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Operation of a MEG pilot regeneration system for organic acid and alkalinity removal during MDEA to FFCI switchover

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ABSTRACT

The switch over from pH stabilisation using MDEA to film forming corrosion inhibitors (FFCI) may be beneficial following formation water breakthrough during hydrocarbon transportation and processing to prevent scaling at elevated pH and to extend the operational lifespan of a field. Where formation water is present, organic acids including acetic can be expected within MEG regeneration systems and can impose a corrosion risk together with carbon dioxide. A case study was performed to evaluate the potential of simultaneous removal of organic acids and MDEA/alkalinity during the switch over from pH stabilisation to film forming corrosion inhibitors (FFCI). Experimental testing was conducted using a MEG pilot regeneration plant operated by the Curtin Corrosion Engineering Industry Centre. Sufficient removal of organic acids was achieved to prevent accumulation within the MEG regeneration loop and subsequent corrosion issues through distillation by lowering the pH of the rich glycol feed to six to promote removal of organic acids with the water distillate. Simultaneously, removal of MDEA and reduction of lean glycol alkalinity was achieved through the reclamation system to facilitate FFCI switchover more rapidly than a comparative industrial operational methodology.

1. Introduction

The formation of natural gas hydrates in hydrocarbon transportation pipelines represents a major flow assurance concern with major implications upon safe and economical process operation. The inhibition of hydrate formation is of critical importance in maintaining process flow and the prevention of damage to process equipment and piping. The annual cost associated with preventing hydrate formation has been estimated to be greater than $500 million through inhibition by methanol injection alone (Daraboina et al., 2013). In many recent oil and gas developments, Mono-Ethylene Glycol (MEG) has seen increasing popularity replacing methanol as the thermodynamic hydrate inhibitor of choice (Haghighi et al., 2009; Pojtanabuntoeng et al., 2017; Zaboon et al., 2017). The preference for MEG over methanol stems from its low volatility, toxicity and flammability, favourable thermodynamic behaviour and simple and proven technology requirements (Bikkina et al., 2012; Haque, 2012).

Post hydrate inhibition, the recovery and reuse of MEG is essential due to the significant volume required to provide effective hydrate control, its high cost and its effects on downstream processes (Haghighi et al., 2009; Pojtanabuntoeng et al., 2017; AlHarooni et al., 2015). Following the three-phase separation from gaseous and liquid hydrocarbons, MEG is removed in combination with water and must be regenerated before it is recycled back to the wellhead for reinjection. The regeneration of MEG is typically performed by distillation to remove surplus water in order to regain a glycol purity between 80 and 90% by weight (Latta et al., 2013; Carroll, 2003).

Alongside hydrate inhibition, the prevention of corrosion in piping and processing systems is a critical aspect of hydrocarbon flow assurance. The majority of natural gas pipelines are manufactured from carbon steel and are susceptible to 'sweet' corrosion due to the presence of carbon dioxide and free water during transport and processing (Pojtanabuntoeng et al., 2017; Papavinasam et al., 2007; Nam et al., 2014). The annual global cost associated with corrosion has been estimated by Koch et al. (Koch et al., 2017) at roughly US $2.5 trillion with up to 60% of corrosion experienced in the oil and gas industry resulting from CO_2 based corrosion (López et al., 2003). To combat corrosion in hydrocarbon pipelines two methods of corrosion control can be applied including the injection of film forming corrosion inhibitors (FFCI) and/or pH stabilisers (Pojtanabuntoeng et al., 2017; Latta et al., 2013; Dong et al., 2008). The presence of MEG itself has also been shown to impede CO_2 corrosion of carbon steels (Pojtanabuntoeng et al., 2017;

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Ramachandran et al., 2006; Gulbrandsen and Morard, 1998).

Corrosion prevention though pH stabilisation can be achieved through the addition of salt based (hydroxide or carbonate salts) or amine based compounds such as methyldiethanolamine (MDEA) (Pojtanabuntoeng et al., 2017; Olsen and Halvorsen, 2015). The basis of pH stabilisation is to promote the formation of an iron carbonate protective film in order to protect the surfaces exposed to corrosion (Pojtanabuntoeng et al., 2017; Olsen and Halvorsen, 2015; Dugstad et al., 2003; Mendez et al., 2005a). pH stabilisation is effective when carbon dioxide is the primary source of corrosion but less so when high levels of hydrogen sulphide are present (Latta et al., 2013). The use of pH stabilisers to inhibit corrosion is limited to pipelines where little to no formation water is present and in some cases can be used in combination with FFCIs (Latta et al., 2013; Olsen and Halvorsen, 2015; Halvorsen and Andersen, 2003; Olsen, 2006). Within systems with large quantities of formation water, pH stabilisation tends to promote the precipitation of divalent salts through reaction with alkalinity (carbonates, hydroxide) at elevated pH (Pojtanabuntoeng et al., 2017; Bikkina et al., 2012; Latta et al., 2013). Where formation water is expected, the injection of film forming corrosion inhibitors is the preferred method of corrosion prevention due to its minimal impact on pH, lessening the potential for scale formation (Bikkina et al., 2012; Latta et al., 2013; Olsen, 2006; Hagerup and Olsen, 2003). Furthermore, pH stabilisers such as MDEA can result in the increased boiling point of lean MEG impacting upon the design and operation of the MEG regenerator and reclaimer systems (Latta et al., 2013).

Once formation water breakthrough occurs and the risk of scaling cannot be managed through alternative means including scale inhibitor injection, it may be beneficial to perform a corrosion strategy switch over from pH stabilisation to FFCIs to extend the life-span of the field (Latta et al., 2013; Lehmann et al., 2014). This process cannot be performed instantaneously, instead, once formation water is detected or anticipated, MDEA must be gradually removed from the system whilst FFCIs are introduced. The removal of MDEA may be accomplished through a vacuum reclamation system by converting MDEA to its salt form at low pH where it is not readily vaporised alongside the MEG solution (Latta et al., 2013). The protonated form of MDEA, $MDEAH^+$ can react within ionic species including chlorides, sulfates, sulfides and organic acid ions to form heat stable salts, a common occurrence in industrial CO_2 and H_2S capture systems using amines (Aronu et al., 2014; Pal et al., 2014; Choi et al., 2010; Haws, 2001; Nainar and Veawab, 2009). However, such low pH within the reclaimer may result in poor organic acid removal rates during reclamation leading to organic acid enrichment within the lean glycol. An increase in organic acids within the MEG regeneration loop may potentially lead to operational issues including corrosion of downstream process equipment and pipelines. The aim of this study is to investigate the feasibility of removing organic acids and MDEA simultaneously by careful adjustment of system pH at critical points within the MEG regeneration system to facilitate switch over from pH stabilisation using MDEA to FFCI.

2. Organic acids within MEG regeneration systems

The presence of organic acids including acetic, propionic and butanoic acids within MEG regeneration systems may arise upon the breakthrough of formation water alongside mineral salts (Latta et al., 2013; Svenningsen and Nyborg, 2014). The degradation of MEG if exposed to excessively high temperatures or oxidation during the regeneration process can also lead to the production of organic acids including glycolic, acetic and formic acids (Haque, 2012; AlHarooni et al., 2015; Svenningsen and Nyborg, 2014; Nazzer and Keogh, 2006). Furthermore, free organic acids may be present with the natural gas within the reservoir and may enter into the MEG regeneration system through the condensed water phase or formation water (Svenningsen and Nyborg, 2014). The presence of organic acids within carbon and mild steel piping has been shown to increase corrosion rates in natural gas and oilfield systems (Dong et al., 2008; Mendez et al., 2005a; Ikeh et al., 2016; Crolet et al., 1999). Top of the Line Corrosion (TLC) may also be experienced within carbon steel systems in the presence of carbon dioxide and acetic acid, with organic acids increasing the rate of TLC (Olsen and Halvorsen, 2015; Svenningsen and Nyborg, 2014; Amri et al., 2009; Mendez et al., 2005b; Sykes and Gunn, 2016; Andersen et al., 2007; Singer et al., 2013).

Organic acids present within the rich MEG can lead to reactions with the alkalinity contained within the MEG solution reducing the effective alkalinity within the system (Halvorsen and Andersen, 2003; Lehmann et al., 2014). Furthermore, organic acids will directly reduce the pH of the solution acting as a proton provider and may be directly reduced on the surface of metals enhancing the anodic reaction of the metal (Mendez et al., 2005a; Hedges and McVeigh, 1999; Joosten et al., 2002). The presence of organic acids and the resulting low pH MEG will also pose a greater corrosion risk to carbon and mild steel piping through increased solubility of iron in the condensing water reducing its efficacy in forming a protective film (Hedges and McVeigh, 1999; Joosten et al., 2002; Svenningsen et al., 2013; Garsany et al., 2002). This effect may be counteracted by use of pH stabilisation chemicals such as MDEA to raise the pH to safer levels and to promote the formation of protective corrosion films (Halvorsen and Andersen, 2003; Mendez et al., 2005b). Furthermore, the work conducted by Amri et al. (Amri et al., 2009) suggests that the presence of acetic acid within the aqueous phase of gas condensate pipelines directly increases the potential for localised corrosion attacks in carbon steel pipelines.

During MEG regeneration by distillation where the water phase is boiled off, if a high pH is maintained in the reboiler, any organic acids present within the rich MEG will exist in their ionic form and accumulate within the regenerated lean MEG and will be recycled back to the wellhead (Olsen and Halvorsen, 2015; Halvorsen and Andersen, 2003). Therefore, if not otherwise removed, acetic acid will begin to build up within the MEG regeneration loop and excessive exposure will begin to occur within process pipelines enhancing the potential for corrosion. To ensure removal of organic acids during MEG regeneration, their removal can be performed through the reclamation system at elevated pH where organic acids will dissociate to their ions forming salts in the presence of monovalent cations (Svenningsen and Nyborg, 2014). The organic salts will subsequently be captured within the vacuum reclamation system whilst the lean MEG is evaporated and recovered to be reused.

3. Operational scenario

The switch over from pH stabilisation (for example, using MDEA) to film forming corrosion inhibitors may be required as part of the hydrocarbon pipeline corrosion inhibition strategy once formation water breakthrough has occurred. Upon the introduction of formation water, pH stabilisation will no longer be suitable due to its tendency to cause scaling issues as a result of the elevated pH (Pojtanabuntoeng et al., 2017; Bikkina et al., 2012; Latta et al., 2013). Therefore, it may be necessary to ‘switch over’ from using a pH stabiliser to a more conventional corrosion inhibitor to limit scaling within the transportation pipelines to ensure flow can be maintained. To facilitate the switch over process, the MDEA must be removed from the MEG regeneration loop with removal through the reclamation system being a possible method (Latta et al., 2013; Olsen, 2006).

To achieve removal of MDEA within the reclamation system, MDEA must first be neutralised to its salt form to allow accumulation within the reclaimer (Latta et al., 2013; Soames et al., 2018). Through prior extensive testing conducted by the Curtin Corrosion Engineering Industry Centre (CCEIC) involving removal of MDEA from lean MEG, a pH level below 8 has been identified as the pH range at which MDEA will begin to experience appreciable removal during reclamation. At a pH of approximately 8 and below, MDEA will be converted to its salt