



AMINE PLANT CORROSION REDUCED BY REMOVAL OF BICINE

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ABSTRACT

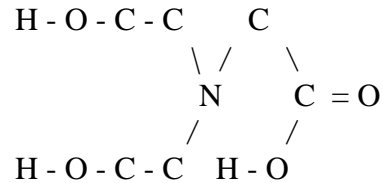
Bicine, an amino acid, has been found in numerous amine gas treating systems including tail gas treating units, certain refinery services, and some natural gas processing plants. Bicines (bicine and other similar amino acids) are formed in amine gas treating systems as a result of amine degradation due to the presence of oxygen and/or sulfur dioxide. The presence of Bicine alone in the amine system is not necessarily corrosive. However, Bicine is a strong chelator with iron and can initiate, in the presence of H₂S, a fast acting corrosion mechanism. Through both laboratory analytical studies and numerous full scale "in plant" Bicine removal projects, it has been demonstrated that amine system corrosion can be reduced when the amine system is cleaned by ion exchange through the removal of Bicine and the precursors of Bicine. Numerous examples and case histories are presented to demonstrate the benefits of removing Bicine from contaminated amine solutions.

AMINE PLANT CORROSION REDUCED BY REMOVAL OF BICINE

BICINE

Bicine is an amino acid that results from amine degradation due to the presence of oxygen and/or sulfur dioxide. The amine solvents experiencing this degradation are MDEA, DEA, TEA, and mixed amine solvents containing any of these amines as components.

Chemical Formula

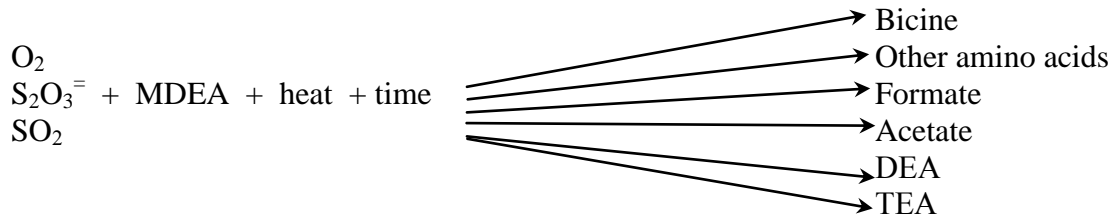


N,N-bis(2-hydroxyethyl)glycine (Bicine)

Formation

Bicine has been shown to form in amine systems utilizing MDEA-based amines when subjected to O₂ contamination. Plant operating experience indicates a slow but continuous formation of Bicine in the amine system when low levels of O₂ and/or SO₂ are present in the amine system feed gas.

Numerous Bicine formation mechanisms have been proposed. The generally accepted O₂ degradation path involves one of two mechanisms: 1) a disproportionation reaction of two moles of DEA to form one mole each of TEA and MEA followed by oxidation of the TEA to form Bicine or 2) a disproportionation reaction of MDEA to TEA and other mixed amines followed by further oxidation of the TEA to Bicine. Regardless of the actual formation mechanism, the Bicine formation reaction can be generally described as depicted below.



Accelerated Bicine formation has been noted after up-sets in the SRU and the hydrogenation section of the TGTU increased the amount of O₂, H₂S, and SO₂ entering the TGTU absorber. The resulting elevated levels of thiosulfate (S₂O₃⁼) contribute to formation of Bicine and other amino acids.^[1,2] Removal of the thiosulfate, a heat stable salt anion precursor for Bicine, soon after a TGTU upset could prevent much of the resulting Bicine formation in the TGTU amine because the Bicine formation mechanism may take several weeks to produce a substantial amount of Bicine and the subsequent corrosion.^[1]

CORROSION

The primary corrosion mechanism in an amine system is H₂S attack on carbon steel with the resultant formation of FeS. In an ideal amine system with a clean amine solution, the protective layer of FeS formed on the carbon steel prevents further corrosion. However, when Bicine is present the protective layer is continuously destroyed or not formed at all. Bicine is a strong chelator and will chelate iron maintaining the iron in a soluble form and preventing or weakening the stable formation of the protective FeS layer. The unprotected carbon steel is once again attacked by the H₂S resulting in an accelerated corrosion rate. [3, 4, 5]

Bicine by itself in an amine solution is not corrosive to carbon steel. As shown in Figure 1, there is no increase in the instantaneous corrosion rate of a 30 wt % MDEA solution when H₂S is not present. The corrosion data presented in Figures 1 and 2 were generated using a Mini-Amine-Plant designed to simulate, as closely as possible, an actual amine plant in operation. The corrosion probe was placed in the 250 °F “reboiler” section. The corrosion studies were conducted using a linear polarization probe to measure instantaneous corrosion rates. The triple electrode probe design eliminates interference by solution conductivity on the indicated corrosion rate. [3]

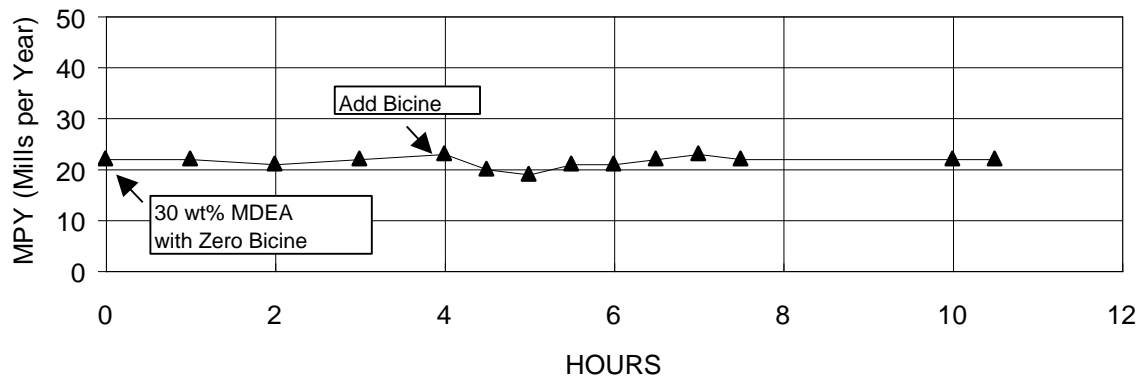
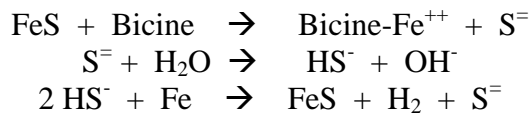


Figure 1 – Corrosion Study
MDEA, Bicine, with Zero H₂S

Bicine prevents the protective FeS passivation layer from forming. The chelating corrosion mechanism involves the removal of the protective FeS layer by dissolution of the Fe⁺⁺ by the chelant (Bicine). The mechanism proposed is as follows:



H₂S must be present and it is the corroding agent as indicated in Figure 2 below. To develop the data presented in Figure 2, a sample of 30 wt % MDEA containing 2 wt % Bicine, taken from a refinery, was utilized. Initially the corrosion probe was conditioned in the sample for several hours, then H₂S was added (the refinery amine had only 0.003 mol/mol Lean Loading). Then additional Bicine was added. The H₂S loading from the point at which Bicine

was added to the end of the test decreased to 0.008 m/m yet the corrosion rate increased significantly over the same period. The contrast of Figures 1 and 2 indicates the role of Bicine in the corrosion process as a chelator rather than as a direct corroder.^[3]

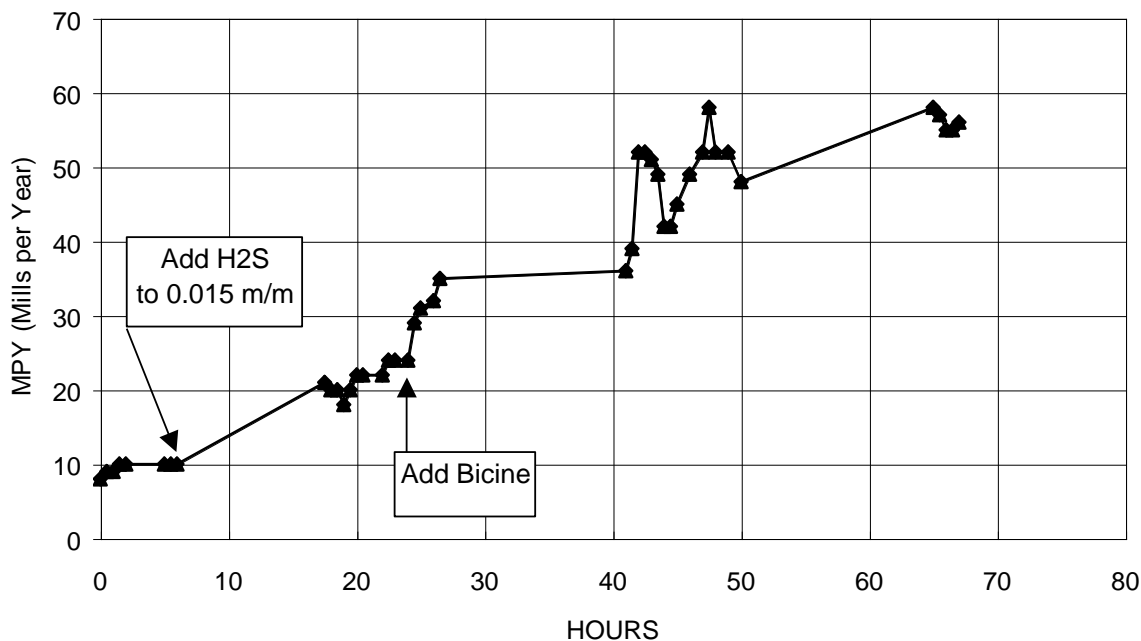


Figure 2 – Corrosion Study
MDEA, Bicine, and H₂S

As long as Bicine and H₂S are present, Fe will be continuously chelated from any available source.

Bicine Removal

Because Bicine is such a strong corrosion enhancer, concentrations of Bicine in an amine system should be kept very, very low – in the low hundreds of ppm. Thus distillation, which focuses on moving the solvent away from impurities, is not an efficient means of removing low levels of Bicine from amine treating units. However, ion exchange plucks the Bicine out of passing solvent with little energy expended to move the solvent. Ion Exchange Technology has proven successful in removing Bicine and Bicine precursors when properly implemented. Several Case Histories are presented below.

Case History 1

A Texas gas plant utilizing a specialty MDEA solvent was experiencing significant corrosion shortly after plant start-up in the carbon steel sections of the amine plant. With the assistance of their amine supplier, the plant determined that the corrosion was being caused by the presence of Bicine generated due to O₂ in the sour gas feed. The incoming oxygen incursion into the amine system could not be eliminated. A combination corrosion inhibitor/oxygen scavenger was added to the amine to scavenge the O₂ and to prevent further degradation of the MDEA to Bicine. The implementation of the O₂ scavenger program did decrease the Bicine

formation rate. However, this action was not totally adequate to control the corrosion. MPR was requested to provide their mobile ion exchange equipment to reduce the Bicine. The Bicine level was reduced from 3,929 ppmw to 471 ppmw in the operating amine system.^[6] Figure 3 depicts the Bicine reduction during the mobile cleaning period. The corrosion was reduced by the mobile cleaning service but returned when the mobile cleaning equipment was removed.

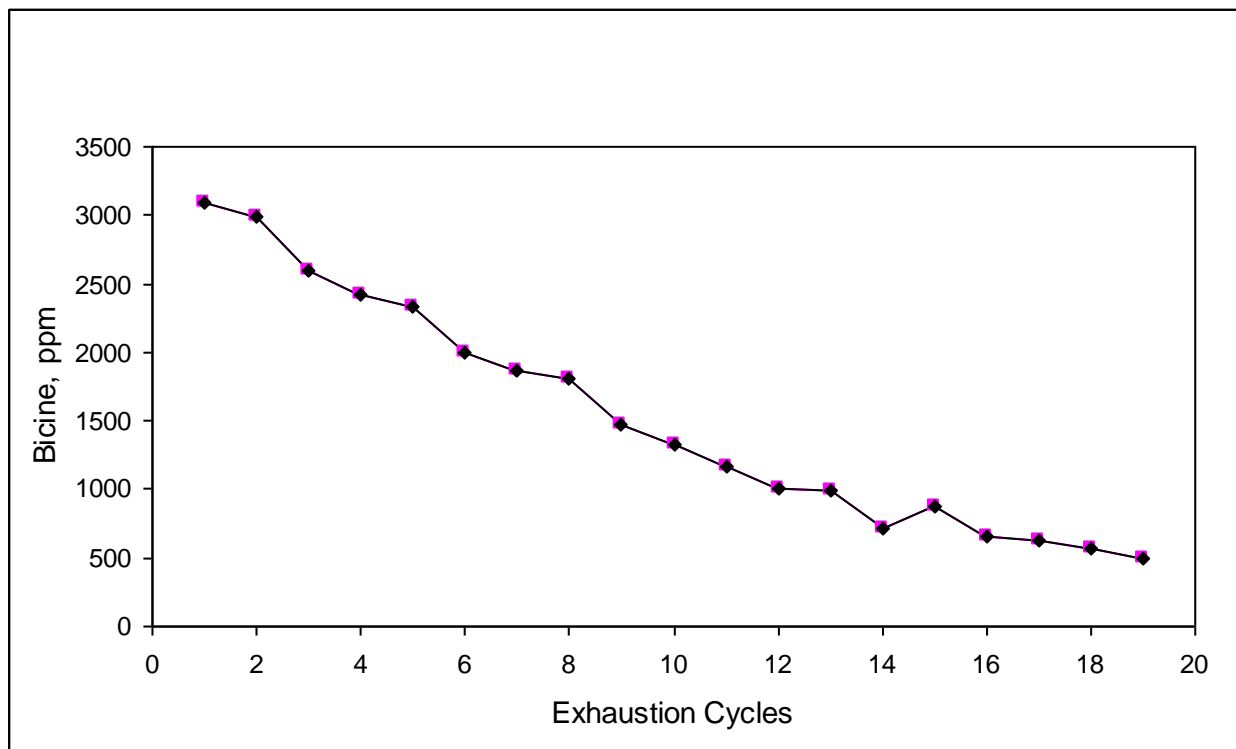


Figure 3 – Bicine Removal

Case History 2

A western U. S. natural gas producer was concerned about corrosion in the amine system due to Bicine. The amine contained about 5,200 ppm amino acids, including 1,825 ppm Bicine. During a turn-around, the amine system was taken offline, and the entire system circulated through mobile ion exchange unit. The Bicine content was reduced to less than 25 ppm (0.0025 wt %).

Case History 3

A tail gas unit located in a gulf coast refinery was experiencing unexplained corrosion. The refiner contacted the amine supplier who identified Bicine as a potential cause. MPR was requested to do additional laboratory analytical work and a laboratory control study on Bicine. The lab work and study performed by MPR confirmed that Bicine was present and that it was the root cause of the corrosion. A demonstration of the custom designed removal process was performed in the lab followed by a successful clean up of the operating system. Bicine was reduced from 3 % to 0.7 %.

Case History 4

In 2002, Pinnacle Gas Treating Inc. (a subsidiary of Anadarko Petroleum) at the Bethel Gas Plant at Tennessee Colony, Texas became concerned when their Bicine level reached the

500 ppm level in their specialty formulated MDEA solvent. The plant began experiencing high corrosion rates, excessive foaming, equipment fouling and unstable plant operations. Chlorides were also elevated and were an additional concern. A mobile ion exchange project successfully reduced the Bicine to less than 40 ppm. Figure 4 shows the Bicine reduction during the mobile cleaning job.

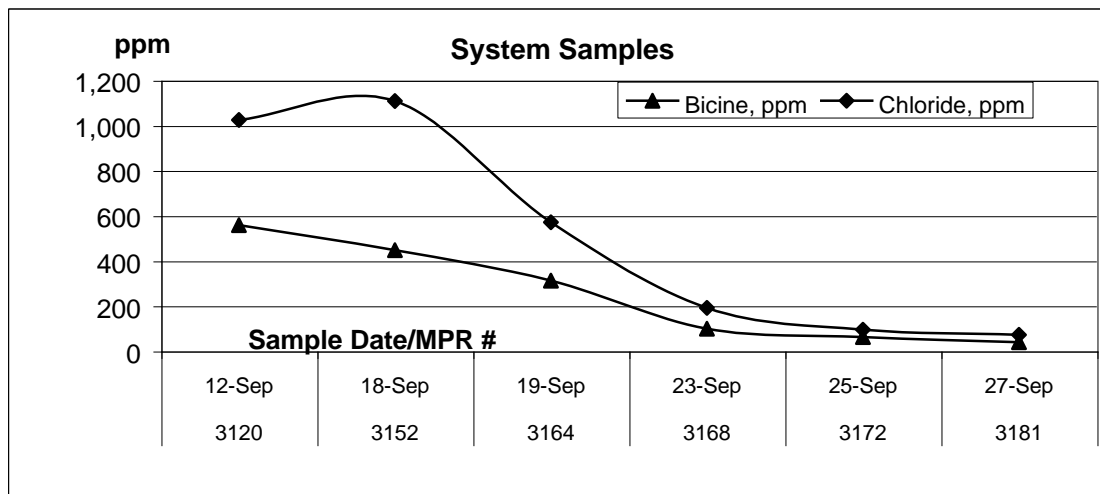


Figure 4 – Bicine and Chloride Removal

The following Table 1 depicts the actual results of other operating systems that have been cleaned by ion exchange technology.

Table 1 – Examples of Bicine Removal Projects

System	Amine	Initial Bicine, Wt. % or ppm	Removal End Point, Wt % or ppm
A	MDEA	4.9	1.8
B	MDEA	3.9	1,200 ppm
C	MDEA	2.1	3,200 ppm
D (Case 3)	MDEA	3.1	0.7
E	MDEA	2.0	0.6
F	DEA	1.2	0.6
G	MDEA	1.0	2,300 ppm
H	MDEA	2.1	1,400 ppm
I	MDEA	3,000 ppm	200 ppm
J (Case 1)	MDEA	4,000 ppm	500 ppm
K (Case 2)	MDEA	1,825 ppm	24 ppm
L (Case 4)	MDEA	500 ppm	40 ppm

The wide range of final end point concentrations shown in Table 1 reflects the specification requested by the plant operator. Several of the data points illustrate that Bicine can be reduced down to the very low part per million range if desired.

BICINE ANALYSIS

Bicine is identified and quantified by Ion Chromatography. Other amino acids are also separated in the ion chromatograph but are not usually identified. Total amino acid content can be estimated from the ion chromatograph and from a combination of charge balance of measurements of ionic compounds in the solution and knowledge of the contribution of amino acids to amine titrations and total heat stable salts tests.

SUMMARY

Bicine is a very corrosive degradation product produced in certain DEA and MDEA systems. Amine system operators should take steps to minimize O₂ and SO₂ incursion into the amine system and should monitor Heat Stable Salts and Amino Acids (Bicine) concentrations in the amine. By skilled application of ion exchange, Bicine can be removed and maintained at very low levels that will reduce or prevent corrosion.

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