

Firestone

INTEROFFICE

DATE September 28, 1979

TO Mr. T. C. Walker

FROM J. A. King ✓

REFERENCE

SUBJECT VCSA MEETING, SAN FRANCISCO, SEPTEMBER 13 & 14, 1979

First, the Agenda:

1. Chemical Industries Institute of Toxicology, R. Fleming, Air Products:

This is an organization devoted to scientific truth with a prime purpose being resistance to ill-founded government regulation. It is not a lobby, nor a lab or consulting body for any member company. Its facility at Research Triangle Park, N.C. cost \$14 million and is due to be fully in operation soon. Its staff numbers 18 PHD's and MD's, 40 MS and BS scientists and 34 others. Its 14 man board is composed of member company representatives. Members are billed according to yearly sales: 0.04% of sales for a 3 year commitment for sales less than \$1 billion/year; 0.06% for \$1-2 billion of sales and 0.08% for over \$2 billion sales. For anyone interested in joining or knowing more, he can write for their annual report. They have done some significant work since incorporation in 1974 even though the permanent facility is just now due for full operation.

• Risk Analysis, Runaway Reactor, Solvent Process, D. Wobser, Union Carbide:

UC started its own program which is simply trying to pre-think what can happen and to develop ways to reduce and control risk. Primary aim is to anticipate and design around hazards and not to provide solutions to problems.

The concept is not new but is just now being intensively applied in the Chemical Industry. ICI is the recognized leader in the field. About ten companies presently use the technique in some form with about three of them using computer analysis.

Generally a combination of events can be pinpointed as the cause of an event with two or three being primary. In about 90% of the cases, human error is involved in some way. The analysis has side benefits: improved safety and communications, reduced design changes and testing planned changes on paper first.

UC sent their people to school for this. Some having such courses are U. of Texas, U. of Tennessee, U. of Washington, George Washington U. and Carnegie-Mellon. They have also used outside consultants in

OCC 2910

training. The weakest area of the method is the lack of good data on the relative frequency of primary hazards; for example, only generic data is available on the industrial frequency of DP cell failure.

The example case, not computer controlled, was analyzed and showed over 3000 combinations of events that could have led to the problem. However, the computer model showed that the design was not at fault. Of the corrections made, a few minor ones were plant tested first. A four man team worked about 30 mandays on the analysis. This included a Process Engineer, Design Engineer, R&D man and an Instrument man. UC does not believe a production man is necessarily required on such a team.

3. Training New People for Safety, R. Henderson, Diamond:

This was preparation for Diamond's Texas VCM plant startup in April 1978 - process is thermal cracking of EDC. All new employees get same training as described.

Best safety comes from knowledge and understanding of process and equipment and Diamond concentrated on these. As construction proceeded the twelve man plant staff developed a Process Operation Manual.

Totally green people got a preliminary course in simple math, physics, etc. Then process people got a four-week training by key supervisors using the Process Operating Manual as an aid. Maintenance and contract maintenance people got two weeks of process and flow diagram instruction followed by special training in their skill areas. The entire group got a four-day fire school course at Texas A&M including the staff and R. Henderson. Then all hands helped on the final plant check out for startup. Diamond thinks it takes a year to fully qualify operators.

Somewhere in all this all people received safety training with actual hands on experience from first line Production and Maintenance Supervisors who had previously developed a Safe Operation Manual. Each employee has his own copy of the manual.

During construction and startup only two lost time accidents occurred and these were not serious. They currently have one Safety and Loss Control Supervisor and one Safety and Environmental Engineer. They consider all supervisors to be Safety Supervisors.

4. VCM Explosion, Recovery System, Dr. B. Terwiesch, PVC Plant
Production Manager, Huels, W. Germany:

The explosion in December, 1978 occurred in the base of a tower where ammonia, used for corrosion protection, was washed out of the inert gas stream. Cost of the damage was about \$1 million, but there were no injuries to humans, since the process is remotely controlled.

Peroxide is believed to have been the cause, but the mystery is how a sufficient amount formed and why in the wash tower. An explosive mixture and runaway polymerization were ruled out.

In recent times they have experienced an increase in impurities in recovered VCM and had raised the allowable oxygen content in the system to 6% from the former 0.8%. Normal content at compressor inlet was 1.5% (vol.).

The conclusions from the Huels study of the event as to the contributing factors and required conditions are:

1. Liquid VCM must be present.
2. Liquid water must be present.
3. Oxygen must be present.
4. Only a slightly elevated temperature is necessary.
5. Presence of other impurities is not as important as the other factors.

Since the explosion the company has:

- A. Started a peroxide monitoring system.
- B. Maintained the system alkaline - phenol is best; sodium ^{HYDROXIDE}~~peroxide~~ is not good enough.
- C. Reduced the oxygen content of the system to 2%.
- D. Started an R&D program - they believe the peroxides must be kept solubilized and not allowed to form the typical large solid lumps. To this Mr. J. Barr of Air Products pointed out that there is a liquid peroxide that will distill.

5. Snuffing a VCM RR Car Fire with Explosives, H. Waltemate, Goodrich:

This fire occurred after a derailment in Princeton, Ky. in October, 1978. Two of five derailed VCM tank cars caught fire. The two were the old type while the other three were the improved version and did not leak. During the entire emergency between 15 and 200 families were evacuated at various stages of assumed danger in areas of up to three miles from the site.

The fires started at once and in five days had half emptied the cars. There was no liquid released. In the first four days the Hulcher Emergency RR Service Co. (Virdon, Ill.) had cleared the site of all but the two burning cars. After three more days the local Fire Marshall called in an Army demolition team from Ft. Knox. On the ninth day the Army blew both cars, but only one fire was snuffed out. On the tenth day a second charge put out the last fire.

The procedure was to blow specially shaped charges below the liquid level and allow the liquid VCM to flow out into the temporarily constructed dike around each car. The hope, of course, was also to blow out the fires. On the successfully blown car, the hole blown was about 2 feet square with edges clean as though cut with a torch. They theorized the non-success was because of ice buildup inside the second car. The leaks from both were from below the liquid level.

5. Operator Training for Regulatory Compliance, D. Frey, Diamond Shamrock, Houston:

This was a last-minute substitution for "Major VCM Excursions and How They are Handled" on the original agenda.

Diamond has two training programs for their Gulf Coast plants: one for new people assigned to the plants and one for everyone after one year on the job. These are handled by two full time instructors who are former plant foremen.

The first program is the normal preliminary training program. The "recycle" program after one year is also given to new assignees to the PVC plants. The latter program includes:

- 1 day - Safety and Environmental
- 1 day - Performing a Job
- 2 days - Process and Quality Control
- 1 week - more advanced training in theory, trouble shooting and quality control.

Diamond recommends full time people for training and sees benefits such as improved production and safety records. In two previous years of VCM releases, two thirds were from operator error. This year they have seen a reduction of about 65% in these.

7. Data Reporting on VCM Monitoring Equipment, W. Clark, Dow:

A PVC plant system was described which includes a Process Control (PC) Computer and a Management (M) Computer. Both are used for other than handling VCM data. The PC computer costs \$50,000, was initially programmed in about 30 days, has shown 99.9% reliability since 1974 and has no backup.

The M Computer costs \$150,000, had 90 days programming, shows 98% reliability and has a backup disc.

GC data from VCM monitoring sensors in two buildings goes to the PC Computer, which feeds into the M Computer. There is a backup GC. Other data is also fed into the M computer, some manually.

The M Computer stores GC and other data and prints out daily reports, physical schedules, training schedules, etc. Some data goes directly to microfilming and this includes OSHA records. This was the only company I heard that has addressed the problem of long term storage of OSHA records.

8. Solvent Absorption as a Final VCM Control Device, G. Schaaf, Goodrich:

The example, essentially a sales pitch, was for a plant process on stream for final compliance in October 1978. It consists of two packed columns, one of which is a stripping column. The solvent is proprietary, inexpensive and commercially available. They are going to license the process. The process was chosen on economic and safety considerations.

They claim they can meet a 5 ppm emission limit. There have been no apparent problems of buildup of impurities in recovered VCM nor in the solvent. They have no COP production at this site.

They see advantages, other than economic, such as: safety - less pollution potential - can locate close to the source.

On economics, the speaker presented a comparison based on EPA's 150 million lbs./year plant and the costs I could note down were:

	<u>Solvent Absorption</u>	<u>Incineration</u>	<u>Carbon Adsorption</u>
Capital Installation	\$475,000	\$425,000	\$600,000
Operating Costs:			
Utilities	\$6.00/hr.	\$2.91/hr.	\$13.94/hr.
Solvent	\$.50/hr.		
Caustic		\$2.34/hr.	
Gain:			
Recovered VCM	\$13.97/hr.		\$13.97/hr.

9. Chloride Stress Cracking, J. Wallace, Esso, Sarnia, Canada:

Prior to the meeting the Questionnaire (A attached) was distributed and 17 responses were received. Firestone's, on pipe cracking only, was one of these. Seven responses were from foreign companies. From these a Working Hypothesis was developed (B attached). Other information by the speaker was:

- Stripping Vessels - at high temperature low pH, 3-4, seems to be significant
- Stripping Towers - are exceeding life expectancies; low oxygen content seems to coincide with no cracking
- Centrifuges - pH may not be significant
- Dryers - pH is not significant; some cracking on baffles and flights
- Piping - less cracking with 316SS (see C attached)
- Recovery Systems - some cracking in condensers, storage vessels and surge vessels
- Miscellaneous - screen frames have shown cracking. Chromium is removed at pH less than 4.0 near welded areas. Intergranular cracking leads to transgranular cracking above 4 pH.

Also attached (D) is a Risk Analysis paper which was prepared prior to the distribution of the Questionnaire for the latest meeting.

The speaker asked for more input from the members, citing the difficulty of making a good analysis from the sometimes incomplete and qualified data he had received. He reminded everyone that the value to everyone depended on good input data and that these could be sent totally anonymous. I suggest our reconsidering giving our full experience history.

10. Governmental Regulatory Effects on VCM and PVC Industries, J. Barr, Air Products - his last attendance in the VCSA:

Mr. Barr formerly handled regulatory liaison and interpretation for VCM and PVC only for all company plants. He now has been assigned full-spectrum responsibility, notification and interpretation for twelve chemical plants, for environmental and product regulations: OSHA, EPA, F&DA, DOT, TSCA, HEW, etc. Some of his comments on all these are below:

OSHA: Inspections: In the last year he knows of 14 companies who were inspected - recommends making a protest if anyone is cited under the new Enforcement Manual of June 4 - trade associations will provide legal help on this if they are asked - OSHA intends to enforce ACGIH and NIH guidelines (acronyms unknown) which are voluntary guidelines - employee representatives must be included in inspections and paid - OSHA is having trouble getting inspection warrants without showing cause.

Lead Standard: Part was remanded but not rate retention. A man removed from an affected area for health reasons cannot have his pay rate reduced.

This provision has a limited term and also depends on his suitability for employment.

Carcinogen Policy: This will probably not be issued until the benzene case is settled. The Fifth District Court has ruled that incremental cost/benefit must be considered. OSHA has appealed.

Fire Brigades: These are now proposed for comment. One feature is that an employee could refuse a hazardous job. duPont has estimated a \$50 million cost for this for all its plants. Air Products estimates \$15 million.

EPA: Carcinogen Policy: This may appear soon in the Federal Register (FR), but may not control all sources of hazardous pollutants. It will probably require a generic leak reduction program at once and Best Available Technology (BAT) as a minimum later with decreasing goals based on residual risk. It would be the same type of program now in force for VCM. New plants would have to have BAT automatically as well as the offset provision. On October 25, industry will meet one last time with EPA's Costle before the FR proposal to try to ease the burden.

VCM Standard Revision: EPA intends no action until after the Carcinogen Policy is published. EDF may not accept the delay. EPA Enforcement wants changes also.

VCM Emergency Relief Valve Discharges: Four companies in NE got Cease and Desist Orders from EPA. (We know of Borden in Region I and Hooker and Tenneco in Region II.) Hooker and Tenneco have filed for judicial review.

Three companies have been given orders to show cause before their violations for emergency discharges are not turned over to the Justice Dept. (We know only of Air Products' Calvert City, Kentucky plant order.)

Water Quality Criteria: These have been issued and the States will now decide how to use them on dischargers. EPA used the old risk analysis and Mr. J. Barr feels the whole thing is a very bad job - no credit for dilution - no aquatic life criteria proposed - etc. If States do not allow for dilution and use the EPA criteria as issued, they will apply directly to point source discharges.

PVC Packaging: This awaits the results of an SOM policy (F&DA's Sensitivity of Analytical Method). This will use acceptable risk calculations to establish residuals. A memo of understanding with EPA on potable water has finally been written. The plastics pipe industry has adopted a voluntary limit of 10 ppm in pipe.

DOT: The department has proposed a four digit international identification system for all containers of hazardous materials: HM-171.

IRLG (acronym unknown): This combines OSHA, EPA, CPSC, F&DA, etc. on identification of carcinogens. It is a first step on a uniform government policy. It uses risk assessment and has many good features, but is generally "too pessimistic" according to Mr. J. Barr.

INTERAGENCY REGULATORY LIAISON GROUP

CONSUMER PRODUCT
SAFETY COMMISSION

IRLG/TSCA: This combination is developing extensive and detailed test methods. TCE will be classed as a carcinogen.

11. Releases, Fires, Explosions, etc.:

Georgia-Pacific: Plant was pushing for record production - using a temporary set up for reactor clean wall additive - operator short cut the procedure - the man was pulled by vacuum into the reactor along with his equipment - temperature was 185°F from steam stripping - agitator on slow speed - no backup man - 15 minutes before anyone knew - man had compound fractures of an arm and a leg, internal injuries and severe burns, but is back at work - Management has assumed responsibility in pushing too hard for production.

Shell: They overfilled a tank car - relief valve lifted - VCM caught fire - stopped five minutes after pump was shutdown - instrument failure.

Goodrich: In PVC compound area, operator fell into a hot water tank - 200°F - burned over 50% of his body - fell from platform 3½ feet from top of tank having no safe bar.

ICI: The computer shut down one VCM transfer pump while a second finished the charge. The second Durco pump then exploded with fire and damage within a 20 ft. radius. All eight 5/8" flange bolts broke - they theorize the cause was heat/pressure buildup with a

OCC 2917

closed discharge. I will write Dr. J. Wilson, ICI Plastics Div., Welwyn Garden City, Herts, England for more detail on this.

Air Products: Ran a 3500 RPM VCM transfer pump against a closed valve and shattered a pipe. One inch relief valve was not large enough. They modified the computer control for faster response.

X Company: Shattered a pipe running a water pump against a closed valve.

Some Answers to FPC Questions:

- I. Removing Setups with Explosives: Air Products has done this for some time. Large and small, glass lined and SS. I will write the Calvert City, Kentucky plant manager for details. They use an outside company for this.
- II. VCM Standard:
 - A. Reactors: Eight companies said they do not open reactors. Goodrich has sight glass in drop line rather than on reactor. Three companies displace with water. Eleven displace with steam. Two displace with nitrogen. Ten measure opening compliance with instruments while four use the bag method as we do.
 - B. Incinerators: Four use boilers as backup. Eleven have no back-ups and, of these five are not planning backups (Pottstown is included here). Georgia-Pacific has temporary approval to use their boiler for VCM while they install an incinerator. One has an HCl limit on a boiler used for VCM. Some neutralize HCl from incineration. Two monitor feed to incineration for explosive mixture. One company monitors each stream to the incinerator and adds nitrogen if in the explosive range.
 - C. Gas Holders: Several plants use gas holders to even out flows. General Tire is the only one having a holder for Emergency Relief Valve Discharges. It is for manual venting and relief valves are not piped to it. Has a rubber seal. Holds one 4000 gal. batch. It was not installed for this purpose originally. They have used it for some years and feel it is an acceptable means. Mr. R. Laundrie would only add that "they have their problems with it".
 - D. Emission Questionnaire: Mr. G. Schaaf, Goodrich reported such poor response that no report could be made. Asked everyone to send these in since it includes data already given to EPA. Mr. J. Barr, Mr. R. Laundrie and several others strongly urged this. I received Perryville's too late to send and have not yet received one from Pottstown.

- III. OSHA: No one allows females into regulated areas. No one appears to be thinking about how to store 30 years of records except Dow.
- IV. Tapes: Personal tapes were banned at last year's meeting in Atlanta. The meeting tape was not taken for the current meeting. Meeting tapes were originally taken on advice of legal counsel of some companies to prove no price fixing, etc. All companies are now asked to respond on their updated views.

Attempting to get all questions answered is quite a chore. If you will ask me again, in writing, I will try via my own questionnaire to get more information for you.

Next October's meeting is in Bermuda.

J. A. King
J. A. King

JAK/rm

Attachment

cc: Mr. T. C. Walker
Mr. C. J. Kleinert
Mr. F. F. Hoy
Mr. K. H. Garner
Mr. P. J. Foley
Mr. C. W. Engblom
Mr. D. M. Connor
Mr. G. D. Lloyd
Mr. R. A. Park
Mr. R. W. Arnold

PS #1 - At a later meeting Mr. Barr corrected a statement. Air Products plant is the only company having received a show cause order before EPA turns over to the Justice Dept. the Calvert City violations for emergency relief valve discharges.

PS #2 - Several plants have PVC dust complaints from neighbors. Goodrich, at least, has installed water scrubbers for suspension dust capture in more than one plant; Pedricktown is one plant using this method.

J. A. King/rm

CHLORIDE STRESS CORROSION RISK MANAGEMENT FAILURE QUESTIONNAIRE

(A)

HAVE YOU EXPERIENCED CHLORIDE STRESS CORROSION CRACKING IN ANY OF THESE MATERIALS -

STAINLESS STEEL TYPE 304 ☐ 304L ☐ 316 ☐ 316L ☐ OTHER

IF SO, PLEASE INDICATE THE CONDITIONS, AS FAR AS THEY ARE KNOWN TO YOU.

TYPE OF EQUIPMENT _____

STEEL TYPE	304	304L	316	316L	OTHER
1. MAXIMUM TEMPERATURE USED					
2. % OF TIME AT THIS TEMPERATURE					
3. YEARS OF SERVICE					
4. IONIC CHLORIDE CONTENT PPM					
5. pH					
6. OXYGEN CONTENT					
7. WERE CONCENTRATING CONDITIONS PRESENT					
8. EXTERNAL OR INTERNAL (MARK E OR I)					
9. IF INTERNAL, LIQUID OR VAPOUR (L OR V)					
10. WAS FOULING PRESENT					
11. SPECIAL CONDITIONS*					

*SPECIAL CONDITIONS INCLUDE STRESSES FROM GRINDING OR WELDING, TEMP. CYCLING, PRESENCE OF CHELATOR.

PLEASE RETURN TO: J.R. WALLACE
ESSO CHEMICAL CANADA
PLASTICS TECHNOLOGY LABORATORY
P.O. BOX 69, S. CHRISTINA STREET
SARNIA, ONTARIO N7T 7H9

OCC 2920

(A)

WORKING HYPOTHESIS

THE MAJORITY OF THE DATA COLLECTED OR REASONABLY ASSUMED, PLUS THE OBSERVATION OF STRESS CRACKS ORIGINATING AS INTERGRANULAR CRACKS IN HEAT AFFECTED ZONES, LEAD TO THE FOLLOWING HYPOTHESES.

- AT pH <4 A REASONABLE GUIDE TO LIFE EXPECTANCE MAY BE OBTAINED FROM THE COMPUTATIONS PRESENTED AT THE LAST MEETING.
- AT pH >4 LIFE EXPECTANCY IS GREATLY INCREASED.
- IN THE CASE OF STRIPPING TOWERS, OPERATION ABOVE ATMOSPHERIC PRESSURE MAY ALSO EXTEND THE LIFE EXPECTANCY BY PREVENTING OXYGEN ENTRY.
- FOULING WAS USUALLY PRESENT, BUT ITS EFFECT WAS NOT CLEARLY RESOLVED.

THE IMPLICATIONS OF THESE HYPOTHESES ARE IMPORTANT AND VERIFICATION OR CORRECTION IS EAGERLY SOUGHT.

YOUR INPUT IS AGAIN REQUESTED, ESPECIALLY TO FIND:

- HAVE YOU EXPERIENCED ANY CRACKING AT pH >4 OR AT DISSOLVED OXYGEN CONTENTS <0.5 PPM (NOT TO BE CONFUSED WITH OXYGEN IN THE CHARGE, WHICH IS CONVERTED TO HCl)?
- CONVERSELY, HAS THE LIFE OF A GROUP OF VESSELS GREATLY EXCEEDED THE PREDICTED LIFE EXPECTANCY UNDER THESE CONDITIONS?
- HAVE YOU ANY OTHER DATA RELEVANT TO THE LIFE EXPECTANCY?

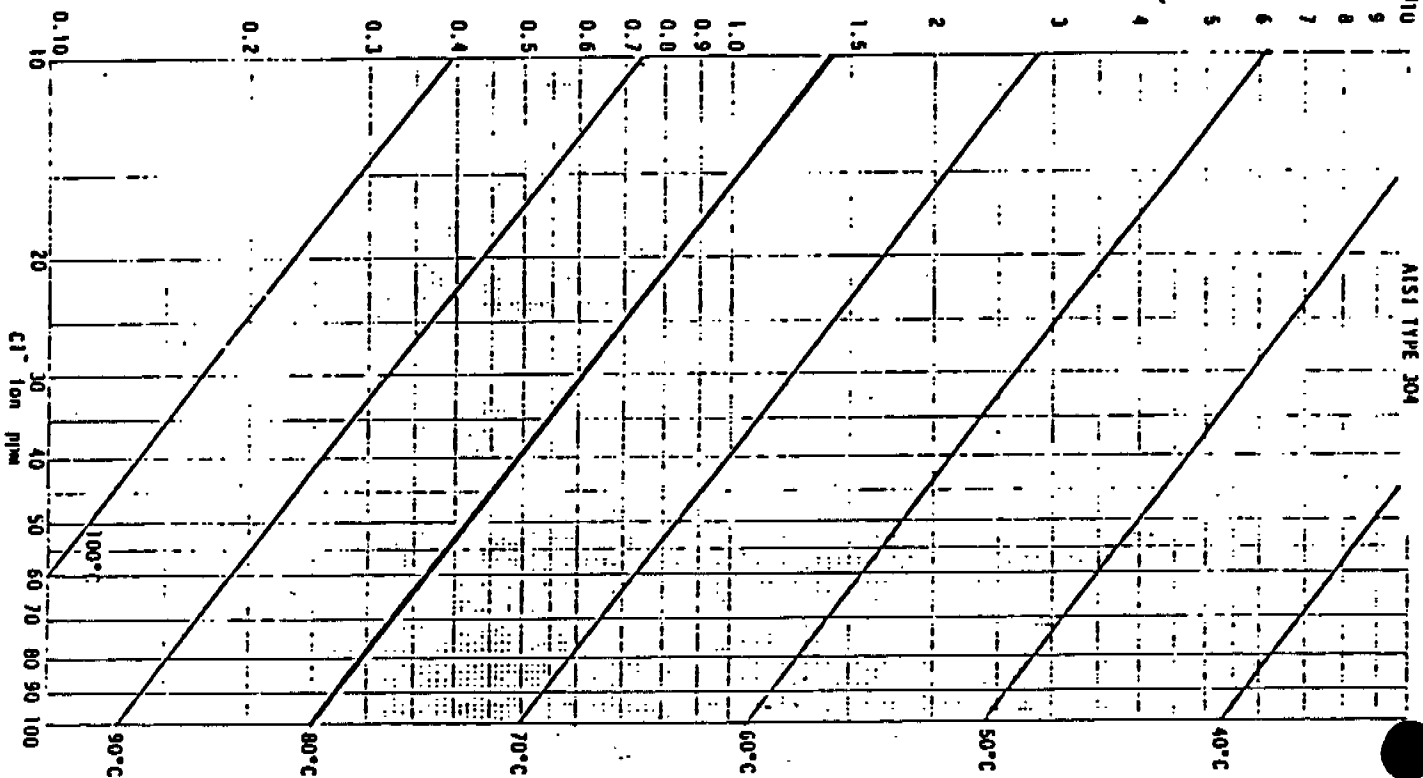
COPIES OF THE ORIGINAL HANDOUT AND QUESTIONNAIRE ARE AVAILABLE FOR GATHERING RESPONSES. ANONYMOUS RESPONSES ARE BETTER THAN NONE.

JRW/cdr
79 09 13

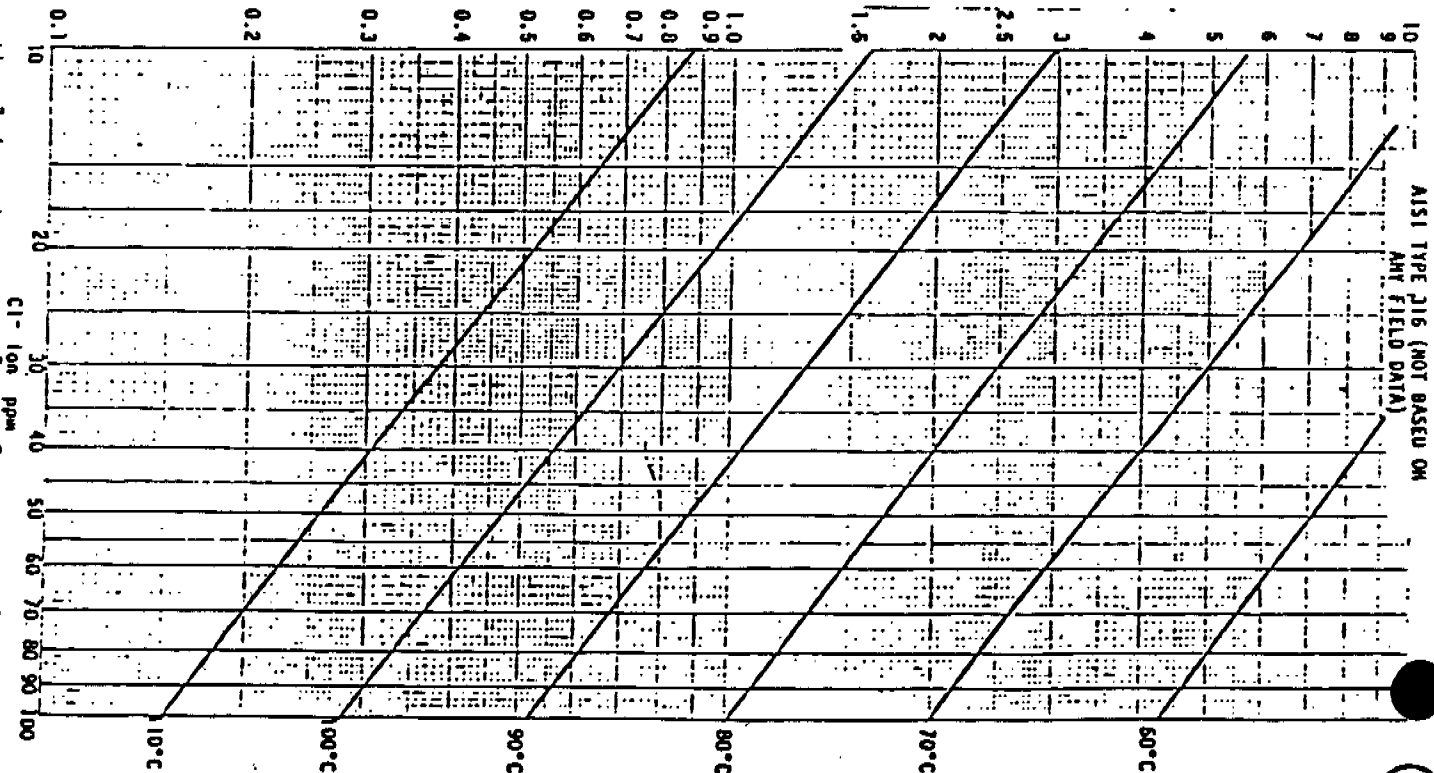
OCC 2921

(B)

LIFE EXPECTED - TOTAL YEARS
OF ACTUAL EXPOSURE



LIFE EXPECTED - TOTAL YEARS
ACTUAL EXPOSURE



These predictions are the best we can make, based largely on the laboratory results of others, plus our field experience with Type 304 stainless steel. No guarantee can be given of performance in any specific circumstances, due to the effect of other variables, as yet not quantified.

CHLORIDE STRESS CORROSION CRACKING (C.S.C.C.) RISK ANALYSIS

(D)

- 1) NUMERICAL ESTIMATES OF PROBABLE C.S.C.C. FAILURE DATES ARE ESSENTIAL FOR DECISION MAKING.
- 2) FROM DATA IN A REVIEW BY E. HOXIE^(a) THE "WICKING TEST" 50% FAILURE TIME $t_{0.5}$ IS ESTIMATED AS
$$t_{0.5} = \text{ANTILOG}_{10} \left(\frac{3679}{T^{\circ}\text{C} + 273} - 0.7586 \log_{10} [\text{Cl}^{-} \text{ ppm}] - 6.045 \right) \text{ HOURS FOR AISI 304.}$$
- 3) ACTUAL STRIP DRUMS AND MIX TANKS OF AISI 304 BADLY FAILED IN 5 TO 7 TIMES $t_{0.5}$.
- 4) MOST PROBABLE FAILURE TIME t_{f304} ESTIMATED AS $3 \times t_{0.5}$ FOR AISI 304
i.e. $t_{f304} = \text{ANTILOG}_{10} \left(\frac{3679}{T^{\circ}\text{C} + 273} - 0.7586 \log_{10} [\text{Cl}^{-} \text{ ppm}] - 9.5105 \right) \text{ YEARS}$
- 5) NOTE (a) FIGURE 13 SUGGESTS FOR AISI 316, $t_{f316} = 4 \times t_{f304}$. NO ACTUAL FAILURE FOUND OR PREDICTED.
- 6) RESULTING PROBABLE FAILURE ESTIMATES ARE PLOTTED IN THE ATTACHMENT.
- 7) FOR REGULAR EXPOSURE OF DIFFERING SEVERITY, E.G. P_a, P_b, P_c % OF TIME AT TEMPERATURES, T_a, T_b, T_c -----ETC.
$$\frac{100}{t_f} = \frac{P_a}{t_{fa}} + \frac{P_b}{t_{fb}} + \frac{P_c}{t_{fc}} \dots \text{ETC.}$$
- 8) FAILURES WERE AT PH 3-4: EFFECT OF PH UNDER INVESTIGATION. ZERO OXYGEN INHIBITS, BUT LOW LEVEL HAS NO EFFECT.
- 9) CORRELATION WITH ONE OTHER PLANT HAS BEEN GOOD. MORE CORRELATIONS NEEDED FOR GOOD RISK MANAGEMENT. YOUR INPUT IS REQUESTED WHERE EQUIPMENT HAS GREATLY EXCEEDED THE PREDICTED FAILURE TIME.

(a) E.C. Hoxie - Some Considerations in the Selection of Stainless Steel for Pressure Vessels and Piping
A.S.M.E. Talk 1975 copies from International Nickel Corp., 1 New York Plaza, New York, N.Y. 10004.

J.R. WALLACE:caw
ESSO CHEMICAL CANADA
PLASTICS TECHNOLOGY LABORATORY
P.O. BOX 69, SARNIA, ONTARIO N7T 7H8
OCTOBER 25, 1978 TEL. (519) 339-2284

OCC 2923

(D)