

# RGD TESTS INVOLVING HYDROGEN SULPHIDE

Element demonstrates that H<sub>2</sub>S is a more hostile gas than CO<sub>2</sub> towards housed elastomeric seals subjected to repeated pressure cycling in RGD tests.

By: Barry Thomson, Michael Lewan, Keyur Somani

Element Materials Technology Hitchin Limited, Wilbury Way, Hitchin, ENGLAND SG0 4TW

## INTRODUCTION

The objective of this work is to introduce rapid gas depressurization (RGD) testing in which hydrogen sulphide (H<sub>2</sub>S) is part of the test gas mixture. Public domain information about this topic has not been found, despite the fact that elastomers have been deployed as seals in highly sour applications (e.g., gas re-injection) for many years. This work is part of an Element programme to investigate, and where possible quantify, the influence of H<sub>2</sub>S on oilfield elastomer performance. HNBR and fluoroelastomer grades are included in the RGD study, but with higher resistance to chemical deterioration the latter are the only realistic candidates for HPHT sour gas sealing applications: other non-metallic sealing options, not discussed here, include EPDM and energized PTFE. The durability of HNBR in sour fluids is of great interest to the industry, but quantification is complicated by the large number of variables which influence performance. Chemical aging of HNBR will be addressed in a future work programme.

Carbon dioxide (CO<sub>2</sub>) is known to be more soluble than methane in oilfield nitrile and fluoroelastomer compounds. Hence, CO<sub>2</sub> has the potential to be more damaging when a seal, saturated with gas at high pressure and elevated temperature, is vented quickly to atmospheric pressure. There is evidence to suggest that H<sub>2</sub>S has an even greater affinity for rubbers, with implications for RGD resistance. The

challenge addressed here is to determine whether RGD testing supports this contention.

## GENERAL COMMENTS – RGD

The factors (Table 1) which influence RGD resistance of a given elastomer compound in O-ring form are well known, but not all are well quantified.

Test procedures for RGD testing of elastomer seal have been available for many years and have evolved to meet the needs of both end users and suppliers of testing services. The most widely employed RGD methodology over the last decade is described in the NORSOK M-710 (Rev. 2) standard.

Work to update the standard was completed in 2010-2011 and the document re-issued as Edition 3 in September 2014: the procedural details are identical to those given in the ISO 23936-2 standard, issued in 2011. The upgrade improved test efficiency and eliminated anomalies in the damage rating system. In practice, the ISO 23936-2 standard has now superseded NORSOK M-710 for RGD assessment.

The standard test does not qualify a material for service, but it does enable comparisons between compounds from different suppliers by third parties. The most widely specified RGD test conditions are 10 cycles, 100 °C, 150 bar of 10/90 mol% CO<sub>2</sub>/CH<sub>4</sub>, and 20 bar/minute vent rate. These provide a reasonably searching test of O-ring RGD resistance. The test is not functional; both sides of the housed seals are exposed to gas.

		<b>Beneficial Level</b>	<b>Reality</b>
<b>Material</b>	Modulus	High	Both cannot be high simultaneously
	Tear Strength	High	
	Diffusion coefficient	High	Little reliable data available
	Gas solubility	Low	
<b>Seal</b>	Processing	No contamination	Always a risk
	Manufacture	Perfect flow in mould	Always risk of “imperfections”
	Section Diameter	Small	Depends on application
	Groove Design	80-85% fill	Some compound benefit
<b>Operational</b>	Temperature	Low	Application Dependent
	Pressure	Low	
	Vent rate	Slow	Often no control
	Gas type	Low/no CO <sub>2</sub>	CO <sub>2</sub> more soluble than CH <sub>4</sub>
	No. of events	Fewer the better	Most damage occurs during first event
	Target pressure	Above atmospheric	Often no control

**Table 1** Factors which influence elastomer O-ring RGD resistance

An end user looking for seals for gas service will expect ISO/NORSOK certification as a minimum. There are corporate RGD test procedures which require that a pressure differential is applied across the test seals.

What the ISO/NORSOK method allows is the testing of just about any O-ring seal under just about any conditions. In practice, the standard acts as a benchmark RGD test for new/revised elastomer compounds being considered for use in high pressure gas applications.

The damage rating system assigns a number (0 through 5) to a sectioned seal surface which characterizes it according to the type and length of cracks present; the number of cracks carries less weight, although total crack length is a factor. The only acceptable ratings are 0 through 3. The user should be aware that the ISO/NORSOK RGD acceptance criterion is such that successful seals can exhibit significant fracture damage. For example, the 3-rated O-ring surfaces shown in Figure 1 are all acceptable. The end user can always insist on zero as the only acceptable rating from the test.

Test	Pressure [Bar]	Temperature [°C]	Gas	Cycles	Vent Rate [bar/min]
1	150	100	CH <sub>4</sub>	2	20
2	300				
3	450				
4	150	125	CO <sub>2</sub>	1	
5	300				
5B	300				
6	450	150	CH <sub>4</sub>	2	
7	150				
8	300				
9	450				

**Table 2** Exploratory RGD Test Conditions

Once a seal compound has been selected, appropriate functional testing should be undertaken to evaluate performance at service-relevant conditions.

In order to illustrate the influence of variables, results from the exploratory RGD programme listed in Table 2 will be discussed. This plan incorporated many sealing compounds in the form of size 312 O-rings and was designed in part to investigate the influence of groove fill. RGD tests of 2 cycle duration are all that is required for comparative testing.

### NOMINALLY SIMILAR COMPOUNDS

It may come as a surprise but the RGD resistance of nominally identical sealing compounds can vary hugely. Developing materials for high pressure gas resistance requires more than just increasing compound stiffness; processing is also important. Four HNBR compounds which on paper are very similar - medium acrylonitrile, peroxide cured HNBR,

hardness around 90 Shore A – are used here to illustrate the “facts of life” about RGD. Their RGD performance is compared in Table 3; the rating system applied was that of ISO 23936-2.

HNBR compounds 1 and 2 are clearly very good performers, with only minor fracture damage appearing occasionally. HNBR4 exhibits poor fracture resistance under all test conditions - remember that these are only 2 cycle tests – while HNBR3 lies somewhere between these extremes.

Seals of HNBRs 3 and 4 were also tested housed in narrower grooves. The results (Table 4) show a clear improvement in performance for HNBR4, but no gain for HNBR3. Groove fill may not have been quite high enough to realize the benefit; the levels reflect as-received seal dimensions. The improvement is also readily apparent when total crack length is plotted against temperature and pressure (Figure 2).

Test	Temp [°C]	Pressure [bar]	O-Ring	HNBR				
				1	2	3	4	
1	100	150	1	0000	0000	3000	4000	
			2	0000	0000	0000	4000	
2		300	1	0000	0000	0000	4444	
			2	0000	0000	0000	4443	
3		450	1	0000	0000	5000	5444	
			2	1000	0000	0000	4444	
4		125	150	1	1000	0000	4440	4444
				2	0000	0000	4440	4430
5			300	1	0000	0000	4400	5554
	2			2000	0000	4000	4433	
6	450		1	0000	0000	2200	4444	
			2	0000	0000	0000	4442	
7	150		150	1	0000	0000	4441	4444
				2	0000	0000	4320	4442
8			300	1	0000	0000	4420	4444
		2		0000	0000	4400	4442	
9		450	1	0000	3000	4420	4443	
			2	0000	0000	4220	4433	
<b>Average Groove Fill [%]</b>				62	65	63	70	

**Table 3** HNBR RGD Performance versus Pressure and Temperature

Higher groove fill does not confer universal improvement in HNBR RGD resistance; this applies also to fluoroelastomers. For compounds such as HNBR4, the gain is noticeable, although complete crack suppression is too much to expect given the extensive fracturing across all conditions in the standard groove. Testing is essential.

The best compounds can be exposed to much harsher conditions – higher temperatures, pressures, cycles – without too much change in performance. For example, seals of HNBR1 subjected to 10 cycle RGD tests (Table 5) are barely affected, even in 100% CO<sub>2</sub>.

Test	Temp [°C]	Pressure [bar]	O-Ring	HNBR				
				Stand	High	Stand	High	
1	100	150	1	3000	0000	4000	0000	
			2	0000	0000	4440	0000	
2		300	1	0000	1100	4444	3000	
			2	0000	0000	4443	3000	
3		450	1	5000	5443	5444	3300	
			2	0000	4433	4444	0000	
4		125	150	1	4440	4000	4444	2100
				2	4440	3000	4430	3310
5			300	1	4400	4400	5554	4333
	2			4000	0000	4433	3000	
6	450		1	2200	0000	4444	3330	
			2	0000	0000	4442	3300	
7	150		150	1	4441	4433	4444	4332
				2	4444	4444	4330	3333
8			300	1	4420	4440	4444	3320
				2	4400	4333	4442	3333
9			450	1	4420	4443	4423	4333
				2	4220	4333	4433	4320
<b>Average groove fill [%]</b>				63	80	70	89	

**Table 4** HNBR RGD performance versus pressure and temperature

The results tabulated below are for low numbers of 312 O-ring seals. It should be evident that the more rubber that is tested - via increased replication and/or increased seal size - the greater the risk of processing flaws and contamination influencing material performance. The total volume of rubber tested is an issue for future consideration.

The recommended 80-85% groove fill level for high pressure gas service may not be appropriate for all gas types. It was intended to provide support for seals which expand during/after gas venting. Another seal growth scenario is one due solely to gas absorption.

HNBR	Pressure [Bar]	Temperature [°C]	Gas	Fill [%]	ISO Rating
1	695	120	100% CO <sub>2</sub>	78	1100,0000
	150	100	10/90% CO <sub>2</sub> /CH <sub>4</sub>	60	1000,0000
2	121	121	10/90% CO <sub>2</sub> /CH <sub>4</sub>	84	3000,0000,0000

**Table 5** HNBR RGD performance in 10 cycles

This is not believed to be a significant issue for methane and methane-rich mixtures, but is relevant for CO<sub>2</sub> and CO<sub>2</sub>-rich formulations. A situation can arise where the housed seal is still capable of absorbing CO<sub>2</sub> and it will keep expanding into available space, such as the clearance in radial housings. Local extrusion can result in tearing, which could ultimately compromise seal function. An example is shown in Figure 3. Here, the O-ring swelled in the test gas, which contained a very high level of CO<sub>2</sub>, and extruded into a vent hole in the fixture end cap causing local material loss.

### CO<sub>2</sub> VERSUS CH<sub>4</sub>

The four HNBR compounds were subjected to a single cycle RGD test at 125 °C with 300 bar CO<sub>2</sub>; test 5B in Table 2. Performance is compared with the 2 cycle methane results (Test 5) in Table 6.

There is little difference in crack length in the standard and narrow grooves with each gas type and the order of resistance is unaltered. The narrower groove does bring improvement, more so in the CO<sub>2</sub> test. It is possible that the greater swelling in CO<sub>2</sub> fills the free space in the groove, giving the seal nowhere to go during/after gas venting.

HNBR	Groove Fill	Test Gas	
		CH <sub>4</sub>	CO <sub>2</sub>
1	Standard	0	0
2	Standard	0	2
3	Standard	20	20
	High	14	5
4	Standard	51	45
	High	17	0

**Table 6** Total crack length (mm): CH<sub>4</sub> versus CO<sub>2</sub>

## RGD TESTING WITH HYDROGEN SULPHIDE

CO<sub>2</sub> is more soluble than methane in oilfield elastomers, although there is little quantitative information in the public domain. Less is known about the affinity of H<sub>2</sub>S for the same materials. It has been common practice to substitute CO<sub>2</sub> for H<sub>2</sub>S in RGD tests. The text below is taken from ISO 23936-2 standard, Annex F:

*“Many service fluids include hydrogen sulphide (H<sub>2</sub>S) in the gas phase. For obvious reasons, RGD testing with H<sub>2</sub>S (or gas mixtures containing H<sub>2</sub>S) is rarely (if ever) undertaken. Currently, CO<sub>2</sub> is considered as a suitable substitute gas but there is evidence, for nitrile elastomers at least, that H<sub>2</sub>S is absorbed more readily and in greater quantities at equilibrium than is carbon dioxide. Hence the strong possibility exists that H<sub>2</sub>S is the more hostile gas, all else being equal, in terms of elastomer RGD resistance. Research activity continues in this area.”*

The above paragraph was included in response to Figure 4, which was generated by Element in 2008. Here, gas sorption by an HNBR1 O-ring was measured using a magnetic (contactless) suspension balance. The seal was placed on a scale within a pressure chamber and the mass of gas absorbed measured by the external six figure balance via the magnetic link. Three size 312 O-ring seals were measured, each exposed at 10 bar pressure and 50 °C to a different pure gas: CH<sub>4</sub>, CO<sub>2</sub> and H<sub>2</sub>S.

With methane, no mass change was recorded and increasing pressure to 20 bar had no effect. In CO<sub>2</sub>, O-ring mass increased by 2.1% with equilibrium attained after approximately 40 hours. The saturation process required only 10 hours in H<sub>2</sub>S and the mass gain was significantly greater, at 5.5%.

The implication of these results is that H<sub>2</sub>S potentially poses a greater threat than CO<sub>2</sub> to elastomers (or nitriles at least) in RGD situations. In other words, the straight substitution of H<sub>2</sub>S by CO<sub>2</sub> may be too

conservative. However, it may not be possible to determine the H<sub>2</sub>S influence at low pressures and with mixed gases because the best performing compounds can resist pure CO<sub>2</sub> at very high pressures (Table 5).

## PRACTICAL CONSIDERATIONS

Element have been undertaking sour RGD tests on a commercial basis for several years, with conditions ranging from a few per cent H<sub>2</sub>S at moderate pressures to very low levels of H<sub>2</sub>S at high pressures. Conditions were always driven by application requirements: in other words, there was no obligation to determine the specific influence of H<sub>2</sub>S on seal RGD resistance. The level of H<sub>2</sub>S was either insufficiently high to have a measurable influence on O-ring RGD resistance or else, at the lower pressures where it may have been a factor, reference tests were not run.

In order to determine whether H<sub>2</sub>S really does have a more detrimental effect (than CO<sub>2</sub>) on elastomer RGD resistance, the H<sub>2</sub>S level in the gas mixture and the test pressure should both be high. Executing RGD tests at high pressures and temperatures with CH<sub>4</sub>/CO<sub>2</sub> mixtures is not difficult but the introduction of even ppm levels of H<sub>2</sub>S requires dedicated boosting, scrubbing and gas detection equipment.

The pressure to which Element boosts sour gas mixtures is dependent on the volume to be pressurized, the concentration of H<sub>2</sub>S in the mixture (which determines cylinder pressure) and the limit of the pumping system. The free volume in the pressure vessel must be low, to enable efficient and safe boosting, venting and scrubbing operations. Vessel sealing and the number of pressure cycles also need to be considered. The test pressure used here was dictated by what could be undertaken safely with the sour gas mixture.

The sour test gas mixture was specified as 25/75 mol% H<sub>2</sub>S/CH<sub>4</sub>. With this mixture, 200 bar was easily

achievable with existing equipment. Moreover, there was no reason to run a full (ISO 23936-2) 8 cycle RGD test since (i) this is not a certification exercise and (ii) the bulk of RGD fracture damage is believed to occur during the first cycle. Hence a 4 cycle test at 200 bar and 100 °C, with venting at 20 bar/minute, was considered to be adequate for the purposes of seal compound comparison.

## ELASTOMER COMPOUNDS

Six elastomer compounds were used in the RGD test programme: two HNBRs and four fluoroelastomers. A total of 24 O-rings of each were tested: size 312 (BS1806), inner diameter 15.24 mm, section diameter 5.33 mm.

The two HNBR grades were selected for their quite different levels of RGD resistance. HNBR1 has a track record of very good performance across many tests undertaken by Element over the last decade. HNBR4 is a less resistant material and is anticipated to perform poorly, but consistently. Disparate performance also directed fluoroelastomer compound choices. Fluoro1 is very resistant to fracture damage in a wide range of pressurized gas tests. Fluoro4 is also a good performer, based on less extensive testing. Fluoro2 has average RGD resistance.

Fluoro3 was not developed for gas service: it is a lower stiffness compound, and is therefore anticipated to fracture readily in all test conditions. HNBR compounds would not normally be selected for sealing applications with this level of H<sub>2</sub>S; the Element long term interest is in fluoroelastomers for this type of service. However, the results are informative.

## RGD TEST METHODOLOGY

The test gases were procured from CK Gas Product Limited: CH<sub>4</sub>, 25/75 mol% CO<sub>2</sub>/CH<sub>4</sub> and 25/75 mol% H<sub>2</sub>S/CH<sub>4</sub>.

Each O-ring was weighed using a calibrated 0.1 milligram densimeter for the calculation of seal volume. O-rings were housed radially in pairs in steel fixtures (Figure 5). Half of the seals in each test were installed on spigots which formed a groove of standard (BS 1806) dimensions when assembled: the other half utilized a spigot which formed a narrower groove. In the standard groove, a correctly dimensioned O-ring fills 66% of the available volume; in the narrower groove, occupancy is closer to 88%. In practice, exact fill levels depend on seal dimensions and ranged from 63% to 93%. O-ring distribution is shown in Table 7.

Compound	Test 1 [CH <sub>4</sub> ]		Test 2 [CO <sub>2</sub> ]		Test 3 [H <sub>2</sub> S]	
	Standard	High	Standard	High	Standard	High
HNBR1	4	4	4	4	4	4
HNBR4	4	4	4	4	4	4
Fluoro1	4	4	4	4	4	4
Fluoro2	4	4	4	4	4	4
Fluoro3	4	4	4	4	4	4
Fluoro4	4	4	4	4	4	4

**Table 7** O-ring replication and groove fill levels

The same pressure vessel was used for all tests, which were undertaken in numerical order. The cell has a working pressure of 1000 bar and was equipped with an internal thermocouple, external band heater, calibrated pressure sensor and isolation needle valve. Venting was performed using a purpose-built rig. Pressure and temperature were recorded by PC running dedicated data acquisition software; the data capture interval was 600 seconds, except during pressurization and venting operations, when it was lowered to 30 seconds.

The 24 fixtures containing the test O-rings were placed in custom spacers within the vessel. These ensured that fixtures were located in the same place for each test, and that vessel free volume was less than one litre.

Once closed, the vessel was leak checked with nitrogen and heated to test temperature. The test gas was then applied using an appropriate booster pump.

After the required interval, the gas was released from the vessel under computer control at 20 bar/minute.

After one hour at atmospheric pressure, the gas pressure was re-applied to start the next cycle. After the final vent, the vessel was left at test temperature with the valve open for 25 hours, before cooling naturally to laboratory ambient temperature. In the sour test, the vented gas was passed through a scrubber to chemically neutralize the hydrogen sulphide; the vessel was flushed with nitrogen before being opened. RGD test details are summarized in Table 8.

The retrieved fixtures were dismantled and the O-rings stored in labelled bags. Each was rated according to the procedure given in ISO 23936-2, Table B.4. The pressure and temperature logs are shown in Figures 6-8.

Test	1	2	3
Gas	25/75% CH <sub>4</sub> / CH <sub>4</sub>	25/75% CO <sub>2</sub> / CH <sub>4</sub>	25/75% H <sub>2</sub> S/ CH <sub>4</sub>
Pressure	200 -0/+10 bar		
Temperature	100 -0/+1 °C		
No. of cycles	4		
Cycle 1 duration	72-72.5 hours		
Cycles 2-4 duration	23 hours		
Dwell time	60 minutes		
Vent rate	20 +0/-1 bar		
Degas time	26 +/- hours at test temperature		
Cooling period	61 hours minimum		

**Table 8** RGD Test Conditions

## RESULTS

The premise is that a series of three gases in which the minor component is 25 mol% CH<sub>4</sub>, CO<sub>2</sub> and H<sub>2</sub>S will be increasingly damaging towards sealing elastomers in multi-cycle RGD tests. As well as housed seals, samples of several semi-translucent thermoplastics were included in each test in the hope was that one would exhibit increasing levels of visible fracture damage after tests 1, 2 and 3.

PrimoSpire®, a self-reinforcing polyphenylene from Solvay, did show such progressive changes (Figure 9). This amorphous polymer is orange when viewed in transmission. Samples of thickness 3 mm were unaffected in methane, but a few isolated fractures appeared with CO<sub>2</sub> in the test gas. The change in appearance after test 3 was spectacular; the polymer deformed, became opaque and was significantly fractured.

Element have observed this change in PrimoSpire® before, but only after exposure in 100% CO<sub>2</sub> at much higher temperature and pressure.

This result alone is compelling evidence to support the contention that H<sub>2</sub>S is a particularly damaging gas.

### HNBR

The ISO ratings for the HNBR seals housed in the standard and narrow grooves are listed in Tables 9 and 10, respectively.

HNBR1 performed as expected in the baseline (methane) test, with no fracture damage recorded. With CO<sub>2</sub> in the gas mixture, minor cracks appeared in two of the four O-rings. In test 3, most seals had at least one rating of 1. The narrower groove (Table 10) may be a factor in the marginal improvement in RGD resistance. Overall, this HNBR is not very sensitive to test gas composition. The seals exhibit moderate compression set (Figure 10) and remained quite flexible after Test 3.

Material	Test 1 [CH <sub>4</sub> ]	Test 2 [CO <sub>2</sub> ]	Test 3 [H <sub>2</sub> S]
HNBR1	0000	0000	0000
	0000	2111	1111
	0000	1000	1100
	0000	0000	1000
HNBR4	4444	4433	“4444”
	4433	5444	“4444”
	4443	4433	“4444”
	4333	3322	“4444”

**Table 9** Ratings for HNBR O-rings RGD tested in standard groove

Material	Test 1 [CH <sub>4</sub> ]	Test 2 [CO <sub>2</sub> ]	Test 3 [H <sub>2</sub> S]
HNBR1	0000	1000	0000
	0000	0000	0000
	1000	1000	1110
	0000	0000	0000
HNBR4	1000	3300	“0000”
	2000	2000	“0000”
	4400	0000	“0000”
	3300	3000	“0000”

**Table 10** Ratings for HNBR O-rings RGD tested in narrow groove

The RGD resistance of HNBR4 is poor in each test gas at 70% groove fill. However, its performance is known to improve when the seal occupies more of the groove. Three of the four Test 1 seals incurred significant fracture damage in the standard groove (Table 9), but only one seal did so when exposed to the same conditions in the narrower channel (Table 10). In both mixtures the gain was also significant, with no large cracks present in the exposed seal sections.

After Test 3, HNBR4 seals were hugely changed in terms of flexibility. In the standard groove, each seal adopted a round cornered rectangular section, with significant fracture damage. Each O-ring was very stiff, so much so that none would bend when flexed by hand. The 4444 rating assigned to each seal was based on the inspection of two surfaces from one seal, which was sectioned with difficulty (Figure 11). This HNBR has clearly undergone significant

chemical aging. In the narrow groove, each seal expanded (groove fill was initially very high at 93%) to adopt an almost square section, which was then “locked” in place as aging proceeded. The 0000 rating was based on inspection of two surfaces of a single seal; the O-ring had to be sawn in two and the surface smoothed with wet/dry abrasive paper. No fracture damage was visible (Figure 12). The only benefit of aging, to form additional chemical crosslinks, is that RGD resistance will improve. Unfortunately, the process also compromises seal function as elasticity is lost.

Chemical aging under these conditions was not expected. It is known that HNBRs stiffen at modestly elevated temperature (e.g., 130 °C) in dry sour gas mixtures and that increasing H<sub>2</sub>S concentration can significantly accelerate the process. The magnitude of the change is all the more surprising given the apparent similarity, on paper, of HNBR1 and HNBR4.

Fill %	Test 1 [CH <sub>4</sub> ]	Test 2 [CO <sub>2</sub> ]	Test 3 [H <sub>2</sub> S]
66	0000	0000	0000
	0000	0000	0000
	0000	0000	1000
	0000	4000	0000
87	0000	0000	3000
	0000	0000	0000
	0000	0000	4430
	0000	0000	3000

**Table 11** Ratings for Fluoro1 O-rings RGD tested at two groove fill levels

## FLUROELASTOMERS

The ISO RGD ratings for the Fluoro1 seals are listed in Table 11.

Fluoro1 seals were intact after pressure cycling in methane, as expected. In the mixture containing CO<sub>2</sub>, performance was also perfect except for a large crack in one seal in the standard groove. The occasional large (4-rated) crack is an example of the seemingly random damage which can appear in even the most consistently resistant compounds.

Inspection of the fracture surfaces did not reveal a contaminant particle – an obvious cause – leaving a discontinuity in the rubber as the likely origin.

In the H<sub>2</sub>S mixture seals in the standard groove are undamaged but fractures appear in three quarters of the O-rings tested in the narrow groove. There is no evidence that Fluoro1 was overly swollen in either gas mixture: such expansion can result in extrusion damage. It is tempting to associate the marked increase in damage with the presence of H<sub>2</sub>S.

However, it could also be fate that this group of seals exhibited more damage. A definitive test would be to run at a higher H<sub>2</sub>S level: if 25% H<sub>2</sub>S represents the approximate lower performance limit, then increasing it to 40% should be sufficient to cause more widespread fracture damage in O-rings of Fluoro1. The level of compression set is low (Figure 13).

The ISO RGD ratings for the Fluoro2 O-rings are listed in Table 12.

Fluoro2 exceeded expectations, with a major crack appearing in just one O-ring in the methane control test. This very good resistance is also apparent in the CO<sub>2</sub> mixture, but not when the minor test gas component is H<sub>2</sub>S. The deterioration in resistance is stark, with just one of the eight seals surviving undamaged. These seals exhibit higher compression set (Figure 14) than those of Fluoro1.

The RGD ratings for the Fluoro3 O-rings are listed in Table 13.

Fluoro3 is a lower hardness grade and not compounded for RGD resistance. Accordingly, each seal fractured extensively (Figure 15) under all test conditions. In the narrow groove, swelling of the

fluoroelastomer in both gas mixtures resulted in local material loss of the type displayed in Figure 3.

The RGD ratings for the Fluoro4 O-rings are shown in Table 14.

Fill %	Test 1 [CH <sub>4</sub> ]	Test 2 [CO <sub>2</sub> ]	Test 3 [H <sub>2</sub> S]
67	4100	0000	5430
	0000	0000	5540
	1000	0000	5544
	1111	1000	5300
89	1000	1100	4433
	1110	1000	4443
	0000	0000	4430
	1000	0000	0000

**Table 12** Ratings for Fluoro2 O-rings RGD tested at two groove fill levels

Fill %	Test 1 [CH <sub>4</sub> ]	Test 2 [CO <sub>2</sub> ]	Test 3 [H <sub>2</sub> S]
66	4433	4444	4444
	4444	4444	4444
	4444	4444	4444
	4444	4444	4444
88	5333	4443	4444
	5433	5444	5544
	5433	4444	4444
	4333	5433	3333

**Table 13** Ratings for Fluoro3 O-rings RGD tested at two groove fill levels

Fill %	Test 1 [CH <sub>4</sub> ]	Test 2 [CO <sub>2</sub> ]	Test 3 [H <sub>2</sub> S]
63	0000	0000	4400
	0000	4200	5552
	4400	0000	4110
	0000	0000	4400
84	0000	0000	5440
	0000	0000	4444
	0000	4300	4433
	0000	0000	5400

**Table 14** Ratings for Fluoro4 O-rings RGD tested at two groove fill levels

Fluoro4 is another material which performed well in Tests 1 and 2. One O-ring was badly fractured in methane and two in the CO<sub>2</sub> mixture. As with Fluoro2, the deterioration in RGD resistance when H<sub>2</sub>S is included in the gas mixture is unambiguous. Fluoro4 has something in common with Fluoro1; there are no witness marks which would indicate excessive swelling in the higher groove fill case. Set is low (Figure 16), similar to the level in Fluoro1.

#### SUMMARY COMMENTS

It is well established that CO<sub>2</sub> poses a greater threat than methane to housed elastomer seals in RGD tests conducted at elevated temperatures and pressures. There is ample test evidence to demonstrate not only increased fracture damage but also to show that oilfield elastomers generally swell to a greater extent in pure CO<sub>2</sub> and CO<sub>2</sub>-rich gas mixtures. In extreme cases, the swelling can lead to extrusion damage.

In contrast, little is known about the affinity that sealing elastomers have for H<sub>2</sub>S, and how this impacts RGD resistance. A simple weighing

experiment involving HNBR seals exposed to low pressure (i) CO<sub>2</sub> and (ii) H<sub>2</sub>S revealed that the latter gas is absorbed to a significantly greater extent. The work described here is the starting point in exploring the consequences of this difference.

Three RGD tests were undertaken at moderate conditions with housed small O-rings of two HNBRs and four fluoroelastomers. Test conditions were identical except for the gas. The control test used pure methane. For the Test 2, the gas mixture contained 25 mol% CO<sub>2</sub> in methane, and for the critical Test 3, the CO<sub>2</sub> was replaced with H<sub>2</sub>S. The elastomers were selected to give a range of RGD resistance, from very good to poor. In addition, several semi-translucent thermoplastics were included because fracture damage is visible.

One thermoplastic showed the required increase in fracture damage as the minor component of the gas was changed from CH<sub>4</sub> to CO<sub>2</sub> to H<sub>2</sub>S, providing strong support for the contention that a high quantity of absorbed H<sub>2</sub>S is the root cause.

The best performing HNBR was negligibly affected by all test conditions. The second HNBR, which is less RGD resistant, showed some improvement when installed in a narrower groove in the methane and CO<sub>2</sub> tests. However, this material aged significantly in the sour RGD test, an unexpected outcome.

The most RGD resistant fluoroelastomer did well in methane and with CO<sub>2</sub> present, but some larger cracks appeared with H<sub>2</sub>S, perhaps indicating that the material is approaching a limit. In contrast, two other fluoroelastomers which showed generally good resistance in Tests 1 and 2, were massively fractured in the H<sub>2</sub>S case. The stark performance difference between the CH<sub>4</sub>/CO<sub>2</sub> and CH<sub>4</sub>/H<sub>2</sub>S gas mixtures is clear evidence that H<sub>2</sub>S is an escalated damage threat to elastomeric seals in high pressure service, where the possibility of venting to atmospheric pressure exists.

## CONCLUSIONS

- H<sub>2</sub>S is more soluble in HNBR than CO<sub>2</sub> and this situation is believed to apply to fluoroelastomers generally.
- H<sub>2</sub>S has been shown to cause a significant increase in RGD fracturing in susceptible elastomers, when compared with CO<sub>2</sub>.
- Both H<sub>2</sub>S and CO<sub>2</sub> cause significant seal expansion during soak at pressure, but the magnitude varies with compound.
- Accordingly, the recommended 85% groove fill level is probably too limiting; in H<sub>2</sub>S and CO<sub>2</sub>, tailoring the groove to seal performance (swelling, RGD) may be the future.
- Substitution of H<sub>2</sub>S by CO<sub>2</sub> when running “sour” RGD tests is too conservative; the level of CO<sub>2</sub> should at least be doubled.

- More needs to be done to characterize swelling of oilfield elastomers in H<sub>2</sub>S and H<sub>2</sub>S-rich mixtures.

## NEXT STEPS

Quantifying the expansion of oilfield elastomers in H<sub>2</sub>S deserves attention. A sapphire windowed vessel can be used to visually quantify the effect of low pressure H<sub>2</sub>S and CO<sub>2</sub> (say 10 bar) on a range of elastomer types. This will provide a good indication of gas diffusivity and solubility characteristics. Running tests with mixtures at higher pressures and temperatures could follow.

Increasing the level of H<sub>2</sub>S in the RGD test gas mixture is also an option: Element could operate with 50% H<sub>2</sub>S but at lower pressure and reduced cycles. Testing with 50/50 mol% H<sub>2</sub>S/CH<sub>4</sub> would be with two compounds only, HNBR1 and Fluoro1; seal replication would be increased. The expectation is that Fluoro1 would be significantly damaged and that HNBR1 would not. It is also of interest to determine whether the higher level of gas has an aging effect on the HNBR.

## FIGURES

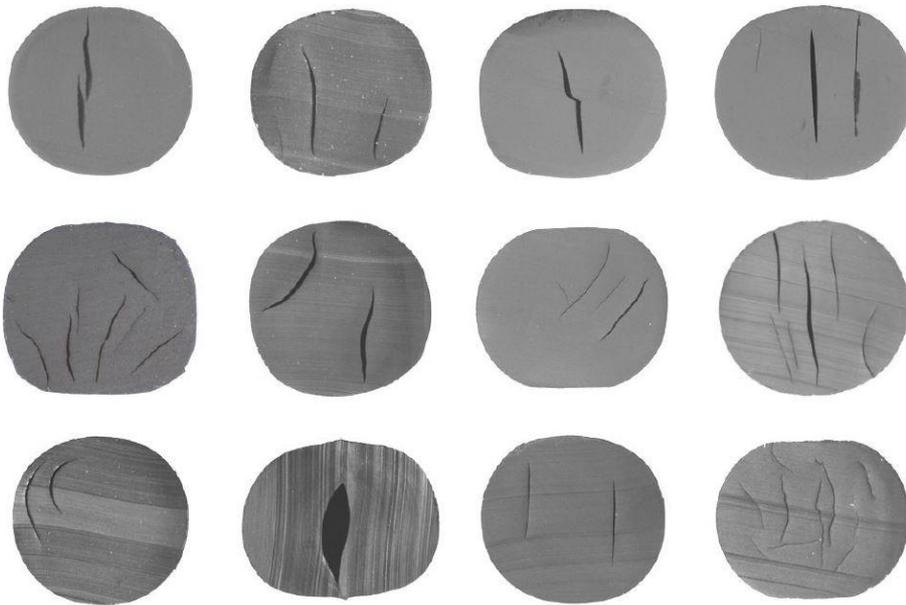


Figure 1 RGD tested O-ring surfaces rated 3 according to ISO 23936-2

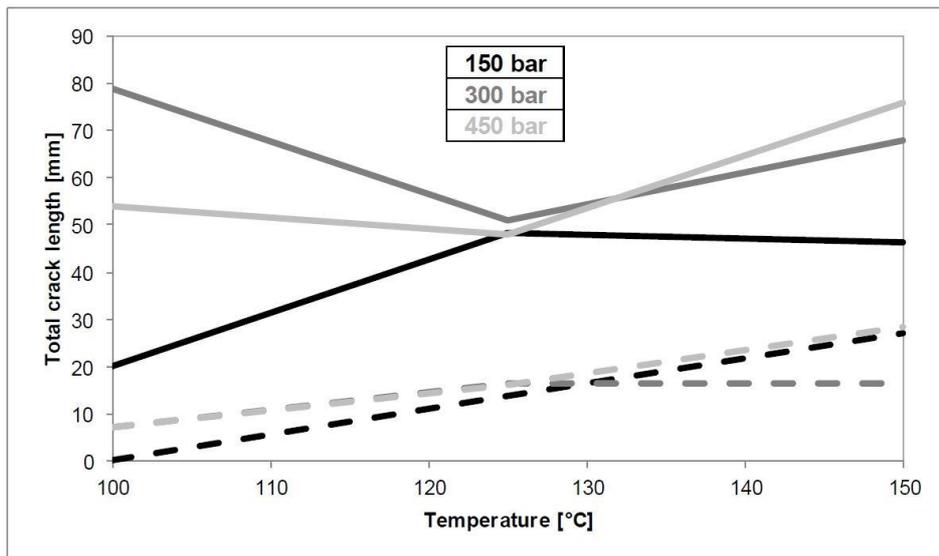
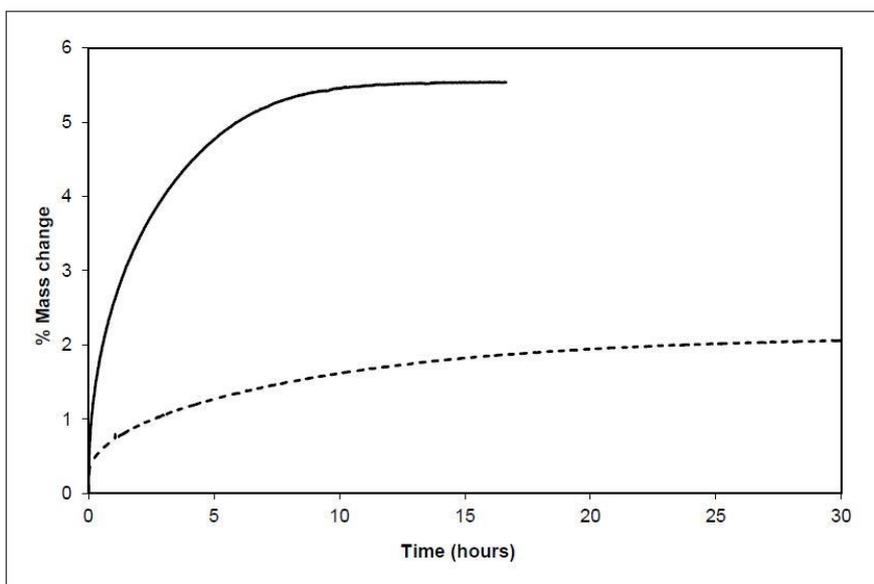


Figure 2 Total crack length vs. RGD test temperature and pressure for HNBR 4 O-rings housed in standard groove (solid lines) and narrow groove (dashed lines)



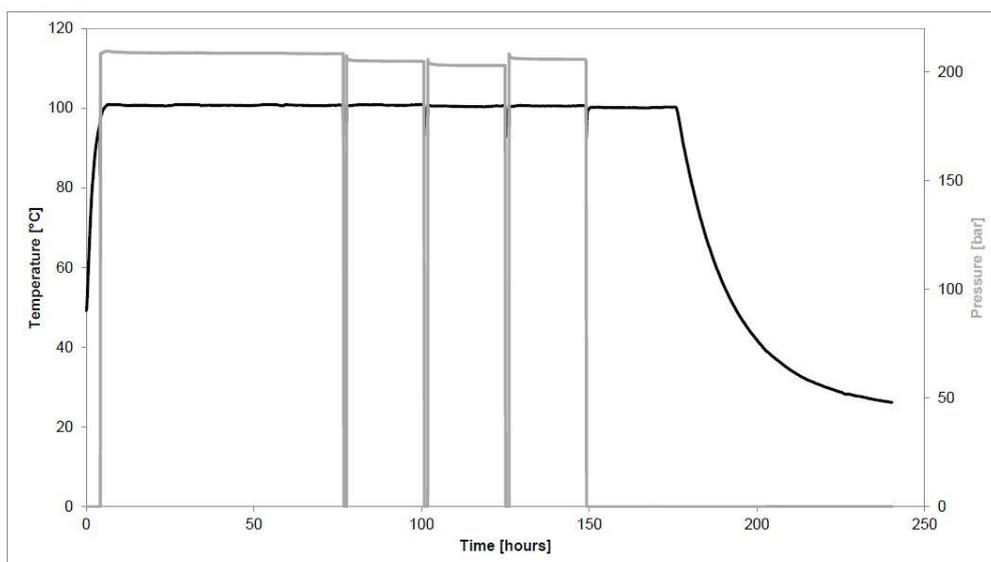
**Figure 3** Fluoro3 seal after CO<sub>2</sub> RGD test, showing material loss due to local extrusion



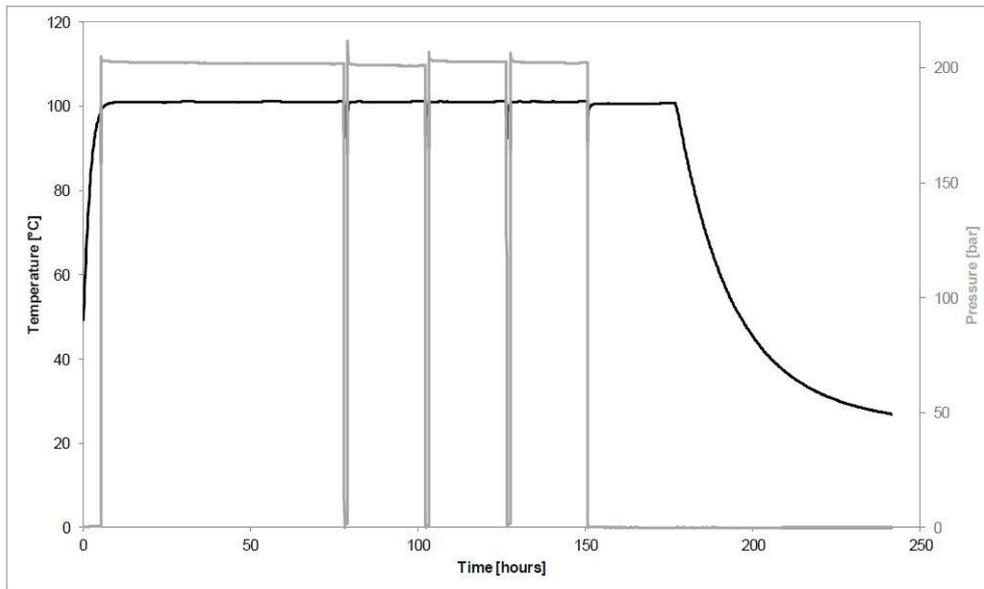
**Figure 4** Change in mass of HNBR1 O-ring at 50°C in 10 bar CO<sub>2</sub> (dashed line) and 10 bar H<sub>2</sub>S (solid line)



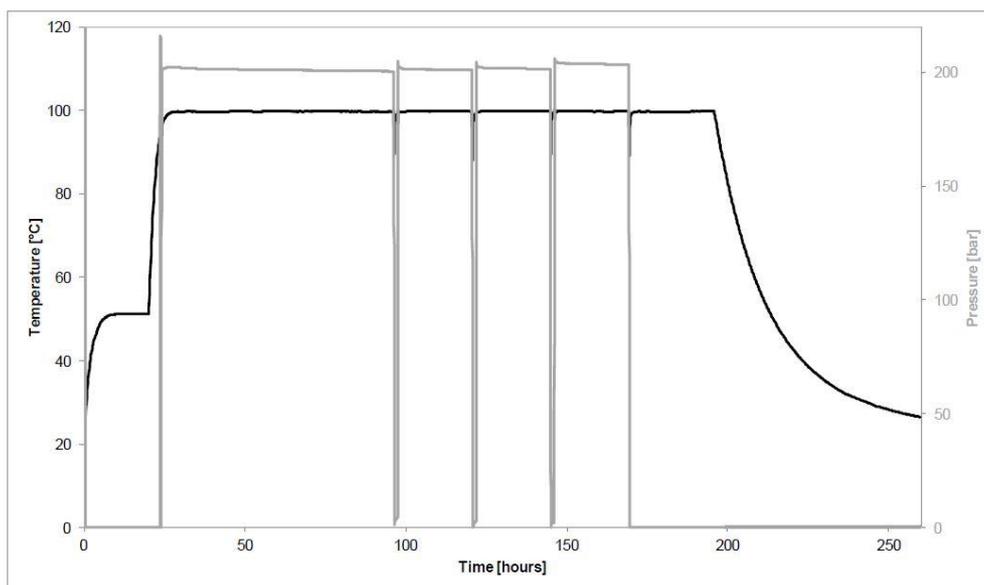
**Figure 5** O-ring RGD test fixture comprising spigot, body, and end caps



**Figure 6** Pressure and temperature logs for Test 1 (100% CH<sub>4</sub>)



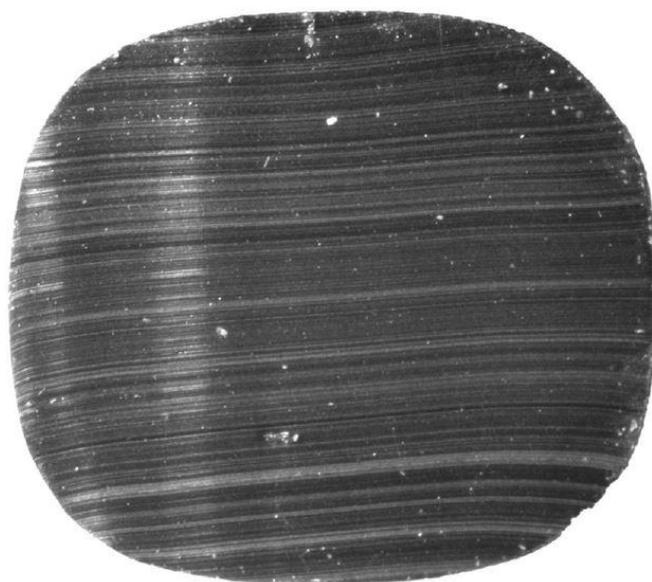
**Figure 7** Pressure and temperature logs for Test 2 (25/75% CO<sub>2</sub>/CH<sub>4</sub>)



**Figure 8** Pressure and temperature logs for Test 3 (25/75% H<sub>2</sub>S/CH<sub>4</sub>)



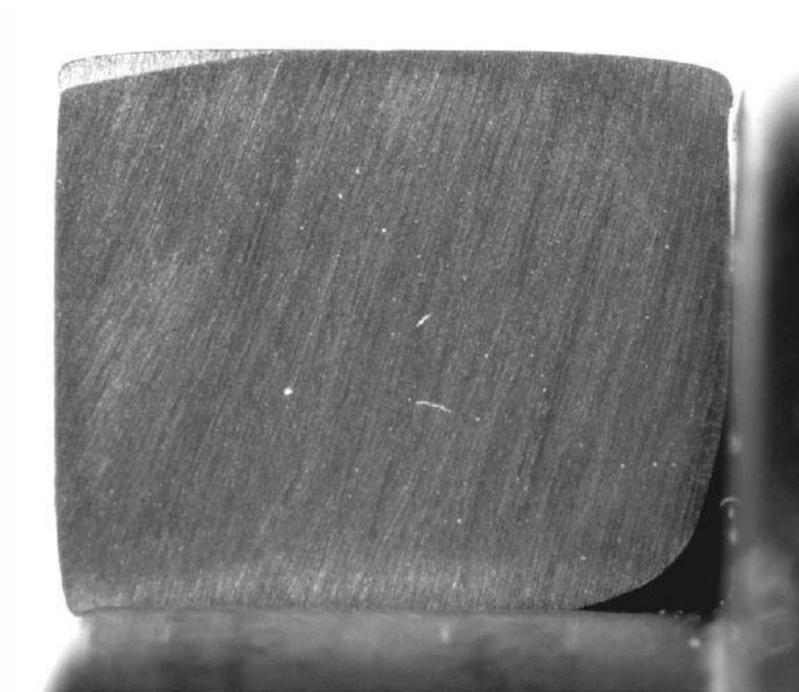
**Figure 9** PrimoSpire® samples from Test 1 (top), Test 2 (center), and Test 3 (bottom)



**Figure 10** HNBR1 section after Test 3, standard groove



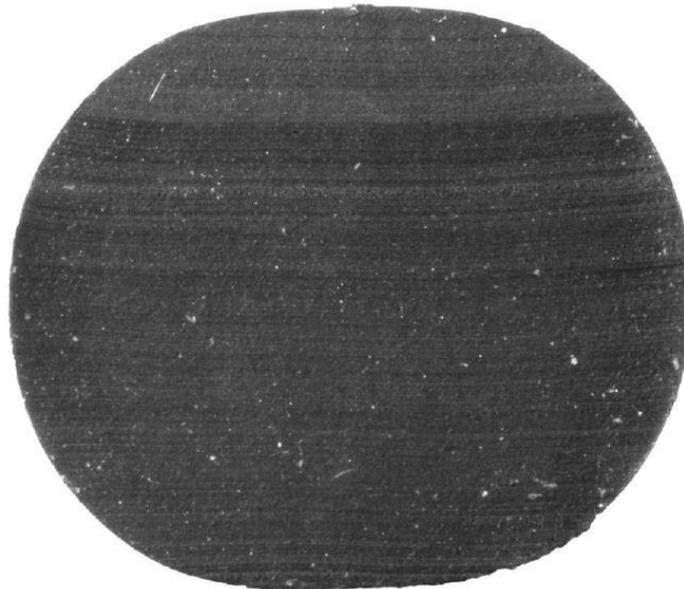
**Figure 11** HNBR4 section after Test 3, standard groove



**Figure 12** HNBR4 section after Test 3, section installed in (narrow) groove



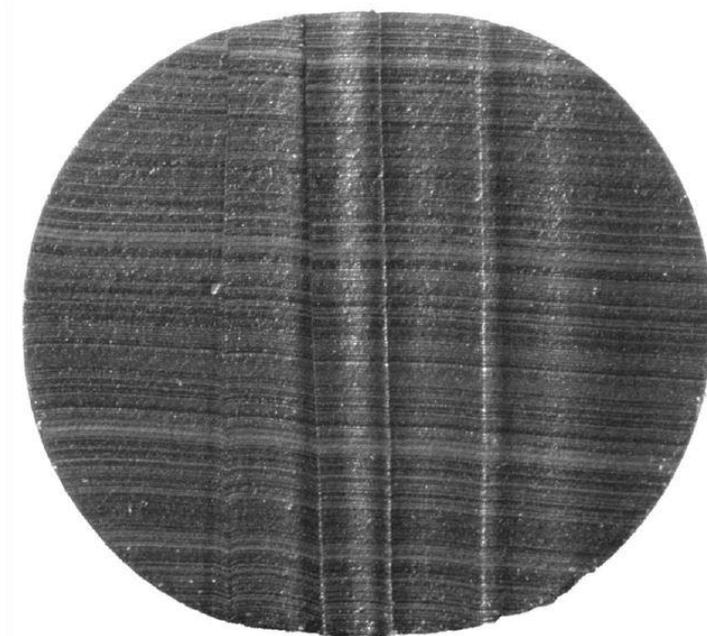
**Figure 13** Fluoro1 section after Test 3, standard groove



**Figure 14** Fluoro2 section after Test 3, standard groove



**Figure 15** Fluoro3 section after Test 3, standard groove



**Figure 16** Fluoro4 section after Test 3, standard groove

### References

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### For more information on the content of this article contact:

Element Materials Technology Limited Hitchin, Wilbury Way, Hitchin, England SG0 4TW

T: +44 1462 427850, F: +44 1462 427851, E: [info.hitchin@element.com](mailto:info.hitchin@element.com)