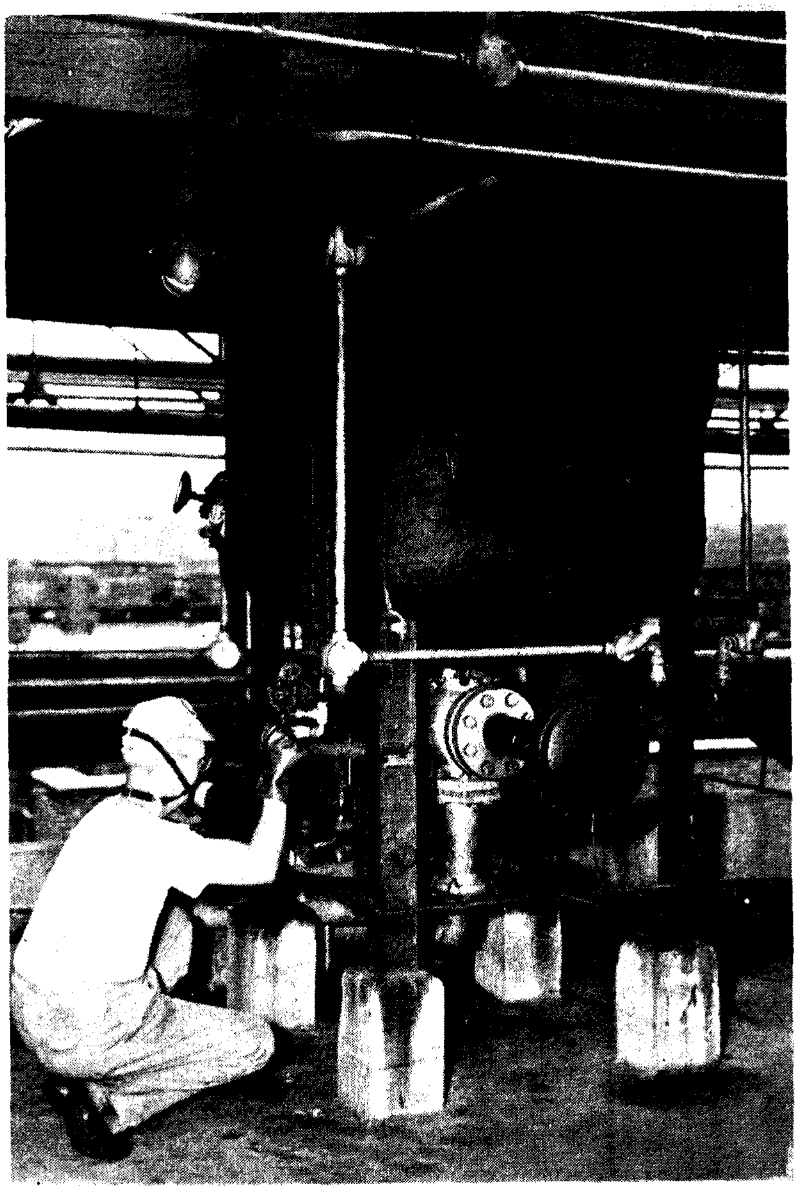

Cyanides from the Coke Oven

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Associate Editor

in collaboration with

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Samples of Liquid Hydrogen Cyanide for Analysis Are Taken from Receiving Tanks at Koppers Plant, Kearny, N. J.

A Staff-Industry Collaborative Report . . .

THE sulfur shortage is upon us and promises to be around for some time. While the brimstone producers slog through Louisiana swamps seeking new sulfur domes, petroleum refiners are looking at their acid sludges as a possible source of more sulfuric acid; ore refiners are viewing sulfurous stack gases with new interest, and coke oven operators are recalculating the economics of sulfur recovery from their off-gases by long established methods. Surface sulfur deposits, pyrites, and even anhydrite, neglected as long as the easily mined domes held out, are now the focus of intense interest. In other words, sulfur, like gold, is where you find it, and sulfuric acid consumers are missing no bets.

At the same time, hydrogen cyanide, long a slow-moving product commercially, has suddenly acquired new interest with the advent of the acrylonitrile fibers and the discovery of a new nylon process, both of which require the deadly gas as a fundamental raw material. It too has been the subject of intense technical and economic research. In 1948 two primary producers, Du Pont and American Cyanamid, made less than 40,000,000 pounds. Pittsburgh Coke and Chemical recovered less than 1,000,000 pounds from coke gases. The 1948 processes were based on sodamide, formamide, and cyanamide. By the end of this year three new primary producers, Rohm & Haas, Carbide and Carbon, and Koppers, will be in the picture and with expansion by the original two producers will boost total production to close to 95,000,000 pounds. Next year Monsanto will get into the act and Du Pont's mammoth 60,000,000-ton plant at Memphis, Tenn., will come on stream; Rohm & Haas and American Cyanamid will expand again to bring the total output to at least 200,000,000 pounds. All this new capacity, with the exception of the American Cyanamid expansion, which will use the cyanamide process, will utilize a reaction between methane and ammonia. All but one of the other new installations will introduce natural gas and ammonia into a reactor and apply high temperatures to make the reaction go to completion. The one exception is the Koppers plant. The Koppers people, like all coke makers, know that this reaction occurs spontaneously in a coke oven. High temperature coke oven gases contain about 60 grains of hydrogen cyanide per 100 cubic feet or about 0.7 pound per ton of coal coked. Disposal of this hydrogen cyanide has actually been a problem for almost as long as coke has been made. Usually the hydrogen cyanide has been decomposed, reacted to produce another product, or simply discharged to the atmosphere or to the sewers. A few producers in Europe and Pittsburgh Coke and Chemical in this country have recovered it as the pure gas, but the processes were not attractive economically, particularly when the market for the material was none too enthusiastic.

Now obviously that situation has changed. The market is strong and appears to be in for a long period of expansion. Furthermore the market for sulfuric acid, which can be produced from another coke gas contaminant, hydrogen sulfide, can only be described as desperate. At this fortuitous point Koppers is developing a process for recovering both hydrogen cyanide and hydrogen sulfide from coke oven gases and has a full scale plant in operation. Such a recovery technique could potentially add 60,000,000 pounds to the annual supply of hydrogen cyanide if it were adopted by all coke oven operators (*14*).

The potential sulfuric acid production that could be effected by this means is more difficult to estimate since it will depend on the sulfur content of the coal processed into coke, but at least it may be said that full hydrogen sulfide recovery should make the coke operators independent of outside sulfuric for their ammonia sulfate operations. Average coal should produce 8 to 10 tons of 100% sulfuric acid per 1000 tons of coal carbonized. Assuming a conservative 100,000,000 tons of coal coked in byproduct ovens in the United States each year this would yield an impressive 1,000,000 tons of acid. Some of this is of course already being recovered by older methods.

Removal of hydrogen sulfide from off-gases is actually an old story to coke oven operators. The gas is apparently formed quite easily by the reduction of the sulfur-containing constituents in the coal and is produced in a greater or lesser extent in all carbonizing operations.

Many effective processes, from the old boxes of wood chips mixed with iron oxide to the current thioarsenate or alkali absorbers, have been used for its removal (*9*).

HYDROGEN CYANIDE RECOVERY PROCESSES

The special value of the Koppers process lies in its recovery of hydrogen cyanide. Cyanides as such are not present in coal. They are never formed in low temperature carbonization processes. The process by which cyanide is formed from hydrocarbons and ammonia has not been fully determined; it obviously requires high temperatures and probably involves one or more of the following reactions (*12*, *13*).

	K cal.
$C_2H_2 + 2NH_3 = 2HCN + 3H_2$	−28.0
$C + NH_3 = HCN + H_2$	−39.5
$CH_4 + NH_3 = HCN + 3H_2$	−60.0
$C_2H_4 + 2NH_3 = 2HCN + 4H_2$	−63.0
$CO + NH_3 = HCN + H_2O$	−10.0

No effective catalysts have been discovered for these reactions.

Regardless of the source of the hydrogen cyanide it is desirable to remove it from some gas streams even if it is not recovered, as cyanide forms complexes with iron and consequently is mildly corrosive to steel equipment. In installation where iron oxide is used to remove hydrogen sulfide the elimination of hydrogen cyanide is especially important because it reacts with the iron oxide to produce a solid deposit of iron complexes which soon clogs the boxes.

Many processes have been devised and are used to eliminate cyanide. However, few of those that have found commercial application have recovered the gas in an unreacted form, primarily because there has been only a limited market for pure hydrogen cyanide in the past. Before World War I British, German, and American coke makers were scrubbing their off-gases with alkali solutions and recovering various iron-cyanide complexes from the solution (*2*, *3*, *6*, *10*, *11*, *18*, *23*). Some of these processes give excellent recoveries and are still in use. Cyanide has also been recovered in nickel and copper complexes and in ammonia-iron compounds (*4*, *5*, *8*). In recent years in the United States, it has been recovered as a thiocyanate, usually by reaction with an ammonium sulfide complex to produce ammonium thiocyanate.

Shortly before World War II a process was introduced in the United States in which the cyanide is reacted with iron sulfate and lime to precipitate calcium ferrocyanide (*19*). This process found large scale application at the Pittsburgh Coke and Chemical plant at Neville Island, Pa. It has now been superseded by a plant built in 1942 which uses a process very similar to the Koppers installation to be described here. In fact it employs identical equipment for the initial removal of cyanide and sulfide from the coke gas stream. The major deviation is in the final separation of hydrogen sulfide from the hydrogen cyanide solution. The Neville Island plant requires several steps for this operation whereas Koppers accomplishes it in a single stripper-rectifier column.

The hydrogen cyanide removed from coke oven gases has in some cases been destroyed by reaction with permanganate. In other instances the thiocyanates produced by the recovery system have been intentionally decomposed by bacterial cultures. Many processes have been suggested and several employed in the past for the conversion of cyanide into more readily marketed ammonia (*1*, *15*). However, none of these processes offered any appreciable economic advantages. Their major function was the control of pollution and reduction of corrosion.

Polymerization

Lack of enthusiastic markets has not been the only deterent to the recovery of hydrogen cyanide. Pure hydrogen cyanide, particularly when in the liquid state, has a disconcerting tendency to polymerize explosively, unless properly stabilized. If the polymerization proceeds slowly as it does in dilute aqueous solutions of hydrogen cyanide, there is little decomposition into the constituent elements. The polymer has a smaller percentage of nitrogen and hydrogen than hydrogen cyanide; a typical analysis is 3.4% hydrogen, 46.15% carbon, and 50.45% nitrogen (*22*) as compared with 3.7% hydrogen, 44.5% carbon, and 51.85% nitrogen in hydrogen cyanide. The excess nitrogen and hydrogen are liberated as ammonia

The reaction is strongly exothermic and is catalyzed by alkaline environments. Consequently the liberation of ammonia makes the reaction autocatalytic if it is not immediately neutralized. The autocatalytic action makes the reaction tend to "run away" and under such a situation the heat liberated partially decomposes the polymer into elemental gases which are expanded with explosive violence.

The structure of the polymer—a black, semicrystalline material—is complex and apparently varies somewhat with the conditions under which it is formed. The linkage probably involves an opening of the carbon-nitrogen triple bond, although it has been suggested that only the isocyanide form, $H-N=C$, is subject to polymerization. Under some circumstances the polymer exhibits a deficiency rather than an excess of carbon. This latter behavior has been attributed to the incorporation of hydrocarbon molecules. When the polymer is formed in the presence of sulfides it usually will include substantial quantities of sulfur which suggests the possibility that a copolymer of sulfide and cyanide has been created. The poisonous nature of hydrogen cyanide gas has apparently discouraged intensive studies of the polymer-forming reaction.

It is believed that pure hydrogen cyanide will not polymerize in this fashion but will form a trimer of fixed composition. However, such a possibility is not of commercial importance. The commercial material will polymerize spontaneously even in acidic environments, but the rate of the reaction under such conditions is negligible. Consequently the established practice has been to stabilize hydrogen cyanide by the addition of inorganic acids. Phosphoric acid, 0.2% by weight, has been the most common additive, although sulfuric and other acids have been used. The added acid merely reacts with the ammonia evolved by the polymerization reaction and holds the rate of the reaction at its nominal minimum.

Maintaining stable conditions throughout the steps of any reasonably complex process has been a difficult problem, and earlier coke makers uniformly solved it by converting the poisonous and potentially explosive gas into some more innocuous compound as soon as possible. The forerunner of the Koppers plant, described in this article, experienced an explosion caused by a run-away polymerization in 1949. However, in building the present plant engineering improvements have been incorporated that ensure continuous inhibition in both liquid and vapor phases at all points in the process stream. The acid inhibition of the cyanide polymerization has been known for some time. It is primarily engineering development that has made the Koppers process practical at a time when new market activity is economically attractive.

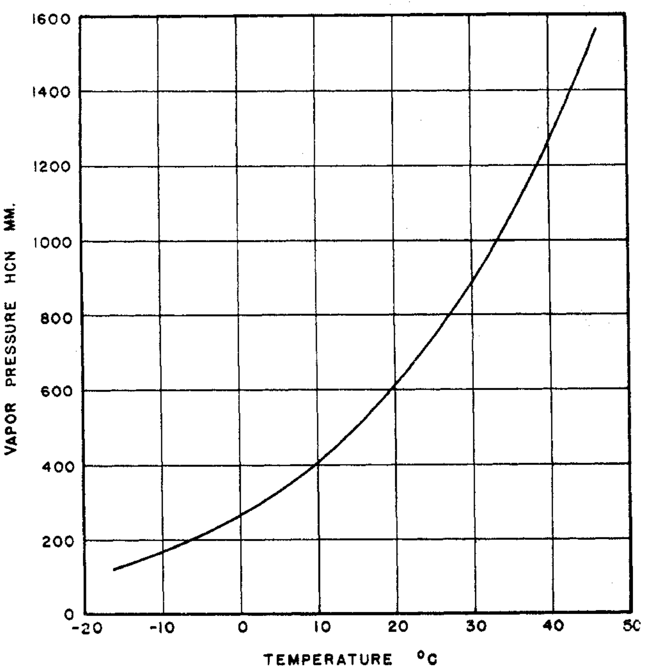


Figure 1. Vapor Pressure of Hydrogen Cyanide

KEARNY, N. J., PLANT OF KOPPERS CO., INC.

The 220 coke ovens at Kearny produce about 48,000,000 standard cubic feet of gas a day. As this gas comes from the ovens it passes immediately through water sprays which condense the tars and dissolve about 10% of the ammonia present. Essentially no hydrogen cyanide is lost in this water scrubbing because at the temperature of the "flushing liquor" (75° C.), the vapor pressure of hydrogen cyanide is so high that solution in the water is negligible (Figure 1). About 300,000 gallons of this flushing liquor pass through the sprays every hour. It is collected from the gas mains and held in settling tanks to separate the tar and aqueous layers. The tars are decanted off and refined in another section of the Kearny plant. Most of the aqueous liquor from the settling tanks (280,000 gallons per hour) passes through heat exchangers which supply the heat required to desorb the gases in the gas "purification" unit. From the heat exchangers the water is recycled to the sprays in the coke oven gas outlets. The flushing liquor picks up some extra water from the coke oven gases. This excess is drawn off the recycling system and fed to a stripping still which removes the dissolved ammonia. The ammonia recovered is returned to the gas stream. The water is discarded.

The coke oven gas stream is cooled to 80° C. and saturated with water vapor by the water sprays. It passes through a cooler which precipitates out the residual tars and is then bubbled through a tower containing dilute sulfuric acid; the acid reacts with the ammonia present to form ammonium sulfate which is subsequently precipitated and recovered. Movement of the gases from the coke ovens through the cooler and ammonia scrubber and into the purifying units is accomplished by centrifugal gas pumps located between the cooler and the acid tower.

Absorption of Hydrogen Cyanide, Hydrogen Sulfide, and Carbon Monoxide

The tar- and ammonia-free coke oven gas contains about 0.48 volume % of hydrogen sulfide and 0.13 volume % of hydrogen cyanide. These gases along with carbon dioxide (Figure 2) are scrubbed out by a dilute solution of sodium carbonate in the Koppers unit. Organic absorbents, notably sodium phenolate (*20*) and the alkynolamines (*14*), are used to absorb hydrogen sulfide from natural gas, refinery gas, and producer gas. However, these are not adaptable to coke oven gases because they will react with the hydrogen cyanide present and lose their absorbing efficiency. Other hydrogen sulfide removal systems used in the coke industry involve reactions between the sulfide and the absorbent so that the hydrogen sulfide cannot be recovered unchanged. Some of these systems recover finely divided molecular sulfur, but this product is usually sold as an agricultural chemical rather than used for sulfuric acid production.

When these other purification systems are used the hydrogen cyanide either remains in the fuel gas, or it is recovered and returned to a fuel gas line. In a few instances where pollution problems are not acute it may be discharged to the air or to the sewer as an aqueous solution.

In the vacuum carbonate process the coke oven gas passes countercurrent to a stream of 6 to 7% aqueous sodium carbonate in an absorber tower packed with West Virginia spruce hurdles (Figure 3). Gas feed is at a rate of 2,300,000 cubic feet per hour. The alkaline absorbent is fed at 32,000 gallons per hour and leaves the tower at 53° C. The pressure in the absorber is about 50 inches of water gage maintained by gas transfer pumps. The absorption involves the reactions

$$Na_2CO_3 + CO_2 + H_2O \rightleftarrows 2NaHCO_3$$

$$Na_2CO_3 + H_2S \rightleftarrows NaHS + NaHCO_3$$

$$Na_2CO_3 + HCN \rightleftarrows NaCN + NaHCO_3$$

The overhead from the absorber contains the light oil and naphthalene fractions as well as the gaseous hydrocarbons of the

Table I. Chemical and Utility Requirements per Day

Coke oven gas feed, stand. cu. ft./day	50,000,000
Vacuum purification (Na_2CO_3), lb.	400
HCN recovery, gal.	
H_2SO_4 (93%)	2.52 2.7
H_3PO_4 (85%)	0.25 1.0
Sulfur recovery, tons	20
165-lb. steam, lb.	
Vacuum purification	
HCN recovery	40.0
Sulfur recovery (heat recovery gives net gain)	(+150,000)
15-lb. steam, lb.	
Vacuum purification	9,600
HCN recovery	2
Sulfur recovery	
Brackish water, gal.	
Vacuum purification	1,844,000
HCN recovery	65.5
Sulfur recovery	50,000
City water, gal.	
Vacuum purification	187,000
HCN recovery	45.5
Sulfur recovery	22,000
Electrical power, kw.-hr.	
Vacuum purification	7,880
HCN recovery	45
Sulfur recovery	4,000
H_2SO_4 (100%), tons	86
HCN (98.5%), lb.	2,940

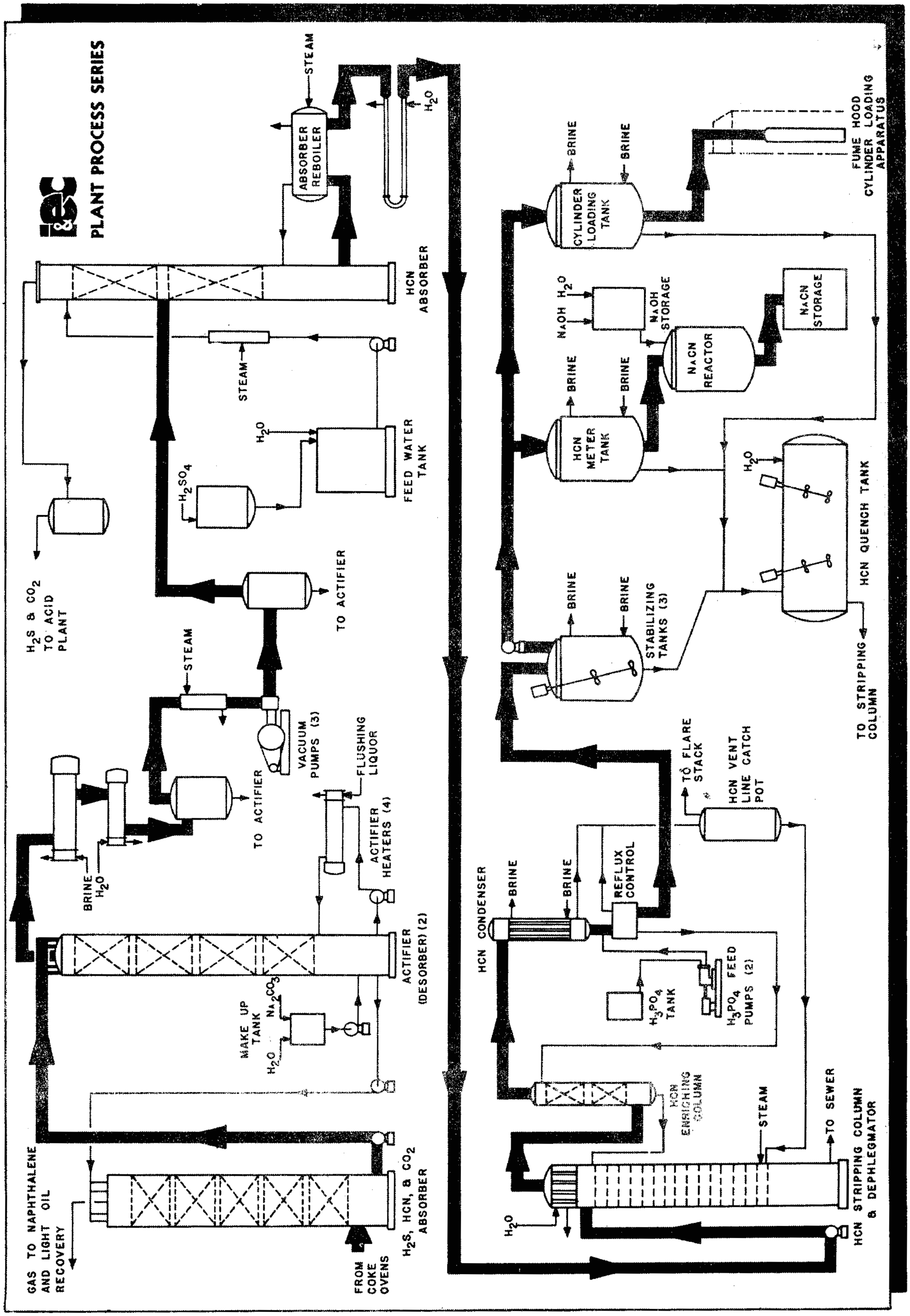


Figure 2. Flow Sheet for the Production of Hydrogen Cyanide at the Kearny, N. J., Plant of Koppers Co., Inc.

original gas: 93% of the hydrogen sulfide, 85 to 90% of the hydrogen cyanide, and virtually all the carbon dioxide have been removed. The residual hydrogen sulfide is removed by passing it through boxes of wood chips impregnated with iron oxide.

Desorption

The alkaline solution from the bottom of the absorber is sprayed into the tops of two parallel desorption columns or "actifiers." The absorption reactions in the liquid purifier system are all reversible, and equilibrium is influenced by pressure and temperature. In the Seaboard process, which was the predecessor of the present operation, desorption was accomplished by heat and aeration of the solution with air or clean fuel gas (*17*). However, such aeration converted some of the sulfide to thiosulfate and most of the cyanide to thiocyanate, thus preventing their recovery as gases. The technique now used at Kearny employs water vapor to strip the gas from the absorbent and maintains a vacuum on the system to reduce the heat required to produce the water vapor (*21*). At the operating pressure of about 4.2 inches of mercury absolute, the volume of vapor required to strip the solution is about the same as it would be at atmospheric pressure, but the weight of the vapor and hence the heat required to produce it is less than one fifth as great. The bottom sections of the desorption columns act as reservoirs for the absorbent. About 2000 gallons are held in each. The total volume of absorbent in the purification system is about 8000 gallons. The absorbent in the bottoms of the desorbing towers is pumped at about 300,000 gallons per hour through exchangers heated by the flushing liquor from the coke gas mains. These exchangers supply all the heat required by the desorption operation. The actifiers operate at about 53° C. An automatic level control operates the outlet valve of a pump that recycles the stripped carbonate solution from the reservoir to the head of the absorber. Return of sulfide or cyanide to the absorber would reduce the absorbing efficiency of the carbonate solution and result in excessive carry-over of these gases in the fuel gas stream.

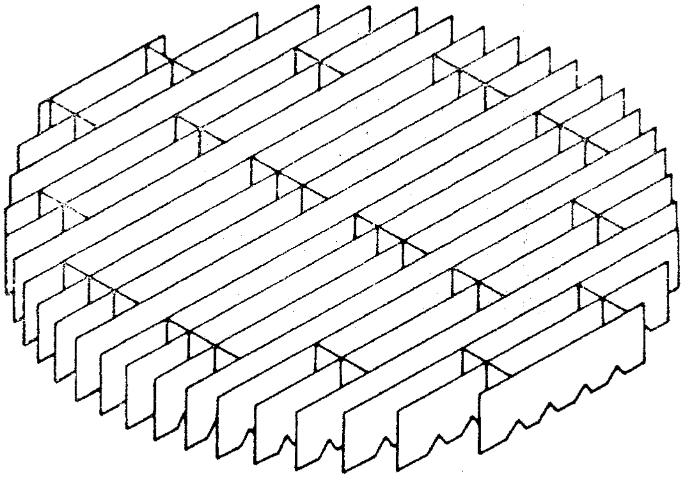


Figure 3. Hurdle Packing

Liquid carry-over from the actifier towers is caught in knockout drums (Figure 4) and returned to the actifier bottoms. However, some absorbent is lost from the top of the absorber column. Under normal operating conditions this loss amounts to about 2400 gallons of water and 400 pounds of sodium carbonate a day.

The gas from the actifiers is about 55% hydrogen sulfide, 15% hydrogen cyanide, and 25% carbon dioxide. A small amount of inert gas, primarily nitrogen, from air leaks in the system and some hydrocarbons and hydrogen may bring the total of minor constituents to as much as 5%. The percentage of hydrogen sulfide in this stream is relatively low since the Kearny plant uses low sulfur (1.0%) West Virginia coals. High sulfur coals contain as much as 5% sulfur, about half of which would be released as hydrogen sulfide to give a mixed gas from the actifiers with as much as 75% hydrogen sulfide. Gas from high-sulfur coals will release more carbon dioxide from the carbonate solution in the actifiers, so that the percentage of hydrogen sulfide in the gas stream does not become as high as might be expected, although the total volume of gas is increased substantially. The percentage of hydrogen cyanide formed is little affected by the composition of the coal being coked.

The desorbed gases pass through a sheet-and-tube condenser cooled with salt water, which reduces the temperature to 38° C., and then through a smaller, fresh water-cooled condenser, which cools it to 21° C. This double condenser system is used because the salt water coolant taken from the brackish inlets adjacent to the plant attains temperatures as high as 31° C. in the summer whereas the temperature of the city-supplied fresh water seldom exceeds 10° C. A knockout drum after the condensers removes entrained water. The condensers and the knockout all drain back to the actifier reservoir. The gas stream containing hydrogen sulfide, hydrogen cyanide, and carbon dioxide passes from the knockout through a short length of steam-jacketed pipe, used as a conditioner in cold weather, and into the reciprocating pumps which maintain the vacuum in the actifier column. There are three of these single-stage, horizontal pumps each with a capacity of 1700 cubic feet per minute, but only two are on the line at any one time.

The vacuum carbonate operations are conducted in the old gas purification area of the plant. They are all relatively standard and may be found in other installations. Lack of space around the existing purification unit necessitated location of the hydrogen cyanide and hydrogen sulfide recovery unit in a new area of the site, about 0.25 mile away. The gas from the carbonate absorption operations is piped to the new area through a 4-inch, carbon steel main by the pressure of the vacuum pumps.

Hydrogen Sulfide and Hydrogen Cyanide Recovery

When the gas stream arrives at the new installations, it is introduced into a knockout drum which removes entrained liquid or condensables from the previous operations. There is actually so little drainage from this drum that only biweekly tapping is required. Steam coils in the bottom prevent freezing in cold weather and drive any dissolved hydrogen sulfide or hydrogen sulfide from the collected water before it is discharged.

From the knockout drum the gas stream goes directly to the center of the hydrogen cyanide absorbing column. Twenty-foot

TABLE II. MATERIALS BALANCE FOR HYDROGEN CYANIDE RECOVERY OPERATION

Feed, lb./hour			
HCN	162		
H_2S	605		
CO_2	277		
Others	56		
City H_2O	8350		
			9450
Products, lb./hour			
Overhead from absorbers			
H_2S	605		
CO_2	277		
Others	56		
		938	
Overhead from stripping still			
HCN	160.4		
H_2O	3.4		
		163.8	
Stripping still bottoms			
HCN	1.6		
H_2O	8346.6		
		8348.2	
			9450

sections above and below the inlet are packed with Berl saddles. Water, acidified with sulfuric acid to pH around 3.0 and heated to 30° C. by direct injection of 165-pound steam is introduced (*6E*) at the head of the column. Gas flow in the absorber is 12,000 cubic feet per hour. The flow of acid solution between 900 and 1100 gallons per hour keeps the hydrogen cyanide content of the overhead discharge below 10 grams per 100 cubic feet (0.02% by volume). Heating the absorbent prevents naphthalene from precipitating out and reduces the vapor velocity in the column.

The packed section of the absorber column below the inlet acts as a rectifier to remove hydrogen sulfide. The solution going into this rectifier section is essentially saturated with hydrogen sulfide (about 2 grams per liter). The rectifier section operates with a top temperature of 30° C. and a bottom temperature of 95° to 100° C.

Sulfuric Acid Production

Hydrogen sulfide and carbon dioxide pass out the top of the absorber, through a knockout drum to remove entrained water picked up in the absorber, and then are sent to the adjacent contact sulfuric acid plant. This gas stream is fed directly into a jet in the acid plant combustion chamber. It contains about 65% hydrogen sulfide, 30% carbon dioxide, and 5% other gases. The carbon dioxide and other inerts in the stream are carried through and ultimately discharged from the vents of the sulfur trioxide absorbers.

The acid plant used at Kearny is a 10-year-old standard type of contact unit. Most modern contact acid plants use a "dry" process—that is, the combustion air is dried before it is admitted into the burner, and the water content of the gases is kept at a minimum throughout the process. However, since the burning of hydrogen sulfide produces water it is impossible to use this type process with the gas recovery system. Consequently, the Kearny operation uses a "wet" process in which the sulfur dioxide gas is dried between the burner and the converters. The new "quench converter" type contact plant in which the conversion is done on the wet sulfur dioxide gas would be particularly applicable to the use of hydrogen sulfide in sulfuric acid manufacture (*16*).

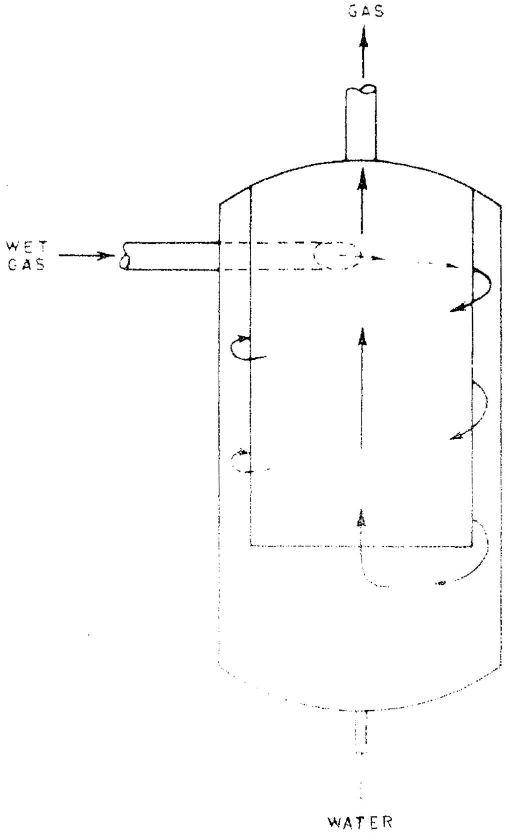


Figure 4. Knockout tank

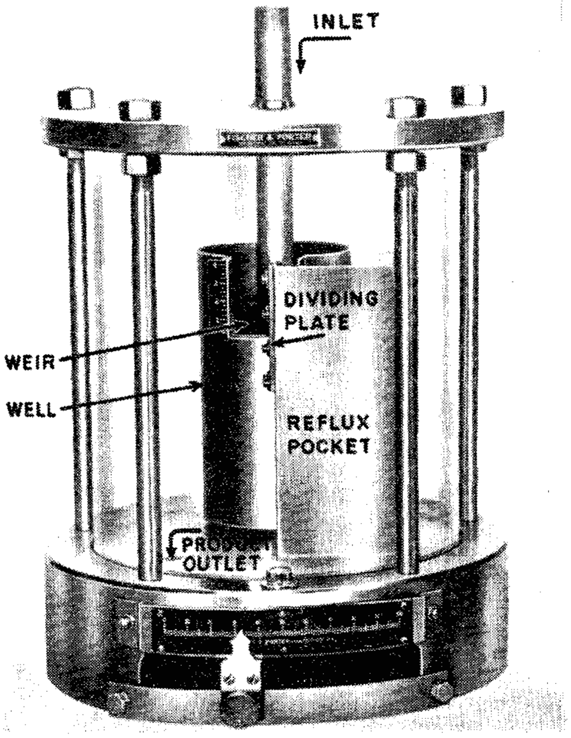


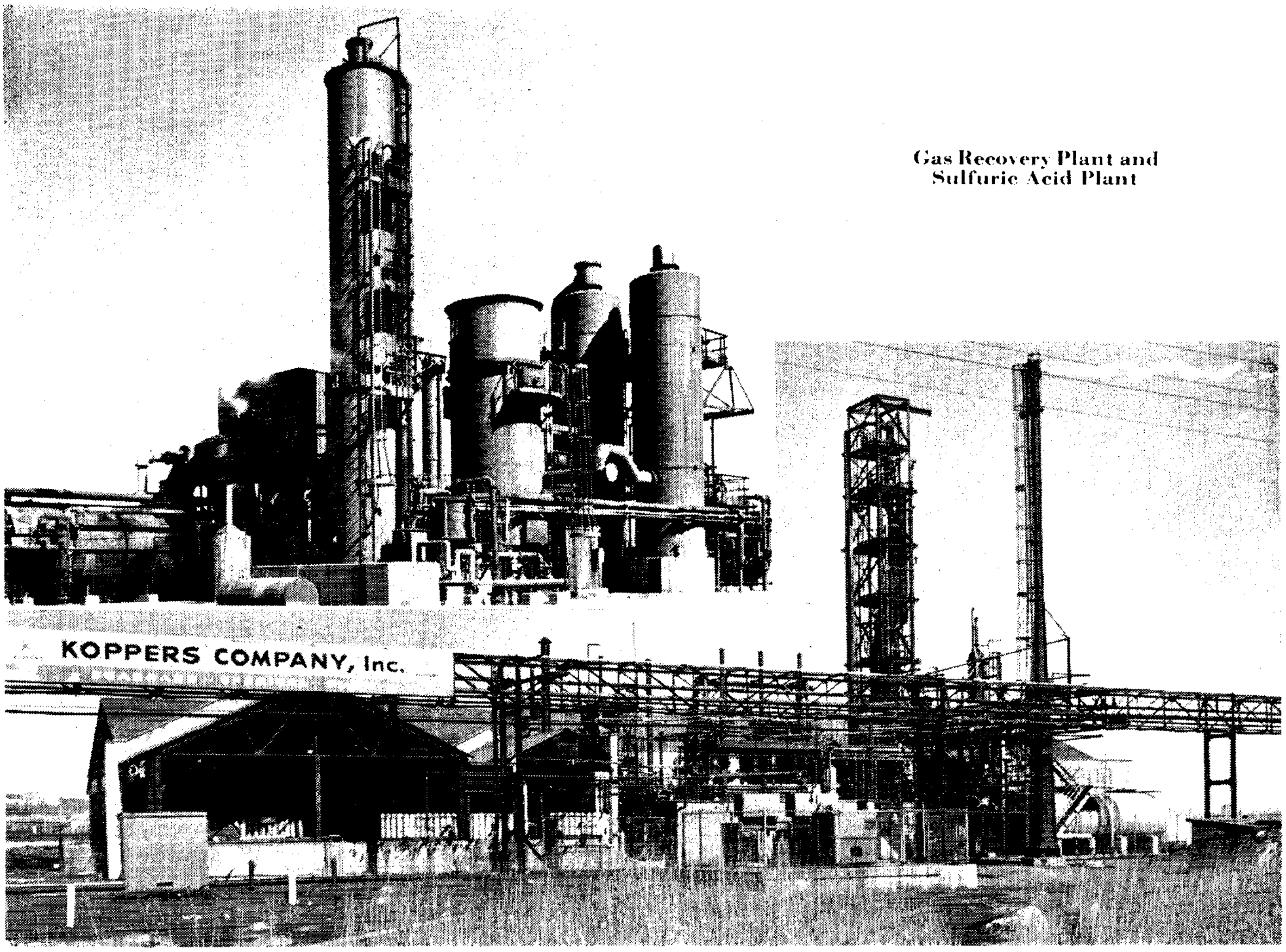
Figure 5. Ratoweir

According to experience at the Kearny plant, it would be possible for the recovery operation described here to produce all the sulfuric acid required to convert the ammonia recovered from the coke gas into ammonium sulfate, if a coal of average sulfur content was being coked. However, the generally accepted minimum economic size for a sulfuric acid plant is about 100 tons of acid per day. A plant of that size would require gases from a very large battery of coke oven—much larger than that at Kearny. About 60% of the acid produced at Kearny is shipped outside the plant. Consequently, a separate burner jet in the acid plant combustion chamber burns molten sulfur to supplement the hydrogen sulfide fuel. Hydrogen sulfide burns with a much hotter flame than sulfur, and this higher temperature must be taken into account in designing an acid plant to burn all or part hydrogen sulfide. The Kearny acid plant feeds about twice as much sulfur as hydrogen sulfide. This results in a temperature of about 1150° C. in the burner compared to about 950° C. in a conventional unit burning all sulfur.

Hydrogen Cyanide Separation

The water solution of hydrogen cyanide from the bottom of the hydrogen cyanide absorber-rectifier is drawn into a shell-and-tube reboiler. Steam to the reboiler tubes is automatically controlled and maintains a pressure drop equal to 5 to 8 inches of water through the rectifier section. Steam and the last traces of hydrogen sulfide stripped from the hydrogen cyanide solution return from the reboiler to the absorber-rectifier column. About 1000 pounds of steam per hour are required to obtain optimum performance on the rectifier. An automatic level controller regulates the flow of solution from the reboiler into a water-cooled, double-pipe, hairpin heat exchanger where it is cooled from 90° to 80° C. to prevent vapor binding in the transfer pumps.

The absorber operates at 5 pounds per square inch pressure maintained by a back pressure controller on the overhead while the



Gas Recovery Plant and Sulfuric Acid Plant

stripper is at atmospheric pressure so that cooling is also necessary to eliminate the possibility of flashing in the stripper.

The cooled stream of what is called "foul solution," containing about 2% hydrogen cyanide, is pumped (*6E*) to the top of a ten-tray stripping still. About 1100 pounds per hour of 165-pound steam are introduced directly into the bottom of the tower to effect the distillation. Water at 100° C. containing less than 0.02% hydrogen cyanide is discharged from the bottom of this column by an automatic level control and sent to the sewer. The overhead stream at 85° C. passes through a small water-cooled, vertical tube condenser called a dephlegmator. Cooling the vapor stream at this point allows the enriching column to operate at a much lower reflux ratio. The condenser also prevents surges of cyanide from flooding the enriching column and reduces the load on the hydrogen cyanide condenser. The vapors leave the dephlegmator, at 55° C., containing about 50% of water. They pass into an enriching column, packed with $^1/_2$-inch ceramic Berl saddles, which completes the removal of water from the stream. The bottoms from the enriching column are returned to the top of the stripper. The enriched hydrogen cyanide vapor at 26° C., containing about 98.5% hydrogen cyanide, is chilled to 5° C. in a brine-cooled, shell-and-tube condenser to avoid polymerization. This liquid hydrogen cyanide stream then passes into an adjustable refluxing weir (Figure 5) (*2E*). Under normal conditions about 50% of the liquefied, stabilized hydrogen cyanide is returned to the top of the enriching column as a reflux. A continuous specific gravity meter on the reflux line provides a constant check on the purity of the product.

About 0.1% of phosphoric acid (0.0235 gallon per hour) is added to the hydrogen cyanide on the refluxing apparatus to inhibit polymerization both in the product and in the stripping still. The phosphoric acid is commercial grade and is pumped from the 50-gallon storage tank by two parallel, positive displacement, pulsating diaphragm type metering pumps (*7E*).

Stabilizing

The liquid hydrogen cyanide product is piped to one of three brine-jacketed, 250-gallon, receiving tanks. The three tanks are used sequentially and will each hold about 8 hours' production. The tanks are stirred with a double-propeller agitator driven by a 1-hp. motor at 350 r.p.m. As soon as a tank is filled it is analyzed for stabilizer content. If the analysis shows less than 0.2% of phosphoric acid, acid is added to make up the difference. Stabilized batches are pumped (*8E*) to a meter tank, brine-cooled to about 2° C. From the meter tank the liquid hydrogen cyanide may be diverted either to the cylinder-filling department or to the reactors in which sodium cyanide is prepared. If it is to be shipped as liquid hydrogen cyanide it is transferred to a brine-cooled (2° C.) loading or surge tank from which it is drawn directly into chilled shipping flasks.

At present Koppers is not shipping any cylindered hydrogen cyanide from Kearny. The entire output of the plant is sold as 30% aqueous sodium cyanide solution. Processing to this end product eliminates the fire and explosion hazard of storage and handling of liquid hydrogen cyanide.

Sodium Cyanide Production

To make the sodium cyanide solution about 400 gallons of commercial 50% aqueous caustic solution are introduced into a reactor and diluted with water to 23 to 29% depending on the atmospheric temperature. Hydrogen cyanide is then introduced from the meter tank through a dip pipe at a decreasing rate until almost all the sodium hydroxide has reacted. The rate of addition of the cyanide must be controlled carefully and the reactor charge agitated vigorously to ensure that the hydrogen cyanide introduced reacts immediately with sodium hydroxide. If a local concentration of sodium cyanide should build up around the dip pipe, free hydrogen cyanide would collect momentarily and, in the alkaline solution, would begin to polymerize. Although the polymerization would not progress very far before the hydrogen cyanide would be reacted, enough polymer would form to discolor the sodium cyanide solution.

As the sodium hydroxide is depleted by reaction to sodium cyanide the added hydrogen cyanide does not react as quickly and the rate of addition must be reduced. The progress of the reaction is followed by frequent density determinations until the end point is approached. The final addition is calculated from a titrimetric analysis. The product contains about 2% free sodium hydroxides to ensure that the stoichiometric point is not exceeded.

Measurement of solutions is by visual observation of calibrations on the feed tanks. The standard batch produces 1000 gallons of 28 to 35% sodium cyanide varying with the time of year. In the winter the low concentrations must be used to avoid solidification in transit. In the warmer months the concentration is increased to save on shipping costs. All billing is on a sodium cyanide content basis.

Performance

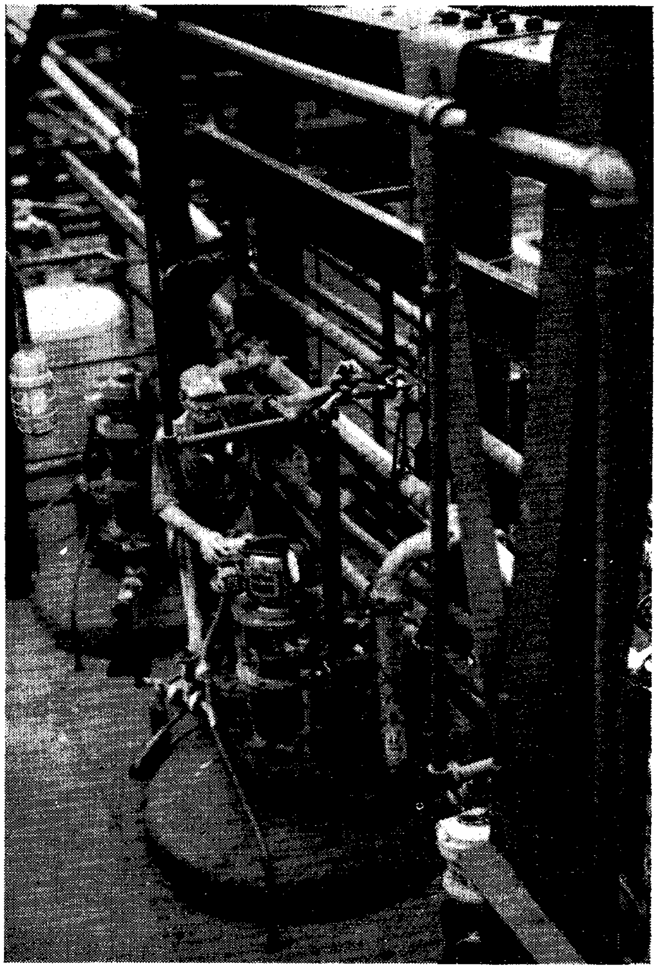
The Kearny plant produces about 172 pounds per hour of 98.5% hydrogen cyanide from a feed rate of mixed gases of about 12,000 standard cubic feet per hour.

Under optimum conditions the yield of hydrogen cyanide calculated on the feed to the hydrogen cyanide absorber is about 99%. The major product loss is incurred in the maximum of 1.6 pounds per hour of hydrogen cyanide that is lost in the bottom discharge of the stripper column.

Recently the operators of the plant discovered a serious corrosion problem in the absorber and the lower sections of the stripping still. Although the Type 304 stainless steel used for this equipment appears to be adequately resistant to the necessary concentrations of sulfuric when tested in the laboratory, rapid corrosion has been experienced in actual use. It is possible that this corrosion was caused by experimental runs in which acetic acid or other supplementary inhibitors were added to the dilute acid absorbent. If acetic acid is used as a vapor phase inhibitor it may be necessary to find some more resistant material for the construction of the process vessels. However, there is some possibility that reducing the acidity of the absorbent will eliminate the corrosion problem without impairing the absorbing efficiency of the column.

Previously the absorbent was held at pH's as low as 2.3. It is hoped that an acid solution with pH as high as 3.5 will give the same absorbing efficiency.

Polymer formation in the equipment containing pure hydrogen cyanide or aqueous solution of hydrogen cyanide in concentrations greater than 50% by weight has apparently been completely eliminated by proper engineering design and the addition of phosphoric acid inhibitor. However, a slow accumulation of polymer has occurred in the absorber section of the recovery plant where dilute solutions of hydrogen cyanide are involved. Although the formation is slow and does not entail any explosive hazard it affects operating conditions and has necessitated several shutdowns. This polymer formation seems to be primarily caused by dead spots in the equipment which are not continually flushed by fresh solution. Under such conditions the acid inhibitor is gradually exhausted by reaction with ammonia released by slow polymerization, and the autocatalytic phase of the polymerization is attained. Vapor phase inhibition of the polymerization by the introduction of sulfur dioxide solutions and sulfur dioxide gas has not been effective in eliminating the polymer formation. Acetic acid added to the sulfuric acid in the absorbent for the same purpose also seemed to have little inhibitory effect on the polymerization and may have increased the corrosion of the absorber. The most promising remedy for this condition seems to be a modification of the internal arrangement of the equipment involved to ensure that fresh solution reaches all surfaces continuously.



Transfer Pumps

Submerged mounting of pumps and off-center introduction of agitator as seen from top of receiving tanks

Operating experience has shown that the simplest and most straightforward start-up procedure is both the safest and most efficient. In lighting off the plant the absorber is first purged with steam to eliminate air and then filled with coke oven gas to prevent air from leaking back in. Acid absorbent is admitted to the top of the absorber, passes down the column and through the reboiler, and is discharged to the sewer. Steam is passed through the reboiler at the regular operating rate and mixed gases are admitted to the absorber. Steam to the reboiler may be adjusted manually to bring the absorber-rectifier to standard operating conditions as quickly as possible. When the discharge from the reboiler is free of hydrogen sulfide it is assumed that the absorber has attained operating equilibrium; overhead gases are sent to the acid plant, and the foul solution from the bottom is admitted to the stripper column. Steam is admitted to the stripper at the standard rate and water is passed through the dephlegmator at the maximum cooling rate. This usually provides a dephlegmator discharge at about 40° C. The overhead vapors enter the enriching column, and the reflux ratio is immediately set at 1:1. The initial product contains less than 10% water, and after a few minutes of reflux operation the product has attained the standard strength of 98.5% hydrogen cyanide.

To shut down the unit the mixed gas feed is by-passed to the stack. The stripper remains operating at standard conditions until there is no more overhead discharge. The flow of absorbent through the absorber and into the stripper is continued until all hydrogen cyanide has been removed from the system. If it is necessary to enter any of the process equipment the vessels are filled with the dilute sulfuric acid absorbent, drained, and purged with steam before they are opened. If the plant was to remain idle for a period of several days this procedure would also be followed to prevent polymer formation by residual hydrogen cyanide.

Acid flushing and steam cleaning are used throughout the plant to clean lines and vessels. No alkaline detergents are used at any time.

In the event a pipe that carries hydrogen cyanide must be replaced or repaired, the section of line is isolated and operators in gas masks and rubber gloves loosen the adjacent flange connections until the hydrogen cyanide begins to drip out. A water hose is played on the connection until the dripping stops and then the line is removed.

Vent System

All vents from the hydrogen cyanide recovery unit including those from the relief valves are connected to a 60-foot flare stack. The stack has two separate flares, one for sulfide gases and one for cyanide, with a single ignition system. The sulfide flare is connected to manual vent valves on the inlet knockout and the hydrogen sulfide knockout drums, to a relief valve set for 10 to 12 pounds per square inch on the hydrogen sulfide knockout, and to a 15 pound per square inch relief valve on the absorber reboiler.

The other flare serves manual vents on the cyanide condenser, the reflux weir, the absorber reboiler, the stabilizers, cylinder loading, and meter tanks, all through a vent line catch pot. Most of the vent lines are 4-inch stainless steel although a few are 2 inches. Flame arresters on both flares prevent a blowback into the system. The stabilizer, loading, and meter tanks also have aluminum rupture disks calibrated to release at 10 to 15 pounds per square inch gage. The stabilizers have 8-inch disks; the others use 6-inch. The rupture disks have individual stacks that rise about 10 feet above the vessel.

Auxiliary Equipment

Refrigeration for the plant is provided by two 20-hp. units using Freon refrigerants (*10E*). The cooling effect is transmitted (*3E*) to the jacketed pipes and tanks by calcium chloride brine with a specific gravity of 1.2.

All instruments and automatic valves are air operated. The air for this service is taken from the general plant service line and dried in a double tower gas dryer. Each tower contains 65 pounds of silica gel. They operate alternately on 24-hour drying and regenerating cycles. Regeneration is by internal steam coils. The unit has a capacity of 25 cubic feet of air per minute to a dew point of 9° C.

Two banks of three nitrogen cylinders are available to replace the instrument air in case of compresser failure or other casualty. Each cylinder can supply air for the entire instrument sytem for 6 minutes.

Materials of Construction

Practically all the equipment in the recovery plant which will come in contact with high concentrations of either hydrogen cyanide or hydrogen sulfide is fabricated of Type 304 stainless steel (*1E*). Although such construction is not absolutely necessary, it prevents discoloration of the product by corrosion products. The sewer that serves the stripper is also of stainless steel since it must handle dilute acid at 100° C. Other sewers are ceramic. Phosphoric acid lines and pumps are of Monel metal.

All process piping is joined by bolted flange joints similar to those commonly used with small soft tubing (*9E*) (Figure 6). Pipe is flared to a conical shape by special tools on the job. Ease of dismantling and replacing sections of line so connected more than compensate for its relatively high initial cost, according to Koppers' engineers.

High temperature lines are steam traced and magnesia lagged. Glass-wool insulation is used on the brine lines and other pipe carrying streams below atmospheric temperatures. Process vessels have 2 inches of glass wool or 85% magnesia insulation plus a weatherproof asphaltic coating.

Safety Features

The major safety provision of the installation is a system of quick-acting valves that make it possible to drop the contents of any container holding liquid hydrogen cyanide into water almost instantaneously.

The three stabilizer tanks, the meter tank, and the cylinder loading tank are all equipped with 4-inch dump valves that will completely empty them into a 6500-gallon horizontal quench tank in 10 seconds in the event of run-away polymerization. The quench tank is always filled with 4500 gallons of water, enough to quench the contents of all the hydrogen cyanide vessels in the event of trouble. It is equipped with two 420-r.p.m. agitators each with two 16-inch square pitch, horizontal paddles (*5E*)

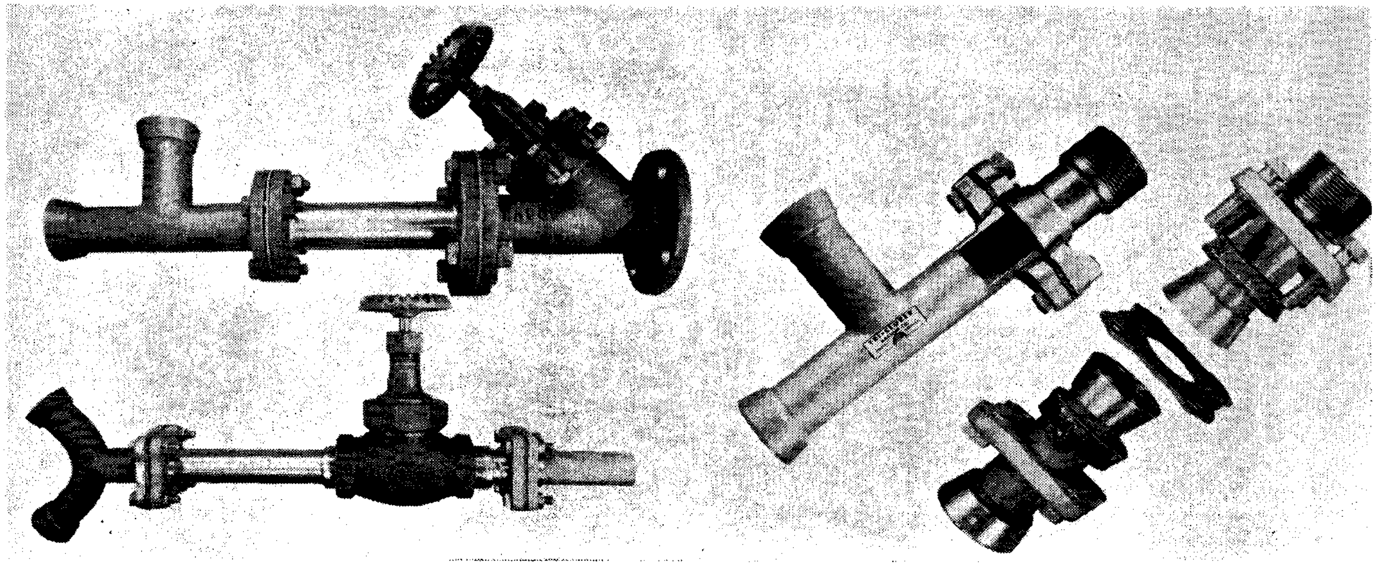


Figure 6. Flanged Conical End Fittings

This precautionary measure has been adopted since the explosion in the initial installation. It has never been necessary to use the quenching system, but if any charge of hydrogen cyanide were quenched in this fashion the contents of the quench tank would be steam stripped in the stripper column and the hydrogen cyanide stripped out would be burned.

The dump valves may be operated manually by individual switches on the control board or they may all be opened simultaneously by a master switch located in the unit's office building. If the temperature in a stabilizer exceeds 10° C. an alarm rings. At 20° C. the valve on that vessel will open automatically. The valves are air operated and controlled by three-way solenoid valves. A standby nitrogen supply is available which will automatically replace the instrument air in case of compressor failure. However, if this standby system fails or the air lines develop a leak that it cannot compensate the valves will open rather than become inoperative in the closed position. Steam valves throughout the plant will automatically close in the event of air pressure failure. In addition to the dump valves the stabilizing tanks are also equipped with 8-inch rupture disks to release the pressure of any explosion or explosive increase in pressure.

As a second major precaution, the plant has been carefully designed to eliminate all pockets where liquid hydrogen cyanide might accumulate. Toward this end, all cyanide-carrying pipes have a minimum slope of 6 inches in every 10 feet. Sharp bends in piping or any other construction that might induce eddies in the flow of liquid hydrogen cyanide have also been avoided.

In addition to the polymer explosion hazard, hydrogen cyanide is also combustible, explosive in the usual sense, and, of course, poisonous. It has an ignition temperature of 585° C. and is explosive in concentrations between 11 and 60% (*22*). It has a toxic limit of 50 p.p.m. and may be absorbed through the skin. Although as a gas it is lighter than air and has a low persistence, it is a liquid below 26° C. and as such will persist for long periods.

Koppers' safety engineers recommend water as the best fire extinguisher for hydrogen cyanide since it will dissolve the material as well as cool it. A manually-triggered sprinkler system fed from a 75,000-gallon tank protects the stabilizer tanks. A dike around these vessels will contain a major spill for added protection.

The toxicity hazard has been beaten by rigid enforcement of regulations regarding the use of gas masks and rubber gloves and especially close attention to the prevention of skin absorption from contaminated clothing. All handling of hydrogen cyanide, even in small sample quantities, must be done within sight of another man. Safety showers and eyewash fountains have been provided generously.

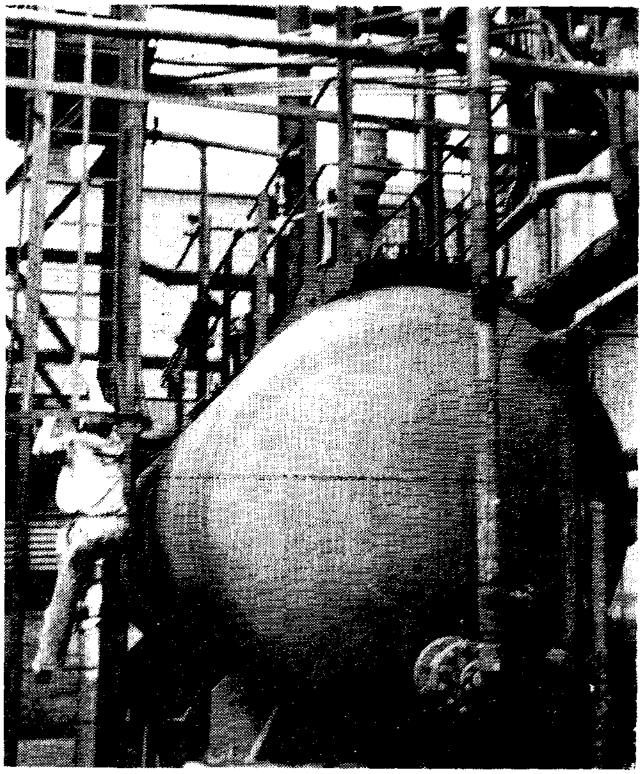
The hydrogen sulfide provides its share of headaches also. It is explosive when present in the air from 4 to 46%, and it will ignite at about 350° C. Furthermore, its toxic limit in the atmosphere is even lower than that of hydrogen cyanide, although its strong odor makes it easier to detect. However, the hydrogen sulfide is handled very little once it is isolated from the mixed gas; it goes directly to the sulfur burner and, consequently, does not introduce as widespread a hazard as the cyanide.

A monthly inspection of all vessels and lines is made to detect structural weaknesses and accumulations of polymer. Checks with cyanide test paper and then an actual gas analysis are made before anyone enters a process vessel.

Chemical Control

Most chemical analyses on the recovery process are run once a day. The mixed gas feed to the hydrogen cyanide absorber is assayed for hydrogen sulfide, hydrogen cyanide, carbon dioxide, and ammonia. The gas going to the sulfuric acid plant is checked for hydrogen cyanide and carbon dioxide. The stripping column feed is analyzed for hydrogen sulfide and hydrogen cyanide, and hydrogen cyanide is run on the stripper bottoms.

While hydrogen cyanide is being run into a stabilizer the tank is checked hourly for cyanide concentration by specific gravity and acid content by titration. If a charge is allowed to stay in the stabilizer for an extended period it is checked for acid stabilizer content once during each shift.



Quench Tank

Any vessel containing HCN can be dumped into this 6500-gallon water tank in 10 seconds

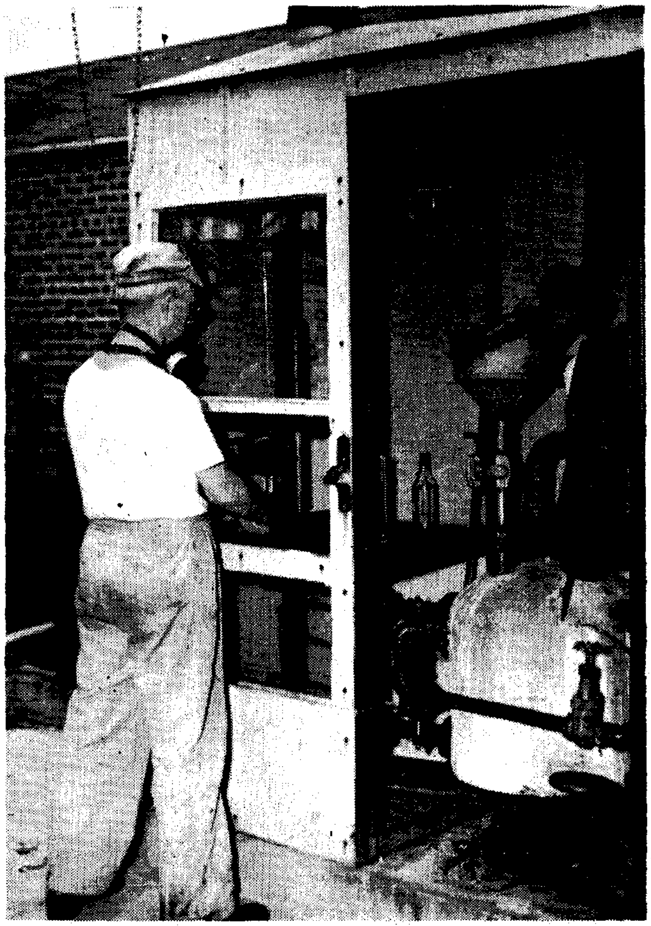
After a stabilizer tank has been filled it is sampled for specific gravity, hydrogen cyanide, total inhibitor content (base titration), phosphoric acid, sulfuric acid, sulfur dioxide, hydrogen sulfide, color, noncondensables, and a standard stability test involving color change after addition of ammonium hydroxide.

POTENTIAL OF THE PROCESS

The coke oven installation of the Koppers Co. at Kearny is a small one as coke oven batteries go these days. Some of the plants associated with steel mills process several times the coke handled at Kearny. However, the Kearny operation is large enough to afford typical operation conditions for a study of the hydrogen cyanide–hydrogen sulfide recovery system. The operating history now available indicates that the recovery operation will be economical. For simple hydrogen sulfide recovery it must compete with a number of other systems. However, that phase of the operation has been available as the "vacuum carbonate purification process" for some time and has proved its competitive position. Its adaptability to cyanide recovery now gives it an added advantage. It is obvious from the much-lamented current state of sulfur supplies that sulfur recovery from hydrocarbon gases will enjoy increasing importance in the years to come.

The present stimulation of the market for cyanides caused by the introduction of acrylonitrile fibers promises the hydrogen cyanide recovery operation a strong market for its product. The new cyanide plants springing up throughout the country give ample evidence that the chemical industry is expecting a boom in the demand for cyanide.

Although the use of cyanide in the form of a 30% sodium cyanide solution is unfamiliar to most consumers, Koppers' marketing



Chemical Analysis Equipment

Equipment adjacent to receiving tanks permits frequent and quick determinations of stabilizer in liquid HCN

experience to date indicates that enough cyanide applications can be modified to use this form of the material to absorb all potential production from coke oven gases. Pittsburgh Coke and Chemical Co. has had little trouble disposing of the solutions they have produced for the past 9 years to large unit consumers within short hauling distance of their plant. Similarly, Koppers has found a ready market for their high purity solutions, particularly among manufacturers of dyestuff intermediates and other fine chemicals. Of course there are some cyanide markets—such as the heat treating of steel which now represents the major single market for sodium cyanide and the recovery of precious metals—in which the cyanide solutions can never compete. Some of the solution has been sold to the plating industry.

It is not yet apparent whether the solution will be suitable for use in the production of acrylonitrile or adiponitrile for synthetic fiber; however, as fiber production absorbs large portions of the primary hydrogen and sodium cyanide supply, the sodium cyanide solutions should find ample applications as a replacement.

The solutions enjoy certain positive advantages, primarily in handling, over both gaseous hydrogen cyanide and solid sodium cyanide. The solutions do not present as serious a toxicity hazard as the gas and are much more easily assayed, measured, and metered than the solid. Furthermore, they can be shipped to the consumer and transferred within the plant with greater ease and less danger.

The gross economics of this process, like that of any by-product recovery, are exceedingly difficult to calculate. In most gas-producing operations it is essential that hydrogen sulfide be removed from the product either to avoid air pollution or corrosion of pipes and tanks or in the case of open-hearth operations to avoid sulfur contamination of the furnace charge. Hydrogen cyanide effluents, either as a gas or in solution, also present a pollution problem although their concentration is usually low enough to avoid being a public nuisance. Both of these gases are highly corrosive and gas plant operators say that their presence in the air at the plant site increases measurably the rate of external corrosion or surface coating failure.

The benefits derived from the elimination of hydrogen sulfide and hydrogen cyanide as plant effluents are at best intangible. Their value will vary with the atmospheric conditions around a given plant and with the pollution control regulations under which it must operate. However, preliminary calculations from the Kearny experience indicate that even disregarding these intangible benefits, the hydrogen sulfide and hydrogen cyanide recovery system should pay for its operation and amortize its initial cost within a reasonable plant life at the present market prices for the recovered materials. Should increased demand raise these prices or should regulations demand that these gases be removed from the plant effluents the operation will offer a definite economic advantage.

BIBLIOGRAPHY

(1) Bueh, J., Ger. Patent 112,459 (1898); Brit. Patent 9075 (1899).
(2) Coleman, W. H., Brit. Patent 27,908 (1912).
(3) Feld, W., Ger. Patent 178,635 (1905).
(4) *Ibid.*, 244,487 (1910).
(5) Forst, von der, *Ibid.*, 182,084 (1906).
(6) Foulis, W., Brit. Patent 9474 (1893).
(7) Gluud, W., "International Handbook of By-Product Coke Industry."
(8) Gluud, W., and Riese, W., Ger. Patent 551,074 (1929); *Ber. Ges. Kohlentech.*, 3, 437–51 (1931).
(9) Gollmar, H. A., "Chemistry of Coal Utilization," pp. 947–1007, New York, John Wiley & Sons, 1945.
(10) Hempel, H., Ger. Patent 404,428 (1923).
(11) Knublauch, O., Brit. Patent 15,164 (1887).
(12) Kuster, H., *Brennstoff-Chem.*, **12**, 329–34 (1931).
(13) Kuster, H., dissertation, Braunschweig (1928); *Ges. Abhandl Kenntnis Kohle*, 11, 608–19 (1931–3).
(14) Lowry, H. H., editor, "Chemistry of Coal Utilization," pp. 1094–1124, New York, John Wiley & Sons, 1945.
(15) Mueller, M. E., *J. Gas Lighting*, **112**, 851–5 (1910); *Proc. Am. Gas Inst.*, **5**, 231–51 (1910).
(16) Olive, T. R., *Chem. Eng.*, **57**, No. 10, 103–7 (1950).
(17) Ramsburg, C. J., U. S. Patent 1,389,980 (1921).
(18) Rowland, W. L., *Ibid.*, 465,600 (1871).
(19) Schreiber, F. D., *Ibid.*, 2,110,244 and 2,113,002 (1938).
(20) Shaw, J. A., *Ibid.*, 2,028,124–5 (1936).
(21) Sperr, F. W., Jr., and Hall, R. E., *Ibid.*, 1,533,773 (1925).
(22) Walker, M., and Eldred, D. N., IND. ENG. CHEM., **17**, 1074–81 (1925).
(23) Wilton, J., *Gasbeleucht*, **37**, 108 (1898).

Processing Equipment

(1E) American Iron & Steel Institute, New York, N. Y., (ASTM A167-44, Grade 3), C = 0.20%; Mn = 2% max.; P = 0.035% max.; S = 0.030% max.; Si = 1.0% max.; C_2 = 18–22%; Ni = 8–11%.
(2E) Fischer & Porter Co., Hatboro, Pa., Rotaweir flow proportioner.
(3E) Harris Pump and Supply, Greenville, S. C., 1-inch, DS6-2, Dayton Dowd type.
(4E) Heresite and Chemical, Inc., Manitowoc, Wis., Herecol.
(5E) Industrial Process Engineers, Newark, N. J., gear motor drive type.
(6E) Ingersoll-Rand, New York, N. Y., Cameron No. 1 Class MCS, single-stage pump.
(7E) Lapp Insulator Co., Inc., LeRoy, N. Y., Lapp Pulsofeeder CPS-1, piston type, Monel.
(8E) Tabor Pump Co., Buffalo, N. Y., Vertical Type No. C-2, 1-hp. sump pump.
(9E) Tri-Clover Manufacturing Co., Kenosha, Wis., Tri-Clover pipe connections.
(10E) York Corporation, York, Pa., 363W York 20-hp. refrigeration units.

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