Conversion of a natural gas pipeline to hydrogen transport and the effects of impurities on the hydrogen quality

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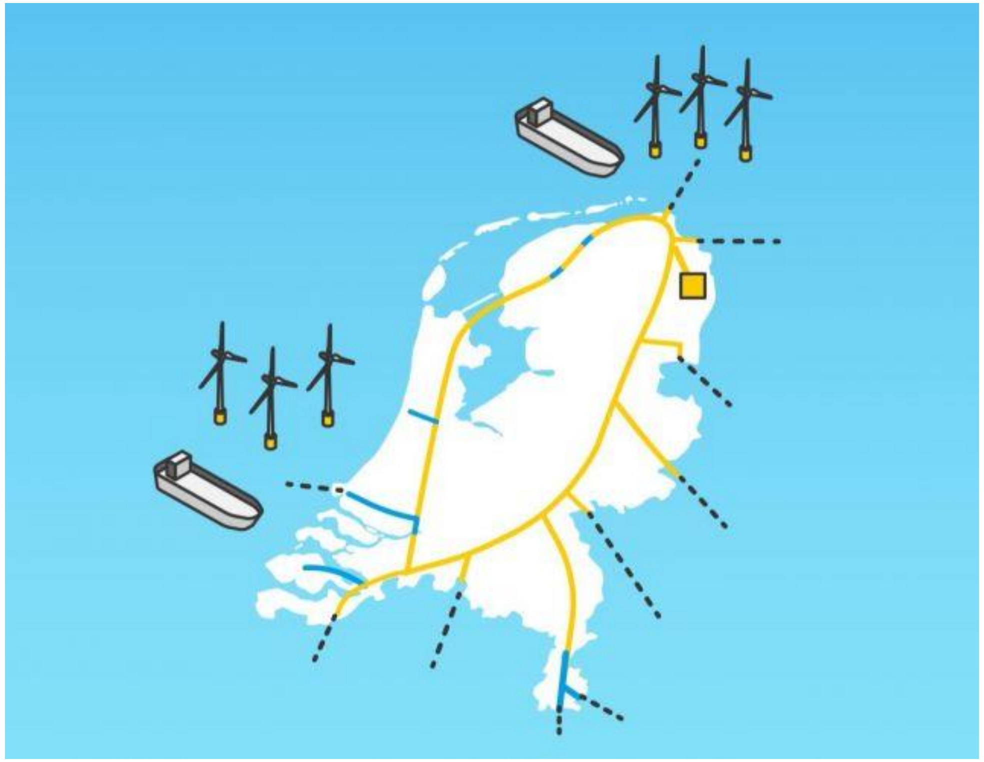
Introduction

The Netherlands must become more sustainable: CO_2 emissions must be zero by 2050. Hydrogen from sustainable sources will play an important role in this sustainability process, starting with the industry.
Hynetwork Services is realizing regional hydrogen pipelines in the industrial clusters in cooperation with local parties. In addition, a national backbone is being constructed to connect all the clusters with each other. A large part of this backbone will exist of former natural gas pipelines.

The first experience with the conversation of a natural gas pipeline to hydrogen transport was done with a relatively short natural gas pipeline between two chemical plants in the Netherlands. This 12 km long 16-inch natural gas pipeline was converted in 2018.



HYNETWORK
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Indicative quality specification hydrogen backbone

Component	Symbol	Unit	Minimum	Maximum
Hydrogen	H_2	mole %	98	
Total sum of hydrocarbons including methane	C_xH_y	mole %		1.5
Total sum of inerts (nitrogen, argon and helium)	N_2, Ar, He	mole %		2.0
Oxygen	O_2	ppm		10
Carbon dioxide	CO_2	ppm		20
Carbon monoxide	CO	ppm		20
Total sulphur including H_2S	S	ppm		5
Formic acid	CH_3OOH	ppm		10
Formaldehyde	CH_2O	ppm		10
Ammonia	NH_3	ppm		10
Halogenated compounds		ppm		0.05
Water dewpoint	H_2O	^oC @ 70 bara		-8

Source: Hynetwork Services, *https://www.hynetwork.nl/downloads*

Cleaning protocol

Based on experience with pigging operations and nitrogen purge of natural gas pipelines, the proposal is to use the following criteria for cleaning natural gas pipelines:

- Liquids/solids/sludge; maximum 1 litre of material for pipe diameters up to 12-inches and up to 2 litres of material for pipe diameters larger than 12-inches (regardless of pipeline length).
- Hydrocarbons up to 1000 ppm.
- Water dewpoint < -8°C @ 70 bar.

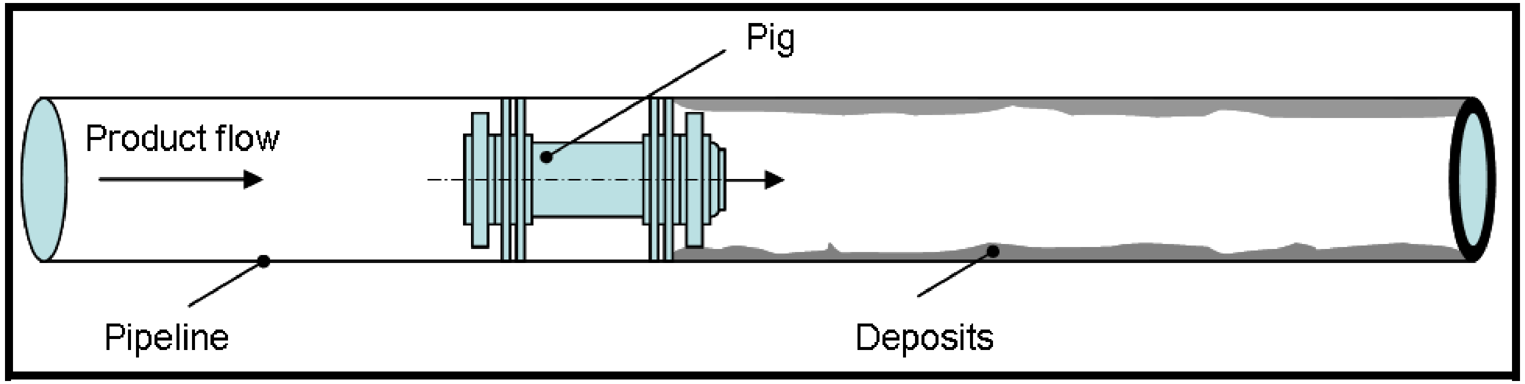
If these criteria are met after cleaning, an existing natural gas pipeline can be converted to hydrogen transport. In order to achieve a cost-effective cleaning method, experience has been included in the conversion of pipelines in the Netherlands. Based on these findings, five steps can be distinguished when converting an existing natural gas pipeline to hydrogen transport:

STEP	DESCRIPTION
1	Pre-clean using cleaning pigs to remove loose dirt and liquids from the pipeline with natural gas
2	Displace natural gas to nitrogen using a pig-run to separate the natural gas from the nitrogen and preserve the pipeline under a low-pressure nitrogen atmosphere
3	Perform maintenance/replacement of valves. Placing caps on branches that are no longer operational
4	Pig-run cleaning under nitrogen atmosphere. Monitoring contaminants in nitrogen and performing tests to see if the criteria to switch over to hydrogen transmission are fulfilled. If criteria are not met, an additional purge with nitrogen is carried out.
5	Displacement from nitrogen to hydrogen using a pig-run to separate the nitrogen from the hydrogen

Pipeline preparations

The existing 16-inch section of the natural gas pipeline was examined using internal Magnetic Flux Leakage (MFL) inspection in 2017. This is a widely used non-destructive testing method for the detection of (internal) corrosion and pitting in steel structures. Before this inspection the natural gas pipeline was cleaned by means of a bi-directional (BIDI) cleaning pig. Approximately 5 litres of sludge (not analysed) came along at that time. Sludge found in natural gas pipelines normally consists of a mixture of natural gas condensates, lube oil and glycol.

Photo: Pig launcher/receiver Ergil



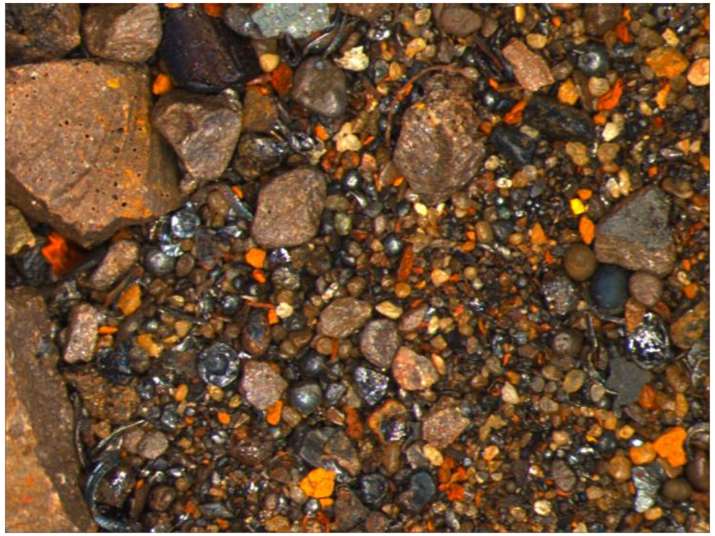
Source: www.theprocesspiping.com

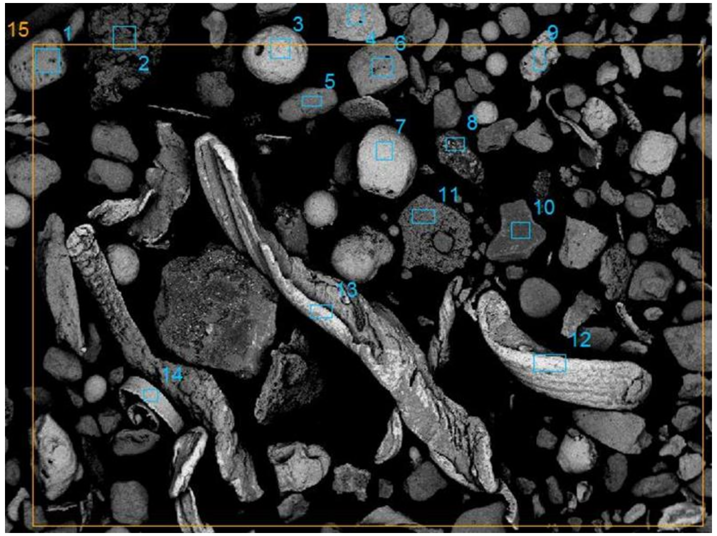
SEM-EDX analysis debris

Scanning Electron Microscope (SEM)-Energy-Dispersive X-ray (EDX) results:

- Minerals
- Rust particles
- Iron oxide balls (welding and grinding)
- Chips of low alloy steel

Element	Symbol	Elemental composition in mass%		
		Average	Minimum	Maximum
Carbon	C	3.6	0.0	39.0
Oxygen	O	26.7	5.3	50.0
Sodium	Na	0.2	0.0	4.1
Magnesium	Mg	0.5	0.0	2.6
Aluminium	Al	2.9	0.0	47.0
Silicon	Si	8.4	0.4	50.4
Sulphur	S	1.6	0.0	18.3
Potassium	K	0.5	0.0	5.0
Calcium	Ca	4.5	0.0	35.8
Titanium	Ti	1.7	0.0	17.1
Manganese	Mn	1.2	0.0	12.3
Iron	Fe	48.0	1.8	91.7





Gas Analysis (1)

Thermo Scientific Trace 1300 Gas Chromatograph with a Flame Ionisation Detector and a Mass Spectrometer ISQ (single quadrupole) in parallel

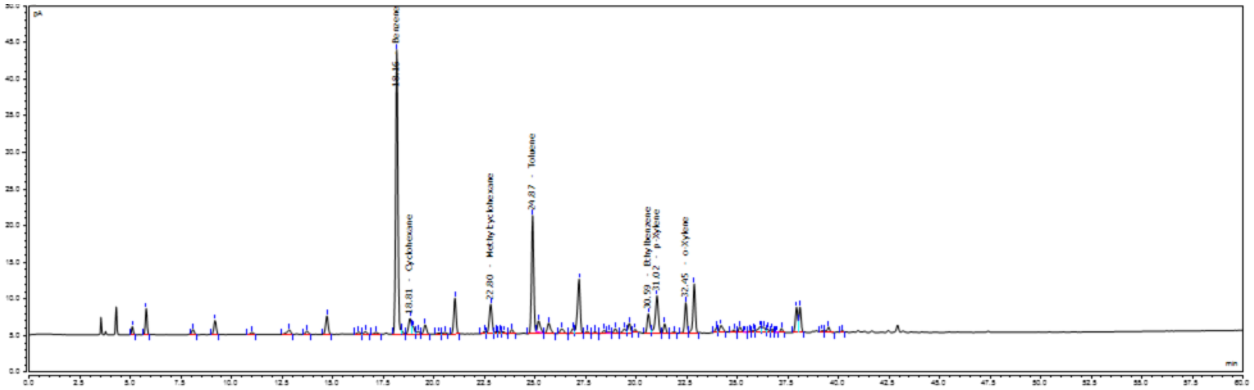
Screening unknows in mass range 20 – 400 amu

GC/MS system DNV, delivered by Interscience

BTEX and cycloalkanes in initial nitrogen samples (June 2018)

Component	Symbol	Retention time (min)	Concentration (ppm)
Benzene	C_6H_6	18.2	43.7
Cyclohexane	C_6H_8	18.8	3.5
Methylcyclohexane	C_7H_{14}	22.8	5.1
Toluene	C_7H_8	24.9	17.2
Ethylbenzene	C_8H_{10}	30.6	3.3
p/m-Xylene	C_8H_{10}	31.0	6.9
o-Xylene	C_8H_{10}	32.4	4.3

Chromatogram RTX-1 5µm 60m x 0.53 mm analytical column



Gas Analysis (2)

Single Ion Mode (SIM) of the mass spectrometer was used to detect 9 common sulphur components in natural gas. Detection limits are in the single digit ppb range.

THT (TetraHydroThiophene) odorant was analysed with an Agilent Technologies 490 PRO micro-GC.

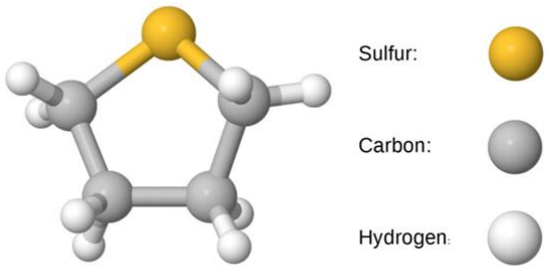
9 common Sulphur components and SIM settings

Component	Symbol	SIM mass (amu)	Retention time (min)
Hydrogen sulfide	H_2S	34	3.99
Carbonyl sulfide	COS	60	4.27
Methyl mercaptan	CH_4S	47	6.00
Ethyl mercaptan	C_2H_6S	62	8.95
Dimethyl sulfide (DMS)	C_2H_6S	62	9.73
Carbon disulfide	CS_2	76	10.88
n-Propyl mercaptan	C_3H_8S	76	14.65
n-Buthyl mercaptan	$C_4H_{10}S$	56	21.25
Tetrahydrothiphene (THT)	C_4H_8S	60	27.11

Components present in initial nitrogen samples (June 2018)

Component	DNV result	Unit
Carbon monoxide	<0.1	ppm
Carbon dioxide	1200	ppm
Ethane	0.6	ppm
Cyclohexane	3.4	ppm
BTEX	75.4	ppm
Other saturated hydrocarbons	40	ppm
Chlorine and organochlorides	*	ppm
Fluoride and organofluorides	*	ppm
Total sulphur (inorganic and organic)	5.5	mg S/Nm^3
Total silicon (including siloxanes)	<0.06	mg Si/Nm^3

*no organic chloride and -fluoride components detected.



tetrahydrothiophene (THT)

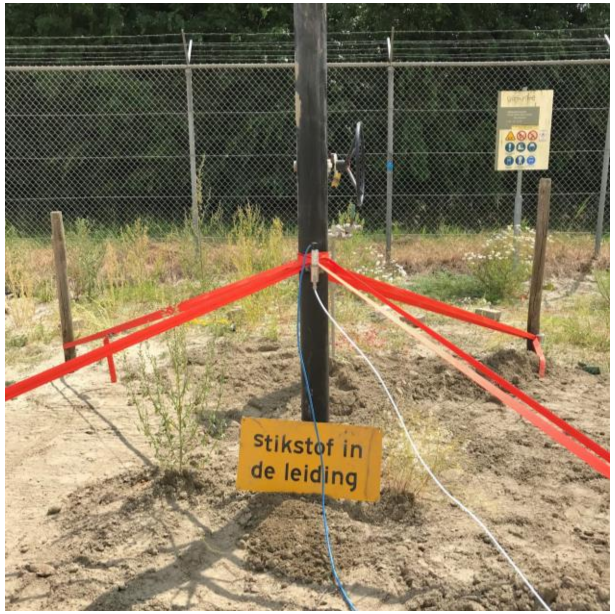
Nitrogen purge (July 2018)

Following an investigation into the residual products in the converted pipeline, which will eventually transport hydrogen, it was found that a number of components have relatively high values. It was decided to purge with nitrogen at one side and to vent it on the other side of the former natural gas pipeline. DNV was asked to monitor this process using a water dewpoint sensor, a flame ionization detector (C_xH_y) and a micro-GC.

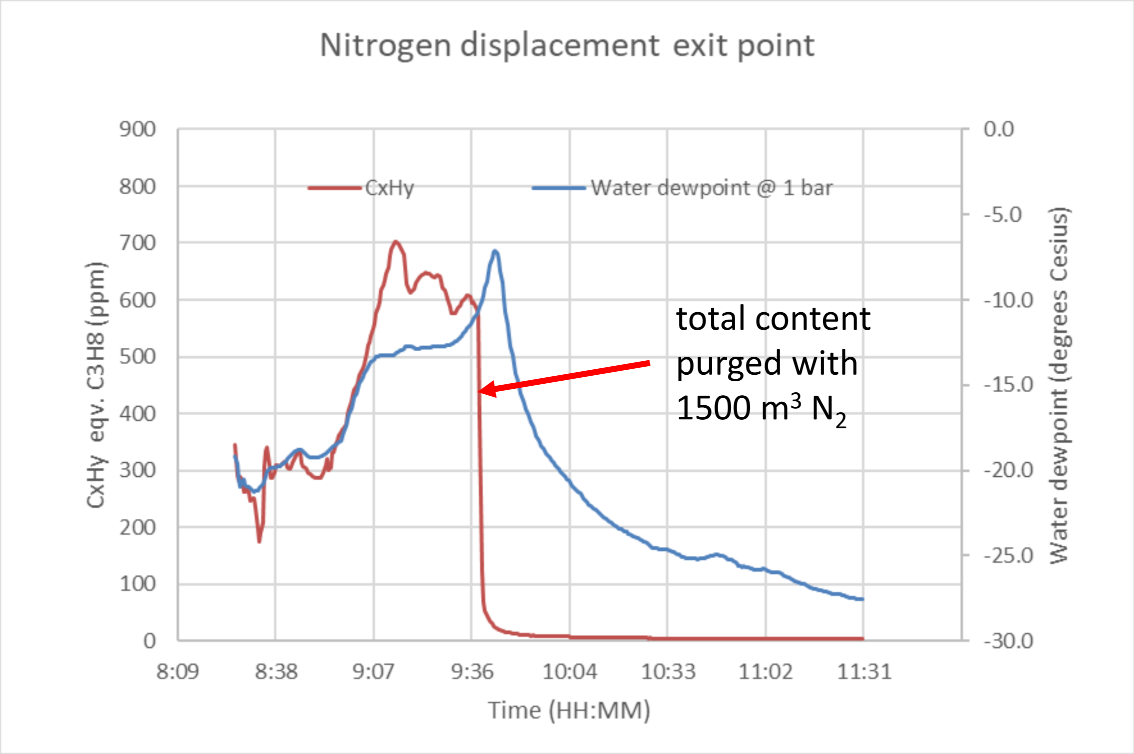
Nitrogen unit WSG

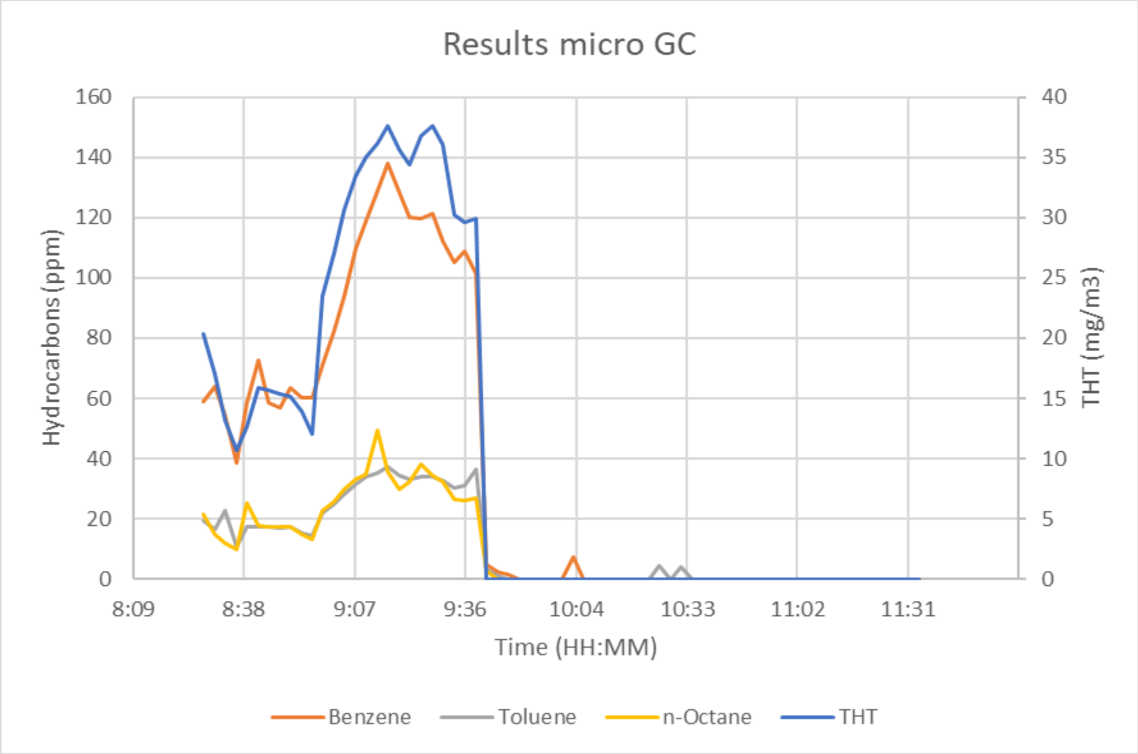
Nitrogen injection DN50 + Coriolis flowmeter

Nitrogen vent DN100 + sampling DNV



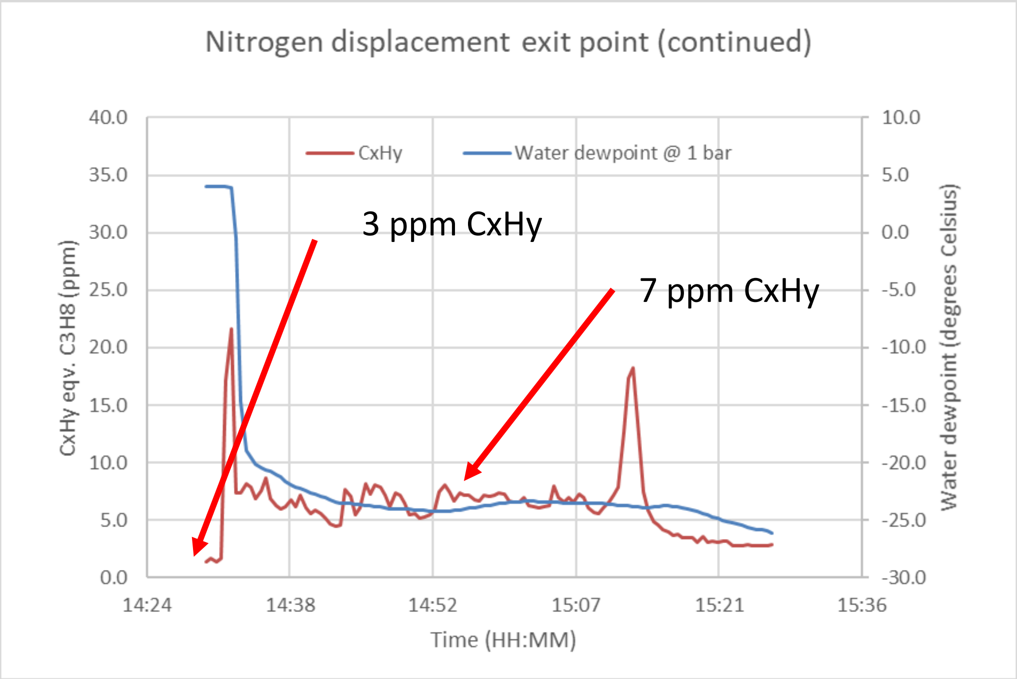
Nitrogen purge results July 2018 (1)





Nitrogen purge results July 2018 (2)

The initially measured high concentrations of contaminants (aromatics and THT) in the nitrogen originated from pores in the inner wall (flow coating) of the former natural gas pipeline. Because the pipeline had been stored under nitrogen for several weeks, the nitrogen was slowly contaminated because of desorption. This same effect could be observed on a shorter time scale after the initial nitrogen displacement. The concentration of hydrocarbons increased from a concentration of 3 ppm to 7 ppm over the entire length of the pipeline within three hours.



Concentrations after (second) nitrogen displacement

Component	Symbol	Concentration in ppb
Hexanes	C_6H_{14}	100
Benzene	C_6H_6	200
Xylenes	C_8H_{10}	300
Octanes	C_8H_{18}	100
THT	C_4H_8S	17.5

Commissioning and monitoring 2018 - 2022

In October 2018 the former natural gas pipeline was commissioned. The purpose was to deliver an oxygen free and clean pipeline. A 16-inch foam pig travelled through the entire pipeline during a final nitrogen purge and it was dry and clean in the pig-receiver. Oxygen concentration was below 1 ppm.

Component	2018 Exit no flow	2019 Exit flow	2020 Exit flow	2020 Entry flow	2022 Exit no flow	2022 Entry no flow	Unit
Carbon dioxide	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	ppm
Oxygen	-	<1.0	8	<1.0	3	<1	ppm
Nitrogen	-	895	1444	1423	601	804	ppm
Cyclohexane	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	ppm
BTEX	0.5	<0.1	<0.1	<0.1	<0.1	<0.1	ppm
Other saturated hydrocarbons	0.2	<0.1	<0.1	<0.1	<0.1	0.2	ppm
Chlorine and organochlorides	*	*	*	*	*	*	ppm
Fluoride and organofluorides	*	*	*	*	*	*	ppm
Total sulphur (inorganic and organic)	0.03	<0.01	<0.01	<0.01	<0.01	<0.01	mg S/Nm^3
Total silicon (including siloxanes)	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	mg Si/Nm^3

**no organic chloride and -fluoride components detected*

Conclusions

1. Initially the natural gas in the 12 km long pipeline was displaced with nitrogen in 2018. After an additional purge in July 2018, the concentration of contaminants decreased very rapidly from 600 ppm C_xH_y to 3 ppm C_xH_y. The initially measured high concentrations of contaminants (aromatics and THT) originated from pores in the inner wall (flow coating) of the former natural gas pipeline. Because the pipeline had been stored under nitrogen for several weeks, the nitrogen was slowly contaminated because of desorption. This same effect could be observed on a shorter time scale after the initial nitrogen displacement. Indeed, the concentration of hydrocarbons increased from a concentration of 3 ppm to 7 ppm over the entire length of the pipeline within three hours.
2. After about five displacements with pure nitrogen in July 2018, the concentrations of almost all contaminants are well below the Hynetwork hydrogen specification.
3. The nitrogen displacement occurred at low pressure conditions (just above atmospheric). The mechanism of desorption is mainly dependent on temperature. Therefore, when the pressure is increased, dilution will occur. In addition, the absolute quantity decreases over time because there is no longer a supply of natural gas components. After commissioning, the pipeline will be deployed with hydrogen at a higher pressure and flow. Under these conditions, the content of all natural gas components will be diluted. It is therefore advised to maintain the pipeline under hydrogen flowing conditions for some time after commissioning.
4. Based on the measurement results in the period 2018 - 2022, it can be concluded that no contaminants/components were found that can be originally related to the former natural gas transport. This applies to both flowing and stationary conditions of the pipeline in question. After all, after a period of standstill, possibly adsorbed components in the inner pipe wall can cause a (temporary) increase in the gas phase.
5. A cleaning protocol has been proposed that consists of five steps.

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