

Investigation of GRP Caustic discharge pipe

Shell Nederland Chemie – Moerdijk

Restricted

This document is made available subject to the condition that the recipient will neither use nor disclose the contents except as agreed in writing with the copyright owner.

Copyright is vested in Shell Global Solutions International B.V., The Hague.

© Shell Global Solutions International B.V., 2005. All rights reserved

Neither the whole nor any part of this document may be reproduced or distributed in any form or by any means (electronic, mechanical, reprographic, recording or otherwise) without the prior written consent of the copyright owner.

Shell Global Solutions

Shell Global Solutions is a trading style used by a network of technology companies of the Royal Dutch/Shell Group.

GS.05.50579

Investigation of GRP Caustic discharge pipe
Shell Nederland Chemie – Moerdijk

by

P.J.M. van Loon

Keywords: GRP, caustic, discharge pipe, SNC, chemical attack, remaining lifetime

Summary

During leak repair of the 8 inch, diameter Glass-fibre Reinforced Epoxy (GRE) caustic discharge line of Shell Nederland Chemie (SNC) Moerdijk significant damage at the internal surface was observed, after only 6 years operation. The above ground, 500 m long caustic discharge line consists of 400 m GRE pipe P-13072, and 100 m Glass-fibre Reinforced Vinyl Ester (GRVE) pipe P-14049.

Shell Global Solutions was requested by SNC to investigate a GRE and GRVE pipe sample to determine main cause for the observed damage and remaining lifetime of the caustic discharge line, and also to give a recommendation on material upgrade.

Degradation of the internal liner of the GRE pipe is caused by the combination of insufficient liner thickness and chemical attack of the glass fibres, resulting in cracking, and de-bonding of the liner. It is concluded that liners reinforced with synthetic fibres, and thickness of at-least 1.5 mm, should be used in caustic soda service.

The GRVE pipe is still in good condition, mainly because presence of a 1.3 mm thick liner, which performed much better, compared to the 0.75 mm thick liner, used in the GRE line.

For long-term, reliable operation, "minimum" required reinforced wall thickness is calculated at 2.8 mm. Based on an average glass corrosion rate of 0.1 mm per year, remaining lifetime for the GRE P-13072 caustic discharge line is predicted at 18 years, i.e. line should be replaced in 2023.

Microscopic investigation of the GRE pipe wall of line P-13072 should be repeated after 5 years, i.e. in 2010, to confirm that the corrosion rate is still within acceptable limits, i.e. less than 0.1 mm per year, and for more reliable prediction of remaining lifetime.

The GRVE pipe is still in very good condition, and remaining lifetime for the P-14049 GRVE caustic discharge line is therefore expected at-least 20 years.

Recommendation on material upgrade, and new GRE piping class for caustic soda service is also given in this report.

Contents

	Page	
1. Introduction	1	
2. Service conditions	1	
3. Pipe samples	1	
3.1 Materials	1	
3.2 Dimensions	2	
3.3 Chemical resistance	2	
4. Investigation	2	
4.1 Ameron Bondstrand 4000 GRE pipe	2	
4.2 Sarplast GRVE pipe	3	
5. Discussion of results	3	
6. Prediction of remaining lifetime	3	
6.1 Operational load	3	
6.2 Occasional load	4	
6.3 Caustic discharge line	4	
7. Material upgrade option	5	
7.1 Material	5	
7.2 Piping classes	5	
8. Conclusions	6	
9. Recommendation	6	
Figure 1	Degraded internal surface of GRE pipe sample, showing "loose" liner	7
Figure 2	Cross section of 5 mm thick GRE pipe sample	7
Figure 3	Microstructure GRE showing degraded glass fibre reinforced structural layer	8
Figure 4	Microstructure of liner GRE pipe, showing severely attacked glass fibres	8

Contents (Cont'd)

	Page
Figure 5	9
Figure 6	9
Figure 7	10
Figure 8	10
Figure 9	11
Figure 10	11
Figure 11	12
Figure 12	12

1. Introduction

During leak repair of the 8 inch, diameter Glass-fibre Reinforced Epoxy (GRE) caustic discharge line of Shell Nederland Chemie (SNC) Moerdijk significant damage at the internal surface was observed, after only 6 years operation. The above ground, 500 m long caustic discharge line consists of 400 m GRE pipe P-13072, and 100 m Glass-fibre Reinforced Vinyl Ester (GRVE) pipe P-14049.

The above ground, 500 m long caustic discharge line runs from jetty-6 to storage tank T-0860, and consists of 400 m GRE pipe P-13072, and 100 m Glass-fibre Reinforced Vinyl Ester (GRVE) pipe P-14049. Pipe sections, 1 m long, were cut from the GRE and GRVE discharge line for further investigation.

Shell Global Solutions was requested by SNC to investigate a GRE and GRVE pipe sample to determine main cause for the observed damage and remaining lifetime of the caustic discharge line, and also to give a recommendation on material upgrade.

2. Service conditions

The service conditions for the caustic discharge line are:

- Sodium hydroxide (NaOH), concentration 50 %;
- Pressure: maximum 6.8 bar;
- Temperature: 25 - 40 °C;

3. Pipe samples

Pipe sections, 1 meter long, were cut from the GRE and GRVE discharge line for further investigation.

3.1 Materials

- Discharge line P-13072, Bondstrand 4000 from Ameron - GRE;
 - Resin: Epikote 827, aromatic amine cured (MDA);
 - Fibre: E-glass roving, Hybon 2062, PPG Industries Fiberglass Products;
 - Liner: Resin rich, reinforced with C-veil, 30 grams/m².
- Discharge line P-14049, Sarplast - GRVE;
 - Resin: Vinyl ester Derakane 411, Dow Chemicals;
 - Fibre: E-glass roving, Owens Corning OCF R25H;
 - Liner: Resin rich, reinforced with C-veil, 33 grams/m².

3.2 Dimensions

- Discharge line P-13072, (GRE);
 - Internal diameter: 209 mm
 - Laminate thickness: 5.1 mm;
 - Liner thickness: 0.75 mm (specified thickness is 1.3 mm).

Discharge line P-14049, (GRVE);

- Internal diameter: 200 mm;
- Laminate thickness: 5.2 mm;
- Liner thickness: 1.3 mm.

3.3 Chemical resistance

According to chemical resistance guide from Ameron, Bondstrand 4000 GRE pipe, used for the P-13072 caustic discharge line, should be resistant against sodium hydroxide, 50 % concentration, up to 82 °C, and therefore chemical attack was not expected.

According to Dow Chemicals, Manufacturer of Derakane 411 vinyl ester resin, used for the P-14049 caustic GRVE discharge line, vinyl ester resin is resistant against sodium hydroxide, 50 % concentration, up to 80 °C. According to the resin Manufacturer, double synthetic veil should be used in liners for caustic service.

4. Investigation

To investigate degradation of the GRE and GRVE pipe, optical microscopic inspection, has been performed on GRP pipe samples.

To determine type of fibres used in the liner, i.e. glass, or synthetic, Scanning Electron Microscopy (SEM) was used.

4.1 Ameron Bondstrand 4000 GRE pipe

The GRE pipe sample, showing significant damage of the internal liner, is shown in Figure 1.

Figure 2 shows a cross section of the GRE pipe wall, showing the "loose" liner. Total thickness of the structural wall is 5.1 mm, and consists of eleven layers (plies). Thickness of the liner is 0.75 mm, i.e. significantly less than 1.3 mm, as specified by the Manufacturer for Bondsrand 4000 pipe.

Figure 3 shows a detail of the 0.45 mm thick inner ply (dark colour), which has been severely attacked. Several cracks in the fibres are observed. In addition, significant reduction in fibre diameter and change in fibre shape has occurred.

Figure 4 shows a cross section of the liner. At several locations glass fibres have completely disappeared, and remaining glass fibres have significantly reduced in size. Figure 5 shows the surface of the liner, showing surface voids, and open channels at locations where glass fibres have completely disappeared.

From the SEM investigation it is concluded that the fibre material used in the resin rich liner is glass, and not synthetic, as recommended by the resin Manufacturer for alkaline service.

4.2 Sarplast GRVE pipe

The GRVE pipe sample, showing the intact pipe, including liner, is shown in Figure 6.

Figure 7 shows a cross section of the GRVE pipe wall, showing the intact laminate, including liner. However, small radial cracks in the liner are observed. Total thickness of the structural wall is 5.2 mm, and consists of six layers (plies). Thickness of the internal liner is 1.3 mm.

Figure 8 shows the surface of the liner, showing small surface voids, and presence of surface cracks.

Figure 9 shows detail of a radial crack in the resin rich layer, and a crack at the fibre/matrix interface. Figure 10 shows further detail of the crack at the fibre / matrix interface, showing chemically attacked glass fibres.

From the SEM investigation it is concluded that the fibre material used in the resin rich liner is glass, and not synthetic, as recommended by the resin Manufacturer for alkaline service.

5. Discussion of results

From investigation of the GRE pipe section it is concluded that degradation of the internal liner is caused by the combination of insufficient liner thickness and chemical attack of the glass fibres. Chemical attack of the glass fibres introduces channels in the liner, and consequently liner will start to deteriorate, resulting in cracking, and de-bonding of the liner, and chemical attack will start at the next glass layer (ply) of the structural wall.

Considering the rather low thickness of the liner, and chemical attack of the glass fibres present in the liner, it is not unreasonable to assume that failure of the liner has occurred within a short period of time, say within one or two years. The observed corrosion attack of the first reinforcement layer (ply) corresponds to an average corrosion rate of 0.1 mm per year, and this is in good agreement with the literature (<http://www.gargscientific.com/>), see Figure 11.

From the microscopic investigation of the GRVE pipe section it is concluded that the GRVE pipe is still in good condition, mainly because presence of the 1.3 mm thick liner, which performed much better, compared to the 0.75 mm thick liner, used in the GRE line.

It is concluded that liners reinforced with synthetic fibres (e.g. Nexus), and thickness of 1.5 - 2 mm, should be used in caustic soda service.

6. Prediction of remaining lifetime

Design life of GRP pipe systems, based on continuous operation, is typically 20 years, as specified in ISO 14692. The aim of structural design for GRP pipe systems is to ensure that they shall perform satisfactorily and sustain all stresses and deformations throughout their service, i.e. stresses stay within the long-term design envelope, see Figure 12.

6.1 Operational load

Operational loads are long-term, and if number of load cycles during design life is less than 7000, design shall be considered as static. The design envelope for sustained loading is based on a safety factor of 1.5 on the long-term strength envelope, as specified in ISO 14692.

6.2 Occasional load

Occasional load is of short-term duration and the number of occurrences during design life is limited. It should be noted that for GRP pipe systems there are no established links between the effects of long-term loading and those of higher loads that are of short-term duration. For steel pipe systems, guidance on duration of occasional loads permitted is given in ANSI/ASME B31.1 (Section 102.2.4) and ANSI/ASME B31.3 (Section 302.2.4).

Concerning duration of occasional loads permitted for GRP pipe systems, the following is recommended:

- Number of load cycles should not exceed 7000 during life of the pipe system;
- Duration should not exceed 10 hr (say half a day) at any one time and no more than 100 hr (say 4 days) per year.

Occasional loads are: hydro-test, water hammer, blast over-pressures, etc.

The design envelope for occasional loading, e.g. hydro-test, is based on a safety factor of 1.1 on the long-term strength envelope, as specified in ISO 14692.

6.3 Caustic discharge line

Loading cycle for the GRP caustic discharge line is every 2 - 3 weeks, i.e. duration exceeds 4 days per year. Therefore the design loading condition for the GRP discharge pipe is considered "sustained", i.e. pipe wall stresses should stay within the sustained design envelope.

In addition, deflection of the pipe should not exceed 12.5 mm, or 0.5 % of span length or support spacing, whichever is smaller, as specified in ISO 14692.

Following mechanical loads have been considered for the P-13072 GRE caustic discharge line:

(a) Pressure load

- Hoop stress = $PD/2t$ (MPa);
- Axial stress = $PD/4t$ (MPa);

Where:

- P is internal pressure (MPa);
- D is internal diameter (mm);
- t is thickness of reinforced wall (mm).

(b) Bending load

$$\text{Bending stress} = QL^2 / 12W \text{ (MPa);}$$

Where:

- Q is distributed load (N/mm);
- L is support span length (mm);
- W is modulus of section (mm^3).

(c) Deflection

$$\text{Maximum deflection, } f = QL^4 / 384EI \text{ (mm);}$$

Where:

- E is bending stiffness (12500 MPa for Bondstand 4000);
- I is moment of inertia (mm^4).

Based on internal pressure of 6.8 bar, support span of maximum 6 m, density 2000 kg/m³ for GRE, and density 1500 kg/m³ for caustic soda, i.e. distributed load of 580 N/m, following stresses and deflections are calculated for the P-13072 GRE caustic discharge line:

(A) Virgin GRE pipe, December 1998 (Position A in Figure 12)

- Reinforced wall thickness: 5.1 mm;
- Hoop stress: 14 MPa;
- Axial stress (pressure induced): 7 MPa;
- Bending stress: 10 MPa;
- Axial (total): 17 MPa;
- Mid span deflection: 8 mm, i.e. well within acceptable limit of 12.5 mm.

(B) Corrosion attacked GRE pipe (Position B in Figure 12)

- Reinforced wall thickness: 2.8 mm;
- Hoop stress: 26 MPa;
- Axial stress (pressure induced): 13 MPa;
- Bending stress: 17 MPa;
- Axial (total): 30 MPa;
- Mid span deflection: 13.5 mm, slightly (8 %) above limit of 12.5 mm.

From the calculations it is concluded that the "minimum" required wall thickness for long-term, and safe operation, is 2.8 mm, i.e. pipe stresses are still within the long-term sustained design envelope (Figure 12). Based on an average corrosion rate of 0.1 mm per year, remaining lifetime for the GRE P-13072 caustic discharge line is predicted at 18 years, i.e. the GRE line should be replaced in 2023.

The GRVE pipe is still in very good condition, and remaining lifetime for the P - 14049 GRVE caustic discharge line is therefore expected at least 20 years.

7. Material upgrade option

7.1 Material

For sodium hydroxide service, up to 80 °C, following non-metallic pipe material should be specified:

- GLASS-fibre Reinforced Epoxy (GRE), aromatic amine cured (MDA), including liner;
- Liner: reinforced with at-least two layers of **synthetic** veil, e.g. Nexus;
- Thickness liner: 1.5 to 2 mm.

7.2 Piping classes

Presently, only the metallic piping class 16021 is available for sodium hydroxide service, temperature range 0 to 150 °C. However, during the project phase for the SNC caustic discharge line, GRP was selected because of significantly lower costs, compared to the metallic option, as recommended in the Shell piping classes. Therefore SNC has asked Shell Global Solutions to also incorporate a GRP piping class for sodium hydroxide service.

The new GRP piping class should specify GRE- amine cured pipe, EPDM gasket material, flat-face flanges, temperature limits 0 to 80 °C, and 10 bar pressure rating, i.e. ASME rating class 150.

8. Conclusions

- (a) Degradation of the internal surface of the Bondstrand 4000 GRE pipe is caused by the combination of insufficient liner thickness and chemical attack of the glass fibres;
- (b) Based on an average glass corrosion rate of 0.1 mm per year, and minimum required reinforced wall thickness of 2.8mm, remaining lifetime for the GRE P-13072 caustic discharge line is predicted at 18 years, i.e. replacement of the GRE line in 2023;
- (c) The GRVE pipe is still in good condition, mainly because presence of the 1.3 mm thick liner, which performed much better, compared to the 0.75 mm thick liner, used in the GRE line. Remaining life for the P-14049 caustic discharge line is expected at least 20 years;
- (d) In caustic soda service, synthetic fibres, e.g. Nexus, should be used in liners, and thickness should be at-least 1.5 mm.

9. Recommendation

Microscopic investigation of the GRE pipe wall of line P-13072 should be repeated after 5 years, i.e. in 2010, to confirm that the corrosion rate is still within acceptable limits, i.e. less than 0.1 mm per year, and for more reliable prediction of remaining lifetime.

Amsterdam, March 2005

mv



Figure 1 Degraded internal surface of GRE pipe sample, showing "loose" liner

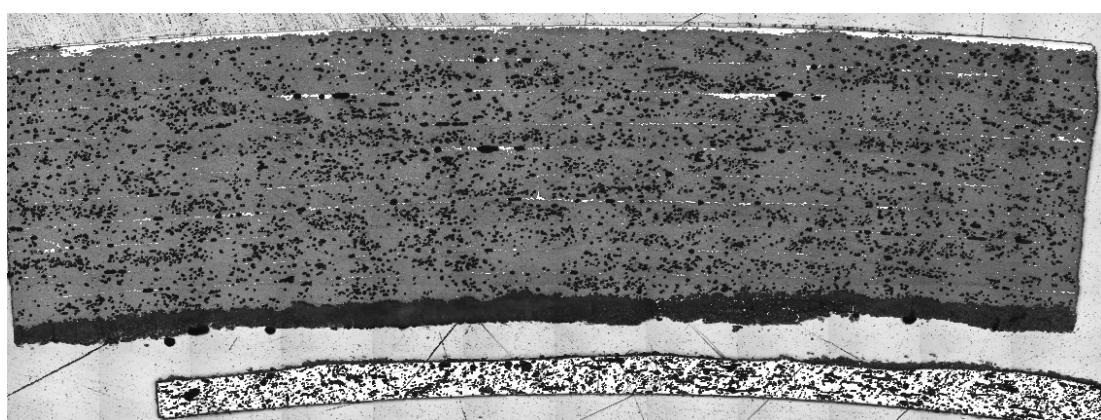


Figure 2 Cross section of 5 mm thick GRE pipe sample

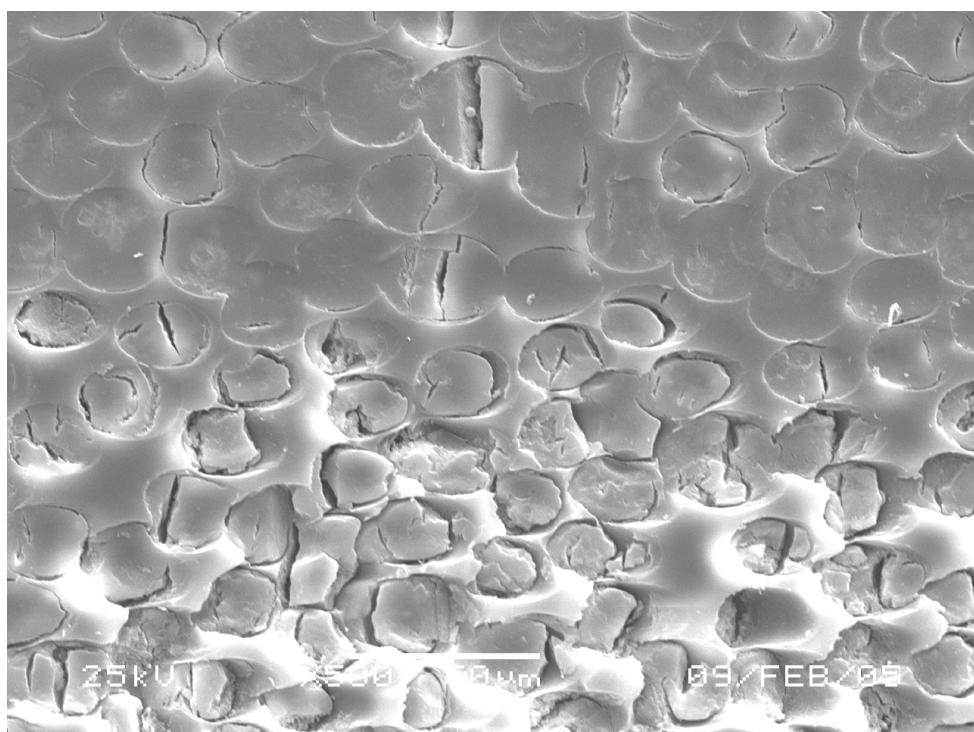


Figure 3 Microstructure GRE showing degraded glass fibre reinforced structural layer

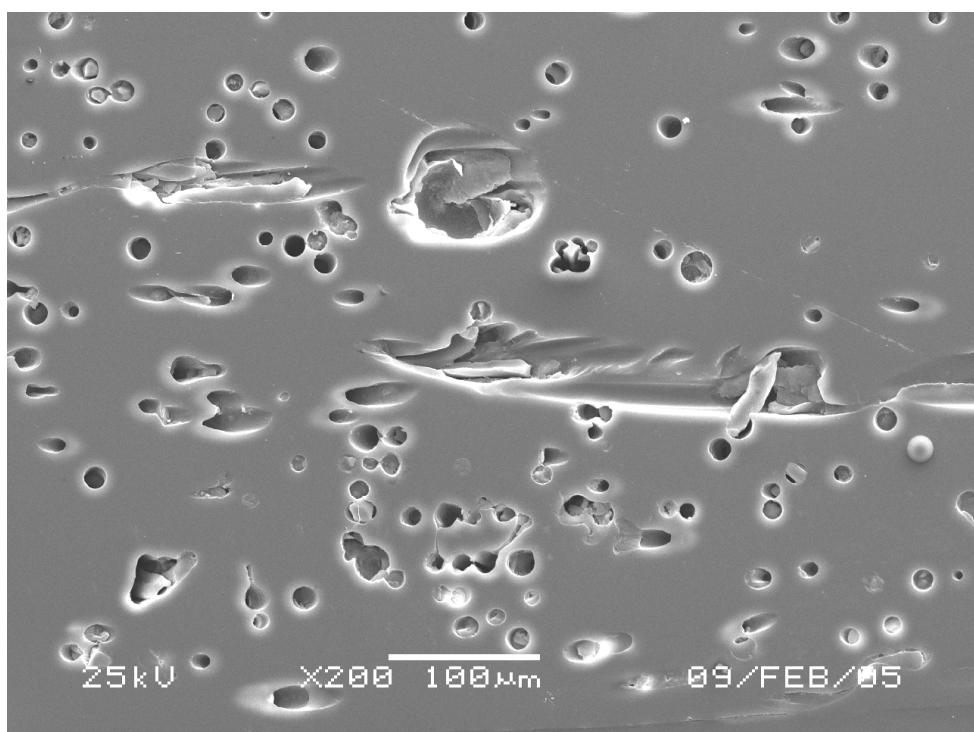


Figure 4 Microstructure of liner GRE pipe, showing severely attacked glass fibres

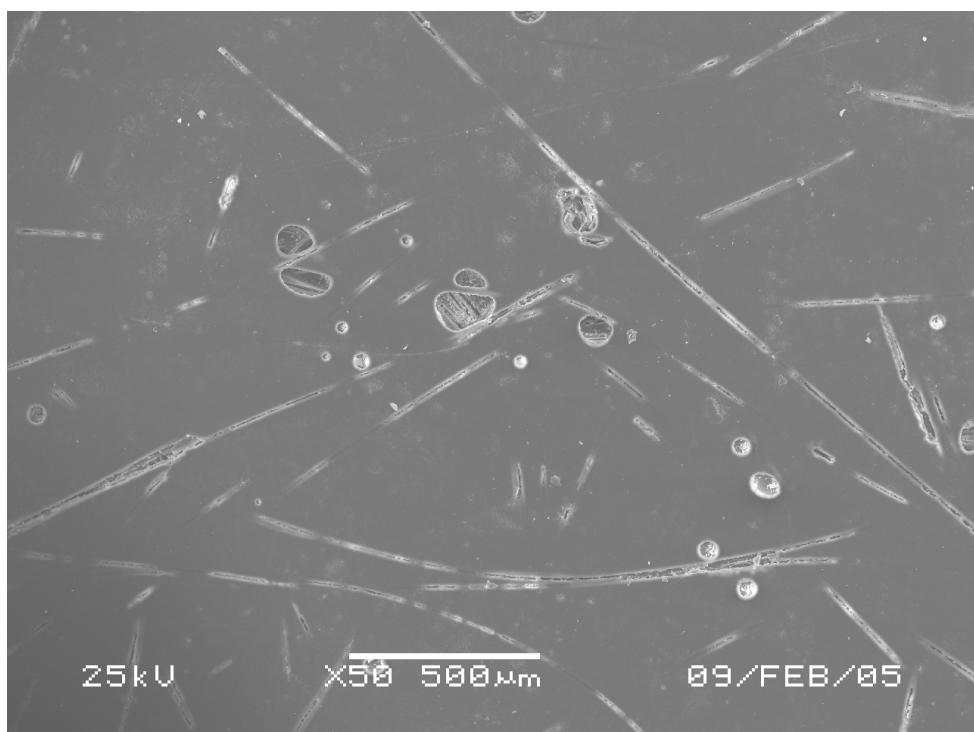


Figure 5 Liner surface of GRE pipe showing surface voids, and open channels



Figure 6 Intact GRVE pipe sample

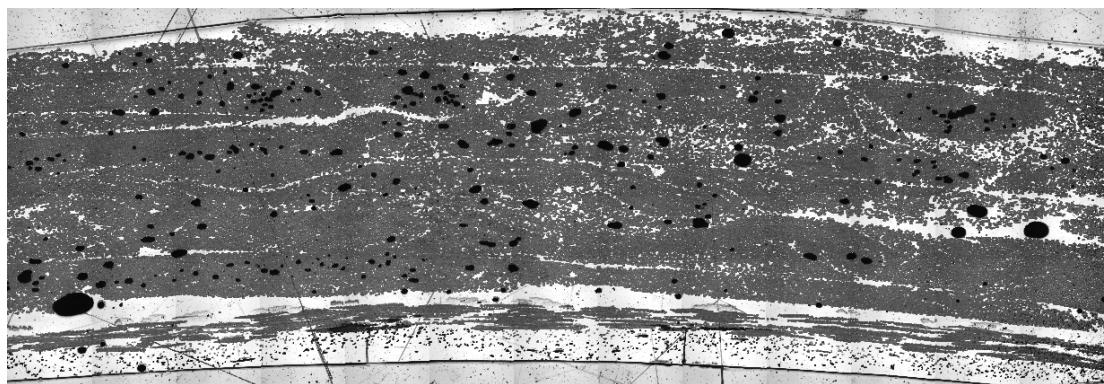


Figure 7 Cross section of 5 mm thick GRVE pipe sample

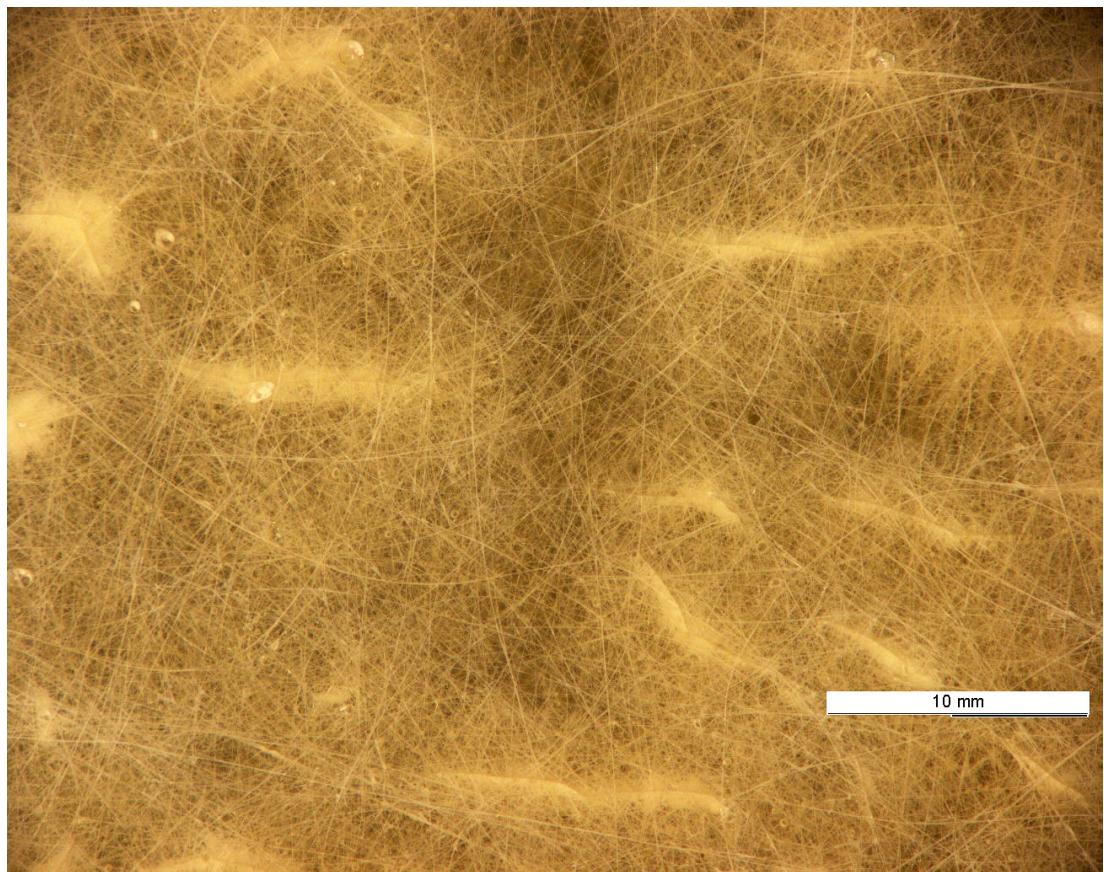


Figure 8 Liner surface of GRVE pipe showing surface voids, and cracks

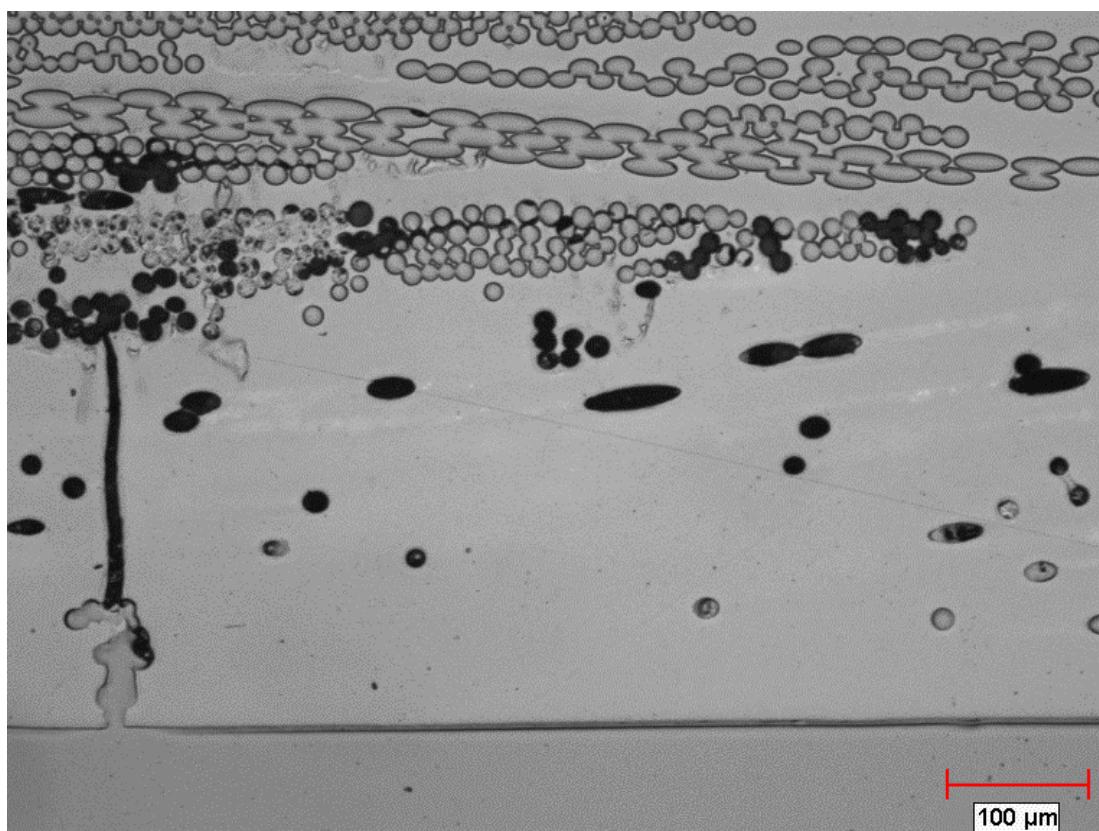


Figure 9 Microstructure of liner GRVE pipe, showing radial, and de-lamination cracks

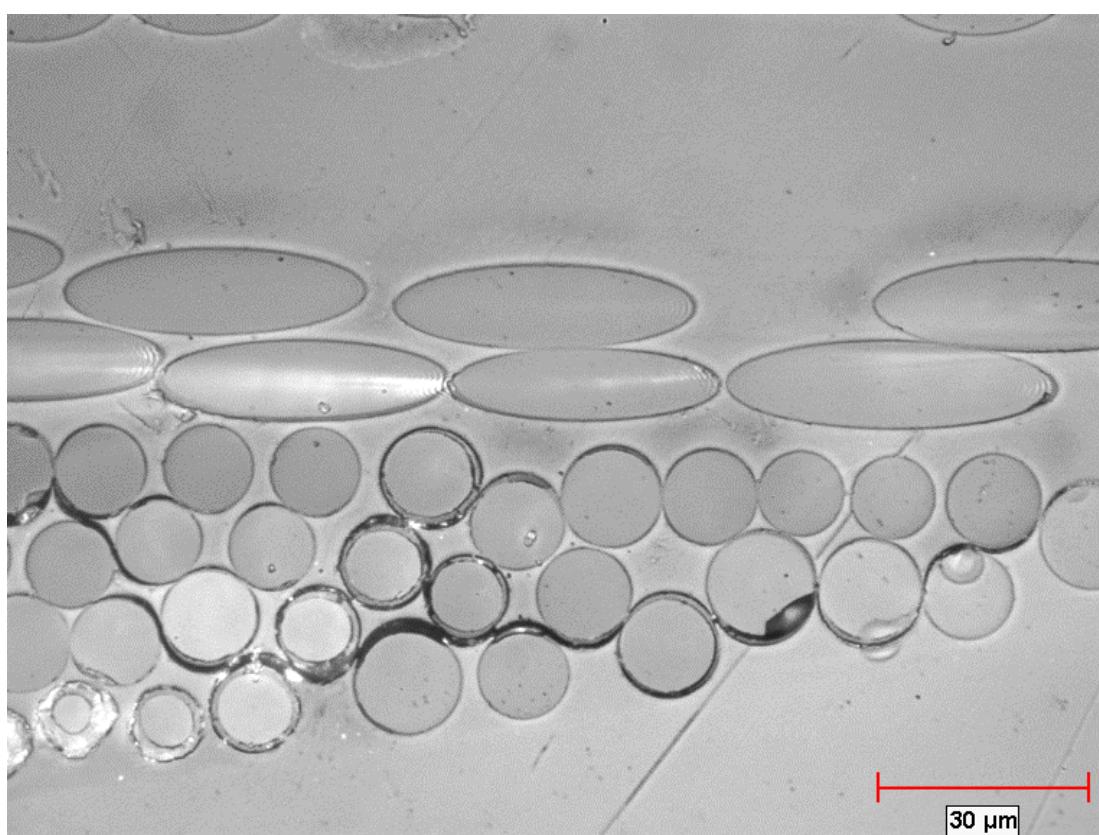


Figure 10 Detail of liner GRVE pipe, showing crack and chemically attacked glass fibres

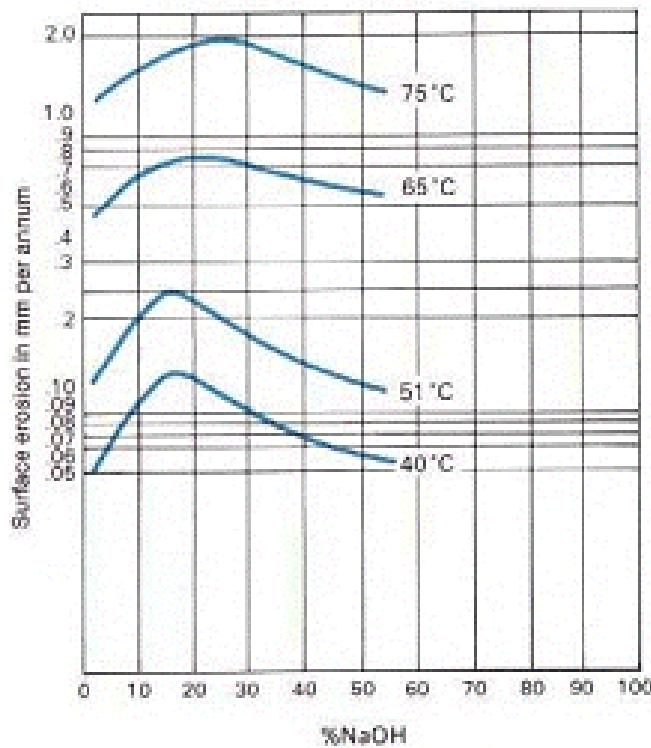


Figure 11 Corrosion rate of glass material in caustic soda

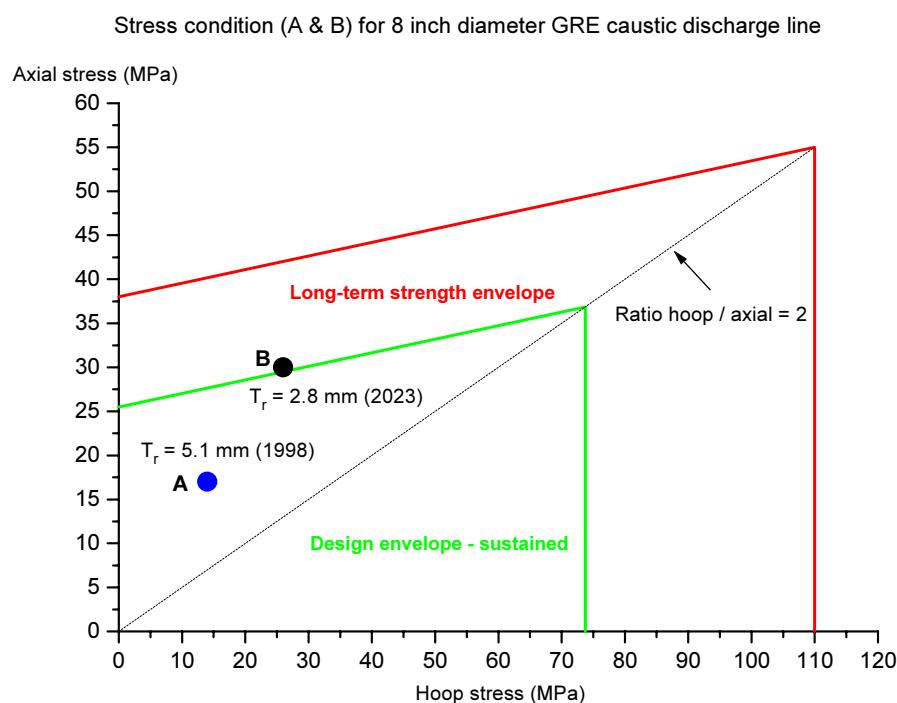


Figure 12 Design envelope for GRE pipe

Administration & Distribution list

This report has been classified as Restricted and is not subject to US Export Control regulations.

Report number	GS.05.50579
Field	Chemicals
Activity no.	53000022
Customer	Shell Nederland Chemie B.V., Moerdijk
Title	Investigation of GRP Caustic discharge pipe Shell Nederland Chemie – Moerdijk
Author(s)	P.J.M. van Loon
Co-worker(s)	
Approver/Reviewer	W.C. Fort/K.R. Lewis
Owner/Custodian	
Keywords	GRP, caustic, discharge line, SNC, chemical attack, remaining lifetime
Restrictions on Distribution	This report can be freely shared with all Shell Global Solutions employees
Additional Distribution	Additional copies can be requested from the library specified in the primary distribution. Please note that permission from the owner may be required for these additional copies.
Issue date	March 2005
Electronic file	GS.05.50579.pdf

Shell Nederland Chemie B.V., Moerdijk

CFD	P.B.J. van Diepen	1
CFD/3	D.P.L.M. Doggen	1
MEOD/3	R.F.A. Habes	1
CEI/212	M.T. van den Hoogen	1
MEOD	R.J. Mooldijk	1
CEI/133	E. de Waard	1

Shell Oil Company, Houston

WTC	1
-----	---

Shell Global Solutions International B.V.

Amsterdam, GSXI	Library	1
GSEI/1	P.J.M. van Loon	1
GSEI/2	L.M. de Mul	1
	K.M. Orzessek	1