Pilot-Scale Laboratory Waste Treatment by Supercritical Water Oxidation

Yoshito Oshima*, Rumiko Hayashi1 and Kazuo Yamamoto2

Department of Environmental Systems, Graduate School of Frontier Sciences, The University of Tokyo, Tokyo, Japan
1Department of Chemical System Engineering, Graduate School of Engineering, The University of Tokyo, Tokyo, Japan
2Environmental Science Center, The University of Tokyo, Tokyo, Japan

(Received December 1, 2005; accepted March 23, 2006)

Key words: supercritical water oxidation, waste treatment, laboratory waste

Supercritical water oxidation (SCWO) is a reaction in which organics in an aqueous solution can be oxidized by O2 to CO2 and H2O at a very high reaction rate. In 2003, The University of Tokyo constructed a facility for the SCWO process, the capacity of which is approximately 20 kl/year, for the purpose of treating organic laboratory waste. Through the operation of this facility, we have demonstrated that most of the organics in laboratory waste including halogenated organic compounds can be successfully treated without the formation of dioxines, suggesting that SCWO is useful as an alternative technology to the conventional incineration process.

1. Introduction

Supercritical water oxidation (SCWO), which operates under conditions in which both temperature and pressure are above the critical point of water (374°C, 22.1 MPa), has attracted attention as a promising technology for waste treatment, particularly for aqueous organic waste streams. The application of this technology to handling practical waste has been widely investigated over the past decades. Although a previous investigation on the application of the SCWO process was limited to the treatment of industrial waste, the application of this technique to the treatment of laboratory waste also seems to be reasonable and feasible, because SCWO is capable of a rapid and complete decomposition of various organics including toxic, poisonous and even refractory species.

*E-mail address: oshima@k.u-tokyo.ac.jp
The University of Tokyo constructed a new facility for the SCWO process for treating chemical organic wastewater from laboratories. Figure 1 shows the breakdown of organic waste in The University of Tokyo. Approximately 30% of the organic waste is a mixture of organics and water, and approximately 20% of the organic waste is halogenated compounds. A large concentration of water in the waste is theoretically unfavorable for the conventional incineration treatment, but it would not be a problem for the SCWO process. Therefore, it is reasonable to use the SCWO technology as an alternative to incineration for the treatment of laboratory waste in our university. In this paper, we introduce the design of equipment and the treatment performance of the new facility for the SCWO process at present.

2. Design of SCWO Equipment

A schematic diagram of SCWO equipment that was constructed in 2003 at Kashiwa campus, The University of Tokyo is shown in Fig. 2. As a reactor system, we adopted the “MODAR-type reactor,” which is an effective method of the treatment of halogenated organic compounds and inorganic salts.(1) The volume of this reactor is approximately 25 L, and the capacity of treatment is approximately 20 tons per year.

The waste solution is mixed with air, which is an oxidizer, and introduced into the reactor through a nozzle. In the reactor, temperature is highest in the vicinity of the nozzle because of the exothermicity of the reaction, and the organic carbon in the waste is quickly oxidized to CO₂ mainly in the upper zone of the reactor. Because the reactor is not equipped with an external heater, a vertical temperature gradient can be naturally achieved, which consequently leads to phase separation into a supercritical zone in the upper portion of the reactor and a liquid zone at the reactor bottom.

![Fig. 1. Breakdown of organic waste in The University of Tokyo (1998–2003).](image-url)
Halogenated organics such as chlorinated hydrocarbons are oxidized in the upper supercritical zone and transformed into acids, which also dissolve in the supercritical water, and discharged along with CO₂ and H₂O from the top of the reactor. The fluid coming out from the upper side is cooled down and neutralized by a stream of an aqueous solution of sodium hydroxide, followed by gas-liquid separation. In the meantime, because of the very low solubility of inorganic compounds in water under the supercritical condition, inorganic salts such as NaCl in the original waste form dense brine droplets or solid precipitates, and move down to the bottom of the reactor because of their weight. At the bottom of the reactor, where water is in the liquid phase, an inorganic salt can be dissolved in the water and is flushed out of the reactor along with the effluent solution of the gas-liquid separator.

Another concept we have adopted for the reactor design is called “Dual Shell Pressure Balanced Vessel (DSPBV),” which is effective for preventing corrosion in the reactor. A Cr-Mo steel, which is known to possess a high mechanical strength against pressure, is used for the outer shell of the reactor vessel; however, this material is not applicable to corrosive conditions such as a condition with a very low pH. To solve this problem, a cylindrical cartridge made of special anticorrosive materials, such as Ta and Ti, is used to prevent the surface of the vessel from being exposed to a corrosive atmosphere. The pressure of air flowing outside the cartridge is slightly higher than the pressure inside the cartridge, and is always controlled so as to keep the pressure difference very small. Although the anticorrosive cartridge is made of special expensive materials, DSPBV enables us to reduce the thickness of the cartridge and to save cost.

3. Achievements and Technical Problems

We have already treated various kinds of wastewater from The University of Tokyo, and the total amount of treated wastewater in the fiscal year 2004 was approximately 3 kl. Table 1 shows several examples of the amounts and compositions of the wastewaters treated by
SCWO equipment at Kashiwa campus in the fiscal year 2004. “Incombustible” waste (1.17 kl) which includes more than 5% water, 1.38 kl of “combustible” waste, and 0.40 kl of “halogenated organic” waste were completely and successfully treated without the formation of dioxines, and problems with corrosion have not been reported so far. The total number of operation days of the treatment process was 74, excluding the days used for the analysis of waste, pretreatment, and treatment of inorganic wastewater. Furthermore, the treatment process was operated continuously to reduce the load to SCWO equipment at the start up and shut down, and the maximum operation period was 8 days.

These achievements imply that SCWO is a promising technology applicable to the treatment of laboratory waste; however, there are several problems still remaining to be solved. One problem is the high capital and running cost of the technology. Particularly, as shown in Fig. 3, the percentage of labor cost to the total running cost is high, which may be partly due to the legal requirement of licensed laborers to operate such a large-scale high-pressure plant. Another problem is salt formation in the reactor. We have experienced a sudden pressure increase during the operation due to the clogging of the tubing at the exit of the reactor caused by salt precipitation. We found from the ICP analysis that the major components of the precipitate were alkaline metals such as Na and K, and Cl. An example of the salt composition is shown in Table 2. These elements were initially present as dissolving salts in the original solution and were presumed to form mixed precipitates under the reaction conditions of SCWO. Barner et al. previously suggested in a paper that inorganic salts such as NaCl and Na₂SO₄ are sticky and tenaciously adhere to solid surfaces with which they come in contact in the SCWO process. We measured the melting point of the precipitated salt, and found it to be approximately 630°C. This value is far lower than the melting points of pure inorganic salts such as NaCl (801°C) and Na₂CO₃ (850°C). We

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Achievements of laboratory waste treatment by SCWO equipment at Kashiwa campus of The University of Tokyo in fiscal year 2004.</th>
</tr>
</thead>
</table>
| **1.17 kl of “incombustible” waste** examples:  
- Acetone (12%), IPA (5%), methanol (5%), acetonitrile (4%), pyridine (1%) in water  
- Dimethyl sulfoxide (6%), cyclodextrine (1%) in water  
- Ethanol (35%), IPA (5%), chloroform (1%), phenol (1%) in water |
| **1.38 kl of “combustible” waste** examples:  
- Ethyl acetate (35%), acetone (27%), n-hexane (19%) toluene (6%), pyridine (3%)  
- Methanol (34%), ethanol (33%), acetone (33%) |
| **0.40 kl of “halogenated organic” waste** example:  
- Dichloromethane (75%), chloroform (12%), acetone (6%), methanol (4%) |
also observed experimentally that the plugging due to the salt formation does not take place when the original solution contains only NaCl. From these observations, it is suggested that the plugging problem in the SCWO treatment of laboratory waste water will be more serious if the original waste contains multiple types of inorganic salt, because of the formation of mixed-salt precipitates that possess low melting points and high adhesivenesses.

In laboratory waste, the concentration of inorganic salt in most organic wastewater is usually on the order of hundreds of ppm or less; however, the obstruction in the reactor may be caused by a very small amount of salt contamination from the waste. Therefore, a thorough identification of the chemical components of the wastewater before SCWO treatment is necessary to avoid the plugging problem caused by salt formation in the reactor.

Table 2
Example of salt composition analyzed by ICP.

<table>
<thead>
<tr>
<th>Element</th>
<th>Percentage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>59.5%</td>
</tr>
<tr>
<td>Na</td>
<td>27.4%</td>
</tr>
<tr>
<td>C</td>
<td>8.6%</td>
</tr>
<tr>
<td>K</td>
<td>2.3%</td>
</tr>
<tr>
<td>S</td>
<td>0.7%</td>
</tr>
<tr>
<td>P</td>
<td>0.5%</td>
</tr>
</tbody>
</table>
4. Conclusion

We constructed a new facility for SCWO for the treatment of waste from laboratories in The University of Tokyo. We adopted the MODAR-type reactor as a reactor system, and the complete decomposition of organic waste, including halogenated compounds was achieved without the problem of corrosion. However, salt formation still remained a problem; thus, we are now investigating possible technical solution to this problem. We will continue to gather the engineering data through the operation of the facility, and develop a better and a more practical treatment process by solving these technical problems.

Acknowledgements

The authors greatly appreciate the financial support in the form of a Research Grant for the Promotion of Science for scientific research on priority areas entitled “Evolution of environmental, health and safety and development of educational program” from the Ministry of Education, Culture, Sports, Science and Technology of Japan. Precious technical data and information for this study were provided by Organo Corporation, which is also greatly appreciated.

Reference