

CHLORINE PLANT OPERATION SEMINAR PROCEEDINGS

25th Meeting

Omni International Hotel

Atlanta, GA.

February 1982



CHLORINE INSTITUTE PAMPHLET

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THE CHLORINE INSTITUTE, INC.

- PROCEEDINGS -

TWENTY-FIFTH CHLORINE PLANT OPERATIONS SEMINAR

Atlanta, Georgia
February 17, 1982

John Forner, Presiding

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THE PLANT OPERATIONS SEMINARS, A RETROSPECTIVE

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(Presented at the Chlorine Institute's
25th Plant Operations Seminar
Atlanta, Georgia, February 17, 1982)

I am delighted to meet with you and to review - briefly you can be sure - the proceedings of the twenty-four Plant Operations Seminars which have led to this, the twenty-fifth. During the twenty-four years over which they have been held the accomplishments have been great; the consequences of those accomplishments have been far-reaching.

The first of these meetings was held in New York City in January of 1957. It is not true that one of the accomplishments of that meeting was that the Commodore Hotel - for that is where the meeting took place - was torn down to provide a skeleton for the Grand Hyatt. It is true that the meeting laid the ground work for one of the most effective of all mutual emergency assistance programs - the program now in place as CHLOREP.

It all began as a public relations problem. Chlorine was then - as it is today - a deadly war gas to the press and to much of the public in general. Whenever chlorine was mentioned in the press it was in connection with some unhappy event, an explosion, an accident, air pollution, or perhaps someone was gassed. Does that sound familiar?

The program for that first meeting was organized around plans for a community relations program. The concept was evolving that the scare headlines and what was perceived as irresponsible reports by news persons could best be countered by educating people about the good things chlorine does. One speaker went so far as to say that, after a spectacular incident was over and the townspeople saw how well the plant handled the emergency, relations with their neighbors improved. To which one attendee retorted that he was unwilling to have a release as a public relations effort.

But even then the germ of CHLOREP was in the making. One speaker described a local mutual assistance agreement and how the public's knowledge of its existence helped inspire confidence among the populace.

The year 1957 was a fateful year. That year the Plant Managers met twice. By the time of the second meeting it had become clear that a Public Information Program - modest though the proposal was - would up the dues of the Institute 35 to 40 per cent. The then President of the Institute commented ruefully that the name of the Program needed to be changed to emphasize Safety. Safety always sells.

The formal program, consistent with its ongoing theme, had a presentation by an outside speaker on the need for individual plant disaster procedures to be linked to civil defense. The speaker may not have been too helpful, however. Most of his remarks had to do with what one - presumably a chlorine plant manager - ought to do after a hydrogen bomb struck. It was something of an anti-climax when one Plant Manager described in detail a well thought out program for taking care of emergencies. Throughout, in these early papers, is concern how to keep roads free of curious onlookers.

The Third Meeting continued the theme of in-house disaster planning. While the records do not show it, by now the hope for a formal Public Information Program was fading. This meeting was chaired by the President of the Institute, not the Chairman of the Public Information Committee. In addition to Disaster Planning, housekeeping as an aid to safety received attention.

A recurrent theme - as it ought to have been - was the place of the Plant Manager in the scheme of Management. Most often the speakers have dealt with how the Plant Manager ought to manage his own people. However, one notable paper appeared in the Third Plant Managers Meeting where Dr. Carl F. Prutton talked about the relationship of corporate top management to chemical plant managers. He was not kind.

The Fourth Meeting in 1959 may have been one of the most significant of all meetings. The theme of that meeting was a hypothetical chlorine accident in which a member other than the shipper was called upon to lend assistance. Very briefly, a chlorine consumer left a chlorine car connected over a week end when unloading was discontinued. The railroad, acting on instructions, pulled the car loose. Chlorine escaped from the car and from a storage tank. The consumer called his chlorine supplier. He was instructed to call a chlorine producer located nearer to his plant than the supplier. The nearby producer sent a technical service man who capped off the leak. Seventeen people were hospitalized and some sued.

The meeting took the form of a critique. The technical service man insisted that his job was to give immediate assistance; the supplier had the responsibility for following through. The lawyer said that since the technical service man performed his part in a competent and reasonable manner his company had no liability. He further said the clear liability rested with the consumer since he left the tank car connected with no one in attendance. He quoted the section of the then ICC regulations with which we are all now so familiar: "...throughout the entire period of unloading or while the car is connected to the unloading device, the car must be attended by the unloader." The doctor discussed treatment for chlorine inhalation and stated that while chlorine inhalation is unpleasant either you recover completely or you die - a choice which is easy to make.

Someone from the audience suggested that member companies of the Institute ought to have an agreement with one another where one company could call on another company nearer the scene of an incident to provide help. The lawyer said he didn't even like to hear the word "agreement" but it was a suggestion to which serious thought should be given.

By the time of the Fifth Meeting there was considerable soul searching as to the direction the Plant Managers group should take. Some thought emergency handling and disaster planning had gone as far as it could go. Others wanted to broaden the scope of problems dealt with but were concerned about the implications of discussing plant problems in open meetings.

At any rate a Task Force was appointed and it decided to break new ground in the Sixth Meeting. For one thing it was held in Cleveland, Ohio. For another, it was the second meeting that year and it was not part of an annual meeting. Most important it had an entirely new agenda.

There were two panel discussions. In the morning the relatively new and controversial subject of chlorine trucking was dealt with. The ever present question of change out of angle valves was tackled. The question of driver training and the carrying of emergency equipment was discussed. The consensus was that trucking was a safe and rational way to move chlorine and the movement was bound to grow.

In the afternoon chlorine storage was discussed. I had the privilege of addressing the group on Storage in Conventional Storage Tanks. I will not say that it was my finest hour. In those days we used a public stenographer to make a verbatim report. I had a little trouble with a question put to me and needed a bit of time. I turned to one of my colleagues in the audience and said, "That's what we do, don't we, Glenn?" To which he replied, "No, Herb, we don't do that at all." The stenographer got it all.

The Seventh Meeting continued the process of diversifying the nature of the Plant Managers Meetings. Members of the Institute had become concerned about possible adverse health aspects of exposure to chlorine and to mercury during normal operations. Wayne State University had been retained to investigate. The meeting had papers on air sampling and on determining mercury in air, matters which were essential to the Wayne State investigation. The members discussed chlorine plant ventilation. A group of papers on nitrogen trichloride as a hazardous by-product of chlorine manufacture was presented. An added starter was a pictorial review of the raising of the chlorine barge which sank off the shore of Natchez, Mississippi. The wildly exaggerated and hysterical reports which almost diverted national attention from the missile crisis in Cuba were noted.

If chlorine is a deadly war gas capable of instilling horrible fear in the minds of people guided by our popular press, nitrogen trichloride is the bete noire among chlorine plant managers. The Eighth Meeting continued the preoccupation with this unpleasant material. Cell room ventilation was another big topic.

By now it was clear that the Plant Managers Seminars were prepared to take on all problems. The seminars had become a forum for discussing almost any problem likely to arise in chlorine production. The participants had gotten used to being able to discuss technical matters in a technical forum. At the same time forbidden matters were scrupulously avoided. In 1966, the Ninth Meeting took on hydrogen and chlorine mixtures together with a heavy dose of measuring chlorine flow and the nature chlorine impurities.

The Tenth Meeting returned to the theme of emergency planning. Here for the first time the Plant Managers recognized the community of interest between chlorine packagers and primary producers. One paper outlined an emergency planning protocol suitable for packagers. While packagers did not constitute the audience one can see interest developing which now is finding fruition in the varied agenda of the Packagers Committee.

One of the important papers at that session described planning and procedures at a Gulf Coast plant to deal with hurricanes. And again the subject of how to deal with the press and with TV came up.

It was at this meeting that A.E. Howerton continued his analysis of the area affected by a chlorine release. In its latest form this is now a separate publication of the Institute. This important paper made use of much of the then new dispersion data developed in the interest of safe operations at atomic energy plants and at missile launching or test sites.

The Eleventh Meeting returned to the subject of chlorine handling. Methods of transferring chlorine by pressure padding, by heated chlorine vapor and by pumps, both submerged and canned, were discussed. The method of heating chlorine to provide a chlorine pad had been adopted, said one speaker, in order to eliminate the need to purge a storage weigh tank delivering chlorine into a pipe line. Vapor recompression received considerable attention. Other papers dealt with atmospheric pressure storage in spheres and such mundane matters as loading of cargo tanks, tank cars, and barges. You will note the similarity of subject matter to current Institute publications but the Plant Managers Seminars long preceded the pamphlets.

The Twelfth Meeting (1969) returned to operations. One session was devoted to compressors in chlorine service: the famous Nash Hytor, conventional reciprocating compressors and the then not so conventional centrifugal compressors. Safety in the electrical systems necessary for electrolytic processes received attention. The meeting closed with substantial unfavorable discussion about the meeting place (The Plaza) and the meeting city (New York).

The next meeting saw a different hotel (The Biltmore) but the meeting was still in New York. It was a time of turmoil. The Wayne State findings on worker exposure to chlorine and to mercury were in. The Williams Steiger Act (OSHA) had not been passed and the uncertainty of future regulation had people in a dither. That meeting looked the facts in the face and almost unanimously agreed that realistic data had to be gathered now for use in the future.

By the time of this meeting the Sub Committee on Emergency Control Planning was virtually ready to announce a formal outside plant emergency control program. The Manual was ready. In reporting to the Plant Managers, the Sub Committee announced their most recent decision: the recommendation for a single central dispatch point. That point was to be the Bureau of Explosives. Clearly CHLOREP was not yet ready but it was getting close.

The Fourteenth Meeting (1971) took place in one of the Institute's favorite meeting places - New Orleans. By now the word, ecology, was on everyones lips and even the purists had given up trying to hold to its real meaning. They seemed resigned to its being used to mean the environment and any change in the environment brought about by man, today or in the past, was harmful and therefore bad.

But the chlorine industry has always been concerned that its operations conform to the highest standards of good neighborliness. It is small wonder that when information on the effect of mercury in the ecosystems came to the fore, the chlorine industry immediately went to work to monitor the amount of mercury escaping and to minimize the amount of mercury in its products.

In this wide ranging meeting the effects of chlorine in air were discussed, particularly those possible emissions in the operation of a chlorine plant. Air borne mercury received attention as well as mercury discharges into the waterways. So that all of the focus would not fall on mercury cell plants, asbestos and lead in air were discussed. The meeting concluded with a panel discussion evaluating the chemical industry's approach to pollution abatement in the seventies. The consensus was that true abatement would cost money but so do paved streets. There seemed to be agreement that expenditures on abatement could have a great reward of their own: the effort could help restore the image of the chemical industry which was once welcome anywhere but at the time of speaking "no more popular than the black plague."

At the Fifteenth Meeting (1972) Fritz Zorn reported that CHLOREP was ready to go. John Zercher of what was then MCA reported on the first five months of CHEMTREC. Long, hard work on the part of Plant Managers was beginning to bear fruit.

For the first time the subject of metal anodes was up for discussion. All of the speakers predicted, quite accurately, that the use of metal anodes would accelerate. All of them praised the higher quality product produced. And all of them lamented the cost.

Also this meeting was noteworthy because OSHA had come into being. At last the Plant Managers had guidelines which they had to follow. One of the papers presented a somewhat detailed analysis of how the Act had functioned up to then. I think the general attitude was one of awe that anything so comprehensive could come about.

By the Sixteenth Meeting (1973) the full impact of OSHA had sunk in. In addition, EPA and the Clean Air Act of 1970 was a matter of concern. The meeting was largely devoted to the impact on cell room design and operation and on electrical systems of what was lumped together as "Recent Regulations." The mood of awe from the 1972 meeting had given way to a mood of "Can They Be Serious?" Speaker after speaker warned that "they" were, indeed, serious and pointed out changes in customary procedures which would have to be made.

As if the Plant Managers did not have enough to deal with, the energy crunch came. The Seventeenth Meeting (1974) was devoted to discussing ways to conserve energy. However, a careful reading of the papers showed that most of the thinking was directed toward identifying sources of energy consumption that might, in a better world, be reduced.

There was no respite. The Eighteenth Meeting (1975) devoted itself to pollution control and further to energy conservation. Asbestos came in for a long, hard look. By now the impact of Federal regulations had been fully felt and a look was taken at state regulations.

A difficult problem for Plant Managers has always been the status of respiratory equipment. As the question of "approved respirators" wended its tortuous way through the regulatory bodies, the Plant Managers received a report on how things stood. It wasn't far different from the report of the year before.

The Nineteen Meeting (1976) was the first at which membrane cell technology was discussed. Since this meeting was held in Montreal it was appropriate that the installation described be a Canadian installation. The date of the meeting was February 4. Those of you who attended that meeting may recall that all of the sessions were extremely well attended. They had bad winters in those days, too.

The Twentieth Meeting moved back to the friendlier weather in New Orleans. Chlorine technology was the subject. Two interesting papers dealt with hydrogen chloride to chlorine processes. It is safe to say, however, that a paper on the Asahi membrane and Asahi membrane technology aroused the most interest.

The Twenty-first Meeting (1978) returned to its first love: public relations. The Public Information, the Government Relations, the Community Relations and the Media Relations programs were separately reviewed. By now the subject of membrane technology was no longer novel and two papers were presented on that subject.

The Twenty-second Meeting was held here at the Omni in 1979. It began with an analysis of how the public looks at the chemical industry as revealed by a public opinion survey. The chemical industry was regarded by all segments of the population as just about the worst offender in all categories of relation with the public. Only in cleaning up water ways did the public think the industry had done a good job. Only the tobacco industry was perceived as more socially irresponsible than the chemical

industry. It should be noted that this survey was with regard to chemical industry generally - not specifically the chlorine industry. We have reason to believe that in general you gentlemen have been instrumental for your plants being held in higher esteem than the industry as a whole.

The EPA tests on the use of foam to repress chlorine evaporation from a spill were reported. New technology received attention. Membrane cell developments were discussed, again in terms of Asahi experience. Cost comparison was made of high and low pressure chlorine compression. The conclusion was that in some cases one is better than the other - a conclusion with which no one could argue.

The Twenty-third Meeting returned to a panel format. One panel was devoted to chlorine storage. One of the papers detailed European Chlorine Storage Practice. Mention of this paper has particular relevance today in the light of the Institute's participation in an international meeting in London this summer to discuss matters of mutual interest with the BITC/GEST group. BITC stands for Bureau International Technique du Chlore and is similar in scope to the Institute. GEST is a technical working group dealing with chlorine storage and transport together with associated equipment.

A second panel brought up to date the status of pollution control in the Chlor Alkali industry. And with ever increasing energy costs it was appropriate that another panel devote its attention to energy conservation.

We come now to the last meeting prior to this Twenty-fifth Meeting. It continued the panel format. As at the beginning, emergency planning was a prime concern. Our meetings began with consideration of how to deal with the media in emergency situations and guess what - that was a subject at our most recent meeting. Also Art Howerton brought us up to date on calculating the amount of chlorine released under various conditions of emission. Remember, he first dealt with the mechanism of dispersion at the tenth seminar.

This meeting dealt also with the effect of various potential exposures to plant personnel and continued the technology review.

And so, gentlemen, I say to you that from a relatively small and simple beginning, the Plant Managers Seminar has evolved into an important and influential body. It has accomplished much. CHLOREP, the most effective industry cooperative effort for dealing with emergencies is in place. Working groups dealing with public information, plant safety and other matters of concern function. A forum for the update of technology awareness exists. People with experience in dealing with the multitude of regulations have been able to share their information to the benefit of all. Even the name has changed and today we speak not of the Plant Managers" Seminar but of the Plant Operations Seminar.

You may well be proud of your antecedents and your prospects are propitious.

PLANT SAFETY COMMITTEE REPORT

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Presented At The

25th Plant Managers Seminar
Atlanta, Georgia
February 17, 1982

During 1981, the Plant Safety Committee was restructured to provide the staffing and responsibility assignment needed to accomplish the established goals. The previous four sub-committees were combined into two sub-committees--Safety Planning and Seminar. Two functioning Task Forces on Respirator Equipment and Electrical Safety continued to operate.

The following summarizes the accomplishments of the sub-committees and task force:

I. SAFETY PLANNING SUBCOMMITTEE - Chairman, Don Hise, B.F. Goodrich

Accomplishments in 1981:

1. Publish the pamphlet "Calculations for Determining the Area Affected by Chlorine Releases" in the first quarter of 1981. The pamphlet has been well received.
2. Completed the first draft of "Mitigation of Cl₂ Release". This publication represents a compilation of techniques used by member companies in dealing with chlorine releases. It will undergo final review prior to release by the Plant Safety Committee in early 1982.
3. The pamphlet "Emergency Control Planning Check List" was reviewed. It is considered to be current and the sub-committee has recommended no modifications at this time.
4. Solicited data from all member companies and released a summary of all data in October 1981. The data indicated that 67 plants reported 511 total recordable incidents (compared to 440 in 1978 and 410 in 1979) with 124 of these being lost work day incidents (compared to 147 in 1978 and 115 in 1979). One fatality occurred and it was classified Falls-Struck By.

Of the various catagories, lost work day percentage incidents fell in the areas of Burns-Chemical, Burns-Thermal, Electrical, Falls Struck By, and Fire-Explosion. Gas inhalation remained at 10%, Strains and others both increased.

II. SEMINAR SUBCOMMITTEE - Chairman, Jack Fonner, Georgia Pacific

Accomplishments in 1981:

1. Solicited suggested topics for the 25th Seminar.
2. Developed the program
3. Organized this seminar.

III. RESPIRATOR TASK FORCE - Chairman, Larry Packard, Dow Chemical

Accomplishments listed in 1981:

1. Respirator pamphlet completed after extensive review by task force and Health and Toxicology Committee and recommended for adoption.
2. Coordinated the study on mouth bit respirators performance. Extensive testing completed with Diamond, Dow and Olin participating. Dr. Pritchards was utilized as a consultant. Data developed is in the final stages of review in anticipation of seeking approval for mouth bit respirator for wider use than escape.

IV. ELECTRICAL TASK FORCE - Chairman, Art Forester - Hooker Chemical

1. Coordinated the final review of the Electrical Safety Training Program developed by Hooker and made it available to the industry. Twenty copies were sold and were well received.

V. GOALS FOR 1982

1. Restructure staffing
 - a. Don Hise, B.F. Goodrich to be Chairman of Plant Safety Committee. Don Wilson of Diamond to be Vice Chairman.
 - b. Chairman to appoint subcommittee chairman and vice chairman.
2. Publish the following pamphlets:
 - a. Respiratory Protection Guidelines by April 1982
 - b. Mitigation of Cl₂ Releases by third quarter after committee approval in May.
 - c. Emergency Planning Check List - revision by 3rd quarter after committee approval in May.
3. Obtain approval for mouth bit respirators and mercury respirators by supporting manufacturers and providing data.

Disclaimer

The views expressed by the author do not necessarily reflect Chlorine Institute policy and under no circumstances is the mention of equipment and/or process methodology to be construed as an Institute endorsement.

Method for Calculating Water Distribution In A Chlorine Condensing System



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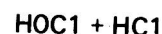
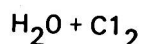
Presented at the
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A method is presented for calculating water distribution between phases in a chlorine condensing system. Examples for condensing systems are developed, illustrating the calculation technique and the results being compared with observed corrosion in a typical system.

The importance of physical configuration of condensers is discussed in terms of enabling the continuous removal of a water-rich second liquid phase, which exists as solid chlorine hydrate at temperatures below 9.6°C.

Corrosion Mechanism — The Chlorine-Water System

The corrosion mechanism for wet chlorine attack on steel is generally accepted as the result of the formation of a water-rich phase in the system. The water-rich phase will not only dissolve a protective layer of ferric chloride, but will also result in the formation of a strongly acid medium by reaction of chlorine with water as follows:



Ketelaar and Kooi show solubilities and vapor pressures of water in the system chlorine-water as a function of temperature,

$$(1) \log_{10} X_s = -7.7/2.30 RT + 4.63$$

$$(2) \log_{10} P_o = -12.5/2.30 RT + 7.65$$

where

X_s = Solubility of Water in Liquid Chlorine in Mole %

P_o = Vapor Pressure, atmospheres

T = System Temperature, °R

R = Gas Constant, 0.001987

Table I shows selected values for the solubility and vapor pressure as calculated by Equations 1 and 2.

Table I
Solubility and Vapor Pressure
Of Water In Liquid Chlorine

Temperature °C	Solubility Of Water In Liquid Chlorine			Vapor Pressure Of Water In System Atmospheres
	Mole %	PPM by Molar Volume	PPM by Weight	
50	0.21	2100	532	123×10^{-3}
40	0.16	1600	406	72.7×10^{-3}
30	0.12	1200	304	41.8×10^{-3}
20	0.076	760	193	21×10^{-3}
10	0.048	480	122	9.85×10^{-3}
0	0.029	290	74	4.35×10^{-3}
-10	0.017	170	43	1.8×10^{-3}
-20	0.0093	93	24	0.70×10^{-3}
-30	0.0050	50	13	0.25×10^{-3}
-40	0.0025	25	6	0.08×10^{-3}

Water combines with chlorine to form solid chlorine hydrate ($\text{Cl}_2 \cdot 8\text{H}_2\text{O}$) at temperatures below 9.6°C. If water in chlorine exceeds the solubility at any given temperature, a water-rich phase is formed; above 9.6°C this phase is liquid and below 9.6°C the phase is solid chlorine hydrate.

Chlorine drying systems generally produce gas with a water content less than 50 ppm by volume. Thus if the solubility data and generally accepted corrosion mechanism are correct, corrosion would not be expected in any liquid system at temperatures above -30°C. With a water content of 50 ppm by volume, even at lower temperatures, (since this is in the region where the second phase is solid chlorine hydrate) corrosion would not be expected to occur.

Corrosion does occur in condensing systems even with a very low water content in the incoming chlorine gas. Ketelaar and Kooi have postulated this results from the fact that the water content is significantly higher in the gas phase leaving a condenser than in the liquid phase thus the water content of the condensed chlorine becomes higher in each progressing series condenser.

Water Distribution In A Chlorine Condensing System

From solubility and vapor pressure data it becomes possible to calculate a water balance for a chlorine condensing system using Raoult's and Dalton's Laws assuming ideal behavior of the gas and liquid phase.

Raoult's Law for ideal solutions is expressed as follows:

$$(3) \bar{P}_O = P_O X_O \text{ where}$$

\bar{P}_O = Partial Pressure of the Component in the Vapor Phase

P_O = Vapor Pressure of the Pure Component at the System Temperature

X_O = Mole Fraction of the Component in the Liquid Phase.

For partially soluble components such as the water-chlorine system, Raoult's Law becomes

$$(4) \bar{P}_O = P_O \frac{X_O}{X_S} \text{ For } X_O < X_S$$

$$(5) \bar{P}_O = P_O \text{ For } X_O \geq X_S$$

Where

X_S = Mole Fraction Solubility of the Component in the Liquid Phase.

A graphic representation of Raoult's Law for partially soluble components is shown in Figure 1.

Dalton's Law for ideal gases is expressed as follows:

$$(6) \bar{P}_O = P_t Y_O \text{ where}$$

Y_O = Mole Fraction Component in Gas Phase

P_t = Total System Pressure

Combining equations (4) and (6) develops a relationship between mole fraction of the partially soluble component in the gas and that in the liquid.

$$(7) P_O \frac{X_O}{X_S} = P_t Y_O$$

$$(8) Y_O = \frac{P_O X_O}{P_t X_S} \text{ For } X_O < X_S$$

$$\text{and } (9) Y_O = \frac{P_O}{P_t} \text{ For } X_O \geq X_S$$

Since P_O , the vapor pressure of water, and X_S , the solubility of water, can be calculated at the system temperature from equations (2) and (1), respectively, equation (8) provides the relationship between the concentration of water in the gas and liquid phases leaving a chlorine condenser. This relationship holds only if the water content leaving in the liquid is less than the solubility.

If there is sufficient water present in the system to exceed the solubility, then equation (9) is used to calculate the concentration of water in the gas phase.

The actual water mass balance across a chlorine condenser is developed from the simultaneous solution of two equations:

Water Balance:

$$(10) G_i Y_i = L_o X_o + G_o Y_o$$

where G_i = Inlet Gas Flow Rate, Moles

Y_i = Inlet Water Concentration, Mole Fraction

L_o = Outlet Liquid Flow Rate, Moles

X_o = Outlet Water Concentration In Liquid, Mole Fraction

G_o = Outlet Gas Flow Rate, Moles

Y_o = Outlet Water Concentration in Gas, Mole Fraction

and

$$(11) \quad Y_o = P_o/P_t X_o/X_s$$

L_o and G_o are calculated using vapor pressure data for chlorine and the quantity of inerts present. Thus there become two unknown in the system, X_o and Y_o , and the simultaneous solution of equations (10) and (11) results in values for X_o and Y_o . If the solution to X_o is greater than X_s then equation (9) is used to calculate Y_o and substitution of Y_o in equation (10) yields X_o .

Application of Water Distribution Calculations In a Chlorine System

The appendix shows a detailed water balance calculation for an actual chlorine condensing system. The system was unique in that external refrigeration was not employed, taking advantage of 10°C maximum year-round available cooling water temperature for heat removal on the primary condenser, and the use of flashing liquid chlorine for heat removal on the secondary condenser.

The results of the water balance calculations are illustrated as Figure 2 with water concentrations presented in ppm by volume.

For an incoming gas at 50 ppm by volume, calculations show the water in liquid chlorine condensed to be 44 ppm and in the outlet gas to be 107 ppm. With a solubility of 523 ppm in liquid chlorine, a second (water rich) liquid phase would not exist and corrosion would not be expected. In actuality there was no corrosion in this primary condenser.

Water distribution calculations on the condensing side of the secondary condenser show the water in the liquid chlorine to be 210 ppm, exceeding the solubility of 50 ppm, hence a second (water rich) phase is formed. As long as the operating temperature remains below the freezing point of chlorine hydrate corrosion will not occur since

the second phase will be as solid chlorine hydrate provided the solid chlorine hydrate does not accumulate in the condenser to melt later into a corrosive phase. With a density of 1.23, chlorine hydrate will float on liquid chlorine and will leave the condenser with the chlorine provided there are no barriers to physically cause the accumulation of hydrate.

The water balance on the flashing side of the secondary condenser shows that chlorine hydrate would accumulate in the condenser. The liquid chlorine condensed in the secondary condenser, containing 210 ppm H_2O , was recycled through the shell side combined with liquid from the primary, containing 44 ppm, for a combined liquid containing 179 ppm. At the shell side operating temperature and pressure the chlorine gas leaving the flashing condenser could contain a maximum of 161 ppm water if saturated hence water was accumulating in the condenser. This resulted in severe corrosion on the flashing side of the condenser since the accumulated chlorine hydrate melted on system shutdown.

The solution to this problem proved to be simple. By using only the lower water content liquid chlorine condensed in the primary as the flashing coolant in the secondary, corrosion was totally eliminated. The results of water balance calculations for this case are shown in Figure III.

The liquid chlorine condensed in the secondary is piped directly to storage where it is combined with the bulk of the liquid produced in the primary. The liquid now used as the flashing coolant on the secondary contains 44 ppm, substantially less than the saturated condition (164 ppm) of the gas formed hence there is no accumulation of chlorine hydrate. In practice, the corrosion on this condenser was totally eliminated by the change in coolant source.

This example illustrates an actual use of vapor distribution calculations in solving an in-plant problem that proved successful. The problem encountered with a second (water rich) phase on the

condensing side of an exchanger is more complex.

Importance of Physical Configuration Of A Condenser

A second example of an actual condensing system illustrates the importance of condenser configuration. Figure IV shows the calculated water concentrations for the third condenser in a series chlorine condensing system.

For this condensing system the water content in the chlorine to the first condenser in series is ≈ 10 ppm by volume. A computer program was developed for water balance calculations for the system with Figure IV showing the results for the tertiary condenser.

For this particular system the secondary and tertiary condensers drain by gravity through a seal leg into a common receiver, the receiver being equalized with the tertiary gas discharge line. The calculated water balance shows the condenser liquid in the tertiary to contain 41 ppm compared with a solubility of 8.6 ppm. Thus a second water-rich phase of solid chlorine hydrate is formed.

With the configuration of the condenser the formed chlorine hydrate accumulated since its density is less than that of liquid chlorine. The actual performance experience of the condenser fits precisely that predicted by the model. The condenser operates for months without any problems, surviving even drying string upsets, until taken out of service for other reasons. Upon restart, the seal leg plugs with ferric chloride, necessitating physical cleanout of the condenser.

The solution to this problem is envisioned as the elimination of the seal leg by installing a level control directly on the condenser. Thus the liquid level can be periodically dropped in the condenser to the point where gas is bypassed thus enabling the second phase chlorine hydrate to be drained from the condenser and into the bulk

liquid chlorine. The water content of the combined liquid chlorine from all condensers is substantially less than the solubility hence the chlorine hydrate from this particular source will go back into solution. The changes in this system are currently being made.

Summary — Importance and Application of Water Balance Model

Observations of chlorine condensing systems indicate the overall model as developed for calculation of water distribution is correct. This leads to the conclusion that the presented corrosion mechanism, the water solubility and vapor pressure data as developed by Ketelaar and Kooi, and that the water-chlorine system approaches ideality are each consistently correct. Thus, a very powerful tool is available for both design and troubleshooting of chlorine condensing systems.

Each individual system must be looked at separately by use of the presented model. This would be done preferably in the design phase. In some cases the use of a drying step between series condenser may be warranted although this would be most difficult from a practical standpoint. In any event, for a condenser with a water-rich second phase in the temperature regime below the freezing point of chlorine hydrate, care must be taken with the physical configuration of the exchanger to prevent the accumulation of this solid phase.