

Sour Under-Deposit Corrosion with Different Iron Sulfides

J. Kvarekvål and M. Tjelta
Institute for Energy Technology
P.O. Box 40, N-2027 Kjeller, Norway
jon.kvarekval@ife.no

ABSTRACT

Under-deposit corrosion experiments were performed to study the corrosive effects of different types/polymorphs of iron sulfides; Pyrite, pyrrhotite and a troilite/pyrrhotite mixture, which were all commercially available, and mackinawite synthesized in-house by corrosion of steel shavings. Prior to testing the commercial iron sulfides were ground in a ball mill under oxygen-free atmosphere to ensure active particle surfaces. The H₂S and CO₂ partial pressures were 10 bar each, the temperature was 25 °C, and the test solutions consisted of high-salinity brine (100 g/L NaCl, 150 ppm bicarbonate). The duration of the tests was around 14 days. Both weight loss corrosion and localized corrosion data were obtained. The entire surfaces of the exposed coupons were scanned with a 3D profilometer, obtaining detailed data on localized corrosion morphology and pit depths. The different iron sulfide deposits exhibited different effects on both weight loss and localized corrosion. The experimental results, and various properties of iron sulfide deposits affecting the corrosion behavior, are discussed on the background of available literature.

Key words: sour corrosion, under-deposit corrosion, galvanic corrosion, H₂S, iron sulphide

INTRODUCTION

The occurrence of under-deposit corrosion (UDC) in the oil and gas industry is mainly confined to stagnant or low-flow regions of production and transmission lines, where the local conditions are favorable for the build-up of surface deposits. UDC with iron sulfide deposits has been identified as a particularly challenging problem, as FeS deposits can increase corrosion rates by limiting inhibitor availability at the steel surface and acting as a high area cathode. Several papers have pointed out that deposits and suspensions of iron sulfide particles can accelerate corrosion, give more severe localized corrosion than inert deposits (e.g. sand, clays), and reduce the effect of corrosion inhibitors [1-10].

In order to increase the understanding of iron sulfide polymorphism on sour under-deposit corrosion, UDC tests with different types of iron sulfides was performed as part of a recent JIP to study the corrosive effects of different types of iron sulfides; commercial pyrite, pyrrhotite, “FeS” (a troilite/pyrrhotite mixture) and freshly synthesized mackinawite.

EXPERIMENTAL

Four UDC experiments with different iron sulphides were carried out in Hastelloy[†] autoclaves. The total volume of each autoclave was 2 litres, and a filling level of 75% was used (1.5 litres of test solution). The test conditions are given in Table 1. A synthetic formation water with 100 g/L NaCl and 0.15 g/L HCO₃ was used as test solution. The initial pH value of 3.6 was measured for these conditions. Three test coupons were exposed in each experiment; one without iron sulfide deposit, one with a 0.3 mm thick deposit layer and one with 4 mm deposit.

Table 1
Experimental parameters for the UDC experiments.

Test ID	Temp. (°C)	H ₂ S (bar)	CO ₂ (bar)	NaCl (g/L)	NaHCO ₃ (g/L)	Deposit	Exp.time (days)
1	25	10	10	100	0.21	“FeS” (commercial troilite/pyrrhotite mix)	14
2	25	10	10	100	0.21	Pyrrhotite. (commercial)	14
3	25	10	10	100	0.21	Pyrite (commercial)	14
4	25	10	10	100	0.21	Mackinawite (fresh synthesized)	15

The iron sulfide deposits were milled with a planetary mill placed in a nitrogen filled glove box (see Figure 1) in order to achieve roughly the same particle size distribution and to obtain fresh (non-oxidized) particle surfaces. The mackinawite deposits were freshly produced by corrosion of steel shavings and were applied without further treatment. Samples with deposits was prepared in a N₂ filled glove box and taken directly to the autoclaves where flushing with nitrogen started immediately.

The test coupons were made of sour service certified UNS K03014 carbon steel with dimensions Ø 24 mm x 3 mm. The elemental composition of the steel is given in Table 2. The exposed surface area was 11.3 cm². All test coupons were mounted horizontally in PTFE holders. 2-3 coupons, of which one was a weight loss corrosion coupon, were exposed in each experiment. The ratio between the test solution volume and exposed surface area was typically 50-75 mL/cm². The autoclaves and coupon holders are shown in Figure 2. The target H₂S and CO₂ partial pressures were achieved by loading and stabilizing with H₂S, and then adding CO₂.

After exposure the test coupons were stored in a dry N₂ atmosphere awaiting further processing. Prior to weight loss measurements and surface profilometry the coupons were stripped by ultrasonic cleaning in Multitreat 5537[†] sulfide solvent (active ingredient: Tetrakis hydroxymethyl phosphonium sulfate). After stripping the test coupons were scanned with a Nanovea ST400[†] optical pen profilometer, providing surface profiles for the entire exposed surface area of each

[†] Trade Name

coupon. An optical pen with a vertical range of 2 mm and resolution of 0.3 μm was used. The raw profiles were post-processed with Mountain Professional 3D software[†] to obtain pit counts, maximum pit depths and distribution of surface area on different depths.

Selected coupons were studied by X-ray diffraction (XRD), both with the outer layer intact and with the outer layer wiped off. To avoid unwanted exposure to oxygen the test coupons were loaded onto a closed dome-shaped sample holder in the N_2 -filled glove box.

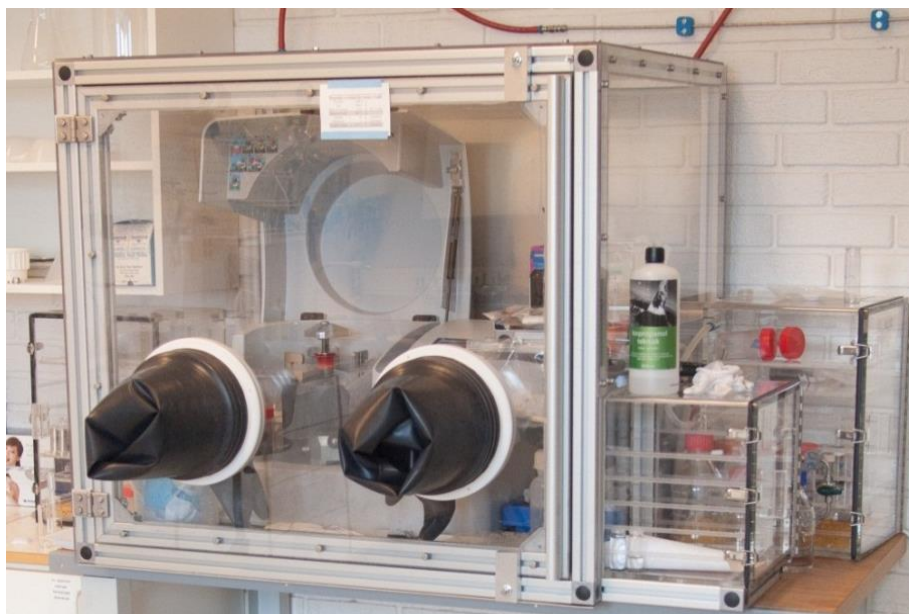


Figure 1: Photo of glove box for milling and preparation of iron sulfide samples



Figure 2: Hastelloy autoclaves (left), sample holder with coupons (right).

Table 12

Elemental composition of the sour service certified pipeline steel used for test coupons.

Steel	C	Si	Mn	S	P	Cr	Ni	V	Mo	Cu	Al	Sn	Nb
UNS K03014	0.06	0.26	1.05	0.001	0.01	0.02	0.26	0.048	0.01	0.01	0.029	0.003	0.047

RESULTS AND DISCUSSION

As described in the previous section four experiments were carried to investigate the effects of different amounts and types of iron sulfides on under-deposit corrosion. A summary of the results is given in Table 3. Average weight loss corrosion rates and pit measurements were obtained for all coupons. The maximum penetration rates ("Max CR") are based on the deepest pit measured by 3D profilometry, and is an average rate over the duration of the experiment.

Table 3
Summary of results for the UDC experiments.

Exp ID	Deposit	Avg CR (mm/y)	Max pit depth (um)	Max CR (mm/y)
1	-	0.63	275	7.17
	0.3 mm FeS	0.95	160	4.17
	4 mm FeS	1.99	259	6.75
2	-	0.35	196	5.09
	0.3 mm pyrrhotite	0.77	150	3.90
	4 mm pyrrhotite	1.43	196	5.09
3	-	0.31	84	2.18
	0.3 mm pyrite	0.48	136	3.52
	4 mm pyrite	0.50	283	7.33
4	-	0.24	125	3.04
	0.3 mm mackinawite	0.87	200	4.87
	4 mm mackinawite	0.38	170	4.14

Figure 3 shows the average corrosion rates for all iron sulfide types plotted against layer thickness. The corrosion rates with troilite/pyrrhotite and pyrrhotite deposits increased with increasing layer thickness, as expected when the galvanic effect of cathodically active iron sulfides is predominant. For pyrite and mackinawite deposits the behavior was different, inasmuch as the corrosion rates increased from 0 to 0.3 mm deposit, but remained constant (pyrite) or decreased (mackinawite) when the layer thickness increased to 4 mm. It is possible that the low corrosion rates under pyrite are due to its low activity for the cathodic reactions, which results in a comparatively small galvanic effect. Mackinawite, on the other hand, was expected to be more active. The reduced corrosion rate for the 4 mm mackinawite layer may be due to local dissolution and precipitation formed a quite compact deposit layer which acted as a barrier against mass