



Condensation corrosion of carbon steel at low to moderate surface temperature and iron carbonate precipitation kinetics



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ABSTRACT

This study investigates the influence of surface temperature and droplet retention time (DRT) on the corrosion rate, FeCO₃ supersaturation, and scaling tendency of carbon steel exposed to water condensation. This corrosion phenomenon is also known as top of the line corrosion (TLC). TLC is found to be governed by surface temperature irrespective of water condensation rates (WCR) at low surface temperature (15 °C). The results also demonstrate that the DRT directly influences FeCO₃ supersaturation and scale formation. A new kinetic constant for the calculation of FeCO₃ precipitation rate under condensing condition at the top of the line is proposed.

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1. Introduction

Corrosion due to water condensation commonly called top-of-the-line corrosion (TLC) occurs in wet gas transportation pipelines operating in stratified flow. Internal corrosion occurs at the upper portion (between 10–2 o'clock positions) where water condenses as a result of temperature difference between the outside environment and the process fluid [1–3]. Dissolved gases such as CO₂, H₂S and volatile organic acids are the prime corrosive constituents of the condensed liquid corroding the inner steel surface due to their acidic nature [4]. Since its discovery in 1960s, extensive laboratory studies and field data identified water condensation rate (WCR), gas temperature (T_g), gas flow rate, partial pressure of acid gases and the presence of organic acids as the controlling factors of TLC [4–9]. However, the most influential and interrelated factors in TLC are WCR, T_g and inner wall temperature or surface temperature (T_s) [10]. It can be anticipated that distinguishing the roles of each parameter could lead to a better understanding and an improvement of prediction models.

Literature has been focusing on the effect of WCR as it is considered to be the dominant parameter determining TLC severity. The critical WCR was estimated to be between 0.15 mL m⁻² s⁻¹ to

0.25 mL m⁻² s⁻¹ in low organic acid environment [10]. Wide ranges of WCR from 0.001 mL m⁻² s⁻¹ to 2.25 mL m⁻² s⁻¹ have been studied [8,10–16]. The direct proportional relationship between WCR and TLC rates has been reported. This is due to the constant replenishment of freshly condensed water prevents the condensed film to be saturated with FeCO₃.

It is apparent that WCR determines the droplet retention time (DRT)—the time at which a water droplet remains in contact with a steel surface before detaching due to gravity. Though the DRT is inversely proportional to WCR, the WCR only provides hypothetical droplet longevity instead of the exact duration. Hence, DRT is important information and may explain TLC mechanism since the water chemistry of a droplet continuously changes with time. Pojtanabuntoeng *et al.* observed the condensation pattern in water-hydrocarbon co-condensation system using a borescope but the longevity of droplet at different condensation rate was not reported [17].

Two dominant reactions; i.e. iron dissolution and iron carbonate precipitation, occur adjacent to the steel surface while undergo corrosion in CO₂ environment [18,19]. Therefore, the thermodynamics and kinetics of both reactions would be governed by T_s rather than T_g . Yet, most studies as well as prediction models addressed the TLC phenomenon as a function of T_g with little attention to T_s [7,20,21]. This is because WCR is assumed to be the governing parameter controlled by T_g .

For example, Nyborg and Dugstad developed an empirical model to calculate sweet TLC rate based on T_g , partial pressure of CO₂,

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and WCR excluding the effect of T_s [7]. According to the model, TLC rate increased from 0.03 mm y^{-1} to 0.14 mm y^{-1} when T_g increased from 30°C to 90°C as a result of an increasing condensation rate. A more advanced TLC prediction model determines TLC rate by taking into account the effect of T_g , CO_2 partial pressure, gas velocity, condensation rate, and acetic acid (HAc) concentration. T_s is calculated implicitly through heat and mass transfer across the pipe wall [9].

The effect of the outer pipe wall temperature on TLC ranging from 5°C to 90°C has been investigated [10,14,20,22]. For instance, Asher et al. reported the effect of pipe wall temperature on TLC based on the mechanistic model and compared it with experimental results at a constant condensation rate of $0.1 \text{ mL m}^{-2} \text{ s}^{-1}$. The study reported a declining trend of TLC rate with increasing wall temperature from 25°C to 90°C [10]. However, TLC scenario at low pipe wall temperature was reported by Qin et al. [22]. In this study, at a constant T_g of 25°C , TLC rates decreased slightly with an increasing wall temperature from 5°C to 15°C . The authors attributed their results to the slow electrochemical reaction kinetics at low temperature. With increasing temperature to 20°C , corrosion rate decreased sharply due to low condensation rate combined with higher tendency of scale formation. It should be noted also that the experimental design applied in this study might produce an unrealistic condensation pattern where the condensed liquids glided vertically from top to bottom on a rotating flat samples instead of forming droplets.

Additionally, limited electrolyte at the top of the line (TOL) challenges the use of conventional electrochemical measurements and it has not been reported in open literature. The measurement of TLC rate has been relied on weight loss method. This method provides an integrated corrosion rate over a long period of exposure and may not capture the continuous changes due to corrosion and scale formation processes at TOL surface. The competitive effect of these two phenomena can be best understood by an instantaneous monitoring of TLC rates and the water chemistry of the condensed water.

This study presents a new design of the TLC setup that is capable of measuring real T_s and *in-situ* collection and analysis of condensed water for its chemistry. With this new setup, the influences of the two interrelated parameters on sweet TLC; i.e. WCR and T_s , are differentiated at low to moderate surface temperatures. Additionally, the thermodynamic and kinetic of FeCO_3 scale formation at TOL are discussed based on DRT and water chemistry of the condensed liquid.

2. Experimental

2.1. Test material

A 1030 carbon steel rod (carbon 0.30%, manganese 0.75%, silicon 0.25%, phosphorous 0.04%, sulphur 0.04% and iron balance) was used as a sample in this study. The 20 mm diameter steel rod was cut into 16 mm long cylindrical samples. After an initial polishing with 600 grit silicon carbide paper and rinsing with deionized (DI) water and ethanol, the samples were electro-coated with cationic epoxy (Powercron™ 6000CX) leaving one circular surface exposed for experiments. A 1.5 mm diameter hole was drilled 10 mm deep from the side of the sample just 1 mm above the exposed surface for inserting the surface temperature probe.

2.2. Experimental procedure

A schematic diagram of TLC set-up is shown in Fig. 1. The exposed surface was polished with silicon carbide paper to 1200 grit surface finish, cleaned with DI water and ethanol, and dried

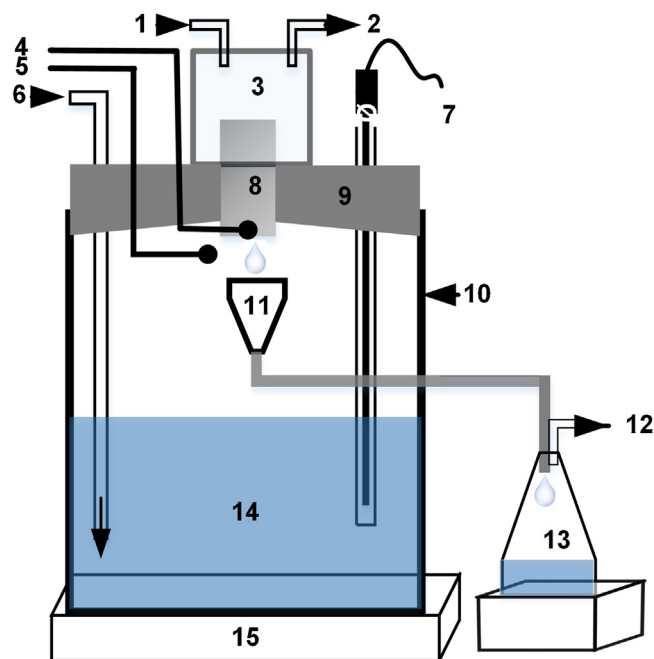


Fig. 1. Schematic of top-of-the-line corrosion (TLC) setup; 1. Cooling water inlet, 2. Cooling water outlet, 3. Stainless steel cooling chamber, 4. Surface temperature probe, 5. Gas temperature probe, 6. CO_2 inlet, 7. Thermocouple, 8. Carbon steel sample, 9. Polyethylene terephthalate lid, 10. Glass vessel of 2 L volume, 11. Condensate collector, 12. CO_2 outlet, 13. Condensate reservoir, 14. High purity water, 15. Heater.

with oil-free compressed air. The prepared carbon steel sample was weighed in an analytical balance which has a resolution of 0.1 mg. It was then inserted into the polyethylene terephthalate (PET) lid in such a way that the top coated portion was suspended into the cooling chamber and the bared portion was exposed to the corrosive environment. The bottom portion of the PET lid was machined at an angle of around 20° to allow any water droplets condensing on the lid to slide away and not mix into the collection cup. This was done to avoid an artificially high water condensation rate and potentially inaccurate assessment of the water chemistry. The temperature probe was inserted into the sample to measure surface temperature (T_s) and the other thermocouple was positioned in the gas phase near the sample to record gas temperature (T_g). The TLC lid was then placed onto a glass cell of 2 L volume assembled with CO_2 inlet and outlet, a thermocouple (to control bulk liquid temperature), and a condensed liquid collection cup. The whole assembly was deoxygenated by sparging with high purity CO_2 gas (99.99%) for 10 min. The cooling chamber was connected to a water bath to maintain the desired T_s .

In a separate container, 1400 mL of high purity water ($18.2 \text{ M}\Omega \text{ cm}$), pre-sparged with high purity CO_2 overnight and pre-heated to a predefined temperature, was transferred to the TLC cell using a peristaltic pump to avoid oxygen contamination. T_g and T_s were controlled by adjusting the bulk liquid temperature and the cooling water temperature, respectively. As soon as T_g and T_s reached the desired value, the experiment started.

The condensed liquid, dropped into the condensate collector placed directly beneath the sample, was transferred immediately into the condensate reservoir at room temperature to avoid any re-evaporation. The liquid was then collected periodically from the reservoir to determine its mass, pH, and ferrous ion concentration. The water condensation rate was calculated by dividing the collected condensed water with surface area and time. The *in-situ* corrosion rate was calculated based on dissolved iron (Fe^{2+}) presenting in the condensed liquid for a certain exposure time according to Eq. (1) [23,24]. The integrated corrosion rate was

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