# MOLTEN SULPHUR TRANSPORT
# REVIEW AND CURRENT THOUGHTS

By
Bill Hannemann
Larry Hopper
Jim Molnar

## General

Recovered elemental sulphur production continues to grow at a rate of about four percent per year.[1] The majority of sulphur shipped in the United States is shipped in its molten, also known as liquid, state. Sulfur melts at approximately 230 degrees Fahrenheit. For maximum mobility molten sulphur is usually heated to between 280 and 300 degrees Fahrenheit. It falls to the producers and the rail industry to find safer and more cost-efficient ways of handling this commodity in its molten state. This presentation reviews some of the work that has been done and brings to light some of the current thoughts on how to improve the protection offered by protective coatings in preventing corrosion damage in this extremely aggressive service.

## History

In the late 70's exceptional corrosion was found in tank cars carrying molten sulphur. Several reports of tank cars splitting open were reported in the early 1980's.

The nineties saw a rail-related incident in Canada that caught the attention of the Canadian Transport Commission and generated a report. This led the AAR[2] to issue regulations covering the transportation of molten sulphur in tank cars.

The National Association of Corrosion Engineers (NACE,) which is a consensus standard organization, in the form of its Land Transportation Group, worked to prepare a standard that would address this problem and help in the selection of lining materials and develop proper application procedures for this service aiming to maximizing the integrity of the tank car. The Task Group (TG 067) that addressed this problem included representatives of the tank car builders, owners, coating manufacturers, shippers of molten sulphur, tank car repair facilities and a representative from the Sulphur Institute.

The Task Group sought to create a multiple part standard with the first part addressing the selection of coating materials through testing and analytical evaluation. The second part addressed the methodology that is consistent with the best available application procedures, taking into account the capabilities of tank car facilities; this included surface preparation; application of coating materials; inspection of the completed coating system both visual and through testing using readily available instruments. The standard

provides guidelines to the builder, owner, shipper, and all those involved in the production and use of rail tank cars intended for the transport of molten sulfur.

The standard (NACE RPO302-2002) was issued in 2002 and was utilized by owners of tank car fleets carrying molten sulphur.

Within two years, reports of earlier than expected coating material failures were coming back to the Land Transportation Group. This lead to the group taking on the task of revising the standard to better serve the industries needs.

## Testing of Coating Materials

The reports indicated that properly applied coating materials, which had passed the material selection testing protocols, were failing, primarily by blistering.

One member worked to develop a cyclical chemical resistance test protocol that replicated at least the physical appearance of the most common failure mode. His test methodology is explained below.

The coating should be applied to vertical and cylindrical surfaces of a tank carbon steel test cell. The test cell should be filled to one-half its capacity with an ambient temperature representative sample of sulfur typically transported in rail tank cars along with tap water equal to 1.5% by weight of the sulfur. The test cell with sulfur and the tap water shall be heated in an oven over a 3.5-hour ramp heating period to 162°C (325°F) and soaked for three hours at a temperature of 162°C (325°F). Five hours shall be allowed for cool down to ambient temperature. This test cycle is then repeated for 25 days or a minimum of 50 cycles.

Although the temperature of the testing exceeds the optimum viscosity range of the material for unloading it does mimic the standards utilized by those engaged in molten sulphur pump design. Our Task Group members also confirmed that the steaming racks used to heat molten sulphur tank cars prior to unloading, had less than perfect ability to control the temperature of the molten sulphur in the tank cars.

Based on the test's ability to replicate the failure phenomena showed by cross referencing, the test was added to the specification.

Some additional qualitative tests that are suggested in the specification are a Dry Heat Resistance Test, a Chemical Resistance Test, an Adhesion Test, an Impact Resistance Test and a Thermal Shock Test (Cyclical).

## Surface Preparation

The surface preparation portion of the specification addresses weld preparation requirements prior to abrasive blasting to a white metal finish in accordance with NACE No. 1/SSPC-SP 5.[3]

This portion of the specification also includes references to the proper grit, problems with the steel surface, potentially contaminated steel and quality assurance.

Tank cars that have been in molten sulphur service must be cleaned of all visible sulphur residues prior to the following steps.

Tank cars that have been in molten sulphur service may have metal loss from the corrosion process. In some cases, this corrosion may be so deep that extensive plate repair or replacement is necessary.

Nonvisible and/or soluble contaminants are a problem that must be addressed. Residual sulfur that is not visually obvious may be on the surface or have soaked into the steel. Iron/sulfur salts may be present. Such contaminants could cause adhesion/blistering problems in service or as early as during the coating cure. Removal methods may include one or more of the following: steaming for 24 hours, scrubbing with 3 to 5% phosphoric acid, high-pressure or ultrahigh-pressure waterjetting and prebaking at 230°C (450°F) for two hours in addition to one or more of the preceding methods. After this(these) step(s) a commercially available test to detect soluble salt contaminants may be performed.

When all of the indicated surface preparation has been completed, the surface should have a pH in the range of 6 to 8 prior to the application of coating.

Coating Application and Inspection

The application section of the specification covers the application to the tank and all parts that receive coating. The procedures for inspection (with an appendix that contains a Rail Tank Car Coating System Inspection Report Form) and touchup of the coating film are included in this specification. Another appendix covers qualifying a shop to perform the coating work.

The current version of this standard is out for ballot.

Working on Life Extension

Some of the Task Group's members are not convinced that the current methods do enough to remove potential problems to a coating in service. The NACE Task Group working on this issue has been investigating various other parts of the standard, most notably the removal of nonvisible contaminants from the substrate of tank cars that have seen molten sulphur service. One idea presented has been to apply steam under pressure to the interior of the tank; other members favor using targeted chemicals to assist in the decontamination process.

It has been suggested by another task group member that nitrogen or another inert gas blanket be utilized in loaded and empty tank cars to attenuate the potential for corrosion damage.

There are costs and shop process drawbacks to the above ideas. Until proven to increase coating life and/or decrease corrosion they do not yet appear to provide a benefit sufficient to be included in the current version of the specification.

## Coating Maintenance

Periodic inspection of a car interior is the only real way to monitor actual coating performance. When looking at tank cars it pays to look for indicators that may show patterns in coating problems. Knowledge of whether the tank car was in molten sulphur service prior to the application of the current coating may indicate a surface that was not completely decontaminated. Some indicators to consider when looking for trends in predicting coating life are the coating material, the application facility and the tank car file size, at the time of that coating application. By considering these tank cars as groups, patterns of coating life may be revealed. Even though it may seem inconvenient to monitor these tank cars so closely, by addressing coating problems promptly, the tank car will likely see less corrosion damage.

The cost of corrosion for not monitoring tank cars by visual inspection can greatly increase the overall cost of transporting molten sulphur by rail. The cost of repair to the tank car for loss of thickness to the tank shell can easily outweigh a conscientious program that continually monitors a molten sulphur fleet.

## Conclusion

Tank car life is legally 50 years, but cars in molten sulphur ladings will not last long without addressing the corrosive nature of this service. A protective coating applied to the interior of these cars has been shown to be one method of extending the usable life of these rolling assets. The AAR currently requires all tank cars in molten sulphur service to be protected in Specification M-1002.

Further studies in molten sulphur corrosion will hopefully define when the stress on the coating is the greatest, whether it is during loading, reheating or in an empty tank car. It could also be during the transition from one activity to the other. Understanding this might provide further insight as how to reduce coating distress and thereby corrosion of tank cars in this service.

A desirable course for some molten sulphur fleet owners/managers is: have an independent laboratory evaluate coating materials that are available utilizing the new test protocols and compare the results; then create a good application specification that includes inspection during the application process; and most importantly of al,l monitor the existing coatings through frequent examination and data gathering.

1. M. Kitto, World Sulphuric Acid Situation, British Sulphur Consultants, Sulphur 2005, Moscow.

2. American Association of Railroads (AAR), 50 F St. NW, Washington DC 20001-1564.

3. NACE No. 1/SSPC-SP 5 (latest revision), "White Metal Blast Cleaning" (Houston, TX: NACE, Pittsburgh, PA: SSPC).

4. U.S. Department of Transportation (DOT), 400 7th St. SW, Washington DC 20590