Treatment of sewage sludge using hydrothermal oxidation – technology application challenges

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Abstract The objective of this paper is to examine the technical feasibility of hydrothermal oxidation as a sewage sludge treatment option. Hydrothermal oxidation involves treatment at temperatures and pressures below and above the critical point for water, 374.2°C and 22.1 MPa. Subcritical water oxidation (SubCWO) achieves incomplete sludge oxidation (<95% COD removal) and produces high-strength liquors containing significant quantities of volatile fatty acids (VFAs). Controlled liquor recycling into the treatment plant can provide a useful carbon source to support biological nutrient removal (BNR). SubCWO also achieves efficient destruction of the organic component of sludge solids, resulting in significant mass and volume reductions. Supercritical water oxidation (SCWO) on the other hand can completely oxidize the organic component of sludge (>99.9% COD reduction), produce high quality effluents and disposable ashes and air emissions. The major engineering challenges associated with developing hydrothermal treatment systems, especially SCWO systems, are solids management, corrosion and safety. The solids management challenge relates to scale formation, including deposition of inorganic salts and transport of suspended particles. The corrosion challenge relates to handling highly halogenated and extreme-pH waste streams. Nevertheless, the available body of technical knowledge supports the design of efficient SCWO sludge treatment systems.

Keywords Hydrothermal oxidation; sludge organic resources; sewage sludge; subcritical water oxidation; supercritical water oxidation

Introduction

The reuse of sludge from domestic wastewater treatment plants for agricultural purposes is an attractive management options. However, the accumulation of toxic heavy metals and toxic organic compounds, the cost of sludge transport from urban centers to areas suitable for land application, and the availability of land and markets to absorb the generated sludge quantities may limit the feasibility of the agricultural reuse option. The growing quantities of sludges generated in urban areas require innovative treatment processes that are capable of achieving significant mass and volume reductions. Technologies that combine efficient sludge mass and volume reductions with the production of reusable sludge products at competitive costs provide the most desirable solutions.

In highly populated urban areas, the difficulties associated with securing landfill sites make the minimization of disposal volume a key objective of sludge management. In such areas, sludge management may involve a combination of options, such as the reuse of sludge organic component to produce compost, fuel, and oil, and the reuse of the inorganic component to produce fill and construction materials (Yasuda, 1991). Municipalities typically use compost material on urban green zones or provide the product to suburban farmers at a nominal cost. In Europe, Japan and the United States, sludge incineration is widely used in highly populated cities as an ultimate sludge treatment option. In some cities in Japan, melting of the inorganic component of sludge following incineration is employed to further minimize the disposal volume through producing reusable products from sludge. Sludge melting locks the heavy metals in the slag, which is typically reused as a construction material (Yashiki and Murakimi, 1991).
While sludge incineration is widely practiced on full-scale basis in many highly populated urban areas in Japan, hydrothermal oxidation, in particular supercritical water oxidation (SCWO), is currently being considered by various research and waste management organizations as an alternative treatment option. SCWO occurs at temperatures and pressures above the critical point, 374.2°C and 22.1 MPa. The major issues in favour of considering hydrothermal oxidation as an alternative to incineration include (Shanableh and Gloyna, 1991; Gloyna and Li, 1998): (1) the ability to achieve efficient treatment in a totally enclosed facility; and (2) lack of harmful emissions. In Japan, concerns regarding harmful emissions including dioxins from incinerators have generated negative community views of the process in general. The community concerns extend to incinerating materials, such as sludge, that do not significantly contribute to emissions of dioxins and other toxic products of incomplete combustion.

The purpose of this paper is to present a brief evaluation of the hydrothermal oxidation technology as a sludge management option and as an alternative to incineration. In addition, the discussion highlights some of the major issues related to selecting and applying the innovative SCWO technology for sludge treatment.

Hydrothermal oxidation

Hydrothermal oxidation as discussed in this paper refers to oxidation of organic matter in water (subcritical or supercritical) as a reaction medium. The discussion presented in the following sections describes the performance of two hydrothermal oxidation processes. These are: (1) subcritical water oxidation (SubCWO), including wet air oxidation (WAO); and (2) supercritical water oxidation (SCWO).

Wet air oxidation (WAO) is a relatively low temperature (120°C to 300°C) and low-pressure (1–10 MPa) process. The process brings together the waste and the oxidant streams under suitable oxidizing conditions. Sludges can be conditioned at low temperatures and oxidized to high level of destruction (80–85%) at higher temperatures. In WAO, the proteins, lipids, starch and fibers that make the sludge solids are converted into simpler dissolved compounds, such as sugars, amino acids, fatty acids and ammonia (Teletzke et al., 1967).

The SCWO process occurs at temperatures and pressures above the critical point (374.2°C and 22.1 MPa). Water becomes a supercritical fluid at temperatures and pressures above the critical point. Supercritical water (SCW) may be viewed as a transition state between the liquid and gas phases. Within the critical zone, the liquid and gaseous phases merge resulting in one phase, or supercritical fluid. The supercritical fluid has unique characteristics, some of which are highly useful for the hydrolysis and oxidation of complex organic waste streams. Oxygen is completely miscible in SCW (Japas and Franck, 1985). SCW also has a high ability to dissolve organic matter (Connolly, 1966; Tsonopoulos and Wilson, 1983) and facilitate mass transport of dissolved matter. The process brings together reactants in an intimate contact in a highly oxidizing environment that rapidly achieves near complete destruction of organic waste streams. Compared to subcritical water, SCW thus has a superior ability to dissolve organic matter and oxygen. Unlike WAO and SubCWO reactions in which the liquid and gas phases remain separate and distinct, reactions in SCW occur in a single phase. The unique characteristics of SCW result in rapid oxidation reactions that are not hindered by oxygen availability or mass transfer limitations (Gloyna and Li, 1998).

The initial SCWO research efforts were focused on developing an effective hazardous organic waste treatment process capable of achieving 99.9999% removal efficiencies. The process was viewed as a competitive alternative to incineration. The first full-scale SCWO facility in the United States transformed the innovative SCWO treatment concept into reality.
The full-scale facility demonstrated that the process is capable of achieving exceptionally efficient treatment results and produce high quality effluents, disposable ashes, and safe air emissions (McBrayer, 1995). The process proved to be environmentally sound and more economical than incineration for the treatment of dilute hazardous organic wastes (Blaney et al., 1995).

Below the critical temperature, the production of thermally resistant by-products such as acetic acid limits the treatment efficiency to a maximum of approximately 90–95%. Using SCWO, the organic component of sludge can be reduced to any desired level in a relatively short reaction time. The required reaction time to achieve near complete oxidation (>99.9% as COD) decreases from approximately 30 minutes near the critical point to few seconds above 600°C.

**Sludge destruction mechanisms**

The various organic components of sludge undergo two major hydrothermal reactions: decomposition (mainly hydrolysis) and oxidation. Hydrothermal decomposition of the complex organic component of sludge results in the formation of simpler organic products, such as sugars, amino acids, and fatty acids. Hydrothermal oxidation results in the formation of oxygenated intermediates and final oxidation products, such as CO₂ and H₂O. The model in Figure 1 represents hydrothermal decomposition and oxidation. The final hydrothermal oxidation products of the initial complex organic matter (represented by C, H, N, O, P, S, Cl) are shown in Eq. 1. The process raises the P, S, and Cl atoms in the waste to their highest oxidation state. Nitrogen products may include ammonia, nitrogen gas, nitrates, and nitrates depending on the original form of nitrogen in the waste and the reaction conditions such as temperature and pH (Shanableh and Crain, 2000).

\[
\text{C, H, N, O, P, S, Cl} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{PO}_4^{3-} + \text{Cl}^- + \text{SO}_4^{2-} + (\text{N}_2 + \text{NH}_4^+ + \text{NO}_2^- + \text{NO}_3^-) + \text{Heat} \quad (1)
\]

**Mass and settled-volume reduction**

The destruction of the solid organic component of sludge, which mainly consists of proteins, lipids, hydrocarbons, and crude fiber, is rapid and proceeds through hydrolysis and oxidation. Hydrothermal treatment can result in significant mass reduction, depending on the organic component of sludge (typically 60–80% VS/TS). This is demonstrated by the selected treatment results presented in Table 1 (Shanableh, 1990). The data were obtained using a 1.5-litre continuous flow tubular reaction zone operated at a constant pressure of 28 MPa and mass flow rate of 50 g/min. The maximum residence time was approximately 30 minutes at the lowest reaction temperature of 280°C decreasing due to fluid expansion to less than 10 minutes at the maximum SCWO reaction temperature of 455°C. The temperature within the tubular reaction zone was not uniform, and the temperatures reported in Column 1 of Table 1 were the maximum measured within the reaction zone. The treated sludge contained approximately 1.8% volatile solids, 3% total solids, 31,900 mg/L total COD, and 29,900 mg/L solids COD. The treatment results indicate that the level of mass reduction reached approximately 55–60% on a dry solids basis. The resulting solids residues settled in 30 minutes to within 10–20% of the original volume of 980 mL/L, which...

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**Figure 1** Simplified sludge hydrothermal oxidation model

A = Complex Organic Matter (Sludge Solids)
B = Thermal Decomposition Products
C = Intermediate Oxidation Products
D = Final Oxidation Products
represented an 81–90% improvement in sludge settlability. The data confirm that the
destruction of sludge solids as measured by solids COD (92.9–99.8%) constantly exceeded
the total COD removal (71.7–96.6%). This is because hydrothermal treatment results in
efficient hydrothermal decomposition of the solid organic matter and the formation of
thermally resistant dissolved organic compounds such as acetic acid.

**Production of soluble organic resources**

SubCWO is practically incapable of achieving complete oxidation of the organic com-
ponent of sludge. This treatment limitation results from the production of large quantities
of thermally resistant soluble by-products, such as acetic acid (Table 1). Acetic acid may
account for as much as 30–80% of the soluble COD in the effluent, depending on the degree
of oxidation achieved (Goto et al., 1998). The data in Table 1 for example indicate that the
contribution of acetic acid to the soluble COD reached approximately 80% when the COD
removal was approximately 84%. The recycling of high strength hydrothermal oxidation
liquors into the treatment process can raise the oxygen demand by 30–50% through increas-
ing the concentration of organic matter in the total flow. Liquor recycling can also increase
the concentration of VFAs in the total flow by 40–50 mg/L as acetic acid (Shanableh, 2000).
The recycled liquor can be of benefit to the treatment process. Researchers (Karllsson, 1990;
Karsson, 1997; Henze and Harremoes, 1990; Barlindhaug and Odegaard, 1996) have suc-
cessfully used the hydrolyzed organic matter from sludge as a carbon source for denitrifica-
tion. Barlindhaug and Odegaard (1996) reported that thermal hydrolysis products
performed as well as biological hydrolysis products in terms of supporting denitrification.
The biological availability of thermal hydrolysis products for supporting enhanced bio-
logical phosphorus removal (EBPR) has been confirmed and demonstrated to be feasible and
effective (Jomaa, in preparation; Jomaa et al., 2000; Shanableh, 2000).

Subcritical hydrothermal treatment, with or without the use of oxidants, is capable of
decomposing the organic solids fraction of sludge and producing high strength liquors. The
use of oxidative hydrothermal treatment can minimize the production of objectionable air
emissions such as carbon monoxide. A disadvantage of hydrothermal production of

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<th>Max. measured temp. (°C)</th>
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<th>Solids COD removal (%)</th>
<th>Increase in soluble COD (%)</th>
<th>Acetic acid contribution to soluble COD (%)</th>
<th>Solids mass reduction (%)</th>
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*Approximately 3,000 mg/L acetic acid, 7,000 mg/L soluble COD
dissolved organic matter is the production of ammonia, which when recycled into the treatment process increases the oxygen demand (Shanableh, 2000).

**Fate of sludge heavy metals and toxic organic chemicals**

Sludge heavy metals are typically incorporated in the ashes in non-leachable forms. Tongdhamachart (1990) detected dissolved Cr (0.1–3.3 mg/L) and Pb (0.3–0.6 mg/L) in supernatants resulting from the treatment of anaerobically digested sludges containing 3% total solids at 300–460°C in a stainless steel grade 316 reactor. Stainless steel grade 316 contains approximately 16.46% by weight Cr, 18.19% Ni and 2.11% Molybdenum. The pH in the treated samples remained in the range of 7.2–8.0. Some Cu was also detected (0.2–0.8 mg/L) at subcritical temperatures but not at supercritical temperatures. Similarly, Shanableh (1990) reported soluble Cr concentrations in the range of 2–3.4 mg/L below 374°C and 0.5–1.1 mg/L above 380°C in supernatants resulting from the treatment of undigested sludges. In the undigested sludge, the treated effluent pH increased in the range of 5.4–7.4 with increased reaction temperatures in the range of 280–460°C. Both Shanableh (1990) and Tongdhamachart (1990) confirmed that most of the original sludge metals remained concentrated in the ash residuals, however with the destruction of solids and possibly as a result of corrosion, the concentrations of metals in the ashes increased by a three to five folds. The leachability of metals in the ashes was assessed using the toxicity characteristic leaching procedure, TCLP. Non of the metals concentrations measured in the TCLP extracts exceeded the specified TCLP limits (Shanableh, 1990; Tongdhamachart, 1990).

In addition to being capable of achieving virtually complete removal of the major organic components of sludge, SCWO treatment is capable of destroying the trace hazardous sludge contaminants, such as PCBs. Crain et al. (1999) reported that the destruction removal efficiency exceeded 99.99% for the PCBs in the sludge following SCWO at 540°C and one minute reaction time at 27.6 MPa. The treatment of PCPs contaminated sludges resulted in a gaseous effluent with non-detectable levels of PCBs, dioxins or furans.

**SCWO process development**

Unlike SubCWO in which water remains in the liquid state, SCWO reactions occur within supercritical water, which is neither a liquid nor a gas. The highly oxidizing SCWO environment coupled with the presence of halogens can lead to rapid metallurgical degradation. The expansion of water under SCWO conditions reduces the density and increases the velocity of the fluid inside the reactor. The low fluid density directly influences the residence time and solids handling in reactors.

A simplified schematic of a hydrothermal treatment system is presented in Figure 2. The system utilizes a pre-heater, reactor, solid-liquid separator, and cooling/energy recovery exchanger. The pre-heater utilizes some of the energy in the effluent to heat the influent. Introduction of the oxidant into the preheated waste stream causes a rapid rise in temperature and an aggressive oxidizing environment within the reactor. The heat exchange/recovery units are particularly susceptible to scaling and corrosion. The corrosion issue may not be a major concern with sludges compared with halogenated waste streams. Gloyna and Li (1998) and Shanableh and Crain (2000) provided a review of suitable materials for SCWO reactions. In general, the most suitable materials for SCWO reactions are expensive and usually lack structural integrity. However, the acceptable corrosion resistant materials can serve as reactor liners. In addition to corrosion, pressure letdown devices are susceptible to erosion as a result of suspended solids in treated effluents. Solids separation prior to effluent discharge can help reduce erosion of pressure letdown devices. Another challenge associated with process development relates to scaling. The deposition of salts on the walls of the reactor and heat exchange devices results from the inability of the low density SCW to
dissolve inorganic salts, which drop out of solution. These challenges continue to be investigated by researchers and various alternative solutions have already been proposed (Gloyna and Li, 1998).

The key engineering design considerations for successful SCWO sludge treatment systems include (McBrayer et al., 1993; Gloyna et al., 1994; Gloyna and Li, 1998): sludge pretreatment; energy considerations; materials; solids separation; treatment conditions; effluent handling; and ash disposal. Treatment to achieve any degree of oxidation requires treatability testing to select the most suitable range of reaction temperatures, pressures, residence times, and oxidants.

As with incineration, SCWO can achieve virtually complete oxidation of the organic component of sludge. However, the major advantages of SCWO as compared to incineration relate to applicability to relatively dilute waste streams and quality of air emissions (Blaney et al., 1995; Gloyna and Li, 1998). The process can meet stringent regulatory requirements for air emissions without the need for extensive air pollution control devices. This feature reduces the operating costs of SCWO compared to incineration. The SCWO process is best suited to treat waste streams that contain adequate organic content to generate enough heat to sustain the reaction temperatures. Highly concentrated waste streams can result in overheating. Sludges thickened to 5–10% solids content can provide the best treatment economics as thickening reduces the required reactor volume and allows the generation of enough heat to sustain the reaction. On the other hand, sludge incineration requires efficient dewatering and drying of sludges and the addition of auxiliary fuels to sustain the reaction temperatures.

Proponents of SCWO claim that the process offers significant operating cost savings when viewed as an alternative to incineration of relatively dilute organic waste streams. This claim (EWT, 1998) has been confirmed by data from the first commercial-scale SCWO facility, which was commissioned in the US in May 1994 at the Huntsman’s Chemical Company in Austin, Texas (McBrayer, 1995). The Texas Austin-based Eco Waste Technologies designed the 1,100 L/h facility for the Huntsman’s Chemical Company.

Conclusions
Hydrothermal oxidation of sludges using SubCWO and SCWO offers a versatile and technically viable sludge treatment concept. Hydrothermal oxidation can be used to achieve any degree of destruction of the organic component of sewage sludge. Subcritical hydrothermal oxidation offers opportunities for combining efficient sludge mass and volume reductions with production of useful organic matter, mainly VFAs, that can be recycled and used to support biological nutrient removal in wastewater treatment plants.
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References


