APPLICABILITY OF COKE PLANT WATER TREATMENT TECHNOLOGY TO COAL GASIFICATION

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Abstract

Historically, some of the most profound early waste treatment research was performed in Europe on liquors from coke and gas plants. The early studies demonstrated that wastewater technology developed for coal gas, producer gas, and by-product coke plants was transferable. It follows that much of wastewater treatment technology developed recently for by-product coke plants will be transferable to tar-producing coal gasification processes. It is expected that the development of virgin wastewater treatment technology will be required for coal gasification processes that operate under tar-free conditions.

Activated sludge technology is adaptable to treatment of condensates from tar-producing coal conversion processes. The application of the data base available from coke plant waste treatment will reduce a research project to a developmental project at a vast saving in time and effort. Coal condensates may be deficient in trace element nutrients such as phosphorous, magnesium, and potassium. Evaluation of nutrient adequacy is recommended in developmental studies. Effluent polishing by dissolved air flotation is worthy of consideration inasmuch as the process is more capable of handling slugs of suspended solids than are filters. In addition, the float separated from the flotation process is a concentrate rather than a dilute filter backwash.

Preliminary absorption of halides is a concept that has potential for improving water management at coal gasification facilities. The separation of a low volume, high salt concentrate would reduce disposal problems and increase the feasibility of water reuse.

Gas lighting with coal-derived gas and water-borne collection of sewage commenced in the cities and towns of England in the early nineteenth century. The technology soon spread throughout Europe and to the Americas. The adoption of gas and sewage technology in conjunction with a large increase in population resulted in gross pollution of receiving waters. A Royal Commission on Sewage Disposal was appointed in 1898 to report on methods for the treatment and disposal of sewage and trade wastes. Not surprisingly, coal gas plant liquors were among the trade wastes included in the early investigations. The evolution of the studies has been documented elsewhere[1,2,3].

A review of highlights of previous studies would show that near the turn of the century studies with biological filters had determined that spent ammonia liquor from a gas plant could be treated as a 0.5 percent admixture with domestic sewage. By 1911, it had been demonstrated experimentally that gas plant ammonia liquor could be treated for substantial periods on biological filters by recirculation of effluent without a requirement for dilution with sewage. The experiments employed recirculation ratios of up to 19 to 1 and preceded by 25 years the frenzied rush in the domestic sewage field to patent every conceivable recirculation scheme for biological filtration.

The treatment of coke plant ammonia still waste in admixture with domestic sewage was tested early in the evolution of the activated sludge process. Based on experiments at Milwaukee in 1920 and subsequent studies, Mohlman[4] concluded that admixtures containing 30 to 40 mg/l of phenol were acceptable for the activated sludge process. He also concluded that admixtures containing 25-35 mg/l phenol were acceptable for intermittent sand filtration. Nolte[5] in the early Thirties, employed the addition of nutrient phosphate to ammonia liquor to enable experimental treatment by activated sludge without domestic sewage dilution.

The recognition of the nutritional deficiency of ammonia still waste was an important observation inasmuch as the performance of biological treatment on undiluted waste had been unreliable over sustained periods of operation. Prototype activated sludge plants were installed at coke plants in Europe and

North America in the early Sixties[6,7,8,9]. The treatment performance has been highly impressive but problems have been experienced in regard to consistency. Activated sludge installations at coke plants have proliferated in recent years.

Thus an analysis of early research on biological treatment of ammonia liquor suggests that the trend of original studies tended to be on liquors from coal gas plants. The result of the studies were somewhat inconsistent but were shown to be transferable to coke plants and to producer gas plants. It follows that many of the refinements in biological treatment more recently developed at coke plants will be transferable to tar producing coal gasification technology. Tar-free coal conversion processes are expected to require the development of virgin waste treatment technology.

Improved gas cleaning technology is being installed at modern coke plants. Coke plant gas cleaning technology is expected to be applicable to the cleaning of cooled producer gas for industrial consumption, but modification would generally be required for the production of substitute natural gas from coal for interstate pipeline transmission.

CURRENT STATUS

Gas Cleaning

Upgraded gas cleaning and water treatment technology have been employed in recent coke plant installations. A generalized block diagram representative of coke plant gas cleaning is given as Figure 1. Primary cooling to about 90° F is advocated to provide for early removal of naphthalene to minimize deposition of naphthalene during gas transport. High efficiency electrostatic tar removal with back-up capability is employed to protect subsequent by-product processes. The selection of the ammonia recovery process depends upon projections of marketability of the recovered by-products, and gas quality criteria. Some recent plants employ the Phosam process for indirect recovery of ammonia as anhydrous ammonia—which offers maximum flexibility for the marketing of the by-product. However, the simpler recovery of ammonia as ammonium sulfate is still the most popular method. When coke plants recover sulfur as sulfuric acid, some of the acid can be consumed in the ammonium sulfate by-product operation.

The trend at modern coke plants for desulfurization has been to employ neutralization processes using ammonia liquor or other alkalies as absorbent, or oxidation processes such as Stretford. A myriad of desulfurization process alternatives exist commercially, but processes applicable to coal gas desulfurization are restricted to those that operate efficiently in the presence of extraneous sulfur and cyanide compounds. The selection of the desulfurization process is dependent upon the design of the gas treatment system and the desired by-product (e.g., H_2SO_4 or S). Neutralization processes are normally designed to achieve gas residuals of 0.1 to 0.3 gr/dscf hydrogen sulfide, whereas oxidation processes can be designed to achieve residuals of 0.01 gr/dscf hydrogen sulfide. Most of the demonstrated desulfurization processes are of limited effectiveness for the removal of organic sulfur compounds (e.g., COS and CS_2).

Ammonia Stripping

The ammonia contained in the flushing liquor condensate separated during primary cooling is recovered by steam stripping. If the coal feed contains appreciable chlorides, a substantial fraction of the ammonia in the flushing liquor will be present as ammonium chloride or other fixed ammonia. Alkaline stripping is required to spring fixed ammonia. Modern ammonia stills at coke plants are usually designed for a residual of about 50 mg/l of total ammonia in the still bottoms. A two-stage stripping operation is usually employed with lime or caustic soda being added to the second stage to spring ammonia from strong acid anions.

Some modern stripping processes, such as Chevron in the petroleum industry and Cyam of U. S. Steel, employ controlled pH in the first stage to preferentially separate weak acid gases (HCN, H_2S, and CO_2). The result is improved biological plant effluent quality inasmuch as cyanide is somewhat refractory to biological processes. In addition to the previously mentioned processes, Bethlehem Steel Company[10] has developed a single-stage alkaline stripping process that features low

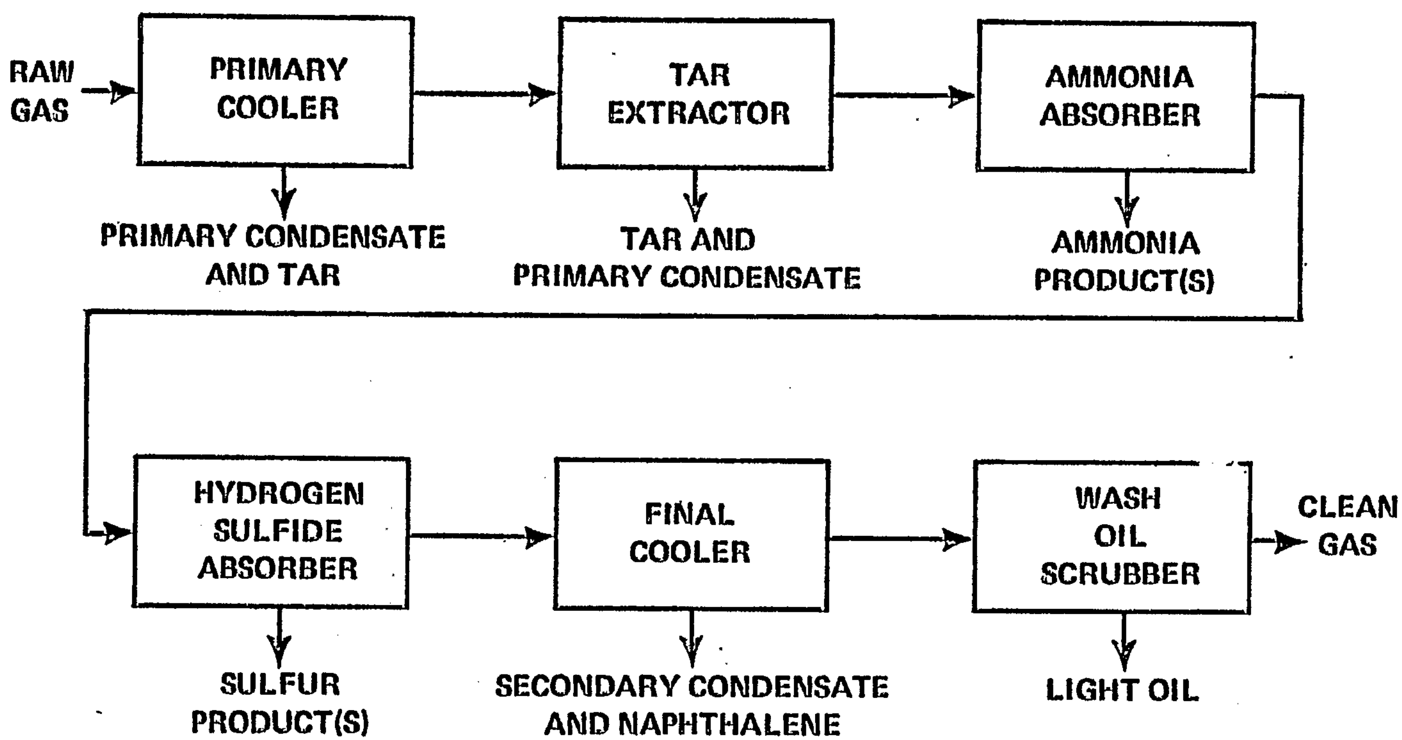

Figure 1. Schematic of coke plant gas purification.

steam consumption and improved ammonia stripping efficiency.

Wastewater Treatment

The present trend at coke plants for wastewater treatment is towards the activated sludge process. The process features remarkable removal of phenol to sub mg/l levels but usually provides somewhat less impressive removal of thiocyanates and cyanides. The limitations of the process include effluent color and occasional inconsistencies in respect to discharge of suspended solids, thiocyanates, and cyanides. Efficient removal of ammonia in the stripping operation will encourage consistent degradation of thiocyanate and cyanide.

Process Performance

The composition of the primary condensates from tar-producing coal gasification processes are basically similar to primary condensates from coke plants operating on similar coal. The gas volume per ton of coal is much larger from gas plants than from coke plants which results in lower concentrations of impurities in the gas and larger units for gas purification. The larger gas volume would also be expected to produce a larger volume of a more dilute primary condensate per ton of coal feed.

The combination of similarity in composition and historical record of similar treatability characteristics should enable the transfer of sufficient gas cleaning and waste treatment technology to justify the substitution of a development study for a much more involved research study. That is, for purposes of experimental design, it can be projected: (a) that a biological process will perform well in the 80 to 95° F range, (b) that pure culture processes are impractical, (c) that the food-to-microorganism ratio will be less than 0.2 lb BOD/lb volatile suspended solids, (d) the yield of cell substance will be from 0.2 to 0.5 lb/lb BOD removed, and (e) that the final clarifier unit solids loading will be from 20 to 30 lb/day=sq ft. It can be further projected that the following concentration ranges will be representative of the settled effluent: (a) suspended solids 60 to 200 mg/l, (b) phenol 0.05 to 0.5 mg/l, (c) thiocyanate 1 to 10 mg/l, (d) cyanide 1 to 10 mg/l, (e) sulfide 0.01 to 0.3 mg/l, and (f) BOD 50 to 150 mg/l. The availability of such guideline information limits the scope of investigative effort and is therefore of great assistance in the design of developmental studies to rapidly verify expected process performance on specific waste flows.

Biological processes are capable of producing a range of effluent qualities. The penalties associated with increased performance are larger aeration units, larger clarification units, and increased energy consumption. Energy consumption is derived primarily from power expended for aeration and agitation of culture—plus heat requirements to maintain acceptable culture temperature in cold weather. It is important that aeration/agitation methodology not adversely affect settleability of the activated sludge culture. Research is indicated to identify optimized design concepts that achieve process objectives at low energy consumption and minimum cost.

Process Development

A vast literature of inconsistent study findings is available to designers of activated sludge processes for coke plants and gas plants. Some degree of rationalization of study findings is sometimes possible by interpretation of literature information within the constraints of process principles. Parenthetically, it should be recognized that coal gas condensates are highly colored and chemically complex so as to pose analytical enigmas. Reported values of biochemical oxygen demand (BOD) may reflect interference due to toxicity. Developmental analytical techniques are recommended for reliable determination of BOD [11]. Chemical oxygen demand tests, using dichromate or permanganate, are subject to interference from chlorides which often are present in abundance. Compensation for chloride interference was tedious prior to modification of the COD test in 1963. The primary condensates contain a host of phenolic substances which may or may not be reported by particular analytical methodology employed in literature studies. Free cyanide will be in equilibrium with metal cyanide complexes and thiocyanate. Therefore, the concentration registered by analysis may depend upon the processing of the sample. Thus, discretion is indicated in the interpretation of literature information. Improved interpretation of previous studies would be possible if reliable correlations between parameters were developed through research.

Most studies of biological treatment of ammonia still wastes have concluded that phosphate is the only mineral nutrient supplement required; whereas some studies advocate addition of phosphate, magnesium, and potassium[12]. Process fundamentals suggest that the waste substrate should supply the microorganisms with the mineral composition required for synthesis of cell substance, possibly similar to the guideline composition given in Table 1. The elements carbon, hydrogen, oxygen, nitrogen, and sulfur are inherently available in adequate quantity with activated sludge treatment of ammonia still waste. The elements phosphorous, sodium, potassium, calcium, magnesium, and iron are normally present in flushing liquor in low concentrations unless opportunity is provided for leaching from gas-borne particulates. Ample calcium is present after stripping in a lime still, but the process effects virtually complete precipitation of magnesium and phosphate. Stripping in a caustic still induces precipitation of calcium and magnesium.

Table 2 presents a hypothetical comparison of approximate quantities of the nutrients present in Synthane coal gasification process condensate and coke plant ammonia still feed, versus bacterial composition from Table 1. The elements contained in Table 2 are of low volatility and therefore tend to report to the char and fines during gasification or coking. The concentration levels in the condensate are presumably dependent upon the degree of leaching from the fines. The coke plant ammonia still feed reflects contributions from Phosam purge and light oil refining as well as flushing liquor. The indicated calcium deficiency would become a surplus if lime were utilized in the ammonia stripping operation. The indicated iron deficiency is generally less at coke plants where higher concentrations of cyanides are present and there is more opportunity for leaching of fines. The difference between the requirement and presence of potassium in the condensate suggests a deficiency, but most coke plant biological treatment processes perform well without supplemental potassium nutrient. It is conceivable that at coke plants potassium is leached from fines or present in other feeds connected to the biological plant.

To date, biological treatment of coke and gas plant wastes has been characterized by limited process stability. Until such occasional problems are resolved. the possible role of trace nutrients should be kept under consideration—especially in view of the variability in coal feeds and the importance of magnesium as an enzyme constituent. Most studies have indicated that phosphate is the only nutrient addition required for biological treatment of wastewater from coke and gas plants, but high efficiency ammonia stripping may lower residuals of magnesium and calcium (caustic stills) and revisions in gas cleaning may reduce the opportunity for leaching from gas-borne particulates. Lower gas cyanide levels could also limit the leaching of metals from particulates. Nutrient requirements for biological processes can be evaluated relatively simply by experimental procedures involving several culture transfers in developmental type determinations of BOD rates[11]. Such evaluations are recommended on a case-by-case basis pending resolution of the question.

Dilution of wastewater is sometimes advocated for biological treatment of coke plant wastes. Dilution will lower the exposure of the microorganisms to refractory substances such

TABLE 1

REPRESENTATIVE ELEMENTAL COMPOSITION OF DRY BACTERIAL PROTOPLASM

	Wt.%		Wt.%
C	50	Na	0.7
H	5.8	K	0.5
O	27	Ca	0.7
N	12	Mg	0.5
P	2.5	Fe	0.1
S	0.7		

Adapted from: R. E. McKinney (13)

TABLE 2

HYPOTHETICAL COMPARISON OF TRACE NUTRIENT COMPOSITION VS. INDICATED BACTERIAL REQUIREMENT FOR SYNTHANE CONDENSATE AND COKE PLANT AMMONIA STILL FEED

	Indicated Requirement lb/1,000 tons	Synthane Condensate[a] Indicated Present lb/1,000 tons	Still Feed Indicated Present lb/1,000 tons
Ca	10	5.1	5.9
Fe	2.8	0.28	3.2
K	14	0.78	16
Mg	14	1.6	3.5
Na	20	19	95
P	70	0.12	57

[a]Illinois #6 Coal, Forney, A. J. et al. (14).

as salts and hard organics, but in the completely mixed activated sludge process, degradable substances are present at effluent concentration levels—suggesting minimum justification for dilution. Dilution can assist in the control of calcium sulfate precipitation resulting from reaction between residual calcium from lime stills and sulfate formed during aeration by bio-oxidation of thiocyanate and reduced sulfur compounds.

Effluent Polishing

High dissolved solids in the feed to activated sludge processes has been associated with increased effluent suspended solids. In addition, the culture of activated sludge systems sometimes loses its ability to settle which results in increased discharge of suspended solids with the effluent. Such periods are sometimes termed "upsets." However, if the process is viewed as operating in dynamic equilibrium rather than in steady state, it is conceivable that periods of loss of culture settleability could be a part of the normal spectrum of operations. In any event, the discharge of excess suspended solids is often difficult, and sometimes impossible, to correct by adjustment of plant operational practices. The implementation of effluent polishing may be required to achieve effluent suspended solids levels associated with domestic sewage activated sludge plants. Granular media filtration has been employed for effluent polishing, but lamella dissolved air flotation has been demonstrated as superior for the capture of significant overages of suspended solids[15]. The flotation process was capable of clarifying feeds with 300 mg/l suspended solids to the 25 to 35 mg/l range. Dissolved air flotation was also advantageous in that the captured solids are collected in a low volume float instead of a large volume backwash.

Research Trends

Preliminary absorption of halides is a concept that has potential for improving water management of coal conversion processes. The concept, illustrated in Figure 2, features a controlled temperature—controlled volume scrubbing operation followed by demisting to capture strong acid salts in a low volume purge. The asset of the concept is that subsequent condensates are low in strong acid salts and therefore more applicable to incorporation in recycle circuits. The low volume characteristic of the purge concentrate will facilitate disposal

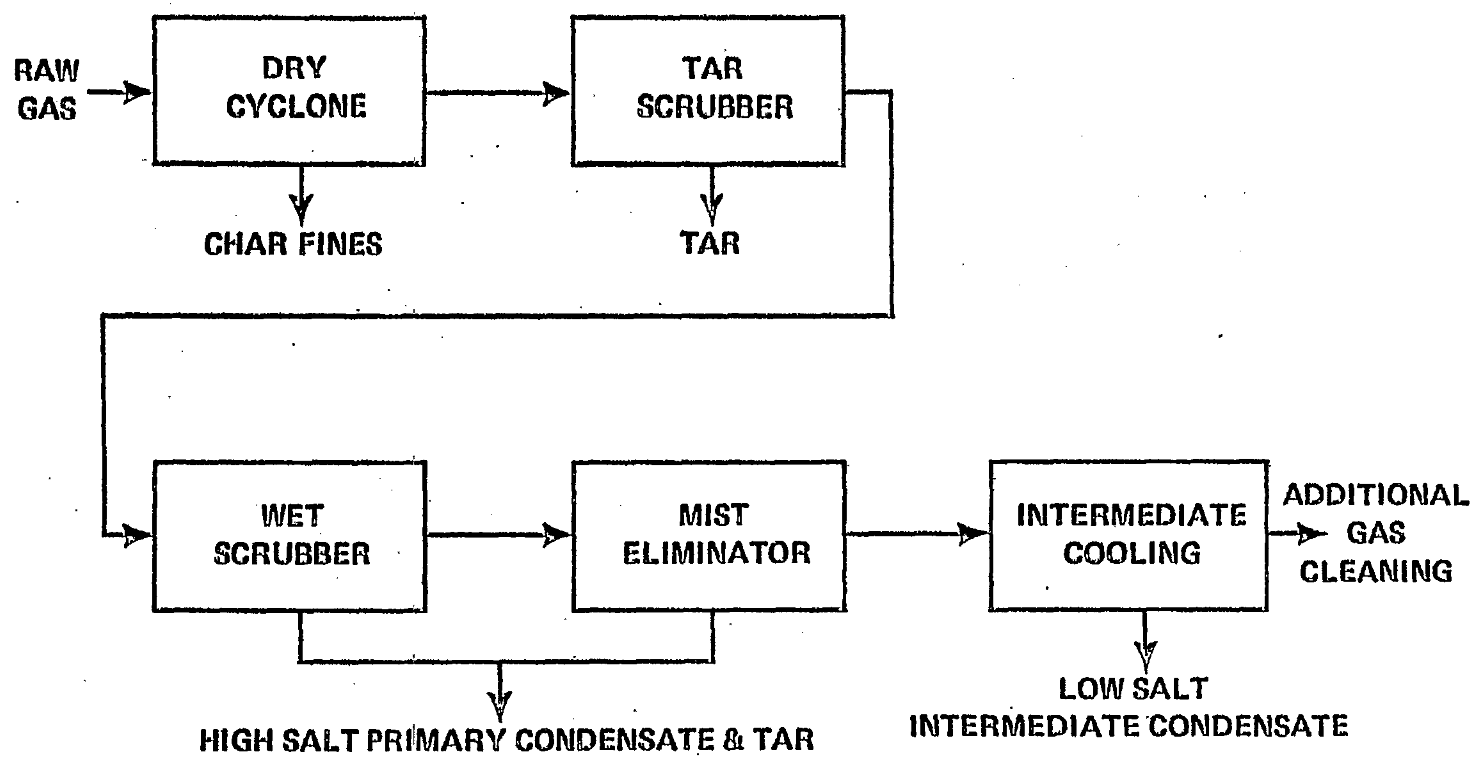

Figure 2. Schematic of preliminary absorption of halides.

or recovery, but the fate of the concentrate is an unresolved aspect of the concept.

SUMMARY AND CONCLUSIONS

Modern coke plants provide fuel gas that is highly acceptable for many industrial purposes. Prior to use, the gas is processed for removal of particulates, naphthalene, ammonia, hydrogen sulfide, and light oils. The proven process technology employed for coke oven gas cleaning is adaptable to the cleaning of cooled producer gas for industrial consumption, but process revisions would be required for the cleaning of substitute natural gas. On a per ton of coal basis, larger volumes of gas and larger volumes of a more dilute condensate will be derived from producer gas operations than from coke plant operations.

The activated sludge process is commonly employed for wastewater treatment at modern coke plants. The process can be designed to provide excellent removal of phenol, thiocyanate, BOD, and cyanide. The limitations of activated sludge treatment of coke plant waste are dark color in the effluent and occasional inconsistencies in performance relative to thiocyanates, cyanides, and suspended solids. Effluent polishing by dissolved air flotation is worthy of consideration inasmuch as the process is better able to handle slugs of suspended solids than filters. In addition, the float separated from the flotation process is a concentrate rather than a dilute filter backwash.

Activated sludge technology is adaptable to treatment of condensates from tar producing coal conversion processes. The application of the data base available from coke plant waste treatment will reduce a research project to a developmental project at a vast saving in time and effort. Coal condensates may be deficient in trace element nutrients such as magnesium and potassium. Evaluation of nutrient adequacy is recommended as part of developmental studies. The nutrient situation may differ depending upon the efficiency of processes for the removal of particulates and ammonia.

Preliminary absorption of halides is a concept that has potential for improving water management at coal gasification facilities. The separation of a low volume, high salt concentrate would reduce disposal problems and increase the feasibility of water reuse.

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