



WP4.D3 / REPORT ON CORROSION AND LIFETIME TESTS FOR SOLAR FLUIDS FINAL DRAFT

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July 2005

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SUMMARY

Overview of tests for corrosivity and lifetime of solar fluids. Standardized methods are available for corrosion tests, no standards are available for the determination of the lifetime of a solar fluid in a given application.

GENERAL CONSIDERATIONS

Most solar fluids are based on glycol/water-mixtures. Temperatures in today's covered solar collectors are well above limits of glycol stability and the fluid degrades with time. Several parameters are known that influence the lifetime of these solar fluids.

STANDARDIZED TESTS

Standardized tests are available to determine the corrosion of metals in a given solar fluid. Examples are ASTM D1384, ASTM E711 and ASTM E745. The focus of these tests is always on the metal corrosion, not on the degradation or lifetime of the solar fluid.

REPORTED TESTING RESULTS

Several authors present results from corrosion and glycol deterioration tests. Corrosion is usually not a problem with most solar fluids on the market, as long as they are applied correctly and have not been deteriorated by high temperatures.

CONCLUSIONS

No standards are available for the determination of the lifetime of solar fluids in a given installation, and the quantitative influences of system parameters on the deterioration of glycols in glycol/water-mixtures are only poorly understood. Further work and the development of standards for these topics are needed.

SUMMARY

In central and northern Europe, solar collectors are usually filled with an antifreeze fluid to prevent bursting of pipes during cold periods. This report gives an overview of corrosion and durability tests of solar fluids as they are described in standards or performed by various laboratories with standardized and non standardized methods. Standardized methods are available for corrosion tests, but no acceptable limit of metal mass loss of specimen are defined. No standards are available up to date for the determination of the lifetime of a solar fluid in a given application, and it is not clear yet which general parameters of a solar fluid shall be used for the measurement of degradation and the determination of the lifetime.

General considerations

Manufacturers and installers of solar thermal systems have the option to choose between different antifreeze products sold by different companies. Among other properties of the fluid, influence on corrosion of containment materials and the lifetime of the fluid are of great importance. There are a number of standardized corrosion tests such as ASTM D1384, E712 and E745 which are usually applied to the unused fluid. Most solar fluids are based on glycol/water mixtures. Manufacturers usually give upper temperature limits for the application of these products of 120 – 175 °C. These temperatures are below stagnation temperatures of modern flat plate collectors, and considerably lower than stagnation temperatures encountered in vacuum tube collectors. Thus, the solar fluid is degrading with time, and its properties change unfavourably. Enhanced corrosion and the formation of particulate matter from degradation products may be observed. These processes can seriously damage the system and lead to plugged pipes, filters and pumps. It is therefore strongly recommended to check the condition of the solar fluid from time to time, and replace it if necessary. There are currently no standardized methods to measure the temperature limits of a solar antifreeze, or to predict its lifetime in a specific installation. Lifetime will be strongly influenced by the conditions the fluid is subjected to, determined by the design and operation of the collector loop. Relevant parameters are temperature of the collector in stagnation, frequency and total time of collector stagnation, pressure and emptying behaviour of the collector field, metals encountered in the containment materials, presence of oxygen and so on. Thus the lifetime of an antifreeze is not a property of the fluid only, but a property of the fluid in a specific type of installation.

Standardized corrosion tests

A number of standardized corrosion test methods for metals in contact with antifreeze have been developed by the American Society for Testing and Materials (ASTM). Other standard testing methods for general corrosion investigations are described by German industry standards (DIN). All these methods have in common that they focus on the corrosion of metals and other materials in contact with the antifreeze, and not on changes of properties of the antifreeze itself or on the lifetime of the antifreeze. It has to be kept in mind that all laboratory tests of accelerated ageing – standardized or not - may give other results as breaking down of fluids in a solar heating plant due to the fact that a locally shifting pH to the acid side may lead to other products in addition to those one will find in laboratory products /Byg86//Byg88/. The most important standards for solar fluids are described in the following sections.

ASTM D1384

This test is a "Standard Test Method for Corrosion Test for Engine Coolants in Glassware" /ASTM D1384/. As the title indicates, this test has not been developed for solar antifreeze, but for engine coolants. Still it is the only standardized corrosion test manufacturers of solar antifreeze refer to in their product declarations /Hal05/.

In this test method, specimens of metals are totally immersed in aerated antifreeze solutions for 336 hours at a constant temperature of 71 or 88 °C, always significantly below the boiling point of the antifreeze. The specimens are usually treated specially before the immersion and electrically isolated from each other during the test. After the test, metal loss of the specimens is to be measured. The test is run in triplicate and it is quite common that the results of one of the three tests is completely out of line, which gives an idea about the difficulties of reproducibility of this kind of testing procedure.

In addition to what is demanded in the standard, the specimens can be observed under the microscope to detect pitting and crevice corrosion. The usefulness of this test for the prediction of antifreeze properties in solar applications is quite limited due to the low temperatures of the test method as compared to temperatures encountered in solar applications.

ASTM E712

This test is a "Laboratory Screening of Metallic Containment Materials for Use With Liquids in Solar Heating and Cooling Systems" /ASTM E712/. As the title indicates, this test has been developed for the prediction of the performance of metals in combination with a specific solar fluid under conditions similar to those in solar thermal applications. Although the focus is not on the lifetime of the antifreeze, it is considered to be essential in these test procedures to detect changes in the nature of the fluid that might significantly alter the corrosivity of the fluid.

This test method covers six laboratory test procedures for evaluating corrosion performance of a metal/fluid pair. The procedures are:

- A Basic Immersion Test at Atmospheric Pressure: This test is very similar to ASTM D1384. Deviations are that it is permissible to use any schedule of times and temperature and that consideration is given to the fact that silicate from the glassware can dissolve in an aqueous fluid and significantly affect the corrosion observed. This effect is insignificant if silicate is already part of the inhibitors used in the commercial fluid. If this is not the case, other containment materials than glassware may be used. This test is considered to be useful for plumbing, pumps, tanks, etc., but not for collector panels.
- B Heat Rejecting Surface Test at Atmospheric Pressure: This test is used for the determination of corrosion of surfaces that are used for heat transfer into the fluid. The heat transfer metal is placed on an electric heater, and a flask containing the fluid with an opening at the bottom is pressed onto the heated specimen with a flange. Provision is made for closing the apparatus and installing a reflux condenser at the top. Any temperature and time schedule may be applied for the heated specimen, and a stirring device may be added. This test is considered to be useful for simulating condition in collector panels.
- C High Pressure Test: Defined Temperature and pressure are applied to the fluid and specimens in an autoclave. The specimens are galvanically isolated and may be totally immersed, partially immersed or in the vapour phase. Any time, temperature and pressure

- profile may be applied. This test is considered to be useful for systems that face high temperatures and are closed to the atmosphere.
- D Repeated Dip Dry Test at Atmospheric Pressure: This test is simulating alternate wetting and drying conditions. An automatic control is dipping the specimen into the solution and pulling them out to dry. Any time schedule may be applied.
 - E Crevice Test at Atmospheric Pressure: This test is similar to ASTM G48, a test for stainless steel. It may be used to evaluate general corrosion resistance and to detect susceptibility to crevice corrosion attack.
 - F Tube Loop Test at Atmospheric Pressure: This test has the same purpose as B, with the difference that the heated section is not a plate but a tube. The tube is heated by a heating tape, and the fluid is pumped through the tube into a reservoir open to the atmosphere.

For all tests described in this standard, a minimum testing time of 30 days is recommended because the time-dependence of corrosion can show substantial non-linearity. It is also recommended that the effect of time of testing be evaluated. Since depletion kinetics can be a strong function of the exposed metal surface area, the ratio of metal surface area to fluid volume should relate to an operating system. Attention is given to the roughness of metal surfaces. The result is measured in mass loss per area of each metal specimen, and by examination at 10x magnification for incidence of localized attack. Changes of the heat transfer fluid such as appearance or odour is reported.

ASTM E745

This test is a "Standard Practice for Simulated Service Testing for Corrosion of Metallic Containment Materials for Use With Heat-Transfer Fluids in Solar Heating and Cooling Systems" /ASTM E745/. Like the other ASTM-tests, the purpose is the determination of the performance of the metallic containment material rather than the detection of fluid deterioration. It describes three practices:

- A Laboratory Exposure Test for Coupon Specimens: The apparatus consists of a mixing shaft which is heated by a hot plate. A pump is used for the circulation of the fluid. This test is not applicable for heat transfer from the test specimen to the fluid. Recommendations are given for cleaning methods for the test specimen. For test conditions that cannot be achieved under open atmosphere, the mixing shaft may be transferred to an autoclave.
- B Laboratory Exposure Test for Components or Subcomponents: The apparatus consists of a storage tank, a pump, plumbing, a process controller and monitoring equipment, as well as heating and cooling devices.
- C Field Exposure Test of Components or Subcomponents: This test consists of a small real outdoor installation which is operated until solar noon and then stopped to go into stagnation as often as possible. This test should be performed for at least one year.

For all tests described in this standard, a minimum testing time of 6 months is recommended and it is also recommended that the effect of time of testing be evaluated (compare remarks above for ASTM 712). Evaluation and reporting procedures are essentially the same as with ASTM D1384 and ASTM E712.

Reported testing results

Frei 1984

Specimens of copper, aluminium, steel, brass and solder were immersed into different fluids in an open beaker corrosion test, similar to ASTM D1384, but with temperature cycles from 20 – 90 °C. Mass loss, crevice and pitting corrosion were reported as well as pH and reserve alkalinity of the fluids /Fre84/. This test method is usually referred to as the "EMPA-test".

Rossiter 1983 and 1985

Already in 1983, Rossiter stated that "because of the lack of information on glycol degradation, it is not possible to predict the time to fluid breakdown, or to draw definite conclusions about the lifetimes of glycolic fluids in general" /Ros83/. Rossiter developed methods for the determination of degradation products of aqueous glycol solutions with ion chromatography. Aqueous glycol solutions without inhibitors were degraded in a way similar to ASTM D1384 (aeration, 100 °C, metal coupons) and then analyzed. With this method, glycolic acid, lactic acid and formic acid were identified among the major degradation products. Precipitates were collected and identified as copper(II)glycolate and copper(II)lactate with infrared spectrophotometry /Ros83/. In a later investigation, variables affecting the thermal degradation were studied (temperature, presence of metals and presence of oxygen). In this study it was concluded that the extent of degradation of the glycol cannot be used as an indicator of the magnitude of the decrease in pH /Ros85/.

Brown 1986 and 1987

Mass spectrometric methods were used to determine the rates of O₂ consumption and CO₂ evolution of ethylene glycol at temperatures in the range of 100-126 °C. Measurements showed that copper had a catalytic effect on glycol degradation, and that the rate limiting step of the reaction to CO₂ was not dependent on the amount of oxygen /Bro86/. In a further investigation, X-ray and IR spectra of synthetically prepared Cu(II)-salts (as found in /Ro85/) were analyzed and compared with results obtained from precipitated salts in degraded fluids /Bro87/.

Stichel 1997 and Schmidt 1998

Stichel and Schmidt performed a number of different tests described in AGK-Arbeitsblatt W1 /AGK88/. They compared results of the ASTM D1384 and the EMPA-test mentioned above with another ASTM test particularly designed for the test of aluminium alloys /ASTM D 4340/, a crevice corrosion test and the FVV Heisstest /FVV86/ /Sti97a/. In addition to this, they introduced a chemical corrosion test using a rotational cylinder /Sti97b/. With this cylinder, tests similar to ASTM D 1384 as well as electrochemical investigations were performed.

Electrochemical criteria included polarisation resistance, length of passive range and hysteresis effects at the anodic part of current density-potential curves.

The authors proposed limits of material depletion in g/m² for different tests and compared them to limits used by the automotive industries for engine coolants. They concluded that the investigated heat transfer fluids for solar applications from German manufacturers all proved excellent protective qualities against corrosion.

It was judged that the ASTM D 1384, the crevice corrosion test, the rotating cylinder test and the electrochemical investigations are the most effective testing methods of those investigated.

Werner 2000

Metal specimens were submerged in different fluids and treated with high temperatures (up to 280 °C) and pressures (up to 60 bar) in autoclaves /Wer00/. The test corresponds more or less to ASTM E712 C. Reporting was done similar to the above mentioned EMPA test.

Wedel 2000

Heat transfer fluids have been heated in U-shaped closed copper tubes to 90 °C (normal operation of solar system) and to 185 °C (stagnation of solar system). The closed copper tubes were only filled half and only one arm was heated alternately by an oil bath, such that evaporation could take place in the heated arm and condensation in the other arm. After the test, pH and reserve alkalinity were measured. According to the authors, IR-Spectroscopy of the fluids did not give any useful information. Change in colour and formation of particles were described /Wed00/.

Hafner 2001

A copper plate in contact with the solar fluid is heated and is visible through a window. The solar fluid can be pumped and is allowed to evaporate. The test consists of cycles between 120 °C and over 300 °C at 2.2 bar. One cycle of heating and cooling takes 25 minutes, and the fluid is kept above 300 °C for 3 minutes. Several samples were drawn during a 47 days test and concentration of inhibitors was measured as well as reserve alkalinity, pH, copper concentration in solution, density of the fluid and refraction index. This test was designed to simulate conditions similar to those in vacuum tube collectors and also focused to some extent on fluid deterioration.

Hillerns 2003, Hausner 2003, Hausner 2001

Heat transfer fluids have been tested in an autoclave at 160, 200 and 235 °C for 14, 28 and 42 days. Pressure in the autoclaves was not reported. Troubling of the fluid, odour and solid residues formed have been reported as well as pH and reserve alkalinity /Hil03/. In one publication, also values for metals in solution after the tests were reported /Hil01/

Madera 2003

A ion chromatographic method was developed to separate and analyse degradation products of aqueous ethylene glycol solutions. Formic acid, acetic acid and glycolic acid were identified as the main degradation products in an overheated field sample /Mad03/.

Conclusions

A number of standardized and non standardized testing methods are available to determine corrosion of metals in contact with fluids used in solar applications. Manufacturers commonly refer to the ASTM D1384 in their product declarations. Maximum allowed depletion in g/m² for different metals are not given in this standard, but proposed in publications by Stichel /Sti97a/. The same author concludes that all heat transfer fluids for solar applications he investigated proved excellent corrosion protection. Corrosion is usually not a problem in solar applications as long as the installation is done professionally, an appropriate solar fluid is chosen and the fluid is in good condition /Sti97a/ /Haf01/.

With increased collector temperatures during stagnation and unfavourable emptying behaviour of collector fields, solar fluids based on glycol-water mixtures may deteriorate with time, leading then to two different types of problems that may be interrelated: metal corrosion, and plugging of pipes, filters or pumps due to degradation products /Haf01/ /Wed00/. It is thus important to test not only the corrosion of metals in a fresh solar fluid, but also the lifetime of solar fluids in a given application. The influencing parameters for a given application may be the number and total time of collector stagnation, pressure in the collector field, type of collector emptying behaviour, presence of metals, presence of oxygen etc.

No standard test method could be found for fluid deterioration and lifetime of solar fluids under specific conditions. Several non standardized investigation methods were developed by different authors /Wed00/ /Hil01/ /Hil03/ /Haf01/ /Wer00/. Sometimes estimations of the lifetime of a solar fluid was based on these investigations. Further work is needed to create a standard test method for the estimation of solar fluid lifetimes /Hal04/.

Acknowledgement

The authors thank the Swiss Federal Office for Education and Science for financial support, as well as R. Werner (EMPA, CH), S. Dahl Wedel (DTI, DK), K.H. Tostmann (STZ, DE), L. Cedheim (SP, SE), F. Hillerns (Tyforop, DE) and M. Hafner (Clariant, DE) for valuable information about solar fluids and corrosion tests.

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