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Napthalene Removal

Dated: 1976

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INTEROFFICE CORRESPONDENCE

Date: July 7, 1976

To: Mr. F.K. Armour

From: N.H. Keyser

Subject: Naphthalene Removal at the Chicago Coke Plant

Reference: D2-005-010

V. Beaucaire
J. Duncan
G. Durkin
R. Nagan
R. Rankin
J. Seaman
R. Winters

Gary Durkin has prepared an informative review on certain practices used to remove naphthalene from coke oven gas. Of interest is the fact that coal gas lines have been flushed out with fuel oil. The oil is then recovered and burned. Gary believes that this method could be adapted as a temporary and immediate means to prevent build up in the coke oven lines until more permanent corrective measures are taken.

Other information presented in the review leads to the conclusion that when the primary and secondary coolers are working in topnotch condition we might expect our coke oven gas to contain naphthalene in a range of 15 grains per 100 cu.ft. in winter to 30 grains per 100 cu.ft. in summer without help from some other means of naphthalene removal. I am told that at one time we sold gas to Youngstown Sheet and Tube with a specification of 5 grains in winter and 15 grains in summer. Therefore, at one time there was a factor that was operating to polish off the naphthalene removal.

The implication is that the condition and the operation of the light oil plant is important to the final clean up of the naphthalene content of gas. At this writing we have no positive information on how much naphthalene was removed or is removed from the gas by the light oil. A typical published analysis of light oil shows a naphthalene content of one percent. A material balance indicates that two percent naphthalene in the light oil coupled with good final cooling would have produced specification gas for Youngstown Sheet & Tube. This seems to me to have been a distinct possibility because naphthalene is very soluble in light oil.

The point of this memo is to urge that there be no delay in putting the light oil plant into topnotch condition. It is a necessary step to avoid continued build up of naphthalene in the gas main.

IS-5018-1-B

There is attached a naphthalene balance which was calculated on the assumption of some typical naphthalene contents of the various products of a coke plant. This balance puts the various points of naphthalene removal in some sort of perspective. It suggests that a correlary to the above implication is that light oil will only add the finishing touches and cannot substitute for poor cooling of the gas.

N H Keyser

meo

NAPHTHALENE BALANCE IN A COKE PLANT
(Based on typical analyses of materials)

Naphthalene, lb/day

17,000 gallons of tar per day

Tar out in hydraulic collector mains,	7%	6,728
Tar out in primary cooler,	26%	7,495
Tar out in electrostatic precipitator	28%	3,457
		17,680

34 million cubic feet of gas per day, 85 gr./100 cu.ft.
into final cooler   4,128

Total naphthalene produced (tar and gas)   21,808

Naphthalene Removal from Gas, 34 million cubic feet per day

Gas into final cooler, 85 gr./100 cu.ft.	4,128
Gas from final cooler, 20 gr./100 cu.ft.	970
Naphthalene removed by final cooler	3,158

Naphthalene entering light oil system, 20 gr./100 cu.ft.	970
Naphthalene remaining in gas @ 5 gr./100 cu.ft.	243
Naphthalene to light oil	727

At 4,800 gallons of light oil per day, specific
gravity 0.886:   35,425 lb. light oil per day

$$\frac{727}{35425 + 727} \times 100 = 2.0\% \text{ naphthalene in light oil}$$

Date: June 1, 1976

To: Mr. N. H. Keyser

From: G. M. Durkin

Subject: Progress Report of Naphthalene Removal at
           Chicago Plant

Reference: D2-002-010

In recent months, gas samples testing for naphthalene content of
the coke oven gas have shown that the majority of naphthalene present
in the gas entering the final gas cooler is removed. In addition, samples
have shown that the light oil recovery system may also have the ability
to remove naphthalene. Before discussing the results of our naphthalene
sampling a short discussion on naphthalene removal in general will be
presented.

General Principle

First, the amount of naphthalene in the gas is dependent on the type
of coal used in the ovens and the ovens operating temperature. The
higher the volatile content of the coal, the greater the byproduct
yield at any given coking temperature. This is due to the fact that
high volatile coal has a higher hydrogen content, so that when destruc-
tively distilled in the oven, low boiling point hydrocarbons are
produced. The effect of carbonizing temperature has much the same
relationship. Table 1 is a copy of a table presented in The Chemistry
of Coal Utilization. The table compares Pratt Coal carbonized at various
temperatures. Summarized, the table shows that coke yield will remain
relatively the same due to the fixed carbon content of the coal.

The gas and light oil yield will increase and the tar yield will decrease
as temperature increases. Note also that the naphthalene content of the
gas increases as the temperature of carbonization increases. Therefore,
a large amount of naphthalene is produced when a combination of high
volatile content coals and high oven temperatures is used.

The basic problem then is how to remove naphthalene from the gas. If
the naphthalene is not removed, condensation of solid phase naphthalene
will result in the gas distribution system. Several approaches to naph-
thalene removal are possible. Chapter 29 of The Chemistry of Coal
Utilization summarizes the methods used to remove naphthalene from gas
plant gas. The section of this chapter relative to naphthalene removal
is presented.

Briefly, there are four basic methods for naphthalene removal from coke
oven gas; 1) condensation by cooling, 2) absorption by solvents in a
washer or scrubber 3) application of solvents, either liquid or vapor
forms to the gas-distribution mains and 4) absorption by solids. These
four systems can be discussed briefly.

TABLE 1.

TABLE VII

YIELDS OF PRIMARY PRODUCTS AND THEIR CONSTITUENTS IN PERCENT BY WEIGHT OF COAL RESULTING FROM THE CARBONIZATION OF PRATT COAL AT TEMPERATURES OF 500 TO 1,100° C [2]

Carbonization Temperature		500°	600°	700°	800°	900°	1,000°	1,100°
Gas	Carbon dioxide	0.65	0.96	1.36	0.75	0.97	1.18	0.88
	Illuminants	0.47	0.76	1.74	2.02	2.41	2.16	2.41
	Oxygen	0.14	0.14	0.17	0.15	0.25	0.20	0.29
	Hydrogen	0.12	0.34	0.79	1.19	1.41	1.83	2.29
	Carbon monoxide	0.19	0.55	1.14	1.60	2.13	2.99	4.81
	Methane	2.52	4.35	5.38	5.87	6.31	6.99	6.15
	Ethane	1.34	1.32	1.26	0.97	0.31	0.14	0.06
	Nitrogen	0.27	0.38	0.56	0.45	0.61	0.61	0.91
	Total	5.70	8.80	12.40	13.00	14.40	16.10	17.80
Light oil	Olefins	0.05	0.08	0.09	0.07	0.05	0.04	0.03
	Naphthalene	Trace	0.0005	0.00	0.001	0.0008	0.0009	0.002
	Benzene	0.02	0.03	0.10	0.26	0.51	0.63	0.56
	Toluene	0.02	0.04	0.10	0.19	0.16	0.14	0.10
	Paraffins	0.18	0.17	0.07	0.06	0.02	0.02	0.01
	Solvent naphtha	0.11	0.14	0.15	0.11	0.09	0.07	0.05
	Total	0.38	0.46	0.51	0.69	0.83	0.90	0.75
Liquor and ammonia	Ammonia	0.01	0.06	0.20	0.20	0.17	0.16	0.11
	Liquor	4.80	5.70	6.00	5.90	5.70	4.70	2.90
	Total	4.81	5.76	6.20	6.10	5.87	4.86	3.01
Tar	Acids	1.30	1.36	1.11	0.62	0.34	0.18	0.08
	Bases	0.11	0.11	0.12	0.11	0.105	0.06	0.04
	Olefins	0.32	0.40	0.28	0.26	0.25	0.18	0.17
	Aromatics	1.53	1.71	1.77	1.76	1.71	1.26	0.82
	Paraffins and naphthenes	1.43	1.22	0.45	0.15	0.105	0.06	0.03
	Residue above 350° C	2.91	3.60	3.57	3.90	3.59	3.26	2.46
	Total	7.60	8.40	7.30	6.80	6.10	5.00	3.60
Coke	Ash	9.20	8.20	8.60	9.00	9.20	9.50	9.30
	Hydrogen	2.50	1.80	1.20	0.80	0.50	0.30	0.20
	Carbon	64.90	63.00	61.70	61.40	61.60	62.10	63.30
	Nitrogen	1.50	1.30	1.10	1.00	1.10	1.00	0.60
	Oxygen	2.60	1.80	1.10	0.70	0.10	0.00	0.20
	Sulfur	0.60	0.50	0.70	0.50	0.60	0.50	0.50
	Total	81.30	76.60	74.40	73.40	73.10	73.40	74.10

Condensation by Cooling: The solubility of naphthalene in coke oven gas is a temperature dependent function. Figure 1 shows the variation of naphthalene in the gas versus gas temperature. Note the sharp increase in solubility between 30°C and 50°C. The principle of removal by cooling relies on this insolubility at low temperature to remove the naphthalene. In practice, the gas is cooled usually by water to a temperature less than the temperature that is expected in the gas system. Thereby not allowing the gas to reach the naphthalene dew point within the main. In some plants, refrigeration is used to cool the gas to 0°C to remove naphthalene and light oil. Without refrigeration, the gas cannot be cooled much below atmospheric temperature if river water or cooling towers are used. If the gas cannot be cooled to a temperature below that expected in the gas mains, then reheating of the gas before it enters the distribution system should be considered.

Absorption by solvent in a washer or scrubber: This method was commonly used in America and England before World War II. As with light oil recovery a solvent oil is used to remove the naphthalene from the gas. However, due to the high solubility of naphthalene in most oils, a small amount of scrubbing oil is needed.   Normally, the gas was washed by an oil in a filled tower or brush scrubber. These systems then allowed large volumes of gas to contact small volumes of oil. The petroleum or tar oil used was seldom regenerated but was usually burned or returned to the part of the gas making operation.

Application of solvents, either liquid or vapor form to gas-distribution mains: This practice was generally used by plants that for any number of reasons developed a naphthalene removal problem. Basically, the idea was to wash the gas in the mains rather than in a scrubber. To do so, a spray system was installed in the main and a solvent oil sprayed in.

The oil consumption would be higher than in a scrubber but the lack of new equipment would lower the cost. The spent solvent oil would simply be removed in the drip legs. Again, the oil would be burned or used in gas making rather than regenerated.

Absorption by solids: This type of operation is basically a variation of the dry oxide box principle. The gas was sent through a filled chamber, the naphthalene would then condense on the fill and the fill either removed or regenerated. Such materials as charcoal, shredded tires and silica gel were used as fill. Although this process was effective for the most part, it was not very popular.

Present System

The present configuration of the by-products operation uses the first principle for naphthalene removal. That is, direct water to gas contact to cool the gas below the dew point expected in the gas mains. The operation is performed by the final cooler system which was constructed by Wilputte in 1953. The system was constructed by converting the first

FIGURE 1. SATURATION OF NAPHTHALENE IN COKE OVEN GAS

NAPHTHALENE, gr-/100 cu.ft
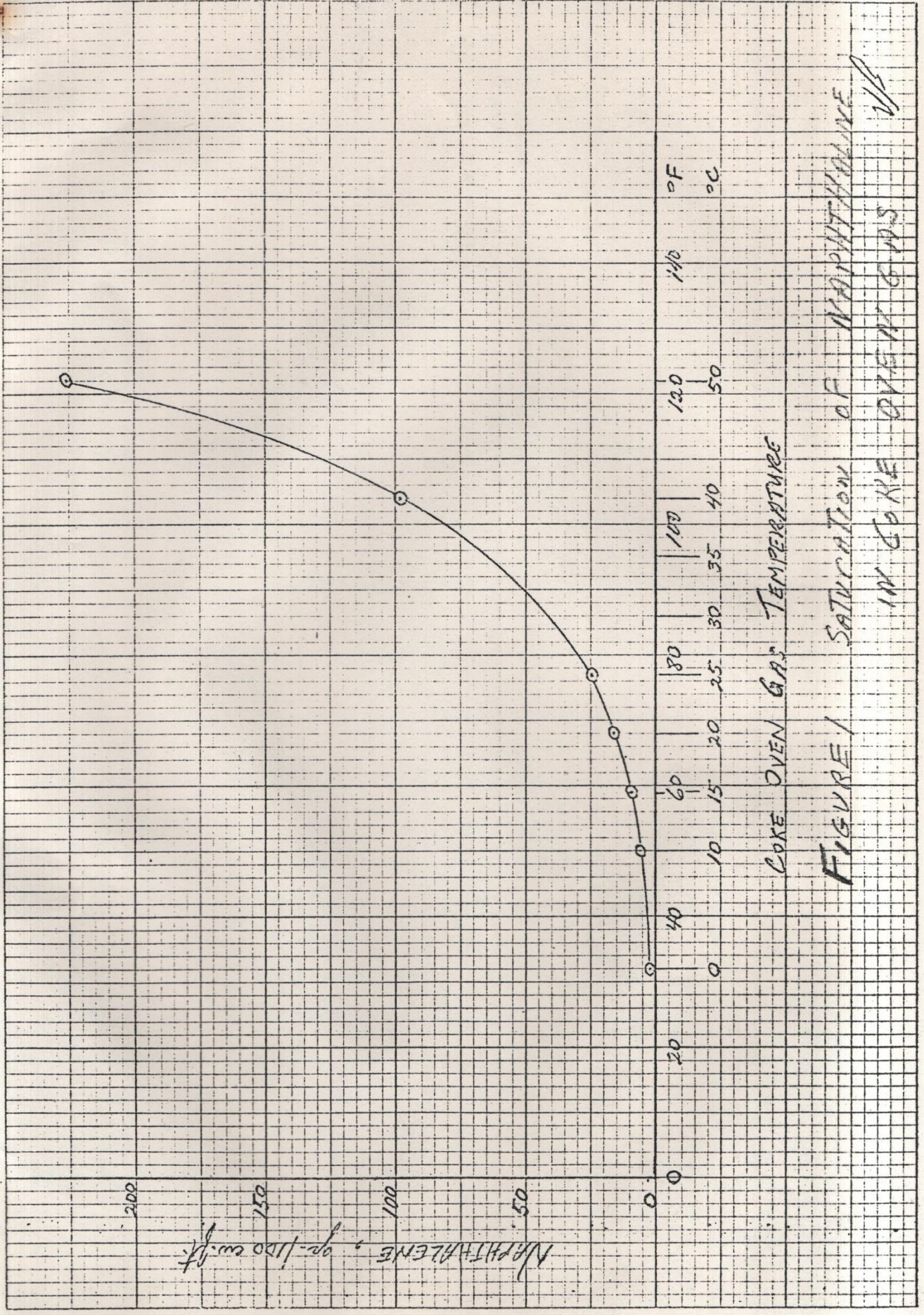
COKE OVEN GAS TEMPERATURE

L.B.A. into a water type final cooler. This tower is 11 feet in diameter and 100 feet high. It is filled with 78 grids and has 16 water sprays located in the top. The water used to cool the gas also flushes condensed naphthalene from the gas. The naphthalene is then floatation separated and the water weired to the hot bay. From the hot bay the water is pumped to the Marley Tower for cooling before being pumped back to the final cooler. The system is a simple recycle with naphthalene separated only by floatation. This system is simple and does not have the refinements that appeared in early gas plants. Many early gas plants used some type of refrigeration to cool the water used in the final cooler so that a lower gas temperature would be insured. Other plants mixed the gas cooling water with a naphthalene solvent oil to remove the naphthalene from the water before it was returned to the gas cooler. In the present operation, the use of a wet deck air cooler, the Marley Tower, makes the gas cooling dependent on atmospheric conditions. Hot, damp days will provide poor gas cooling. Also, the simple floatation separation of naphthalene leads to respray of naphthalene into the gas cooler due to poor separation. The possibility of using floatation chemical agents in the final cooler will be examined.

In defense of the system, the tower itself is capable of very close temperature approaches. That is, the gas will be cooled to the temperature of the input water within one or two degrees centigrade. Also, at the current low water flow rates that have developed due to poor pumping, the tower still reaches the one or two degree approach. The problem being that at low water flow rates the tower is not properly scrubbed and frequent steam cleaning is needed. In addition, low water flow causes slow cooling of the gas which may effect the size of naphthalene particles.

However, the problems of naphthalene in the final product gas remains and methods needed to eliminate the problem must be found. It should be noted that since 1953 until about three years ago the naphthalene content of the gas was within limits. What forces then have resulted in the high naphthalene level.

From the standpoint of the final cooler system, there has been a general deterioration in the water pump and in the Marley cooler. This has resulted in low water flow rates and high water temperatures. These two areas must be high on the list of problem causers. Currently, the Engineering and Research Departments are working in this area. The final cooler pumps are worn and obsolete, therefore larger capacity new pumps have been sized. The piping system is capable of handling the higher water flow rates. Therefore, only modifications to the pump's inlets will be needed in the pipe system. The new pumps will require larger horsepower motors and therefore modifications to the starters and switch gear will be needed. The replacement pumps will cost roughly $12,000 for pumps alone, not including the cost of switch gear and pipe modifications. In addition, drawings have been prepared, parts ordered to repair the existing Marley Tower water distribution system. The total

for temporary repair parts is roughly $500. Also, a proposal has been presented by Marley for a replacement wooden cooling tower. This tower would handle the 1000 gpm flow rate and be able to cool 3,000,000 BTU/hr. The tower would cost $26,959 delivered and assembled. A copy of the proposal is attached. The new tower would fit over the existing basin so that installation costs would be low. When this work is completed, the final cooler system should have enough water flow and water temperature to return to its' earlier satisfactory operation.

Two things should be noted relative to the final cooler. The system was designed and built not for the production of the present oven system but rather for the production of the Semet Solvay 6, 7, 8 series of ovens. Therefore, the system may not be properly sized for the present operation. For this reason, the repairs to the pumps and Marley Tower will increase pump and water cooling capacity. Also, since the coal blend now used is higher in volatile content and oven temperatures are higher, the amount of naphthalene to be removed by the system may be greater than originally designed. Therefore, the additional capacity being designed into the system should overcome any deficiency.

Finally, as far as gas cooling to remove naphthalene is concerned, there is a need for additional equipment that could aid in cooling. The use of artificial refrigeration of the water to remove the dependence on weather conditions should be considered.

The simplest type of equipment for water chilling is a vacuum flash evaporator. Such a device could be used to cool part or all of the water sent to the final cooler itself. The device is basically a barometric steam condenser that uses the vacuum produced by steam condensation to evaporate the process water. Such a system is shown in Figure 1. This type of unit is basically a barometric condenser which is used to condense steam, thereby creating a vacuum in a chill tank. The vacuum is increased by supping the steam through Venturi booster sections. The water to be cooled is pumped into the chill tank where evaporation occurs and cooling results. Such a unit would require steam for power and water for steam condensation. The system could be used to cool all or part of the heat load with the Marley cooler removing the remainder of the load. The Marley cooler would send to the atmosphere the heat drawn from the gas by the final cooler plus the heat of the steam used to drive the chiller. The chiller would handle part of the final cooler flow so that a low gas temperature is insured under all conditions. The use of a vacuum water chiller would have the advantage of good gas cooling, it would not be an alternative to repair or replacement of the Marley cooler and pump but must be used together with these repairs.

In conclusion, the present gas cooling equipment is not functioning properly. Repairs are needed to the pumps and the Marley cooling tower. A system of water chilling would be adaptable to the system. However, any gas cooling system, unless it is cooling to less than $0^{\circ}C$ will not remove all traces of naphthalene. For this reason, other methods of removal were developed.

principle

Figure 2.   Flash Evaporator

Water literally chills itself in a Croll-Reynolds CHILL-VACTOR. The principles of the process are as simple as the boiling of a liquid. It is well known that water boils at lower temperatures at high altitudes than at sea level. For instance, if water is heated to a temperature of 175 degrees F. at sea level and carried at constant temperature and pressure to the top of Pike's Peak, the water will boil instantly and continue boiling until its vapor pressure is equal to the pressure of the surrounding rarefied atmosphere. The heat required for boiling comes from the water itself primarily, along with a small amount from the container. Some of the sensible heat of the water is used to supply the latent heat of vaporization for boiling. This loss of heat causes the temperature of the water to drop.

The rarefied atmosphere at high elevations corresponds to a partial vacuum created artificially at sea level. If the pressure is lowered sufficiently, any temperature down to the freezing point can be produced. It is even possible to sub-cool ice from the solid to the vapor phase by means of direct evaporation. This process is used commercially and is called "freeze drying."

Vacuum refrigeration finds its widest application in chilling water for air conditioning, food processing and industrial uses. Water is chilled usually to temperatures in the range of 35 to 60 degrees F., although in many processes liquids are cooled to much lower temperatures. The drawing shows how the Croll-Reynolds CHILL-VACTOR uses this principle in a typical water-chilling unit. Water to be chilled enters the chill tank and flows over a weir or through perforations in the weir plate. When the water comes in contact with the vacuum in the chill tank, it boils instantly. The energy released as the water vapor expands causes turbulence that breaks up the water into small drops and lowers its temperature. The chilled water is then removed by a barometric leg or pump. It is circulated through heat exchangers, air-conditioning equipment or other process equipment and returned to the chill tank. If part or all of the water is required for process use, fresh water is fed continuously into the chill tank. In circulating systems, make-up water amounting to approximately 1% for each 10 degree F. of cooling is added.

Steam at high velocity in the EVACTOR booster entrains water vapor from the chill tank, producing a partial vacuum in the chill tank and removing the water vapor. The combined stream of motivating steam and water vapor leaving the booster is condensed in the condenser by water from a cooling tower or industrial water supply. The drawing shows a barometric condenser, the most frequently used type in vacuum refrigeration because it is the most economical. This type of condenser requires a discharge or barometric leg about 36 feet long to remove the water by gravity and overcome friction. A pump may be used where sufficient height is not available. When the condensate must be recovered, a surface condenser is used, raising the cost of the installation. A CHILL-VACTOR with a surface condenser not only recovers the motivating steam as condensate but provides an additional amount of condensate from the water vapor handled and requires no barometric leg.
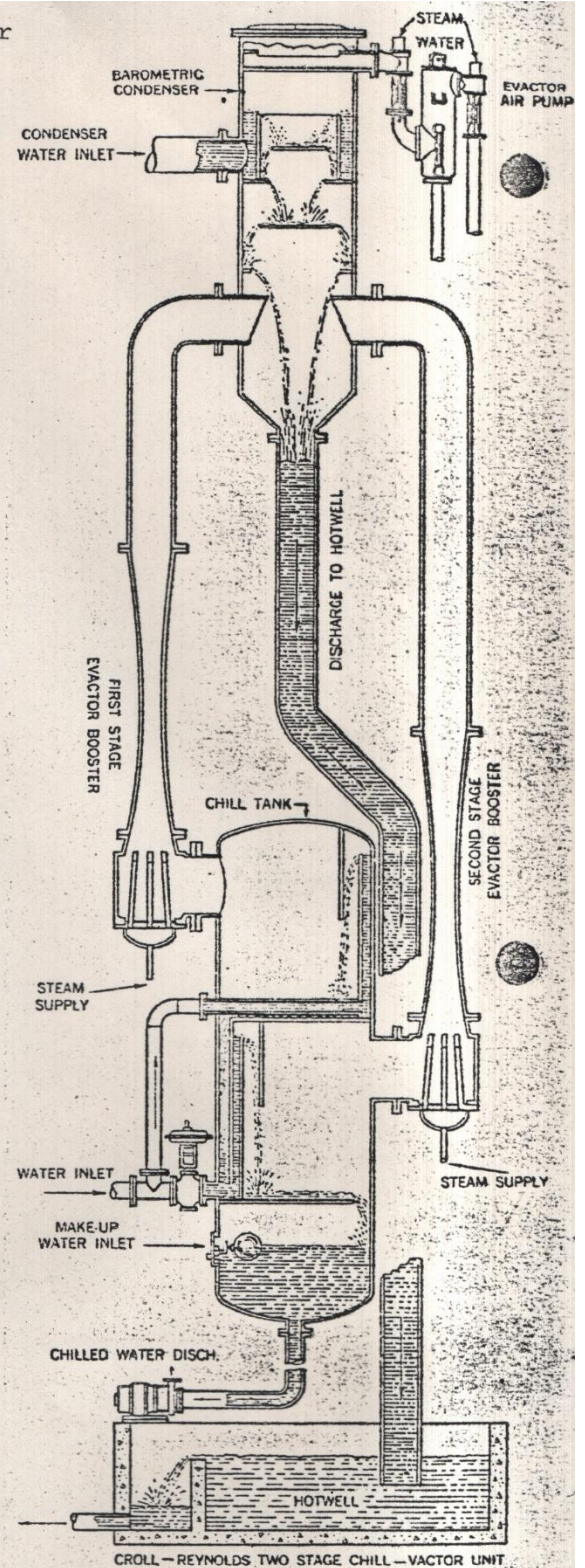
CROLL-REYNOLDS TWO STAGE CHILL-VACTOR UNIT

Absorption by solvents in a washer or scrubber: These systems were
popular in the early days of gas plants due to the high efficiency of
this process. The gas and oil samples taken thusfar have shown that
naphthalene is removed by the absorption oil in the benzol scrubbers but
that the naphthalene is not removed from the oil in the debenzolizing
still. A conclusion can be drawn from the results so far. The use of
solvent extraction for naphthalene removal is possible within the present
benzol absorption system, LBA1, LBA2). The major problem is to find a
method by which the naphthalene rich wash oil could be regenerated.
The normal practice was to burn the oil after it had been saturated with
naphthalene. This could be done by sending spent oil to the blast furnace.
One method of wash oil regeneration will be investigated that is to use
the same type of flash evaporator described earlier to flash evaporate water
from hot absorption oil as it leaves the debenzolizing still. The
evaporation of water would cool the absorption oil and the vacuum within
the chiller may evaporate or sublime the naphthalene from the wash oil.
This system would then cool and regenerate the wash oil. This possibility
will be investigated and reported at a later date.

Also, the sampling for naphthalene will be extended to determine the
benzol and other light oil fractions present in the gas as it moves
through the LBA1 and LBA2. This information will establish in which
LBA the light oil is removed. It may be possible to operate one LBA for
light oil recovery and the other LBA for napthalene removal. No definite
conclusions can be made at this time but the investigation into this area
will continue.

Application of solvents either liquid or vapor form to the gas-distribution
mains: As described earlier, the concept was to use the gas mains as
the scrubbers by injecting solvents into the mains and allowing the drip
legs to remove the spent solvent. To apply the concept of washing within
the mains, the solvent should be sprayed into the main on the coke plant
side so that the gas travels through the main deficient in naphthalene.
Such an injection point is available on the coke plant side. Figure 2
shows a rough map of the gas main as it leaves the coke plant. The main
runs north and south after leaving the booster station to a point roughly
in the center of the oven coal bin. From that point, the main runs east
and up at a slight angle to the point where it reaches 4 belt and turns
northeast. It is in the section running uphill and east that solvent could
be injected through two existing taps. The spent oil would then condense
and run to the drips on the coke plant side. Oil remaining in the gas would
condense farther down the main and may aid in removal of the existing
deposit. Such a system could be easily installed and could use such solvent
oils as fuel oil, kerosene and light oil. The oil collected at the drips
could then be burned in the furnaces.

A simple mass balance would provide an indication of the solvent oil
consumption. First, with poor gas cooling, a naphthalene content of
50 grains/100 cu. ft. could be expected. The gas flow is roughly
18,000,000 cu. ft./day or 750,000 cu. ft./hr. Calculating the load on
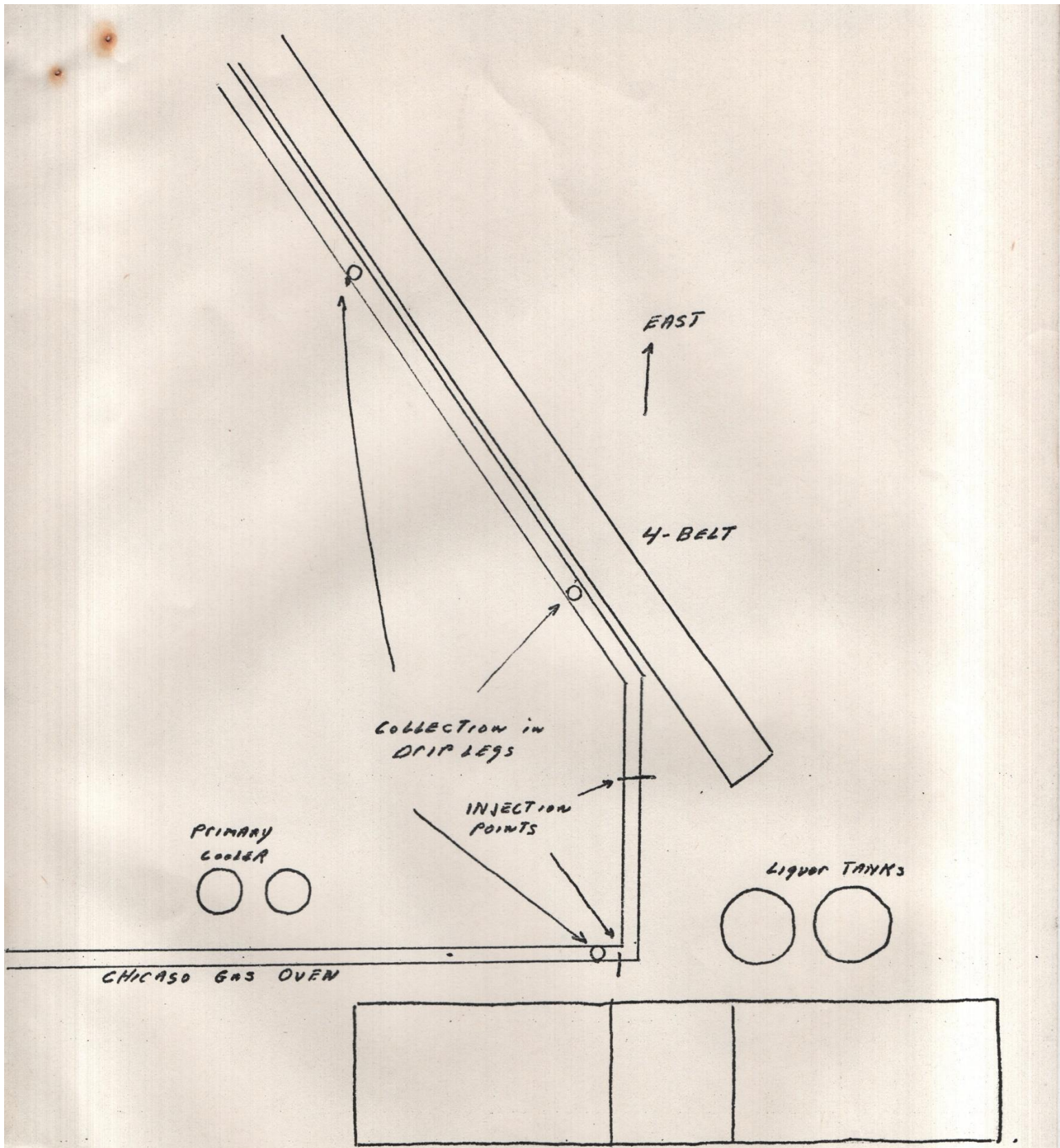an hourly base:

EAST

4-BELT

COLLECTION IN
DRIP LEGS

INJECTION
POINTS

PRIMARY
COOLER

LIQUOR TANKS

CHICAGO GAS OVEN

FIGURE 3 · SOLVENT INJECTION POINTS

$$750,000 \ \frac{cu.ft.}{hr.} \ x \ \frac{50 \ grains}{100 \ cu. \ ft.} \ = \ 375,000 \ grains/hr.$$

$$375,000 \ grains/hr. \ x \ .000142 = 53 \ lb./hr.$$

Therefore, the amount of naphthalene to be removed is 53 lb./hr. If
the solvent is capable of 5 weight percent solubility of naphthalene the
weight of solvent would be 1,060 lb./hr. If kerosene is the solvent,
the system would require 158 gal./hr. Such a system was used only when
the existing facility did not lend itself to naphthalene removal or as
a method to reduce a problem due to inadequate by-product facilities. The
injection of solvent oil into the main on the coke plant side could be
a method to relieve the problem without major capital expense as a
temporary solution.

Absorption by solids: The final method does not apply to the present
operation due to the fact that no spare gas handling equipment exists. In
addition, the labor involved in replacement of solid absorbers makes this
process unattractive.

Conclusion

Napthalene removal will be improved by the repair of the existing gas
cooling equipment. Progress is being made toward this end. In addition,
the use of chilled water for gas cooling and the use of the light oil
recovery system for naphthalene removal are being investigated. Finally,
I suggest that consideration be given to injection of solvent oils into
the gas main on the coke plant side to remove naphthalene from the gas
and possibly from the main until repairs can be completed.

G. M. Durkin

GMD/paj