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### Corrosion of CO<sub>2</sub> absorbers – whys and wherefores Ramakrishnan Seshagiri

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#### ABSTRACT

 $CO_2$  absorber columns using Giammarco Vetrocoke (GV) solution are widely constructed from Carbon Steel, have reported to become a major concern for the sweetening units, corrosion being the major cause for the leakages. As a result of the leakage, the ammonia plants are taken for shutdowns leading to substantial losses in productivity. Various manifestations of corrosion are in the form of grooving, impingement, erosion-corrosion, deposition of GV solution on the internals viz. nozzles and tray supporting ring (TSR). The corrosion protection is offered by passivation treatment using Vanadium Pentoxide (V<sub>2</sub>O<sub>5</sub>), which when affected is predominant cause of corrosion of carbon steel. Various parameters like Iron content, solid contents, ratio of V<sub>5</sub>/V<sub>t</sub>, gas velocity, inlet and outlet CO<sub>2</sub> concentration, solution concentration and temperature needs to be monitored to understand any disruption in the system.

Research on the factors affecting the meta-vanadate passive layer leads a path to arrive on the causes of failure. A few cases are addressed in the present study wherein the bottom portion of the absorber walls were found to be predominantly affected due to passivation layer destabilization. High velocity of inlet gas, higher CO<sub>2</sub> concentrations in inlet gas, high solution velocity, channeling and deposition of GV solution, Iron carbonate solid contaminants have found to cause depassivation and subsequent corrosion, erosion-corrosion of the absorber walls. Two case studies are discussed in this paper.

Keywords: CO2 absorber; GV solution; passivation; corrosion; erosion corrosion.

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#### INTRODUCTION

 $CO_2$  removal is an integrated part of ammonia plants wherein  $CO_2$  from synthesis gas needs to be removed so that the synthesis gas in combination with nitrogen is used for producing ammonia. The  $CO_2$  gas that is removed is usually used for producing Urea.  $CO_2$  is removed from synthesis gas by absorption using GV solution or amines. GV solution comprises of hot aqueous solution containing ~ 30% Potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) partly converted to Potassium bicarbonate (KHCO<sub>3</sub>). GV solution also contains glycine and di-ethanolamine as activators for improving the efficiency of  $CO_2$ absorption and  $V_2O_5$  as corrosion inhibitor. GV solution at boiling temperatures along with  $CO_2$  in inlet synthesis gas is highly corrosive as  $CO_2$  absorbers are made of carbon steel and which is why passivation by pentavalent Vanadium is used<sup>1</sup>.  $V_2O_5$  added as the corrosion inhibitor, reacts with carbon steel and forms a layer of meta-vanadate which acts as a passivation layer to protect the underlying carbon steel from the corrosive environment.

The  $CO_2$  absorption is done in two stages. The synthesis gas from shift converter is fed into the Vetrocoke absorber via the process gas inlet nozzle which is usually at the bottom. The absorber consists of multiple layer bed packed with stainless steel packing material. Semi-lean GV solution is fed into the middle section of the absorber where it comes in contact with the process gas and much of the  $CO_2$  absorption takes place here. The process gas with reduced  $CO_2$  vapor pressure rises up where lean GV solution comes into contact. Rich solution containing absorbed  $CO_2$  leaves the absorber bottom and is transferred to a two stage regeneration system where  $CO_2$  is recovered and is sent for Urea production. The process gas free of  $CO_2$  (usually less than 500 ppm) leaves from the top of the absorber and is sent for ammonia production.

In recent times, there have been a number of reported cases of leakage in  $CO_2$  absorber sections which had led to plant shut downs, stalling production. The leakages predominantly had occurred on the lower bed of the Vetrocoke absorber where process gas inlet nozzle is located. The paper discusses two case studies on leakage and reduction of wall thickness of  $CO_2$  absorbers.

#### **CORROSION PROBLEMS IN CO2 ABSORBERS**

Plant experience shows that there are number of problems associated with corrosion of Carbon steel in hot aqueous  $K_2CO_3$  solutions saturated with  $CO_2$  where dissolved  $CO_2$  being the major culprit<sup>2</sup>. Saturated  $CO_2$  in solution dissolves more iron and thus aggravating the corrosion rate<sup>2</sup>. Gary et al<sup>3</sup> reported that carbon steel corrodes at the rate of 340 mils per year in 40%  $K_2CO_3$  solution saturated with  $CO_2$ .

Grooving of absorber walls have been constantly reported as a problem as it leads to loss of wall thickness. Grooving is a result of erosion-corrosion that occurs when there is higher  $CO_2$  concentration in inlet feed gas, decreased strength of  $V_2O_5$  in solution, presence of suspended solids like Iron carbonate in solution. Deep grooves are observed when there is lack of passivation due to semi-lean and lean solutions. Pitting is observed when the concentration of H<sub>2</sub>S is higher in inlet feed gas. Most of the problems are a result of improper passivation of the absorber shell or when the adequately passivated layer is disturbed eventually leading to corrosion. The meta-vanadate passivation layer is sensitive to destabilizing upsets.

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#### FACTORS AFFECTING CORROSION OF ABSORBER

The ratio of  $K_2CO_3/KHCO_3$  plays a key role in the corrosion of the Vetrocoke absorber. Higher the bicarbonate concentration, higher is the corrosion rate and moreover, corrosion due to high bicarbonate cannot be reduced by introducing meta-vanadate in the system. Gary et al<sup>3</sup> also reported that, minimum corrosion rate is observed when  $K_2CO_3/KHCO_3$  ratio is around 0.1 - 0.2. Any ratio lesser than this could have serious effect on the corrosion rate. The corrosion depiction being gullying or general corrosion. Presence of interlocked stresses in the fabricated vessel coupled with corrosive acid gases and hot potash solution may lead to stress corrosion cracking (SCC).

Temperature has a significant effect on the corrosion rate. For an increase in temperature from 20°C to 80°C, the corrosion rate increases two fold. Another major factor affecting the corrosion of absorber walls is solution velocity. At higher velocities, erosion plays an important role. A high velocity fluid stream has much higher force and exerts shear stress enough to damage the passivation layer and causes erosion-corrosion. High erosion also occurs when there is turbulence due to high inlet gas velocity that causes impingement of acid gas and solution on to the absorber walls that may lead to punctures<sup>3</sup>.

Flow conditions have influence on the corrosion rate and formation of protective film when solid contaminants like Iron carbonate is present. At over  $60^{\circ}$ C, in the presence of Iron carbonate, corrosion rate can go as high up to 18 mm per year<sup>4</sup>. The passivation by meta-vanadate is affected or becomes inadequate when there is less than 20% V as V<sub>2</sub>O<sub>5</sub>. Aeration is done to oxidize V<sup>+4</sup> to V<sup>+5</sup> that in turn forms meta-vanadate passive layer. When there is inadequate aeration, V<sup>+5</sup> fails to reach the required concentration and thus leading to inadequate passivation. Upsets in operation also leads to disruption in the passivation layer. Sudden depressurization of the absorber by sudden operation of the downstream vent valve occurs during short shut downs and startups which could potentially damage the vetrocoke absorber wall<sup>5</sup>.

#### CASE STUDY – 1

In plant 1, leakage was reported in  $CO_2$  absorber section in one of its Ammonia plant. Post leakage, the plant was taken for shutdown and the  $CO_2$  absorber was opened up for investigation.

#### OBSERVATION

Grooving of absorber walls were observed at 0° to 50° and from 180° to 360° taking reference from process gas inlet nozzle which is located between bed 1 and bed 5 (Figure 1). Metal loss ranged from 7 mm to 18 mm along the grooving. Puncture/hole was observed at 22° near the distributor lateral end hole. Impingement marks were observed at 40° and 180° where maximum metal loss up to 33 mm occurred. Much of the grooving was observed adjacent to the process gas inlet nozzle. The top portion of the process gas inlet nozzle was found badly corroded and heavy deposition of GV solution was also observed. The tray supporting ring experienced heavy GV solution deposition and was corroded beyond repair. Rest of the bed portions like middle section and top sections of the absorber walls were not affected. The corroded portions of absorber shell, process gas inlet nozzle and tray supporting ring are shown in Figure 2.

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Figure 1. Schematic of CO<sub>2</sub> absorber of Plant 1



Figure 2. Plant 1 – CO<sub>2</sub> absorber section a) Grooving on absorber walls b) Corroded portion of process gas inlet nozzle c) Corroded tray supporting ring

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#### ANALYSIS

#### 1. Plant data analysis

The shells of the CO<sub>2</sub> absorber, process gas inlet nozzle and tray supporting ring are of carbon steel metallurgy. 45 days plant data prior to leakage was analyzed. Increase in Fe content (up to 95 ppm) was observed whenever the lean and semi lean solution flows were increased to maintain the rate of CO<sub>2</sub> absorption. Subsequent decrease in solution flow to counteract increase in Fe loss, spiked up the CO<sub>2</sub> slip at process gas exit. This is supported by the plant data evidence wherein the CO<sub>2</sub> slip measured (up to 2000 ppm) at process gas exit was constantly above the ideal range of CO<sub>2</sub> slip, which is 900 ppm and at most of the times was above 1500 ppm with maximum CO<sub>2</sub> slip of about 2000 ppm. Higher CO<sub>2</sub> in process gas signifies that either there is higher CO<sub>2</sub> concentration at inlet process gas or improper CO<sub>2</sub> absorption by GV solution.

#### 2. Visual observation

Cut samples from the corroded process gas inlet nozzle and tray supporting ring were brought from the plant for analysis. Top portion of inlet nozzle showed heavy deposition of GV solution and complete metal loss portion (Figure 2). Solution flow patterns were also observed on the top portion of the nozzle.

Profound thinning and extensive corrosion were observed on the tray supporting ring (Figure 2). A portion of of the tray supporting ring had experienced complete metal loss beyond repair.

#### 3. Positive Material Identification (PMI)

PMI using Oxford X-Met 5000 was carried out on nozzle and tray supporting ring samples. PMI on inlet nozzle revealed 4.48 % to 5.17 % V on the passivated inside portion and 0.18 % to 0.56 % V on the corroded outside portion. This clearly indicates that, the outside top portion of the nozzle is de-passivated. The concentration of elements from various affected and unaffected portions of the inlet nozzle and tray supporting ring are tabulated in Table 1.

Element (wt %)	Nozzle N7 sample 1 eroded region	Nozzle N7 sample 1 unaffec ted region	Nozzle N7 sample 2 eroded region	Nozzle N7 sample 2 unaffce ted region	TSR sample 1 eroded region	TSR sample 2 eroded region top side	TSR sample 2 eroded region bottom side	TSR weld region
V	0.56	5.17	0.18	4.48	0.28	0.16	0.13	0.14
Cr	0.32	0.24	0.09	0.15	0.1	0.03	0.04	0.08
Mn	0.96	0.79	0.91	0.44	1.03	1.29	1.21	1.18
Fe	96.69	94.49	98.08	95.93	97.88	97.46	97.48	97.49
Ni	0.14	0.29	0.01	0.2	0.04	0.25	0.02	0.04
Cu	0.01	0.31	-	0.21	0.02	-	0.08	0.01
Мо	0.06	-	-	0.05	0.01	0.01	0.02	0.02

Table 1. PMI results of nozzle and tray supporting ring samples

#### 4. pH test

pH test was done on nozzle and tray supporting ring samples in which both had a pH of 9 and this alkalinity is the result of deposition of GV solution, which by itself is alkaline in nature.

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#### 5. Metallography

Cross section of samples from nozzle and tray supporting ring samples were cut, polished and etched in 2% nital solution and observed under Olympus GX51 optical microscope at 500x magnification which revealed banded microstructure ferrite-pearlite (Figure 3) indicating base material and dendritic microstructure indicating nozzle weld.



## Figure 3. a) Microstructure of process gas inlet nozzle parent metal b) Microstructure of tray supporting ring c) Microstructure of process gas inlet nozzle weld region

#### 6. Hardness

Hardness was measured on the cross section of the mounted TSR sample using Futuretech FV-700 microhardness tester. No major anomalies were observed in hardness test as hardness was well under 22 HRc for both nozzle and tray supporting ring.

#### Probable causes of leakage

The failure of the process gas inlet nozzle and the tray supporting ring may be attributed to channeling of GV solution which caused excessive GV solution deposition. Improper bed and packing arrangement, destabilizing upsets might have caused channeling of GV solution flow. Due to excess GV solution flow on the nozzle and tray supporting ring, the meta-vanadate passivation layer was affected resulting in rupture of passivation layer and subsequent corrosion which is substantiated by the very low V content in PMI results.

Plant data shows higher  $CO_2$  slip in the process gas exit to the order of 2 to 2.5 times higher than the allowable limit of 900 ppm.  $CO_2$  slip was constantly over 1200 ppm right from 45 days prior to leakage. Maximum  $CO_2$  slip measured was around 2000 ppm which indicated either there is higher concentration of  $CO_2$  in the inlet process gas or improper  $CO_2$  absorption inside the Vetrocoke absorber both of which are bound to cause corrosion of absorber walls. The type of grooves observed inside the absorber walls (Figure 2) is typical of acid gas corrosion by high concentration of  $CO_2$  (acid gas) and high inlet gas velocities. Contamination by Iron carbonate is suspected as could have accelerated metal loss leading to puncture in a short period of time. The reason for the areas adjacent to the process gas inlet on either sides were severely affected can be attributed to acid gas flashing from the failed process gas inlet nozzle. Leakage can be attributed to the puncture near the distributor lateral end hole and impingement due to acid gas flashing.

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#### CASE STUDY - 2

Leakage was reported from bottom of bed 1 of CO<sub>2</sub> absorber section at an Ammonia Plant in Plant 2 and subsequently the plant was taken for a shutdown. The absorber suffered a puncture through which the leakage was observed near the long seam of the first shell located at bottom of bed 1. Profound reduction in wall thickness was observed in the region between longitudinal seam at 315° and 135°. Severe attack on the bed 1 tray supporting ring was also observed. Region where reduction in wall thickness had occurred is observed with groove marks which are typical to erosion-corrosion. Accelerated metal loss led to the failure of absorber in a relatively short time. The photographs of the affected portions of the absorber are shown in Figure 4.



a)

b)

# Figure 4. Plant 2 – CO<sub>2</sub> absorber a) Corroded tray supporting ring b) Affected and unaffected portions of absorber walls

#### ANALYSIS

#### 1. Plant data analysis

2 months plant data prior to leakage was analyzed. The rich GV solution outlet temperature was greater than 114°C throughout the analysis period and the ratio of  $V_5/V_t$  was constantly above 40 % indicating no major anomalies. However, sudden increase of Fe content from 50 ppm to 200 ppm was observed probably indicating the onset of corrosion and thereafter Fe content was constantly above 200 ppm till leakage.

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#### 2. PMI

Chipped off samples (Figure 5) from the  $CO_2$  absorber were analyzed by Oxford X-Met 5000 PMI on both passivated and debase metal portion of the chipped sample (Table 2). PMI results show 3 wt% V on the passivated portion and 0.1 wt% V on the carbon steel base metal portion.



Figure 5. Chipped off carbon steel sample from  $CO_2$  absorber a) Passivated portion b) base metal portion

Element (wt %)	Passivated portion	Base metal portion
Fe	96.1	98.6
Mn	0.9	1.2
V	3	0.1
Cu	-	0.1

Table 2. Results of PMI analysis on chipped off steel specimen

#### 3. Energy dispersive X-ray spectroscopy (EDS) analysis

EDS analysis was carried out on both passivated and base metal portions of the chipped off sample (Figure 6). The results shows 2.22 wt% V on the passivated portion in line with PMI results. No significant V peak was observed on the base metal portion of the sample.



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#### Figure 6. a) EDS results of passivated portion of the chipped sample. b) EDS results of depassivated portion of the chipped sample

#### 4. Microstructural analysis

The chipped off sample from the absorber wall was cut along the cross section, polished and etched with 2% nital and examined under metallurgical Olympus FV-700 microscope at 50 to 500x magnification to analyze the microstructure. A banded microstructure consisting of a mixture of ferrite and pearlite was observed (Figure 7) which is typical to a rolled carbon steel plate.



Figure 7. Microstructure of the chipped off specimen at 500x.

#### Probable cause of leakage

The flow of acid gas loaded GV solution with higher velocity along the walls of shell of the bed-1 region could likely be the reason for the chemical attack and erosion-corrosion. This is possible due to damaged gasket in liquid distributor tray, which might have caused liquid flow along the wall between  $315^{\circ}$  and  $135^{\circ}$ , thereby damaging the passivation layer and eroding/corroding the metal beneath. The solution might have gained velocity while flowing along the shell of bed-1 region and probably exceeded critical velocity at the lowest shell course of the bed-1 region, due to which erosion-corrosion of the shell occurred. It appears that the long seam at  $315^{\circ}$  and  $135^{\circ}$  degree had thwarted the erosive action of the rich solution, due to their slight higher hardness as compared to parent material. At the dummy bed region, entire shell internal diameter was eroded/corroded, which can be probably attributed the turbulence created by  $CO_2$  gas, which is entering at that region. Below the liquid level, it is obvious that no corrosion would occur since passive layer is intact (absence of erosion).

Stress corrosion cracking (SCC) is another possibility that cannot be overlooked wherein the corrosive environment (acid gas + GV solution) coupled with interlocked stresses that might have led to the rupture and the subsequent leakage.

#### DISCUSSION

Two case studies of  $CO_2$  absorber leakages at two different ammonia plants are discussed and analyzed for probable cause of failure. In both the cases, the  $CO_2$  absorber experienced extensive groove marks and impingement marks and a rupture point from where leakage occurred. The extensive groove marks are typical indications of acid gas corrosion by  $CO_2$  and coupled with GV solution Grooving of absorber walls is likely to happen when there is higher concentration of  $CO_2$  in inlet process gas, improper  $CO_2$  absorption leading to more  $CO_2$  at process gas exit which is substantiated in the first case study where  $CO_2$  at process gas exit was constantly over 1500 ppm and reached a maximum of 2000 ppm.

Corrosion, erosion-corrosion of absorber walls is bound to happen when passivation layer is disturbed and consequently the underlying carbon steel is prone to corrosion by the inlet process gas and boiling GV solution. Weakened passivation is substantiated in the first case where the corroded top portion of the process gas inlet nozzle had only 0.18% to 0.56% V, whereas the unaffected inside diameter portion showed 4.48% to 5.17% V indicating intact passivation. There are several factors like ratio of K<sub>2</sub>CO<sub>3</sub>/KHCO<sub>3</sub>, V<sub>5</sub>/V<sub>t</sub>, channeling of GV solution etc which led to inadequate or weak passivation.

#### CONCLUSION

In case 1, erosion-corrosion coupled with acid gas flashing is suspected to have caused the leakage of the absorber shell. Channeling of GV solution leading to excessive GV solution deposition is suspected to be the likely cause of failure of process gas inlet nozzle and TSR. In case 2, high solution velocity might have ruptured the meta-vanadate passive layer and subsequent erosion-corrosion is suspected to have caused the absorber shell rupture and the subsequent leakage.

In both the case studies, no anomalies were observed in the ratio of  $K_2CO_3/KHCO_3$  and  $V_5/V_t$ . Probably high acid gas inlet and solid particulates have caused active and erosion corrosion of the Vetrocoke absorbers. The factors that must be taken care of for smooth operation of the  $CO_2$  absorber are ratio of  $K_2CO_3/KHCO_3$ ,  $V_5/V_t$ , concentration of  $CO_2$  in process gas inlet, solution velocity, temperature, bed and packing arrangement, destabilizing upsets during operation,  $H_2S$  content in feed gas and suspended solid contamination.

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