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From Michael D. McGee

Date January 18, 1977

CONFIDENTIAL

Subject Trip Report on Meeting with Akzo Representative

Meetings with Mr. Anthony Beekwilder, Chief Process Engineer for Akzo, were held on November 30 and December 1 at the Lake Charles VCM Plant. The objectives of the meetings were to evaluate the Akzo HCl recovery technology, discuss the operating performance of their installation, and in general to utilize Mr. Beekwilder's technical assistance on chlorinated hydrocarbon incineration and HCl recovery. Mr. Beekwilder proved to be extremely knowledgeable in this field. Certainly his visit was well worthwhile considering the immediate application for several of his recommendations. Conoco personnel attending the meeting were:

J. H. McCulley - VCM Plant (part-time)
J. R. Holcomb - VCM Plant (part-time)
C. R. Parker - CED
M. D. McGee - PED

Akzo's incineration and HCl recovery unit is located in their VCM plant in Rotterdam, Netherlands. The capital cost of their incinerator and HCl recovery unit, excluding the tank farm and site preparation, was \$5.0-5.5 MM (1976 dollars). The unit has operated only 6 months since completion in 1972 because economics have favored disposal of chlorinated wastes at sea on ships equipped to incinerate the wastes. Akzo currently plans to begin operating the unit continuously in February, 1977. Feed to the unit is a mixture of tars produced in the VCM plant and waste chlorinated hydrocarbon liquids from outside sources.

Akzo employs the Nittetu submerged combustion technology for incineration. The HCl recovery process was developed by Akzo and represents a significant departure from other available recovery methods. A process flow diagram of the incineration and HCl recovery unit is attached. The most unique aspects of their process are 1) a partial condenser is used to remove most of HCl from the quenched incinerator flue gases and 2) the HCl stripper is operated at elevated pressure (37 psig) which reduces the azeotrope composition to 18 weight percent HCl (from 20.2% HCl at 1 atm.). Mr. Beekwilder did not think their process could be economically applied to our application because of the relatively low HCl/H₂O ratio in our combustion gases. A preliminary engineering study would be required to determine the

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utilities requirements and approximate capital costs of their system. Mr. Beekwilder estimated the approximate cost of the study at \$20,000 and about 6 weeks required for completion. Further consideration of this alternative does not appear warranted in light of Mr. Beekwilders' recommendation that the calcium chloride process is more suited for our installation. Additional information obtained during the meeting is listed in the following sections.

INCINERATION

1. Sodium salts in the feed liquids can cause rapid failure of the firebrick in the incinerator. Sodium carbonate forms low freezing point eutectic mixtures which vigorously attack the brick. Akzo established a maximum sodium concentration of 100 ppm on contracted liquids to prevent rapid deterioration of the brick lining. The tars from Akzo's VCM plant contain very little sodium (<< 100 ppm).
2. Water washing of the liquids to remove the salts was attempted in the laboratory. This approach was abandoned because a stable emulsion was formed by the wash.
3. Installation of sodium resistant brick in the incinerator was also rejected because of the extremely high cost. Also, sodium resistant brick are susceptible to deterioration from thermal shock.
4. Akzo expects 15,000-20,000 hours service life from the Molite fire brick installed in their incinerator. The following specifications were placed on the firebrick.

$\text{CaO} + \text{MgO} < 0.6 \text{ wt. } \%$
Alumina = 72-75 wt. %
Porosity < 16 %

5. Two types of sodium resistant brick were suggested; a fused Molite (very low porosity), Corhart-manufactured by Corning Glass.
6. Gradual heating and cooling of the incinerator during start-up and shut-down (< 180°F/hour) is recommended to avoid thermal shock damage.
7. The waste liquids pass through an 80 mesh (177 microns) basket-type filter before injection into the incinerator. Filter elements are changed once per day. Smaller mesh size elements were tested and plugged rapidly.

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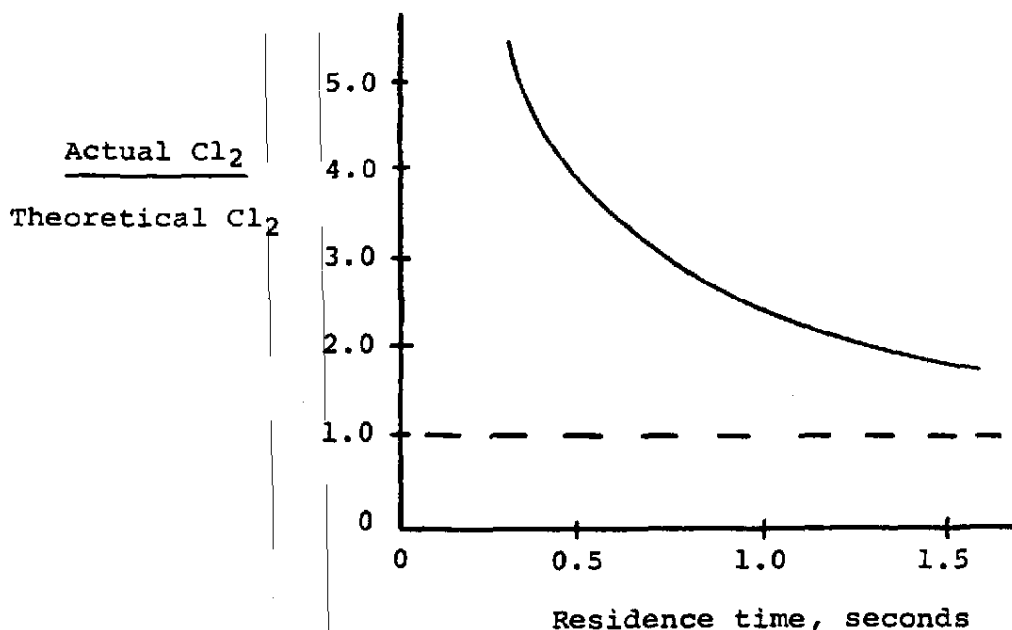
INCINERATION (Continued)

8. Burner guns are designed to produce liquid droplets below 200 microns in diameter. No problems with burner plugging have been encountered by Akzo. One of the Nittetu installations in Japan has experienced nozzle plugging which was attributed to inadequate liquids filtration.
9. Low-alloy, centrifugal waste liquid feed pumps were originally installed. These pumps have been replaced, due to excessive wear, with other centrifugal pumps with a single mechanical seal. Filtered liquid is used as a flush fluid. Mr. Beekwilder was not sure of the current material of construction, but indicated he would send this information. Reciprocating pumps were not selected because of pressure fluctuations and valve sticking during shut-down.
10. Air atomization of the waste liquids was strongly recommended over steam atomization. One of the Nittetu installations had experienced severe corrosion of the burner tip with steam atomization. The steam hydrolyzes the chlorinated liquids to form HCl which is highly corrosive at the elevated temperature of the burner. Polymerization of any isoprene present in the tars could also be caused by steam atomization. Water in the feed tars in concentrations above 200 ppm will also lead to burner corrosion due to hydrolysis.
11. An air atomization rate of 4.3 - 5.2 SCF per pound of waste was recommended.
12. Atomization air is supplied by an oil sealed, rotating vane compressor. The atomization air to liquids ratio is not controlled.
13. No automatic controls are utilized on the incinerator. Combustion air and steam rates are adjusted manually to maintain the desired excess oxygen (i.e. 15-20% excess air) and chlorine levels in the combustion chamber. During start-up the response of the incinerator was too complex to allow automatic control. Once the system has reached steady-state, Beekwilder thought automatic control would be feasible. The line between the ample point and the oxygen analyzer should be as short as possible.
14. The chlorine concentration leaving the incinerator has ranged from 1000-2000 ppm (normally between 1000-1500 ppm) which is approximately 4-5 times the equilibrium value predicted by the Deacon equation. Nittetu has developed some data which shows the ratio of actual chlorine

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INCINERATION (Continued)

production to the theoretically production decreases as the residence time in the incinerator increases. Since the data is proprietary Nittetu information we could not obtain a copy of the correlation. The basic shape of the curve is shown below:



15. Their incinerator design incorporated an elaborate inter-lock system for start-up and emergency shut-downs. The primary objectives of the system are to prevent explosive conditions in the firebox and to limit the rate of heating and cooling of the incinerator. Two flame scanners were utilized; one monitors the main flame and the other is on the pilot. The start-up is aborted by the inter-lock if the pilot does not ignite within four seconds. Initial start-up attempts were thwarted by this feature. A material, opaque to ultraviolet light, was originally installed by error in the flame monitor window. The inter-lock would not allow start-up because it appeared the pilot had not ignited. If the main flame is lost, the incinerator is purged with 5-7 volumes of air before re-ignition is attempted. The purge gas rate is 170 SCFM. Nitrogen is available as a standby purge gas because the purge air blowers are not equipped with emergency power. If the firebox temperature does not drop below 2300°F the main burner can be reignited without using the pilot burner.

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INCINERATION (Continued)

16. During shut down, purge air is circulated by the wind-box, inspection windows, manholes and any other metal surfaces to provide cooling from back radiation from the firebrick.
17. Cooling of the downcomer tube between the incineration chamber and the quench chamber is from splashing of acid onto the outside of the tube. Normally the Nittetu submerged combustion units can operate no lower than 60% of capacity because at low-gas rates the decreased turbulence does not provide complete wetting of the tube. Akzo has circumvented this limitation by diverting high rates of air into the downcomer.
18. The primary operating problem encountered with the Akzo incineration section is incomplete combustion of small carbon particles (80-120 micron diameter) present in the feed liquid. They are currently testing a 'gorator' pump which will grind the particles to less than 30-40 microns in diameter. There is adequate residence time in the firebox to completely combust of this diameter particle. Preliminary investigations show rapid wear of the internal gears may present problems with this approach. They are planning on testing burner nozzles with 90° and greater spray angles to produce a short flame front and possibly increase the combustion of soot. The original nozzles produced a 60° spray angle.
19. Feed liquids to the incinerator are blended to provide a homogeneous composition prior to pumping to incineration. A feed storage tank volume of 560,000 gallons provides approximately 27 days of residence time at the maximum feed rate (about 4 tons/hr.). The feed tank is equipped with jet mixers to keep the suspended solids in suspension. A large manhole to provide access for clean-out was suggested.
20. A radiation pyrometer, preferably with aluminum sheathing, is the only type of temperature sensor Beekwilder thought could be successful applied in this application.
21. Mr. Beekwilder was quite interested in our incinerator design and was anxious to find out the eventual performance of the unit (especially the waste heat boiler). Based on their evaluation that was made in 1970-71, he expressed some reservations on certain aspects of the system. The service life of the waste heat boiler with liquids firing was one of his primary reservations. The higher chlorine

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INCINERATION (Continued)

concentrations resulting from liquids combustion will substantially increase the corrosion rates of carbon steel in the boiler. He cited the high corrosion rates of carbon steel by chlorine above 300°F. At 450°F, ignition occurs when pure chlorine contacts carbon steel. Presumably the ignition is caused by ferric chloride formed by attack of chlorine on carbon steel. The presence of salts in the liquids and difficulty of maintaining a constant fire box temperatures were two additional aspects of liquids firing that he believed would have a deleterious effect on the life of a waste heat boiler. Chlorine formation in the Nittetu installations is suppressed by steam addition, rather than water addition specified in our design. He indicated there is a potential for spalling of the fire brick from contact with water near the injection port during normal operation. Also, if tight shut off is not maintained, leaks of water would cause spalling during shutdown.

Shell had a waste heat boiler in chlorinated hydrocarbon liquids incineration service that was started up in 1968. The performance of the boiler was so poor that it limited the steam factor of the plant. The unit has now been shut down. Shell specified during long term incineration negotiations with Akzo that they would not enter into an agreement if a waste heat boiler was utilized in the unit.

ANHYDROUS HCl RECOVERY

General

1. Akzo evaluated both the calcium chloride and the typical above the azeotrope distillation processes (as licensed by Hoescht-Uhde and Union Carbide). The above-the azeotrope distillation processes were rejected because both the capital and operating costs were higher than for the process developed by Akzo. The calcium chloride process normally utilized by Nittetu was rejected because at Akzo's high cost of boiler feed water quality water required for scrubbing and the high iron content of the feed liquids (1000 ppm). (Based on information presented by Nittetu, this iron concentration would require a complete purge of the calcium chloride solution every three weeks to avoid exceeding the solubility limit of iron chloride).
2. Akzo visited three of Nittetu's installations in Japan at VCM plants owned by Kashima VCM, Mitsubishi-Monsanto and Mitsubishi Chemicals. They were not allowed to walk through the Kashima unit, however, technical discussions were held with operations and engineering personnel at the plant site. At the time of their visits none of the units were producing

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ANHYDROUS HCl RECOVERY (Continued)

anhydrous HCl. Rather, the vapors from the water cooled condenser were absorber in a water scrubber to produce a 35 weight percent acid. The reason for producing a strong acid was the high price of 35% HCl and not any operating problems associated with anhydrous production. Equipment plugging was encountered only at the Mitsubishi-Monsanto installation, which was the only plant which did not use a boiler feed water quality (low TDS) scrubbing water. The river water used for scrubbing the HCl contained a high sulfate ion concentration. Calcium sulfate precipitated on the packing in the stripper and formed a scale on the reboiler tubes. Inorganic impurities in the feed acid do not interfere with the ability of calcium chloride to break the azeotrope. Only when the concentration exceeds the solubility do inorganics create any operating problems. Nittetu originally installed polypropylene telleretes packing in the caustic scrubber which failed due to embrittlement from hypochlorite attack. The packing was replaced with PVC telleretes which also failed from embrittlement. They are now using trayed columns with titanium internals. The only other operating problem the Japanese companies have experienced with the recovery section is leakage of HCl past the single mechanical seals on centrifugal, acid pumps.

3. The only installation of the Union Carbide process that is purported to have produced anhydrous HCl is B. F. Goodrich's unit at Calvert City, Kentucky. According to Beekwilder the unit was never able to manufacture anhydrous HCl.

Materials of Construction

4. All of the vessels in the Akzo recovery unit are constructed of rubber-lined steel. The HCl stripping tower is also lined with two layers of brick-acid resistant brick on the inside with carbon brick next to the rubber-lined walls. No corrosion problems have been encountered in any of the vessels.
5. Low quality rubber-lined pipe was installed through out the system except for carbon steel lines on the anhydrous HCl service. All of the original lined pipe had to be replaced because of holes present in the lining. A high quality rubber lined pipe was used for replacement.
6. For hot acid service, he recommended teflon lined pipe for our system. For cold acid service (< 160°F) Kynar-lined pipe was recommended for diameters less than 6 inches.

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ANHYDROUS HCl RECOVERY (Continued)

7. Expansion joints between all major pieces of equipment in hot acid service was strongly recommended.

HCl Absorber

8. The adiabatic absorber contains three packed sections, each with 10 feet of 2 inch polypropylene pall rings. The minimum liquid loading is approximately 4 gpm per square feet. Warm scrubbing water (149°F) is feed to the top section of the absorber to avoid fog formation which results from cold water addition. Liquid leakage through the trap-out trays is the only operating difficulty experienced with the absorber.
9. A polypropylene or Haveq, sieve tray absorber would be specified in their next design rather than the packed absorber. The primary advantage with the seive tray is they can operate at lower liquid to gas ratios which eliminates the necessity for recirculation of acid. Approximately 10 actual trays would be required in the absorber. Stacked, removable trays were recommended. Cemented Haveq trays have caused cracks at the tower walls due to shrinkage of the trays as they cool.
10. Less than 1 percent at the total HCl formed by incineration remains in the exhaust gases from the absorber.
11. The acid leaving the bottom of the absorber is at its boiling point. Forty minutes of liquid residence time is provided in the bottom of the absorber.

Pumps, Piping and Instrumentation

12. Two automatic acid strength monitors were installed in the recovery system; neither of which are not being used. A Quick-fit analyzer which monitored condenser outlet acid concentration by boiling point determination was destroyed during start-up and has not been replaced. The acid strength in the top section of the absorber is checked by specific gravity analysis on hand drawn samples. The continuous analyzer using conductivity measurement which was installed on this stream is not used because it was not accurate. Plant personnel did not work on the instrument to determine if the accuracy could be improved. Although Beekwilder thought the analyzer could be adjusted to function properly, he did not believe the high amount of maintenance needed was justified since the concentration varied little after start-up.

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ANHYDROUS HCl RECOVERY (Continued)

13. All of the acid transfer pumps are solid epoxy construction. Each of the acid pumps are spared. For hot acid service ($> 165^{\circ}\text{F}$). Either impervious graphite or stoneware construction was recommended. The Nittetu installations have had good performance from the stoneware pumps except when water hammer is encountered the impeller is rapidly destroyed. Double mechanical seals with a water purge is recommended.
14. Saunders membrane (pinch) control valves were recommended for acid service with a teflon or glass lined body and teflon membrane. Akzo has experienced good performance with teflon lined ball valves in HCl service.
15. Glass-lined thermowells with a tantalum tip were specified by Akzo and have performed satisfactorily.

Hastelloy C relieve valves and rupture discs were specified in their unit. Rupture discs are installed on both sides of the relief valve since they relieve to the HCl absorber.

Caustic Scrubber

16. A spray-type caustic scrubber was specified because of the problems Nittetu experienced with packed towers. The caustic consumption rate is 0.1 pounds of NaOH per pound of HCl produced. Approximately 2.5 times the stoichiometric caustic required for HCl and Cl_2 neutralization is fed to the scrubber. The excess caustic is consumed by carbon dioxide absorbed from the flue gases. Beekwilder cautioned against attempting to partially spend a strong caustic solution in a scrubber. Their experience indicates that any excess caustic added will be spent by the resulting increased carbon dioxide absorption.
17. The vent gases contain less than 10 ppm chlorine.
18. Spray nozzles are constructed of titanium.
19. Rubber lining of the scrubbing tower was specified to provide corrosion protection during periods of upset in the HCl absorber. During normal operation carbon steel would be adequate for the caustic service. However, rapid corrosion rates will result if large amounts of acid are carried over from the absorber.
20. Sulfite, thiosulfate and urea have been used to reduce the hypochlorites formed by scrubbing chlorine with caustic. At current prices in Europe, thiosulfate is the least expensive reducing agent.

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ANHYDROUS HCl RECOVERY (Continued)

21. Beekwilder thought porcelin Intalox Saddes was the best packing choice for the scrubber. At temperatures above 150°F and pH above 10, silica will dissolve out of the packing.
22. Both the stripping column preheater and reboiler are impervious graphite, cylindrical exchangers. The preheater shell is teflon-lined steel; the reboiler has a carbon steel shell. The preheater has not performed satisfactorily because of by-pass at the baffles. A plate-type, impervious graphite preheater would be specified in their next design. Great care must be taken in fitting the cylindrical blocks together to avoid leaks between the shell and tube side fluids. An impervious graphite, shell and tube reboiler is now preferred because of the lower cost of this exchanger type. The maximum shell side pressure is 175 psig from Holland manufactures which contrasts to the 75 psig maximum available in the U.S.
23. Acid cleaning of the graphite exchangers is recommended, rather than mechanical cleaning which may damage the exchangers.
24. The overhead condensers and the product interchanger are impervious graphite shell and tube exchangers.
25. The product interchanger is designed to heat the HCl to 40°F above its dew point to avoid corrosion in the compressor.
26. A carbon steel, air-cooled exchanger equipped for air recirculation is used for intercooling the HCl during compression. Air cooling was selected to avoid cooling of the HCl below its dew point in the winter.
27. The overall heat transfer coefficient in the reboiler is 200-250 BTU/hr ft²°F. At the outlet end of the acid cooler the overall coefficient is 20-25 BTU/hr ft²°F.
28. The HCl chiller and refrigeration unit should be designed with enough spare capacity to accomodate upsets in the HCl condenser. Excess capacity also allows anhydrous HCl production during the initial stages of start-up.
29. Ethylene glycol is used as an intermediate heat transfer fluid in the HCl chiller. Ammonia is the working fluid in the refrigeration unit.
30. None of the exchangers are spared. Replacement tubes and cylindrical exchanger sections are kept on hand.

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ANHYDROUS HCl RECOVERY (Continued)

HCl Stripper

31. A total of twenty feet of 2 inch, impervious graphite raschig rings are included in the tower. Raschig rings, which are made from the excess length cut from exchanger tubes, were chosen because of their low cost.
32. Above 275°F ceramic packing will be dissolved by dilute hydrochloric acid.
33. Two hours of feed storage capacity is provide in the bottom of the HCl condenser.
34. No problems have been encountered with using anhydrous HCl in the oxychlorination unit.
35. The maximum allowable temperature of anhydrous HCl in contact with carbon steel is 212°F. Above this temperature ferric chloride has an appreciable vapor pressure. Since the ferric chloride film is continuously evaporating, a high corrosion rate results.
36. During start-up the column is operated at total reflux. Nitrogen is circulated through the compressor with a small purge to the absorber. The line to the oxychlorination unit is purged with nitrogen and blocked in until the overhead reaches temperature and pressure. Once the outlet gas temperature from the absorber reaches 5°F the product HCl is dry enough for compression. Approximately 12-20 hours is required for the system to reach equilibrium during start-up.
37. A two stage centrifugal compressor manufactured by Sundyne is used by Akzo. The internals are 316 stainless steel. A spare compressor is kept in the shop. Approximately 6 hours is required to install the spare. Reciprocating compressors are considerably more expensive than the centrifugal type for this service.
38. The product HCl line is steam traced to avoid condensation during the winter.
39. The product HCl contains less than 100 ppm water.
40. Approximately 18-24 months would be required for mechanical design and construction of their unit. The process design would require at least 3 months.

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If there are any questions concerning the information presented in this report please contact me.

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