

## **WET AIR OXIDATION PROCESS FOR SLUDGE TREATMENT (ZIMPRO PROCESS)**

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*Abstract: With rapid world population growth and strict environmental regulations, increasingly large volumes of sludge are being produced in today's wastewater treatment plants (WWTP) with limited disposal routes. Sludge treatment has become an essential process in WWTP, representing 50% of operational costs. Sludge destruction and resource recovery technologies are therefore of great ongoing interest. Wet air oxidation (WAO) can be used for the final sludge destruction and also potentially producing industrially useful by-products such as acetic acid. In essence, this technology uses high pressure and temperature in the presence of an oxidizing agent to deconstruct municipal biosolids. And also studies on the kinetics and mechanism of wet oxidation and advantages and disadvantages. This paper reviews roles of wet air oxidation in sludge treatment, and challenges faced by these technologies. WAO is a wide range of treatment temperatures with different temperatures suitable for treatment of different wastes. The wet oxidation scenario displayed a significant positive impact on global warming and eutrophication compared to land filling, but displayed a relatively high energy requirement. Overall, this technology has potential for significant improvements in biosolids management. By applying this technology to municipal biosolids, a substantive mass reduction of more than 90 per cent was achieved. In addition, process conditions were chosen such that readily degradable carbon compounds, such as acetic acid, were formed.*

**Keywords:** Acetic acid, sludge, Supercritical Water Oxidation (SCWO), Wet air oxidation(WAO), Zimpro process.

### **INTRODUCTION**

In a world of increasing demand for sustainable waste management, drivers for reducing waste volumes to landfills have become important. This includes finding alternative management strategies for the large percentage of municipal biosolids currently being land filled. A wet oxidation process for municipal biosolids was investigated as a potential technology to avoid these biosolids from going to landfill[3].

The WAO process can be defined as “the oxidation of organic and inorganic substances in an aqueous solution or suspension by means of oxygen or air at elevated temperatures and pressures either in the presence or absence of catalysts”.

Wet air oxidation (WAO), sub-critical water oxidation and supercritical water oxidation on the other hand utilize oxygen (or any suitable oxidant) with the aim, in most cases, to completely degrade organic compounds into carbon dioxide and water. In order to achieve this, high temperature (and subsequently pressures) conditions are required. The severity of conditions can determine the extent of oxidation achieved, and this feature allows oxidative hydrothermal processes to be used, besides sludge treatment, for the production of useful by-products – namely, acetic acid[5].

Zimpro process was a WAO technology originally designed in the 1930's for the manufacture of artificial vanilla flavoring, which was later adopted in sludge treatment with the aim of oxidizing the solids in sludge and destroy up to 65% chemical oxygen demand (COD) using temperatures up to 250 °C. However, problems with corrosion and high strength COD liquor caused a drop in popularity for its use. The Zimpro process was later modified into a lower temperature process, at 200 °C, called thermal sludge conditioning[1].

### LITERATURE REVIEW

**Zhu et al.**, studied that Investigated the complete digestion of mixture of primary and surplus sludge using wet oxidation without catalysts. The wet oxidation was carried out in an autoclave at 250 °C with holding times ranging from 30 to 120 minutes. A digestion efficiency of volatile suspended solids (VSS) of 94 – 96% was achieved. However, the organic matter content was high in the product liquid, which necessitated subsequent biological denitrification[8].

**Kevin Hii et al.**, studied that Hydrothermal processes such as thermal hydrolysis and wet oxidation technologies are becoming an essential part of sludge management strategies adopted in modern wastewater treatment plants. These technologies contribute not only to the reduction of waste volume, but also to the improvement of their environmental performance. Enhanced biogas production, energetically self-sufficient processes, value-added by-products, decreased greenhouse gas emissions and reduced reactor volumes are some of the benefits that can be expected from these technologies[5].

**D. Fytili, A. Zabaniotou**, studied that The review future trends in sludge handling, focusing mainly at thermal processes (e.g. Pyrolysis, wet oxidation, gasification) and the utilization of sewage sludge in cement manufacture as a co-fuel[2].

**Teletzke, G. H.**, studied that The low-pressure Zimpro treatment, which operates in the range of 150–300 psi at about 300°F. He portrayed low-pressure wet-air oxidation as an economical and flexible method of producing a sterile, drainable, and completely acceptable end-product for ultimate disposal[7].

### WET AIR OXIDATION PROCESS (ZIMPRO PROCESS)

The Zimpro process is a relatively innovative treatment for sludge. It operates on the basic principles that (1) organic matter contained in an aqueous solution can be oxidized, and whatever heat value it contains released, and (2) oxidation at this stage is more effective than if the water were first evaporated and the residue used as fuel in a conventional boiler. Because heat is liberated by a fuel only when it is subjected to combustion in the presence of air, the Zimpro process depends on air being forced into a reactor vessel. One objective of

this process is the production of the maximum number of Btu's from the organic matter in a waste effluent per pound of compressed air fed into the reactor.

Because the Zimpro process eliminates conventional filters, chemicals, sludge digestion units, incinerators, and auxiliary equipment, it reduces space and land requirements. The end-products are steam, nitrogen, CO<sub>2</sub>, and ash. The effluent gases from the reactor, having been "scrubbed" with water, contain no fly ash and are practically odourless.

In the treatment of sewage sludge, oxidation is brought about by continuously pumping the sludge and a proportionate amount of air (both sludge and air at elevated temperatures and pressures) into a reactor vessel. Combustion occurs as the oxygen in the compressed air combines with the organic matter in the sludge to form CO<sub>2</sub>, N<sub>2</sub>, and steam, while the ash remains in the residual water. The reactor, and the whole process system, is automatically maintained at a constant pressure and the products of the combustion are continuously removed from the reactor. If the concentration of volatile matter is high and the sewage sludge concentration is great enough (>5%), the steam, plus the gases (CO<sub>2</sub> and N<sub>2</sub>), which are products of combustion, will contain more than enough energy to run the air compressors and pumps used in the process. The residual hot water from the reactors is used in heat exchangers that raise the temperature of the incoming sludge and air sufficiently to cause oxidation to begin as soon as they come together in the reactor. In this way, once the process is started, no external heat or power is required to sustain the combustion.

Equipment required for the Zimpro process includes: compressor, air receiver, high-pressure sludge pump, sludge-storage tank with agitators, heat exchangers, reactor, separator, and cooler.

A schematic drawing of the process is presented in Units achieve 80 to 90% reduction of insoluble organic content of sewage sludge by oxidation without flame. Sludge is burned without de-watering or pretreating. The unit operates continuously at pressures of 500 to 600 psig and temperatures of 420°F. End products are substantially inorganic, inert, biologically stable ash; residual water; and odour - free gaseous products of combustion (carbon dioxide, nitrogen, and steam). The plant is designed for automatic operation with minimal maintenance. An air compressor and sludge pump are the only equipment components with moving parts. Power requirement is approximately 50 hp for a one-ton unit (dry weight). Building and land-space requirements are nominal[4].

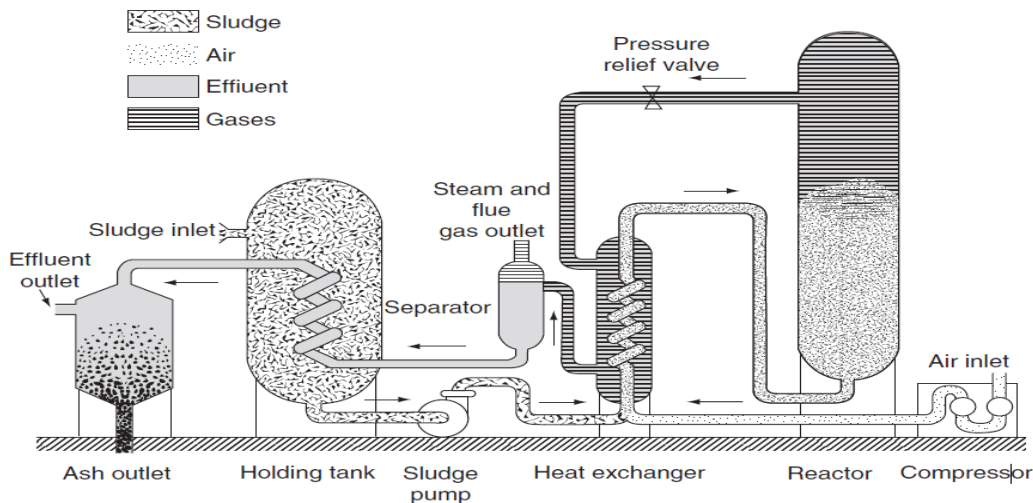


Figure 1 : Schematic diagram of the Zimpro process for sewage-sludge oxidation

Source : [4]

Problems with this process comes in the handling of the supernatant( larger secondary treatment facilities), the acid condition of the sludge (which may require ventilation), and odour problems from the gases generated ( may need a catalytic combustion unit)[6].

### KINETICS AND MECHANISMS OF WAO

The composition of sewage sludge can vary greatly but the main components are carbohydrates, proteins and lipids. The first stage in the WAO of sludge involves a large proportion of the insoluble organic content being converted into simpler soluble organic compounds (sugars, amino acids, fatty acids, etc.). The smaller molecules are then oxidized into easily biodegradable and oxygenated products (carbon dioxide, inorganic salts and water). This conversion is achieved through a number of hydrolysis and oxidation reactions occurring in series. These series of reactions are propagated by an organic radical obtained through oxidation of C-H bonds. The organic radicals produced are able to oxidize all organic compounds that contain hydrogen via hydrogen abstraction. The organic compounds are gradually decomposed into more stable intermediates which are finally oxidized to carbon dioxide and water. The overall reaction rate slows down as the easily oxidized compounds are gradually removed and acetic acid and other stable intermediates are formed.

To simplify the reaction mechanism for WAO, it can be assumed that the destruction of sludge proceeds via two pathways – it can proceed either directly or indirectly. In the direct pathway, all initial relatively unstable intermediates in sludge come into direct contact with oxygen and are converted into carbon dioxide. In the indirect pathway, these initial relatively unstable intermediates first undergo hydrolysis to form relatively refractory intermediates such as acetic acid. These intermediates are later oxidized into carbon dioxide.

However, sludge contains a complex mixture of compounds. Through the series of reactions involved in WAO, some of the organic compounds are fully oxidized, whereas some are transformed to intermediate products of lower reactivity.

Imteaz and Shanableh (2004) have developed a model for the WAO of wastewater sludge using a simplified first-order reaction scheme. The proposed alternative WAO reaction model aimed to present a more convenient method to describe the oxidation of sludge. Instead of describing the WAO process in terms of oxidation of unstable and stable compounds, the authors simplified the reaction scheme in terms of solubilisation and oxidation of all the COD in sludge. The global reaction model proposed is shown in Equation:

$$\frac{d(X + Y)}{dt} = -ke^{-\frac{E}{RT}}(X + Y)^m(O)^n$$

where

(X + Y) = total COD

O = concentration of oxidant

m = order of reaction with respect to organic reactant

n = order of reaction with respect to oxidant

Here, it is assumed that the destruction of COD biosolids may proceeds via a single pathway involving two reaction steps. Any solid COD in the sludge must first solubilise via hydrolysis before it can come into contact with the oxidants and finally oxidize[5].

## PRODUCTION OF USEFUL BY - PRODUCT IN WAO PROCESS

It is well known that the WAO process is able to produce chemical products such as volatile fatty acids (VFA), mainly acetic acid, which can be recovered for use. The production of acetic acid using WAO at sub-critical conditions for use as the organic reactants necessary in denitrification processes in WWTPs.

The WAO effectively hydrolyses sludge solids but achieves incomplete oxidation of the organic components. This produced COD-rich liquors containing 10% wt/wt acetate, which accounted for up to 80% of soluble COD. So, that the formation of organic acids increased with reaction temperature. More organic acids were formed as intermediates when the reaction temperature increases. Acetic acid production increased by four times as temperature was increased from 180 °C to 240°C, at 40 minute reaction time.

Two-step process to improve acetic acid production which consisted both of a hydrothermal reaction process in the absence of oxygen and a reaction process with oxidant supplied afterward. In the first step, the formation of furans is accelerated as the oxidation of these compounds leads to large amounts of acetic acid. In the second step, these furans are further converted to acetic acid by oxidation with fresh supplies of oxygen. The acetic acid obtained was of a high purity.

The WAO process achieved yield and purity of acetic acid of 12% and 38% respectively. On the other hand, the two-stage process achieved 8% yield and purity of 25%.

These works highlight the potential of using WAO to produce acetic acid from sludge. The production of useful chemical products may become an incentive for the implementation of WAO processing in sludge treatment, as research continues on the conditions which affect the production of acetic acid in WAO processing of sludge[5].

## ADVANTAGES AND DISADVANTAGES

### A. Advantages

1) Reduces solids mass, 2) Operating cost of this process is less compare to chemical conditioning, 3) Solids produced are more concentrated and much easier to dewater, 4) process is virtually free of upsets due to types of sludge and loading, 5) Eliminates chemicals and increases production, 6) The operator is not exposed to the sludge as a daily routine, 7) Mass transfer is rapid, 8) Completely destroys organic material, including carcinogens and pathogens, 9) System can operate more cheaply but with the same efficiency as the incineration process, 10) Complete destruction of a variety of wastes in short residence times, 11) Excellent dewatering[7].

### B. Disadvantages

1) Serious odor problems, 2) Pressure and heat could damage the equipment and could be a safety problem to operators, 3) High construction cost, 4) High maintenance cost, 5) Liquid recycle creates unwanted processing issues, 6) Volatile solids not reduced, 7) Not a stable product, 8) Problems of corrosion of equipment, 9) Must be stored and distributed dry[7].

## CONCLUSION

- WAO is a wide range of treatment temperatures with different temperatures suitable for treatment of different wastes.
- The production of useful by-products from WAO has been identified in several works and is acetic acid to be a beneficial characteristic of the process.

- The main output of this process is sludge containing more than 95% of mineral components and less than 3% of low-molecular organic substances. The sludge is dewatered (i.e. belt filter press) and then recycled or land filled.

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