
Question 58: In your experience has a non-phosphorous corrosion inhibitor been successfully used to mitigate naphthenic acid corrosion? In what circumstances and under what conditions are non-phosphorous corrosion inhibitors used?

Doug Meyne (Champion)

Phosphorus-based naphthenic acid corrosion inhibitors have been successfully used in the refining industry since the early 1980's. Phosphorus provides its protection to steel by corroding it and forming a passive layer that, under SEM/EDS, proves to be an Iron/Phosphorus/Sulfur blend. With rare exception, the protection comes from high TAN liquid attack of the affected metal, which is a good match for non-volatile filmers in pump-arounds like an HVGO. However, when there are zones being attacked by condensing naphthenic acids, the opportunity for contact, and hence mitigation by the inhibitor, is impaired. The P-S-Fe bond is pretty tenacious, with a bonding energy higher than the activation energy for naphthenic acid corrosion. In addition, this bonding is also effective at dispersing existing FeS in a dirty system which can result in downstream fouling issues and/or pluggage of HDS reactor beds. Naphthenic acid corrosion occurs from ~500F to ~650F. non-phosphorus inhibitors can work, but those in commercial use have temperature limitations. Their bonding energy is much lower than the phosphorus-based products, and at elevated temperatures (> 500F) they are simply inefficient at adsorption. Non-phosphorus inhibitors have been successful at the lower end of the temperature range in atmospheric columns. Products that also have a sulfur component are largely dependent on their sulfidation capability for resistance. The controlled application of a reactive sulfur causing sulfidation can be helpful in the sweeter acidic crudes, such as some of those coming out of western Africa with less than 0.5% sulfur. However, their effectiveness is substantially reduced when the crude already has sufficient H₂S to create and maintain a thin sulfide layer, and they are ineffective in crudes that produce enough H₂S to cause sulfidic corrosion.

Jim Johnson (Marathon Petroleum)

We use phosphorous based inhibitor at one of our refineries and have phosphorous based inhibitor on hand at another, but not using. We have no experience with a non-phosphorous inhibitor.

Sam Lordo (Nalco Company)

Nalco has successfully applied sulfur based high temperature corrosion inhibitors to mitigate naphthenic acid corrosion in all streams affected by naph acid, sidestreams, tower bottoms and in a few cases furnace transfer lines since 1992 using patented chemistries. The protective barrier formed by a sulfur-based inhibitor is not as persistent as the phosphorous based product so the use in these is recommend

in high shear areas such as vacuum furnace transfer lines.

Nalco routinely uses this product when there is concern, valid or not, of downstream phosphorous impacts if a phosphorous inhibitor is used. The sulfur-based products are also used when the circuit to be protected contains fuels such as diesel or jet.

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