

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 corro-

sion 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, 1968¹. 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 coolers². 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-

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

²R. L. Piehl, "Survey of Corrosion in Hydrocracker Effluent Air Coolers," *Materials Performance*, January 1979.

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% $\text{NH}_3 \times \text{mole}\% \text{H}_2\text{S}$, 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 97⁷. 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

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

⁶C. 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.

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

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

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



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 corro-

sion 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 Piehl⁸ 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-

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

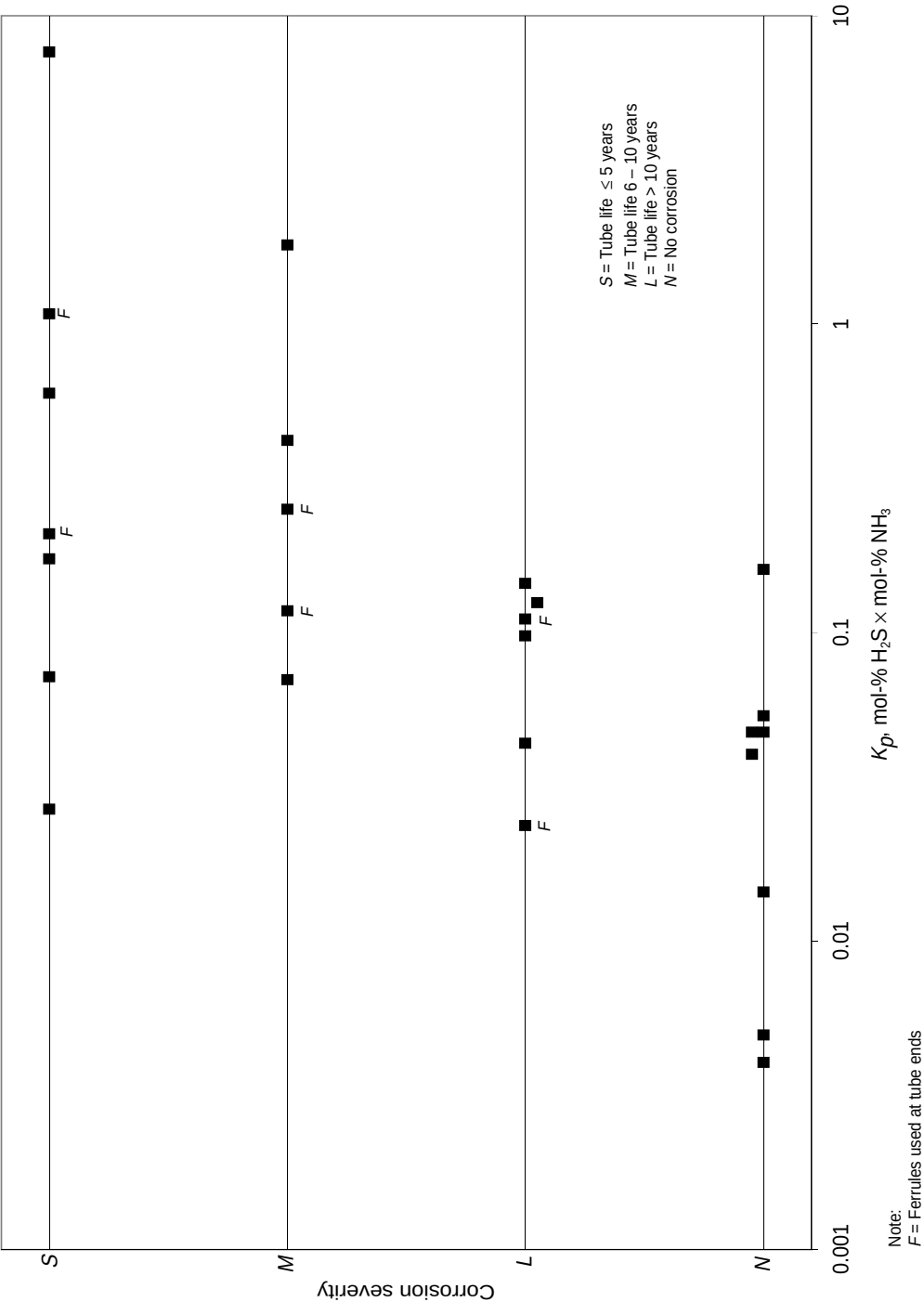


Figure 1—Effect of K_p on REAC Tube Corrosion (from Ref. 7)

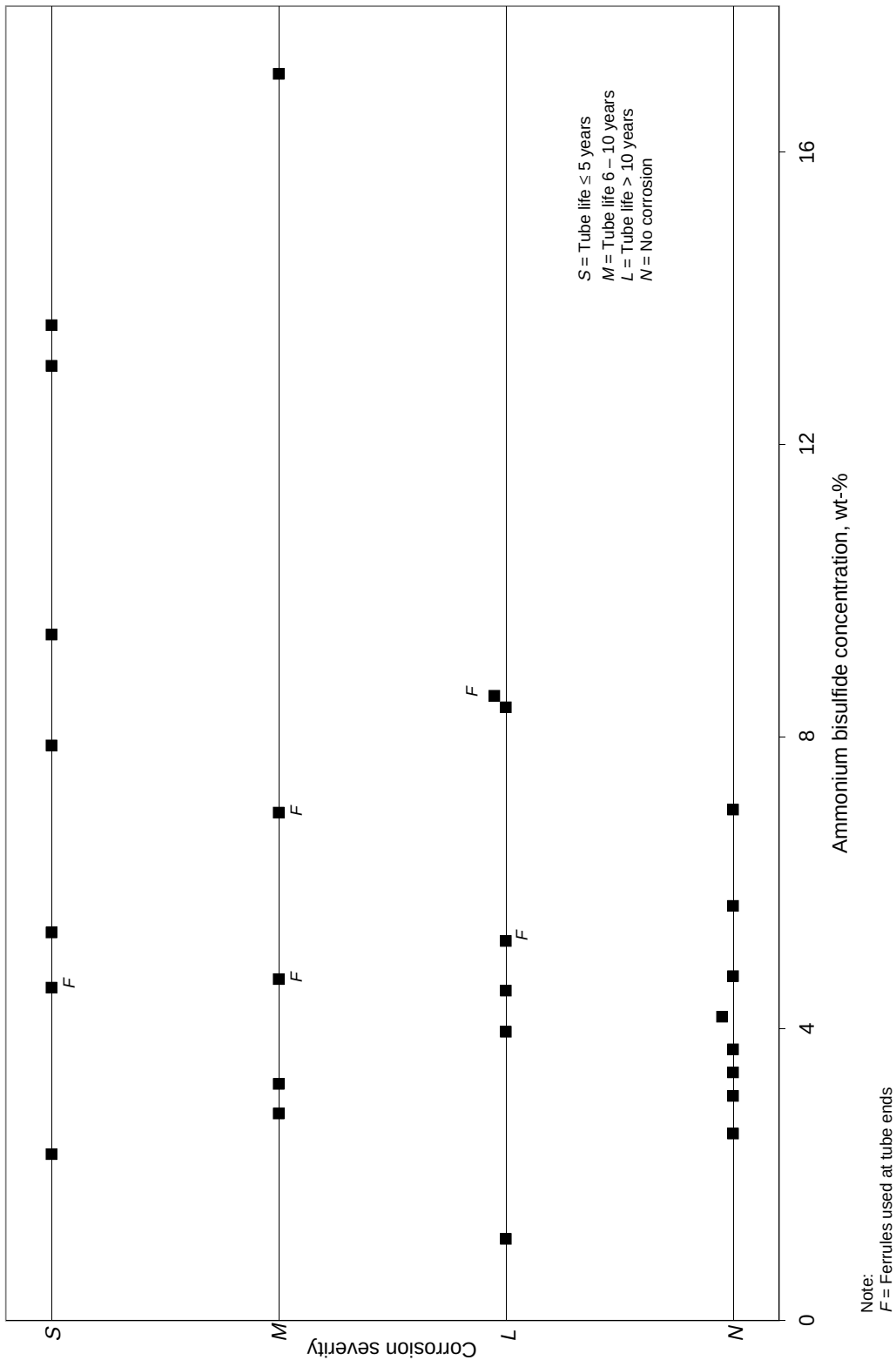


Figure 2—Effect of NH₄HS Concentration in the Downstream Separator on REAC Tube Corrosion (from Ref. 7)

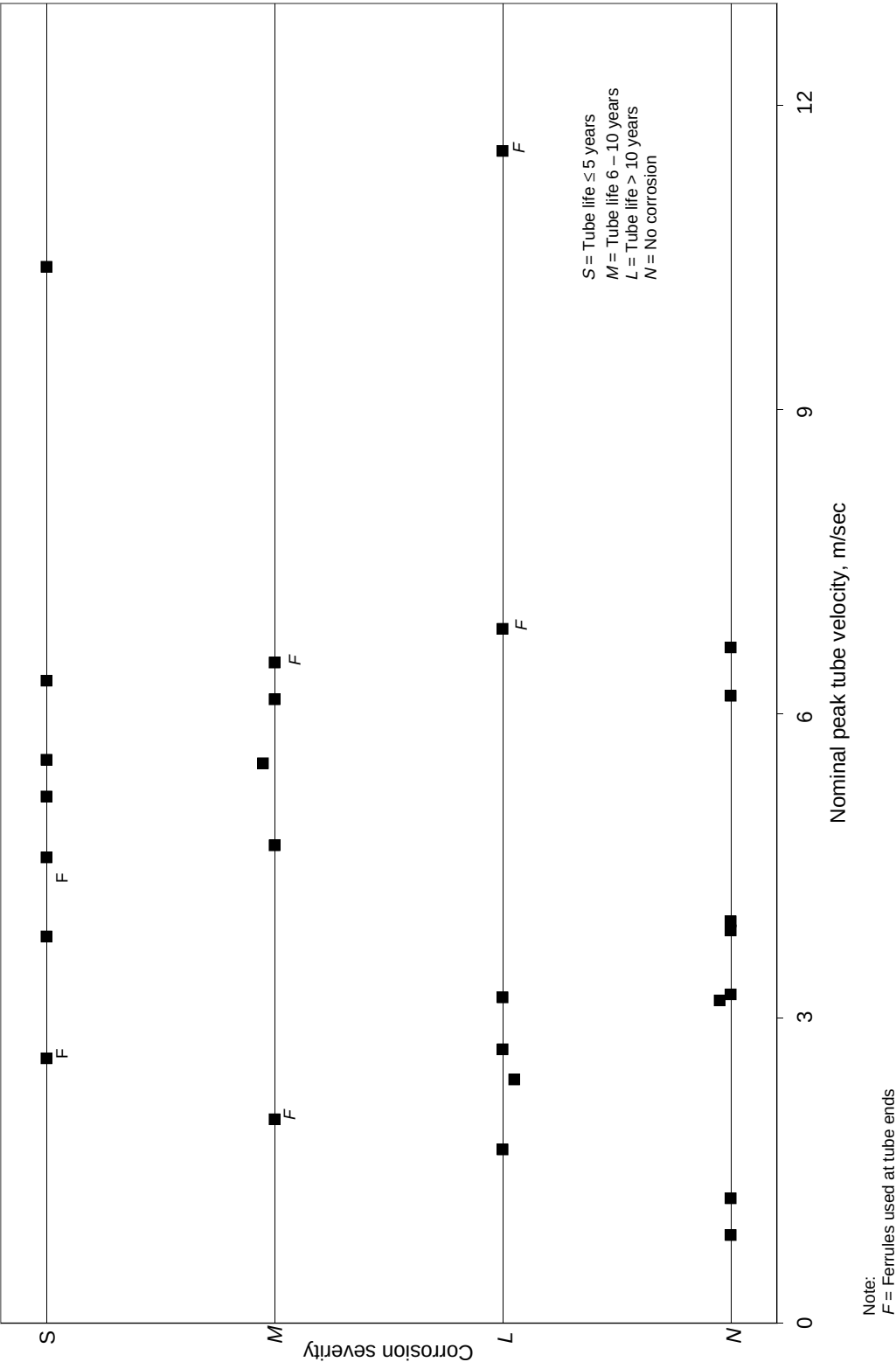


Figure 3—Effect of Velocity on REAC Tube Corrosion (from Ref. 7)

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 con-

tained 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:

<i>HCU</i>	hydrocracking
<i>HTU</i>	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.)

Table 2—Preliminary Survey Results

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

To test the validity of the selection of companies for interview, their responses to the preliminary survey were sepa-

rated 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