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Survey of Biological Treatment in the Iron and Steel Industry

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Survey of Biological Treatment in the Iron and Steel Industry

by

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ABSTRACT

This study was conducted with the objective of surveying the current uses of biological methods of treatment for wastewaters produced by the U.S. iron and steel industry.

Topics considered in this survey included identification and characterization of wastestreams receiving treatment on a pollutant component basis, capabilities of biological treatment, advantages and disadvantages of various biological systems, nitrification and denitrification, current utilization of biological treatment by the industry and possible options to standard biological methods.

Results of the survey indicate that coke plant wastewaters, particularly waste ammonia liquor, containing phenol, ammonia, cyanide, thiocyanate, carbonate, sulfide, oil, suspended solids and dissolved solids are the primary wastewater source for biological treatment units. Advantages of biological treatment include the capability of meeting the 1983 BATEA guidelines for phenol removal and providing reduced levels of ammonia, cyanide and thiocyanate. Disadvantages include susceptibility of the system to upset due to increases in influent temperature or component concentrations, and in some cases, cost.

Biological treatment of wastewater is capable of attaining as high as 99% removal of phenolic constituents. Increased retention times, in conjunction with other operational parameters, will allow for increased removal of ammonia, cyanide and thiocyanate. Where nitrification and denitrification units are provided, as much as 90% of influent ammonia may be oxidized.

Current use of biological treatment in the iron and steel industry for coke plant wastewaters is limited. Where it is utilized, interest is centered upon phenol removal. Suspended growth systems are the biological methods employed, with little attention paid to fixed growth, either for primary treatment, roughing or polishing.

Options to standard biological treatment include physical/chemical treatment and variations of the activated sludge process. Pilot studies have shown some methods to be competitive with biological treatment.

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SECTION 1

INTRODUCTION

The American iron and steel industry comprises approximately 400 plants. Of this number, however, only 63 are classified as integrated mills, that is, a steel plant which has facilities for coking, iron, and steel making, and for rolling and finishing. Steel production from such a plant requires between 84,500 to 135,200 ℓ of water per tonne (metric ton) of steel produced. Of this amount of water, 20-40 percent comes into direct contact with process gas or product. Major water-using operations are coke plants, sintering, blast furnace, steelmaking, hot forming, pickling, cold rolling, and coatings.[1] Of these operations, the wastewater most commonly treated by biological processes is the waste ammonia liquor from coke byproduct plants.

During the 1920s production from byproduct coke ovens surpassed that of beehive ovens. This resulted from three advantages of the byproduct process: 1) improved coke quality, 2) the chemical recovery made possible by the process, and 3) the fact that the byproduct process produced significantly less air pollution.

Since the mid-1960s, coke production has remained constant at 54-63 million tonnes per year. Chemical recovery, however, has grown progressively less economical. Concurrent with this change, and particularly since the advent of the Federal Water Pollution Control Act Amendment of 1972 (PL 92-500), attention has been directed toward a fourth difference between the coking operations. That difference is the water pollution problems which are a direct result of chemical recovery processes.

The present study has focused on wastewaters treated by biological methods, problems associated with these methods, and preventive measures to avoid these problems.

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[1]Kwasnoski D. Water Pollution Control in an Integrated Steelplant. International Metallurgical Reviews, Vol. 20, 1975, pp.137-145.

SECTION 2

CONCLUSIONS

1. Biological methods of treating coke plant wastewaters are capable of meeting the 1983 Best Available Technology Economically Achievable (BATEA) guidelines for phenolics and possibly ammonia.

2. Although biological oxidation of wastewaters is an accepted treatment method, it is utilized by less than 20 percent of the integrated steel plants in the United States. Where biological treatment units are operating, they are utilized essentially for phenol removal, with little attention given to other pollutants.

3. The variable nature of coke plant wastewater will produce system shock and upset. Methods utilized to avert upset conditions are 2 to 7 day equalization capacity, auxiliary basins, and dilution.

4. After a system is upset, recovery times will vary from 24 hours to 2 or more weeks. Recovery time varies with the type of loading in the waste stream (e.g., high organic concentration) and its effect upon resident microorganisms.

5. Single-stage activated sludge systems will remove more than 99 percent of the phenolic compounds with a retention time of approximately 24 hours. Increased retention times and proper hydraulic loadings will provide greater levels of ammonia, cyanide, and thiocyanate removal.

6. A multi-stage activated sludge unit with carbonaceous, nitrification, and denitrification tanks will provide high levels of phenolic and ammonia degradation. These units are, however, difficult to operate and maintain due to the susceptibility of the microorganisms involved to fluctuations in temperature and component concentrations in the effluent.

7. Coke oven wastewaters are deficient in certain nutrients required by the resident microorganisms. In single-stage activated sludge systems phosphate is provided as phosphoric acid.

8. Polishing steps in conjunction with biological treatment are not utilized due to expense. Where polishing is necessary, a physical/chemical treatment system may be selected rather than biological.

9. The applicability of rotating biological contactors and trickling filters in the treatment of coke plant wastes has received little attention because of wastewater composition and limited treatment capacity.

10. Real estate requirements are a function of the volume of wastewater and the levels to which it is to be treated.

11. There is question as to whether biological treatment will remain competitive with physical/chemical processes. As additional waste streams are added or levels of treatment increased, the size and therefore cost of the system increases.

SECTION 3

RECOMMENDATIONS

1. The economic feasibility of biological treatment vs. physical/chemical treatment must be studied in terms of what compounds are removed and in what quantities, and the treatment of additional wastewaters.

2. Economic and operational studies are necessary to determine the feasibility of the use of trickling filters and rotating biological contactors as roughing or polishing steps in conjunction with activated sludge.

3. More investigations of multi-stage and parallel treatment systems are necessary. All operating problems and solutions must be defined and system economics evaluated.

4. Methods to decrease "down time" following system upset must be developed. Such materials as dried biological matter should be considered.

5. Automatic on-stream analyzers should be utilized. Such units would detect wastewater variations before reaching the treatment system and automatically shunt the "loaded" wastewater to an auxiliary basin from where it could be added to the treatment system at a controlled hydraulic rate.

6. Research is necessary to clarify methods which will reduce retention times.

7. Cooperative pilot plant studies and demonstration projects are necessary for the elucidation of process problems and solutions in various biological and physical/chemical treatment processes. Favorable results and reliable operation would probably result in an increased interest on the part of industry.

8. Possible uses of treated coke plant wastewater should be determined.

9. Studies should be conducted to identify treatment methods used by other industries, and their possible application to the iron and steel industry. Such studies will require detailed evaluations of operating characteristics, treatment potential, and economics.

10. Multi-media effects of various operations such as stripping should be investigated with regard to air pollution.

SECTION 4

THE COKING PROCESS AND WASTEWATER SOURCES

The coking process involves heating coal (average charge, 14-18 tonnes) in the absence of air for 16-20 hours at temperatures between 870°-1260°C. Organic compounds within the coal are released as gases and drawn off through exhaust pipes for processing and recovery. Wastewaters orginate from these prime sources: moisture within the coal during decomposition, and gas treatment/chemical recovery (process water). The largest wastewater fraction is process water and may account for 60-85 percent of the total flow of 400-1000 ℓ/tonne of coal. Process waters may be grouped into six categories:[2]

1. tar still wastewater
2. waste ammonia liquor
3. ammonia absorber and crystalyzer blowdown
4. final cooler wastewater blowdown
5. benzol plant wastewater
6. desulfurizer and cyanide stripper wastewater

Wastewaters from coke plants are saline and contain a variety of pollutants such as ammonia, phenols, cyanide, thiocyanate, sulfides, oil and grease, and suspended solids. In PL 92-500, the E.P.A. has indicated the maximum allowable concentration of these constituents by 1983, as shown in Table 1.

TABLE 1. 1983 EFFLUENT LIMITATIONS FOR BYPRODUCT COKE OPERATIONS BASED ON (340 ℓ/tonne) DISCHARGE VOLUME

Pollutant Parameter	Concentration, mg/ℓ
Cyanide	0.25
Phenol	0.5
Ammonia as N	10
Sulfide	0.3
Oil and grease	10
Suspended solids	10
pH	6.0-9.0

[2]Dunlap, R.W., and F.C. McMichael. Treatment Technology is Suggested for Reducing Coke Plant Effluent. Environmental Science and Technology, 10(7): 654-657, 1976.

SECTION 5

BIOLOGICAL OXIDATION OF COKE PLANT WASTEWATERS

Biological oxidation of coke plant wastewaters can best be understood in terms of certain fundamentals of the oxidative process involved. These include the fact that the microorganisms involved are ubiquitous, require an organic or inorganic carbon source, nutrients, controlled pH and temperature, and in most organisms, require molecular oxygen. Based on these needs, microorganisms will multiply according to species predominance and diversity.

Organisms that require molecular oxygen, either dissolved in water or from the air, are known as aerobic microoganisms. Those which exist in the absence of molecular oxygen are anaerobic microorganisms. A number of anaerobic species may obtain oxygen from radicals such as nitrate (NO_3) or sulfate (SO_4), and are termed denitrifiers or sulfate reducers. In the development of most biological wastewater treatment units, however, aerobic microorganisms are of the greatest interest.

BIOLOGICAL TREATMENT SYSTEM DESIGN

Biological wastewater treatment systems fall into two categories: suspended growth (activated sludge) and fixed growth (trickling filters and rotating biological contactors).

Suspended Growth Systems

Of the various types of activated sludge systems, two of the most common are the completely-mixed and contact-stabilization versions. The flexibility of the former in allowing adjustments in wasteload variations, makes it a very popular treatment process for wastewaters containing a relatively high organic concentration. It has seen some success in the treatment of industrial wastes with a high concentration of suspended and colloidal organics. During the contact stabilization process, biological solids are brought into contact with the wastewater for a short time period. They are then separated and reaerated in order to degrade sorbed organics.

Activated sludge plant design should consider four major aspects:

1. influent composition stability
2. mixing and aeration
3. nutrient addition
4. retention time

Influent Composition Stability--

Batch or intermittent wastewater operations are often included in the waste to be treated. The fluctuating composition of the waste must be minimized if effluent of consistent quality is to be produced. A holding tank may be utilized to offset such fluctuations, but the addition of the contents of the holding tank to the unit must be carefully monitored.

Mixing and Aeration--

Concentrations of components which are toxic to the microorganisms occurring in activated sludge units must be reduced to low levels throughout the aeration tank. Rapid dispersion of the influent stream through the vessel by a completely mixed system will provide the most favorable environment for efficient treatment.

Aeration provides the oxygen levels required by the microorganisms for respiration and also allows the sludge to make contact with the components to be treated.

Nutrient Addition--

The amount of nutrient addition necessary varies from wastewater to wastewater. Generally, only phosphate is necessary and is added as phosphoric acid.

Retention Time--

Retention time has a great influence on the size and cost of a treatment unit, therefore this parameter should be minimized as much as possible, though a sufficient margin of safety should be built in to handle overloads. The retention time has a direct effect on effluent quality. However, theoretical retention times for given wastewater component concentrations may have to be increased due to organic and inorganic inhibitors or dilution.

Another process capable of equaling the organic removal of activated sludge systems is the aerated lagoon. These lagoons, however, are less desirable options. They are sensitve to temperature fluctuation and need much more real estate due to the longer hydraulic retention time required for a given degree of treatment, as measured in days rather than hours.

Fixed Growth Systems

Trickling filter systems generally utilize a rock or synthetic substrate upon which a biological film will grow. As the wastewater passes over this medium, soluble organics are extracted and degraded. Only the top 1-2 mm of the film is completely aerobic. As depth increases the microorganisms found are facultative anaerobes and finally obligate anaerobes which do not perform as the system is intended. As a result there is a build-up of inactive biological material. This process has seen use as a roughing or pretreatment process for wastewaters due to its inability to produce consistently high-quality effluent.[3] Trickling filters are used at some plants for treatment of in-plant sewage and in at least one case, the effluent is recycled to other water using operations.[4]

The rotating biological contactor is another type of fixed growth system which has received attention in recent years. In this process a thin, large diameter disc provides the substrate upon which the biological film grows. Many discs are placed closely together on a rotating shaft. Approximately 1/3 of the rotating disc is immersed in a trough through which the wastewater flows. Aeration occurs when the disc is brought through the water and into the air.

The rotating disc system provides certain advantages over both the trickling filter system and activated sludge process. In particular, the rotating disc provides a shearing force which prevents the build-up of inactive biological material seen in the trickling filter and provides the spread of oxygen through the biological film at all times. The unit also requires less energy for operation than activated sludge systems, and may do without sludge recirculation, which reduces sludge handling problems.[5] The rotating disc does, however, have a disadvantage. In order to treat wastewaters containing high concentrations of organics, it requires many discs, which leads to a high capital cost. Additionally, if the organics are refractory, long contact periods are required and it is possible that less than optimal reduction will be attained.

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[3] Ford, D.L., and L.F. Tischler. Biological System Developments. Chemical Engineering, 84(17):131-135, 1977.

[4] Hydrotechnic Corporation. Integrated Steel Plant Pollution Study for Zero Water and Minimum Air Discharge. Progress Report, EPA Contract 68-02-2626, July 7, 1977.

[5] The British Carbonization Research Association. The Biological Treatment of Coke Oven Effluents: Laboratory Studies Using the Rotating Disc Process. Carbonization Research Report No.23, December 1975.

TREATMENT OF COKE PLANT WASTEWATER CONSTITUENTS

Constituents of coke plant wastewaters which are of concern to regulatory authorities and are at the same time amenable to biological treatment are phenol, ammonia, cyanide, thiocyanate, and sulfide. Typical concentration ranges are shown in Table 2.

TABLE 2. CONCENTRATION RANGES OF COKE PLANT WASTEWATER CONSTITUENTS[6]

Constituents	Range (mg/ℓ)
Phenolics	300-4000
Free Ammonia, as NH_3	1300-2000
Fixed Ammonia, as NH_3	2600-4000
Carbonate, as CO_3	2300-2600
Cyanide, as CN	10-100
Thiocyanate, as SCN	50-500
Oils and Tars	20-40
Suspended Solids	80-120
Total Dissolved Solids	4000-13,000

Phenol Oxidation

A number of miroorganisms capable of oxidizing phenolic compounds have been identified. Among these microogranisms are representatives of the genera *Pseudomonas*, *Bacillus*, *Achromobacter*, and *Micrococcus*. Certain strains have been reported to tolerate phenol in concentrations above 10,000 mg/ℓ.[7]

Many phenolic compounds, such as cresol, resorcinol, benzene, and catechol, etc., which are believed to be present in coke plant wastewater, have also been biologically oxidized.

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[6]Jablin, R., and G.P. Chanko. A New Process for Total Treatment of Coke Plant Waste Liquor. AICHE Symposium Series-Water, 70(136):713-722, 1973.

[7]DeFalco, A.J. Biological Treatment of Coke Plant Wastewaters. Iron and Steel Engineer, 52(6):39-41, 1975.

It is not uncommon to read of reported phenol removals of 99.8-99.9 percent.[8] These levels, however, are regulated by wastewater temperature, pH, and the tolerance of the microorganisms involved to other wastewater components such as ammonia, cyanide, and thiocyanate.

Cyanide Oxidation

Cyanide is produced during the cooling operation due to the formation of hydrogen cyanide. The hydrogen cyanide is highly soluble in water and therefore the gas cooling water will absorb the compound.

Cyanide removals of 10-87 percent have been reported in pilot plant operations. There has been some question whether the removal process is biological or air stripping.[8] The former, however, has been shown to be the case more than 99 percent of the time.[9]

Cyanide has also been shown to exert an inhibitory effect upon thiocyanate removal and nitrification. Free cyanide above 3 mg/ℓ completely inhibits thiocyanate removal, while nitrification does not commence until cyanide is reduced to levels below 0.5 mg/ℓ.[9]

Other researchers have shown that cyanide can be biologically treated when retention times are directly proportional to influent cyanide concentrations.[10] For high cyanide concentrations, however, this observation may be academic because of the capital costs which would be incurred in constructing a treatment unit with an adequate retention time.

Thiocyanate Oxidation

The oxidation of thiocyanate is considered the rate-controlling step in the biological oxidation of coke oven wastewater.[11]

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[8]Barker, J.E., and R.J. Thompson. Biological Oxidation of Coke Plant Waste. Paper presented at AISI Regional Technical Meeting, Chicago, 1971.

[9]Wong-Chong, G.M., and S.C. Caruso. Biological Oxidation of Coke Plant Wastewaters for the Control of Nitrogen Compounds in a Single-Stage Reactor. Report prepared for American Iron and Steel Institute.

[10]The British Coke Research Association. New Advances in the Biochemical Oxidation of Liquid Effluents. Coke Research Report No.64, March 1971,

[11]Pearce A.S., and S.E. Punt. Biological Treatment of Liquid Toxic Wastes, Part II. Effluent and Water Treatment Journal, 15(1):87-95, 1975.

Thiocyanate oxidation does not commence until most of the phenolic constituents of the waste liquor have been removed, and, as stated above, until cyanides have been reduced to 3 mg/ℓ. Thiocyanate also exerts an inhibitory effect upon nitrification, though not as extensively as cyanide.

It has been reported that thiocyanate removal may be obtained and retention times decreased by the addition of para-aminobenzoic acid.[10] Other researchers have indicated that reduced wastewater strength will lead to an increase in thiocyanate degradation.[8]

Ammonia Control

Biological control of ammonia is achieved through the process of nitrification-denitrification. This process is accomplished primarily by two specialized genera of bacteria, *Nitrobacter* and *Nitrosomonas*. The nitrification stage is oxidative when ammoniacal nitrogen is oxidized to nitrite by bacteria of the genus *Nitrosomonas* and the subsequent nitrite to nitrate oxidation is controlled by the genus *Nitrobacter*. Denitrification consists of reduction of oxidized nitrogen compounds to gaseous nitrogen. The process is controlled by many organisms (e.g., *Thiobacillis denitrificans*).

Coke oven wastewater frequently contains ammonia in concentrations as high as 2000 mg/ℓ. Biological organisms are not capable of existing in such an environment, thereby necessitating a means for ammonia reduction to levels amenable to biological treatment. This is generally accomplished with the use of an ammonia still which, if operating efficiently, will produce an effluent containing approximately 200 mg/ℓ free ammonia. If a still is not utilized, dilution water must be provided. This will increase the hydraulic load, giving increased retention times and either increased overflow or a larger and more expensive facility.

The oxidation of ammoniacal nitrogen to nitrite produces acid, with the resultant decrease in pH. Nitrification has been reported to be most efficient in the pH range of 7.8 to 8.3, which may be adjusted with sodium hydroxide.[12]

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[12]Adams, C.E., and W.W. Eckenfelder, Jr. Nitrification Design Approach for High Strength Ammonia Wastewaters. Journal of the Water Pollution Control Federation, 49(3):413-421, 1977.

Nitrifiers also require an inorganic carbon source for the synthesis of organic compounds necessary for metabolism. To a limited extent this inorganic carbon may be obtained from the wastewaster itself, but generally a material such as sodium carbonate must be added. Pilot plant studies indicate that a near optimum alkalinity concentration is approximately 100 mg/ℓ, which may be difficult to maintain.[8] This is due to conversion of alkalinity to carbon dioxide as pH is reduced by acid formation. Also, if lime is used for pH control in place of sodium hydroxide, calcium carbonate may be precipitated with the concomitant reduction in inorganic carbon, thereby limiting the system.

The requirements for denitrification are significantly different from those of nitrification. Denitrification proceeds anaerobically and also requires the addition of an organic, rather than inorganic carbon source. Among the carbon sources which have received attention are methanol, sucrose, methylethylketone, formaldehyde, acetone, glucose, and molasses, with methanol being frequently recommended.

Temperature, pH, and alkalinity are not as critical to denitrification as to nitrification; however, acid addition may be required if pH rises too high.

Ammonia control through nitrification and denitrification is extremely complicated. Many variables exist, any one of which can halt the treatment process. In pilot and laboratory studies, however, ammonia removals have been reported to exceed 90 percent.

SECTION 6

CURRENT UTILIZATION OF BIOLOGICAL TREATMENT PROCESSES

Of the 63 integrated steel plants in the United States, fewer than 20 percent are currently operating a biological treatment unit for wastewaters other than sanitary sewage.

TREATMENT METHOD SELECTION

The decision to construct a biological treatment system is based upon such criteria as cost, treatment potential, real estate availability, potential for upset and recovery, and prior experience with such units. This decision may be precipitated by the construction of new coke ovens, or notification by the local municipal district that it can no longer accept a plant's wastewater for treatment.

The construction of a biological treatment plant is a significant capital investment for any mill. It has been reported that a single-stage treatment unit with a capacity of 250 gpm costs approximately $6 million for all components (clarifiers, stream stripper, chemical tanks, etc.). This does not include operation costs or real estate acquisition, if necessary. Of this amount, approximately 40 percent is attributable to the biological components. The total expenditure will vary with the size and capabilities of a new treatment unit, but the 40 percent biological component is expected to remain relatively constant. If stepped or multi-stage units are constructed, however, both the total expenditure and percent contribution of the biological components will increase. Costs also increase if polishing steps are required to meet a given effluent quality standard.

An advantage of biological treatment methods is their abilitiy to meet the 1983 effluent limitations for phenolics and possibly ammonia; however, the degree of treatment attained is dependent upon the characteristics of the wastewater. It is for this reason that many of the presently operational systems have been constructed.

Conversely, a decision may be made against construction of a biological treatment unit in view of the fact that such systems may be upset by variations in wastewater temperature or component concentrations. If a treatment system is upset, a long period of time may elapse (often more than two weeks) before the unit is operating efficiently again. During this time any discharge of coke oven wastewaters would put the plant out of compliance with effluent limitations. Therefore, the avoidance of such a situation appears highly desirable in the eyes of the industry. Another, and much more basic, reason for non-selection of biological treatment systems is the fact that the industry is not extremely knowledgeable about biological treatment processes. It has not invested the money, as have other industries, to attain the working knowledge necessary to apply the process to coke oven wastewaters. Other treatment methods are better known and understood, and therefore stand a better chance of selection.

Operation

Currently operating biological treatment systems are generally single stage activated sludge units. The capacities of these systems are highly variable, but certain parameters are common to all systems. Temperatures in the treatment units are between 24-36^{o}C. Influent suspended solids are in the range of 30-100 mg/ℓ, mixed liquor suspended solids are 2,000-12,000 mg/ℓ, and the final effluent is usually between 75-100 mg/ℓ. Currently operating systems and those under construction are not achieving oxidation of all compounds. Most systems are treating specifically for phenolics, reducing influent concentrations of 1100-1400 mg/ℓ by approximately 99 percent. Less attention is given to cyanide, thiocyanate, and ammonia in these units, with removals of 20-50 percent being reported for cyanide and thiocyanate and almost no removal of ammonia. Retention times in the aeration basin sometimes exceed 35 hours, with 24 hours being common. An approximately two day equalization capacity is generally maintained, but, depending on the design of the system, as much as a seven day capacity may be recommended. Sludge wasteage rates are extremely variable as is sludge disposal. If sludge wasteage occurs infrequently, the sludge may be disposed of in the blast furnace. Otherwise it is either dewatered or combined with lime to achieve a 12-15 percent solids content, and is then hauled to a landfill. As the wastewater is deficient in phosphate, all operating or planned units provide for the addition of phosphoric acid. No units are reported to respond adversely to changes in ambient temperatures, but, as mentioned earlier, changes in influent wastewater temperature may shock the system. There are also no known plans for variations on the activated sludge process (e.g., Zurn-Attisholz process), stepped or multi-stage treatment, or roughing and polishing steps, the latter being due to excessive cost.

SYSTEM UPSETS

A number of factors can lead to the shut-down of a biological treatment system or to its operation at reduced efficiencies: increased wastewater temperature, transient loadings of wastewater constituents such as cyanide and ammonia, and mechanical failure. Depending upon the event or combination of events which lead to upset conditions, recovery time can vary greatly. In some cases, improvement may be seen in 24 hours where no curative steps have been taken other than to return the wastewater stream to its normal composition. In others, a period of two or more weeks may be required to obtain and acclimate a "starter" culture and return the system to efficient operation. A "starter" culture is activated sludge trucked ~~to~~ from a municipal sewage treatment plant already treating industrial wastewater to the coke plant wastewater treatment facility. Some operators also add soil taken from the areas proximal to the coke ovens, in the belief that the organisms inhabiting that soil are the same organisms which function in biological treatment units.

OPTIMIZATION OF BIOLOGICAL TREATMENT UNITS

As stated earlier, the oxidative process which occurs in the biological treatment of wastewaters is an extremely complex one, and is highly sensitive to any local changes in its environment. Therefore, maximum attention must be given to providing for the needs of the microorganisms which carry out the treatment process. A number of steps may be taken to prevent upset conditions and optimize the treatment process. These are discussed in the following sections.

Equalization

Auxiliary basins collect wastewaters containing abnormally high concentrations of one or more pollutants. The water is stored in these basins and then delivered to the biological treatment system at a controlled rate. When such basins are used, the diversion of abnormal wastewaters is accomplished by the use of an automatic on-stream analyzer.

Dilution

Heavily loaded waste streams are sometimes diluted with water containing lower pollutant concentrations where it is know that the undiluted influent stream will shock or upset the treatment system. Treatment will continue even at these somewhat reduced food/microorganism ratios because the oxidative mechanism is more sensitive to toxic or inhibitory compound concentration than to substrate concentration. Surface or ground water, once-through cooling water, or blowdown from the in-plant utilities provide sources of dilution water.

Stripping

The reduction of high organic and inorganic loads and the sequestering of wastewater variations can be achieved through steam or solvent stripping.

The resulting wastewater is then much more amenable to biological treatment.

Recently however, attention has been given to the multi-media effects of such stripping practices, notably the potential problem of air pollution.

Increased Sludge Inventory

An increased sludge inventory in the biological treatment unit provides a greater number of active microorganisms per unit area, thereby reducing any deleterious effects which are exerted by influent variations. Sludge inventory may be increased by reducing sludge wasteage and/or increasing the sludge recycle ratio.

Sludge inventory is related to food/microorganism ratio, F/M. At increased F/M ratios, the microorganisms approach their maximum growth rate. The type of "food," or substrate available, however, is very important. If the substrate is a complex organic compound, it must first be reduced to simple substrates before it can be utilized by the microorganisms. This will provide a reduced growth rate, although the F/M ratio is high.

Sludge Age

Sludge age is defined as the average contact time between the microorganisms and substrate. The optimum sludge age for treatment of coke oven wastewaters is dependent upon the complexity and concentrations of the influent components and the aeration basin temperature. Other parameters of importance include retention time in the aeration basin and food/microorganism ratio.

Enhancement of Nitrification

Nitrification provides a means to keep ammonia levels within discharge limits. The nitrifying microorganisms, however, are highly sensitive to influent variations and temperature. The two-stage activated sludge process is capable of providing nitrification, although it is much more expensive than conventional activated sludge units. The first stage removes the carbonaceous oxygen demand from the wastewater, which then flows to the second stage for nitrification. Nitrification can also be achieved in extended aeration single-stage units which are operated for the purpose, and by the rotating biological disc.

Activated Carbon Treatment

The use of activated carbon in conjunction with biological oxidation has apparently received little attention from the iron and steel industry. It has been suggested as a polishing step before discharge or reuse for the removal of any remaining organic compounds, certain toxic constituents, and residual color. The primary drawback of this combined method is the total cost of the treatment operation.

Studies have been conducted, however, using activated carbon as part of a physical/chemical treatment process for coke plant wastewaters.[13] Results indicate that nearly complete organic, color, and suspended solids removal can be achieved. Free cyanide is then removed by catalytic oxidation on the granular carbon.

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[13]Van Stone, G. R. Treatment of Coke Plant Waste Effluent. Iron and Steel Engineer, 49(4):63-66, 1972

SECTION 7

POSSIBLE TREATMENT OPTIONS TO STANDARD BIOLOGICAL TREATMENT

Treatment options to the standard biological treatment techniques include the use of nitrification-denitrification systems, physical/chemical treatment schemes and variations on the activated sludge process, such as the Zurn-Attisholz process.

NITRIFICATION-DENITRIFICATION

Difficulties encountered in operating biological nitrification-denitrification units and their increased cost have been among the reasons for the limited use of these systems in treating coke plant wastewaters. Pilot and laboratory studies have shown, however, that such systems can reduce the levels of certain compounds (e.g., phenol, ammonia) which meet stringent discharge limitations, while achieving a reduction in concentrations of cyanide and thiocyanate.[9, 14]

Nitrification-denitrification treatment systems require three stages for operation. The first stage is the carbon removal unit, followed by nitrification, and then denitrification.

Wastewater enters the carbon removal unit where phenolic compounds are degraded. Temperatures are maintained between 27-38°C with a retention time of approximately 24 hours. Phosphate addition occurs in this unit. Phenolic removals in this unit may exceed 99 percent. Some cyanide and thiocyanate removal may be observed.

Effluent from the carbon removal system flows to the nitrification unit. Inorganic carbon addition and pH control are necessary to aid in ammonia degradation. Studies indicate that under proper conditions, 90 percent of influent ammonia can be oxidized.

Wastewater then flows from the nitrification unit to the denitrification unit where oxidized nitrogen is converted to nitrogen gas under anaerobic

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[14] Barker, J.E., and R.J. Thompson. Biological Removal of Carbon and Nitrogen Compounds from Coke Plant Wastes. EPA-R2-73-167, U.S. Environmental Protection Agency, Ada, Oklahoma, 1973.

conditions. With controlled rates of addition, approximately 95 percent of the oxidized nitrogen can be converted.

PHYSICAL/CHEMICAL TREATMENT OF COKE PLANT WASTEWATERS

Many components of coke plant wastewater are removable by physical/chemical treatment methods. Organics are frequently removed through the use of activated carbon or dephenolizers with ammonia removal accomplished by steam stripping. Cyanides are removed by catalytic oxidation or precipitation during the clarification process.[13, 15]

A pilot study has shown that activated carbon is capable of removing organics from barometric condenser water.[15] However, problems arise with the addition of other coke plant wastewater sources to the activated carbon, notably waste ammonia liquor. The phenol content of ammonia liquor is as much as 50 time greater than other wastewaters. The increased load on the activated carbon makes frequent carbon regeneration necessary, contributing to increased operating costs. The study determined that ammonia liquor can be treated in an economic manner by passing it through virgin activated carbon or reducing phenol levels through the use of dephenolizer before activated carbon treatment.

Ammonia removal is achieved through steam stripping of highly loaded wastewaters. Removal is pH dependent and does not occur below pH 7, necessitating the addition of alkaline materials such as lime or caustic soda. The latter has been recommended for its ability to eliminate or reduce disadvantages associated with lime addition.[15]

Wastewater clarification is a third major operation in physical/chemical treatment of coke plant wastewater. To avoid coating the activated carbon, oils (free and emulsified) must be first removed. One method of accomplishing this is agglomeration of oil on an iron precipitate, produced by adding spent pickle liquor and caustic soda to the wastewater.[15] Upon removal of the agglomerated oil, the wastewater is ready for treatment of other contaminants.

The economics of activated carbon treatment for industrial wastewaters compares favorably with other treatment options, owing primarily to the reactivation capabilities of the carbon.[13] However, physical/chemical treatment of coke oven wastewater does not exhibit a vast superiority over other

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[15]J.W. Schroeder, and A.C. Naso. A New Method of Treating Coke Plant Waste Water. Iron and Steel Engineer, 53(12):60-66, 1976.

treatment options. Therefore, the selection of the type of treatment which will provide the desired pollutant reduction most economically will have to be made on an individual coke plant basis.

ZURN-ATTISHOLZ PROCESS

The Zurn-Attisholz process has achieved greatest utility in Europe, where more than 50 installations are operating. In the United States, 11 Zurn-Attisholz installations are in operation, the majority treating the wastewaters of the pulp and paper industry.

The Zurn-Attisholz process is a two-stage high-rate system marked by a high sludge recycle rate and sludge age. In operation, the first stage maintains a 6,000-8,000 mg/ℓ mixed liquor suspended solids (MLSS) concentration, 0.1-0.5 mg/ℓ dissolved oxygen and a 200 percent sludge recycle. Characteristics of the second stage are approximately 2,000 mg/ℓ MLSS, 2.0 ppm dissolved oxygen and 150 percent sludge recycle. Suspended solids and biochemical oxygen demand removals exceed 98 percent with retention times of 2.5 hours per stage.

The applicability of this process to coke oven wastewaters has not been adequately investigated. The second stage of the system can be designed for ammonia removal; however, the levels of removal which may be achieved are not known. The problem of cyanide and thiocyanate removal, with respect to the Zurn-Attisholz process, has not been adequately researched. The Zurn-Attisholz process for the biological treatment of wastewaters has, where implemented, been highly successful. No Zurn-Attisholz systems are known to be treating coke plant wastes, but there is no indication that studies have not been carried out on the applicability of the process to such wastes. Due to the impressive results of this process with wastewaters from other industries, investigations (economic and operational) should be conducted on its applicability to coke plant wastes and other wastewater streams.

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16. ABSTRACT The report gives results of a survey of current uses of biological treatment methods for U.S. iron and steel industry wastewater. It includes identification and characterization, on a pollutant component basis, of waste streams receiving treatment; capabilities of biological treatment; advantages and disadvantages of various biological systems; nitrification and denitrification; current utilization of biological treatment by the industry; and possible alternatives to current biological methods. The coke plant, particularly its waste ammonia liquor, is the major wastewater source for biological treatment. The liquor contains phenol, ammonia, cyanide, thiocyanate, carbonate, sulfide, oil, suspended solids, and dissolved solids. Biological treatment of wastewater can remove 99% of its phenolic constituents. Adjusting operational parameters, including increasing retention time, increases removal of ammonia, cyanide, and thiocyanate. Ammonia reduction exceeding 90% is achievable in nitrification and denitrification units; however, biological systems are susceptible to upsets due to fluctuations in temperature or waste loading. Current use of biological treatment is limited, with interest centered on phenol removal. Pilot studies have shown some physical/chemical methods to be competitive with biological treatment.

17. KEY WORDS AND DOCUMENT ANALYSIS

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Iron and Steel Industry		Stationary Sources	11F	
Biology	Ammonia	Biological Treatment	06C	07B
Waste Water	Phenols	Denitrification		
Water Treatment				
Nitrification			07C	

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