

SUMMARY

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Carbon dioxide (CO_2) removal from ammonia synthesis gas (SG) is an important part of a SG production unit. Presence of CO_2 in SG is not desirable since it poisons the ammonia synthesis catalyst and the poisonous effect on the catalyst is irreversible thereby effecting the overall plant performance. Other factors which calls for the removal of CO_2 are (1) Its presence creates various operational problems like liquifaction when the SG is compressed, (2) Solid CO_2 plugging in liquid nitrogen wash system, (3) CO_2 is one of the starting material for the manufacture of Urea, Ammonium sulfate, (4) Presence of CO_2 dilutes the SG mixture.

Many methods are available for the removal of CO_2 to suit the different needs of the manufacturers, all of which can be classified into three categories w.r.t. the solvent - CO_2 interaction viz. (1) Chemical absorption process, (2) Physical absorption process, (3) a combination of chemical and physical processes. Giammarco Vetrocoke (GV) solution which uses potassium carbonate activated by arsenic trioxide, Benfield (BF) solution which uses potassium carbonate and diethanol amine with vanadium pentoxide inhibitor and GV solution using glycine and monoethanol amine, are some of the widely used CO_2 removal systems in the manufacture of ammonia.

In one of our ammonia plants, the CO_2 absorber which is used for removal of CO_2 using GV solution (potassium carbonate - arsenic trioxide), grooving and fine cracks had been observed after years of service. CO_2 absorber is a vertical column made of carbon steel material having a height of 39.16 meters and a wall thickness of 40 mm. In the absorber, GV lean solution having an index of carbonation ($\text{IC} = \text{mole of } \text{CO}_2 \text{ per mole of } \text{K}_2\text{O}$) 0.9, is fed at the top of upper

section at 70 degree C, GV semi lean solution having IC = 1.1 enters the absorber mid way through the column at 85 degree C and GV rich solution (IC = 1.6) leaves from the bottom part of the absorber at 100 degree C. The SG mixture for CO₂ stripping enters the absorber from bottom part at 130 degree C.

In continuation with the study carried out pertaining to corrosion problems vs corrosion inhibitors, by electrochemical methods, in potassium carbonate-glycine solution, in the present work, I had tried to evaluate the corrosive nature of GV solutions on CS material in laboratory controlled conditions.

It is observed from the literature survey that carbon steel material used in the absorbers/ regenerators and other equipment in carbon dioxide removal system is prone to general thinning and Stress Corrosion Cracking.

MEA/ DEA units solutions, when used with controlled lower percentage can minimize corrosion problems to some extent, but hot potash and GV systems are prone to such type of problems. It is also seen that the carbonate solutions, upon saturation with more carbon dioxide, is capable of dissolving more iron and increasing the corrosion rate. Carbon steel material is sensitive to Stress Corrosion Cracking (SCC) in potash solution and for this material, the specificity of the corrodent like hydroxyl ions, carbonate/ bicarbonate ions is well known.

Especially with GV split stream method, the concentration of these SCC causing ions are more at the splash zone of the absorber, where semi lean solution from the regenerator half way is taken out and splashed at the middle portion of the absorber, which results in fine, shallow cracks and general thinning. The cracking in high pressure

GV systems had lead to explosions, culminating into major industrial disasters. The welding seams and the heat affected zones are particularly prone to SCC due to interlocked stresses. Transverse cracks, leading to circular grooves are formed near attacked areas.

The packing material, using Intalox saddles made of stainless steel or porcelain material causes pitting along the contour of saddles.

General corrosion also leads to excessive sludge formation leading to concentration pockets.

In MEA/ DEA Systems, the fact that degradation products cause more corrosion problems and intergranular SCC, especially in MEA units, is proved beyond doubt.

DEA units, in which corrosion problems are encountered at lesser intervals up to now, are also facing corrosion problems with extensive cracking at the repair welds.

General methods for corrosion control, by certain operational practices and design features are always followed world wide, does not eliminate the problem altogether, but certainly reduces the chances and frequency of problem considerably.

Removing the residual stresses, in the carbon steel material by stress relieving methods is very costly and cumbersome. To spot the personnel for carrying out such techniques is also very difficult and it is also extremely difficult to get 100% reproducible result in towers of the height of more than 30 meters.

The use of inhibitors to passivate the carbon steel material is the most widely used corrosion prevention method in these systems.

The inhibitor used, has to act as a passivator, by reducing the corrosion current and also shifting the potential of the carbon steel material to the passive state far away from the potential range at which SCC occurs, thereby preventing both general corrosion and SCC. Many inhibitors and its combinations are studied and recommended for such use in hot potash and GV system. Potassium dichromate, vanadium pentoxide and sodium nitrite are some example of single inhibitor system.

Many combinations are also extensively studied. Compounds of vanadium and antimony, antimony and iron, vanadium and iron, potassium nitrite with various combinations of vanadates, alkali metal sulfide and sulfur, bismuth oxide and sodium silicate are some examples of this combinations.

For MEA/DEA units, inhibition is achieved by addition of salts of vanadium and cobalt. Amine guard ST also works as a inhibitor package. Nowadays copolymers are studied in combination with nickel compounds in these systems.

With special reference to Gujarat State Fertilizers Co. Ltd., it is experienced that after 15 years of service period CO₂ absorber walls had been affected by severe corrosion leading to crack initiation.

SCOPE OF WORK

1. A Search of an inhibitor or a combination of inhibitors which when added to the GV solution in small concentration will effectively control the corrosion problems.
2. Apply electrochemical evaluation technique to understand the mechanistic aspects of corrosion phenomena and its inhibition.

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3. Detailed studies of selected inhibitor for its compatibility and efficiency at the lowest possible concentration to economize the large volume handling system.
 4. Narrow down the compatibility and efficiency contributing factors by diversified views like impedance, pearlite leaching for surface characterization.
 5. To substantiate the performance of selected inhibitor on its availability, handling, safety, economy and operational viability.

The techniques used for the present study are open circuit potential measurements, polarization scan, AC impedance spectroscopy and pearlite leaching tests using sophisticated electronic instruments like EG & G AC Impedance system Model 368, Petrolite Potentiodyne Analyser and metallurgical inverted microscope. Experiments were carried out using specially designed laboratory glassware and AR grade chemicals as per known standards.

It is also noted that weight loss studies is not helpful for accurate measurements of corrosion rates since even without inhibitors the corrosion rate is very low. The important criterion for stress corrosion cracking is the redox potential of CS in the solution. Inhibitors shifting this potential towards more positive values are also studied. SCC potential of CS in a typical GV solution was found out to be -0.6 to -0.7 V vs SCE. The importance of potential measurement during the plant in operation is also stressed.

The lower OCP value of CS in plant lean and semilean solution than in rich solution at lower temperature is noteworthy. Lower carbonation index of lean and semilean solution is also interesting.

Experiments carried out using GVSL solutions collected at various intervals of days and with and without aeration showed that there was definite changes in its electrochemical characteristics. Four GVSL solutions collected within a span of around two months had shown higher OCP values, lower i_{cc} and i_p values, E_{pp} and E_p in almost all cases are very much comparable with OCPs of CS. There is also a marked difference in these values with and without aeration of GVSL solution. Insufficient aeration of GVSL solution in the plant had shown lower OCP and higher i_{cc} and i_p values at first but after aeration in the plant and the experiments without aeration showed that these values were much lower than the conventional values, showing the effect of Sb_2O_3 and ferric ions.

Corrosion rates calculated from B_a , B_c and I_{corr} values shows that for all inhibitors ($K_2Cr_2O_7$, V_2O_5 , $NaNO_2$, metavanadate) and its various combinations, there is an increase in corrosion rate giving negative efficiencies, except for metavanadate-nitrite combination with ferric ions, where it is positive. Thus it is seen that these inhibitor combinations do not act as good inhibitors for the system.

Sb_2O_3 additions to syn. GVSL solution shows aggressive action of ferric ions in lower concentrations (up to 0.02%), however, further addition of ferric ions play an important role in the synergistic action of ferric and antimony ions and thus at higher concentration of ferric ions the protective action of the inhibitors is observed. However, only at the Sb_2O_3 concentration of 0.15%, the protective properties of ferric-antimony combination is observed even at the lowest concentration (0.01%) of ferric ions and increases with an increase in its concentration up to 0.03%. Thus this combination of Sb_2O_3 and ferric ions is the ideal combination for the system. This is also observed in the zonal graphs where the OCP lies in passivation zone. Polarization resistance (R_p) calculated from the values obtained from

polarization curves is found to be the highest for CS in syn. GVSL solution containing 0.15% Sb_2O_3 and 0.03% ferric ions.

In order to understand the inhibitive action of the synergistic effect of ferric ions and Sb_2O_3 , R_p values are also derived from impedance data where lower perturbations of the double layer maintains the system at almost a steady state. The R_p values derived by this method show a slightly different trend. The addition of 0.01% ferric ions decreases the R_p initially, however, further additions of ferric ions increase R_p and only at 0.03% ferric ions and 0.15% Sb_2O_3 it is maximum, as is observed from polarization data.

High R_p and low C_{dl} values for 0.15% Sb_2O_3 and 0.03% ferric ion concentration in syn. GVSL solution amply establishes the passivation characteristics on CS as is the case with OCP and polarization studies.

Therefore, it is seen that Sb_2O_3 - ferric ion inhibitor combination works as an anodic inhibitor synergistically to control corrosion by lowering corrosion current, thereby lowering anodic Tafel and giving low corrosion rate and high polarization resistance values. The lowering of critical current density and passive current values also takes place consequently. Thus it is shown that how current values associated with the polarization studies can be used to identify the utility of various inhibitors for controlling corrosion.

CS in GVSL solution with 0.15% Sb_2O_3 and 0.03% ferric ions at an OCP of - 305 mV, shows only very mildly etched pearlitic phase, but inclusions are non affected. The almost intact nature of the pearlitic phase and the absence of any localised features and corrosion products coupled with an OCP of - 305 mV shows that the surface is well passivated. The minor leaching observed adjacent to elongated

inclusions may be attributed to the formation of passive layer. Thus the shift in potential to the passivation zone not only had arrested general corrosion, but also had reduced susceptibility of CS to SCC. This confirms the observations from polarization and AC impedance results. Thus the influence of inhibitor combination on the pearlite leaching of CS in GV solutions is established and by addition of antimony oxide and ferric ions reduces, to a great extent, the leaching of pearlite from the CS surface, and almost completely arrests general corrosion.

The iron removal system by side stream plant which is a part of the CO₂ removal system also faces choking problems due to ferrous/ ferric ions in the GV solution. The heat exchanger tubes and other cold zones also faces sludge formation problems due to the precipitation of iron complexes with arsenic.

By addition of Sb₂O₃, we not only achieve passivation of CS in such system, but also the aeration is controlled and therefore any undue conversion of As₂O₃ to As₂O₅ is also avoided. Excessive aeration which leads to the presence of oxygen in the methanator section is also controlled well. The load on the iron removal system is also greatly reduced by controlled aeration. It is necessary to point here that after passivation of the CS in GVSL solution, the concentration of iron in the solution will become steady.

The corrosion of CS in synthetic and plant GVSL solutions studied by polarization, AC impedance, pearlite leaching and measurement of corrosion potential have been discussed. The theories discussed and the references cited shows the inhibitive action of antimony trioxide in conjunction with ferric ions and air. Of all the inhibitors studied chromates and vanadates seem to have negative effect of iron

on their inhibitive action. Nitrite alongwith vanadate and tartrate with vanadate are unaffected by presence of ferric ions in the solution.

However, the presence of ferric ions above a certain level and aeration in the solution containing antimony trioxide renders the metal surface passive, thereby reducing corrosion current, double layer capacitance, corrosion rate, leaching of pearlitic phase and increasing polarization resistance, corrosion potential and inhibitor efficiency, substantiated by electrochemical theory of corrosion and its inhibition, potential - pH relationship, thermodynamics of oxidation - reduction of antimonite ions and phase characterisation leading to following conclusions.

1. Antimony trioxide and ferric ions, when added to the GV solution, effectively controls the corrosion problems like general corrosion and localised corrosion (SCC). This is achieved by a shift of corrosion potential towards more noble values and supported by lowering of current values, thereby achieving passivation.
2. Antimony trioxide in the range of 0.14% to 0.15% and ferric ions at 0.02% to 0.03% was found to be the critical range of concentration which gives good compatibility and highest efficiency. Thus, synergistic effect of antimony trioxide and ferric ions was established with potential measurements, polarization studies confirmed by AC impedance, pearlite leaching studies.
3. Application of diversified techniques for inhibitor evaluation like AC impedance technique and pearlite leaching studies confirmed the compatibility and efficiency of these critical concentration of antimony trioxide and ferric ions.

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4. **Addition of antimony trioxide and ferric ions in the real system and assessment of the inhibitor performance afterwards, substantiated the fact that antimony trioxide and ferric ions, in combination, are capable of combating corrosion problems in CO₂ removal system.**

 5. **Easy availability, safety in handling, economically and operationally viable and low concentration required, considering large volume to be handled, substantiates the use of antimony trioxide in CO₂ removal system using potassium carbonate-arsenic oxide solution.**