

SOFC Sealing with Thermiculite 866 and Thermiculite 866 LS

J R Hoyes^a and M Rautanen^b

^a Flexitallic Ltd, Hunsworth Lane , Cleckheaton, West Yorkshire , BD19 4LN, UK

^b VTT, PO Box 1000, Biologinkuja 5, Espoo, FI-02044 VTT , Finland

This paper outlines the structure and properties of a unique compression sealing material that is entirely free of any organic component which has been giving excellent sealing in SOFC service for a number of years. The paper also discusses a new material that combines the advantages of a compression seal with that of a glass seal to provide a compression sealing material needing as little as 0.1 MPa surface stress in order to achieve excellent levels of tightness.

Introduction

Flexitallic has been a manufacturer of industrial sealing materials since before 1871 and has an enviable record of innovation of sealing materials and gaskets. The well known spiral wound gasket, used in a huge range on industrial sealing applications around the world, was invented by Flexitallic in 1913, USP 1,089,134.

Recently, innovation by the sealing industry in terms of types of sealing materials has blossomed as the industry has developed materials to replace the traditional ones based upon asbestos fibre. Asbestos fibre was used in a very high proportion of all the sealing materials available and was, in particular, the basis of the materials having the highest application temperature which was about 550 °C.

Flexitallic has been to the fore of this surge of innovation to replace asbestos based sealing materials with one new form of sealing material, Thermiculite, being of particular relevance to the sealing of solid oxide fuel cells. The Thermiculite technology developed and patented by Flexitallic, for instance USP 2004/0214032, is capable of excellent service at up to 1000 °C and was initially conceived after it became obvious that the then most promising material for high temperature sealing, exfoliated graphite, suffered disastrous service failures due to oxidation at temperatures as low as 350 °C.

More recently, once it became obvious that there was a need for a compression gasket suitable for SOFC sealing, the Thermiculite range of sealing materials was extended to include Thermiculite 866 which has since been proven around the world to provide reliable SOFC sealing. The structure, capability and service experience of Thermiculite 866 is outlined in this paper and the benefits that it can provide to the groups around the world who are developing SOFC stacks are indicated.

As a result of the experience gained with Thermiculite 866 and the development of a production plant for its large scale manufacture, further members of the Thermiculite range targeted at SOFC sealing have been, or are being, developed either in collaboration with SOFC development teams or in accordance with their requirements. The first of

these new materials, Thermiculite 866 LS, developed in collaboration with VTT is also discussed.

Thermiculite Technology

This technology is based upon the use of vermiculite, a naturally occurring mineral of the phyllosilicate grouping. The members of this group of minerals are all plate silicates and are noted for their high temperature capability and chemical resistance. Two other members of the group are china clay and mica.

The mica family of minerals within the phyllosilicate group consists of a number of well known mineral species such as muscovite and biotite, both of which are widely used in industry because of their thermal and electrical resistance. Together with another member of the group, phlogopite, biotite forms a series of minerals which can be naturally modified over eons of time by hydrothermal action into a mineral known as vermiculite. This mineral, available in large, easily mined, deposits around the world is also used widely in industry because of its temperature capability and its thermal insulating properties.

A key feature of vermiculite is that the individual crystal sheets which stack together to form the plates can be separated from each other, exfoliated, by practical means, a feature that is unique to vermiculite. The simplest way of achieving this exfoliation, although incompletely, is by the application of heat to the plates as mined. This causes the plates to open up into “books” to produce the familiar and widely used material that is the basis of a wide range of industrial products ranging from thermal insulation to garden compost. This material is known as thermally exfoliated vermiculite.

This type of exfoliation is not practical with other members of the mica group. Micas such as muscovite, biotite and phlogopite can be milled to produce a fine powder but that process only produces particles of low aspect ratio having increasingly smaller dimensions. Exfoliation of these micas by the application in the same way that vermiculite can be transformed into “books” is not possible.

For vermiculite far more efficient method of exfoliation than by heat is by chemical means as by this route the plates can be opened up into individual sheets of thickness measured in nanometres. This material, known as chemically exfoliated vermiculite, CEV, together with diluent fillers and elastomer forms the basis of the Thermiculite grades 815, 835 and 715 intended for general industrial sealing. These are all providing excellent service in a diverse range of industrial applications around the world.

The individual sheets of the CEV are very flexible and can be used to form very thin films of vermiculite. This film forming capability, as a result of the sheets adhering one to another, is very useful forms the basis of the use of Thermiculite in SOFC applications.

Thermiculite 866

Thermiculite 866 consists of only CEV and steatite, another phyllosilicate mineral also known as talc; there is no other component and no organic binder. The sheets of the

CEV act as a binder to hold the whole together to form a flexible sheet that is robust enough to be cut into complex shapes.

A compression sealing material is dependent upon an external load being applied to it so that a seal is created. In order to maintain the seal, the material has to ensure that the load is maintained under service conditions for a long as is required.

To be successful a sealing material has to have certain features which can be summarised as:

Conformability --- the material has to be soft enough to be able to conform to the irregularities of the surfaces being sealed so that a seal is created.

Stress retention --- the material has to resist the tendency for its thickness to reduce under load or as a result of the application of heat or as the result of the burn off of any components at the service temperature. If the thickness reduces then if the stress imposed upon it via the elastic stack tie bars will reduce.

Sealing --- the structure of the material has to be such that the medium being sealed cannot penetrate through it or between it and the surfaces being sealed at any temperature up to the service temperature.

Thermiculite 866 and Thermiculite 866 LS meet all of these objectives.

The Structure of Thermiculite 866

Figure 1A illustrates the structure of Thermiculite 866. This shows why the sealing is so good as the highly aligned sheets of the CEV interspersed with the steatite create a very tortuous path along which any gas molecules would have to travel in order to escape.

In contrast, Figure 1B shows the structure of a traditional mica sheet material. This shows the thick & blocky nature of the mica, relative to the CEV of Figure 1A. These materials rely upon the inclusion of an elastomer in the material to bind it together. If too much elastomer is added, to ensure good ambient temperature sealing, then the creep characteristics will be poor. At elevated temperature the binder will burn off creating a higher leakage rate than at ambient temperature.

The Properties of Thermiculite 866

Thermiculite 866 is available in a thickness range of 0.3 to 1.0 mm at a density of 1.9 gm / cm³. The standard thicknesses available are 0.3 mm, 0.5 mm, 0.7 mm and 1.0 mm, with intermediate thicknesses being available as required. The material is made at a width of 450 mm and is supplied in sheets of any length up to 1000 mm with 450 mm by 350 mm being a standard sheet size.

The conformability or compression characteristics as a function of both the applied stress and material thickness are given in Figure 2. This shows that there is sufficient conformability in the material to compensate for the irregularities in the surfaces.

The stress retention capability of a sealing material is dependent upon two key aspects of the material :

- 1 Whether or not the material creeps under load thus reducing the thickness and therefore allowing a reduction of extension of the stack tie bars with the load on the gasket reducing as a consequence. If this happens then the level of sealing achieved will reduce.
- 2 Whether or not the thickness of the material under load reduces due to the burn off of any component of the material.

In both cases Thermiculite 866 has minimal tendencies to allow stress loss due to thickness reduction. Figure 3 shows that the creep resistance of Thermiculite 866, which contains no organic content to burn off, is superb even at 20 MPa at both ambient temperature and also elevated temperature. This means that the stress retention in a stack of Thermiculite 866 will be outstanding.

A comparison of the performance of Thermiculite 866 and a mica sheet sealing material is given in Figure 4. It can be seen, even at ambient temperature where the elastomer in the mica sheet would still be present, that the superiority of Thermiculite 866 is very significant. It will be appreciated that at SOFC temperatures after burn off of the elastomer, the difference will be even more significant.

The sealing capability of Thermiculite 866 increases as the stress imposed upon the gasket increases. For a given loading from the tie bars of an SOFC stack the stress on the gasket can be maximised by reducing the gasket area as far as is possible. Sometimes this can be achieved by design changes but otherwise the area can only be reduced by changing the dimensions of the gasket. Figures 5A and 5B illustrate how the sealing of Thermiculite 866 varies as a function of the landwidth of the gasket, the landwidth being the difference between the inner & outer dimensions of the gasket along the radial direction from the centre of the gasket, the stress on the gasket and the pressure being contained. The landwidth should not be reduced below about 4 mm as cut gaskets with landwidths below this value become less robust and the sealing achieved for a given stress reduces as the landwidth reduces.

The combination of the excellent creep resistance, minimal burn off at service temperature and inherent sealing capability mean that Thermiculite 866 provides excellent sealing performance in SOFC service. This is illustrated by Figure 6A and Figure 6B where sealing data collected by a customer during actual stack testing are shown. It can be seen that the level of sealing achieved was well below the required level and that thermal cycling down to 100 °C did not reduce the level of seal achieved.

Apart from creating and maintaining a seal to the required level of sealing, Thermiculite 866 also provides electrical isolation. The electrical insulating resistance of Thermiculite 866, as determined by IE 167 [BS 2782 : Part 2 :1992], is given below in Table I.

TABLE I.

Thickness	As Received [MΩ]	After 50°C for 24 hours [MΩ]
0.5 mm	0.33	7.5
0.7 mm	0.50	7.5

Thermiculite 866 as a Precision Component of the Stack

As well as its sealing and isolation benefits, Thermiculite 866 can act as an engineering component in the stack because the robustness of its manufacturing process makes it possible to ensure that under the assembly load the thickness of the gasket is held within tight tolerances. Similarly, the level of conformability of Thermiculite 866 under the assembly load can be controlled so that the manufacturing tolerances of other components can be accommodated thus avoiding the cost of better tolerance control of those components.

Gaskets are generally expected to just seal two rigid and, at least approximately, parallel surfaces. The thickness of the gasket is generally not critically important. This may be the case in SOFC applications but we have learnt that there are distinct advantages to the SOFC stack designer if the thickness as a function of applied stress can be controlled to limits much tighter than those current for traditional industrial sealing or the conformability at the stress required to achieve the required level of sealing can be tightly controlled.

The manufacturing process for Thermiculite 866 is similar to the traditional tape casting processes and was developed to provide very tight control of the weight per unit area of the product across and along the sheet and between production runs. The simplicity of the Thermiculite 866 formulation, just two components, and the use of computer controlled dispensing, mixing and casting systems, ensure that the dough from which the product is made is highly consistent. Given control of the weight per unit area and of the ratio of the two ingredients, it is possible to supply Thermiculite 866 such that under the specified stress the thickness is controlled to +/- 0.02 mm.

Gasket Cutting

Thermiculite 866 can be easily cut with a knife or scissors and cut gaskets are robust provided that the landwidth is not reduced significantly below about 4 mm. Gasket cutting by the use of laser or water jet methods is not recommended. Where quantities of gaskets or gaskets with complex shapes are required then they should be cut by those organisations that specialise in the supply of cut gaskets to their users. These can be found in every city in the industrial world. Flexitallic offers a gasket cutting service to assist its customers. A confidentiality agreement can be signed where required so that

confidential gasket shape information can be supplied with security in order to allow the production of the necessary gasket cutting tooling.

Thermiculite 866 LS

Lowering the stress that has to be imposed upon a compression gasket to achieve the required level of sealing has significant advantages for the SOFC stack designer. As the loading required on the gasket falls so the cost of the raw materials of the stack falls. Similarly, components made of brittle materials that could not survive the higher loads can be successfully utilized.

There are two types of leakages from a compression seal; they are interfacial, the leakage between the surface to be sealed and the gasket, and permeation, the leakage through the core of the gasket. The relative magnitude of the two types of leakage depends upon many factors, not least the pressure and nature of the gas to be sealed. Figure 7 shows how the sealing of Thermiculite 866 is influenced by material thickness when the surfaces to be sealed are either smooth or spirally grooved. The difference, for a given thickness, between the results from the two types of surface finish gives an indication of the magnitude of the interfacial leakage component and the intercepts give an indication of the magnitude of the permeation leakage component. In parallel, Figure 8 gives an indication of how the pressure of the gas being contained influences the sealing performance of Thermiculite 866.

One user of Thermiculite 866 for a number of years has been the VTT Technical Research Centre of Finland, one of the leading research institutes in fuel cell research in the Nordic countries. The focus of the SOFC research at VTT is to develop new technology and to provide information for industrial enterprises in order to support development work on SOFC based power plants. VTT also supports the development of stacks, the development of balance of plant components, and the application of SOFC power plants. A further purpose is to increase the understanding of the fundamentals of SOFC science and systems.

As the result of collaboration over the supply of tailored forms of Thermiculite 866 to VTT to assist their SOFC development work, a very positive relationship developed between Flexitallic and VTT. One important requirement from VTT was for an SOFC sealing material with a sealing stress requirement well below that of Thermiculite 866. In order to cover the reduction of both types of leakage without duplication of effort the necessary work was shared between VTT & Flexitallic. VTT concentrated on the reduction of the interfacial leakage component of compression gasket materials whilst Flexitallic concentrated on the reduction of the permeation component of the leakage because the latter was formulation dependent and the former was not.

VTT were highly successful in their work. The interfacial leakage reduction method developed by VTT is based upon the application to each surface of the gasket of a glass powder having a melting point lower than the service temperature so that under service conditions the glass becomes a highly viscous paste which blocks off the leakage paths. This work has resulted in excellent sealing at stresses below 0.5 MPa.

Figure 9 compares the sealing achieved at stresses of both 0.1 and 0.4 MPa for standard Thermiculite 866 and Thermiculite 866 plus the glass containing coating known as Thermiculite 866 LS. The dramatic gain in sealing can be clearly seen Figure 10 shows the surface of Thermiculite 866 LS with the glass particles being clearly visible.

Figure 11 shows the effect of time and thermal cycling on the sealing of Thermiculite 866 and Thermiculite 866 LS at a temperature of 700 °C. The gasket stress during these tests was 0.1 MPa and during the overall test period of over 600 hours, using 4% H₂ in N₂, a series of five thermal cycles down to 150°C were carried out between the 300 to 530 hour periods of the test. The sealing performance of the coated material was throughout the tests very significantly lower than the standard Thermiculite 866 and it was constant. The sealing performance of the plain Thermiculite 866 increased somewhat during the tests, an effect that has been reported by a number of users. The thermal cycles had no significant impact on the performance of either type of gasket indicating that the thin glass coating provides excellent performance without the cracking and excessive leakage associated with the use of conventional wholly glass seals.

In parallel with this work by VTT, Flexitallic has been investigating formulation changes aimed at creating a material with lower permeation than Thermiculite 866 which simultaneously has a higher level of conformability. This work, as yet not completed, is progressing well as can be seen in Figure 12 where the thickness dependency of the leakage from the development material can be seen to be minimal.

Conversion Factor for Helium Leakage Rates

At STP 1 mg /m/s of He = 3.306 ml/cm/min He = 0.361 ml/mm/min He.

Acknowledgments

The work of all the laboratory staff at both Flexitallic and VTT without which these products and this paper would not have been possible, is gratefully acknowledged. Also, our thanks are due to the Thermiculite customer who allowed us to include in this paper some of the stack sealing data that they had generated.

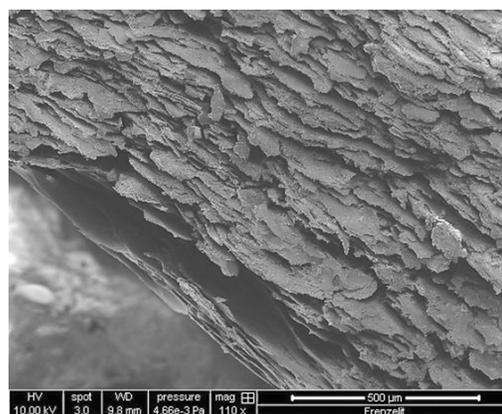
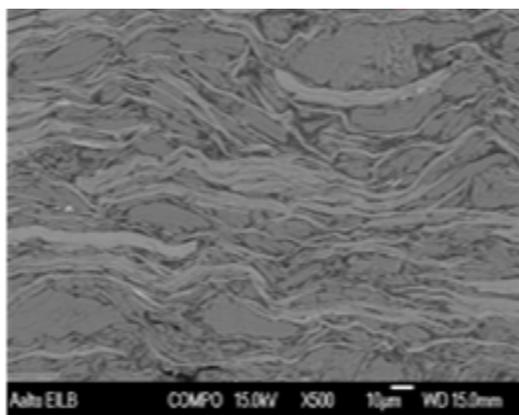


Figure 1A Thermiculite 866

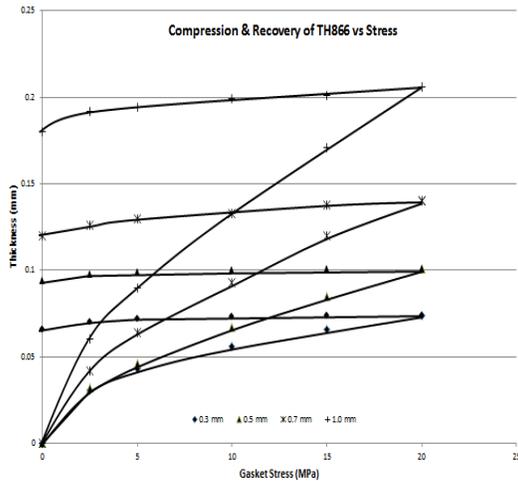


Figure 2 Compression

Figure 1B Traditional Mica Sheet

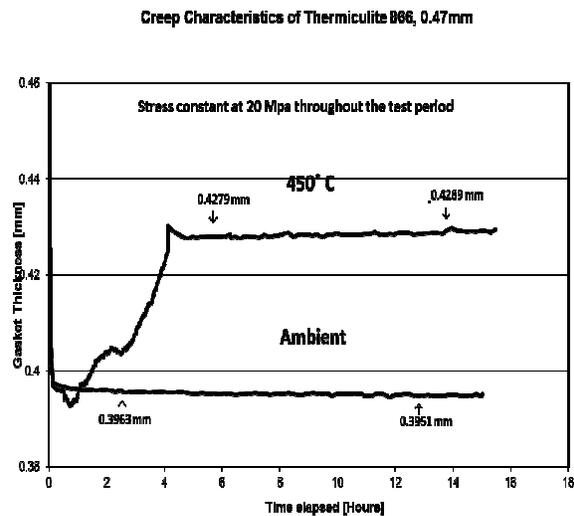


Figure 3 Creep Resistance

Comparison of Sealing of Thermiculite 866 And Mica

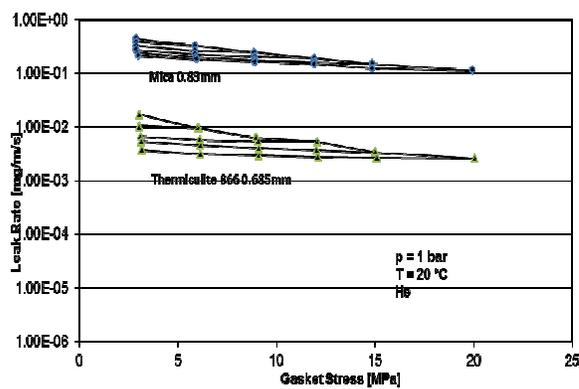
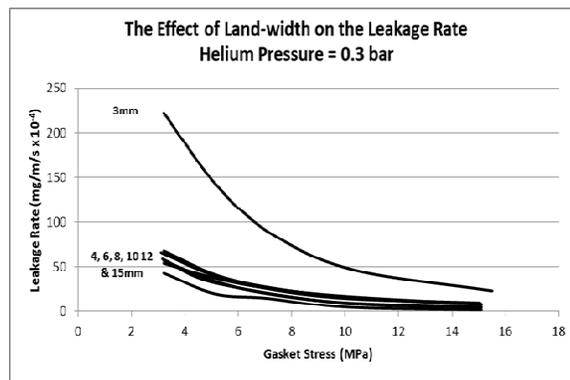
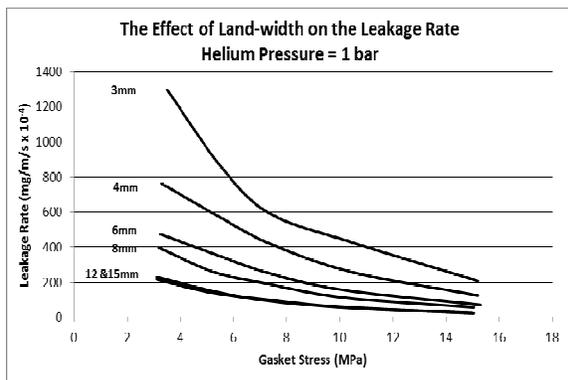
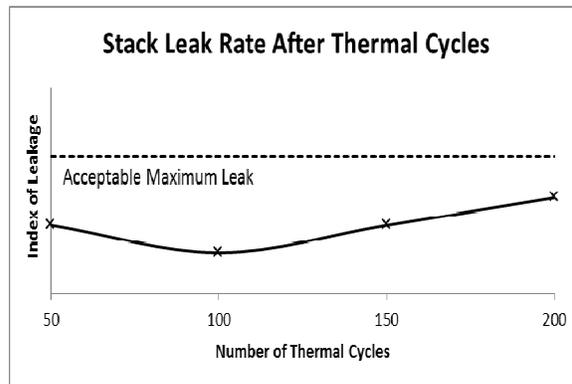
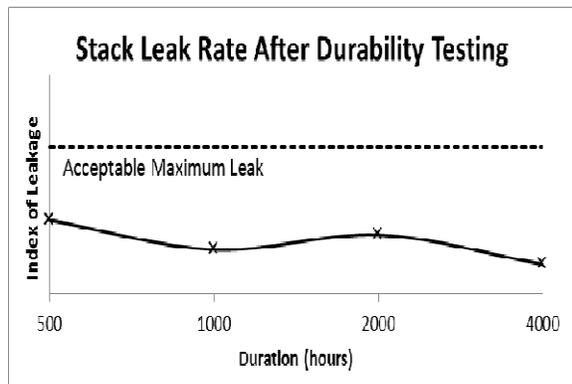


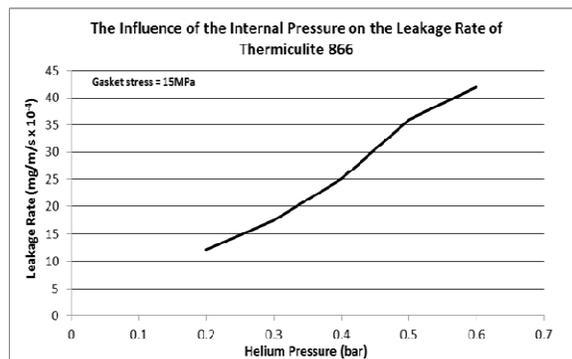
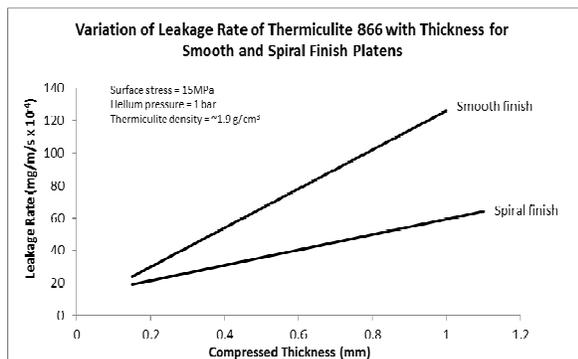
Figure 4 Comparison of sealing Characteristics of Mica and Thermiculite 866



Figures 5A and 5B Effect of Landwidth on Sealing of Thermiculite 866



Figures 6A and 6B Thermiculite 866 Stability of Service in SOFC Stack Service



Figures 7 and 8 Influence of Surface Finish and Pressure on the Sealing Performance of Thermiculite 866

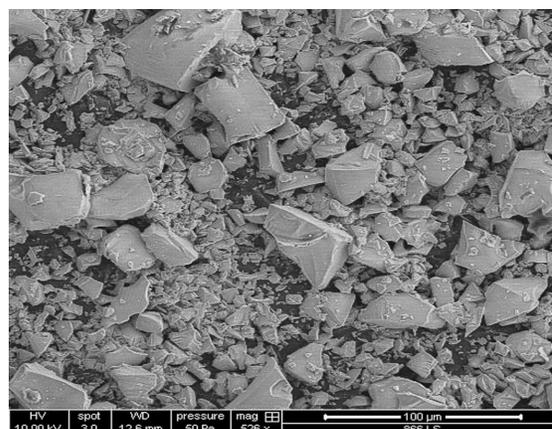
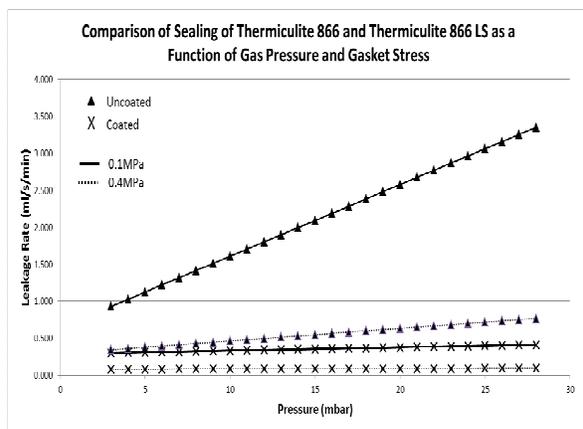
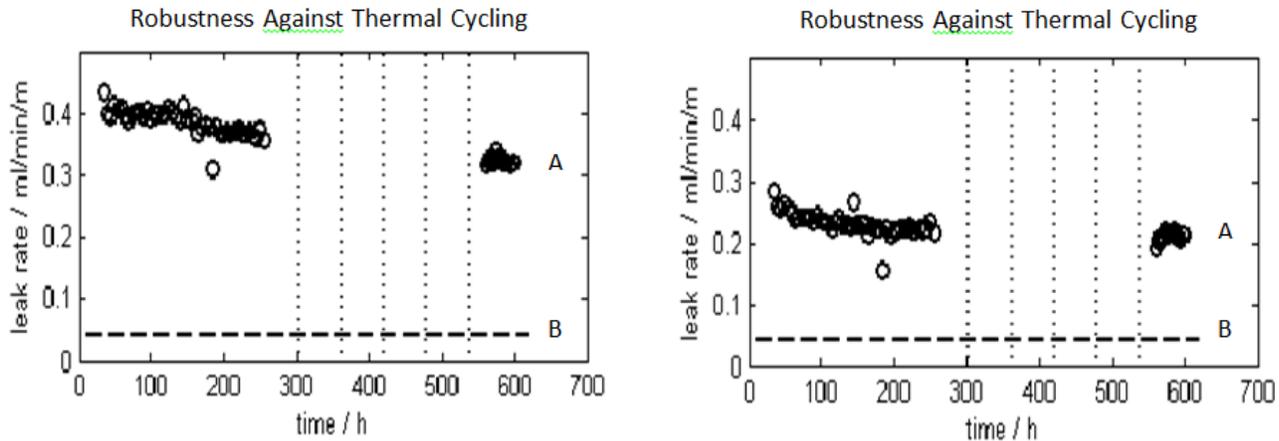


Figure 9 Thermiculite 866 LS Sealing

Figure 10 The Coating on Thermiculite

866 LS



A – Thermiculite 866 alone; B – Thermiculite 866 with glass coating; $\Delta p = 25$ mBar

Figure 11 The Robustness and Sealing Performance of Thermiculite 866 and Thermiculite 866 LS

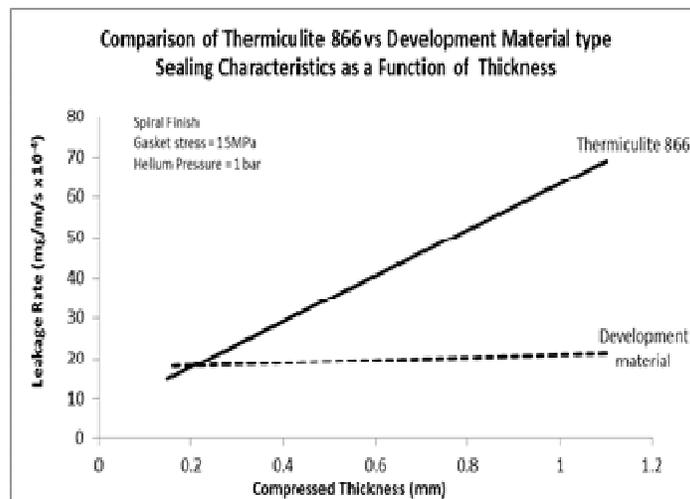


Figure 12 Progress on the Development of Further Materials