Gas/Liquid Membranes For Natural Gas Upgrading

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To

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DISCLAIMER

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ABSTRACT

Efforts this quarter have concentrated on field site selection. ChevronTexaco has signed a contract with Kværner process Systems for the 50 MM scf/d dehydration skid at their Headlee Gas Plant in Odessa, TX for a commercial-scale test. This will allow the test to go forth. A new test schedule was established with testing beyond the existing contract completion date. Potting and module materials testing continued. Construction of the bench-scale equipment was started. Additional funding to support the test was obtained through a contract with Research Partnership for Secure Energy for America.

TABLE OF CONTENTS

INTRODUCTION

Gas Technology Institute (GTI) is conducting this research program whose objective is to develop gas/liquid membranes for natural gas upgrading to assist DOE in achieving their goal of developing novel methods of upgrading low quality natural gas to meet pipeline specifications.

Kværner Process Systems (KPS) and W. L. Gore & Associates (GORE) gas/liquid membrane contactors are based on expanded polytetrafluoroethylene (ePTFE) membranes acting as the contacting barrier between the contaminated gas stream and the absorbing liquid. These resilient membranes provide much greater surface area for transfer than other tower internals, with packing densities five to ten times greater, resulting in equipment 50 – 70% smaller and lower weight for the same treating service.

The scope of the research program is to (1) build and install a laboratory- and a field-scale gas/liquid membrane absorber; (2) operate the units with a low quality natural gas feed stream for sufficient time to verify the simulation model of the contactors and to project membrane life in this severe service; and (3) conducted an economic evaluation, based on the data, to quantify the impact of the technology. Chevron, one of the major producers of natural gas, has offered to host the test at a gas treating plant. KPS will use their position as a recognized leader in the construction of commercial amine plants for building the unit along with GORE providing the membranes. GTI will provide operator and data collection support during lab- and field-testing to assure proper analytical procedures are used. Kværner and GTI will perform the final economic evaluation. GTI will provide project management and be responsible for reporting and interactions with DOE on this project.

EXECUTIVE SUMMARY

The cofunding agreement with ChevronTexaco continues under discussion. ChevronTexaco's Chinchaga Gas Plant in Alberta, Canada will not be increasing capacity as planned. Since they do not have a commercial need for the contactor, they have withdrawn that site and are seeking another suitable location. We continue seeking alternative hosts and sites as a backup. A meeting was held with ChevronTexaco in Denver last quarter, 2002 to identify potential locations. Most of their needs are outside the North American market.

Early in 2003, ChevronTexaco identified a potential test site in West Texas. The application here is for a full-scale dehydration unit, similar in size as originally proposed, but for a different natural gas processing application. A meeting was held with ChevronTexaco, GTI and KPS at the Headlee Gas Plant in Odessa, TX, to investigate testing, contract terms, schedules, and responsibilities. A design review meeting (originally planned as a HazOp review, but served more as design) was conducted at KPS offices in Houston, TX during the third quarter, 2003. For this analysis, focus was on issues directly affecting the planned tie-ins.

A meeting was held with Tony Zammerilli, DOE Project Manager, in Morgantown, PA to review status of the project during the third quarter, 2003. This project has been delayed due to the time required to secure an appropriate site after the originally proposed site became unavailable. GTI has slowed down the project so that the original funding would be available. However, the cost of the test has increased. KPS and ChevronTexaco have increased their planned co-funding, but there is still a gap. He indicated that there is no out-year funding for Gas Processing projects in the DOE budget. He indicated that he would be responsive to reasonable changes in the program direction to help ensure the test occurs, within the bounds of the contract. The Contract Administrators must approve any changes to schedule and costs.

GTI was awarded a research contract from Research Partnership for Secure Energy for America (RPSEA) that will provide cofunding for this project. The objective of the proposed project is to develop gas/liquid membrane contactors for deep, offshore processing of natural gas to decrease the overall cost to bring these valuable reserves to the market. The scope of work for this program is to design, construct, install, and operate a 50 million standard cubic feet per day commercial-scale dehydration absorber in a gas plant environment at 900 psi, in conjunction with the DOE Project. This

absorber will be designed to offshore specifications so that it can be moved to platform operations, if successfully demonstrated. Prior to installation, a novel membrane protection system will be tested in the laboratory to study response time under simulated failure modes. An engineering research study will design the dehydration system for a typical deepwater, offshore Gulf of Mexico application and then conceptualize a subsea installation utilizing the technology. Work will begin first quarter, 2004.

EXPERIMENTAL

ChevronTexaco module:

The contract between ChevronTexaco and KPS was signed November 6, 2003 for the 50 MM scf/d dehydration unit. The contract spells out specific performance criteria that must be demonstrated during the test before ChevronTexaco will accept the unit. It is anticipated that the test skid will then be moved to an offshore platform for dehydration service. The revised schedule for the project is given in Figure 1.

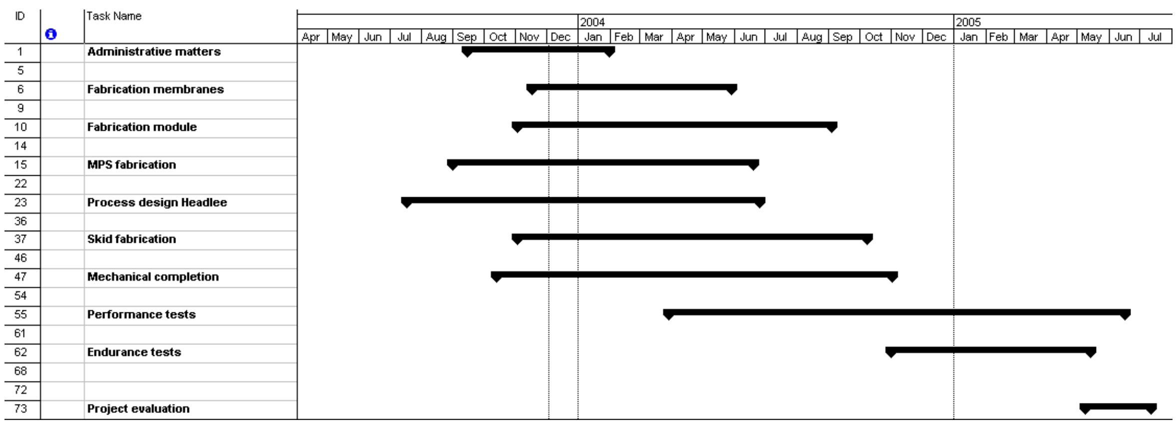


Figure 1 Project Schedule for Headlee Dehydration Test

An Advisory Committee meeting was held in Houston this quarter to review progress and set responsibilities for the project. It was agreed that the existing glycol pumps would be sufficient for our testing, therefore the pump skid was eliminated from the design basis. KPS and local contractors completed all tie-in work on time, allowing us to make our test tie-ins without disrupting the plant operations. The current flowsheet is shown Figure 2.

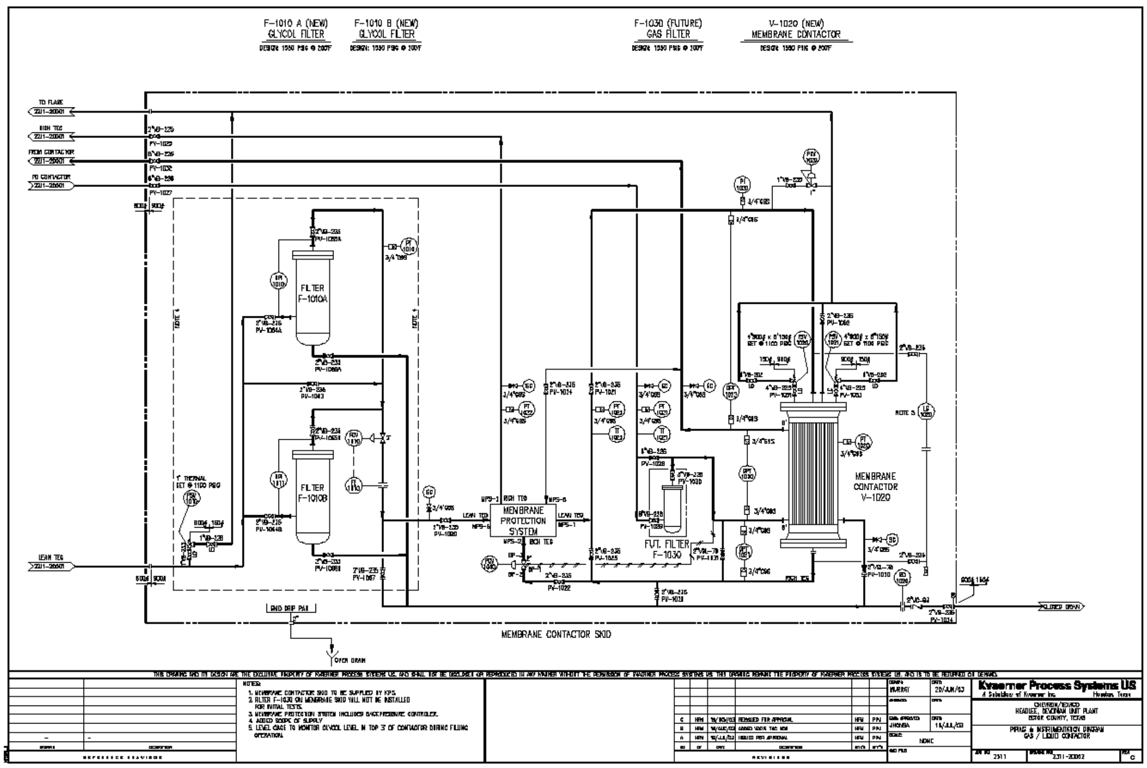


Figure 2 Headlee Test Skid P&ID

GTI will be responsible for the collection of data, and will install a separate analytical/office trailer at the site. The trailer will be equipped with the needed analytical equipment and data collecting systems. GTI will also supply (to be borrowed for testing period) an on-line Ametek moisture analyzer for dry gas analysis (water in dry gas). The wet gas water content will be calculated and verified by a water mass balance (dry and wet gas and lean and rich TEG). The sampling plan and procedures will be prepared prior to the HAZOP meeting planned for March 2004. The possibility of reducing the water content in the lean TEG at the plant during the testing is being investigated. This would require increasing the temperature in the reboiler and, if possible, adding some stripping gas. The variation of water content in the glycol will add important data points for the evaluation of the performance and the simulation tool. While it will be a benefit if one of the tests can be operated with 7 pound water/MMscf in the dry gas, this can be a challenge at Headlee due to the large amount of water in the gas and the high water content in the lean glycol.

As part of their cofunding, a purchase order has been issued to W.L. Gore to build the ribbon-tube-membrane coating equipment for the ChevronTexaco module, to optimize the coating process with this new equipment, and to develop a method to measure the characteristic performance of the coating layer (permeability, coating thickness) – both for the Colorado-membranes and for the new ChevronTexaco-membranes. When that work is completed and the results are satisfactory (ChevronTexaco-membrane performance compared to Colorado-membrane performance), a purchase order for the membrane production will be issued by KPS.

Potting Testing

The present potting material has its limitation in the casting of larger diameters due to high exothermic peak and subsequent cracking of cured material. Therefore, a search for a new thermosetting material was initiated.

<u>Chemical immersion test:</u>

The most common gas treatment absorbents were picked out for the test where resin samples (including membrane and spacer) are exposed for 24 weeks at 60°C. The following solvents were chosen:

- TEG
- MEA
- MDEA
- aMDEA (highly activated from BASF)
- Morphysorb
- Selexol/Genosorb

As a measure for chemical resistance, the adhesion between membrane/PTFE and resin was chosen in addition to swelling of sample. Chemical resistance test will be performed after 6, 12, and 24 weeks. The test was completed this quarter.

Parallel to the chemical testing, the following activities will be performed:

- potting simulations, i.e. study of the rheological behavior of approx. 3 kg samples of the various resins in a plexiglass mould of length/diameter 720 mm which is filled with membrane sheets and spacer material
- building dummies of the full size diameter and thickness (approx. 40 kg resin), both to see the rheological behavior and the curing performance in full scale
- identify the new potting material.

Laboratory Testing

<u>Summary</u>

Design efforts have been initiated towards fabrication of the facilities to perform the next phase of gas-liquid membrane tests. A first-pass at the major process flow has been formulated, including a simplified P&ID and a Design Basis. Mechanical overviews of the pressure vessel are presented, to facilitate evaluation of options for fabrication of the membrane module. Review and comments have been solicited by KPS to allow movement to the next stages of program design and implementation.

<u>Introduction</u>

The approach is (1) to modify an existing high-pressure facility, within an enclosure in the south west corner of Laboratory 636 at Des Plaines and (2) to utilize the high-pressure compressor / circulation system, which has been installed for the scavenger test rig, to supply the primary gas requirements.

As these facilities are upgrades for the gas-liquid membrane program, existing equipment will be left in place as much as possible in the facilities, which will facilitate future flexibility for comparing the gas/liquid membrane with conventional contactors.

The current plan is to conduct primarily sweetening operations, in a sequence as follows

1— Carbon dioxide removal (from a nitrogen-based stream)

2--- Hydrogen sulfide removal (also from a nitrogen-based stream)

3--- Other components, such as water (in a nitrogen stream)

<u>Process Flow</u>

The proposed process flow is shown in the simplified P&ID in Figure 3. Major vessels have been included, as well as most of the process piping, with line sizes. However, only primary process controllers, such as flow and pressure controllers have been included at this point. Items such as line or vessel heaters, safety and interlock systems, a membrane-protection system, and other details will be added at a later stage.

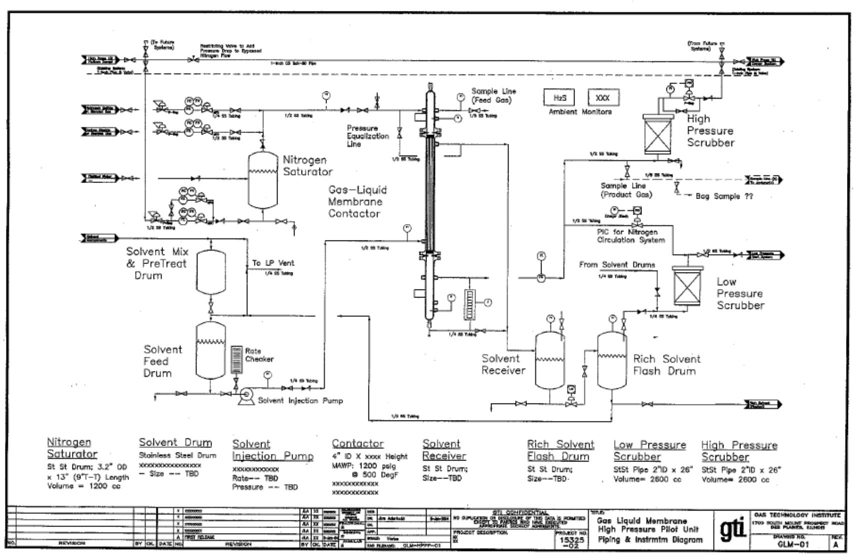


Figure 3 Proposed Laboratory Test Unit P&ID

The center of the experiment system will be the membrane module, which will contain tubes of membranes enclosed in a pressure vessel. For this first pass, we have assumed that the membrane module can be mounted vertically. The feed gas stream would be passed down through the membrane tubes. It is assumed that the solvent will be flowing upward on the shell side of the membrane module.

The bulk of the gas flow will be nitrogen and will come from the circulating compressor system, which was installed recently by the Gas Processing team at GTI for the “scavenging” test stand. A connection to this source of high-pressure nitrogen is currently being implemented. There are two features of this system, which need to be mentioned. First, there is currently no high-pressure make up capability for the compressor system (other than bottled gases), so the high-pressure nitrogen must be cleaned up at the gas-liquid membrane test facility and recycled back to the compressor suction. Second, the compressor is a positive-displacement machine, so the flow rate range is relatively fixed. Since the flow rate is substantially more than that desired for the gas-liquid membrane program, a bypass will be included as the connection is made from the compressor system to the gas-liquid membrane facility, so that most of the high-pressure nitrogen stream is recycled back to the compressor suction. Only a slip stream of the overall high-pressure nitrogen circulation is routed to the gas-liquid membrane unit.

The existing system contains parallel mass flow controllers for the nitrogen feed, which can each give about 1000 scfh at 1000 psig. There also exists a mass flow controller (for lower flow rates) to feed concentrated hydrogen sulfide blends into the feed gas stream. Another mass flow controller will be added to deliver concentrated carbon dioxide for studies at about 800 psig. The existing system has a bubbler (“Nitrogen Saturator”) in line for the nitrogen feed stream so that water can be added, if it is necessary to humidify the feed gas.

Liquid flow rates in the existing system are very low, on the order of a couple gallons per day. We expect that the solvent rates will be considerably higher for the gas-liquid membrane project, probably on the order of several liters per minute. This is one area to which we will devote much more effort in the next stage of design. We have not yet attempted to size the solvent vessels beyond what exists.

Membrane Module – Mechanical Design

It would be expedient to utilize pieces of the existing contactor for the membrane module in the gas-liquid membrane experimental studies. This section will review some of the options. A mechanical drawing is shown below, with major dimensions given. These dimensions are not precise values, but rather estimates which we made mostly from the exterior of the assembled column. These dimensions will be utilized for scoping calculations at this point, but the column would have to be disassembled and checked more precisely to validate many of the measurements before construction of a membrane module could be attempted.

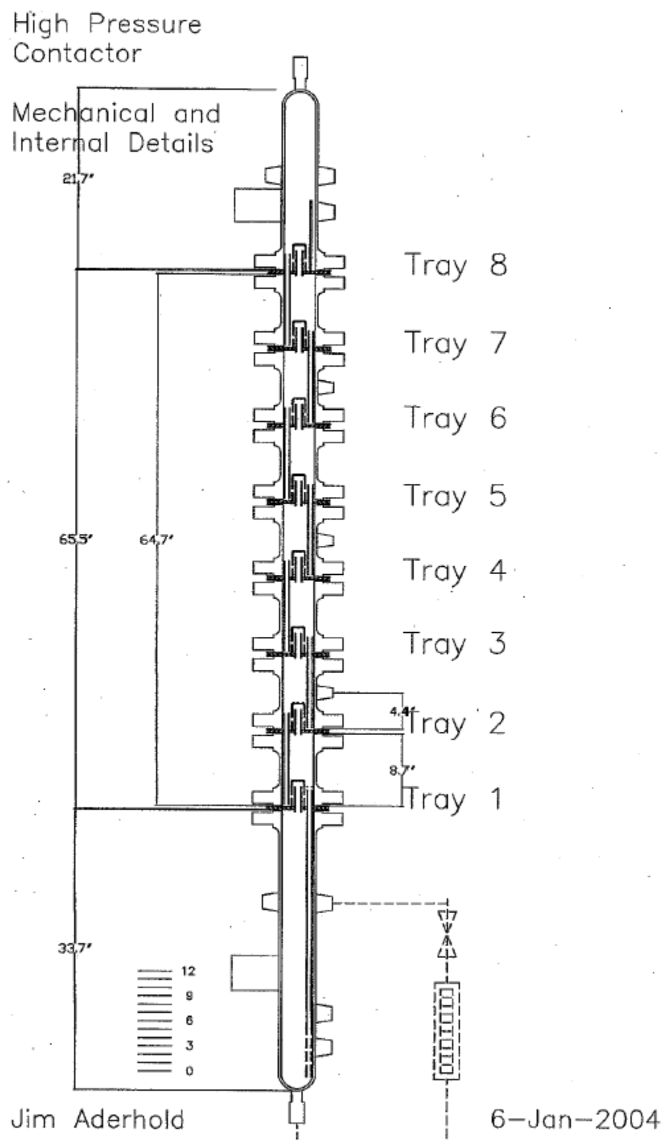
In general, most of our measurements are consistent with the following assumptions:

Pipe = 4-inch, Sched-80 (Possibly Sched-40)

Flanges = 4-inch, 600 psi service

Material = carbon steel

First, assume that only the two end pieces ("heads") of the existing contactor were employed. In other words, if all the middle spool pieces and trays in the existing contactor were removed, a new spool piece with the membrane module could be inserted directly into the system with relative ease, employing the end sections from the existing contactor. As the contactor is supported now, this new spool piece would be about 66 inches in length, including the ends, which would have to be 4-inch, 600 psi nominal flanges. It would be relatively straightforward to remount one of the existing "heads", so the length of a new spool piece could be less than 66 inches, but ceiling limitations would preclude anything more than about 72 inches in length for a whole new spool piece with a membrane module.



Second, another approach would be to fabricate a membrane module, which could be inserted into the existing column, after the current internals had been removed. The contactor could be reassembled with between two and seven spool pieces containing the membrane module and the existing "heads". The second mechanical drawing shows the two types of existing spool pieces – three spool pieces with nozzles in the middle of the pipe section and four spool pieces without nozzles. Two of the spool pieces, which have threaded nozzles, could be used for solvent inlet and outlet points; the other spool pieces could be utilized as fillers in between. The standard spiral-wound gaskets are about 3/16-inch thick, so each section of the membrane module would be close to 9 inches in length. This approach could be used to produce membrane sections of 18, 27, 36, 45, 54, or 63 inches in length. This option would eliminate the need for any new pressure vessel sections, but it would present the challenging opportunity of sealing the shell side from the tube side at both ends. One end of the membrane module could be fabricated similar to the current trays in the contactor – that is, in the form of a large washer, which could be sealed between two gaskets at the flange connection. However, the other end would have to be small enough to be inserted into the spool pieces, so it would seal against the wall of the pipe in a spool piece.

Design Basis

	Nominal	Maximum	Minimum	Notes
Feed Gas				
Primary Component	Nitrogen	----------	---------	
Flow Rate, SCFH	1000	1500	100	
SLPM	500	750	50	
Feed Gas Components				
Carbon Dioxide, Vol %	5	10	---	(1)
Hydrogen Sulfide, ppm	50	200	10	(2)
Liquid Solvent				
Rate, GPH	1	25	1	(3)
LPM	---	1.5	0.1	
Membrane Processing Conditions				
Pressure, psig	800	1000	300	
Temperature, ^oF	80	150	60	

Notes:

(1) – At the total make gas rate of 1000 SCFH, percentage levels of carbon dioxide would be a logistical challenge, and we have several alternatives which need to firmed up, a good possibility of requiring at liquid CO_2 supply.

(2) – These levels of hydrogen sulfide are probably too dilute, but they are close to the upper limit from a gaseous supply of hydrogen sulfide, a good possibility of requiring a liquid H_2S supply also to get hydrogen sulfide concentrations at percentage levels requiring the need to upgrade the existing scrubber.

(3) – These solvent rates are very preliminary, which we will update in the next stage of design.

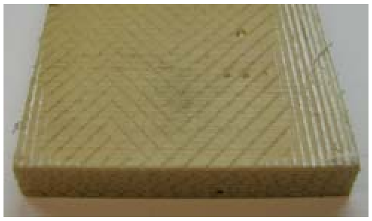
(4) – In general, a movement to lower gas rates for the pilot plant design would be preferred. Movement to higher gas rates significantly increases operating costs and makes the logistics much more difficult.

RESULTS AND DISCUSSION

Chemical immersion in TEG – First Test Series:

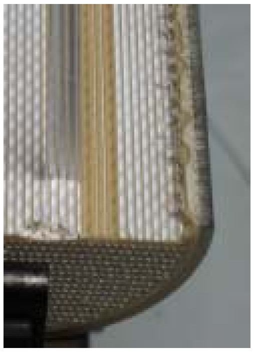
Fuller – 27 weeks

The first test series was terminated after 27 weeks of immersion. Only one of the tested systems show acceptable chemical resistance in TEG defined as swelling behavior and hardness. This is an epoxy system from Vantico. The swelling is expressed as a percentage increase in sample thickness. The Vantico-system swelled by 8% and the reference system from Fuller (used in Colorado) by 11%. The hardness of these two systems are 3-4 for Vantico (4=hard/1=soft) and 2 for the Fuller system. Fuller system has also a pronounced discoloration.



Vantico – 27 weeks

After the 27 weeks of immersion, the samples were tested with regard to adhesion and mechanical bending.



Mechanical peeling test

Adhesion test or mechanical peeling tests express the force necessary to peel the membrane from the potting material. For the two samples of Fuller and Vantico, the force has been reduced by 18% and 20%, respectively, which is assumed to be very good results.

The bending strength for the Fuller material was 23 N/mm^2 prior to testing, but was not measurable after testing due to the softness of the sample. Similar measurements for the Vantico system were 64 N/mm^2 prior to testing and 20 N/mm^2 after 27 weeks, which is comparable to the Fuller system prior to testing.

Chemical immersion in TEG – Second Test Series:

From the test series1, only one system was satisfactory. Based on the fact that we want at least 2 different potting systems for the TEG application and that we also want a system which is working for the physical solvent, a second test series was initiated with 4 new potting systems.

The samples are now tested for 13 weeks, and the results are pretty good. None of the potting systems seems to cover all the solvents (TEG, amines and physical solvents). What we may comment so far is that it seems that we got at least one alternative for TEG-application, and one of the systems performs also very well in Morphysorb.

Dummy Tests:

The pure Vantico resin system (without membranes and spacers) has been potted in a full scale mould (720 mm) to check the behavior of the material while curing (tensions, cracks, temperature rise).

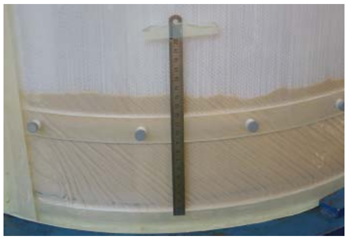
The exothermic peak in the middle of the 40 kg sample was 145°C, which is relatively low compared to earlier results with Fuller resin (above 200°). In comparison, a 3 kg sample measured 112°C exothermic peak.

The cured sample was cut in slices (see picture) and checked for defects. No cracks or pores or other defects was detected which indicates a controlled curing reaction.


Pure resin – full scale mould


Pure resin – cut in slices for inspection

A half dummy filled with membranes and spacers was made by injection of approx. 20 kg of epoxy resin into the mould. The potting material was leveling quite well before setting even though the leveling at the injection inlet could be improved. The exothermic peak temperature was measured to 109°C, and inspection of the sliced potting (see picture) showed no visual defects.


Injection of resin into the stack


Slices of potted membranes

The chemical immersion test series 2 will go on. From these tests, one or two systems will be picked out for potting simulation and dummy tests. For the Vantico-system already tested in dummy tests, there will be done some additional potting simulation tests to optimize the leveling performance of the system

CONCLUSION

Conclusion of the chemical TEG immersion test is that a new potting system which seems to be significant better than the “old” Fuller system with regard to chemical resistance has been identified. In addition to the chemical resistance towards TEG, the Vantico system seems also to work very well in MEA (30%), MDEA (43%), aMDEA (100%). However, in Selexol and especially in Morphysorb, the performance is not very good, with parts of the material dissolving.

REFERENCES

None