A Study of Corrosion in Hydroprocess Reactor Effluent Air Cooler Systems

API PUBLICATION 932-A
SEPTEMBER 2002

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Downstream Segment

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A Study of Corrosion in Hydroprocess Reactor Effluent Air Cooler Systems

This study was sponsored by the American Petroleum Institute (API), Committee on Refinery Equipment, Subcommittee on Corrosion and Materials Research. The purpose of the study was to provide technical background, based on industry experience and consensus practice, for controlling corrosion in hydroprocess reactor effluent systems. The findings reported herein will be used as an interim resource by the industry and as a basis for a future API recommended practice document.

1 Introduction

The treatment of crude distillation products with hydrogen to produce higher yields of gasoline and jet fuel became a major part of refinery technology with the introduction of hydrocracking in the 1950s. Later, other hydrofining processes for removal of impurities from products were introduced. These technologies all had similar corrosion experiences that eventually were identified as being associated with the presence of hydrogen sulfide (H_2S) and ammonia (NH_3), and their reaction product ammonium bisulfide (NH_4HS), in the reactor effluents. Minor contaminants such as chlorides and oxygen were also believed to have an influence on corrosion. But in general, corrosion was associated with salt deposition, concentrated solutions of ammonium bisulfide and the flow velocity.

In 1976, R. L. Piehl (Standard Oil of California) conducted a survey for the National Association of Corrosion Engineers (NACE) on corrosion in Reactor Effluent Air Cooler (REAC) systems. Industry-wide experience was gathered and analyzed to establish guidelines to minimize REAC corrosion. In 1996, Unocal/UOP conducted an extensive survey of their licensees world wide. Their conclusions confirmed the validity of the original parametric guidelines and contributed to the importance of certain design features in avoiding corrosion problems. Since the earlier survey, failures have continued to occur and while it is believed that most have resulted from operation outside of the guidelines, there has been no systematic study of the experience or open documentation of individual events.

2 Preamble

Information for this report has been gathered from open literature, private company reports and interviews with representatives of major refining companies. The terminology used by each of these sources to describe some of the corrosion events has varied slightly and may have introduced some double meanings. Every effort has been made in this document to maintain consistency and avoid confusion. Specifically, we have tried to differentiate between “localized corrosion” as a category of corrosion phenomena (e.g., pitting, crevice corrosion or stress corrosion cracking) and corrosion that has been confined to a small area of the corroding surface at a specific location in the process equipment. For the most part, localized corrosion will refer to the latter, i.e., corrosion occurring on a small area, or at a specific location in the process. Where a specific type of corrosion has occurred the proper description, for example, pitting, or stress corrosion cracking, will be used.

Throughout the report, reference is made to the effects of velocity on corrosion. It is commonly acknowledged that velocity induces accelerated attack by a mechanism involving the erosive effect of the high velocity liquid. The many contributors have frequently referred to this phenomenon as erosion. The consensus however appears to be that the mechanism is one of accelerated corrosion. This should more properly be categorized as erosion-corrosion. Thus, unless otherwise stated, the use of the term erosion-corrosion is meant to describe the severe corrosion experienced by high velocity fluid flow.

3 1975 NACE Survey

Prior to this survey, R. L. Piehl had presented the results of studies conducted by his company at an API Division of Refining meeting in Philadelphia, May 15 – 17, 1968[1]. These studies provided the earliest insights into the corrosion problems associated with this new technology and attempted to identify critical parameters contributing to the corrosion of carbon steel equipment.

Among the important conclusions reached at that time was the recognition that sulfide corrosion in an alkaline environment was the primary cause of corrosion. The quantities and relative ratios of ammonia and hydrogen sulfide were perceived as important and the possible influence of minor contaminants such as chlorides and oxygen were acknowledged. The study concluded that the dominant mode of attack was erosion-corrosion of air cooler tube ends and some flow velocity limitations were suggested to avoid the problem.

It was subsequently recognized that the subject was much more complex than originally thought and that other equipment, especially piping, was also affected. To broaden the data base and capture as much experience as possible, NACE Group Committee T-8 (Refining Industry Corrosion) set up Task Group T-8-1 to conduct a survey of the T-8 membership on the subject of corrosion of hydroprocess effluent air coolers[2]. Information was gathered on forty-two plants from fifteen refining companies, mostly in the United States. In general, the results were supportive of the original definition of the prob-

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[1] R. L. Piehl, “How to Cope with Corrosion in Hydrocracker Effluent Coolers,” *Oil & Gas Journal*, July 8, 1968.

[2] R. L. Piehl, “Survey of Corrosion in Hydrocracker Effluent Air Coolers,” *Materials Performance*, January 1976.

lem, but tended to underscore the complexity of the problem rather than provide clearer guidance. The ability of both ammonium chloride and ammonium bisulfide to condense as solids from the vapor phase and thereby cause blockage of the flow path was the motivation to introduce a water wash to solubilize the deposited material. Unfortunately, the resulting aqueous solutions are extremely corrosive unless substantially diluted, and are in fact the cause of the corrosion problems in these systems.

The survey gathered data on the chemical composition of the effluent stream including contaminants, and attempted to define the corrosivity of the aqueous phase by factoring in the amount of water added to the system and its velocity. The concentration of bisulfide solution was measured in most cases at the downstream water separator and this value was used as a measure of the aggressiveness of the process stream. It was observed that at a concentration of 2% bisulfide or below corrosion was mild but at 3% – 4% or more, significant corrosion began to occur.

The results helped to support a previously suggested relationship between the bisulfide concentration and velocity, wherein the bisulfide level was represented by the product of mole% $NH_3 \times$ mole% H_2S, designated as the K_p (Piehl) factor. It was proposed that for K_p values of 0.1 – 0.5, velocities in the range 15 ft/s – 20 ft/s would be appropriate but for K_p values above 0.5 there was no suitable velocity. The higher the K_p value the tighter the tolerance on velocity. It was also found that velocities of 10 ft/s – 12 ft/s could result in stagnant deposits underneath which severe corrosion could occur, hence a lower limit of 10 ft/s was suggested, with an upper limit of 20 ft/s and an optimum of 15 ft/s.

A major conclusion drawn from this survey was that air cooler corrosion is a complex phenomenon having numerous interdependent variables. This reduces the prospects of successfully eliminating corrosion by control of one or even several of the variables.

4 1996 UOP Survey

In the 20 years following the NACE survey the problems with corrosion continued, giving rise to a number of publications discussing various aspects of the phenomenon[3,4]. Air cooler tubes continued to be the principal focus of the discussions although piping problems were also recognized. Laboratory studies of corrosion were unable to clarify the use of parametric variables in controlling corrosion[5,6]. Thus, in 1996, Unocal/UOP initiated a survey of its licensees to expand the experience data base and possibly identify any new factors in the corrosion of REACs and related piping.

The survey consisted of a comprehensive 10-page questionnaire covering a variety of process and mechanical design information and corrosion experience. Topics included general operating conditions such as process mode, feedstocks, gas flow rates, contaminants (H_2S, NH_3, Cl, CN), water wash details, and flow velocities. Air cooler and piping design and layout, materials and corrosion experience were also covered.

Forty-six responses were received from operators of five different types of hydroprocess unit. The information in the responses was compiled into tabulated formats and analyses made of the effects of certain variables on the corrosion experienced. Not all the respondents were able to provide values for each of the key parameters requested so that UOP had to provide estimated values by calculation from key operating data such as feed quality, charge rates, reactor efficiencies, flow rates, temperatures, pressures, and tube and piping flow areas. Note that these calculations, in particular velocities, were not based on rigorous process simulation but rather on factored estimates based on representative models for each unit configuration. To ensure consistency, UOP calculated values for K_p, NH_4HS concentration and velocities for all of the units.

The results were presented in Paper 490 at Corrosion 97[7]. The diversity in the responses is illustrated in Table 1, which summarizes the range of values received for the key variables; however, it cannot be construed that such a range of values in the key parameters will necessarily result in wide pattern of corrosion behaviors because of the interdependency of corrosion on several parameters at the same time. Only if all the parameters are at one end of the range or the other can extreme behavior be anticipated. In addressing corrosion of carbon steel air cooler tubes, the effect of K_p factor on the severity of corrosion was evaluated by plotting K_p factor versus level of corrosion experienced. The level of corrosion was associated with tube life and the following rankings used.

Severe (S)	Tube life of 5 years or less
Moderate (M)	Tube life of 6 – 10 years
Low (L)	Tube life greater than 10 years with reported corrosion occurring
None (N)	No corrosion reported

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[3] A. M. Alvarez and C. A. Robertson, “Materials and Design Considerations in High Pressure HDS Effluent Coolers,” *Materials Protection and Performance*, May 1973.

[4] E. F. Ehmke, “Corrosion Correlations with Ammonia and Hydrogen Sulfide in Air Coolers,” *Materials Performance*, July 1975.

[5] D. G. Damin and J. D. McCoy, “Prevention of Corrosion in Hydrodesulfurizer Air Coolers,” *Materials Performance*, December 1978.

[6] C. Scherrer, M. Durrieu and G. Jarno, “Distillate and Resid Hydroprocessing: Coping with Corrosion with High Concentrations of Ammonium Bisulfide in the Process Water,” *Materials Performance*, November 1980.

[7] A. Singh, C. Harvey and R. L. Piehl, “Corrosion of Reactor Effluent Air Coolers” Paper 490, Corrosion 97.

Table 1—Summary of REAC Environments

	Minimum Value	Median Value	Maximum Value
K_p	0.00	0.17	8.1
Wash water rate, vol-% feed	0.5	5.2	15.7
Foul water NH_4HS content, wt-%[a]	0.6	4.8	17.2
REAC tube velocity, ft/s	3.0	~ 13.0	39.0
REAC outlet piping velocity, ft/s	4.3	15.1	44.9

Note:

[a] Interpreted to mean NH_4HS content of sour water in downstream separator.

A plot of the data is shown in Figure 1. The four horizontal bands represent the four levels of corrosion but it can be seen that there is considerable overlap in the range of K_p factors at each level. The best conclusion that can be drawn is that there is a trend showing that the severity of corrosion increases with increase of K_p, confirming Piehl's observation. The imprecise nature of the correlation however does not permit a useful guideline to be developed. Similar plots were developed for corrosion severity versus:

1. Downstream separator bisulfide concentration (see Figure 2),
2. Maximum air cooler tube velocity (see Figure 3).

Note: Where values were not reported by the plants, values calculated by UOP were used. These calculated values are valid only for balanced systems with assumed uniform flow distribution. They may be inaccurate where less than full condensation has occurred. As presented, the data were so scattered that no correlation or inference could be drawn. It was evident that occurrences of corrosion do not correlate well with individual parameters partly because of the inaccuracies just discussed and in addition, because of the interdependency of some of the parameters. By simultaneously plotting the level of corrosion against both bisulfide concentration and velocity, only a very slight improvement was obtained (see Appendix A, Figure A-1). However, when the influence of piping symmetry on the distribution of flow through the air coolers was introduced as a fourth parameter, more striking relationships were apparent (see Appendix A, Figures A-2 through A-5).

The air cooler piping system consists of a single inlet pipe connected to a branched manifold system called the inlet header, which distributes the flow equally to each cell of the air cooler. The outlet flow from each cell is gathered by a similar manifold arrangement called the outlet header, which reduces to a single outlet pipe leading to the separator. With the piping headers (inlet and outlet) hydraulically balanced (see Figure A-3), no corrosion or low corrosion of the air cooler tubes is apparent. Several moderate corrosion points appeared, but two of these were associated with very high bisulfide concentrations. Similarly, where the inlet piping header is balanced, corrosion tends to be low (see Figure A-4). On the other hand, when both headers were unbalanced (see Figure A-5), corrosion of the tubes was predominantly severe or moderate. It is clear that uneven distribution of flow through the air cooler creates conditions of either low or high velocities where corrosion can occur. Unfortunately, in most cases reported, neither the bisulfide concentration nor the magnitude of the velocity at the location where corrosion occurs is known, so that a more refined correlation is not possible. The data were screened to exclude air coolers with return bend tubes and those with ferrules. All of the plots are included in Appendix A (see Figures A-1 to A-5).

The above analytical approach was also applied to the associated REAC piping. Piping failures have been the cause of some of the most serious incidents in these units. Discussions of experiences with REAC piping corrosion can be found in the NACE T-8 committee minutes and have been documented by Piehl[8] as well as the UOP study.

Appendix B (see Figures B-1 to B-7) are data plots for outlet headers and piping corresponding to the air cooler tube series. Two sets of data have been used, one for the maximum velocity in the air cooler outlet header and the other for maximum velocity in the piping from the header system to the separator, if greater. Since the piping has a greater thickness than air cooler tubing, the classification of corrosion severity has been changed. Severe corrosion is considered as less than 10 years life, moderate corrosion between 10 and 20 years and low corrosion as measurable but with a greater than 20 year predicted life.

The conclusions are similar to those for the air coolers showing an unclear relationship when just two or three parameters are plotted and an improvement when the fourth parameter is added. Figure B-1 shows the combined effect of bisulfide concentration and header velocity on corrosion. The exceptions to good performance generally lie in the regime of high bisulfide and high velocity. There are however several severe corrosion data points that fall below 4% bisulfide and less than 20 ft/s velocity, a regime that is normally regarded as acceptable. If the maximum piping velocity is included in the data (see Figure B-2), severe corrosion shifts to the right indicating that corrosion is associated with higher velocities. The correlation is stronger when only the maximum outlet piping velocity is plotted (see Figure B-3), and severe corrosion is shown only when velocities are greater than 25 ft/s.

Figure B-4 includes the effect of the header configuration and indicates that serious corrosion has been experienced only when the system is unbalanced whereas with balanced headers experience has been favorable even at surprisingly high veloc-

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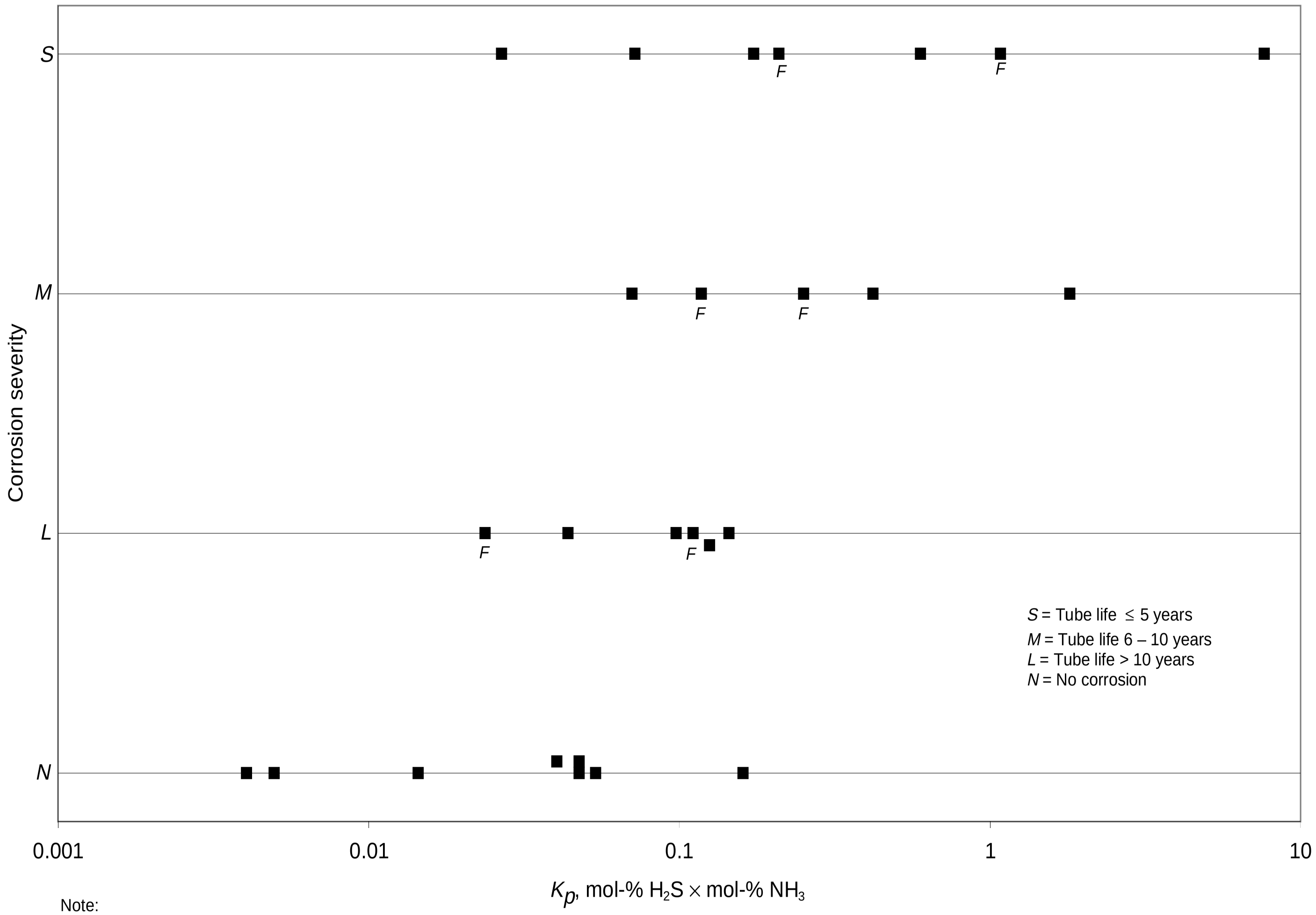
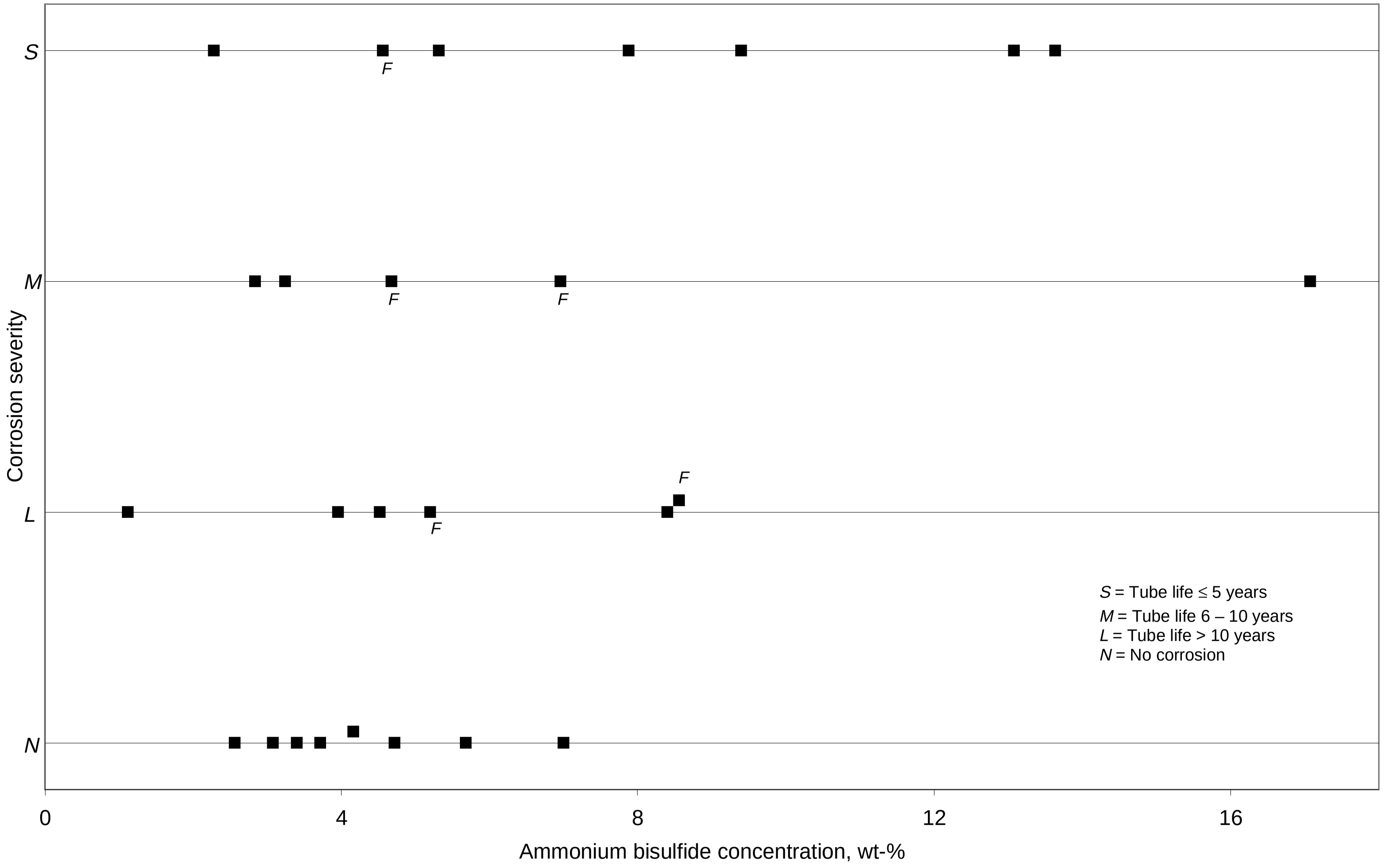
[8] R. L. Piehl, "Survey of Corrosion in Hydrocracker Effluent Air Coolers," *Materials Performance*, January 1976.



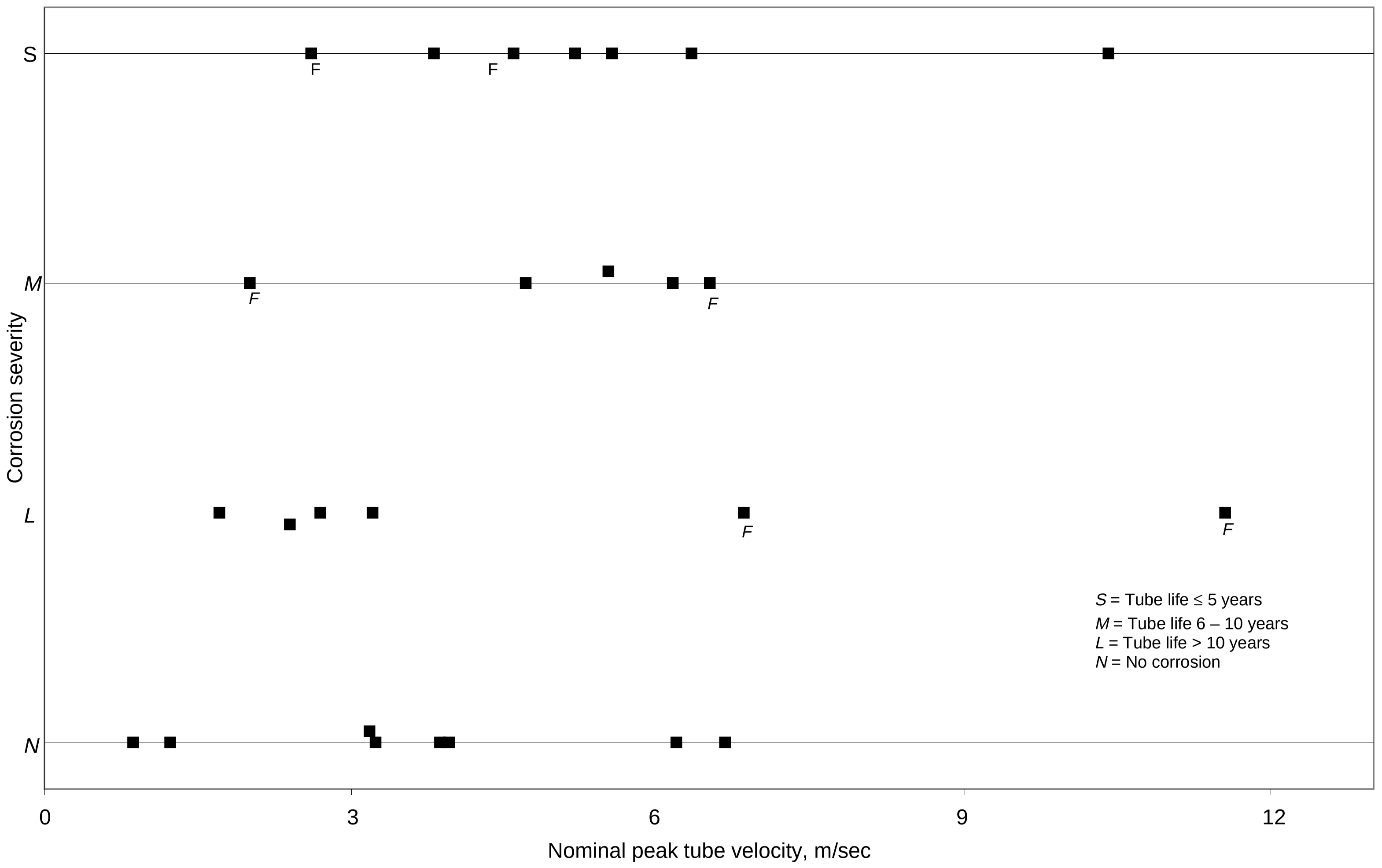
Note:
F = Ferrules used at tube ends

Figure 1—Effect of K_p on REAC Tube Corrosion (from Ref. 7)



Note:
F = Ferrules used at tube ends

Figure 2—Effect of NH_4HS Concentration in the Downstream Separator on REAC Tube Corrosion (from Ref. 7)



Note:
F = Ferrules used at tube ends

Figure 3—Effect of Velocity on REAC Tube Corrosion (from Ref. 7)

ities and bisulfide concentrations. The data in Figure B-4 is clarified by showing the effect of each configuration separately as in Figures B-5, B-6, and B-7. Unfortunately, these observations do not provide any precise guidance as to corrosion behavior with velocity but on the other hand are not in conflict with the suggested ranges proposed by Piehl. A serious shortcoming is the lack of predictability of erosion-corrosion in terms of both the velocity conditions that initiate it and the locations where it might occur.

The UOP survey also reported on the performance of various alloys for REAC tubes and piping, corrosion of other components and in addition discussed air cooler tube fouling. The report concluded with a list of design and operating recommendations which support the 1975 NACE study but did not add any further enlightenment or provide new guidelines for dealing with the problem.

5 1998 API Survey

The present study was initiated in 1997 and consisted of two parts:

1. A preliminary survey to obtain a broad overview of the problem within the task group members' experience.
2. An interview process of selected companies in which details of their corrosion experiences were explored.

5.1 PRELIMINARY SURVEY—BROAD OVERVIEW

A brief questionnaire was sent to all task group members inviting them to provide general information about two units within their company's operations where the corrosion experience in one unit was significantly different from the other. Any unit that had experienced a catastrophic event such as an explosion or fire was to be included. Where possible the second unit would be one that had a predictable and essentially trouble free corrosion record.

The preliminary questionnaire is shown in Figure 4. The survey was divided into three major categories.

1. *Level of distress.* This was intended to give a measure of the severity of the corrosion problems experienced for each unit and to identify units with poor experience from those with good experience.
2. *Economic levels.* Another measure of the seriousness of the corrosion problem is the frequency with which equipment replacements have to be made or if a large capital investment in alloy replacements is believed to be necessary. This category provided some insight into those aspects.
3. *Corrosion control.* The level of effort needed to keep corrosion under control is an indication of the seriousness of the problem to the owner. Included in this category were some corrosion control measures and the quality of inspection.

Unfortunately, in attempting to keep the survey brief to elicit maximum and timely response, some line items contained more than one subject. This ambiguity has been taken into account in drawing conclusions from the responses and does not appear to be a major deterrent to the usefulness of the results.

Table 2 is a complete compilation of the responses received. The categories discussed above are listed at the left side of the table. Each column represents an individual unit identified by a code letter which has been used consistently through the remainder of this report. The type of unit is identified by a code letter as follows:

HCU	hydrocracking
HTU	hydrotreating—this includes hydrodesulfurization and hydrodenitrification units.

Table 3 summarizes the data from the responses and the following conclusions have been drawn.

a. Out of 24 units included in the survey:
   - Five units reported fires and explosions.
   - Four units reported unscheduled outages.
   - Ten units reported experiencing corrosion but manage it by regular replacement of carbon steel or have substituted alloy for carbon steel.
   - Five units reported no significant corrosion.

b. A total of 12 units have substituted alloy for carbon steel.

c. Ten units use alloy extensively.

d. Two units report low corrosion rates but have experienced fires. This indicates localized corrosion resulting in a serious leak.

e. Only two units report using inhibition. One of these had an unscheduled outage.

f. Fifteen plants use regular inspection, that is, inspections conducted at planned intervals, usually at unit turnarounds.

g. Eleven plants use extensive inspection. The thickness measuring locations have been increased or 100% UT inspection is used to detect localized corrosion.

h. Seventeen plants use special frequent inspection. This includes on-line UT and radiography.

There is no distinction of behavior by type of unit. Both hydrocrackers and hydrotreaters have had comparable corrosion experiences. The experience is clearly diverse although it is apparent that those units that have suffered a catastrophic event have upgraded to alloy even when corrosion is generally mild, whereas some units have never had a problem and carbon steel has been quite satisfactory for all equipment items. Inhibition is not a widely used method of corrosion control but those who use it clearly perceive an economic advantage in doing so. It is evident that many reactor effluent systems are subjected to more rigorous inspection than other refinery units as indicated by the number of units receiving frequent or special inspections. The latter include techniques that are detailed and time consuming but are more thorough than alternative methods.

Levels of distress

a) No corrosion or corrosion requiring replacement of equipment on a scheduled basis.

b) Corrosion requiring replacement of equipment on an unscheduled basis.

c) Corrosion causing an outage (unscheduled and sudden).

d) Corrosion causing a fire, explosion, and property damage.

Economic levels

a) Replacement of carbon steel items i) exchanger bundles, ii) piping, iii) weld repair.

b) Frequent extensive in-kind replacement of carbon steel items.

c) Replacement of carbon steel with alloy.

d) Replacement of alloy with alloy.

e) Prolonged outage for replacement.

f) Unit reconstruction.

Corrosion Monitoring Control (Mark as many as are applicable.)

a) Mild corrosion monitored by regular maintenance.

b) Extensive use of alloy in critical locations.

c) Successful use of inhibition.

d) Extensive inspection—all equipment frequently.

e) Special inspection techniques/frequent inspection. (Define frequent as less than 1 year interval.)

f) Use of chemical analysis indicators—e.g., K_p factors, NH_4HS concentration.

g) Wash water quality.

h) Wash water quantity.

Comments (Please add additional pages as needed.)

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Figure 4—Preliminary Survey of Subcommittee Participants for Levels of Experience

Table 2—Preliminary Survey Results

		A	B	C	D	E	F	G	W	H	J	K	L	M	N	Y	O	R	U	DD	P	Q	S	T	X
			HCU	HTU	HCU	HTU	HTU		HCU	HCU		HTU	HCU	HCU		HCU	HTU	HCU	HTU			HCU	HTU	HTU	HTU
Level of Distress																									
a)	No corrosion					X														X	X	X	X	X	X
b)	Scheduled replacement									X	X	X	X	X	X	X	X	X	X	X					
c)	Unscheduled outage						X	X	X	X															
d)	Explosion, fire	X	X	X	X	X																			
Economic Levels																									
e)	Replacement carbon steel		X					X		X			X	X	X	X	X	X	X	X	X	X	X	X	X
f)	Frequent, extensive CS replacement						X		X																
g)	Alloy for CS	X	X	X	X	X				X	X	X		X				X	X			X			
h)	Alloy replacement					X										X				X					
i)	Prolonged outage		X		X	X																			
j)	Unit reconstruction					X																			
Corrosion Control																									
k)	Mild corrosion, regular inspection		X				X	X	X	X	X	X		X		X			X	X		X	X	X	X
l)	Extensive use of alloy	X	X	X	X	X				X		X		X				X				X			
m)	Inhibition								X													X			
n)	Extensive, frequent inspection	X	X		X	X			X	X	X	X		X							X	X			
o)	Special, frequent inspection		X	X	X	X	X	X			X		X	X	X	X	X	X	X			X	X	X	
p)	Chemical analyses: K_p factors	X	X	X	X	X			X	X	X	X	X	X	X	X	X	X	X		X	X			X
q)	Wash water—quality		X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X
r)	Wash water—quantity		X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X

Comments: A: C.S. pipe— > 825; 444 exchanger tubes; > 0.5 mm/yr; velocity = 6 m/s; bisulfide = 4 wt%

B: Replacement of carbon steel in exchangers; (see column E above)

C: Four large leaks; three fires, all related to bisulfide/Cl corrosion

H: Wash—8 kg/hr at 19.2 mbsd

M: Wash—6.8 kg/hr at 14.0 mbsd

O: Cl corrosion at water injection point

R: Cl, F corrosion at water injection point

X: No significant replacement of carbon steel items for many years (see column E above)

Table 3—Summary of Preliminary Survey Results

		SUBTOTALS			
Level of Distress					
a)	No corrosion				5
b)	Scheduled replacement			10	
c)	Unscheduled outage		4		
d)	Explosion, fire	5			
Economic Levels					
e)	Replacement carbon steel	1	2	8	5
f)	Frequent, extensive CS replacement	0	2	0	0
g)	Alloy for CS	5	1	5	1
h)	Alloy replacement	1	0	2	0
i)	Prolonged outage	3	0	0	0
j)	Unit reconstruction	1	0	0	0
Corrosion Control					
k)	Mild corrosion, regular inspection	1	4	6	4
l)	Extensive use of alloy	5	1	3	1
m)	Inhibition	0	1	0	1
n)	Extensive, frequent inspection	4	2	3	2
o)	Special, frequent inspection	4	2	8	3
p)	Chemical analyses: K_p factors	5	2	9	3
q)	Wash water—quality	4	4	10	5
r)	Wash water—quantity	4	4	10	5

The results of this brief survey clearly invite a more detailed investigation into the differences between those units that have experienced no significant corrosion and those that have had explosions or fires. It is also evident that some operators are required to spend more time and money in maintaining their units than others. Previous attempts to address these issues by studying the underlying factors known to affect corrosion behavior have failed to produce a clear picture of the differences. This is believed to be due to the complexity of factors and the lack of precise control of those factors throughout the system.

The next step in this present survey was designed, therefore, to take a different approach to test the above premise. It was decided that instead of gathering broad, detailed information on each of the units selected for study, the information sought would be relevant to a specific corrosion experience only. In this way, it was hoped to separate local aberrations from general unit performance and possibly improve the parametric relationships between causes and effects.

To accomplish this, a selection was made of a number of operating companies that met the following criteria.

1. They operate units with experience at both ends of the spectrum.
2. They were known to have reliable engineering resource.

The number of locations visited was influenced by budgetry considerations.

To test the validity of the selection of companies for interview, their responses to the preliminary survey were separated from Table 2 and are presented in Table 4. A summary of the information is given in Table 5. Comparing Tables 3 and 5 it can be seen that the percentage of units falling into each category is approximately the same in both cases indicating that the selected units are representative of the total population.

5.2 INTERVIEW PROCESS

Following review of the responses, a number of companies were selected and arrangements made to interview key personnel with respect to reactor effluent system corrosion. These interview arrangements were made through the task group members but a request was made to have present appropriate staff engineers with an intimate knowledge of corrosion, process and inspection aspects involved in each of the units selected for study. All of the participants were very co-operative, but it was evident in some companies that staff reductions and re-assignments had an effect on the time available for such studies. Few engineers remain that have a lifetime of experience with these units.

Prior to the visits, a detailed questionnaire (shown in Appendix C) was sent to the interviewees to provide a basis for the discussions and indicate the quality of information being sought. The UOP survey demanded a substantial amount of detailed information, which was needed to compute values for the process parameters of interest. The present survey was designed to avoid imposing an unnecessary burden on the respondents in requesting extraneous process data that would not have a foreseeable use. However, a certain

Table 4—Preliminary Survey Results (Showing Only Units Selected for Site Visits)

		B	C	E	W	I	Y	O	R	U	Q	X	SUBTOTALS		
		HCU	HTU	HTU	HCU	HCU	HCU	HTU	HCU	HTU	HCU	HTU			
Level of Distress															
a)	No corrosion			**X**							**X**	**X**			2
b)	Scheduled replacement					**X**	**X**	**X**	**X**	**X**				6	
c)	Unscheduled outage				**X**										
d)	Explosion, fire	**X**	**X**	**X**									3		
Economic Levels															
e)	Replacement carbon steel	**X**					**X**	**X**	**X**	**X**	**X**	**X**	1	4	2
f)	Frequent, extensive CS replacement				**X**	**X**							0	2	0
g)	Alloy for CS	**X**	**X**	**X**		**X**			**X**	**X**	**X**		3	3	1
h)	Alloy replacement			**X**			**X**						1	1	0
i)	Prolonged outage	**X**		**X**									2	0	0
j)	Unit reconstruction			**X**									1	0	0
Corrosion Control															
k)	Mild corrosion, regular inspection	**X**			**X**	**X**	**X**			**X**	**X**	**X**	1	4	2
l)	Extensive use of alloy	**X**	**X**	**X**					**X**		**X**		3	1	1
m)	Inhibition				**X**						**X**		0	1	1
n)	Extensive, frequent inspection	**X**		**X**	**X**						**X**		2	1	1
o)	Special, frequent inspection	**X**	**X**	**X**			**X**	**X**	**X**	**X**	**X**		3	4	1
p)	Chemical analyses: K_p factors	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	3	6	2
q)	Wash water—quality	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	3	6	2
r)	Wash water—quantity	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	**X**	3	6	2
K_p Values		**0.12**	**0.03**	**0.33**	**0.45**	**0.23**	**0.34**	**0.3 – 0.45**		**0.4 – 1**	**0.04**	**0.05**			

Comments:
B: Replacement of carbon steel in exchangers (see column E above)
C: Four large leaks; three fires, all related to bisulfide/Cl corrosion
O: Cl corrosion at water injection point
R: Cl, F corrosion at water injection point
X: No significant replacement of carbon steel items for many years (see column E above)

Table 5—Summary of Preliminary Survey Results (Showing Only Units Selected for Site Visits)

		SUBTOTALS		
Level of Distress				
a)	No corrosion			2
b)	Scheduled replacement		6	
c)	Unscheduled outage			
d)	Explosion, fire	3		
Economic Levels				
e)	Replacement carbon steel	1	4	2
f)	Frequent, extensive CS replacement	0	2	0
g)	Alloy for CS	3	3	1
h)	Alloy replacement	1	1	0
i)	Prolonged outage	2	0	0
j)	Unit reconstruction	1	0	0
Corrosion Control				
k)	Mild corrosion, regular inspection	1	4	2
l)	Extensive use of alloy	3	1	1
m)	Inhibition	0	1	1
n)	Extensive, frequent inspection	2	1	1
o)	Special, frequent inspection	3	4	1
p)	Chemical analyses: K_p factors	3	6	2
q)	Wash water—quality	3	6	2
r)	Wash water—quantity	3	6	2

amount of detail to evaluate each experience was requested. It was decided that the data collected would be specific to each corrosion incident discussed. In this way, the parameters affecting each incidence of corrosion would be available, but the laborious task of gathering all the process, operating and maintenance records could be eliminated. This made the information base more manageable. The questionnaire covered all of the subjects pertinent to corrosion in REAC systems and served as an agenda for the discussions.

The contents of each interview were recorded as hand-written notes backed up by copies of relevant data sheets, flow diagrams and reports. Each significant corrosion experience was discussed in chronological order until the entire history of the unit was completed. The results of these discussions were compiled into a spreadsheet presented in Table 6.

5.3 REACTOR EFFLUENT AIR COOLERS

All of the data relevant to the reactor effluent air coolers have been sorted from Table 6 and is presented separately in Table 7. The table identifies the plant and type of unit and gives a brief description of the corrosion problem, including the apparent cause. Where additional background information or observations are available, they have been added as comments. Numerical data has been compiled separately in Table 8.

There has been a wide variety of experience with air coolers in terms of useful life. Tube failures have occurred in as little as a few months in the worst case (Plant C), but in another unit (Plant U), carbon steel tubes have lasted 25 years with no failures. In the first case, corrosion was due to deposition of ammonium salts in the air cooler tubes with probably just enough water present to create an aggressive concentrated salt solution. Subsequent efforts to solve the problem by substituting chrome steels and later stainless steels were unsuccessful until Alloy 800 was installed some 14 years later. The maximum tube velocities in this air cooler were high with respect to Piehl's guidelines and the ammonium bisulfide concentration in the downstream separator was 13% suggesting that this too might have been a contributing factor. In the second case, the operating conditions are very mild. There has never been any plugging or corrosion because the air cooler operates at an outlet temperature above the salt condensation point (150°F). It is interesting that this unit also has unbalanced outlet piping, which apparently is not a factor because the deposition of salts does not come into play.

One of the earliest problems with carbon steel air cooler tubes was severe localized corrosion of the tube ends (Plants W, EE, and Y). This was caused by high velocity and turbulence at the entrance to the tube and in some cases at the outlet end of the tube. This type of attack is thought by many to be an example of erosion-corrosion. The problem has been solved by the use of alloy ferrules with carbon steel tubes. Both stainless steel and Alloy 800 ferrules are used. Where ferrules are used, they must be designed with a tapered end so that there is no abrupt transition from the ferrule to the tube causing downstream eddies. Loose fitting ferrules can admit corrosive solutions to the annulus with the tube wall and initiate crevice corrosion (Plant W). Alloy 800 tubes have not been reported to have tube end corrosion problems.

The results of discussions with respondents indicated that velocity must be controlled to avoid corrosion problems. Although the data in Table 8 is incomplete, it can be seen that serious corrosion is associated with either high bisulfide concentrations or high velocity, or both (Plants C, W, AA, and EE). Conditions of high bulk fluid velocity also lead to turbulence and localized corrosion or erosion-corrosion. The data in Table 8 is not in conflict with 20 ft/s as a reasonable upper limit on tube velocity when associated with 4% bisulfide. Plant Y appears to be in conflict with this conclusion, however the lower velocities could have resulted in underdeposit corrosion from salt build-up when the bisulfide concentration was 7% – 8%. The data for Plant O in Table 8 indicates that higher velocities can be tolerated if the bisulfide concentrations are low.

One of the factors emphasized by this review is the critical role of wash water. Plants that experienced severe corrosion early in their history have attributed the problem to lack of wash water (Plants B, R, and Y) and have often been able to correct the problem by increasing the water rate. There is a wide variation from process to process in the amount of injected water that vaporizes when introduced to the process stream. None of the respondents reported more than 75% vaporization, indicating a minimum of 25% of the injected water remains as liquid after introduction. When a single injection point is used, the aqueous phase has to distribute itself through the inlet piping header system and the air cooler tube bundles in proportion to the effluent flows in that equipment. To eliminate the influence of an unbalanced piping header system, some operators use multiple injection points (see Table 11). These are usually located on the air cooler inlet nozzle close to the tube bundle inlet. The purpose is to ensure that each bundle receives the same amount of wash water. However, individual monitoring of each injection line is required, and frequent manual adjustment of the flow control valves is often needed. The small diameter water lines and injectors are also prone to plugging depending on the quality of water used. Wash water preferences will be discussed below when that specific topic is addressed.

Where corrosion has been serious and persistent, unit operators have sometimes invested in Alloy 800 or Alloy 825 as a permanent solution. Alloy 800 has been used for at least 17 years with no major failures (Plant B); however, pitting corrosion has been reported (Plants Q and E) so that the long-term reliability has been put in question. One of these cases reported a chloride content of 50 ppm in the separator water. The level at which chlorides are significant with respect to pitting of Alloy 800 has not been established although laboratory tests[9] identify 100 ppm as harmful. One operator also received laminated Alloy 800 tubes that were not discovered until they had been in service some time.

5.4 REAC INLET AND OUTLET PIPING

All comments relating to inlet and outlet piping associated with the REACs have been sorted from the general comments in Table 6 and presented as a separate compilation in Table 9. The numerical data have been reformatted and are presented in Table 10.

The piping system discussed in this section covers the piping from the water injection point, the inlet headers to the air cooled exchangers, and the outlet headers and piping to the separator drums.

Out of the 12 units included in the detailed survey, one half experienced piping corrosion problems. Of the better performing group two were inhibited, two use alloy and two did not experience any significant corrosion. Corrosion has been experienced on both the inlet and outlet sides of the REACs. The corrosion has often been localized at tees, elbows or as grooving of straight run pipe. Depending on upstream factors, such as type of catalyst and feedstock quality, condensed salts can be ammonium fluoride, chloride or bisulfide, or combinations of the three. Some operators employ fluoride catalyst activators giving rise to residual fluorides in the system (Plant R). The deposition temperature for the chloride salt is higher than the fluoride salt deposition temperature which in turn is higher than the bisulfide condensation temperature. Apparently, the aggressiveness of the salts is in the same order. Severe corrosion by deposition of ammonium chloride is the most prevalent type of attack.

5.4.1 Inlet Piping

Corrosion of the inlet piping was reported for two areas, immediately around the water injection point and in the headers before the REACs. Around the injection point, direct water impingement has been a problem. When excessive vaporization occurs, the amount of liquid water remaining could be too low and this results in concentrated aqueous salt corrosion. Salt deposits in the feed/effluent exchangers upstream of the water injection point have resulted in severe corrosion when water has come in contact with the deposits, from either splashing or saturation above the dew point. One solution has been to use an alloy lining in the immediate area. One operator has used Alloy 625 successfully for this purpose. Localized corrosion can also occur as a concentrated aqueous phase resulting from insufficient wash water flows through the piping system. At elbows where surface velocities can increase due to turbulence, the attack may be particularly severe. Both straight-pipe corrosion and erosion-corrosion of elbows have been reported by respondents. Again, the solution has been to use alloy for protection. In one case, Plant Q, installing Alloy

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[9] C. Scherrer, M. Durrieu and G. Jarno, “Distillate and Resid Hydroprocessing: Coping with Corrosion with High Concentrations of Ammonium Bisulfide in the Process Water,” *Materials Performance*, November 1980.

Table 6—Compilation of Information from Plant Interviews

Plant	Unit	Location of Corrosion	Type of Corrosion	Causative Factors	Comments
B	**HCU**	Air cooler tubes	Bisulfide corrosion	Lack of wash water.	Installed 1971; failed in 6 years (fire); replaced with Alloy 800.
		A/C outlet piping	Grooving and channeling	25 ft/s attack in turbulent area downstream of elbow. Now corroding at 50 mpy. Suspect oxygen and chlorides. No corrosion when oxygen and chlorides under control.	Original 18" replaced with 22" in 1994.
		Trim cooler	U-bend corrosion	Lower velocity and lower temperature than A/C. Lower rate of corrosion.	Replaced carbon steel with Alloy 800 in 1981 (10 years).
		Effluent/ fractionator feed exchanger	Tube thinning (24 years); bisulfide corrosion	Suspect oxygen (50 ppb) involved; inlet piping @ 29 ft/s—still in service.	Failed in 1995 after 24 years at < 5 mpy.
Q	**HCU**	A/C inlet piping (c.s.)	Bisulfide corrosion	High velocity—43 ft/s: low water injection.	Non-symmetrical piping layout; 14" pipe. Installed Alloy 800 elbows in inlet until pipe replaced with 825. Both inlet and outlet piping now 825.
		A/C outlet piping (c.s.)	Bisulfide corrosion	High velocity—34 ft/s: low water injection.	
		A/C tubes (c.s.)	Tube thinning—bisulfide corrosion	Alloy 800 replacement; have found pitting. Also experienced leaks from external corrosion.	Thirty-six tube leaks from 1967 – 1983. Installed ferrules in 1983. After 1 month, one tube leak. Retubed with Alloy 800 tubes in 1984 – 1985.
		Fractionator feed/effluent exchanger	Tube corrosion	Bisulfide corrosion from water in fractionator feed; retubed in 1981 with Alloy 800.	Startup 1967 with carbon steel tubes. Eighty-six U-bend tubes plugged by 1976 leak. Leak in 1978 caused outage. Retubed with carbon steel in 1981. Retubed with Alloy 800 in 1983.
		Trim cooler	Bisulfide corrosion; also water side attack	Suspect oxygen involved. Filming amine added in 1994.	Water side corrosion by MIC; poor chlorination; 10 mpy – 15 mpy on channels. Retubed in 1983 with carbon steel.
C	**HTU**	A/C tubes (c.s.)	Bisulfide corrosion	13% bisulfide; 25 ft/s.	Failure 77 days (1967). Tried 12 Cr, 17 Cr, and 18-8 upgrades. Alloy 800 installed in 1981. 17% max (13% average) ammonium bisulfide; 25 ft/s.
		A/C outlet piping	Bisulfide corrosion	Swirling grooved pattern.	Upgraded to Alloy 800. Now 825 because of PTA.
		Compressor suction line	Bisulfide corrosion	10% – 15% bisulfide. Rates of 100 mpy – 500 mpy in turbulent flow behind weld protrusion. High NH_3 in gas phase reduced by lowering wash water temperature.	Problem caused by high ammonia in vapor causing bisulfide salt deposit. Pinhole just behind weld jetted onto operator resulting in shut down. Near miss. Corrosion in column tolerable at 10% but not 15% bisulfide.
		Hydrogen recycle dead leg	Ammonium chloride corrosion	Dead leg allowed condensate to form.	Gas oil HT hydrogen. 12 Cr dead leg 6" pipe large enough to allow circulation and salt accumulation.
O	**HTU**	Separator liquid/reactor effluent	Ammonium chloride corrosion	Not enough intermittent wash water. Wetted but non-flowing deposits.	Operational defect. Solid deposits pushed downstream into exchanger. 300 mpy – 400 mpy. Now 625 overlaid.
		A/C tubes	No corrosion	No corrosion because of 3-phase flow.	No solids deposits; 1% bisulfide in separator; 26 ft/s.
R	**HCU**	A/C tubes	Ammonium fluoride/chloride corrosion	Underdeposit corrosion. Inadequate wash water (distribution).	Fluorides from hydrocracking catalyst. Needs re-fluorination. Upgraded to type 410 stainless steel (1984). Designed for annular flow. Weirs in inlet header. Corrosion in tubes < 1 mpy since 1984.
		Water injection point	Corrosion-erosion adjacent to inlet	Insufficient wash water. 1 in. metal loss in 10 years.	Severe attack (65 mpy). Redesigned with spray nozzle and weld overlaid with Inconel 625. Installed static mixer.
		A/C inlet piping	Ammonium fluoride corrosion	400 mils in 20 years. NH_4F or NH_4Cl ; too hot for bisulfide.	Replaced in 1978. Lasted to 1997.

Table 6—Compilation of Information from Plant Interviews (Continued)

Plant	Unit	Location of Corrosion	Type of Corrosion	Causative Factors	Comments
W	**HCU**	A/C inlet piping	Thinning at exchanger inlet. Balanced piping	High nitrogen feed; $K_p > 0.45$; 8% bisulfide.	After first experience with carbon steel, used 12 Cr. Intermittent wash to prevent salt fouling. Use inhibitor.
		A/C tubes	Recurring problems with carbon steel tubes; bisulfide corrosion	8% bisulfide; < 20 ft/s velocity in tubes; carbon steel tubes.	1968 – 1980 unscheduled replacement; after 1980 went to 5-year schedule. Four leaks since. Four years minimum, average > 5 years. Erosion at outlet of last pass. Use type 304 ferrules—pitted in annulus due to chlorides.
		A/C outlet header	Bisulfide corrosion	Required replacement of headers. Unbalanced piping.	Wash water adjusted according to bisulfide content, nitrogen content, and feed rate. 75% non-vaporizing.
		A/C outlet piping	No serious corrosion—no replacement	Some Ls overlaid with 309/18-8. Indicates erosion-corrosion at > 20 ft/s.	Strict control of bisulfide in accumulator (8%).
W(2)	**HCU**	A/C outlet piping	Severe bisulfide erosion—fire	Increased velocity because of 10% increase in liquid feed.	Unsymmetrical piping with impingement due to sharp turns. Velocity change from 20 ft/s – 27 ft/s.
X	**HTU**	All carbon steel equipment	No serious corrosion problems	K_p = 0.05; 2% – 3% bisulfide; 15 ft/s tube velocity.	Balanced piping; annular flow; stripped sour water wash, 60% vaporized; low chlorides.
EE	**HCU**	A/C tubes	Bisulfide corrosion	Tube thinning. Ferrules installed on inlet of row 2. Thinning of inlets to 3rd and 4th rows. Never had tube plugging.	Carbon steel tubes, Alloy 800 ferrules. Original top row type 304 stainless steel—changed to Alloy 800. Tube life has varied from 5 – 16 years. All tubes changed to Alloy 800 in 1997. K_p = 0.12 – 0.2; bisulfide = 4% at separator.
		A/C piping	No significant corrosion	Low bisulfide; Velocities ~ 30 ft/s.	
I	**HCU**	All carbon steel equipment	No serious corrosion problems	Unbalanced piping; bisulfide ~ 4%. Velocities not provided. K_p = 0.23.	
Y	**HCU**	A/C tubes	Bisulfide corrosion	K_ps increased from 0.09 to 0.32 over time. Velocities in 10 ft/s – 15 ft/s range. 4% bisulfide.	Carbon steel—initial problems tube end corrosion. Perforation came later. Retubed with carbon steel approximately every 5 years. Plan to upgrade to Alloy 825 on next retube. Formerly single wash water point—now multiple. Poor water distribution.
		A/C piping	Bisulfide corrosion inlet headers	Velocities in inlet header system of 17 ft/s – 27 ft/s.	Unbalanced inlet and outlet piping. > 20 mpy. Possible chloride problem due to inadequate water in inlet. Piping upgraded to Alloy 825 on small sizes. Alloy 625 overlay on large carbon steel piping.
					Possible chloride problem due to inadequate water.
		HP Separator	Bisulfide corrosion-erosion	Impingement attack.	Stainless steel impingement plate of adequate size.
Z	**HTU**	A/C tubes	Bisulfide corrosion—thinning leading to fire	Type 410 stainless steel tubes. Failure after 7 years. 20 mpy – 25 mpy. Bottom tube grooving. Bisulfides concentrated to 19% in outer cells. Poor water distribution.	Non-symmetrical piping and single point water injection. Tubes upgraded to Alloy 825. Throughput increased before failure.
		A/C piping	No corrosion	Alloy 825.	Header boxes and outlet piping verified 825. No velocities available.
AA	**HTU**	A/C outlet piping	Corrosion-erosion of carbon steel piping	Bisulfide corrosion.	Replaced elbows with Alloy 800. Velocities 18 ft/s – 32 ft/s. Within 2 years upgraded all pipe to Alloy 800. Changed to Alloy 825 because of polythionic acid cracking—installation error. Balanced inlet and outlet. 14% – 15% bisulfide.
		A/C tubes	No corrosion	Alloy 800 tubes and Alloy 800 boxes.	Original tubes Alloy 800. Velocities 18 ft/s – 20 ft/s.
		Effluent/fractionator feed exchanger	Ammonium chloride deposition	Corrosion upstream of water injection.	Added intermittent injection points. Metallurgy upgraded from 17Cr to 2205 duplex SS.

Table 6—Compilation of Information from Plant Interviews (Continued)

Plant	Unit	Location of Corrosion	Type of Corrosion	Causative Factors	Comments
		HPLT separator water outlet pipe	Bisulfide corrosion	Level control problem. Stratified flow with concentrated bisufide at steel surface 8% – 28% bisulfide in aqueous phase, normally 15% – 16%.	Swirl pattern of attack terminated at weld protrusion which acted as a flow straightener. Local attack immediately after weld. CS replaced with Alloy 800.
		HPLT separator outlet pipe—hydrocarbon	Bisulfide corrosion due to water entrainment	Water carryover from high level in separator. Extreme corrosion up to 1-in. loss in one week.	Severe corrosion of weldolet. Detected by radiography before failure occurred. Near miss.
		LPLT separator off gas piping	Impingement attack	Sulfur deposit buildup caused restricted flow and erosion-corrosion. Requires liquid carryover.	Probably erosion-corrosion from droplet impingement.
		By-pass dead legs	Bisulfide corrosion	(See Plant C for same problem.) Corrosive deposits formed by circulation in open dead leg.	Localized attack over 1 ft^2 area.
		Equipment downstream of separators	Problems caused by bisulfides and cyanides	Occurs where salt concentration takes place.	Stripper overhead receiver vapor line had to be replaced at 6 month intervals.
BB	**HCU**	Feed/effluent exchanger	Chloride pitting of tubes on feed side	Type 321 stainless steel tubes pitted due to Cl in feed.	Fail every 2 years. Upgraded to 254SMO. No desalter.
		Effluent piping upstream A/C	Under deposit attack	Ammonium chloride.	Corrosion around water injection point and downstream piping.
		A/C tubes	Carbon steel tubes	High velocities up to 60 ft/s in inlets. Velocities reduced to 15 ft/s – 17 ft/s. Unbalanced piping.	9% bisulfide max.; 3.5% – 4% avg. Changed from 4-pass to 2-pass to reduce velocities—solved problem. Water accumulation in lower pressure drop tube banks caused sealing and increased flow in open banks.
CC	**HCU**	Effluent piping from exchangers to separator	Bisulfide corrosion	6% – 6.8% bisulfide. Velocities up to 32 ft/s.	Extra heavy CS replaced every 8 years. Upgraded to Alloy 825 because of increasing N in feed.
		1st stage effluent trim cooler	Bisulfide corrosion	~ 6.5% bisulfide.	U-tube exchanger. Upgraded from CS to monel after 2 years.
		1st stage effluent/feed exchanger	Bisulfide corrosion	~ 6.5% bisulfide Velocity 38 ft/s – 40 ft/s.	Original CS > 10 years life. Upgraded to 3RE60 duplex alloy.
		2nd stage effluent feed exchanger	Bisulfide corosion		Changed tubes from 17 Cr to 3RE60 after 15 years.
E	**HTU**	A/C tubes	Alloy 800—found pitting after 7 years	Original 800 tubes and header boxes. Found pitting and delaminations. Upgraded to Alloy 825. Suspect chlorides caused pitting. Tube velocities 12 ft/s – 17 ft/s.	
		A/C piping	Corrosion-erosion of outlet elbow resulting in fire	Carbon steel piping. Inlet piping balanced; outlet piping unbalanced. Bisulfide < 8%. Velocities 9 ft/s – 26 ft/s.	Unit modified to include HPHT separator for process reasons. Failure occurred after 9 months. Failure occurred in outlet elbow after installation of HPHT separator. Reduced water wash, increased bisulfide, and unbalanced fan operation. Increased H_2.
		Effluent/feed exchanger	No corrosion	Operates at 400+ with no salt deposits. No water wash on this item.	Plan to increase operation to 500 degrees. Concern with naphthenic acids. Effluent has 5 ppm – 10 ppm chlorides.
U	**HTU**	A/C tubes	No corrosion	H_2S in excess of ammonia. 6% bisulfide. Velocity 10 ft/s.	No plugging. Discontinued upstream water wash. Ammonia low; temperatures high. Single point water injection—totally vaporized. Carbon steel tubes. 5 Cr channels. Four bays to two after addition of HPHT separator due to reduced throughput.
		A/C piping	No corrosion	Currently carbon steel—upgrading to Alloy 825. Unbalanced outlet piping. REAC inlet velocity 21 ft/s.	Planning addition of HPHT separator. K_p = 0.8. Alloy 825 piping from injection point to separator.

Table 7—Compilation of Information from Plant Interviews—Air Cooler Tubes

Plant	Unit	Location of Corrosion	Type of Corrosion	Causative Factors	Comments
B	**HCU**	Air cooler tubes	Bisulfide corrosion	Lack of wash water.	Installed 1971; failed in 6 years (fire); replaced with Alloy 800.
Q	**HCU**	A/C tubes (c.s.)	Tube thinning—bisulfide corrosion	Alloy 800 replacement; have found pitting. Also experienced leaks from external corrosion.	36 tube leaks from 1967 – 1983. Installed ferrules in 1983. After 1 month, 1 tube leak. Retubed with Alloy 800 tubes in 1984 – 1985.
C	**HTU**	A/C tubes (c.s.)	Bisulfide corrosion	13% bisulfide; 25 ft/s.	Failure 77 days (1967). Tried 12 Cr, 17 Cr, and 18-8 upgrades. Alloy 800 installed in 1981. 17% max (13% average) ammonium bisulfide; 25 ft/s.
O	**HTU**	A/C tubes	No corrosion	No corrosion because of 3-phase flow.	No solids deposits; 1% bisulfide in separator; 26 ft/s.
R	**HCU**	A/C tubes	Ammonium fluoride/chloride corrosion	F condensation temperature > chlorides.	Fluorides from hydrocracking catalyst. Needs re-fluorination. Upgraded to type 410 stainless steel (1984). Designed for annular flow. Weirs in inlet header. Corrosion in tubes < 1 mpy since 1984.
W	**HCU**	A/C tubes	Recurring problems with carbon steel tubes; bisulfide corrosion	8% bisulfide; < 20 ft/s velocity in tubes; carbon steel tubes.	1968 – 1980 unscheduled replacement; after 1980 went to 5 year schedule. Four leaks since. Four years minimum, average > 5 years. Erosion-corrosion at outlet of last pass. Use type 304 ferrules—pitted in annulus due to chlorides.
X	**HTU**	All carbon steel equipment	No serious corrosion problems	K_p = 0.05; 2% – 3% bisulfide; 15 ft/s tube velocity.	Balanced piping; annular flow; stripped sour water wash, 60% vaporized; low chlorides.
EE	**HCU**	A/C tubes	Bisulfide corrosion	Tube thinning. Ferrules installed on inlet of row 2. Thinning of inlets to 3rd and 4th rows. Never had tube plugging.	Carbon steel tubes, Alloy 800 ferrules. Original top row type 304 stainless steel—changed to Alloy 800. Tube life has varied from 5 – 16 years. All tubes changed to Alloy 800 in 1997. K_p = 0.12 – 0.2; bisulfide = 4% at separator.
I	**HCU**	All carbon steel equipment	No serious corrosion problems	Unbalanced piping; bisulfide ~ 4%. Velocities not provided. K_p = 0.23.	
Y	**HCU**	A/C tubes	Bisulfide corrosion	K_ps increased from 0.09 to 0.32 over time. Velocities in 10 ft/s – 15 ft/s range. 7% – 8% bisulfide.	Carbon steel—initial problems tube end corrosion. Perforation came later. Retubed with carbon steel approximately every 5 years. Plan to upgrade to Alloy 825 on next retube. Formerly single wash water point—now multiple. Poor water distribution.
Z	**HTU**	A/C tubes	Bisulfide corrosion—thinning leading to fire	Type 410 stainless steel tubes. Failure after 7 years. 20 mpy – 25 mpy. Bottom tube grooving. Bisulfides concentrated to 19% in outer cells. Poor water distribution.	Non-symmetrical piping and single point water injection. Tubes upgraded to Alloy 825. Throughput increased before failure.
AA	**HTU**	A/C tubes	No corrosion	Alloy 800 tubes and Alloy 800 boxes.	Original tubes Alloy 800. Velocities 18 ft/s – 20 ft/s.
BB	**HCU**	A/C tubes	Carbon steel tubes	High velocities up to 60 ft/s in inlets. Velocities reduced to 15 ft/s – 17 ft/s. Unbalanced piping.	9% bisulfide max.; 3.5% – 4% avg. Changed from 4-pass to 2-pass to reduce velocities—solved problem. Water accumulation in lower pressure drop tube banks caused sealing and increased flow in open banks.
E	**HTU**	A/C tubes	Alloy 800—found pitting after 7 years	Original 800 tubes and header boxes. Found pitting and delaminations. Upgraded to Alloy 825. Suspect chlorides caused pitting. Tube velocities 12 ft/s – 17 ft/s.	
U	**HTU**	A/C tubes	No corrosion	H_2S in excess of ammonia. 6% bisulfide. Velocity 10 ft/s.	No plugging. Discontinued upstream water wash. Ammonia low; temperatures high. Single point water injection—totally vaporized. Carbon steel tubes. 5 Cr channels. Four bays to two after addition of HTHP separator due to reduced throughput.

Table 8—Air Cooler Tube Experience from Survey

					Type of Corrosion							
Plant	Unit	Original Material	Corrosion rate (life)	Material Upgrade (life to date)	Erosion-Corrosion	Salt deposit	Thinning	Other	Cause of Corrosion	HS concentration (%)	Velocity (ft/s)	K_p
B	**HCU**	CS	18 mpy (6 years)	Alloy 800 (17 years)		X	X		Insufficient wash water	5% – 22 % (calculated)	17 – 19	0.2
Q	**HCU**	CS		Alloy 800 (14 years—pitting)			X		Bisulfide corrosion		19	0.014 – 0.040
C	**HTU**	CS	500 mpy (77 days)	Various to Alloy 825[a] (9 years)			X		High bisulfides; high velocity	13 average; 17 max.	25	0.2 – 0.5
O	**HTU**	CS		None		No			Low bisulfide	1%	26	0.22
R	**HCU**	CS	200 mpy (6 months)	12 Cr[b]		X	X		Fluorides/chlorides—high deposition temperature. Insufficient wash water			
W	**HCU**	CS		Use 304 SS ferrules[c]	X				High exit velocity	8%	Currently < 20	> 0.45
X	**HTU**	CS	Since 1972	None		No			Favorable operating parameters	2% – 3%	15	0.05
EE	**HCU**	CS w/ 800 ferrules; 304 top row	20 mpy	Alloy 800 (new)	X	No	X		High velocity and low water wash	4%	30 in; 20 out	0.12 – 0.2
I	**HCU**	CS		None						4%		0.23
Y	**HCU**	CS	25 mpy (est.)	CS, Alloy 825 next upgrade	X	?		Pitting	Low water rate; poor distribution	7% – 8% (reduced to 4%)	11 – 15 in; 8 – 11 out	0.34
Z	**HTU**	17 Cr	20 mpy – 25 mpy	Alloy 825		No	X		High bisulfide	Up to 19% in low flow cells		
AA	**HTU**	Alloy 800	13 years						No corrosion	12 – 15%	18 – 20	
BB	**HCU**	CS		None			X		High tube end velocities caused by uneven flow	3.5% – 4% avg.; 9% max.	60 ft/s reduced to 15 ft/s – 17 ft/s	
E	**HTU**	Alloy 800		Alloy 825				Pitting[d]	Suspect chlorides	< 8%	12 – 17	6.1
U	**HTU**	CS		None		No			Low NH_3	3.9 average; 6.0%	10	~0.8

Notes: [a] Carbon steel failed in 77 days.

[b] Replaced failure with CS. Changed to 12Cr for process reasons.

[c] Chloride corrosion behind the outlet ferrule.

[d] Manufacturing defects.

Table 9—Compilation of Information from Plant Interviews—Piping Information

Plant	Unit	Location of Corrosion	Type of Corrosion	Causative Factors	Comments
B	**HCU**	A/C outlet piping	Grooving and channeling.	25 ft/s attack in turbulent area downstream of elbow. Now corroding at 50 mpy. Suspect oxygen and chlorides. No corrosion when oxygen and chlorides under control.	Original 18" replaced with 22" in 1994.
Q	**HCU**	A/C inlet piping (c.s.)	Bisulfide corrosion.	High velocity—43 ft/s: low water injection.	Non-symmetrical piping layout; 14" pipe. Installed Alloy 800 elbows in inlet until pipe replaced with 825. Both inlet and outlet piping now 825.
		A/C outlet piping (c.s.)	Bisulfide corrosion.	High velocity—34 ft/s: low water injection.	
C	**HTU**	A/C outlet piping	Bisulfide corrosion.	Sequential addition of Alloy 600 to downstream piping. Failure occurred downstream of last upgrade in remaining carbon steel section.	Occurred in 1982. No info on parameters.
R	**HCU**	A/C piping	NH_4F corrosion. 100 mpy.	1 mil in 10 years. Ammonium fluoride.	Replaced in 1978 and again in 1996.
W	**HCU**	A/C inlet piping	Thinning at exchanger inlet. Balanced piping.	High nitrogen feed; K_p > 0.45; 8% bisulfide.	After first experience with carbon steel used 12 Cr. Intermittent wash to prevent salt fouling. Use inhibitor.
		A/C outlet piping	No serious corrosion—no replacement.	Some ells overlaid with 309 / 18-8. Indicates erosion-corrosion at > 20 ft/s.	Strict control of bisulfide in accumulator (8%).
W(2)	**HCU**	A/C outlet piping	Severe erosion-corrosion—fire.	Increased velocity because of 10% increase in liquid feed.	Unsymmetrical piping with impingement due to sharp turns. Velocity change from 20 ft/s – 27 ft/s.
X	**HTU**	All carbon steel equipment	No serious corrosion problems.	K_p = 0.05; 2% – 3% bisulfide; 15 ft/s tube velocity.	Balanced piping; annular flow; stripped sour water wash, 60% vaporized; low chlorides.
EE	**HCU**	A/C piping	No significant corrosion.	Low bisulfide; Velocities ~ 30 ft/s.	
I	**HCU**	All carbon steel equipment	No serious corrosion problems.	Unbalanced piping; bisulfide ~ 4%. Velocities not provided. K_p = 0.23.	
Y	**HCU**	A/C piping	Bisulfide corrosion inlet headers.	Velocities in inlet header system of 17ft/s – 27 ft/s.	Unbalanced inlet and outlet piping. > 20 mpy. Possible chloride problem due to inadequate water in inlet. Piping upgraded to Alloy 825 on small sizes. Alloy 625 overlay on large carbon steel piping.
Z	**HTU**	A/C piping	No corrosion.	Alloy 825.	Header boxes and outlet piping verified 825. No velocities available.
AA	**HTU**	A/C outlet piping	Erosion-corrosion of carbon steel piping.	Bisulfide corrosion.	Replaced elbows with Alloy 800. Velocities 18 ft/s – 32 ft/s. Within 2 years upgraded all pipe to Alloy 800. Changed to Alloy 825 because of polythionic acid cracking—installation error. Balanced inlet and outlet. 14% – 15% bisulfide.
		HPLT separator outlet pipe	Bisulfide corrosion.	Carbon steel pipe replaced with Alloy 800.	12% – 15% bisulfide in aqueous phase.
		HPLT separator outlet pipe— hydrocarbon	Bisulfide corrosion due to water entrainment; near miss.		
		LPLT separator off gas piping	Impingement attack downstream of sulfur deposits.	Deposit buildup restricted flow and caused erosion-corrosion. Requires water carryover.	
BB	**HCU**	Effluent piping upstream A/C	Under deposit attack.	Ammonium chloride.	Corrosion around water injection point and downstream piping.
CC	**HCU**	Effluent piping from exchangers to separator	Bisulfide corrosion.	6% – 6.8 % bisulfide. Velocities up to 32 ft/s.	Extra heavy CS replaced every 8 years. Upgraded to Alloy 825 because of increasing N_2 in feed.
E	**HTU**	A/C piping	Erosion-corrosion of outlet elbow resulting in fire.	Carbon steel piping. Inlet piping balanced; outlet piping unbalanced. Bisulfide < 8%. Velocities 9 ft/s – 26 ft/s.	Unit modified to include HTHP separator for process reasons. Failure occurred after 9 months. Failure occurred in outlet elbow after installation of HTHP separator. Reduced water wash, increased bisulfide, and unbalanced fan operation. Increased H_2.
U	**HTU**	A/C piping	No corrosion.	Currently carbon steel—upgrading to Alloy 825. Unbalanced outlet piping. REAC inlet velocity 21 ft/s.	Planning addition of HPHT separator. K_p = 0.8. Alloy 825 piping from injection point to separator.

Table 10—Piping Experience from Survey

								Water injection point					
Plant	Unit	Inlet—(I) Outlet—(O)	Original Material	Corrosion Rate (life)	Material Upgrade (life to date)	Balanced	Unbalanced	Single	Multiple	Water wash rate (gpm)	HS concentration (%)	Velocity (ft/s)	K_p
B	**HCU**	O	CS	50 mpy[a] grooving	none	X		X		120	n.a.	25	0.12
Q	**HCU**	I	CS; added 800 elbows	Inhibited	Alloy 825		X			low		43	
		O	CS	Inhibited	Alloy 825		X					34	0.04
C	**HTU**	O	CS; Alloy 600 liner	No corrosion	Alloy 825				X	None (originally 12 gpm)	7% – 10%		
R	**HCU**	I	CS	65 mpy NH_4F corrosion	Weld overlay Alloy 625 around injection point			X		156 gpm	4%	n.a.	
W	**HCU**	I	CS	Thinning[b]	Lined with 321 SS	X			X	Adjusted 12 gpm – 32 gpm	8%	< 20	> 0.45
		O	CS	Thinning[b]	Weld overlay 309/18-8 elbows		X				8%	< 20[c]	> 0.45
W2	**HCU**	O	CS	Impingement corrosion	Duplex 2205		X			n.a		27	
I	**HCU**	I & O	CS	No serious corrosion	None		X		X	60 gpm	4%		0.23
Z	**HCU**	I & O	Alloy 825	None			X	X		n.a	n.a	n.a	
AA	**HTU**	O	CS	Erosion-corrosion of piping	Alloy 800 to 825 later due to PTA cracking	X			X	n.a.	14% – 15%	18 – 34	
E	**HTU**	O	CS	Erosion-corrosion of elbows (fire)	Alloy 825		X			170 gpm (target)	6% – 7%	9 – 26	n.a.
U	**HTU**	I	CS	No corrosion	None	X		X		16 gpm	4.6% average	21	0.4 – 1
		O					X						
I	**HCU**	I & O	CS	No serious corrosion	None		X		X	60 gpm	4%		0.23
Z	**HCU**	I & O	Alloy 825	None			X	X		n.a	n.a	n.a	
AA	**HTU**	O	CS	Erosion-corrosion of piping	Alloy 800 to 825 later due to PTA cracking	X			X	n.a.	14% – 15%	18 – 34	
E	**HTU**	O	CS	Erosion-corrosion of elbows (fire)	Alloy 825		X			170 gpm (target)	6% – 7%	9 – 26	n.a.
U	**HTU**	I	CS	No corrosion	None	X		X		16 gpm	4.6% average	21	0.4 – 1
		O					X						

Notes: [a] Current measured rate—suspect oxygen and chlorides

[b] Added inhibition after early experience

[c] Velocities > 20 ft/s caused erosion-corrosion requiring weld overlay

Table 11—Wash Water Details

			Source of Wash Water											
Plant	**Original Capacity (bbls/d)**	**Present Capacity (bbls/d)**	**Steam Condensate**	**Stripped Sour Water**	**Boiler Feed Water**	**Oxygen (ppb)**	**Other**	**Rate gpm (original)**	**% Vaporization**	**gpm Per Cooler Bundle**	**Single Injection Pt.**	**Multiple Injection Pts.**	**Inlet Piping**	**Outlet Piping**
B	35,000	52000	X		X	< 20[a,b,c]		120		7.5	X		*U*	*U*
Q	22,000	40,000	X				Inhibited	21				X	*U*	*U*
O			X			< 100	10 ppm Cl	68	51		X			
				X		< 100	< 50 ppm Cl[d]							
R			X			< 100	50 ppm Cl	156	< 50	19.5	X		*U*	*U*
				X		< 100	< 30 ppm Cl[d]							
C			X			100	5 ppm Cl	38	51	6 (min.)		X		
				X		0	80 ppm Cl							
W	40,000	50,000		X		< 15	50 ppm Cl	12 – 32	25			X	*B*	*U*
			X			present	Fe	adjustable						
							Inhibited							
X			10%	90%		330			< 60		X		*B*	*B*
I	25,000		X					60		10		X	*U*	
EE	45 TDB	55 TDB	X			de-aerated		27	66		X		*U*	*U*
Z				X					< 75		X		*U*	*U*
Y	11,500		20%	24%	56%	100[b]	6 ppm – 10 ppm Cl[d]	35	< 75		X		*U*	*U*
AA	45,000	65,000	X	X		50 ppb[a,b]	Significant	100		8.3		X[e]	*B*	*B*
CC	36,000				X	< 5	0 ppm Cl	105		n.a.			n.a	n.a.
E	30,000		X	X		low	20 ppm – 50 ppm Cl	170	20	21		X	*B*	*U*
U	14,000		X	X		> 40	10 ppm Cl[d]	16	> 50	4	X		*B*	*U*

Notes: [a] Reduced from 1 ppm – 4ppm

[b] Use an oxygen scavenger and nitrogen blanket

[c] Eliminated pump seal leakage

[d] Trace NH_4HS

[e] No individual flow indicators or monitors—unbalanced water distribution

Water line plugs from contaminated process water

B = balanced

U = unbalanced

800 elbows allowed the continued use of carbon steel piping until the entire piping was replaced with Alloy 825. In another plant (Plant W), the piping was upgraded to 12 Cr.

Plant Q also reported that the inlet piping system was unbalanced, the velocities were high (43 ft/s) and that the water injection rate was too low. However, this was not the case with Plant W where the piping was balanced and velocities were under 20 ft/s. The amount of wash water appeared adequate and yet corrosion was severe.

5.4.2 Outlet Piping

Similar problems to those reported in the inlet piping were also reported in the outlet piping and in some cases appeared in both locations. In the two systems discussed above, Q and W, the REAC tube bundles also corroded. This indicates that the corrosivity of the process fluid is sustained throughout the system and the corrosive is not necessarily depleted. It has been reported that pipe thinning is localized and usually takes the form of grooving. This is descriptive of a continuous channel cut into the pipe wall following the liquid flow path of the corrosive water phase. The groove may be at the bottom of the pipe but often follows a spiral, or swirl pattern. These patterns are seen going into vertical nozzles or emerging from elbows on the horizontal pipe run. Grooving in elbows tends to follow the outer radius of the bend as expected but can be offset and hence escape detection by spot ultrasonic inspection.

The most prevalent problem in the outlet piping was erosion-corrosion in turbulent areas. This commonly occurs in elbows and in some cases protecting the elbows is sufficient to extend the life of the piping system. For example, Plant Q used three 800 elbows with carbon steel pipe runs until the carbon steel life was exhausted and Alloy 825 was substituted for both components. Plant W utilized stainless steel weld overlay on the elbows only, but their experience with respect to the carbon steel pipe is tempered by the use of inhibitor. Note also the experience of Plant C, where the lining was extended downstream during successive turnarounds but failure occurred in the last remaining segment of carbon steel, where the swirl pattern of attack was missed by pulse-echo ultrasonic inspection. In another plant (Plant W2), impingement attack of the air cooler outlet header piping resulted in perforation of the pipe and a fire ensued. In this case, the sub headers were connected to the headers by vertical nozzles, with no elbows such that the flow impinged directly on the horizontal pipe under the nozzle. Severe metal loss occurred directly under the nozzle.

Unbalanced piping configurations have been implicated with piping system corrosion, as illustrated in the data plots from the UOP survey. While it is logical to deduce that an unbalanced system will produce velocity differences in the header system, and, therefore, some parts of the system may be subjected to higher risk of erosion-corrosion, not all cases clearly follow this pattern. For example, Plants I and U have not experienced any significant corrosion. This is evidence that velocity must be linked to other factors, such as the corrosivity of the process, and is not a stand alone parameter. It is also evident that compliance with the guidelines for linear velocity does not ensure freedom from high localized turbulence or impingement and consequential damage (Plant W2).

It should also be noted that imbalance in the flow patterns through the headers may also be caused by differences in the rate of cooling through the various cells of the REAC. One operator reported an air cooler design where reduced cooling was obtained by shutting down or reducing speed of the fans on the middle group of cells while maintaining higher fan speeds on the outer cells. This clearly created a thermal imbalance over the REAC.

A number of different alloys have been used in piping replacements with varying degrees of success. Austenitic stainless steels apparently have satisfactory general corrosion resistance but are prone to pitting attack and stress corrosion cracking where significant chlorides are present. There is no clear definition of a limiting concentration of chlorides so that many operators are unwilling to take the risk and opt for the stress cracking resistance of other alloys.

Among those that have been used are Alloy 800, Alloy 825, Alloy 625, Alloy 400 and duplex Alloy 2205. Until recently, Alloy 800 has been very popular, but several operators have encountered polythionic acid stress corrosion cracking as a result of sensitization of the alloy during field welding. Inadvertent use of Alloy 800H, a higher carbon version, has exacerbated the problem. Reports of pitting in Alloy 800 REAC tubing have also dampened enthusiasm for the alloy in piping replacements. Current upgrades favor Alloy 825, which so far has not experienced any of the problems associated with Alloy 800.

5.5 WATER WASH TECHNOLOGY

Table 11 is a compilation of all the data made available through this survey on factors influencing the role of wash water in corrosion control. This does not address the economic issues nor does it discuss the various operational difficulties experienced with the injection systems including the specific hardware requirements. The purpose is to provide a basis of comparison of the quantities and qualities of the wash water used in each of the various units.

There are three aspects to be considered:

1. A quantity of water sufficient to solubilize the salts and dilute the aqueous phase sufficiently that it is not overly aggressive.
2. A quality of water that does not introduce contaminants into the process stream that aggravate corrosion.
3. Adequate water/vapor contact at the point of injection to ensure removal of acidic components from the vapor.

Discussion of the problem with the various respondents indicated that process restraints and economics often dictate the availability and quality of water and the freedom of choice is limited. Some uncertainty exists as to how to establish the required amount and what level of contaminants are acceptable.

An early rule of thumb for determining the amount of wash water to be injected was 1 gallon per minute of water for every 1000 barrels of feed processed. This survey did not find any consistency with this guideline. Injection rates from 1 gpm/ 1000 bbls – 6 gpm/1000 bbls were reported and it is possible that other rules have been used. (See Turner [Reference 8].) The amount provided to each air cooler bundle varied from 4 gpm – 21 gpm. It is likely that operators adjust the rates until each finds a rate that is economical and provides satisfactory results. This trial and error approach has been costly in some cases where severe corrosion has been attributed to insufficient wash water. Several respondents claimed improved corrosion performance after the wash water had been increased. Examination of the data in Table 11 shows a wide variation in the amount of wash water relative to the capacity of the unit. For example, for Plant Q, based on a unit capacity of 22,000 bbls/d, a water injection rate of 22 gpm would be required by the above rule. The reported amount of 21 gpm is, therefore, consistent with the rule. However, for Plant B the amount of water per 1000 bbls/d is almost four times higher than the rule requires and yet this unit experienced severe corrosion of carbon steel REAC tubes and Alloy 800 tubes were substituted.

According to this survey, there is no consensus with respect to wash water requirements, either as total quantity injected or the amount distributed to each air cooler bundle. This may in part be due to the variations in nitrogen content of the feed from unit to unit as discussed later. The survey shows, however, that all operators introduce enough water that at least 25% remains unvaporized after flashing.

Another issue with respect to water injection is single-versus-multiple injection points. With single injection points, a number of operators have experienced localized corrosion at the injection point. This has been successfully countered by the use of alloy protection of the pipe in the vicinity of the water entry and atomization of the spray to prevent impingement attack and increase scrubbing efficiency. Static in-line mixers are sometimes used to give good water/vapor contact (scrubbing) after the injection point.

Multiple injection points are useful when the inlet header system is unbalanced. This design ensures that the water is evenly distributed to each cell in the REACs provided the system is properly monitored and maintained. Water is injected just ahead of the air cooler bundles, usually in the inlet nozzles. Each injection point requires a flow monitoring device and a flow controller, usually a manually operated valve. A strainer is often used in the water supply piping to prevent injector plugging. The proper flow of water to each point must be checked daily to prevent a potential buildup of deposits. The best systems employ a control house indicator on the process control board.

All the surveyed units with single injection points and unbalanced inlet piping experienced severe corrosion of the REACs. On the other hand, two units with balanced piping systems have not experienced corrosion even with single injection points. There is no clear improvement from using multiple injection points. Severe corrosion has been reported in units with both balanced and unbalanced inlet and outlet piping.

It was desired to include in Table 11 a measure of the severity of corrosion for each of the units so that the influence of the wash water conditions on corrosion might be assessed. Unfortunately, a suitable system for conveniently expressing the corrosion experience for each unit as a simple index was not realized.

5.6 WATER SOURCES

Several sources of water are used and, depending on availability, are used separately or mixed. These are boiler feed water, steam condensate, the stripped bottoms from a sour water stripper and recycle sour water from the downstream cold separator. Each of these sources varies in purity and may contain one or several of the following contaminants; oxygen, carbon dioxide, ammonia, chlorides, cyanides and iron. Boiler feed water is a very good source of water since it has been de-oxygenated but may still contain chlorides. Steam condensate is most likely to contain oxygen and carbon dioxide and for this reason should be degassed and de-oxygenated and stored under a nitrogen blanket before introducing into the process. Not all respondents admitted to using these procedures. Stripped sour water may contain all of the above listed contaminants in varying degrees and is often the primary source of wash water with steam condensate or boiler feed water being used as back up.

Although the role of oxygen in the corrosion process has not been clearly resolved, most operators take steps to minimize the amount of oxygen introduced with the wash water. Most units target the oxygen level at 100 ppb maximum but a number try to maintain oxygen between 20 ppb – 50 ppb. In one unit where corrosion inhibition is used, an oxygen level of 330 ppb was tolerated. One operator reported that oxygen was being admitted to the process from air drawn into leaking pump seals. The seals were, therefore, boxed in and an oxygen free purge provided.

Because cyanides, when present, are below the limits of detection, none of the operators consider them a controllable factor and have no knowledge whether or not they are harmful.

5.7 INSPECTION

The importance of proper inspection of these units is linked to the inconsistent nature of the corrosion experience. The corrosion experience in REAC systems is usually unpredictable and often highly localized. This means that the number of thickness measurement locations (TMLs) must be greater than for a system where the corrosion is more general and predictable. The two types of equipment of prime interest—air coolers and the associated piping—both have their own particular set of difficulties with respect to inspection.

The purpose of the survey was to determine the extent and frequency of inspections used by the individual operators interviewed. At the same time, the inspection methodology was explored to detect any correlation between the quality of inspection and the unit performance from a materials standpoint.

The information gathered with respect to inspection procedures and frequencies is summarized in Table 12. It is apparent from the interviews that an internal rotating inspection system (IRIS) is preferred by operators for inspection of air cooler tubing. This consists of traversing the bore of each tube with a special probe that measures the wall thickness ultrasonically. The method requires the unit to be shut down and the tube surfaces to be well cleaned, usually by high pressure water jetting. The inspection frequency depends on the turnaround interval for the unit and in most cases a 2- to 3-year interval is used. The maximum interval between inspections is 5 years. One operator had access to his unit every year and conducted tube inspections annually.

Piping is especially difficult to inspect because of the extensive surface area that is often difficult to access. The history of erratic flow patterns in the form of spiraling grooves introduces a problem of ensuring adequate coverage by selecting a sufficient number of TMLs. Random-spot UT is clearly unreliable and continuous scan techniques are preferred. There is a considerable effort required to conduct 100% scans of all the piping. Most operators conduct piping inspections on a $2^1/_2$- to 3-year interval but more frequent inspections (6 – 12 months) may be carried out at water injection points or other known problem areas. The relatively low process temperatures allow on-line inspection of piping but not air coolers. Where experience justifies it, the inspection period can be extended to 5-year intervals. Several plants with little or no corrosion are able to do this.

Ultrasonic inspection is most frequently used, but many plants employ radiography to look for localized corrosion or spiral grooving that may have been missed by close interval UT. Radiography has also been used on fittings, especially elbows, to detect localized corrosion. Radiography of large diameter thick wall piping requires a cobalt source which results in a grainy image and less reliable interpretation.

Inspection intervals are set by annual turnaround schedules and the thoroughness of inspection during the turnaround is a function of available manpower and time restraints. Several respondents indicated that upgrading to alloy extended the inspection interval for the items where alloy was employed.

Table 12—Inspection Summary

Plant	Equipment Item	Inspection Interval (years)	Type of Inspection	Operating Factor
B, Q	Piping	2.5 (5 max.)	UT	98%
		one time only	RT	
	A/C tubes	2.5 (5 max.)	IRIS, RFEC	
R, O, C	Wash water injection point	3	UT/B-scan	
	HP separator; LP separator	3 – 6	WFMPT, T-scan	
	A/C tubes	3 – 6	IRIS	
	Piping	3	UT, RT	
		6	B-scan	
W	All	2		
	A/C tubes		100% IRIS	
	Piping ells; headers	1	close interval UT	
X	Air coolers	5		
	Piping	3 – 5		
Y	Air coolers	2	100% IRIS	
	Piping	2	UT	
	Wash water injection point	2	RT	
CC	All	2.5		91%
AA, BB	All	3	UT, RT	
	Selected items	0.5 – 1	100% B-scan, RT	
U	A/C tubes	1	VT, UT (IRIS)	
	Feed/effluent exchangers	5	VT, UT	
	Separators	5	VT, UT, WFMPT	
E	All	4	VT, UT, RT	
	Vessels		API 510	
	Piping	1	API 570	

Wherever possible, on-line inspection should be employed to provide closer monitoring of potential problem areas. Operators have reported avoiding serious consequences by finding a problem area before a leak occurred. It is expected that hydroprocess units will receive a high priority from risk based inspection planning. These survey results show that there is a relatively low incidence of failure but a very serious consequence when failure occurs.

5.8 CORROSION

It is generally recognized that corrosion in hydroprocessing REAC systems can occur at any place between the point of water injection and the point of water separation. However, this survey also reveals that carryover and entrainment of water in the hydrocarbon streams beyond the separators has been a persistent and worrisome problem for some operators. Corrosion has also occurred in bypass piping (deadlegs) around feed/effluent exchangers when the piping is configured such that deposited salts can accumulate and become corrosive in the presence of water.

The general locations where the survey showed most operators to have experienced problems have been summarized in Table 13. The list of locations is familiar and has been well covered in previous surveys. Table 13 shows that most of the units surveyed have experienced either REAC or piping corrosion in their early history. Also listed in Table 13 are the types of attack associated with the corrosion experience. These fall into three categories, salt deposit attack, aqueous salt corrosion and velocity influenced corrosion. These problems have been countered by either carefully implemented process controls or by the use of corrosion resistant alloys.

The primary corrosive in the majority of cases was believed by respondents to be ammonium bisulfide, and the severity of attack dependent on concentration and velocity. However, it is believed that oxygen can be an accelerant of the corrosion process and is an undesirable component. The majority of operators take care to minimize or control the amount of oxygen entering the system. One unit reported improvement in their corrosion experience when the oxygen in the water wash was reduced from 1 ppm – 4 ppm to 50 ppb. Some operators believe that oxygen should be kept below 50 ppb, or even as low as 20 ppb, in the water injected into the system. There are however many units that allow up to 100 ppb oxygen. It is interesting to note that some of the units that have a relatively benign corrosion history take no special steps to minimize oxygen. The role of oxygen and other oxidants in the corrosion process is not clearly understood by the corrosion community but the effort to control them to low levels appears to be justified by the experiences reported. Plants that employ deaerated steam condensate, for example (EE) and (I), have reported a relatively good corrosion performance (see Table 7). Plant B maintains low oxygen and was able to use carbon steel REAC outlet piping for 24 years. During a period when the oxygen levels were higher than usual, corrosion rates of 50 mpy on the CS pipe were experienced.

The potential harm of chlorides was recognized in two ways:

1. Deposition of ammonium chloride in the effluent cooling train with serious corrosion consequences, (see Plants C, O and R, Table 7); and
2. Potential effects on alloy materials performance such as pitting and stress corrosion cracking (see Plants Q, W, BB and E).

One operator believed that chlorides were always involved with bisulfide corrosion and had evidence of a difference between 1 ppm and 5 ppm on the severity of attack. Chlorides enter the system with the feed, from the reactor catalyst, with make-up hydrogen, especially if unscrubbed reformer gas is used, and with the wash water. One or two plants do not have a crude desalter so that the chloride levels are inherently high. Steps to control the ingress of chlorides from all sources seems prudent. Unfortunately, insufficient data was available from this survey to correlate any distinctive influence of chlorides on the severity of corrosion experienced by any particular unit other than clear cases of NH_4Cl deposition.

The survey was unable to determine the importance of cyanides in the corrosion process. Most units reported undetectable levels of cyanides and, therefore, were unable to determine whether or not the minute quantities present had any effect or not; however, the presence of cyanides was reported by several respondents who either observed the Prussian blue color of corrosion deposits on piping or found it by analysis of the deposits. One operator reported no apparent problems with cyanides in the REAC system but a very definite influence on corrosion of a downstream coker unit.

5.9 ALLOY SUBSTITUTION TO PREVENT CORROSION

The alloy solution is costly. A recent study[10] concluded that to upgrade REAC exchanger and piping materials from carbon steel to Alloy 825 would cost $1 million for a hydrocracker unit with 6,160 ft^2 of air cooler surface. Alternative solutions, however, carry more risk. This is because the parameters affecting corrosion are not quantitatively well defined and there often is great difficulty predicting the sites where the process parameters may fall outside of the guidelines.

Some of the alternative materials selections to replace or upgrade from carbon steel have been discussed by Singh et al.[11], and Shargay and Lewis[12]. A few additional items have

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[10] C. A. Shargay and K. R. Lewis, "Cost Comparison of Materials Options for Hydroprocessing Effluent Equipment and Piping," NACE, Corrosion 96, Paper 600.

[11] A. Singh, C. Harvey and R. L. Piehl, "Corrosion of Reactor Effluent Air Coolers," Paper 490, Corrosion 97.

[12] C. A. Shargay and K. R. Lewis, "Cost Comparison of Materials Options for Hydroprocessing Effluent Equipment and Piping," NACE, Corrosion 96, Paper 600.

Table 13—Corrosion Experience

Corrosion Description	**Plants Matching Description**
Air cooler tube thinning from bisulfide corrosion	
Underdeposit attack	B, R
Flow corrosion	C, Z
Inlet end erosion-corrosion	Y
Outlet end erosion-corrosion	W, Y
Other	Q, R
Reasons	
Insufficient wash water	B,R
High bisulfide concentration at separator	C, Z
Too high velocity	C, W, Y
Unbalanced header system	Z,R
Ammonium fluoride	R
Water injection point corrosion	R, Y
No with alloy protection	C, R
Air cooler inlet piping corrosion	Q, R, W, BB
Elbows	Q
Headers	W, Y
Header boxes	Y
Reasons	
Insufficient wash water	R, W, Y
High bisulfide concentration at separator	
Too high velocity	Q, W, Y
Suspect O_2 and Cl	R, BB
Air cooler outlet piping corrosion	Q, C
Thinning	B, C, W, CC, AA
Headers	Y
Header boxes	Y
Elbows	C, AA, E
Dead leg	C, O
Reasons	
Insufficient wash water	Y, AA, E
High bisulfide concentration at separator	AA, C
Too high velocity	Q, W, Y, AA, CC
Unbalanced header system	W, Y
Suspect Cl and O_2	B, W
Feed/effluent exchanger corrosion	
Bisulfide corrosion	B, Q, CC
Suspect O_2	B
Chlorides	O, AA, E, BB
Insufficient wash water	O, AA
Trim cooler corrosion	
Bisulfide corrosion	B, Q
U-bend corrosion	B
Reasons	
Insufficient wash water	
High bisulfide concentration at separator	
Too high velocity	
Unbalanced header system	
Suspect O_2	Q
Downstream of separator	C, Y, AA
High bisulfide	C, AA
High velocity	C, Y, R
O_2	
By-pass dead legs	AA

been picked up by this survey. Austenitic stainless steels are avoided by most operators because of the potential for stress corrosion cracking and pitting corrosion. Some units use them in the form of linings for pipe or as weld overlay where the integrity of the pressure boundary is less threatened and the risk of catastrophic failure is greatly reduced. Experience with pitting of Alloy 800 tubes and polythionic acid cracking of Alloy 800 piping has introduced concerns about the use of this alloy. There is a preference for using Alloy 825, which has a higher alloy content and stabilizing elements to combat both these modes of attack.

Another approach to avoiding these problems was to employ duplex alloys which have inherent resistance to both phenomena. 3RE60 has been used successfully (Plant CC) downstream of the water injection point for more than 18 years with no plans to replace it. Alloy 2205 has been used for both air cooler tubes and piping with varying success. Problems can arise if the material is not properly specified and fabricated[13]. High residual hardness after welding can lead to sulfide stress cracking and must be avoided. In addition one respondent reported selective leaching of the ferrite phase by ammonium chloride.

Alloy 400 has been used successfully for tubes in water cooled exchangers for more than 20 years but this survey did not reveal any air cooler applications.

5.10 INHIBITION

Only two units surveyed used chemical inhibition to control corrosion. One unit employs a filming amine type of inhibitor and the other uses a proprietary chemical. Both units, however, continue to exercise control over some of the critical parameters such as bisulfide concentrations, velocities and contaminants. It appears that the application of the inhibitors does permit the use of carbon steel where it might otherwise have to be substituted. The decision to use an inhibitor is, therefore, an economic choice versus an alloy upgrade.

6 Discussion and Analysis of Survey Responses

The following section is an interpretation of the information supplied by the respondents from a more generalized viewpoint. These interpretations include ideas and opinions expressed by the engineers interviewed that were not necessarily substantiated with actual scientific or engineering data.

6.1 GENERAL EQUIPMENT CONSIDERATIONS

This study has been broadly directed at hydroprocess reactor effluent streams. This includes the products of reaction from both hydrotreating and hydrocracking processes. Within those processes are differences in the equipment arrangements that affect where corrosion might most be expected. Hydrocracking may involve two stages of catalytic reactions, the first is essentially a hydrotreating step in which sulfur, nitrogen and chloride contaminants are converted to H_2S, NH_3 and HCl respectively. These corrosive compounds are normally removed before the hydrocarbon stream enters the second stage so that the second stage effluent would be expected to be less aggressive than the first stage effluent. This does not preclude the requirement for alloy in these systems, as reported for Plant CC.

Downstream of the reactor there are two flow schemes that influence the amount of equipment to be protected and the wash water flow scheme. In one scheme, the total reactor effluent is sent to a single bank of air coolers and the to a high pressure low temperature (HPLT) separator. In the second scheme, a high pressure high temperature (HPHT) separator is employed and only its vapor stream is water washed. The HPHT separator liquid hydrocarbon is unwashed and carries dissolved H_2S, NH_3 and HCl to the downstream product stripper tower. This can result in corrosion problems in the stripper.

Clearly, each of the above process schemes has economic trade-offs, which also include the number of equipment items to be monitored and inspected, the amount of alloy employed, and the distribution of wash water. The corrosion processes are the same since the reactants are unchanged but the severity may be affected by the distribution in terms of concentrations and flows.

Many operators have reported problems in equipment downstream of the separators. This includes the separator vessels, piping and strippers. These items have experienced various modes of attack from general bisulfide and chloride promoted corrosion to hydrogen related cracking. It is beyond the scope of this study to detail these incidences but the experience serves to emphasize the aggressive nature of aqueous solutions of the ammonium salts wherever they occur. Operators should be aware that poor separation or entrainment of the aqueous phase can result in the same problems that have plagued REAC systems. The penalty for allowing the aqueous phase to carry through the separators is increased corrosion requiring an increased scope of inspection and maintenance activities.

6.2 NITROGEN CONTENT OF THE FEED

A number of respondents have reported observing an increase in corrosion severity when the nitrogen content of the feed has been increased, or the throughput increased for the same size equipment. The relationship between nitrogen in the feedstock and the severity of corrosion is simply that increased nitrogen will increase the amount of ammonia after hydrogenation and since the number of moles of bisulfide is essentially equal to number of moles of ammonia, this will result in an increase in bisulfide. The bisulfide content in mols/hr is determined by the difference between the lbs/hr nitrogen in the feed and the lbs/hr nitrogen in the product divided by the molecular weight of 14. To determine the bisulfide concentration in condensed water, the following relationships are used;

$$\text{For wt\% } H_2S < 2 \times \text{wt\% } NH_3,$$
$$\text{then wt\% } NH_4HS = 1.5 \times \text{wt\% } H_2S$$

$$\text{For wt\% } H_2S > 2 \times \text{wt\% } NH_3,$$
$$\text{then wt\% } NH_4HS = 3 \times \text{wt\% } NH_3.$$

The amount of ammonia produced for any given amount of nitrogen in the feed is a function of both the process and the

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[13] A. K. Singh, R. J. Gaugler and A. J. Bagdasarian, “Duplex Stainless Steel in Refinery Hydroprocessing Units, Success and Failure Stories,” “Proceedings of 4th International Conference on Duplex Stainless Steels,” Paper no.16, Glasgow, Scotland, Nov. 1994.

efficiency of conversion within the process. In the first case, for example, naphtha hydrotreaters are usually low in nitrogen and may not require continuous water wash, whereas diesel hydrotreaters will require a water wash. In addition, the catalytic efficiency of the process will vary from unit to unit for the same amount of nitrogen. Some units process feedstocks with varying nitrogen contents, resulting in fluctuating ammonia concentrations in the reactor effluent. Add to that the changes in catalyst activity during its normal cycle and it is clear that ammonia contents of the effluent may vary considerably over a period of time. This in turn influences the amount of wash water needed at any one time. It is for this reason that some operators use adjustable wash water rates that are determined by the amount of nitrogen in the feed.

Superficially, the data from this survey appear to indicate that units that experience severe corrosion are dealing with nitrogen contents in the feed of 1200 ppm or greater, and those units not experiencing significant corrosion have feedstocks of less than 600 ppm nitrogen. However, from the foregoing it is clear that such inferences can be grossly inaccurate.

Careful examination of the UOP survey data showed a non-linear relationship between the nitrogen in the feed and the ammonia in the air cooler inlet gas. The amount of ammonia increased with the increase in nitrogen level as expected. However, the ammonia contents reported for a given nitrogen level covered a range of values. Consequently, with such a scatter of data, the correlation between the ammonia content and the severity of corrosion is weak and at best indicates a trend rather than a specific relationship.

Note: Both parameters in this relationship are variable. This is analogous to the relationship between K_p factor and corrosion severity. Therefore it appears that the use of nitrogen content as a guide to potential corrosion severity is no more reliable than the K_p factor.

Although the severity of corrosion due to increased quantity of nitrogen in the feedstock is not predictable, the experience shows a trend towards increased problems. The practice of changing feed stocks or increasing unit throughput without regard for the corrosion consequences has penalized some operators.

6.3 SALT DEPOSITION AND TEMPERATURE

Corrosion can be caused by deposition of either ammonium chlorides or ammonium bisulfides or both (excluding plants where fluorides may be present). The deposition temperatures of the two salts are considerably different. Ammonium chloride usually deposits at 350°F – 400°F, whereas bisulfides deposit in the range of 80°F – 150°F. Deposition temperatures increase with the amount of chloride or nitrogen in the feed. The prediction of the precise deposition temperatures for any particular set of process conditions has been studied extensively. Yiing-Mei Wu[14] has used a thermodynamic approach to predict the temperature at which salt deposits, the kind of salt that deposits and an approximation of the amount. Turner[15] and others[16] make use of deposition charts to predict salt crystallization temperatures.

The temperature at the point of water injection is another critical process parameter. When the unit is being designed to meet a 25% unvaporized water criterion, the amount of wash water can vary by 1.5 – 2.5 times for a 100°F difference. This is directly tied to heat exchanger design and performance.

It is clear that there is an important relationship between process design and operation and control of corrosion. The information needed to provide the best system of corrosion control requires computational understanding and skills normally out of the range of traditional metallurgists and corrosion engineers. Few respondents to this survey volunteered an understanding of the process aspects in this area, although several indicated awareness of the influence of the process conditions on the corrosion performance of their units.

6.4 MANAGEMENT OF CORROSION

Successful management of corrosion in these units requires integrated team effort involving process, mechanical, inspection and corrosion engineers. This is not only for design or expansion but for day-to-day operating decisions. As discussed below, the effect of the process conditions on wash water management is an important aspect of corrosion control; in addition, a joint effort is needed to resolve the effectiveness of changes in ammonia levels and bulk fluid flow velocities. Some units have been successful in persuading their management to recognize the importance of observing the process parameter guidelines and keeping the corrosion engineer informed of any changes in operating conditions that could affect those parameters. The advent of federal requirements for process safety management has introduced procedures that several respondents rely on, namely the management of change. This requires that when a process change is introduced, all affected disciplines are notified and are given the opportunity to discuss the consequences and to propose any necessary remedial action.

6.5 FACTORS INFLUENCING CORROSION

The key factors influencing corrosion in REAC systems are unanimously recognized as bisulfide concentration and velocity. It is also realized that these two parameters interact in the effect on corrosion severity.

A widely observed influence of velocity has been the severe, localized metal loss experienced at changes of flow direction, such as in piping elbows, the u-bends on exchanger tubes, or the spiral gouging that occurs in straight piping. It is

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[14] Y. M. Wu, "Calculations Estimate Process Stream Depositions," *Oil & Gas Journal*, January 1994, p. 38.

[15] J. Turner, "Design of Hydroprocessing Effluent Water Wash Systems," Paper 593, Corrosion 98.

[16] E. F. Ehmke, "Corrosion Correlations with Ammonia and Hydrogen Sulfide in Air Coolers," *Materials Performance*, July 1975.

this writer's opinion that the mechanism is more properly described as erosion-corrosion. The difference between erosion-corrosion and mechanical erosion is that in the first event it is the susceptibility of the corrosion product film to mechanical disruption that is the controlling factor. In the case of mechanical erosion, both the corrosion product film and the underlying metal are removed mechanically. In erosion-corrosion, the accelerated loss of metal is caused by high corrosion rates of the metal surface by constant removal of the partially protective corrosion product film as it is formed and re-formed. The importance of this distinction is that it is the quality of the corrosion product film that is most influential in the resistance of the material to the effect of velocity. Thus, factors that affect the chemical and mechanical properties of the corrosion product film may have a significant effect on its ability to resist breakdown caused by increased velocity. It is for this reason that the presence of contaminants is important where they are perceived to affect the protectiveness of the surface film. It is beyond the scope of this study to pursue this complex subject further.

Discussion of this subject with corrosion engineers indicated that the effects of contaminants, such as oxygen, chlorides and cyanides, on the corrosion film properties were not sufficiently understood to allow customized control of the outcome. However, through empirical experience, many engineers have strong convictions regarding the influence of some, if not all the contaminants, and use their own guidelines based on their experience. This study could have revealed some consistent correlation between differences in contaminant levels and the severity of corrosion experienced. The variability of the aggressiveness from unit to unit and the lack of precision in the measurement of the contaminants made this an extremely difficult task.

6.6 CORROSION CONTROL

The history of corrosion in REAC systems has been a succession of surprise events. Among the first problems encountered were tube end erosion-corrosion and tube thinning in the air coolers. This was followed by corrosion of the REAC inlet piping and subsequently outlet piping. These problems lacked universal consistency. Some units had problems, and the location of each problem varied. Differences in bisulfide concentration and velocity accounted for much of the variability and the broad guidelines developed encompassed many of the variations. Problems persist because the conditions at the locations where corrosion occurs cannot be observed and monitored and are difficult to forecast. One example is plugging occurs in air cooler tubes, causing increased flow and subsequent attack on unplugged tubes. Monitoring such an event requires frequent on-line inspection, which is costly and runs the risk of being unsuccessful. In addition to limits on bisulfide concentration and velocity, the crux of corrosion control has been to make the system as balanced as possible with respect to stream compositions and flow distribution. Thus, balanced flow paths into, through and out of the air coolers, sufficient quantity and uniform distribution of the wash water have been an essential part of the corrosion control strategy.

6.7 WATER WASHING

Water washing is an essential control measure but requires sufficient water to be effective. It is important that water be introduced into the system in such a way that it does not create additional problems. Liquid water must be available at all locations where salts condense from the effluent stream in sufficient quantity, to dissolve the solids and move them through the system. A sufficient quantity of water is needed to maintain a mildly corrosive solution throughout its passage to the separators. This survey did not find any consistency in the amount of water used by the various units, some units using as much as six times as much as others in proportion to the feed rate.

A detailed discussion of the subject has been presented by J. Turner[17], who indicated two guidelines that are commonly used for determining the amount of wash water to be injected.

1. The maximum bisulfide concentration in the cold separator, and
2. The amount of washwater required to ensure that 25% water remains in the aqueous phase at the point of injection.

The two guidelines differ greatly in their influence on the design requirements to achieve each goal. The amount of ammonia that goes into solution at the point of injection is a function of temperature, and it is assumed that almost total solubility is achieved below 150°F – 200°F. The concentration of the bisulfide solution depends then on the ammonia produced by de-nitrification. Simulation analyses have shown that the bisulfide concentration at the point of injection is less than in the downstream separator water. It is likely that corrosion will be worse downstream of the air coolers and bisulfide concentrations will be higher. In this case, it does not seem as important to maintain 25% unvaporized at the point of injection. There is in fact an advantage to distributing the water as vapor rather than liquid to the point of condensation within the air cooler tubes. Insufficient water, however, could produce high concentrations of salts at the point of condensation downstream, especially chlorides. For this reason, it is prudent to maintain a minimum of 25% unvaporized water, as practiced unanimously by the respondents to this survey.

The actual amount of water required for any particular unit is not, therefore, a matter of simple rules of thumb but requires a careful assessment of the process parameters. It

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[17] J. Turner, "Design of Hydroprocessing Effluent Water Wash Systems," Paper 593, Corrosion 98.

requires knowing the chemical equilibria and the temperature at the wash water injection point.

The water quality is also important. The contaminants introduced with the wash water should not have any significant contribution to downstream corrosion. A few of the respondents mentioned control of iron entering the system with wash water. Insoluble sulfides will quickly form from any iron ions entering these sour water systems and will lead to deposits. For example, 50 gpm of wash water containing 1 ppm iron can deposit as much as 300 lbs iron sulfide per year in the system.

In an effort to obtain good distribution of the wash water, there has been a progression of improvements in the injection devices starting with an open tee, to quills and spray nozzles with downstream inline mixers. Experience with these different devices has varied from unit to unit. The use of single versus multiple injection points is controversial. To improve uniformity of distribution through the air coolers, many operators use multiple injection points. This has not worked infallibly and corrosion of tubes has been experienced in spite of multiple injections showing that corrosion may not depend on wash water distribution alone, assuming each injection point is working properly.

6.8 CORROSION ASSESSMENT

A major difficulty in assessing the performance of individual process units is the problem of quantifying corrosion experience. A unit that performs generally well can suffer a local failure that is disastrous. This unit is then classified as a "serious" corrosion case and the process and engineering parameters used for comparison with "moderate" or "mild" cases. Attempts to correlate individual process parameters with severity of corrosion are inherently flawed by the inclusion of extreme behavior for the stated process conditions, whereas the conditions at the point of failure are probably quite different. Plotting corrosion severity against another general parameter, such as K_p factor or nitrogen content in the feed, only compounds the error and the resulting plots are extremely scattered.

The precise conditions prevailing at the location of corrosion may be difficult, if not impossible, to quantify and control. The options available to rectify the problem often include a lesser but continued risk. The distinct trend towards use of expensive alloys to replace carbon steel probably reflects the desire to minimize the risk. There are definite trends toward the use of higher alloys such as 2205, 800 and 825 for air coolers and related piping especially for replacements and expansions. At the same time, alloy substitution allows more process flexibility, including higher nitrogen feedstocks and higher conversion efficiencies, reduced inspection and reduced maintenance. As an example, units that employ carbon steel air cooler tubes strive to maintain 4% – 8% bisulfide in the separator water but allow increasing amounts of bisulfide depending on the alloy used. Typically, for 8% – 15% bisulfide, Alloy 800 would be employed.

6.9 FLOW EFFECTS

Velocity limits also depend on the alloy being used. With carbon steel tubes an upper velocity limit of 20 ft/s is generally observed, whereas with alloy tubes, higher velocities are permitted. For example, velocities up to 40 ft/s have been used with Alloy 800 tubes. Another aspect of flow through the system is the importance of maintaining high enough velocities to minimize phase separation between the vapor, water and hydrocarbon phases. The importance of flow regime has been discussed by Ehmke[18], whose experience indicated that least corrosion was experienced in a stratified or annular flow pattern where the liquid was in laminar flow at the wall. The present survey showed that most operators try to maintain annular flow in the air cooler tubes to avoid possible problems.

7 Conclusions

The cause of corrosion in reactor effluent air cooler systems is reasonably well understood and has been attributed to the formation of ammonium chloride and ammonium bisulfide salts. To prevent plugging of the flow paths by condensed solid deposits, water is injected into the process to solubilize the salts. The aqueous solutions thus formed may be extremely aggressive to carbon steel and even cause problems for some alloys. Experience has shown that the problem can be controlled by strict limitations on aqueous salt concentration and velocity. This simple strategy, however, is complicated by numerous factors such as the even distribution of flow through the equipment and the complexity of controlling the flow patterns to avoid high velocity turbulent conditions. Maintaining uniform concentration of the salt solutions throughout the equipment by avoiding deposit build-ups or evaporative conditions is another complication. The corrosion history of these units has been characterized by highly localized failures. Severe thinning has occurred over relatively small areas where local conditions have been very aggressive. This has made the task of inspection of the equipment more difficult. The inspection intervals have been shortened and the coverage increased. But in spite of this, serious failures have occurred.

The extent to which these factors can be manipulated for the best control is often dictated by economic considerations. There is evidence that a hydraulically balanced piping system around the air coolers alleviates corrosion in some but not all systems. For that reason, there has been a trend toward the use of Alloy 825 for air cooler tubes and related air cooler piping. This alloy has been used successfully under some process conditions for up to 15 years with no adverse experience. Currently, users allow up to 40 ft/s velocity. There is no

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[18] E. F. Ehmke, "Corrosion Correlations with Ammonia and Hydrogen Sulfide in Air Coolers," *Materials Performance*, July 1975.

known limit with respect to bisulfide concentrations, but laboratory research has indicated low corrosion up to 45% bisulfide under very low flow conditions. No pitting corrosion or cracking problems have been reported. The prospects of providing trouble-free equipment with minimal risk of a catastrophic failure, that allows flexibility in operating conditions, is to some companies worth the considerable investment.

The design and control of the water wash addition to the process is one of the most critical factors in controlling the corrosion problem, especially with carbon steel equipment. The proper amount of water needed to keep the system flushed of salt deposits and to control its distribution through split flow paths to ensure uniform washing of all the equipment. The water quality is also important and is suspected to affect details of the corrosion process such that the corrosion product films can vary in their degree of protectiveness. This in turn affects the tolerance to bisulfide concentration and velocity. For this reason, care is exercised by limiting oxygen and chloride contents of the wash water, though the maximum permissible levels of both these elements are not known. Other contaminants, such as mineral salts and heavy metal ions, can cause plugging problems in the water system and contribute to fouling in the process equipment.

The most critical task is to determine the amount of water needed at the point of injection. One criterion is to maintain at least 25% water in the liquid state after injection. The amount of vaporization is a function of the temperature and pressure. The amount of water injected also depends on the ammonia concentration which is a function of the nitrogen content of the feed and the efficiency of de-nitrification. The amount of ammonia that goes into solution depends on the temperature at the wash water injection point and may be calculated using thermodynamic modelling. Many operators base the quantity of injection water on the concentration of bisulfide in the low pressure separator. Typically, they try to maintain a level of 4% – 8% bisulfide in the sour water. This apparently has been a successful strategy for those who use it according to the reported performance of their units. It is not clear whether the target concentration is achieved simply by adjusting the water addition or whether the more sophisticated analyses just discussed are employed. It is recommended that a proper process evaluation be used, taking into account conditions at the point of water injection to maintain 25% unvaporized water, as well as the bisulfide concentration at the separator.

It is clear that chemical engineering techniques are needed to determine the water wash requirements and also to predict the deposition temperature of the ammonia salts and the amount of salt depositing. These factors bring into play the heat balance of the process and affect equipment performance. This is especially true during the design of the unit but should also apply to any process changes that are subsequently made. For this reason, cost-effective corrosion control of these units requires a continuous team effort by operating engineers and those responsible for corrosion performance, to monitor and control the process parameters and to implement effective change management procedures when significant adjustments are made.

8 Future Research

The survey/interview approach used in this study and in previous studies has clearly exhausted the possibility of uncovering new or unique information leading to resolution of some of the unanswered questions. It is evident that there is a need for a new approach, such as the generation of reliable laboratory data that serves as a baseline to predict materials performance under the various conditions encountered in these processes.

The referenced literature used in this report includes several laboratory studies [5,6,9] that cover different aspects of the problem. The tests by Damin and McCoy[5] were conducted under essentially stagnant conditions while those of Scherrer et al.[6] utilized a simulated process flow scheme. Bonner et al.[9] studied the effects of oxidants and explored the effect of pH. A combination of the latter two studies might be most useful in providing realistic corrosion rate data and providing insight into the mechanisms of the corrosion processes. Two types of study are suggested, possibly in sequence.

The first study would consist of a series of tests under simulated process conditions reproducing the natural process conditions as closely as possible. The objective would be to generate corrosion on various alloys including carbon steel that matched the mode and severity of that observed in plant equipment under the same conditions. Assuming that this could be achieved, the studies would then be broadened to introduce the effects of different variables, especially velocity and oxygen, chlorides and cyanides. The objective would be to provide a clearer picture of the influence of velocity on corrosion and determine the effect of contaminants on both corrosion and erosion-corrosion performance of the various alloys.

In a second series of studies the more fundamental aspects could be explored. The following is a suggested list of topics.

1. The corrosion product film needs to be characterized in terms of chemical composition and properties and differences in protective and nonprotective films determined. This could include studies of alloys as well as carbon steel.
2. The effect of process contaminants, such as oxygen, chlorides and cyanides, should be studied with respect to the films characterized in item 1 above. Studies of film formation under truly anaerobic conditions are needed as a baseline for comparison with the presence of oxidants.
3. Determine the desirable film properties that provide resistance to the effects of flow velocity, and how best to achieve those properties.

APPENDIX A—PLOTS OF CORROSION SEVERITY VERSUS VARIOUS PARAMETERS FROM THE UOP SURVEY DATA FOR ALL COOLER TUBES (REFERENCE 7)

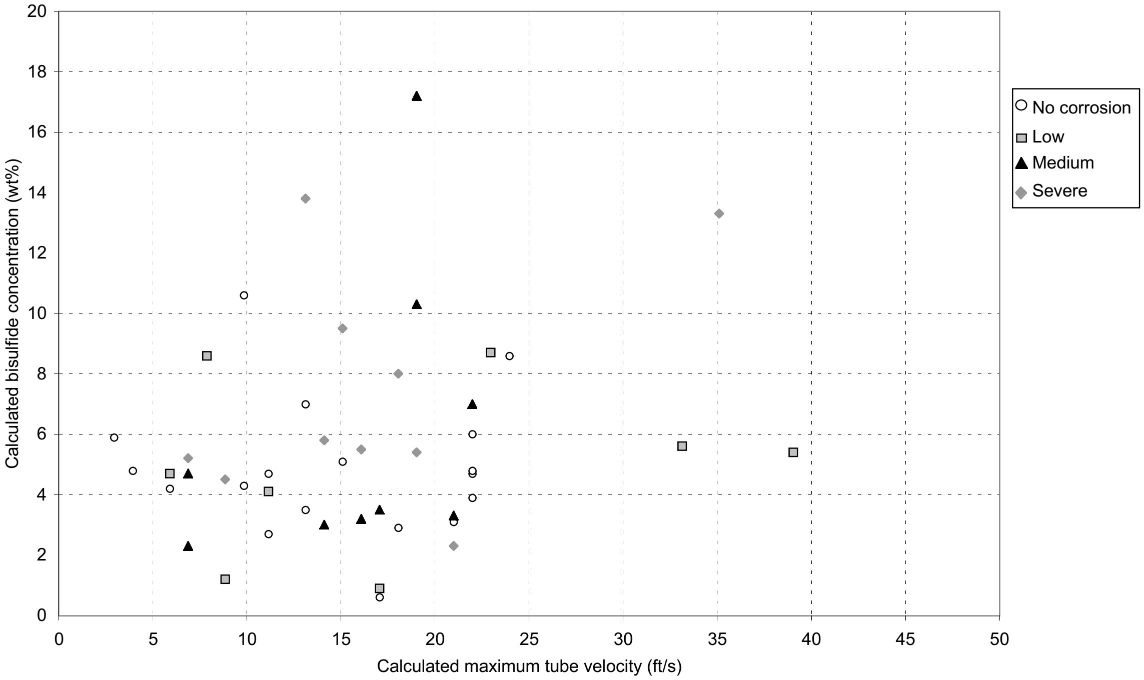

Figure A-1—Corrosion of Air Cooler Tubes—The Combined Effect of Calculated Ammonium Bisulfide Concentration in the Downstream Separator and Calculated Maximum Tube Velocity (ft/s) on Corrosion Severity

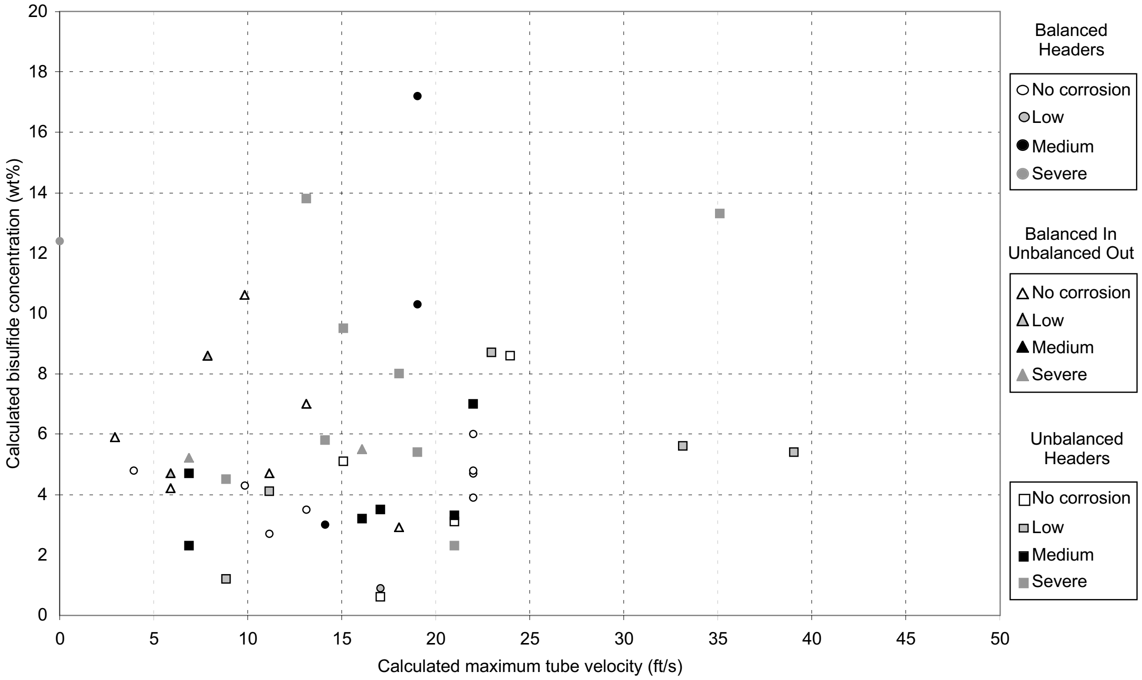

Figure A-2—Corrosion of Air Cooler Tubes—The Combined Effect of Calculated Ammonium Bisulfide Concentration in the Downstream Separator and Calculated Maximum Tube Velocity (ft/s) on Corrosion Severity for Balanced and Unbalanced Headers

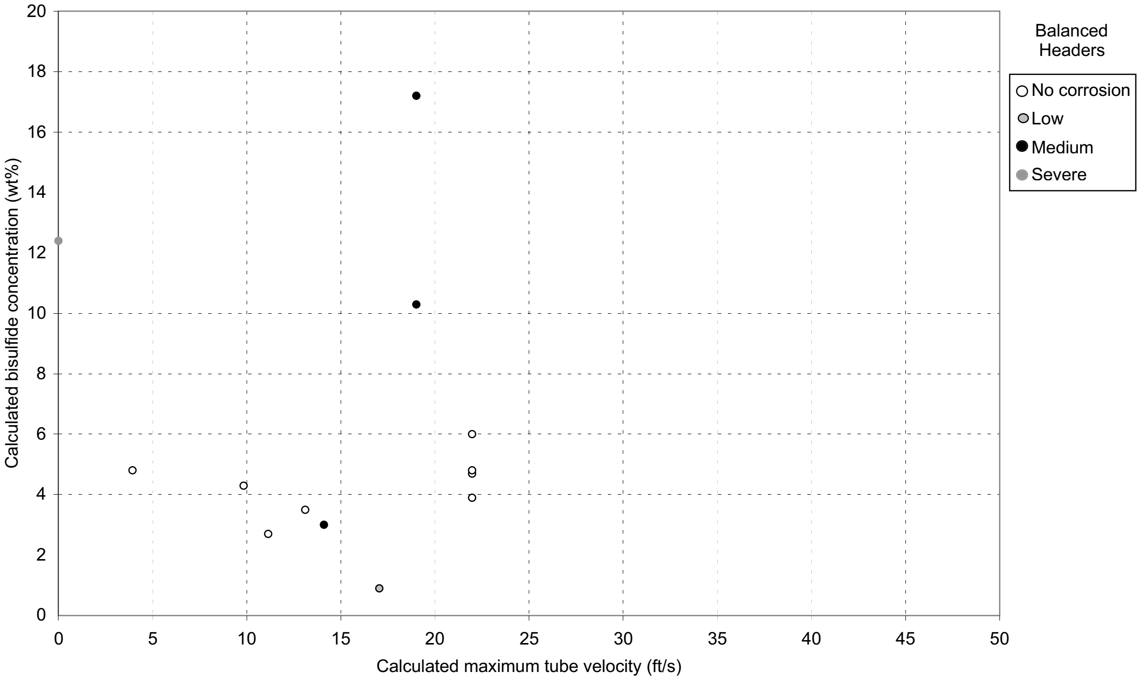

Figure A-3—Corrosion of Air Cooler Tubes—The Combined Effect of Calculated Ammonium Bisulfide Concentration in the Downstream Separator and Calculated Maximum Tube Velocity (ft/s) on Corrosion Severity for Balanced Header Systems

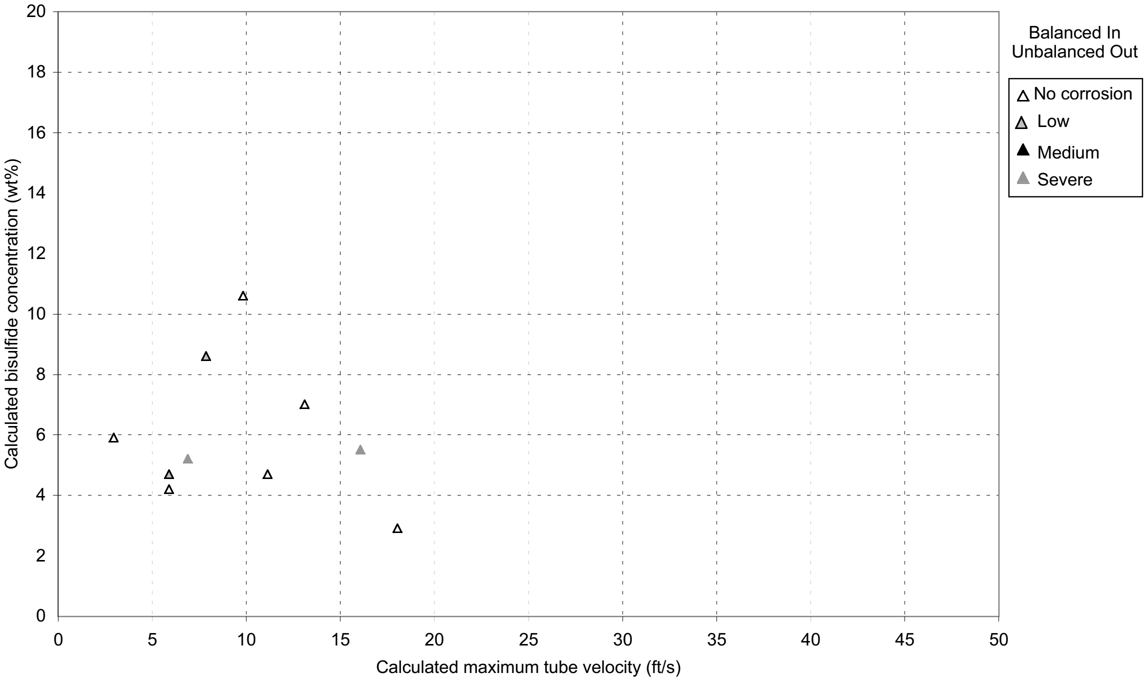

Figure A-4—Corrosion of Air Cooler Tubes—The Combined Effect of Calculated Ammonium Bisulfide Concentration in the Downstream Separator and Calculated Maximum Tube Velocity (ft/s) on Corrosion Severity for Balanced Inlet and Unbalanced Outlet Header Systems

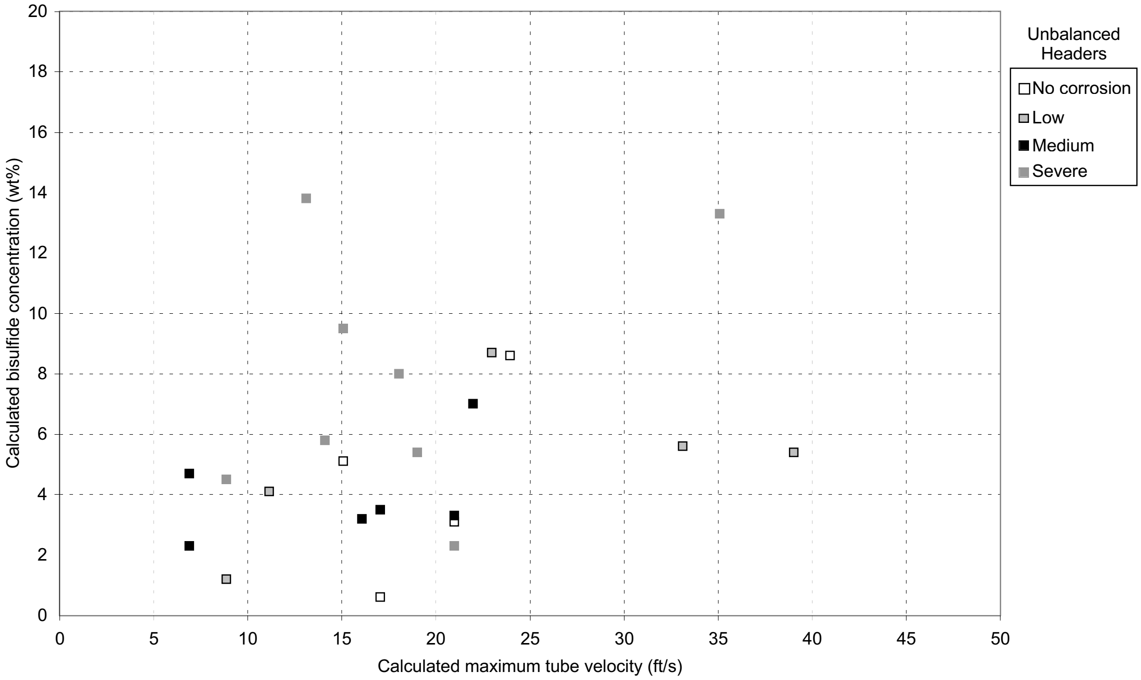

Figure A-5—Corrosion of Air Cooler Tubes—The Combined Effect of Calculated Ammonium Bisulfide Concentration in the Downstream Separator and Calculated Maximum Tube Velocity (ft/s) on Corrosion Severity for Unbalanced Header Systems

APPENDIX B—PLOTS OF CORROSION SEVERITY VERSUS VARIOUS PARAMETERS FROM THE UOP SURVEY DATA FOR REAC PIPING (REFERENCE 7)

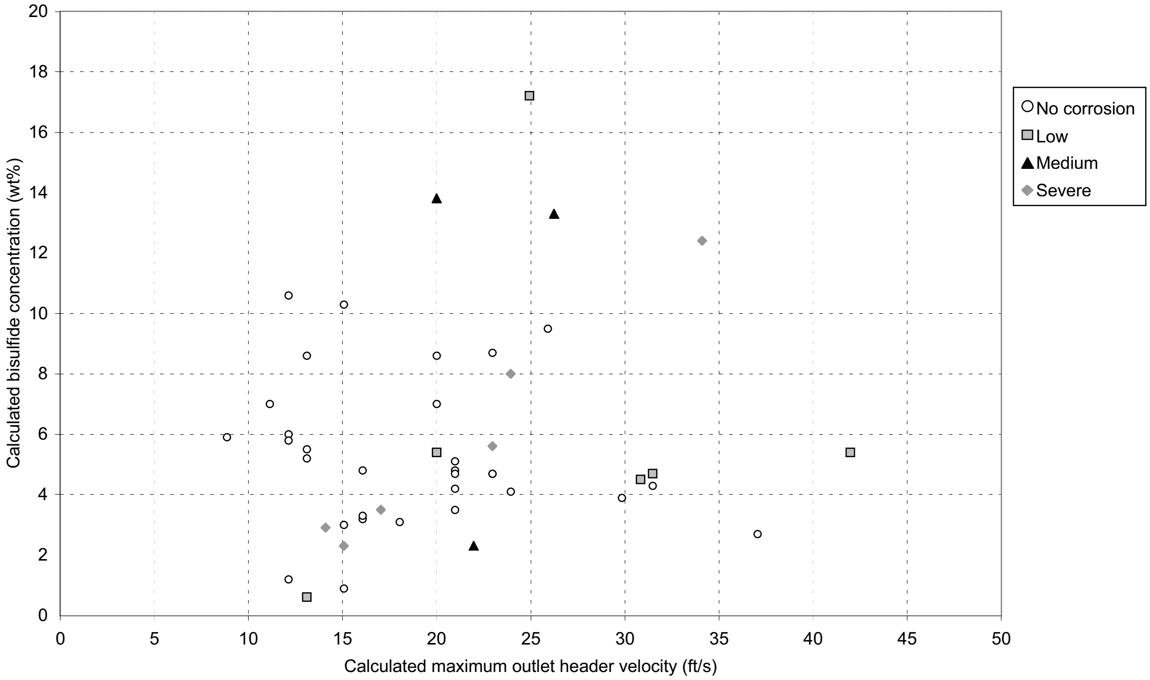

Figure B-1—Corrosion of REAC Outlet Header—The Combined Effect of Calculated Ammonium Bisulfide Concentration in the Downstream Separator and Calculated Maximum Outlet Header Velocity (ft/s) on Corrosion Severity

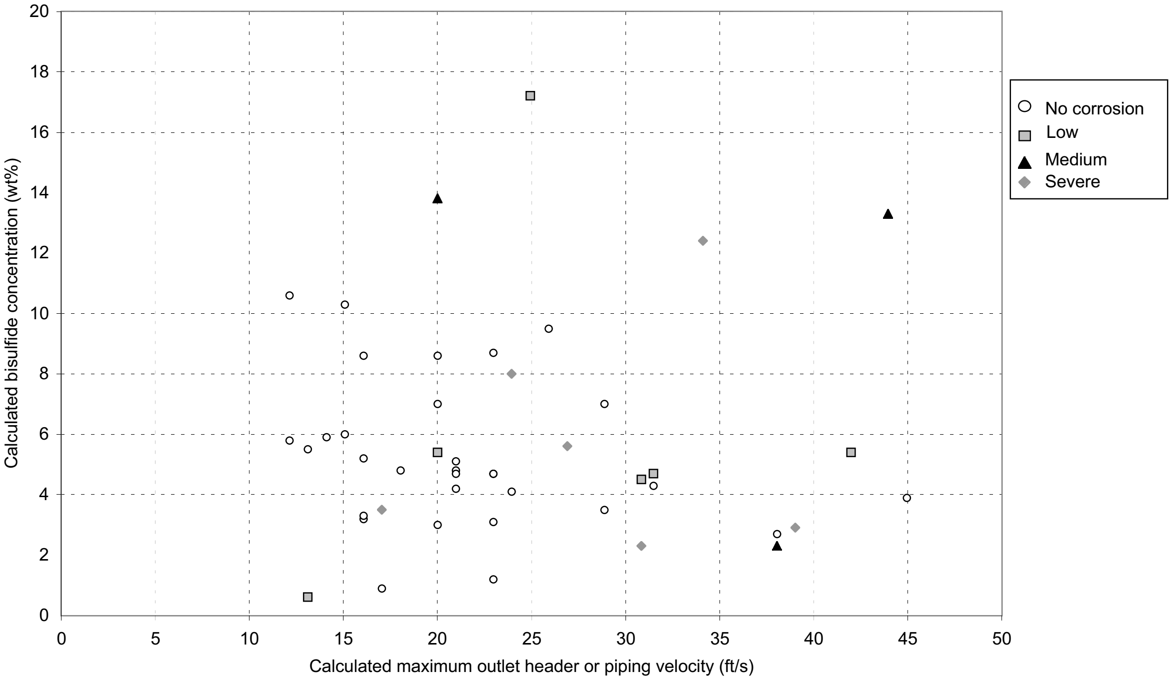

Figure B-2—Corrosion of REAC Outlet Header or Piping—The Combined Effect of Calculated Ammonium Bisulfide Concentration in the Downstream Separator and Calculated Maximum Velocity (ft/s) in the Outlet Header or Piping on Corrosion Severity

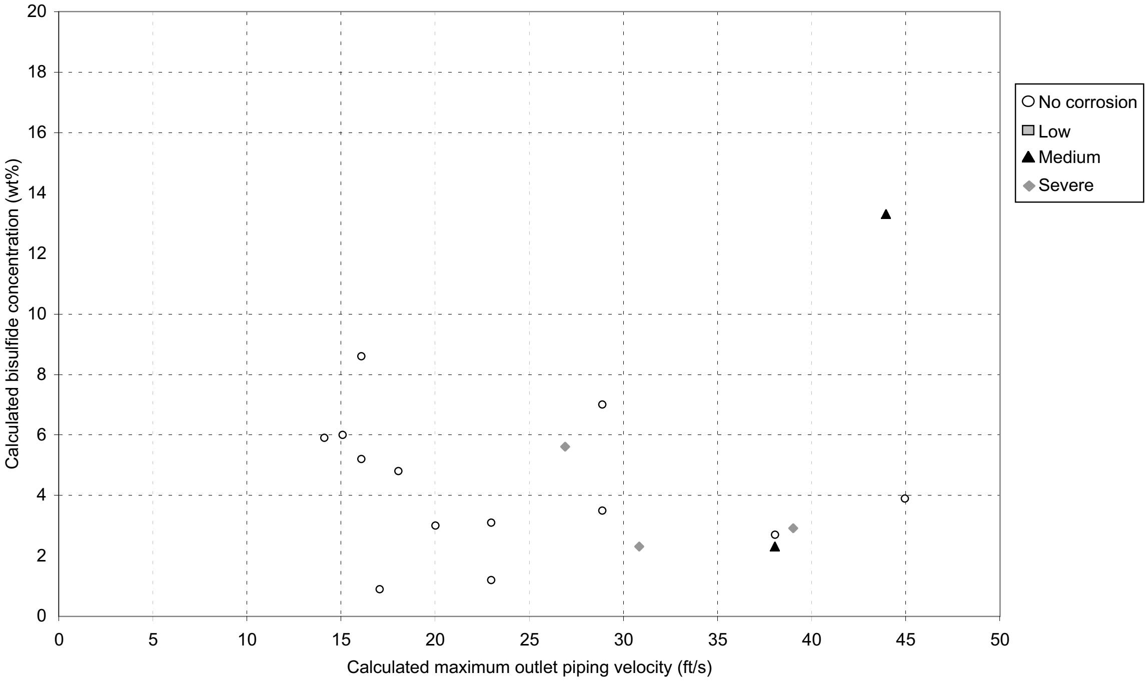

Figure B-3—Corrosion of REAC Outlet Piping—The Combined Effect of Calculated Ammonium Bisulfide Concentration in the Downstream Separator and Calculated Maximum Outlet Piping Velocity (ft/s) on Corrosion Severity

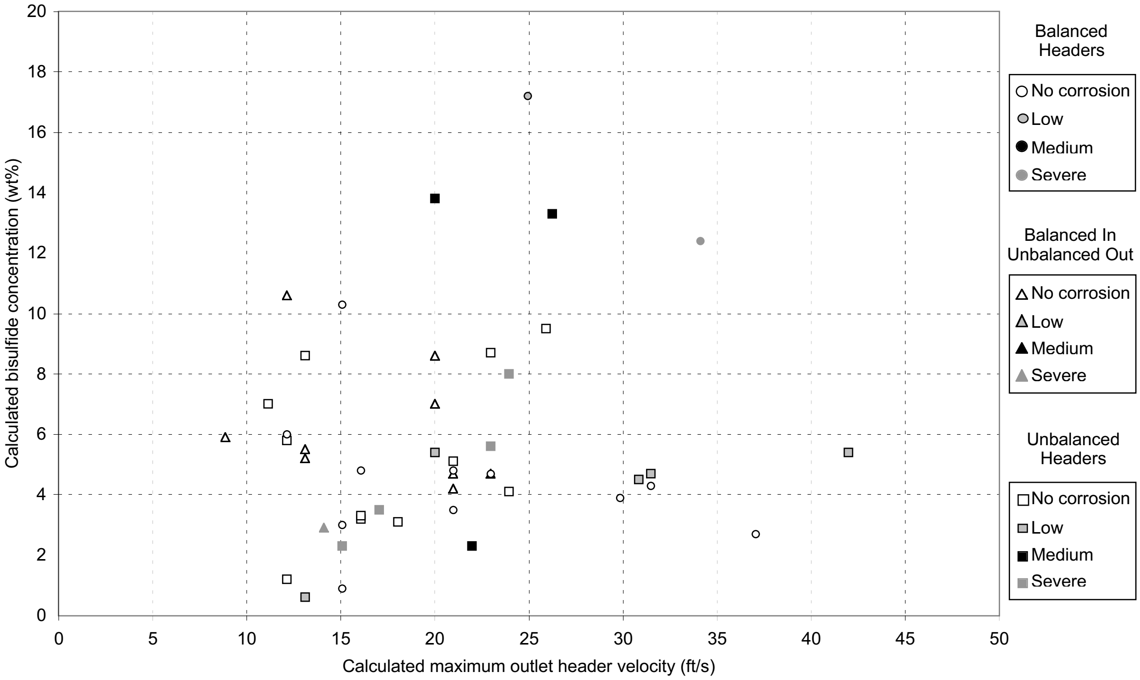

Figure B-4—Corrosion of REAC Outlet Header—The Combined Effect of Calculated Ammonium Bisulfide Concentration in the Downstream Separator and Calculated Maximum Outlet Header Velocity (ft/s) on Corrosion Severity for Balanced and Unbalanced Header Systems

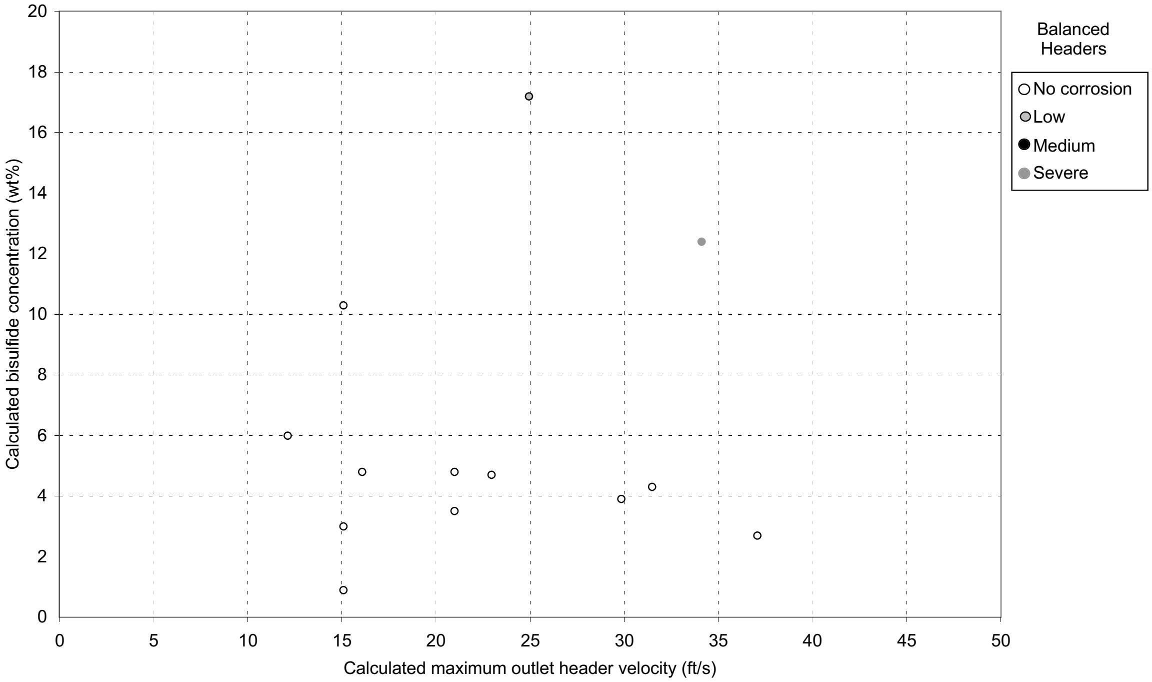

Figure B-5—Corrosion of REAC Outlet Header—The Combined Effect of Calculated Ammonium Bisulfide Concentration in the Downstream Separator and Calculated Maximum Outlet Header Velocity (ft/s) on Corrosion Severity for Balanced Header Systems

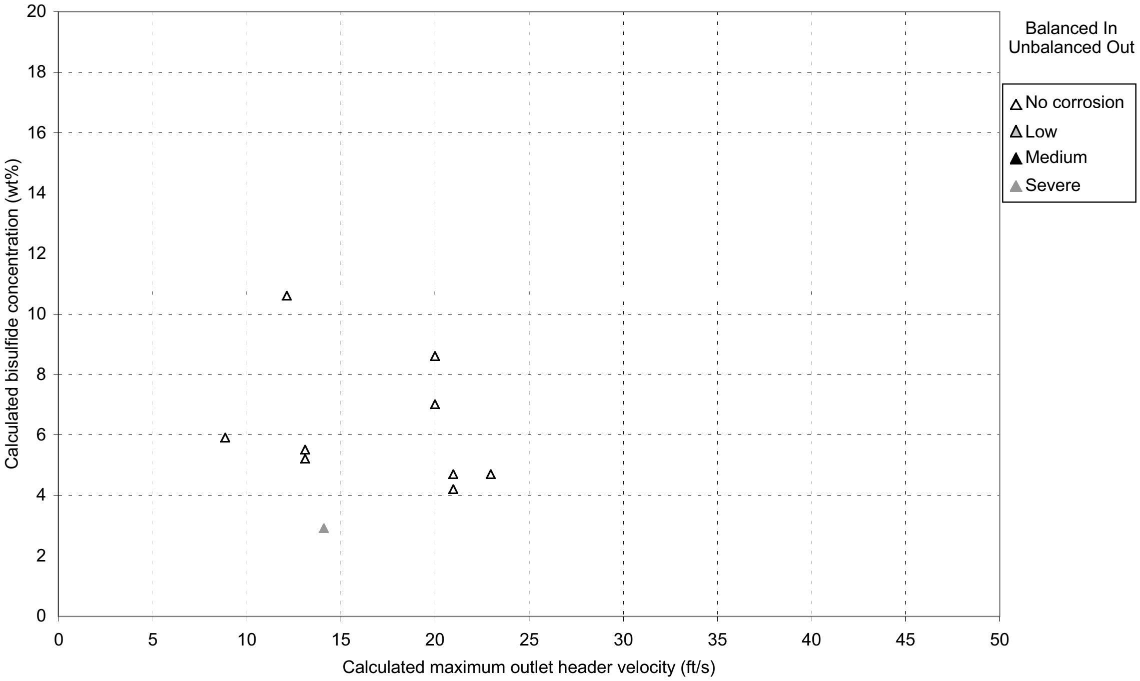

Figure B-6—Corrosion of REAC Outlet Header—The Combined Effect of Calculated Ammonium Bisulfide Concentration in the Downstream Separator and Calculated Maximum Outlet Header Velocity (ft/s) on Corrosion Severity for Balanced Inlet and Unbalanced Outlet Header Systems

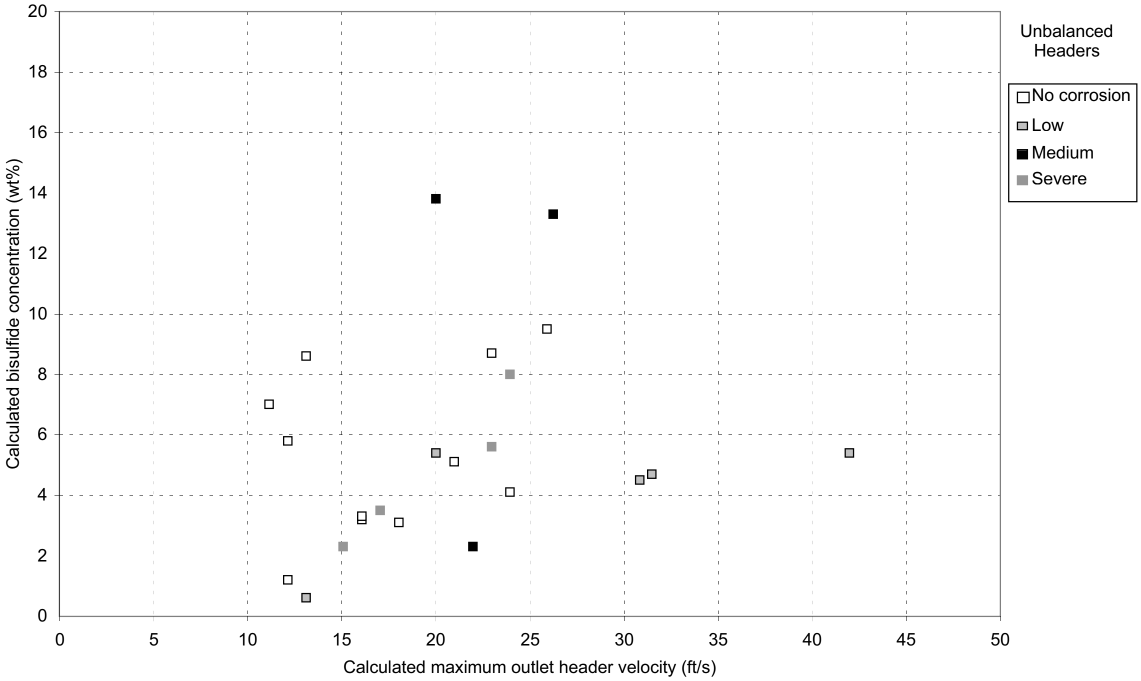

Figure B-7—Corrosion of REAC Outlet Header—The Combined Effect of Calculated Ammonium Bisulfide Concentration in the Downstream Separator and Calculated Maximum Outlet Header Velocity (ft/s) on Corrosion Severity for Unbalanced Header Systems

APPENDIX C—QUESTIONNAIRE

SURVEY OF HYDROPROCESS REACTOR EFFLUENT SYSTEM CORROSION

To: All selected recipients

Thank you for your participation in this important task to determine recommended practices to minimize corrosion through design, operation and maintenance of hydroprocess effluent systems. From your response to the preliminary questionnaire it appears that your experience will be of great value to this effort and we would like to obtain more detailed information. We would like to follow up with a visit to your office or refinery to conduct personal interviews and discussions with the people most knowledgeable about corrosion in the hydroprocess unit(s) you have identified.

We ask that the following information be available at the time of the visit as a minimum basis for the discussions. As much as possible should be available as hard copies to turn over to the consultant for subsequent analysis. Any or all of the documents furnished can be returned to the engineers at the conclusion of the project.

SECTION 1—SCHEMATIC DRAWINGS

Please provide the following schematic drawings. *Single page (11" × 17" max.) reductions of process flow diagrams are acceptable provided, they are legible. Mechanical flow sheets and piping layout drawings should not be submitted at this time but may be requested later.*

a. Process flow schematic from the reactor to low pressure separator (show design pressures and temperatures and major control instruments).
b. Overhead air cooler piping arrangement with location of water injection points.

Comments (use a separate page if necessary):

____
____
____
____
____
____

SECTION 2—OPERATING CONDITIONS

(a) Temperature and Pressure

	Normal Range	Maximum Upset High/Low
Temperatures		
Reactor effluent		
Air cooler inlet		
Air cooler outlet		
Hot high pressure separator		
Cold high pressure separator		
Hot low pressure separator		
Cold low pressure separator		
Pressures		
Reactor effluent		
Air cooler inlet		
Air cooler outlet		
Hot high pressure separator		
Cold high pressure separator		
Hot low pressure separator		
Cold low pressure separator		

Annual operating cycle—scheduled annual operating hours__________
actual operating hours (history) ___________
scheduled outage ______________________

Comments (use a separate page if necessary):

____
____
____
____
____
____

(b) Process Conditions

It is desirable to know as much as possible about the chemical composition of the process streams from the outlet of the reactor to the discharge of the low-pressure, low-temperature separator. It is generally recognized that compounds of H_2S, NH_3, halogens, cyanides and oxidants such as oxygen are the principal contributors to corrosion. We need to identify the presence and concentration of each salt to match with the corrosion experience for each of the units reported.

Please provide the following flow stream compositions (typically found on the bottom of the PFD). Please give moles/hr or ppm, mol wt of component, and total moles in the stream. If available please also provide gals/hr or scfm. Include all components in the stream and indicate the phases present (e.g., liquid, vapor).

Component	Reactor A/C				High Pressure Separator		Low Pressure Separator	
	Inlet		Outlet		In*		In*	
Temperature °F								
Pressure psig								
$C_1 - C_7$ (total hydrocarbons)								
Hydrogen								
Hydrogen Sulfide								
Hydrogen Cyanide								
Ammonia								
Water								
Oxygen								

* give both hot & cold

In addition, please address the following:

1. NH_4HS Concentration in liquid phase________%
   Location of measurement _____________________
   Temperature __________ Pressure _____________
   K_p Factor (mol% $H_2S \times$ mol% NH_3) ____________
2. Chlorides Concentration ___________ ppm
   Location _____________ Temperature _______ Pressure _________
3. Fluorides Concentration ___________ ppm
   Location _____________ Temperature _______ Pressure _________

(c) Flow Conditions

In addition to the above information on the quantities of vapors and liquids moving through the system, it is desirable to define the actual flow conditions at certain critical areas. Of particular interest is the dispersion of the injected wash water and distribution to the air cooler tubes, the flow through the air cooler tubes and the flow in the outlet manifolds, especially the elbows. The injection and distribution of wash water is explored in a later section. This section will address conditions around the air coolers.

Please answer the following:

What is the condition of the stream entering the air coolers? Is it all vapor or does it have some liquid?

At what point does condensation of a) water and b) hydrocarbon take place in the cooler tubes?

What are the flow characteristics in the cooler tubes? Please indicate the bulk velocity and flow regime (annular, stratified, plug, etc.?).

Give the flow characteristics of the outlet piping.

Additional Comments:

SECTION 3—METALLURGY

Please provide a Materials Selection Diagram or marked-up flow sheet indicating the principal materials of construction for vessels and piping.

Manufacturers Vessel and Exchanger Data Sheets may be submitted provided the information is up-to-date, including any changes and the approximate date of the change, and that all items exposed to the operating stream are included.

Inspection Data Sheets and computer graphics may also be used with the same provisions as above. If inspection documents are submitted in response to Section 4, they need not be duplicated for this section provided they contain all the required information as indicated next.

- All materials should be properly identified with a) a specification number such as ASTM, ASME or API, b) the material description (e.g., alloy name), c) thickness, and d) corrosion allowance.
- Piping and tubing should be designated as welded or seamless.
- Any stress relief heat treatment should be noted.

In general, only materials exposed to the operating environment need be described in detail. The following equipment must be included:

Reactor exit piping
Reactor feed/effluent exchangers (effluent side only)
Piping to the air coolers
Air coolers (header boxes and tubes)
Trim cooler
Piping to the separators
Hot high pressure separator
Cold high pressure separator
Hot low pressure separator
Cold low pressure separator

SECTION 4—WATER WASH

Source of wash water____

List all chemical contaminants and their concentrations. The following are suggested as a starter list:
Ammonium salts or ammonia; hydrogen sulfide, other sulfides or sulfur compounds, cyanides, chlorides, HCl, fluorides, oxygen and oxidizing agents.

____
____
____
____

pH?__________
Quantity of water injected (gals/min) _______________
Number of injection points _______________ One for each bundle? _______________
Based on number of air cooler bundles, what quantity of water is provided per cooler?__________________________
____

If not covered in Section 1, please provide a sketch or describe the air cooler piping arrangement from the inlet line through the manifolds and individual inlets to the cooler headers, as well as the outlet arrangement. __________________________
____
____

What chemical analyses are performed on the air cooler effluent?______________________________________
____
____

Describe the method of determining ammonium bi-sulfide concentration in the AC effluent. Include the sampling procedure and analytical method. ____
____
____

SECTION 5—INSPECTION

To avoid accumulation of a large number of documents, it is preferable that, where possible, *summary* sheets of the inspection records for each equipment item be submitted. The purpose of gathering this information is to determine whether the level and quality of inspection has had a bearing on the performance of the unit. It is also important to learn if any indications of a potential problem developed over a long period of time or if they developed suddenly—the time frame can be used to relate to the process conditions in the same time period.

It is suggested that a separate sheet or sheets be provided for each item of equipment discussed. The items listed below are the minimum information required.
Name of item (reactor, piping, etc.) ____
Frequency of inspection____
Last inspected____
Type of inspection (visual, UT, eddy current, etc.)

____
Inspection method—please indicate the extent of inspection for each item, especially piping (i.e., whether it is random, fixed location or grid readings).
Inspection record—year, observations, readings.
Please attach Inspection Data Sheets for each item reported.

SECTION 6—CORROSION

Please provide a summary narrative of the corrosion experience with the unit.

This section should include corrosion data acquired by coupons, probes or test pieces, as well as visual observations and inspection thickness data.

In answering the following questions please address each item of equipment separately. Do not be confined by the space provided, attach additional sheets if needed.

Since the unit was commissioned, has any item experienced severe corrosion requiring it be replaced? If so, describe.

Has the same item been replaced more than once?

Were there any changes made in the metallurgy, such as a different corrosion allowance, or different material?

Have any non-metallurgical changes been made, such as inhibition, or process modification?

Have the changes been successful in controlling the problem?

Has the problem diminished without making changes?

If so, what was responsible for the improvement?

Were process changes made for reasons other than corrosion control?

Has corrosion ever led to an unscheduled shutdown? If "yes" describe the incident.

Has there ever been a catastrophic incident?

What changes have been made to avoid a repetition of the event?

SECTION 7—INHIBITION

The following information is requested with respect to the use of chemical inhibitors in the effluent system.

Type of inhibitor (trade name or generic description)

Water soluble? ____________ Hydrocarbon soluble? ____________

Point of addition

Method of injection

Continuous? ____________ Intermittent? ____________

Dosage?

Number of years in use

Effectiveness—is corrosion rate reduced or is corrosion essentially eliminated? ____

____

____

Have other inhibitors been tried which were unsuccessful? Please describe. ____

____

____

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