



MPR Services, Inc.

**Technical Article
Presented at
GAS PROCESSORS ASSOCIATION
EUROPEAN CHAPTER
18 February 1998**

Controlling Corrosion in Gas Treating Solutions

Arthur L. Cummings, MPR Services, Inc., Dickinson, Texas (PRESENTER)
Shade M. Mecum, MPR Services, Inc., Charlotte, North Carolina
Fred C. Veatch, MPR Services, Inc., Dickinson, Texas

ABSTRACT

Alkanolamine solutions and glycol solutions present operational problems while performing vital gas treating functions. Most of the operational problems are related to or caused by corrosion. In alkanolamine systems, capacity, effectiveness, economy, and operational ease are shown to be greatly enhanced and corrosion reduced by reducing heat-stable salt (HSS) concentrations. The removal of HSS is shown to be much more effective than other control methods, such as strong base addition. In glycol systems, salts and acid gases create corrosion products that contribute to plugging, fouling, and foaming. Methods are presented for controlling salts and corrosion products in operating alkanolamine and glycol systems, thereby improving performance, economy and production.

INTRODUCTION

Gas treating solutions such as alkanolamines and glycols rarely work trouble-free. Yet their design is simple: the solution absorbs unwanted substances from gas, circulates to the regeneration section, releases the absorbed substances such that they can be collected, then circulates back to absorbing section. The principle is wonderful. The solution can be circulated indefinitely, performing its function flawlessly. The reality is, however, that the solution becomes contaminated and operational problems result.

When operational problems arise, a common response is add something -- anti-foam, corrosion inhibitor, neutralizer, fresh solvent, etc. However, additives can change solution properties or eventually contribute to problems. For example, it is well accepted that too much anti-foam can cause foaming in amine systems. Viscosity, surface tension, thermal conductivity, electrical conductivity, are important characteristics of the solution that can be altered by accumulating additives and contaminants. Operators become accustomed to gas treating systems that have problems because the composition of the solvent (amine or glycol) is always much different than the pure solvent due to contamination and additives..

This paper looks at methods of eliminating operational problems by removing contaminants and minimizing additives. We propose that corrosion is best controlled by removing corrosion enhancers and corrosion products. Contaminants that enhance corrosion or are products of corrosion contribute to most of the operational problems associated with the gas treating solutions. Removing the contaminants allows operation with a solution that is most like the solution for which the system was designed. Plants can approach trouble-free operation by maintaining chemically clean solvents.

EXPERIENCES WITH CONTAMINANT REMOVAL

A refiner experienced severe corrosion problems evidenced by the need to change filter elements 1 to 3 times a day. Amine system upsets frequently curtailed production and caused flaring. Heat Stable Salt contamination was up to about 5 wt% as MDEA in solution. The patented HSSX® Process (utilizing ion exchange) was contracted to remove heat stable salts. Salt levels were reduced to under 1 wt% as MDEA. The next filter change out was performed a month later, not because of need, but to inspect the filters, which were found to be in good condition. Corrosion had been controlled by removing contaminants. Flaring incidents ceased for 6 months. Only after heat stable salt levels increased again did operational problems recur and filter change out frequency increased. Operational problems had been controlled by removing contaminants.

An amine system (Flexsorb) could not keep up with the gas processing demand. Production was limited by the amine system. Extra coolers were brought in to reduce contactor temperature in order to increase absorption of acid gas. Production was still limited. The HSSX® Process was contracted to remove heat stable salts. Approximately 60,000 kg of heat stable salts were removed. As a result, capacity of the amine system increased, the extra cooling was turned off and unit production increased by 25,000 bpd. Circulation rates were also reduced resulting in an additional savings of steam cost. The cost of cleaning was recovered in a few days of operation. Operational problems had been eliminated by removing contaminants.

A gas plant associated with salt dome storage experienced carry over of sodium chloride into its TEG system during periods of heavy gas demand. The sodium chloride level exceeded its solubility level at some points in the system causing fouling of reboilers. A proprietary process (the Glycolex™ Process utilizing ion exchange) was contracted to remove the

chloride. While the regenerators were off line, the glycol system was cleaned producing a product with less than 20 ppm chloride without glycol loss. Salt removal continued until precipitated salt was redissolved and the chloride level in the system was less than 200 ppm. Operational problems had been eliminated by removal of contaminants.

A MEG system at a gas plant associated with a pipeline was plagued by operations and maintenance problems because of the precipitation of iron carbonate. This precipitation occurred in heat exchangers and regenerators. Additionally extremely fine particulate iron carbonate defied filtration, but added to the fouling in the heat exchangers and tower elements. Agglomerated particles formed during regeneration collected on filters in the regeneration trains necessitating 6 or more filter changes per day. The Glycolex™ Process, a proprietary process, was contracted that could remove dissolved iron and salts. Glycol from the rich and lean storage tanks containing dissolved iron, agglomerated particulate iron, fine particulate iron, condensed hydrocarbon and sodium chloride were cleaned. From black, particulate-laden glycol containing over 6000 ppm sodium chloride, dissolved and particulate iron ranging from hundreds to thousands of ppm, and condensed organics, a product was produced that was clear, colorless glycol containing consistently less than 1 ppm iron, 20 ppm chloride, and 20 ppm sodium, with pH at the desired level. As the plant used this cleaned glycol in their system, operators became very happy: filter changes dropped to less than 1 per day. Operational problems were reduced by removal of contaminants.

An EG system at a gas plant associated with a pipeline contained over 4900 ppm sodium chloride. The Glycolex™ Process was employed to reduce the sodium and the chloride. The desired level of less than 350 ppm chloride and less than 300 ppm sodium was achieved by processing a slip stream of glycol while the system continued to treat gas. Corrosion concerns were eliminated by removal of contaminants.

EXPERIENCE COMPARING CAUSTIC ADDITION WITH SALT REMOVAL

Caustic Addition

A refinery upgrading heavy sour crudes had a large rate of heat stable salt buildup, sometimes as much as 450 kg per day in a "formulated" MDEA solvent system. Heat stable salt anion (formate, acetate, thiocyanate, chloride, thiosulfate and sulfate) levels in the range of to 7 to 12 wt% as MDEA (or up to 25% of the total amine bound with heat stable salts) were quite common. The refinery practiced neutralization as recommended by their amine supplier, usually adding caustic to reduce the amine heat stable salts (bound amine) to less than 2 wt% MDEA. Caustic addition was advertised to significantly reduce corrosion, improve amine performance, and return the bound amine to active amine. Only the last objective was ever achieved, and only to a limited extent.

Corrosion rates all over the system increased tremendously as extensive efforts to control amine losses resulted in increased heat stable salt anion concentrations in the system. Regenerators corroded so rapidly that weld overlays were required almost yearly. An additional set of

lean/rich exchangers was purchased so that fouling and corrosion failures in one set of exchanges would not shut the regenerator down. Reboiler fouling occurred so often that isolation valves had to be installed to clean the exchangers on line. Filter costs reached nearly \$0.4 million per year. Eventually a third regenerator train was installed to allow for one train to be down for repairs. Still, this did not prevent loss of hydrocarbon throughput due to corrosion/fouling problems.

Performance of the amine operations at this level of heat stable salts were poor at best. Contactors and regenerators were constantly foaming leading to large losses and sulfur plant upsets. Liquid treaters lost large amounts of amine overhead leading to many water treatment plant permit excursions. Amine system operation was a major bottleneck to hydrocarbon throughput.

Caustic addition was then supplemented with an electro dialysis based heat stable salt removal unit. Caustic additions were to control the bound amine at low levels while the electro dialysis unit would try to hold the heat stable salts anion levels equivalent to about 7 wt% MDEA. This was done on the assumption that the bound amine content was the cause of corrosion acceleration, rather than the heat stable salt anion content. Maintenance of the high salt anion level was also required for maximum efficiency of the electro dialysis and to minimize the amine losses to its waste brine. Going to lower salt anion levels increased the power requirement for the separation which made more amine cross the membranes into the brine, eventually rendering the brine untreatable. As with the caustic addition alone, the caustic plus electro dialysis program produced the same poor results in corrosion control and amine system performance.

Contaminant Removal

After 3 years of the neutralization/electro dialysis program, a patented ion exchange based heat stable salt removal process (the HSSX® Process) was employed to remove heat stable salts and sodium. Heat stable salt levels were reduced to 1 wt% as anions (2.3 wt% as MDEA) and 0.5 wt% sodium. These much lower levels of salt anions can be achieved because the heat stable salt anion removal efficiency and the regenerant waste stream characteristics of the patented ion exchange based removal system are not affected by salt anion concentration in the amine solution.

The ion exchange process frees the amine from the heat stable salt anions, sends the freed amine back to the amine system, and sends the heat stable salts (as innocuous sodium salts) to waste. Amine strength (capacity) is increased. Unlike caustic neutralization, the ion exchange process removes the undesirable heat stable salt anion from the amine system.

Immediately after the initial cleanup by the patented ion exchange based heat stable salt removal process, heat exchanger fouling problems were eliminated. Filtration costs were cut in half. Antifoam usage dropped by 90%. The system stabilized enough to allow record crude, coker and cat cracker runs simultaneously, while amine consumption was cut in half.

As the heat stable salt anion level rose after the initial cleanup, the problems associated with high anion levels began to resume. The HSSX® Process cleanup was employed again restoring the system to smooth operations. It was decided at that point to go to continuous removal and maintenance of low salt anion and sodium levels using an HSSX® Kidney.

As the HSSX® Kidney reduced the contaminant levels to about 0.5-0.8 wt% anions (~1-2 wt% as MDEA) and sodium less than 1000 ppm, even greater operational benefits have resulted. Filtration costs have been cut by 80%. All the heat exchangers show little, if any, fouling. Amine losses have been reduced by 90% without detrimental build-up of heat stable salts. Amine purges have obviously been unnecessary as a mode of HSS control.

The operational results of heat stable salt removal are compared to those of caustic addition in Table I. Corrosion and operational problems were controlled by removing contaminants.

WHY CONTAMINANT REMOVAL HELPS OPERATIONS

The amine and glycol systems described above were operating with gas treating solutions that were far from the ideal solutions for which they were designed. Effects of dissolved salts, particulates and hydrocarbons are not included in theoretical models. The contaminant removal described above produced gas treating solutions that were very close to the pure solutions for which the systems were designed.

Suspended particles are known to aggravate the foaming loss problems by helping any hydrocarbon contamination in the amine form foam stabilizing gelatinous layers at the amine/hydrocarbon interfaces.¹ The benefits of filtration are well accepted.

The role played by contaminants, particularly dissolved contaminants, has not been fully appreciated. Heat stable salts in amine systems, for example, have long been tolerated at high levels. Their role in corrosion rate enhancement has not been understood, so the typical treatment has been to free the amine by caustic addition and allow the salts to build up until "natural" losses of amine controlled the salt concentration. The above examples show there is a better way to deal with salts -- remove them without amine loss -- that also improves operations. Recent corrosion investigations have shown how heat stable salts enhance the corrosion rate in amine systems.^{2,3,4}

Table II shows corrosion rate reductions as heat stable salts (HSS) anions were removed from operating amine systems.² MDEA systems 1 and 2 samples were drawn from two operating amine systems while HSS were being removed by the HSSX® Process on a slip stream. MDEA system 3 amine was drawn from the operating system, then the HSS were removed in the laboratory. Corrosion rates are dramatically reduced by removal of HSS.

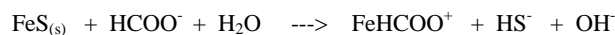
Similar tests of MDEA system 4 amine as received from the refinery and after addition of caustic in the laboratory show why that operator did not add caustic. Caustic increased the observed corrosion rates.

DEA and MEA corrosion rates are also given in Table II from similar tests on amine from system 5 and system 6, respectively. Caustic addition to “neutralize” (convert) all the amine HSS to sodium HSS did reduce corrosion rate somewhat in DEA. Removal of the HSS and the sodium by the HSSX® Process reduced corrosion rate much more. MEA corrosion rates are all much higher than DEA and MDEA, because of the much higher H₂S lean loading of this sample. Probes were clean carbon steel, so corrosion rates include acid gas corrosion rates as enhanced by HSS. Clearly, HSS enhanced corrosion rates even with high acid gas concentrations.

To more accurately show effects of HSS on corrosion in an operating amine system, a Mini-amine-plant/corrosion monitoring cell (MAP/CMC) was constructed.²⁻⁴ Figures 1 and 2 are graphs of the corrosion rates in mils per year (thousandths of an inch per year) versus the time of the experiment. Each solution change event is marked in the figures. Clearly the experimental data show the expected increase in corrosion rates when acid gas is added to the amine and when heat stable salts are added to the amine. This data also gives a clear indication that maintaining low heat stable salt levels provides effective protection against corrosion rate acceleration by heat stable salts.

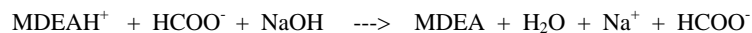
Contrary to conventional wisdom, however, the data show that corrosion rates can increase or remain nearly the same after caustic addition to amine solution with heat stable salts. The only significant drop is found in the DEA case where CO₂ is a major part of both the lean loading and the corrosion mechanism. Even there, with time the corrosion rate increased again, suggesting the benefit of caustic addition was temporary.

The acceleration of the corrosion rates, as evidenced by the data, is caused when the heat stable salt anions act to remove ionic iron trapped in the iron sulfide on the surface of the carbon steel probe. This is illustrated in the equation.



This process may be better understood by the realization that there is always a very small amount of Fe⁺⁺ and S⁼ in equilibrium with the FeS_(s) near the surface. Heat stable salt anions can attract the Fe⁺⁺ away from the surface and then transport it far away in the flowing amine solution. At the FeS_(s) surface, meanwhile, equilibrium dictates dissolution of another FeS to Fe⁺⁺ and S⁼. In the MAP/CMC this process can be completed, just as in an operating amine system.

Addition of caustic changes amine salts to sodium (or potassium) salts:



Changing from an amine salt to a sodium salt does not alter the concentration of the salt anion, which is the cause of the acceleration of iron sulfide film removal and thus corrosion

rates. Corrosion rates are especially increased in the hot, lean sections of the unit because of the low H₂S content of the solution is insufficient to keep the iron sulfide precipitated.

When the lean amine containing the iron complex is returned to the contactor, the higher H₂S content of the solution pulls the ionic iron away from the heat stable salt anion and re-precipitates it as iron sulfide particles.

Bicarbonate (HCO₃⁻) has a great affect on the corrosion rate in H₂S laden amine systems. It not only provides a strong sink for a corrosion product (Fe⁺⁺ --> FeCO₃), but it also has a proton available for the cathodic reaction. Its presence in an amine solution also has the effect of changing caustic addition from a corrosion enhancing to an apparent corrosion reducing procedure, at least in the short term (Figure 2). Figure 3, where bicarbonate concentration and corrosion rate are graphed together, shows the correlation. The understanding of this lies in the effect of pH on the relative concentrations of acid species in solution. The pH of the solution is governed by the fraction of amine that is in the bound (protonated: DEAH⁺) form. In the pH range governed by the bound DEA excursions in the MAP test, as a fraction of total solvated CO₂, the bicarbonate (HCO₃⁻) fell from 94% to 33%, upon the first caustic addition. Simultaneously, the carbonate (CO₃⁻) rose from 6% to 67% of the CO₂ in solution. The drop in bicarbonate concentration is responsible for the drop in corrosivity of the solution. The carbonate's proton must be an important part of the corrosivity of CO₂ lean loadings. The correlation between bicarbonate concentration and corrosion rate is unquestionable in the caustic section of the experiment.

The rise in carbonate probably caused the immediate reduction in total CO₂ in solution noted above. This can be explained. The sudden jump in carbonate, as pH increased sharply by caustic addition, precipitated FeCO₃ by reacting with dissolved Fe⁺⁺ from earlier corrosion and may have exchanged with some FeS. As time and corrosion progressed, however, the FeCO₃ gradually redissolved, replaced by less soluble FeS. This explains the observed gradual decrease in H₂S and increase in total dissolved CO₂ with time. One can conclude that the addition of base (caustic) to HSS laden DEA solutions in the presence of acid gases (H₂S and CO₂) can decrease the corrosion rate in the short term, but increases the longer term corrosive nature of the solution.

Glycol solutions exposed to carbon dioxide (CO₂) will also develop significant levels of bicarbonate. Depending on pH, bicarbonate may also play an important role in corrosion rates in glycol systems.

CONCLUSIONS

Operational problems of alkanolamine and glycol systems can be reduced significantly by removal of dissolved contaminants, such as salts. Corrosion can also be reduced by removal of dissolved contaminants and by maintenance of low levels of all contaminants. The path to smooth operations includes removal of corrosion products and corrosion enhancers.

REFERENCES

1. Pauley, C. R., Hashemi, R., and Caothien, S., "Analysis of Foaming Mechanisms in Amine Plants", paper presented at AIChE Summer Meeting, Denver, Colorado, August 22-24, 1988.
2. Cummings, A.L., Veatch, F.C., Keller, A.E., "Corrosion and Corrosion Control Methods in Amine Systems Containing H₂S", Paper 97341, NACE Corrosion/97, March 1997.
3. Cummings, A.L., Veatch, F.C., Keller, A.E., "Corrosion and Corrosion Control Methods in Amine Systems Containing Hydrogen Sulfide", *Materials Performance*, 37(1), January 1998, pp. 42 - 48. (abridgment of Reference 2)
4. Mecum, S.M., Veatch, F.C., and Cummings, A.L., "Why Caustic Addition is Bad for Amine Systems", *Hydrocarbon Processing*, October 1997, pp. 115-19.

TABLE I
AMINE SYSTEM OPERATIONS IMPROVED BY ION EXCHANGE REMOVAL OF
HEAT STABLE SALTS, NOT BY CAUSTIC ADDITION

	DURING (and Before) CAUSTIC PROGRAM	MAINTAINING LOW HEAT STABLE SALTS BY HSSX®
CORROSION	Heat Exchanger Fouling and Failure Regenerator Weld Overlay Annually Reboiler Fouling -- Frequent Cleaning Filter Costs High Extra Regenerator Train Installed to Cover Down-time	NO FOULING FILTER COSTS CUT 80%
PERFORMANCE	Foaming continually Amine Losses large Sulfur Plant Upsets Water Treatment Plant Excursions Lean Loading high Bottleneck for hydrocarbon throughput	ANTI-FOAM REDUCED 90% AMINE LOSSES CUT 90% LOWER LEAN LOADING RECORD CRUDE, COKER, and CAT CRACKER RUNS

TABLE II
CORROSION RATES OF LEAN AMINES FROM OPERATING SYSTEMS
REDUCED BY HEAT STABLE SALTS (HSS) REMOVAL

Amine	Total Amine wt%	HSS as Amine wt%	Caustic Added as Amine wt %	CORROSION RATE		
				at T=150 F mpy	at T=200 F mpy	at T=250 F mpy
MDEA, Sys 1	34	4.0	0	18	50	115
MDEA, Sys 1 HSS reduced		1.5		5	15	35
MDEA, Sys 1 HSS reduced		0.7		5	10	18
MDEA, Sys 2	30	3.6	0	20	65	190
MDEA, Sys 2 HSS reduced		2.6		18	30	65
MDEA, Sys 2 HSS reduced		0.9		10	12	15
MDEA, Sys 3	40	12.8	8.9	20	50	140
MDEA, Sys 3 HSS removed		<0.2	<0.2	<5	<5	<5
MDEA, Sys 4	35	4.9	0	10	25	70
MDEA, Sys 4 + Caustic		4.9	3.9	10	30	130
DEA, Sys 5	24	3.6	1.6	14	32	62
DEA, Sys 5, + Caustic		3.6	3.6	13	18	30
DEA, Sys 5, HSS removed		<0.2	<0.2	3	4	5
MEA, Sys 6,	19	2.1	0	80	200	>350
MEA, Sys 6, HSS removed	19	0		30	55	100
MEA, Sys 6, sans HSS & LL	19	0		20	22	25

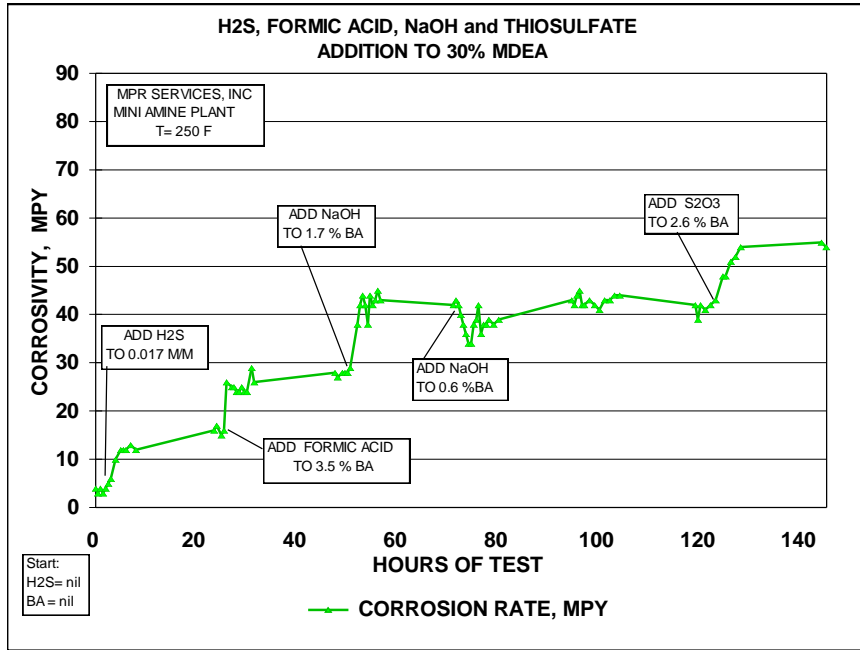


Figure 1
Effects of Heat Stable Salts and Caustic Addition on Corrosion Rate in MDEA
 1 mpy = 0.025 mm per year

Comment [AC1]: Page: 9
DEA MAP test c:\alc\slides\dea2show.cgm
from dea2show.wb1:dea2show

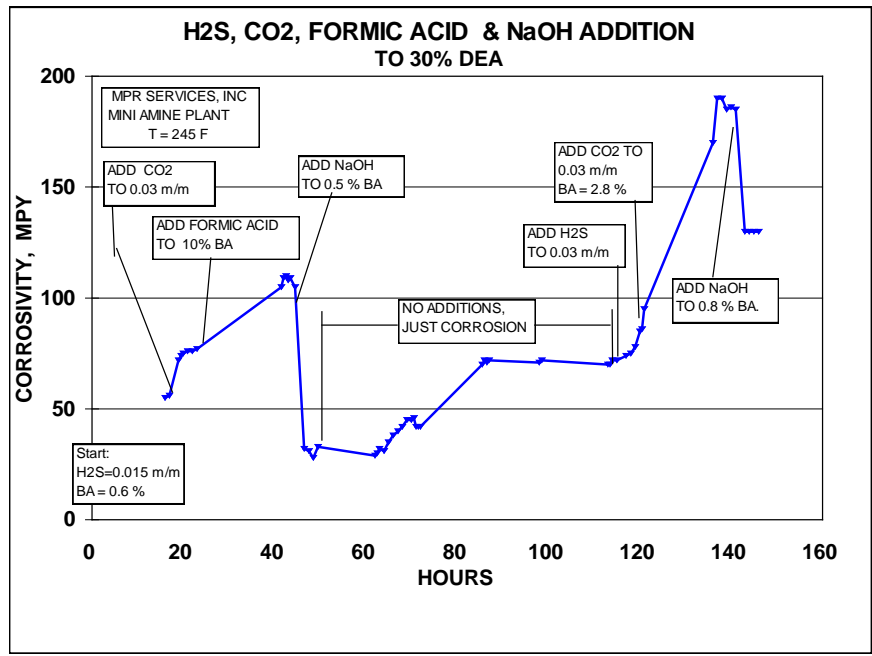
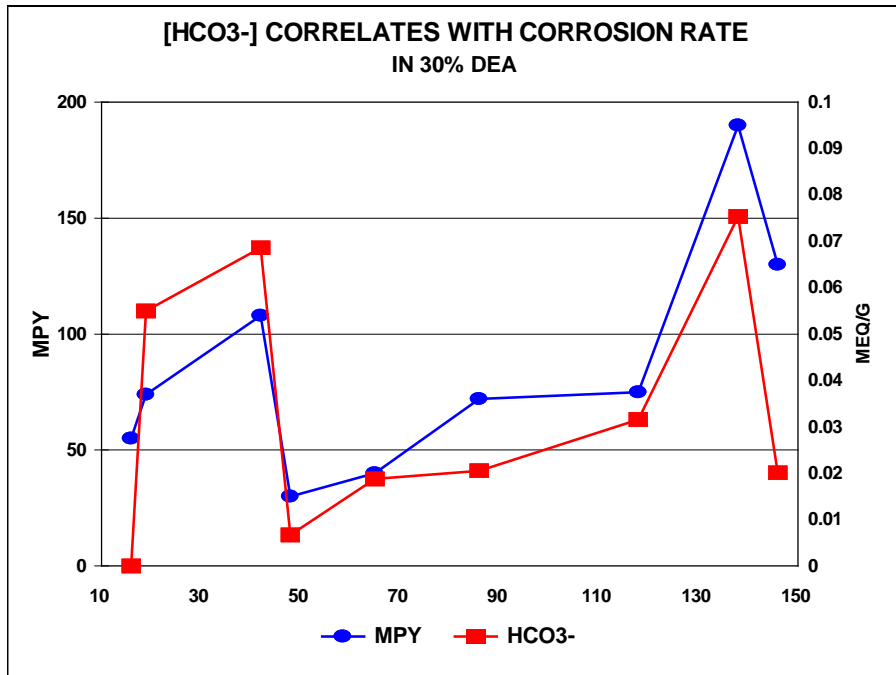


Figure 2
Effects of Heat Stable Salts and Caustic Addition on Corrosion Rate in DEA



Comment [ALC2]: DEA MAP test
 c:\alc\slides\hco3cor.cgm from
 c:\alc\resrch\fred\FVaudea3.wb1:ioncorr

Figure 3
Correlation of Corrosion Rate with Bicarbonate concentration in MAP Test of DEA
 Corrosion rate (mpy) and bicarbonate concentration (meq/g) versus test hours (see Figure 2)