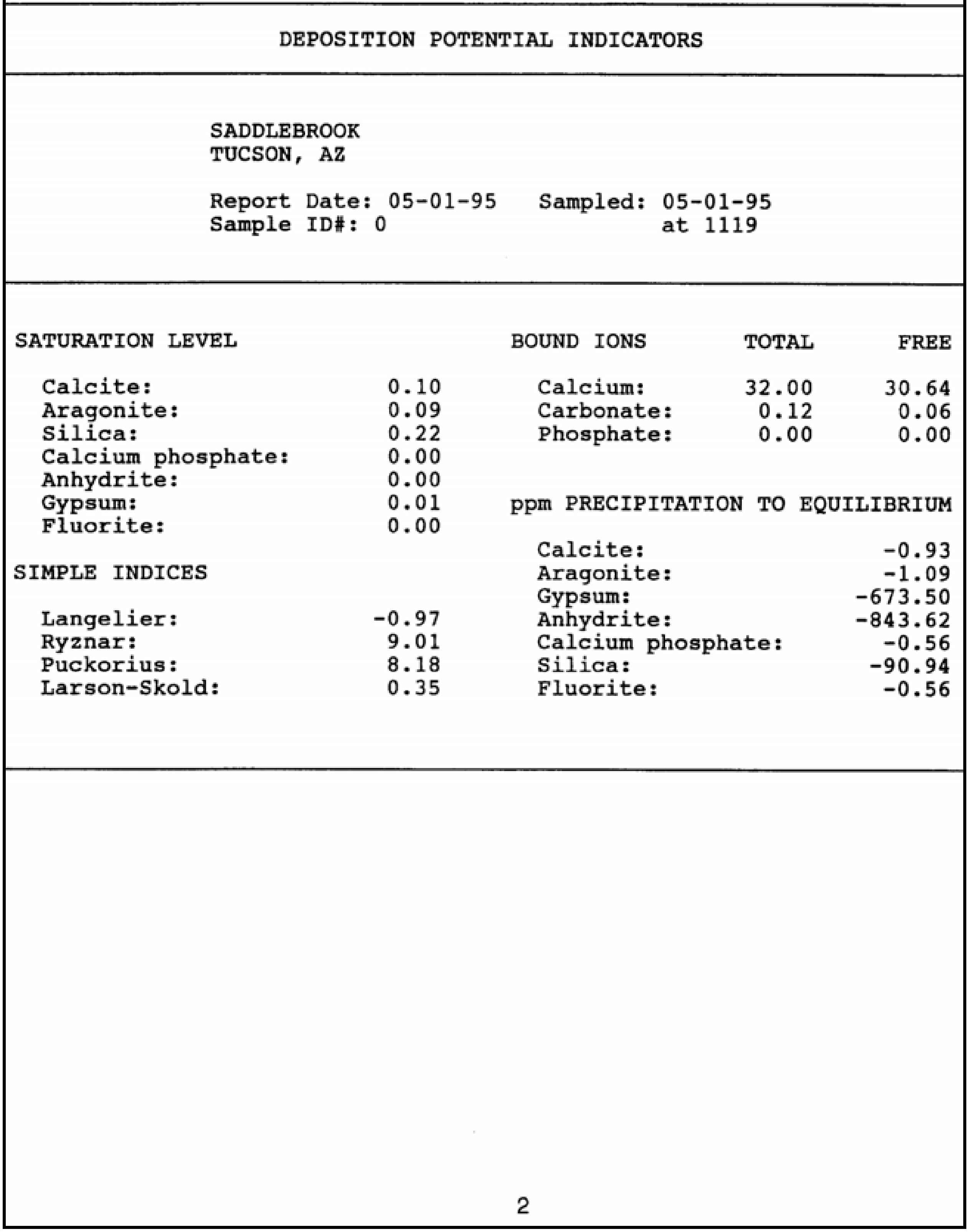
2

Table B



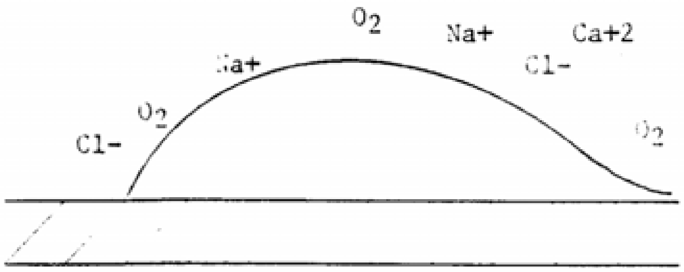
```
                    WATER CHEMISTRY INPUT

          SADDLEBROOK
          TUCSON, AZ

          Report Date: 05-01-95   Sampled: 05-01-95
          Sample ID#: 0                    at 1119

CATIONS                            ANIONS

  Calcium           32.00            Chloride             8.00
  Magnesium          4.80            Sulfate             21.00
  Sodium            13.55            "M" Alkalinity      96.00
  Potassium          0.00            "P" Alkalinity       0.00
  Iron               0.00            Silica              26.10
  Ammonia            0.00            Phosphate            0.00
  Aluminum           0.00            H2S                  0.00
  Boron              0.00            Fluoride             0.00

PARAMETERS                         COMMENTS

  pH                 7.06
  Temperature       65.00

                              1
```

Table B

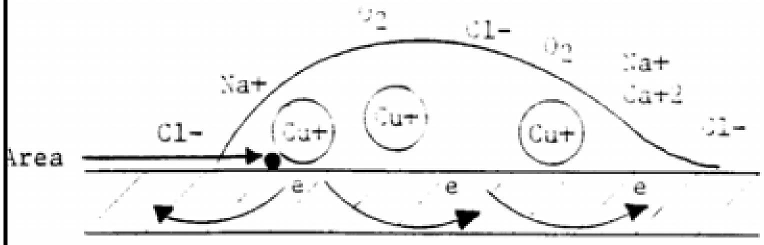


```
                    DEPOSITION POTENTIAL INDICATORS

              SADDLEBROOK
              TUCSON, AZ

              Report Date: 05-01-95   Sampled: 05-01-95
              Sample ID#: 0                    at 1119

SATURATION LEVEL                         BOUND IONS       TOTAL      FREE

  Calcite:                  0.10           Calcium:       32.00     30.64
  Aragonite:                0.09           Carbonate:      0.12      0.06
  Silica:                   0.22           Phosphate:      0.00      0.00
  Calcium phosphate:        0.00
  Anhydrite:                0.00
  Gypsum:                   0.01         ppm PRECIPITATION TO EQUILIBRIUM
  Fluorite:                 0.00
                                           Calcite:                 -0.93
SIMPLE INDICES                             Aragonite:               -1.09
                                           Gypsum:                -673.50
  Langelier:               -0.97           Anhydrite:             -843.62
  Ryznar:                   9.01           Calcium phosphate:       -0.56
  Puckorius:                8.18           Silica:                 -90.94
  Larson-Skold:             0.35           Fluorite:                -0.56

                                  2
```

Table C



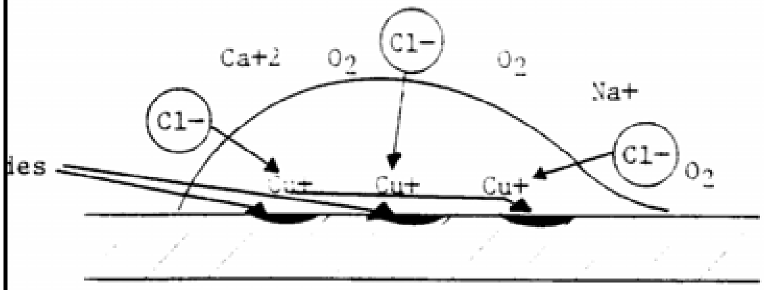
DEPOSIT SETTLES ON METAL SURFACE



OXYGEN CAN REACH METAL ONLY AT OPEN SURFACE

CATHODIC REACTION

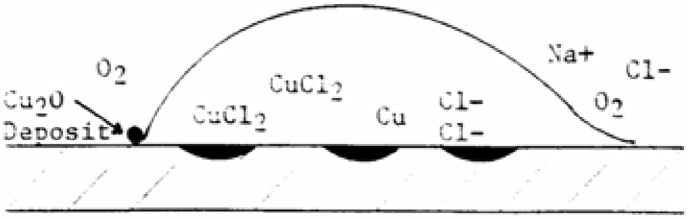
$O_2 + H_2O + 4e \rightarrow 4OH-$



OXYGEN CONTINUES TO DEPOLARIZE THE CATHODIC AREA
WHILE CHLORIDE DIFFUSES INTO THE POROUS DEPOSIT

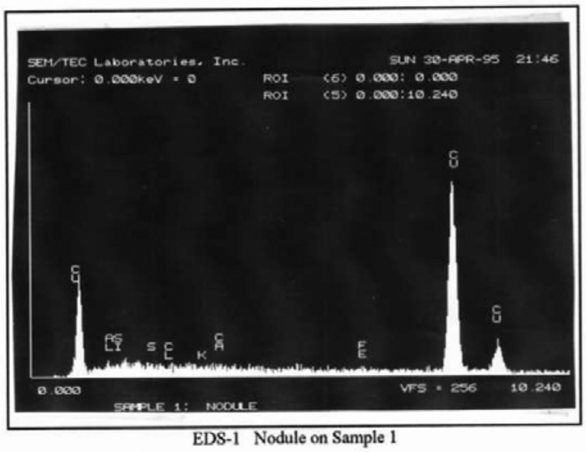
CATHODIC REACTION CONTINU

$O_2 + 2H_2O + 4e \rightarrow 4OH-$

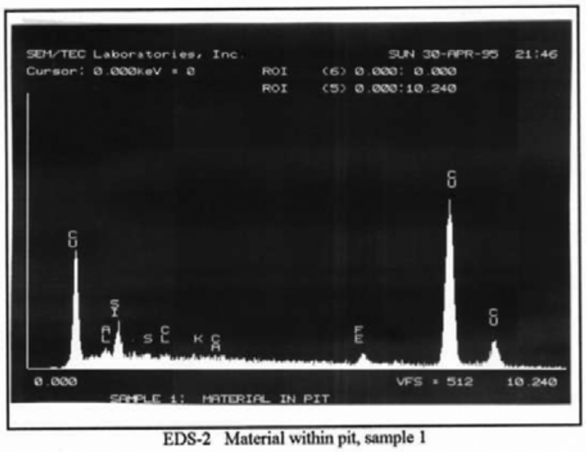


$O_2 + 2H_2O + 4e \rightarrow 4OH-$

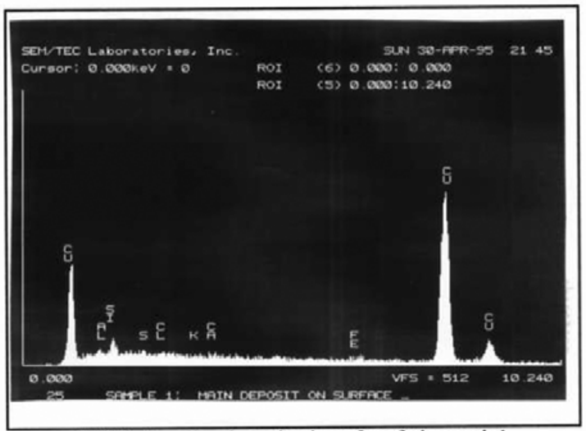
THE COPPER WITHIN THE DEPOSIT REMAINS SOLUBLE AS Cu+
IN THE ABSENCE OF O_2 CORROSION INCREASES AS IONIC
STRENGTH IN THE DEPOSIT INCREASES



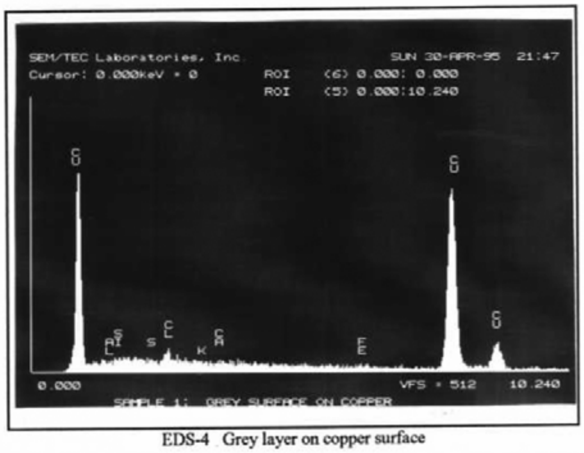
EDS-1 Nodule on Sample 1



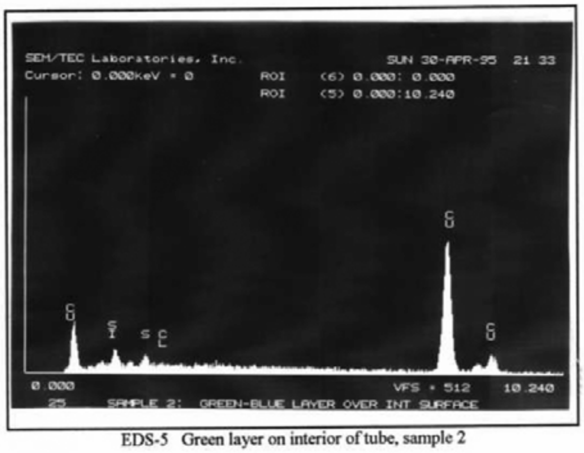
EDS-2 Material within pit, sample 1



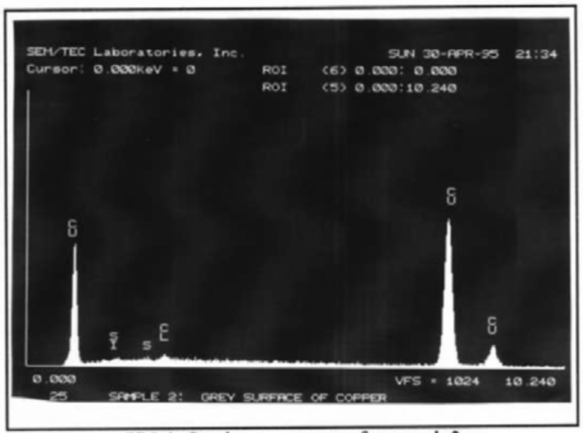
EDS-3 Green deposit over interior surface of tube, sample 1



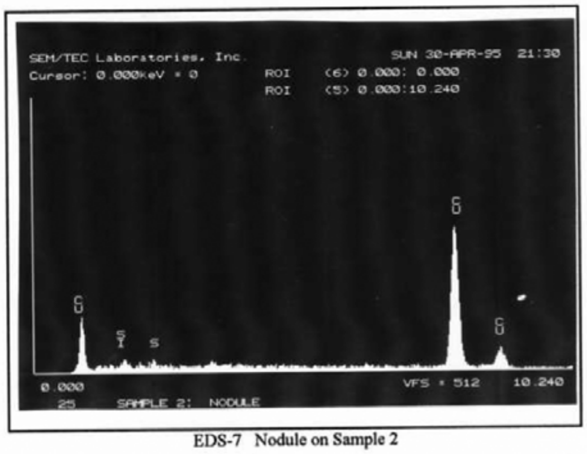
EDS-4 Grey layer on copper surface



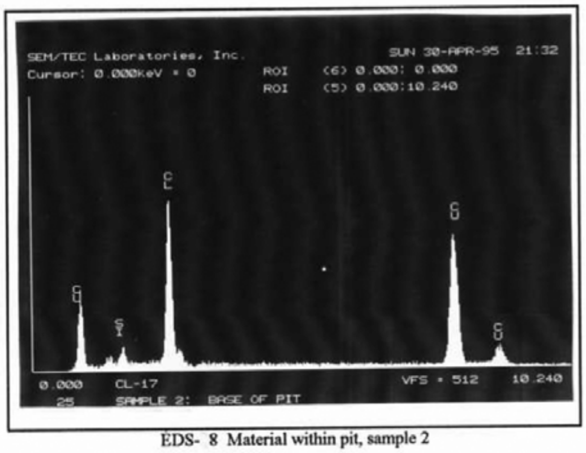
EDS-5 Green layer on interior of tube, sample 2



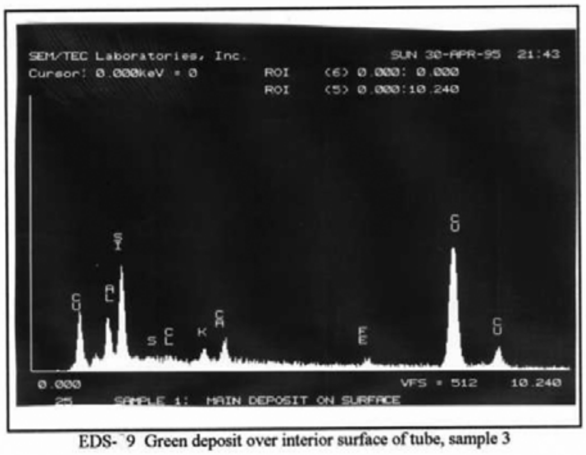
EDS-6 Grey layer on copper surface, sample 2



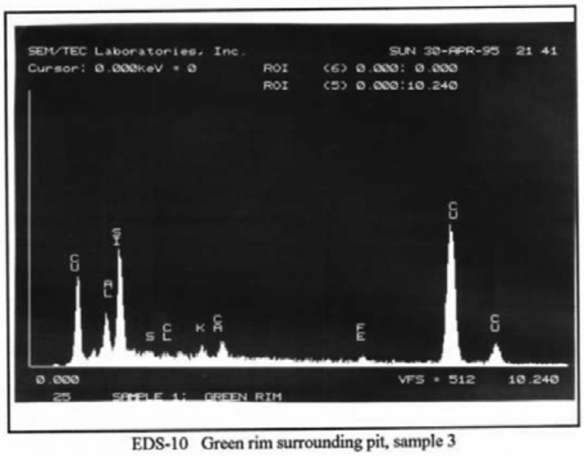
EDS-7 Nodule on Sample 2



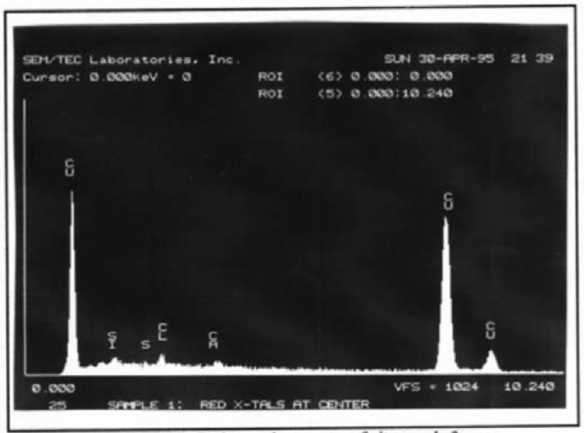
EDS- 8 Material within pit, sample 2



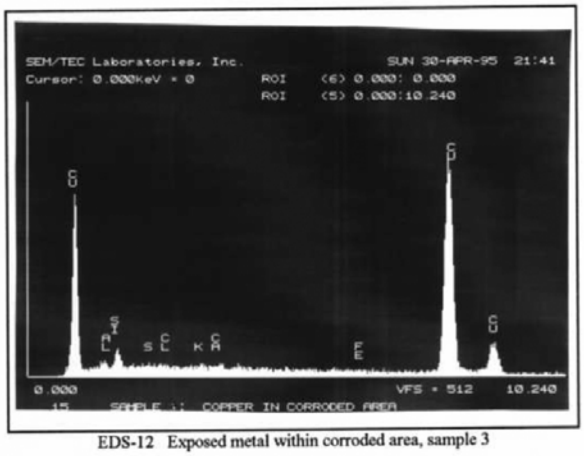
EDS- 9 Green deposit over interior surface of tube, sample 3



EDS-10 Green rim surrounding pit, sample 3

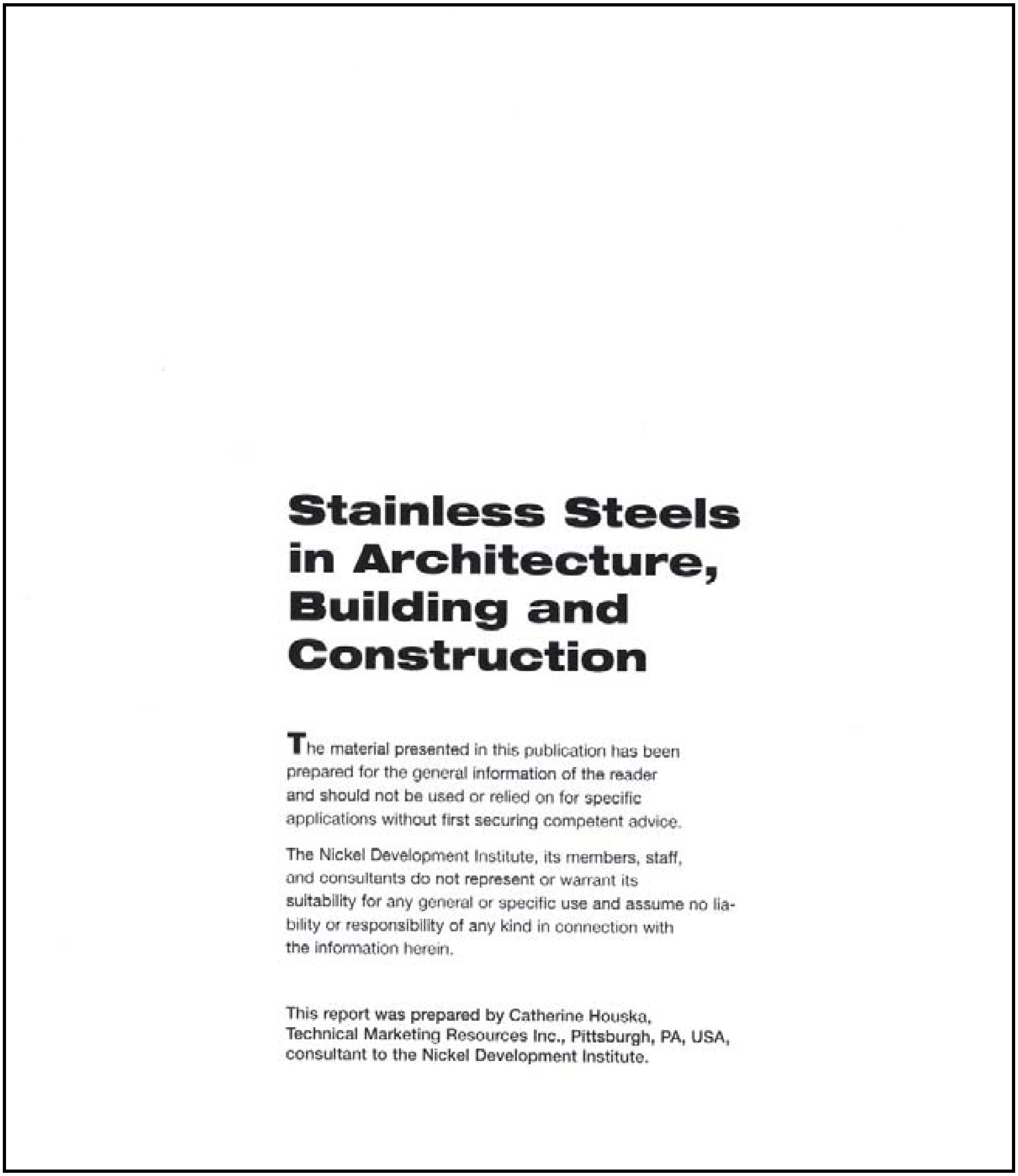


EDS-11 Red crystals at center of pit, sample 3



EDS-12 Exposed metal within corroded area, sample 3

The following material from the Nickel Institute is provided with permission from Catherine Houska, Nickel Institute.

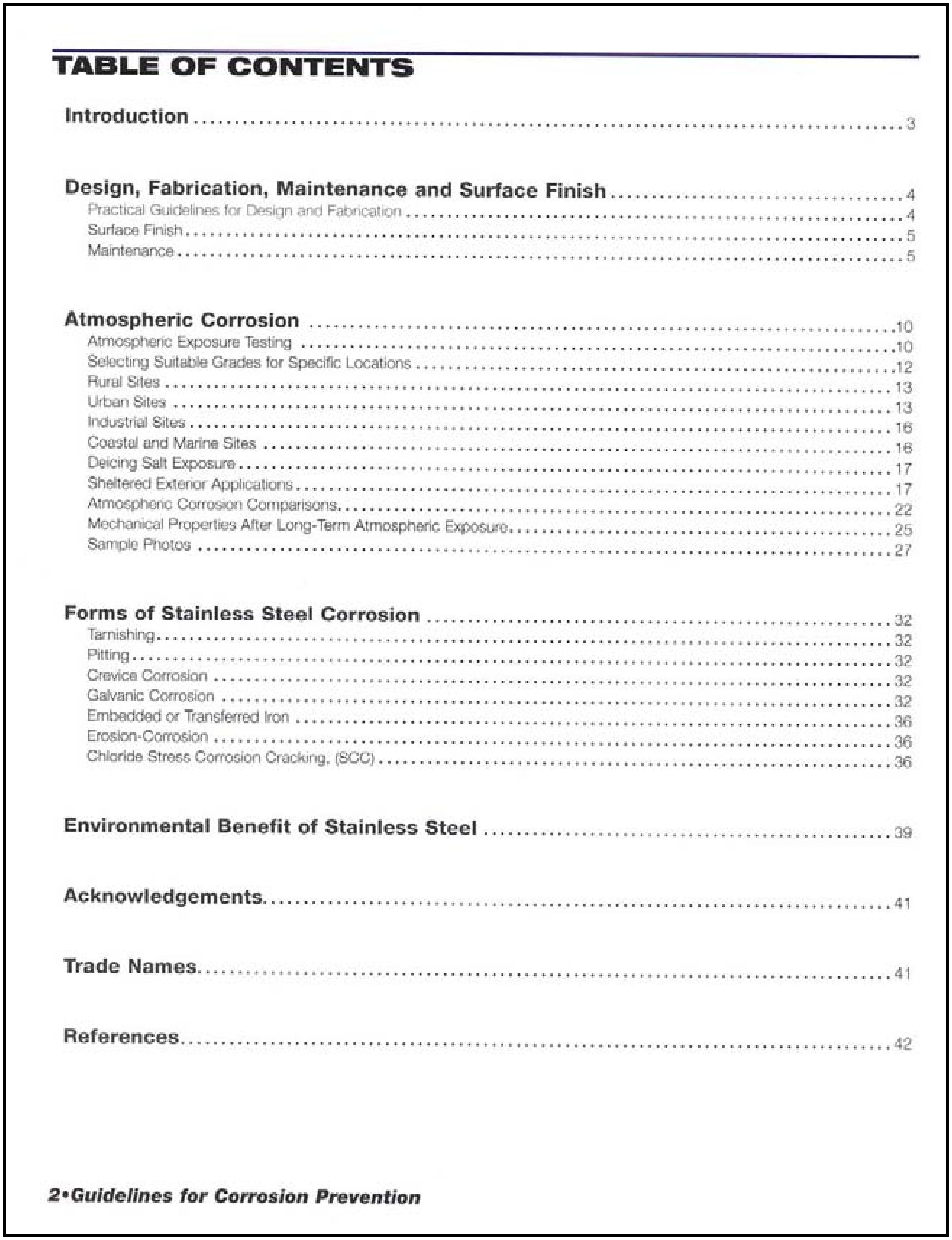


Stainless Steels in Architecture, Building and Construction

The material presented in this publication has been prepared for the general information of the reader and should not be used or relied on for specific applications without first securing competent advice.

The Nickel Development Institute, its members, staff, and consultants do not represent or warrant its suitability for any general or specific use and assume no liability or responsibility of any kind in connection with the information herein.

This report was prepared by Catherine Houska, Technical Marketing Resources Inc., Pittsburgh, PA, USA, consultant to the Nickel Development Institute.



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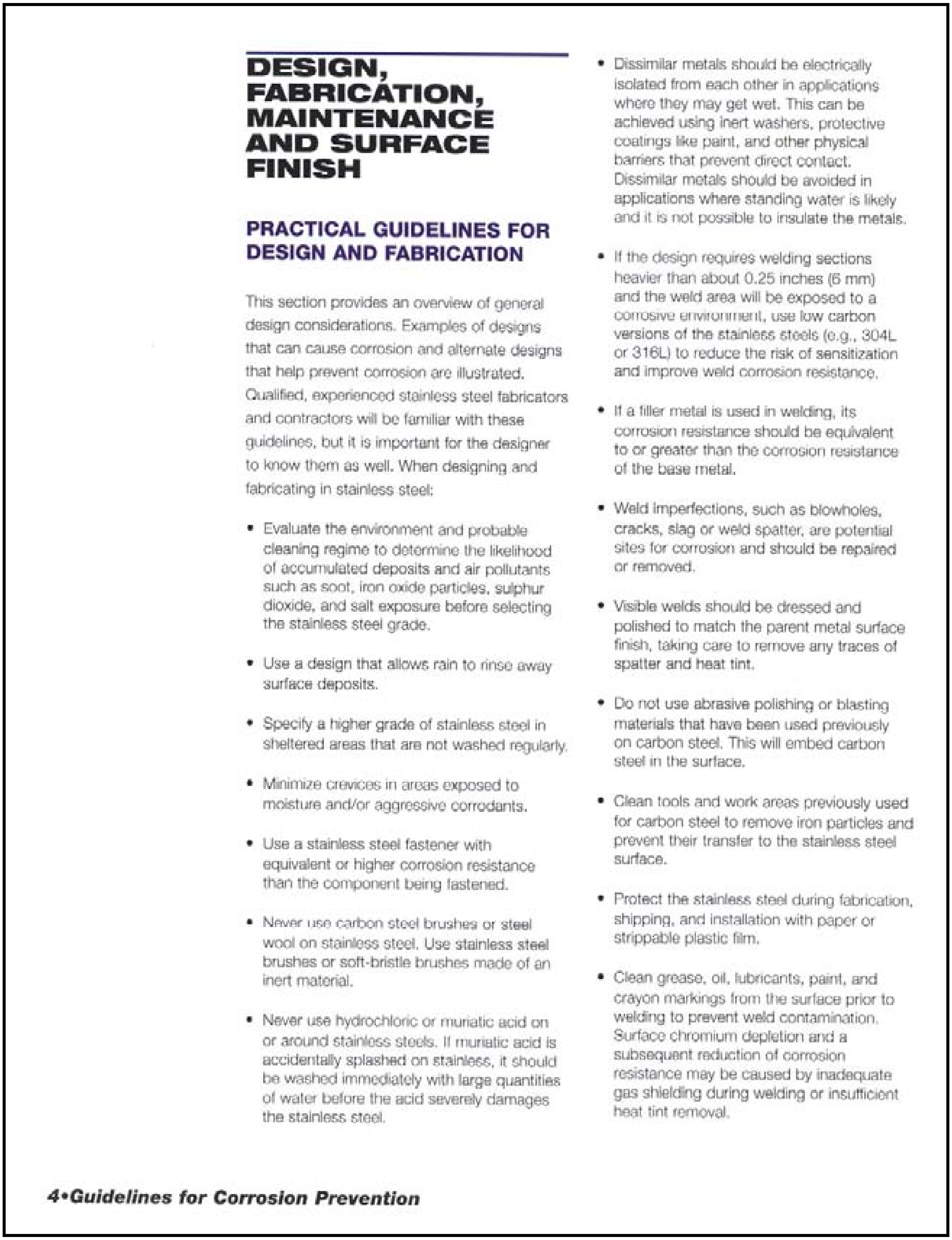
INTRODUCTION

Stainless steel is one of the most durable materials used in architecture, building, and construction. With appropriate grade and finish selection, design, fabrication, and maintenance, the appearance and properties of the stainless steel will remain unchanged over the life of the building. These properties make stainless steel a popular choice for buildings designed to last 50 or more years, aggressive environments, applications where security is a concern, and high traffic areas.

Stainless steels are corrosion-resistant because they form a thin, protective passive film on their surface. This film forms spontaneously when chromium in the stainless steel reacts with oxygen in the air. If the film is damaged or removed during fabrication or polishing, it self-repairs quickly as long as the stainless steel surface is clean. Because stainless steels do not suffer general corrosion and become thinner, the term "corrosion allowance" has no meaning in stainless steel structural design.

Atmospheric corrosion, tarnishing, pitting, crevice corrosion, embedded iron, erosion/corrosion, galvanic corrosion, and stress corrosion cracking can impact the performance and appearance of building materials. This brochure discusses these issues and stainless steel's performance relative to other construction materials.

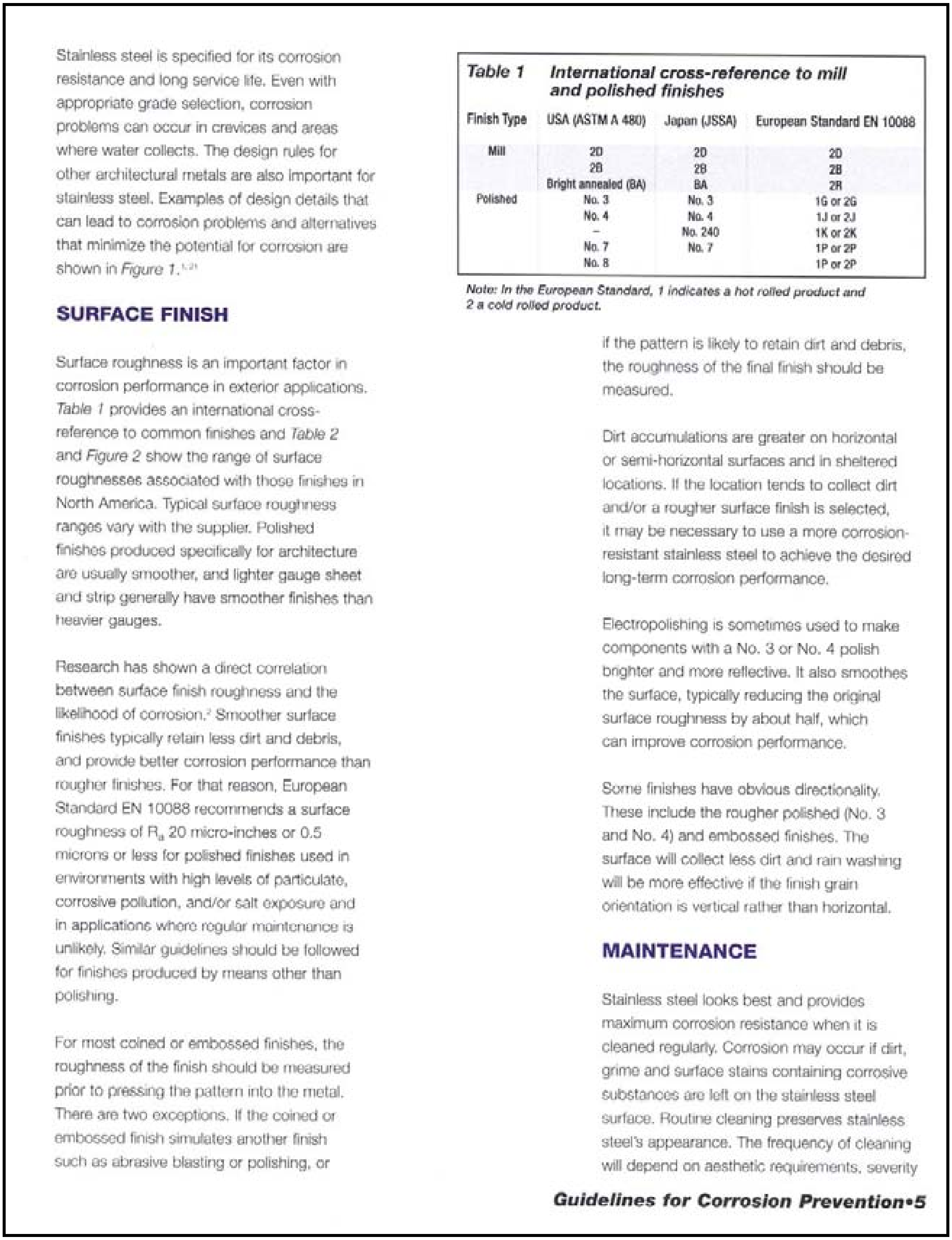


DESIGN, FABRICATION, MAINTENANCE AND SURFACE FINISH

PRACTICAL GUIDELINES FOR DESIGN AND FABRICATION

This section provides an overview of general design considerations. Examples of designs that can cause corrosion and alternate designs that help prevent corrosion are illustrated. Qualified, experienced stainless steel fabricators and contractors will be familiar with these guidelines, but it is important for the designer to know them as well. When designing and fabricating in stainless steel:

- Evaluate the environment and probable cleaning regime to determine the likelihood of accumulated deposits and air pollutants such as soot, iron oxide particles, sulphur dioxide, and salt exposure before selecting the stainless steel grade.
- Use a design that allows rain to rinse away surface deposits.
- Specify a higher grade of stainless steel in sheltered areas that are not washed regularly.
- Minimize crevices in areas exposed to moisture and/or aggressive corrodants.
- Use a stainless steel fastener with equivalent or higher corrosion resistance than the component being fastened.
- Never use carbon steel brushes or steel wool on stainless steel. Use stainless steel brushes or soft-bristle brushes made of an inert material.
- Never use hydrochloric or muriatic acid on or around stainless steels. If muriatic acid is accidentally splashed on stainless, it should be washed immediately with large quantities of water before the acid severely damages the stainless steel.
- Dissimilar metals should be electrically isolated from each other in applications where they may get wet. This can be achieved using inert washers, protective coatings like paint, and other physical barriers that prevent direct contact. Dissimilar metals should be avoided in applications where standing water is likely and it is not possible to insulate the metals.
- If the design requires welding sections heavier than about 0.25 inches (6 mm) and the weld area will be exposed to a corrosive environment, use low carbon versions of the stainless steels (e.g., 304L or 316L) to reduce the risk of sensitization and improve weld corrosion resistance.
- If a filler metal is used in welding, its corrosion resistance should be equivalent to or greater than the corrosion resistance of the base metal.
- Weld imperfections, such as blowholes, cracks, slag or weld spatter, are potential sites for corrosion and should be repaired or removed.
- Visible welds should be dressed and polished to match the parent metal surface finish, taking care to remove any traces of spatter and heat tint.
- Do not use abrasive polishing or blasting materials that have been used previously on carbon steel. This will embed carbon steel in the surface.
- Clean tools and work areas previously used for carbon steel to remove iron particles and prevent their transfer to the stainless steel surface.
- Protect the stainless steel during fabrication, shipping, and installation with paper or strippable plastic film.
- Clean grease, oil, lubricants, paint, and crayon markings from the surface prior to welding to prevent weld contamination. Surface chromium depletion and a subsequent reduction of corrosion resistance may be caused by inadequate gas shielding during welding or insufficient heat tint removal.



Stainless steel is specified for its corrosion resistance and long service life. Even with appropriate grade selection, corrosion problems can occur in crevices and areas where water collects. The design rules for other architectural metals are also important for stainless steel. Examples of design details that can lead to corrosion problems and alternatives that minimize the potential for corrosion are shown in *Figure 1*.[1,2]

SURFACE FINISH

Surface roughness is an important factor in corrosion performance in exterior applications. *Table 1* provides an international cross-reference to common finishes and *Table 2* and *Figure 2* show the range of surface roughnesses associated with those finishes in North America. Typical surface roughness ranges vary with the supplier. Polished finishes produced specifically for architecture are usually smoother, and lighter gauge sheet and strip generally have smoother finishes than heavier gauges.

Research has shown a direct correlation between surface finish roughness and the likelihood of corrosion.[2] Smoother surface finishes typically retain less dirt and debris, and provide better corrosion performance than rougher finishes. For that reason, European Standard EN 10088 recommends a surface roughness of R_a 20 micro-inches or 0.5 microns or less for polished finishes used in environments with high levels of particulate, corrosive pollution, and/or salt exposure and in applications where regular maintenance is unlikely. Similar guidelines should be followed for finishes produced by means other than polishing.

Table 1 ***International cross-reference to mill and polished finishes***

Finish Type	USA (ASTM A 480)	Japan (JSSA)	European Standard EN 10088
Mill	2D	2D	2D
	2B	2B	2B
	Bright annealed (BA)	BA	2R
Polished	No. 3	No. 3	1G or 2G
	No. 4	No. 4	1J or 2J
	–	No. 240	1K or 2K
	No. 7	No. 7	1P or 2P
	No. 8		1P or 2P

Note: In the European Standard, 1 indicates a hot rolled product and 2 a cold rolled product.

For most coined or embossed finishes, the roughness of the finish should be measured prior to pressing the pattern into the metal. There are two exceptions. If the coined or embossed finish simulates another finish such as abrasive blasting or polishing, or if the pattern is likely to retain dirt and debris, the roughness of the final finish should be measured.

Dirt accumulations are greater on horizontal or semi-horizontal surfaces and in sheltered locations. If the location tends to collect dirt and/or a rougher surface finish is selected, it may be necessary to use a more corrosion-resistant stainless steel to achieve the desired long-term corrosion performance.

Electropolishing is sometimes used to make components with a No. 3 or No. 4 polish brighter and more reflective. It also smoothes the surface, typically reducing the original surface roughness by about half, which can improve corrosion performance.

Some finishes have obvious directionality. These include the rougher polished (No. 3 and No. 4) and embossed finishes. The surface will collect less dirt and rain washing will be more effective if the finish grain orientation is vertical rather than horizontal.

MAINTENANCE

Stainless steel looks best and provides maximum corrosion resistance when it is cleaned regularly. Corrosion may occur if dirt, grime and surface stains containing corrosive substances are left on the stainless steel surface. Routine cleaning preserves stainless steel's appearance. The frequency of cleaning will depend on aesthetic requirements, severity

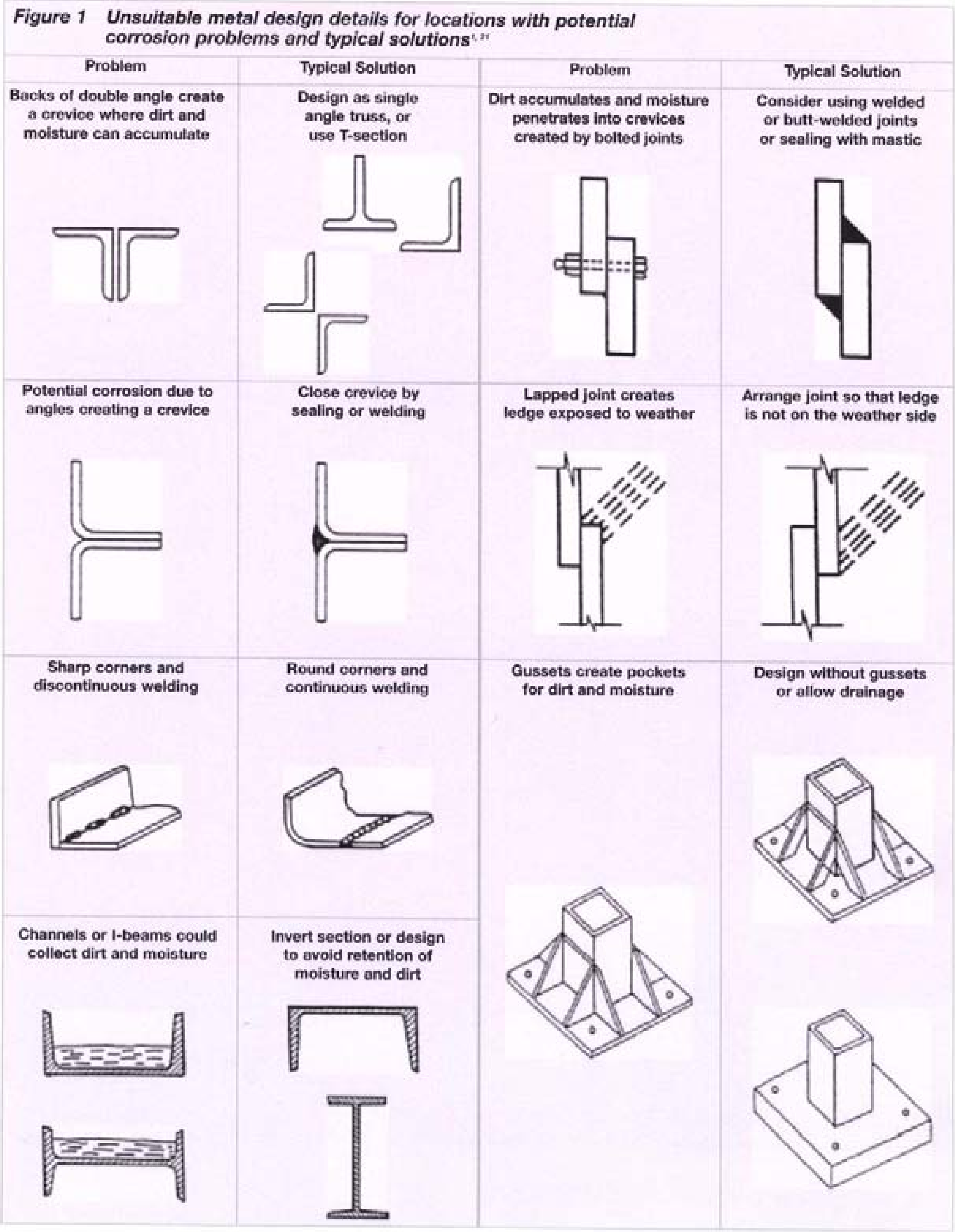
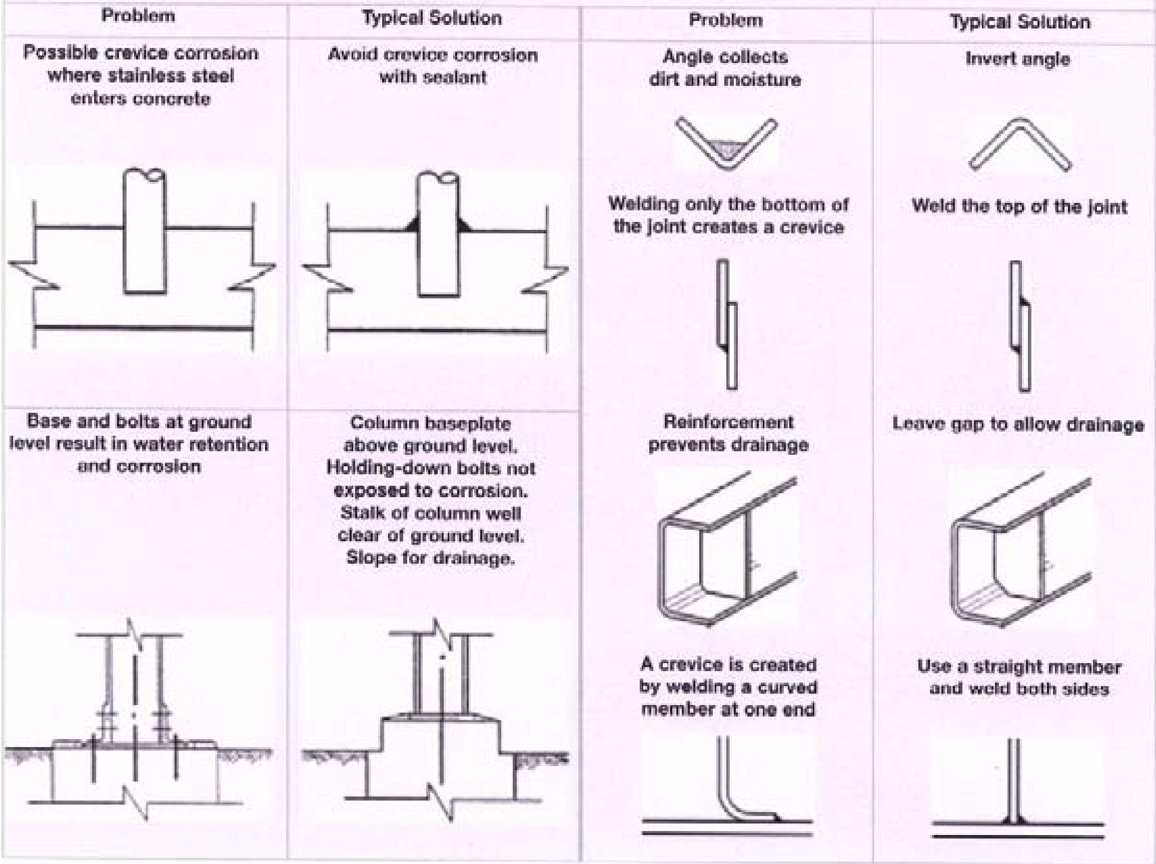


Figure 1 Unsuitable metal design details for locations with potential corrosion problems and typical solutions[1, 21]

Problem	Typical Solution	Problem	Typical Solution
Backs of double angle create a crevice where dirt and moisture can accumulate	Design as single angle truss, or use T-section	Dirt accumulates and moisture penetrates into crevices created by bolted joints	Consider using welded or butt-welded joints or sealing with mastic
Potential corrosion due to angles creating a crevice	Close crevice by sealing or welding	Lapped joint creates ledge exposed to weather	Arrange joint so that ledge is not on the weather side
Sharp corners and discontinuous welding	Round corners and continuous welding	Gussets create pockets for dirt and moisture	Design without gussets or allow drainage
Channels or I-beams could collect dirt and moisture	Invert section or design to avoid retention of moisture and dirt		

6•Guidelines for Corrosion Prevention

Figure 1 (cont'd) *Unsuitable metal design details for locations with potential corrosion problems and typical solutions*[1, 21]



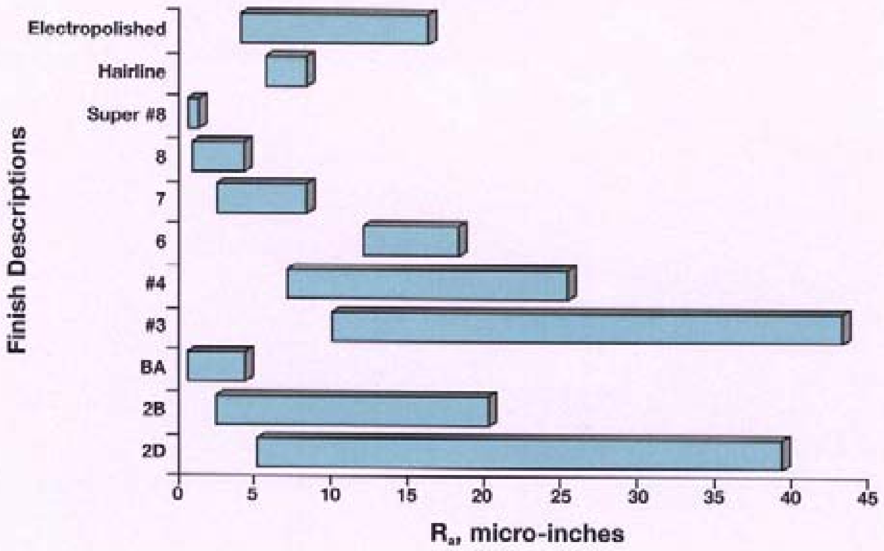
Problem	Typical Solution	Problem	Typical Solution
Possible crevice corrosion where stainless steel enters concrete	Avoid crevice corrosion with sealant	Angle collects dirt and moisture	Invert angle
		Welding only the bottom of the joint creates a crevice	Weld the top of the joint
Base and bolts at ground level result in water retention and corrosion	Column baseplate above ground level. Holding-down bolts not exposed to corrosion. Stalk of column well clear of ground level. Slope for drainage.	Reinforcement prevents drainage	Leave gap to allow drainage
		A crevice is created by welding a curved member at one end	Use a straight member and weld both sides

Table 2 *Typical surface roughness ranges for cold rolled sheet and strip from North American stainless steel suppliers*

ASTM A 480 Finish Descriptions	R_a and RMS Surface Roughness Equivalents			
	R_a, micro-inches	R_a, microns	RMS, micro-inches	RMS, microns
2D	5.0–39.0	0.13–1.0	6.4–49.2	0.16–1.25
2B	2.4–20.0	0.06–0.51	3.0–25.1	0.08–0.64
BA	0.5–4.0	0.01–0.10	0.49–4.9	0.01–0.13
#3	10.0–43.0	0.25–1.10	12.3–54.1	0.31–1.37
#4	7.0–25.0	0.18–0.64	8.9–31.5	0.23–0.80
6	12.0–18.0	0.30–0.46	14.8–22.6	0.37–0.57
7	2.4–8.0	0.06–0.20	3.0–9.8	0.07–0.25
8	0.74–4.0	0.019–0.10	0.9–4.9	0.02–0.13
Super No. 8	0.4–0.8	0.01–0.02	0.5–1.0	0.01–0.03
Hairline	5.5–8.0	0.14–0.20	6.9–9.8	0.18–0.25
Electropolished	4.0–16.0	0.10–0.41	4.9–20.2	0.13–0.50

Note: Data for sheet and strip were obtained from North American suppliers. The highest and lowest values were used to create the surface roughness range and include both light and heavy gauges. Lighter gauges generally have smoother finishes than heavier gauges and would be at the bottom end of the range. Surface roughness will vary across sheet width and length.

Figure 2 ***Typical surface roughness ranges for cold rolled sheet and strip from North American stainless steel suppliers***

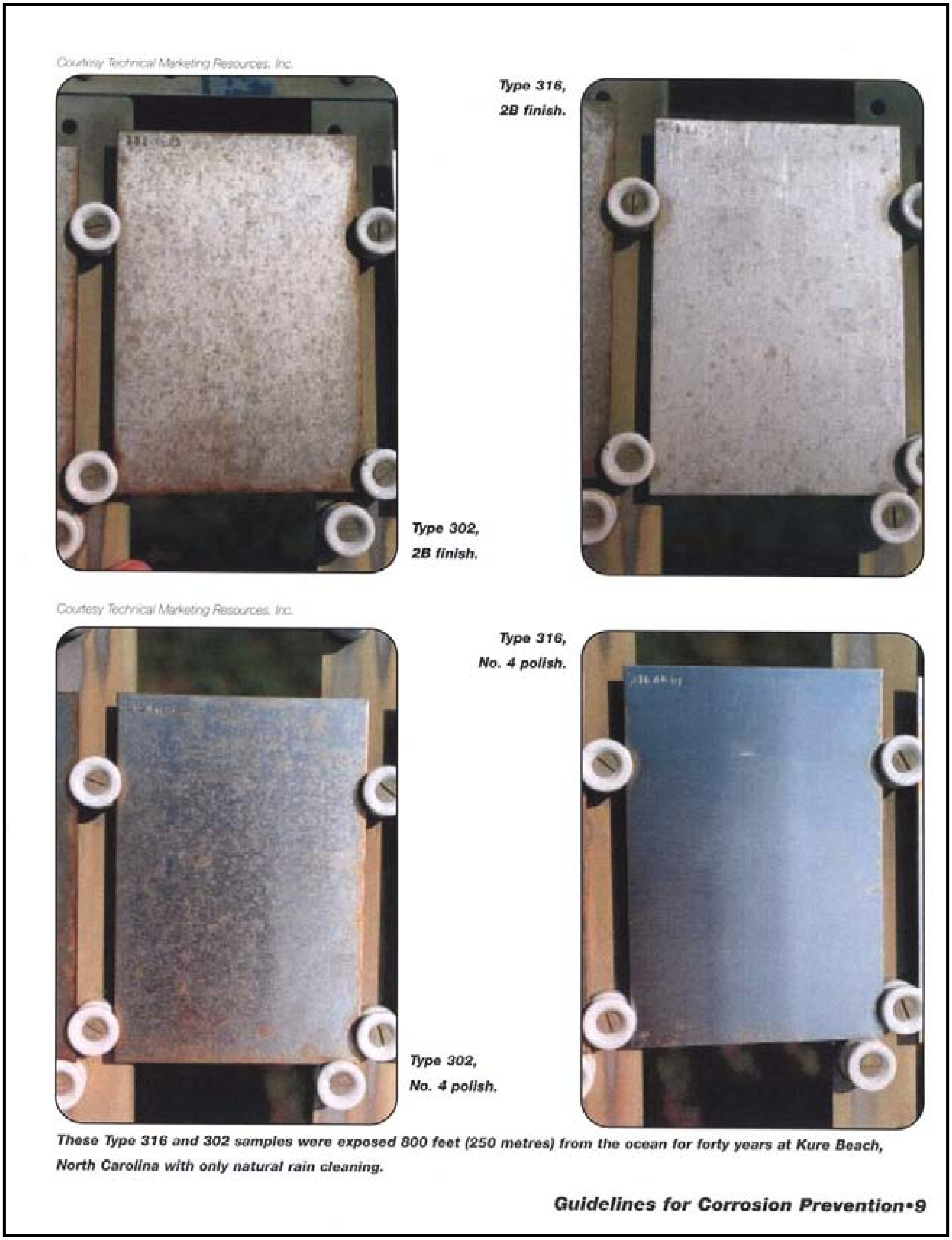


of the environment, suitability of the stainless steel grade and finish for that environment, the presence or lack of heavy rains to clean the surface, and the design.

When possible, designs should take advantage of natural rain washing and include building washing systems. Designing for rain cleaning and stainless steel grade and finish selection are particularly important in structures that will never or rarely be cleaned, like industrial buildings and monumental structures such as the Gateway Arch.

Stainless steel is easy to clean and regular cleaning with appropriate products will not change the appearance of the finish over time. Loose dirt is rinsed off with clean water. A mild detergent or 5% ammonia and water solution is applied with a soft clean cloth. This is rinsed off with clean water and then wiped or squeegeed dry. A soft-bristle brush can be used to loosen dirt and a degreaser to remove oil stains. Cleaning products should not contain chlorides or harsh abrasives.

If the surface has been neglected or there are stubborn deposits, a mild, non-acidic, non-scratching, abrasive powder that does not contain chlorides can be used on bare stainless steel. More aggressive cleaning can damage the finish and the supplier should be consulted before proceeding. It is best to test cleaning products on a stainless steel sample or inconspicuous location before use. Although buildings can often be restored to their original appearance after many years of neglect, remedial cleaning is more costly and can have uncertain results. Cleaning guidelines can be found in the NiDI publication 11 014, *Guidelines for Maintenance and Cleaning*.



Courtesy Technical Marketing Resources, Inc.

Type 316, 2B finish.

Type 302, 2B finish.

Courtesy Technical Marketing Resources, Inc.

Type 316, No. 4 polish.

Type 302, No. 4 polish.

These Type 316 and 302 samples were exposed 800 feet (250 metres) from the ocean for forty years at Kure Beach, North Carolina with only natural rain cleaning.

Guidelines for Corrosion Prevention•9

ATMOSPHERIC CORROSION

ATMOSPHERIC EXPOSURE TESTING

Potentially corrosive atmospheric pollutants, wind-borne marine salt, temperature, humidity, rainfall, and deicing salt exposure must be taken into consideration when selecting an appropriate stainless steel. Localized pollution and the direction of the prevailing winds can cause differences in the corrosiveness of sites that are only a few miles or kilometres apart.

Courtesy Specialty Steel Industry of North America

The Inland Steel Building (completed in 1957) is on a busy street in downtown Chicago and has Type 302 exterior wall panels with a No. 4 polish. They are exposed to deicing salt and pollution. The panels have always been cleaned three to four times per year when the windows are washed. It is in excellent condition.

For testing and material selection, service environments are classified as rural, urban, industrial, and marine. These categories refer to the general environment and not to localized conditions such as the immediate proximity of a source of strong pollution like a smokestack. Possible environmental changes during the building life should be evaluated. For example, will a rural site become urban or industrial?

Within each category, levels of severity have been established. To classify the severity of an environment, rainfall, air temperature, pollution and other factors have been monitored. Because no two environments are exactly alike, the data should be used as a general performance guideline for localities with similar pollution levels and climate in conjunction with the guidelines in *Table 3*.

Carbon steel calibrating samples are used to compare the severity of atmospheric corrosion test sites around the world.[3,4] See *Table 4*. Comparative metal corrosion data from many of these sites is provided in this brochure. This data can be used in conjunction with *Table 4* and a thorough evaluation of the site to predict probable metal performance in locations with similar environments and carbon steel corrosion rates. Although some of these sites are in locations where deicing salts are used, the calibrating samples were not exposed to salt. Salt exposure makes an environment much more aggressive. The likelihood of deicing salt exposure should be considered when evaluating the severity of sites.

An electrolyte must be present for corrosion to occur. An electrolyte is a water solution that can conduct an electric current because it contains chemicals, such as chlorides. The water could come from rain, condensation of

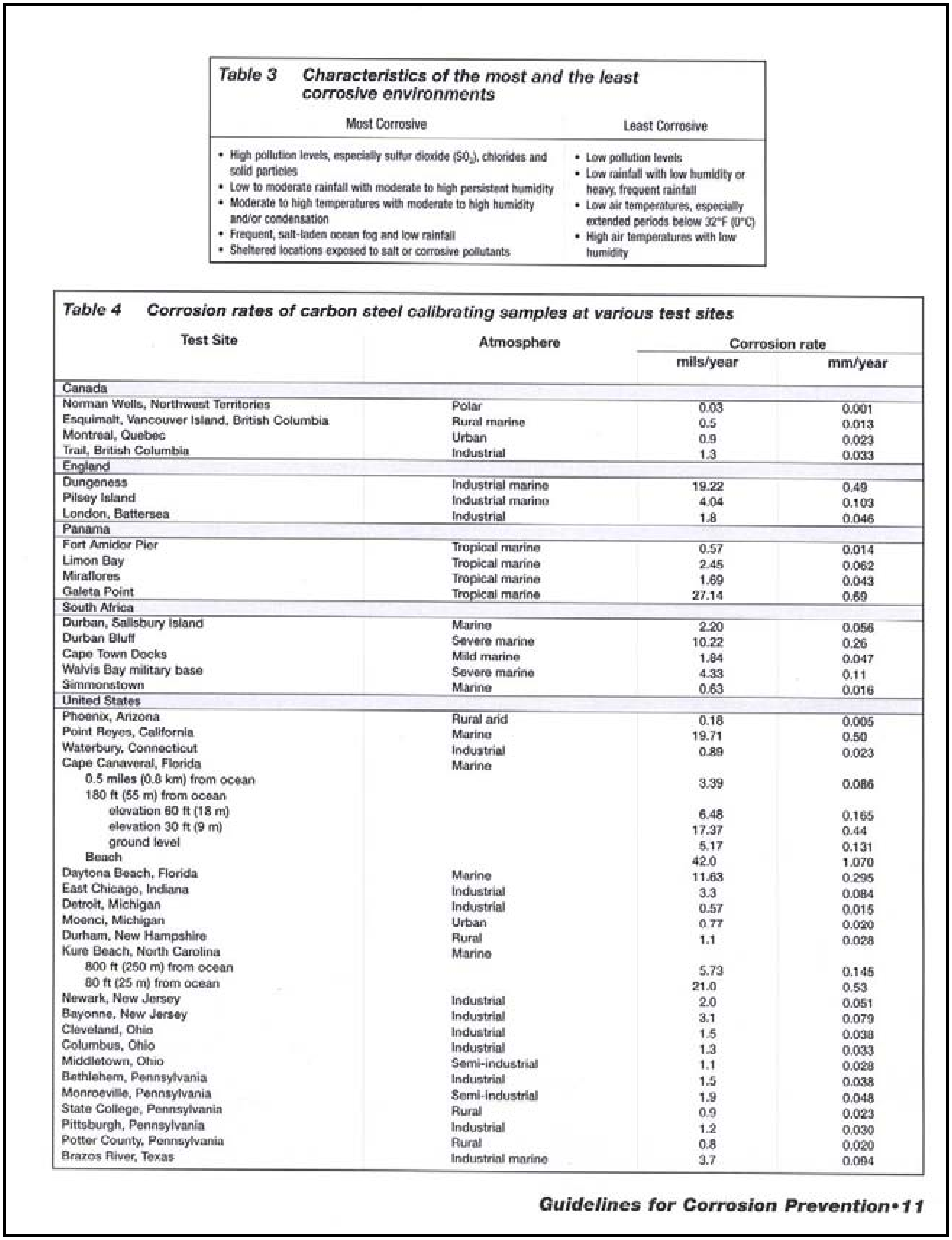
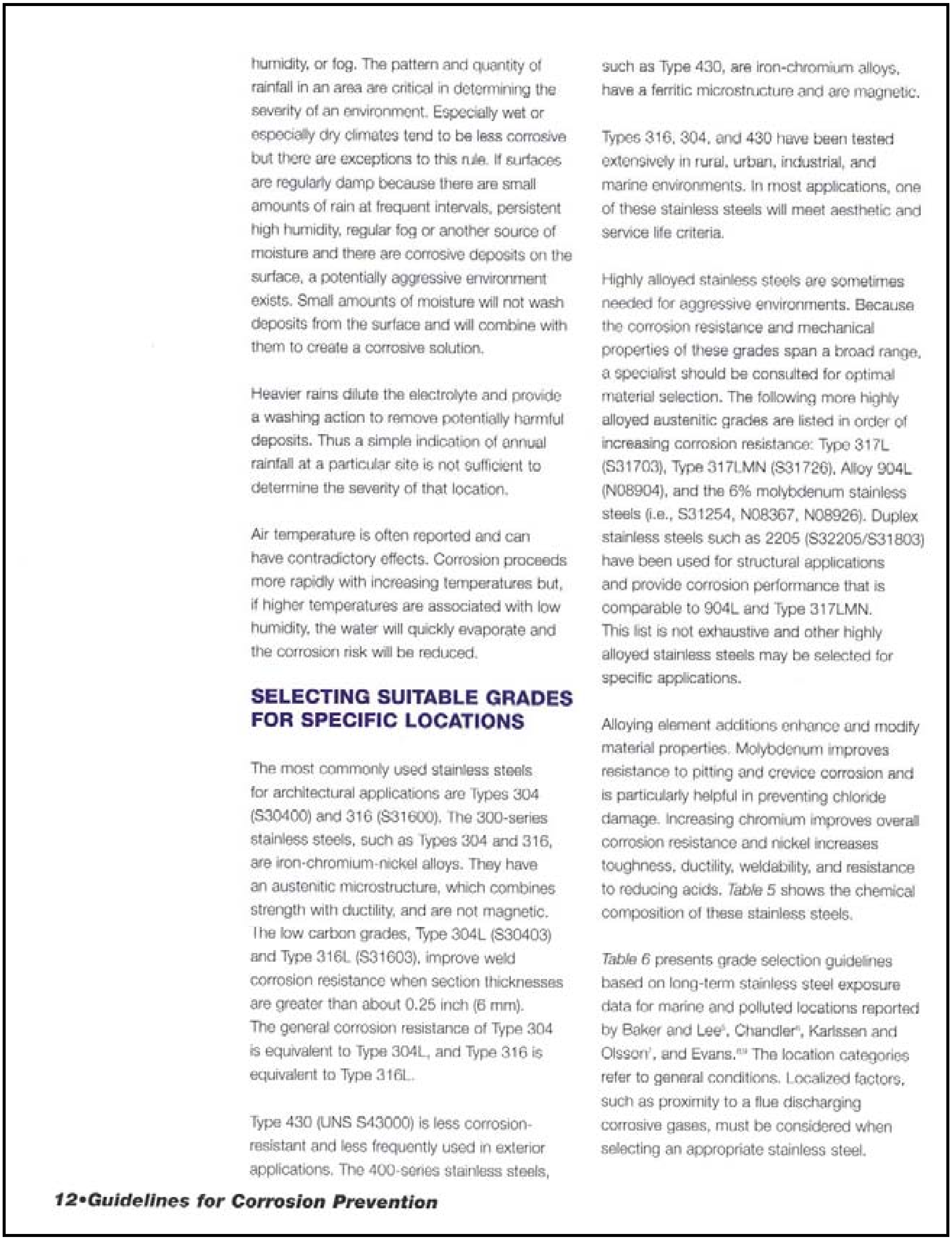


Table 3 Characteristics of the most and the least corrosive environments

Most Corrosive	Least Corrosive
• High pollution levels, especially sulfur dioxide (SO_2), chlorides and solid particles • Low to moderate rainfall with moderate to high persistent humidity • Moderate to high temperatures with moderate to high humidity and/or condensation • Frequent, salt-laden ocean fog and low rainfall • Sheltered locations exposed to salt or corrosive pollutants	• Low pollution levels • Low rainfall with low humidity or heavy, frequent rainfall • Low air temperatures, especially extended periods below 32°F (0°C) • High air temperatures with low humidity

Table 4 Corrosion rates of carbon steel calibrating samples at various test sites

Test Site	Atmosphere	Corrosion rate	
		mils/year	mm/year
Canada			
Norman Wells, Northwest Territories	Polar	0.03	0.001
Esquimalt, Vancouver Island, British Columbia	Rural marine	0.5	0.013
Montreal, Quebec	Urban	0.9	0.023
Trail, British Columbia	Industrial	1.3	0.033
England			
Dungeness	Industrial marine	19.22	0.49
Pilsey Island	Industrial marine	4.04	0.103
London, Battersea	Industrial	1.8	0.046
Panama			
Fort Amidor Pier	Tropical marine	0.57	0.014
Limon Bay	Tropical marine	2.45	0.062
Miraflores	Tropical marine	1.69	0.043
Galeta Point	Tropical marine	27.14	0.69
South Africa			
Durban, Salisbury Island	Marine	2.20	0.056
Durban Bluff	Severe marine	10.22	0.26
Cape Town Docks	Mild marine	1.84	0.047
Walvis Bay military base	Severe marine	4.33	0.11
Simmonstown	Marine	0.63	0.016
United States			
Phoenix, Arizona	Rural arid	0.18	0.005
Point Reyes, California	Marine	19.71	0.50
Waterbury, Connecticut	Industrial	0.89	0.023
Cape Canaveral, Florida	Marine		
0.5 miles (0.8 km) from ocean		3.39	0.086
180 ft (55 m) from ocean			
elevation 60 ft (18 m)		6.48	0.165
elevation 30 ft (9 m)		17.37	0.44
ground level		5.17	0.131
Beach		42.0	1.070
Daytona Beach, Florida	Marine	11.63	0.295
East Chicago, Indiana	Industrial	3.3	0.084
Detroit, Michigan	Industrial	0.57	0.015
Moenci, Michigan	Urban	0.77	0.020
Durham, New Hampshire	Rural	1.1	0.028
Kure Beach, North Carolina	Marine		
800 ft (250 m) from ocean		5.73	0.145
80 ft (25 m) from ocean		21.0	0.53
Newark, New Jersey	Industrial	2.0	0.051
Bayonne, New Jersey	Industrial	3.1	0.079
Cleveland, Ohio	Industrial	1.5	0.038
Columbus, Ohio	Industrial	1.3	0.033
Middletown, Ohio	Semi-industrial	1.1	0.028
Bethlehem, Pennsylvania	Industrial	1.5	0.038
Monroeville, Pennsylvania	Semi-industrial	1.9	0.048
State College, Pennsylvania	Rural	0.9	0.023
Pittsburgh, Pennsylvania	Industrial	1.2	0.030
Potter County, Pennsylvania	Rural	0.8	0.020
Brazos River, Texas	Industrial marine	3.7	0.094



humidity, or fog. The pattern and quantity of rainfall in an area are critical in determining the severity of an environment. Especially wet or especially dry climates tend to be less corrosive but there are exceptions to this rule. If surfaces are regularly damp because there are small amounts of rain at frequent intervals, persistent high humidity, regular fog or another source of moisture and there are corrosive deposits on the surface, a potentially aggressive environment exists. Small amounts of moisture will not wash deposits from the surface and will combine with them to create a corrosive solution.

Heavier rains dilute the electrolyte and provide a washing action to remove potentially harmful deposits. Thus a simple indication of annual rainfall at a particular site is not sufficient to determine the severity of that location.

Air temperature is often reported and can have contradictory effects. Corrosion proceeds more rapidly with increasing temperatures but, if higher temperatures are associated with low humidity, the water will quickly evaporate and the corrosion risk will be reduced.

SELECTING SUITABLE GRADES FOR SPECIFIC LOCATIONS

The most commonly used stainless steels for architectural applications are Types 304 (S30400) and 316 (S31600). The 300-series stainless steels, such as Types 304 and 316, are iron-chromium-nickel alloys. They have an austenitic microstructure, which combines strength with ductility, and are not magnetic. The low carbon grades, Type 304L (S30403) and Type 316L (S31603), improve weld corrosion resistance when section thicknesses are greater than about 0.25 inch (6 mm). The general corrosion resistance of Type 304 is equivalent to Type 304L, and Type 316 is equivalent to Type 316L.

Type 430 (UNS S43000) is less corrosion-resistant and less frequently used in exterior applications. The 400-series stainless steels, such as Type 430, are iron-chromium alloys, have a ferritic microstructure and are magnetic.

Types 316, 304, and 430 have been tested extensively in rural, urban, industrial, and marine environments. In most applications, one of these stainless steels will meet aesthetic and service life criteria.

Highly alloyed stainless steels are sometimes needed for aggressive environments. Because the corrosion resistance and mechanical properties of these grades span a broad range, a specialist should be consulted for optimal material selection. The following more highly alloyed austenitic grades are listed in order of increasing corrosion resistance: Type 317L (S31703), Type 317LMN (S31726), Alloy 904L (N08904), and the 6% molybdenum stainless steels (i.e., S31254, N08367, N08926). Duplex stainless steels such as 2205 (S32205/S31803) have been used for structural applications and provide corrosion performance that is comparable to 904L and Type 317LMN. This list is not exhaustive and other highly alloyed stainless steels may be selected for specific applications.

Alloying element additions enhance and modify material properties. Molybdenum improves resistance to pitting and crevice corrosion and is particularly helpful in preventing chloride damage. Increasing chromium improves overall corrosion resistance and nickel increases toughness, ductility, weldability, and resistance to reducing acids. *Table 5* shows the chemical composition of these stainless steels.

Table 6 presents grade selection guidelines based on long-term stainless steel exposure data for marine and polluted locations reported by Baker and Lee[5], Chandler[6], Karlssen and Olsson[7], and Evans.[8,9] The location categories refer to general conditions. Localized factors, such as proximity to a flue discharging corrosive gases, must be considered when selecting an appropriate stainless steel.

Table 5 ***Unified Numbering System (UNS) chemical compositions****

UNS No.	Common or Trade Name	C	Cr	Cu	Mn	Mo	N	Ni	P	S	Si	Fe
S43000	430	0.12	16.0–18.0	–	1.00	–	–	–	0.040	0.030	1.00	rem
S30400	304	0.08	18.0–20.0	–	2.00	–	–	8.0–10.5	0.045	0.030	1.00	rem
S31254	254 SMO	0.020	19.5–20.5	0.50–1.00	1.00	6.0–6.5	0.180–0.220	17.5–18.5	0.030	0.010	0.80	rem
S31600	316	0.08	16.0–18.0	–	2.00	2.00–3.00	–	10.0–14.0	0.045	0.030	1.00	rem
S31703	317L	0.030	18.0–20.0	–	2.00	3.0–4.0	–	11.0–15.0	0.045	0.030	1.00	rem
S31726	317LMN	0.03	17.0–20.0	0.75	2.00	4.0–5.0	0.10–0.20	13.5–17.5	0.045	0.030	0.75	rem
S31803	2205	0.030	21.0–23.0	–	2.00	2.5–3.5	0.08–0.20	4.5–6.5	0.030	0.020	1.00	rem
S32205	2205	0.030	22.0–23.0	–	2.00	3.0–3.5	0.14–0.20	4.5–6.5	0.030	0.020	1.00	rem
N08367	AL-6XN	0.030	20.0–22.0	–	2.00	6.0–7.0	0.18–0.25	23.5–25.5	0.040	0.030	1.00	rem
N08904	904L	0.020	19.0–23.0	1.00–2.00	2.00	4.0–5.0	–	23.0–28.0	0.045	0.035	1.00	rem
N08926		0.020	19.0–21.0	0.5–1.5	2.00	6.0–7.0	0.15–0.25	24.0–26.0	0.030	0.010	0.50	rem

* *Maximum unless a range is given.*

RURAL SITES

Locations categorized as "rural" are not exposed to industrial atmospheric discharges or coastal or deicing salts. Suburban areas with low population densities and light, non-polluting industry may also be categorized as rural. Both migrant air pollution and future development should be considered when categorizing a site.

Type 430 will suffer light to moderate staining and rusting on both exposed and sheltered surfaces. Smoother surface finishes and regular washing help reduce corrosion, although some loss of brightness should be expected.

Type 304/304L exposed surfaces are virtually unattacked but sheltered surfaces could experience minor discolouration.

Smoother surface finishes provide better resistance to tarnishing and regular washing helps retain a pristine finish.

Type 316/316L with a smooth surface finish retains a bright appearance. Rougher surface finishes like a No. 3 or No. 4 polish may experience slight tarnishing. Washing is not generally necessary to maintain corrosion performance although dirt film removal improves appearance.

URBAN SITES

Urban sites include residential, commercial and light industrial locations with low to moderate pollution from vehicular traffic and similar sources.

Type 430 can become quite heavily rusted, especially in sheltered areas where pollutants

Table 6 ***Grade selection guidelines***

Grade (Type)	Location											
	Rural/Suburb			Urban			Industrial			Marine/Deicing Salt		
	L	M	H	L	M	H	L	M	H	L	M	H
Highly Alloyed	■	■	■	■	■	■	■	■	●	■	■	●
316, 316L	■	■	■	■	●	●	●	●	(●)	●	●	(●)
304, 304L	●	●	●	●	●	(●)	(●)	(●)	✖	●	(●)	✖
430	●	(●)	(●)	✖	✖	✖	✖	✖	✖	✖	✖	✖

L *Least corrosive conditions within that category due to low humidity and low temperatures*
M *Fairly typical of category*
H *Corrosion is likely to be higher than typical for the category due to persistently high humidity, high ambient temperatures, and/or particularly aggressive air pollution*
■ *Good service, but may be over-specified*
● *Most economical choice*
✖ *Corrosion likely*
( ) *Indicates that the grade may be suitable if a smooth surface finish is selected and it is washed regularly*

Courtesy Allegheny Ludlum Corp.

Above the third floor, New York City's 150 East 42nd Street (completed in 1954) has Type 302 exterior wall panels with a 2B finish (surface roughness of R_a 15 micro inches or R_a 0.3 μm). Although their height protected them from deicing salt, they were exposed to pollution and coastal salt. They were cleaned for the first time in 1995, restoring their appearance. The Chrysler Building can be seen in the background. It is also Type 302 and has the same finish and surface roughness. It has been cleaned twice since 1930.

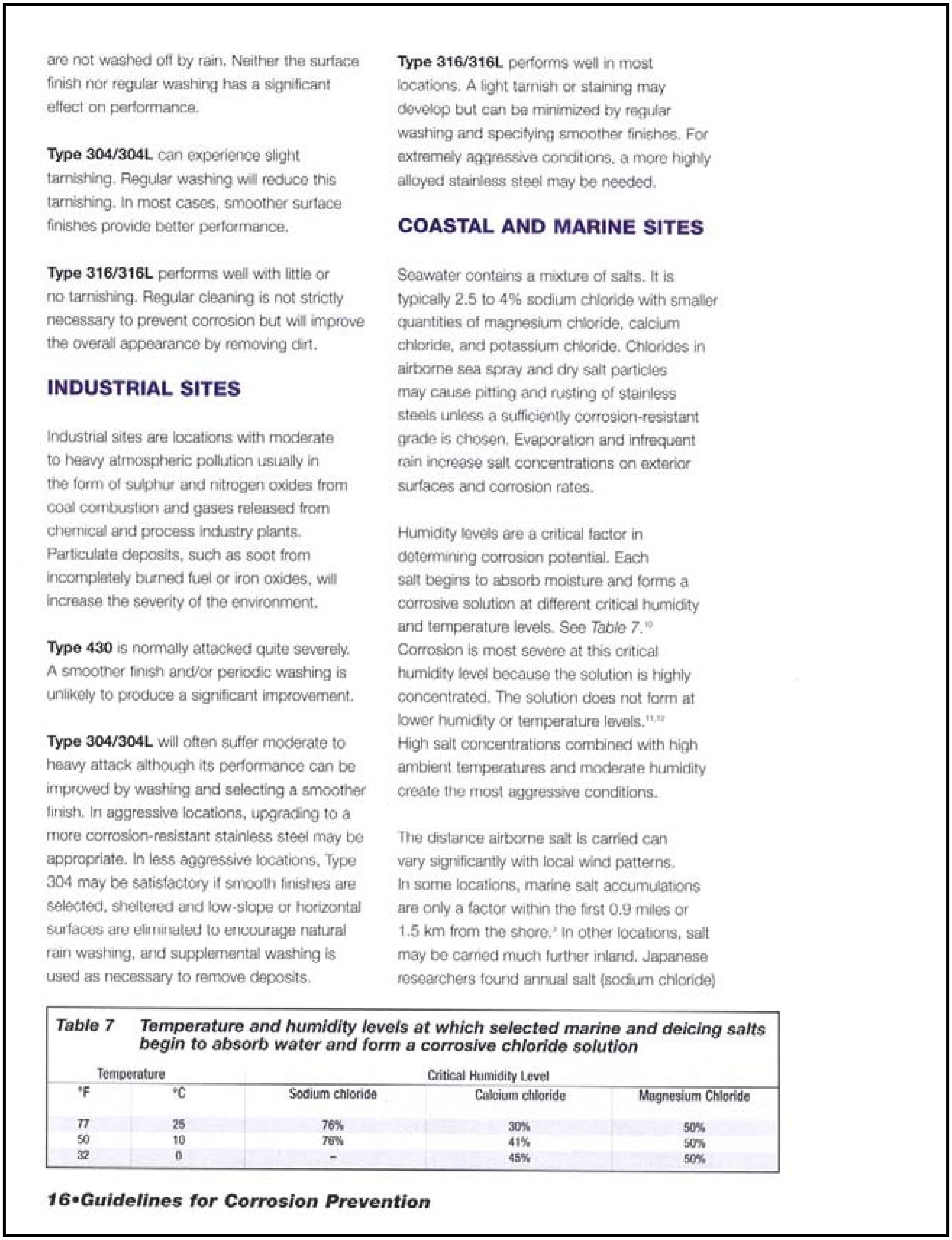
Courtesy J & L Specialty Steel

These Jones Beach, New York street lights (installed in 1967) are Type 316 with a No. 4 polished finish. They are exposed to coastal and deicing salts.

Courtesy Alpha Manufacturing, Orlando, Florida

Type 316 toll booths are used in Massachusetts, New Jersey, Florida and where they are exposed to coastal salt, automotive pollution, and, in the northern states, deicing salt.

Guidelines for Corrosion Prevention•15



are not washed off by rain. Neither the surface finish nor regular washing has a significant effect on performance.

Type 304/304L can experience slight tarnishing. Regular washing will reduce this tarnishing. In most cases, smoother surface finishes provide better performance.

Type 316/316L performs well with little or no tarnishing. Regular cleaning is not strictly necessary to prevent corrosion but will improve the overall appearance by removing dirt.

INDUSTRIAL SITES

Industrial sites are locations with moderate to heavy atmospheric pollution usually in the form of sulphur and nitrogen oxides from coal combustion and gases released from chemical and process industry plants. Particulate deposits, such as soot from incompletely burned fuel or iron oxides, will increase the severity of the environment.

Type 430 is normally attacked quite severely. A smoother finish and/or periodic washing is unlikely to produce a significant improvement.

Type 304/304L will often suffer moderate to heavy attack although its performance can be improved by washing and selecting a smoother finish. In aggressive locations, upgrading to a more corrosion-resistant stainless steel may be appropriate. In less aggressive locations, Type 304 may be satisfactory if smooth finishes are selected, sheltered and low-slope or horizontal surfaces are eliminated to encourage natural rain washing, and supplemental washing is used as necessary to remove deposits.

Type 316/316L performs well in most locations. A light tarnish or staining may develop but can be minimized by regular washing and specifying smoother finishes. For extremely aggressive conditions, a more highly alloyed stainless steel may be needed.

COASTAL AND MARINE SITES

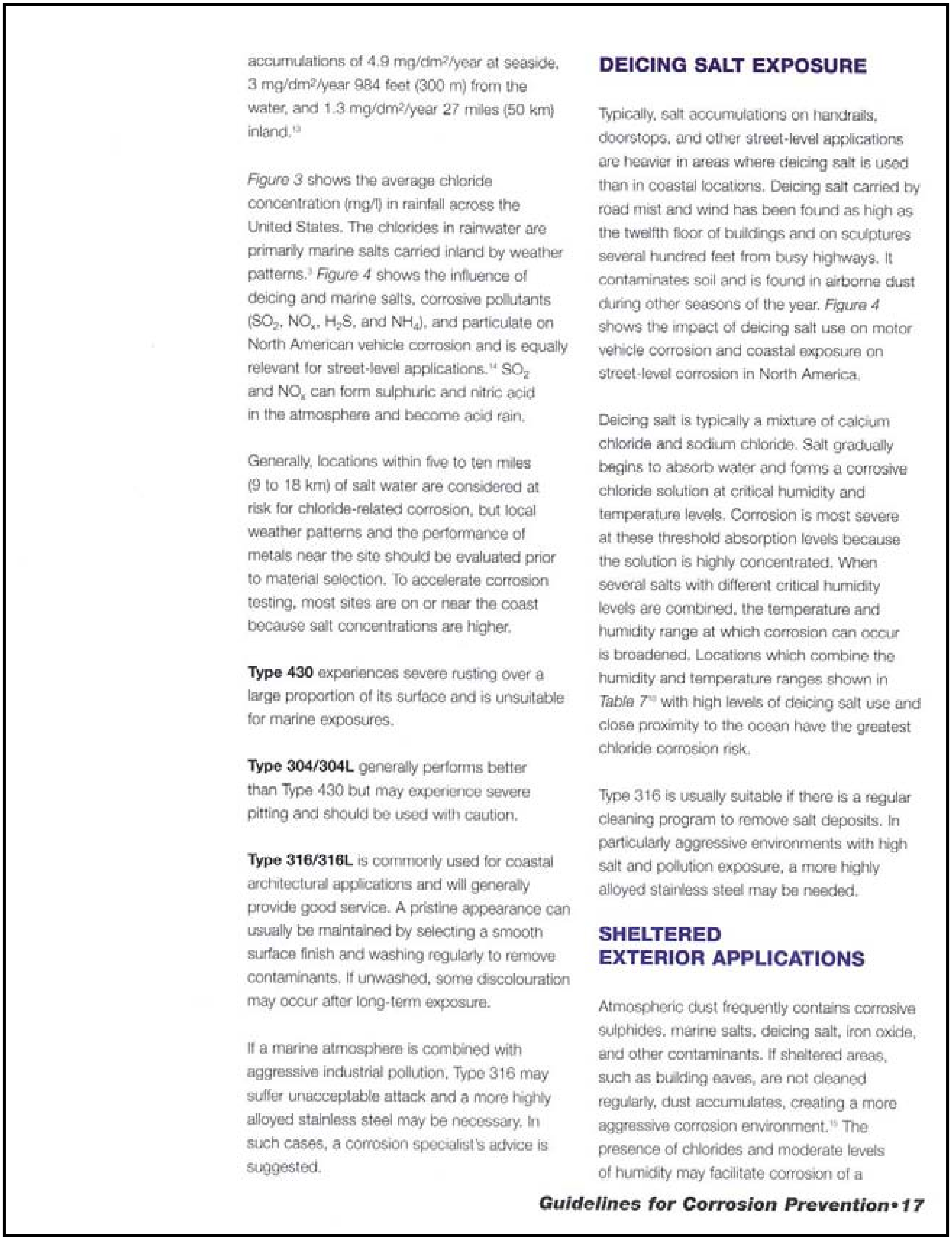
Seawater contains a mixture of salts. It is typically 2.5 to 4% sodium chloride with smaller quantities of magnesium chloride, calcium chloride, and potassium chloride. Chlorides in airborne sea spray and dry salt particles may cause pitting and rusting of stainless steels unless a sufficiently corrosion-resistant grade is chosen. Evaporation and infrequent rain increase salt concentrations on exterior surfaces and corrosion rates.

Humidity levels are a critical factor in determining corrosion potential. Each salt begins to absorb moisture and forms a corrosive solution at different critical humidity and temperature levels. See *Table 7*.[10] Corrosion is most severe at this critical humidity level because the solution is highly concentrated. The solution does not form at lower humidity or temperature levels.[11,12] High salt concentrations combined with high ambient temperatures and moderate humidity create the most aggressive conditions.

The distance airborne salt is carried can vary significantly with local wind patterns. In some locations, marine salt accumulations are only a factor within the first 0.9 miles or 1.5 km from the shore.[3] In other locations, salt may be carried much further inland. Japanese researchers found annual salt (sodium chloride)

Table 7 ***Temperature and humidity levels at which selected marine and deicing salts begin to absorb water and form a corrosive chloride solution***

Temperature		Critical Humidity Level		
°F	°C	Sodium chloride	Calcium chloride	Magnesium Chloride
77	25	76%	30%	50%
50	10	76%	41%	50%
32	0	–	45%	50%



accumulations of 4.9 $mg/dm^2/year$ at seaside, 3 $mg/dm^2/year$ 984 feet (300 m) from the water, and 1.3 $mg/dm^2/year$ 27 miles (50 km) inland.[13]

Figure 3 shows the average chloride concentration (mg/l) in rainfall across the United States. The chlorides in rainwater are primarily marine salts carried inland by weather patterns.[3] *Figure 4* shows the influence of deicing and marine salts, corrosive pollutants (SO_2, NO_x, H_2S, and NH_4), and particulate on North American vehicle corrosion and is equally relevant for street-level applications.[14] SO_2 and NO_x can form sulphuric and nitric acid in the atmosphere and become acid rain.

Generally, locations within five to ten miles (9 to 18 km) of salt water are considered at risk for chloride-related corrosion, but local weather patterns and the performance of metals near the site should be evaluated prior to material selection. To accelerate corrosion testing, most sites are on or near the coast because salt concentrations are higher.

Type 430 experiences severe rusting over a large proportion of its surface and is unsuitable for marine exposures.

Type 304/304L generally performs better than Type 430 but may experience severe pitting and should be used with caution.

Type 316/316L is commonly used for coastal architectural applications and will generally provide good service. A pristine appearance can usually be maintained by selecting a smooth surface finish and washing regularly to remove contaminants. If unwashed, some discolouration may occur after long-term exposure.

If a marine atmosphere is combined with aggressive industrial pollution, Type 316 may suffer unacceptable attack and a more highly alloyed stainless steel may be necessary. In such cases, a corrosion specialist's advice is suggested.

DEICING SALT EXPOSURE

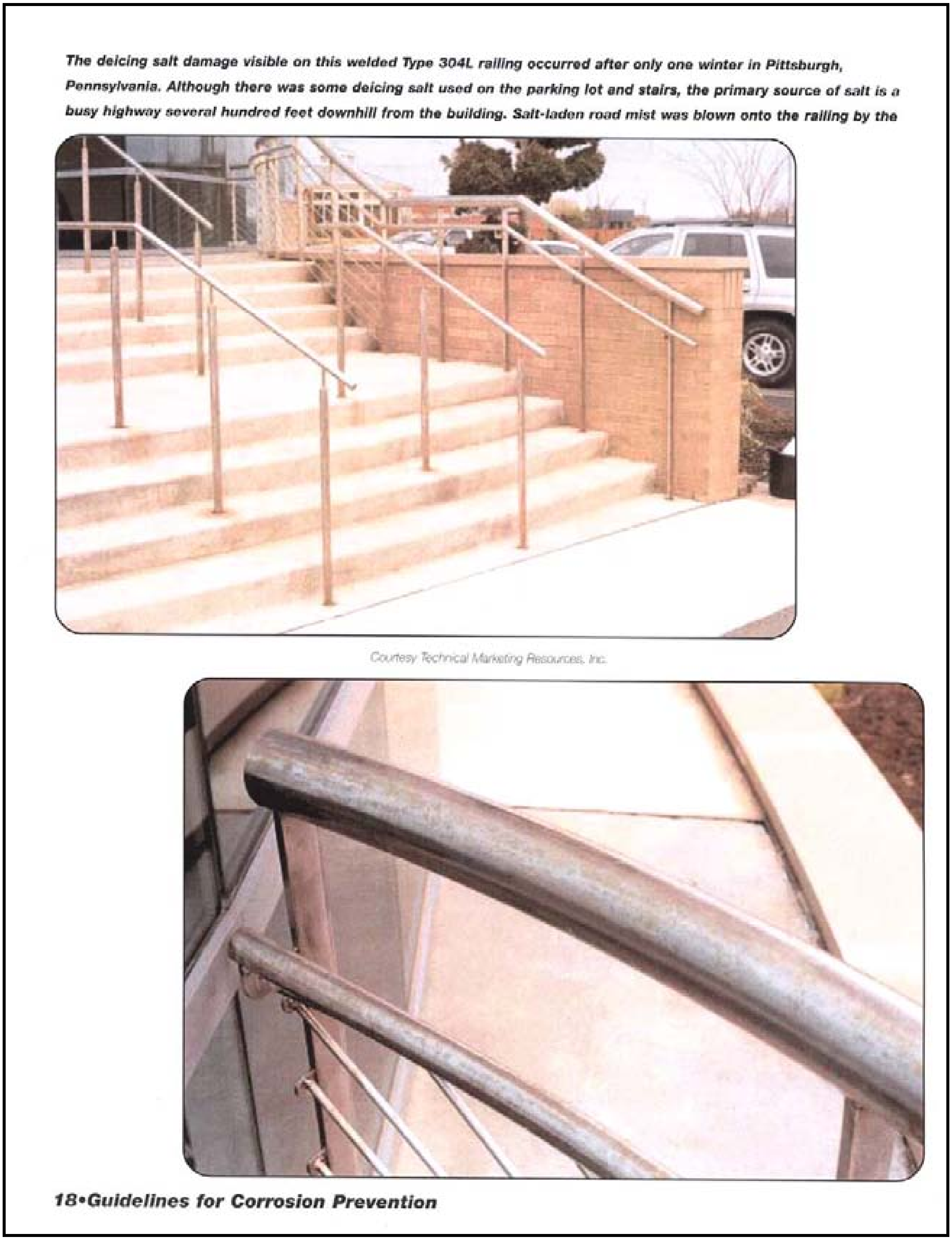
Typically, salt accumulations on handrails, doorstops, and other street-level applications are heavier in areas where deicing salt is used than in coastal locations. Deicing salt carried by road mist and wind has been found as high as the twelfth floor of buildings and on sculptures several hundred feet from busy highways. It contaminates soil and is found in airborne dust during other seasons of the year. *Figure 4* shows the impact of deicing salt use on motor vehicle corrosion and coastal exposure on street-level corrosion in North America.

Deicing salt is typically a mixture of calcium chloride and sodium chloride. Salt gradually begins to absorb water and forms a corrosive chloride solution at critical humidity and temperature levels. Corrosion is most severe at these threshold absorption levels because the solution is highly concentrated. When several salts with different critical humidity levels are combined, the temperature and humidity range at which corrosion can occur is broadened. Locations which combine the humidity and temperature ranges shown in *Table 7*[10] with high levels of deicing salt use and close proximity to the ocean have the greatest chloride corrosion risk.

Type 316 is usually suitable if there is a regular cleaning program to remove salt deposits. In particularly aggressive environments with high salt and pollution exposure, a more highly alloyed stainless steel may be needed.

SHELTERED EXTERIOR APPLICATIONS

Atmospheric dust frequently contains corrosive sulphides, marine salts, deicing salt, iron oxide, and other contaminants. If sheltered areas, such as building eaves, are not cleaned regularly, dust accumulates, creating a more aggressive corrosion environment.[15] The presence of chlorides and moderate levels of humidity may facilitate corrosion of a



The deicing salt damage visible on this welded Type 304L railing occurred after only one winter in Pittsburgh, Pennsylvania. Although there was some deicing salt used on the parking lot and stairs, the primary source of salt is a busy highway several hundred feet downhill from the building. Salt-laden road mist was blown onto the railing by the

Courtesy Technical Marketing Resources, Inc.

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wind and deposited salt. The rough mill finish increased salt adherence. The discolouration was removed with a mild abrasive cleaner. Corrosion damage could have been avoided or minimized with frequent cleaning or selection of Type 316L with smooth finish.

Courtesy Technical Marketing Resources, Inc.

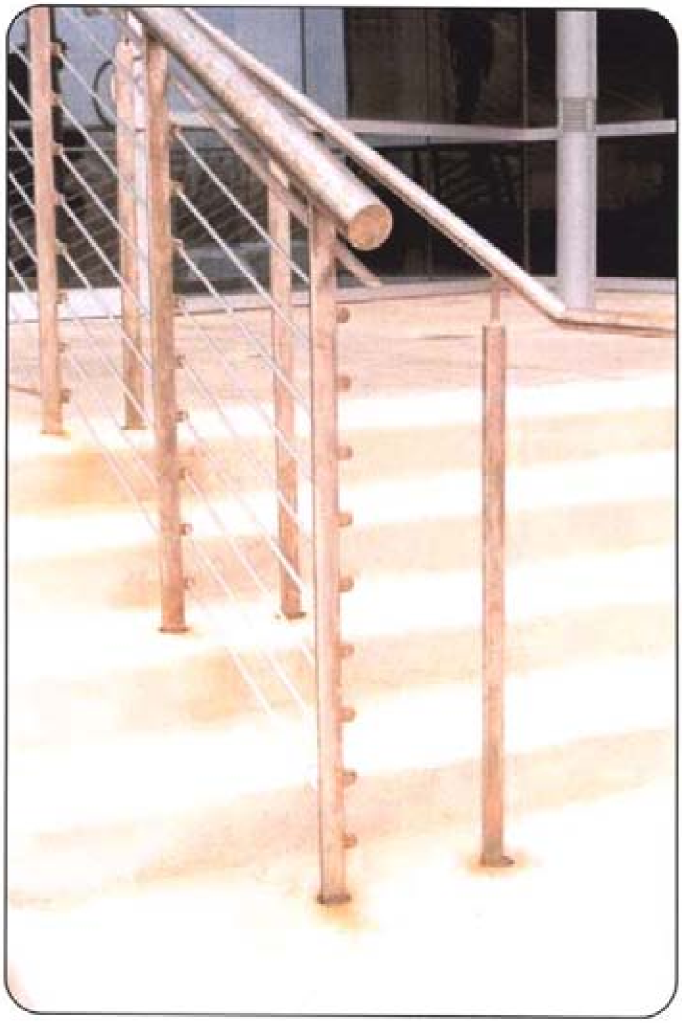


Figure 3 *Average chloride concentration (mg/l) in rainwater in the United States and the eastern coast of Canada*

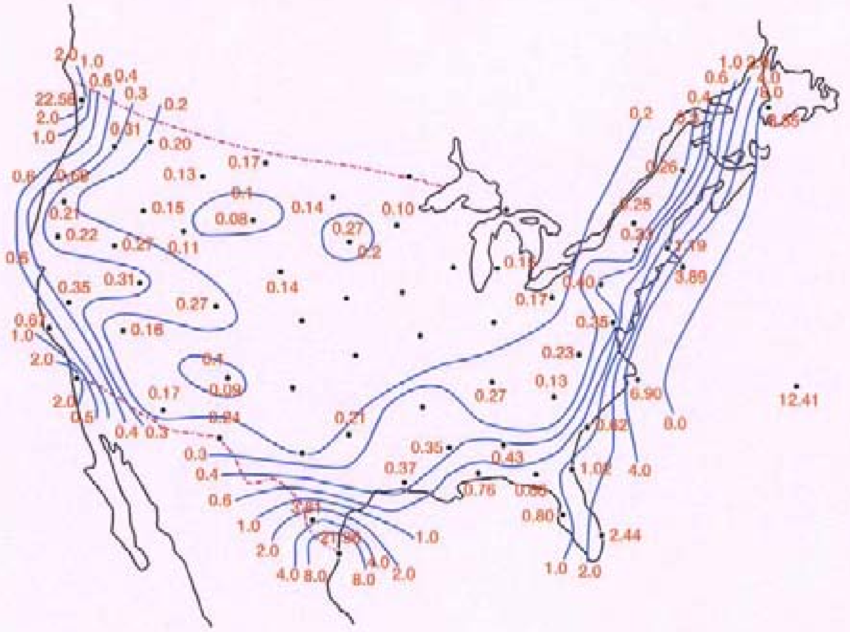
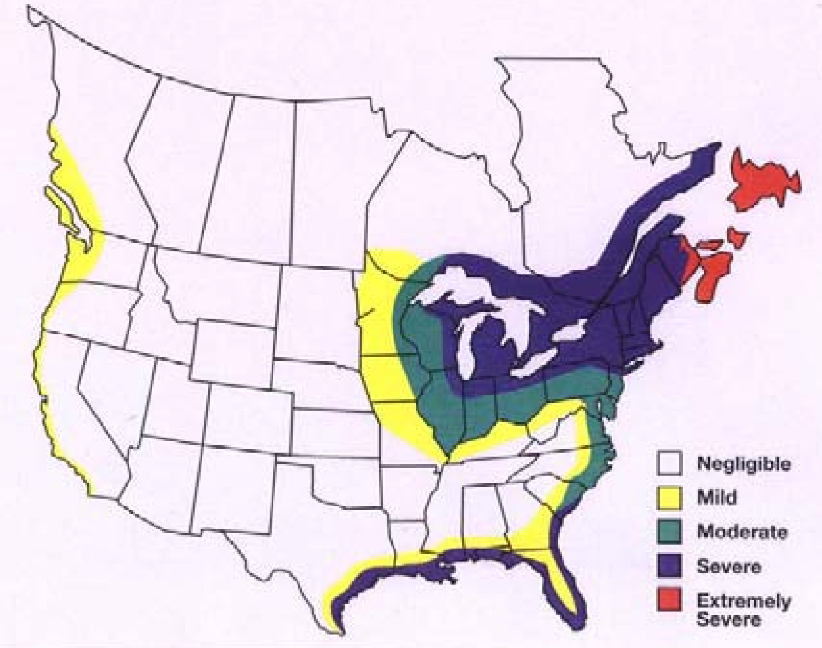
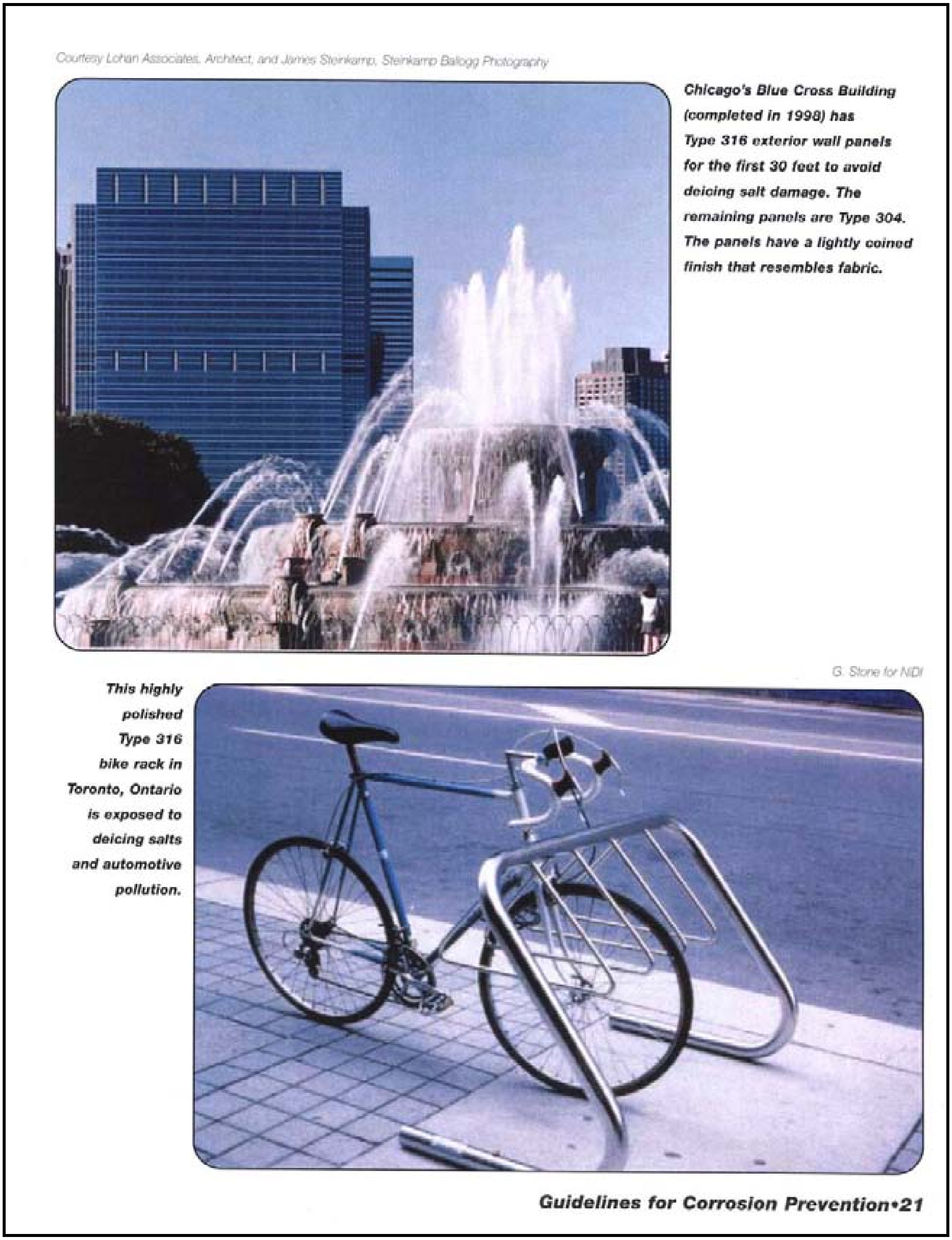


Figure 4 *North American corrosion environment for vehicles and street-level applications*





Courtesy Lohan Associates, Architect, and James Steinkamp, Steinkamp Ballogg Photography

Chicago's Blue Cross Building (completed in 1998) has Type 316 exterior wall panels for the first 30 feet to avoid deicing salt damage. The remaining panels are Type 304. The panels have a lightly coined finish that resembles fabric.

G. Stone for NiDI

This highly polished Type 316 bike rack in Toronto, Ontario is exposed to deicing salts and automotive pollution.

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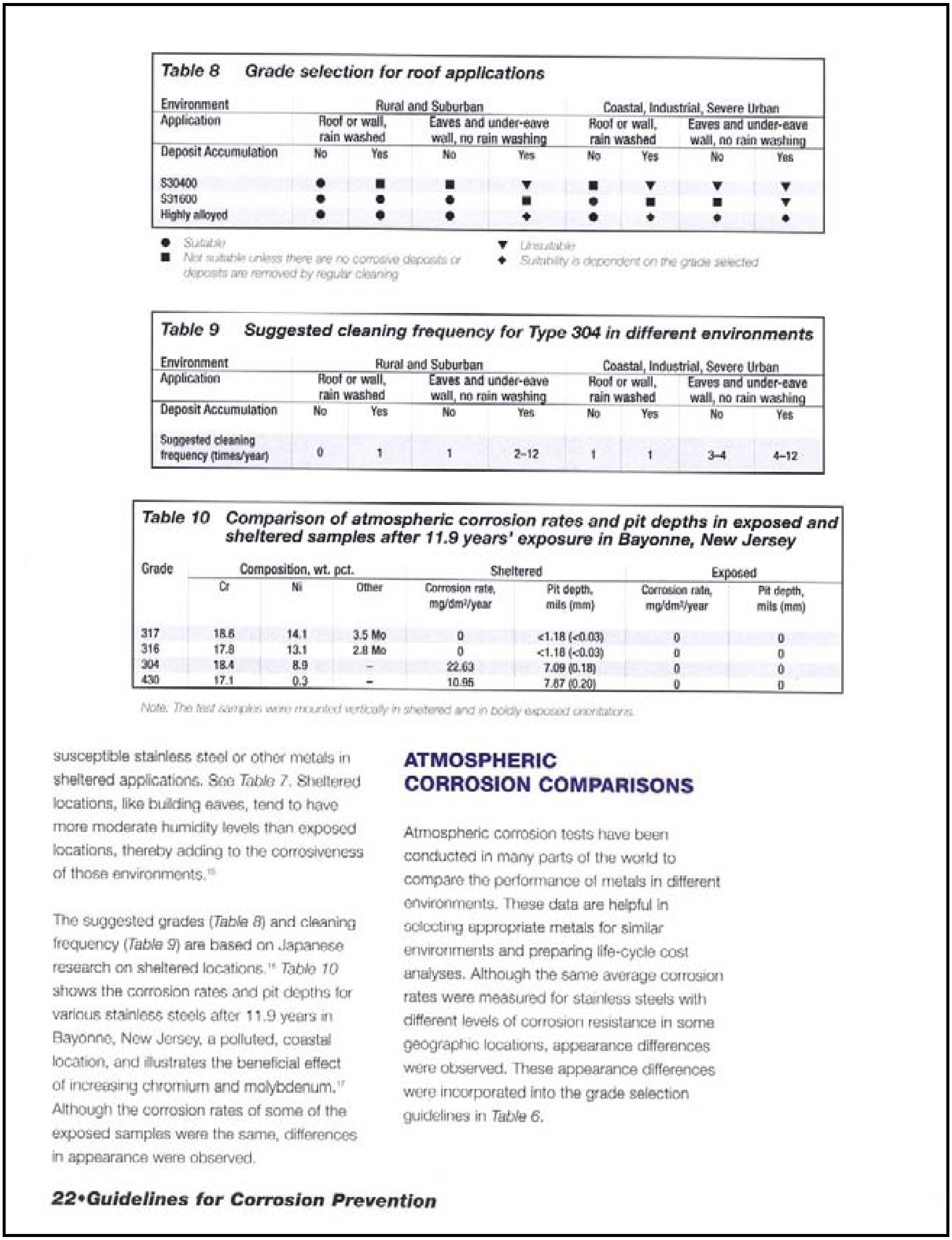


Table 8 Grade selection for roof applications

Environment	Rural and Suburban				Coastal, Industrial, Severe Urban			
Application	Roof or wall, rain washed		Eaves and under-eave wall, no rain washing		Roof or wall, rain washed		Eaves and under-eave wall, no rain washing	
Deposit Accumulation	No	Yes	No	Yes	No	Yes	No	Yes
S30400	●	■	■	▼	■	▼	▼	▼
S31600	●	●	●	■	●	■	■	▼
Highly alloyed	●	●	●	◆	●	◆	◆	◆

- ● *Suitable*
- ■ *Not suitable unless there are no corrosive deposits or deposits are removed by regular cleaning*
- ▼ *Unsuitable*
- ◆ *Suitability is dependent on the grade selected*

Table 9 Suggested cleaning frequency for Type 304 in different environments

Environment	Rural and Suburban				Coastal, Industrial, Severe Urban			
Application	Roof or wall, rain washed		Eaves and under-eave wall, no rain washing		Roof or wall, rain washed		Eaves and under-eave wall, no rain washing	
Deposit Accumulation	No	Yes	No	Yes	No	Yes	No	Yes
Suggested cleaning frequency (times/year)	0	1	1	2–12	1	1	3–4	4–12

Table 10 Comparison of atmospheric corrosion rates and pit depths in exposed and sheltered samples after 11.9 years' exposure in Bayonne, New Jersey

Grade	Composition, wt. pct.			Sheltered		Exposed	
	Cr	Ni	Other	Corrosion rate, mg/dm^2/year	Pit depth, mils (mm)	Corrosion rate, mg/dm^2/year	Pit depth, mils (mm)
317	18.6	14.1	3.5 Mo	0	<1.18 (<0.03)	0	0
316	17.8	13.1	2.8 Mo	0	<1.18 (<0.03)	0	0
304	18.4	8.9	–	22.63	7.09 (0.18)	0	0
430	17.1	0.3	–	10.95	7.87 (0.20)	0	0

Note: The test samples were mounted vertically in sheltered and in boldly exposed orientations.

susceptible stainless steel or other metals in sheltered applications. See *Table 7*. Sheltered locations, like building eaves, tend to have more moderate humidity levels than exposed locations, thereby adding to the corrosiveness of those environments.[15]

The suggested grades (*Table 8*) and cleaning frequency (*Table 9*) are based on Japanese research on sheltered locations.[16] *Table 10* shows the corrosion rates and pit depths for various stainless steels after 11.9 years in Bayonne, New Jersey, a polluted, coastal location, and illustrates the beneficial effect of increasing chromium and molybdenum.[17] Although the corrosion rates of some of the exposed samples were the same, differences in appearance were observed.

ATMOSPHERIC CORROSION COMPARISONS

Atmospheric corrosion tests have been conducted in many parts of the world to compare the performance of metals in different environments. These data are helpful in selecting appropriate metals for similar environments and preparing life-cycle cost analyses. Although the same average corrosion rates were measured for stainless steels with different levels of corrosion resistance in some geographic locations, appearance differences were observed. These appearance differences were incorporated into the grade selection guidelines in *Table 6*.

Table 11 Average corrosion weight loss in mils/year (mm/year) at Japanese sites after four or five years' exposure

Material	Pacific Coast		Sea of Japan, coastal	Inland		Industrial	
City	Omaezaki	Makurazaki	Wajima	Takayama	Obihiro	Kawasaki	Tokyo
Type 304	0.003 (0.00008)	0.006 (0.00015)	0.0035 (0.00009)	0.0055 (0.00014)	0.0059 (0.00015)	0.033 (0.00084)	0.037 (0.00093)
Aluminum	0.157 (0.004)	0.118 (0.003)	0.118 (0.003)	0.071 (0.0018)	0.122 (0.0031)	2.421 (0.0615)	0.118 (0.003)
Weathering steel	30.12 (0.765)	20.63 (0.524)*	19.29 (0.490)	14.094 (0.358)	14.45 (0.367)*	72.24 (1.835)	44.13 (1.121)
Carbon steel	41.42 (1.052)	32.05 (0.814)	27.68 (0.703)	19.21 (0.488)	16.97 (0.431)	156.81 (3.983)	70.75 (1.797)

** Samples were exposed for four years.*

The corrosion weight loss of carbon steel, weathering steel, Type 304, and aluminum were measured after either four or five years' exposure at seven coastal, inland, and industrial sites in Japan. The results are summarized in *Table 11*.[18]

Tropical environments can range from arid deserts to humid, industrial sites. The U.S. Naval Research Laboratory in Washington, D.C. conducted a 16-year study of 54 metals at two sites in Panama. The Miraflores site is 4.3 miles (8 km) from the coast in a semi-urban location with prevailing winds from the land to the ocean. The Cristobal site is a marine location on a roof 52 feet (16 m) above the shore, facing wind from the ocean. In both locations, the panels were angled 30 degrees from the horizontal. See *Table 12*.[19]

In the United States, extensive marine testing of metals has been conducted at Kure Beach, North Carolina. *Table 13* compares the average corrosion rates of Types 304 and 316 with carbon steel, Galvalume™, and galvanized steel.[3,20]

Table 12 Atmospheric corrosion data for two tropical sites in Panama

Constituent mg/10m^3	Cristobal (coastal)			Miraflores (inland)		
	Max.	Min.	Avg.	Max.	Min.	Avg.
Total dissolved solids	19.35	1.06	2.47	9.11	0.53	3.04
Organic and volatile matter	6.07	0.56	2.81	2.44	0.39	1.20
Sulphate	2.26	0.11	0.71	3.99	0.04	0.88
Chloride	1.48	0.12	0.81	0.56	0.05	0.19
Nitrate	0.39	0.00	0.11	0.42	0.00	0.14

Metal	Avg. metal loss after 16 years, mils (mm)	Avg. annual corrosion rate, mils/year (mm/year)	Deepest pit, mils (mm)	Avg. metal loss after 16 years, mils (mm)	Avg. annual corrosion rate, mils/year (mm/year)	Deepest pit, mils (mm)
Type 316	<0.01 (<0.0003)	<0.01 (<0.0003)	<4.92 (<0.125)	0 (0)	0 (0)	<4.92 (<0.125)
Aluminum 1100	0.11 (0.0028)	<0.01 (<0.0003)	<4.92 (<0.125)	0.07 (0.0019)	<0.01 (<0.0003)	<4.92 (<0.125)
Aluminum 6061-T6	0.11 (0.0028)	<0.01 (<0.0003)	<4.92 (<0.125)	0.06 (0.0015)	<0.01 (<0.0003)	<4.92 (<0.125)
Nickel (99.9%)	0.20 (0.005)	<0.01 (<0.0003)	<4.92 (<0.125)	0.09 (0.0024)	<0.01 (<0.0003)	<4.92 (<0.125)
Alloy 400	0.22 (0.0056)	<0.01 (<0.0003)	<4.92 (<0.125)	0.14 (0.0036)	<0.01 (<0.0003)	<4.92 (<0.125)
Cartridge brass	0.33 (0.0084)	0.02 (0.0005)	<4.92 (<0.125)	0.25 (0.0063)	<0.01 (<0.0003)	<4.92 (<0.125)
Nickel-silver	0.37 (0.0094)	0.02 (0.0005)	<4.92 (<0.125)	0.28 (0.0071)	0.02 (0.0005)	<4.92 (<0.125)
Muntz metal	0.43 (0.011)	0.03 (0.0008)	<4.92 (<0.125)	0.32 (0.0081)	<0.01 (<0.0003)	<4.92 (<0.125)
Cast bronze	0.79 (0.020)	0.02 (0.0005)	5.98 (0.152)	0.39 (0.0099)	<0.01 (<0.0003)	32.99 (0.838)
Copper (99.9%)	0.79 (0.020)	0.03 (0.0008)	<4.92 (<0.125)	0.26 (0.0069)	<0.01 (<0.0003)	<4.92 (<0.125)
Lead (99%)	0.79 (0.020)	0.05 (0.0013)	<4.92 (<0.125)	0.55 (0.014)	0.04 (0.001)	<4.92 (<0.125)
Low alloy steel	7.80 (0.198)	0.04 (0.001)	17.01 (0.432)	5.67 (0.144)	0.28 (0.007)	22.01 (0.559)
Cast gray iron	7.72 (0.196)	0.32 (0.0081)	37.01 (0.940)	5.94 (0.151)	0.28 (0.007)	37.01 (0.940)
Cast iron (18% Ni)	9.17 (0.233)	0.59 (0.015)	59.02 (1.499)	2.91 (0.074)	0.24 (0.006)	9.02 (0.229)
Carbon steel	10.63 (0.270)	0.47 (0.012)	39.02 (0.991)	8.58 (0.218)	0.43 (0.011)	25.98 (0.660)
Wrought iron	18.70 (0.475)	0.94 (0.024)	60.98 (1.549)	12.20 (0.310)	0.63 (0.016)	37.01 (0.940)

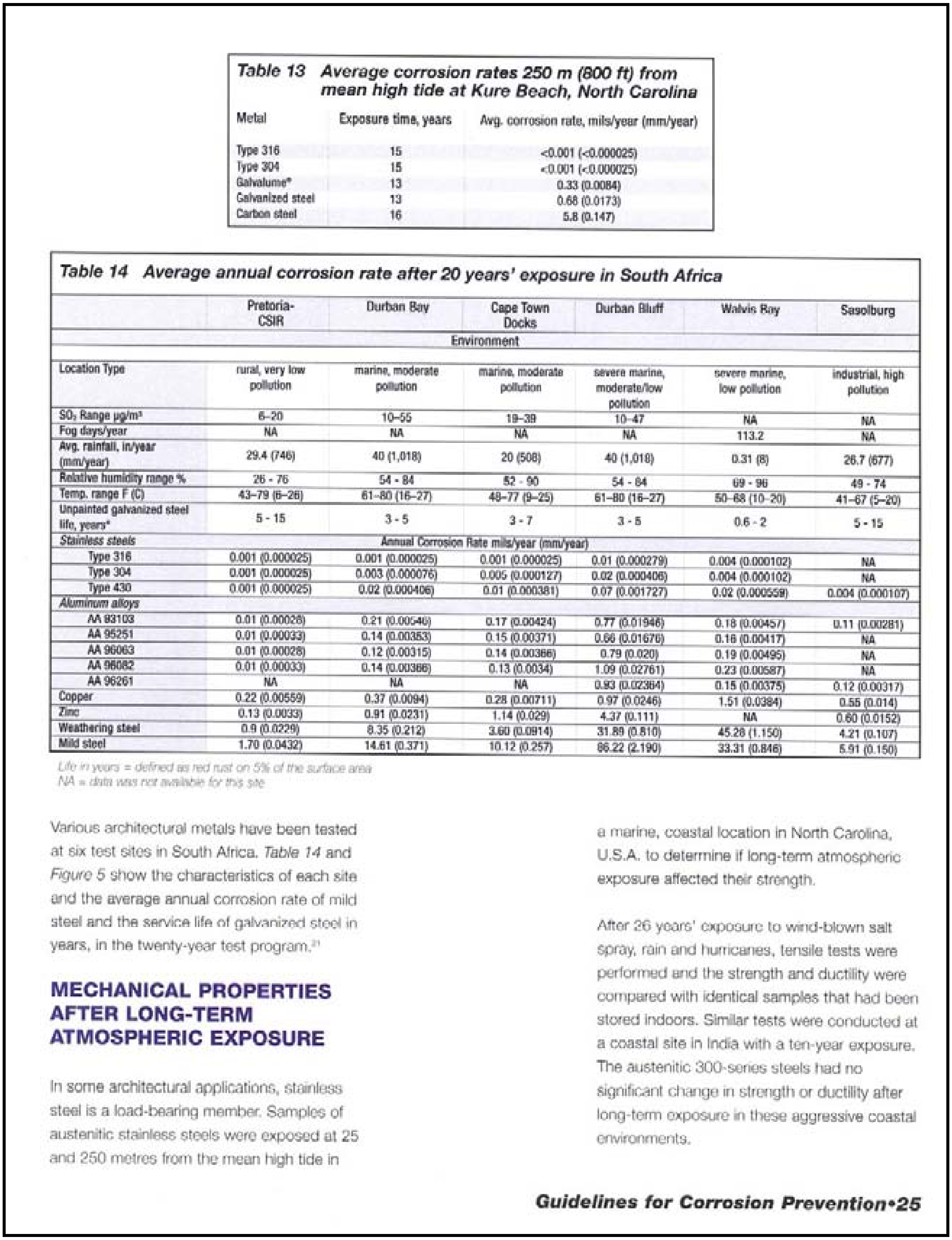


Table 13 Average corrosion rates 250 m (800 ft) from mean high tide at Kure Beach, North Carolina

Metal	Exposure time, years	Avg. corrosion rate, mils/year (mm/year)
Type 316	15	<0.001 (<0.000025)
Type 304	15	<0.001 (<0.000025)
Galvalume*	13	0.33 (0.0084)
Galvanized steel	13	0.68 (0.0173)
Carbon steel	16	5.8 (0.147)

Table 14 Average annual corrosion rate after 20 years' exposure in South Africa

	Pretoria-CSIR	Durban Bay	Cape Town Docks	Durban Bluff	Walvis Bay	Sasolburg
			Environment			
Location Type	rural, very low pollution	marine, moderate pollution	marine, moderate pollution	severe marine, moderate/low pollution	severe marine, low pollution	industrial, high pollution
SO_2 Range µg/m³	6–20	10–55	19–39	10–47	NA	NA
Fog days/year	NA	NA	NA	NA	113.2	NA
Avg. rainfall, in/year (mm/year)	29.4 (746)	40 (1,018)	20 (508)	40 (1,018)	0.31 (8)	26.7 (677)
Relative humidity range %	26 - 76	54 - 84	52 - 90	54 - 84	69 - 96	49 - 74
Temp. range F (C)	43–79 (6–26)	61–80 (16–27)	48–77 (9–25)	61–80 (16–27)	50–68 (10–20)	41–67 (5–20)
Unpainted galvanized steel life, years*	5 - 15	3 - 5	3 - 7	3 - 5	0.6 - 2	5 - 15
Stainless steels			Annual Corrosion Rate mils/year (mm/year)			
Type 316	0.001 (0.000025)	0.001 (0.000025)	0.001 (0.000025)	0.01 (0.000279)	0.004 (0.000102)	NA
Type 304	0.001 (0.000025)	0.003 (0.000076)	0.005 (0.000127)	0.02 (0.000406)	0.004 (0.000102)	NA
Type 430	0.001 (0.000025)	0.02 (0.000406)	0.01 (0.000381)	0.07 (0.001727)	0.02 (0.000559)	0.004 (0.000107)
Aluminum alloys						
AA 93103	0.01 (0.00028)	0.21 (0.00546)	0.17 (0.00424)	0.77 (0.01946)	0.18 (0.00457)	0.11 (0.00281)
AA 95251	0.01 (0.00033)	0.14 (0.00353)	0.15 (0.00371)	0.66 (0.01670)	0.16 (0.00417)	NA
AA 96063	0.01 (0.00028)	0.12 (0.00315)	0.14 (0.00366)	0.79 (0.020)	0.19 (0.00495)	NA
AA 96082	0.01 (0.00033)	0.14 (0.00366)	0.13 (0.0034)	1.09 (0.02761)	0.23 (0.00587)	NA
AA 96261	NA	NA	NA	0.93 (0.02364)	0.15 (0.00375)	0.12 (0.00317)
Copper	0.22 (0.00559)	0.37 (0.0094)	0.28 (0.00711)	0.97 (0.0246)	1.51 (0.0384)	0.55 (0.014)
Zinc	0.13 (0.0033)	0.91 (0.0231)	1.14 (0.029)	4.37 (0.111)	NA	0.60 (0.0152)
Weathering steel	0.9 (0.0229)	8.35 (0.212)	3.60 (0.0914)	31.89 (0.810)	45.28 (1.150)	4.21 (0.107)
Mild steel	1.70 (0.0432)	14.61 (0.371)	10.12 (0.257)	86.22 (2.190)	33.31 (0.846)	5.91 (0.150)

Life in years = defined as red rust on 5% of the surface area
NA = data was not available for this site

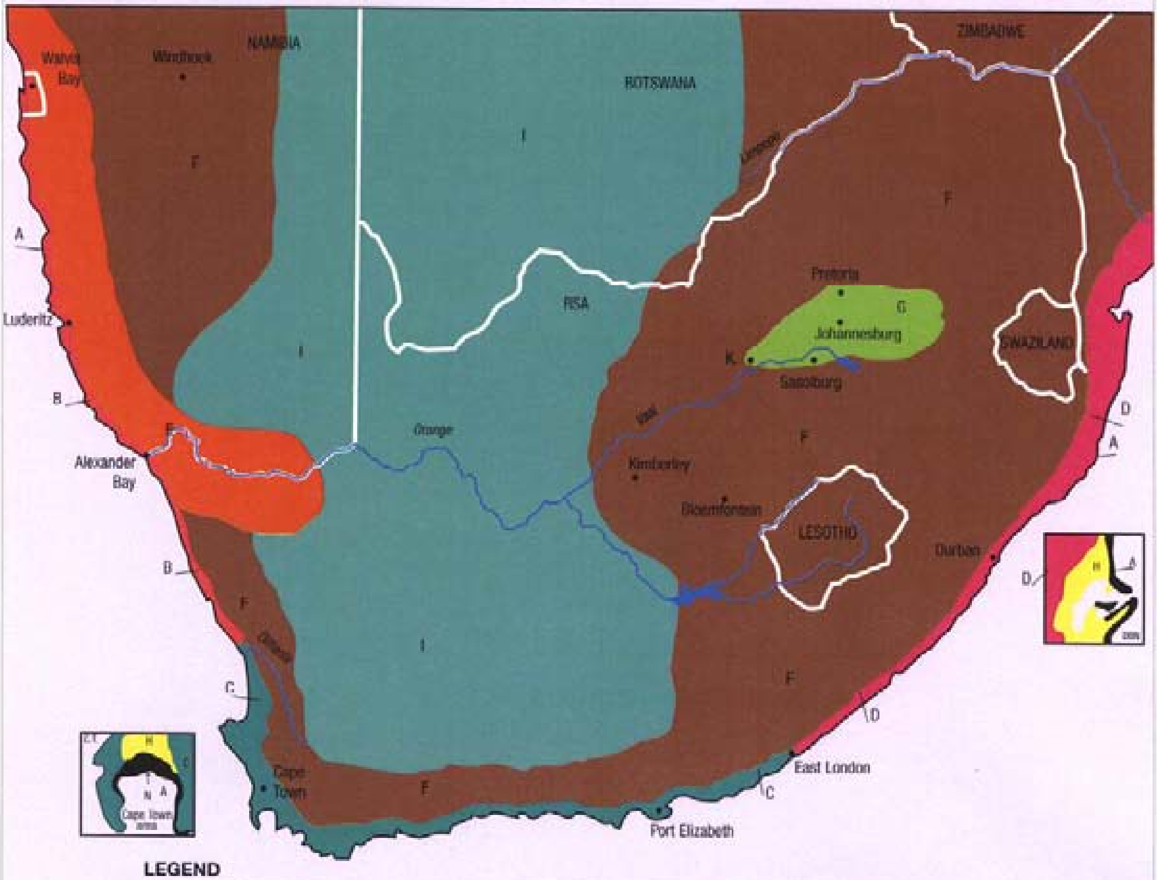
Various architectural metals have been tested at six test sites in South Africa. *Table 14* and *Figure 5* show the characteristics of each site and the average annual corrosion rate of mild steel and the service life of galvanized steel in years, in the twenty-year test program.[21]

MECHANICAL PROPERTIES AFTER LONG-TERM ATMOSPHERIC EXPOSURE

In some architectural applications, stainless steel is a load-bearing member. Samples of austenitic stainless steels were exposed at 25 and 250 metres from the mean high tide in a marine, coastal location in North Carolina, U.S.A. to determine if long-term atmospheric exposure affected their strength.

After 26 years' exposure to wind-blown salt spray, rain and hurricanes, tensile tests were performed and the strength and ductility were compared with identical samples that had been stored indoors. Similar tests were conducted at a coastal site in India with a ten-year exposure. The austenitic 300-series steels had no significant change in strength or ductility after long-term exposure in these aggressive coastal environments.

Figure 5 Atmospheric corrosion map of South Africa



LEGEND

Code	Description	Map identif.	Type of corrosion	Mild steel* corrosion rate µm/yr	Galvanized steel sheet** life in years†
A	Intertidal to 5 km inland	⬛	Severe marine	100 – 300	Up to 3
B	Desert marine (mists)	🟥	Severe marine	80 – 100	0.5 – 2
C	Temperate marine	🟦	Marine	30 – 50	3 – 7
D	Subtropical marine	🟥	Medium to severe marine	50 – 80	3 – 5
E	Desert inland dry	🟧	Desert	< 5	> 30
F	Inland	🟫	Rural	10 – 20	> 20
G	Inland urban	🟩	Inland industrial††	15 – 40	5 – 15
H	Urban coastal	🟨	Marine industrial††	50 – 150	1 – 3
I	Inland arid	🟦	Semi desert	5 – 10	> 30

* Higher corrosion rate usually indicates proximity of sea.

** Commercial grade Z 275 g/m² (unpainted)

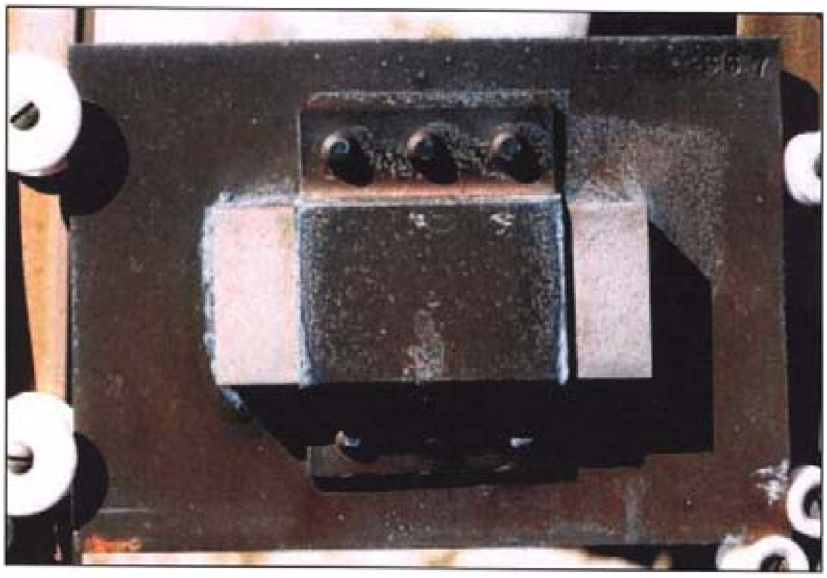
† Life in years – until 5% of surface area showing red rust.

†† Industrial implies pollution present in atmosphere.

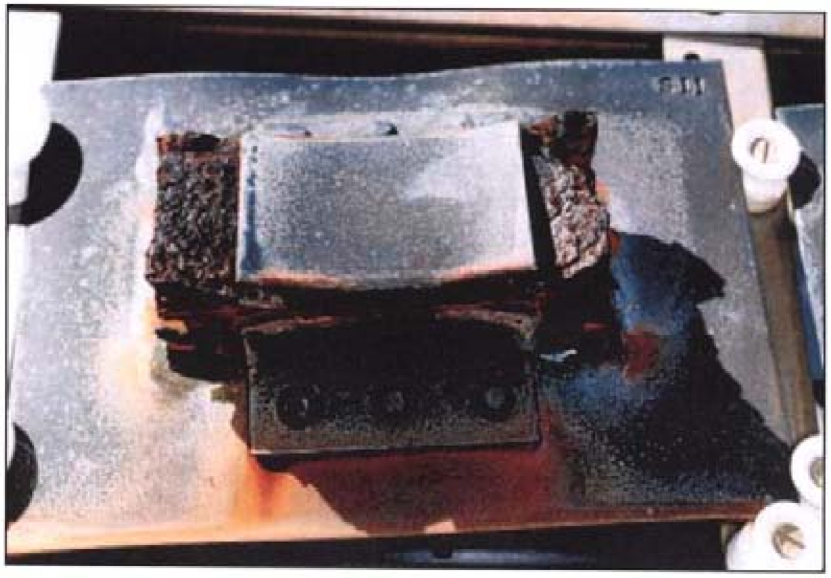
C and D usually from 5 km inland up to first mountain range.

ATMOSPHERIC CORROSION SAMPLE PHOTOS

The atmospheric corrosion test samples shown in the following 13 photos are at the LaQue Center for Corrosion Technology, Inc., an internationally respected corrosion research facility in Kure Beach, North Carolina. The samples have been exposed to the elements and are only cleaned by rain. Except where noted, the samples are 820 feet (250 m) from the ocean's mean high tide. These photos were taken in 2000.

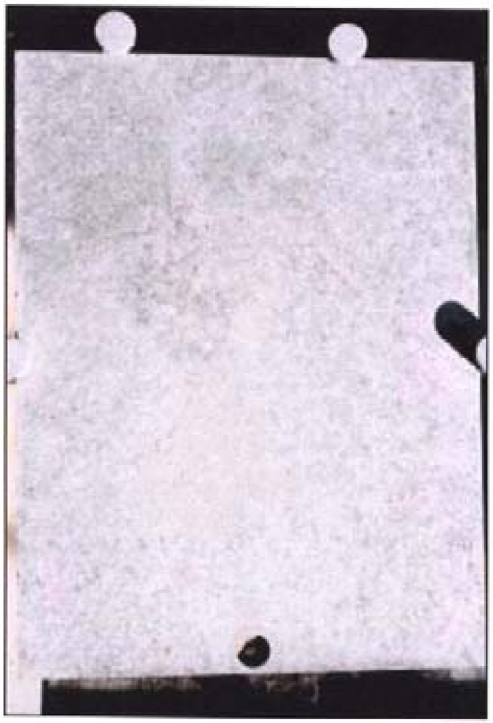


Type 316 stainless steel and copper combination is performing well.

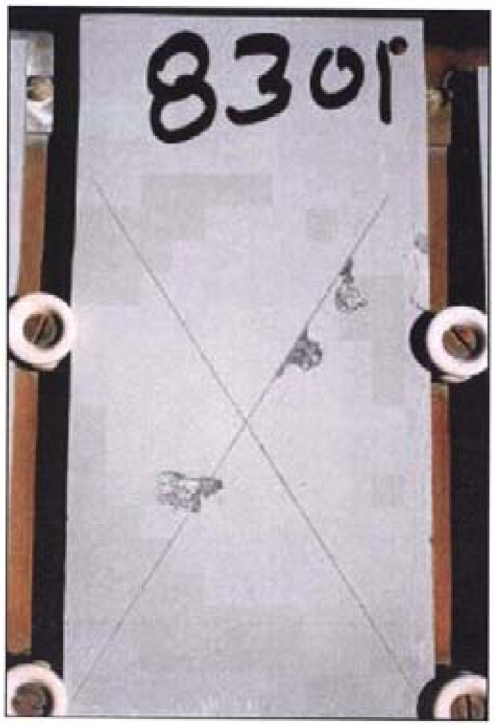


The mild steel plate's corrosion product has expanded and broken the copper saddle.

The above Statue of Liberty corrosion demonstration panels have been in place since 1984. Type 316 and carbon steel plate samples were attached to copper sheets with a saddle which is riveted in place.

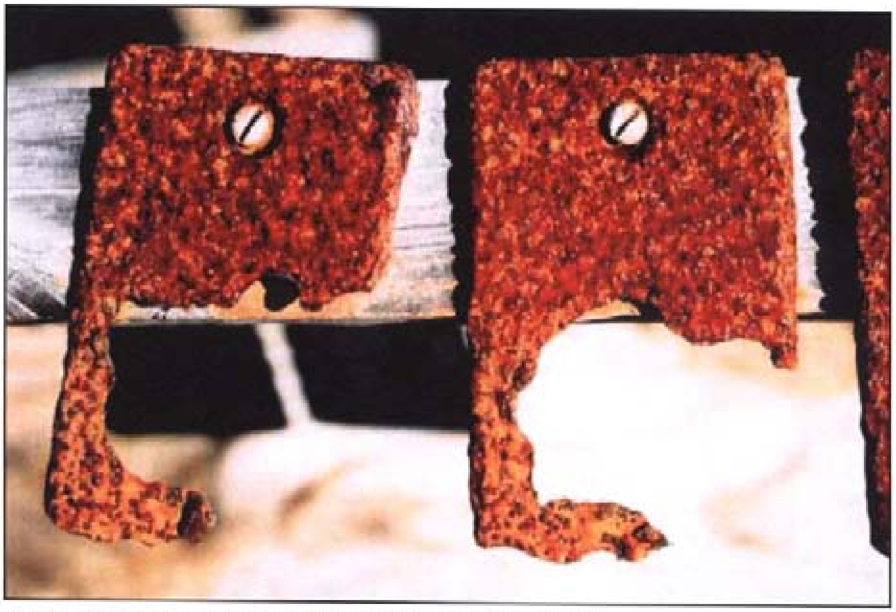


Aluminum alloy 6061 exposed since 1982 about 82 feet (25 m) from the mean high tide.

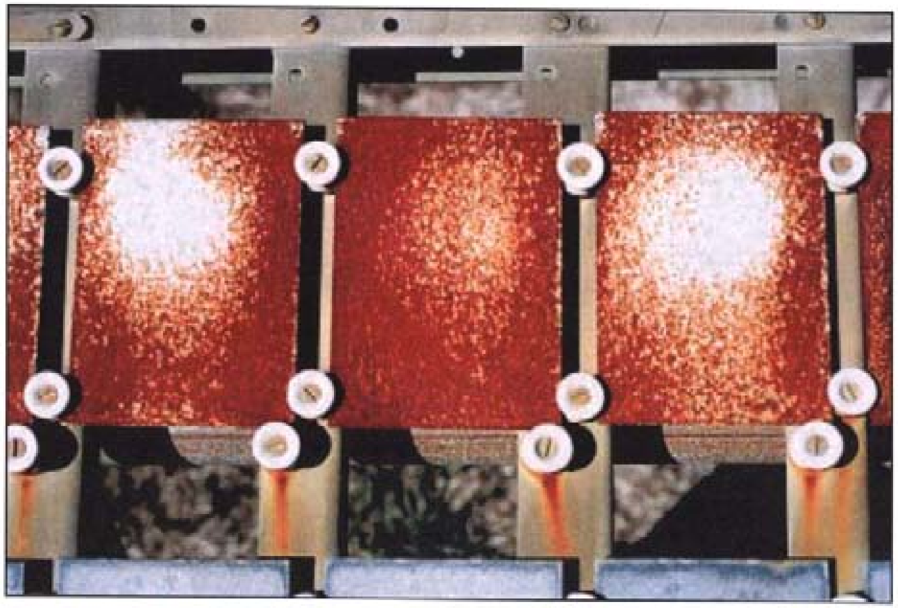


Painted cast aluminum alloy 360 exposed since 1988.

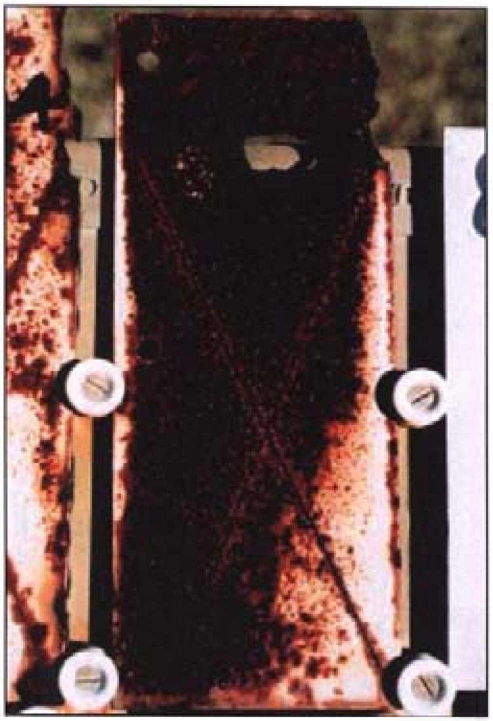
Anodized aluminum exposed since 1942.



Coated (60 Zn, 20 Al, 20 Mg) carbon steel exposed since 1952.



Bare G-90 galvanized steel exposed since 1981.



Painted cold rolled steel exposed since 1988.

High-strength, low-alloy weathering steel exposed since 1968.

Type 304 exposed since 1941.

Type 316 exposed since 1941.

Zinc tin alloy exposed since 1960 about 82 feet (25 m) from the mean high tide.

Pure zinc exposed since 1960 about 82 feet (25 m) from the mean high tide.

FORMS OF STAINLESS STEEL CORROSION

If stainless steel is selected, installed, and maintained correctly, it does not suffer corrosion. However, if the environment exceeds the corrosion resistance of a particular stainless steel in a specific location, some corrosion may occur. Only certain types of corrosion may affect stainless steels.

TARNISHING

Tarnishing is a fairly uniform discolouration of a metal's surface. With exterior stainless steel applications, there may be a slight yellow tarnishing of the surface and some loss of brightness, especially if fine particles of dirt are incorporated into the surface deposit. Some improvement may be obtained from washing but the overall effect on appearance is small and may not be apparent when viewed from a distance.

PITTING

If a stainless steel corrodes, pitting is the most likely form of corrosion. If the environment overwhelms the capability of the stainless steel, the protective, passive film is disrupted and cannot heal itself. This is shown schematically in *Figure 6*. (See Atmospheric Corrosion section.) Pitting starts as tiny points of attack and is usually black or dark brown in colour. In the most severe cases, the number and depth of the pits can increase to give an extensively corroded appearance. If the attack is mild, the pits may not detract from the general appearance but the area below them may be stained as rust leaches out. Selecting an appropriate stainless steel and cleaning regularly to remove surface deposits reduce the potential of pitting damage.

CREVICE CORROSION

Crevice corrosion is similar to pitting but occurs over a larger area when deposits or other materials block the oxygen access needed to maintain the passive film. Corrosion can occur if chloride-containing rainwater or condensation is present in a tight crevice and conditions are created which exceed the corrosion resistance of a particular stainless steel. It is more likely with lower-alloyed stainless steels, particularly where the crevice gap is very small (a tight washer) and the path to free oxygen is long (a large diameter washer). Correct design reduces the potential for crevice corrosion. In areas exposed to water, designers should minimize crevices, seal them, or consider a more corrosion-resistant, higher-alloyed grade. See *Figure 7*.

GALVANIC CORROSION

Galvanic or "bimetallic" corrosion can occur when two metals of differing electrochemical potential are electrically coupled in a conducting liquid, usually called an electrolyte. Several factors determine galvanic corrosion potential: the electrochemical potential difference, the

Figure 6 Pitting corrosion

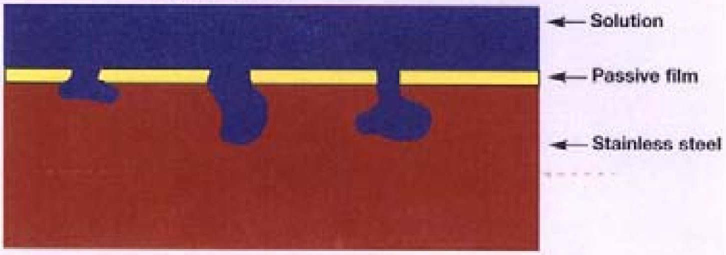
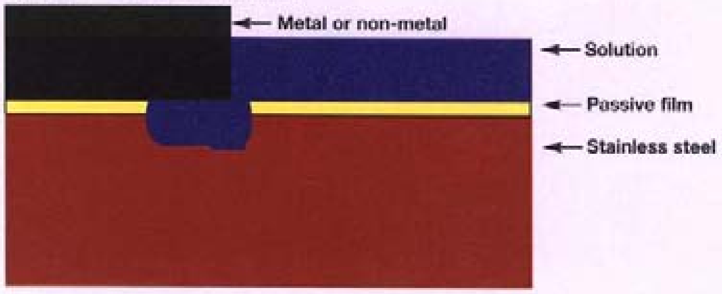


Figure 7 *Crevice corrosion*



presence of moisture to connect the metals on a regular basis, and the relative surface area ratio of the metals. If no moisture is present or an inert, electrically insulating material prevents electrical contact, galvanic corrosion cannot occur.

Figure 8 illustrates galvanic corrosion. *Figure 9* shows examples of when galvanic corrosion can and cannot occur. *Figure 10* shows the galvanic series in seawater. The metals are arranged in order from the least noble (least corrosion-resistant) to the most noble (most corrosion-resistant). Environment affects a metal's potential. Some metals are shown twice along with the terms "active" or "passive". In extremely severe corrosion environments like strong acids, a stainless steel may not be able to maintain its protective passive film and may begin to corrode actively. This might occur in an industrial equipment application. These conditions are not present in architectural applications and stainless steels can be considered to be in the passive state.

Galvanic corrosion may be a concern if there is a significant difference in electrochemical potential and the metals are not electrically isolated from one another. If two metals are close together in the galvanic series (e.g., two stainless steels or copper and stainless steel), the potential for galvanic corrosion is low in all but the most aggressive environments.

The relative surface area of the two metals is important. When the surface area of the more corrosion-resistant metal is large relative to the less corrosion-resistant metal, an unfavourable ratio exists and there is an increase in the corrosion rate of the less corrosion-resistant metal. For example, coupling a small piece of carbon steel to a large piece of stainless steel could cause rapid corrosion of the carbon steel. If the ratio is reversed and the less corrosion-resistant material has a large surface area, the corrosion rate of the less corrosion-resistant metal is only slightly increased.

Figure 8 *Galvanic corrosion*

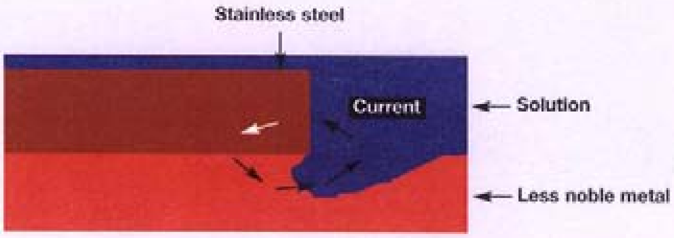
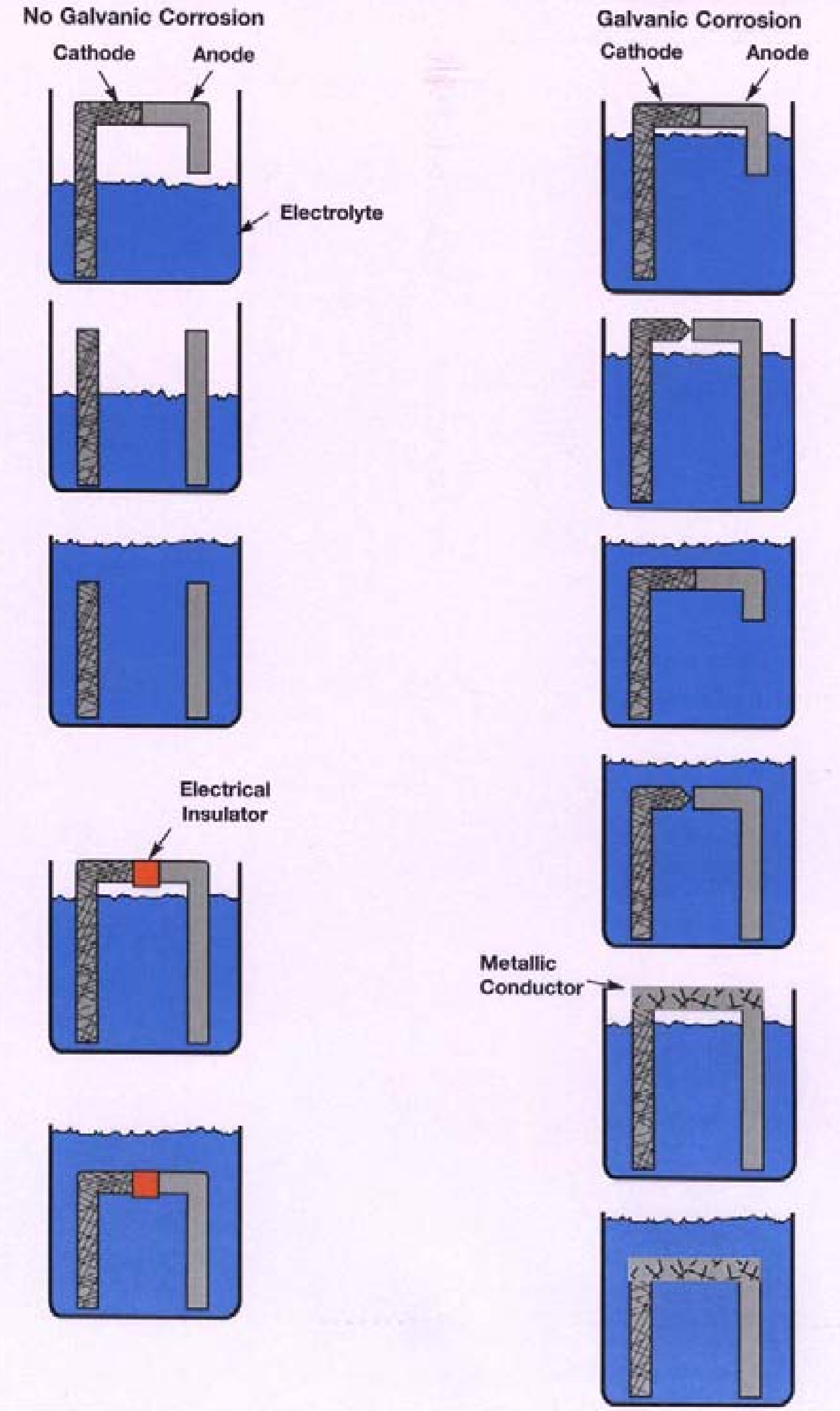


Figure 9 **Dissimilar metal and electrolyte combinations where galvanic corrosion can and cannot occur**



34•Guidelines for Corrosion Prevention

Figure 10 Galvanic series in seawater at 77°F (25°C)[22]

Least noble = anodic = most susceptible to corrosion

Magnesium and its alloys
Zinc
Galvanized steel or galvanized wrought iron
Aluminum alloys 3004, 3003, 1100, in this order
Cadmium
Low carbon steel
Wrought iron
Cast iron
Nickel cast irons
Stainless steel, Type 410 (active)
50-50 lead-tin solder
Stainless steel, Type 304 (active)
Stainless steel, Type 316 (active)
Lead
Tin
Muntz metal, C28000
Alloy 200 (active)
Alloy 600 (active)
Yellow brass, C27000
Aluminum bronzes, C61400
Red brass, C23000
Commercially pure copper, C11000
Silicon bronze, C65500
Alloy 200 (passive)
Alloy 600 (passive)
Alloy 400
Stainless steel, Type 410 (passive)
Stainless steel, Type 304 (passive)
Stainless steel, Type 316 (passive)
Alloy 825
Alloy 625
Alloy C
Silver
Titanium
Gold

Most noble = cathodic = most corrosion-resistant

Dissimilar metal combinations should be avoided in areas where moisture is likely to accumulate and remain for long periods. In well-drained exterior applications, dissimilar metals can be used together if a favourable surface ratio exists, but they should be electrically insulated from one another. Neoprene washers, roofing felt, paint, and other inert materials or coatings are effective barriers. When painted carbon steel and stainless steel are welded together in an exterior application, the welded joint should be painted. Hidden and exposed stainless steel fasteners with neoprene or other inert washers are used regularly in aluminum, zinc, and painted galvanized steel roof applications. The inert washer separates the metals in case water is frequently present or infiltrates under the head of the fastener.

EMBEDDED OR TRANSFERRED IRON

Iron or carbon steel can become transferred to or embedded in the surface of stainless steel and other architectural metals and begin to rust within a few hours or days. This can give the incorrect impression that the material underneath is rusting. However, in severe cases, the rusting steel may actually cause the stainless steel under it to corrode because the protective passive film cannot re-form.

The source of iron can be steel tools, abrasive polishing or blasting media or fabrication areas previously used on carbon or low-alloy steels, use of carbon steel wool or carbon steel brushes during cleaning, and accidental scratching. Ideally, the fabrication area should be dedicated to stainless steel. If that is not possible, the area should be cleaned prior to stainless steel fabrication to remove residual iron particles. To prevent accidental contamination, the stainless steel surface should be protected with protective paper or strippable plastic films during fabrication, handling, storage and transport.

The purchaser can specify that stainless steel products pass one of several non-destructive tests for detection of embedded iron such as ASTM A 967. A particularly simple and straightforward test is to thoroughly wet the surface with clean water and wait for 24 hours to see if rust appears. Additional information about preventing, detecting and removing embedded iron and steel can be found in the Nickel Development Institute publication, *Fabrication and post-fabrication cleanup of stainless steels*, No. 10 004.

EROSION-CORROSION

Erosion-corrosion is accelerated metal loss caused by a flowing corrosive liquid which contains abrasive particles such as sand or debris. It can be a problem with aluminum, copper and other susceptible materials in applications like piping and roof drainage systems. Resistance to erosion-corrosion is not related to hardness or strength, but flow velocity, high turbulence, or changes in flow direction can have a significant impact on performance in susceptible metals.[23] Stainless steels are virtually immune to erosion-corrosion because they form thin, tightly adherent, protective passive films. High flow velocities are beneficial to stainless steel corrosion performance because they help keep the stainless steel surface clean.

CHLORIDE STRESS CORROSION CRACKING (SCC)

Chloride stress corrosion cracking (SCC) may occur in Types 304 and 316 exposed to chlorides and tensile residual stress at temperatures above about 150°F (65°C). These conditions are unlikely in most architectural applications.

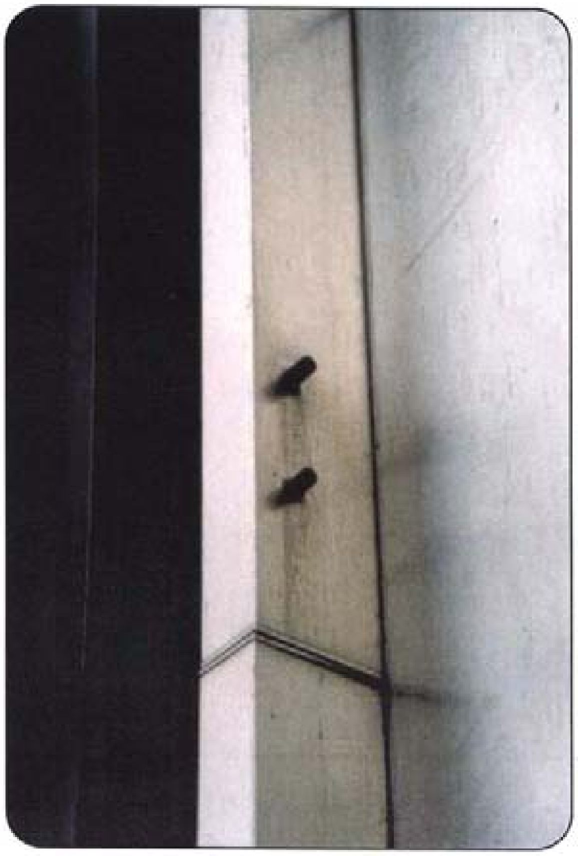
SCC has occurred at lower temperatures in unusually severe indoor environments, such as swimming pool suspended ceilings. The

C. Houska for NiDI

This infrequently cleaned statue of Sun Yat Sen (installed in the 1930s) in San Francisco's Chinatown combines stainless steel (body) and copper (hands and head). Moisture is only present for short periods of time. The two metals are in close proximity in the galvanic series and there is no sign of galvanic corrosion.

C. Houska for NiDI

The ratio between the dissimilar metals is important in evaluating the potential for galvanic corrosion. The fastener should always be of equivalent or higher corrosion resistance. Stainless steel fasteners with inert washers are often used for Weathering steel (left), carbon steel, copper aluminum and zinc roof and wall panels. Galvanized steel fasteners should never be used for stainless steel panels (below).



Nickel Development Institute publication No. 12 010, *Stainless steel in swimming pool buildings*, provides additional information about appropriate grades for this application.

The potential for SCC in an aggressive marine environment was evaluated in a five-year study of 300-series stainless steels in three metallurgical conditions: annealed (the normal as-delivered mill condition), as welded, and cold-worked. The site for these tests, Kure Beach, North Carolina, U.S.A., experiences hot summers. The underside of the panels reached temperatures of about 120°F (50°C) and the exposed side 140°F (60°C).[24] None of the samples experienced stress corrosion cracking.

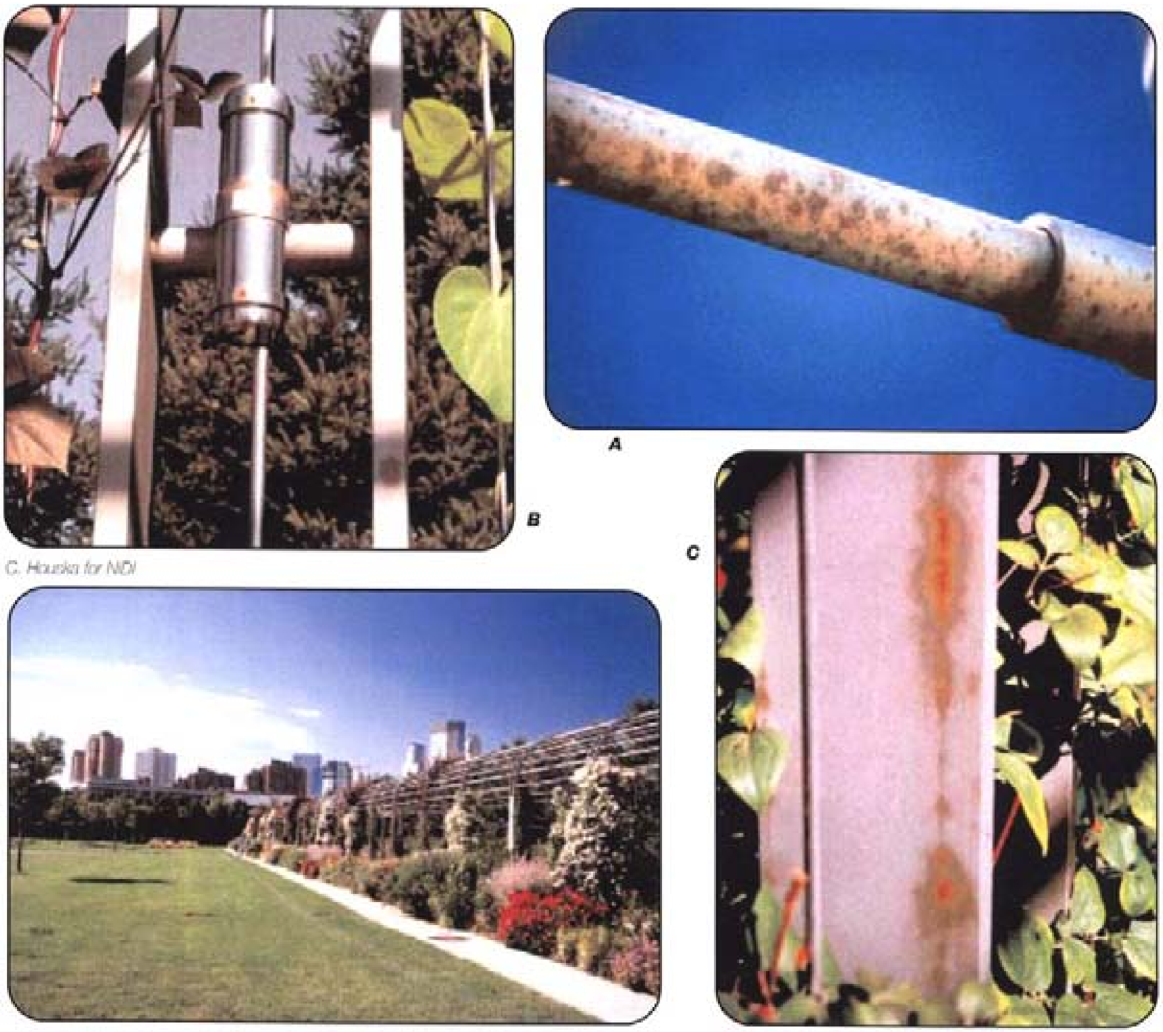
ENVIRONMENTAL BENEFIT OF STAINLESS STEEL

The environmental impact of construction materials is a growing concern. If an appropriate grade and finish are selected, there should be no need to replace stainless steel, even if the building life spans hundreds of years. Stainless steel scrap has a high value – so it is not discarded. Stainless steel is 100% recyclable and there is no limit to how much recycled scrap can be used to produce new stainless steel.

Metal loss due to corrosion can potentially add toxic elements to the environment and the lost metal cannot be recycled. Replacing lost metal adds an additional environmental burden (energy consumption, mining, mineral extraction). Stainless steel corrosion loses are negligible. (See comparative corrosion data.)

Because stainless steels are inherently corrosion-resistant, no protective coatings are needed, and the adverse environmental impact associated with coatings (out-gassing of volatile organic compounds [VOC], replacement, and removal for recycling) is eliminated. No acids or harsh chemicals are needed to clean stainless steel.

Stainless fasteners and anchors help ensure that stone, masonry, pressure-treated lumber, slate, and tile reach their full service life potential.

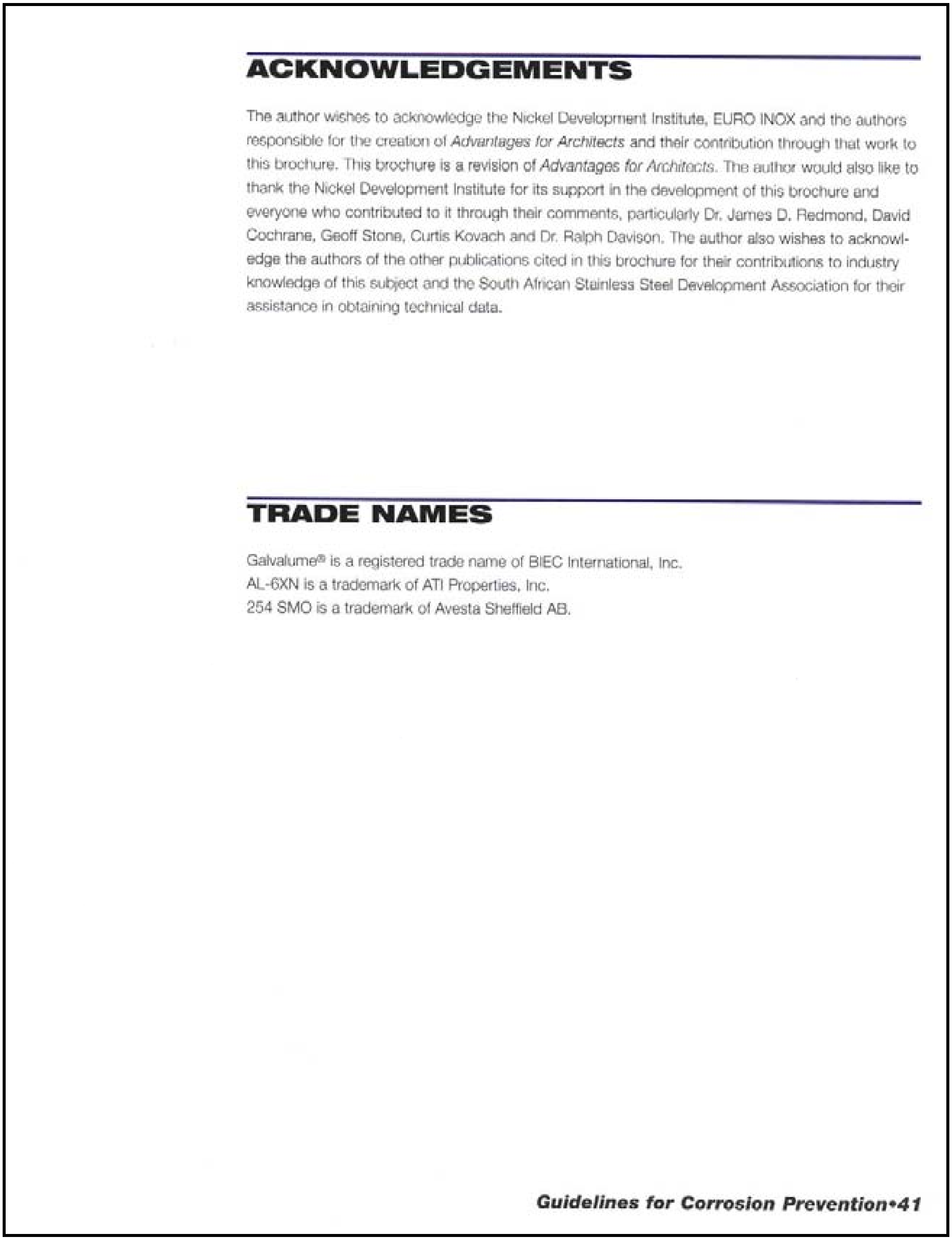


C. Houska for NDI

Careful evaluation of a site is important because factors that influence the corrosiveness of a site may not be immediately apparent. This stainless steel arbour is in a park in a suburban area adjoining downtown Minneapolis. Normally a location of this type would be considered a low to moderately corrosive urban environment, but this park is beside an elevated highway and deicing salt laden road mist blows into the park, making the environment more aggressive.

All the arbour's components are rough, abrasive blasted Type 304 (surface roughness of R_a 281 micro-inches or 7.3 μm) except for the tension rods and lights which are highly polished Type 316. Photo A shows Type 304 deicing salt damage. The rough finish retains more salt, making natural rain washing less effective. Sheltered surfaces experienced significantly more corrosion than components boldly exposed to rain. The Type 316 was untouched by the deicing salt except where crevices trapped salt and water. Photo B shows crevice corrosion. Photo C shows embedded iron on one of the Type 304 vertical support members.

Corrosion of the attractive design could have been avoided if the entire arbour were Type 316 with a smooth finish, crevices were sealed or eliminated, salt had been washed off the arbour in the spring, and the surfaces were protected from embedded iron during transport, fabrication and installation.



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TRADE NAMES

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AL-6XN is a trademark of ATI Properties, Inc.
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Section 4. Bibliography

This bibliography contains reports and other reference materials relating to copper corrosion.

1996 Aboveground and Underground Storage Tank Conference Proceedings, 1996. NACE Storage Tank Conference, Houston, Texas, January 16–18, 1996. D.E. Krause and J.A. Lehmann (eds.).

Abstract: Risks of storage tank failure and ground contamination are just two of the problems facing storage tank owners and operators today. As governmental concern for public safety increases, so does the pressure on operators to implement the necessary changes to satisfy the new regulations within a specific time frame. The papers published in these proceedings not only cover pending legislation on aboveground storage tanks, but also prospective legislation. Besides the important regulatory issues, these proceedings cover corrosion, leak detection and prevention, contingency planning, emergency response, asset preservation, design, construction, and maintenance.

Alhajji, J.N., and M.R. Reda, 1996. Role of Solution Chemistry on Corrosion of Copper in Synthetic Solutions: Effect of Bicarbonate Ion Concentration on Uniform and Localised Attack, *British Corrosion Journal*. Vol. 31, No. 2, pp. 125-131. ISSN 00070599.

Abstract: Pitting of copper pipes was simulated in the laboratory in synthetic tap waters with various water chemistries under stagnant conditions at room temperature. The primary interest was the effect of bicarbonate ion concentration on uniform and localized attack. Long term experiences were conducted by immersion tests (weight loss) of 8 months duration. Short term tests were conducted using electrochemical tests. It was found that increasing the bicarbonate concentration in tap waters results in a decrease in the corrosion rate due to uniform attack and increases the tendency to pit. This is irrespective of the $[HCO_3^-]/[SO_4^{2-}]$ concentration ratio. Pitting of copper can be enhanced if the solution contains an oxidising agent such as ferric ions which are recognised to be a common constituent in water supply systems. A mechanism is presented that predicts the observed relationship between bicarbonate ion concentration and corrosion rate and is supported by experimental data.

Al-Kharafi, F.M., and H.M. Shalaby, 1995. Corrosion Behavior of Annealed and Hard-Drawn Copper in Soft Tap Water, *Corrosion,* Vol. 51, No. 6, June 1995, pp. 469-481.

Abstract: The corrosion behavior of annealed and hard-drawn copper pipes was studied in soft tap water at room temperature. The work was carried out under stagnant and flow conditions on short- and long-term bases using electrochemical techniques. As-received copper pipes did not suffer from pitting regardless of whether the water was flowing or stagnant. The pipes experienced only mild general corrosion, which was more apparent in the hard-drawn copper. However, the pipes suffered from pitting when their initial air-formed oxide film was removed. The pitting attack occurred only when an external potential was applied and the water was stagnant. When general corrosion occurred, the protective oxide film thickened but did not separate from the metal surface. When pitting occurred, a thin and translucent cuprous oxide scale was formed. This scale separated from the metal surface, creating the occluded cell required for pitting initiation. The number of pits was ~7 pits/cm^2 to 10 pits/cm^2 for both types of copper and remained almost unchanged with polarization time. The average pit diameter was larger in the annealed copper than in the hard-drawn, but the average pit depth was almost equal in both types. Impedance measurements revealed that a mixture of capacitive and faradaic behaviors existed during the developmental stages of pitting, with an increase in the faradaic component as pitting progressed. Thus, the growth of pitting appeared to be dependent on mass transport through the oxide scale.

Al-Kharafi, F., H.M. Shalaby, and V.K. Gouda, 1987. Failure of Copper Pipes in Kuwait's Domestic Tap Water, *10th International Congress on Metallic Corrosion: November 7-11, 1987, Madras, India*, Trans Tech Publications, pp. 767-781. ISBN 0878495746.

Abstract: Annealed phosphorus deoxidized copper water pipes which failed after 16 and 20 months of service in hot and cold water piping, respectively, were investigated. When the pipes were sectioned, some areas were covered by bluish-green crusts and the rest by a dark-greyish layer. Pits were found along a longitudinal axis. The pits were hemispherical in shape, and intergranular corrosion was observed inside and around the pits. Residual carbon found on the internal surfaces of the pipes varied from 1.2 to 4.7 mg/dm^2. The water contains high levels of chloride, sulphate, and a lower level of bicarbonate. The pH ranges from 7 to 9, and the water was treated with a silicate-phosphate inhibitor. The crust covering the pits were essentially composed of sulphate and phosphate while chloride was identified inside the pits. The pitting potential of copper in Kuwait tap water was found to be 320 mVH.

Al-Kharafi, F.M., H.M. Shalaby, and V.K. Gouda, 1989. Pitting of Copper Under Laboratory and Field Conditions, *British Corrosion Journal,* Vol. 2, No. 4, pp. 284-290. ISSN 00070599.

Abstract: An investigation of the pitting in soft tap water of copper has revealed that fresh specimens tested under accelerated laboratory conditions behave similarly to copper tubes that have failed during service. In both cases, the pits are hemispherical in shape and are surrounded by an intergranularly attacked metal surface. They contain cuprous oxide and chloride crystals and are covered with an adherent oxide scale. Bluish green mounds, composed of basic copper sulphate crystals, are observed on top of the scale of the laboratory tested specimens. On the failed tubes, the deposits were composed mainly of sulphate, phosphate, and chloride. SEM examination of specimens after polarisation experiments revealed that the scale is initially separated from the bare metal surface by a layer of cuprous oxide crystals. Pits initiate irregularly along grain boundaries and later develop into a hemispherical shape. The development in shape is associated with precipitation of cuprous chloride inside the pits and on the metal surface below the scale. This is followed by precipitation of basic sulphate crystals and readhesion of the scale to the underlying metal surface.

ASM Engineered Materials Handbook, Desk Edition, 1996, ASM International. ISBN 0-87170-283-5.

Abstract: Contains information on the basic nonmetallic structural engineering materials—plastics, composites, ceramics, and glasses. Provides data on properties, selection, applications, and testing. Includes a "Guide to Materials Selection" that gives comparative information about the characteristics and advantages/disadvantages of these materials. New sections have been added on recycling plastics, metallizing of plastics, recycling, and environmental impact of ceramics and ceramic-matrix composites.

Baba, H., T. Kodama, and T. Fujii, 1986. Measurements of Pitting Potential and Effect of Oxidizing Agents in Water on the Pitting Potential of Copper Tubes in Hot Water, *Transactions of National Research Institute for Metals*, Vol. 28, No. 3, pp. 248-257. ISSN 045329222.

Abstract: Critical pitting potential was measured for copper tubes in flowing synthetic water at 60°C. The chemical composition of the synthetic water (HCO_3^- 36.6, Cl^- 42.6, and SO_4^{2-} 76.8 mg/l) was selected from chemical analysis data of types of water prone to pitting. Anodic polarization curves did not show a rise in current due to pitting. Thus, it was impossible to determine the critical potential from the polarization curves alone. The critical pitting potential of 150 mV vs. SCE was determined by an optical microscopic examination of the potentiostatically polarized copper surfaces at various potential values. The X-ray and EPMA analysis showed that the products inside a pit were Cu_2O and CuCl, and that the green product overlaying the pit was $Cu_4(OH)_6\,SO_4$. The structure and morphology of the pit were the same as those reported for the type 2 pitting of copper, which is commonly observed in soft type water with low $[HCO_3^-]/[SO_4^{2-}]$ ratio. Potential measurements were carried out for copper tubes in flowing synthetic water at 60±1°C with and without the addition of oxidizing agents, dissolved oxygen and residual chlorine. Also measured were the concentration levels of the oxidizing agents for bringing the potential of copper above the critical potential, Ep=150 mV vs. SCE. In the types of water saturated with dissolved oxygen (po_2 = 1 atm) and containing 3, 5, and 10 mg/l residual chlorine, copper specimens were brought to a potential nobler than Ep. In these cases, a numerous amount of pits were observed. It has been demonstrated that residual chlorine is the most detrimental factor for copper pitting in spite of the fact that its concentration level is far lower than that of dissolved oxygen. The pit morphology and corrosion products were classified as type 2 and were the same as those formed by the electrochemical method.

Boulay, N., and M. Edwards, 2001. Role of Temperature, Chlorine, and Organic Matter in Copper Corrosion By-Product Release in Soft Water, *Water Resources*, Vol. 35, No. 3, pp. 683-690.

<u>Abstract:</u> Soft, low alkalinity drinking waters tend to cause relatively high copper corrosion by-product release in plumbing systems. Long-term tests (6-8 months) in a synthetic, microbially stable soft tap water confirmed that lower pHs and higher temperatures increased copper release to water. Soluble copper release increased at lower temperature and lower pH. Low levels of free chlorine (0.7 mg/L) slightly increased copper release at pH 9.5, in marked contrast to the dramatic reductions in copper release that have been observed in soft waters in which Type III pitting corrosion is occurring. Gum xanthan and sodium alginate produced a microbially unstable water that reduced the pH and DO during stagnation in pipes — these indirect effects far outweighed their possible role in chelation or other modes of direct attack on copper surfaces.

Cohen, A., and W.S. Lyman, 1972. Service Experience with Copper Plumbing Tube, *Materials Protection and Performance*, Vol. 11, No. 2, February 1972, pp. 48-53. ISSN 00255378.

<u>Abstract:</u> Seven billion lbs (over 6 million miles) of copper plumbing tube has been put in service since World War II. During the past five years, an average of 71 incidents of failure of copper plumbing tube in the U.S. were investigated by the Copper Development Association, Inc. (CDA) each year. These incidents of failure break down as follows: pitting attack occurred in 24 of the cases; impingement attack, 12; general corrosion, 3, channel attack, 8; sulfide gas attack, 6; underground corrosion, 2; faulty workmanship, 8; and special cases due to come peculiar extraneous condition, 8. This distribution was fairly constant from year to year and probably reflects accurately the distribution of causes of all incidents of corrosive attack that led to failure in service for copper plumbing tube.

Cohen, A., and J.R. Myers, 1984. Mitigation of Copper Tube Cold Water Pitting by Water Treatment, *Corrosion/84*, The International Corrosion Forum Devoted Exclusively to the Protection and Performance of Materials, April 2-6, 1984, New Orleans, Louisiana.

<u>Abstract:</u> Copper is essentially immune to water-side corrosion. However, on occasion, pitting corrosion has been experienced in some communities supplied with water from well sources.

Such pitting can be prevented by treating the water. Successful treatments that have been demonstrated in the U.S. include the addition of soda ash, lime or caustic or simple aeration.

A computer program has been used to highlight the relative contributions to pitting aggressiveness of the various chemical constituents in potable waters.

Cohen, A., and J.R. Myers, 1987. Mitigating Copper Pitting Through Water Treatment, *Journal of the American Water Works Association*, Vol. 79, No. 2, February 1987, pp. 58-61. ISSN 0003150X.

Abstract: In July 1978, the first of about 25 pitting corrosion failures occurred in the residential plumbing systems of private homes and condominiums in the Highland Greens subdivision of Fort Shawnee, Ohio. An investigation showed that the water distributed to the community promoted and supported the pitting corrosion. Treatment of the water supply by addition of sodium carbonate to increase the pH and to eliminate the dissolved carbon dioxide was introduced. Pitting attack diminished almost immediately, and new reports of leakage ceased within six months. Two corrosion test loops containing 100 tube specimens were exposed to raw and treated waters. The 50 specimens exposed to the treated water showed no pitting attack. About 20 percent of the 50 tubes exposed to the raw water displayed major pitting, with lesser but still observable attack in the remainder of the tube specimens.

Cohen, A., and J.R. Myers, 1996. Overcoming Corrosion Concerns in Copper Tube Systems, *Materials Performance*, September 1996, pp. 53-55.

Abstract: Copper water tube systems have a long and successful application history. On rare occasions concerns about aggressive water, system design, material selection, system operation, and defective workmanship occur. Proper materials selection, system design and operations, correct workmanship practices, and effective water treatment alternatives for mitigating corrosion concerns are described, while concurrently enabling the 1991 Lead – Copper Rule Amendment of the 1974 Safe Drinking Water Act to be satisfied.

Cohen, A., and J.R. Myers, 1999. More on Copper Pipe Pitting, *Materials Performance*, MP Forum, January 1999. NACE International.

Abstract: Arthur Cohen and James Myers respond in a letter to the editor to a previous *Materials Performance* Failure Avoidance article by Richard A. Corbett (Well Water Causes Copper Pipe Pitting, November 1998, page 61). They first state that the article contains material that was published previously by Myers and Cohen in *Materials Performance* (October 1995, Vol. 34, No. 10, pp. 60-62) without being referenced. They also argue that the author neglected to indicate which of the optional water treatment techniques corrected the pitting corrosion concern in this incident. Corbett replies to Cohen and Myers' letter by saying the present study represented just about everything that could go wrong and could contribute to cold water copper pitting, and describes the corrective water treatment used.

Control of Corrosion on the Secondary Side of Steam Generators, 1996. R. Staehle (ed.). NACE. ISBN 1-57590-008-4.

Abstract: This book features 41 papers from 10 sessions of an October 1995 conference sponsored by the Electric Power Research Institute (EPRI) and Argonne National Laboratory. Topics covered include: modes and submodes of SCC; metallurgical definition; initiation and growth of SCC; local chemistry and electrochemistry; relationship between bulk and local chemistry; modeling and prediction for occurrence and minimization; stepwise approach and critical elements; and research priorities.

Cornwell, F.J., G. Wildsmith, and P.T. Gilbert, 1973. Pitting Corrosion in Copper Tubes in Cold Water Service, *British Corrosion Journal*, Vol. 8, No. 5, pp. 202-209. ISSN 00070599.

Abstract: Exposure trials in different water supplies have been carried out using copper tubes having various degrees of carbon contamination in the bore. On exposure to a water that supports pitting, the electrode potential of highly-contaminated tubes increases to a value greater than the critical potential for pitting. On the other hand, tubes abrasively cleaned with iron or alumina grit to reduce the carbon to a low level have potentials less than the critical value. Experiments were carried out in which uncleaned tubes were transferred from a water that supports pitting to one that does not and vice-versa. The results lead to the conclusion that in a water that does not support pitting, cathodic polarisation occurs to such an extent that the electrode potential never exceeds the critical value for pitting, even in the presence of considerable carbon contamination.

Corrosion-Resistant Alloys in Oil and Gas Production, 1996. J. Kolts and S. Ciaraldi (eds.). NACE. ISBN 1-877914-92-4.

Abstract: This 2-volume book features 103 classic pages from NACE as well as the SPE, ASM, GDM, TMS, and other publications. This book is divided into seven section: martensitic stainless steels; austenitic stainless steels; duplex stainless steels; precipitation-hardened nickel alloys; solid solution nickel/cobalt base alloys; other alloys; and acidizing corrosion-resistant alloys.

Edwards, M., and J.F. Ferguson, 1993. Accelerated Testing of Copper Corrosion, *Journal of the American Water Works Association*, Vol. 85, No. 10, October 1993, pp. 105-113. ISSN 0003150X.

Abstract: An innovative, short-term corrosion test has been developed that can predict long-term copper corrosion behavior. When used in a six-day study on uniform copper corrosion in five waters, the test predicted corrosion rates that were in good qualitative and quantitative agreement with known long-term (210-day) results. A second phase of the study examined the poorly understood phenomenon of soft-water pitting. Initial work successfully reproduced soft-water copper pitting in the laboratory using a synthetic water, facilitating future studies of pit initiation and potential remedies. Relative pitting tendencies were predicted using the short-term test, as was the long-term release of the by-products of copper corrosion. Pitting severity increased with increased pH and duration of stagnation and decreased in the presence of natural organic matter or chlorine residuals.

Edwards, M., J.F. Ferguson, and S.H. Reiber, 1994. The Pitting Corrosion of Copper, *Journal of the American Water Works Association*, Vol. 86, No. 7, July 1994, pp. 74-90. ISSN 0003150X.

Abstract: Some current theories of copper pitting are contradicted by practical experience. Although it has been theorized that chloride initiates copper pitting attack, simple experiments show that the presence of chloride ion actually tends to decrease the likelihood that pitting will occur. In contrast, sulfate plays no role in pitting theory, yet sulfate has consistently demonstrated a propensity to initiate and propagate copper pitting. New theories are required to reconcile pitting theory and practical observation in order to allow the rational mitigation of copper pitting problems. In addition, the presence of natural organic matter (NOM) in water supplies prevents or inhibits certain copper corrosion problems. As a result, recent efforts to remove NOM as a means of controlling disinfection by-products may lead to increased copper corrosion problems.

Evaluating Elastomeric Materials in Sour Liquid Environments, 1996. NACE Standard TM0296-96. ISBN 1-57590-010-6.

Abstract: New standard to serve as a tool in the process of evaluating elastomeric materials for use in the oil field and other energy-related areas where sour liquid environments are encountered. Describes an accelerated aging procedure with additional information on sour environment testing under pressures greater than atmospheric pressure, allowing data from separate laboratories to be compared if specified test conditions are used. Designed for testing O-rings or specimens of elastomeric vulcanizates cut from standard sheets.

Evaluation of Pipeline and Pressure Vessel Steels for Resistance to Hydrogen-Induced Cracking, 1996. NACE Standard TM0284-96. ISBN 1-57590-020-3.

Abstract: Provides a standard set of test conditions for consistent evaluation of pipeline and pressure vessel steels and test results from different laboratories pertaining to the results of the absorption of hydrogen generated by corrosion of steel in wet H_2S. Describes two test solutions, Solution A and Solution B, and includes special procedures for testing small-diameter, thin-wall, electric-resistance welded and seamless line pipe. Test is intended to evaluate resistance to hydrogen-induced (stepwise) cracking only, and not other adverse effects of sour environments such as sulfide stress cracking, pitting, or weight loss from corrosion.

Extruded Polyolefin Resin Coating Systems with Soft Adhesives for Underground or Submerged Pipe, 1996. NACE Standard RP0185-96. ISBN 1-57590-017-3.

Abstract: This standard details materials and methods of application for two types of polyolefin resin coating systems extruded over soft adhesives on pipe for underground or submerged service. The standard addresses surface preparation, application methods, electrical inspection, pipe handling techniques, and coating system repair methods. The two types of coating systems are (1) polyolefin resin that is crosshead-extruded on the pipe as a seamless coating over a hot-applied mastic adhesive and (2) polyolefin resin that is extruded spirally around the pipe to fuse and form as a seamless coating over an extruded butyl-rubber adhesive.

Fernandes, P.J.L., 1998. Type I Pitting of Copper Tubes From a Water Distribution System, *Engineering Failure Analysis*. Vol. 5, No. 1, pp. 35-40. Elsevier Science Ltd.

Abstract: Samples of copper tubes from a cold water distribution system which had failed due to pitting whilst in service were subjected to a detailed failure investigation. Analysis of the tubes showed that failure was a result of Type I pitting attack. While the exact cause of pitting was unknown, it was hypothesized that it could have been due to changes in the water quality and/or content. The tubes were found to be made from phosphorus de-oxidised copper and no anomalies were evident in either the chemical composition or the microstructure which could have caused the pitting observed. It was recommended that the tubes be replaced and that due attention be given to ensure that the new tubes are free of internal carbonaceous deposits or other foreign matter.

Fischer, W., H.H. Paradies, D. Wagner, and I. Hänßel, 1992. Copper Deterioration in a Water Distribution System of a County Hospital in Germany Caused by Microbially Induced Corrosion – I. Description of the Problem, *Werkstoffe und Korrosion*, Vol. 43, No. 2, pp. 56-62. ISSN 00432822.

Abstract: A severe copper corrosion process in the water distribution system of a County Hospital has been detected in the cold and warm water sections shortly after the opening of the Hospital. The damaged copper pipes showed pitting corrosion phenomena that could not be attributed to known types of pitting. The results of a first sampling revealed the same kind of corrosion in all installation areas. A thorough examination of the samples (perforations and hole depths) proved an influence of design and operating conditions on the extent of corrosion.

The analysis of the corrosion products showed that some products could be attributed to microbial activities in the copper pipes. A polymeric layer, the so-called “biofilm,” could be detected beneath the corrosion products. The presence of a biofilm indicates microbially induced corrosion. First countermeasures are being taken in the County Hospital to prevent further damages.

Fischer, W.R., D.H.J. Wagner, and H.H. Paradies, 1994. An Evaluation of Countermeasures to Microbiologically Influenced Corrosion (MIC) in Copper Potable Water Supplies, *ASTM Special Technical Publication*, pp. 275-282.

Abstract: Unexpected pitting of copper pipes in drinking water installations has appeared mainly in public buildings (often in hospitals) at a small number of places around the world (for example, Germany, Scotland, Saudi-Arabia). Experience and scientific based knowledge about pitting corrosion of copper does not indicate a remarkable susceptibility in the respective drinking water installations. Because substances of biological origin were mixed with the solid corrosion products, the following hypothesis was generally accepted: microbiologically influenced corrosion (MIC).

Though the mechanism of MIC is by no means clear in detail, promising countermeasures have to be developed substantiated and introduced into practice to protect existing installations. In this paper, the arguments for qualified actions are described and, when available, the success of these measures are mentioned. It can be stated that the likelihood of MIC in copper can be reduced to technically acceptable or even to negligible values by a combination of some well-known methods of corrosion protection.

Francis, R., 1996. Carbon Film Causes Pitting, *Materials Performance*, Letters to the editor, March 1996. NACE International.

Abstract: Dr. Roger Francis responds in a letter to the editor to a previous article in *Materials Performance* by James Myers and Arthur Cohen (Pitting Corrosion of Copper in Cold Portable Water Systems, October 1995, page 60). He disagrees with their dismissal of carbon films as a source of pitting corrosion problems in copper alloys. In his experience, he argues, he has seen many copper tube failures due to Type 1 pitting produced by the combined effects of an aggressive water and a “carbon” film, which is produced by the breakdown of drawing lubricant during bright annealing. He argues that carbon films do contribute to Type 1 pitting, although it is believed that they have no role in Type 2 and Type 3 pitting.

Fujii, T., 1988. Localized Corrosion and its Prevention for Copper in Water, *Transactions of National Research Institute for Metals,* Vol. 30, No. 2, pp. 81-86. ISSN 04539222.

Abstract: Localized corrosion modes of copper encountered in water were reviewed to elucidate the mechanism and establish preventive measures. First, the corrosivity of soft water in Japan was evaluated in relation to the performance of plumbing materials. Subsequently, typical corrosion failures due to pitting, erosion-corrosion and cuprosolvency were discussed and finally a pitting corrosion mechanism was proposed. It was concluded that pitting can occur, when the transition from cathodic control to anodic one due to passivation is combined with the presence of chloride and highly oxidizing agents like residual chlorine.

Fuji, T., T. Kodama, and H. Baba, 1984. The Effect of Water Quality on Pitting Corrosion of Copper Tube in Hot Soft Water, *Corrosion Science*, Vol. 24, No. 10, pp. 901-912.

Abstract: Laboratory reproduction of pitting on copper was attempted in a hot, circulating water loop for the purpose of clarifying the mechanism and establishing countermeasures to the pitting. Type 2 pitting was observed to occur on the internal surface of copper tubes after long-time exposure to Tokyo water, when it was heated to 60°C and residual chlorine of 2~3 mg/l was added. After prolonged loop testing, the electrode potential of copper exceeded the critical value, +150 mV (SCE). The pits were deep and acute, and were covered with greenish glue products, which were identified as basic copper sulfate. Pitting did not occur in water free of residual chlorine even under air-saturated conditions, in which copper retained a low potential value.

Gan, F, C. Der-Tau, and A.K. Meitz, 1996. Laboratory Evaluation of Ozone as a Corrosion Inhibitor for Carbon Steel, Copper, and Galvanized Steel in Cooling Water, *ASHRAE Transactions*, Vol. 102, No. 1, pp. 395-409. ISSN 00012505.

Abstract: An experimental study has been made to evaluate ozone as a corrosion inhibitor for use in cooling water systems. Corrosion of AISI 1010 carbon steel, CDA 122 copper, and hot-dipped galvanized steel in soft and hard water containing 0 to 0.1 ppm of ozone as examined at 90°F (32°C) over a range of water velocity of 0.5-0.5 ft/s (0.15-2.9 m/s). The mechanism of ozone affecting metal corrosion was studied with an electrochemical polarization technique and the change in the chemical composition of test water during the corrosion tests. It was found that in soft water corrosion of carbon steel was inhibited by ozone. The corrosion rate of carbon steel in soft water was: 22-60 mpy (0.56-1.5 mm/yr) without ozone and 14-27 mpy (0.35-0.68 mm/yr) in the presence of 0.1 ppm of ozone. Pitting corrosion occurred on all carbon steel coupons in soft water; ozone decreased pit density, pit size and pit depth. In hard water, corrosion of carbon steel was accelerated by ozone. Uniform corrosion occurred on all carbon steel coupons in hard water. The extent of corrosion acceleration by ozone decreased with increasing water velocity; at a high velocity of 9.5 ft/s (2/9 m/s) the corrosion rates of carbon steel with and without ozone became approximately the same at 20 mpy (0.51 mm/yr). Corrosion of copper in both soft and hard water was accelerated by ozone. In the presence of 0.1 ppm ozone, the corrosion rate of copper was: 0.6-1.5 mpy (0.016-0.038 mm/yr) in soft water, and 0.8-1.4 mpy (0.02-0.036 mm/yr) in hard water. Corrosion of galvanized steel in both soft and hard water was inhibited by ozone. The inhibition efficiency increased with increasing water velocity.

Harju, T., and O. Oy. The Effect of Water Quality vs. Tube Surface Quality on the Corrosion of Copper.

Abstract: The corrosion behaviour of copper tubes was followed at six waterworks in southern Finland. All tests were performed in cold water over a period of about twelve months. The 'passivation' process of four different copper qualities was followed by means of electrochemical measurements. Corrosion behaviour of these four surface qualities differed only slightly in good supply waters, while in an 'aggressive' water the differences were more pronounced. These observations indicate that the quality of the supply water plays a dominant role in the passivation of copper tubes.

Hatch, G.B., 1961. Unusual Cases of Copper Corrosion, *Journal of the American Water Works Association*, Vol. 53, pp. 1417-1428. ISSN 0003150X.

Abstract: The consumer generally feels that copper tubing should last a lifetime, and usually he is not disappointed. But in those rate instances when pitting occurs in copper tubing, holes may be formed after approximately a year of operation.

Copper, like other metals used for potable-water tubing, can be damaged from both general and localized corrosion. General corrosion of copper tubing in water service produces harmful side effects but seldom causes an appreciable decrease in the life of the tubing. Further, general corrosion usually can be controlled rather simply by treating the water. Localized corrosion markedly decreases the life of tubing. Most problems of copper pitting still remain to be solved by the corrosion investigator, but some puzzling instances of pitting encountered by the author may be of interest.

Hughes, H.C., and T. Pyle, 1982. Importance of Some Aspects of Water Quality on the Corrosion of Copper and Stainless Steel in Solar Hot Water Heaters, *Conference 22, Australasian Corrosion Association, Technical Papers (Preprints)*, Hobart, Tasmania, Australia, November 8, 1982.

Abstract: The pitting corrosion of copper and crevice or pitting corrosion of stainless steels have been discussed in terms of factors such as temperature, chloride concentration, pH and bicarbonate concentration all of which affect the corrosion and hence the use of these metals in domestic solar hot water heater manufacture. A thermodynamic approach indicates that the desired basic copper carbonate protective film will not be formed on copper in some waters at high temperatures and an experimental approach in which the potting potentials are determined indicates that the safety margin for the corrosion potentials of stainless steel is small in similar waters.

Impressed Current Anodes for Underground Cathodic Protection, 1996. NACE Publication 10A196.

Abstract: Addresses six commonly used anode materials: graphite; high-silicon chromium cast iron; mixed-metal oxide; platinum-coated niobium, titanium, and tantalum; polymeric materials; and scrap steel. The report describes the nature of each material; reported consumption rates; typical applications; anode configurations; handling, packaging, and connections; environmental considerations; and history and limitations. The report is intended to provide an overview of impressed current anode materials for individuals new to the cathodic protection field and to serve as a reference for more experienced personnel.

Jacobs, S., S. Reiber, and M. Edwards, 1998. Sulfide-Induced Copper Corrosion, *Journal of the American Water Works Association*, Vol. 90, No. 7, pp. 62-73. ISSN 0003150X.

Abstract: The presence of sulfides in potable water increases copper pitting and the release of copper corrosion by-products. After 3 h of stagnation in a copper pipe, the average by-product release of a synthetic drinking water that contained sulfides was 8.0 mg/L at pH 6.5 and 4.4 mg/L at pH 9.2. These concentrations represented a 5- and 30-fold increase compared with water without sulfides. Sulfide-induced corrosion problems might be ameliorated by removal of sulfides from the water, mechanical removal of the sulfide scale, chlorination, or deaeration. However, in the laboratory only mechanical removal of the sulfide scale and removal of sulfides from water were effective within a month. Utility case studies strongly support a relation between sulfides and increased copper corrosion problems.

Kearns, J.R., and B.J. Little (eds.), 1994. Microbiologically Influenced Corrosion Testing, *Symposium on Microbiologically Influenced Corrosion Testing*, American Society for Testing and Materials, pp. 253-265. ISBN 0-8031-1892-0.

Abstract: A copper-corrosion process of unknown origin was observed in the cold and warm water supplies shortly after commissioning a county hospital in Germany. The cause of the damage could be attributed to microbial-influenced corrosion (MIC). An evaluation of the damage showed that corrosion is most likely to occur in intensively branched, horizontal pipework during prolonged periods of stagnation. The influences of operating conditions and design installation on the corrosion process could not be separated. The operating conditions and design installation can be separated in test rigs using the occurrence manifestation characteristics for this corrosion process as a measure for the likelihood of corrosion. After an induction period of 200 days the corrosion is most often found under intermittent and stagnant conditions in the test rigs. Furthermore, a seasonal influence can be observed. It was shown in experiments performed in the laboratory that it should be possible to considerably minimize this induction period found in the test rigs.

Keating, K.L., 1974. I*nvestigation of Copper Tubing Failures at Chula Vista Development in Nogales, Arizona*, September 29, 1974.

Abstract: In 1974, an investigator for the Arizona State Registrar of Contractors discussed a problem with the author concerning leaking water pipes in a home development in Nogales, Arizona. Several home owners in the development had filed a complaint with the Registrar of Contractors to the effect that the plumbing in their homes was faulty. About 20 leaks had developed in various homes in the 120-home development. The author was asked to help determine the cause of the leaks, or at least if the contractor was at fault. Based on his investigation of the copper tubing samples and the information given to him by the investigator, the author believes that this corrosion is the same type of problem that he has encountered in the Tucson area. Furthermore, he believes that the evidence indicates it is the same corrosion problem that other investigators have reported from other parts of the country and the world.

Keating, K.L. *Corrosion of Copper*.

Abstract: Copper and its alloys are generally considered to have good resistance to corrosion. Copper can and does corrode in certain environments, however. There is a pitting corrosion phenomenon that takes place on copper tubing that carries fresh water. The phenomenon has been observed in the United States and other parts of the world. One way to attack a problem of this sort is to try to duplicate in the laboratory those conditions that seem to develop the problem in actual practice. This approach was taken by the author of this paper. The presentation will show how these conditions were synthesized in the laboratory and were able to develop a scale similar to that formed in copper tubes perforated in actual situations. A possible solution to the problem will also be presented.

Komukai, S., and K. Kasahara, 1994. On the Requirements for a Reasonable Extreme Value Prediction of Maximum Pits on Hot-Water-Supply Copper Tubing, *Journal of Research of the National Institute of Standards and Technology*, Vol. 99, No. 4, July–August 1994, pp. 321-326.

Abstract: Application of extreme value statistics to the problem of Type-II pits growth prediction on hot-water-supply copper tubing is described. A recommendation is suggested for optimum combinations of the number and the size of unit samples required for reasonable extreme value predictions.

Korshin, G.V., S.A.L. Perry, and J.F. Ferguson, 1996. Influence of NOM on Copper Corrosion, *Journal of the American Water Works Association*. Vol. 88, No. 7, July 1996, pp. 36-47. IRN 10391836.

Abstract: Natural organic matter (NOM) profoundly affected the corrosion of copper in a moderately alkaline synthetic water. It decreased the rate of corrosion, increased the rate of copper leaching, and dispersed crystalline inorganic corrosion products. The interaction of NOM with corrosion products was modeled using separate phases of malachite and cuprous oxide. The authors concluded that NOM promotes the formation of pits in a certain narrow range of concentrations (0.1–0.2 mg/L in laboratory tests) and suppresses this type of corrosion at higher dosages. At low DOC concentrations, the main interaction between NOM and the surfaces of corroding metal and corrosion products is adsorption. The influence of NOM on corrosion of metals in real distribution systems must be studied in relation to long periods of surface aging, flow rate, concentration and type of oxidants, pH, and alkalinity.

Lin, Y., and H. Yasuda, 1996. Effect of Plasma Polymer Deposition Methods on Copper Corrosion Protection, *Journal of Applied Polymer Science*, Vol. 60, No. 4, pp. 543-555. ISSN 00218995.

Abstract: The behavior of plasma polymer coating for Cu corrosion protection was investigated in dc cathodic polymerization, with and without anode magnetron enhancement, af magnetron glow discharge polymerization, and rf glow discharge polymerization. The combination of visual and scanning electron microscopy observations established general trends in an accelerated wet/dry cycle corrosion testing environment containing 0.1*N* chloride ions. Dc anodic magnetron cathodic polymerization of TMS offered the best Cu corrosion protection due to an enhanced deposition uniformity and adhesion of the deposited plasma polymer to the Cu substrate. No corrosion was observed after 25 wet/dry cycle accelerated corrosion tests when uncoated Cu suffered a severely generalized attack in one cycle. Superior corrosion protection was also performed by an af plasma polymerized coating of $C_4F_{10} + H_2$ (1:1) at a low-energy input density and of methane at high-energy input and high deposition thickness carried out in the range of this study. The application of plasma polymers which showed high water vapor permeation resistance and surface dynamic stability greatly reduced the pitting densities.

Lucey, V.F., 1967. Mechanisms of Pitting Corrosion of Copper in Supply Waters, *British Corrosion Journal*, Vol. 2, September 1967, pp. 175-185.

Abstract: Detailed examination of a large number of copper water tanks and pipes showing pitting corrosion (taken from certain districts to which pitting is confined) revealed features that could not be reconciled with the conventional explanation based on the presence of large cathodic areas surrounding small anodic corrosion sites. A new theory of pitting corrosion of copper is proposed which explains the features observed. Pitting arises when a pocket of cuprous chloride forms beneath a porous electrically conducting membrane (usually cuprous

oxide). The anodic and cathodic processes occur on the inner and outer surfaces of the membrane. Dissolution of copper occurs by reaction with the anodic product beneath the membrane and deposition of calcium carbonate occurs by reaction of hardness salts in the water with the cathodic product above the membrane.

Pockets of cuprous chloride capable of developing into corrosion pits can only form if the potential of the copper rises above 90 mV E_H during the period of film formation. Control of the potential below this value by coupling to a small sacrificial aluminum anode has been shown to prevent formation of pits in copper tanks and cylinders in service.

Lucey, V.F, 1977. Prevention of Pitting Corrosion of Copper Water Tanks and Cylinders, *EROCOR '77 Eur Congr on Met Corros*, 99nd Event of the Eur Fed of Corros, London, England, September 19-23, 1977, Published by the Society of Chemical Ind., London, England, pp. 261-264.

Abstract: A basic understanding of the mechanism of pitting corrosion of copper has led to the development by BNF of the now well established method of protecting copper tanks and cylinders from Type 1 pitting corrosion using aluminum protector rods. More recent fundamental work now suggests that the action of the protector rod is not to influence the type of oxide film formed on the copper as previously thought but to prevent the formation of mobile copper corrosion products which are instrumental in pit initiation.

Managing Corrosion with Plastics, Volume XI, 1993. *Proceedings of the 12th Biennial Managing Corrosion with Plastics Symposium*, November 1–4, 1993, Baltimore, Maryland. NACE. ISBN 1-877914-68-1.

Abstract: Promotes cost-effective use of plastics in solving corrosion problems. Emphasizes the importance of plastics selection, specification, fabrication, installation, inspection, and maintenance. Topics covered include: acoustic emission intensity, design, fabrication and inspection of RTP tanks for corrosive chemical service, evaluation of fiber-reinforced plastics for solvent resistance and containment, failure analysis of FRP pipe and tanks, hand portable face planning vs. traditional abrasion methods for FRP laminates, fluoropolymer linings technologies, reliability of high-density polyethylene pipe bonds in high-pressure applications, double containment systems and much more.

Mattson, E., 1968. Corrosion Investigation of Water Heaters with Heating Coils of Copper Tubes, Proceedings of the 5th Scandanavian Corrosion Congress, October 7-10, 1968, Copenhagen, Denmark. Vol. 2, Pap. 39, 16 p.

Abstract: In certain parts of western and northern Sweden pitting has occurred in the heating coils of copper tube used in water heater batteries. The results of this investigation do not indicate that the pitting can be eliminated by a change from phosphorized copper to oxygen-bearing or arsenical copper as material for the coils. A considerable decrease in the pitting has been attained, however, by alkalization of the water to a pH- value of about 8.3.

Mattsson, E., 1979. Corrosion of Copper and Brass. Practical Experience in Relation to Basic Data, *Metaux: Corrosion-Industrie*. Vol. 55, No. 645, May 1979, pp. 173-185. ISSN 00261084.

Abstract: During the period 1965–1979 the author has — in co-operation with various co-workers — investigated some of the corrosion phenomena occurring in the application of copper materials. A survey is given of some conclusions reached in investigations on the following subjects:

- the electrode kinetics of cooper in acidic copper sulphate solution;
- atmospheric corrosion and patina formation;
- the pitting of copper water tubes;
- the erosion corrosion of copper water tubes;
- the dezincification of brass;
- the stress corrosion cracking of brass;
- the hydrogen embrittlement of copper;
- the corrosion resistance of copper canisters for final disposal of spent nuclear fuel.

Mattsson, E., 1987. Focus on Copper in Modern Corrosion Research, *National Association of Corrosion Engineers,* April 1987, pp. 9-16.

Abstract: A survey is given of recent development work on the corrosion of copper and its alloys. Corrosion on electronic equipment has been studied with the aid of x-ray photo-electron spectroscopy and the quartz crystal micro-balance technique. Sulfur and nitrogen oxides have shown a strongly synergistic effect on the corrosion of copper. For assessment of the corrosivity of atmospheres, copper coupons are exposed, and the corrosion products are analyzed by cathodic reduction. Copper pipes are increasingly used for hot and cold tap water. Type 1 pitting, generally ascribed to a continuous carbon film inside the pipe, is considered in new specifications limiting the carbon film contamination. Type 3 pitting can apparently be counteracted by increasing the alkalinity of the water so that protective basic copper carbonate can form. Traces of copper dissolved in the tap water may kill bacteria in the water. A copper-nickel sheathing of offshore jacket structures has been found cost effective for controlling corrosion and fouling. Corrosion inhibitors for copper have been studied simultaneously using surface-enhanced Raman spectroscopy, ellipsometry, and an electrochemical technique in situ, and new inhibitors have been tailored. In a new underground application, copper canisters have been considered for final disposal of spent nuclear fuel at 500-m depth in granite rock. The canister corrosion has been estimated considering thermodynamically possible reactions and the supply of corrosive species. For assessment of the stress corrosion resistance of copper alloys, an ammonia test has been developed as an alternative to the mercurous nitrate test. Finally, studies are reported of stress corrosion in pure copper resulting from the action of nitrite.

Mattsson, E., 1988. Counteraction of Pitting in Copper Water Pipes by Bicarbonate Dosing, *Werkstoffe und Korrosion*, Vol. 39, No. 11, pp. 499-503. ISSN 00432822.

Abstract: Copper pipes are extensively used for tap water installations and generally perform well. Exceptionally, however, copper pipes are perforated due to pitting. Three main types of pitting (I, II and III) have been identified, but as for the causes and the mechanisms these have not yet been fully clarified.

Through case studies, model experiments, thermodynamic calculations, and service tests, evidence has been obtained that waters having a pitting propensity for copper pipes can be made less corrosive by an increase of the HCO_3^- content. On water treatment the following water composition should be aimed at:

- a pH value of at least 7
- an HCO_3^- content of at least 70 mg/l, preferably 100 mg/l
- As low as SO_4^{2-} content as possible, or at least lower than the HCO_3^- content (both in mg/l).

Mattsson, E., and A.-M. Fredriksson, 1968. Pitting Corrosion in Copper Tubes – Cause of Corrosion and Counter-Measures, *British Corrosion Journal*, Vol. 3, No. 5, pp. 246-257. ISSN 00070599.

Abstract: An abstract of failures of hard-drawn copper water pipes (phosphorus-deoxidised copper) in service due to pitting corrosions was conducted from November 1962 to February 1965. Fifteen cases were reported. All those about which information could be obtained came from hot water installations and occurred in water with a low pH (≤7) and a HCO_3^- content of, at the most, 100 mg/l but generally below 50 mg/l. Failures not due to pitting corrosion (i.e., caused by erosion and corrosion or corrosion fatigue) occurred in waters with a higher pH and higher HCO_3^- content.

A laboratory investigation into the ability of the corrosion products to counteract further corrosion in different types of water was also carried out, using an electrolytic cell which, in principle, was a model of an active pit in a copper tube. This led to the following conclusions, which are in good agreement with the results obtained from the examination of service failures:

If the pH value of the water is high enough, the copper dissolved by the corrosion can be precipitated as basic cooper salt. At low pH values such precipitation does not take place.

If the $[HCO_3^-]/[SO_4^{2-}]$ ratio in the water is high, dissolved copper can be precipitated as basic copper carbonate in the neighbourhood of the corrosion site and counteract further corrosion.

At a low $[HCO_3^-]/[SO_4^{2-}]$, crusts of basic copper sulphate will be precipitated at some distance from the corrosion site and may lead to a high corrosion rate.

Pitting is not likely to occur in hot water tubes of hard copper if the pH is $\geq 7 \cdot 4$ and the $[HCO_3^-]/[SO_4^{2-}]$ ratio ≥ 1 (the concentration given in mg/l). The critical values mentioned are approximate and may be adjusted in the light of future experience.

Minamoto, K., and S. Inagaki, 1990. Corrosion Behavior of Copper Tube in Hot Water Supply Systems, *Kobelco Technology Review*, No. 7, pp. 22-25.

Abstract: This paper describes a comprehensive survey of the causes of corrosion problems in copper tubing used in hot water supply systems for buildings. In particular, the effects of HCO_3^- / SO_4^{2-} ratio, residual chlorine and SiO_2 on pitting corrosion and possible countermeasures are examined in depth from a new viewpoint. Also, the characteristics of pitting corrosion resistant alloy “ANPIC-TUBE” and results of its field tests are reported.

Monticelli, C., G. Brunoro, G. Trabanelli, and A. Frignani, 1986. Corrosion in Solar Heating Systems. I. Copper Behaviour in Water/Glycol Solutions, *Werkstoffe und Korrosion*, Vol. 37, No. 9, pp. 479-484. ISSN 00432822.

Abstract: A research programme has been developed in order to investigate the corrosion behaviour of metallic materials commonly used in solar heating systems.

This paper presents the results of an experimental study on copper corrosion resistance in ethylene and propylene glycol/water solutions (1:1 by volume) constituting the most common bases of heat transfer fluids. Long time gravimetric tests were carried out on electrolytic copper at 80°C, even in glycol/water solutions previously degraded at their boiling temperature or polluted with 200 ppm chlorides.

Chemical compositions, semiconducting properties and morphological characteristics of all surface products were investigated by X-ray diffraction analysis, pulse photopotential technique and SEM observations, respectively. Heat transfer effects on copper corrosion and copper/6351 aluminum alloy couple efficiency were evaluated by electrochemical tests.

The following results were obtained:

- Ethylene and propylene glycol/water solutions are low corrosive media. Nevertheless, chloride pollution and/or high temperature degradation of glycols markedly increase their aggressivity. Under all the experimental conditions, copper corrosion rates are higher in ethylene than propylene glycol solutions.
- In chloride-free solutions, heat transfer stimulates the cathodic reaction of the copper corrosion process.
- Galvanic contact between copper and aluminum alloy always causes pitting corrosion on aluminum electrodes. The severity of the pitting attack is enhanced by the presence of heat transfer conditions on copper and/or chloride ions in the solutions, particularly in ethylene glycol.

Muhlibauer, W.K., 1996. *Pipeline Risk Management Manual, Second Edition*. Gulf Publishing Company. ISBN 0-88415-668-0.

Abstract: This reference guides you in managing the risks involved in pipeline operations. Pipeline engineers, designers, operators, and managers rely on this book's basic risk assessment model—a practical, straightforward method for analyzing pipeline risks. Covers many additional aspects of pipeline risk management including: risk and cost of service interruption; risk of sabotage; methods to assess environmentally sensitive and high-value areas; workplace stress; and human error potential. Covers ways to create a resource allocation model by linking risk with cost. Also addresses offshore pipelines and distribution system pipelines as well as cross-country liquid and gas transmission pipelines.

Myers, J.R., and A. Cohen, 1994. Soldering Flux-Induced Pitting of Copper Water Lines, *Materials Performance*, October 1994, pp. 62-63.

Abstract: Soldering flux-induced pitting attack is becoming more frequent on the inside surfaces of copper tubes and fittings in both domestic plumbing and sprinkler systems. It occurs preferentially in cold-water lines. The problem can be effectively mitigated by requiring plumbing technicians to use industry-standard materials and workmanship.

Myers, J.R., and A. Cohen, 1995. Pitting Corrosion of Copper in Cold Potable Water Systems, *Materials Performance*, October 1995, pp. 60-62.

Abstract: Copper tubing in potable water systems is highly resistant to corrosion. However, pitting attack will occur in tubing carrying cold water with an aggressive chemistry (typically, pH of 7.0 to 7.7 and dissolved carbon dioxide of at least 25 mg/L). The most cost-effective method for preventing this pitting is altering the water chemistry by raising the pH and reducing the carbon dioxide content.

Rambow, C.A., and R.S. Holmgren, Jr., 1966. Technical and Legal Aspects of Copper Tube Corrosion, *Journal of the American Water Works Association*, Vol. 58, pp. 347-353. ISSN 0003150X.

Abstract: The use of copper for conveying drinking water dates from the early days of civilization, but only within the past 50 years or so has copper tubing come into widespread use for domestic water applications. This rapid acceptance stems from its ease of installation and its record of satisfactory service. In addition, the cost differential between copper and other pipe has largely disappeared in recent years because the former, although relatively expensive, can be installed with less labor. For these reasons, it is expected that the use of copper tubing for domestic water service will continue to increase.

Although copper tube is a high-quality, trouble-free, corrosion-resistant, and otherwise generally satisfactory material, this very fact has led many users to assume that copper would not corrode under any conditions of exposure to domestic water. This is not the case. The authors are aware of several instances in which copper tube has failed owing to corrosion-caused leaks. There have been other instances in which corrosion did not result in leaks but in which the copper content of the water so increased that the suitability of the water for domestic purposes was affected.

Riedl, R., and J. Klimbacher, 1989. Pitting Corrosion in Copper Water Pipes, *International Journal of Materials and Product Technology,* Vol. 4, No. 2, pp. 159-166. Inderscience Enterprises, Ltd. ISSN 02681900.

Abstract: Copper as a material for water supplying installation is used to an increasing degree in Austria as it also is elsewhere. Pipes of copper are used in cold- and warm-water supply because good economy is promised by the easy machinability, handling, very good soldering properties and the good corrosion resistance. In spite of the good corrosion resistance there have been corrosion problems leading to great damage which has had to be covered by technical insurance either of the owner or the manufacturer. Corrosion attack occurs as pitting corrosion; three different types are known. The conditions for pitting corrosion will be shown; in most cases a characteristic analysis of the water may be assigned. This does not mean though, that certain waters automatically cause corrosion. Further conditions must be fulfilled to make corrosion damage probable. Conditions depending on fabrication, handling and use of copper pipe systems will be discussed.

Rossum, J.R., 1985. Pitting in Copper Water Tubing, *Journal of the American Water Works Association*, Vol. 77, No. 10, October 1985, pp. 70-73. ISSN 0003150X.

Abstract: Investigation of leaks in copper water tubing led to evidence that internal pitting corrosion of copper is the result of failure to thoroughly flush household plumbing rather than a result of corrosive water or defective material.

Sandenbergh, R.F., 1993. Pitting Corrosion of Copper Tubing in Domestic Waters, *Corrosion and Coatings South Africa*, Vol. 20, Issue 2, pp. 4-8, 12, George Warman Publications (PTY) Ltd., IRN 10023100.

<u>Abstract:</u> The corrosion of copper tubing in domestic waters is discussed with special reference to pitting corrosion. Critical factors in the initiation of pitting corrosion such as the water quality and the presence of surface films on the copper are pointed out. The electrochemical pitting cell is used to evaluate waters from the Pretoria Region and some sub-surface waters were found to be conducive to pitting corrosion. Steps that can be taken to avoid pitting corrosion in copper tubing are discussed. The potential benefits of a water database and a test capable of evaluating surface films in relatively short times are pointed out.

Schock, M.R., and D.A. Lytle, 1994. Critical Issues in Water and Wastewater Treatment. *Proceedings of the 1994 National Conference on Environmental Engineering*, J.N. Ryan and M. Edwards (eds.). American Society of Civil Engineers, Boulder, Colorado, July 11-13, 1994, pp. 17-25. ISBN 0-7844-0031-8.

<u>Abstract:</u> Historically, uniform copper corrosion has been of little concern. Numerous forms of pitting corrosion and consequent pipe failures have been documented and classified. Recently, because of the monitoring introduced by the Lead and Copper Rule, cuprosolvency (copper solubility) has forced many utilities to undertake corrosion control studies and treatment, rather than the replacement of pipes perforated by pitting. The development of a useful model for cuprosolvency in drinking water is constrained by several areas of uncertainty, many of which were addressed in a recent study. These areas are: the nature of field data; the selection of appropriate aqueous and solid species for drinking water systems; the uncertainties in selection of the most accurate equilibrium constant data; the role of metastable phases in cuprosolvency control; the effects of temperature; and residual oxidants in the plumbing systems.

Sequeira, C.A.C., 1995. Inorganic, Physicochemical, and Microbial Aspects of Copper Corrosion: Literature Survey, *British Corrosion Journal*, Vol. 30, No. 2, pp. 137-153. ISSN 00070599.

<u>Abstract:</u> A literature survey on the corrosion of copper in aqueous solutions, with particular relevance to potable water, is presented. Coverage is of inorganic and physicochemical aspects of copper corrosion, namely those dealing with the thermodynamics of copper corrosion reactions, oxygen reduction at copper surfaces, and the photoelectrochemistry of the copper copper oxide–electrolyte system. Microbially induced pitting corrosion and transport in associated biomembranes are also considered.

Shalaby, H.M., F.M. Al-Kharafi, and V.K. Gouda, 1989. A Morphological Study of Pitting Corrosion of Copper in Soft Tap Water, *Corrosion*, Vol. 45, No. 7, July 1989, pp. 536-547.

Abstract: A morphological study was carried out on the pitting corrosion of copper in soft tap water at room temperature. Pitting corrosion was initiated through localized breakdown of a relatively thin protective cuprous oxide film. This film increased in thickness and became a scale that separated from the metal surface by cuprous oxide crystals. The oxide crystals ruptured the scale and extruded from it forming mounds at sites that corresponded to grain boundaries. The initiation of pitting attack was observed along the grain boundaries, and the pits developed into hemispherical shapes. After the pits were already established, basic copper sulfate corrosion products were formed on top of the scale through a precipitation reaction that involved basic copper chloride crystals grown underneath the scale.

A new mechanism is proposed that can explain pitting corrosion of copper in soft and hard waters. The presence of chloride ions is a prerequisite in the breakdown of the film and the initiation of pitting attack. Furthermore, the pit morphology depends on the deformation of the grains, and the composition of corrosion products inside the pits is the same whether the water is soft or hard. The concentration of the chemical species present in the water determines the composition of the corrosion products covering the pits.

Smith, S., and R. Francis, 1990. Use of Electrochemical Current Noise to Detect Initiation of Pitting Conditions on Copper Tubes, *British Corrosion Journal*, Vol. 25, No. 4, pp. 285-291. ISSN 00070599.

Abstract: Many failures in copper pipes used for cold water transportation result from type 1 pitting. This occurs when tubes containing a deleterious film from the manufacturing process are exposed in an aggressive water. Present tests to detect the presence of deleterious films are unsatisfactory and a possible alternative rapid test method has been studied. The technique involves collection and analysis of the electrochemical current noise signals emitted by the copper tube during corrosion. Tubes with different amounts of carbon contamination, produced at BNF and deliberately engineered by industry, have been studied using an electrochemical current noise technique. After only 20 h on test, the standard deviation and coefficient of variation of electrochemical noise signals clearly distinguished between grit blasted tube and contaminated tube. A longer, 30 h, test was needed to separate those that were borderline but satisfactory from those that were borderline/unsatisfactory.

Sosa, M., S. Patel, and M. Edwards, 1999. Concentration Cells and Pitting Corrosion of Copper, *Corrosion Science*, Vol. 55, No. 11, November 1999, pp. 1069-1076.

Abstract: Certain aspects of copper tube failure in drinking water systems are inconsistent with the "membrane cell theory" of copper pit propagation, which postulates that cathodic reactions occur immediately above the pit tubercle. To examine the basis for this theory, classic experiments of Lucey were revisited and alternative interpretations were apparent that are consistent with concentration cell effects. In fact, under chemical conditions thought to support Type I copper pitting, more than 90% of electron loss at the anode was accounted for by concentration cell effects rather than cathodic reactions occurring above the pit. In addition, the qualitative trends in currents arising from concentration cells are consistent with practical observations regarding the role of bulk solution pH in Type I pitting; that is, waters between pH 6.5 and pH 7.8 sustain currents that support pitting, but at pH < 6.5 or pH > 7.8, currents become self-limiting.

Storage Tanks—Advances in Environmental Control Technology, 1996. P.N. Cheremisinoff (ed.). Gulf Publishing Company. ISBN 0-87201-332-4.

Abstract: This volume helps in identifying and assessing problems regarding the technical issues are well as regulatory requirements regarding storage tank use, replacement, and remediation. This volume is divided into ten chapters dealing with aboveground and underground storage tanks composition; underground storage tanks; aboveground tanks; aboveground storage tanks regulations and engineering; aboveground tank farm specifications; a comparison of steel and fiberglass construction for underground storage tanks; fuel dispensing tanks—factors to consider in location; a comparison of steel fiberglass construction; air stripping VOCs from groundwater; and minimizing ecological damage during cleanup of terrestrial and wetland oil spills.

Sulfide Stress Cracking Resistant Metallic Materials for Oilfield Equipment, 1996. NACE Standard MR0175-96. ISBN 1-57590-021-1.

Abstract: Presents metallic material requirements for resistance to sulfide stress cracking for petroleum production, drilling, gathering and flowline equipment, and field processing facilities to be used in H_2S-bearing hydrocarbon service.

Survey of CRA Tubular Usage, 1996. NACE Publication 1F196.

Abstract: New technical committee report contains data solicited from oil and gas companies on use of CRA tubulars in oil and gas production. Data have been analyzed in terms of total quantity of pipe reported for specific environmental conditions, including bottomhole temperature, H_2S concentration, H_2S partial pressure, and CO_2 concentration.

Suzuki, I., 1984. The Prediction of Pit Initiation Time for Copper Tubes in Hot Water From Water Composition, *Corrosion Science*, Vol. 24, No. 5, pp. 429-437.

Abstract: Chlorite ion, formed by disproportionation of hypochlorite, is a cause of pitting corrosion of copper tubes in hot water. The attack of chlorite ion depends on the corrosion product layer on copper, the properties of which are influenced by water composition. A new method to predict the initiation time of pitting from water composition was presented on basis of quantitative relationships between the attack of chlorite ion and the corrosion product layer formed in various water compositions.

Suzuki, I., Y. Ishikawa, and Y. Hisamatsu, 1983. The Pitting Corrosion of Copper Tubes in Hot Water, *Corrosion Science*, Vol. 23, No. 11, pp. 1095-1106.

Abstract: The electrode potential of copper tube used in hot water distribution system in buildings rises gradually with time of exposure and then attains to a critical value of pitting potential after a long incubation period. The process of potential rise proceeds in two stages. The first stage is the formation of a cuprous oxide layer in the potential range $\leq$60 mV (SCE) and the second stage is due to the reactions of chlorite ions accumulated in the cuprous oxide layer in the potential range >60 mV (SCE). Oxyacids and oxyanions of chlorine formed in the water, to which chlorine gas or hypochlorite was added for sterilizing process, accelerate the formation of cuprous oxide layer in the first stage, and the reaction of chlorite ions increase the electrode potential of copper tube in the second stage.

Taxén, C., 2000. Pitting Corrosion of Copper, Equilibrium – Mass Transport Limitations, *Mat. Res. Soc. Symp. Proc.*, Vol. 608, pp. 103-108.

Abstract: Predictions from a mathematical model of the propagation of a corrosion pit in copper are reported. The model uses equilibrium data for solid and aqueous species to calculate local chemical and electrochemical equilibria in small volume elements. Mass transport between elements under local internal equilibrium is calculated using aqueous diffusion coefficients with the constraint of electrical neutrality. Propagation of a corrosion pit is deemed possible when the fraction of the oxidised copper that forms solid corrosion products, at the copper metal, is insufficient to completely cover the underlying metal. The effect of pH and salt concentrations in the bulk water was studied by varying the composition of the water.

Results are presented in the form of $E\text{-}\log[Cl^-]$ diagrams where E is the applied potential and $[Cl^-]$ is the total bulk concentration of chloride. The $E\text{-}\log[Cl^-]$ diagram shows two separate areas where pitting is found to be possible. One region at low chloride concentration and high potential and one region at high chloride concentration and low potential. Increased sulphate concentration is found to be detrimental with respect to pitting corrosion, particularly in the high potential region. Increased carbonate concentration is found to be beneficial, particularly in the low potential region. Pitting corrosion of copper can be described as a case of galvanic corrosion where cuprous oxide at a pH similar to that of the bulk is the cathode material for oxygen reduction and copper metal at the local, lower pH in a corrosion pit may behave as the anode.

Treseder, R.S., and R.N. Tuttle, 1996. *CORROSION UPDATE: Oil and Gas Production, 1996 Edition*. corUPdate, Inc.

Abstract: Excellent reference tool for designers, builders, and operators of oil and gas facilities. Summarized papers published in 1995 and papers presented at CORROSION/96.

Wilson, J.T., 1997. *Microanalysis Project Report*, Materials Analytical Services, submitted to John Harrison of Florida Solar Energy Center, Cocoa, Florida.

Abstract: The objective of the performed analyses was to determine the most probable cause of the leaking in the submitted tubes taken from various ICS solar collectors. Based on the performed analyses the most probable cause of the leaking appears to be localized pitting corrosion as the result of iron precipitation from the incoming city water supply.

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