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Corrosion Effects of Magnesium Chloride and Sodium Chloride on Automobile Components

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16. Abstract
The project consisted of two phases. In the Phase I study, the relative corrosiveness of the two salts were examined by SAE J2334 test and ASTM B117 test. In the Phase II study, SAE J2334 test and NACE TM-01-69 test (as modified by the Pacific North States) were applied. Representative metals examined in the project included stainless steel 410 and 304L, aluminum 2024 and 5086, coated automobile body sheets, copper wires, and mild steels.

Experimental results of SAE J2334 test indicated that $MgCl_2$ was more corrosive than NaCl to the bare metals tested. However, the experimental results of ASTM B117 test showed opposite conclusions. Because of the conflicting conclusions, further tests were conducted using NACE TM-01-69 (as modified by the Pacific Northwest Snowfighters). Again, opposite conclusions were obtained from SAE J2334 and NACE TM-01-69 tests. In order to investigate the causes responsible for the inconsistency, the experimental conditions of both SAE J2334 and NACE TM-01-69 tests were modified and various modified modes of the two tests were conducted.

It was found that the inconsistency in the test results was not a result of different chemical concentrations of chloride solution, different immersion times, testing periods, or testing temperatures. The inconsistency was attributed to the different moisture conditions and different properties of the two salts under high humidity environment. There are three basic moisture conditions in the three testing methods used in the project: dry, wet (saturated moisture), and dip (immersion). Since the $MgCl_2$ solution has higher viscosity and stronger hydraphilicity than the NaCl solution, it is much easier for the $MgCl_2$ solution to stick and crystallize on the surface of the metals under the dry condition, and then become solution on the metal surface under the wet condition. This dry-wet effect is responsible for the different corrosion behaviors of $MgCl_2$ under different testing conditions.

Therefore, depending on service conditions experienced by automobile components, $MgCl_2$ is more corrosive than NaCl under humid environments, and NaCl is more corrosive under immersion and arid environments. This conclusion was obtained based on the experiments with the deicing salts used in the state of Colorado.

Implementation
Study findings resulted in specification changes for deicing chemicals used by CDOT. The new specification on corrosiveness requires magnesium chloride used by CDOT to be no more corrosive than sodium chloride on aluminum and stainless steel as tested by the NACE TM-01-69 method.

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Corrosion Effects of Magnesium Chloride and Sodium Chloride on Automobile Components

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Abstract

Magnesium chloride has been used on the roads for anti-icing and deicing in Colorado for several years. Some concerns have surfaced that this chemical may have higher corrosion effect than sodium chloride. The objective of this investigation is to compare the relative corrosiveness of the two chlorides to the metals used in automobile components.

The project consisted of two phases. In the Phase I study, the relative corrosiveness of the two salts were examined by SAE J2334 test and ASTM B117 test. In the Phase II study, SAE J2334 test and NACE TM-01-69 Test (as modified by the Pacific North States) were applied. Representative metals examined in the project included stainless steel 410 and 304L, aluminum 2024 and 5086, coated automobile body sheets, copper wires, and mild steels.

Experimental results of SAE J2334 test indicated that $MgCl_2$ was more corrosive than NaCl to the bare metals tested. However, the experimental results of ASTM B117 test showed opposite conclusion: $MgCl_2$ was less corrosive than NaCl. Because of the conflicting conclusions, further tests were conducted using NACE TM-01-69 (as modified by the Pacific North States). Again, opposite conclusions were obtained from SAE J2334 and NACE TM-01-69 tests. In order to investigate the causes responsible for the inconsistence, the experimental conditions of both SAE J2334 and NACE TM-01-69 tests were modified and various modified modes of the two tests were conducted.

It was found that the inconsistence in the test results was not resulted from different chemical concentrations of chloride solution, not from different immersion times, testing periods, and testing temperatures. The inconsistence was attributed to the different moisture conditions and to the different properties of the two salts under high humidity environment. There are three basic moisture conditions in the three testing methods used in the project: dry, wet (saturated moisture), and dip (immersion). Since the $MgCl_2$ solution has higher viscosity and stronger hydraphilicity than the NaCl solution, it is much easier for the $MgCl_2$ solution to stick and crystallize on the surface of the metals under the dry condition, and then become solution on the metal surface under the web condition. This dry-wet effect is the main reason responsible for the different corrosion behaviors of $MgCl_2$ under the different testing conditions.

Therefore, depending on service conditions experienced by automobile components, $MgCl_2$ is more corrosive than NaCl under humid environment, and NaCl is more corrosive under immersion and arid environment. This conclusion was obtained based on the experiments with the deicing salts used in the state of Colorado.

Acknowledgements

Executive Summary

Statistics showed that road salt costs about $55 per ton, however, it causes about more than $1543/ ton worth of damage to vehicles, bridges, and the environment (Hudson, 1987). A recent study by CC Technologies Laboratories, Inc. in 2001 on corrosion related costs in the U.S. showed that $7.7 billion were used for corrosion resistant alloys, $8.3 billion/year for highway bridges, and $109 billion for epoxy coating; a total of 3% of Gross National Products (GNP) was spent in the U.S. for corrosion related problems (For more information: www.corrosioncost.com).

The Colorado Department of Transportation (CDOT) has been using $MgCl_2$ for anti-icing and deicing for several years. Some concerns have surfaced that the chemical may affect various components of cars and trucks. Most of the complaints pointed out that $MgCl_2$ tarnished or created spotting on vehicles. There are also concerns about corrosion that could lead to structural failure of vehicle components. This study, sponsored by CDOT, is aimed to answer the following questions: how stainless steel is affected; if $MgCl_2$ attacks Cr components; what the effect of $MgCl_2$ is on Al; how $MgCl_2$ affects electrical components; and whether there is a chemical reaction between the $MgCl_2$ and NaCl that are used in the sand and salt mixture.

The project consisted of two phases, the Phase I compared the relative corrosiveness of the two salts by SAE J2334 test and ASTM B117 test; in the Phase II study, another test – NACE TM-01-69 (as modified by the Pacific North States) was applied. In addition, modified SAE J2334 tests and modified NACE TM-01-69 tests were conducted. All test data were analyzed and compared.

The Phase I study started with an extensive literature review on the relevant information. Based on the collected information, two experimental methods and several types of metal specimens were selected for the experimental program of Phase I. Then, a comprehensive experimental study was performed. The metal specimens tested in Phase I were selected from the commonly used metal coupons used by the automobile industry, including stainless steel SS410 and SS304L, aluminum Al2024 and Al5086. In addition, a few coated coupons of automobile body sheet were also tested. Two testing methods were applied to the selected metals, one was SAE J2334, an accelerated cyclic test, and the other was ASTM B117, a continuous spraying test. The former was a typical cyclic corrosion test representing the in-service environments; the later provided a different corrosive environment and mechanism. In each of the two selected testing methods, two salts, i.e., sodium chloride and magnesium chloride, were used as corrosive medium, respectively. After the designated testing cycles or hours were reached, visual observation and weight loss analyses were conducted, and the difference in the corrosion of the metals caused by the two chlorides were compared.

Experimental results obtained by the cyclic exposure test (SAE J2334) on the bare metals indicated that $MgCl_2$ was more corrosive than NaCl. The rate of corrosion varied from metal to metal. For stainless steel SS410, the corrosion rate caused by $MgCl_2$ was 5 to 13 times higher than that by NaCl; for aluminum AL2024, the corrosion rate caused by $MgCl_2$ was one to two times higher. Experimental results obtained by the continuous spray test (ASTM B117) showed

inconsistencies when compared with the results of SAE J2334 test, especially for the stainless steel SS410, for which NaCl was more corrosive than $MgCl_2$.

The coated automobile body panels with the treatment of electroplating or hot-dip alloying exhibited very high corrosion resistance. No significant corrosion products were observed on the coupons even if the panels were scratched and the outer coating was damaged. Some coupons of coated cold roll sheets were also tested, which showed poor corrosion resistance.

As conflicting test results were shown in the Phase I study based on the two selected testing methods, the third test, NACE TM-01-69 (as modified by the Pacific North States), was applied together with SAE J2334 in the Phase II study to compare the corrosiveness of NaCl and $MgCl_2$. Again, conflicting test results were obtained: from SAE J2334, $MgCl_2$ is more corrosive than NaCl (consistent with Phase I); and from NACE TM-01-69, $MgCl_2$ is less corrosive than NaCl.

It is very clear that a consistent conclusion cannot be reached without a detailed study on the corrosion mechanisms involved in the selected testing method. Although both SAE J2334 and NACE TM-01-69 are cyclic corrosion tests, the experimental parameters used in the two testing methods are substantially different. In order to investigate the possible causes responsible for the conflicting results, the experimental parameters specified in the two testing methods were modified. For instance, the concentration of the chemical solution for SAE J2334 was changed, and the testing temperature, immersion time, testing period for NACE TM-01-69 were modified. A systematic experimental study by using the modified testing methods were conducted.

For the two deicing chemicals tested in the project, $MgCl_2$ has higher viscosity and higher hydraphilicity than NaCl. For the two testing methods used in the Phase II, SAE J2334 involves three conditions: dry, wet (saturated moisture), and dip (immersion in the chloride solution); and NACE TM-01-69 involves only two conditions: dry and dip. The systematic test results obtained in the Phase II showed that the differences in chemical concentration, immersion time, testing period, and testing temperature do not have significant effect on the high corrosiveness of $MgCl_2$ by SAE J2334, and that it is the combined effect of the wet condition (in SAE J234) and high viscosity and hydraphilicity of $MgCl_2$ that leads to the high corrosiveness of $MgCl_2$. Because of the high viscosity of $MgCl_2$ solution, it is much easier for the $MgCl_2$ to stick on the surface of the coupons and crystalline under the dry condition; because of the high hydraphilicity of $MgCl_2$, the crystallined $MgCl_2$ turns base into solution under the subsequent wet condition, which leads to high corrosion rate on the metals.

Therefore, depending on the service conditions experienced by automobile components, $MgCl_2$ is more corrosive than NaCl under humid environment, and NaCl is more corrosive under immersion and arid environment. This conclusion was obtained based on the experiments with the deicing salts used in the state of Colorado.

Implementation Statement

Various impacts of magnesium chloride on the safety of transportation, highway maintenance, durability of infrastructure, and the environment are very complicated and closed related issues. This study focused only on a very specific topic. More comprehensive and systematic studies will be necessary and important for evaluating the overall performance of the deicing chemical.

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Part I: The Phase I study

1. Background

The Colorado Department of Transportation (CDOT) has chosen what they consider to be the most effective and cost efficient chemical deicer, magnesium chloride ($MgCl_2$), to apply on Colorado's roads and highways. In conjunction with magnesium chloride, CDOT also uses a dry mixture of sodium chloride and sand in certain areas of the state. Liquid magnesium chloride is used as both an anti-icing and a deicing agent. Some trucking companies believe the use of magnesium chloride has led to increased vehicle maintenance costs and may cause an increased risk to vehicle safety. Because of the nature of the industry and customer demands, trucks are counted on to deliver freight regardless of road and weather conditions. Additionally, trucks often travel the same route on a daily basis, and subsequently encounter a higher level of chemical deicers than many passenger cars.

Anecdotal information provided by Colorado trucking companies revealed widespread belief that magnesium chloride is responsible for excessive pitting and corrosion, increased vehicle maintenance and cleaning costs, accelerated metal component wear, breakdown of electrical systems, and increased safety risks due to loss of visibility, wet highways, and affected brake systems.

In response to these concerns, the CDOT Research Division agreed to sponsor this study to investigate the effect (if any) liquid magnesium chloride has on vehicles in Colorado. It is hoped the private sector will benefit from the identification of causal factors, costs, and solutions regarding the use of liquid deicers. The public sector will benefit from testing, under laboratory and real-world conditions, the impact upon vehicle components caused by current deicing methods. Additional benefits include the opportunity for industry and government to work together toward creating solutions and building a viable partnership for the future.

The American Trucking Associations Foundation (ATAF) and the University of Colorado (CU) were contracted by the CDOT Research Division to investigate the impacts of deicers on commercial vehicles. This study included both qualitative research conducted by the ATAF, and laboratory analysis, which was conducted by the Department of Civil, Environmental and Architectural Engineering, the University of Colorado at Boulder. The Research Team (ATAF and CU) also worked with the trucking industry to identify specific concerns and perceptions from the use of magnesium chloride.

The goals of the study were to conduct experimental testing of the effect of magnesium chloride on the metals most commonly used in manufacturing trucks. Representative metals were selected from the automobile industry to compare corrosion behaviors after exposure to two deicing salts - sodium chloride (NaCl) and magnesium chloride ($MgCl_2$). Metals were selected from conventional coupons used in automobile and steel industries, which do not include mild steel. The main concern was the corrosion behavior of aluminum and alloy steel (especially stainless steel) and various coatings. Additional information was collected from CDOT and other state transportation departments in the Western U.S. to further investigate deicing procedures and methods. Information was also collected directly from trucking companies to determine

perceptions and opinions on whether the use of magnesium chloride affects trucks and trucking operations in Colorado. The issues addressed in the study included:

- How stainless steel is affected;
- If $MgCl_2$ attacks Cr (chromium) components;
- What the affect of $MgCl_2$ is on Al (aluminum);
- Is a mixture of MgCl2 and NaCl more corrosive than either chemical alone?
- How $MgCl_2$ affects electrical components;
- Identifying the concerns/problems trucking companies attribute to deicer use;
- Documenting and analyzing the costs and benefits to the trucking industry from the use of deicers;
- Identifying the costs and benefits of various deicers used by CDOT;
- Identifying and evaluating possible alternatives to current deicers and evaluating possible alternatives to current application methods and processes.

2. Literature Reviews

2.1 Corrosion Theory of Metallic Materials

Pure metals and their alloys tend to enter into chemical union with the elements of a corrosive medium to form stable compounds similar to those found in nature. When metal loss occurs in this way, the compound formed is referred to as the **corrosion product**, and the metal surface is spoken of as being **corroded**. Corrosion is a complex phenomenon that may take any one or more of several forms. It is usually confined to the metal surface, and this is called **general corrosion**. But it sometimes occurs along grain boundaries or other lines of weakness because of a difference in resistance to attack or local electrolytic action, this is called **localized corrosion** (Perry and Chilton 1973). Localized corrosion includes:

Intergranular Corrosion: Selective corrosion in the grain boundaries of a metal or an alloy without appreciable attack on the grains or crystal. Austenitic stainless steels and some aluminum alloys, when improperly heated, become susceptible to intergranular corrosion because of the precipitation of intergranular compounds.

Stress Corrosion: Corrosion can be accelerated by the applied stresses.

Galvanic Corrosion: A corrosion rate that is faster than usual, which is associated with the flow of current to a less active metal (cathode) in contact with a more active metal (anode) in the same environment.

Crevice Corrosion: It occurs within or adjacent to a crevice formed by contact with another piece of the same or another metal or with a non-metallic material. This form of corrosion can result because of a deficiency of oxygen in the crevice, acidity changes in the crevice, buildup of ions in the crevice, or depletion of an inhibitor.

Pitting Corrosion: It develops in highly localized areas on a metal surface.

According to the electrochemical theory, a complete corrosion reaction is divided into an anodic portion and a cathodic portion, occurring simultaneously at discrete points on metallic surfaces. The flow of electricity from the anodic to the cathodic areas may be generated by local cells set up either on a single metallic surface (because of local point-to-point differences on the surface) or between dissimilar metals. When a solution exists, electrons are captured by the cation in the solution, which causes the movement of electrons to continue. The active metal gradually becomes ionic and dissolves into the solution. By this time, we consider that the metal is corroded. Taking the corrosion of iron as an example, the following are the chemical reactions involved in the corrosion process:

1). At anode, iron ions enter solution in the form:

$$2Fe \rightarrow 2Fe^{2+} + 4e \qquad (1)$$
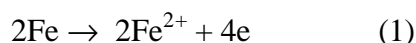
2). At cathode, the hydrogen ions in water accept electrons:

$$4H^+ + O_2 + 4e \rightarrow 2H_2O \qquad (2)$$
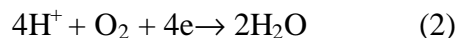
3). Ions of iron combine with OH ions in water to form $Fe(OH)_2$:

$$2Fe^{2+} + 4OH^- \rightarrow 2Fe(OH)_2 \qquad (3)$$
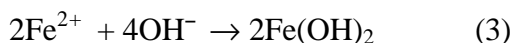
4). $Fe(OH)_2$ is further oxidized into $Fe(OH)_3$:

$$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3 \qquad (4)$$
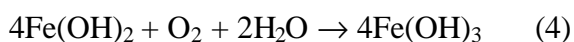
2.2 Corrosion of Metallic Materials Caused by Deicing Salts

According to the adsorption theory, Cl^- adsorbs on the metal surface in competition with dissolved O_2 or OH^- . Once in contact with the metal surface, Cl^- favors hydration of metal ions and increases the ease with which metal ions enter into solution, opposite to the effect of adsorbed oxygen, which decreases the rate of metal dissolution. In other words, iron and stainless steel are not readily passivated anodically in solutions containing an appreciable concentration of Cl^-. Breakdown of passivity by Cl^- occurs locally rather than generally over the passive surface. As results, minute anodes of active metal are formed surrounded by large cathodic areas of metals. There is a potential difference between the two areas, and thus resulted cell is called a passive-active cell. This cell will lead to pitting corrosion.

Chloride ions do not chemically react with the metals. Chloride ions only assume a role as a medium or catalyst in the electrochemical process. Chloride anions in the solution could help to remove the metal cations accumulated on the anode by forming soluble compounds, and this contributes to an accelerated anodic reaction and thus faster rusting of the metals. This hypothesis is supported by the research of Ambat and Dwarakadasa (1993), who found the concentration of chloride had great effect on the corrosion rate of aluminum alloys in the region of neutral pH. They considered that the strong dependence of the corrosion rate of aluminum on chloride ion concentration in a neutral environment may be explained by the adherent oxide film that is present on the surface of the alloy. In such cases, the presence of chloride ions can accelerate the corrosion by retarding film repair. At the film/solution interface, chloride ions lead to a local thinning of the passive layer and to pitting corrosion.

Since the oxide film on the surface of the aluminum is soluble in both low and high pH solutions, the change of pH has a great influence on aluminum corrosion. This influence is profound because the solutions of NaCl, $CaCl_2$, $MgCl_2$ and so on have different pH values even with the same weight percentage concentration.

The presence of chloride ions from the deicing salts in solution can create extensive localized attack by their adsorption on weak parts of the oxide film on the surface of metals, thus forming soluble complexes. This process can be further accelerated by several microstructural features of the alloy. The presence of other ions such as OH^-, SO_4^{2-}, and CO^{2-} in solution and factors such as pH and temperature, can all lead to accelerated corrosion (Srivatsan et al. 1989).

Chloride ions breaks down passivity or prevent its formation on the surfaces of iron and stainless steel. From the point view of the oxide film theory, Cl^- ions penetrate the oxide film through pores or defects easier than other ions, because of their small size and great mobility. Or Cl^- may colloidally disperse the oxide film and increase its permeability. There is another mechanism about Cl^-: when chloride ions are present in the solution, ferrous chloride will be formed at the anode and sodium hydroxide at the cathode. These two products will then react to form ferrous hydroxide and sodium chloride. The ferrous hydroxide is then oxidized into the rust.

2.3 Inhabitation and Inhibitors

There are several classes of inhibitors. In highway applications, passivators and organic inhibitors are usually incorporated into the deicers.

Most of the passivators are inorganic oxidizing substances, including chromates (CrO_4^{2-}), nitrites ($NO2^-$), or molybdates (MoO_4^{2-}). They can also be organic substances such as benozoate (C_6H_5COONa) and cinnamate ($C_6H_6^.CH^.CH^.COONa$). They can passivate the metal and reduce the corrosion rate. They can further be divided into anodic inhibitors and cathodic inhibitors. Anodic inhibitors are those chemicals that function by stifling the reaction at the anode, while cathodic inhibitors act at the cathode but not as effective as does the anodic inhibitors.

The organic inhibitors work in a different way. They usually form a multilayer protective film by physical adhesion on the surface of the metal and prevent the corrosive ions from contacting to the metal. Some organic inhibitors, such as pickling inhibitors, function by forming an adsorbed layer on the metal surface, probably no more than a monolayer in thickness, which essentially blocks discharge of H^+ and dissolution of metal ions. Compounds serving as pickling inhibitors require a favorable polar group or groups by which the molecule can attach itself to the metal surface. These include the organic N, amine, S, and OH groups.

The concentration of corrosion inhibitors must exceed a certain critical value. Below this concentration, passivators behave as active depolarizers and increase the corrosion rate at localized area (formation of microcell). It is similar to the chromium content in stainless steel, corrosion occurs in a stainless steel if the chromium content of the steel is too low. The critical concentration for CrO_4^{2-}, NO^{2-}, MoO_4^{2-} is about 10^{-3} to 10^{-4} M. Chloride ions and elevated temperatures increase the critical concentrations. At 70 to 90°C, for example, the critical concentration of CrO_4^{2-} and NO^{2-} become 10^{-2} M. For this reason, it is important to maintain the concentration of passivators above the critical values. For organic inhibitors, the concentration should also be higher than the critical value to facilitate the formation of the multilayer protective film.

2.4 Corrosion Research in the Automotive Industry

Statistics showed that road salt costs about $55 per ton, and its use results in more than $1543/ ton worth of damage to vehicles, bridges, and the environment (Hudson, 1987). As early as the 1960's, Jameston (Cargill Inc. 1968) investigated the effect of inhibited deicing salt on corrosion rates of metals used in automobiles by performing tests under driving conditions. Redmerski et al. (Colt Industries 1978) studied the corrosion behavior of metals in automotive trim applications. The tested materials included stainless steels, stainless clad aluminum, and anodized aluminum. The experiment by Redmerski et al dealt with the behaviors of the different metals under same corrosion condition. It did not compare the corrosiveness of different chemicals.

Gluszek and Nitsch (1982) determined the susceptibility to stress cracking corrosion and pitting corrosion of 304L steel in boiling NaCl, $CaCl_2$ and $MgCl_2$ solutions at 5N concentration. They found the order of corrosiveness of the solutions was $NaCl > CaCl_2 > MgCl_2$, with pHs of 7.0, 6.3 and 5.4, respectively. This conclusion, however, cannot be applied to other occasions, since boiling reduces the role of oxygen in the corrosion process. For the corrosion of automobile metals, oxidization of steel should be the first mechanism and chloride is only one of the participators in the electrochemical process.

Tarutani et al. (Sumitomo Metal Industries 1991) studied the performance of ferritic stainless steels for automobile muffler corrosion. They examined the corrosion behavior of ferritic stainless steel (409L and 410L) in artificial exhaust gas condensates containing corrosive ions such as Cl^- and SO_4^{2-}. The test results clarified that Type 436L ferritic stainless steel, the material for the automobile muffler, exhibited acceptable corrosion resistance.

Koyama and Sakauchi (Australia 1982) proposed a test method for evaluating the chipping resistance of outer panels. It was reported that the test affords superior accuracy and repeatability as well as excellent applicability for quantitative evaluation of the corrosion resistance. In 1990, the Society of Automotive Engineers (SAE) published a standard road test procedure (SAE J1293) for comparing the corrosion resistance of both coated and uncoated sheet steels in an undervehicle deicing salt environment. Whitton (Ford Motor 1995) presented a report on their research results on vehicle component corrosion resistant coatings and test methods comparison. The corrosion resistance of the coating was evaluated on automobile automatic transmission oil pans. Three test methods, including salt spray, accelerated corrosion test track testing and customer vehicles, were evaluated. The most informative and most severe test method was found to be the accelerated corrosion test track method.

Androsch (Voest-Alpine 1995) investigated the corrosion behavior of various coating systems in different types of automotive corrosion tests. He found that for the same site, test and coating type, the creepage results could differ significantly, depending on which season the exposure began.

Bednar et al (AK Steel Corp. 1995) researched the corrosion behavior of automotive body panels in normal vehicle service under severe conditions of intense deicing salt usage. The study included, in addition to visual evaluation and rating of doors, a metallographic

investigation of the manner of paint coating failure on steel and zinc/zinc-alloy coating substrates and the corrosion behavior of metallic coatings.

Altmayer (Scientific Control Laboratories 1996) provided guidelines to assist in choosing the most appropriate accelerated corrosion test for a given application. Simpson et al. (Bethlehem Steel 1998) introduced US automotive corrosion trends over the past decade. The paper reported the results of five surveys conducted to date. The surveys, consisting of closed car parking lot surveys checking for perforation, blisters, and surface rust, were carried out in the Detroit, Michigan area. More recently, the research group published another article on a license plate corrosion test (Townsend et al. 1999). They mounted coupons on the vehicles, and the conditions of the scribe creep of the coupons are given in Table 1.

The corrosiveness of deicing salts to the automobile was studied mainly based on commonly used NaCl and $CaCl_2$. Other salts were hardly investigated in experiments. We found that the only research dealing with different deicing salts in automobile industry was by McCrum (1989). In the study, calcium magnesium acetate (CMA), sodium chloride and magnesium chloride were used in highway and bridge structures. The corrosiveness of these salts was compared. McCrum found that CMA was definitely less corrosive than NaCl or $MgCl_2$, and rust inhibitor mix could provide superior (less) corrosion performance over distilled water.

We can also find some useful data regarding the corrosiveness of $MgCl_2$ and NaCl to the metal materials. The data in Table 2 is from the *Chemical Engineers' Handbook (5th Edition).* This data, obtained from unidentified test procedures, indicate that there is no obvious difference between the corrosiveness of the two chlorides to the materials.

Table 1: Scribe Creep Results in Canada On-vehicle Tests (mm)

Materials	1 year	2 years	3 years	4 years	5 years
EG30	0.8	1.4	2.2	3.7	5.4
EG70	0.7	0.8	1.1	1.2	1.9
GA67	1.0	1.0	1.0	1.4	1.6
Zn44	1.5	1.7	2.0	2.4	3.2
CRSB	3.0	8.6	12.5	17.4	23.4

Table 2: Corrosiveness of MgCl$_2$ and NaCl to some materials (inch/year)

Materials	MgCl$_2$	NaCl
Al	**<0.005** (10%, 75°F)	**<0.005** (10%, 75°F)
Copper, Al Bronze, Tin Bronze	**<0.02** (10%, 75°F)	**<0.02** (10%, 75°F)
Stainless Steel (12% Cr)	**<0.02** (10%, 75°F)	**<0.02** (10%, 75°F)
Stainless Steel (17% Cr)	**0.02~0.05** (10%, 75°F)	**<0.02** (10%, 75°F)
Glass	**<0.005** (25%, 225°F)	**<0.005** (30%, 225°F)
Polyethylene	Complete resistance (50%, 150°F)	Complete resistance (25%, 125°F)
Polyvinyl Chloride, unplasticized	Complete resistance (25%, 150°F)	Complete resistance (25%, 125°F)
Butyl Rubber	Satisfactory (25%, 75°F)	Satisfactory (25%, 75°F)

2.5 Research Activities on Deicers

Recent studies on the nature of liquid magnesium chloride as an anti-icer for winter highway maintenance is a topic of great interest throughout the United States, Canada and Europe. Major themes in the literature center around the benefits of using liquid magnesium chloride for winter road use versus other forms of materials such as rock salt (Thunder Sword Resources, Inc., 1988). The benefits listed in most of the research on liquid magnesium chloride include its efficiency in use, lower maintenance costs to state and federal authorities, and the assurance of a better method of protecting the environment. Other products currently in use have been known to cause considerable harm to the environment.

The Department of Geological and Atmospheric Sciences at Iowa State University verified the contribution of rock salt deicers as a corrosive material on highways and a cause of groundwater contamination (Cody, R.D. et al). The study conducted by the Center for Transportation Research and Education (CTRE) noted a "considerable interest in new deicers, especially magnesium chloride because of its anti-icing properties and its effectiveness at lower temperatures than rock salt, and calcium magnesium acetate because it reduces steel corrosion and groundwater chloride contamination" (Ibid., p. 4).

Other important benefits reflected in the most recent research include effects on air quality. "Another stimulus for switching to liquid deicers is new air quality guidelines in the U.S. which regulate the level of fine particulates in the air. This restricts the use of sand/salt mixtures which tend to increase the level of airborne particulates." (Thunder Sword Resources, Inc., 1988). This is vital for states such as Colorado that use sand and other abrasives which contribute to "20% of Denver's persistent winter air quality problems" (Federal Highway Administration).

Evidences of the stimulus of state governmental agencies to work closely with federal agencies to further investigate snow and ice control on roadways are visible in various case studies developed by the Strategic Highway Research Program (SHRP) (Federal Highway Administration). The Strategic Highway Program is a project established by Congress in 1987 to develop and evaluate innovative technologies for roadway construction, maintenance, and operations in cooperation with the Federal Highway Administration (http:// www.ota.fhwa.dot. Gtov/roadsvr/). Some of the states conducting research on anti-icing techniques include Colorado, Kansas, Iowa, Washington, Missouri, and Oregon. The University of Nevada-Reno prepared summary reports of the findings of the SHRP/FHWA anti-icing studies based on a benefits-versus-cost analysis developed by the Texas Transportation Institute, of the research completed on this particular project (Federal Highway Administration, 1998). Similar to a majority of the studies conducted by various state and federal agencies, the main focus of the research was to highlight the benefits of liquid magnesium chloride coupled with a road weather information system. Little is mentioned in the reports of the effects of corrosiveness on the roadways or other chemical problems associated with the use of the product.

The Federal Highway Administration's field evaluation tests on liquid magnesium chloride performed by the U.S. Army Corps of Engineers Cold Regions Research and Engineering laboratory also provided positive results concerning this product as a deicer and non-corrosive agent (U.S. Army Cold Regions Research and Engineering Laboratory, 1996). This study is vital because the research eventually led to the publication of the Federal Highway Administration's Manual of Practices for an Effective Highway Anti-Icing Program (Federal Highway Administration, 1997). Private companies in Canada also contributed to the literature by conducting studies on accident occurrences using liquid magnesium chloride compared to traditional salting and sand (Insurance Corporation of British Columbia, 1998). The findings stated that new methods of deicing had reduced the number of road accidents by 75% (Thundersword Resources, Inc., 1998).

Other important studies were developed by the SALT Institute. Although somewhat dated, the Snowfighter's Handbook is still considered a viable source for studies in relation to snow and ice control (SALT Institute, 1991).

We can look to the future of the research to be a focus on environmental concerns. A consortium was developed between Washington, Oregon, Montana, Idaho, and British Columbia to "develop specifications for chemicals related to snow and ice control" (Thundersword Resources, Inc., 1998) and also address environmental issues based on public interest.

2.6 Standards of Corrosion Testing

2.6.1 ASTM standards
In general, the objective of an accelerated test is to create the degradation phenomena in a period of time shorter than the natural period, without changing the failure mechanisms. In particular, for metal corrosion the acceleration can be accomplished using various electrochemical techniques. Different accelerated testing methods have been developed, such as simple immersion tests, cabinet tests, simulated service tests, and in situ field service tests. The

ability to predict actual service performance based on test results of a specific testing method increases with the length and the degree of complexity of the test.

The oldest and the most widely used standard laboratory corrosion test is the ASTM Method of Salt Spray (Fog) Testing (B117). According to this standard, specimens are exposed to a constant mist/spray of aerated, neutral pH, 5 wt. % NaCl solution. Specimens are exposed for several hundred hours.

A project about accelerated laboratory testing methods conducted by Alcoa Center was about painted aluminum automotive body sheets (Moran et al. 1995). Ten test methods and six materials were used in this study, including aluminum alloys 2036, 2008, 6111, 5182, and steel 1008 with and without coating. The results showed that the test method which correlated best with the outdoor exposures was ASTM B117, the continuous salt spray method.

2.6.2 Accelerated Corrosion Test Methods in the Automobile Industry

Corrosion testing is an important part in the development, selection, and qualification of coated metal sheet products for corrosion-resistant automobiles. Although most of the reliable corrosion data comes from long-term monitoring of the performance of road-driven vehicles, the time and cost for these long-term tests are very high. On the other hand, laboratory accelerated corrosion tests are relatively quick and inexpensive, but are often of questionable reliability. For example, test results from the salt spray test (ASTM B117) have shown poor correlation with service performance of steel sheets. This is because the corrosion mechanisms occurring in a continuously wet salt-spray cabinet are significantly different from those taking place in the wet and dry conditions experienced by road-driven vehicles (Doppke, and Bryant, 1983; Money, and Kain, 1988).

In the last two decades, much effort has been made to develop a laboratory test method for cosmetic corrosion of painted panels that can realistically simulate the in-service exposure. Various multi-stage cyclic testing methods (e.g., alternating salt and humidity exposures) have been developed and compared to the salt spray method (ASTM B117).

From 1990 to 1995, AISI and SAE carried out a comprehensive, cooperative research program to correlate various testing methods including ASTM standards and other methods used in the automobile industry. In the program, the accelerated and outdoor exposure tests were compared to four-year on-vehicle exposure tests from Montreal, Quebec and St. John's, Newfoundland, Canada using a variety of statistical techniques. Of the 28 test procedures compared, CCT-IV and GM9540P/B provided the best overall performances for the ten "standard" coated sheet materials, which has been widely used in corrosion studies throughout the automotive community.

CCT-IV is a cyclic testing method, consisting of three different environmental conditions: salt spray per ASTM B117, dry-off at 60°C and ambient relative humidity (RH), and humidity at 60°C and 95% RH. Salt spray is applied for ten minutes, followed by 155 minutes of dry-off, and 75 minutes of humidity. Then, five repetitive cycles of 160 minutes dry-off and

80 minutes humidity complete the 24 hour cycle. The total exposure time is 50 cycles (five cycles per week and weekends at ambient conditions).

GM9540P/B is a GM standard, in which the first part consists of eight hours exposure to ambient conditions, with five min. salt spray period at the first four 90 minutes time intervals. Spray was applied manually using a spray bottle. The second part is a high humidity exposure (49°C, 95% RH) for eight hours. The third part provides an eight hour exposure at 60°C, and less than 30% RH. Total exposure period was 40 cycles (5 cycles per week, weekends at ambient lab conditions).

Another project about accelerated laboratory testing methods conducted by Alcoa Center was about painted aluminum automotive body sheets (Moran et al. 1995). Six materials were used in this study, including aluminum alloys 2036, 2008, 6111, 5182, and steel 1008 with and without coating. The results showed that the test method which correlated best with the outdoor exposures was ASTM B117, the continuous salt spray method. This study confirmed that the two lab methods favored by SAE for evaluating steels were GM9540P/B and CCT-IV. For aluminum alloys, however, these two test methods are not optimal.

Cyclic corrosion tests involving repeated exposure to salt water, humidity, and drying conditions have been developed to overcome some of the deficiencies of the salt spray test. Many types of cyclic tests have been developed, and the results vary significantly. Moreover, the effects of the various cyclic-test parameters such as time, temperature, relative humidity, and salt composition were not well understood. Therefore, there was a pressing need for improving and standardizing the laboratory cyclic corrosion test. For this purpose, a corrosion task force was organized and funded by AISI and SAE. In 1995, funding of the Task Force was taken over by the Auto/Steel Partnership (A/SP), a consortium of North American automobile and steel producers. This joint work led to the successful development of a new cyclic cosmetic corrosion test, designated as SAE J2334 (Townsend et al. 1998).

On-vehicle cosmetic corrosion tests were performed in Canada during the research program. Montreal, Quebec and St. John's, Newfoundland were chosen for on-vehicle tests since these environments are known to be among the world's most corrosive. Performance of the materials was determined after a five-year exposure by removing loose paint next to the scribed region of the panels, and measuring the extent of paint undercutting.

Table 3: Ranking of Cosmetic Corrosion Test Methods

Test	Duration	R^2	C	Sum
SAE J2334	80 cycles	0.96	0.97	1.93
CCT-IV	35 cycles	0.74	0.86	1.60
GM9540P/B (GM)	50 cycles	0.84	0.59	1.43
B117 Salt spray	4 weeks	0.19	0.05	0.24

Many cosmetic corrosion test methods were evaluated in the research program. These test methods included laboratory, automotive proving ground, and static outdoor scab tests. To quantitatively compare the results of these tests to those obtained from the real-world, a least-squares linear regression method was adopted and part of the results are shown in Table 3. In the

Table, R is the correlation coefficient, and R^2 indicates the fraction of the variation that is accounted for by the least-squares line. The closer R^2 is to unity, the more the lab test data and the real world experimental data agree. Another coefficient C in Table 3 is the ratio of the real creep of the tested materials to the value of creep that would be predicted by the least-squares line. An ideal test would have a R^2 of one and a C of one, and the sum R^2+C would be equal to two. From the Table, it is clear that SAE J2334 test is a significant improvement over existing tests. It is also noted that the ASTM B117 salt spray test results do not correlate well with real-world performance.

Corrosion mechanisms were analyzed by using equipment such as light microscopy, scanning electron microscopy, energy dispersive X-ray mapping, X-ray diffraction, and Mossbauer spectroscopy. The results showed a good match of the corrosion products and morphologies of attack for SAE J2334 and the on-vehicle tests, thus providing a strong fundamental basis for the correlation of the corrosion-test results.

3. Surveys and Interviews with Road Maintenance Departments and Trucking Companies
(This section of the report was prepared by Dr. Patricia Olsgard, formerly of the American Trucking Association Foundation)

3.1 Survey of Colorado Trucking Companies

The American Trucking Association Foundation developed a two-page survey to determine the level of concern among the trucking industry regarding the use of magnesium chloride on Colorado's highways. The survey was pilot tested and refined prior to being faxed to more than 150 trucking companies with operations in Colorado. These companies were asked to provide information relating to costs, safety issues and general opinions/attitudes concerning Colorado's use of magnesium chloride.

Trucking companies were identified from two main sources: the membership of Colorado Motor Carriers Association, and the National Motor Carrier Directory. Fifty-three surveys were returned, providing a response rate of 34.8%. This response rate is very acceptable for a single mailing, voluntary response survey.

The survey was divided into three sections: company information; vehicle wear attributed to magnesium chloride; and general questions regarding Colorado's use of magnesium chloride.

3.2 Survey Results

Of the companies that responded to the survey, 80% were for-hire companies (hired to carry freight). Private trucking companies (haul primarily company goods) represented the remaining 20% of the respondents. Companies reported an average of 62% of total fleet miles was driven within Colorado. While many of the companies were interstate carriers, 33 of the respondents reported being intrastate or pickup/delivery carriers. Additionally, the trucking companies that responded operate in all areas of the state, with a concentration on the I-25/front range corridor.

Seventy-two percent of the respondents reported noticing increased wear on their equipment since Colorado began using magnesium chloride. Twenty-eight percent reported no problems associated with the use of magnesium chloride.

Companies reported the most damage to chrome, tractor or trailer bodies, aluminum parts, wheels, hoses and connectors, and electrical parts. The specific type of damage mentioned most often included corrosion, pitting, staining/tarnishing, discoloration, drying/cracking (hoses), and accelerated rust.

Chrome, aluminum parts, and electrical wiring were reported to have received heavy damage requiring replacement. However, 25% of respondents reported no damage to electrical wiring or chrome, indicating certain types of wiring/connections and chrome may be more susceptible than others to damage.

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Fifty-three percent of the companies reported they have not changed their procedures to limit vehicle damage caused by magnesium chloride or other deicing methods. Those companies that have implemented changes to their operations to limit or repair damage caused by deicing primarily increased the frequency of vehicle washing. On average, these companies increased the frequency of truck washing by 28% in the months that magnesium chloride is used. In addition to increasing the number of washings, 62% of companies reported magnesium chloride was difficult to remove requiring more labor, additional brushing, and stronger cleaning chemicals to eliminate the residue.

General attitudes about the benefits of magnesium chloride were mixed. A narrow majority of respondents do *not* believe that the use of magnesium chloride has made truck driving less safe or affected the safety of their equipment. Companies which disagreed cited such reasons as: magnesium chloride sticks to the highway even when there is no snow so the highways are continually wet; magnesium chloride creates a film on the windshield that is difficult to remove and impairs visibility; and magnesium chloride corrodes electrical connections which lead to electrical failures. Eight respondents reported that increased electrical failures affected vehicle safety.

The majority of respondents (62%) believe that magnesium chloride has *not* reduced the number of winter road closures in Colorado. A similar majority also prefers previous methods of deicing (primarily salt/sand mixtures) to the current methods used by CDOT.

Companies were asked to quantify the costs they associated with the use of magnesium chloride. Eighteen companies detailed costs relating to increased maintenance, accelerated parts/wiring replacement, etc. The total annual cost associated with those 18 companies was over $260,000, with an average annual cost per company of $14,500. Twenty-five companies detailed annual costs associated with additional truck washing (including different/extra chemicals, additional labor, etc.) totaling nearly $200,000, with an average annual cost per company of $8,000.

Thirteen companies further detailed costs relating to the use of magnesium chloride. The average cost per company per year is presented as a general reference to the types of costs motor carriers are attributing to the use of magnesium chloride, associated with various truck components.

Paint:	$13,000
Chrome:	$48,000
Tractor/Trailer body:	$ 6,950
Aluminum parts:	$ 7,050
Other metal parts:	$ 1,890
Lights:	$ 4,546
Windshield:	$ 682
Tires:	$ 2,000
Wheels:	$ 6,850
Hoses:	$ 1,080
Wiring:	$ 4,244

3.3 Interview of Other States

Interviews were conducted with winter road maintenance departments in twelve western states. Information was collected about winter road maintenance, deicing/anti-icing procedures, application methods, budgets, research plans and other topics regarding magnesium chloride. The results of those interviews are summarized below.

The information below reflects statements made by DOT employees in other states, and many include opinions. The statements were not substantiated through this research project, and do not reflect the opinions of the Research Team.

Colorado:

We use magnesium chloride with a low thermal inhibitor because it lasts 30% longer than the salt/sand method and is more environmentally friendly. It reduces the air and water pollution and it helps prevent road closures. We use about four million gallons statewide per year, and we are cutting back on using sand. Magnesium chloride is the most cost effective at 30 cents a gallon.

Colorado uses a mixture of 27–30 wt.% magnesium chloride and 70–73 wt.% water. Magnesium chloride is a trade off—it causes sloppy messes but we do not have the ice buildup on roads we used to have. We do have to continually monitor and clean road signs because the magnesium chloride causes a build-up of grime. Magnesium chloride "locks" down fine materials, whereas road-sanding produces dust particulates, affecting the environment and causing pollution. Rock salt used in sand mixes with the magnesium chloride and is more corrosive.

We are experimenting with "Ice Slicer", which is a granular product. It involves using 1/3 less product and requires no sweeping. It is very expensive ($75 per ton) but keeps the roads wet. We used Ice Ban for a while. It worked well, but it costs two to two and one-half times more than magnesium chloride. It also has a high phosphorous level, which caused higher algae growth.   We are now testing Calabran M 1000 (an alcohol-based solution), which works better than magnesium chloride in colder weather and is less corrosive. However, it is two to two and one half times more expensive than magnesium chloride, at a cost of about 75 cents per gallon. CDOT's average annual maintenance budget is $2.5 million. In 1999, CDOT spent $627,000 on salt/sand and $300,000 on magnesium chloride.

CDOT used to have a lot of chipped paint and windshield damage complaints when we used the salt/sand mixture. The biggest complaint we hear with the magnesium chloride is the continual water spray from wet highways and that it is hard to clean off vehicles. We have a training manual for our maintenance crews. We stress safety and customer service. We use PowerPoint slides as a learning tool. One of the things we teach is that we don't anti-ice on curved highways because of the difference in skid resistance.

California:

Most of the products we use are for anti-icing and anti-frosting. We use magnesium chloride, rock salt and salt brine, depending on the area. Once we explained to the public that the magnesium chloride had reduced the number of accidents, the public was more receptive. We use 28-38 gallons per lane mile. We make our own tanks and we spread it based on gear speed. We have 15 spray tanks to cover 1,700 miles of road.

Our magnesium chloride costs 50 cents per gallon. It is supposed to be equal in corrosion to salt/sand but the mist from magnesium chloride is more noticeable since it covers the entire vehicle.   We do not use magnesium chloride as a bond breaker. With magnesium chloride we'll go 5 to 7 days between applications, compared to daily applications of rock salt.

We also use a lot of salt brine since it is much cheaper (6 cents a gallon). We purchased two salt brine-mixing machines and mix it ourselves.   We are presently experimenting with Freeze Guard and PCI—both products have a corrosion inhibitor.

Idaho:
Magnesium chloride is our primary anti- and deicer but we also use a sand/salt mixture (5% salt). We have been using magnesium chloride for a few years and it is working well.   We wanted more of an anti-icing product than we got with salt/sand, so we switched to magnesium chloride.   It is a growing program as we are adding more roads to our deicing system, and magnesium chloride seems to be more cost effective.

We have had some complaints about our deicers pitting and corroding aluminum parts, sticking to the windshields and being difficult to remove. We have also had complaints that when magnesium chloride with an inhibitor was first applied at the beginning of the season, it created slick conditions on the highways.   We are researching this using a skid meter. Additionally, we are researching to see if different structured highways and traffic volumes make a difference when magnesium chloride is put down.   Our annual road maintenance budget is around $50 million, $13 million of which is our anti/deicing budget.

Kansas:
We use salt, pre-wetted salt and salt brine for both anti- and deicing. We use magnesium chloride with a corrosion inhibitor only in the Kansas City Metro area where there is heavy traffic volume and large structures. Kansas has an abundance of salt so it is more cost effective (less than 3 cents a gallon) than any other deicers on the market. In some instances we use pure salt, but other times we mix three parts sand to one part salt.

We did try Ice Ban with a corrosion inhibitor along with the salt brine but we had a lot of complaints about how slimy it was and how it stuck to the vehicles. Our staff did not like using it either because of the offensive odor. Lab tests showed Ice Ban did reduce corrosion of the salt but it did not drop the effective temperature of the salt. Ice Ban is also more costly per gallon.

Montana:
Magnesium chloride is used in the urban areas, and a combination of magnesium chloride and salt/sand is used elsewhere. We use 2 ½-5% salt in stockpiles to provide traction. We use approximately 2 ½ million gallons of magnesium chloride by winter's end. Magnesium chloride

is a trade-off between cosmetics and traction. It could save lives, which is invaluable.   We have been using magnesium chloride since 1993 and most of our complaints are about corrosion of "after market" items that are not clear coated. Aluminum wheel damage seems to be the biggest complaint.

Our sand trucks are equipped with side tanks filled with liquid chemical. We inject the sand with this liquid chemical. The abrasive, wetted down with the liquid chemical, keeps the sand from being thrown to the side of the track—making a sandpaper effect. It isn't thrown from the wheel path, reducing both windshield damage and dust/pollution.

We quit using salt/sand mixtures because of environmental issues.   Magnesium chloride provides better air quality and performance. Anything we use has to be 70% less corrosive than salt. We use salt brine on steel for testing and comparison purposes. We found calcium chloride to be more corrosive than the other products we have used.

Nebraska:
Our Road Maintenance Department uses salt brine (sodium chloride), magnesium chloride and Ice Ban for our deicing program. We were a test state for Ice Ban.   We use an estimated 80,000 gallons of Ice Ban liquid a year. Ice Ban is not fool proof and it is somewhat expensive. It is reddish in color and smells like syrup. We use it on our new concrete highways because it is non-corrosive, but when the temperature reaches below 24 degrees, Ice Ban becomes a skating rink.

Temperature and humidity dictate what product we will use on any given day. We use a lot of pre-wetted salt. Some salt/sand (aggregate) is used but we are using it less often as it creates a major clean-up problem and we get better results with the chemical deicers. The salt brine is cheap to use and any new deicer product would have to be equal or less costly, in order for us to change.

We have not had many complaints with our deicers. Vehicle manufacturers are doing a better job of zinc coating, which prevents a lot of the corrosion.

Nevada:
We use magnesium chloride and salt grind tanks as winter road storm control. We use the magnesium chloride as an anti-icer and salt/sand mixture during and after the storm. Both methods work well. We haven't used enough of the magnesium chloride to have complaints from the public. We did use magnesium chloride on a parking lot to keep the dust down and had a lot of complaints about corrosion. Ten to fifteen percent of our overall road maintenance budget is used for anti-deicing.

In the mountains near Reno we use brine as an anti-icing agent to prevent snow and ice buildup.   We send out sand trucks with liquid tanks on the sides, to monitor an area in case of changing conditions. The problem with magnesium chloride (PCI inhibitor) is the high cost and spotty availability of the product. Salt water is cheaper and less corrosive.

We used to be in the top 10 most polluted areas when we used salt/sand. We now use harder sand (standard is 5 parts sand to 1 part salt), and we check it every 500 yards on the highways.

We also use road sensors to monitor temperatures. A DTM (Doppler radar system) is used to help in controlling winter driving conditions. This gives the Department opportunities to utilize alternate de-icing chemicals, make optimal use of materials and staff, and practice anti-icing techniques developed through years of research.

North Dakota:
We have never tried the magnesium chloride. We use rock salt for anti and deicing. We have salt brine makers all over the state and make it as needed. Until two years ago we did not use an anti-icer, but now, we use the salt brine for that purpose as well. We like the price of rock salt.

Oregon:
We have been using CMA (Calcium Magnesium Acetate, a vinegar-like product) for three to four years. CF2 (potassium), a combination of CMA and DF2 magnesium chloride with an inhibitor. CMA is used prior to a storm and works best at 24 degrees and above. We never use salt, but do use a lot of sand. In some areas of the state, we have used rock salt without a corrosive inhibitor and have received no complaints.

We believe magnesium chloride is a better anti-icer and breaks up the ice better than CMA during and after a storm. It is also cheaper to use than the others we have tried. It is more environmentally safe since it does not get in the water.

South Dakota:
We use abrasive materials--anywhere from 15 to 70% salt/sand.   We use about 20 tons of salt a year. We put down both pre-wetted salt/sand, as well as dry sand that we wet after application. We also use magnesium/chloride as an anti-icer, as well as a deicer. We use a corrosion inhibitor with it. We like it because our pavement returns to bare pavement days earlier than when we use the salt/sand method and it is easier to clean up after a storm.

Next year we are testing Ice Ban as a pre-wetting for abrasive materials under limited application. We are developing a deicer of our own that is neutral in pH factor. It is a dry pellet and manufacturing it is not yet economical.

Utah:
We use sodium chloride (NaCl) 50/50 sand/salt mix as a deicer. We mix the NaCl ourselves. We have the usual complaints when using NaCl of pitting windshields. We are now pre-wetting with brine solution (20-23 % sodium chloride) as an anti-icer, and are using all liquid trucks. We just plow if it gets below 20 degrees and freezes.

We have been experimenting with magnesium chloride and calcium chloride. Calcium magnesium acetate is less corrosive but more expensive to use. We were told that it works with temperatures as low as –60 degrees. We have High Performance Salt that is mined in Utah and

absorbs energy from the sun. There is also Morton Salt that is white and we add dye to it. We are running lab tests to see what effect, if any, white, red or blue sand has on our deicer program.

Washington:

We use magnesium chloride with Ice Ban as an inhibitor in most areas. We also use CMA and calcium chloride. Magnesium chloride is the least expensive. CMA works the best and it doesn't corrode, but is far more expensive. Calcium chloride does the most damage to aluminum. We use 10-15 gallons of magnesium chloride per mile as an anti-icer. In extreme conditions, we will also use salt/sand. We do not use pre-wetted salt or sand. We used to use granular products for both anti and deicing (urea and salt/sand), but we stopped using the salt/sand method when it became an environmental issue.

Our biggest concern in anti/deicing is the uniformity both in training and application. Road surfaces vary, therefore, you cannot treat a new highway with anti-icing and deicers the same way you treat an older highway that has had a lot of use, dirt and oil on it. Human factors of over applying or not knowing when and how much to apply are a lot of the problems associated with deicers. Anti/deicing is an ongoing learning process in our state. We have had some complaints about the magnesium chloride and Ice Ban being corrosive and hard to remove. We advise people to wash their vehicles as often as possible.

We are a member of Pacific Northwest States (PNS) that sets the anti/deicer criteria in many states.   They set the specification for what is used. They plan to try other methods, especially if the cost is right.   FHWA reported CMA is coming out with a cheese whey by-product that may work as good as the original but not nearly as costly.

Ice Ban is really good as a buffer for the chloride but its smell and color are objectionable to humans, although it is not a toxic product. The Ice Ban is a by-product of beer and is a real hazard where animals are concerned as they get out on the highways to lick it and sometimes get hit by vehicles.

4. Phase I Research Procedures and Methods

4.1 Corrosion Testing Methods Used in the Project

Based on an extensive literature review of corrosion testing methods, modified SAE J2334 and ASTM B117 were selected as the testing methods in the project to compare the effects of different salts on the selected metals. It should be pointed out that both of the selected testing methods were designed for specific purpose of testing. SAE J2334 is a typical cyclic corrosion test representing the corrosion effect of in-service environments to various coating systems; while ASTM B117 simulates a corrosive environment in coastal areas. The primary reason for using these two testing methods in the present study was to create different corrosive environments and mechanisms that can be possibly encountered on the roads. The selected coupons included coated and uncoated metals. In each of the two selected testing methods, two salts (sodium chloride and magnesium chloride), were used as the corrosive medium, respectively. After the designated testing cycles or hours were reached, the difference in the corrosiveness of the metals caused by the two chlorides were compared.

The laboratory experiments were conducted by the following procedures:

- Prepare (clean and dry) the coupons according to the procedures specified by ASTM G1-96 "Practice for preparing, cleaning, and evaluating corrosion test specimens." All coupons were degreased by ethanol and rinsed thoroughly with water, before being dried in the oven.
- Weigh the coupons to a precision of $\pm$ 0.001 g.
- Carry out corrosion experiments in accordance with SAE J2334 and ASTM B117, respectively. In each run of the tests by SAE J2334, two coupons were tested for each type of material, while in each run of the tests by ASTM B117 only one coupon was used.

The ASTM B117 test is a continuous spray test lasting for 800 hours at a temperature of 38ºC. The basic procedures for a modified SAE J2334 can be seen in Figure 1. A few modifications were made to the standard SAE J2334 when the test was conducted. One of the modifications was that the tests were not interrupted during weekends and holidays in order to provide a constant and continuous environment to the coupons. Another modification was that two different chemicals (NaCl and $MgCl_2$) were used as two separate testing solutions to compare their corrosiveness, while in the standard method, several chemicals are mixed in one solution with a fixed composition. The magnesium chloride was obtained from CDOT's Region 6 maintenance facility. The chemical analysis showed that the concentration of the sample solution was 22 wt.%. Based on the concentration, the solution for the corrosion test was made to a concentrations 1.0 wt.%.

After the designated cycles or hours were reached, the coupons were taken out for cleaning and evaluating, following the procedures specified by ASTM G1-96. Stainless steel coupons were dipped in nitric acid of 10 vol.% for 20 min. at 60ºC. Aluminum coupons were dipped in nitric acid (HNO_3, sp gr 1.42) for 15 min. at room temperature. The coupons were

rinsed with water and dried before being weighed again. All coupons were photographed at two-week intervals after the beginning of the test.
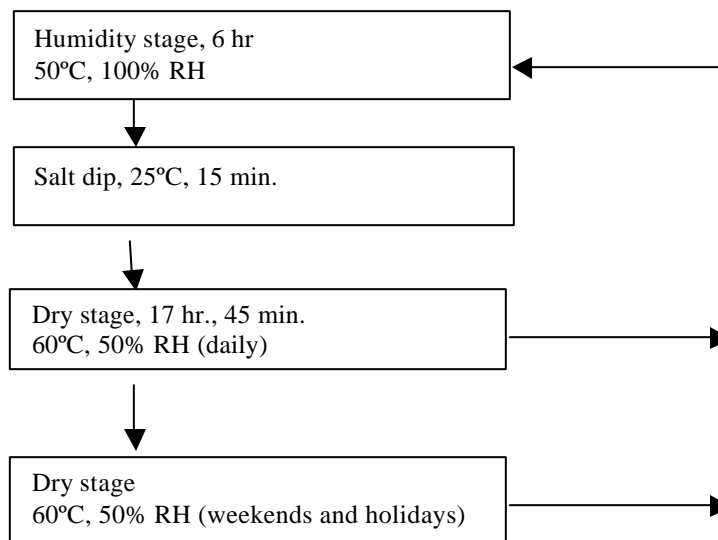
Figure 1: Schematic of SAE J2334 (manual mode).

4.2 Experiment Materials

As far as materials used in trucks, there is a very wide variety depending on the component. Following would be most common for main truck components.

Truck Cab:

Cold Rolled carbon and galvanized steels - pretreated with zinc phosphate, e-coat primed and top coated; Aluminum sheet and extrusion alloys (3000, 5000 and 6000 series) -pretreated with zinc phosphate, e-coat primed and top coated

Exterior Decorative Bright Parts:

Chrome Plated Cold Rolled or Hot Rolled Steels; Chrome Plated 5000 Series Aluminum; Chrome Plated Zinc Die Castings; Chrome Plated Plastics; 430 & 434 Bright Annealed Stainless Steels; 300 Series (301, 302 and 304) pre-buffed Stainless Steels

Exterior Light Weight Components:

Fuel Tank - Bare 3000 and 5000 Series Aluminum Sheet Alloys
Wheels - Bare 2000 and 6000 series aluminum forging alloys

Chassis:

Hot Rolled Carbon & High Strength Low Alloy Steels Primed and Top Coated
Nodular and gray Iron Casting with e-coat or casting sealer and Top Coated

Based on the common materials used by the automobile industry, following materials were selected in the project for both Phase I and Phase II studies. Two types of stainless steels: 304L and 410. 304L has higher chrome (18.11%) and nickel(8.05%) than 410 (12.5% Cr, trace Ni). Two types of aluminum alloys: 2024 and 5086. 5086 has higher magnesium content (3.5 ~ 4.5%) than 2024 (0.25 to 0.5), but with similar contents of other elements like Cu, Fe, Si, Mn, Ti and so on. Following are the analyses of the coupons:

a. Al 2024, a representative of aluminum with low magnesium

Cr:	<0.1
Cu:	1.0~2.0
Mg:	0.25~0.5
Si:	<0.6
Zn:	<0.25
Mn:	0.1~0.4
Fe:	<0.5
Ti:	<0.1

b. Al 5086, a representative of aluminum with high magnesium

Cr:	0.050/0.250
Cu:	0.100 max
Fe:	0.500 max
Al:	balance
Mn:	0.200/0.700
Si:	0.400 max
Ti:	0.150 max
Mg:	3.500/4.500
Zn:	0.250

c. SS 304L, a representative of stainless steel with high chromium and nickel

C:	0.018
Cr:	18.110
Cu:	0.38
Fe:	balance
Mn:	1.810
Mo:	0.350
N:	0.080
Ni:	8.050
P:	0.028
S:	0.001
Si:	0.520

d. SS 410, a representative of stainless steel with low chromium

C:	0.150 max.
Cr:	2.500
Fe:	balance
Others:	minimal

e. ACT cold roll sheet, coated, one of the standard corrosion coupons
f. ACT Zn/Fe A45, coated, one of the standard corrosion coupons
g. ACT E60 EZG, coated, one of the standard corrosion coupons

All three ACT coupons (Type e, f, and g) have the same coating system:

Ecoat: U32AD400
Primer: G27AD258 Powder
Basecoat: R164WE936 Stone white
Clearcoat: R126CG2001
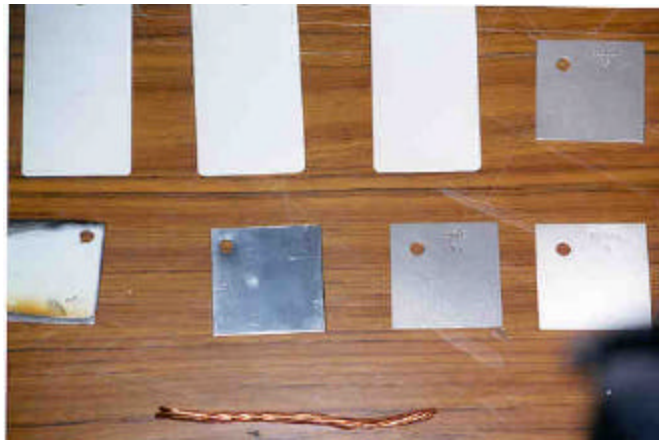
Figure 2: A photograph of the coupons.

Figure 3: Experimental setups.

4.3 Equipment

a. Two environmental chambers (see Figure 3), with temperature range from ambient to 65°C, and the humidity range from ambient to 100% RH;

b. Precision balance, 210 ± 0.001g;
c. Continuously spray unit (see Figure 3), $38°C \pm 1°C$;
d. Optical microscope of 200x with a CCD camera connected to a PC with an image grabber;
e. Digital Multimeter, Model Bel Merit DX360T;
f. Microcomputer pH meter, Model HI 8424.

4.4 Field Testing Procedures

(This Section of the report was prepared by Dr. Patricia Olsgard,
formerly of the American Trucking Association Foundation)

The in-service exposure test was carried out on Colorado highways during the winter of 1999 to verify the results from the laboratory experiments. Five metal coupons, identical to those used in the laboratory tests, were bolted to a Plexiglas sheet approximately the size of a license plate. Ten of these Plexiglas plates were mounted on trucks for exposure on the highway starting the first week of November 1999. The plates were removed from the various trucks and returned to CU-Boulder for analysis in May 2000.

Fig.4 Coupons on the trucks

Four plates were mounted on CAST Transportation trucks; three plates were mounted on HVH Transportation trucks, and the remaining three plates were mounted on CDOT Region 6 Maintenance trucks. While both CAST and HVH have interstate operations, the participating carriers were asked to mount the plates on trucks that ran miles only in Colorado to guard against exposure to other state's deicing chemicals.

- HVH Transportation is a large for-hire trucking company that operates primarily in Colorado. Test plates were installed on two trucks that operate between Denver and Grand Junction, and one truck that operates between Pueblo and Denver.
- CAST Transportation is a large for-hire trucking company that operates primarily in Colorado. Test plates were installed on four trucks that operate mainly on the I-70 and I-25 corridors.
- Colorado Department of Transportation Region 6 Maintenance Department is responsible for Highway Maintenance along the Front Range and in the Denver metropolitan area, including C-470 and parts of I-25. Test plates were installed on two vehicles that apply magnesium chloride and one vehicle utilized by the Road Maintenance Supervisor.

5. Phase I -Experimental Results and Discussions

5.1 Cyclic Exposure Test by the SAE J2334 Method

The cyclic exposure test provided a severe corrosive environment in which cyclic changes in temperature, humidity and concentration of the solutions took place simultaneously. In total, five runs were conducted by the SAE J2334 method. Each run lasted for two months. Some runs were extended after two months of testing, which will be explained later. In Run 1 and Run 2, NaCl and MgCl₂ reagents (pure chemicals, not obtained from CDOT) were used, respectively. In Run 3 and Run 4, NaCl and MgCl₂ deicing salts were applied. In Run 5, a mixed solution of NaCl and MgCl₂ was used. In the first four runs, 1.0 wt.% was the concentration for NaCl and MgCl₂ solutions. In Run 5, the solution contained 0.5 wt.% NaCl and 0.5 wt.% MgCl₂.

In this report, reagent salts means pure chemical solution; practical salts means the deicing salts used on the road by CDOT, with the magnesium chloride solution containing rusting inhibitor.

Among the metals tested, SS410 has less corrosion resistance as compared to SS304L. Similarly, Al2024 has less corrosion resistance compared to Al5086. We noticed that SS410 contains less chrome than SS304L and Al2024 contains less magnesium than Al5086. These may be among the reasons for the different corrosion resistances.

Figure 5 and Figure 6 show the test results by reagents and road salts, respectively. It is seen that MgCl₂ behaves more corrosively than NaCl to all the metals tested, either with pure chemical solutions or with practical salt solutions. A comparison of the results attained respectively with the reagent MgCl₂ (without corrosion inhibitor) and the magnesium chloride used on the road (with corrosion inhibitor) indicates that the inhibitor reduces corrosion of AL2024 by 60%, but increases that of SS410 by 216%.

In the figures, the corrosion rates are shown in mpy (mils per year) and calculated following procedures outlined by the ASTM G28 standard. According to this standard, the corrosion rates are given by the following formula:

$$\text{Corrosion Rate} = \frac{K \times W}{A \times T \times D}$$

in which

$K =$ a constant 3.45×10^6, mpy.

T = time of exposure, in hours

A = area in cm^2

W = mass lost in grams

D = density in g/cm^3, $steel\,410 : 7.7, steel\,304 : 7.94, Al\,2024 : 2.78, Al\,5086 : 2.66$
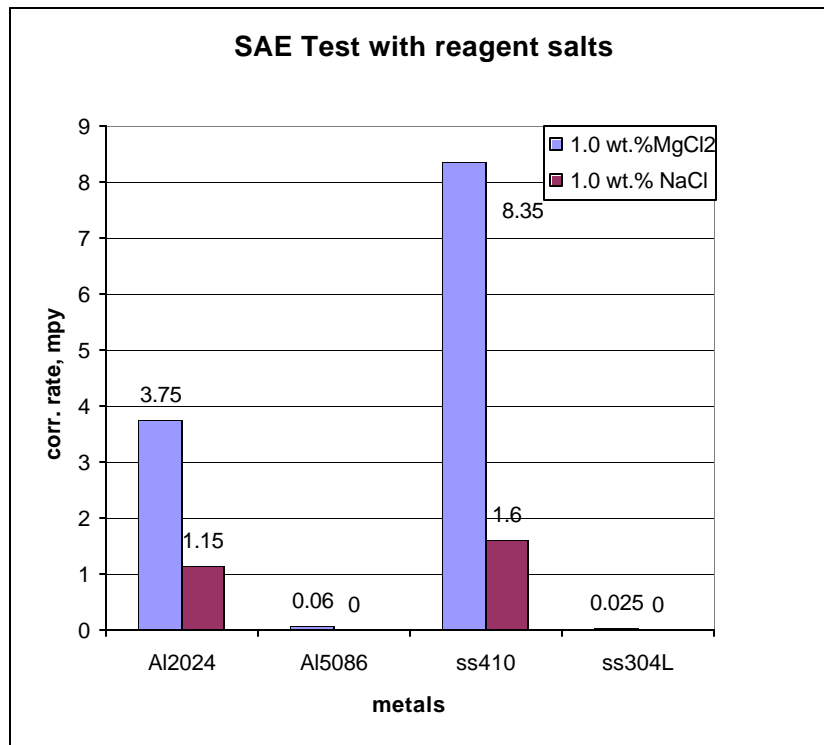
Fig.5 SAE test with reagent salts
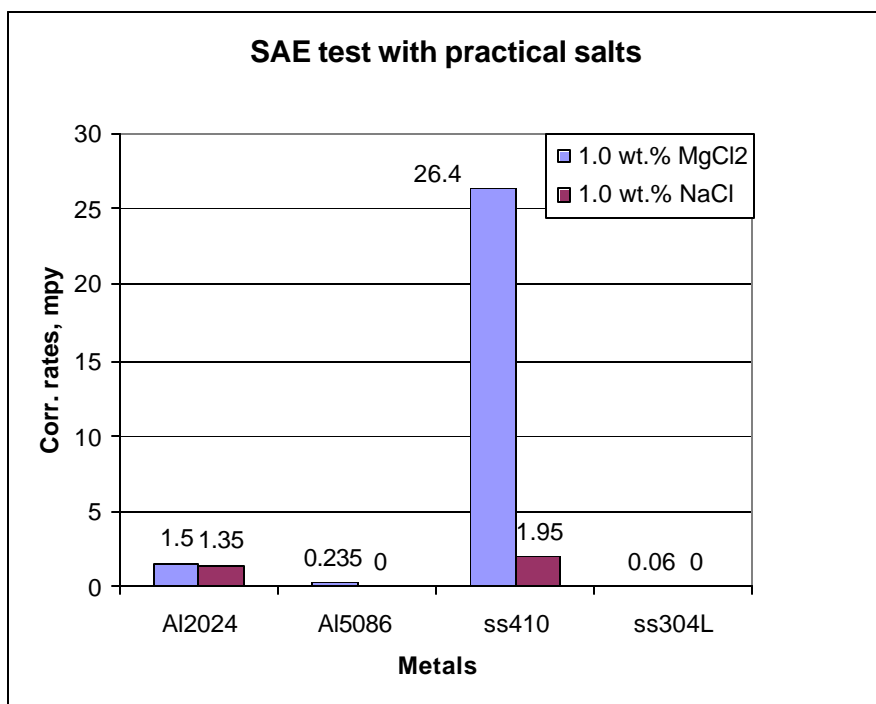
Fig.6 SAE test with the practical salts
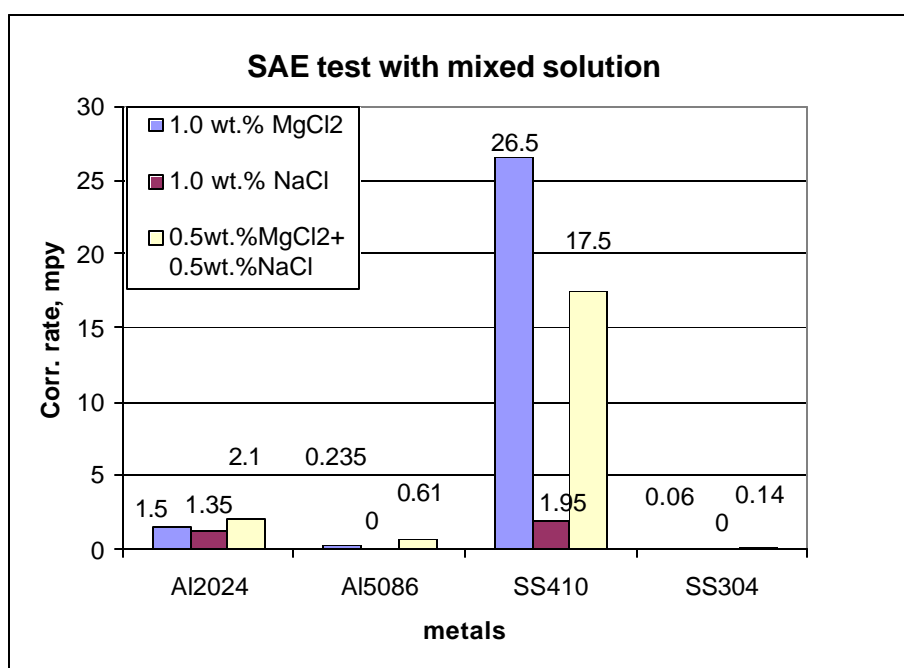
Fig.7 SAE tests with mixed solution

The experimental results of the cyclic test Run 5 with mixture of NaCl and $MgCl_2$ (practical salts) are given in Table 8 (Appendix 1) and shown in Fig.7. Mixed solution was used to compare with single salt, in order to assess the possibility of a possible coupling effect between $MgCl_2$ and NaCl. Intuitively, the mixed solution of NaCl and $MgCl_2$ should be less

corrosive than MgCl$_2$ alone, since NaCl (less corrosive) is added to the solution. Fig. 8 shows that the mixed solution of NaCl and MgCl$_2$ seems more corrosive than the MgCl$_2$ solution for Al2024, Al5086 and SS304L. However, the differences among the three values of the same type of metal are quite small, so the coupling effect is not significant. For SS410 the mixed solution caused even a smaller corrosion rate than MgCl$_2$ solution, but higher than NaCl solution.

For ACT coupons (i.e. ACT cold roll sheets, ACT Zn/Fe A45, and ACT E60 EZG), different chlorides used in the cyclic tests did not lead to any significant difference in the corrosion damage, as shown in Figure 8. The cold roll sheet was corroded by both NaCl and MgCl$_2$ to the same extent. However, no corrosion occurred to the other two ACT sheet materials, (ACT Zn/Fe A45 and ACT E60 EZG) even after the cyclic tests were extended from two months to four months. One should notice that a scratch which penetrated the coating layer was made on every ACT coupon. Previous research showed that the scratches help accelerate the corrosion of the metals. The tests indicate that the treatments of electroplating or the hot-dip alloying during the manufacturing of the coupons enable the two ACT coupons to withstand cyclic chloride corrosion.

Figure 8: Coupons Corroded by a mixture of NaCl and MgCl$_2$
(practical salts)

Figures 9 and 10 are photographs of the corroded coupons at different stages caused by reagents and practical salts, respectively.
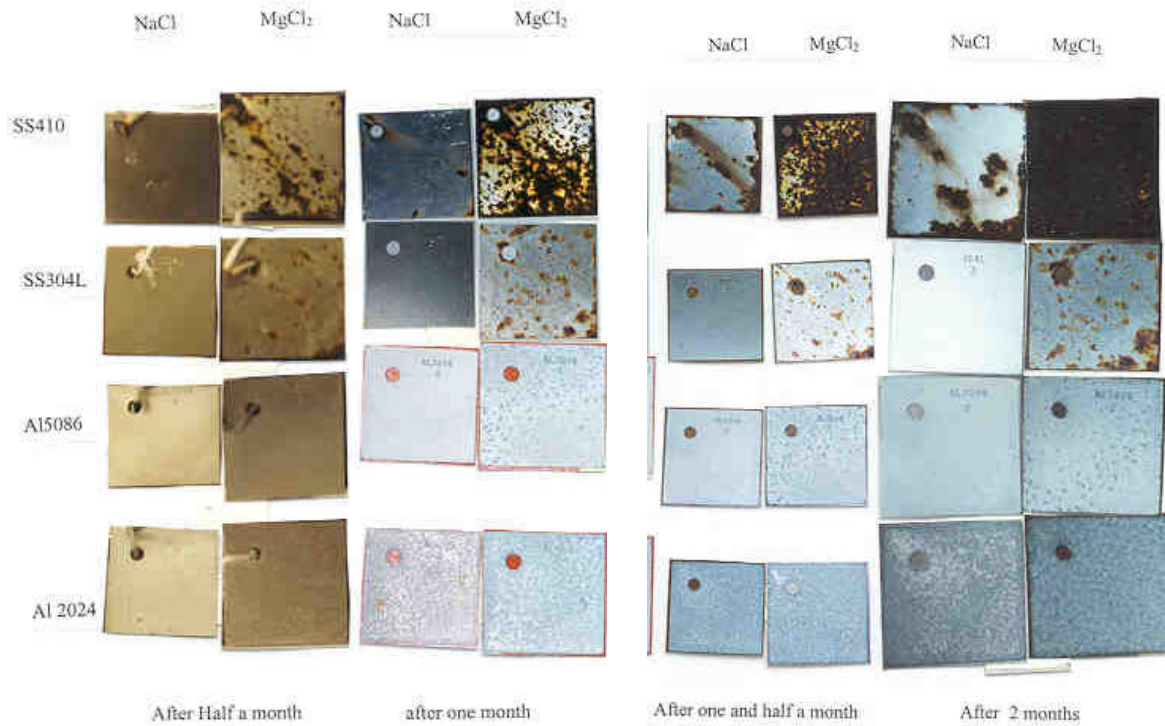
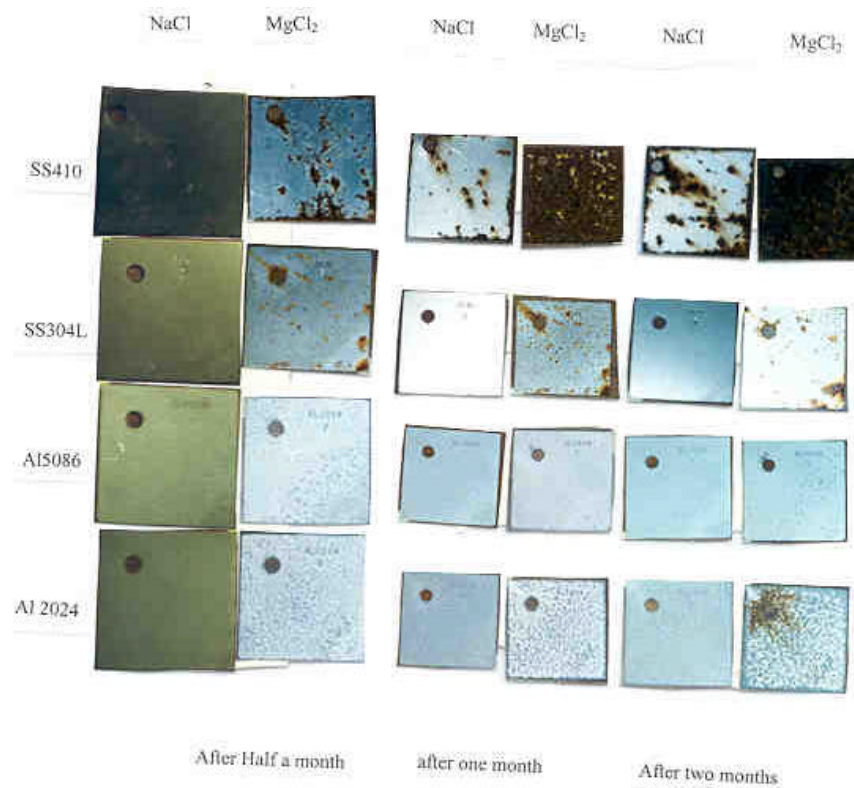**Figure 9: Coupons after testing by SAE J2334 (with reagents)**

Figure 10: Coupons corroded by practical salts in J2334 test
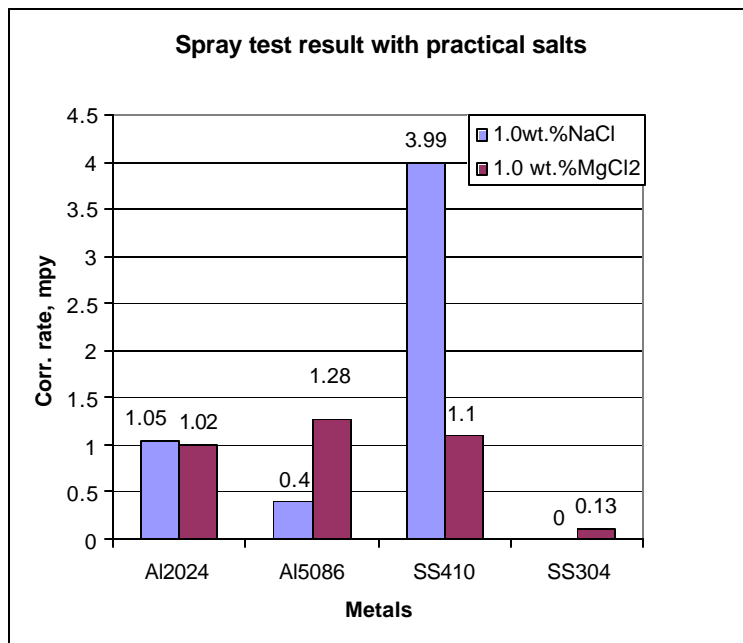
Fig.11 Spray test with the practical salts
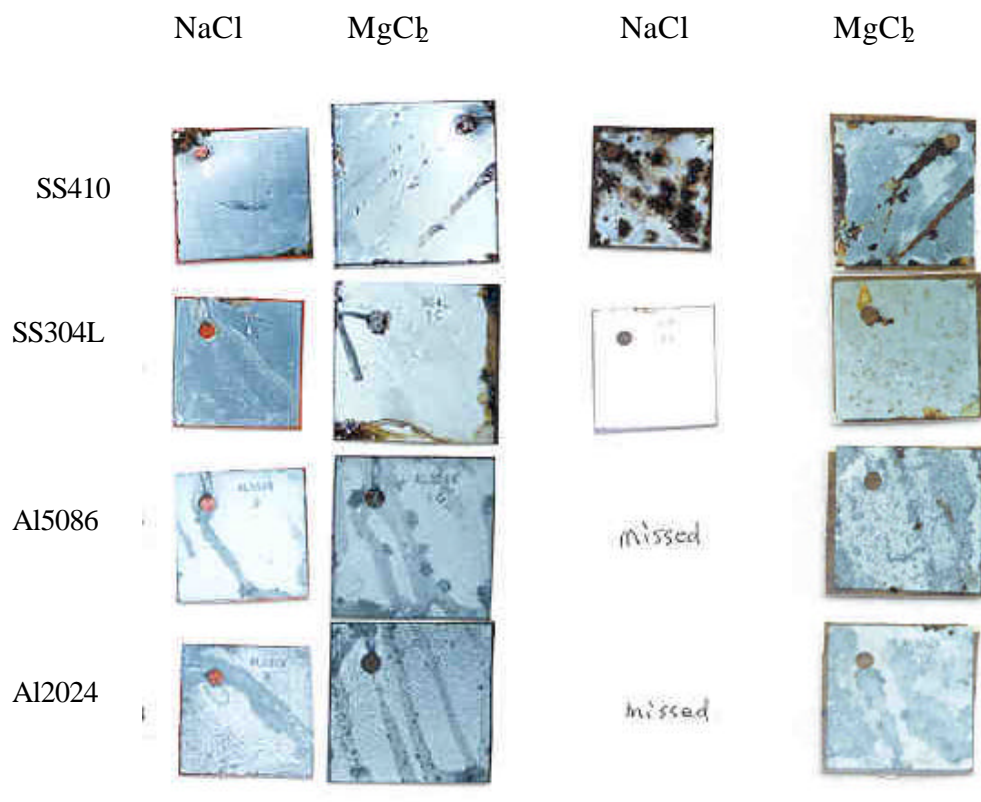
Figure 12: The test samples of the ASTM B117 test with practical salts.

5.2 Continuous Spray Test by the ASTM B117 Method

For the continuous spray test (ASTM B117), two runs were carried out with 4.0 wt.% solution of NaCl and MgCl₂ (practical salts), respectively. There were a total of 800 hours of continuous spray for each run. We originally considered extending the spray time from 800 hours to 1600 hours. However, the spray test was terminated after 800 hours because too much chloride gas was accumulated in the laboratory. The detailed test results are given in Table 9 and Table 10 (Appendix 1) and are also shown in Figure 11. The photos for the samples of the continuous spray test are shown in Figure 12.

5.3 Comparison of the Cyclic Exposure Test and the Continuous Spray Test

Comparing the results shown in Figures 5, 6, 7, and 11 one can see that the absolute corrosion rates of SS410 and Al2024 obtained from the cyclic exposure test (SAE J2334) are higher than those from the continuous spray test. This may be due to the fact that in the spray test (ASTM B117) the coupons were rested in a nearly closed environment. A mixture of salt fog and a small fraction of air was blown into the chamber. The oxygen concentration in the chamber was very low. In this circumstance, the electrochemical corrosion process was impeded, just as in the case when the coupons were immersed in the salt solutions.

In order to confirm the role of oxygen in the electrochemical corrosion process, another experiment was performed, in which SS410 and copper wires were immersed in 30 wt.% NaCl solution and 30 wt. % MgCl₂ solutions for two months, respectively. Although the two materials suffered severe corrosion under other test environments, hardly any corrosion occurred in the immersion test (Figure13). This indicates the importance of oxygen in the corrosion process.
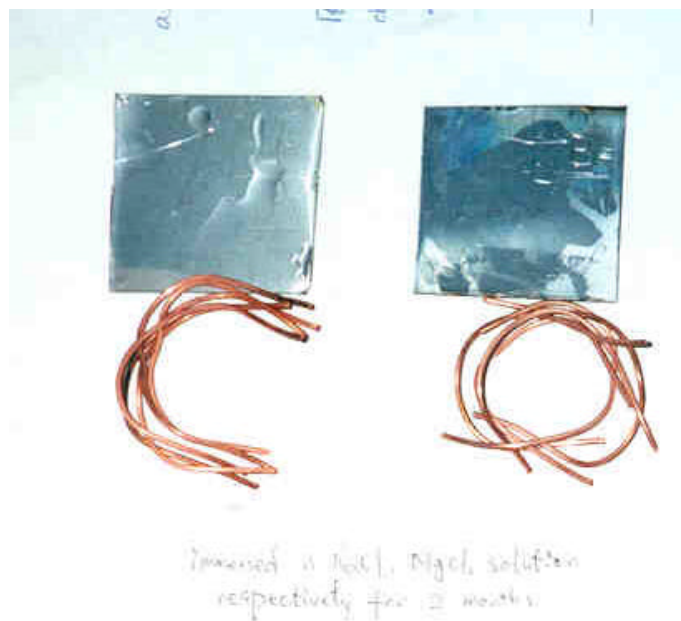
Figure 13: Immersion tests of SS410 and copper wires.

5.4 The Corrosion of Copper wires

The corrosion tests for copper tubes by both SAE J2334, In the test, two different chloride solutions were used with the same concentration (3.0 wt.%). Different corrosion damages were observed. The corroded coupons are shown in Figures 14. The photo indicate that $MgCl_2$ causes more severe corrosion to the copper specimens than NaCl. The coupons subjected to $MgCl_2$ solution had more green rust (CuO) on the corroded surface than that subjected to NaCl solution.
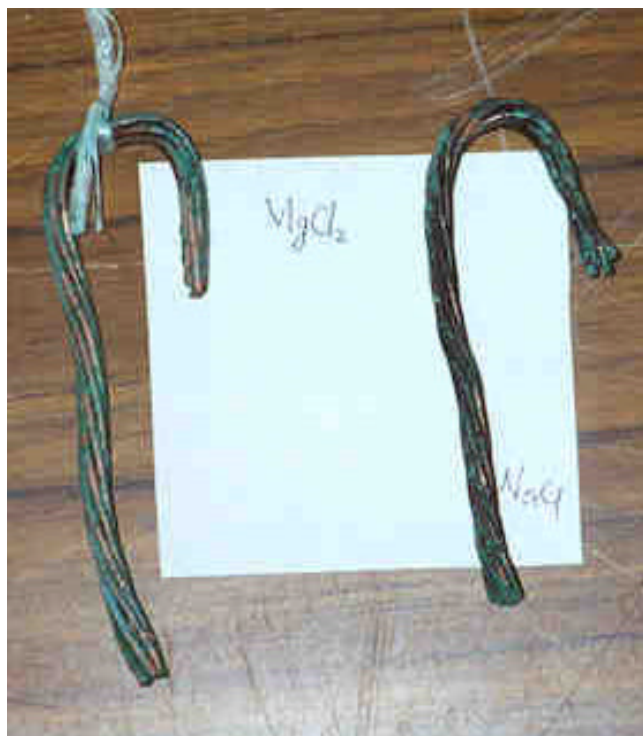
Figure 14: Corroded copper wires after SAE J2334 testing

5.5 In-service Tests
(This Section of the report was prepared by Dr. Patricia Olsgard,
formerly of the American Trucking Association Foundation)

The coupons mounted on the trucks of CDOT, HVH, and CAST were sent back to CU-Boulder for laboratory testing after being exposed for one winter (1999). The results are given in Table 11 (Appendix 1) and shown in Figure 15a, b, c, and d. It appears trucks #295, #1169, #1159, #1166, #1158, #1576, and #3066 had been exposed to a more severe corrosion environment than the others.

Coupons 3088, 3067, and 3066 were mounted on HVH trucks. Trucks 3066 and 3088 ran 5-6 days each week on I-70 between Denver and Grand Junction. Truck 3066 ran six nights per week and was driven a total of 81,305 miles while the test coupons were installed. Truck 3088 ran five days per week from Grand Junction to Denver and was driven a total of 78,986 miles. Truck 3067 ran 2 trips per day, five days per week from Pueblo to Denver and was driven a total of 70,254 miles during the test period. Based on testing completed by CU-Boulder, the trucks driven between Denver and Grand Junction (3066 and 3088) suffered more corrosion damage than the truck driven between Denver and Pueblo.

Coupons 1169, 1159, 1158, and 1166 were installed on trucks driven by CAST Transportation. Truck 1158 was driven throughout the Colorado during the testing period and was driven a total of 60,459 miles. Truck 1159 and 1166 operated between Denver and Grand Junction and were driven 98,313 and 39,826 miles. Truck 1169 operated between Denver and Climax and was driven 37, 236 miles during the test period.

Since the records of the salt application on these roads were not available. This in-service experiment did not lead to further conclusion.

Fig.15a Corrosion of SS304L

Fig.15b Corrosion of SS410

Fig. 15c Corrosion of Al2024

Fig.15d Corrosion of Al5086
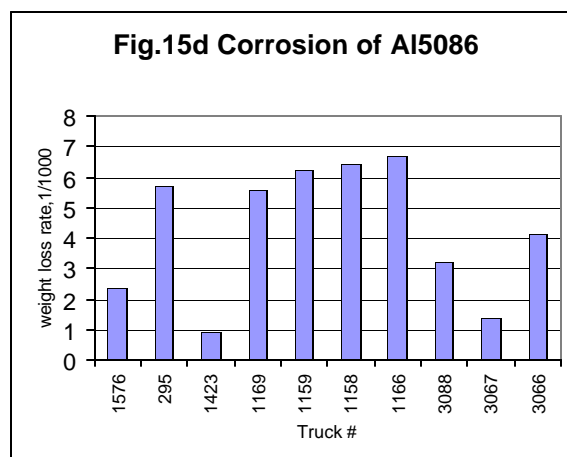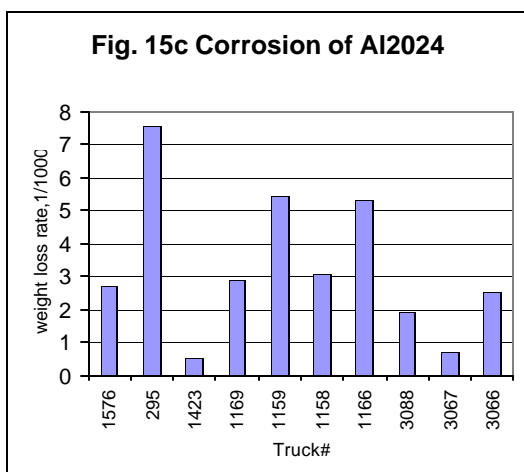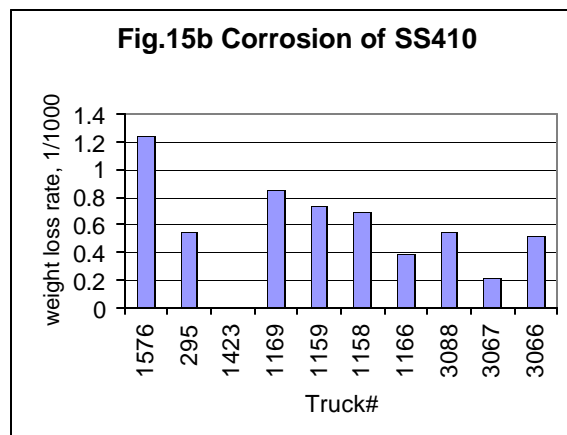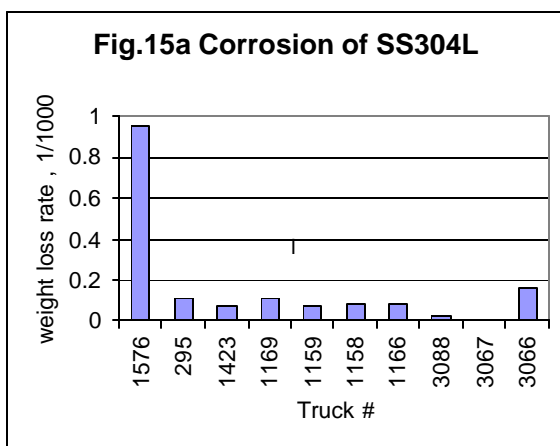
Figure 15 Corrosion rates of the coupons mounted on the trucks

5.6 Chemical and Microscopic Analyses

In order to understand and further explain some of the test results, chemical and microscopic analyses were performed. Figure 16a through Figure 16h are the microscope photographs of the corroded coupons subjected to the cyclic exposure corrosion test. It can be seen that regardless of the corrosion medium used, the same morphological feature of the corrosion products is observed for the same metal. Different amounts of the corrosion products can be seen for different metals under attacks by different chlorides. All corrosion products are in amorphous or glass states.
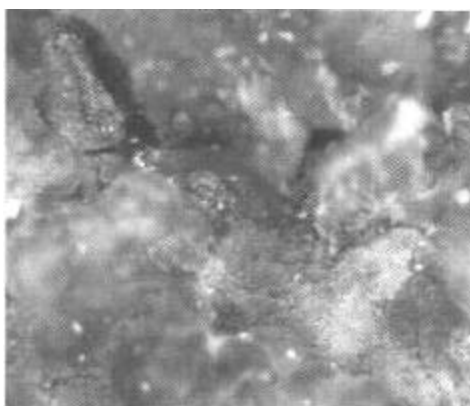
Figure 16a, SS410, MgCl$_2$, x150
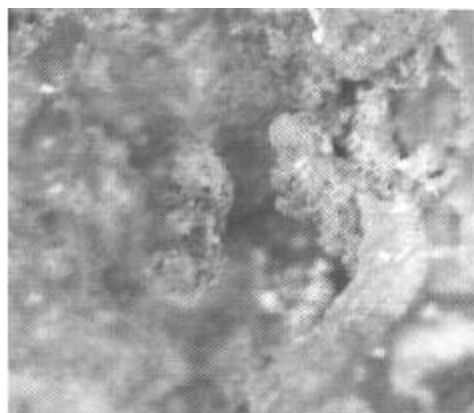
Figure 16b, SS410, NaCl, x150

Figure 16c SS304L, MgCl$_2$, (x 150)
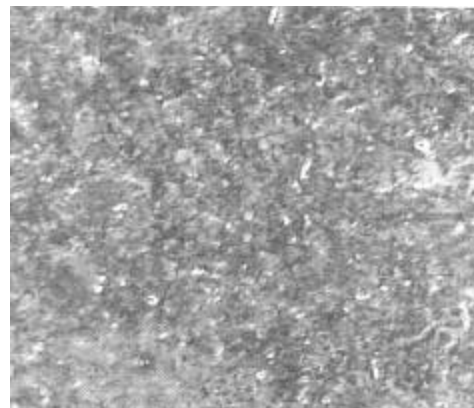
Figure 16d SS304L, NaCl, (x 150)
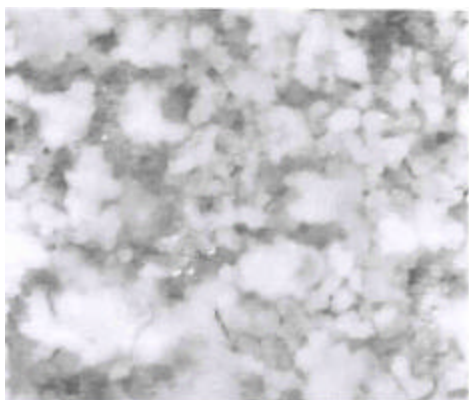
Figure 16e Al2024, MgCl₂, (x 150)
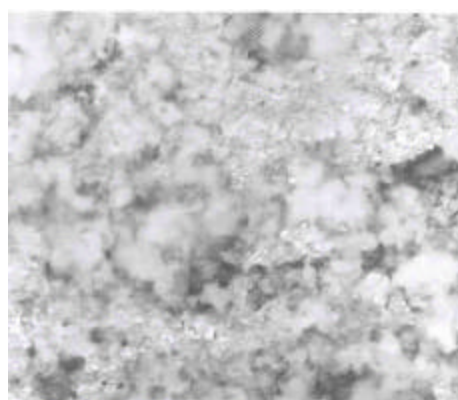
Figure 16f Al2024, NaCl, (x 150)
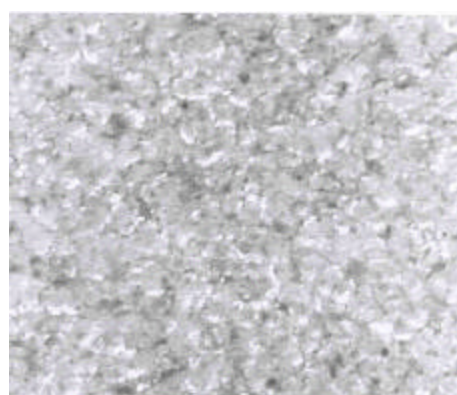
Figure 16g Al 5086, MgCl₂, (x 150)
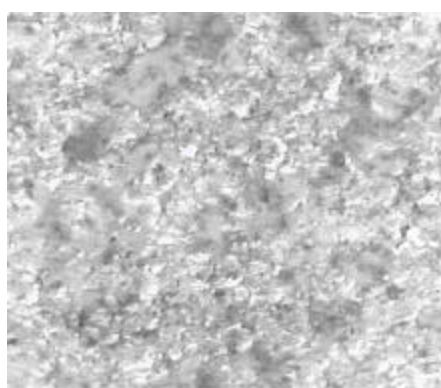
Figure 16h Al 5086, NaCl, (x 150)

Figures 16: Microscope photographs of the corroded coupons subjected to the cyclic exposure corrosion test
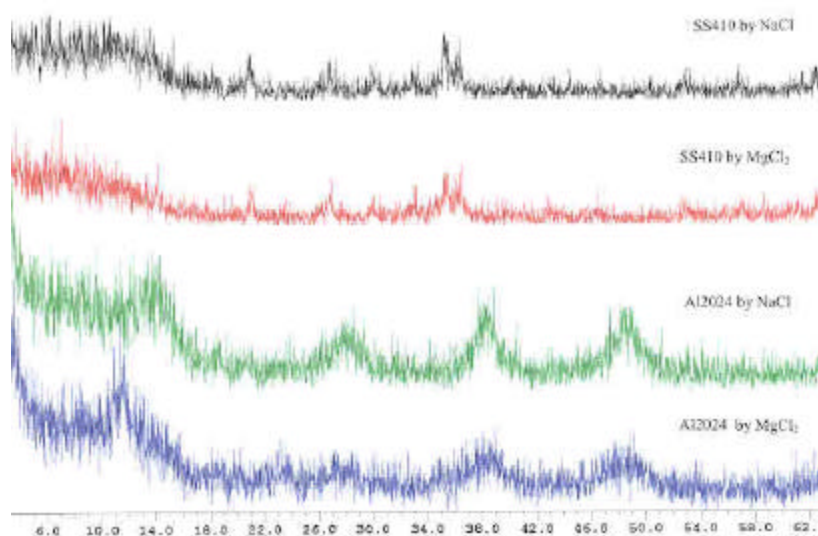
Figure 17: Corrosion products from SAE J2334 test, analyzed by XRD

The corrosion products collected from those coupons in SAE J2334 test were analyzed by X-ray diffraction (XRD) (see Figure 17). The XRD results show these corrosion products are aluminum oxide hydroxide (bohmite) for the aluminum, and a mixture of iron oxide (magnetite) and iron oxide hydroxide (lepidocrocite) for the steel. These corrosion products are in low crystallinity, without incorporation of chloride. Our results agree with the study by Kajiyama and his colleague (1995), who studied the chemical composition of the corrosion products of steel on vehicles used in North America, as well as the growth mechanism of the corrosion products. Quantitative analyses of the crystalline compositions were performed on the rust formed on the outer panel surface and in the crevice of the lapped portion on the vehicles. Characteristic regions of the rust compositions were found in the α-FeOOH/(Fe$_3$O$_4$ + γ-FeOOH)/(β-FeOOH + amorphous rust) ternary diagram. The rust from the crevice in the lapped portion contained more (γ-FeOOH + Fe$_3$O$_4$) than that from the outer steel panel.

All these observations and analyses suggest that the corrosions of the bare metals including iron, aluminum and copper under cyclic exposure to deicing salts are typical electrochemical corrosion processes, rather than a direct chemical reaction between the metal and chloride. At the anode areas the following reactions take place:

Steel: $Fe \rightarrow Fe^{2+} + 2e$ (5)
Aluminum: $Al \rightarrow Al^{3+} + 3e$ (6)
Copper: $Cu \rightarrow Cu^{2+} + 2e$ (7)
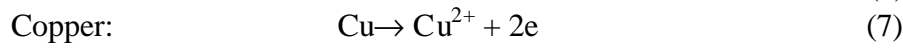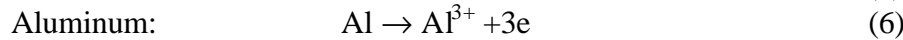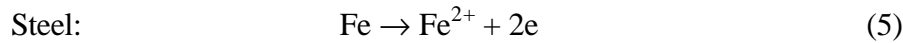
At the cathode areas, the hydrogen ions in water accept electrons:

$$4H^+ + O_2 + 4e \rightarrow 2H_2O \qquad (8)$$

Ions of the metals may further combine with OH ions in water to form hydroxides,

$$2Fe^{2+} + 4OH^- \rightarrow 2Fe(OH)_2 \qquad (9)$$
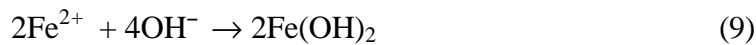
and Fe(OH)$_2$ is further oxidized into Fe(OH)$_3$:

$$4Fe(OH)_2 + O_2 + 2H_2O \rightarrow 4Fe(OH)_3 \qquad (10)$$

5.7 Corrosion induced by MgCl$_2$

When reasoning why MgCl$_2$ leads to higher corrosiveness than NaCl in the SAE test, one may think about its lower pH value, compared to NaCl solution of the same weight percentage concentration.

With the same concentration level, the MgCl$_2$ solution has lower pH values than the NaCl solution. This is because MgCl$_2$ may hydrolyze according to MgCl$_2$ + H$_2$O $\rightarrow$ Mg(OH)Cl + HCl (Silcock, 1979). This means there are more hydrogen ions in the corrosion medium when MgCl$_2$

is used as the road salt. Since higher concentrations of hydrogen ions can promote the cathode reaction (see Equation 8), thus the metals subjected to the $MgCl_2$ solution have a higher corrosion rate. However, measurement of pH values of 1.0 wt.% chloride solutions with a microcomputer pH meter (Model HI 8424) did not support this explanation. It demonstrated that sodium and magnesium chloride solution had almost the same pH values at the concentration of 1.0 wt.%. Moreover, this assumption can not explain the result by ASTM B117 test, in which NaCl solution exhibited higher corrosiveness than $MgCl_2$. Therefore, further study is needed to identify the reasons.

6. Conclusions from the Phase I study

The Colorado Department of Transportation has been using magnesium chloride for anti-icing and deicing for several years with good results in snow and ice control. However, over the same period, there have surfaced some concerns that the chemicals affect various components of cars and trucks. Although the corrosion inhibitor present in the magnesium chloride used by CDOT should prevent or minimize corrosive effects, the question remains if the chemicals attack aluminum and other vehicle components. The Colorado Motor Carriers Association, in response to complaints from their members, requested a study be performed to provide objective facts to address these concerns.

The results from the industry survey show the high degree of concern, ranging from comments about tarnished and dulled paint finishes to ruined components in need of replacement. The overall cost to the industry is difficult to quantify, but could potentially reach into the thousands of dollars for each power unit or trailer. While the survey provided a great deal of information from trucking companies relating to attitudes and opinions about Colorado's deicing program, along with basic cost data attributed to the use of magnesium chloride, it could not prove magnesium chloride was corrosive. To address this important point, the University of Colorado at Boulder conducted laboratory tests.

In summary, from the Phase I study the following conclusions can be drawn:

- Experimental results obtained by the cyclic exposure test (SAE J2334) indicated that $MgCl_2$ was more corrosive than NaCl to the most of the bare metals tested. The rates of corrosion varied from metal to metal. For stainless steel SS410, the corrosion rate caused by $MgCl_2$ was 5 to 13 times higher than by NaCl; for aluminum AL2024, the corrosion rate caused by $MgCl_2$ was one to two times higher. $MgCl_2$ was also more corrosive than NaCl to the electronic components made of copper.
- Experimental results obtained by the continuous spray test (ASTM B117) showed inconsistencies when compared with the results of the SAE J2334 test, which suggested that NaCl was more corrosive than $MgCl_2$ for most of the metals tested, especially for the less corrosion-resistant metals -SS410 and Al2024.

- For the metals with weak resistant to corrosion such as SS410, and Al2024, the corrosion rates obtained by SAE J2334 test were higher than those obtained by ASTM B117 test.
- The mixture of $MgCl_2$ and NaCl under the SAE testing condition did not cause more severe corrosion to most of the metals than did any single salt (either $MgCl_2$ or NaCl). With one exception for SS410, the mixture of NaCl and $MgCl_2$ resulted in higher corrosion than NaCl. Since only one solution concentration was used in the test, more detailed study is needed to confirm about the coupling effect.
- The coated automobile body panels with the treatment of electroplating or hot-dip alloying exhibited very high corrosion resistance. No significant corrosion products were observed on the coupons even when the panels were scratched and the outer coating was damaged. However, the coated cold roll sheets show poor corrosion resistance.

Part II: The Phase II study

After the Phase I study, the Phase II study started with a main focus: using another test (other than ASTM B117 and SAE J2334) to verify the relative corrosiveness of the two deicing chemicals, and investigate why different testing methods result in different corrosiveness. The importance and the significance of the Phase II study can be described from two different points of view. From the viewpoint of a government agency, it is important to know which testing method can simulate more realistically the real service condition so that the testing method can be specified as a proper industry standard. From the viewpoint of academic research, understanding the effect(s) of controlling parameters on the corrosion mechanisms of different deicing chemicals is a key issue of the corrosion science, and an essential topic for developing optimal deicing chemicals.

7. The NACE test

As a test procedure for selection of deicing agent, NACE standard TM-01-69 modified by the North Pacific States (PNS) is adopted by several state DOTs. According to the criteria adopted by the PNS, "only corrosion inhibited chemical products are at least 70% less corrosive than reagent grade sodium chloride may be used". The NACE test was used in the Phase II study.

The coupons used in the NACE test are ½" (approximately 1.38 x 0.56 x 0.11 in) flat steel washers with a density of about 7.85 g/cm^3, supplied by AD-TEK Inc. (Boring, OR).

All deicing chemicals used in the Phase II study were real deicing salt from CDOT. Before testing, 3% solutions of deicing agent were prepared by using distilled water. For the solid chemicals such as NaCl, 3% solution was prepared as weight percentage, while for the liquid chemical products, three parts liquid chemical product (as received) was mixed with 97 parts distilled water to produce the test solution. All solutions including the distilled water were covered and allowed to sit for a minimum of 12 hours to stabilize and reach equilibrium.

When testing, approximately 300 ml of each solution was put into a 500 ml glass flask. Each flask was covered by tape and left with a small hole to allow a nylon string to run through. Two washers were contained in a flask without contact each other. The strings holding the coupons were attached to a frame which was controlled by a timer to move up and down. When the frame moves up and down, the coupons were immersed in the solutions for 10 min. and then dried in air for 50 min. The experimental setup of the NACE test is shown in Fig.2-1.

The corroded coupons were removed from the solution after 72 hours. They were placed in a beaker containing the cleaning acid, concentrated hydrochloric acid containing 50 g/l $SnCl_2$ and 20 g/l $SbCl_3$. After 15 min. of cleaning the coupons were removed from the acid, rinsed with tap water and then distilled water, and wiped with paper tissue. The dried coupons were weighed for weight loss to 0.001g.
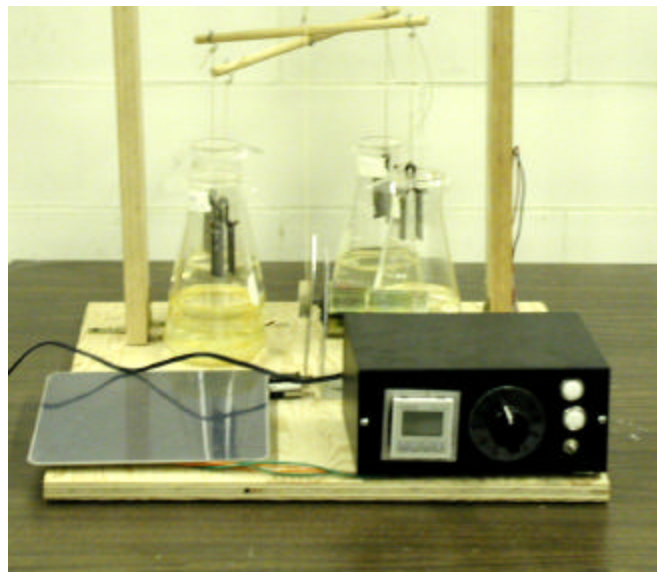
Fig.2-1 Experimental setup for the NACE TM-01-69 test

The corrosion rates in Phase II study are calculated by the following formula:

$$\text{Corrosion Rate} = \frac{K \times W}{A \times T \times D}$$

where

K = a constant 3.45x10^6, mpy.

T = time of exposure, in hours

A = area in cm^2

W = mass lost in grams

D = density in g/cm^3, $steel\,410 : 7.7, steel\,304 : 7.94, Al\,2024 : 2.78, Al\,5086 : 2.66, A36 : 7.85,$ $Washer : 7.85,$

The results of three NACE tests were given in Table 2-1 (Appendix II) and diagrammatically shown in Fig. 2-2. The room temperatures of the testing laboratory were 26 ±1.0 ºC (79 ± 1.7 ºF). One can see that $MgCl_2$ with inhibitor is less corrosive than NaCl, but not 70% less.
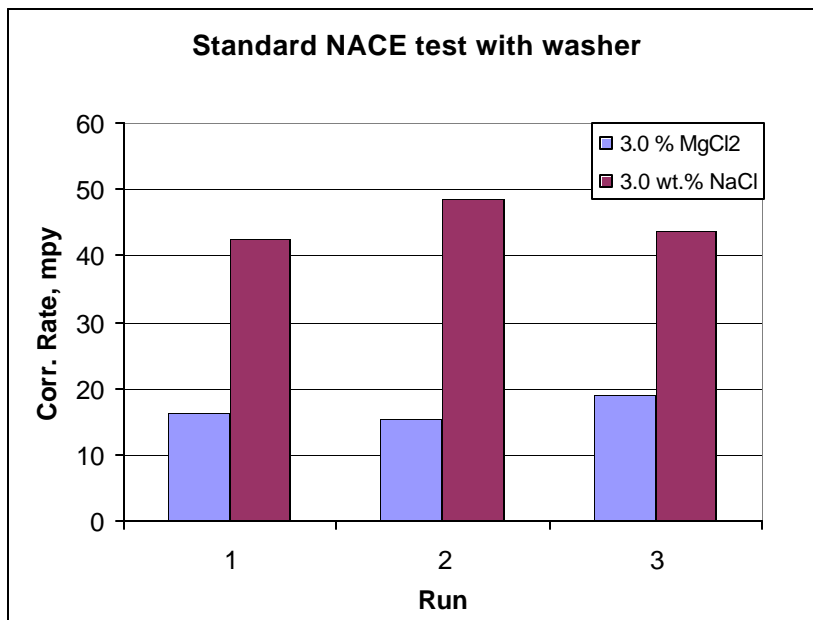
Fig. 2-2 Standard NACE test with washer as coupons
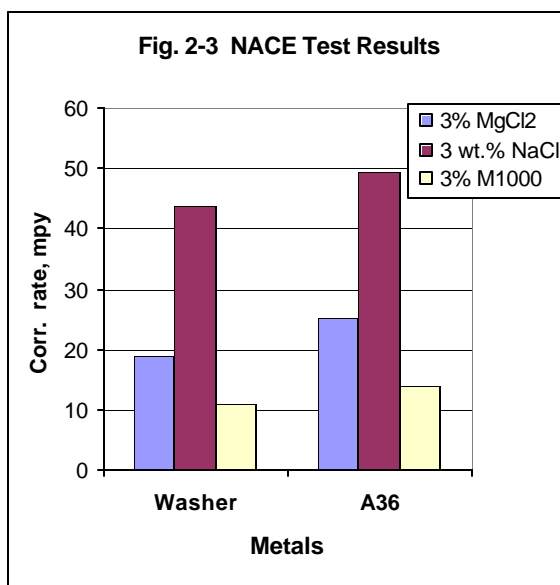
Fig.2-3 NACE test Results with washers and A36

In addition to the standard NACE test as shown above, modified NACE tests were carried out in the Phase II study. The modifications included the use of A36 steel coupons, and the use of various concentrations of $MgCl_2$ solutions. The test results are given in Figs. 2-3 and 2-4. Detailed test data can be found in Table 2-2 (Appendix II). From Fig. 2-3, one can see that NaCl caused the highest level of corrosion among the three deicing chemicals, and M1000 the least. The changes in the concentration of $MgCl_2$ solution in the range of 3% to 12% (or 0.84 wt.% to 3.36 wt.%) do not increase the corrosion rates of A36 and washer. To the contrary, a decreased tendency is observed (Fig.2-4). This may be due to the effect of inhibitor in the $MgCl_2$ solution, which has an increased concentration in the solution of 12% $MgCl_2$. It is now very clear that using the NACE test, NaCl is more corrosive than $MgCl_2$, even $MgCl_2$ solution is increased to the same level of the 3.0 wt. % as NaCl solution.

Other metal coupons, i.e., SS410, SS304, Al2024 and Al5086, were also tested by the NACE method. However, the NACE test cannot create any significant corrosion on these metals, because the testing time of 72 hours is apparently too short to generate any detectable corrosion on the metals.
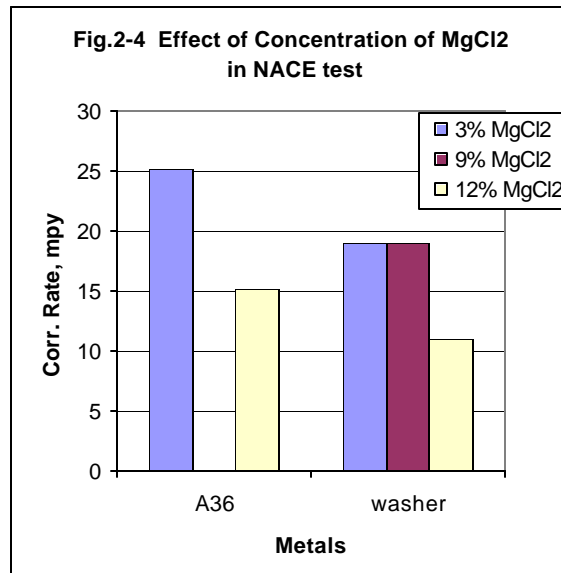
Fig. 2-4 Effect of concentration of $MgCl_2$ in the NACE test

8. More SAE J2334 tests

In this part of the Phase II study, A36 steel and the PNS standard washer were tested by SAE J2334 test. Considering the fact that the NACE method and the SAE method are specified under different concentrations of the solutions, we modified the concentrations in the SAE test according to the NACE standard, that is, NaCl at 3.0 wt. %, and $MgCl_2$ at 3.0% (3 parts of the liquid as received and 97 parts distilled water). The purpose of these modified SAE J2334 tests was to run the SAE test with the same concentration condition and same coupons as used in the NACE method, and to see if these changes would lead to different results from the Phase I study.

These SAE tests continued for 58 days before stopped. The A36 and NACE washer coupons were cleaned by the same procedure as described early in the NACE test. It is very important to see that with A36 and washer as coupons, the corrosion rates resulted from NaCl and $MgCl_2$ solutions became comparable (see Fig.2-5), which is different from the results of the Phase I with other metals.
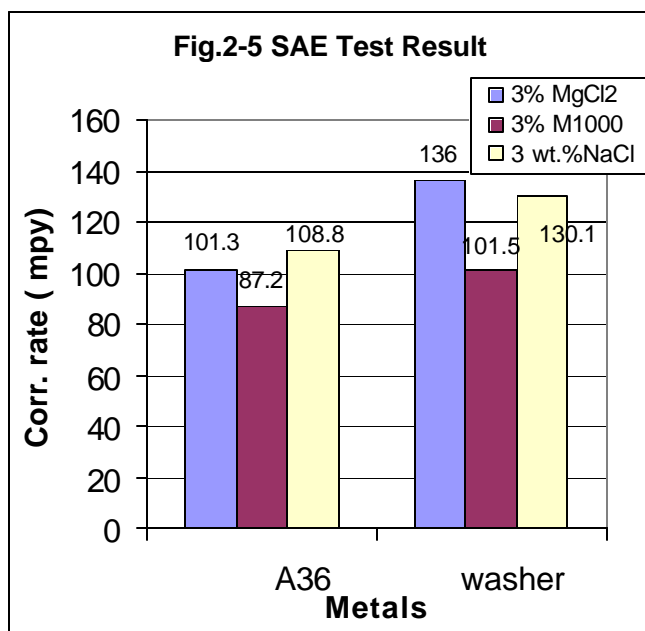
Fig. 2-5 SAE test results

Another deicing solution, Caliber M1000 was also evaluated by the SAE test to compare with NaCl The result indicated that when using NACE washer and A36 as testing coupons, 3.0% M1000 was less corrosive than 3.0 wt. % NaCl, or 3.0% $MgCl_2$ (Fig.2-5).

An chemical analysis indicated that the 3.0% $MgCl_2$ used in the above tests had an equivalent weight percentage of 0.84 wt.%, because the three parts of $MgCl_2$ liquid as received is not 100% pure chemical. Therefore, there was a quite large difference between the solution concentrations of the two salts used in the above tests: 3.0 wt.% of NaCl and 0.84 wt.% of $MgCl_2$. The comparison was not based on the same concentration of the solutions. For this reason, further study was conducted using various concentrations of NaCl solution. The results showed that when the concentration of NaCl was reduced to 1.5 wt. %, the corresponding corrosion rate decreased by about 20%.   When the concentration of NaCl was increased to 6.0 wt. %, the corresponding corrosion rate remained the same as that by 3.0 wt. % NaCl (see Fig. 2-6). 1.5 wt. % and 6.0 wt. % were used because 1.5 wt. % is a half of the concentration specified by NACE (3.0 wt. %), and 6.0 wt. % is two times of the specified concentration.

When the results from 1.5 wt. % NaCl solutions and 3.0 % $MgCl_2$ (or 0.84 wt. %) are compared, as shown by Fig. 2-7, $MgCl_2$ has a higher corrosion rate than NaCl. Therefore, the SAE test leads to a conclusion that $MgCl_2$ is more corrosive than NaCl for all three concentrations used in the tests (1.5 wt.%, 3.0 wt.%, and 6.0 wt.%). This conclusion, different from the NACE test, was further confirmed later by long term SAE tests of 81 days (see Fig. 2-14).
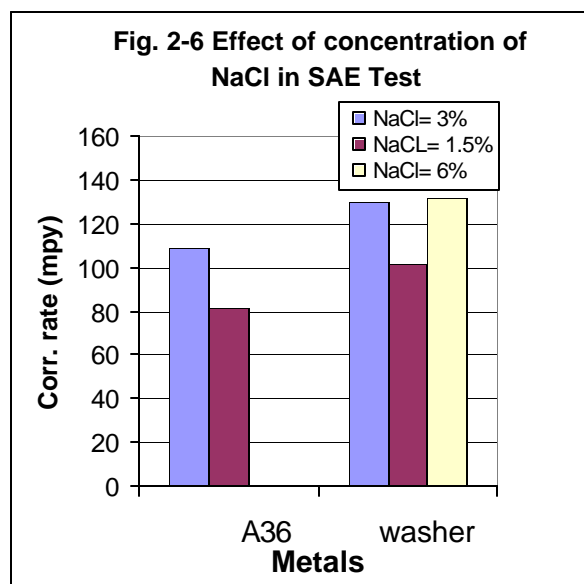
Fig. 2-6 Effect of concentration of NaCl in the SAE test
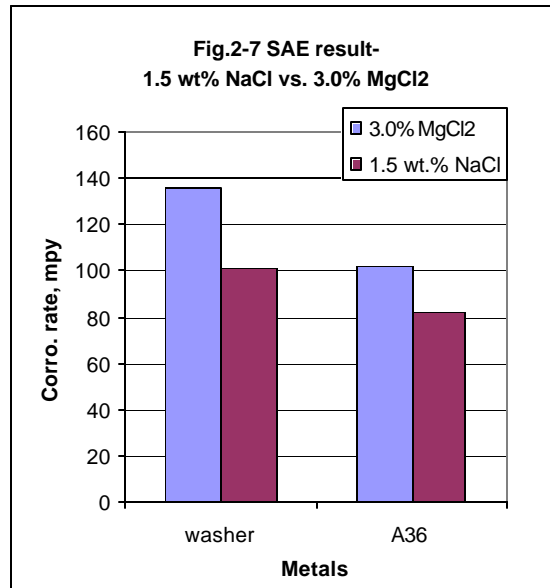
Fig. 2-7 SAE result- 1.5 wt. % NaCl vs. 3.0% MgCl$_2$

Detailed experimental data are provided in Tables 2-3 and 2-4 (Appendix II).

As one can see, there is a significant inconsistency between the results from the SAE and NACE tests, even if the same type of coupons and same concentration condition were used. If we use the SAE test on the washers, the MgCl$_2$ solution would not be less corrosive than NaCl, therefore, the CDOT specification would not been satisfied (Fig. 2-5); on the other hand, if we use the standard NACE test method (Fig. 2-3), then the MgCl$_2$ solution would be much less corrosive than NaCl. In order to investigate further the controlling parameters responsible for the different corrosion rates under different testing methods, systematic tests were conducted in the following three sections.

9. Tests with distilled water

For the purpose of comparing the relative corrosiveness of the testing environments of the NACE method and the SAE method, distilled water was used as a corrosive solution in the two tests.

Fig. 2-8 Distilled water tank after 81 days
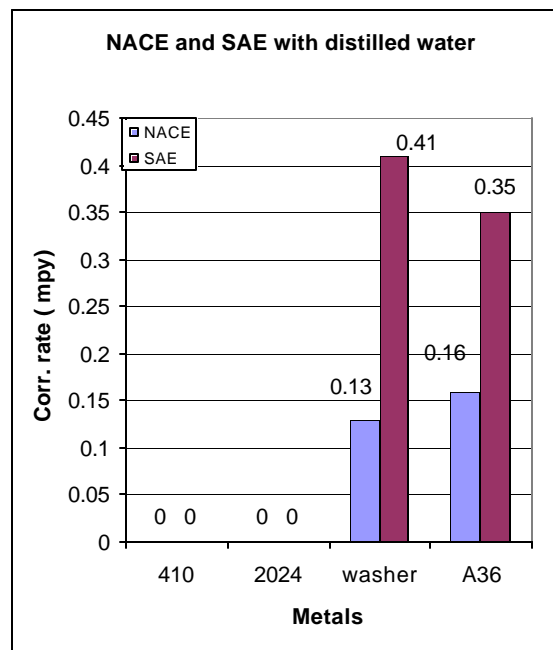
Fig. 2-9   Comparison of the SAE and SAE tests with distilled water

The SAE test with distilled water was started from August 18, 2001. After 81 days of testing, a very thin layer of rust appeared on the surfaces of A36 coupons and NACE washers. There was almost no visible rust on the surface of SS410 and Al2024 coupons. The water used as corrosion medium was clear without significant rust accumulation (Fig.2-8), which is an indication of the absence of rust accumulation.

The NACE test with distilled water was started from July 22, 2001. The testing period of the NACE test was extended significantly to compare with the testing period of the SAE test. After 109 days, the NACE test was stopped and the corrosion rate was measured. The calculated corrosion rates for the two tests are shown in Fig. 2-9. Comparing the SAE test to the NACE test with distilled water, it is evidenced that the SAE test had resulted in one to two times higher degrees of corrosion to the washers and A36 coupons. This suggests that the SAE test provides a much more aggressive testing environment than the NACE method, which may be due to the elevated temperature or high humidity, or the combination of the two. The appearance of the coupons before cleaning is shown in Fig. 2-10.

Fig. 2-10 Coupons exposed to distilled water
(Upper: from the NACE test of 109 days, lower: from the SAE test of 81 days)

10. Effect of testing duration and Concentration of Solution

There is a large difference in the testing durations between the NACE and SAE tests. The duration of the NACE test is 72 hours (three days), and the duration of the SAE test is two months or longer. The duration of test may have a major effect on the corrosion result. In addition, the concentration of the solution used in the SAE tests in the Phase I study was 1.0 wt. %. In order to assess the effects of testing duration and solution concentration, in the Phase II study, both the NACE and SAE tests were conducted for extended durations. At the same time, 3.0 wt. % solutions were used to keep the concentration of $MgCl_2$ in accordance with that of NaCl.

Our experiences showed that the qualitative assessment by visual inspection on the appearance of coupons and the color of solutions is consistent with quantitative weight loss analysis. Visual inspection is fast, direct, and cost less. Therefore, in this part of the study, the results from both visual inspection and weight loss analysis are included.

10.1 Visual inspection of the coupons in the extended NACE Test

The NACE tests with both NaCl and $MgCl_2$ solutions were started from July 1, 2001 and stopped after 128 days. The tested coupons included SS410, Al2024, Al5086 and SS304L. The visual inspection results of the NACE tests can be summarized in Tables 2-5 and 2-6.

The descriptions of the level of corrosion in the above tables (i.e. no, minor, moderate, and severe) are based on visual observation. One can simply observe the surface of coupons and color of the solutions to compare different corrosion rates for SS410 and Al2024, while for SS304 and Al5086, no any change was found in their solution color. The level of corrosion induced by different corrosion media can be observed in Fig. 11a and Fig. 11b, in which the dark brown colored solution is the NaCl solution with accumulated rust in it, and the light brown one is the $MgCl_2$ solution. The coupons in the solutions are SS410. The photos were taken after 69 days of test. Apparently, NaCl is more corrosive than $MgCl_2$.

Table 2-5 MgCl₂ solution as corrosion medium (the NACE test,128 days)

Metal	SS410	Al2024	Al5086	SS304
Corrosion	Moderate	Minor	No	No

Table 2-6 NaCl solution as corrosion medium (the NACE test, 128 days)

Metal	SS410	Al2024	Al5086	SS304
Corrosion	Severe	Severe	No	No

Fig. 2-11a. The NaCl solution in the NACE test (at 69 days)

Fig.2-11b The MgCl$_2$ solution in the NACE test (at 69 days)

10.2 Visual inspection of the coupons in the SAE Test

The SAE tests with NaCl and MgCl$_2$ solutions were started from August 18, 2001 and stopped after 81 days. This test served as a confirmation test for the SAE tests conducted in the Phase I. In this test, both of the solution concentration of NaCl and MgCl$_2$ were increased to 3.0 wt.%, instead of 1.0 wt.% in the Phase I. Fig. 2-12 shows the appearance of the coupons after 20 days of test. Since the coupons of the same type of metals exhibit similar extent of corrosion when exposed to different solutions, a simple visual inspection of surface appearance cannot tell the difference (e.g. a thick layer of rust covers the surface of the coupons of mild steel). The exact level of corrosion must be evaluated by weight loss analysis. However, an approximate assessment can be made by observing the colors of the solutions used in the test, as shown in Fig. 2-13a Fig. 2-13b. From the figure, it is apparent that MgCl$_2$ is more corrosive than NaCl, which is consistent to the results obtained in the Phase I. This confirms the conclusion achieved in the Phase I that MgCl$_2$ is more corrosive than NaCl by the SAE test.

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Fig. 2-12 The coupons of the SAE test at 20 days

Fig. 2-13a The 3 wt.% MgCl$_2$ solution used in the SAE test after 20 days
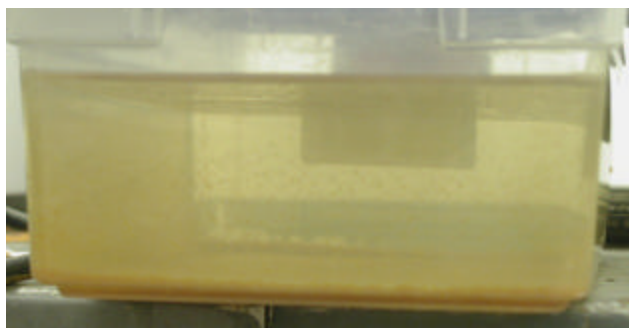
Fig. 2-13b The 3 wt.% NaCl solution used in the SAE test after 20 days
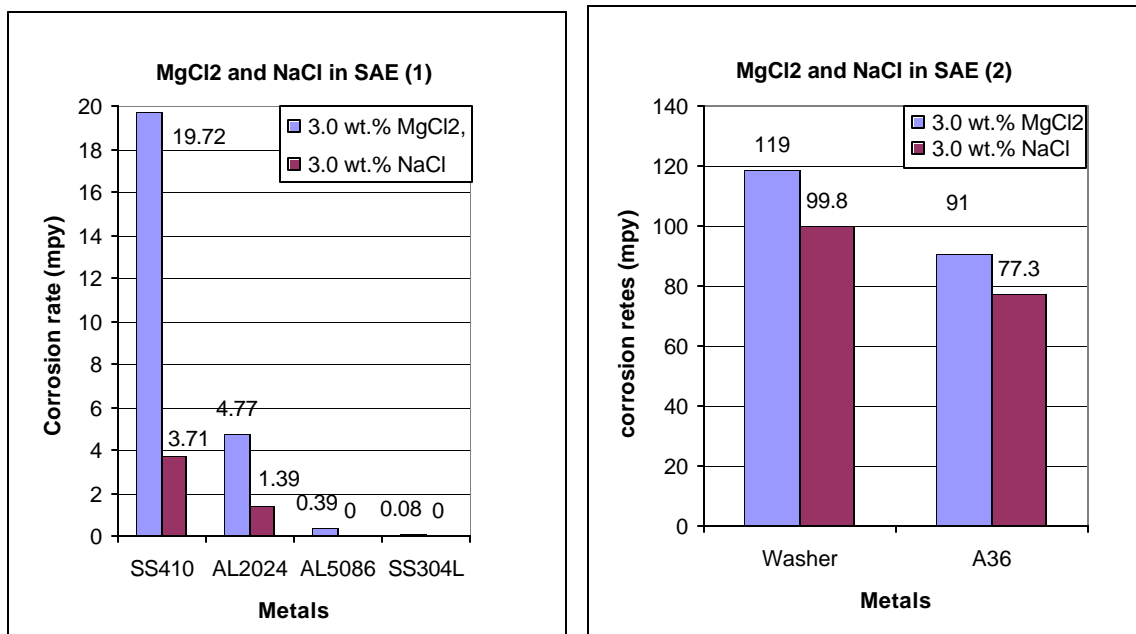
Fig. 2-14 Comparison of the corrosion rates by the SAE test after 81 days

10.3 Quantitative corrosion rate analysis

The results of the corrosion rate analysis are listed in Table 2-7 and Table 2-8 (Appendix II). The unit of the corrosion rate used in the tables is mils per year (mpy). The absolute weight loss (in gram) is also listed in the appendix. The same data are shown in Fig. 2-14 and Fig. 2-15, respectively. The corroded coupons are shown in Fig. 2-16 and Fig. 2-17.

It is important to note that the corrosion rates of the coupons exposed to the $MgCl_2$ increased greatly from the NACE test to the SAE test, for instance, SS410 from 0.3 in Fig. 2-15 to 19.72 in Fig. 2-14. While the corrosion rates of the coupons exposed to the NaCl did not increase in the same magnitude, SS410 from 1.28 in Fig. 2-15 to 3.71 in Fig. 2-14.

From the NACE test, the $MgCl_2$ with inhibitors is much less corrosive than the NaCl (Fig. 2-15), regardless of the concentration of the solution and the testing duration used in the test. From the SAE test, however, the $MgCl_2$ with inhibitors is more corrosive than the NaCl (Fig. 2-14); the same results as obtained in the Phase I study.
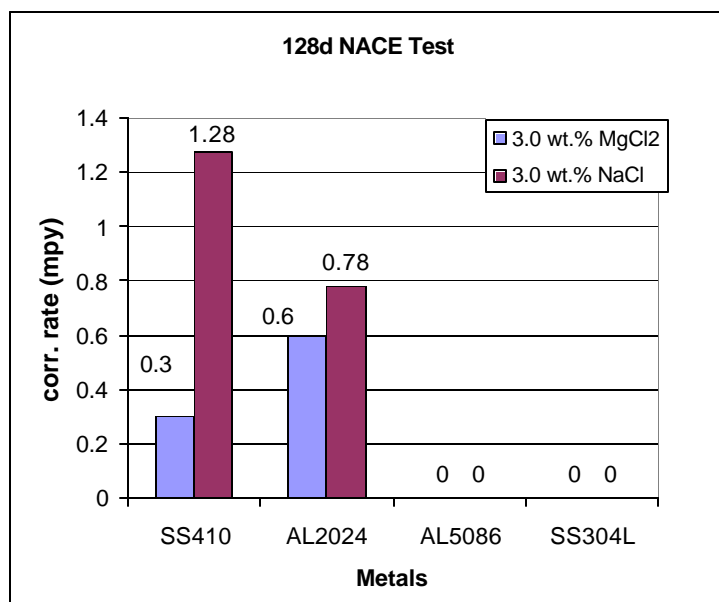
Fig. 2-15 128 days NACE test

Fig. 2-16 Coupons after the NACE test
(Upper: exposed to the MgCl₂ solution, lower: exposed to the NaCl solution)

Fig.2-17 Coupons after the SAE test
(Upper: exposed to the NaCl solution, lower: exposed to the MgCl$_2$ solution)

11. The effects of temperature and immersion time

Another major difference in the NACE test and the SAE test is the testing temperature. The NACE test is conducted under ambient temperature, while the SAE test is conducted under two elevated temperatures for the dry stage (60 ºC) and the humidity stage (50 ºC). In general, a higher temperature leads to a higher reaction rate. In order to assess the effect of temperature on the corrosion result, the NACE test was modified to have the testing temperature as 50ºC (122 ºF). At the same time, the immersion time of coupons in the solution was also modified. Instead of 10 min. in the solution and 50 min. in the air, the NACE test was modified to have coupons 30 min. in the solution and 30 min. in the air for each one-hour cycle. In this way, the contact time with chloride solutions is increased.
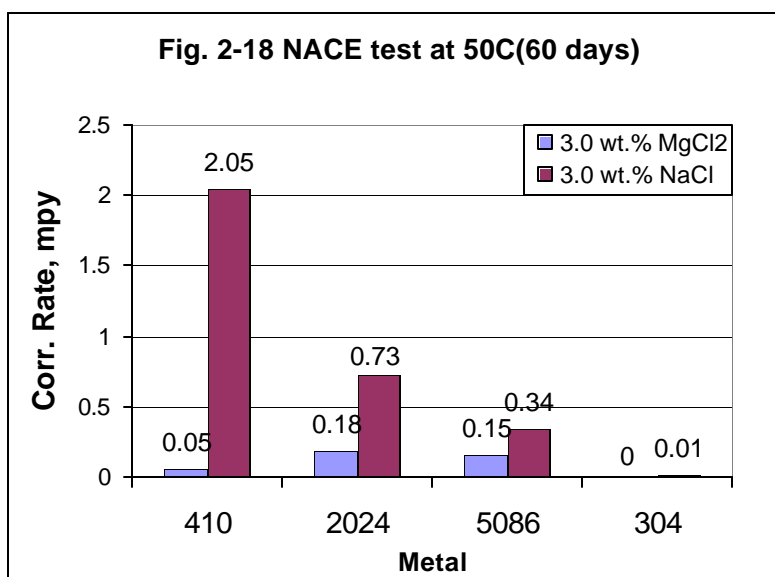
Fig.2-18 NACE test at 50°C (60 days)

The modified NACE test continued for 60 days. The results are shown in Fig. 2-18 and Table 2-9 (Appendix II). From Fig. 2-18, it is obvious that the NaCl is still more corrosive than the MgCl₂. Therefore, similar to the testing duration, the temperature and the immersion time are not the controlling parameter responsible for the difference between the NACE test and the SAE test.

12. Corrosion mechanisms involved in the tests

The two standard testing methods (SAE J2334 and NACE TM-01-69) led to different conclusions in terms of the relative corrosiveness of NaCl and $MgCl_2$ to the metals selected in this study. This suggests that the test results by ASTM B117 in the Phase I study was not an accidental phenomenon, it is reconfirmed by NACE TM-01-69 test in the Phase II study, both suggesting that NaCl has a higher corrosive ability than $MgCl_2$. The reason(s) for the difference should be identified.

It was already discussed that different testing methods have different environmental conditions, and which led to different corrosion rates of a metal with different media. In the case of NaCl, the corrosion rates of the coupons showed quite small changes from one testing environment to another. But in the case of $MgCl_2$, the corrosion rates increased drastically from the NACE testing condition to the SAE testing condition. The corrosion rate induced by $MgCl_2$ exceeds the corrosion rate of the same metal in NaCl in the SAE environment. We also noticed that the corrosion rates of the metals in distilled water have also been affected significantly by the testing conditions.

At first, we attributed the inconsistency in testing results to the effects of temperature, immersion time, the duration of testing, and the concentration of media. However, it was proved by the systematic experimental study that all these differences in testing parameters do not alter the corrosiveness order of the two salts. Further comparing the NACE test with the SAE J2334 test, we find that the only difference between the two testing methods that has not examined so far is that the SAE method has a "wet" stage of 6 hours at 50ºC and 100% relative humidity. It is believed that this stage is responsible for the different corrosion results.

We further examined the exposure histories experienced by the coupons in the two tests, respectively. In the NACE test, after the immersion period of 10 min, the coupons are raised from the solutions. On a fresh coupon with smooth surface, the chloride solution could not form an uniform and stable film when the coupon just comes out of the solution. Instead, the solution film disappears in a very short time under the action of surface tension and remains only on a small part of the surface, especially on the lower edge of the coupon. At the beginning of this stage, $MgCl_2$ solution is able to cover larger surface area than NaCl does, due to its high viscosity, but soon it dries up just like NaCl solution. Therefore, during most of the dry stage in the NACE test, the coupons have very short time to contact with the corrosive solution, thus this stage does not contribute much to the final corrosion result.

Most of the corrosion reaction is considered to take place during the immersion period. The immersion period of the NACE test is quite short, only 10 min. Frequent movement of the coupons in and out of the solution makes the solution somewhat like an aerated solution with high oxygen concentration. This situation is different from the one described in Fig. 13, in which the long-term immersion test was conducted. The rate of corrosion in the immersion test was very low because the solution was a stagnant solution with low oxygen concentration.

With increasing time of the tests, the surface of the coupons gradually becomes rough and is able to keep more solution on it, more corrosion takes place during this stage. However,

we must note that only the coupons evolving higher level of corrosion during the immersion period have rougher surfaces. For this reason, *it is believed that the NACE test basically represents the result of a continuous immersion test or a continuous spray test.* In fact, the NACE test has a similar total immersion time (not exactly the same) as the immersion time of the SAE test. The coupons in the solution during the NACE test is 720 min. (i.e. 10 min. per hour for 72 hours), while the SAE test has 900 min. immersion time (i.e. 15 min. immersion period each day for 60 days). The NACE test demonstrates that under the condition of continuous, direct contact between salt solutions and metals, NaCl solution is more aggressive than $MgCl_2$ solution. The test data obtained by ASTM B117 also support this conclusion.

When the environmental temperature is increased to 50 ºC, as in the modified NACE test, the surface of coupons becomes dried much faster. The contribution of the dry stage to the final corrosion result becomes even less. So, this modification can not alter the characteristic of the NACE test.
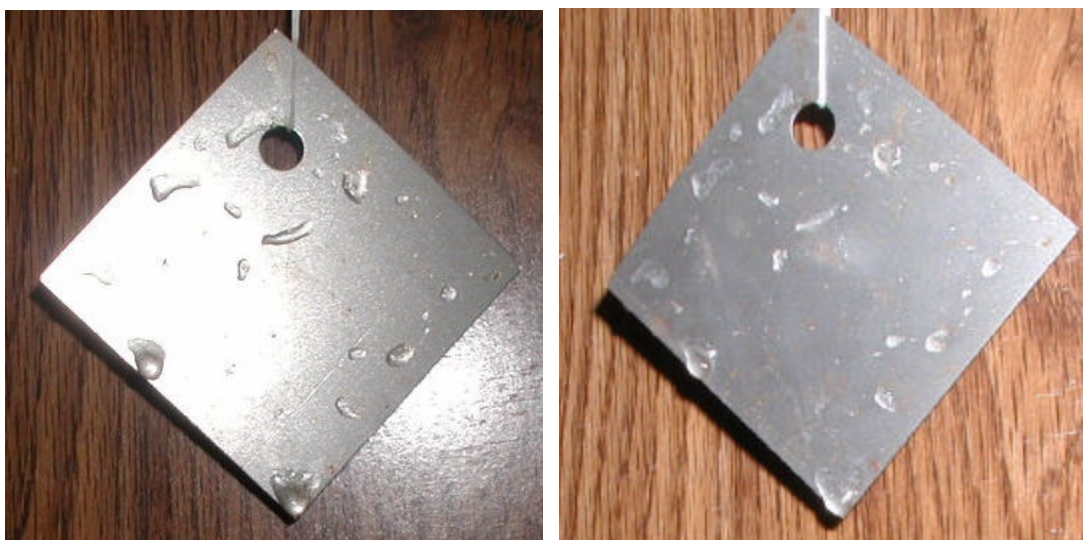
Fig.2-19 Condensed MgCl2 on the surface of metal after pulled out of the solution

With the SAE test, it has a wet stage of six hours at 50ºC, 100% relative humidity. This stage is very important to the total corrosion result, as suggested by the distilled water test. With the high humidity in this stage, a more corrosive environment is formed, in which all essential conditions for the corrosion process to take place, i.e. moisture, oxygen and metal, exist. In the case of $MgCl_2$ solution, with its high viscosity, $MgCl_2$ tends to adsorb and then condense on the surface of the coupons at the dry stage. This phenomenon can be seen in Fig. 2-19. The pictures show that crystallization has occurred on the surfaces of the solution beads. Due to its extremely high hydrophilicity, the condensed $MgCl_2$ solid will then absorb moisture and become solution as soon as the wet stage starts. This solution film does not evaporate in the high humidity condition during this stage. The coexistence of $MgCl_2$, water, oxygen and metal initiates the corrosion of metal coupons. After the condensation of $MgCl_2$ during the dry stage, the concentration of $MgCl_2$ on the surface of coupons in the subsequent wet stage is much higher

than the concentration of the testing solution, the high concentration definitely accelerates the corrosion, and moreover, the elevated temperature at the wet stage (50ºC) accelerates the corrosion as well. With more corrosion product developed, the surface of coupons becomes rougher and rougher, and the surface is able to keep more $MgCl_2$ solution at the dry stage, which in turn accelerates the corrosion in the wet stage. This explains the high corrosion rate by $MgCl_2$ in the SAE test.

For NaCl solution, there is less liquid kept on the surface than for the $MgCl_2$ when coupons are raised from the solution, this is mainly because of the low viscosity of NaCl solution. Therefore, when the surface becomes dry, not much solid salt exists on the coupon surface. In the wet stage, it is very hard for the NaCl solid to become solution because of its low absorbability to water. Without participation of the salt, the wet stage would not provide as severe corrosive condition to the metal as in the case of $MgCl_2$.

(Original states)   (8 min. late)   (6 hr. late)
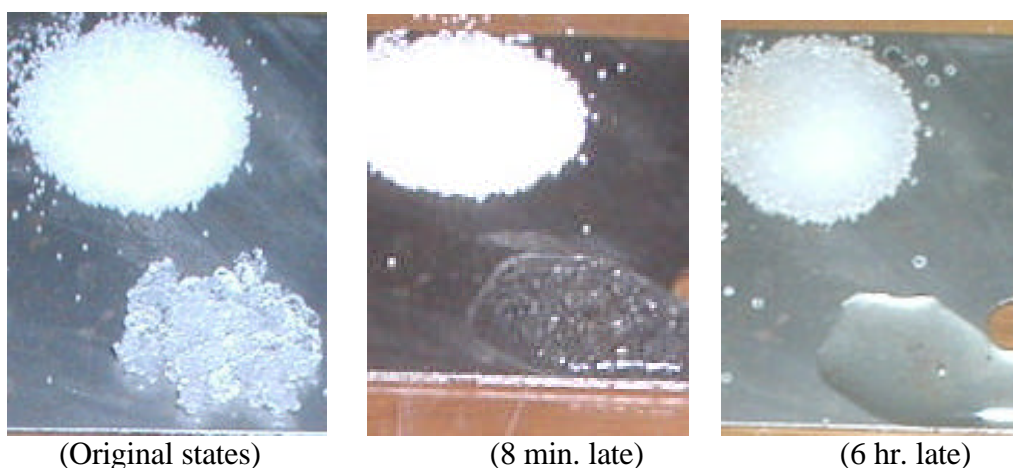
Fig. 2-20 Comparison of hydrophilicities between MgCl2 and NaCl

A simple experiment demonstrates the difference in hydrophilic behaviors of the two chlorides and physical changes experienced by them during the dry-wet process: both sodium and magnesium chlorides are placed in a chamber of 50°C and 100% relative humidity. It is observed that $MgCl_2$ solid dissolves into solution by absorbing moisture within a few minutes, while NaCl remains in solid state even after six hours, as shown in Fig.2-20.
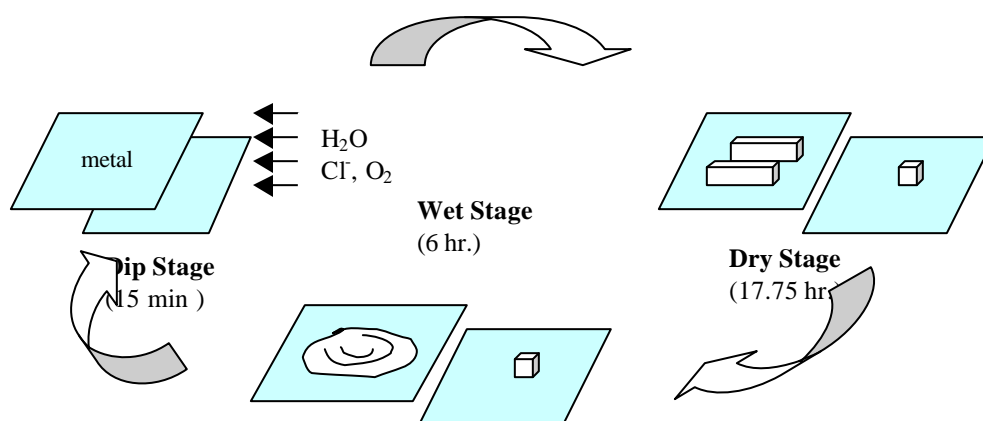
Fig.2-21 Physical changes of chlorides in the three stages in the SAE test
(Dip stage: coupons are attacked by chloride solution; Dry stage: chlorides dry up and become crystal, more $MgCl_2$ is kept on the surface than NaCl; Wet stage: $MgCl_2$ dissolves into solution, NaCl remains in solid state)

The corrosion process in the SAE test can be illustrated in Fig. 2-21. One can see that the NACE test mainly consisting of the "dip stage" and the "dry stage", while the SAE test has an additional "wet stage". As NaCl has higher corrosiveness than $MgCl_2$ when metal coupons are immersed in the solutions, NaCl causes higher corrosion rate than $MgCl_2$ in the NACE test. The SAE test has a short immersion period and a long "wet stage", which has an effect significant enough to change the corrosiveness order of the two salts. ASTM B117 test has only one stage, which is similar to the "dip state". As a result, it produces a similar result to the NACE test.

Strictly speaking, the NACE test is not exactly a cyclic exposure test, it may be considered as a test close to the category of immersion test. The NACE test is able to create a higher corrosion rate than a pure immersion test, mainly due to the frequent switch between the dry and the wet stages. The oxygen concentration on the surface of coupons increases drastically, which increases the corrosion rate.

In conclusion, the NACE test is more like a continuous immersion test than a cyclic exposure test. This explains the consistent results obtained by the NACE test and ASTM B117. At the same time, it also explains the contradictive results between the NACE test and SAE J2334.

The phenomenon shown in Figs. 2-19, 2-20, and 2-21 can be referred to as dry-wet effect, that is, a salt adsorbs on the surface of the metal at dry condition and then absorbs moisture to form solution at a subsequent wet condition. The dry-wet effect is especially profound for the salts with high viscosity and hydrophilicity, which can greatly increase corrosiveness of the salt. The dry-wet effect should be further investigated in the future studies.

13. Confirmation tests

In order to verify the corrosion mechanisms proposed in the previous section, additional experiments were designed and conducted. The results are shown and discussed in this section.

13.1 The NACE test at 50°C and 100% relative humidity

In this test, the coupons were placed in a chamber of 50°C and 100% relative humidity. The other testing conditions are the same as a standard NACE test, i.e. 10 min. dip in solution and 50 min. in air. The coupons in this test are either immersed in the solutions or stayed in saturated air. In both cases, the surface of the coupons was continuously covered by a liquid film. Therefore, this test is similar to a continuous immersion test. As expected, NaCl behaves more aggressively in this type of environment. The coupons tested by the modified NACE test after seven days are shown in Fig. 2-22a, which shows that NaCl solution indeed has higher corroding ability than $MgCl_2$. The corresponding corrosion rates are given in Fig. 2-22b.
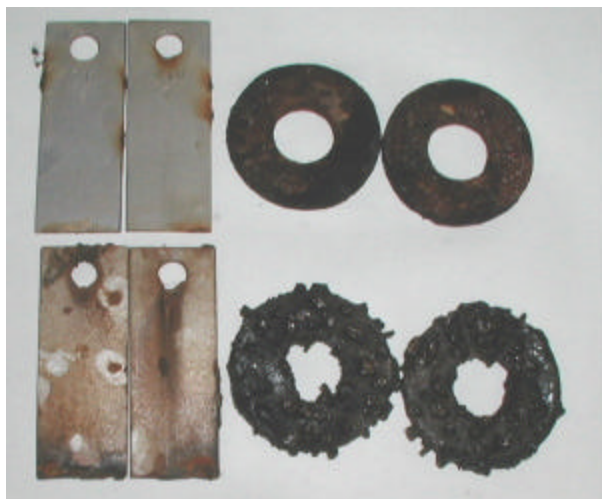
Fig. 2-22a Coupons in the NACE test at 50°C and 100% RH after 7 days
(upper: by $MgCl_2$; lower: by NaCl)
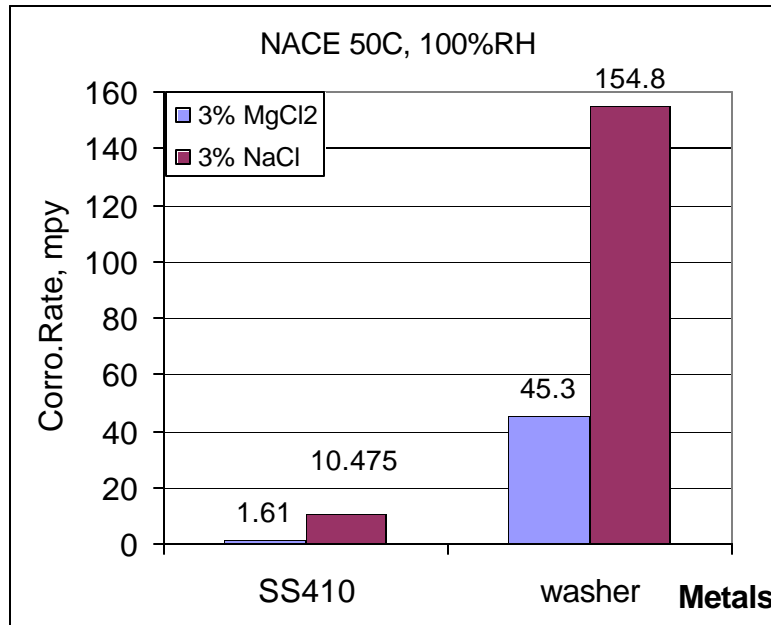
Fig. 2-22b Corrosion rates from the NACE test at 50°C and 100% RH after 7 days

13.2 The SAE test without the wet stage

This test consists of two stages in each 24-hour cycle: 15 min. dip in 25°C solution, followed by a dry stage of 23 hr. and 45 min. (60°C, 50% RH), i.e., a SAE J2334 test without the wet stage. As mentioned before, the coupons will become dry soon after placed in the dry chamber. It is very difficult for the corrosion to take place in the dry stage. Therefore, the corrosion during this modified SAE test takes place almost solely within the 15 min. dip stage in every 24 hours cycle. So, it is a intermittent immersion test, similar to the standard NACE test. The coupons tested for seven days are shown in Fig. 2-23a and the corrosion rates are given in Fig. 23b. It is very clear that minor corrosion was developed on the washer subjected to NaCl, consistent with the standard NACE test data, and all other coupons remained intact.
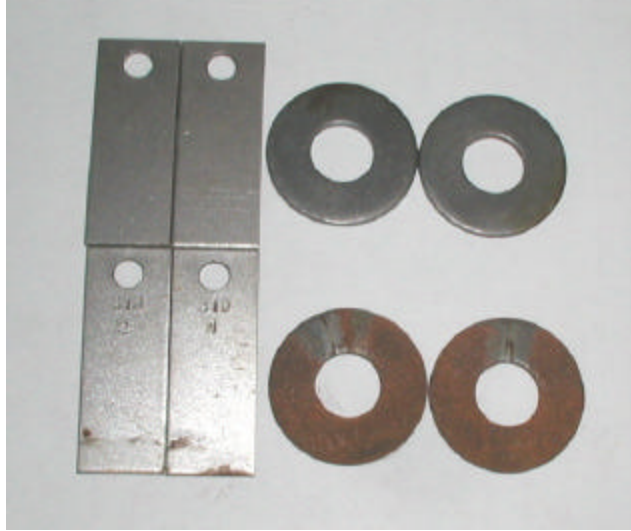
Fig. 2-23a Coupons by the SAE test without the wet stage after 7 days
(Upper: by MgCl₂; lower: by NaCl)
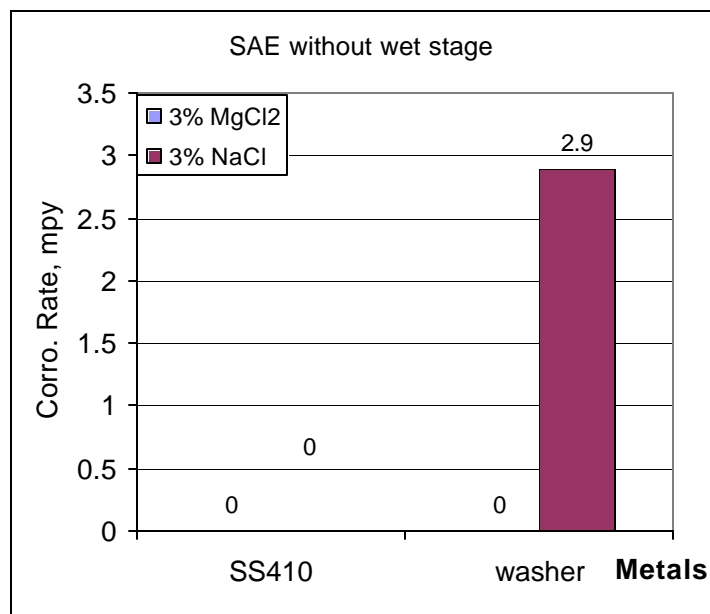
Fig. 2-23b Corrosion rates by the SAE test without the wet stage after 7 days

This test provides the most important evidence that the SAE test without the wet stage is similar to the standard NACE test, and that the wet stage is the crucial stage for the development of the corrosion from MgCl₂.

13.3 The SAE test without the dry stage

This test consists of two stages in every 24-hour cycle: 15 min. dip in 25°C solutions, followed by a wet chamber stage (50°C, 100%RH) of 23hr. and 45 min., i.e., the SAE J2334 test without the dry stage. Compared to the modified NACE test at 50°C and 100% RH (Section 13.1), this test has shorter dip period and at lower temperature: only a 15 min. dip period every 24 hours under 25°C. It can be seen from Figs. 2-24a and 2-24b that the results obtained by this test are different from those present in Section 13.1. The difference reflects the importance of immersion stage and its condition to the corrosion results. In the NACE test, the coupons are immersed in hot solutions of 50°C and have a total immersion time of 10 x 24 = 240 min. every 24 hours. As result, NaCl resulted in severe corrosion, as observed from Fig. 2-22a. In the case of the SAE test without the dry stage, the coupons have only a 15 min. dip period in 25°C solutions every 24 hours, as a result, the corresponding corrosion is much less severe than the NACE test (compare Fig. 2-22a and Fig. 2-24a).

Fig. 2-24a Coupons by the SAE test without the dry stage after 7 days
(upper: by MgCl$_2$; lower: by NaCl)
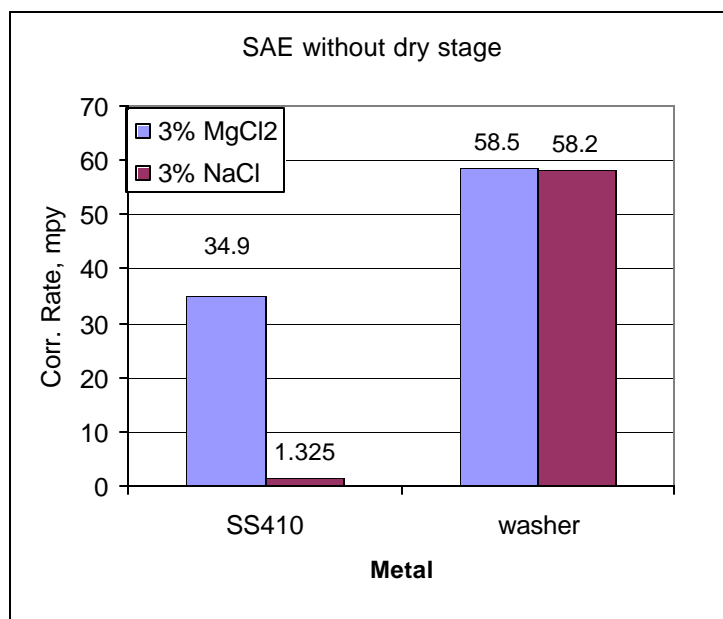
Fig. 2-24b Corrosion rates by the SAE test without the dry stage after 7 days

There is one important phenomenon in this test, i.e., with NaCl as medium, the wet chamber stage seems much less corrosive than the dip stage to the coupons, which can be seen by comparing the coupons with NaCl in Fig. 2-22a and Fig. 2-24a. With $MgCl_2$ as medium, the wet chamber stage resulted in very high corrosion rates than the dip stage, which can also be seen by comparing the coupons with $MgCl_2$ in Fig. 2-22a and Fig. 2-24a. The mechanisms responsible for the phenomenon have not been fully understood. Nevertheless, these confirmation tests reiterate such a fact: under high humidity environment, $MgCl_2$ tends to cause higher levels of corrosion, and in dip condition NaCl results in higher corrosion.

14. Discussion and conclusions

14.1 About corrosion inhibitors

Some corrosion inhibitors contain biodegradable ingredients, which may decompose after exposed to elevated temperatures. We took into account the degradation effect of corrosion inhibitor in the SAE test. Does the failure of the inhibitor in $MgCl_2$ solution lead to high level of corrosion in the SAE J2334 test?

To answer this question, a small bottle of $MgCl_2$ solution was included in the SAE test. The $MgCl_2$ solution with inhibitors went through the same temperature cycles with the coupons. When the SAE test was stopped, the chemical compositions of the $MgCl_2$ solution and the original $MgCl_2$ solution were analyzed and compared. The difference in chemical composition of the solutions, if any, is an indication of the degradation of the corrosion inhibitor under the testing environment.

After 60 days of the SAE test, the chemical compositions of the $MgCl_2$ solutions were analyzed. The result indicated that the original $MgCl_2$ solutions contained 280 mg/L of organic carbon and the $MgCl_2$ solution after the SAE test contained 700 mg/L of organic carbon. It seems that the inhibitor in the $MgCl_2$ solution was not decomposed by the SAE testing condition. The increase in the concentration of organic carbon can be explained by the evaporation of water from the solution, as we noted that the sample of the solution was highly crystallized and there was a significant decrease in the volume when it was taken out from the testing chamber.

From the chemical analysis, one can see that there was no decrease in the organic carbon content of the inhibitor after the elevated temperature. However, we can not completely rule out the possibility of the degradation of the inhibitor in the $MgCl_2$ solution, because, besides the organic carbon content, we are still not sure if any other change has occurred in the chemical composition of the inhibitor. On the other hand, Fig.2-5 suggests that the inhibitor functions quite well, reducing the corrosion rate of SS410 from 26.4 mpy to 14 mpy when the concentration of $MgCl_2$ increased from 1.0% to 3.0%. More researches are apparently needed on the degradation of the corrosion inhibitors under elevated and cyclic temperature environment.

In general, corrosion inhibitors are metal-specific and salt-specific. In another words, there are no corrosion inhibitors that work very well for all metals and all deicing salts. Because CDOT requires specifically that $MgCl_2$ must be 70% less corrosive than NaCl, and because the NACE (PNS standard) requires specifically the use of the washer (mild steel) as coupon for the NACE test, the corrosion inhibitors developed by the suppliers in PNS region may work especially well with $MgCl_2$ and the mild steel, but not equivalently well with other metals. This explains the large variation in corrosiveness when different metals were used in both the SAE test and the NACE test.

14.2 Which testing method is more realistic for simulating service condition?

The testing methods used in the present study can be grouped into two categories. The first category, with the immersion effect as the dominant corrosion mechanism, includes ASTM

B117 and the NACE TM-01-09 test. The other category, with the dry-wet effect as the controlling corrosion mechanism, includes SAE J2334 test.

On the road, vehicles or parts of vehicles may experience elevated temperatures and high humidity. One case is the parts close to or connected to high temperature components (e.g. hood) and/or in humid environment (e.g. lower part of front door); another case is the vehicle under direct sunlight. For these cases, the SAE testing method may provide a more realistic evaluation of the corrosiveness of the deicing chemicals. For those parts of vehicles that remain under immersion condition and arid environment, the NACE testing method may provide a better estimation of the corrosiveness of the deicing chemicals. In the real service situation, a vehicle may be exposed to a very specific and complicated condition, which may not be represented by either one of the testing methods.

Although both the NACE method and the SAE method are considered to be accelerated corrosion tests, the SAE method creates a more aggressive environment for all metals tested and for all corrosion medium used in the study.

14.3 Sodium chloride or magnesium chloride?

Comparing the corrosiveness of the two chloride solutions when directly contacting a metal, $MgCl_2$ is less aggressive than NaCl, as indicated by test data from ASTM B117 and NACE TM-01-69. However, $MgCl_2$ solution has high viscosity, high crystallization potential and strong hydrophilicity, so, it can stick on the surface of a metal and becomes solution again in humid environment. Eventually, it may lead to more severe corrosion than NaCl, especially to the components with coarse surfaces. Therefore, $MgCl_2$ may have higher or lower corrosiveness than NaCl, depending on the specific exposure conditions experienced by a vehicle.

The present test data indicate that using magnesium chloride in combination with sodium chloride does not cause higher corrosion for most of the metals tested than using just sodium chloride. Although the coupling effect was observed for SS410, it has been studied only briefly by the SAE test, more systematic and comparative studies are needed in the future.

We only examined the corrosion effect of magnesium chloride on various metals, other effects of magnesium chloride should also be considered, such as the impacts to concrete pavements, to steel bridges, and to the environment.

14.4 Conclusions of the phase II study

- The experimental results show that NACE TM-01-09 test and ASTM B117 test lead to similar results regarding the relative corrosiveness of the deicing salts: NaCl is more corrosive than $MgCl_2$. SAE J2334 test leads to different results: $MgCl_2$ is more corrosive than NaCl. It is experimentally demonstrated that the difference in the test results is not due to the effects of different testing temperatures, different durations of testing, different immersion time, and different concentrations of deicing chemicals in the tests. The difference is due to the wet stage in SAE 2334 test.

- MgCl₂ solution has higher viscosity than NaCl solution, and thus, MgCl₂ solution tends to stick and crystallize on the surface of the metal coupons in the dry stage of SAE 2334. MgCl₂ crystals have higher hydrophilicity than NaCl crystals, and thus, MgCl₂ crystals absorb moisture and turn into solution in the wet stage in SAE 2334 (which is right after the dry stage). The dry-wet effect is the primary cause responsible for the different corrosion test results between SAE 2334 and the NACE test methods.

- Different corrosion mechanisms are involved under immersion condition and wet condition for NaCl and MgCl₂. Under high humidity condition (wet), MgCl₂ tends to cause higher levels of corrosion; and under dip condition (immersion), NaCl results in higher level of corrosion. It must be mentioned that this conclusion was made based on experiments with the deicing chemicals used in the state of Colorado.

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Appendix 1. Results of corrosion tests of the Phase I study

Table 4 Test results with MgCl₂ reagent by SAE J2334

Metal	Original weight (g)	Weight after test (g)	Weight loss (g)	Loss in %	Corrosion rate (mpy)	Average rate (mpy)
Al2024	5.698	5.468	0.23	4.0365	3.7	3.75
Al2024	5.706	5.469	0.237	4.1535	3.8	
Al5086	5.426	5.425	0.001	0.0184	0.02	0.06
Al5086	5.435	5.432	0.003	0.0552	0.1	
SS410	15.057	13.644	1.413	9.3843	8.3	8.35
SS410	15.199	13.766	1.433	9.4283	8.4	
SS304L	17.801	17.798	0.003	0.0168	0.02	0.025
SS304L	17.908	17.903	0.005	0.0279	0.03	

Table 5 Test results with NaCl reagent by SAE J2334

Metal	Original weight (g)	Weight after test (g)	Weight loss (g)	Loss in %	Corrosion rate mpy	Average rate mpy
Al2024	5.693	5.623	0.07	1.2296	1.1	1.15
Al2024	5.713	5.639	0.074	1.2953	1.2	
Al5086	5.429	5.445	0	0	0	0
Al5086	5.432	5.448	0	0	0	
SS410	15.299	15.068	0.231	1.5099	1.4	1.6
SS410	15.416	15.111	0.305	1.9785	1.8	
SS304L	17.816	17.816	0	0	0	0
SS304L	17.871	17.871	0	0	0	

Table 6 Test results with MgCl₂ practical salt by SAE J2334

Metal	Original weight (g)	Weight after test (g)	Weight loss (g)	Loss in %	Corrosion rate (mpy)	Average rate (mpy)
Al2024	5.721	5.6333	0.088	1.5382	1.4	1.5
Al2024	5.726	5.63	0.096	1.6766	1.6	
Al5086	5.438	5.42	0.018	0.331	0.3	0.235
Al5086	5.424	5.414	0.01	0.1844	0.17	
SS410	15.087	10.688	4.399	29.1576	25.7	26.4
SS410	15.39	10.761	4.629	30.078	27.1	
SS304L	17.795	17.783	0.012	0.0674	0.07	0.06
SS304L	17.915	17.906	0.009	0.0502	0.05	

Table 7 Test results with NaCl practical salt by SAE J2334

Metal	Original weight (g)	Weight after test (g)	Weight loss (g)	Loss in %	Corrosion rate (mpy)	Average rate (mpy)
Al2024	5.718	5.61	0.108	1.8888	1.7	1.35
Al2024	5.718	5.654	0.064	1.1193	1	
Al5086	5.436	5.447	0	0	0	0
Al5086	5.434	5.447	0	0	0	
SS410	15.444	15.076	0.368	2.3828	2.2	1.95
SS410	15.413	15.122	0.291	1.888	1.7	
SS304L	17.809	17.809	0	0	0	0
SS304L	18.354	18.354	0	0	0	

Table 8 Test results with NaCl + MgCl$_2$ practical salts by SAE J2334

Metal	Original weight (g)	Weight after test (g)	Weight loss (g)	Loss in %	Corrosion rate (mpy)
Al2024	5.715	5.585	0.13	2.2747	2.1
Al5086	5.434	5.398	0.036	0.6625	0.61
SS304L	17.813	17.789	0.024	0.1347	0.14
SS410	30.195	27.2	2.995	9.9189	17.5

Table 9 Test results with NaCl practical salt by ASTM B117

Metal	Original weight (g)	Weight after test (g)	Weight loss (g)	Loss in %	Corrosion rate (mpy)
Al2024	5.718	5.682	0.036	0.6296	1.05
Al5086	5.432	5.419	0.013	0.2393	0.4
SS410	15.306	14.927	0.379	2.4761	3.99
SS304L	17.885	17.885	0	0	0

Table 10 Test results with MgCl$_2$ practical salt by ASTM B117

Metal	Original weight (g)	Weight after test (g)	Weight loss (g)	Loss in %	Corrosion rate (mpy)
Al2024	5.715	5.68	0.035	0.6124	1.02
Al5086	5.435	5.393	0.042	0.7728	1.28
SS410	15.141	15.036	0.105	0.6935	1.1
SS304L	18.406	18.393	0.013	0.0706	0.13

Table 11 Corrosion of the metal coupons mounted on the trucks

Truck #	1576	295	1423	1169	1159	1158	1166	3088	3067	3066
SS304L	#1	#2	#3	#4	#5	#6	#7	#8	#9	#10
Orig. wt	35.5	36.652	36.717	36.818	36.846	36.446	36.593	36.228	36.148	36.69
after corr.	35.47	36.65	36.71	36.814	36.843	36.443	36.59	36.227	36.149	36.684
wt loss, g	0.034	0.004	0.003	0.004	0.003	0.003	0.003	0.001	0	0.006
loss, %	0.957	0.109	0.081	0.108	0.081	0.082	0.081	0.027	0	0.163
SS410										
Orig. wt	30.601	30.692	30.572	30.652	28.712	30.186	30.572	29.72	28.461	30.579
After corr.	30.563	30.675	30.581	30.626	28.691	30.165	30.56	29.704	28.455	30.563
wt loss, g	0.038	0.017	0	0.026	0.021	0.021	0.012	0.016	0.006	0.016
Loss, %	1.241	0.553	0	0.848	0.731	0.695	0.392	0.538	0.210	0.523
Al2024										
Orig. wt	11.475	11.476	11.472	11.475	11.468	11.449	11.433	11.456	11.438	11.45
After corr.	11.444	11.389	11.466	11.442	11.406	11.414	11.372	11.434	11.43	11.421
wt loss, g	0.031	0.087	0.006	0.033	0.062	0.035	0.061	0.022	0.008	0.029
Loss, %	2.701	7.581	0.523	2.875	5.406	3.057	5.335	1.920	0.699	2.532
Al5086										
orig. wt	10.908	10.899	10.902	10.906	10.896	10.902	10.899	10.896	10.899	10.903
after corr.	10.882	10.837	10.892	10.845	10.828	10.832	10.826	10.861	10.884	10.858
wt loss, g	0.026	0.062	0.01	0.061	0.068	0.07	0.073	0.035	0.015	0.045
loss, %	2.383	5.688	0.917	5.593	6.240	6.420	6.697	3.212	1.376	4.127

Appendix II. Results of corrosion tests of the Phase II study

Table 2-1 NACE test results

RUN	medium	Orig. wt. (g)	After corr. (g)	Corr rate (mpy)	ratio %
RUN 1	MgCl2	32.954	32.848	16.17	38.1
	NaCl	32.751	32.473	42.42	100
RUN 1	MgCl2	32.828	32.728	15.26	31.3
	NaCl	33.029	32.71	48.68	100
RUN 1	MgCl2	32.959	32.835	18.92	43.2
	NaCl	33.003	32.716	43.79	100

Table 2-2 NACE test

Concentration	Metal	Original wt. (g)	Wt. After test (g)	corrosion rate (mpy)
3% MgCl2	washer	32.959	32.835	18.92137
	Washer	32.943	32.821	18.61619
	A36	53.467	53.274	25.185
9% MgCl2	Washer	32.724	32.6	18.92137
12%MgCl2	Washer	32.854	32.782	10.9866
	A36	49.989	49.873	15.1371
3% NaCl	Washer	33.003	32.716	43.79382
	Washer	32.815	32.556	39.52125
	A36	56.218	55.839	49.45655

Table 2-3 SAE test with MgCl2 in Phase II study

Materials	Original wt. (g)	Wt. After test (g)	Corrosion rate (mpy)
A36	27.711	20.438	98.17964
A36	27.743	20.015	104.3218
washer	32.915	15.664	136.1565

Table 2-4 SAE test with different NaCl concentrations

Solution	Metal	Original wt. (g)	Wt. After test (g)	corrosion rate (mpy)
1.5% NaCl	A36	56.046	43.515	81.75989
	Washer	32.75	19.41	101.7787
3.0% NaCl	A36	27.85	19.335	111.1141
	A36	27.964	19.804	106.4816
	Washer	32.87	15.817	130.1073
6.0% NaCl	Washer	32.73	15.522	131.2899

Table 2-7. NACE test results after 128 days (mpy)

	NaCl	MgCl$_2$	H$_2$O (109 days)
SS410	1.28	0.3	0
AL2024	0.78	0.6	0
Al5086	0	0	
SS304L	0	0	
Washer			0.133
A36			0.16

Table 2-8. SAE test results after 81 days (mpy)

	NaCl	MgCl$_2$	H$_2$O
SS410	3.71	19.71	0
AL2024	1.39	4.77	0
Al5086	0	0.39	
SS304L	0	0.09	
Washer	91	119	0.415
A36	77.3	99.8	0.355

Table 2-9a NACE test with MgCl2 at 50 ºC

Metal	orig. wt (g)	wt. after test, (g)	Corrosion rate (mpy)
410	21.78	21.773	0.051538
2024	8.346	8.337	0.183535
5086	8.154	8.147	0.149189
304	21.515	21.515	0

Table 2-9b NACE test with NaCl at 50 ºC

	Orig. wt. (g)	wt. after test, (g)	Corrosion rate (mpy)
410	21.801	21.522	2.054161
2024	8.351	8.315	0.73414
5086	8.17	8.154	0.341004
304	21.453	21.451	0.01428

Table 2-10 NACE in wet chamber, 7 days, with MgCl2

	Original wt.	After Corr.	Wt. Loss,	Corr. Rate	Average
	g	g	G	mpy	mpy
410	11.645	11.626	0.019	1.2	1.61
410	11.553	11.537	0.016	2.02	
washer	32.885	32.193	0.692	45.3	45.3

Table 2-11 NACE in wet chamber, 7 days, with NaCl

	Original wt.	After Corr.	Wt. Loss,	Corr. Rate	Average
	g	g	G	mpy	mpy
410	11.67	11.59	0.08	10.1	10.475
410	11.962	11.876	0.086	10.85	
washer	32.885	30.518	2.367	154.8	154.8

Table 2-12 SAE with dip and wet chamber, 7days, with MgCl2

	Original wt.	After Corr.	Wt. Loss,	Corr. Rate	Average
	g	g	G	mpy	mpy
410	10.891	10.6	0.291	36.73	34.9
410	10.907	10.645	0.262	33.07	
washer	32.845	31.95	0.895	58.5	58.5

Table 2-13 SAE with dip and wet chamber, 7 days, with NaCl

	Original wt.	After Corr.	Wt. Loss,	Corr. Rate	Average
	g	g	g	mpy	mpy
410	10.91	10.9	0.01	1.26	1.325
410	10.885	10.874	0.011	1.39	
washer	33.015	32.125	0.89	58.2	58.2

Table 2-14 SAE with dip and dry chamber, 7days, with MgCl2

	Original wt.	After Corr.	Wt. Loss,	Corr. Rate	Average
	g	g	g	mpy	mpy
410	10.885	10.885	0	0	0
410	10.893	10.893	0	0	
washer	33.036	33.036	0	0	0

Table 2-15 SAE with dip and dry chamber, 7 days, with NaCl

	Original wt.	After Corr.	Wt. Loss,	Corr. Rate	Average
	g	g	g	mpy	mpy
410	11.007	11.007	0	0	0
410	10.928	10.928	0	0	
washer	32.887	32.843	0.044	2.9	2.9