EPDM and Fluorocarbon Seal Materials: A Comparison of Performance for Nuclear Fuel Transport Flasks

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SUMMARY

The lid seals on the flasks used to transport spent fuel from U.K. AGR and Magnox Power Stations are fluorocarbon elastomer 'O' rings. Currently, only this material is qualified for the purpose and it was decided to investigate the possibility of qualifying other materials. One material that is already in use in similar applications is an Ethylene Propylene Diene Monomer (EPDM). The work presented in this paper compares the performance of the existing material with three candidate types of EPDM. The areas considered were:

- Extrusion and blow-out resistance when subjected to various steam pressures and temperatures at a range of flange separations,
- Permeability to water, caesium salt solution and hydrogen (as a typical 'benchmark' gas)
- Radiation resistance in warm (60°C) aqueous conditions

It is concluded that the performance of the EPDM materials is good in respect of mechanical properties, radiation and water resistance. However, while permeation rates for gas and water can be higher than for fluorocarbon, this might be mitigated by assessing the actual radioactive burden in the permeate. In the case of dissolved salts, the test results indicate that this will be very low.

1 INTRODUCTION

Spent fuel from the UK AGR and Magnox Power Stations is transported in water-filled Nuclear Fuel Transport Flasks. The lids of these flasks are sealed to the bodies using two elastomer 'O' rings housed in rectangular grooves with seal retention features. The flasks have two additional through-wall penetrations equipped with valves. These are for water level control and to purge the ullage atmosphere above the water. These valves are also sealed with elastomer seals.

The 'O' rings currently in service are made from a fluorocarbon material supplied by DuPont Dow and known as Viton E60C. A specific formulation is used by the seal manufacturer to mould the flask seals.

Currently only this specific material is qualified for use on the flask penetrations, and this presents an operational risk to fuel transport should it become unavailable. To mitigate this risk it was decided to investigate the use of an alternative material for use in these applications. This paper summarises some of the supporting work undertaken.

2 BACKGROUND

The safety cases for the flasks cover the integrity of the sealing arrangement under routine operation and postulated accident conditions, and conform to the UK National Regulations (based on the IAEA Regulations) for Safe Transport of Radioactive Material. Under normal conditions a range of seal temperatures and internal flask pressures are cited. These, together with seal leakage estimates derived from predespatch leakage test criteria, are used to determine maximum radioactive leak rates for the seals. The leakage will consist of by-pass leakage (that which flows through defects in the interface between the seals and the sealing faces) and permeation leakage (that which passes through the elastomer by diffusion). The fluids that are considered to contribute to the leakage in this way are gases, water, dissolved salts and suspended particulate matter. One of the strongly pessimistic assumptions in the way that the safety cases address permeation is in calculating the activity release due to the permeation of water. It is assumed that the same concentration of dissolved salts and particulate matter exists in the water that has permeated, as exists in the flask water upstream. This assumption is challenged by work described later in this report. For gas permeation, hydrogen flow rates are used as a typical 'benchmark', as hydrogen is one of the most rapidly permeating gases.

Under accident conditions the flasks are considered to suffer a particular impact that might affect the integrity of the lid seal joint, and a fire that would generate a temperature excursion. This could compromise the elastomeric seals and would generate increased pressures inside the flasks.

An extensive programme of experimental tests designed to simulate the effects of impact and fire accident criteria was carried out in the 1980's. The parameters considered in this early programme of tests included the following:

- Effect of pre-soaking seals in water to simulate an extended period of normal operation prior to the accident scenario.
- Effect of a period of radiation exposure to simulate the effect of ageing on the seals.
- The temperature and pressure excursion to which the seals would be subject in the fire accident.
- Extrusion or blow-out through any gaps that might be induced between the lid and its seal face caused by firstly the impact and secondly the thermal distortion that might occur as a result of the fire.
- The possible presence of water in the interspace between the two seals and the pressure developed therein by the effect of the ensuing fire.
- The ability of the seals to retain fluids after the accident criteria had been imposed (as disclosed by a leak test)
- The compression set of the seals as a result of the normal operation and then the accident criteria imposed.

The tests rigs used full cross-section seals with a reduced planform to make them a manageable size.

The extensive test programme described above focussed on the accident performance of the Viton E60C material, and in the configurations used on the flask the material met the requirements satisfactorily. A smaller programme was also carried out on two particular Ethylene Propylene Diene Monomer (EPDM) elastomers; one was resin-cured the other peroxide-cured. In all aspects tested the EPDM materials showed better performance than the equivalent tests with Viton E60C. They showed superior blow-out/extrusion resistance and the accumulated compression set was better. However, as the Viton E60C had met the required criteria, a conservative decision was taken to continue with the use of this material in service.

A third EPDM material known as EPDM 30H has recently been specified as the seal material for a number of flask applications. Some test work has been carried out on this particular formulation, see for example Ref. 1. In general it has performed well, particularly in situations where the elevated temperature period was limited or where its exposure to atmospheric oxygen was limited. Other examples of the use of EPDM in high temperatures in relatively anaerobic conditions have shown very good performance. See for example Ref. 2.

3 CHOICE OF MATERIAL AND FURTHER TEST WORK

In view of the good performance of resin-cured and the peroxide-cured EPDM and the widespread use of EPDM 30H it was decided to carry out further test work on these materials. The areas that required further information were:

- The permeation rates of the EPDM materials for water, gas and salt solution.
- The comparative extrusion and blow-out resistance of the EPDM 30H compared with Viton E60C and the two other EPDMs.
- The radiation and water resistance of EPDM 30H and the resin-cured EPDM compared with Viton E60C.

This further test work was carried out under contract and was jointly managed between British Nuclear Group and British Energy.

4 RESULTS AND INTERPRETATION

4.1 Permeation

It should be noted that water permeation data are sometimes quoted in units of kg s^{-1} m^{-1} Pa^{-1}, and sometimes in units of m^3 s^{-1} m^{-1} Pa^{-1} (or m^2 s^{-1} Pa^{-1}) treating water as if it were an ideal gas. Using the principle that one mole of a gas occupies 22.4 litres at standard temperature and pressure, the mass data may be converted to volume data by multiplying by 1.244 (ie 22.4/18). The volumetric units are also often quoted as cm^3 s^{-1} cm^{-1} atm^{-1}, or cm^3 s^{-1} cm^{-1} bar^{-1}. Ignoring the difference between bar and atmospheres, these units may be scaled to the metre-Pascal equivalents by multiplying by 10^{-9}.

Previous experimental work to establish the permeation coefficients for water, hydrogen and other gases through Viton E60C had been carried out. This used a test rig where a thin diaphragm of elastomer had been clamped between flanges and exposed to the test fluid on one side and the permeate collected from the other. Similar test facilities were used in the salt solution and hydrogen tests reported here.

4.1.1 Salt solution and Water Permeation

Only EPDM 30H was used in the experiments. Caesium nitrate salt was used, dissolved in de-ionised water. A concentration of 1000 ppm (0.1%) was used. Caesium was considered to be the most relevant ion as it contributes the majority of the radioactive release calculated for soluble radionuclides. The concentration was chosen for experimental convenience. The test set up was to use an unsupported 80mm diameter diaphragm, 2mm thick. The exposed area was of 50mm diameter. The pressurised solution was put on one side of the diaphragm and the permeate was collected from the low pressure side. The diaphragm and the solution were held at 100°C, the permeate was collected at room temperature. Two main tests and a water control test were carried out. The water control test was conducted at 110°C. The individual tests were run over several days and the quantities of water collected were 0.6 ml, 1.8 ml and 1.5 ml respectively.

The concentration of salt in the permeate was measured in two ways. In the first instance an ion specific electrode was used to determine nitrate concentration. In the second (only used for the caesium salt tests, not the control) measurements were made on samples sent to an independent laboratory where analysis for caesium was carried out.

The control tests showed negligible nitrate. The salt tests showed some inconsistency between the values of nitrate and caesium detected, but as these were very low (less than 0.05% of the source solution caesium concentration, and up to 0.25% of the nitrate concentration) the inconsistency is attributed to experimental error. The caesium concentration was considered the more reliable. In either case the salt concentration in the permeate was very low, with the elastomer acting as a very effective 'filter'.

The control test usefully provided a water permeation measurement, and the flows of water from the salt solutions were very similar. The value is presented in Table 1.

Limited data are also available from Ref. 3. Here permeation rates for two EPDM materials are given for water vapour at 'room temperature' (assumed to be 20°C) and give a range of 0.55×10^{-5} to 3.7×10^{-5} cm^3 sec^{-1} cm^{-1} bar^{-1} (0.55×10^{-14} to 3.7×10^{-14} m^3 s^{-1} m^{-1} Pa^{-1}).

4.1.2 Gas

The experimental results investigating the permeation of gas through EPDM materials only used hydrogen as the test medium. The test samples comprised elastomer sheets nominally 2mm thick. The sheets were mounted on a porous support. Hydrogen at a pressure of 20 barg was applied to one side of the sheet. Temperature was varied between 50°C and 200°C.

The raw data from the experiments have been analysed on the basis that they conform to an Arrhenius relationship (ie that there is a linear relationship between the log of the value and the reciprocal absolute temperature) and they have been plotted in Fig 1. Also included in this figure are the previously measured data for Viton E60C.

It may be seen that there is very close agreement between the data for Viton E60C from the two experimental programmes, and that this agreement persists throughout the temperature range. It may also be seen that the permeation rate for hydrogen through the EPDM materials is greater than that through the Viton E60C. At low temperatures the permeation rate through EPDM is about five times greater than that through the Viton E60C. At high temperatures (200°C) there is very little difference.

Data from Ref 3 have been added to the graph.

4.2 Extrusion and Blow-out Resistance

The experimental work used 0.275 inch (7 mm) cord diameter 'O' ring seals contained in grooves, and sealing against a flat plate. Seal compression, and hence the extrusion gap was varied by insertion of shims. Temperature and pressure were also varied, but not all materials were tested under all conditions. Only relatively low compressions (ranging from 5% to 11%) were used, as failure conditions were being sought.

Four test conditions were used:

i. Seals in the presence of water at 60°C for 14 days, with pressure from equilibrium vapour pressure plus air pressure enhanced by the temperature rise.
ii. as i) but pressure enhanced to 83 bar (1200 psi) using nitrogen.
iii. seals in the presence of water held at 260°C for 30 minutes.
iv. as iii) but pressure enhanced to 83 bar (1200 psi) using nitrogen.

In addition hardness, elongation and tensile properties were measured prior to testing, and, where possible, after testing. For statistical reasons, three tests were carried out at each set of conditions for each material.

All materials survived tests i) and ii) even at the lowest compression (5%). At the end of the test period the EPDM materials showed enhanced tensile strength and elongation at break, whereas the results for some of the Viton E60C samples showed reductions in these properties. However, the variation could be within the experimental scatter.

In test iii) at 5% compression, one failure by blow out of the Viton E60C was seen. In test iv) with the high pressure, all the Viton E60C tests failed at all compressions tested (up to 9%), and all EPDM 30H tests showed failures at 5% compression. The other two EPDM materials survived. Again, there was a trend for the EPDM materials to show enhanced tensile strength and elongation at break. Where measurements were possible, the E60C material gave variable results.

On balance it is deduced that the best performing material was the resin-cured EPDM, followed by the peroxide-cured EPDM, then EPDM 30H and finally the Viton E60C.

From these tests, it may be concluded that the mechanical performance of all of the EPDM materials tested is superior to that of the Viton E60C at 260°C.

4.3 Radiation

EPDM 30H, the resin-cured EPDM and Viton E60C were subjected to radiation. The materials were in the form of nominally 0.275 inch cord diameter 'O' rings, and these were mounted in grooves and compressed by a nominal 16% against a flat face. Tests were conducted at 60°C both wet and dry, but not pressurised. Radiation dose rates were between 15 and 23 Gray h^{-1}. The primary experimental measurement was compression set. This was measured periodically and comparisons between materials made at common accumulated dose. Control tests were also conducted in the absence of radiation. Here comparisons were made on a time basis.

Under irradiated conditions the results did not show any obvious difference between wet and dry conditions. The compression set values for the two EPDM materials were very similar, and significantly lower than the Viton E60C.

In the absence of radiation the compression set was lower. Here the Viton E60C material showed an enhanced set when wet, compared with dry conditions. For the EPDM materials there was no discernible effect due to the presence of water. Under wet conditions the compression set performance for the two EPDM materials was significantly better than the Viton E60C.

5 DISCUSSION

5.1 Water Permeation

The data presented in Table 1 shows the measured permeation rate to be lower than that of the Viton E60C at 110 °C. The published data from Ref 3 however, show it to be greater at room temperature by about a factor of 10.

5.2 Permeation of Salts

The current methodology assumes that the concentration of radionuclides in the water remains constant as it permeates through the seals. The new data show that for the EPDM material tested, this assumption is very pessimistic. The data show the downstream caesium concentration in the permeate is at least a factor of 400 (probably 2000) lower than the upstream concentration. It is judged that this low permeation rate is not specific to the EPDM 30H elastomer, and that similar results would probably be obtained if experiments were conducted on E60C or any other of the EPDM elastomers.

5.3 Gas permeation

Figure 1 shows the hydrogen gas permeation data obtained from this programme. The measured permeation rates for the EPDM materials are typically higher than Viton E60C for temperatures below about 200°C. The published data from Ref 3 show higher values than those measured.

5.4 Chemical Effects

It is important to note that EPDM elastomers are incompatible with mineral oils (Ref 3). Thus if the Viton E60C seals were to be substituted with EPDM, then it is essential that they do not come into contact with mineral oil products. All seals would need to be assembled into their grooves in the absence of such materials and where mineral oil lubricants are used on screwed fittings (e.g. valve or lid bolts) it would be necessary to ensure that contact with the seals be avoided.

5.5 Overall Review

The general picture emerging from these tests is that the EPDMs are better than the Viton E60C material for

- High temperature blow-out and extrusion resistance
- Radiation and water resistance (together or separately)

As regards the water permeability, the published data (at room temperature) range towards significantly higher values than the measured value for the Viton. However, the measured values at 110°C show EPDM to have a lower value than the Viton. Also, the possible concern over the published higher values is offset by the finding that the majority of the dissolved radionuclides are left behind when the water permeates through.

The hydrogen measurements on the EPDMs relative to Viton show reasonable parity at 200°C, and are up to a factor of 5 higher at 50°C; and, similar to the water situation, the published data for hydrogen range towards significantly higher values. In the context of gas permeation, specific assessments of the individual radioisotopes (eg Krypton and Xenon) may result in reduced calculated radioactive release rates.

In addition to the measurement and analysis work described above, the case for justifying the use of EPDM elastomers to substitute the existing Viton would be reviewed in the context of the guidance provided by the UK Department for Transport (Ref 4)

6 CONCLUSIONS

It is concluded from the work reported above that the performance of the EPDM materials is good in respect of mechanical properties, radiation and water resistance. However, while permeation rates for gas and water can be higher than for Viton, this might be mitigated by assessing the actual radioactive burden in the permeate. In the case of dissolved salts, the test results indicate that this will be very low.

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8 ACKNOWLEDGEMENT

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Table 1 Permeation Coefficients for Water and Steam through Various Elastomers

TEMPERATURE	20°C	50°C	100°C	110°C	150°C
EPDM 30H (measured, water phase)				0.84	
EPDM Ref 3 Minimum	0.55				
EPDM Ref 3 Maximum	3.7				
Viton E60C (measured, water phase)	0.38	0.720	1.67	1.91	3.15
Viton E60C (measured, steam phase)			1.93	2.09	2.76

Units: STP $m^3\ m^{-1}\ s^{-1}\ Pa^{-1} \times 10^{-14}$

Fig 1 Hydrogen Permeation Coefficients: Published Data and Measured Values

Units for permeation are STP $m^3\ s^{-1} m^{-1} Pa^{-1}$