

SYNTACTIC FOAM THERMAL INSULATION FOR ULTRADEEP HIGH TEMPERATURE APPLICATIONS

by

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ABSTRACT

This paper addresses a major challenge facing deepwater production of oil and gas: how to assure continuous flow of product under the pressures and temperatures found on the ocean floor. Syntactic foam promises to overcome the limitations exhibited by conventional insulation materials in the past. New hybrid glass and polymer chemistries with improved "hot, wet" performance survive in conditions that were formerly thought impossible. This paper presents the latest laboratory test data on these new materials, and proposes models for predicting long-term performance.

INTRODUCTION

Offshore production of hydrocarbons has spread rapidly into deep water, moving from a thousand meters or less to depths well in excess of two thousand meters. As the water depth has increased, so too has the temperature of the product, from under 100° C to more than 150° C. At the same time, the size of fields and length of transport are growing, worsening the risk of blockage due to thermal precipitates. In response, a number of different flow assurance measures have evolved, including insulation of flowlines, risers, and wellhead equipment. Until recently, however, the effectiveness of insulation materials was limited by their vulnerability to the subsea environment. To meet this challenge, specialized syntactic foam systems have recently undergone a remarkably intense period of research and development.

SYNTACTIC FOAM

Syntactic foam is a lightweight composite material made from tiny hollow glass microspheres in a polymeric resin binder, along with other fillers and additives. Because the microspheres are filled with air, syntactic foam is low in both density and thermal conductivity. The choice of syntactic materials typically includes the following:

Rigid Binders: A rigid binder will add support and reinforcement to the glass microspheres, giving greater strength for a given density. However, excessive rigidity may result in cracking, particularly under thermal shock and cycling. The most common rigid binder resin choice is epoxy, because of its superior strength and resistance to hot, wet conditions. The choice of hardener may be either anhydride or amine curing agents, each of which has distinct advantages and disadvantages.

Flexible Binders: Flexibility is useful in many applications, and can offer some protection against cracking. However, flexible binders must be carefully designed to avoid degradation under hot, wet conditions. Polyurethane, for example, may show reversion or hydrolysis, and rubbers often suffer from oxidation. Another problem is that flexible binders do not reinforce microsphere fillers, detracting from their effectiveness in density and thermal conductivity.

MATERIAL VARIABLES

Many different kinds of materials can be used for subsea insulation, including epoxy, hydrocarbon resins, polyurethane, silicone, polypropylene, and various rubbers. Each material has distinct advantages and disadvantages. Extensive testing has shown that thermosetting epoxy resins have superior properties in most hot, wet applications, especially in ultradeep service. For that reason, the rest of this paper will concentrate on epoxy-based syntactic foam. An epoxy syntactic normally consists of at least four components: the basic epoxy, a hardening agent (or curative), one or more fillers, and additives, such as diluents, catalysts, modifiers, and coupling agents. Desirable properties include ease of processing, long life under service conditions, high efficiency, and acceptable economics. (1) The choice of epoxy chemistry is often between an amine curative and an anhydride curative. The tradeoffs between these chemistries are summarized in **Table 1**, below:

Curing Agent	Anhydride	Amine
Cost	low	high
Viscosity	good	good
Heat resistance	fair	good
Water resistance	good	good
Chemical resistance	fair	fair
Toxicity	low	high
Processing	easy	difficult

Table 1

COMPARISON OF EPOXY CHEMISTRIES

CHOICE OF FILLERS

Generally speaking, fillers, such as metal, ceramic, carbon, or glass particles, are added to the resin matrix in order to improve polymer properties, raise continuous use temperature, and to reduce the cost. However, such fillers may also decrease the elongation, water resistance, and cross-link density. The most commonly used fillers for epoxy resin are glass microspheres. The typical sizes of glass microspheres range from 15 to 120 microns, and their density varies from 0.125 to 0.6 g/cc. Normally, filler loading in epoxy resin is 30 to 50% by volume, but the maximum can be as high as 68%.

There have been concerns regarding glass microspheres performance under hot, wet conditions, and some tests have shown deterioration. This may be caused by breakage during cure, failure of adhesion to the glass surface, and/or expansion mismatch during heating and cooling. These effects can be mitigated by careful selection of glass chemistry and addition of appropriate coatings and coupling agents. **Figure 1** illustrates the effect of glass surface treatment. Sample 1 is an epoxy syntactic foam sample with untreated glass microspheres, and Sample 2 is the same, but with glass surface treatment. After 22 weeks of exposure, Sample 1 gained over four times as much water as did Sample 2. Another way to avoid microsphere failure is to use different types of fillers, such as ceramics (2). The disadvantages of ceramic microspheres are higher density

and thermal conductivity, and possible problems in processing. However, some ceramic fillers can provide very good results under hot-wet conditions, as shown in **Figure 2**.

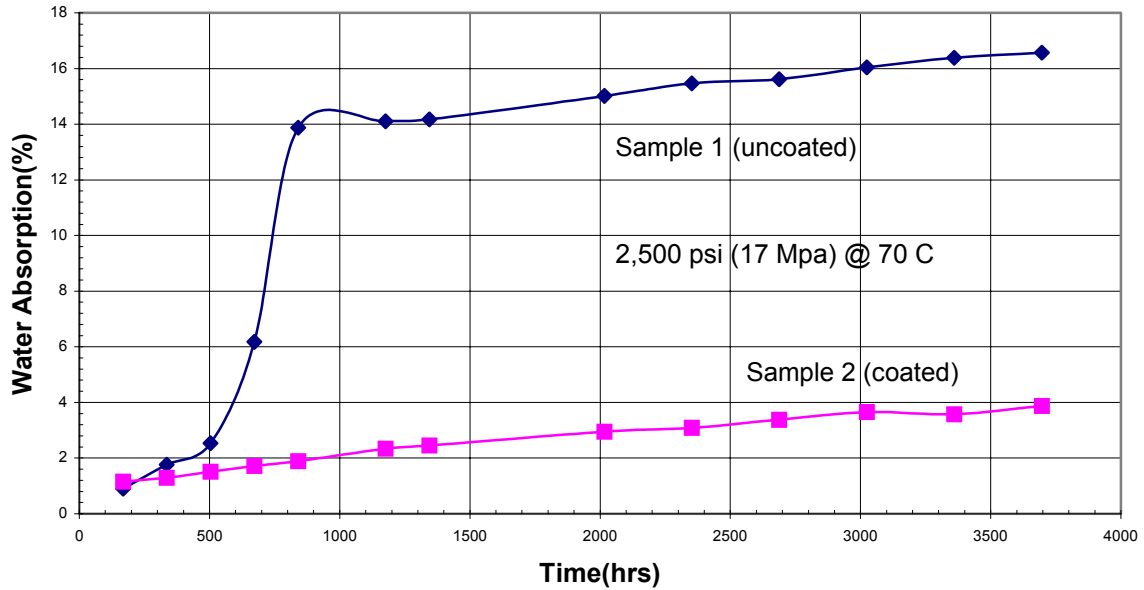


Figure 1
EFFECTS OF GLASS MICROSPHERE COATINGS

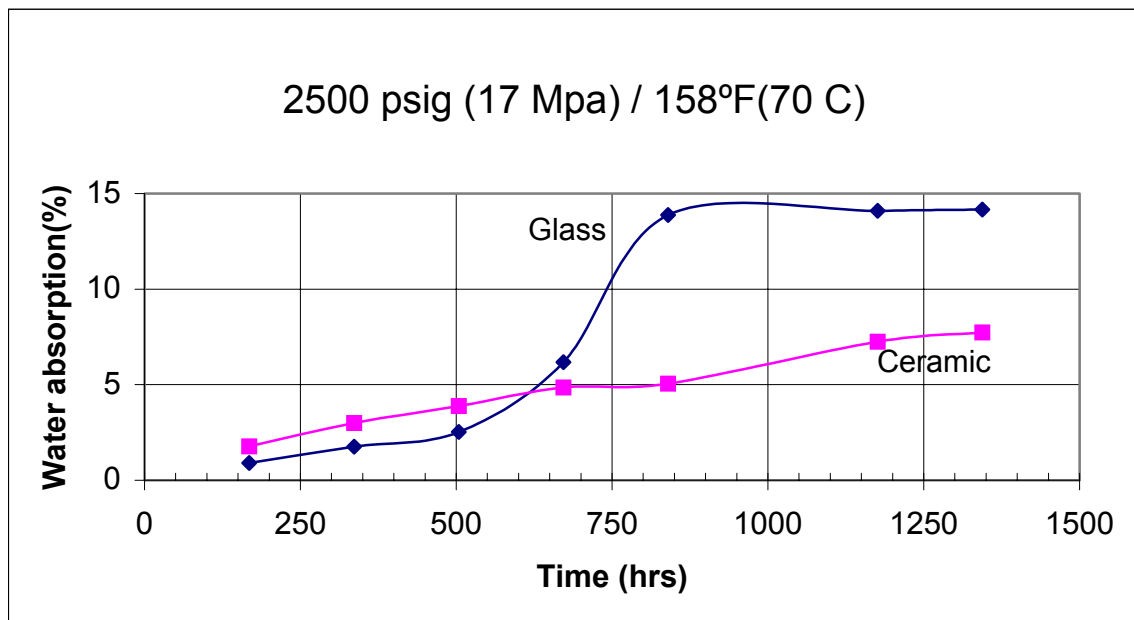


Figure 2

CHOICE OF BINDER RESINS

Most epoxy resins are rigid, especially those with good high temperature performance. Because they are so rigid, epoxies may be difficult to cast directly onto pipe without cracks. One solution is to add toughening agents or flexibilizers. The most commonly used flexibilizers are CTBN or castor oil, the purpose being to create a two-phase matrix. Unfortunately, the effect of added flexibilizer is to reduce hot-wet performance. Another disadvantage is aging. Most polybutadiene materials, for example, perform well in the initial stages, but deteriorate after thermal aging. As a result, it is important to choose flexibilizing agents carefully and to balance long-term performance with flexibility.

Another way to avoid cracking is to use so-called "soft" materials, such as naturally flexible epoxy, or an elastomer such as polyurethane. Unfortunately, most flexible materials do not provide good high temperature performance, often showing high water absorption and cracks. There is much debate regarding polyurethane as a high temperature insulation material. A concern is the possibility of hydrolysis after the material is exposed to hot-wet conditions for a long period. Extensive testing has shown that most polyurethanes perform well at temperatures below 70 °C, but, above this temperature, the materials lose their water resistance and some even show reversion. This effect is shown in **Figure 3**. Therefore, a general conclusion is that polyurethanes should only be used in subsea insulation at temperatures of 70°C or less. Other disadvantages of polyurethane include its high cost and difficult processing issues.

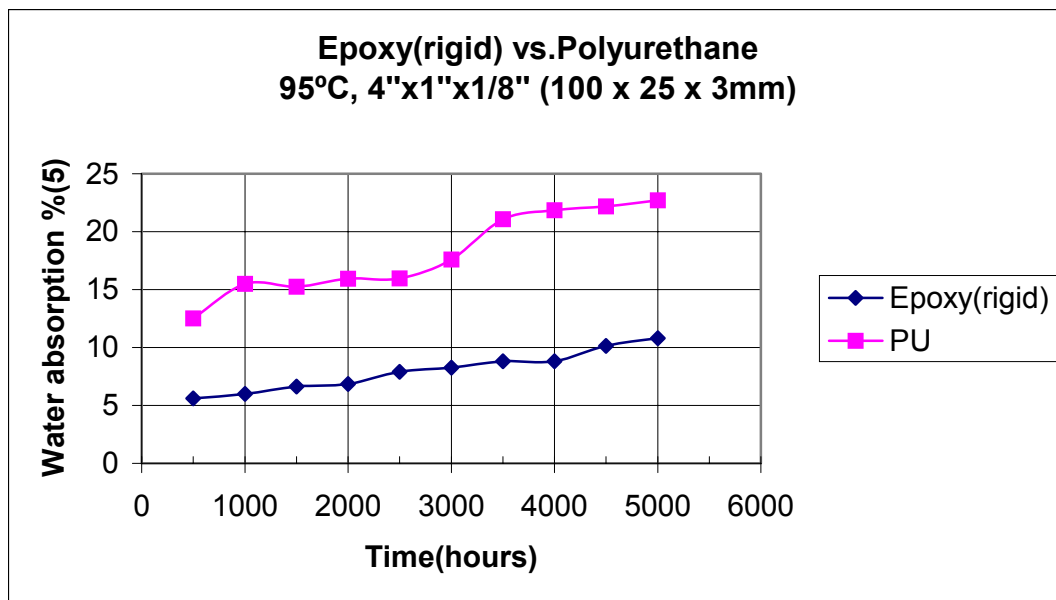


Figure 3

TESTING METHODS AND EQUIPMENT

First stage: Screening Test: Three different temperature (50, 70, 95°C) water baths to measure water absorption at atmospheric pressure for different formulation samples (similar to ASTM D570)⁽⁴⁾. Test durations range from 24 hours to 10,000 hours.

Second stage: Properties Tests: including mechanical properties (density, hardness, compression, tensile, creep, shear and impact), thermal properties (thermal conductivity, glass transition temperature, specific heat), hydrostatic properties (water absorption at different temperatures and pressures, crush pressures) and aging properties (thermal and humid aging).

Third stage: Simulated Service Test: performed under the most realistic conditions possible, such as the testing service provided by Heriot-Watt University. A standard test is 28 days, although longer periods are desirable.

INTERPRETATION OF TEST DATA

EFFECTS OF TEMPERATURE

The goal of long-term testing is to provide data that can be used to predict performance for twenty years or more. In First Stage Testing, materials are subjected to 50, 70, and 95 °C water for periods from 24 hours to 10,000 hours. Typical sample sizes are 1"x 4"x1/8" (100 x 25 x 3 mm). The data is normally analyzed by the Arrhenius law to simulate accelerated aging:

$$R = A \exp (-B/T)$$

Where R= rate of phenomena, A and B are constants, T is the absolute temperature (°K)

It is very difficult to apply this rule to syntactic foam material, because the aging process of these materials is complex, involving the base material, fillers, glass transition temperature, pressure, and so on. In **Figure 4**, we see two identical formulations tested at different temperatures. At the beginning, the higher temperature sample shows more water absorption, but as time goes on, the results approach each other. This leads to the conclusion that, so long as the application temperature is significantly lower than the maximum temperature at which the insulation material will survive, the final water absorption results will be very similar, no matter what the application temperature is.

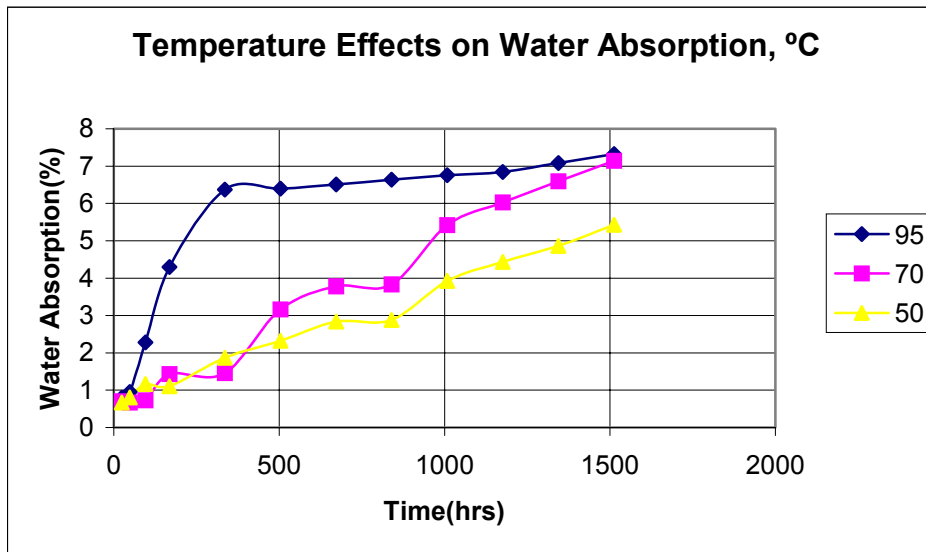


Figure 4

EFFECTS OF THICKNESS

Another question that frequently arises has to do with the suitability of sample size and test method. Are ASTM standards appropriate for this new application? It seems at this point that no one has the “perfect” method or model for predicting insulation material performance after twenty years in the ocean. So far, the best way at this time appears to be the “Simulated Service Test” which attempts to duplicate the actual application: hot oil flowing inside the pipe and pressurized cold water outside the insulation. This kind of test is very expensive and time consuming, and not suitable for screening large numbers of candidate materials. For that reason, the atmospheric pressure water bath test is used as the initial screening test. The key is to set up the test and establish an acceptance range that is both accurate and realistic. To do that, we must understand the mechanism of water absorption.

As the binder material cures, a number of “micro voids” form in the resin matrix. When the material is immersed in water, water molecules fill these voids. Most commonly used models estimate the rate of water absorption according to Fick’s laws of diffusion (3), in which only one phase is considered, and the filling rate is governed by diffusion. Other models consider two phases, such as the Langmuir model. The second source of absorption is the polar attraction between base material and water. This effect tends to disappear at higher temperature. After the water migrates into the matrix, it starts to attack the fillers and the resin itself, resulting in an increase in the absorption rate. The question is, how far can the water go? To understand this better, a sample that had been already exposed to high temperature water for a long period of time (85°C / 1,848 hrs) was examined under a SEM. The water was seen to have penetrated no more than 50 microns. As shown in **Figure 5**, the thickness of the insulation affects both water absorption and long-term performance. This is why larger-scale tests are required.

Fick’s law (3):

$$M_t/M_\infty = 1 - 8/\pi^2 \sum 1/(2n+1)^2 \exp\{-D(2n+1)^2 \pi^2 t/h^2\}$$

Where:

M_t : weight at time t (h)

M_∞ : weight at infinite time(saturation)

D : diffusion coeff. (mm^2/h)

h : thickness (mm)

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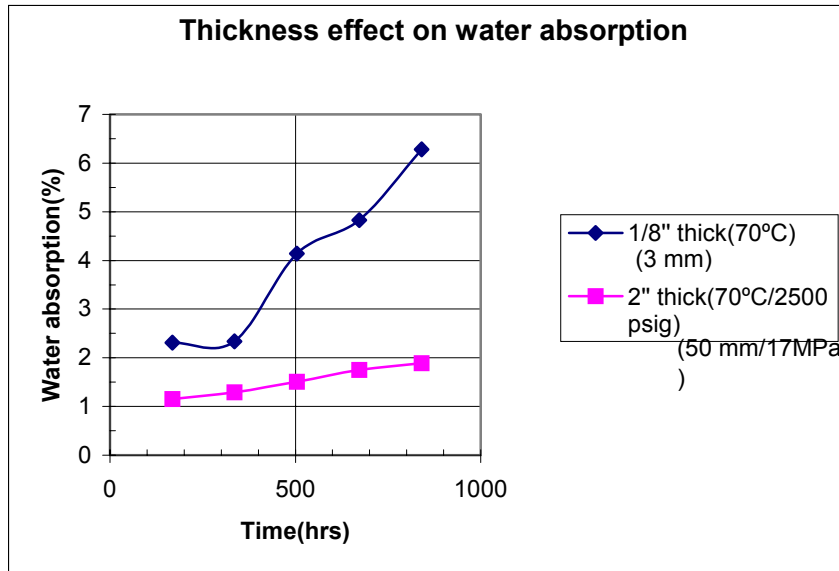


Figure 5.

EFFECTS ON THERMAL CONDUCTIVITY

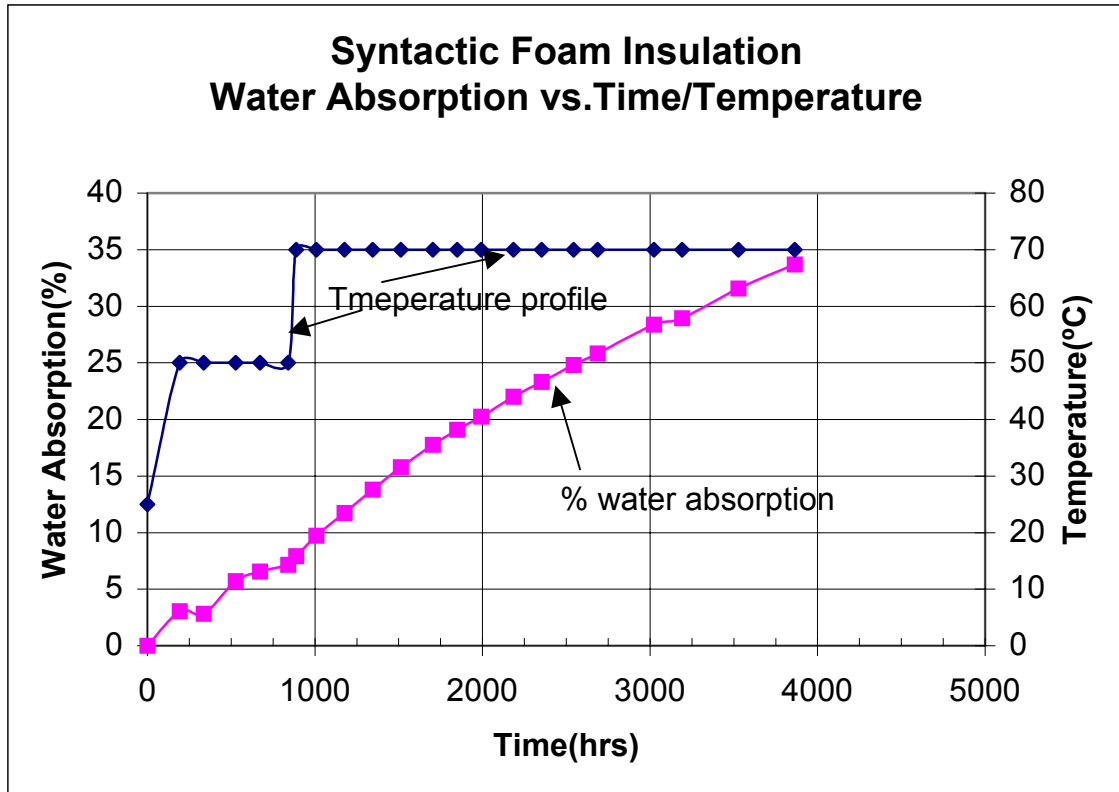
How will water absorption affect the thermal conductivity (K-value) of the insulation material? To answer this question, another experiment was performed. A block of porous “pack-in-place” syntactic foam (12”x12”x 2”, or 300 x 300 x 50 mm) was prepared with an initial dry density of 25.5 pcf (0.41 g/cc) and an initial dry thermal conductivity value of 0.05 BTU-ft/hr-ft²-°F (0.09 W/m-K). Thermal conductivity testing was performed per the procedure outlined in the Holometrix Operation Manual for the Lambda 2000 Series Heat Flow Meter in accordance with ASTM C518. The sample was wrapped in plastic film prior to thermal conductivity measurements, to prevent any escape of water from the sample during testing.

To accelerate the absorption process, the syntactic foam specimen was placed in a controlled water bath containing distilled water warmed to 122°F (50°C). The specimen was removed from the bath periodically in order to measure water weight gain, density, and thermal conductivity. The water absorption rate was further accelerated by raising the temperature of the water bath to 158°F (70°C) after 3864 hours (161 days). The temperature and absorption profiles are represented graphically in **Figure 6**. **Figure 7** shows the impact of this absorption on thermal conductivity.

A direct relationship can be drawn from the charts to appreciate the impact of water absorption and density increase on thermal conductivity. The results are in line with expected theoretical analysis. Thermal conductivity of the syntactic foam increases with increasing water absorption and resulting density, but at a *decreasing* rate. Density increases in a linear relationship with increasing water absorption. Even though density increased 29.7% during the test, the thermal conductivity still is in a range that would be considered highly effective for subsea insulation. Note that the absorption of this porous

specimen was artificially induced by pressurization. Water absorption of non-porous syntactic foam under normal subsea conditions is expected to be in the 5-10% range.

Figure 6



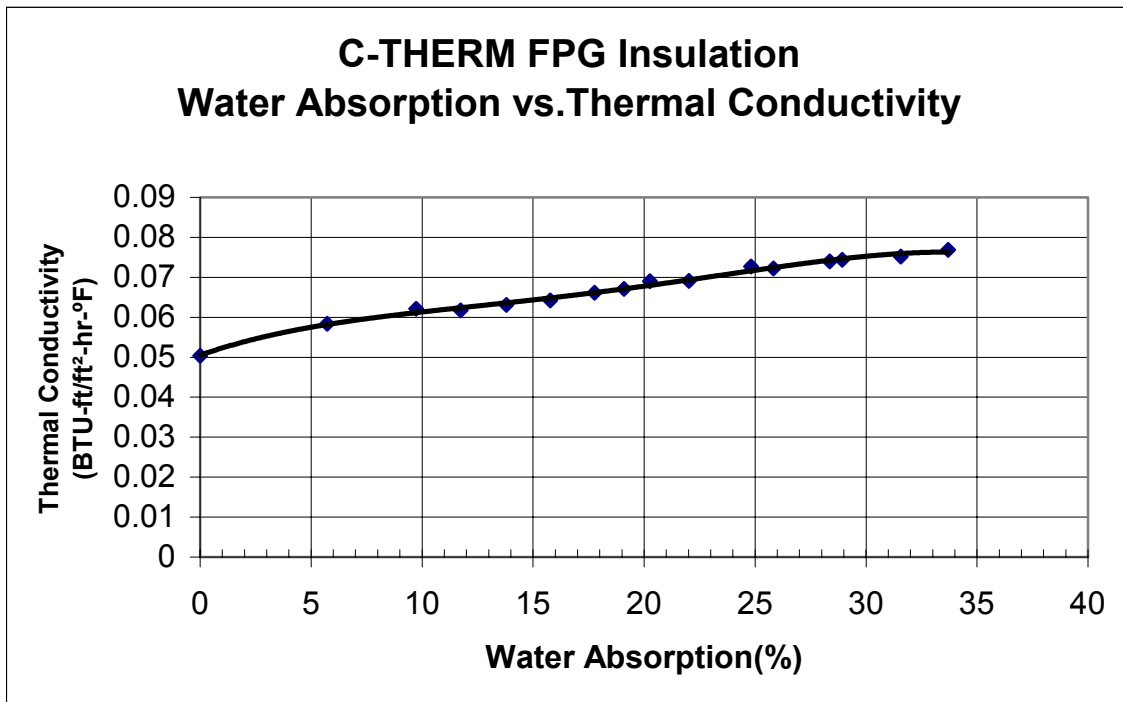


Figure 7

SIMULATED SERVICE VESSEL

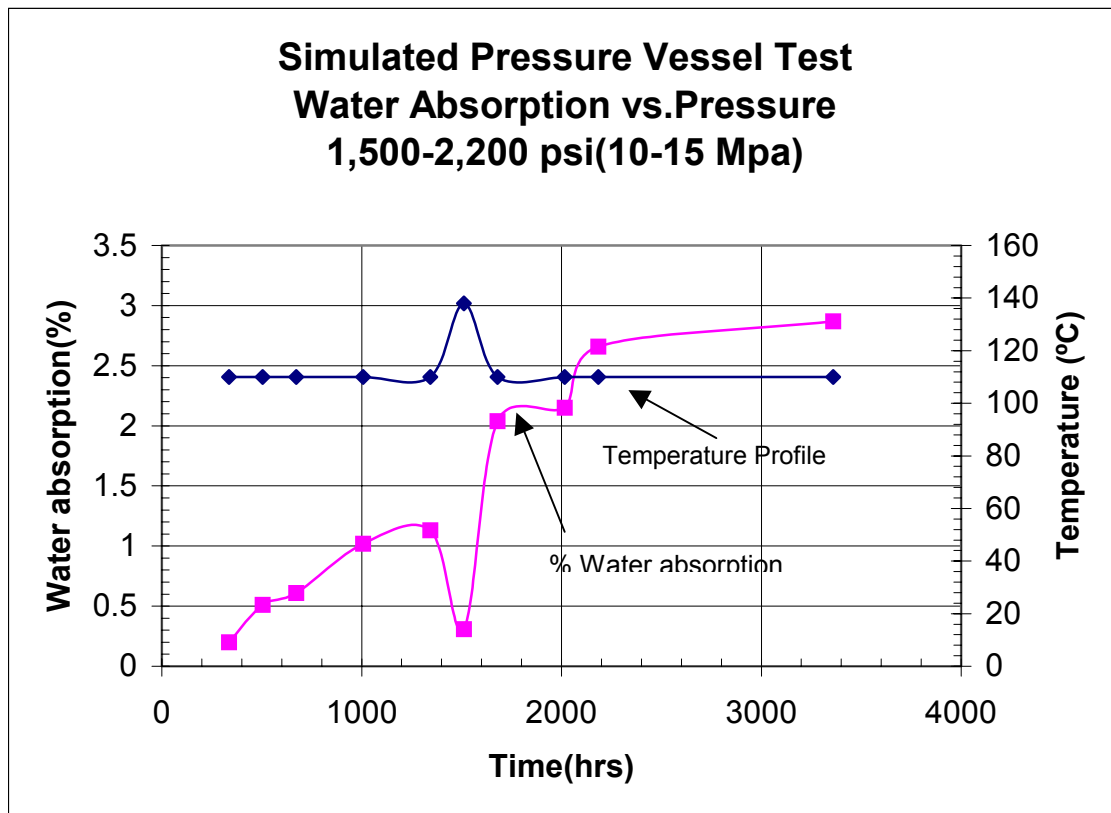
The best way known to test insulation material is by using a Simulated Service Vessel (SSV). The SSV can provide reliable data on material behavior under combined pressure and temperature. The SSV that we use in our testing can operate up to 175 °C and 20 MPa. The vessel can test insulation samples cast onto 8" nominal pipe (219 mm) up to 1.5 m long. In order to generate more data per unit time, we normally limit our samples to 0.5 m long each, and test three samples simultaneously. The apparatus, which is shown in **Figure 8**, consists of five major parts: pressure vessel, oil heater, water chiller, temperature and pressure controller, and emergency pressure relieve valve.

The test conditions that created the data shown in **Figure 9** are an initial temperature of 110 °C inside the core pipe for eight weeks, increased to 138 °C for two weeks, then returned to 110 °C for another two weeks. Water temperature was held constant at 4 °C during the entire test period. Hydrostatic pressure was 10 MPa for the first two weeks, and then 15 MPa for twenty (20) weeks. The vessel was opened every week to visually inspect the insulation material and weigh the samples to calculate water absorption. During the opening and closing process, the insulation material experienced both thermal shock and pressure cycling. As result, the SSV test is more severe than its intended application, and the data tends to be conservative.



Figure 8 – Photograph of SSV

Figure 9



SUMMARY AND CONCLUSIONS

1. Syntactic foam insulation materials are available to meet almost any present subsea insulation requirement, with epoxy-based syntactics being the most versatile and capable systems known at this time.
2. Long-term materials behavior can be predicted by testing small size samples under appropriate conditions. However, the conditions and procedures must be very carefully selected, and the results properly analyzed.
3. Materials performance is driven by both temperature and pressure. Temperature is the key driver in short-term “ hot, wet” conditions. Hydrostatic pressure, so long as it is well below the crush pressure, primarily impacts long-term performance.
4. Considering Point 3, the Arrhenius equation must be used with great caution in extrapolating water absorption from short-term data. The differing time constants of temperature and pressure effects must be taken into account.
5. The best way known for testing insulation material is the Simulated Service Vessel (SSV), but it is also the most expensive and inconvenient method. Further, SSV test duration is a topic requiring more study and discussion.
6. While it is every engineer’s goal to design a 100 % waterproof system, the possibility always exists for some leakage to occur during twenty or more years under high hydrostatic pressure. Therefore, it is advisable to design and test insulation materials under conservative “hot, wet” conditions.

ACKNOWLEDGEMENT

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