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KRAFT MILL GASEOUS RECOVERY AND ODOR ABATEMENT

SUMMARY

Some kraft pulp producers, realizing the economic potential, are making a concerted effort to recover the maximum chemicals and heat from their mill gaseous effluent. The limitations of insufficient knowledge of the sulfur-containing odoriferous compounds and techniques to capture them are rapidly being overcome today. Through co-operative research, two different, adequate sampling and analytical procedures have been developed. One major producer's research team is attempting to establish odor thresholds for individual odorous compounds and groups of these compounds.

A critical and objective analysis of the kraft gaseous effluent situation today indicates a serious need for further co-operative effort to establish on a scientific basis and to perfect techniques for the capture and processing of gaseous effluents with an aim toward better economy of chemicals and heat and a cleaner and more healthful atmosphere in which to work and live.

THE INSTITUTE OF PAPER CHEMISTRY

INTRODUCTION

The paper industry, with perhaps several minor exceptions, has not been particularly accused of serious atmospheric pollution. Within the industry, however, we are cognizant of the particulate and odorous emissions which surround the mill sites. Many of us, in fact, have come to associate these with a good, healthy feeling of a prosperous industry. Perhaps on the other hand, if we take a critical look at this particulate and gaseous emission, we could make observations which would improve the industry and make it even more prosperous.

Although both the soda and sulfite process mills have an effluent emission problem, the one of greatest concern to the public today is the malodorous effluent from the kraft pulp mill. A look at the kraft mill gaseous recovery program of even a few of the available mills assures us that there are nearly as many programs as mills. This of course is due in great part to different woods available, different products manufactured, and, thus, different technical procedures for processing. On the other hand, all these recovery programs have common goals. It is the intention of this project to combine the several aspects of these common goals and to attempt an improvement by a critical analysis.

From an economy point of view, it is apparent that the needless emission of particulate solids from a kraft or soda recovery process is wasteful--even to the extent of 5 to 10% loss. Likewise, it is becoming better appreciated that the emission of gaseous sulfur-containing compounds is costly from both a heat and chemical standpoint.

These effluents, both particulate and gaseous, are now collectable within reasonable limits, as has been demonstrated in several parts of the world, principally by Tomlinson (1), Wright (2), Trobeck (3), Collins (4), and Hisey (5). Needless to say, there have been others who have made contributions, some of major importance, to the goal of attaining the most economical and odorless kraft mill by maximum heat and chemical recovery of all effluent sources.

To plan and design an integrated program for total mill pollution abatement and maximum chemical and heat recovery, every possible source of emission should be firmly established as a valid threat, or not. Once each source has been established, the next logical step is to ascertain the most efficient method applicable to minimize that emission. Efficiency here should encompass the economic as well as the pollution abatement aspect. Care must be exerted not to duplicate equipment in considering the individual effluents. By objective planning, one should consider the admonition of Witheridge (6) and others, that the installation of gaseous emission abatement equipment costs as high as $10 per cubic foot per minute as compared with $1.00 for simple dust removal. Thus, every possible alternative in operating procedure should be examined for reducing gaseous emission. Oxidation of the black liquor in a kraft mill recovery process has been well established as an extremely important means of decreasing the odor of hydrogen sulfide and the organic sulfur compounds. Inadequate or partial oxidation, on the other hand, makes the odor problem worse than no treatment.

Condensing of the blow gas steam substantially reduces the volume of gaseous effluent to be treated from this souce. Also, the operation of a mill on a scheduled production basis serves as a means of smoothing out the gaseous effluent volumes. In order to consider the many facets of the whole gaseous recovery-odor abatement program, obviously one must first have a good understanding of the components of the kraft mill effluents. This understanding can best be obtained by a study of the sampling, analyses, and treatments of the several sources of emission.

ANALYSIS OF PROBLEM AND PRESENT CONTROL EFFORTS

EFFLUENT SAMPLING AND ANALYSIS

It is quite common knowledge that hydrogen sulfide occurs in relatively large quantities in digester blow and relief gases, evaporator gases and condensate, and recovery furnace stack effluents. Methyl mercaptan, methyl sulfide, and a large number of other sulfur compounds are also included in varying amounts in these effluents. The significance of these individual compounds, as concerns atmospheric pollution and/or odor control, is not fully established. Odor thresholds for many organic compounds have been established and some are known to be included in kraft mill effluents. However, the grouping of several compounds in various combinations, such as found in kraft mill gaseous emissions, has an odor effect often different from that of the individual gases alone.

Some of these malodorous sulfur-containing compounds of kraft mill effluents apparently are present in the minutest amounts, yet sufficiently high above the odor threshold so as to be detectable by the human nose. To make even a cursory attempt to analyze the effluents requires extremely sensitive instruments. The broad variety of compounds found in the gaseous effluents and their chemical similarity makes the task even more difficult. Some of these compounds occur also as natural effluents of household and industrial heating plant products of combustion, thus aiding the confusion of source definition.

These and other problems have historically inhibited the progress of developing simple yet adequate procedures for a complete qualitative and quantitative analysis of kraft pulp mill effluents.

Recently the development of analytical procedures based more on physical rather than chemical methods have been advanced in many industrial fields.

There are on the market today many types of semi- and fully automatic samplers, some of which collect periodically, and others continuously, very minute yet adequate sample data which are reproducible.

The method of thermally depositing or precipitating particulate matter has been used for years for obtaining small, thin films for visual or electron-microscopic examination. Another reliable device for dust collecting is the portable electrostatic precipitator. Silverman (7) has described a high-speed air sampler for obtaining adequate quantities of dust from aerial atmosphere. This apparatus is portable, simple to use, and has become very popular with civil and state air pollution boards.

Only a few years ago, most particulate samples were spot checked by chemical analysis for one component or another and recorded as a certain weight per thousand cubic feet of air sampled. Even at best, the chemical analysis was a long, involved, laborious task with somewhat questionable accuracy. Today one may choose whichever is more convenient among a number of quick, accurate, and simple methods for analysis. There are, for example, x-ray and electron diffraction, emission spectroscopy, light microscopy, and flame and absorption spectrophotometry. Each of these methods identifies by the physical characteristics of the particulate in question and by comparison of these characteristics with a known. At least, ideally, each element or compound present may be identified by its unique physical characteristics. Adams (8), by means of x-ray diffraction, has determined the percentage of cement in dust collected at ten locations. Schmelzer (9), using the same method, has separated percentages of cement and barite. It should be possible to develop this method further to encompass sulfur, lime, and specific sodium compounds.

A procedure for simultaneous collection of particulate and gaseous effluent samples was devised at the University of Florida for the National Council for Stream Improvement. This procedure, as reported by Hendrickson (10), requires a Whatman paper filter for particulate followed by three impingement bottles in parallel to collect separately sulfur dioxide, hydrogen sulfide, and total sulfur. By use of a vacuum source and three Sprague 1A gas meters, adequate samples have been obtained in an hour from recovery furnace stacks. The sampling procedure is simple and the equipment sufficiently portable to be convenient for abatement program testing within a mill or from one mill to another. The sample-collecting bottles can be made up in units so that handling them as a portable device is quite satisfactory. Analysis of the gas effluent samples can be done in an analytical laboratory by colorimetric methods.

To measure the aerial conditions of a kraft mill neighborhood, several continuous recording devices are available on the commercial market which analyze for sulfur-containing compounds. Notable examples are the Thomas Autometer, the Titrilog, and the Rubicon. These instruments were developed to determine sulfur dioxide and/or hydrogen sulfide concentrations and have a reported accuracy range of 0.1 to 500 parts per million. The Autometer and Titrilog record the effective total content of many oxidizable gases such as hydrogen sulfide, mercaptans, and unsaturated hydrocarbons as well as sulfur dioxide. In the Titrilog, these certain compounds are oxidized by elemental bromine in bubbling the gas sample through the electrolyte bath of sulfuric acid-potassium bromide solution. By potentiometric measurement, the instrument determines the reduction in bromine and automatically calls for more to be generated. The Titrilog then measures the electrical current required to generate this bromine, which is proportional to the quantity of the oxidizable gases in the sample.

These instruments are practical for general level of sulfur-containing emissions higher than the odor threshold levels of the odorous sulfur compounds. Nader and Dolphin (11) have developed a circuit modification which increases the Titrilog sensitivity threefold. This development should provide sufficiently close accuracy to measure at least the higher threshold malodorous gases. In fact, at least one kraft producer has used the Titrilog thus modified to govern the control of a multi-scrubber gaseous recovery system. Automatic sampling is by far the simplest mode of obtaining continuous recorded data. The Titrilog maintenance is reported as not a serious problem and the technically trained labor required is probably close to the minimum for the data obtainable. Three fluid absorbers, incorporated in the Titrilog, permit absorption of the chemically similar groups of compounds before the sample enters the reactive cell. Thus, it is possible to obtain analyses for total sulfur, hydrogen sulfide, and a mercaptan, for example. A timing device automatically routes the gas sample directly to the electrolyte cell or through the absorbers. Normally, fifteen minutes are required for each cycle. As an alternative, the use of the absorbers can be replaced and a total sulfur content may be determined for four separate sample streams. The usefulness of the data obtained by the Titrilog is limited to total sulfur content and/or three separate groups of sulfur compounds.

In recent years, it is appreciated that as industry becomes capable of approaching the odor threshold limits of many of the sulfur-containing compounds with modern abatement programs, it becomes more desirable to analyze for the specific malodorous compounds. Chemical analytical methods for the quantitative determination of the individual sulfur-containing compounds are difficult and sometimes unreliable because of the similarity of the compounds' chemical behavior.

The need for improved, faster, yet reliable methods for determining quantities of the particular mercaptans, organic sulfides and disulfides has become more urgent as the methods of possible odor abatement programs have been developed.

The current industrial interest in the development of simpler and more adequate sampling and analysis methods for specific malodorous sulfur-containing compounds is almost without boundary. The grants made by private industry and through co-operative effort in recent years have spurred development progress.

The research group at Washington State University headed by Donald F. Adams (12) has established a technique for condensation and/or adsorption sampling at -78.5°C., heat and vacuum desorption, and liquid-gas chromatographic analysis of the gaseous sulfur-containing compounds in kraft mill effluents. This was accomplished as a research project sponsored by the National Council for Stream Improvement over a period of several years. The initial work was an attempt to separate and determine quantitatively the parts of a mixture of 15 known sulfur-containing compounds by gas-liquid chromatography. This analysis was quite successful by use of Triton x305 as a column liquid and the two-temperature (30 and 100°C.) method. Since many of the sulfur compounds thus analyzed were known to be present in actual kraft mill effluents, the next logical step was to develop a satisfactory method for sampling. Atmospheric pollution samples for chromatographic analysis have been collected by thermal condensation or adsorption as shown by Barnebey and Davis (13). These procedures were modified as necessary to provide adequate samples which gave reproducible results both by chemical analysis and by the gas-liquid chromatography method.

At this time, Adams and his group are in the process of evaluating data obtained from 9 kraft mills using the condensation-adsorption sampling and gas-liquid chromatographic analysis. The results of this research will be reported within a few months, encompassing two purposes: (a) extensive field usage of the new techniques and (b) evaluation of the various types of odor control being used by the different mills (14).

John S. Nader (15) has developed an odor evaluation apparatus which can be used either in the laboratory or field. By manipulation of pure odor-free air and, thus, dilution of odoriferous gases, the apparatus, by means of an individual or a panel, can establish the odor threshold quite accurately. An industrial research laboratory is currently attempting to establish odor thresholds for individual sulfur-containing compounds found in kraft mill effluents. After establishing these individual thresholds, they will attempt to develop the thresholds for various combinations of the compounds.

Perhaps within a reasonable time we can expect to establish the kraft mill gaseous effluent abatement program on a firm, scientific basis. The problem of odor abatement and gaseous recovery will become considerably more exact if we can establish identification and the quantity of the specific compounds, and if we can learn the individual odor thresholds.

RECOVERY FURNACE EFFLUENT COLLECTION

Several kraft producers have already attempted to make a systematic study of the possibility of improving their existing recovery system. Some mills, by trial-and-error methods, have been quite successful in their attempt to attain good recovery and odor abatement.

Let us consider some of the aspects of the more successful installations, some of which have three or more stages for gaseous effluent scrubbing. These multiscrubbing stages are generally in addition to condensation equipment for the digester and blowpit gases and, in some cases, a black liquor oxidation equipment. Practically every mill includes an electrostatic precipitator following the recovery furnace, although there are a few equipped only with wet scrubbers. Obviously, each system has a number of advantages. The electrostatic, with a higher capital investment cost, is less expensive to operate because of the lower (in fact, almost negligible) pressure drop when compared with the venturi-type scrubber and, thus, low fan power requirement. Some wet scrubbers, spraying black liquor as the wetting medium, have the advantage of increased evaporation and, thus, higher thermal efficiency in the recovery system.

Although electrostatic precipitators used in industry for the past fifty years are basically the same design, many technical improvements have been made. A wet-bottom-type, tile-construction electrostatic precipitator typical of today's kraft mill installation can usually capture nearly 99% of the rated inlet loading of particulate solids (16). This is accomplished by adequate design based on theoretical, predictable, maximum loading conditions. Multiple-chamber design also enhances the over-all particulate collection by reducing the wrapping cycle and down-time capture losses. The black liquor, after processing in the multi-effect evaporator, normally flows by gravity or is pumped into the precipitator bottom. Flowing from the precipitator, the black liquor, fortified by the captured particulate solids, is pumped to the throat of a cyclone evaporator at the recovery furnace gas outlet. This promotes additional furnace heat recovery in three ways: higher solids content of black liquor both by evaporation and particulate capture, and higher black liquor inlet temperature by heat transfer from flue gases. Numerous mills are mixing a portion of this hot, strong, black liquor with salt cake make-up prior to firing in the recovery furnace.

For additional particulate capture and gaseous recovery from the recovery furnace electrostatic precipitator effluent, there are installed a variety of wet scrubber types. Recently, one mill has placed in operation adjoining the precipitator two Pease-Anthony-type scrubbers. These cyclonic-type, fine-mist-spray scrubbers are noted for their capture of gaseous and submicron-size particulate effluents. They also have the advantage of a very low pressure drop compared with the venturi-type scrubber. Because of the low pressure drop, the power requirement is moderate and, in fact, often negligible with some systems. Water usage, for the Pease-Anthony-type scrubber with recirculation, averages about 1 gallon per 1000 c.f.m. of effluent gas. Recirculation here is important for several reasons, but mainly to obtain a higher concentration of recovered chemicals to be used in the causticizing or white liquor make-up process.

Multi-tower wet scrubbers have been found satisfactory for particulate and gaseous recovery by several kraft producers. Such towers are relatively inexpensive to install, have a low pressure drop and power requirement, but do require considerable space. The systems using towers without an electrostatic precipitator for particulate capture depend entirely on the force of gravity, or centrifugal force, along with the extremely large amount of sprayed black liquor and water to remove the particulate solids. Usually oxidized, weak black liquor, by recirculation, is sprayed in large volumes through fine mist nozzles in one or more of the towers. Following the black liquor spray towers is a cyclone-type device to recover any entrained liquor. The gases then are conducted through a heat exchanger to provide hot water production from flue gas heat, as a steam-saving advantage. Also, it is now recognized that hot stock washing and screening not only improves the washing of the pulp but saves capital investment and adds to the mill thermal efficiency. For example, the black liquor coming at about 160°F. from the hot screening and brown stock washers will oxidize with a shorter retention time in the oxidation towers.

At least two mills have used a small amount of chlorine gas to further oxidize the sulfur-containing effluent gases prior to their release to the atmosphere. One mill has added 4 to 5 pounds of chlorine per ton pulp production to the effluent stack. Another has installed a reactor chamber before the final gaseous scrubbing stage and by trial and error method has determined that between 1/2 and 1 pound per ton production is sufficient for complete odor control of this recovery furnace effluent gas. Both of these kraft producers are located within an urban area where odor control is of utmost concern.

DIGESTER EFFLUENT COLLECTION

The second source of odorous sulfur compounds emanating from the kraft mill is the digester relief and blow gases. This effluent, particularly in the batch digester mills, is by far the most difficult to control. Even mills operating on a scheduled production basis have an extreme variation in the flow rate of effluent gases. Obviously, during the early and intermediate period of cooking there is no effluent at all; then at blow time a tremendous volume of noncondensable gases plus steam is released. Thus in some twenty minutes, three-fourths of the effluent is released for an average cooking cycle of perhaps five hours. The first and most obvious effort to smooth out this variation in process is to separate the steam by condensation. In some mills the noncondensable gases are temporarily stored in large tanks or spheres and thence are fed into the treatment program at a moderate and relatively steady rate of flow. Although the treatment of the noncondensable digester and blow gases shows much variance from mill to mill, there are four principal systems used: oxidizing in black liquor oxidation towers, burning in the lime kiln, mixing with residual bleach, and treatment in multiple chemical scrubbers. The first three mentioned are by far the least expensive to install and to operate. Little or no power is required and the equipment needs are mainly ducting, instruments, and safety devices. With these methods, however, there is usually a problem of co-ordinating the several equipment units since the system is out of balance for relatively short periods of time, which reduces their effectiveness in odor abatement.

Probably the simplest of these systems is the black liquor oxidation, which consists essentially of a duct connecting the noncondensable gas accumulator with the oxidation tower's air inlet. Where black liquor oxidation equipment is utilized, no further equipment is required and the existing power facilities are normally adequate.

The lime kiln burning of the noncondensable gases requires the installation of flame arresters in the duct system and an air fan to dilute the gases about 20 to 1 to prevent explosions. There was a time when explosions were potentially a serious hazard and perhaps a deterring effect on the development of this rather economical method of disposing of digester gaseous effluent. The products of combustion, along with the lime fumes, can be removed by means of a wet scrubber installation.

Injection of noncondensable gases into the vacuum leg of a chlorine or hypo bleaching-stage washer has proved satisfactory for the requirements of many mills. The residual chlorine oxidizes the sulfur-containing compounds--provided, of course, that an adequate supply of residual chlorine is maintained. Installation of an oxidation reduction potential (ORP) cell enables quite close chlorine control under usual conditions. However, sudden chlorine demand changes (over about 20%) unfortunately require hand operation of the chlorine for a few minutes. One modification of the above process consists of pumping the residual bleach to a chemical scrubber for treatment of the digester and blow gases and has been used by one or more producers. This, of course, is somewhat more expensive, although perhaps more effective for odor control.

Undoubtedly the most expensive system to install and operate for control of the noncondensable digester gases is the multiple scrubber system. It is, however, the most effective from an odor abatement standpoint. Installation of this system could very likely be justified only where the mill area is located within a highly populated area. The experiences of several mills have indicated that single-stage chlorination alone is insufficient for complete odor control. One kraft pulp producer, surrounded by an urban neighborhood, has installed a three-stage scrubbing process to recover maximum chemicals and to deodorize as completely as possible. The equipment includes a tray-type reactor for scrubbing noncondensable gases with air and hot condensate water, a chlorination tower, followed by a venturi scrubber with white water spray. The chlorination tower uses about 6-1/2 pounds of gaseous chlorine per ton of pulp production. The gaseous chlorine use is predicated on the advantage of a homogeneous gas reaction over that of absorption or desorption, and a chemical reaction by using bleach liquor (17). The air and water treatment in the first stage has proved quite effective in reducing the detectable odor. Blow gas control has proved a problem because of the instrument time lag.

As mentioned previously, this same producer has installed a five-stage particulate collecting and tower scrubbing system on the black liquor recovery furnace stack gases. This system includes a particulate collector, a tower scrubber with spent alkaline solution sprays for absorption of sulfur dioxide, a scrubber with water sprays, a gaseous chlorine tower (about 1/2 pound per ton production), followed by a white water scrubber. After such a rigorous scrubbing system, it seems likely that this mill should be nearly odorless, as reported.

The reported total chlorine consumption for both the digester noncondensables and recovery furnace effluent was about seven (6-1/2 plus 1/2) pounds per ton of pulp production. At carload price for chlorine gas, approximately 30 cents per ton of pulp for this additional odor abatement sounds reasonable. Locally produced chlorine gas, of course, would be even less expensive. All the odor level tests at this mill were made with a Titrilog instrument. When compared with a panel of human noses, the Titrilog was more sensitive. That is to say, it was found allowable to have a slight positive test without any discernible odor present. This positive test is believed to be due to interference of other gases on the Titrilog instrument.

BLACK LIQUOR OXIDATION

In many kraft mills, sulfur, in the form of sulfur-containing effluent gases, is lost from the system independent of the loss of sodium. Black liquor oxidation can eliminate at least a large portion of this loss, particularly from the recovery furnace flue gas and to some extent from the multi-effect evaporators. Oxidation of black liquor is well recognized as an extremely important means of decreasing the odor of hydrogen sulfide and organic sulfur compounds. This is accomplished by converting the odorous sulfur compounds to a more stable form so that they are not released by evaporation and further recovery process. In addition to decreasing the odors of these sulfur compounds, there are several other advantages to black liquor oxidation. Some of the numerous reports in recent years of black liquor oxidation advantages are: smoother operation of the multi-effect evaporators with higher solids obtainable and somewhat reduced steam requirements, less corrosion of evaporators and recovery system (and thereby longer life expectancy), better control of sulfidity enabling more desirable cooking conditions, and perhaps the most important advantage--less loss of sulfur from the system. Also, the oxidation equipment has a potential evaporation effect of about 1%, depending upon the temperature and relative humidity of the air involved in the actual process.

Chemical economy appears well founded as a means of financial justification of black liquor oxidation equipment and a gaseous recovery system. As pointed out by Tomlinson (18), black liquor oxidation, or stabilization, is the key point in the sulfur economy of a kraft recovery system. It is the key not only for the sulfur savings but because of further processing and heat recovery attainable by stabilization of the sulfur compounds. Sulfur savings have made it possible to utilize a partial make-up by soda ash and other less expensive sodium compounds. The normal reaction of salt cake decomposition to sodium sulfide requires nearly 7000 B.t.u. per pound (as sodium sulfide) of salt cake. This thermal gain is made possible by the substitution of the gaseous recovered sulfur for salt cake addition.

By oxidizing the black liquor prior to evaporation, as is the usual practice, it is possible to spray the liquor into a cyclonic direct-contact evaporator and thereby increase the black liquor solids content to the evaporators, recovering some heat energy from the flue gases without subsequent raising of the odor level. This allows an increase in evaporator production in the form of higher temperature and higher solids content of the input black liquor. Also, the now-odorless hot condensate from the evaporators at 60 to 70°C. can be utilized in the causticizing stage, thereby making a further steam economy possible. Stabilization of the sulfur compounds has reduced the corrosion potential by elimination of hydrogen sulfide in the multi-effect evaporator and recovery furnace when operated with adequate excess oxygen conditions.

Several kraft producers have indicated advantages to operation with a higher range of sulfidity than formerly attainable prior to black liquor oxidation (3, 4, and 19). This, of course, has been accomplished without subsequent increase in odor level in the area surrounding the mill.

In the industry, oxidation of kraft black liquor is accomplished by several different methods. These have been developed methodically over a period of years. Early research published on studies of black liquor include the work of Bergstrom (20). He discerned in 1939 that kraft black liquor sulfide content would oxidize at 80°C. in a few minutes from 1.99 to 0.14 grams per liter. This reaction was found to take 3 to 5 minutes; then after some thirty minutes of apparently no activity, another slower reaction proceeded. Wright (21) confirmed this two-phase reaction and went on to explore the temperature effect, establishing apparently little oxidation rate change between 140 and 180°F. and substantial decrease in reaction rate below this temperature range. Thus, we realize the necessity of adequate time of exposure and temperature to promote good oxidation reaction for kraft black liquor. Other parameters have been explored by Tomlinson (1), Hisey (5), DeHaas (19), Trobeck (22), Sylwan (23), and Murray (24). Concurrent flow of an adequate air supply and increased surface of exposure have a very marked effect on the oxidation reaction. By the use of two concentric glass tubes as a packed oxidation tower, actual changes in parameters could be observed readily. The outside glass tube was used as a water jacket so that temperature could be controlled, yet direct observation of foaming and wetted surface of packing material could be made. The results of these tests showed the very definite limits of packing material, black liquor concentration, and flow rates of liquor and air necessary to stabilize or oxidize one particular black liquor for one producer's particular cooking conditions.

After considerable testing on a pilot scale, the mill was equipped with a full-scale oxidation tower based on the established data using concurrent air flow and 4-inch cross-section packing tile. This mill was able to discontinue the normal addition of some 3000 pounds of elemental sulfur per day because of increased gaseous recovery after the installation of the oxidation equipment. This is a significant sulfur saving of 17 pounds per ton of pulp produced. Recent changes of this particular installation have included use of corrugated stainless steel plate packing material.

Another very widely used black liquor oxidation system is that of Trobeck, which depends upon foaming as a means of surface exposure. Although both processes of oxidation react the liquor directly from the brown stock pulp washers at 15 to 20% solids content, from this point on they differ widely. In contrast to the method described formerly, the Trobeck method purposely whips the black liquor into a foam by an air blower. The foam is then drawn off into a specially designed foam breaker tank of a size and capacity depending upon the particular black liquor needs.

Numerous installations of both oxidation methods have reported satisfactory results; however, there is an additional equipment cost and increased power required for the Trobeck system over that for the tower system. The pressure drop across the towers packed with vertical hanging plates could be expected to average 3 to 5 inches of water, whereas that of the foam tank could range a foot or more of water. This indicates a substantial difference in power requirements, not including the additional power necessary to run the mechanical foam breakers in the Trobeck system. Most pulp production methods preferably shun any foaming whenever possible in the process because of the problems of deaerating. As a matter of fact, one of the kraft industry's most difficult problems today is excess foaming of the black liquor oxidation process when used on southern kraft liquor. A very few southern kraft producers who have attempted oxidation have not been successful.

RECENT DEVELOPMENTS

In an attempt to provide black liquor oxidation with a minimum of foaming, commercial oxygen gas has been tried. The latest reported attempt, made by Fones and Sapp (25), showed prohibitive costs at the present oxygen prices. Excess foam has proved a serious drawback in the oxidation of southern kraft black liquor and thus inhibits odor abatement in that region. Under the sponsorship of the National Council for Stream Improvement, a major research program is currently under way at Louisiana State University in an attempt to devise methods for oxidation with a minimum of foaming. Needless to say, the solution of this problem would enhance the odor abatement program extensively.

This problem which unfortunately confronts a large portion of the kraft industry brings to mind a number of development projects which have at least a historical value and warrant a brief mention. As is often true, some developments are reasonably inexpensive and yet their contribution to the industry has been considerable; others have cost many thousands of dollars without any gain.

Multi-effect evaporators equipped with stainless steel wire mesh entrainment separators have proved substantially more efficient. This more recent development is now being utilized in many mills to good advantage. The separator cost is very moderate, and the results reported have been encouraging enough to promote extensive usage. Smoother operation is possible, and the added thermal efficiency justifies the minor investment within a few months' time.

Catalytic systems have been utilized for a variety of hydrogenation, reduction, and oxidation reactions in the chemical industry (26). Most of the odorous, sulfur-containing compounds which are of concern to the kraft pulp producer are quite readily oxidized. It follows then that some catalytic system might be a logical answer to the kraft odor problem. Attempts made on several occasions have not been successful for a significant period of time because of severe coating of the catalyst. This factor is not confined to the kraft effluent alone since other attempts have proved futile because of particulate, metallic vapor or other poisonous agents deposited on the catalyst. This does not preclude, however, the possibility that a catalyst may some day be brought forth that will be ideal for this purpose. The problem of minute quantities of the odoriferous sulfur compounds mixed with tremendous volumes of other noncondensable gases, on the other hand, is quite compatible with catalytic systems, as has been demonstrated in the natural gas purification. Another successful application has been on waste gases from the manufacture of formaldehyde from methanol. Here, the heat energy recovered from the effluent is sufficient to maintain the necessary combustion. Certainly, the field appears sufficiently fruitful to be considered another hopeful avenue for fundamental research.

West (27) has studied the comparison of two kraft mill oxidation towers connected in parallel *versus* in series. By varying the black liquor rate over the same range (thereby doubling the mass flow rate in the series-connected towers), increased oxidation was indicated with the towers in series for part of this range. Beyond a certain black liquor flow, the oxidation rate apparently was the same whether the towers were connected in parallel or in series. Analysis of oxidation tower characteristics is problematical because of the complexity of the gas absorption and chemical reaction. As previously pointed out, the process varies according to surface of exposure, concentration of black liquor, partial pressure of oxygen, and rate of agitation. The indicated increase of oxidation in the series towers, as shown under certain conditions, might well be accounted for by a combination of factors including increased wetted area and/or agitation. It is possible that recirculation of a portion of the black liquor might have produced an increase in the oxidation reaction.

Kielback (28) has described a floating bed scrubber which uses light-weight plastic balls, or spheres, as a packing medium. The full-sized unit has proved successful to scrub out fluoride emissions from an aluminum smelting plant effluent where plugging of most other packing material by tars and alumina has been a major problem for years. The plastic spheres actually clean themselves continuously by tumbling over one another. A pilot-size unit has been tried as an oxidation tower for kraft mill black liquor with fair success. A second pilot tower will be tested on the west coast this year. This type of tower appears to be another possibility for gaseous scrubbing in the over-all abatement program as well as for oxidation use.

SYSTEMATIC ENGINEERING PROGRAM

EQUIPMENT PREDICTION

With an adequate knowledge of the individual odorous sulfur-containing compounds, it should be possible to make a systematic investigation of each effluent source to determine on a scientific basis which source is responsible for the emission of a certain compound. Much more advantage can be obtained from a definite knowledge of the specific components of an existing effluent recovery system.

From such studies it is likely that improved gaseous recovery developments may be advanced which are presently unsuspected. It also is realized, however, that new principles are exceedingly rare and that they cannot be anticipated with much confidence. Probably the most important advantage of a systematic and scientific analysis of a gaseous recovery system would be the possibility of equipment performance prediction. Obviously, in order to be able to predict the capture performance of a proposed piece of equipment, one must have a sound, theoretical knowledge, or at least a rational basis for generalizing the factors which are encountered.

The capture of gaseous undesirables from a total gaseous medium with known present-day equipment is accomplished by adsorption, absorption, and/or one or more chemical reactions or a combination of two or more of these. Theoretically, with an increasing number of chemically different compounds, the process usually becomes more intricate.

Compared with gas collection, the concept of aerosol particulate collection is thought of as quite simple. The actual performance of the equipment to capture the particulate from a gaseous medium is sometimes considered in three phases, namely: deposition, retention, and removal. It is apparent that even though all of the undesirable particulate matter becomes deposited, it cannot be considered as captured until it is successfully retained and entirely removed from the effluent stream. It should be realized also that one or all of these phases of capture performance can be affected by the aerosol physical characteristics (size range, shape, and density), the fluid flow pattern, and the mechanical characteristics of the equipment. For a basic piece of equipment operated at predetermined specific conditions of gaseous flow and average aerosol physical characteristics, it is possible to establish adequate capture performance data. Perhaps these data are not sufficient for a theoretical prediction, which of course is the desirable ultimate conclusion. Such data are adequate, however, for an engineering rationalization. And, admittedly, a majority of our present-day industrial odor abatement systems have been based on such an engineering rationalization because of the lack of a real knowledge of the individual odorous compounds as a basis upon which to make a truly scientific equipment performance prediction.

With a particular aerosol having inherently the minimum of size range, shape, and density variables, and once again operating the basic equipment at specific conditions, data which approach the theoretical predictable should be plausible. By careful manipulation of a single parameter at one time, the data obviously can be expanded within reasonable limits to enable the experienced engineer to make a number of practical predictions. Once these limiting boundaries are overstepped, however, we are once again in the field of rationalization.

From the foregoing discussion on particulate capture, it seems evident that generally the aspect of gaseous capture similarly can be approached, once we are in command of the theoretical knowledge of the specific sulfur-containing compounds involved in the kraft mill effluents. These data, established by systematic analysis, should provide the foundation for specific gaseous recovery equipment performance prediction on a firm scientific basis. This concept does not imply an assembly of myriads of performance data on a wide variety of equipment. In contrast, it indicates the present-day urgent need for a critical, quantitative evaluation of representative devices at clearly defined, specific conditions. In place of the usual trial-and-error method, equipment prediction data provide a valid means of application of the right equipment for the specific conditions encountered. Equipment prediction data should enable the experienced engineer to provide: (1) an economic justification based upon the proposed heat and chemical savings, (2) the optimum odor abatement installation for the investment, and (3) the maximum recovery obtainable on a planned basis. This should logically apply to the engineering of either a new installation or an existing installation modification for better heat and chemicals recovery and more effective odor abatement. Such an engineering program eliminates the emotional and expedient problems and also, by logical steps on a scientific basis, brings about the most economical and efficient installation.

SCHEDULED ULTIMATE PRODUCTION CAPACITY

The most highly engineered gaseous recovery system, when installed within a kraft mill not producing on a scheduled basis, is incidental to efficient chemical and heat recovery and good atmospheric pollution abatement. Scheduled production here means operating the mill at sufficiently under maximum capacity to maintain smooth, controllable, and profitable production.

Most production people agree that a kraft mill designed to produce 250 tons of pulp per day could turn out 300 tons or more at times. While it is recognized that this is the most obvious way of reducing cost per ton of production, there are, however, certain limitations to this course of action. Increased production is accomplished by overloading the capacity of certain pieces of equipment. These will be the first limitation to the production capacity. By making revisions or additions to these limitations, a new production capacity may be reached and once again, certain limitations of other equipment are met. Thus, these limitations help to establish the maximum production possible for the existing equipment. Regardless of the designed capacity, the maximum production possible under smooth, controllable, and profitable conditions is foremost in importance to the mill profits.

While it is readily recognized that operation of equipment beyond a certain established maximum capacity increases the maintenance cost, down time, lost production, etc., let us consider some of the effects of this type of operation to the chemical and thermal recovery and odor abatement program.

In the kraft recovery furnace, secondary air is extremely important from an odor control point of view as well as thermal efficiency. Overloading the recovery furnace usually means difficulty in maintaining sufficient free oxygen, necessary in the combustion gases. If insufficient free oxygen is not maintained, some of the sulfur-containing compounds can be chemically reduced to yield again odoriferous gases in the effluent. One producer, by installation of an oversize recovery furnace, has saved the capital investment of a power boiler. The recovery furnace, designed for 400 tons nominal pulp capacity, is now operated at one-half capacity and the black liquor is supplemented with heavy fuel oil as needed to maintain adequate steam. As future production demands, a power boiler can be added and for a considerable time the recovery furnace will not be overloaded.

Partially oxidized sulfur compounds, as previously pointed out, are far more odoriferous than nonoxidized. Overloading of the black liquor oxidation system beyond its full oxidizing capacity could release volumes of partially oxidized sulfur compounds not controllable by the gaseous scrubbing system. This could possibly cause release of gaseous hydrogen sulfide in the multi-effect evaporator and thereby reduce the thermal efficiency as well as overload the evaporator capacity. Pushing the evaporators beyond their capacity reduces the black liquor solids content to the recovery furnace and, hence, steam production is lowered.

These and other facets of equipment overloading can seriously affect the chemical and thermal recovery as well as the atmospheric pollution abatement program of a kraft mill.

This, of course, is not to say that a 250-ton per day designed mill cannot be operated successfully at 300 tons, but, rather, that it is important to establish the ultimate production capacity of a mill to give both maximum profitable production and recovery with the existing equipment.

Thus, a mill operating consistently on a scheduled basis at the optimum production capacity yields the best return for the investment in three ways: chemical and thermal recovery, atmospheric pollution abatement, and pulp production.

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