

Supercritical Water-A Useful Medium for Waste Destruction

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ABSTRACT. Water is a supercritical fluid at temperatures and pressures above the critical point, 374.2 °C and 22.1 MPa. The unique properties of supercritical water (SCW) include complete solubility of oxygen and organic compounds, poor solubility of inorganic salts, improved mixing, enhanced mass transfer rates, and strong ability to dissolve organic solids. The recently developed supercritical water oxidation (SCWO) technology relies on the properties of SCW to create a useful and effective oxidation reaction medium. The oxidation of hazardous organic wastes and sludges can proceed to completion in SCW, and this can be achieved in a totally enclosed treatment facility. This paper describes an investigation of SCWO for destruction of a highly contaminated biological sludge. The destruction of the organic contaminants was virtually complete in relatively short residence times. Above 99 percent chemical oxygen demand (COD) reduction was achieved within 5 minutes at 450 °C, 15 minutes at 425 °C and 25 minutes at 400 °C. The process produced a clear and odorless effluent and a disposable ash with good settling characteristics. The process is applicable to a wide range of hazardous wastes and sludges and can become thermally self sustaining at low concentrations of organic wastes.

As the complexity of environmental management continues to increase, environmental contaminants must be contained and destroyed. Otherwise, the destruction of toxic organic wastes and sludges becomes an overwhelming problem. The growing quantities of hazardous wastes and sludges require special attention and innovative treatment processes. The options for complete destruction of aqueous

hazardous wastes and sludges are limited. Incineration, while potentially achieving complete combustion, does not provide total enclosure and the burning and cleaning processes are expensive and difficult to control. Low temperature water oxidation systems, such as wet air oxidation, cannot achieve total destruction and generate, when applied for sludge treatment, strong liquors that require significant treatment. On the other hand, supercritical water oxidation (SCWO) can provide complete destruction of hazardous wastes and sludges in totally enclosed treatment facilities.

Properties of Supercritical Water

Water is a supercritical fluid at temperatures and pressures above the critical point, 374.2 °C and 22.1 MPa. Under these conditions, the boundaries between the phases disappear, and supercritical water (SCW), oxygen and a wide variety of organic compounds become completely miscible. The high diffusivity and high temperatures assist in destroying the organic solids, and supercritical water dissolves the organic compounds. Intimate contact between reactants in SCW results in a rapid and efficient destruction of the organic component of the waste.

Solubility of oxygen. The rate of wet oxidation at temperatures below the critical point is typically limited by oxygen solubility. This mass transfer limitation results when the rate of oxygen transfer between the gas and liquid phases and the subsequent rate of oxygen diffusion and mixing limit the rate of oxidation reactions at elevated temperatures. Reactions limited by oxygen transfer require extended reaction times and achieve inefficient oxidation results (Gloyna 1988). Under SCWO conditions, the boundaries between the phases disappear (Marshall 1975), and supercritical water and oxygen become completely miscible (Japas and Franck 1985, Thomason and Model 1984). Complete solubility eliminates oxygen mass transfer limitations in SCW.

Solubility of organic and inorganic compounds and SCW dissociation. Under SCWO conditions, SCW, oxygen and a wide variety of organic compounds become completely miscible (Thomason and Model 1984). SCW is an excellent solvent of non-polar organic compounds that are sparingly soluble at ambient temperatures (Josephson 1982). This results from the decline in hydrogen bonding as reflected in low static dielectric constant, ϵ . For example, ϵ is equal to approximately 80 at standard temperatures and pressures (STP) and approximately 5 under SCW conditions (Franck 1963).

While the solubility of organic compounds increases as hydrogen bonding and ϵ decrease, the solubility of inorganic salts decreases. For example, the solubility of CaCl_2 in water decreases from a maximum of 70 percent at subcritical temperatures

to 10 mg/L at 500 °C (Martynova 1976). Accordingly, fewer ions exist in solution under SCWO conditions. The dissociation of water itself is limited under SCWO conditions. The ionic product constant for water (k_w) declines from a typical value of approximately 10^{-14} at ambient conditions to $10^{-21.6}$ at 25 MPa and 475 °C (Marshall and Frantz 1987).

Density, viscosity and heat capacity. The reduced density and viscosity of SCW results in enhanced mobility and diffusivity of molecules. For example, at 27.6 MPa, the density of SCW is 1.01 g/mL at 25 °C, 0.538 g/mL at 375 °C and 0.128 at 450 °C (Gloyna *et al.* 1995). Similarly, the viscosity decreases from 8.86×10^{-4} Pa.s at 25 °C, to 2.98×10^{-5} Pa.s at 450 °C. In addition, SCW is an excellent carrier of thermal energy with the specific heat capacity orders of magnitude larger than its value at ambient conditions (Gloyna *et al.* 1995).

SCWO Research and Development

Although SCWO technology is relatively new, significant research and development effort has been undertaken (USEPA 1992, Jensen 1994, Gloyna *et al.* 1995). The effectiveness of SCWO in destroying a variety of contaminants has been demonstrated (Gloyna 1988, Gloyna *et al.* 1995, Li *et al.* 1993, Muralikishna *et al.* 1993, Shanableh 1994, 1995, Shanableh and Gloyna 1991, USEPA 1992). The applicability of the process for treatment of a variety of organic wastes from municipal and industrial sources is summarized in Table 1 (Gloyna 1988, Oxidyne 1988). Jensen (1994) summarized the current research and development efforts in the United States. The US Department of Defense and Energy, US Navy, General Atomics Corporation, GNI Group, MODAR, MODEC, EcoWASTE Technologies and many research organizations are leading the development of specific SCWO applications. A number of SCWO commercial waste treatment facilities are either under construction and initial testing or started operation in 1994/1995.

The data presented and discussed in this paper describe the destruction of a highly contaminated waste sludge obtained from an industrial waste activated sludge treatment plant. The sludge contained organic solids as well as dissolved organic compounds. The results demonstrate the effectiveness of SCWO in destroying the organic component of the waste. The paper also describes the specialized SCWO reactor models developed for the purposes of this study.

Equipment

Destruction of sludge was evaluated using laboratory-scale batch and continuous-flow reactors. A schematic of the batch reactor vessel assembly is

presented in Fig. 1. The reaction vessel consisted of a horizontal coil-tube reaction vessel (SS 316, 6.35 mm O.D. x 4.57 mm I.D. x 1.22 m long), pressure transducer, a thermocouple, and a reactor holder. Temperature and pressure variations during the course of the reaction were displayed and recorded. During a typical batch test, the reactor was charged with a homogenized sludge sample, mounted on the shaker,

Table 1. Applicability of Subcritical and SCWO (Gloyna 1988, Oxidyne 1988)

| Waste Stream | Subcritical Water Oxidation | SCWO |
|---|-----------------------------|------|
| Industrial Organic Chemicals | X | X |
| Plastics Synthetics | X | X |
| Drug Manufacturing | X | X |
| Paints and Allied Products | | X |
| Industrial Organics | X | X |
| Agricultural Chemicals | | X |
| Explosives | X | X |
| Petroleum and Coal Products | X | X |
| Rubber and Miscellaneous Plastic Products | X | X |
| Acrylonitrile Wastewaters | X | X |
| Cyanide Wastewaters | X | X |
| Polychlorinated Biphenyls (PCBs) | | X |
| Pesticide Wastewaters | X | X |
| Halogenated Aliphatics | | X |
| Halogenated Aromatics | | X |
| Aromatic Hydrocarbons | X | X |
| Ketones (MEK) | | X |
| Organic Nitrogen Compounds | | X |

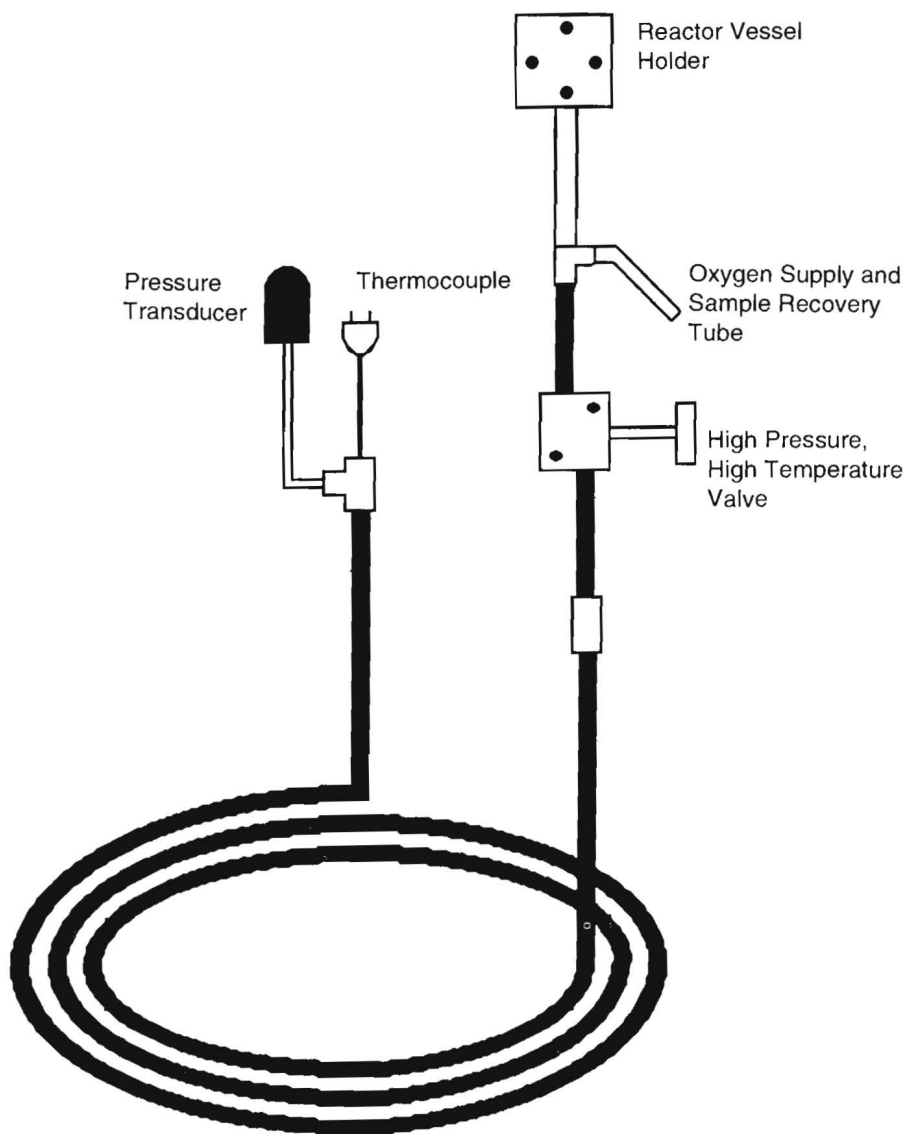


Fig. 1. Schematic of the batch reactor system.

pressurized with oxygen, checked for leaks, immersed in a heated fluidized sand bed for the desired reaction time, then removed and submerged in a water bath to terminate the reaction. On the average, 30 seconds were required to heat the reactor vessel and contents to the desired reaction temperature.

A schematic of the continuous-flow, vertical reactor is presented in Fig. 2. The reactor consisted of two concentric stainless steel 316 (SS 316) tubes. The outer tube dimensions were: 50.8 mm outside diameter (O.D.) x 25.4 mm inside diameter (I.D.) x 5.74 m long. The inner reactor tube dimensions were: 12.7 mm O.D. x 10.9 mm I.D. x 5.74 m long. The reactor surface was initially heated using nine electric band heaters distributed along the reactor. Pressure was controlled by a back pressure regulator and was measured using a pressure transducer interfaced with a digital display. Temperatures were monitored at 16 different locations within the annular space and the core. The operator was protected behind a polycarbonate safety shield.

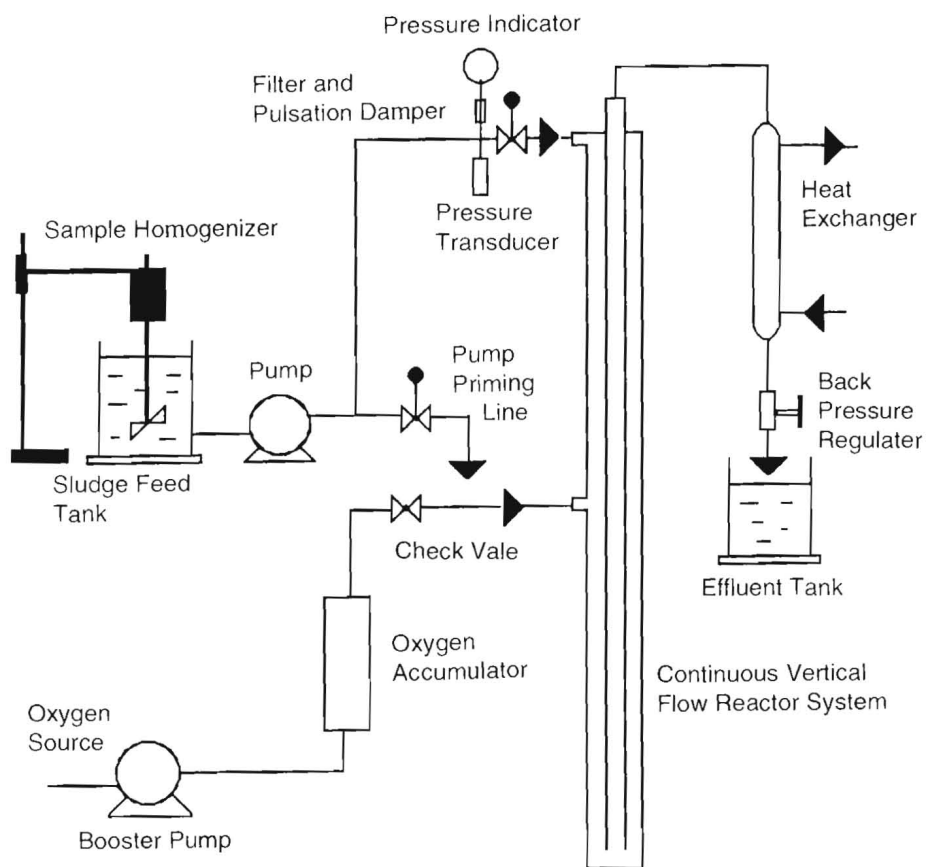


Fig. 2. Simplified schematic of the continuous-flow, vertical reactor system.

Materials and Methods

This project dealt with a highly contaminated activated sludge obtained from a plant which treated wastewaters from a papermill, refinery and petrochemical sources. The sludge contained paper fibres and some oil. Ammonia, pH, and organic content (as measured by the chemical oxygen demand; COD) were measured using standard analytical procedures (APHA 1989). Acetic and propionic acids were measured using a Tracor 550 Gas Chromatograph equipped with a flame ionization detector (FID) and recorder. A 122 cm long x 6.4 mm O.D. x 4 mm I.D. glass column packed with GP Carbowax 20M/0.1 percent H_3PO_4 was used. The column temperature was maintained at 100 °C. The column inlet and outlet temperatures were maintained at 190 °C. The detector temperature was maintained at 160 °C. The carrier gas was nitrogen and the flow rate was 40 cm³/min. Samples and standards were acidified by the addition of one mL of H_3PO_4 to 10 mL sample and the sample injection volume was 0.4 μ L.

Results and Discussion

The destruction of organic solids in SCW proceeds by two mechanism. In the direct mechanism, the organic solid matter in contact with oxygen is directly oxidized to end products. In the indirect mechanism, the solid organic matter is first dissolved by SCW, then the dissolved organic compounds are oxidized. Thermal destruction and solubilization of solid organic matter prior to oxidation (pyrolysis) results in the formation of intermediate organic products, including volatile fatty acids such as acetic and propionic acids. Both acids were detected as transformation products of incomplete oxidation. The organic component of biological sludge contains a variety of organic compounds including carbohydrates, lipids and proteins. Some of the organic compounds are easy to oxidize and others, including reaction products such as acetic acid, require extended reaction times to become fully oxidized. The destruction of proteins results in ammonia as a reaction by-product.

The data presented in Fig. 3 illustrate the destruction of activated sludge subjected to subcritical and supercritical temperatures in the batch reactor. The temperature was varied from 300 °C to 450 °C and the density of supercritical water was maintained at approximately 0.25 g/mL. The initial total solids (TS) concentration was 3 percent. The initial COD of the liquid and solid fraction of the sludge (TCOD) was 30,300 mg/L. As the temperature was increased between 300 °C and 450 °C, COD destruction increased at all residence times. However, to achieve

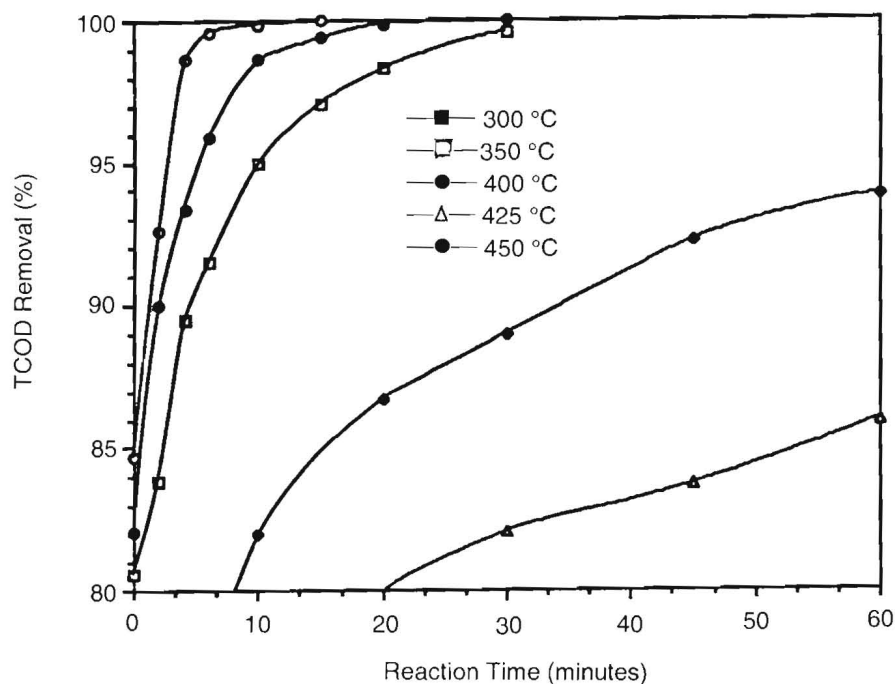


Fig. 3. Destruction of sludge in the batch reactor using subcritical and SCWO.

virtually complete destruction of COD, the temperature had to be above the supercritical point of 374 °C. More than 80 percent of the COD of the raw sludge was reduced during heatup to supercritical reaction temperatures. The heatup time, approximately 30 seconds, was not considered part of the residence time in Fig. 3. For example, five minutes residence time was equivalent to five minutes and 30 seconds total reaction time, of which 30 seconds were heatup time. The remaining COD after heatup required longer residence times for improved destruction and was designated as the difficult-to-oxidise sludge component or reaction transformation product. The difficult-to-oxidise sludge component was mostly (more than 60 to 80 percent) acetic acid (Table 2).

The continuous-flow reactor was operated at constant flow rate and constant pressure. The residence time within the reaction zone was dependent on the reaction temperature. As the reaction temperature increased, the fluid expanded and the

Table 2. Transformation of ammonia and acetic acid in the batch reactor (mg/L)

| Substance | 5 minutes | 10 minutes | 15 minutes | 20 minutes | 30 minutes |
|----------------------|-----------|------------|------------|------------|------------|
| Acetic Acid (350 °C) | 2800 | 2590 | 2100 | 1660 | 725 |
| Acetic Acid (400 °C) | 1220 | 310 | 110 | 40 | – |
| Acetic Acid (425 °C) | 380 | 20 | 15 | – | – |
| Ammonia (350 °C) | 550 | 550 | 560 | 550 | 450 |
| Ammonia (400 °C) | 590 | 590 | 540 | 470 | 260 |
| Ammonia (425 °C) | 460 | 270 | 125 | 25 | – |

residence time decreased. Nevertheless, the degree of sludge destruction increased with increased temperatures. The sludge was destroyed in two regions of the continuous-flow reactor. The first region was at the top of the reactor above the point where oxygen was introduced. In this region, sludge was subjected to thermal decomposition. The second region was below the point where oxygen was introduced. In this region, sludge destruction was due to both thermal decomposition and oxidation. The data presented in Fig. 4 and Table 3 were based on an influent TS

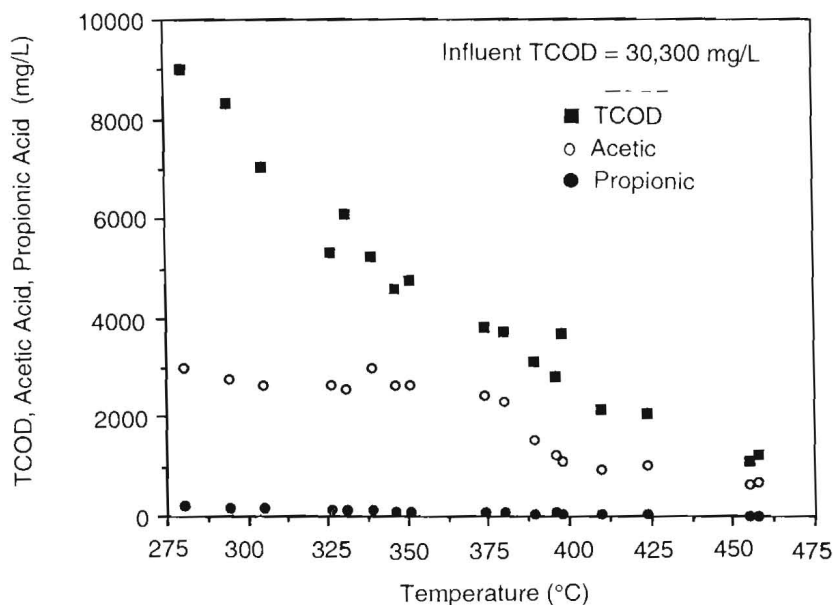
**Fig. 4.** Transformation of the organic component of sludge in the continuous flow reactor.

Table 3. Performance of the continuous flow SCWO reactor system

| Maximum Reactor Temperature (°C) | TCOD (mg/L) | Acetic Acid (mg/L) | Propionic Acid (mg/L) |
|----------------------------------|-------------|--------------------|-----------------------|
| Feed | 30,300 | – | – |
| 302 | 10060 | 2745 | 210 |
| 310 | 10200 | 2745 | 210 |
| 331 | 9270 | 2810 | 190 |
| 329 | 9150 | 2650 | 195 |
| 357 | 7040 | 2940 | 140 |
| 363 | 6650 | 2615 | 105 |
| 378 | 5360 | 2680 | 100 |
| 376 | 5210 | 2450 | 100 |
| 407 | 4140 | 1995 | 85 |
| 409 | 4270 | 1795 | 95 |
| 441 | 3830 | 1700 | 80 |
| 435 | 3780 | 1600 | 85 |
| 456 | 3180 | 1665 | 65 |
| 450 | 2460 | 1305 | 45 |

concentration of 3 percent, a pressure of 40 MPa, and a wet sludge flow of 50 g/min. The amount of oxygen was based on stoichiometric requirements (influent COD) plus 100 percent excess. The resulting COD destruction increased from approximately 75 percent at 300 °C to 97 percent at 450 °C.

Acetic acid was produced in large quantities at subcritical temperatures. Below 375 °C, the concentration of acetic acid in the effluent reached approximately 2,750 mg/L (Fig. 4). Supercritical temperatures were required to oxidize acetic acid. The concentration of acetic acid decreased from 2,750 mg/L at 375 °C to below 600 mg/L above 375 °C. The short residence at supercritical temperatures in the continuous reactor limited COD removal to 97 percent and resulted in a residual acetic acid in the effluent. In the batch reactor, the destruction of acetic acid was virtually complete at SCWO temperatures (Table 2). The concentration of propionic acid in the effluent was low compared with the concentration of acetic acid. Below

325 °C, propionic acid concentrations of 200 mg/L were produced. Above 325 °C, the concentration of propionic acid decreased as the temperature increased from 200 mg/L at 325 °C to 10 mg/L at 450 °C.

The production and transformation of ammonia was an important aspect of sludge destruction. A comparison of the production and transformation of ammonia at subcritical and supercritical temperatures in the batch reactor is presented in Table 2. The data indicate that ammonia was removed at supercritical temperatures, subject to temperature and residence conditions, while at subcritical temperatures, ammonia was not removed. Below 650 °C, the products of organic nitrogen and ammonia are N_2 and N_2O (Gloyna 1988). N_2O decomposes to form N_2 and O_2 .

SCWO resulted in significant sludge mass and volume reduction. While the original sludge containing 3 percent total solids, paper fibres and oils, settled to a volume of 980 mL/L after two hours, the ashes, containing approximately one percent solids, settled to a volume of approximately 110 mL/L in 30 minutes.

Conclusions

SCWO, including temperatures just below the critical point, offers an effective treatment concept that is applicable to a wide range of hazardous wastes and sludges. Using SCWO, the destruction of the organic component of sludge was virtually complete within a relatively short residence time. The process produced a clear and odorless effluent and a settleable ash, and significantly reduced the mass and volume of sludge.

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(Received 20/01/1996;
in revised form 01/07/1996)

الماء في حالته فوق الحرجة : وسط فعال لتحطيم الملوثات

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يصل الماء فوق درجة الحرارة الحرجة ، ٣٧٤ درجة مئوية ، والضغط الحرج ، ٢٢١ ضغط جوي ، إلى حالته المائعة فوق الحرجة . وتتميز حالة الماء هذه بخصائص فريدة منها قدرته الفائقة على إذابة الأكسجين والمواد العضوية . وباعتماد خصائص الماء في حالته فوق الحرجة ، فقد تم حديثاً تطوير تكنولوجيا فعالة لأكسدة الملوثات في هذا الوسط ، ولاحتماء هذا الوسط على كميات كافية من الأكسجين والمواد العضوية المذابة تحت درجات حرارة عالية ، فإنه من الممكن أكسدة المواد العضوية بسرعة كبيرة . ويمكن باستخدام هذه الطريقة التوصل إلى أكسدة كاملة للملوثات العضوية في مفاعلات مغلقة تمنع تسرب الملوثات إلى البيئة المحيطة .

يقدم هذا البحث وصف لتكنولوجيا أكسدة المواد العضوية باستخدام الماء في حالته فوق الحرجة كوسط للتفاعل ، بالإضافة إلى نتائج معالجة حمأة منشطة تحتوي على ملوثات عضوية صلبة من محطة تنقية لمعالجة ملوثات صناعية من مصادر متعددة . وقد اثبتت التجارب أنه من الممكن تحطيم الملوثات

العضوية في الحمأة المنشطة بفعالية تزيد على ٩٩٪ في أقل من خمسة دقائق في هذا الوسط . أما مخلفات التفاعل فقد كانت ماء معالج بدون لون أو رائحة يحتوي على الرماد غير العضوي والذي تم فصله من الماء بسهولة بالترسيب .