



INHIBITING CORROSION IN TRANSPORT PIPELINES BY VpCI ADDITIVES TO CRUDE OIL

Sanja MARTINEZ¹, Boris MIKŠIĆ², Ivan ROGAN³, Antonio IVANKOVIĆ¹

¹University of Zagreb, Faculty of Chemical Engineering and Technology, Croatia, sanja.martinez@fkit.hr

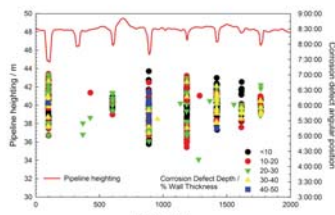
²Cortec Corporation, USA, boris@cortecvci.com,

³CortecCros, Croatia, ivan.rogan@cortecros.hr



INTERNAL CORROSION OF AGEING PIPELINES

1 Crude oil transmission pipelines, due to the basic sediment and water limit usually set to < 0.5%, have a long history without significant levels of internal corrosion. However, for ageing pipelines, it became obvious after decades of problem free operation, that corrosion may shorten the pipeline's life cycle and can lead to costly repairs, leaks and release of hazardous materials into the environment. At some point in the pipeline's life, operators are bound to initiate various measures to ensure integrity and safe operation for the remaining operation period.

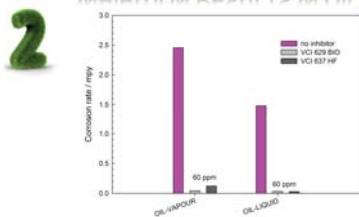


Characteristic pattern of corrosion damage observed in a crude oil pipeline suffering from free water accumulation at low spots.



Removal of paraffin and sludge at the cleaning pig exit of a large diameter crude oil transport pipeline.

INHIBITION RESULTS IN OIL AND VAPOUR PHASE

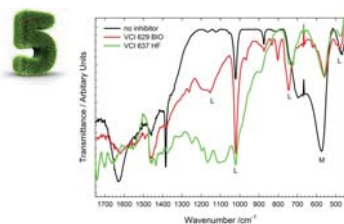


Corrosion rates of X52 5L coupons in liquid crude oil and crude oil vapour phase, calculated from mass loss experiments.



Experimental setup for the mass loss measurements. In each bottle, a coupon was laid at the bottom, with its upper side exposed to the liquid, and its bottom side isolated with tape. Also, in each bottle, one coupon was suspended above crude oil.

FTIR SPECTRA OF THE CORROSION PRODUCT LAYERS



Characteristic FTIR fingerprint region of the corrosion product layers, formed on LPR pin electrodes, in the inhibitor free solution and the inhibitor bearing solutions, after experiments mimicking batch inhibitor application.



Appearance of the rust layer after 30 days of exposure to: a) inhibitor free solution, b) 60 ppm of VCI 629 BIO in 3.5% NaCl and c) 2000 ppm of VCI 629 BIO in 3.5% NaCl. Black layer presents magnetite and brown-orange lepidocrocite.

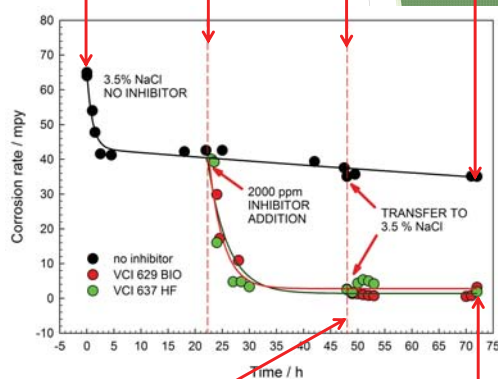
Spectra of the rust layers formed in the presence of inhibitors show multiple overlapping peaks that are not present in the rust formed without inhibitors. These bands are probably due to organic components of the inhibitor present within the corrosion product layer. The rust was sampled after transference to 3.5% NaCl, and additional 24 h of exposure. Hence, these results show that the inhibitors have adsorbed irreversibly, and were retained in the layer.

In the inhibitor free solution, magnetite band is more pronounced than the lepidocrocite band. This has also been confirmed visually, due to the specific colour of the compounds. Magnetite formation is known to be favoured in more aggressive environments where the oxidation process is faster.

SIMULATION OF BATCH INHIBITOR ADDITION INTO THE FLOWING ELECTROLYTE



FINAL RESULT WITHOUT INHIBITOR

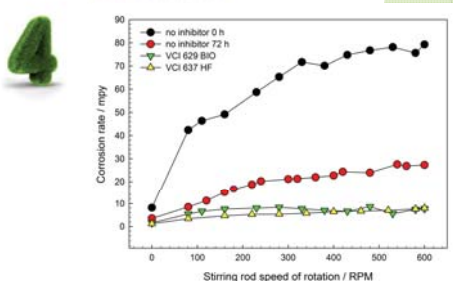


Corrosion rates in batch inhibitor application simulation, measured on LPR probe in stirred 3.5% NaCl, with stirring rod rate equal to 600 RPM.



FINAL RESULT WITH INHIBITOR

TESTING OF THE INHIBITOR PERSISTENCE AT THE SURFACE



Corrosion rates dependence the stirring rate, of electrodes preconditioned in: (i) stagnant 3.5% NaCl for 0 h, (ii) stagnant 3.5% NaCl for 72 h, (iii) stagnant 3.5% NaCl for 24 h and then for further 48 hour after 2000 ppm VCI 629 BIO or VCI 637 HF addition.

CONCLUSIONS

Two vapour phase inhibitors, VCI 629 BIO or VCI 637 HF, have been investigated in the present study. A set of experiments was designed to assess the inhibitor effectiveness at conditions that can be extended to those characteristic for the crude oil transport pipeline. The inhibitors were tested in crude oil and 3.5% NaCl, under stagnant and flowing conditions. They have been applied to clean and pre-rusted steel. Continuous and batch regimes of inhibitor addition have been simulated. Significant improvement of rust layer protectiveness against metal dissolution was observed when the rust layer was exposed to any of the tested inhibitors for 24 h. Under all circumstances, including those most harsh (after termination of batch application, in aerated 3.5% NaCl, under turbulent flow), the inhibitors limited the corrosion rate to < 2 mpy. Taken the typical wall thicknesses in oil transport and storage systems of 6-12 mm, the rate < 2 mpy is acceptable and will ensure long-term problem free operation.