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INVESTIGATIONS OF HEAT TREATMENT FOR PAPER MILL SLUDGE CONDITIONING



Industrial Environmental Research Laboratory
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INVESTIGATIONS OF HEAT TREATMENT
FOR PAPER MILL SLUDGE CONDITIONING

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

Sludges produced by pulp and paper mills and biological treatment of their waste streams need to be disposed of in a dewatered and environmentally sound state. Sludge dewatering is made easier by conditioning. Discussed herein is thermo-conditioning of pulp and paper mill sludges including process, chemical, and biological sludges. This paper is useful to those evaluating sludge dewatering alternatives and the sludge conditioning methods to be employed. For more information contact the Food and Wood Products Branch of the Industrial Pollution Control Division.

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ABSTRACT

The capability of oxidative and nonoxidative heat treatment processes for the conditioning of hydrous sludges originating in pulp and paper industry manufacturing or wastewater treatment operations was defined on the basis of laboratory scale investigation. Sludges employed in the study included (a) alum water treatment sludge, (b) groundwood fines, (c) alum-coagulated biological solids and (d) waste activated sludge. The benefit of acid assisted oxidative conditioning of the latter was also assessed. Results were related in terms of improved filtration properties, the extent and significance of solids solubilization and the resulting impact on filtrate quality.

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SECTION 1

INTRODUCTION

The wider application of high rate biological treatment, as well as the technology proposed to meet evolving effluent standards, will amplify existing sludge disposal problems and broaden the range of sludges requiring disposal to those of physical-chemical origin. Included among the latter would be residuals resulting from wastewater filtration or chemical coagulation of biologically treated effluents and process waters. Moreover, hydrous sludges associated with primary treatment from certain manufacturing operations, groundwood sludges for example, will continue to pose tenuous problems.

The magnitude of sludge disposal difficulties has and continues to warrant several levels of investigation. To illustrate, surface properties of hydrogels have been investigated in previous NCASI research conducted by Zettlemoyer (1). In addition, the significance of the polysaccharadic nature of cellular components to water retention was the subject of a two-year study sponsored by the National Council at the Institute of Paper Chemistry (2). Such fundamental knowledge is prerequisite to development of new approaches to sludge dewatering. For the present, the capability of known technologies for the conditioning and/or dewatering of excess sludges must be understood and considered as an integral part of any waste treatment system. It is within this context that this investigation of thermal processes for the conditioning of hydrous sludges was carried out.

CHARACTERIZATION OF THERMAL CONDITIONING REGIMES

Nonoxidative Conditioning

If a hydrogel is sufficiently heated, bound water will be liberated from within the gel framework. High temperatures induce this phenomenon identified as syneresis by sufficiently increasing molecular movement to overcome electrostatic repulsion. The increased internal contact of the gel's structural elements will result in a breakdown of the hydrogel structure. Lumb (3) reports that the temperature to achieve the full effect with sludges ranges from 290° to 369°F (143° to 187°C). The response of sludge constituents to hydrolysis reactions at those conditions has been detailed by Brooks (4) and would indicate

that mechanism to be of great significance to hydrogel destruction by thermal means.

Harrison's work (5) conducted at the Virginia Polytechnic Institute indicates that maximum filter loading rates could be attained at temperatures ranging from 347° to 365°F (175° to 185°C) corresponding closely with the 349.7°F (176.5°C) optimum reported by Jepson and Klein (6). Brooks (4) and Harrison (5) concur that filtration is not appreciably improved until the temperature is in excess of 266°F (130°C).

Results of Follett's investigation (7) are compatible with the previously cited studies. At conditioning temperatures approaching 266°F (130°C), filterability was actually inferior to the nonconditioned control. However, conditioning at 365°F (185°C) effected dramatic improvement.

W. K. Porteus is credited with the initial patent of a heat conditioning process incorporating the aforementioned principles and operating conditions over 35 years ago. Commercially available systems are characterized by reactor detention times of 30 to 40 minutes at temperatures from 338° to 401°F (170° to 205°C), and corresponding pressures of 150 to 300 psi.

Oxidative Conditioning

In conjunction with syneresis and hydrolysis effects, destruction of the hydrogel structure characteristic of secondary sludges may be further accelerated by thermal oxidation. In theory, any organic compound can be oxidized in aqueous solution, if sufficient energy in the form of heat and/or pressure is provided to complete the reaction.

Figure 1, developed from data collected in previous NCASI study, parallels the results reported by others (8) in illustrating the impact of progressive sludge oxidation upon specific resistance. Of note is the significant reduction in resistance with only 10 to 15 percent oxidation. This should not be interpreted, however, as establishing oxidation as the dominant mechanism. Such a degree of oxidation is accomplished in commercially available equipment at temperatures from 300° to 400°F (150° to 204°C) with associated pressures from 150 to 300 psi, and detention times from 30 to 45 minutes.

The primary effect of low degrees of oxidation is hydrolysis of the large macro-molecules to constituent compounds. The hydrolyses which break up the water binding protein and lipid macro-molecules have been cited as a mechanism for the dramatic increase in filterability at low degrees of oxidation (9).

As oxidation increases, the products of hydrolysis are found in lower concentration, indicating that wet air oxidation

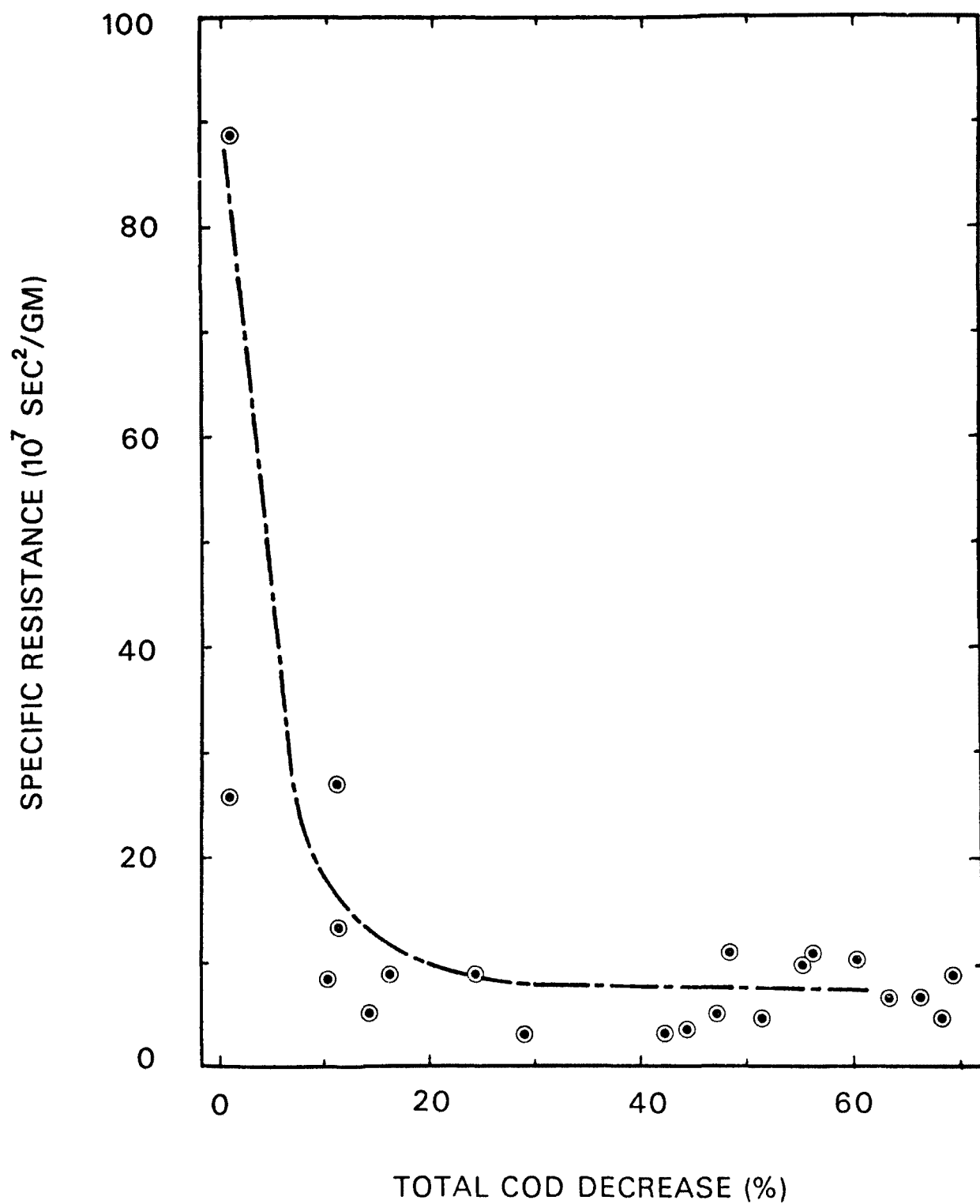


Figure 1. Impact of sludge oxidation upon filterability.

proceeds through hydrolysis followed by oxidation of the smaller molecules to carbon dioxide and water. At high degrees of oxidation only the more stable of the hydrolysis and oxidation products such as acetic acid remain (4). In commercial equipment, high levels of oxidation are affected at temperatures of 450° to 600°F (232° to 315°C), corresponding pressures of 500 to 3000 psi and detention times of 30 to 45 minutes.

From a sludge conditioning perspective, lower degrees of oxidation are, in most cases, economically advantageous in comparison to higher degrees of oxidation (5). Though perhaps possessing only a somewhat lower specific resistance, highly oxidized sludges have a much smaller volume of residual solids remaining for ultimate disposal. However, ash handling may pose a problem for high oxidation systems. Observations have been made that the resulting finely divided ash is not amenable to vacuum filtration (10).

RESPONSES TO PROCESS VARIABLES

The overall response of sludges to thermal conditioning must be understood in terms of the effects of variations in process temperature, reaction time and operational regime upon the extent of solids "destruction" and associated supernatant quality, as well as solids filterability. Observations documented within the literature may be most appropriately related within the framework of previous NCASI investigation (11) evaluating such effects upon a waste activated sludge generated in the treatment of wastewaters associated with bleached kraft/combined NSSC manufacturing. That study was conceived:

1. To assess from a sludge conditioning perspective the relative performance of oxidative and nonoxidative processes over a broad temperature range.
2. To determine the magnitude of solids hydrolysis associated with those processes and the resulting impact upon organic strength, as well as nitrogen, and phosphorous concentrations, contained in the heat treatment liquors. Figures 2 through 9 are illustrative of results from that study.

Filtration Properties

Figures 2 and 3, respectively, illustrate the time-temperature dependency of nonoxidative and oxidative conditioning processes. The former figure demonstrates the benefit of greater detention times at the specified reactor temperature. Comparatively, extending the retention time at a given temperature proved to be of less benefit than conditioning at higher temperatures. Similarly, Everett and Brooks (12) reported that a given degree of conditioning was attainable in less time at greater

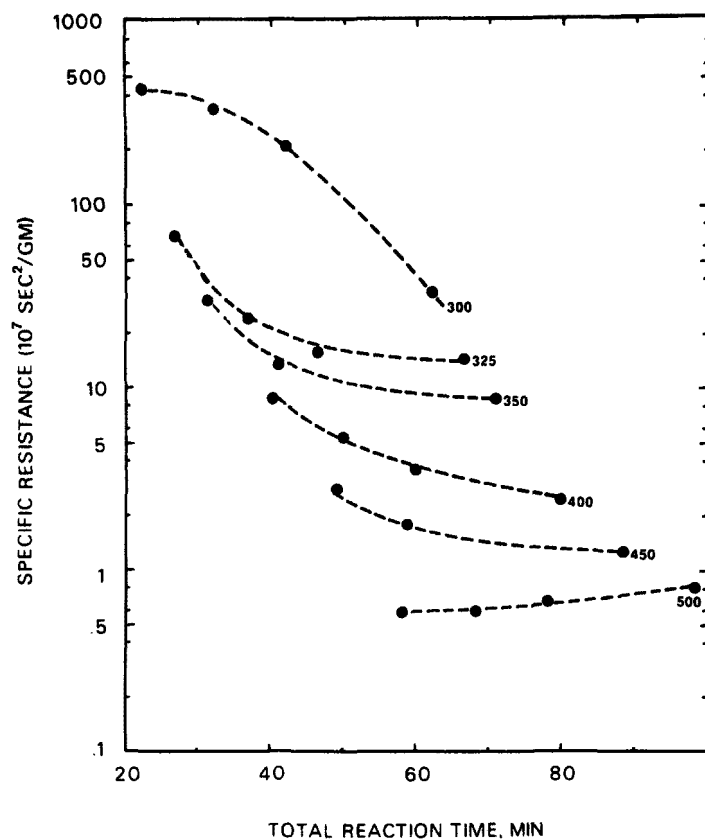


Figure 2. Response of sludge filterability to nonoxidative thermal conditioning.

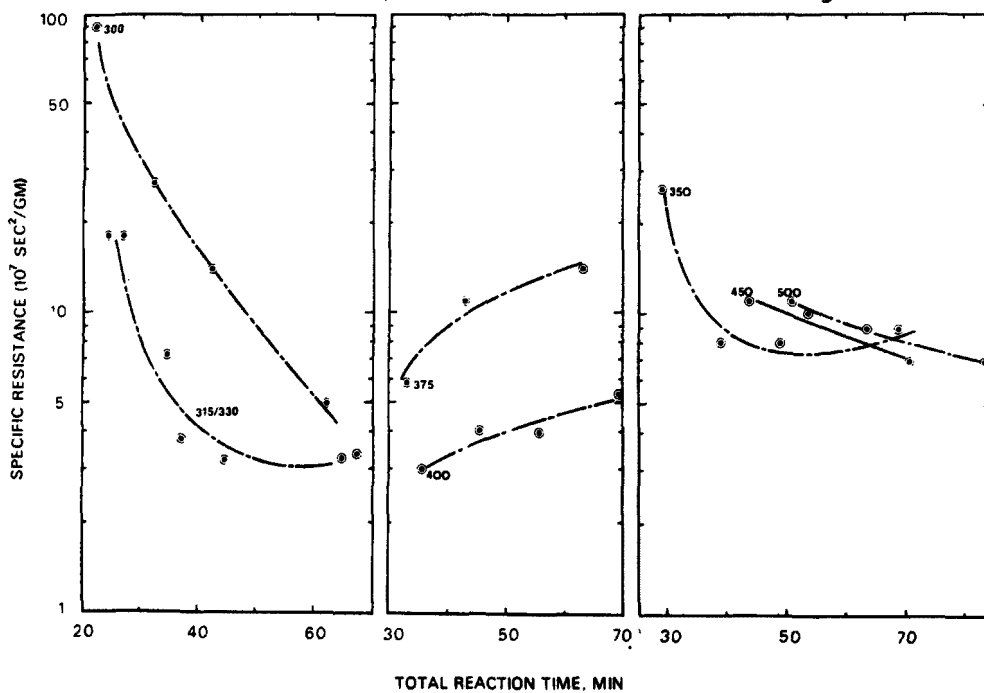


Figure 3. Response of sludge filterability to oxidative thermal conditioning.

temperatures. Within a temperature range of 350° to 400°F (177° to 204°C) specific resistance was reduced to within 3 to 10 (10^7) sec^2/gm , well into the range cited for successful filtration. Values as low as 7.5 (10^6) were attainable at 500°F (260°C). Little further benefit was seen at 600°F (315°C). However, the practical benefit of conditioning at those elevated temperatures would be dependent upon the relative economy of higher temperature reactors as opposed to expanded filter capacity. As shown by Figure 3 dramatic improvement in sludge filterability by oxidative conditioning was observed for even the lowest temperature studied. While additional benefit to increasing the reaction temperature to 315°F (157°C) is apparent, subsequent increase to 330°F (166°C) was of little further advantage. The conditioning effects at 350°F (177°C) would appear to be less suitable were it not for the fact that the resistance of the raw sludge used for the 350°F (177°C) series was 60 percent greater than that of those remaining sludges conditioned at temperatures less than 400°F (204°C).

The apparent departure for the results at 350°F (177°C) illustrates the importance of original sludge composition. It is reasonable to assert that original sludge characteristics other than specific resistance are of undoubted significance to thermal conditioning processes. As a consequence, extrapolation of results for a given sludge to others will require caution. In addition, the influence which the normal compositional variation in sludges originating from a given source exerts upon predictability of process performance requires further study. Lacking that predictability will require inherent process flexibility most readily attainable by designing for operation over a span of temperature conditions. At oxidative temperatures of 375°F (191°C) and 400°F (204°C), sludge filterability worsened as retention time was extended. Conditions associated with those temperatures would appear to constitute a transition range in which further alteration of the sludge structure is detrimental. Experience reported by Everett (13) affirms the existence of a minimum specific resistance, which varies for different sludge types. He relates this phenomena to heat treatment effects upon increased solubilization of sludge organic matter, citing that having attained that minimum specific resistance, additional solids solubilization will not further decrease specific resistance; but, in fact, may increase it. Increasing temperatures to 450°F (232°C) did result in improvement in filtration properties as reaction time was extended. However, results were not significantly better than those observed at 350°F. It should be added that original specific resistances for sludges conditioned at the above three temperatures were of the same order of magnitude [$1000\text{--}1300(10^7)$ sec^2/gm]. Considering the relative performance of conditioning at those temperatures, it would appear that oxidative conditioning beyond 350°F (177°C) is not of substantial benefit to sludge filterability. In any event, within the temperature range of 300° to 350°F (149° to 177°C), the same as

quoted for low level wet oxidation, sludge specific resistance was reduced to within (3 to 7) $10^7 \text{ sec}^2/\text{gm}$.

Thus, nonoxidative and oxidative thermal conditioning processes in temperature ranges of equipment currently available were capable of reducing sludge specific resistance to similar levels. At least from a sludge conditioning standpoint, the processes would appear comparable. That is not to suggest that the processes are or are not economically competitive, all factors considered.

Solids Hydrolysis

A graphical comparison for each conditioning regime indicated that the magnitude of solids hydrolyzed increased as a function of time to some limiting value dependent upon the reaction temperature. As shown by Figure 4, that limiting value increased linearly with the reaction temperature. Furthermore, at a given temperature up to 450°F (232°C), the quantity of solids undergoing reaction by oxidative conditioning was approximately double that for the nonoxidative means. That relationship assumes a reaction environment which is not oxygen limiting. Where oxygen is limiting, solids available for reaction would conceivably lie between the two curves. Sludge hydrolysis by nonoxidative means is limited at temperatures up to 600°F (316°C) to approximately 60 percent; whereas, hydrolysis by oxidative conditioning would appear to be limited only by the volatile content of the secondary sludge. The data would also illustrate that solids hydrolysis exceeding 60 percent is of no further benefit to sludge filterability.

Takamatsu (14), in his study of the thermal decomposition kinetics of activated sludge, concluded that solids hydrolysis could be approximated as a first order relationship, and, as such, would be independent of initial sludge concentration. This would corroborate previously reported data indicating that volatile matter reduction is independent of sludge solids concentration (15). However, where the proportion of initial sludge solids available for reaction at a given temperature is greater, it would follow that the required destruction of the hydrogel components would be accelerated. Thus, because a greater fraction of solids is available for reaction under oxidative conditions, it is reasonable to expect that equivalent conditioning by oxidative means, in contrast to nonoxidative, could be accomplished at lower temperatures. Furthermore, the magnitude of solids reacted could likely be regulated by extent of oxygen availability.

The impact of solids hydrolysis upon filtration properties is illustrated by Figure 5. The linear curves shown were developed for and are limited to results in which the magnitude of sludge hydrolysis was 56 percent and less.

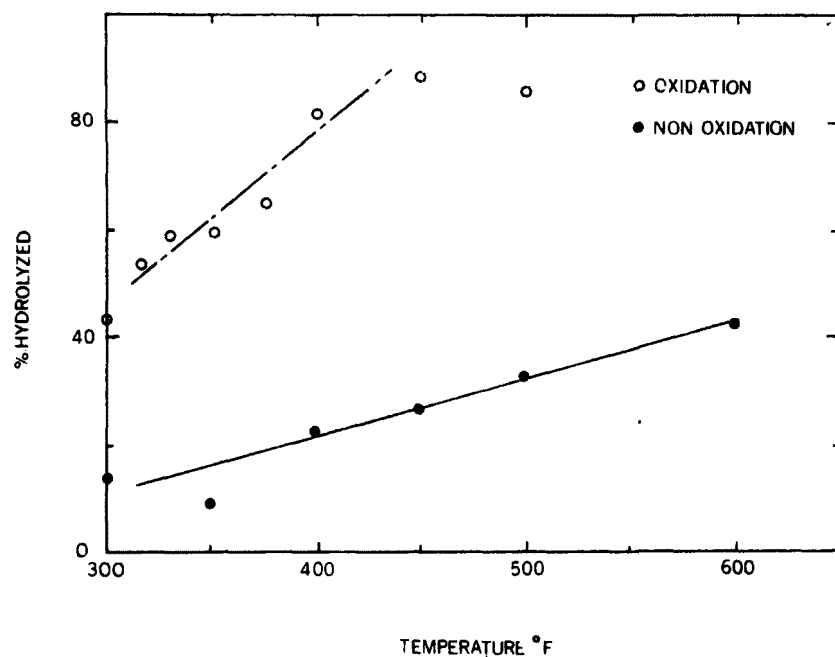


Figure 4. Reactive solids.

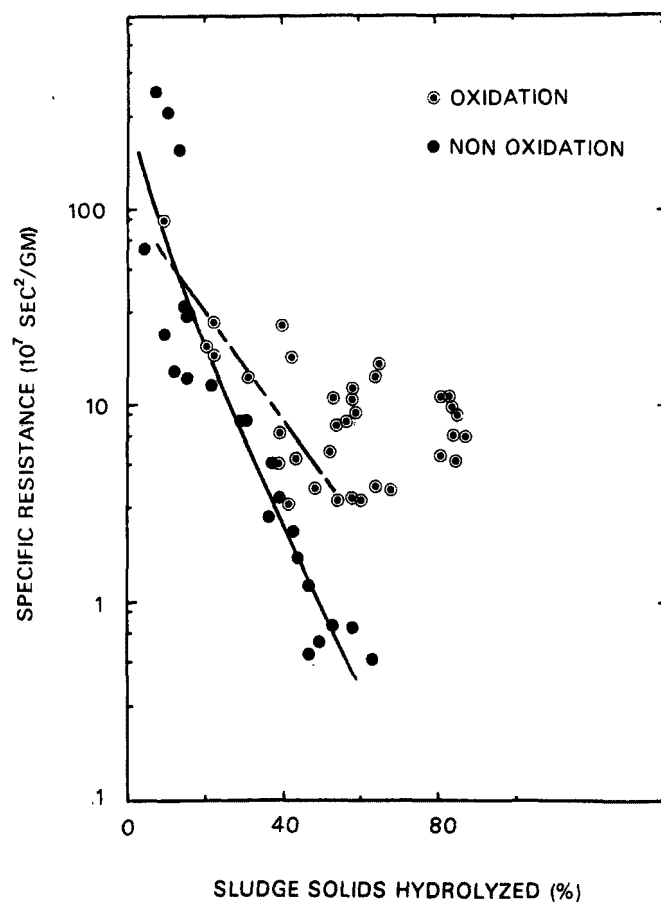


Figure 5. Impact of solids hydrolysis upon sludge filterability.

A similar relationship has been documented by Everett (13) in his studies of the nonoxidative regime of conditioning. The curves suggest that conditioning by low level oxidative and non-oxidative means to a specific resistance of $5 (10^7) \text{ sec}^2/\text{gm}$, would be accompanied by respective solids hydrolyses on the order of 50 percent and 35 percent.

Supernatant Quality

Whatever the benefit of solids hydrolysis to filterability, it is of additional consequence to the composition of sludge filtrates that require further processing prior to discharge to receiving waters. Brooks (16) has concluded that the COD of heat treatment liquors is proportional to the solids hydrolyzed. As shown in Figure 6, a similar trend is indicated by the data developed in this study where sludge solids hydrolysis does not exceed 55 percent. A dramatic decline in liquor COD is apparent at hydrolysis levels beyond 60 percent, a region limited to oxidative conditioning. Results indicate that nonoxidative conditioning of a 1 percent sludge within a temperature range of 350° to 400°F (177° to 204°C) would yield an increased filtrate COD of approximately 4300 mg/liter. With oxidation at temperatures of 300° to 350°F (149° to 177°C), filtrate COD for a similar sludge would be increased to 4800 mg/liter. High level oxidation produced filtrate COD increases ranging from 2600 to 4000 mg/liter. For the entire range of nonoxidative conditioning, as well as oxidation reactions less intense than 450°F (232°C) for 20 minutes, BOD constituted a relatively consistent 58 percent fraction of the measured COD.

Further, sludge oxidation under higher level conditions increased that ratio to an average 74 percent. However, the ratio was highly variable at sludge hydrolyses beyond 80 percent. At those conditions, filtrate composition is no longer predominantly a function of solids reactions, but rather filtrate oxidation. A more direct comparison of measured BOD with solids hydrolysis is presented in Figure 7. The pattern is comparable to the similar relationship for COD with the notable exception that the decline of filtrate BOD associated with high level oxidation is not so dramatic.

Representative BOD concentrations observed for the low level oxidation regime were approximately 3400 mg/liter, in comparison with a 3000 mg/liter magnitude for nonoxidative conditioning in the 350° to 400°F (177° to 204°C) range. High level oxidation was intermediate. Thus, conditions for either process adequate to reduce sludge specific resistance to a range of 3 to 10 (10^7) sec^2/gm would not yield heat treatment liquors with significantly different BOD concentrations.

The cumulative effect of recycling thermal conditioning liquors would impose an additional organic load of at least

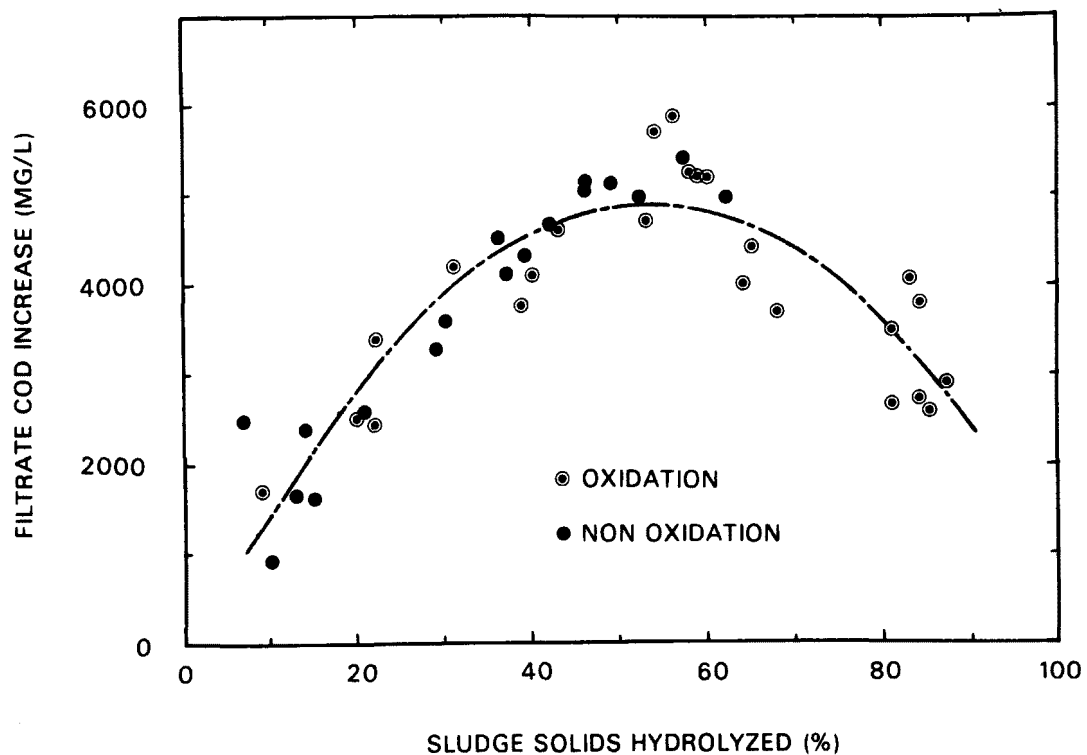


Figure 6. Increase in filtrate COD resulting from heat induced sludge hydrolysis.

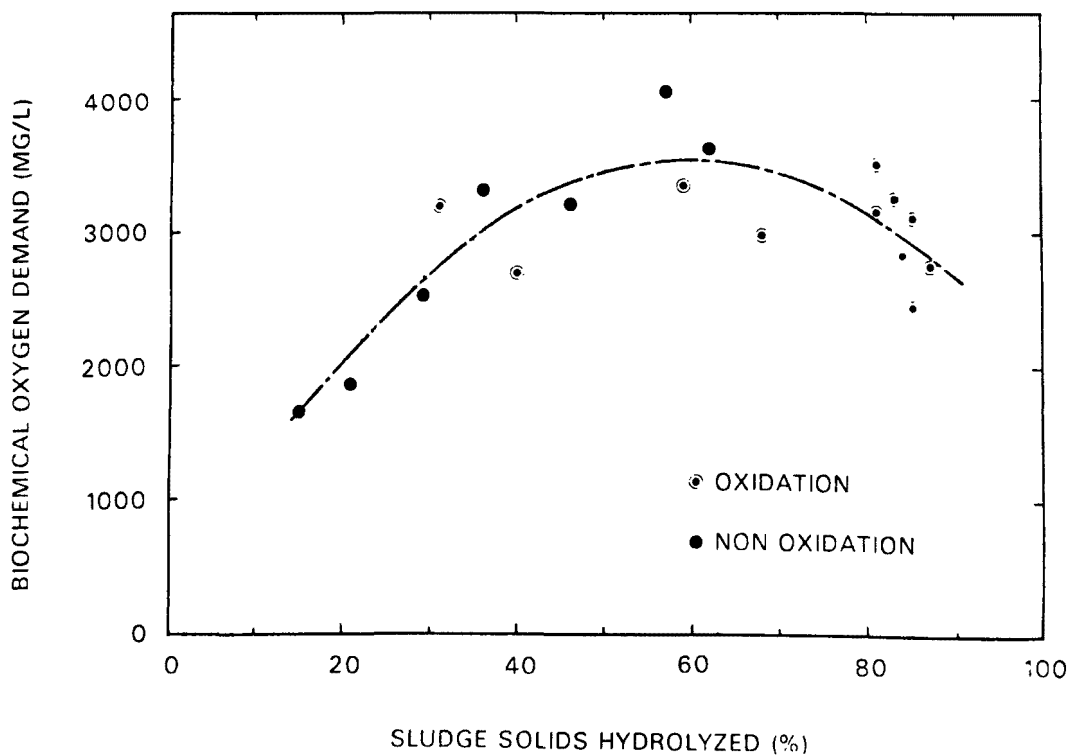


Figure 7. Increase in filtrate BOD resulting from heat induced solids hydrolysis.

20 percent upon the treatment system, assuming a sludge yield of 0.5 lb solids/lb BOD. The subsequent costs for additional treatment, as well as the associated additional sludge conditioning capacity, must be considered in assessing costs of handling the original sludge mass.

Results herein, and those of other investigators, imply that concentrations of organics and other constituents in filtrates associated with the thermal conditioning of a 1 percent consistency sludge may be extrapolated to similar sludges of greater consistency. Brooks (16), as well as Everett (15), have demonstrated that concentration of individual components in a heat treatment liquor increased in proportion to the feed solids concentration. That result would also be corollary to the previously described first order kinetics.

The brown color characteristic of heat treatment liquors has been attributed to high molecular weight compounds originating from the high temperature combination of reducing sugars and amino acids (4). Dark supernatant color persisted over the entire spectrum of nonoxidative conditioning. However, with oxidative conditioning at 400°F (204°C), supernatant color evolved from dark brown to colorless as reaction time was increased. Colorless supernatants were subsequently encountered at more intense conditions.

Filtrate nitrogen concentrations, as shown in Figure 8, increased dramatically with progressive solids hydrolysis. At hydrolysis levels of 50 percent and greater, attainable by wet oxidation, the concentration approached 270 mg/liter, approximately three-fourths of the available nitrogen. In the temperature range typical of nonoxidative conditioning processes, filtrate nitrogen did not exceed 180 mg/liter. Thus, oxidation would appear to return greater quantities of nitrogen.

In work since reported on, Everett (17) cites studies by others indicating that nonoxidative conditioning of digested sewage sludges released approximately 72 percent of the sludge nitrogen. Considering the potential for differing degrees of hydrolysis and the predigestion, such a result is not incompatible.

When exposed to conditions of heat treatment, bacterial nucleic acids, which contain up to 50 percent of cellular phosphorous, may either polymerize into an amorphous mass or hydrolyze, releasing soluble phosphorous (9). For a given intensity of conditioning, as manifested by sludge hydrolysis, filtrate phosphorous concentrations associated with oxidative conditioning consistently exceeded values observed for nonoxidation, as shown by Figure 9. The oxidative environment or its chemical end products apparently accelerates the solubilization of the phosphorous constituents in the sludge mass. Subsequent hydrolysis

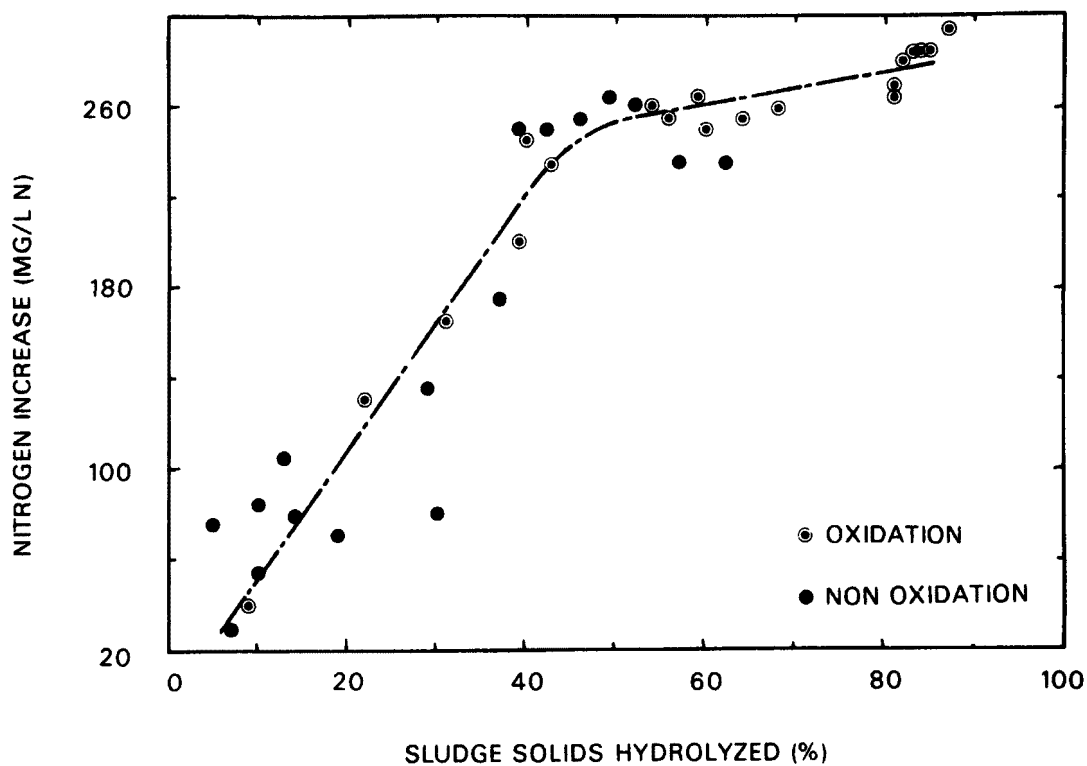


Figure 8. Effect upon filtrate nitrogen of heat induced solids hydrolysis

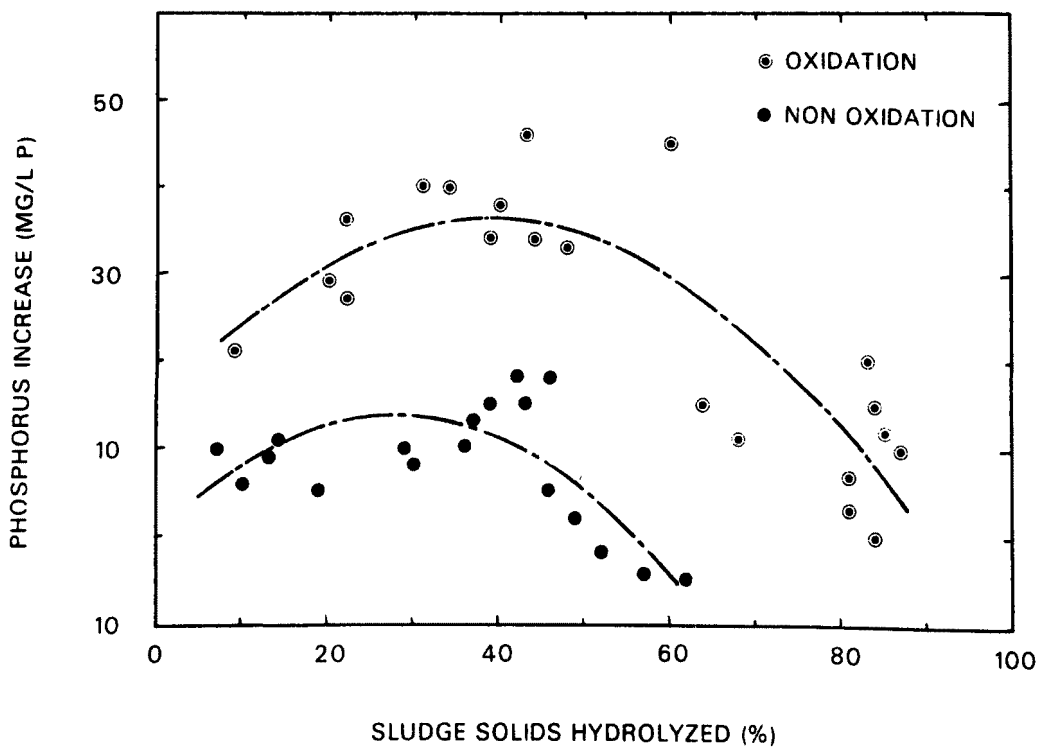


Figure 9. Effect upon filtrate phosphorus of heat induced solids hydrolysis

to the orthophosphate form and reaction with such anions as calcium would result in phosphate precipitation. An observation of decreasing filtrate phosphorous concentrations was made in pilot scale thermal conditioning of sludges generated in treatment of lime neutralized wastewaters of sulfite mill origin (18). As data in Figure 9 illustrates, the latter reaction appears to dominate where conditioning intensity has resulted in respective solids hydrolyses of 35 percent and 50 percent for the nonoxidative and oxidative regimes.

Both oxidative and nonoxidative conditioning results in the recycling of nitrogen compounds in excess of that required for biological oxidation of the filtrate organic constituents, assuming a required ratio of BOD to nitrogen of 20:1. Low level oxidation yielded a 50 percent excess quantity of nitrogen, whereas nonoxidative conditioning produced a 30 percent surplus at temperatures associated with the 35 percent hydrolysis level. Filtrates associated with low level oxidative conditioning contained a quantity of phosphorous adequate to meet an assumed BOD to phosphorous requirement of 100:1. However, nonoxidative conditioning in the 350° to 400°F (177° to 204°C) range made available only half that quantity.

Summary

Malina (19) advances the major advantages of heat treatment systems as the elimination of odor, elimination of the need for chemical conditioning of sludges, and the production of a sterilized filter cake. Cited as major disadvantages are fuel requirements necessary to sustain process temperatures, where necessary, and the need for treatment of supernatant liquor.

Past investigation would suggest that solids hydrolysis represents the principal mechanism for destruction of hydrogel properties by both nonoxidative and low level oxidative thermal conditioning. Both processes are capable of affecting equivalent degrees of sludge conditioning, which, for a given sludge, is dependent upon the magnitude of solids hydrolyzed.

The capacity of thermal conditioning processes to hydrolyze sludge solids is predominantly a function of temperature, with greater degrees of hydrolysis attainable in an oxidative environment. However, the capacity of temperatures within the range of 300° to 400°F (149° to 204°C) to decompose the hydrophilic sludge constituents would appear to lend little justification from a sludge conditioning perspective for further decomposition through utilization of higher temperatures.

Heat treatment liquors associated with oxidative and nonoxidative conditioning processes contain BOD concentrations of significant and comparable magnitude. Liquors generated with the processing of biological sludges of pulp mill origin contained

nitrogen concentrations up to 50 percent greater than required for their biological treatment. Low level oxidation contained at best, phosphorous adequate only for biological assimilation of the organic constituents contained therein. Liquors associated with nonoxidative conditioning or high level oxidation were significantly deficient in phosphorous.

FURTHER CONSIDERATIONS

Incremental Benefits of Acid Hydrolysis

The conditioning of hydrous residues prior to dewatering has been commonly approached by chemical means, with thermal processes receiving only more recent widespread application, predominantly in the municipal treatment sector. However, it is conceivable that the benefits of chemical energy could be extended by use in some optimum combination with thermal processes. It would follow that a corresponding reduction in the necessary intensity of thermal conditioning processes could be affected. Accordingly, interest in acid hydrolysis in conjunction with thermal conditioning processes has recently emerged.

Everett (20) reports that pH was found to have a marked effect both on solubilization and specific resistance of sludges exposed to nonoxidative conditioning. His results, showing effects on the specific resistance of sludge by varying the pH in heat treatment by sulfuric acid addition, are shown in Figure 10. At 338°F (170°C) lowering the pH from 5.5 to 2.5 reduced the specific resistance by between two and three orders of magnitude. At 356°F (180°C), a minimum specific resistance was attained at a pH of 4.0. At a pH less than 4, specific resistance increased, suggesting an "overcooking" phenomenon only found previously at temperatures of 428°F (220°C) or more. Everett attributed the benefit of acid addition to accelerated sludge solubilization. However, Everett concedes that the operation of conventional, nonoxidative heat treatment equipment at low pH would be difficult due to corrosion and other operational problems.

Such a limitation would not apply to the same extent in equipment conventionally applied to oxidative conditioning, due to its inherent design for accommodating more corrosive environments. A similar benefit of acid addition to sludge oxidation has been reported by Seto and Smith (21). As shown in Figure 11, high level oxidation of sewage sludge is achieved at less intense reactor temperatures with acid addition than without. Both the rate and extent of sludge oxidation were reported to increase with acid addition at an operating temperature of 450°F (232°C). That is not to imply, however, any inherent benefit to the dewaterability of the residual solids at that temperature. More importantly from a solids conditioning perspective, the question remains as to the extent to which acceptable filtration

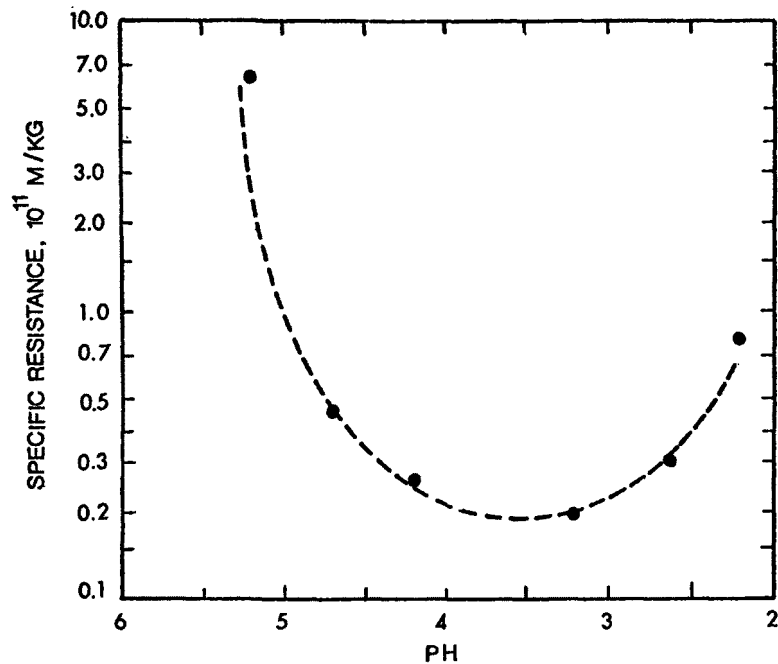


Figure 10. Effect on the specific resistance by varying the pH in heat treatment [after Everett (18)].

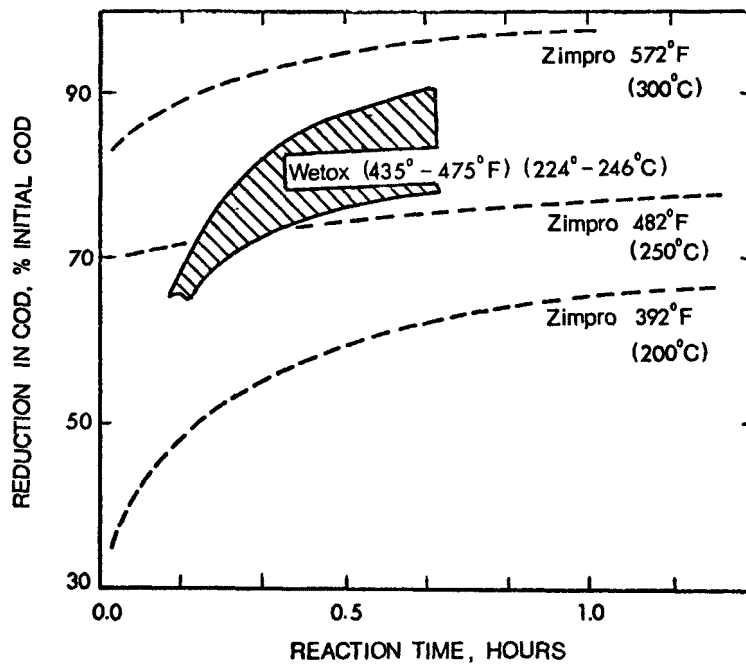


Figure 11. Comparison of laboratory scale Wetox and Zimpro processes for wet oxidation of sewage sludge [after Seto and Smith (19)].

properties can be achieved with less intense reactor temperatures than normally associated with low level oxidative conditioning.

Chemical Sludges

The literature is largely void of experience with the use of thermal processes for the conditioning of chemical sludges. Hudgens and Silveston (22) do describe results of studies with high level wet oxidation for the destructive oxidation of mixed chemical-biological sludges produced by chemical precipitation of nutrients and other components in several conventional municipal waste treatment plants. However, emphasis is given to the degree of destruction of organic matter, and the fate of organic carbon and phosphorous during progressive oxidation at temperatures of 450°F (232°C) or greater. Conditioning benefits at that and lower levels require further assessment.

Conditioning of Cellulosic Residuals

From studies dealing with the relationship between the constitution and dewatering properties of hydrous sludges, Attala (2) infers that groundwood fines should be amenable to conditioning by conventional thermal conditioning means. In laboratory studies, Khanh (23) is reported to have observed the complete destruction of peat moss slurried in water during wet air oxidation at temperatures between 450° to 550°F (232° to 288°C). However, the conditioning of hydrous cellulosic fines at conditions of lower intensity would seem less assured. Teletzke et al. (9) cites that the cellulosic components of sewage sludges are among the more resistant to degradation during wet oxidation, a phenomenon which accounts for their beneficial presence in the vacuum filtration of sewage sludges exposed to low level wet oxidation. Thus, the capacity of low level thermal conditioning processes to improve the filterability of groundwood fines would seem in question.

Summary

The preponderance of investigative activity dealing with the thermal conditioning of sludges has been concentrated upon primary and secondary sludges resulting from conventional wastewater treatment. Furthermore, those studies have typically been oriented toward wastes of domestic origin. What little attention that has been given to chemical sludges, or cellulosic residuals for that matter, has been directed toward their thermal destruction in contrast to the potential conditioning benefits associated with less intense reactions.

Similarly, identification of the benefits of acid hydrolysis in oxidative thermal processes has been limited to high level destructive regimes. The documented benefit of acid hydrolysis in reducing the intensity of nonoxidative conditioning necessary

to maximize sludge filterability would seemingly warrant determination if such a result could be extended to low level oxidative conditioning as well. Accordingly, it was the objective of this study to assess such issues in the applicability of nondestructive heat treatment techniques for the processing of waste sludges anticipated from manufacturing and waste treatment operation associated with the pulp and paper industry. More specifically, to:

1. Evaluate the capabilities of nondestructive heat treatment for the conditioning of hydrous sludges (a) from treatment of effluents from pulp and paper manufacturing and (b) those from physical-chemical treatment of biologically treated effluents and process water treatment.
2. Determine the benefit of acid hydrolysis in reducing the intensity of nondestructive oxidative heat treatment for the conditioning of hydrous sludges.

SECTION 2

CONCLUSIONS

Hydrous groundwood fines and waste activated sludges associated with the treatment of wastewaters from pulp and paper manufacturing, inclusive of sludges resulting from chemical treatment of biologically treated effluents, were all demonstrated to be highly responsive to thermal conditioning. That was not the case for alum based water treatment sludge. For waste activated sludge, acid assisted oxidative conditioning offered only a very slight, if any, advantage beyond that achieved with only a non-oxygen limiting environment.

Improvement in sludge filterability is related to the solubilization of sludge volatile constituents up to some optimum solubilization level between 40 and 60 percent. Beyond that degree of solubilization, a capability limited to oxidative conditioning, solids dewaterability exhibited a classical reversion.

Oxidative conditioning in a nonoxygen limiting environment poses no distinct conditioning advantage over nonoxidative processes. In fact, in the case of alum coagulated biological solids, filter leaf tests confirmed results with conventional filtration parameters showing that oxidative conditioning was less effective than conditioning in the absence of oxygen. However, the presence of oxygen accelerates the rate and extent of volatile solids solubilization.

Regardless of the mode of conditioning or acid addition, solubilization of activated sludge volatile constituents resulted in an associated supernatant COD increase equivalent to approximately 50 percent of the mass of volatile solids hydrolyzed. The corresponding ratio for the alum coagulated biological solids was less, suggesting the possible importance of aeration system sludge age to the character of the supernatant. The ratio of filtrate BOD to COD for groundwood fines and waste activated sludge including when acidified was 0.5 to 0.6--in comparison to 0.3 for the alum coagulated biological solids.

Heat treatment represents a viable means of conditioning the most difficult of sludges. However, technical personnel at installations contemplating its use should be aware of (a) its implications to significantly increased raw waste and color load

and (b) such reported operational problems as corrosion, scale, equipment maintenance and possible odor generation.

SECTION 3

RECOMMENDATIONS

Existing evidence to suggest that the extent of thermal conditioning is affected by sludge solids concentration suggests the existence of an optimum consistency where combined thermal and dewatering costs will be minimized. Definition of such a limit will require further evaluation employing prototype equipment for the dewatering of sludge thermally conditioned at varying consistencies.

Though this study has identified the capabilities of thermal processes for the conditioning of hydrous sludges, questions remain regarding the relative extent to which those results can be achieved with prototype equipment of existing proprietary systems. Factors contributing to potential differences would include the nature of reactor mixing, as well as heat and/or oxygen transfer characteristics. Differences between available alternative systems can be resolved only through comparative pilot testing analogous to process performance studies proposed by the Los Angeles/Orange County Metropolitan area (46). The conduct of such a program would also allow (a) assessment of day-to-day variability in process performance, (b) detection of such operational problems as scale, abrasion or plugging and (c) the response of actual prototype dewatering equipment. Objective cost comparisons would constitute an appropriate addition.

If thermal conditioning is to find application in the pulp and paper industry, the penalty represented by the incremental increase in raw waste and color load must be satisfactorily dealt with. Its contribution to effluent character must either be recognized in individual mill discharge permit limitations or alternative measures must be found for the processing and ultimate disposal of the waste liquors by means other than the wastewater treatment system. For integrated mills, in-process disposal options warrant a systematic, but cautious assessment.

SECTION 4

EXPERIMENTAL PROCEDURES

ANALYTICAL METHODS

Filtration Properties

Capillary suction time (CST) as described by Baskerville and Gale (24) was selected as a parameter by which sludge filtration properties were compared. In addition, where sludge volumes permitted, sludge specific resistance, as proposed by Coakley and Jones (25) was determined as an additional basis for comparison. In doing so, a Whatman No. 2 filter media and a vacuum of 15 inches of mercury were utilized. Data analysis and computation paralleled that proposed by Lutin (26).

A comparison of the two parameters for an unconditioned biological sludge over an array of solids consistencies is shown in Figure 12. The comparison illustrates the linear dependence of capillary suction time upon slurry consistency, whereas a different order relationship is suggested for specific resistance. However, specific resistance did not vary significantly over the range of 1 to 2 percent solids consistency. Correlation of the two dewatering indices is most conveniently made by comparing capillary suction time with the product of specific resistance and sludge solids concentration (24), as graphically shown by Figure 13. A near linear relationship is observed for capillary suction times ranging from approximately 30 seconds to 125 seconds. This corresponds to consistencies up to 2 percent.

It should, perhaps, be added here that such a dependence upon slurry consistency was seen to deteriorate with highly conditioned sludges, as illustrated in Figure 14, developed from study data. It suggests that observations within the range of consistencies encountered in this study were largely independent of consistency. Everett (15) makes a similar observation for thermally conditioned sludges at consistencies up to 8 percent. In addition, specific resistance data previously collected by the Council staff in the course of thermal conditioning pilot studies conducted by others showed comparable values for sludges evaluated at 1.4 and 7 percent solids consistency (18).

Nevertheless, in the determination of capillary suction time (CST), consistencies were adjusted to the original consistency

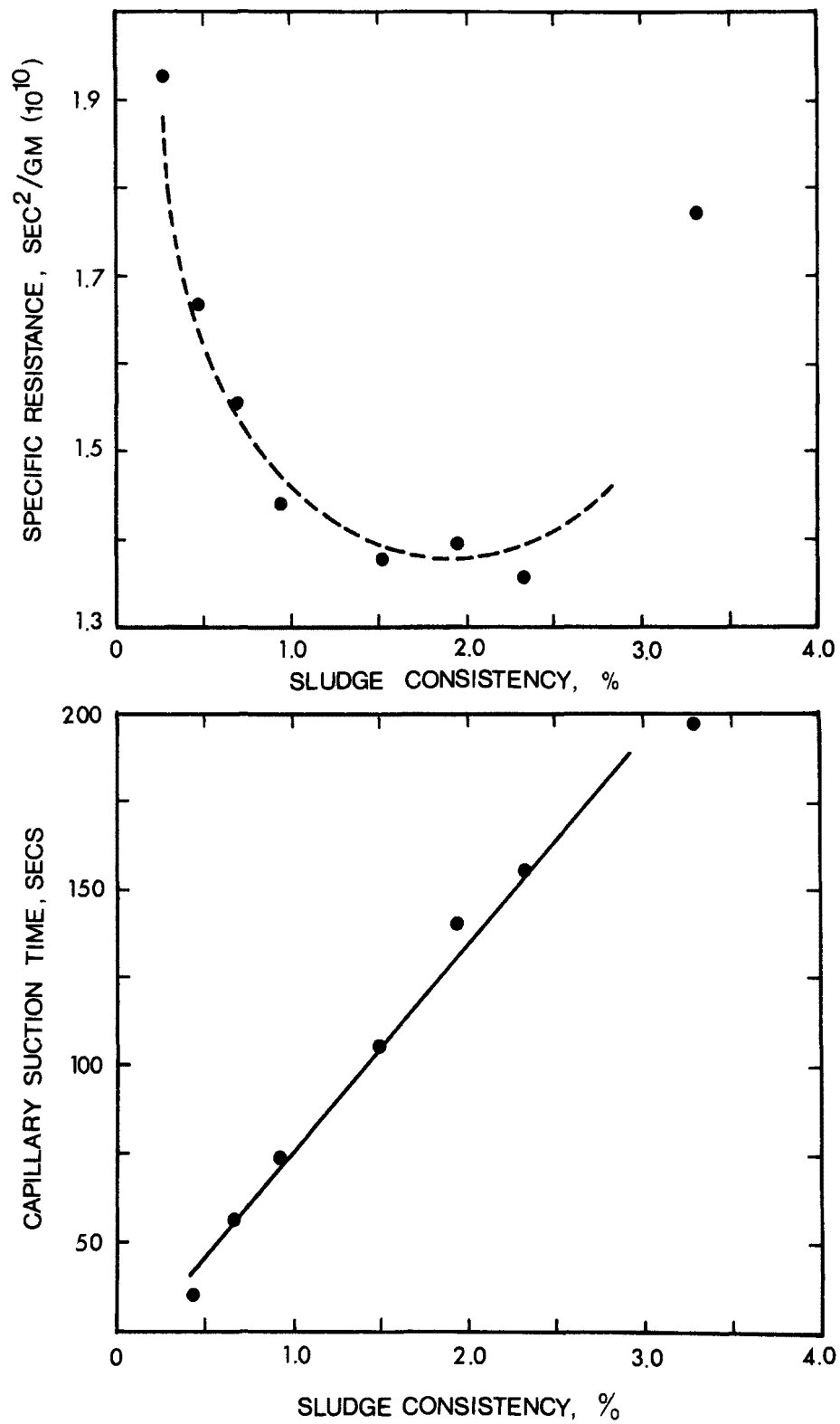


Figure 12. Biological sludge filterability characteristics.

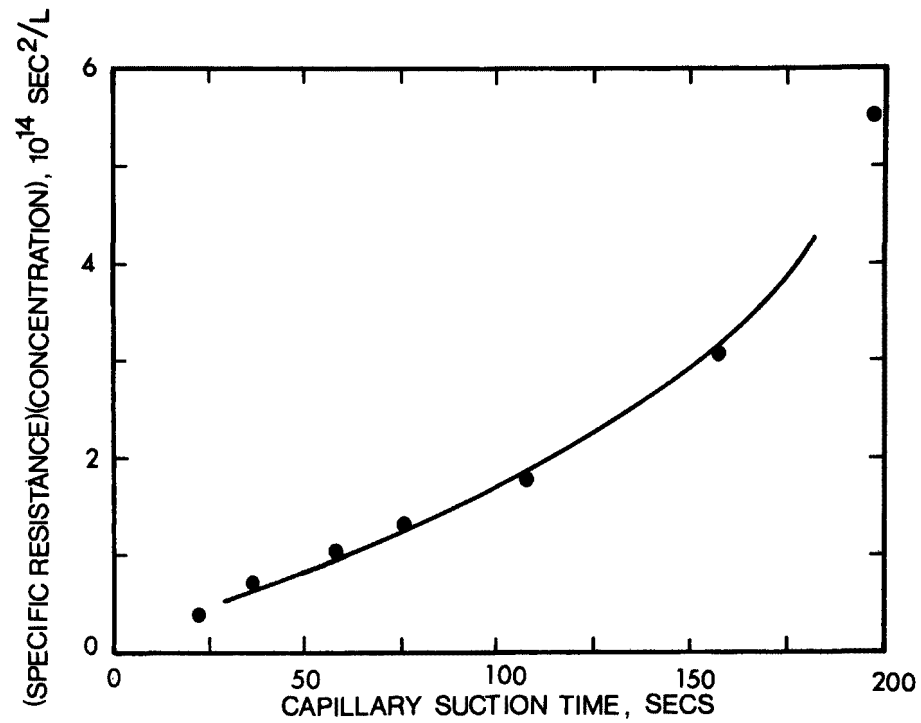


Figure 13. Relationship of specific resistance to capillary suction time.

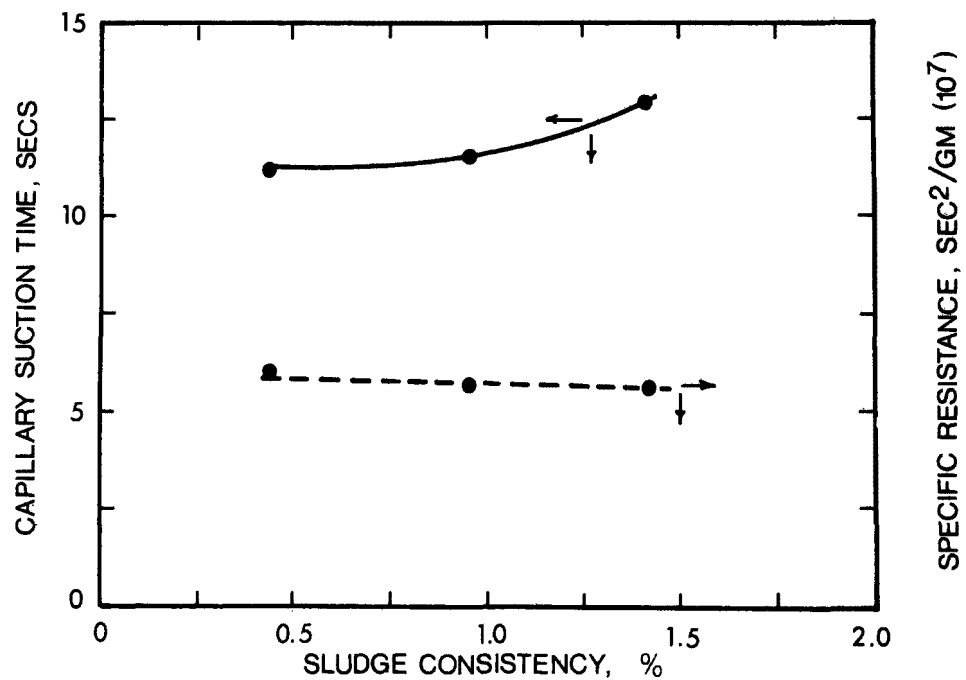


Figure 14. Sensitivity of filtration parameters to sludge consistency for well conditioned sludges.

exposed to thermal conditioning where sample volumes permitted. Reported values represent the average of three replicates. Reported values for specific resistance are the result of a single assessment conducted at conditioned sludge consistency.

Though specific resistance and capillary suction time are useful means for comparing conditioning effects, they bear little correlation with absolute dewatering performance on prototype equipment. For instance, with vacuum filtration, unlike Buchner funnel testing, forces of gravity and pressures of flow are opposing. In addition, Buchner funnel results are not equally dependent upon the cohesive or adhesive qualities of the filter cake. As a consequence, for the two most prominent sludges employed in this study, supplemental vacuum filter leaf testing was conducted. Procedures are outlined in NCASI Technical Bulletin 190 (27). In each case a 15-inch Hg vacuum was used.

Suspended Matter

Concentration of suspended matter contained in unconditioned sludges was calculated as the difference between total and filterable residue. Total residue was assessed by evaporating to dryness a known sludge volume in a forced draft oven maintained at 217°F (103°C). Filterable residue was determined by similarly drying a filtrate sample obtained by filtering through a glass fiber filter media sludge supernatant separated from the raw sludge by centrifugation.

Suspended matter concentrations remaining in conditioned sludges were evaluated by filtration of a known volume of sludge through a Gooch crucible fitted with a glass fiber filter disc, supplemented with Celite Filter Aid as outlined in NCASI Technical Bulletin 230 (28). In all cases, sludge volumes were measured by a cut-off pipette. Volatile matter was also assessed in accordance with methods cited in Bulletin 230.

Organic Concentrations

Chemical oxygen demand (COD) of filtrates was determined in accordance with Standard Methods (29). Biochemical oxygen demand (BOD) of filtrates was evaluated by the direct dilution technique outlined in NCASI Technical Bulletin No. 230.

EQUIPMENT DESCRIPTION AND OPERATION

Thermal conditioning of sludges was accomplished in a two-liter magedrive Autoclave, Model AFP-1005, manufactured by Autoclave Engineers, Inc. The basic autoclave unit is illustrated in Figure 15.

Modifications to the basic autoclave unit to effect ease and rapidity of sludge introduction and sample removal are

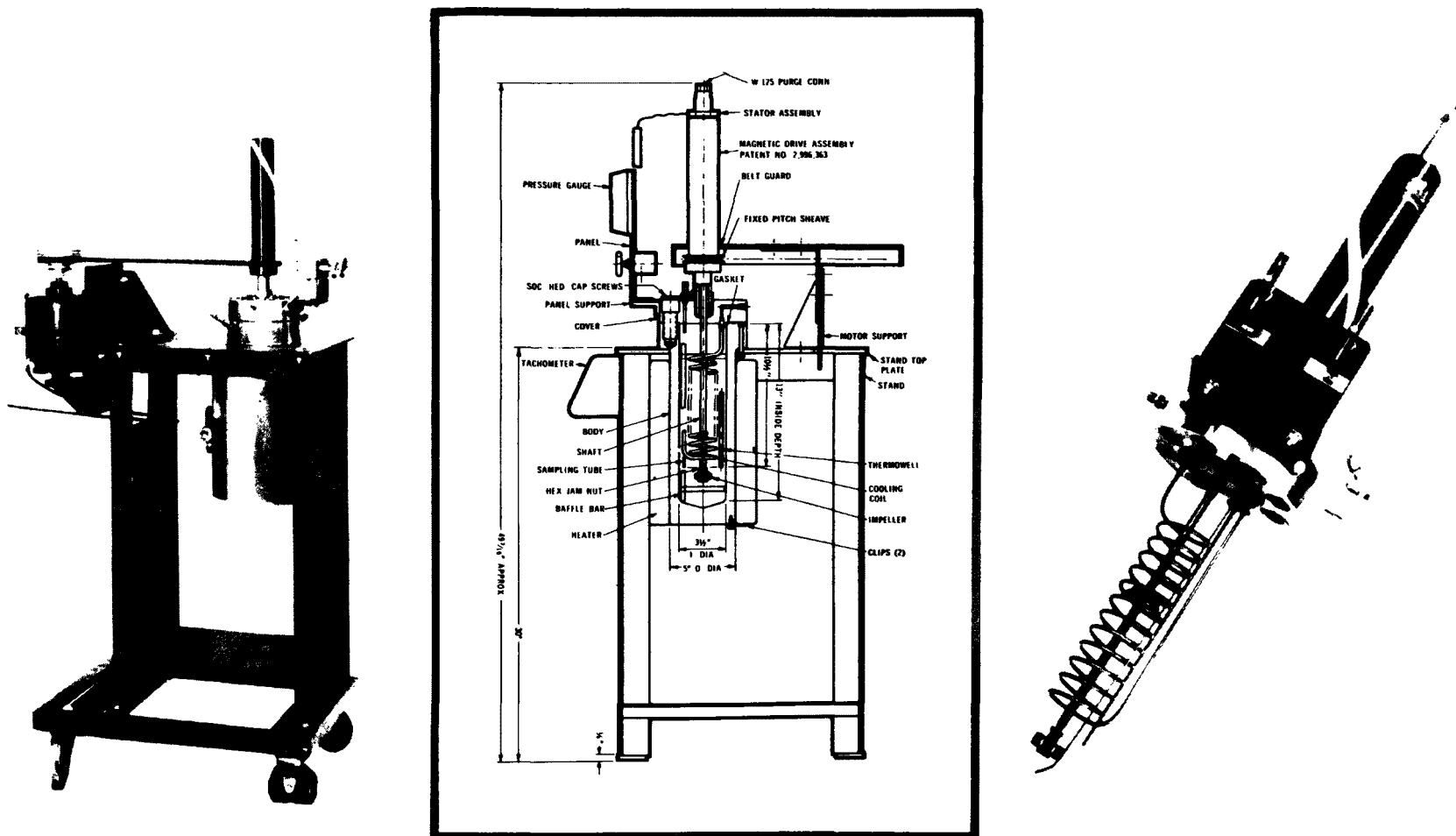


Figure 15. Autoclave utilized for thermal conditioning.

illustrated in Figure 16. Valved openings into the autoclave included a sludge inlet line extending to the bottom center of the unit; a sampling line, open also from the bottom of the unit; and a pressure relief valve located in the cover above the liquid level. A non-valved protective rupture disc was also present in the autoclave cover as a safety requirement. Pressure was monitored via a 0-3000 psi Bourdon tube gage connected into the autoclave cover. Temperature was monitored via a West Model J30BlVS26 thermocouple introduced into a thermowell in the reactor cover plate. Reactor temperature was subsequently displayed on a thermocouple activated temperature indicator, West Model 1.

Reactor heating was provided by a 2.1 kilowatt jacket-type electric heater regulated by a Barber Coleman Model 72C temperature controller in conjunction with a Type K thermocouple. Temperature excursions beyond preset levels were countered by passing cooling water through the internal coil until temperature was reduced.

A two-liter stainless steel Whitey pressure bomb preceded the autoclave in the sample inlet line. A three-way valve at the bottom of the bomb allowed the vessel to be evacuated or permitted sludge to be forced into the autoclave. A three-way valve at the top of the pressure vessel allowed sludge to be drawn into the bomb after evacuation and subsequent pressurization of the vessel via high pressure nitrogen or oxygen tanks.

Equipment operation consisted of five basic elements: (1) autoclave preparation, (2) a preheating of sludge supernatant, (3) injection of the sludge sample, (4) withdrawal of conditioned sludge samples at prescribed time intervals and (5) a final washing of residual solids from the autoclave.

Autoclave Preparation

Prior to supernatant injection the pressure cylinder was evacuated, filled with tap water, and repressurized with nitrogen. The autoclave was subsequently charged with the water and further pressurized with nitrogen through the pressure cylinder. After 2 to 5 minutes agitation, the autoclave was drained.

Supernatant Preheating

Having prepared and purged the autoclave, the pressure cylinder was again evacuated, filled with 500 ml of sludge supernatant and pressurized with nitrogen to 500 psi. The autoclave was then charged with the supernatant and the residual nitrogen bled off to achieve atmospheric pressure. The supernatant was subsequently heated to a temperature approximately 90°F (32°C) greater than the desired conditioning temperature.

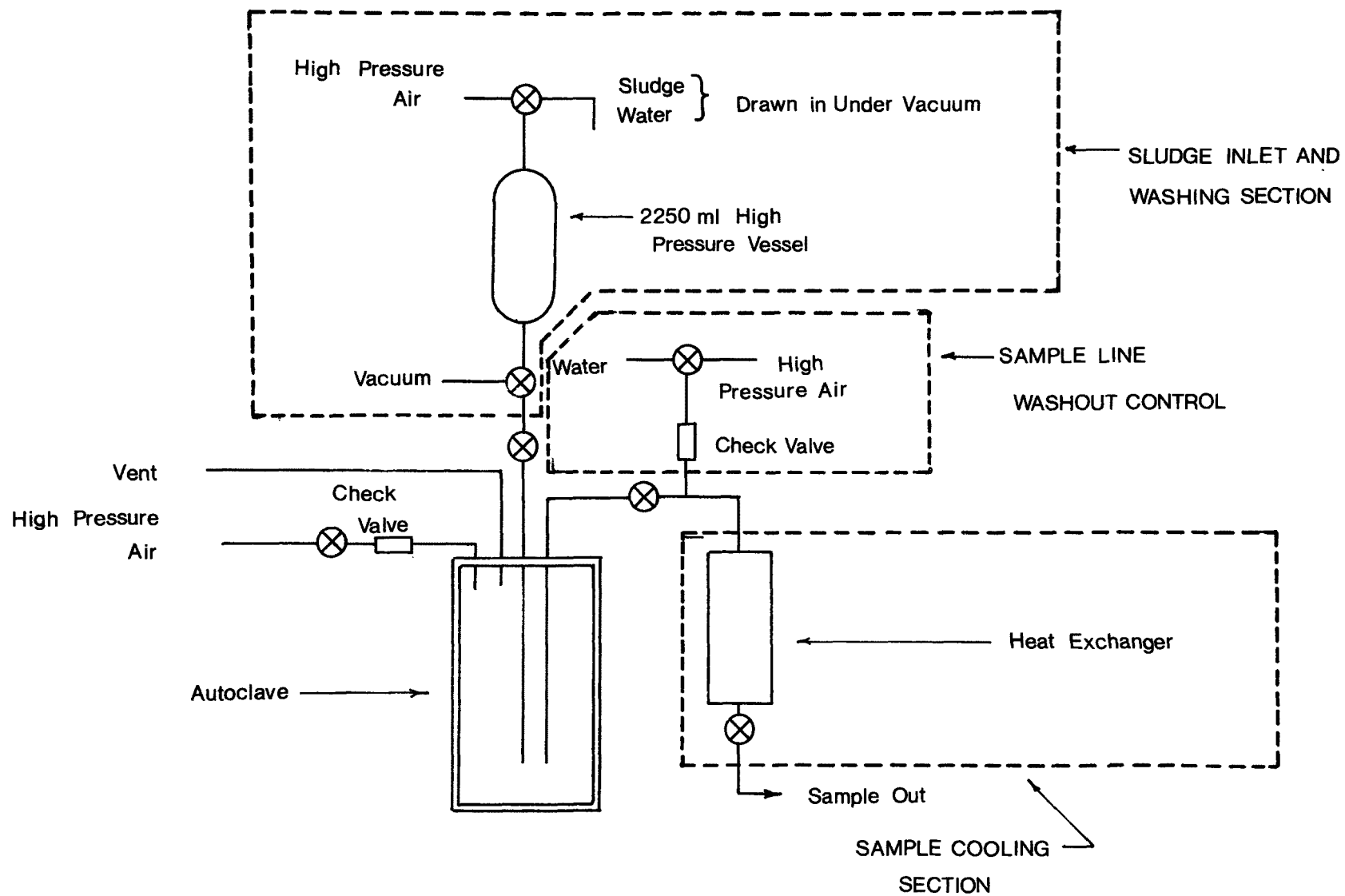


Figure 16. Schematic diagram of thermal conditioning apparatus.

Sludge Injection

During the preheating period, the pressure cylinder was evacuated and filled with 1000 ml of sludge. The cylinder was pressurized with either nitrogen or oxygen (dependent upon the conditioning regime) to a pressure exceeding ultimate autoclave pressure by 500 psi. Once having reached the desired preheating temperature, the autoclave was charged with the sludge. After an initial immediate temperature drop of 75° to 150°F (24° to 66°C) the desired conditioning temperature was established in 3 to 8 minutes and maintained there by periodic bursts of cold water through the autoclave cooling coil. Unless otherwise indicated, in subsequent discussion, reaction time is measured from the point at which specified operating temperatures are attained. Autoclave pressure was maintained at approximately 500 psi in excess of the vapor pressure of water at the conditioning temperature by either nitrogen or oxygen addition, dependent upon the conditioning regime. In the case of oxidative conditioning, the oxygen environment was restored at approximately five-minute intervals.

Sample Withdrawal

At the conclusion of the conditioning period, the autoclave sample valve was opened, allowing passage of a controlled volume of the autoclave contents through the heat exchanger for subsequent collection and analysis. During the course of the study, two approaches were taken in sample extraction, sequential and complete.

In the sequential sampling mode, portions of the autoclave contents were periodically removed at selected time intervals up to one hour as the conditioning progressed. Prior to doing so, the sample line was purged; and following the sample collection, the heat exchanger portion of the sample line was flushed and drained. Sequential sampling was utilized to determine relative compositional characteristics of the autoclave contents with progressive conditioning. However, it was found to be inadequate for assessing the concentration or mass of sludge/filtrate constituents.

To do so for any given conditioning time, it was necessary to completely remove the autoclave contents; that is, collect the complete contents. This sampling mode was employed to determine solids and filtrate COD concentrations. In addition, the availability of larger sample volumes permitted determination of sludge specific resistance.

Autoclave Washing

At the conclusion of all sampling and removal of the autoclave contents, the autoclave was charged with 1800 ml of

distilled water in a manner similar to autoclave preparation. After 3 minutes agitation, the wash water was removed. In the case of complete sampling, the wash water was collected and analyzed for suspended and volatile solids concentrations.

RAW SLUDGE CHARACTERIZATION AND PROCESSING

Composition and filtration characteristics of the sludges employed in this investigation are shown in Table 1.

Biological Sludge

The biological sludge was generated in an activated sludge plant treating wastewaters originating from an integrated bleached kraft mill with combined NSSC production. Characteristics of the system include (a) a 25.4 mgd [$6.7(10^4)$ liters per minute] wastewater feed, (b) a sludge recycle ratio of 24 percent, (c) an average mixed liquor suspended solids of 2000 mg/liter and (d) a detention time of 2.4 hours.

Most commonly during the course of the study, this sludge was added to the autoclave at a nominal 3 percent consistency. During that phase of study dealing with acid assisted hydrolysis, the biological sludge was acidified to a pH of 4.5 ± 0.1 by addition of 1N sulfuric acid. The pH was selected based upon results previously reported by Everett (20), as well as acid requirements in a range commonly cited for a proprietary thermal process employing acidification.

Alum Coagulated Biological Solids

This chemical sludge was generated by the alum coagulation of biologically treated effluent from an integrated bleached kraft mill. The 21.4 million gallon [$81.0(10^6)$ liters] daily flow from the mill is aerated in a basin of 2.8 days detention time. Residual solids are separated in a secondary clarifier following addition of 250 mg/liter alum supplemented with polymer. Of the nonorganic fraction in the sludge, 50 percent is assessed to be alum. Autoclave addition consistency was approximately 3 percent.

Alum Water Treatment Sludge

The alum water treatment sludge utilized had been previously thickened from 0.6 percent solids to 4 percent consistency in a flotation thickener following a 6 lb/ton (3 mg/gm) polymer addition. Feed consistency to the autoclave was approximately 2.5 percent.

TABLE 1. RAW SLUDGE CHARACTERISTICS

	Sludge description	Volatile content, %	Filterability			
			Capillary suction time, sec	Capillary suction time test consistency, %	Specific resistance, 10 ⁸ sec ² /gm	Specific re- sistance test consistency, %
30	Waste activated sludge	72	189.0	3.3	178	3.3
	Alum coagulated biological residue	63	49.1	3.0	52	1.3
	Alum water treatment sludge	33	58.0	2.5	--	--
	Screened groundwood fines	51	25.5	1.5	--	--

Groundwood Sludge

Primary sludge was obtained from a newsprint mill in which groundwood constituted 61 percent of total mill production. Fines were segregated by removing sludge components retained on a 60-mesh screen, based upon Attala's observation (2) that particles finer than 60 mesh pose the most difficult dewatering problems. The thickened fines were charged to the autoclave at 1.4 percent consistency.

After collection and thickening of the sludges at the respective mills, 5 mg/liter formaldehyde was added prior to shipment via surface transportation to the NCASI Central-Lake States Center. In addition, a 5-gallon sample, unpreserved, was shipped by air and subsequently utilized for developing sludge BOD/COD relationships.

SECTION 5

RESULTS

It should, perhaps, be indicated here at the outset that the conduct of this study was not intended to duplicate process conditions associated with existing or proposed proprietary processes for the thermal conditioning of sludges or other waste residuals. Furthermore, performance of equipment utilized in the investigation does not necessarily simulate, from the standpoint of process kinetics, operating characteristics of prototype reactors finding application in commercial systems. Rather, it is intended herein to develop wider public understanding of the potential responses of a variety of pulp and paper industry sludges to conditioning by thermal means.

WASTE ACTIVATED SLUDGES

Filtration Properties

Possibly the most striking observation made in this segment of the study and which the equipment configuration used in the previously cited NCASI investigation did not permit was the rapidity of the conditioning reaction. Figure 17, which illustrates the filtration properties of sludge progressively sampled over an 8-minute interval between the time the sludge was injected into the reactor and its attaining the desired conditioning temperature, would suggest that acceptable conditioning is virtually complete in a matter of several minutes. The congruence of the oxidative and nonoxidative profiles is also noteworthy.

Data pertinent to improvement in filtration properties as a consequence of oxidative and nonoxidative conditioning is shown respectively in Tables 2 and 3 and graphically summarized as Figure 18. In the figure, the range of observations for all detention times at the indicated temperature is shown about a curve drawn through points specific to a 20-minute reaction period. Examination of the data indicates no practically significant difference between the two conditioning regimes. Both were capable of achieving capillary suction times (CST) of 10 to 15 seconds, most commonly within a temperature range of 360° to 400°F (182° to 204°C). As might be anticipated from the demonstrated rapidity of the reaction, the detention time was of consequence principally at temperatures less than 350°F (177°C);

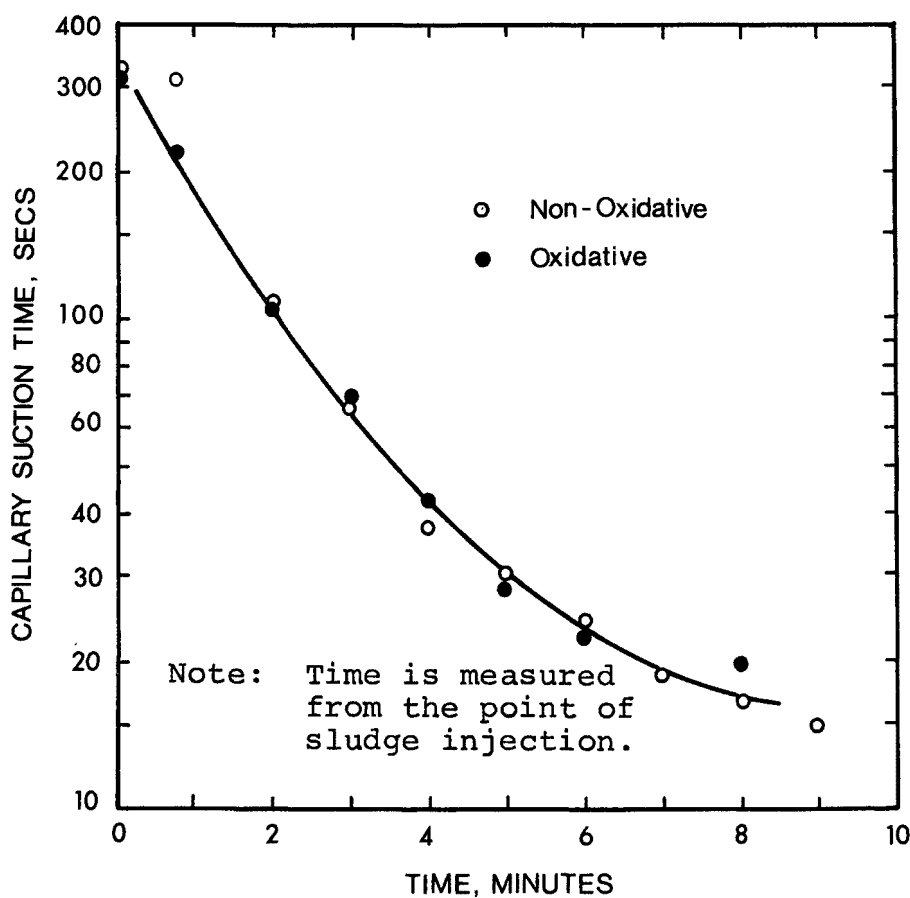
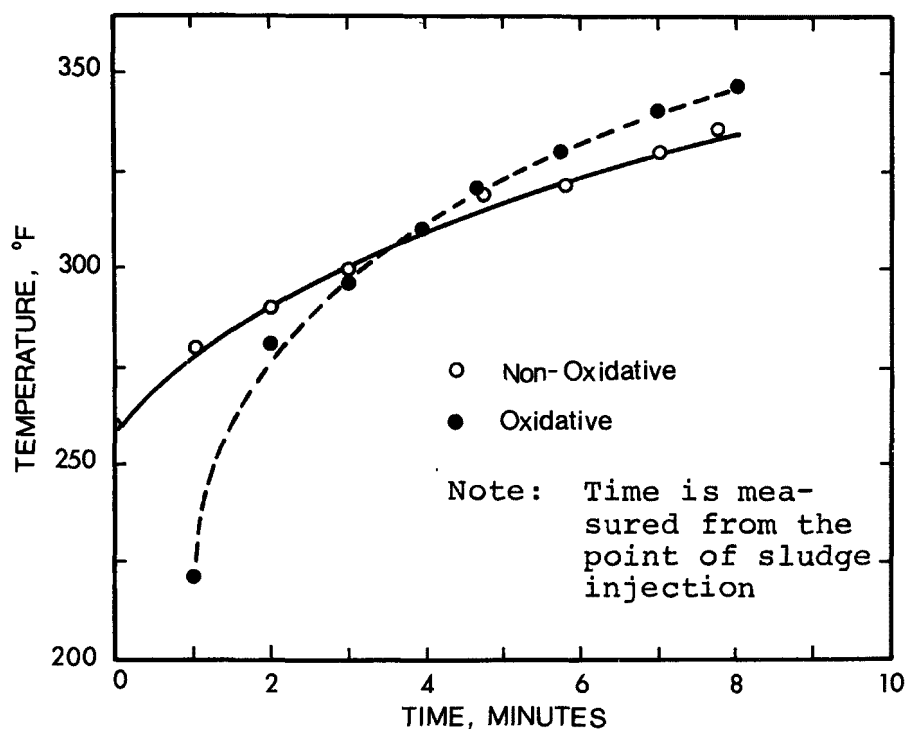


Figure 17. Filtration response as a function of conditioning time.

TABLE 2. SLUDGE FILTERABILITY RESPONSE TO OXIDATIVE CONDITIONING

Temperature	Time, min	Number of observations	Capillary suction time, sec	
			range	average
300°F (150°C)	0	4	20.1-38.0	25.9
	5	2	18.2-23.2	20.7
	10	4	18.0-21.4	19.7
	15	2	16.4-18.3	17.4
	20	5	15.9-19.6	17.8
	25	1	--	16.8
	30	1	--	15.9
	40	3	16.6-18.6	17.6
	50	1	--	13.9
	60	1	--	13.0
315°F (157°C)	0	1	--	29.8
	5	1	--	15.8
	10	1	--	17.4
	15	1	--	16.2
	20	1	--	16.5
	25	1	--	16.7
	30	1	--	16.2
330°F (166°C)	0	1	--	26.0
	5	1	--	18.6
	10	1	--	17.3
	15	1	--	18.4
	20	1	--	16.4
	25	1	--	17.5
	30	1	--	16.7
345°F (174°C)	0	1		23.8
	5	2	16.6-20.8	18.7
	10	2	16.0-18.7	17.4
	15	2	15.0-18.8	16.9
	20	2	13.3-17.4	15.4
	25	1	--	13.3
	30	--	--	17.4
	40	--	--	16.6
	50	--	--	15.5
	60	--	--	15.5
350°F (177°C)	0	2	16.8-17.8	17.3
	10	2	16.4-20.1	18.3
	20	2	16.0-18.7	17.4
	40	3	15.5-20.0	17.4

Note: Time is measured from the point at which the specified operating temperature is attained.

(continued)

TABLE 2 (continued)

Temperature	Time, min	Number of observations	Capillary suction time, sec	
			range	average
360°F (182°C)	0	2	18.6-19.7	19.2
	5	2	14.7-16.4	15.6
	10	2	13.7-13.8	13.8
	15	2	12.6-15.8	14.2
	20	2	12.1-14.3	13.2
	25	1	--	15.3
	30	2	10.8-16.9	13.9
	40	1	--	11.1
	50	1	--	10.6
	60	1	--	11.0
380°F (193°C)	0	2	11.7-17.0	14.4
	5	2	10.4-16.1	13.3
	10	3	10.0-16.2	14.2
	15	2	9.1-12.1	10.6
	20	3	10.4-15.0	13.1
	25	2	0.6-15.0	12.3
	30	3	9.2-18.0	12.5
400°F (204°C)	0	3	12.8-21.0	16.3
	5	1	--	14.7
	10	3	13.9-19.4	16.2
	15	1	--	14.1
	20	3	13.5-19.1	15.5
	25	1	--	16.7
	30	1	--	17.1
	40	2	15.5-30.0	22.8
425°F (218°C)	0	1	--	13.2
	5	1	--	13.2
	10	1	--	10.9
	15	1	--	13.2
	20	1	--	13.6
	25	1	--	13.2
	30	1	--	13.2
450°F (232°C)	0	2	15.3-18.9	17.1
	10	2	16.6-23.1	19.9
	20	2	15.4-24.0	19.7
	40	2	13.4-18.4	15.9

Note: Time is measured from the point at which the specified operating temperature is attained.

TABLE 3. SLUDGE FILTERABILITY RESPONSE TO
NONOXIDATIVE CONDITIONING

Temperature	Time, min	Number of observations	Capillary suction time, sec	
			range	average
300°F (150°C)	0	4	22.7-31.5	33.8
	5	2	21.3-24.3	22.8
	10	4	17.5-20.5	19.2
	15	2	15.7-20.8	18.3
	20	5	16.5-20.9	18.5
	25	1	--	14.9
	30	2	14.0-19.9	17.0
	40	4	15.9-18.9	17.2
	50	1	--	14.7
	60	1	--	18.7
315°F (157°C)	0	1	--	19.6
	5	1	--	19.2
	10	1	--	20.5
	15	1	--	18.7
	20	1	--	19.2
	25	1	--	16.3
	30	1	--	15.8
345°F (174°C)	0	2	22.2-24.2	23.2
	5	2	19.1-20.7	19.9
	10	2	17.1-17.2	17.2
	15	2	17.2-17.5	17.4
	20	2	16.9-17.7	17.3
	25	1	--	15.3
	30	1	--	16.8
	40	1	--	17.4
	50	1	--	14.6
	60	1	--	13.9
350°F (177°C)	0	2	15.3-19.3	17.3
	10	2	17.1-17.4	17.3
	20	3	18.6-20.9	18.2
	40	3	14.3-16.7	15.3
360°F (182°C)	0	2	16.7-17.4	17.0
	5	2	16.0-17.9	17.0
	10	2	14.1-19.1	16.6
	15	2	13.8-15.4	14.6
	20	2	13.8-17.6	15.7
	25	1	--	15.6
	30	2	13.7-15.0	14.4
	40	1	--	15.5
	50	1	--	12.6
	60	1	--	13.5

(continued)

TABLE 3 (continued)

Temperature	Time, min	Number of observations	Capillary suction time, sec	
			range	average
380°F (193°C)	0	2	12.5-24.5	18.5
	5	2	12.5-18.6	15.6
	10	3	12.0-17.3	14.2
	15	2	11.6-18.4	15.0
	20	3	10.8-16.4	13.0
	25	2	11.5-17.5	14.5
	30	2	10.7-16.7	13.7
400°F (204°C)	0	3	18.3-19.3	18.8
	5	2	16.1-24.1	20.1
	10	3	16.3-19.2	17.3
	15	--	--	--
	20	4	12.2-19.1	15.5
	25	1	--	13.4
	30	2	13.0-14.1	13.6
	40	3	10.3-14.2	12.8
	50	1	--	13.0
425°F (218°C)	60	1	--	14.7
	0	1	--	20.0
	5	1	--	15.3
	10	1	--	15.8
	15	1	--	15.6
	20	1	--	14.9
	25	1	--	12.3
450°F (232°C)	30	1	--	14.0
	0	3	13.6-20.1	17.0
	5	1	--	16.4
	10	3	12.1-15.9	14.2
	15	1	--	16.0
	20	3	12.1-15.5	13.5
	25	1	--	15.1
	30	1	--	16.6
	40	2	11.8-12.0	11.9

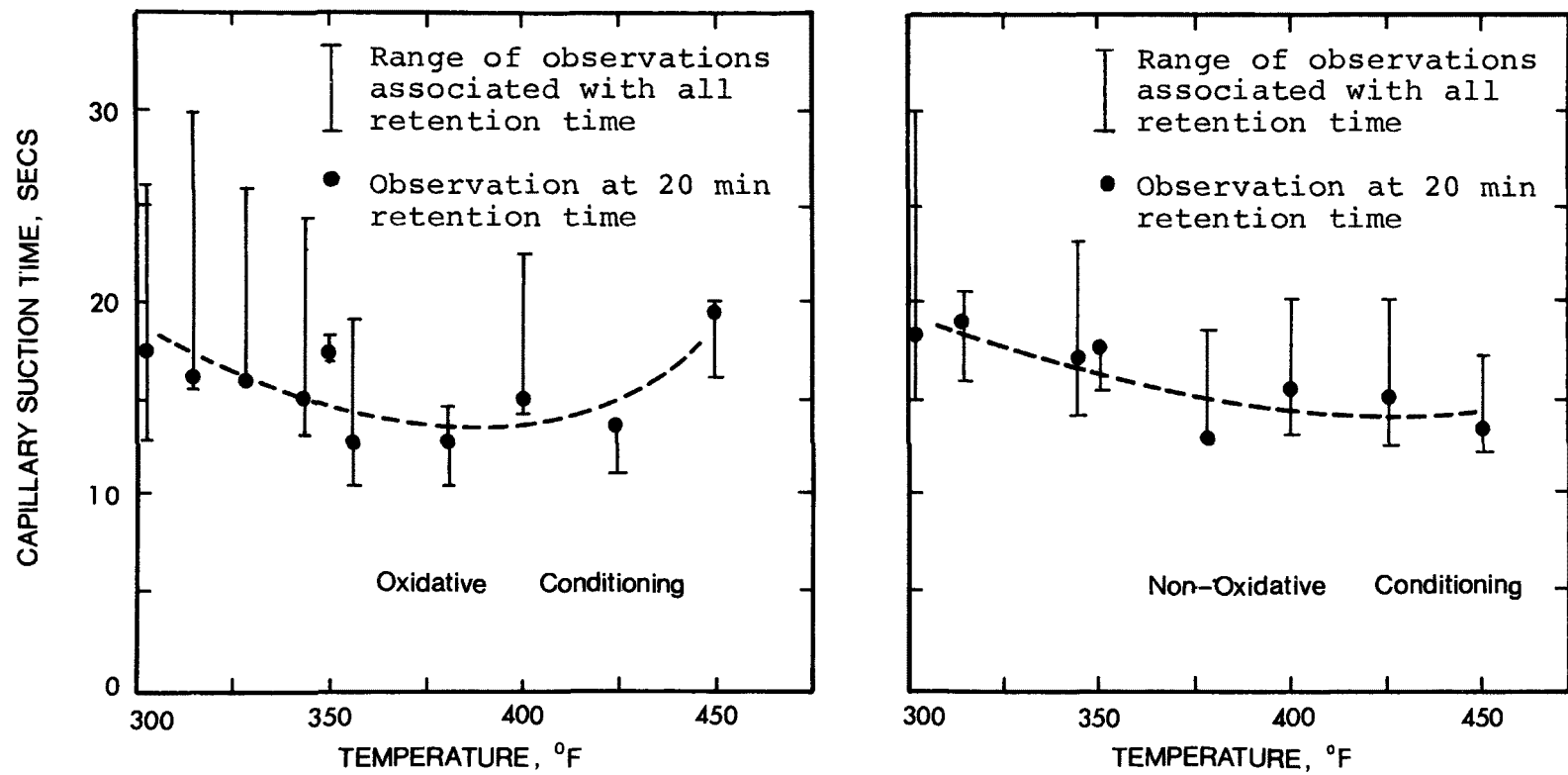


Figure 18. Sludge filterability response to thermal conditioning.

even there, little further improvement, if any, was experienced beyond 5 minutes. That is not to infer, however, that comparable mixing, mass transfer, or associated kinetics can be expected in large scale prototype reactors. With oxidative conditioning, a nominal reversion is suggested by the CST data.

Results of supplemental filter leaf testing conducted at respective form and dry times of 2 and 4 minutes, at a vacuum of 15 inches of mercury are shown in Table 4. In comparing the respective loading rates associated with the two conditioning regimes, the relative sludge consistencies at which the tests were conducted should be noted. In extrapolating a curve correlating nonoxidative loading rates with consistency to a 2.4 percent solids level and assuming a consistency exponent of 1.0, a filter loading rate comparable to that indicated for the sludge conditioned oxidatively is suggested. Doing so cannot be considered conclusive, however. While the sludges were conditioned at differing temperatures, CST data would dispute a lower operating temperature dewaterability advantage for the oxidative regime.

TABLE 4. FILTER LEAF RESULTS WITH
THERMALLY CONDITIONED BIOLOGICAL SLUDGE

Nature of conditioning	Unconditioned	Nonoxidative 400°F/204°C for 40 min		Oxidative 350°F/177°C for 30 min
Specific resistance sec ² /gm	160 (10 ⁷)	7.9	(10 ⁷)	16.1 (10 ⁷)
Sludge consistency, %	3.9	3.9	7.0	2.4
Cake solids, %	16.3	24.3	23.4	30.4
Solids recovery, %	9.0	99.0	99.0	94.0
Filter loading rate lb/ft ² /hr	0.4	6.0	10.7	2.4

Effects of Solids Solubilization

Data tabulated in Table 5 and graphically arrayed in Figure 19 illustrates the importance of the magnitude of volatile solids hydrolysis in achieving optimal conditioning. Lowest values of CST, as well as specific resistance occurred within the range of 40 to 60 percent solids hydrolysis. The curves would indicate that the lowest specific resistance achievable with oxidative

TABLE 5. COMPARISON OF SOLIDS HYDROLYSIS AND FILTERABILITY

	Temperature	Time, min	% Volatile solids hydrolyzed	CST, sec	Specific resistance sec ² /gm
Oxidative	300°F (150°C)	0	11	20.1	34.1
		10	27	18.0	15.4
		20	33	18.2	11.4
		20	43	18.3	--
		40	49	18.6	18.5
	350°F (177°C)	0	34	16.8	11.3
		10	56	20.1	8.9
		20	65	18.7	8.2
		40	67	16.7	--
		40	67	20.0	9.3
	400°F (204°C)	0	66	21.1	9.9
		10	74	19.4	29.2
		20	67	19.1	23.5
		20	66	20.6	--
		40	77	30.1	29.4
	450°F (232°C)	0	72	18.9	25.3
		10	88	23.1	37.4
		20	85	23.5	--
		20	86	24.0	43.7
		40	92	18.4	26.4
Nonoxidative	300°F (150°C)	0	17	22.7	50.0
		0	14	40.5	--
		10	25	18.2	15.6
		20	18	20.9	--
		20	21	17.7	15.3
		40	30	15.9	12.8
		40	29	16.9	--
	350°F (177°C)	0	16	15.3	11.3
		10	30	17.1	7.9
		20	22	18.6	5.1
		20	17	20.9	--
		40	28	14.3	5.0
		40	43	16.7	--
	400°F (204°C)	0	35	18.3	7.7
		10	41	16.3	5.9
		20	49	15.6	4.3
		20	37	15.6	--
		40	49	13.8	2.5
	450°F (232°C)	0	44	17.2	17.0
		10	45	14.5	3.4
		10	44	16.3	3.7
		20	47	13.0	3.5
		40	53	11.8	3.3

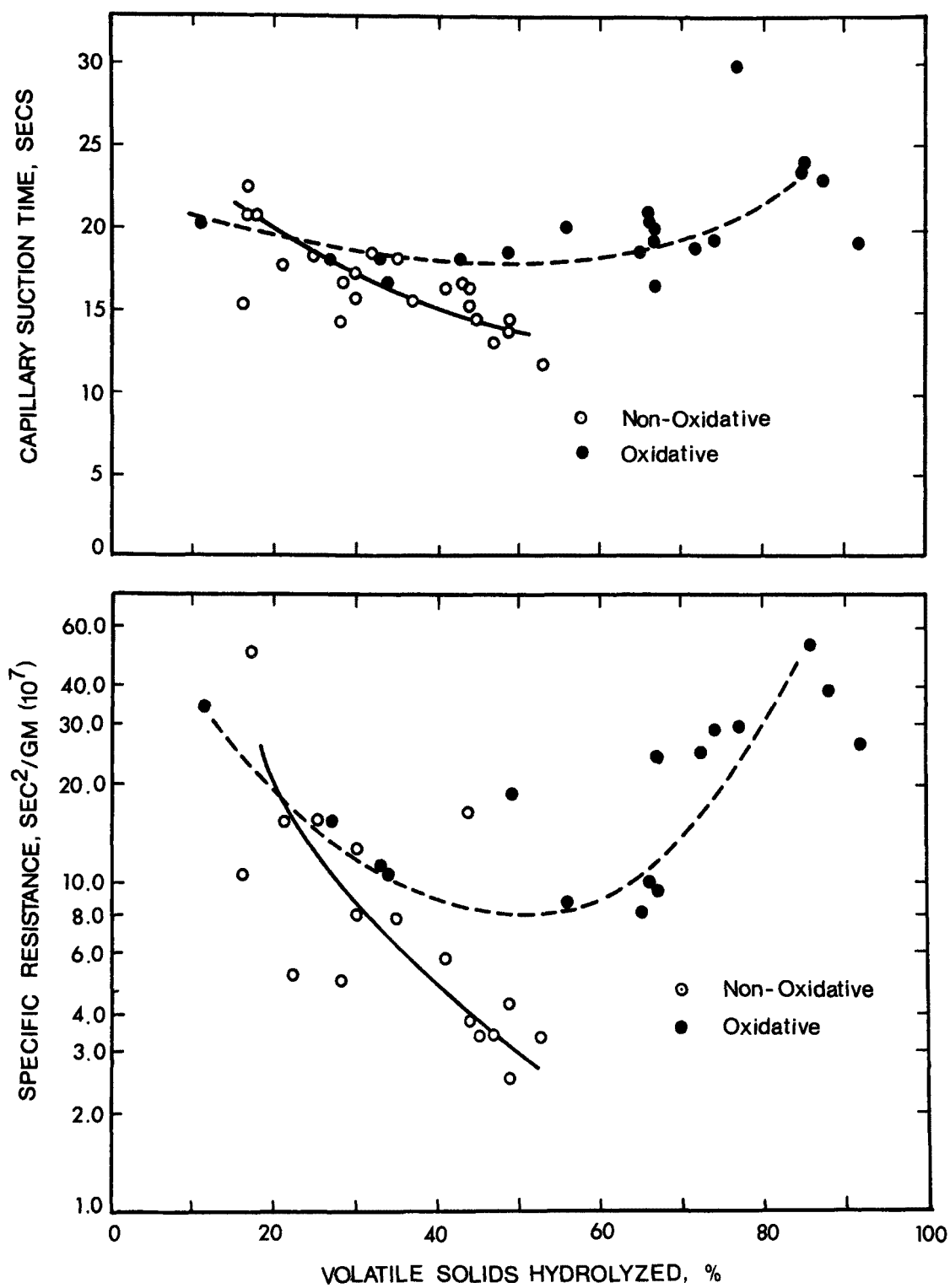


Figure 19. Significance of solids hydrolysis to sludge filterability.

conditioning occurs at a solubilization level of 50 percent. An equivalent degree of conditioning was accomplished with hydrolysis of 30 percent of the volatile solids during nonoxidative conditioning. The data would further suggest that such degrees of hydrolysis are attainable at comparable temperature levels. However, oxidative conditioning, where oxygen is not limiting, would yield fewer solids requiring ultimate disposal.

It should, perhaps, also be noted here that comparison of the CST and specific resistance curves would indicate the latter to be the more sensitive parameter for detecting differences among well-conditioned sludges.

Supernatant Quality

Highest values of filtrate COD observed in the study were on the order of 11 to 13000 mg/liter and generally associated with oxidative conditioning at 350°F (177°C) for extended detention times (40 minutes). At extreme levels of nonoxidative conditioning, values in excess of 10000 mg/liter were encountered as well. The incremental increase in filtrate COD as a consequence of volatile solids hydrolysis is shown in Figure 20, developed from data presented in Table 6. The trend of the data indicates that approximately 50 percent of the mass of volatile solids hydrolyzed is reflected as filtrate COD. The relationship seems common to both conditioning regimes with the exception that a decrease appears to be associated with oxidative conditioning at temperatures of 400° to 450°F (204° to 232°C). A filtrate BOD to COD ratio of 0.5 was consistent over the entire range of conditions, as illustrated in Figure 21.

ACID ASSISTED OXIDATED CONDITIONING

Acid requirements to reduce sludge to 4.5 were in excess of 0.3 gm/liter of sludge solids, or, as shown in Figure 22, greater than the 3 gm/liter threshold indicated by Seto and Smith (21). As expected, acid addition was accompanied by the evolution of hydrogen sulfide and foaming, a phenomenon which complicated the quantitative transfer of solids.

Filtration Properties

CST data shown in Table 7 shows no significant advantage to acid pre-hydrolysis over that associated with conventional oxidative conditioning insofar as its capacity to improve sludge dewaterability. This is, perhaps, better illustrated in Figure 23 in which the range of capillary suction times (CST) corresponding with various reaction temperatures are superimposed on the similar relationship (designated by the shaded area) developed in the previous section for activated sludge without acid addition.

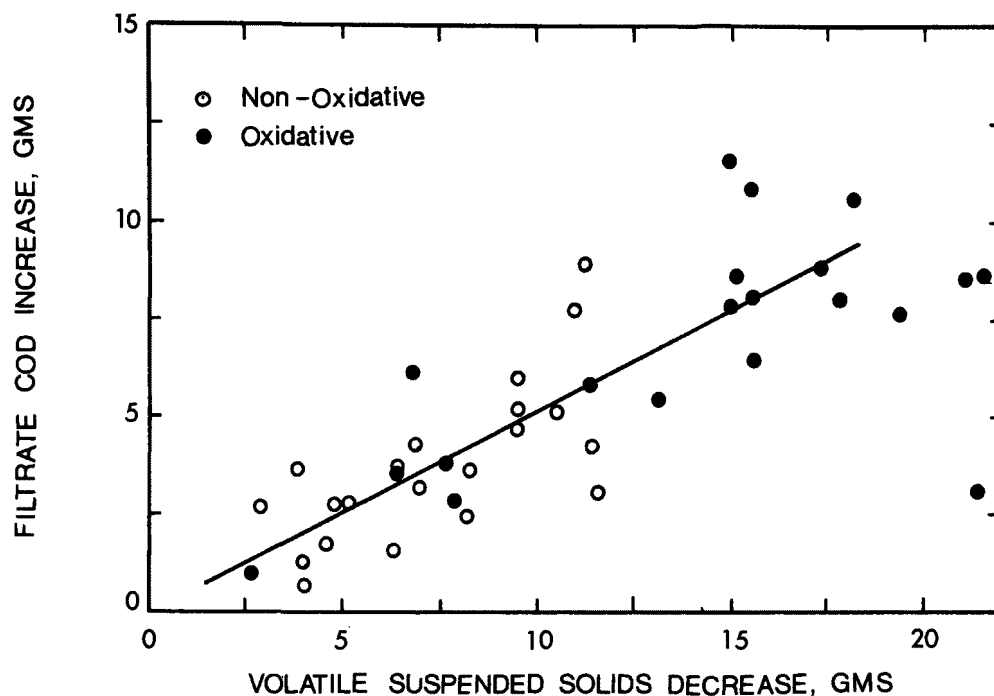


Figure 20. Effect of solids hydrolysis upon filtrate COD.

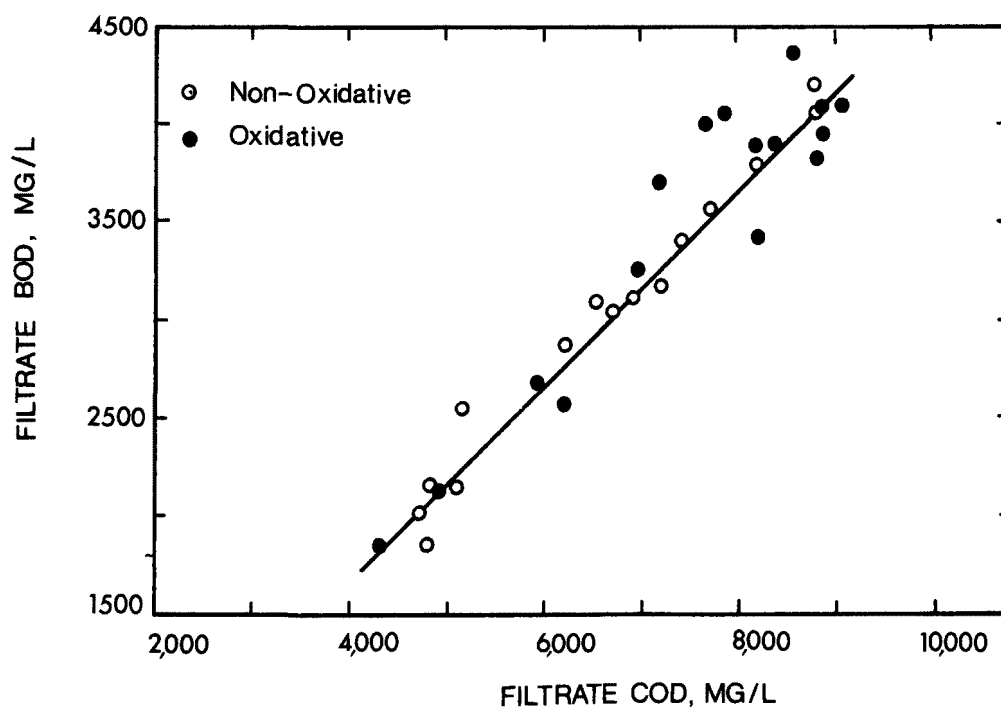


Figure 21. Correlation of filtrate COD-BOD concentrations.

TABLE 6. CORRESPONDING CHANGES IN SLUDGE VOLATILE
SOLIDS AND FILTRATE COD

	Temperature	Time, min	Sludge volatile	Filtrate COD
			suspended solids decrease, gm	increase, gm
Oxidative	300°F (150°C)	0	2.6	1.0
		10	6.4	3.5
		20	7.7	3.8
		20	6.8	6.2
		40	11.4	5.8
	350°F (177°C)	0	7.9	2.9
		10	13.1	5.5
		20	15.0	7.9
		40	15.6	10.9
		40	15.0	11.7
	400°F (204°C)	0	15.6	6.5
		10	17.3	8.8
		20	15.6	8.2
		20	15.2	8.7
		40	17.9	8.1
	450°F (232°C)	0	18.1	10.6
		10	21.7	8.6
		20	21.2	8.6
		20	19.4	7.7
		40	21.4	6.7
Nonoxidative	300°F (150°C)	0	4.0	1.3
		0	2.9	2.7
		10	6.3	1.6
		20	4.1	0.7
		20	4.7	1.9
		20	7.0	3.3
	350°F (177°C)	40	6.9	1.7
		0	5.2	2.9
		10	6.9	4.5
		20	4.9	2.8
		20	3.9	3.8
		40	9.5	4.8
	400°F (204°C)	40	6.5	3.9
		0	8.2	2.5
		10	9.5	4.3
		20	11.5	4.3
		20	8.3	3.7
	450°F (232°C)	40	11.3	9.0
		0	11.6	3.1
		10	10.5	5.2
		10	9.5	6.2
		20	11.0	7.9
		40	--	--

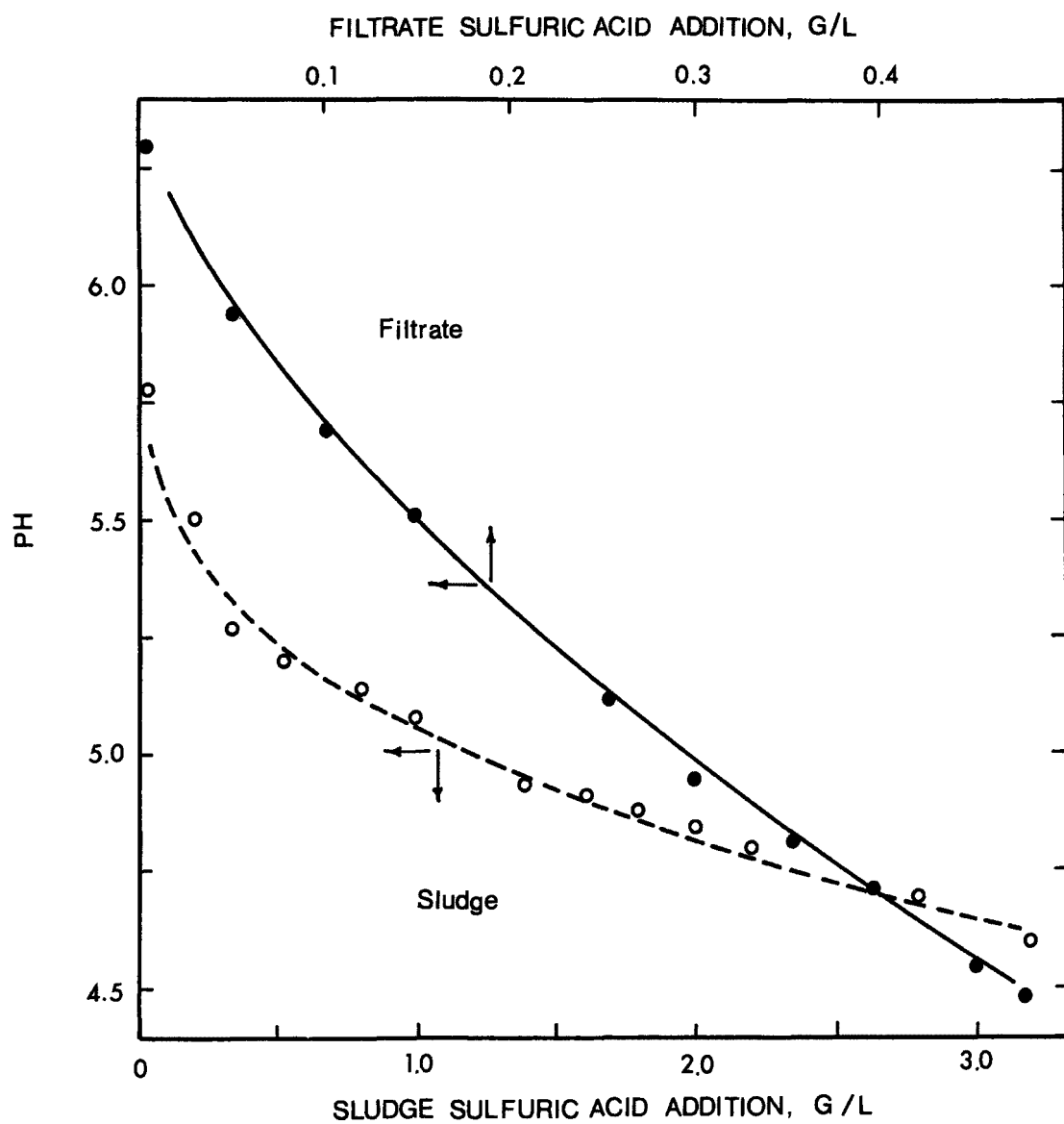


Figure 22. Effect of incremental acid addition upon pH.

TABLE 7. SLUDGE FILTERABILITY AFTER ACID ASSISTED
OXIDATIVE CONDITIONING

Temperature	Time, min	Capillary suction time*, sec		Specific resistance, 10 ⁷ sec ² /gm	
		observations	average	observations	average
300°F (150°C)	0	20.1	20.4	42.6	31.8
		20.6	--	21.0	--
	10	14.5	17.1	4.2	9.4
		19.6	--	14.5	--
	20	17.0	17.0	7.6	7.6
	40	15.6	16.7	4.4	7.0
		17.7	--	9.5	--
350°F (177°C)	0	24.7	20.4	43.8	24.4
		16.0	--	4.9	--
	10	18.3	17.8	8.6	8.6
		17.2	--	--	--
	20	13.3	14.0	2.7	3.8
		14.7	--	4.8	--
	40	10.7	14.4	6.2	10.7
400°F (204°C)		18.0	--	15.2	--
	0	11.5	13.2	5.6	5.2
		14.8	--	4.8	--
	10	16.0	14.6	12.0	9.2
		13.2	--	6.4	--
	20	13.9	13.9	11.5	11.5
	40	10.6	--	3.5	11.2
450°F (232°C)		28.9	19.8	19.0	--
	0	12.4	14.1	6.6	6.2
		15.8	--	5.8	--
	10	21.0	18.5	8.8	8.8
		16.0	--	--	--
	20	15.0	--	1.9	8.1
		17.3	16.7	--	--
		17.9	--	14.3	--
	40	11.8	13.6	4.4	7.7
		15.4	--	10.9	--

* Original sludge capillary suction time was 189 sec at 3.3 per-
cent consistency.

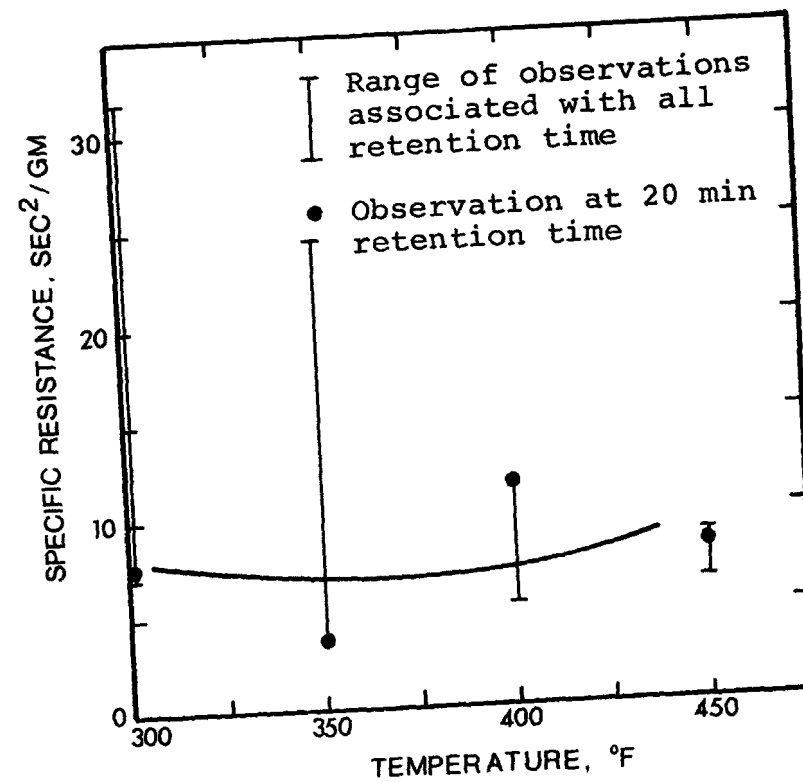
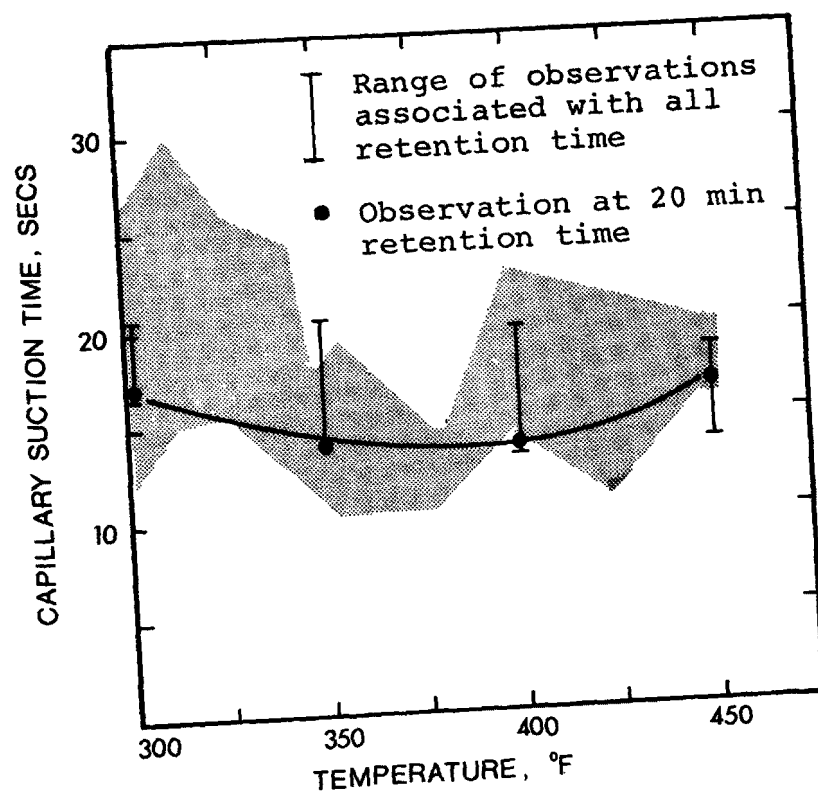


Figure 23. Sludge filterability response to acid assisted oxidative conditioning.

The rapidity with which conventional oxidative conditioning was observed to occur masked any ability of acid to accelerate the process. That is not to suggest that in prototype reactors an acid benefit would not be realized; only that such a distinction could not be made, given the kinetics associated with equipment utilized in this study and the sludge consistencies employed.

Solids Hydrolysis Effects

The relationship of solids filtration properties to volatile solids hydrolyzed is shown in Figure 24 and was developed from data shown in Tables 7 and 8 for acid assisted oxidative conditioning. Comparison with the similar relationship for nonacid conditioning, Figure 19, indicates somewhat better dewaterability with the acid assist as hydrolysis progresses. However, optimum filtration continues to fall in the 40 to 60 percent hydrolysis range. Furthermore, acid addition dampened the reversion potential at extreme levels of hydrolysis. Thus, smaller residuals can be handled without so great a sacrifice in their dewatering properties.

Filtrate Quality

The incremental increase in filtrate COD as a consequence of solid hydrolysis is approximately the same as that for non-acid conditioning, as shown in Figure 25, compiled from data in Table 8. However, there was some evidence to suggest a decrease in the ratio with conditioning for extended times (40 minutes) at temperatures exceeding 350°F (177°C). The ratio of BOD to COD was observed to be 0.6, as taken from Figure 26.

CHEMICAL BASED SLUDGES

Other than its chemical content, the most distinguishing quality between the alum coagulated biological solids and the conventional waste activated sludge was the extraordinarily long sludge age of the former resulting from high degrees of sludge recycle.

Filtration Properties

A comparison of filtration properties associated with the oxidative and nonoxidative conditioning of the alum coagulated biological solids, tabulated in Tables 9 and 10 respectively, indicates the latter conditioning regime to be the better. The average of CST observations at individual times for oxidative temperatures of 350°F (177°C) and less was never below 20 seconds, though that did occur at the initial 400°F (204°C) and 450°F (232°C) conditions. Reversion was evident at more intensive conditions. However, with nonoxidative conditioning CST's of less than 20 seconds were attainable at all temperatures,

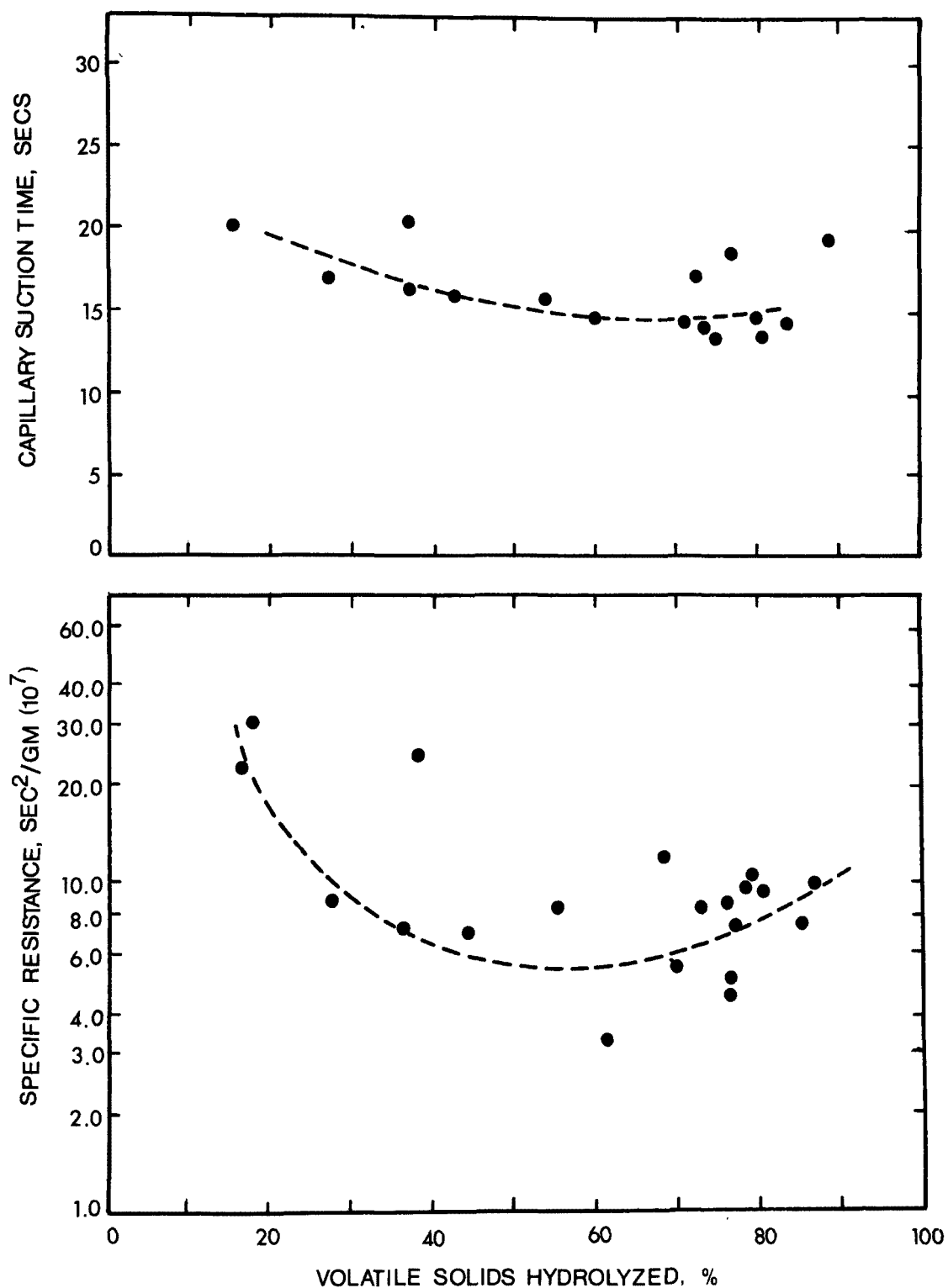


Figure 24. Significance of solids solubilization to the filterability of sludge exposed to acid assisted oxidative conditioning.

TABLE 8. CORRESPONDING CHANGES IN SLUDGE VOLATILE SOLIDS AND FILTRATE COD ASSOCIATED WITH ACID ASSISTED OXIDATIVE CONDITIONING

Temperature	Time, min	Sludge volatile suspended solids decrease, gm		Filtrate COD increase, gm	
		observations	average	observations	average
300°F (150°C)	0	3.9	3.9	0.5	0.5
		4.0	--	--	--
	10	7.9	6.6	5.3	4.2
		5.3	--	3.1	--
	20	8.1	8.1	5.5	5.5
	40	14.0	10.7	5.9	5.3
350°F (177°C)		7.4	--	4.6	--
	0	7.9	8.6	2.1	2.1
		9.3	--	--	--
	10	12.1	12.9	6.9	7.0
		13.6	--	7.1	--
	20	12.9	13.6	9.6	8.9
400°F (204°C)		14.2	--	8.2	--
	40	17.1	18.6	7.7	5.8
		20.0	--	3.8	--
	0	19.7	18.1	4.3	4.0
		16.5	--	3.6	--
	10	16.0	16.0	4.6	4.6
450°F (232°C)		18.7	18.7	8.0	8.0
	20	20.3	19.6	3.9	6.0
		18.8	--	8.0	--
	0	15.7	16.0	6.3	4.5
		16.3	--	2.7	--
	10	19.6	17.9	9.2	9.2
450°F (232°C)		15.5	--	7.0	--
		18.6	--	11.4	--
	20	18.8	16.0	8.8	6.0
		14.2	--	4.4	--
		15.1	--	4.7	--
	40	21.2	17.7	9.0	7.0
450°F (232°C)		12.8	--	4.4	--
		19.0	--	7.7	--

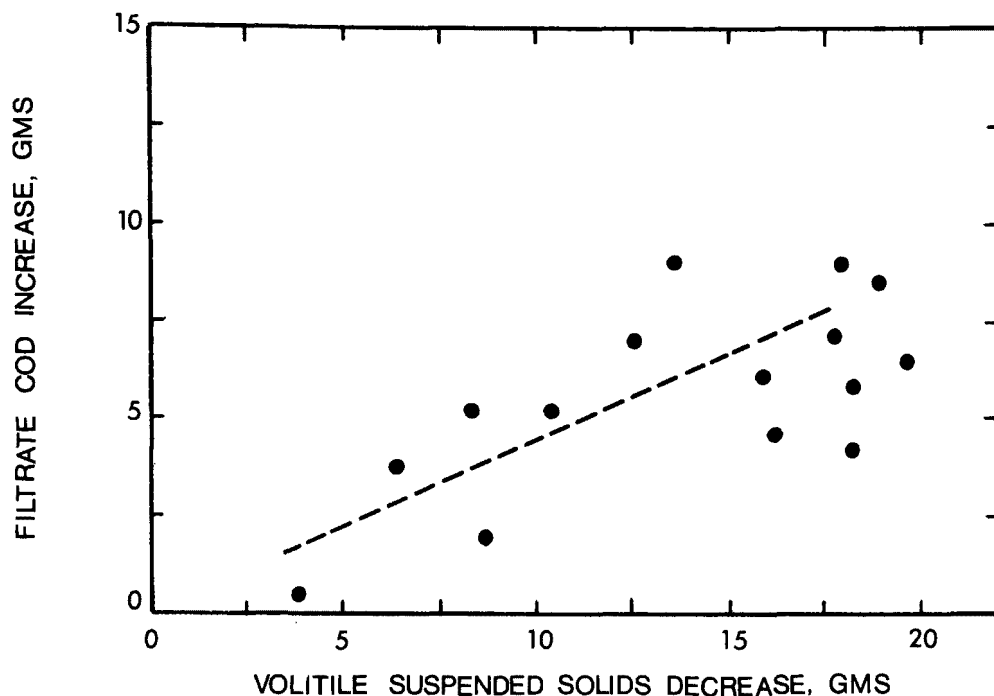


Figure 25. Effect of solids solubilization upon the COD of sludge filtrates following acid assisted oxidative conditioning.

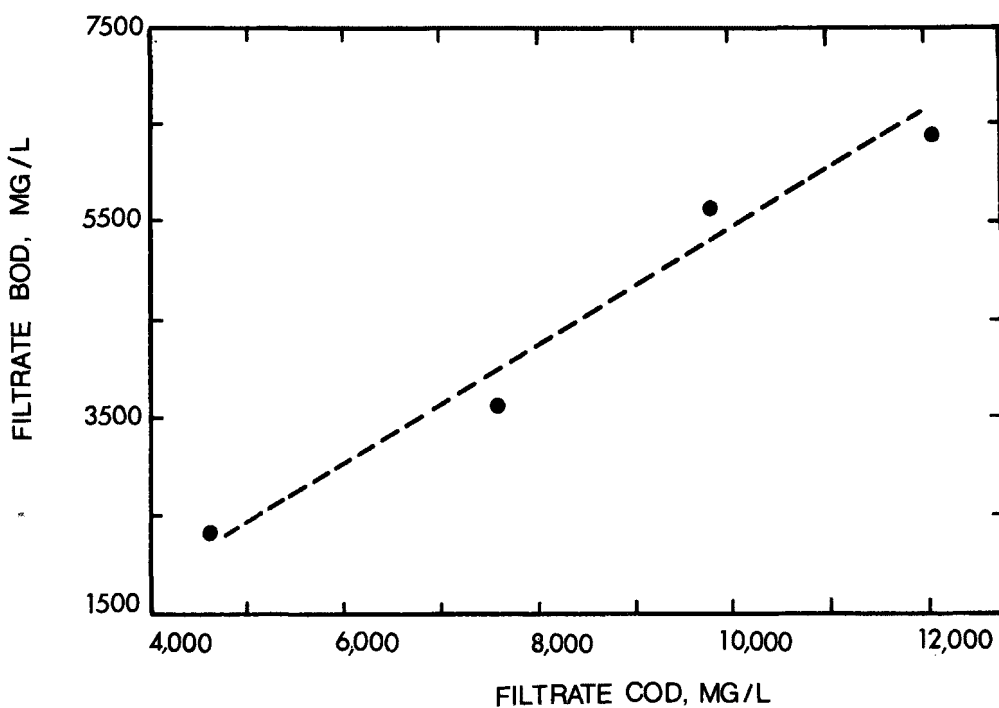


Figure 26. Relative COD-BOD concentrations in filtrates from sludges after acid assisted oxidative conditioning.

TABLE 9. FILTRATION PROPERTIES OF ALUM-COAGULATED
BIOLOGICAL SOLIDS AFTER THERMAL CONDITIONING
(Oxidative)

Temperature	Time, min	Capillary suction time, sec		Specific resistance, $10^7 \text{ sec}^2/\text{gm}$
		observations	average	observations
300°F (150°C)	0	22.2	21.7	25.5
		21.2	--	--
	10	29.3	23.6	25.6
		17.9	--	--
	20	25.1	21.3	--
		17.4	--	25.8
	40	25.0	23.2	2.8
		21.3	--	25.7
350°F (177°C)	0	25.2	20.4	23.3
		15.5	--	--
	10	25.8	22.6	35.5
		19.4	--	--
	20	32.1	23.8	39.6
		15.4	--	--
	40	30.0	23.4	55.6
		16.8	--	--
400°F (204°C)	0	20.7	18.5	12.6
		16.2	--	--
	10	32.6	25.7	43.8
		18.8	--	--
	20	39.6	30.5	60.1
		21.4	--	--
	40	38.0	27.3	61.0
		16.5	--	--
450°F (232°C)	0	22.1	18.9	14.9
		19.3	--	31.1
	10	15.4	--	--
		44.0	30.0	94.5
	20	15.9	--	--
		24.1	22.1	21.6
	40	20.1	--	--
		33.3	27.6	80.1
		21.8	--	--

TABLE 10. FILTRATION PROPERTIES OF ALUM-COAGULATED
BIOLOGICAL SOLIDS AFTER THERMAL CONDITIONING
(Nonoxidative)

Temperature	Time, min	Capillary suction time, sec		Specific resistance, $10^7 \text{ sec}^2/\text{gm}$
		observations	average	observations
300°F (150°C)	0	27.2	37.8	--
		23.6		74.4
		79.6		140.0
	10	20.6	--	--
		32.2	27.3	50.6
		20.4		--
		29.3	--	60.0
	20	32.7	25.9	40.4
		19.0		--
	40	16.9	16.5	8.3
		14.2		11.7
		18.4		--
350°F (177°C)	0	25.0	20.9	30.4
		16.8		--
	10	23.0	20.7	14.9
		18.3		--
	20	19.8	17.6	14.3
		15.4		--
	40	16.0	18.6	5.7
		20.3		--
400°F (204°C)	0	22.0	19.7	15.3
		17.4		--
	10	16.1	15.6	6.9
		15.1		--
	20	15.1	14.3	6.3
		13.4		--
	40	15.7	15.3	6.7
		14.8		--
450°F (232°C)	0	--	16.1	3.0
		15.6		6.4
		16.5		--
	10	14.9	15.5	4.9
		16.0		--
	20	17.5	16.6	6.7
		15.6		--
	40	--	15.5	3.6
		14.1		--
		16.3		4.4
		16.1		--

with the necessary reaction time becoming progressively shorter as temperature increased. A similar scenario could be made for specific resistance results.

Results of vacuum filter leaf testing, shown in Table 11, confirm the advantage of nonoxidative conditioning. At comparable conditions of consistency and form time, respectively 4 to 5 percent and 2 minutes, the loading rate was 5 lb/ft²/hr (24 Kg/m²/hr) for the nonoxidative sludge. The oxidized sludge exhibited a 3 lb/ft²/hr (15 Kg/m²/hr) loading rate.

TABLE 11. FILTER LEAF RESULTS WITH THERMALLY CONDITIONED ALUM COAGULATED BIOLOGICAL SOLIDS

Nature of conditioning	Unconditioned	Nonoxidative 400°F/204°C for 40 min			Oxidative 350°F/177°C for 30 min	
Specific resistance*, sec ² /gm	160 (10 ⁷)	7.9 (10 ⁷)			16.1 (10 ⁷)	
Capillary suction time, sec	65	27.5	38		33	
Sludge consistency, %	3.2	4-5	7-8		4-5	
Form time, min	2	2	2	1	1	2
Dry time, min	4	4	4	2	2	4
Cake solids, %	17	18	18	17	20	21
Solids recovery, %	82	90	96	92	84	86
Filter loading rate, lb/ft ² /hr	1.8	5	9	13	4	3

* Sludge utilized herein differed from that previously described and possessed better dewatering properties in both the conditioned and unconditioned states.

Solids Hydrolysis Effects

Figure 27, compiled from data contained in Tables 9, 10 and 12, displays the relative effects of volatile solids hydrolysis upon resulting filtration properties. It indicates, for oxidative conditioning, that filtration properties do not improve beyond initial hydrolysis levels and degenerate where hydrolysis

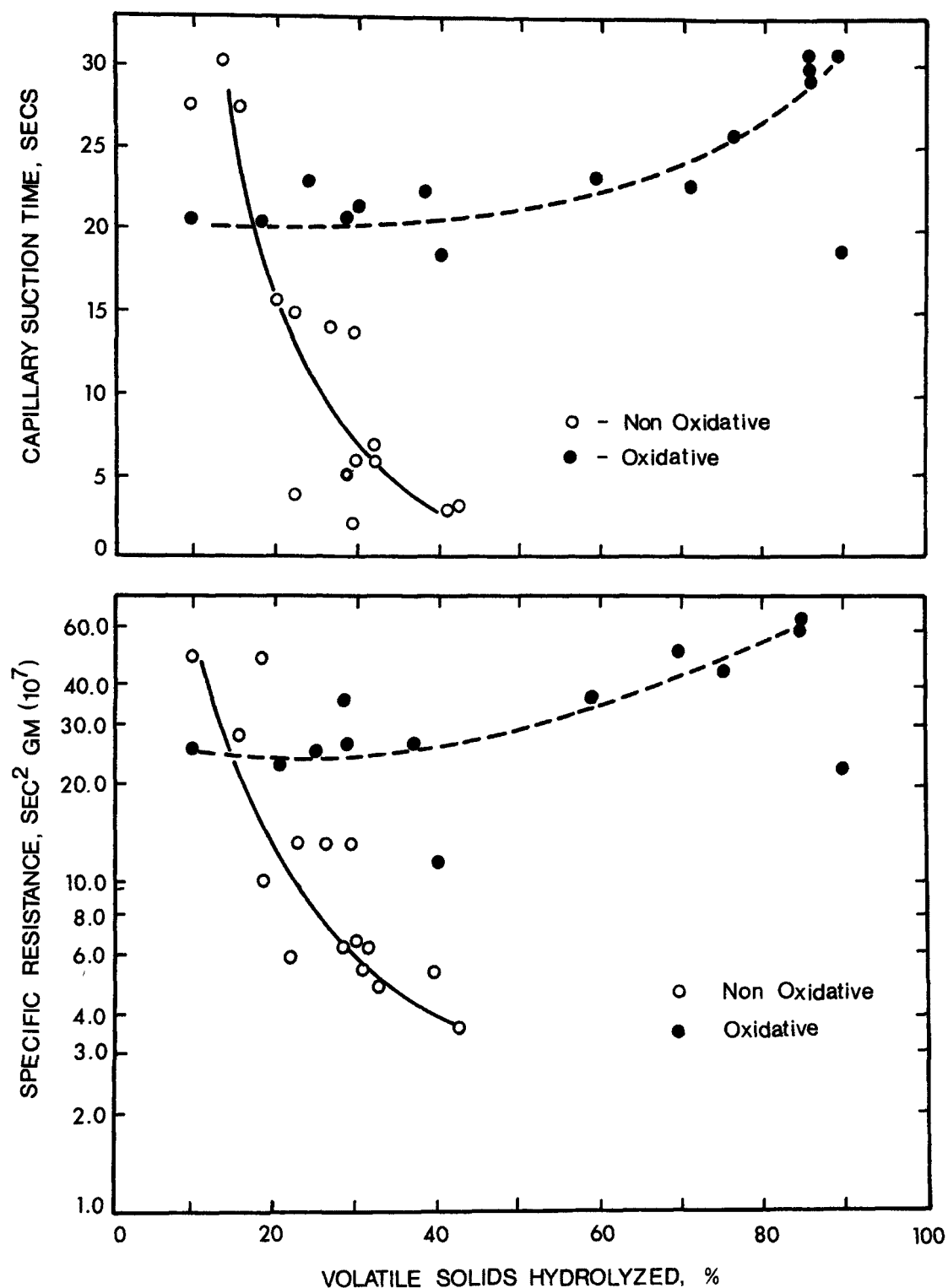


Figure 27. Impact of volatile solids solubilization upon the dewatering properties of alum coagulated biological solids after heat treatment.

TABLE 12. CORRESPONDING CHANGES IN SLUDGE VOLATILE SOLIDS AND FILTRATE COD FOR CHEMICALLY COAGULATED AERATED BASIN RESIDUES EXPOSED TO THERMAL CONDITIONING

Temperature	Time, min	Oxidative		Nonoxidative	
		volatile solids hydrolyzed, %	filtrate COD, mg/liter	volatile solids hydrolyzed, %	filtrate COD, mg/liter
300°F (150°C)	0	10	5205	9	4333
	10	26	4935	17	3924
	20	29	5920	9	4695
	40	38	5960	19	4072
350°F (177°C)	0	20	5863	16	5049
	10	29	5081	21	4681
	20	62	6316	26	5127
	40	71	6820	22	5953
400°F (204°C)	0	41	6660	28	4941
	10	75	7137	32	5228
	20	85	6448	27	5335
	40	85	4990	28	4825
450°F (232°C)	0	89	6101	29	5294
	10	89	6068	31	5552
	20	--	--	42	5296
	40	85	4408	41	4765

levels exceed 40 percent. However, nonoxidative filtration properties exhibit progressive improvement up to the 40 percent hydrolysis limit.

Filtrate Quality

As shown in Figure 28, filtrate COD resulting from solids solubilization ranged from approximately 4000 to 7000 mg/liter, significantly below that associated with conventional activated sludge conditioned at a comparable consistency. At all but the most intensive condition, oxidative filtrate COD exceeded that associated with the nonoxidative regime, as shown in Table 10. COD yield, based upon the mass of volatile solids hydrolyzed, was estimated to be approximately half that associated with conventional activated sludge. Moreover, the ratio of filtrate BOD to COD was approximately 0.3, as shown in Figure 29. These differences are possibly attributable to an altered nature of the biological solids resulting from their extended aeration.

To the extent that the results of the alum water treatment sludge is indicative, the effect of heat treatment on the alum coagulated biological solids cannot be attributed to its effect upon the alum component. As shown in Table 13, thermal conditioning had very little effect on water treatment sludge filterability. Seldom were capillary suction times less than 35 seconds. Associated measurement of specific resistance indicated values ranging between 100 and 200 (10^7) sec^2/gm .

GROUNDWOOD FINES

Results tabulated in Table 14 indicate groundwood fines to be amenable to thermal conditioning. On the basis of capillary suction time, there would seem to be little practical difference between the oxidative and nonoxidative modes. However, specific resistance values exhibit a nominal oxidative reversion at extreme temperature conditions, whereas filterability is seen to progressively improve with increasing temperatures during non-oxidative conditioning.

Filterability was not seen to be highly sensitive to the magnitude of volatile solids hydrolyzed, as shown by Figure 30. However, with oxidative conditioning, a slight reversion at solids hydrolysis levels exceeding 40 percent was suggested by the specific resistance data.

As shown in Table 15, filtrate COD ranged between 3000 and 5000 mg/liter, with no clear distinction between conditioning regime. Data comparing the COD yield with the extent of solids hydrolysis was too widely scattered to suggest any trend. However, filtrate BOD represented approximately half the filtrate COD, as shown in Figure 31.

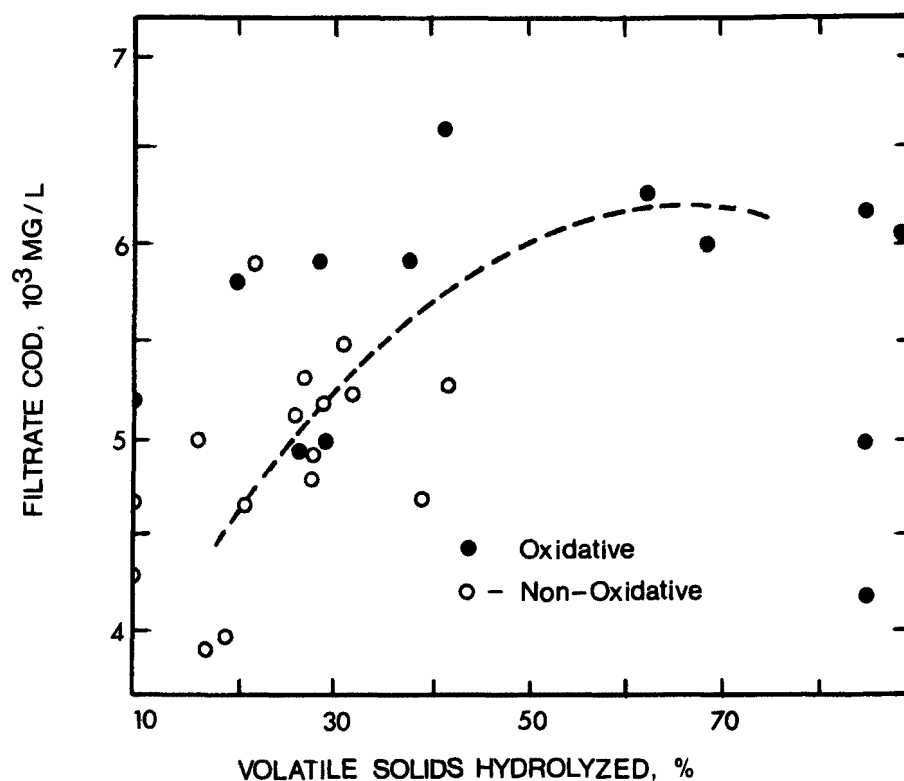


Figure 28. Relationship between filtrate COD and volatile solids solubilization resulting from the thermal conditioning of alum coagulated biological solids.

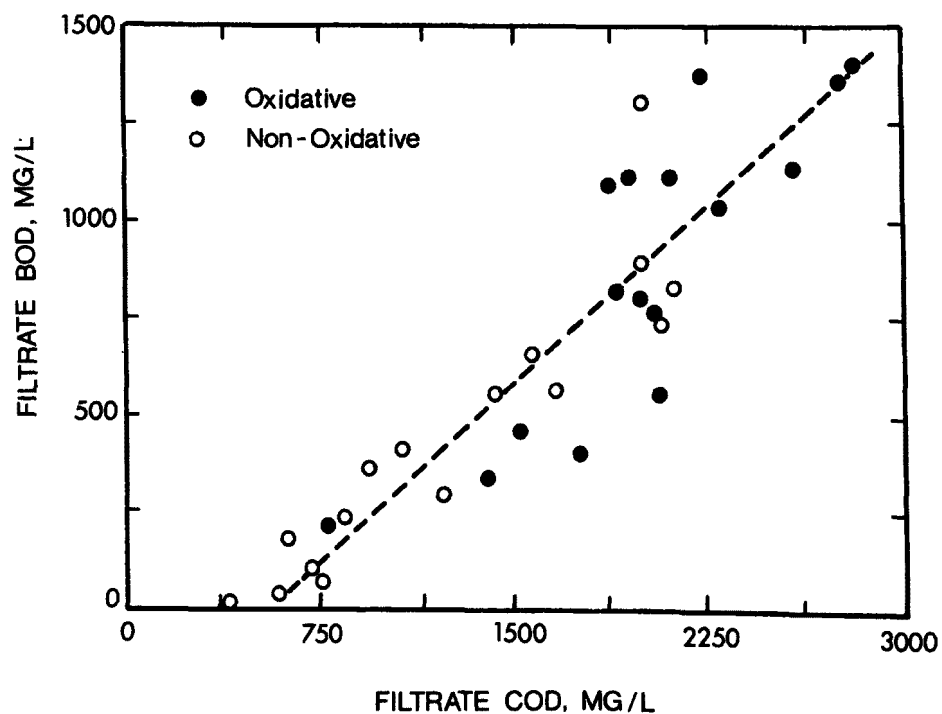


Figure 29. Correlation of BOD/COD for filtrates resulting from the thermal conditioning of alum coagulated biological solids.

TABLE 13. FILTRATION PROPERTIES OF A THERMALLY CONDITIONED
ALUM WATER TREATMENT SLUDGE

	Reaction temperature	Capillary suction time, sec						
		Reaction time, 0-30 min						30
		0	5	10	15	20	25	
Oxidative	300°F (150°C)	--	--	--	--	--	--	--
	315°F (157°C)	--	--	--	--	--	--	--
	330°F (166°C)	37.5	35.2	37.5	38.1	36.0	36.5	37.5
	345°F (174°C)	48.5	--	38.6	39.2	49.8	39.1	42.0
	360°F (182°C)	34.7	32.1	30.5	35.6	35.0	35.1	33.7
	400°F (204°C)	41.3	--	--	37.2	36.3	34.5	32.9
	425°F (218°C)	--	--	--	--	--	--	--
Nonoxidative	300°F (150°C)	40.9	39.7	42.7	38.6	45.1	47.7	38.3
	315°F (157°C)	33.3	27.8	30.6	31.4	29.0	26.5	34.1
	330°F (166°C)	40.1	39.9	34.9	44.1	45.4	57.7	50.0
	345°F (174°C)	45.8	49.8	46.3	49.7	--	37.1	42.0
	360°F (182°C)	36.4	--	34.5	36.0	--	38.5	34.9
	400°F (204°C)	--	--	--	--	--	--	--
	425°F (218°C)	36.4	--	34.5	36.0	--	38.5	34.9

Note: Original sludge capillary suction time was 58.0 sec at
2.5 percent solids consistency.

TABLE 14. FILTRATION PROPERTIES OF GROUNDWOOD FINES
FOLLOWING THERMAL CONDITIONING

	Temperature	Time, min	Capillary suction time, sec	Specific resistance, $10^7 \text{ sec}^2/\text{gm}$
Oxidative	300°F (150°C)	0	11.8	11.5
		10	10.2	6.7
		20	7.2	7.0
		40	11.0	8.0
	350°F (177°C)	0	9.6	6.6
		10	13.7	8.1
		20	13.8	8.1
		40	9.7	17.1
	400°F (204°C)	0	10.0	6.6
		10	9.4	22.7
		20	12.7	7.2
		40	11.2	15.2
	450°F (232°C)	0	9.2	12.0
		10	11.5	13.8
		20	12.4	10.5
		40	10.4	11.3
Nonoxidative	300°F (150°C)	0	8.9	16.0
		10	9.8	7.3
		20	12.5	6.1
		40	8.1	6.7
	350°F (177°C)	0	9.6	6.2
		10	10.6	5.0
		20	8.2	4.3
		40	9.3	3.6
	400°F (204°C)	0	8.6	5.3
		10	8.4	4.3
		20	7.0	3.8
		40	7.5	1.7
	450°F (232°C)	0	8.5	3.7
		10	9.2	3.2
		20	7.0	3.3
		40	8.0	3.4

Note: Original sludge capillary suction time was 25.5 sec at 1.5 percent consistency.

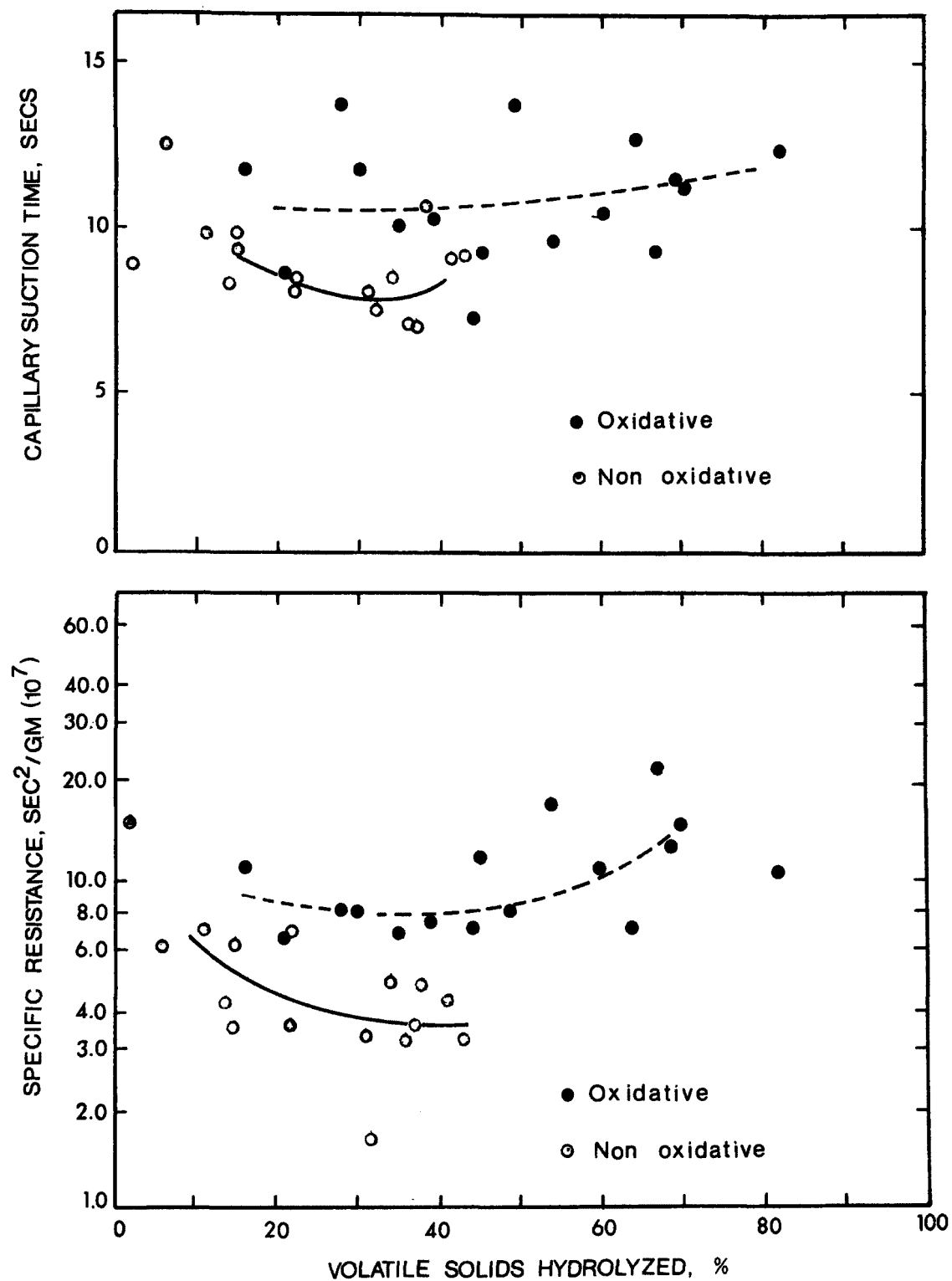


Figure 30. Impact of solids solubilization on the filterability of thermally conditioned groundwood fines.

TABLE 15. CORRESPONDING CHANGES IN SLUDGE VOLATILE SOLIDS AND FILTRATE COD FOR
GROUNDWOOD FINES EXPOSED TO THERMAL CONDITIONING

Temperature	Time, min	Oxidative		Nonoxidative	
		volatile solids hydrolyzed, %	filtrate COD, mg/liter	volatile solids hydrolyzed, %	filtrate COD, mg/liter
300°F (150°C)	0	16	4730	2	4070
	10	29	4590	11	4810
	20	44	3610	6	4590
	40	30	3780	22	4620
350°F (177°C)	0	21	4520	15	4670
	10	28	5120	38	4300
	20	49	3250	14	4240
	40	54	5720	15	3950
400°F (204°C)	0	35	5630	34	4630
	10	67	3350	41	3990
	20	64	2990	37	4620
	40	70	3150	32	3810
450°F (232°C)	0	45	3000	22	4830
	10	69	5860	43	4060
	20	--	--	36	4410
	40	82	4940	31	3360

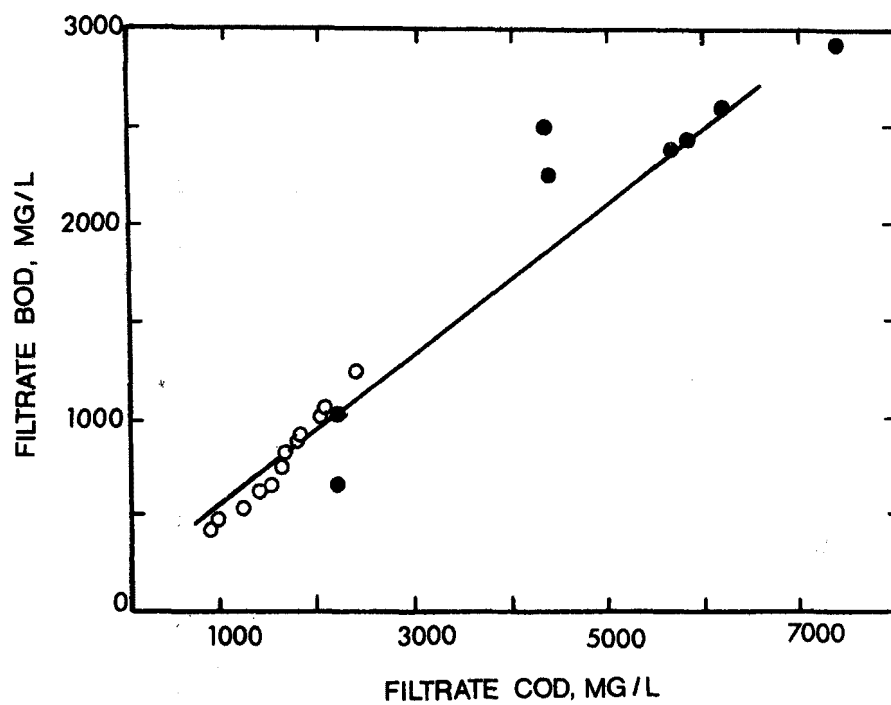


Figure 31. Correlation of BOD/COD for filtrates from thermally conditioned groundwood fines.

SECTION 6

GENERAL DISCUSSION

Though not specifically within the scope of this study, the potential for application of thermal conditioning processes to pulp and paper industry sludge sources warrants at least passing attention to experience reported elsewhere dealing with (a) liquor treatability, (b) factors impacting on cost and (c) full scale plant operational concerns.

LIQUOR TREATABILITY

Given the significant incremental addition to raw waste load which heat treatment liquors constitute, their relative treatability is an issue of considerable concern. While some controversy would seem to exist within the literature dealing with liquor treatability, Everett (30) concludes that there appears to be no reason why heat treatment liquors should not recirculate with incoming wastewaters through the treatment system. This is common practice with heat treatment systems in the United States. Difficulties with doing so, in some cases, have been attributed to installation of systems at older plants (31). This underscores the importance of anticipating the incremental load in plant design. Erikson and Knopp (32) do conclude that direct recirculation of the undiluted liquors to the treatment plant will result in a 10 percent increase in effluent BOD. However, they estimate that elimination of an effluent BOD increase would require separate biological treatment prior to recirculation.

Pilot treatability studies for the separate processing of oxidative heat treatment liquors were carried out by the City of Kalamazoo. However, the approach was not considered further for plant scale application due to (a) potential odors, (b) foaming problems and (c) the necessity for extensive liquor dilution as a consequence of its high strength and temperature (33). Rather, given the compatibility of the liquors for treatment along with the incoming wastewaters, it was considered preferable to provide additional treatment capacity for the overall plant as opposed to installation of a segregated system. In at least two U.S. installations, however, provisions have been made to overcome the above cited difficulties in segregated treatment where doing so has been considered advantageous in permitting

single stage nitrification (34). Long term operating experience is not yet available.

COST CONSIDERATIONS

In the development of economic comparisons for various sludge processing options leading up to incineration available to a 1000 TPD bleach kraft mill, Evans (35) concludes that lowest overall investment involved (a) segregation of the mill primary and secondary sludges, (b) dewatering the former by relatively conventional means and (c) processing the biological sludge by means of heat treatment and subsequent centrifugation.

Considering the highly capital intensive nature of thermal processes, economic comparisons may be easily skewed dependent upon the selection of an amortization period and interest rate. Economic assessments offered in the literature (36) (37) (38) (40) (40) frequently feature periods of 15 years or longer as did Evans (35). His assessment is illustrative, however, in suggesting the potential existence of a situation in which the dewatering of primary and secondary sludges is most economically done independently. Miner *et al.* (41) cites other instances where sludge segregation is desirable. It is under those circumstances where heat treatment of the hydrous fraction alone is most appropriately considered, along with other technologies or conditioning options, such as described elsewhere (41), capable of handling such solids.

Relative unit capital and operating costs furnished by a firm marketing a heat treatment process are shown in Figures 32 and 33 as a function of plant capacity and feed sludge consistency, respectively. These indicate the greatest applicability at large installations, as well as the importance of optimizing feed sludge consistency. However, Everett (15) in extrapolating specific resistance data has suggested that an optimum heat treatment feed sludge consistency exists beyond which conditioning and associated filter yield at a given temperature is adversely affected. Thus, it is conceivable that such process performance limitations pose an upper limit to achieving heat treatment economy alone in the interest of minimizing overall conditioning and dewatering costs.

Kalinske (42) cites English experience where recycling of heat treatment liquors represented an overall 30 percent increase in raw waste load to the plant and goes on to conclude that total costs of such sludge processing systems can be correctly evaluated only if the resulting costs of handling the incremental waste load are considered. One equipment supplier urges the design of solids handling capacities 10 percent greater than that anticipated in the absence of heat treatment. In doing so, Doyle and Gruenwald (43) estimate an incremental cost of nearly \$10.00 per ton of original sludge solids, based upon a recycled liquor

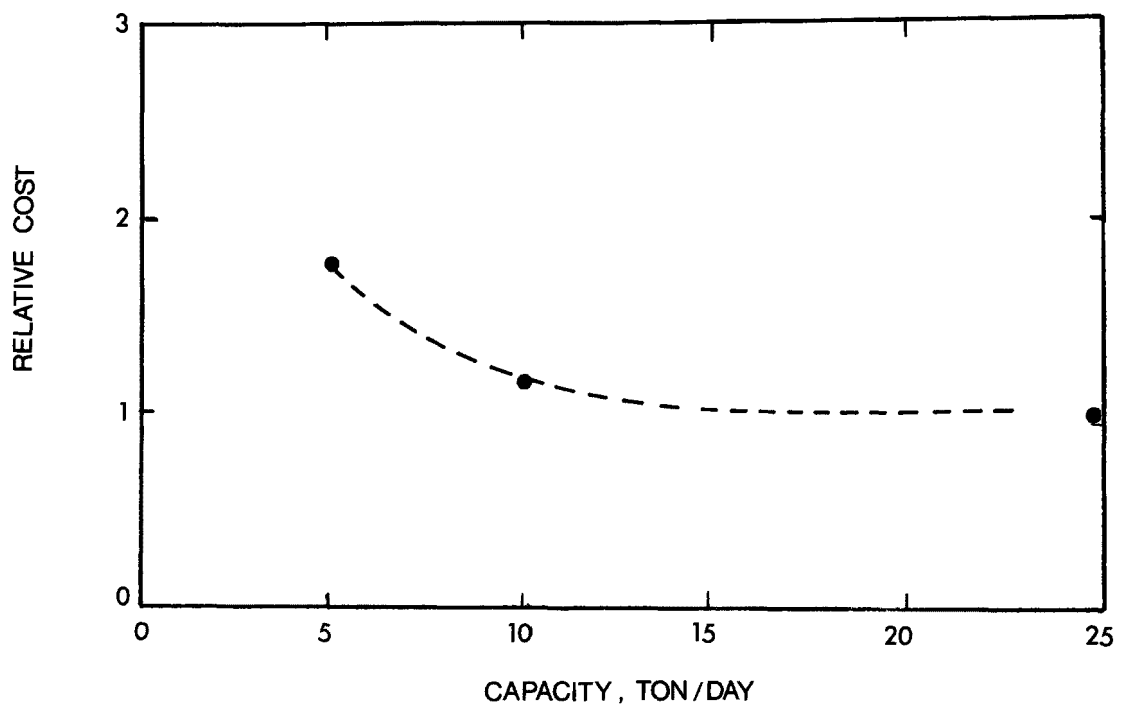


Figure 32. Significance of plant capacity to costs.

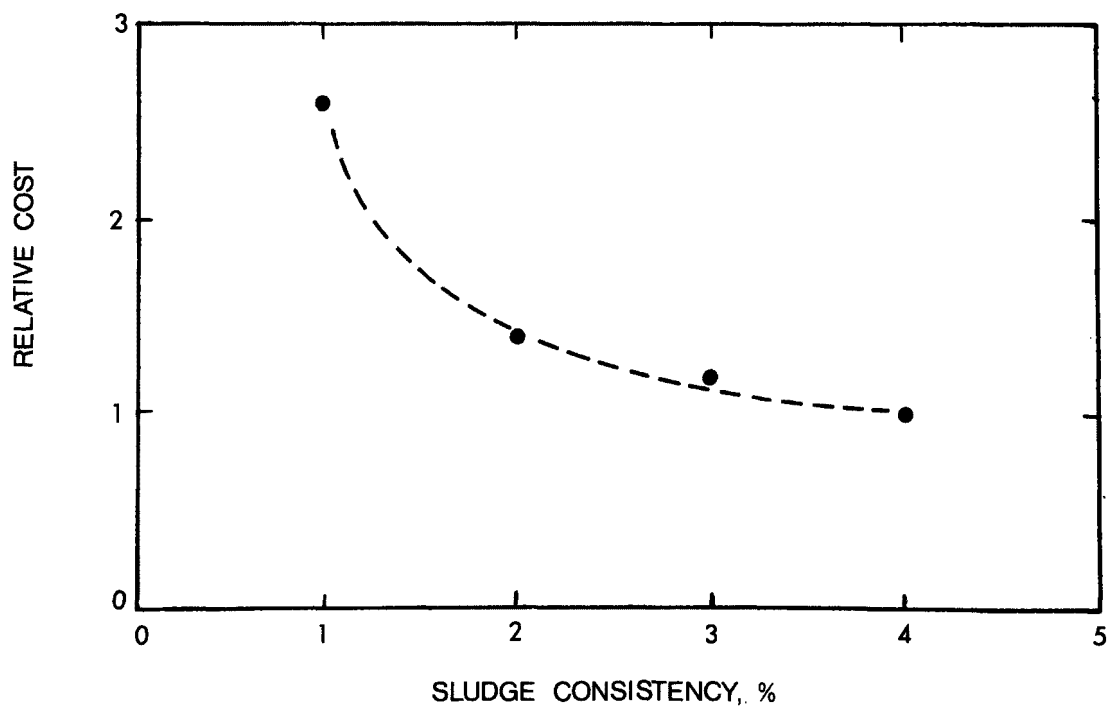


Figure 33. Significance of sludge consistency to plant costs.

BOD load of 21 percent of that entering the Colorado Springs plant and suspended solids contributions of 30 percent of the incoming load.

OPERATIONAL CONCERNS

Municipal Experience

In one compilation of case histories of sludge treatment by high temperature and pressure (31) it was indicated that several U.S. installations had ceased operating heat treatment systems due to (a) effluent quality problems and high process costs associated with a much higher degree of sludge solubilization than anticipated and (b) high costs of maintenance.

Recently cited studies in England (42) have shown that anywhere from 35 to 60 percent of sludge suspended solids are solubilized by heat treatment, with higher values associated with activated sludges. This range is consistent with results reported herein.

Additional English experience reports operating problems with scaling of heat exchanger surfaces. Kalinske (42) also cites continual formation of hard calcium sulfate on heat exchangers as a potentially serious problem as well as corrosion in the presence of high chloride concentrations.

Yet another troublesome problem which has emerged with oxidative systems, as well as nonoxidative, has been odor in the plant vicinity. Corrective measures taken include vapor incineration, water scrubbing, and carbon adsorption. Diffusion within mixed liquor aeration tanks poses an additional option.

The recitation of such a list of potential operational problems is not meant to imply that heat treatment systems are unworkable or are not worthy of consideration in residual management strategies. Their widespread application in municipal sludge management systems provides ample evidence that such problems can be endured where active measures are anticipated or taken to control or minimize them.

Industry Related Experience

Pilot experience with the nonoxidative conditioning of waste activated sludge resulting from waste treatment at a sulfite mill has been detailed by Moss et al. (42). Results reported therein indicated suspended solids decreases ranging from 28 to 35 percent dependent upon reaction temperature, which was varied from 340° to 390°F (171° to 199°C), and detention time. The incremental increase in supernatant BOD constituted approximately 38 percent of the mass of solids solubilized. Limited additional analysis (18) showed a corresponding ratio

of approximately 7 percent for total kjeldahl nitrogen. The associated supernatant color increase was observed to range from 8600 to 11000 platinum cobalt units (PCU), again dependent upon reaction conditions. Moreover, the uncondensed vent gas from the unit contained 10000 odor units per ft³, indicating the possible need for external odor control equipment. Condensates from the vent gases were seen to contribute an additional BOD of 1300 mg/liter. Perhaps of greatest consequence, however, was a scale/plugging problem resulting from precipitation of calcium salts on the vertical reactor standpipe, sludge-steam mixing nozzles, and the hot side of the heat exchanger.

The authors (44) concluded that cake discharge would pose a problem with vacuum filtration, though cake consistencies up to 22 percent were reported. A similar observation was made in leaf test evaluations conducted concurrently by NCASI staff (18). Within the range of acceptable loading rates and solids losses less than 10 percent, cake thicknesses did not exceed 0.2 inches (5 mm). Moreover, fines retained within the filter media were difficult to remove, further suggesting that cake removal might be difficult. Additional dewatering effort cited by Moss et al. (44) indicated that heat conditioned sludge could be dewatered to 19 percent at a rate of 100 gpm (379 lpm) while achieving 88 percent recovery when fed to a Sharples P5400. In contrast, non-heat conditioned secondary sludge is centrifuged to an 11 to 15 percent consistency at comparable recovery only after polymer conditioning costs reported at \$60.00 per ton of production (\$66.00 per metric ton) (45).

To date there are no large scale applications of oxidative conditioning within the paper industry. However, one mill employing high level wet oxidation for liquor recovery intends to dispose of its waste activated sludge within that system.

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