

Experimental study of black powder formation in field TEG solutions

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ABSTRACT

The paper discusses black powder formation in the corrosion experiments with field TEG and lab mixed TEG. TEG samples were collected at the gas receiving facilities and in the TEG dehydration units that delivered gas to a pipeline network. The objective was to determine the corrosion rates and production rate of solids, to better understand the rate controlling mechanisms and to find means to reduce the black powder problem. The experiments were run at 5, 25 and 40 °C, with the test gas consisting of 100 kPa CO₂ and 40 Pa H₂S and the salt content of 100 to 10000 ppm. The test duration varied from 60 to 102 days. Corrosion rates were determined from weight loss measurements and varied in the range 1-30 μm/year. The experiments showed that the corrosion rate increased significantly when solid iron sulfide accumulated on the steel surface and the liquid contained high amounts of dissolved salt.

Key words: Black powder, Corrosion, TEG, CO₂, H₂S

INTRODUCTION

Black powder is a term that describes the particulate materials that collect in gas pipelines.¹⁻³ It can be various types of corrosion products in addition to other contaminants as salts, sand and dirt. The corrosion products (FeS_x, FeCO₃, Fe₃O₄ + other oxides) are formed when the internal steel surface is wetted with a water containing phase with dissolved CO₂, H₂S, organic acids and/or O₂. The composition and the morphology of the products depend on the composition of the liquid phase and the relative concentration of the corrosive gases.

The export gas is usually dried in glycol contactors (see Figure 1) to meet the export gas specification (ref NORSOK M506⁴) before entering the pipeline. The gas will be saturated with the TEG from the glycol contactor and the amount is determined by the operational conditions of the scrubber after the TEG-contactor. TEG will condense as the temperature and pressure of the gas decreases after entering the riser/pipeline, and form a glycol film on the pipe wall.

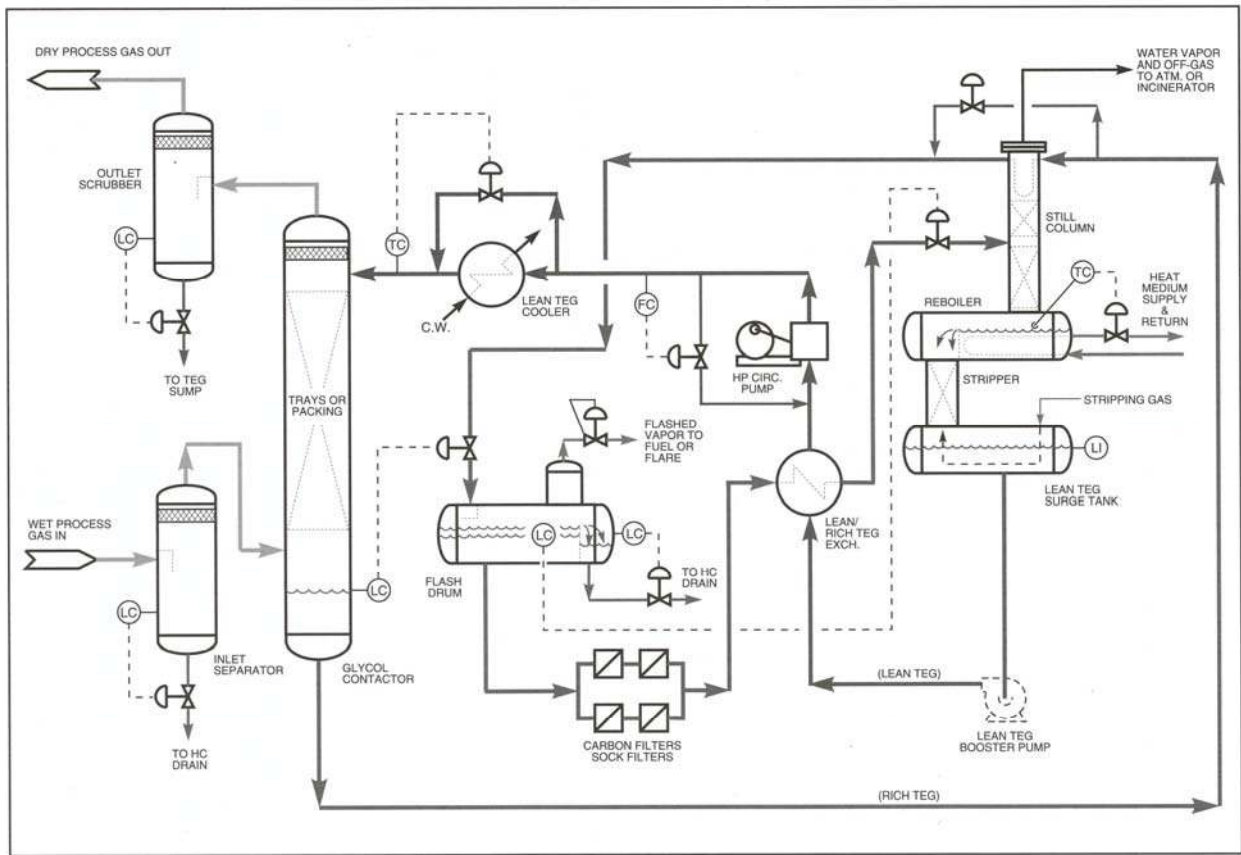


Figure 1: Basic Glycol Dehydration Unit⁵

Glycol is hygroscopic and will extract water from the gas. Simulations with PVTsim⁶ at 5 °C and 15 MPa gives a liquid phase containing 5-10 wt% water when the pipeline is operated within the NORSOK specifications⁴ for dry gas. During operational disturbances the simulations show that the water in the TEG phase may increase to more than 20 wt% at the same temperature and pressure.

The TEG-water mixture is corrosive, although much less corrosive than pure water. Studies reported by DeWaard et al.⁷⁻⁸ (also confirmed in a number of other studies) showed that the corrosion rate in glycol-water mixtures decreases with increasing glycol content and that the effect of MEG, DEG and TEG can be expressed by the empirical glycol correction factor f :

$$\log f = 1.6(\log(W\%)-2) \quad (1)$$

where $W\%$ is the mass percentage of water in the water-glycol mixture. The glycol correction factor f is a multiplier that gives the corrosion rate in the $X\%$ glycol solution when multiplied by the corrosion rate obtained in a glycol-free solution of the same temperature, pH and CO_2 partial pressure:

The glycol factor is < 0.01 in systems with TEG concentrations above 95 wt% and the expected corrosion rates are low (< 0.1 mm/year). Corrosion should therefore not be a problem for the integrity of the pipeline as long as galvanic corrosion and localized attack is not an issue. Corrosion rate as low as 0.001 mm/year, however, can give several tons of corrosion product per year for long pipelines (100-300 km) when the whole surface is wetted and attacked. If the solids are mobilized it can accumulate locally and constrict the pipeline, clog filters, contaminate the sale gas etc.

The motivation for the present study was the finding in a rich gas pipeline that was cleaned by operational pigging after 15 years operation within the specifications for dry gas. A black slurry was

collected in the pig receiver after the pigging operation. Five years later a new field was connected to the pipeline at the same time as the glycol process was optimized. The first operational pigging after the modification caused a lot of problems in the facility plant as the residue now was a powder and not a slurry. Operational pigging was initiated as the pressure changed in the pipeline due to the accumulated powder. The solids from the pig trap were analyzed by XRD and ESEM. The results showed an amorphous material, FeS and probably Fe₉S₈, in addition to magnetite and siderite.

TEG samples were collected at the gas receiving facilities and in the TEG dehydration units that delivered gas to the pipeline network. The paper discusses the results from about 70 corrosion experimental runs with the field TEG and lab mixed TEG. The objective was to determine the corrosion rates and production rate of solids, to better understand the rate controlling mechanisms and to find means to reduce the black powder problem.

EXPERIMENTAL PROCEDURE

Reference test with pure CO₂

X-65 carbon steel sheets (30 cm²) were exposed 14-21 days under semi stagnant conditions in 90, 94 and 98 wt% TEG solutions respectively. The liquid volume to steel surface ratio was 10. There was no stirring, only convection caused by gently bubbling with CO₂. The steel sheets were acid etched just before the exposure as it reduced the likelihood for getting passive films on the steel surfaces.

The corrosion rate was determined by iron counts (Fe²⁺ analysis by photospectrometer) during the exposure and by weight loss after the exposure.

Testing of field TEG with CO₂ and H₂S

Test specimens and test equipment. Disc/cup shaped steel specimens (ID 22 mm and internal height 3 mm) filled with a 2.5 mm thick layer of TEG solution were placed on a plate mounted in a glass cell as shown in see Figure 1. The cell was continuously flushed with CO₂ containing small amounts of H₂S (40 Pa). The total pressure was 100 kPa.

The liquid was added with a syringe after the system was deoxygenated. The steel cup was not completely filled with liquid, but most of the remaining inner wall was wetted, giving an exposed surface area of 5.5 to 5.9 cm² depending on the height of the menisci.

The test specimens were machined from a Ferrite-pearlite X65 pipeline steel and ground with 1000 mesh paper. The composition (wt-%) in addition to Fe was: C (0.08), Si (0.25), Mn (1.54), S (0.001), P (0.019), Cr (0.04), Ni (0.05), V (0.095), Mo (0.01), Cu (0.02), Al (0.038), Sn (0.001), Nb (0.043)

Five test cells were used, two were run at 5 °C, two at 25 °C and one at 40 °C. Each cell could contain up to 20 cups. The test cells were immersed in a thermostatic controlled bath. The flushing gas was bubbled through a liquid layer (similar to the test solution used in the cups) in the bottom of the test cell in order to saturate the gas with water and glycol vapor. Without the pre-saturation of the gas the liquid in the cups would slowly evaporate and eventually dry the test cups.

Three cells (operated at 5, 25 and 40 °C) were opened after 60 days exposure and two (5 and 25 °C) after 102 days.

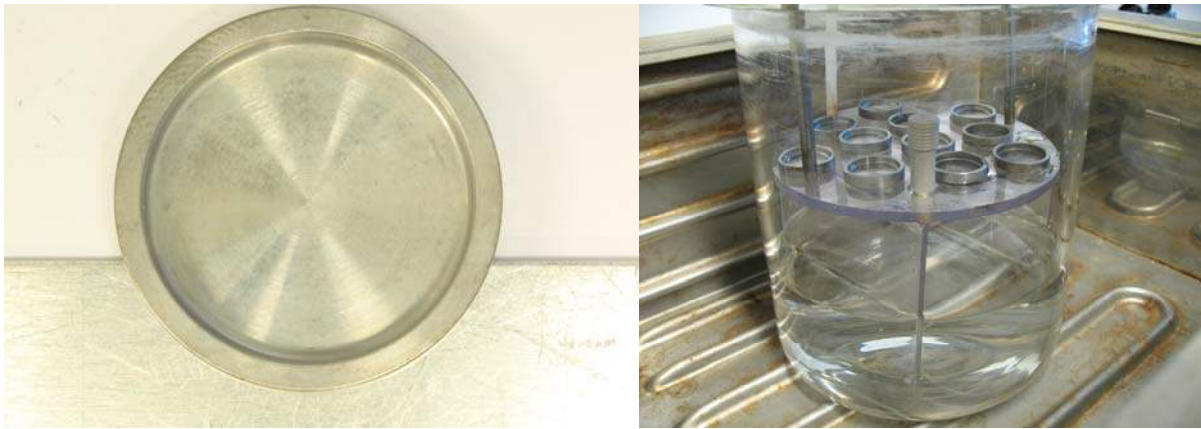


Figure 1: Left: Disc/cup used in the experiments. Right: Test cell with discs

Test solutions: The composition of the test solutions are given in Table 1. The first five solutions were lab mixed 95 wt% TEG (technical grade) added small amount of either HCl or NaOH. Test solution 6 was slurry of TEG and black powder (mainly FeS) collected at the receiving end of the gas pipeline. The solid fraction in the slurry was about 60 wt%. The rest of the solutions were dry (lean) and wet (rich) TEG received from the various TEG dehydration units that deliver gas to the pipeline network feeding the main pipeline.

**Table 1
Composition of test solutions**

No	Sample labeling	Alkalinity mM	TEG wt%	pH (^A)	Cl ⁻ ppm	Br ⁻ Ppm	SO ₄ ²⁻ ppm	Na ⁺ ppm	K ⁺ ppm	Ca ²⁺ ppm	Mg ²⁺ ppm	Fe ²⁺ ppm
Lab mixed solutions												
1	95wt% TEG		95	4.1	<1							
2	95wt% TEG +1 mM HCl		95	1.8	35							
3	95wt% TEG +0.1 mM HCl		95	3.2	3.5							
4	95wt% TEG +1 mM NaOH		95	5			23					
5	95wt% TEG +0.1 mM NaOH		95	4.2			2.3					
TEG slurries, pipeline outlet												
6	FeS particle slurry I	270			102			6700	23	<1	<1	43
TEG from drying units												
7	A, Wet TEG	32.5	≈95	7.7	0	<1	9.4	23	66	36	<1	<2
8	A, Dry TEG	37.0	≈95	8.5	0	<1	7.2	21	38	5	<1	<2
9	B, Wet TEG	8.0	≈98	8.0	36	<1	6.6	31	32	5.5	<1	<2
10	B, Dry TEG	8.3	≈95	8.1	18	<1	4.4	33	34	5.5	<1	<2
11	C, Wet TEG	4.4	≈98	7.1	24	<1	1.2	144	34	7.5	<1	<2
12	D, Wet TEG	2.8	≈95	4.9	959	5	150	350	11	16	49	86
13	E, Wet TEG	1.1	≈95	7.3	7	<1	3	19	18	5.5	<1	3
14	F, Wet TEG	0.9	≈95	8.2	4.7	Low	Low	<10	5	<1	<1	<2
15	G, Wet TEG	40	≈95	9.2	39	Low	Low	<10	32	1.5	<1	<2

^(A)pH measured in the solution before corrosion. The electrode was calibrated with water based buffer solutions

Determination of corrosion products and material loss: The test cups were emptied immediately after exposure, flushed with alcohol and dried. The amount of corrosion products in the removed liquid was determined by iron counts and the corrosion rates were determined from weight loss. The steel cups were weighed before and after the exposure and after the corrosion film was stripped. A small amount of non-corroded metal is removed during the stripping process. The uncertainty in the stripping and the weighing procedure is estimated to be around ± 0.5 mg. Half a mg material loss corresponds to a uniform corrosion rate of $0.6 \mu\text{m/year}$ and $0.35 \mu\text{m/year}$ for the 60 and 102 days exposure, respectively.

The corrosion products were investigated by scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS).

RESULTS

Reference test with pure CO₂

Table 2 summarizes corrosion rates measured in TEG solutions bubbled with pure CO₂. One sample was exposed in each test. The 5 °C experiments were run 21 days and the 25 and 40 °C experiments 14 days. Very little corrosion film formed on the steel surfaces and iron counts indicated that the corrosion rate stabilized after a few days. The corrosion rates (assuming uniform corrosion rates) given in the table are based on iron counts the last week of the exposure.

Table 2
Corrosion rates measured in TEG/water and pure CO₂

TEG wt%	Corrosion rate, $\mu\text{m/year}$		
	Temp: 5 °C	Temp: 25 °C	Temp: 40 °C
90	5	15	20
94	3	12	14
98	3	5	10

Testing of field TEG with CO₂ and H₂S

Table 3 and Figure 2 summarize the measured corrosion rates after 60 and 102 days corrosion. The corrosion rates measured in the 15 different test environments did not vary much except for the FeS slurry samples and solution D that contained the highest concentration of iron and salt. For most of the solutions, it is seen that the material loss corrosion rate was slightly reduced in the long duration tests.

The amount of particles and dissolved corrosion products that was removed when the steel cups were emptied and flushed with ethanol is given in Table 4 and Figure 3. The numbers represent only the “new” corrosion products and do not include the particles and dissolved corrosion products that were added in the cups in the beginning of the exposure. The amount of mobile corrosion products not attached to the steel surface varied a lot. It should be noted that although the amount produced per time unit is less after 102 days than 60 days, the actual amount is higher after 102 days.

Table 3
Corrosion rates measured after 60 and 102 days exposure

		Mass loss corrosion rate, $\mu\text{m}/\text{year}$					
		Temperature		5 °C		40 °C	
		Duration		60 d	102 d	60 d	102 d
				$\mu\text{m}/\text{y}$	$\mu\text{m}/\text{y}$	$\mu\text{m}/\text{y}$	$\mu\text{m}/\text{y}$
No	Lab mixed samples						
1	95wt% TEG	1.3	1.1	0.6	1.3	2.0	
2	95wt% TEG +1 mM HCl	2.2	1.8	0.9	1.7	3.9	
3	95wt% TEG +0.1 mM HCl	1.1	1.1	0.9	1.0	2.0	
4	95wt% TEG +1 mM NaOH			1.4	1.9		
5	95wt% TEG +0.1 mM NaOH			1.6	1.8		
	TEG slurries from pipeline outlet						
6	FeS slurry, parallel I	13.2	11	15.8	10.8	23.7	
6	FeS slurry, parallel II	16.9	13.2	10.8	9.1	23.5	
	TEG from drying units						
7	A, Wet TEG	0.9	1.2	0.4	0.9	1.1	
8	A, Dry TEG	1.7	1.1	0.7	0.6	0.7	
9	B, Wet TEG	1.7	1.3	0.9	0.9	2.0	
10	B, Dry TEG	1.3	1.1	0.7	0.8	1.7	
11	C, Wet TEG	0.7	1.4	1.3	1.3	2.2	
12	D, Wet TEG	17.6	15.2	23.7	20.0	30.1	
13	E, Wet TEG	1.7	1.4	1.1	0.8	2.2	
14	F, Wet TEG,	1.3	0.9	0.9	0.9	1.1	
15	G, Wet TEG	1.5	0.6	0.6	0.8	0.9	

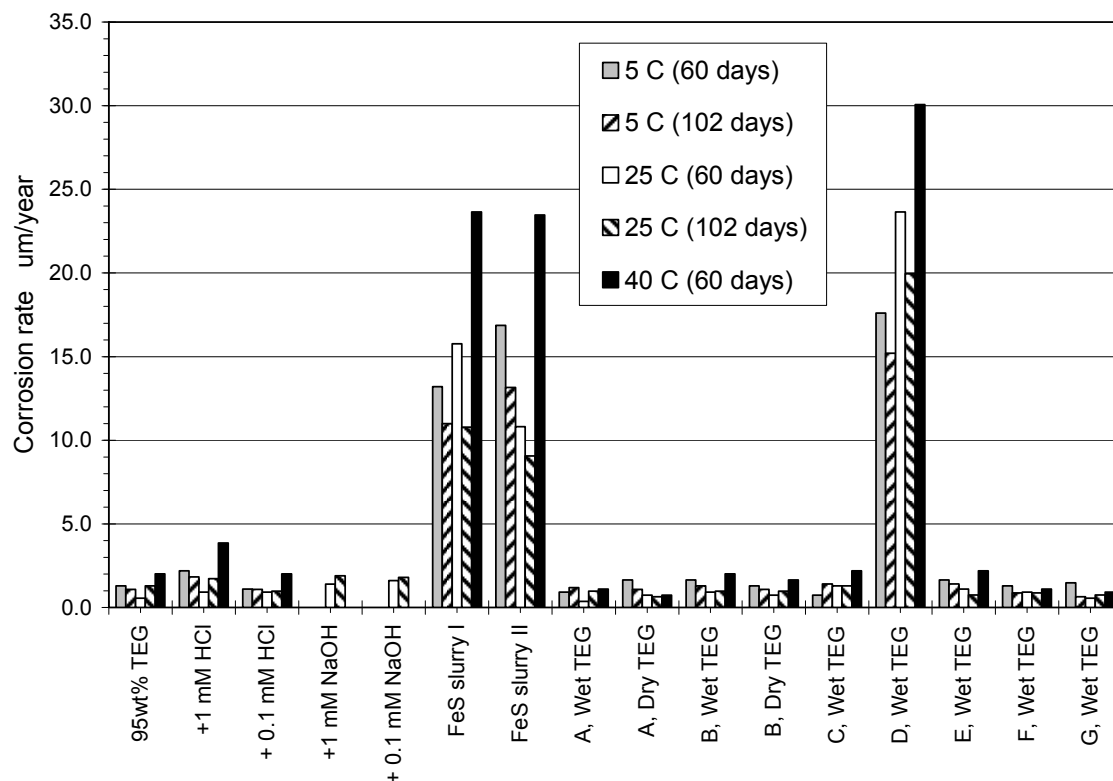


Figure 2: Measured corrosion rates, see Table 3

Table 4
Dissolved and solid corrosion products that did not stick to the steel surface

No	Lab mixed samples	Temperature		5 °C		25 °C		40 °C	
		Duration		60 d	102 d	60 d	102 d	60 d	102 d
				g/m ² /y	g/m ² /y	g/m ² /y	g/m ² /y	g/m ² /y	g/m ² /y
1	95wt% TEG			<0.5	0.7	<0.5	0.6	<0.5	
2	95wt% TEG +1 mM HCl			2.0	2.6	<0.5	1.0	2.0	
3	95wt% TEG +0.1 mM HCl			<0.5	<0.5	<0.5	<0.5	<0.5	
4	95wt% TEG +1 mM NaOH					2.0	<0.5		
5	95wt% TEG +0.1 mM NaOH					1.2	<0.5		
TEG slurries from pipeline outlet									
6	FeS slurry, parallel I			222	157	146	106	304	
6	FeS slurry, parallel II			176	130	208	128	307	
TEG from drying units									
7	A, Wet TEG			2.7	1.6	2.4	1.7	3.9	
8	A, Dry TEG			3.0	1.6	2.8	1.5	2.9	
9	B, Wet TEG			1.8	1.0	1.8	1.0	2.4	
10	B, Dry TEG			1.9	1.1	1.9	1.4	2.6	
11	C, Wet TEG			1.7	1.1	0.9	1.0	2.3	
12	D, Wet TEG			285.8	181.3	226.2	169.3	281.4	
13	E, Wet TEG			0.8	0.6	<0.5	0.6	0.8	
14	F, Wet TEG,			<0.5	<0.5	<0.5	<0.5	<0.5	
15	G, Wet TEG			1.0	0.8		0.6	3.5	

SEM and EDS analyses showed that the steel was covered with a thin layer of iron sulfide and a lot of small particles, 1-2 μm . The particles were found both in the liquid phase and loosely adhered to the

steel surface. Most of the particles were removed when the steel cups were flushed with ethanol after the exposure. Examples of particles that were attached to the surface after gently flushing are shown in Figure 4 and surfaces with removed particles are shown in Figure 5. It was interesting to note that the particles adhered better in the lab mixed solutions than in TEG solutions from the field. When the particles were removed some of the surface film was apparently also removed leaving the craters seen in Figure 5.

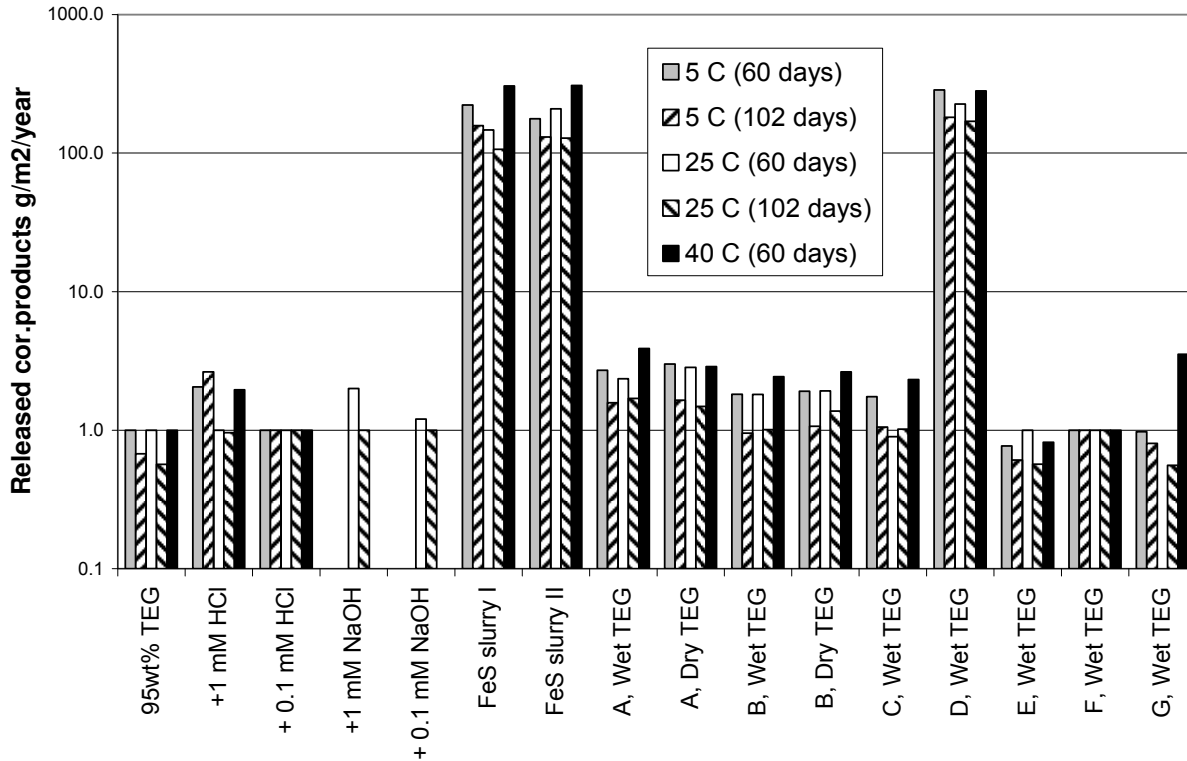


Figure 3: Mobile corrosion products, see Table 4

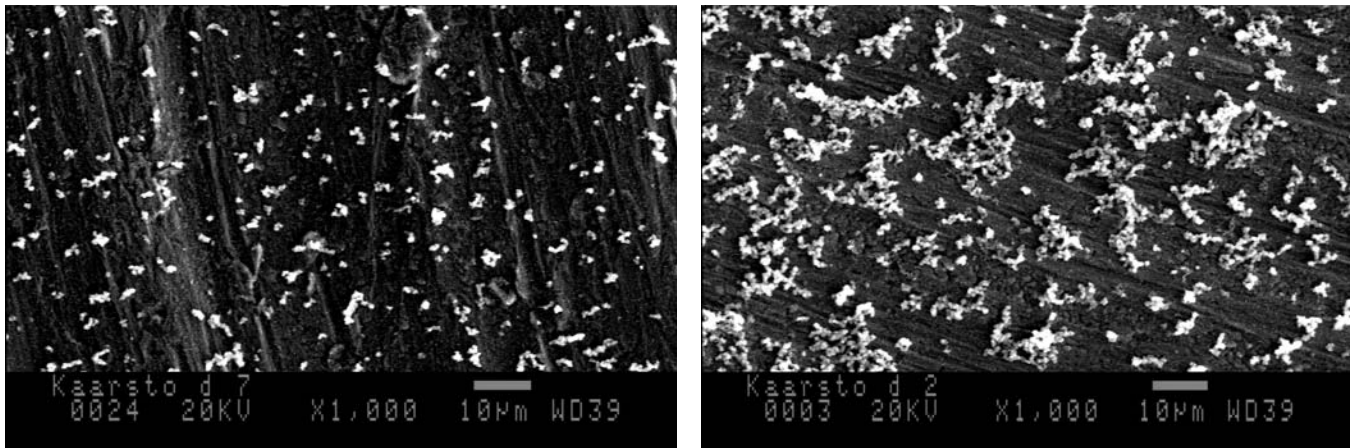


Figure 4: Loosely attached particles formed in 95 wt% TEG with 0.1 mM NaOH after 60 days (left) and 102 days (right) exposure

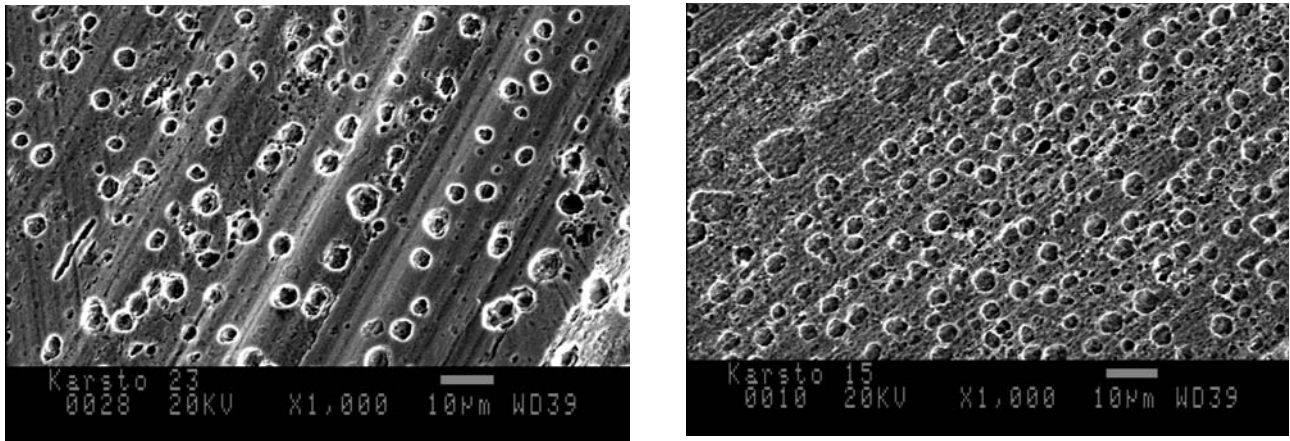


Figure 5: Surface appearance after exposure and flushing with ethanol. Left: solution G, 102 days exposure, 25 °C. Right: solution A Wet, 102 days exposure, 25 °C

DISCUSSION / CONCLUSIONS

Corrosion rates in TEG solutions

The measured corrosion rates with 95 wt% TEG and pure CO₂ are in the same range as estimated with NORSOK M506 model that uses the glycol factor (equation 1) suggested by de Ward, see Figure 6. It should be noted that the NORSOK model apply the glycol factor up to 95 wt % only and then uses the 95 wt% factor between 95 and 100 wt%. The curves in Figure 6 show the estimated corrosion rates when the glycol factor is used in the whole TEG range.

The corrosion rates in field TEG solutions varied from less than 1 to about 30 µm/year. Only a few cups corroded more than 2 µm/year. This is less than the corrosion rate measured in 90-98 wt% TEG and pure CO₂. The CO₂ experiments were carried out with a higher volume/surface ratio (10) than the CO₂/H₂S experiments (0.2). A low volume/surface ratio gives rapid supersaturation of corrosion products and can facilitate the formation of corrosion product films. The lower corrosion rates in the CO₂/H₂S experiments indicate that the iron sulfide dominated corrosion film formed fast and gave reasonable good protection. Localized attack or pitting attack was not seen.

The corrosion rate was much higher in the cups filled with field TEG-solutions that contained large amount of solid FeS and large amount of dissolved salt, namely samples 6 and 12 in Table 3. The accumulation of iron sulfide particles might increase the cathodic area, facilitate the cathodic reaction and thus increase the corrosion rate. When the salt content is high (as for the wet TEG D test), the increased corrosion rate might be attributed to increased conductivity giving larger galvanic effects and/or destabilization of the protective films. It is difficult to conclude which of the proposed mechanisms is dominating.

When experiments are run with freshly ground steel samples a higher corrosion rate is expected in the start of the exposure until a protective layer is formed. If pits are formed, or a conductive layer of corrosion products accumulate on the surface giving under deposit corrosion (UDC), the corrosion rate might increase again with time. When the corrosion rate is measured with weight loss, as in the present project, the increase will not be seen unless the material loss in the second period is higher than the material loss in the first period of the exposure. A slight increase in the corrosion rate with time was registered in solutions 1-5 (25 °C), A-wet TEG (5 °C) and C-wet TEG (5 °C). It might also have been an increase in the other solutions, but this increase was below the detection limit.

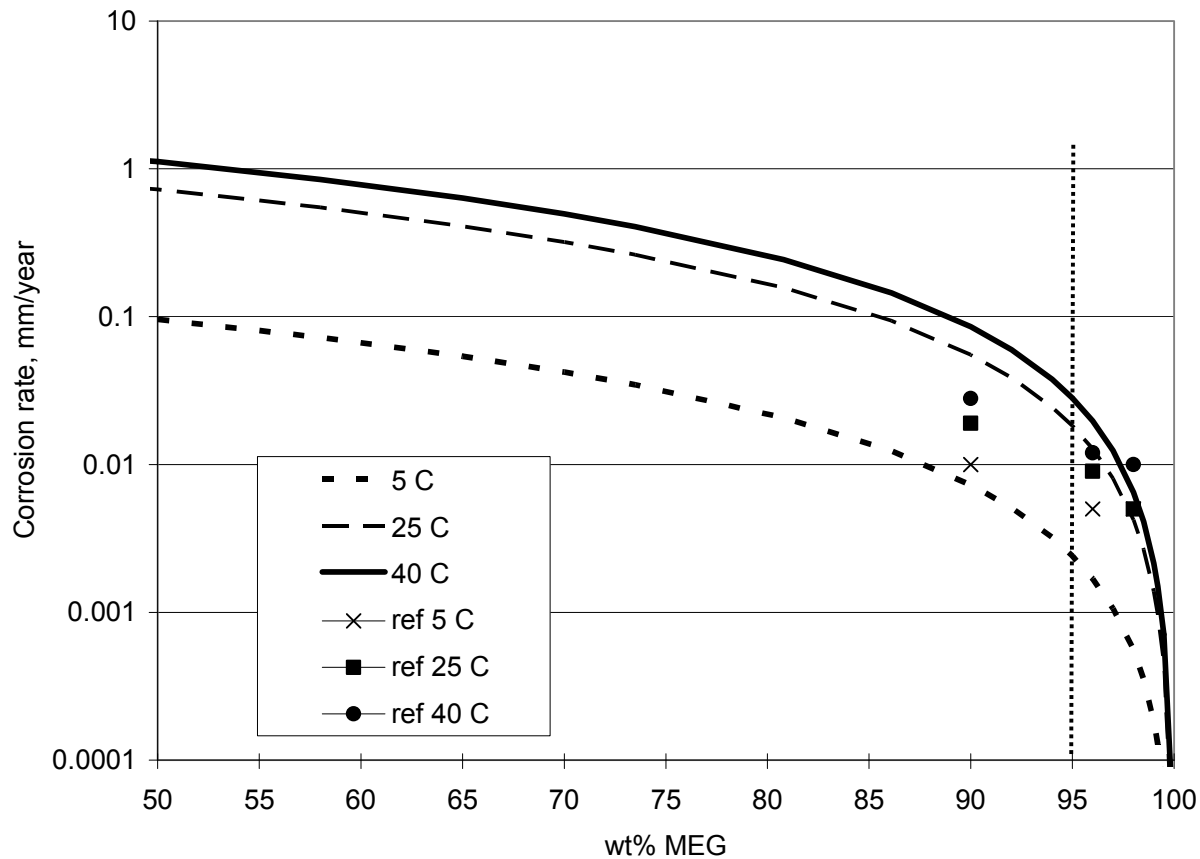


Figure 6: Corrosion rates estimated with the Norsok M 506 model and the results obtained in the reference corrosion tests

Effect of changing conditions

If the H_2S content in the gas is reduced, the corrosion rate can be governed by CO_2 corrosion and the formation of iron carbonate. Under such conditions it is expected higher corrosion rates (same range as shown in Figure 6) until a protective layer is formed. The H_2S concentration where the stability and formation of the corrosion film changes from FeS to $FeCO_3$ is not known for the TEG system, but it is expected to be much lower than the H_2S concentration used in the present experiments. Without any alkalinity in the TEG the dissolved iron concentration can be high (> 100 ppm) if the H_2S content is below the limit for FeS formation. The dissolved iron will precipitate when the H_2S content increases and/or the temperature is increased. This has been seen in other glycol systems when the temperature is increased. Increasing the pH slightly can reduce the corrosion rate and the amount of dissolved iron under these conditions.⁹⁻¹⁰

The amount of liquid in the pipe will depend on the amount of TEG carry over, the dew point and the heating/cooling of the pipeline. In periods with lower dew point, part of the liquid may evaporate and give a higher salt content in the remaining liquid. The possible detrimental effect of dissolved salt can then become worse. If salt turns out to be a problem the corrosion rate and the formation rate of black powder can be reduced if the pipe is "washed" with glycol. In order to ensure a low corrosion rate and low solubility of dissolved corrosion product it is recommended to add small amount of organic base to the washing glycol as higher pH enhances formation of protective surface films like $FeCO_3$.⁹⁻¹⁰

Without pipeline cleaning, the production of solid products containing FeS might accelerate due to salt accumulation and under deposit corrosion.¹¹ Cleaning the pipeline will then be a compromise between the cost of increased dust handling and the cost of cleaning.

Particle formation in the pipeline

The experiments have shown that iron sulfide formed in all test environments. The corrosion films were thin and a large fraction of the corroded iron formed particles on top of the film. The particles were loosely adhered and most of them could be easily removed when the samples were rinsed with alcohol. The typical particle size was 1-2 μm . The size of the particles did not increase significantly going from 60 to 102 days exposure. The number of particles however was larger after 102 days.

The particles in the liquid phase might be transported to the gas phase when liquid droplets are entrained by the gas. When the gas is heated the droplets can evaporate and the particles will remain in the gas as fine dust. It is expected that part of the pipeline surface can alternate between dry and wet depending on production rate and changes in temperature profile. The particles are assumed to be more easily detached from the surface when the pipe wall is dry.

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REFERENCES

1. M. M. Trabulsi, "Black powder in sales gas transmission pipelines," *Global Pipeline Monthly*, 3 (8) (2007).
2. A. M. Sherik, S. R. Zaidi, E. V. Tuzan, and J. P. Perez, "Black powder in gas transmission systems," *CORROSION/2008*, paper no. 08415 (Houston, TX: NACE International, 2008).
3. A. M. Sherik, J. P. Perez, S. P. Jutaily, and A. I. Abdulhadi, "Composition, Source and Formation mechanisms of black powder in sales gas transmission pipelines," *Eurocorr 2007*, September (2007)
4. NORSOK M506.
<http://www.standard.no/en/Sectors/Petroleum/NORSOK-Standard-Categories/M-Material/M-5061/>
5. John M. Campbell: "Gas Conditioning and Processing vol. 2: The Equipment Modules", 8th ed. 1966-2000
6. Commercial software package from Calsep, <http://www.pvtsim.com/index.aspx>
7. DeWaard, C.; Lotz, U.; Milliams, D. E.: "Predictive Model For CO₂ Corrosion Engineering In Wet Natural Gas Pipelines", *Corrosion 91*, Paper No 577, NACE, Houston, 1991.
8. DeWaard,C.; Lotz,U.; Dugstad,A.: "Effect of Liquid Flow velocity on CO₂ Corrosion. A Semi-Empirical model", *Corrosion 95*, Paper No. 128, NACE, Houston 1995.
9. S. Olsen, O. Lunde and A. Dugstad: pH-Stabilization in the Troll Gas-Condensate Pipelines. *CORROSION/99*, Paper No. 19, San Antonio, 25-30 April 1999.

10. A. Dugstad and P. E. Drønen: Efficient Corrosion Control of Gas Condensate Pipelines by pH-Stabilisation. CORROSION/99, Paper No. 20, San Antonio, 25-30 April 1999.
- 11 M. Achour, J. Kolts, P. Humble, R. Hudgins: "Experimental Evaluation of Corrosion Inhibitor Performance in Presence of Iron Sulfide in CO₂/H₂S Environment", CORROSION/2008, paper no. 08415 (Houston, TX: NACE International, 2008).