**2023**
**SOUTH DAKOTA DEPARTMENT OF TRANSPORTATION**
**MAGNESIUM CHLORIDE SPECIFICATIONS**
**AND TEST PROTOCOLS**

## I. SPECIFICATIONS

Clear Roads provides guidance and administration of the Qualified Products List (QPL), which was originally established through the Pacific Northwest Snowfighters. The QPL was created to review, test, and approve products used for winter maintenance and to provide guidance in the selection and purchasing of environmentally responsible products. The QPL can be found at https://clearroads.org/qualified-product-list/

To bid a product under these specifications, products must be on the current QPL, as shown in section VI.F of these specifications.

Any material change to a product listed on the QPL by either the manufacturer or the supplier, which in any way makes the product different from the original qualified product, disqualifies the product for use by SDDOT under these specifications.

The supplier of any product that is delivered or applied, which is found to be contaminated or is cause for environmental concern, will be responsible for all clean up expenses. The term “clean up expenses” includes but is not limited to clean up measures required for the storage facility, yard, equipment, and roadside.

A. No submitted product containing any constituent in excess of the following established total concentration limits as tested in accordance with the listed test methodology from Section V will be accepted. Results are stated as Parts per Million (ppm).

| | | |
|---|---|---|
| 1. | Arsenic | 5.0 |
| 2. | Barium | 100.0 |
| 3. | Cadmium | 0.20 |
| 4. | Chromium | 1.0 |
| 5. | Copper | 1.0 |
| 6. | Cyanide | 0.20 |
| 7. | Lead | 1.0 |
| 8. | Mercury | 0.05 |
| 9. | Phosphorus | 2500.0 |
| 10. | Selenium | 5.0 |
| 11. | Zinc | 10.00 |

Note: Liquid products are tested as received.

B. To meet these specifications, a corrosion inhibited chemical product must successfully complete the National Association of Corrosion Engineers (NACE) Standard TM0169-95, as modified by Clear Roads, and found to have a Corrosion Value of at least 70% less than that of sodium chloride (salt).

C. The Supplier will be liable for any unanticipated or extraordinary damage to equipment used in the storage or distribution of the chemical product. This determination will be in the sole discretion of the South Dakota Department of Transportation (SDDOT).

D. The SDDOT, in its sole discretion, has the right to accept or reject any product based on the materials used to produce the product, or the product’s potential to adversely affect the safety of the public or the environment.

E. Award will be made to the lowest responsible, responsive bidder except as specified herein. Past performance may be taken into consideration as a basis for award.

F. The following requirements also apply to liquid magnesium chloride products:

1. Product must contain no less than 28% and no more than 32% magnesium chloride by weight. Product is to be tested in accordance with test method number 1, Section V of these specifications.
2. Weight per gallon will be established according to the specific gravity and percentage of magnesium chloride contained in the product bid. Product is to be tested in accordance with test method number 2, Section V of these specifications.
3. Product will contain the corrosion control inhibitor in quantities not less than those indicated by the Supplier. The finished deicing product, including corrosion inhibitors, must be completely accomplished at the original manufacturing plant location prior to loading on the transport. Post adding of corrosion inhibitors or any other ingredients after the product has left the original manufacturing plant, and splash mixing, are unacceptable. Product is to be tested in accordance with test method number 3, Section V of these specifications.
4. Product pH must be between 6.0 and 9.0. Product is to be tested in accordance with test method number 4, Section V of these specifications.
5. Product will not contain greater than 1.0% (V/V) Total Settleable Solids and will have ninety-nine percent (99.0%) of the Solids Passing through a Number 10 sieve after being stored at -17.8° C +/- 1° C (0° F +/- 2° F) for 168 hours (Seven days). Product is to be tested in accordance with test method number 5, Section V of these specifications.

## II. BID PROCESS

A. Bids must be accompanied by an analysis of the product being bid. This analysis must contain the following information for each type of product being bid:

1. Corrosion test data obtained according to NACE Standard TM0169-95 as modified by PNS.
2. Analytical results of all constituents for which limits have been set by these Specifications.
3. Specific gravity chart with correlating weight percentage and freeze point information presented in 1% increments beginning with a five percent solution. The chart must contain information up to, including, and exceeding by 5% (or the solubility limits of the product) the concentration being bid.

B. Bids will be accompanied by the most recent detailed product specification sheet and Material Safety Data Sheet (MSDS) including the MSDS of the inhibitor. All documents must be clearly legible.

## III. ORDERS, DELIVERIES, AND INVOICING OF PRODUCTS.

A. SDDOT will place all orders by either phone or email. The official order date will be the date of the phone call or email transmittal if sent by the SDDOT before 2:00 p.m., or the next day if sent by the SDDOT after 2:00 p.m. (All order times reflect Purchaser's time.) The Supplier will call or email back to the SDDOT within 2 business hours a confirmation of receipt of the order and an estimate of the order shipment date.

B. Supplier will make all deliveries during normal working hours (Monday through Friday between the hours of 7:00 a.m. and 4:00 p.m. CST or MST, respective of the time zone in which the delivery is received). Supplier will provide a minimum of 24 hours advance notice of delivery time, unless otherwise requested or agreed to by the SDDOT. Any delivery made without proper advance notification or outside of the established delivery times, unless otherwise authorized by SDDOT in advance, will be assessed a liquidated damages assessment of 10% of the purchase price of the product. Any liquidated damages assessed pursuant to this section will be in addition to any liquidated damages assessed pursuant to Section VI for deviations from these specifications.

C. Supplier will make all deliveries within seven (7) calendar days of the order date. If the Supplier does not deliver within this required time, Supplier will pay SDDOT a liquidated damages assessment of 5% per day for each day of delay, beginning with day 8, and continuing until delivery is made. If the Supplier has not made satisfactory arrangements with the SDDOT Maintenance Shop (Point of Delivery) personnel by the required delivery date, the SDDOT may, at its sole discretion, order from another vendor and the Supplier will pay SDDOT for any additional cost. Any pattern of late deliveries, which in the sole determination of the SDDOT Operations Support Program Manager causes operational issues for SDDOT, will be grounds for the SDDOT to terminate the contract.

D. During the months of November 1 through April 1, each inclusive, if the SDDOT places an order larger than 2 transports for any location, the Supplier will deliver at least 2 transports of that order within the specified time period or liquidated damages will apply. If the Supplier cannot deliver the entire order at once, the balance must be delivered on daily deliveries beginning immediately after the first delivery, until the order is fulfilled, or as otherwise agreed to by the SDDOT.

E. During the months of November 1 through April 1, each inclusive, SDDOT may place orders, clearly designated by SDDOT as “emergency orders.” Delivery of an emergency order within 48 hours of placement of the order will carry a 10% premium above the contract price. The 10% premium is to compensate Supplier for the short notice expenses Supplier may incur and to offer an incentive for Supplier to make every effort to make delivery within the shortened time frame. Supplier will notify SDDOT within 2 hours of placement of an emergency order stating an expected delivery time. If the expected delivery time is not within the 48-hour time frame, SDDOT may go to alternate suppliers in an attempt to fill the order. If the Supplier attempts to make the 48-hour delivery, but does not do so, SDDOT will pay the “as bid” contract price.

F. Supplier will communicate any objection to liquidated damages assessed for a late delivery or specification deviation within seven (7) calendar days of receipt of the liquidated damages assessment. The Supplier will communicate the objection in writing, to the Operations Support Program Manager. The decision of the Operations Support Program Manager to accept or to deny the objection will be final.

G. Supplier will be responsible for all necessary equipment to transfer liquid chemical products to SDDOT’S storage tanks. SDDOT will fit each storage tank with a two-inch male pipe fitting or a large non-connective opening to allow for unloading of product.

H. Supplier will include a current and clearly legible MSDS with each delivery.

I. Supplier will make available an anti-foaming agent for use as needed, at no additional charge to the SDDOT, to control foaming during loading, unloading, and agitation of liquid chemical products.

J. The bill of lading for each shipment must contain the following information:

1. Name of product.
2. Supplier and manufacturer of product.
3. Delivery destination.
4. Total number of units being delivered.
5. Total weight of delivery using a certified scale ticket.
6. The Lot number of product being delivered. The lot number must enable SDDOT to track a delivered product back to its manufacture point, date of manufacture, and specific batch.
7. Transport information—Name of transporting company, tank, trailer, or rail car number, point and date of origin.
8. The Percent Concentration and Specific Gravity, and the test results of both.

K. The invoice must include all the above and the following information:

1. A copy of the original bill of lading.

2. Contract unit of measure.
3. Total number of units delivered.
4. Contract unit price for product delivered.
5. Total price for the units delivered.

L. Fuel Cost Adjustments – The Purchaser will base the price change on a four- or five-week average, to the nearest hundredth of a dollar ($0.01) using the rounding procedures from the DOT Materials Manual, located on the Purchaser's web site. The Purchaser will use the "Weekly Retail On Highway Diesel Prices" for "All Types" using Midwest Prices as reported in the Energy Information Administration (EIA) of the US Department of Energy weekly publication. A 4-week average will be used for months having 4 Mondays and a 5-week average will be used for months having 5 Mondays. The amended contract price will be reviewed monthly during the last week of the month by the Operations Support Office of the SDDOT; therefore, initiating a new contract price effective for deliveries made the following month through the Office of Procurement Management. Should fuel prices increase or decrease beyond 10% from the base price of $3.781 as determined from the EIA publication – Midwest Div. on May 29, 2023, the contract price will be amended as follows:

Calculations have shown that fuel consumption is approximately 50% of the total transportation costs for the delivered loads. Therefore, when a fuel cost adjustment is needed according to the terms of this contract the following procedure will be used. A base price of $.66/gal has been assumed for magnesium chloride being delivered to the sites. The total transportation costs are then determined by subtracting the base price for alternative chemical deicers and magnesium chloride, $.66/per gal., from the Supplier's bid price for that delivery location. Then 50% of that amount will be used for the calculated fuel cost.

Example: The bid price of magnesium chloride is $1.30/gal. Then the transportation cost would be ($1.30-$.66) or $.64/gal. Then 50% of that amount or $.32/gal will be used for the calculated fuel cost.

The percentage applied to the calculated fuel cost would be the amount over 10% to the nearest 0.1%.

Example: The current four- or five-week average fuel price, rounded to the nearest hundredth of a dollar, is $5.00/gal and the published price as of May 29th ,2023 is $3.781/gal. The total percentage increase in fuel price is $5.00 - $3.781 = $1.219/$3.781 or 32.2%. Therefore, the amount applied to the calculated fuel cost would be 32.2% - 10% or 22.2%.

Therefore, the cost increase applied to the contract price would be 22.2% times the calculated fuel cost.

Example: $.32 x 22.2% = $.0710/gal, therefore, use $.071/gal increase. So, $1.30/gal plus $.071/gal for an amended contract price of $1.371/gal.

The same calculations would hold true if the cost of fuel were to fall more than 10% below the published price on May 29th, 2023.

M. Split Loads: Any time a Purchase Order directs that a load be split between more than one delivery location, Supplier will charge no more than $100.00 as a drop fee charged to each location following the first delivery. Supplier will confirm any drop shipment fees in its order confirmation.

## IV. FIELD INSPECTION, UNLOADING, SAMPLING AND TESTING

All product is subject to field and laboratory inspection, sampling, and testing on an as delivered basis. Inspection, sampling, and testing may be done at the sole discretion of the SDDOT. The Supplier will not off load any product without affording the SDDOT an opportunity to conduct the inspection, sampling, and testing. Off-loading of product without affording the SDDOT an opportunity to conduct the inspection, sampling, and testing will deem the delivered product non-compliant and subject to total rejection. The Supplier will only off load product without inspection, testing, and sampling by the SDDOT, when SDDOT point of delivery representative grants prior approval.

A. FIELD INSPECTION

Before allowing any product to be unloaded, SDDOT'S personnel will be allowed the opportunity to perform the following procedures and any other tests or inspections as may be deemed necessary in the sole discretion of SDDOT:

1. Document and maintain records on all deliveries, including those that are rejected.
2. Check to assure that the product is being delivered according to the terms of the contract. This includes but is not limited to the following:
    a. Date of the order.
    b. Date and time of delivery.
    c. Verification of advance delivery notification.
    d. Was the product delivered within allowable times?
    e. Name of the delivery company and license plate numbers of the semi and trailer(s).
    f. Are any liquidated damage assessments required?
    g. Is the product being delivered the product that was ordered?
    h. Document all procedures prior to unloading of product.
    i. Verify that all papers required of a delivery are present, complete, and legible.
        - Is the bill of lading or the invoice accurate, complete, and legible?
        - Legible and current MSDS sheet.
        - Certified weight slip.
3. Verify separation or non-separation of product.
4. Visually inspect the load to determine if there are any obvious reason(s) why the load should be rejected.
5. No precipitate or flocculation in liquid products will be allowed in excess of the specification limits. Product portraying these or other uncharacteristic traits when delivered may be immediately rejected at the option of the SDDOT.
6. Any problems should be noted at the point of delivery by agency personnel, documented, and relayed to their agency representative for action.

B. SAMPLING AND TESTING

One or more samples may be taken from the delivered shipment for laboratory testing after the shipment has passed the initial inspection and is approved for unloading. The sample(s) will be used for testing at the SDDOT'S expense to ensure product quality. Test results from the South Dakota Agricultural Laboratory will be final and conclusive. Test results will be forwarded to the Supplier within 2 business days of receipt from the testing laboratory.

1. A one-gallon (or 2 half gallon) sample will be taken from the transfer hose in three equal parts. Each part will be mixed together with the other parts to make up the one-gallon sample to be

submitted to the laboratory for testing. The three equal sample portions will be collected during unloading as the first third, the second third, and the last third of the product being delivered. If the trailer or pup has compartments, the three equal samples will be taken from only one compartment to complete the sample.

2. Samples sent to the laboratory will be tested for conformance to specifications. If the product is suspected of containing deleterious materials which may be harmful to people, equipment, the roadway, or the environment, samples may be tested for those materials and properties as well.

## V. TEST METHODS

**Number 1 - Percent Concentration of Active Ingredient In The Liquid**

Test Method: Atomic Absorption or Inductively Coupled Plasma Spectrophotometry as described in the most recent version of "Standard Methods for the Examination of Water and Waste Water," APHA-AWWA-WPCF. Test Method "A" in Appendix A is used to determine percent concentration of Magnesium Chloride by Atomic Absorption. The operator should be aware that the high solids content of the samples can present special considerations when conducting the analysis.

**Number 2 - Weight Per Gallon**

Test Method: Specific Gravity as described in the most recent version of ASTM D 1429 Test Method A - Pycnometer at 20° C +/- 1° C.

**Number 3 - Corrosion Control Inhibitor Presence and Concentration**

Test Method: The Materials Laboratory may use the test procedures provided by the Supplier or manufacturer for testing quantitative concentrations of additives.

**Number 4 - pH**

Test Method: ASTM D 1293 except a dilution will be made of 1 part chemical product to 4 parts distilled water before attempting a reading.

**Number 5 - Percent Total Settleable Solids and Percent Solids Passing a 10 Sieve**

Test Method: This procedure is listed as Test Method "C" in Appendix A.

**Corrosion Rate**

Test Method: NACE Standard TM0169-95 (1995 revision) as modified by PNS. This test is shown as Test Method "B" in Appendix A.

**Total Phosphorus**

Test Method: Total Phosphorous as described in the most recent version of "Standard Methods for the examination of Water and Waste Water," APHA-AWWA-WPCF.

**Total Cyanide**

Test Method: Total Cyanide as described in the most recent version of "Standard Methods for the examination of Water and Waste Water," APHA-AWWA-WPCF.

**Total Arsenic, Barium, Cadmium, Chromium, Copper, Lead, Selenium, and Zinc.**

Test Method: Atomic Absorption Spectrophotometry or Plasma Emission Spectroscopy as described in the most recent version of "Standard Methods for the examination of Water and Waste Water," APHA-AWWA-WPCF.

**Total Mercury**

Test Method: Cold Vapor Atomic Absorption Spectrophotometry as described in the most recent version of "Standard Methods for the examination of Water and Waste Water," APHA-AWWA-WPCF.

**Milliequivalents or "meq"**

Test Method: This is a measure of the amount of unreacted base in the product. "meq" means milliequivalents or the milligrams of acetic acid to neutralize 1 gram of unreacted base.

Method for measuring unreacted base is a standard acid/base titration procedure. A fixed volume of acid (30 ml of 0.1 N HCl) is added to 1-gram sample of CMA. The excess acid is titrated with a standard base (0.1 N NaOH) to phenopthalein endpoint, pH of 8.6.

**Moisture Content of Solid Chemical Products.**

Test Method: According to ASTM E 534

**Visual Inspection and Field Observations.**

Test Method: Visual inspection and field observations to assure that the product remains clean and free of extraneous matter, free from hard caking, does not segregate, and remains suitable for the intended purpose and as otherwise outlined in Section IV. NOTE: SDDOT may use any laboratory test method necessary to verify conclusions from visual inspections.

## VI. LIQUIDATED DAMAGES FOR DEVIATIONS FROM SPECIFICATIONS

Liquidated damages will be assessed based on product costs. Determination of the liquidated damages to be applied will be based on the testing procedures as outlined in the specifications. Liquidated damages are to be accumulatively applied. In other words, a shipment failing two tests will be assessed the sum of the liquidated damages of the two tests. This summation is to continue until zero payment is due but cannot continue into the negative.

The Supplier will be required to replace any rejected product, plus any stored product contaminated by the rejected product, at the Supplier's cost. The Supplier will remove and replace any rejected product with product that meets the product specifications, together with handling and transportation charges, at no additional cost to the SDDOT. Removal includes the removal of all product contaminated by the non-specification product. SDDOT personnel will establish the amount of stored product that was contaminated.

Two shipments per contract year of product found by SDDOT to be beyond any specification range will be grounds for contract termination.

SDDOT will not pay for product delivered until SDDOT receives satisfactory test results from its testing lab. SDDOT may use the product prior to receipt of test results. Use does not constitute acceptance. SDDOT reserves the right to price adjust or reject all product received.

No forbearance on the part of the SDDOT will constitute a waiver, nor bind the SDDOT to a waiver of any similar or succeeding breach of same or any other term or provision of these specifications.

### A. LIQUIDATED DAMAGES BASED ON MAGNESIUM CHLORIDE

Field samples taken of the delivered liquid chemical products will be tested for the appropriate Magnesium Chloride concentration in percent according to Test Method 1. Only elements or compounds specific to the product being bid will count towards the percent concentration of Magnesium Chloride. No credit will be given for trace materials such as Calcium Chloride or Sodium Chloride.

Liquidated damages for chemical products below the minimum concentration are as follows:

Concentration Ranges

25.0% to 27.9% ---------- 50% liquidated damages assessment

≤24.9 % ---------- 100% liquidated damages assessment

**B. LIQUIDATED DAMAGES FOR TOTAL METALS, TOTAL PHOSPHORUS, AND TOTAL CYANIDE**

Materials tested for the total concentration of Arsenic, Barium, Cadmium, Chromium, Copper, Lead, Mercury, Selenium, Zinc, Phosphorus and Cyanide and found to have exceeded the specification limits are subject to Liquidated Damages. The liquidated damages will be taken according to the following table.

| Percentage Over the Specified Limit | Liquidated Damage |
|---|---|
| 0 to 5.0 | 10% |
| 5.1 to 20.0 | 15% |
| 20.1 to 40.0 | 25% |
| 40.1 to 75.0 | 35% |
| 75.1 to 100.0 | 50% |
| Over 100.1 | 100% |

**C. LIQUIDATED DAMAGES FOR THE PERCENT CORROSION EFFECTIVENESS**

Products tested for Corrosion Effectiveness and found to be outside the specification limit of 70% less than that of Sodium Chloride are subject to Liquidated Damages (i.e., an acceptable corrosion rate is less than or equal to 30%). The Liquidated Damages will be taken according to the following tables.

| Percent Corrosion Rate | Liquidated Damage |
|---|---|
| 30.1% to 35.0% | 15% |
| 35.1% to 40.0% | 50% |
| 40.1% or greater | 100% or Rejection |

**D. LIQUIDATED DAMAGES FOR TOTAL SETTLEABLE SOLIDS AND PERCENT PASSING THE NO. 10 SIEVE**

Products tested for the Total Settleable Solids and Percent Solids Passing a No. 10 sieve and found to have exceeded the specification limits are subject to Liquidated Damages. The Liquidated Damages will be taken according to the following tables.

TOTAL SETTLEABLE SOLIDS (Less than or equal to 1% is acceptable)

| Percent Settleable | Solids Liquidated Damage |
|---|---|
| 1.1 to 1.5 | 15% |
| 1.6 to 3.5 | 25% |
| 3.6 to 5.0 | 50% |
| 5.1 to 7.5 | 75% |
| 7.6 and above | 100% or Rejection |

PERCENT SOLIDS PASSING A NO. 10 SIEVE (Greater than or equal to 99% is acceptable)

| Percent Passing the No. 10 Sieve | Liquidated Damage |
|---|---|
| 98.5 to 98.9 | 15% |
| 98.0 to 98.4 | 35% |
| 97.5 to 97.9 | 50% |
| 97.4 and below | 100% or Rejection |

**E. LIQUIDATED DAMAGES FOR pH**

The pH analysis will be on the finished product. The Liquidated Damages will be taken according to the following table:

| pH Analysis | Liquidated Damage |
|---|---|
| 5.5 – 6.0 | 15% |
| 5.0 – 5.4 | 25% |
| 4.5 – 4.9 | 50% |
| < 4.5 | 100% |

## F. QUALIFIED PRODUCTS LIST

**Clear Roads Qualified Product List**
**Date of Listing: September 16, 2022**
**Category 1 – Corrosion Inhibited Liquid Magnesium Chloride**

| Product Name | Manufacturer | Corrosion Rate % Effectiveness | % Concentration | Expiration |
|---|---|---|---|---|
| Iceban 200* | Earth Friendly Chem. | 8.4 | 26% | 12/31/2024 |
| Caliber M1000 AP | Envirotech Services Inc. | 20.8 | 28% | 12/31/2024 |
| Meltdown with Shield AP | Envirotech Services Inc. | 25.9 | 30% | 12/31/2024 |
| Hydro-Melt Green | Cargill | 24.3 | 28.5% | 12/31/2024 |
| Meltdown APEX with Shield AP | Envirotech Services Inc. | 25.1 | 30% | 12/31/2024 |
| FreezGard CI Plus | Compass Mineral | 12.2 | 30% | 12/31/2024 |
| FreezGard LITE CI Plus | Compass Mineral | 12.3 | 27% | 12/31/2024 |
| Hydromelt Liquid Deicer | Cargill | 28 | 28.6% | 12/31/2024 |
| FreezeGard CI Plus Sub Zero | Compass Mineral | 14.1 | 27.5% | 12/31/2024 |
| Ice Ban 305 | GMCO Corporation | 25.3 | 26.6% | 12/31/2024 |
| FreezGard 0 CCI | GMCO Corporation | 21.2 | 30.0% | 12/31/2024 |
| Meltdown Apex | Envirotech Services Inc. | 22.4 | 30.0% | 12/31/2024 |
| Meltdown Inhibited | Envirotech Services Inc. | 24.1 | 30.0% | 12/31/2024 |
| ProMelt MAG 30 INH | Innovative Surface Solutions | 25.2 | 30.0% | 12/31/2024 |
| ProMelt Ultra 1000 INH | Innovative Surface Solutions | 28.2 | 27.0% | 12/31/2024 |
| NexGen Torch | GMCO Corporation | 25 | 30.0% | 12/31/2024 |
| NexGen Liquid De-Icer | Paradigm Group | 25 | 30.0% | 12/31/2024 |

Note-Iceban 200 was formerly Iceban Performance Plus M
Those products marked with an asterisk (*) indicates that the stratification can be seen, and agitation is required

## APPENDIX A

**TEST METHOD "A" – Concentration Percentage of Active Ingredient In Liquid Chemical Products**

**TEST METHOD "B" – Corrosion Control Inhibitor Presence and Concentration**

**TEST METHOD "C" – Percent Total Settleable Solids and Percent Solids Passing A No. 10 Sieve**

### TEST METHOD A. Concentration Percentage of Active Ingredient In Liquid Chemical Product

**I. Test Method**

Atomic Absorption Spectrophotometry as described in “Standard Methods for the Examination of Water and Waste Water,” APHA-AWWA-WPCF

**II. Apparatus**

Atomic Absorption Spectrophotometer

250, 500 ml Graduated Cylinders

2000 ml Beaker

100, 500, 1000 ml Volumetric Flasks

5, 10, 15, 20, 25, 30 ml Volumetric Pipettes (Class A)

100 microliter Eppendorf Pipette

**III. Reagents**

ASTM D 1193 Type II Distilled Water

1000 ppm Magnesium Stock Solution

Concentrated Hydrochloric Acid (HCl)

Concentrated Nitric Acid (HNO3 )

Lanthanum Oxide (La2O3)

**IV. Preparation of Lanthanum Chloride; Calcium Chloride and Magnesium Chloride Calibration Standards and Blanks; Quality Control Solutions; and Calcium Chloride and Magnesium Chloride Deicer Solutions.**

1. Preparation of 10% Lanthanum Chloride Stock Solution

   In a 2000-ml beaker add 200 ml of distilled water to 117.28 g of Reagent Grade Lanthanum Oxide. While stirring, very slowly add 500 ml of concentrated HCl (25 ml at a time). ***CAUTION!*** This reaction is extremely violent. Care should be taken so the solution does not overflow the beaker. When the solution has cooled to room temperature, transfer to a 1000-ml volumetric flask and dilute to volume with distilled water. (Lanthanum Chloride is the Ionization Suppressant used in determining Calcium and Magnesium concentrations by Atomic Absorption).

2. Magnesium Chloride Calibration Standards

   A. 100 ppm Magnesium Stock Solution for Dilutions: Pipette 10 ml of the 1000 ppm Magnesium reagent solution into a 100-ml volumetric flask. Using an Eppendorf pipette add 0.1 ml concentrated HNO3 acid and dilute to volume with distilled water.

   B. Magnesium Standards for Calibration (10, 15, 20 ppm): Pipette aliquots of 10, 15, and 20 ml of the above 100 ppm Magnesium solution into three separate 100-ml volumetric flasks. Add 20 ml of the 10% Lanthanum Chloride solution to each flask before diluting to volume with distilled water. The standard solutions should be prepared daily.

3. Blank Solution

   Blank Solution for Calibration: Pipette 20 ml of 10% Lanthanum Chloride solution into a 100 ml volumetric flask and dilute to volume with distilled water. The blank solution should be prepared daily.

4. Quality Control Solutions

   Magnesium Chloride Quality Control Check: Weigh 1.5056g (non-dried) MgCl2-6H2O and place into 1000-ml volumetric flask. Add 1 ml of concentrated HNO3 and dilute to volume with distilled water. From this solution, pipette 10 ml into a 100-ml volumetric flask, add 20 ml of the 10% Lanthanum Chloride solution and bring to volume with distilled water. This will be the working Quality Control Standard and have a value of 18.00 ppm Magnesium. (Note: The 18.00

ppm Magnesium concentration is equal to a 28.2% brine concentration of Magnesium Chloride based on a 2.5-gram sample size.)

**V. Preparation of Liquid Chemical Products Sample Solution**

Solution A

1. Weigh approximately 2.500 grams of the liquid chemical product into a tared 500-ml volumetric flask. Record the sample weight to the nearest mg for final calculations. Add l ml HNO3. Rinse the neck of the volumetric flask with a slight amount of distilled water and allow the sample to digest for one hour. Dilute to volume with distilled water. Label as solution A.

Solution B (Working Chemical Product Solution)

2. Pipette 5 ml of Solution A into a 100-ml volumetric flask. Add 20 ml of 10% Lanthanum Chloride solution and dilute to volume with distilled water. Label as solution B (Dilution factor of 20).

3. Repeat Step 2 so that each chemical product sample has a duplicate working solution.

**VI. Atomic Absorption Spectrophotometer Operation**

Magnesium

1. Set up the spectrophotometer (absorption) with the Magnesium lamp using a wavelength setting of 285.4 nm, and a slit width of 0.2 nm. An Air Acetylene flame should be used with the 10-cm burner head set at a 450. The flame, burner, and instrument are to be optimized for best detection.
2. Calibrate the instrument using the blank, 10-ppm, 15-ppm, and 20-ppm standards for Magnesium.
3. Run the Magnesium Quality Control solution. This result must be within plus or minus 0.15 ppm of the known 18.00-ppm concentration before proceeding.
4. Once the Quality Control solution is within allowable limits, run the chemical product samples and their duplicates and record the results.
5. Run the Magnesium Quality Control solution again to assure accurate results.
6. Following the analysis calculate the percent concentration of the sample and the duplicate sample for each chemical product using the following formulas. These test results must be repeatable within plus or minus 0.3% concentration of each other to be acceptable for reporting. If the results are outside this allowable limit, perform the dilutions over and retest until the samples are repeatable within the 0.3% limit.

**VII. Calculations**

Calculations for MgCl2 base on a sample weighing 2.550 grams*:*

$$\text{Factor} = \frac{(95.211\ \text{MgCl2})\ (1\%)(\text{Dilution factor})(\text{Initial vol.})}{(24.305\ \text{Mg})\ (10{,}000\ \text{ppm})} = \frac{(20)\quad(500\ \text{ml})}{} = 3.9173$$

$$\%\ \text{MgCl2} = \frac{(\text{X ppm from AA})\ (\text{Factor})}{\text{grams of sample}}$$

$$\text{Example: } \frac{(18.87\ \text{ppm})\ (3.9173)}{2.5500\text{g chemical product}} = 29.0\%\ \text{MgCl2}$$

**TEST METHOD B. Corrosion Rate As Conducted From the NACE Standard TM0169-95 (1995 Revision) and As Modified By The Pacific Northwest States**

Products submitted to meet the Corrosion Rate Test and have a Percent Effectiveness determined will be tested according to the National Association of Corrosion Engineers (NACE) Standard TM0169-95 as modified by the PNS. The PNS modified this procedure to use 30 ml of a 3% chemical product solution as

received per square inch of coupon surface area for the corrosion test. Corrosion inhibited chemical product must have a Percent Effectiveness value of at least 70% less than Sodium Chloride (salt) to be acceptable.

## I. PREPARING THE COUPONS

The coupons used are ½" (approximately 1.38 in. x 0.56 in. x 0.11 in.) flat steel washers displaying a density of approximately 7.85 grams per cubic centimeter. (Note: No galvanized coupons may be used even after removing the zinc with acid. Hot dipped galvanization creates a Fe-Zn metallurgical surface bond that changes the characteristics of the steel. Coupons must meet ASTM F 436, Type 1, with a Rockwell Hardness of C 38-45. Each coupon used in the test procedure is subjected to the following process to assure accuracy in test results.

- Examine each coupon for metallurgical abnormalities and reject those that are suspect to flaws.
- All coupons are tested for Rockwell Hardness of C 38-45. Coupons having hardness outside of this range are rejected.
- Acceptable coupons are stamped for identification.
- Wipe with suitable solvent to remove grease and oil.
- Coupons are placed in a 1-liter plastic bottle with 1 tablespoon of phosphate free labware grade detergent (such as Contrex) and 200 ml of warm tap water. Gently agitate for fifteen minutes then rinse coupons with tap water. Coupons are then placed into a 1 Liter plastic bottle with 3 tablespoons of Bon Ami cleaning powder and 200 ml warm tap water. Gently agitate the coupons for fifteen minutes drain and rinse with distilled water and wipe dry.
- Coupons are acid etched with 1 + 1 HCl for 3 minutes.
- The coupons are then quickly rinsed with tap water, distilled water, wiped dried, and placed in chloroform.
- When the coupons are removed from the chloroform for use, they are placed on a paper-lined tray (not touching each other) and allowed to air dry in a ventilated hood for a minimum of 15 minutes.
- Coupons are measured as specified. (Note: If latex gloves are not worn during measuring, the coupons should be rinsed again and dried as prescribe above prior to weighing. This will remove any oils that may be transferred to the coupons.)
- Each coupon will be weighed to a constant weight. The constant weight will be two consecutive weights of each coupon within a minimum of 0.5 milligrams of each other. Removal of incidental flash rusting prior to weighing is not necessary.
- Three coupons are used in each flask for testing the chemical product solutions and determining the distilled water and sodium chloride control standard values.

## II. MEASURING THE COUPONS

The outside diameter, inside diameter, and the thickness of each coupon are measured twice at 90 degrees from each initial reading and the averages calculated for each measurement. The averages are then used to calculate the surface area of each coupon with the following formula:

$$A = (3.1416/2)(D2 - d2) + 3.1416(t)(D) + 3.1416(t)(d)$$

Where D = average outside diameter

d = average inside diameter

t = average thickness

**Example:**

$$A = (1.5708)(1.9044-0.3136) + 0.4768949 + 0.1935226$$

$$A = (1.5708)(1.5908) + 0.4768949 + 0.1935226$$

A = 2.4988286 + 0.4768949 + 0.1935226

A = 3.1692461 square inches (Total surface area of the coupon.)

A = 3.17 square inches

## III. PREPARING THE SOLUTIONS

ASTM D 1193 Type II distilled water is used to prepare each solution, blank, and control standard. The sodium chloride (NaCl) used to prepare the salt standard will be of "ANALYZED REAGENT GRADE" quality.

A 3% solution of NaCl is prepared by weight, using the reagent grade salt and distilled water (W/V).

A 3% solution of each chemical product to be tested is prepared using distilled water to dissolve and or dilute the chemical product. For liquid chemical products, three parts liquid chemical product (as received) is mixed with 97 parts distilled water to produce the test solution (V/V). If the chemical product is a dry product, the 3% solution is made by weight (W/V).

All solutions including the distilled water blank are covered and allowed to sit a minimum of 12 hours to stabilize and reach equilibrium, ensure solubility, and to account for any reactivity that may occur.

## IV. THE CORROSION TEST

Approximately 300 milliliters (actual volume is determined by the surface area of test coupons) of each solution is mixed with distilled water and is put into a 500 milliliter Erlenmeyer flask. Each flask is stoppered with a rubber stopper that has been drilled to allow a monofilament line to run through it. The hole in the rubber stopper is 3-4 millimeters in diameter. The hole should not be greater than 4 millimeters as it will allow the vapor phase within the neck of the flask to vent excessively and can skew the results. One end of the line is attached to the up/down bar of the corrosion machine and the other end of the line is attached to a plastic frame made to hold coupons inside the flask where the three coupons are attached to each plastic frame. The bar is controlled by an electric timer that lowers the coupons into the solution for 10 minutes then raises the coupons out of the solution for 50 minutes, but still keeps the coupons inside the air space of the flask for the entire duration of the test. This allows the coupons to be exposed to the test solution 10 minutes of each hour. The corrosion test runs for 72 hours starting with the coupons being lowered into the solution. No agitation of the solution is made during the corrosion test.

Corrosion tests are conducted at 21-23 degrees Centigrade. The room temperature is to be recorded daily during the operation of the test. The room temperature will be taken with a calibrated thermometer located next to the corrosion-testing instrument.

## V. CLEANING THE CORRODED COUPONS

The coupons are removed from the solution after 72 hours on the end cycle where the coupons are suspended in the air space of the flask. The coupons are pre-washed under running tap water to remove any loosely adherent corrosion products. The coupons are then placed into glass beakers containing the cleaning acid, which is composed of concentrated hydrochloric acid (HCL) containing 50 grams/liter $SnCl_2$ (stannous chloride) and 20 grams/liter $SbCl_3$ (antimony trichloride). The two salts are added to the HCL to stop the reaction of the HCL with the steel once the rust or corrosion is removed. (Note: The gas fumes given off by the acid during this cleaning process contain antimony and are extremely hazardous. This portion of the cleaning must be conducted under a well-ventilated hood.)

Allow the coupons to soak in the cleaning acid for a total of 15 minutes. Remove the coupons from the acid and rinse with tap water followed by distilled water. Wipe with a paper towel or cloth to clean any residual deposit from the coupons. The coupons are then returned to the cleaning acid and the procedure is repeated. After cleaning, the coupons are rinsed in chloroform, air dried for 15 minutes and weighed. Each coupon will be weighed to a constant weight. The constant weight will be two consecutive weights of each coupon within a minimum of 0.5 milligrams of each other.

## VI. EVALUATING THE CORROSION

The weight loss of each coupon is determined by subtracting the final weight from the original weight. The corrosion rate for each coupon is expressed as mils penetration per year (MPY) by the following formula:

MPY = (weight loss (milligrams)) (534) / ((area) (time) (metal density))

**OR**

MPY = (weight loss (milligrams)) (534) divided by ((area) (time) (metal density*))

(Density is 7.85 g/cc for steel*)

The final MPY value for each solution is determined by calculating the average MPY of the three individual coupons. The average MPY from this point forward will be referred to as only MPY of the solution being tested. (Note: Wide variation of MPY of individual coupons inside the same flask typically indicates contamination of a coupon. If variation of individual MPY is too great to determine consistent data, the test should be run over again. Typically, coupon variation may run plus or minus 3 MPY.)

## VII. EXPLANATION

To put the information into perspective it is necessary to briefly recap the corrosion test process. The corrosion value of the distilled water and the reagent grade sodium chloride is critical to this whole process. These are the two base lines used to determine product's acceptability in terms of corrosion value only.

In the following table the distilled water proved to have a corrosion value of 5.00 MPY and the salt had a value of 55.00 MPY. The chart shows that the reagent grade sodium chloride has a water corrected corrosion value of 50.00 MPY. This means that the original corrosion value of the reagent grade sodium chloride and the distilled water (in a 3% solution) was 55.00 MPY. That is, 5.00 MPY for the distilled water and 50.00 MPY for the reagent grade sodium chloride. The 5.00 MPY value for the distilled water is subtracted from the original 55.00 MPY for the reagent grade sodium chloride and distilled water solution to arrive at the distilled water corrected value of 50.00 MPY for the reagent grade sodium chloride.

The corrosion value of 5.00 MPY for the distilled water is subtracted from the total MPY for each of the 3% solutions for each product tested. When this calculation is completed for each product being tested the resulting value indicates the corrected corrosion value.

According to criteria adopted by PNS, "Only corrosion inhibited chemical products that are at least 70% less corrosive than reagent grade sodium chloride may be used." To determine if a product is acceptable, take the corrected corrosion value of the reagent grade sodium chloride and multiply it by 30%. In this case, 50.00 MPY multiplied by 30% equals 15.00 MPY which is the highest acceptable corrected corrosion value for any product in this test. No product in this test producing a MPY value higher than 15.00 MPY is acceptable.

## VIII. NEGATIVE NUMBERS

Some products actually end up with a negative number as a corrected MPY value. A negative number is exceptionally good and actually indicates that the product when mixed with distilled water in a 3% solution is less corrosive than distilled water.

To show an example of a negative number, refer to one Table 1. The 3% solution of Wondermelt-A had a corrected corrosion value of -5.18 MPY resulting in a Percent Effectiveness of -10.36. The more negative the number the better a product is in terms of corrosion inhibiting abilities.

## IX. REPORTING RESULTS

Results will be reported in Percent Effectiveness. Percent values equal to or less than 30% are passing. The distilled water corrected values of the chemical product and the salt are used to make

this calculation. The corrected value of the chemical product is divided by the corrected value of the salt; this value is then multiplied by 100 to give percent.

Example: Magic Melter II has a corrected value of 10.15

Salt has a corrected value of 50.00

Therefore: (10.15 / 50.00) X 100 = 20.3% Pass

Acme Melter has a corrected value of 19.99

Therefore: (19.99 / 50.00) X 100 = 40.0% Fail

**TABLE 1**
**CHEMICAL PRODUCTS CORROSION TEST RESULTS**

| PRODUCT | INITIAL CORROSION VALUE (MPY) | WATER CORRECTED CORROSION VALUE (MPY) | PERCENT EFFECTIVENESS (%) |
|---|---|---|---|
| ***Super Stuff** | **4.97** | **-0.03** | **-0.06** |
| ***Ice Melter** | **5.04** | **0.04** | **0.07** |
| ***Magic Melter** | **6.00** | **1.00** | **2.00** |
| ***Magic Melter II** | **15.15** | **10.15** | **20.30** |
| **Acme Melter** | **24.99** | **19.99** | **39.98** |
| **Acme Melter-1** | **28.71** | **23.71** | **47.42** |
| **Wondermelt** | **59.07** | **54.07** | **108.14** |
| ***Wondermelt -A** | **-0.18** | **-5.18** | **-10.36** |
| **Stuff** | **22.00** | **17.00** | **34.00** |
| **SALT** | **55.00** | **50.00** | **100.00** |
| **Distilled Water** | **5.00** | **0.00** | |

* ACCEPTABLE PRODUCT

Note: The results used in this table are for example only and are not firm numbers. The MPY corrosion values of the distilled water and the reagent grade sodium chloride may vary from test to test.

**TEST METHOD C. Percent Total Settleable Solids and Percent Solids Passing a No.10 Sieve**

This test method is used to determine the amount of total settleable solids and the percent of solids passing the No.10 sieve that are generated from a liquid chemical product when stored at a specified cold temperature without agitation.

Settleable Solids for this procedure are typically formed from chemical precipitation, chemical crystallization, or by the dense settlement of any other components of the deicing product.

Chemical precipitates are formed when specific chemical constituents within the liquid chemical product react together chemically.

Chemical crystallization begins to form when a solution is cooled below its chemical saturation point. Crystallization is the physical characteristic by which a liquid begins to turn to a solid. This physical characteristic is typically used to identify the freezing point of a liquid. This test will determine if the deicing solution can maintain its liquid state at the supplied concentration and at the specified testing temperature with no agitation.

The settlement or separation of additional component(s) (i.e., inhibitors) of the product will be examined for the formation of a dense solid layer and the ability of the chemical product to maintain a non-stratified suspension without agitation.

Total settleable solids will consist of all described parameters excluding soft settling stratification as outlined in the test methodology.

Percent Solids Passing on the No.10 Sieve will be measured by subtracting the volume of solids retained on the sieve from the total sample volume.

## I. Apparatus

1-Liter Graduated Imhoff Cone

ASTM E 11 No.10 sieve

Rubber policeman

Graduated cylinder

Watch glass

Freezer

## II. Test Method

Place 1000 ml of a well-mixed (non-diluted) liquid chemical product into a graduated one-liter Imhoff cone. Place this sample into a freezer which has been precalibrated and stabilized to the correct specified temperature as established in each liquid chemical product category. Cover the sample with a watch glass. The sample will remain in the freezer unagitated for a period of 168 hours. Record the temperature of the freezer daily to assure proper testing temperature. After 168 hours the sample is carefully removed from the freezer for testing.

1. Total Settleable Solids

   This test method will be used to determine if the liquid chemical product is usable and if it requires agitation. This test method will determine the detrimental amount of settlement formed from chemical precipitation, chemical crystallization, or by the dense settlement of any other component(s) of the deicing product.

   The formation of chemical precipitation or chemical crystallization above the prescribed limit is cause for rejection. These characteristics are observed by a dense formation of precipitate or crystals in the cone. Various levels of crystallization may be present if the chemical product concentration is at or near its freezing point.

   The settlement of other chemical product components that can produce a dense solid layer above the prescribed limit will be cause for rejection. Stratification of material exhibiting a phase separation, or a soft settlement is not to be interpreted as a dense solid layer. This type of separation is a result of the chemical product not staying homogenous through the test conditions. Samples submitted that exhibit stratification but pass all other specifications will be passed and will be categorized as “Requires Agitation.”

   The time used to evaluate each sample should be kept to a minimum because as the deicing solutions warm the physical characteristics within the solution change

   Remove the sample contained in the Imhoff cone from the freezer. Determine readings as soon as possible because sample temperature begins to rise immediately after being removed. Measure and record the volume of settleable solids using the calibrated gradations on the cone. (Note: If the settled matter contains pockets of liquid between large settled particles, estimate the volume of these pockets of liquid and subtract this volume from the volume of settled solids.) For transparent liquids this is easily determined by directly reading the volume of the settleable solids in the bottom of the cone. For liquids that are not clear due to hazy, cloudy, or opaque solutions, or due to indefinite stratified zones, the following method can be used.

   Place the sample in a room with no light. Then using a light capable of producing a concentrated beam, such as a flashlight with adjustable light features, back light the sample. With this procedure determine the amount of settlement in the bottom of the cone and the phase separation interfaces. Record the settlement value and the stratification interface volumes if present.

   To determine if this settlement is a dense formation or soft settling due to a phase separation use an eight-millimeter diameter solid glass rod of sufficient length to reach the bottom of the cone. The rod diameter should allow the rod to be inserted to the bottom of the cone and be large enough to determine the slightest resistance. Gently insert the rod into the chemical product and gradually lower the rod to the bottom of the cone. If resistance is felt, mark the rod

level at the top of the cone and remove. Place the rod on the outside of the cone with the mark even with the top of the cone. Read and record the volume where resistance was felt from the gradations on the cone corresponding to the tip of the rod. This volume reading is to be interpreted as a dense settlement and must not exceed the specification limit. If the rod goes completely to the bottom of the cone with no resistance, record that no dense settlement was found.

If stratification is present, gently hand stir the chemical product in a clockwise direction for 45 revolutions in one minute to see if the sample will re-homogenize. Examine the chemical product again, with the light, if necessary, to determine phase stratification interface levels remaining, if any. Record new levels if present. If no levels are detectable and the solution is returned to a homogenous state exhibiting no stratified layers the chemical product will be marked “Requires Agitation.” If levels of stratification are still present, mark as “Requires Extreme Agitation.”

The total settleable solids volume will consist of the accumulated amounts of chemical precipitation, chemical crystallization, and the dense portion of any other constituents. The total settleable solids are reported in percent based upon the volume to volume (V/V) ratio of the settleable solids to the initial sample size.

2. Percent Solids Passing the 10 Sieve

   This procedure must be conducted as fast as possible after determining the total settleable solids so that any frozen chemical crystalline materials are adequately evaluated.

   Immediately after determining the total settleable solids invert the cone (or remove the tip on some models) and pour the sample through an ASTM E 11 certified Number 10 sieve. The sieve should be kept in a mixture of ice and water to keep it cold before using and between samples. Rinse the sieve with water to remove any traces of the previous sample prior to placing in the ice bath. Before using the sieve briefly shake excess water from the sieve. The sample should be poured through one-quarter section of the sieve, if possible, to reduce the surface area from which the sample must be retrieved. The sample on the sieve is not rinsed or pushed through the sieve by any means. All material not flowing through the sieve is rubber policed from the sieve into a graduated cylinder and the volume measured and recorded. Rubber police only the side of the sieve the product was placed on to pass through. Material that is trapped in the mesh of the sieve and does not come loose on the face of the sieve is considered passing and is not included. This volume is subtracted from the total volume of the sample to calculate the sample volume passing. The solids passing the No.10 sieve are reported in percent based upon the volume to volume (V/V) ratio of sample volume passing to the initial sample size.