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## High Temperature, High Pressure Oxidation of Primary Sludges

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HIGH TEMPERATURE, HIGH PRESSURE OXIDATION OF  
PRIMARY SLUDGES

by

Dale R. St. Peter

A Thesis Submitted to the  
Faculty of the Department of Paper Science and Engineering

in Partial Fulfillment

of the

Degree of Bachelor of Science

Western Michigan University

Kalamazoo, Michigan

April, 1971

### Acknowledgment

The author would like to express his appreciation to Mr. Duane Marshall, Mr. Corless Abbott, and Mr. John Fisher for their guidance and advice. He also wishes to thank Mr. Charles Soukup of Zimpro Inc. who was kind enough to wet oxidize a sample of sludge. He is also indebted to Mr. Tom Krieg and Mr. John Nease of Engelhard Minerals and Chemicals for their invaluable aid in obtaining an abrasion number for the product of the oxidation process.

## Abstract

The problem of disposal of high ash papermill sludges has yet to be resolved. High temperature, high pressure wet air oxidation may have the potential to fill this gap in our technology.

A sample of high ash primary sludge was obtained, thickened, wet air oxidized, purified, and evaluated for brightness and abrasiveness. The product was grossly discolored with iron oxide. However, removal of the oxide yielded a high brightness product with low abrasiveness. This product appeared to be well suited for use as a filler material.

In order for this process to be acceptable as a method for obtaining a reusable product from high ash papermill sludge, it will be necessary to keep the iron oxide out of the product.

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## Introduction

In the production of paper and board, large amounts of solid wastes are discharged from the mills as a water suspension. These effluents must be treated so as to reduce the amount of damage they do to our environment. The portion of the effluent which is sent to the rivers must be non-toxic to aquatic life and have a low biochemical oxygen demand. The solids portion must be disposed of by some economical means.

The best means of disposal of any solid waste is through reuse. Of course, this does not always seem possible. The processing necessary to make wastes reusable is very often impractical from an economic standpoint and, in many other instances, the technology which would yield a suitable product for reuse has not even been developed. The latter seems to be the case with the reuse of high ash sludges<sup>1</sup> in the paper industry. The products obtained from the processing of these materials by present methods either do not have the optical properties necessary for utilization as either a coating or a filler material or else they are too abrasive.

<sup>1</sup> The term "high ash sludge" as used in this paper refers to primary sludges having an ash content of roughly forty percent or greater.

The purpose of this investigation is to determine if a high temperature, high pressure wet air oxidation of a high ash sludge is capable of yielding a product which is suitable for reuse as a filler material.

### Literature Review

Some of the methods which have possible application for disposal of the solid wastes are incineration, burning as fuel, land disposal, and wet air oxidation. It should be noted that the applicability of a given process of disposal depends on many factors, one of which is the nature of the solid wastes.

For instance, in order for incineration to be a practical disposal method, the sludge must be at a high solids concentration; otherwise, excessive fuel is required to maintain oxidation. This is due to the fact that heat is required to evaporate the accompanying water. Also, the volume reduction afforded by incineration decreases with increasing ash content. In the processing of a high ash sludge, the ash content is high enough that incineration alone would not be an effective means of disposal.

The ash which remains after incineration can be made bright enough for use as a filler material by keeping the incineration temperature about 1300° F. or higher. However, temperatures of this magnitude cause the water of hydration to be driven off. This converts the kaolin into a very abrasive material (1). This product is marketed to the paper industry but its use is not widespread due to the machine wear that results from using



an abrasive filler or coating material.

The same principles apply to using thickened sludge as a fuel. It is necessary to have a solids content of more than thirty-five percent for combustion of a fifty percent ash sludge to be self-supporting.(1). Even in those instances where the dewatering of the sludge is no problem, just as with incineration, the volume reduction of a high ash sludge would not be sufficient to make burning an effective means of disposal.

Disposal on land is a very short sighted solution to the problem. This practice is carried on by a large number of mills producing high ash sludges. The availability of land is a major factor in this method. Land values are increasing and this method of disposal is no longer as inexpensive as it once was. It can also be argued from the environmental standpoint that this constitutes a very poor and unaesthetic use of land.

Some high ash sludge has found utility in organized landfill. It has been used as a cover material for sanitary landfill. This does not seem to be widely practiced, however.

A wet oxidation process carried out at high temperature and pressure is one possible solution to the problem when coupled with a system for reusing the product of the process. This would work out best if the product could be reused as a filler in the paper being produced. High temperature and

pressure are desirable because of the faster reaction rate and the resulting high degree of oxidation (2,3,4,5). However, 205° F., water's critical temperature, is the maximum permissible temperature (2).

Zimpro Inc. of Rothschild, Wisconsin is working on the utilization of their wet oxidation process for processing high ash sludges. Since they are presently in the developmental stages, they have not given out a great deal of information concerning their results. However, they have implied some degree of success in treating the sludge from mills which make an effort to keep iron contamination to a minimum. This is necessary in mills where iron gets into the system because of iron oxide which is otherwise present in the product. The iron oxide tints the product reddish-brown and reduces the brightness (6).

It is unlikely that the gases given off by this oxidation will be a great problem. Those given off when sewage sludge is treated are somewhat obnoxious, but can be effectively eliminated using a catalytic combustion unit (7).

The wet oxidation process is a method of oxidizing the combustibles while they remain in a liquid water suspension. The water does not have to be removed from the sludge to the degree that is necessary for most other forms of disposal (3). For land disposal, it is usually desirable to dewater the sludge so that it can be hauled more conveniently. The large quantities

of water which would accompany the sludge if it were simply pumped to a disposal site without any dewatering would be excessive and prohibitive. For any type of a burning process it is necessary to dewater the sludge to a great extent as heat will be absorbed in evaporating the residual water and supplemental fuel will be required to maintain combustion. In a wet oxidation process, the water is a very necessary part of the sludge. It is the means by which the combustibles are transported through the process and it also carries the oxygen necessary for combustion (2,3). The amount of water desired is determined by the pumping characteristics of the sludge at different concentrations, the desired treatment rate (combustibles, solids, or ash basis), and the heat required from the combustion process to make the process self-sustaining.

Oxygen is supplied by air which is dissolved in the water by means of a compressor. The temperature and pressure are increased by a series of heat exchangers and a high pressure pump (2,3). The energy used to heat the incoming sludge is supplied by the oxidized sludge which is channeled back countercurrently through the heat exchangers (2,8). When necessary, steam is usually used to supply the additional heat required to raise the incoming sludge to the desired temperature for entering the reactor. Ideally, this is necessary only during start-ups. However, if the chemical oxygen demand falls

below a critical value, which depends on the characteristics of the sludge being treated, the heat supplied to the sludge by the oxidation will not be sufficient to raise the temperature of the incoming sludge to the desired temperature (8). The pressure is maintained at a level which is higher than the vapor pressure of water at the temperature of the sludge (2). A basic flow diagram of a wet air oxidation unit is shown in the appendix.

When practical, provisions can be made to use the excess heat produced by oxidizing high solids sludges to produce electric power. When this is done the process can be made self-sustaining even to the point of supplying the electricity to run the pumps (2).

### Experimental Design

The experimental procedure used in this investigation consisted of obtaining a sample of primary sludge, concentrating the sludge, wet oxidizing the sludge at high temperature and pressure, improving the brightness of the product, and testing the product for its utility as a filler.

The sludge sample was obtained from the Kalamazoo Paper Division of the Georgia Pacific Corporation. It was the product of two processes, the production of fine papers and the deinking of waste papers. The sludge was concentrated by gravity sedimentation.

The sample was then processed by Zimpro Inc. of Rothschild, Wisconsin. It was oxidized at about 570° F. and at a pressure in the neighborhood of 2000 p.s.i. for one hour.

The product of the oxidation was treated with oxalic acid to remove the color due to the iron oxide which was present. The original sludge was then tested for iron content using the 1,10-phenanthroline colorimetric technique described in "Colorimetric Determination of Elements" by Gaston Charlot (New York, 1964).

The product was observed under a microscope at 430 X both before and after the oxalic acid treatment to determine

if there was any visible change in the appearance of the product. A pellet was prepared using the powder press supplied with the Elrepho Color Meter and following the procedure dictated by the instruction manual for the instrument. The brightness of the pellet was measured using the G. E. Photovolt Brightness Tester.

The product was then tested for abrasion using the Valley Abrasion Tester. This test was run by Engelhard Minerals and Chemicals of Menlo Park, New Jersey.

### Discussion

The sludge obtained originally contained 1.47 percent solids. It was thickened to 5.4 percent solids. It contained 50 percent ash (27 g/l). Since the product of the oxidation process lost 18.7 percent upon ashing at 650° C., 27 g/l of ash implies 33 g/l of product.

The product of the oxidation was very heavily contaminated with iron oxide. The reddish-brown color of the iron oxide made the product unacceptable as a filler material. There was 610 mg/l of iron oxide present in the original sample (6). Most of this was due to contamination of the sample as it was obtained. Another sample of sludge was obtained in a plastic container and thickened in the same way as the original sample. The colorimetric determination of iron gave a value of 27 mg/l as  $\text{Fe}_2\text{O}_3$  when based on the same expected amount of product as that from the original sample (33 g/l). The amount of iron oxide is less than one part per thousand of the total amount of product expected. However, judging by the gross discoloration caused by the 610 mg/l of iron oxide, even this lesser amount would probably reduce the brightness to an unacceptable level. The product was also contaminated with a small number of dark specks which were easily removed by screening.

The microscopic examination of the product showed only one notable difference between the untreated product and the oxalic acid treated product. That difference was the presence of iron oxide particles in the untreated product. These particles were larger than the average product particles and appeared to be completely separate entities. They were not physically connected in any way with the other product particles. The similarity in the product particles gave evidence that the oxalic acid treatment probably removed the iron oxide without altering the main portion of the product.

The brightness of the product as measured on the G. E. Photovolt Brightness Tester was 85.5 percent MgO. This is very good for a filler material as anything over eighty is considered acceptable.

Due to the limited amount of product, it was not possible to use the standard procedure for the Valley Abrasion Test. It was necessary to run the test using a reduced volume of slurry. The value obtained is considered reliable as a control run was made using another filler and corrections were made to compensate for the variation in procedure. The abrasion number was 21 mg. This is well within the limits for a filler material.

The total cost of purchasing and operating a 200 ton per day low pressure oxidation unit was estimated in 1963 to be



\$23.30 per dry ton of sludge processed (8). This amount would be increased for a smaller unit; especially a high temperature, high pressure unit which would require more sophisticated equipment.

A fifty percent ash sludge would yield 0.615 tons of product per dry ton of sludge. In order to obtain one ton of product, 1.63 dry tons of sludge must be oxidized. Even at \$23.30 per dry ton, the price per ton of product is \$38. The delivered cost of 82 to 83 brightness filler clay is approximately \$36 per ton. Since the \$38 per ton figure is extremely conservative, a wet oxidation unit probably cannot be justified simply on economic grounds unless present disposal methods are costly. However, it must be taken into consideration that the process is capable of effectively disposing of the high ash sludge. It could also be used on a part time basis for treatment of secondary sludges.

### Conclusion

This study has shown that high temperature, high pressure wet oxidation may be a solution to the disposal problem associated with high ash papermill wastes. The product obtained has low abrasion characteristics and high brightness when free from iron oxide.

In order for this process to be implemented, however, it will be necessary to make provisions for keeping iron out of the system or for removing the iron oxide after the oxidation process.

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## Appendix

Simplified Flow Diagram of a Wet Oxidation Process

